



T.R.

EGE UNIVERSITY

Graduate School of Applied and Natural Science



**INVESTIGATION OF CATALYTIC PERFORMANCES OF LAYERED
DOUBLE HYDROXIDES IN THE REMOVAL OF OXYTETRACYCLINE
HYDROCHLORIDE FROM AQUEOUS SOLUTIONS**

MSc THESIS

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Chemical Engineering Department

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2023

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Chemical Engineering Department

Chemical Engineering Second Cycle Programme

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Merve BARAÇ tarafından yüksek lisans tezi çalışması olarak sunulan **“Investigation of catalytic performances of Layered Double Hydroxides in the Removal of oxytetracycline hydrochloride from Aqueous Solutions (Oksitetrasiklin Hidroklorürün Sulu Çözeltilerden Ayrılmasında Çift Katmanlı Hidroksitlerin Katalitik Performanslarının Araştırılması)”** isimli bu çalışma EU Lisansüstü Eğitim ve Öğretim Yönetmeliği ile EÜ Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümlerine istinaden tarafımızca değerlendirilerek savunmaya değer görülmüştür, **30/01/2023** tarihinde gerçekleşen tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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30/01/2023

Merve BARAÇ



ÖZET

Oksitetrasiklin Hidroklorürün Sulu Çözeltilerden Ayrılmasında Çift Katmanlı Hidroksitlerin Katalitik Performanslarının Araştırılması

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Bu tezde, Oksitetrasiklin HCl'nin (OTC-HCl) çift katmanlı hidroksit katalizörleri kullanılarak Foto Fenton Benzeri Oksidasyon ve Katalitik Islak Hava Oksidasyonunun aktiviteleri incelenmiştir. Yöntemlerin performansları üç farklı çift katmanlı katalizör (Cu-Fe Layered Double Hydroxide, Co-Fe Layered Double Hydroxide ve Ni-Fe Layered Double Hydroxide) kullanılarak karşılaştırılmıştır. Her yöntem için en seçici katalizör belirlenmiştir. Bağımsız değişkenlerin yanıt fonksiyonu üzerindeki etkilerini araştırmak ve oksitetrasiklin giderim yüzdesini maksimize eden optimum koşulları belirlemek için Box Behnken istatistiksel deney tasarımı ve yanıt yüzeyi metodolojisi kullanılmıştır.

OTC-HCl'nin Foto Fenton Benzeri Oksidasyonu için optimum reaksiyon koşulları, görünür ışık varlığında Ni-Fe LDH katalizörü varlığında katalizör yükü = 1.5 g/L, H_2O_2 konsantrasyonu = 1.5 mM, pH=5 olarak belirlenmiştir. Bu koşullarda yaklaşık % 68 giderim elde edilmiştir. Bu optimum koşullarda kinetik çalışma yapılmış ve sistemin birinci dereceden bir adım kinetik modele uyduğu birinci dereceden reaksiyon kinetiğine uyduğu görülmüştür.

Oksitetrasiklin atıksuyunun Katalitik Islak Hava oksidasyonu için en seçici katalizörün Cu-Fe LDH katalizörü olduğu belirlenmiştir. Optimum koşullar 0.5 g/L Cu-Fe LDH katalizör yüklemesi, pH 7 ve 70°C sıcaklıkta olarak belirlenmiştir. Bu

koşullarda giderim yüzdesi %92 civarındadır. Kinetik çalışmalara göre, oksitetrasiklin'in ıslak hava oksidasyonu ile gideriminin iki adımdan oluşan birinci dereceden reaksiyon kinetiğine uyduğu gözlemlenmiştir.

Toksisite testlerine göre, foto fenton benzeri oksidasyon yönteminin (Relative Root Growth %52) atıksudaki toksisiteyi azaltmada daha az etkili olduğu, ıslak hava oksidasyonunun ise daha etkili olduğu (Relative Root Growth %64) sonucuna varılmıştır.

Anahtar Sözcükler: Çift katmanlı hidroksit, Fotokatalitik oksidasyon, Katalitik ıslak hava oksidasyon, Oksitetrasiklin

ABSTRACT

Investigation of Catalytic Performances of Layered Double Hydroxides in the Removal of Oxytetracycline Hydrochloride from Aqueous Solutions

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In this thesis, the performance of photo fenton-like oxidation and catalytic wet air oxidation of oxytetracycline HCl (OTC-HCl) using double-layer hydroxide catalysts was investigated. The performances of methods were compared with three different double-layer catalysts (Cu-Fe LDH, Co-Fe LDH and Ni-Fe LDH). The most selective catalyst was determined for each method. 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 oxytetracycline.

For the photo Fenton-like oxidation of OTC-HCl, the optimum reaction conditions were determined as catalyst loading = 1.5 g/L, H_2O_2 concentration = 1.5 mM, pH = 5 in the presence Ni-Fe LDH catalyst in the presence of visible light source. The degradation efficiency was evaluated as around 68% at these optimum conditions. Kinetic studies were performed at these optimum conditions and it is found that the system fits first order one step kinetic model.

For the Catalytic Wet Air oxidation of oxytetracycline wastewater the most selective catalyst was determined as Cu-Fe LDH catalyst. The optimum conditions were determined as 0.5 g/L Cu-Fe LDH catalyst loading, at pH 7 and at temperature of 70°C. At these conditions the removal percentage was around 92%. According to the kinetic studies it was observed that the removal of oxytetracycline by CWAO process follows two steps second order reaction.

According to the toxicity tests, it was concluded that the photofenton-like oxidation method (Relative Root Growth 52%) was less effective in reducing the toxicity in wastewater, while the wet air oxidation was more effective (Relative Root Growth 64%).

Keywords: Double layer hydroxide, Photocatalytic oxidation, Catalytic wet air oxidation, Oxytetracycline



ÖNSÖZ

Su kirliliğinin dünyadaki en ciddi çevre sorunlarından biri haline geldiği bilinmektedir. Atık sudaki organik kirleticiler insan sağlığına, canlılara ve tüm çevreye zarar vermektedir. Özellikle atık su ortamında bulunana antibiyotiklerin neden olduğu çevresel sorunlar son yıllarda büyük ölçüde endişeye sebep olmaktadır. Bu tip atık suların gideriminde birçok yöntem test edilmiş olmasına rağmen çoğu, antibiyotiği tam parçalayamamakta, yüksek enerji ve işletme maliyeti gerektirmekte ya da toksik yan ürünler ile sonuçlanmaktadır. Dezavantajları azaltabilmek için var olan yöntemlerden, ileri oksidasyon yöntemleri tercih edilmektedir.

Veterinerlik antibiyotikleri içeren atık suların arıtılmasının ileri oksidasyon yöntemleri ile uygulanabilirliğini incelemiştir. Çift katmanlı hidroksitler (ÇKH) olarak adlandırılan anyonik killer içeren katalizörlerin hazırlanmış ve karakterizasyonu yapılmıştır. Hedef veteriner antibiyotik (oksitetrasiklin hidroklorür) ile hazırlanmış sentetik atıksuyun gideriminin fotokatalitik oksidasyon ve katalitik ıslak hava oksidasyonu ile araştırılmıştır. Bu yöntemler arasında uygun olanın belirlenmiştir. Hazırlanan katalizörlerin katalitik performanslarının test edilmiştir. Hedef veteriner antibiyotiğin (oksitetrasiklin hidroklorür) arıtılması için kinetik modellerin türetilmiştir.

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Merve BARAÇ

PREFACE

In this thesis, removal of oxytetracycline hydrochloride from wastewater was evaluated. It is desired to find innovative, environmentally friendly, inexpensive and keep up treatment methods and materials.

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İZMİR

Merve Baraç

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1. INTRODUCTION

The protection and reusability of water resources is extremely important for the health and life of living things. In recent times, because of the rise of industrialization, climate change and the serious decrease in groundwater levels have reached a scary level. Unconscious use of water resources causes natural water resources to be depleted rapidly. Wastewater produced from various industries is dangerous for the health of living things with the organic compounds it contains. In the long term, water containing pharmaceutical waste water poses a significant risk to nature and animal health. Proper disposal of these wastewaters is very important for human and environmental health.

The problem of water scarcity leads researchers to water purification and protection of water resources. Pharmaceutical wastes pose a serious threat to water resources, and antibiotics in this group are very effective and important drug sources in water resource pollution. Because most of antibiotic compounds are released into the environment without being broken down as active ingredients. Various purification methods are used to prevent these compounds from being released into the environment without removal.

Many methods are used in the treatment of wastewater. Conventional ways are often inadequate to completely remove micro-pollutants from the wastewater. The different nature of the pollutants and the low efficiency of the traditional methods used lead researchers to apply new methods. Advanced Oxidation Processes (AOP) show promise with researchers with more efficient purification.

Research has revealed that advanced oxidation processes create oxidizing species with a high reactivity. This radical ($\text{OH}^\bullet$) is radical responsible for the oxidative breakdown of various most commonly occurring organic compounds. Hydroxyl and other radicals oxidize non-biodegradables to simple products and inert products. It is very important to develop oxidation methods. Wet Air Oxidation (WAO), Fenton and Photo Fenton Like Oxidation methods are highly effective process.

Wet Air Oxidation Process, WAO is used to treat wastewater that is overloaded and not too diluted to be disposed of by incineration. The addition of catalysts is very important in WAO. In this way, removal is realized under milder conditions (low pressure, low temperature). Adding Catalyst to the reaction increases its speed and thus shortens the reaction time. The catalyst increases the speed and thus shortens the time. Catalytic wet air oxidation (CWAO) is cheap and ecofriendly methods for hazardous, and non-convertible pollutants, and it is carried out with the addition of a catalyst to wet air oxidation. CWAO also provides a wide operating range of 50 bar up to 250° C. According to the method, organic pollutants are oxidized with O₂ using a catalyst and converted into biodegradable inorganic salts, water and CO₂ (Benitez et al., 2011). CWAO, which is used in the treatment of wastewater containing veterinary antibiotics, is a frequently investigated method.

Another method frequently used in antibiotic wastewater treatment is Photo Fenton Like Oxidation (PFLO). This method is used to reduce various organic and inorganic compounds. In Fenton Reaction, with a light source is very important, so that organic compounds mineralize quickly. Ultraviolet light or visible light be able to used as a light source (Turbay, 2013). Studies on the treatment of wastewater containing veterinary antibiotics with PFLO are increasing day by day.

Studies on the use of cheaper, more environmentally friendly and more effective catalysts in antibiotic wastewater treatment with advanced oxidation method are of great importance today. In this thesis, the feasibility of treating wastewater containing veterinary antibiotics with advanced oxidation methods has been tested. In this study, the performances of PFLO and CWAO methods are compared using double-layer hydroxide (LDH) catalysts. By replacing traditional catalysts with ones with higher efficiency and fewer environmental consequences, existing environmental conditions will be protected and contributed to the improvement.

The aims of this thesis project can be listed as follows:

- a. Preparation and characterization of LDH catalysts.
- b. Investigation of treatment of synthetic wastewaters prepared with target veterinary antibiotics by PFLO and CWAO methods.
- c. Determination of the suitable method.
- d. Derivation of kinetic models for purification of target veterinary antibiotic.

2.0 THEORETICAL BACKGROUND

2.1. Wastewater from Industries

Water is used in production in industry, tons of cubic meters of water are consumed every day. However, while only a small part of the water is used efficiently, a significant part is discharged into the canal as wastewater. In industrial facilities, only 10% of the water is used in the process and the remaining 90% is sent to the canal as waste water. It is transported via the canal to a treatment plant or to the sea via rivers. Therefore, it is very important to treat wastewater. Industrial wastewater may have different contents according to the sector that produces it. Wastewaters may contain biodegradable or resistant compounds. Compounds resistant to removal may contain heavy metals, for example. Therefore the release of industrial wastewater into the environment is of great concern (Kim, 2008).

2.2. Pharmaceutical Wastewater

Pharmaceutical wastewater is the most dangerous member of the industrial wastewater group. If disposed of with insufficient treatment, it can harm the environment and groundwater resources. Due to its variable, toxic and heavy composition, different treatment methods are used for each pharmaceutical wastewater. General treatment cannot be used for all types of pharmaceutical wastewater. Various treatability studies have been conducted to adequately treat pharmaceutical wastewater, making it safe and compliant with legal standards. The use of antibiotics in aquaculture as well as in human and veterinary medicine has increased significantly in recent years (Wang et al., 2020). The most commonly used group among veterinary antibiotics is the tetracycline group.

2.2.1 Oxytetracycline Hydrochloride

The tetracyclines belong to the group of broad-spectrum antibiotics that are very similar in nature and derived from a tetracyclic compound, naphthacenecarboxamide. Tetracyclines create a bacteriostatic effect by inhibiting protein synthesis in bacterial ribosomes. Tetracyclines are known to be effective against a large number of bacteria from various groups, as well as rickettsia, chlamydia, spirochetes, mycoplasmas, leptospores and some protozoa. Therefore, they are the broadest spectrum antibiotics. Major types of Tetracyclines are: Tetracycline and Oxytetracycline, Dimethylchlorotetracycline, Doxycycline and Minocycline (Gurses, 2004).

Oxytetracycline is the second member of the most widely used and broad-spectrum tetracycline antibiotic group. Oxytetracycline tries to prevent the bacteria from producing protein and living and multiplying. It has the purpose of preventing the growth of bacteria. Oxytetracycline stops the infection from increasing. Oxytetracycline is a broad-spectrum antibiotic effective against bacteria. In recent years, some bacteria have developed immunity to this antibiotic. It has led to a decrease in the effectiveness of antibiotics in the treatment of some types of infections. In Figure 2.1, the molecular structure of oxytetracycline is schematized.

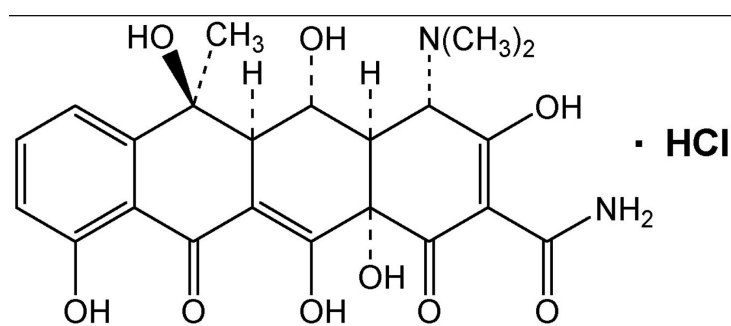


Figure 2.1 : Oxytetracycline molecular schema

2.3 Layered Double Hydroxide (LDH)

Layered double hydroxides can be called anionic clay materials (Braterman et al., 2004). There are many types of natural occurrence silicate-based cationic clays. However, there are anionic clays that naturally occurring in nature, but most anionic clays can be easily synthesized artificially. This category of clay is frequently preferred in the pharmaceutical industry. LDHs have attracted worldwide attention because they can be used in wastewater treatment, medicine and health in either initial or derived form as anion scavengers (Braterman et al., 2004).

Layered double hydroxides (LDH) are inorganic compounds with positively charged layers consisting of metal ions (with different oxidation rate) and hydroxide ions. Hydroxide ions have mobile anions in the inter-layer space.

The number of hydroxides is constant. LDH is determined by its cation composition (Anions A-n in the interlayer space are easily replaced). It is possible to change the composition of the cationic layer so that its charge and hence the distance between layers, number of anions in interlayer space become changeable. With the entry of bipolar anions (eg surfactants) into the interlayer spaces, the polarity of the environment changes. This ensures that the LDH particles are split into separate fragments (up to monolayers). This process is reversible. However, the length of these structures is quite effective. The longer these structures are in length, the more difficult they are to reverse (Cavani et al., 1991).

Recently, LDH catalysts are preferred in many different areas due to their special layered structure. They are particularly important in nanotechnology applications. Two-dimensional (2D) nanoreactors can be used in many fields of study, such as two-dimensional model systems in energy transfer processes (Forano et al., 2006).

LDHs exhibit shape-selective intercalation properties. LDH intercalates are used in suspensions for self-cleaning of surfaces and good compatibility of LDH with inorganic materials. The LDH Molecule Schema is shown in Figure 2.2. LDH layers can be composed of rhombohedral cells or hexagonal unit cells. Most synthetic LDHs are in the form of hexagonal unit cells; only LDH with M^{2+}/M^{3+} ratio equal to 1 exhibits orthorhombic unit cell (Evans and Slade, 2006).

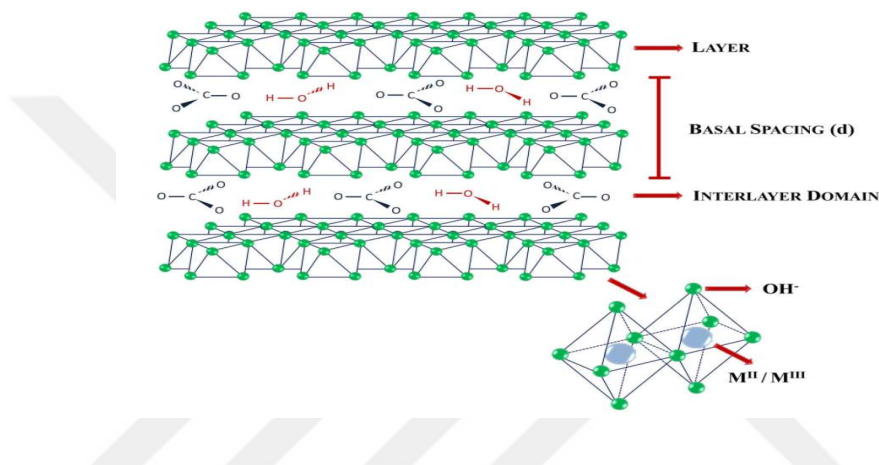


Figure 2.2 : Layered Double Hydroxides Molecule Schema (Evans and Slade, 2006)

2.4. Pharmaceutical Industry Wastewater Treatment

Wastewater produced in the pharmaceutical industry varies according to the intensity of the process used in drug production, the raw materials used and the processes. Pharmaceutical wastewater is usually produced by a series of chemical-synthetic processes and therefore has high toxicity. For this reason, traditional treatment methods are not generally recommended directly. Many types of wastewater treatment methods are used in the pharmaceutical industry. Generally, the polluting factor can be treated by chemical or biological removal means. Obtaining reusable water is essential for sustainability. Recently, it has become popular to apply more environmentally friendly and cheaper production techniques in the pharmaceutical industry. Some of the traditional methods that can be applied are:

1. Biological Treatment
2. Physicochemical Treatment Methods

2.4.1. Biological Treatment

In biological treatment methods, there is a separation of wastewater into more stable and degradable end products by using microorganisms, especially bacteria. Some of the waste is converted into CO₂, H₂O and other stable end products. Biological treatment methods are divided into two depending on the presence of dissolved oxygen. These are aerobic and anaerobic (Muralikrishna et al., 2017). Biological treatment is shown as appropriate method alternative in the treatment of wastewater. However, due to their chemical structures, these wastewaters cannot be directly biologically treated, so they must be pre-treated. The reason why the wastewater containing antibiotics, which contains non-biodegradable substances in high concentration, is not directly given to the biological treatment, is that a good treatment efficiency cannot be obtained. The reason for not getting good efficiency is that microorganisms living in water are inhibited by creating toxic effects and their presence leads to the formation of resistant bacteria (Ferrari et al., 2003). For this reason, a chemical pre-treatment process should be applied to the medicated wastewater that causes inhibition at high concentrations in biological treatment plants before being given to biological treatment.

2.4.2. Physicochemical Treatment Methods

Physicochemical treatment is based on changing the physical state of colloidal particles. It works by using chemicals that help make them more stable and coagulable for further purification or filtration purposes. These treatment methods have been used for many years together with biological treatment methods. These methods are frequently used in industrial water treatment, conditioning of wastewater sludge as part of pretreatment, with increasing efficiency and decreasing costs. Physicochemical treatment can have a major impact on the bioremoval potential of organic matter in wastewater.

2.4.3. Advanced Oxidation Processes (AOP)

Advanced oxidation processes show promise in pharmaceutical wastewater method, consisting of removal of toxins that occur naturally, pollutants, and many studies have been carried out with these methods in the last years. AOP includes a number of techniques for producing hydroxyl radicals, superoxide anion radicals, hydrogen peroxide. The hydroxyl radical is generally preferred species in the activity of AOP. Generally, organic compounds want to form a carbon-centered radical, so they react with the hydroxyl radical by way of example or removal of hydrogen. AOP include various oxidation processes such as Photo-Fenton, Photocatalysis, radiolysis.

2.4.3.1. Ozonization

Ozonation is the most preferred and most suitable alternative method for color removal. Ozone has high reactivity towards C-C double bonds. This method causes a decrease in foaming ability and color removal.

2.4.3.2. Ion exchange

This method is widely preferred method using synthetic resins used to remove contaminants from wastewater. . Polymeric resins are generally preferred in the ion exchange method. It is due to the transfer of ions between solid and liquid phases. The negative aspect of this process is that ion exchange processes are costly (Rengaraj et al., 2001).

2.4.3.3. Photocatalysis

Today, there are two different photocatalytic methods to be used in wastewater treatment. These light sources are solar light and ultraviolet (UV) light. On both light sources, studies may be carried out at different temperatures to decompose pollutants. Solar photocatalysis method because sunlight is used. It is cheaper and environmentally friendly method. The equipment required is very little. Photocatalysis method is used to break down organic substances and various inorganic molecules. It is also used as a Photocatalysis catalyst with nanoparticles (Müller et al., 2010).

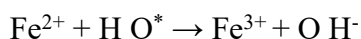
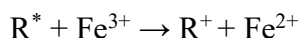
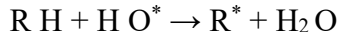
2.4.3.4. Electrochemical Processes

Electrochemical Processes are frequently preferred in studies today due to their environmental friendliness. In this method, they can generate large amounts of hydroxyl radicals with the utilised current. In this purification method, anodes with high O₂ fluctuation are used. Examples of these are hydroxyl radicals and lead dioxide anodes.

2.4.3.5. Fenton Process

The fenton reaction generates hydroxyl radicals from hydrogen peroxide. This process is catalytic. It is basically the electron transfer between H₂O₂ and Fe ions. It is founded on formation of -OH, has a high oxidation potential value, which can separate pollutants at a high rate. Fenton technology is a suitable method for the treatment of wastewater containing non-biodegradable organic pollutants (Nidheesh et al., 2013).

Removal mechanism by Fenton reaction:



2.4.3.6. Photo-Fenton Process

The Photo-Fenton method is often used to get rid of organic compounds by integrating it into an existing water treatment process. It works even at low pollutant concentrations. It usually completely mineralizes the compound and can convert it to a less toxic nature. This process is most effective at pH 2.8. In addition to this process, pH neutral values can also be studied by adding complexing agents suitable for Fe(III). Its wide working range increases its preference. It has been observed that Fenton reaction systems increase the removal of some pollutants as a result of working with UV/Visible light.

2.4.3.7. Photo Fenton Like Oxidation (PFLO)

Photo Fenton Like oxidation is a type of advanced oxidation. It is applied by the interaction of hydrogen peroxide using iron ions or another catalyst using a light source such as UV. PFLO is a frequently used method today as a low-cost, effective method to remove resistant contaminants from water. In addition, advanced equipment and expensive reagents are not required. It is preferred to use less harmful chemicals in the application of this method (Ameta et al., 2018). For all these reasons, it was found appropriate to use this method in this study.

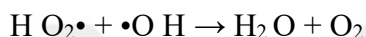
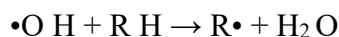
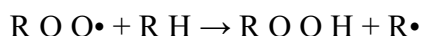
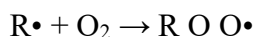
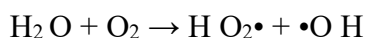
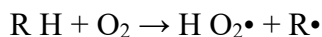
In Photo-Fenton-like oxidation, a H_2O_2 molecule is split into two H_2O^* components by UV light as shown in the first equation. In addition, H_2O^* can be formed by the reaction of H_2O_2 and Fe^{2+} in Fenton oxidation, and H_2O^* can be formed due to the reduction from Fe^{3+} to Fe^{2+} by UV light in the Photo Fenton Oxidation (Han et al., 2020).



2.4.3.8. Catalytic Wet Air Oxidation (CWAO)

Catalytic wet air oxidation is the preferred method for the treatment of toxic and non-biodegradable pollutants. In this method, wastewater is oxidized with dissolved molecular O_2 using a solid catalyst. The use of catalysts provides higher oxidation. Lower temperature and pressure conditions can be used to reduce the chemical oxygen demand. Two oxidants commonly used in catalytic wet air oxidation reactions are oxygen and hydrogen peroxide. The reason why other oxidizers are not used in this method is that the oxidizers are produced in situ. Investigation of reaction mechanisms and reaction kinetics is very important in removing the pollutant factor.

The main reactions with organic compounds are as follows (Zhou et al., 2010).



In the wet air oxidation process, high temperature and high pressure conditions can be applied in order to produce active oxygen species. Therefore, it has great potential for the method of heavy waste in relation to high organic material (COD) and toxic pollutants. Extreme reaction conditions cause high cost and therefore limit its use. Recently, attention has been paid to the development of catalytic wet air oxidation using innovative catalysts. The most common catalysts in CWAO are heterogeneous catalysts. The heterogeneous catalyst has significant advantages like easy separation, high activity and no secondary harmful products. Heterogeneous catalysts are of two types, noble metal (Cu, Mn, Co, Ni etc) and non-noble metal catalysts. It could be one or more of the items. The reason why noble metal catalysts are preferred over other metals is that they are cheaper. But their catalytic activity is lower. The task of the active parts of the inert metal catalyst is to improve the stability of the inert metal catalysts (Abbasi et al., 2019).

Reaction kinetics is very important to interpret the effects of parameters. It is very important to find the appropriate model in order to decide on the appropriate design and operation. In studies, kinetic models suggested demonstrate the removal of organic compounds in CWAO. In most cases, the reaction kinetics of the organic component in CWAO can be reduced to a general rate equation set up as a simple reaction mechanism involving indirect and direct pathways.

3.0 LITERATURE SURVEY

There are many studies in the literature on treatment of veterinary antibiotic wastewaters. Some studies in the literature on wastewater treatment by PFLO and CWAO methods are summarized below.

In 2018, Li et al. studied the activity of the Ag/AgBr/Ag₂WO₄ that they prepared. Prepared Ag/AgBr/Ag₂WO₄ catalyst provided effective removal of tetracycline hydrochloride (TC) antibiotic by the enhanced Photocatalytic oxidation method under visible light. The effect of triple catalyst combination was observed, with quite assertive activity increase and good durability. Superoxide radicals are responsible for removing the polluting factor. A viable Photo-catalytic mechanism on Ag/AgBr/Ag₂WO₄ has been proposed. Their high performance is due to the suppressed recombination of charge carriers (Li et al., 2018).

In 2012, Fan et al. studied anion exchange precipitation process to synthesize bifunctional Ag/AgBr/Co–Ni–NO₃ LDH nanocomposites to add AgNO₃ solution to Co–Ni–Br LDH suspension. It was observed that Ag/AgBr nanoparticles were widely spread on Co–Ni–NO₃LDH layers. Nanocomposites have been used to absorb and photo-catalytically decompose organic pollutants from water. For the removal of dyes and phenol, the Photocatalytic activities of nanocomposites were found to be higher than Co–Ni–Br LDH and Ag/AgBr. This aimed method may be preferred in the preparation of other LDH/silver salt compositions. It was concluded this kind nanostructures have extensive applications in treatment thanks to their high absorption capacity and high Photocatalytic activity (Fan et al., 2012).

In 2019, Panplada et. al studied on the effective degradation of tetracycline (TC) antibiotic from wastewater. Mixed metal hydroxides (MMHs) that can act as sorbent to remove TC from an aqueous solution using LDH components with in situ adsorption removal were expected to produce immediate precipitation formation. With this method, 100% removal of TC within 4 minutes under optimized conditions is considered to be achievable. The results reveal that the method used results in superior

removal performance with the choice of LDH as a sorbent, both in terms of degradation kinetics and yield. Recovery of TC was tested in the presence of anions. Due to the high charge density, 98% recovery was obtained by using dalai phosphate. It was concluded that it is an effective combination in yield degradation of TC in real wastewater (Panplado et al., 2019).

In 2019, Ao et al. studied middle pressure UV/peroxymonosulfate (MPUV/PMS) oxidation process in the presence of sulfate radical to remove tetracycline (TTC) in water. Optimum removal was achieved at an initial TTC concentration of 11.25 μM at pH=3.7, a PMS dose of 0.2 μM , and a UV dose of 250 mJcm^{-2} . As a result, 82% of TTC was observed to be corrupted by MPUV/PMS (Ao et al., 2019).

In 2019, Chen et al. investigated the photocatalytic performance of LDH catalyst is limited. It is associated with slow interface mobility and high recombination rate of Photogenerated electron hole pairs in the material. A new combination was tried to increase the low Photo-catalytic yield. This combination is $\text{Ag}_2\text{O}/\text{Ag}$ decor LDH (LDH- $\text{Ag}_2\text{O}/\text{Ag}$). By accumulating Ag_2O on the LDH surface, the catalyst was successfully synthesized and converted into Ag° nanoparticles in the correct position after heat treatment. It was observed that the Photocatalytic activities of the synthesized LDH- $\text{Ag}_2\text{O}/\text{Ag}$ composites increased substantially. The optimum Photo-catalytic yieald of LDH- Ag_{10} (0.0184 min^{-1}) is approximately 46 times higher than that of LDH (0.0004 min^{-1}). The result of active species capture experiments showed that $\bullet\text{OH}$, h^+ and $\bullet\text{O}^{2-}$ have a significant effect on TC removal. At this stage, OH played a dominant role during the Photocatalytic process (Chen et al., 2019).

In 2021, Zhu et al. investigated Cu-Fe/LDH@BiOI_{1.5} composite Photocatalyst designed with a simple hydrothermal synthesis method and prepared not to be used in removal. A characterization study was carried out to determine the structural performance and visible light response of this composite photocatalyst. Photocatalytic removal test of TC was tested with three different catalyst combinations. The highest removal was achieved with 1:10 Cu-Fe/LDH@BiOI_{1.5} composite with 73% in 75 minutes. Other combinations showed lower removal, including Cu-Fe LDH and pure

BiOI_{1.5}. In this study, key active substances were obtained with O²⁻ and h⁺ in the capture test (Zhu et al., 2021).

In 2021, Wu and others studied the Photo-Fenton method. This method shows great potential in environmental remediation, but the most important problem is the low charge carrier efficiency and the slow reaction kinetics caused by the active radicals present. In this work, FeNi-LDH/BMNSs + H₂O₂+Vis system achieved 95.76% removal in 60 minutes under optimum conditions. Also, high TC-HCl removal rates (over 80%) were obtained over a wide pH range. After 4 iterations, a total organic carbon (TOC) removal rate of 48.98%. In this study, the Photo-Fenton system showed high removal for oxycycline. It showed excellent performance for TC-HCl removal. With this work, Photo-Fenton provided a new method to produce 2D/2D active heterogeneous catalysts for catalytic application (Wu et al., 2021).

In 2019, Gonçalves et al. studied LDH synthesis containing CoCr-LDH with or without Fe₃O₄ done to investigate the effect of magnetite extension into LDH in structural and catalytic terms. Characterization studies were carried out for these materials. Studies continued with Fenton like and Photo Fenton like methods. The analyzes showed successful incorporation of magnetite into LDH. The adsorption and oxidation processes using Fe₃O₄/LDH composite showed that it is more efficient than pure LDH. The reason for this high performance is explained by its higher surface area with the Fe₃O₄/LDH catalyst and larger pores that provide more effective contact with the paint solution (Goncalves et al., 2019).

In 2021, Serge et al. studied the catalytic activity of LDH using a heterogeneous Fenton process for the removal sulfatiazole (STZ), using two different catalysts (copper added and non-copper added catalyst). With the characterization studies carried out, the layered structures created by the overlapping of the layers containing magnesium, iron and copper cations were revealed. It achieved complete degradation of the STZ after 90 minutes. X-ray Photoelectron spectroscopy analysis revealed the presence of Cu(II) and Cu(I) surface regions that contribute to the formation of hydroxyl and hydroperoxyl/superoxide radicals. In addition, there was an increase in the Cu(I) content after use. For both materials, but especially for copper-free LDH, the addition

of tert-butyl alcohol and p-benzoquinone inhibited STZ scavenging, indicating very important of hydroxyl and hydroperoxyl/superoxide radicals in the scavenging process, respectively. At the end of the study, she demonstrated the potential of copper-modified MgFe-CO_3 (Serge et al., 2021).

In 2017, Bai et al. investigated Co-Fe LDH prepared by co-precipitation was and they suggested as catalyst for nitro-benzene removal. The properties of the prepared catalysts were evaluated by analysis. The effect of many factors on the removal of the pollutant factor was investigated. These factors are; initial pH, hydrogen peroxide concentration, catalyst dosage, and nitrobenzene concentration. Yield (100%) was obtained under optimum conditions. These conditions are; For the initial concentration nitrobenzene: 50 mg/L, pH = 2.7, $[\text{H}_2\text{O}_2]_0 = 500$ mg/L, catalyst dosage=1g/L. Co-Fe LDH retained catalytic activity after five repeat cycles. Intermediate product were detected by LC/MS. and Co-Fe is suggested as a different route for nitrobenzene degradation in the LDH and H_2O_2 system (Bai et al., 2017).

In 2020, Qiao et al. studied tetracycline (TC) removal together novel magnetic graphene oxide/ZnO nanocomposites (MZ). Experiments were carried out to examine the tetracycline removal performance of MZ. MZ catalyst shows high adsorption capacity for TC contaminant and can be easily separated from water. The 2nd order kinetic model can well explain the adsorption process of TC. When various results were analyzed. In TC's Photocatalytic removal experiments, graphene oxide served as the structure. ZnO acts as an effective Photocatalyst. MZ remained at relatively high degradation levels after 4 cycles. This study showed that MZ has great potential as a highly effective adsorbent and Photocatalyst for the removal of tetracycline contaminants from water. Tetracycline was removed by adsorption and Photocatalytic oxidation methods. Graphene oxide / zinc oxide is used as a catalyst. It has great potential as a highly yield adsorbent and photocatalyst. Maximum adsorption capacity at pH 6.0 is 1590.28 mg/g. It has good activity, suitable for long-term use (Qiao et al., 2020).

Studies in the literature are summarized in the table below:

Table 3.1 : Table of Literature Survey

Method	Polluting Factor	Catalyst	Optimum Condition	Results	References
medium pressure UV/peroxymonosulfate (MPUV/PMS) oxidation process	tetracyclines	sulfate radical	initial TTC concentration of 11.25 μ m at pH=3.7, a PMS dose of 0.2 μ m, and a UV dose of 250mJcm ⁻² .	TC removal removal efficiency of 82%	(Ao et al., 2019)
under visible light Photocatalytic oxidation	RhB dye and TC antibiotic	triple catalyst Ag/AgBr/Ag ₂ WO ₄	The removal rate constant AgBr=8.6, Ag ₂ WO ₄ =22.9, Ag/AgBr= 3.5 AgBr/Ag ₂ WO ₄ =2.4 for 0.0575min ⁻¹	The presence of ternary composites results in an extraordinary increase in activity and high durability. Superoxide radicals are considered responsible for RhB removal.	(Li et al., 2018)
Adsorption and Photo-Catalytic Oxidation	wastewater	Ag/AgBr/Co–Ni–NO ₃ LDH	MO solutions initial concentration = 25 mg L ⁻¹ temp.=95°C time=5h Co:Ni and Ag:Br molar ratios are about 6:1 and 3:4 Co–Ni–Br LDH, which has two absorption peaks at 620-660nm	In the dark, nanocomposites rapidly adsorb methyl orange. It has been observed that the adsorption capacity of 230 mgg ⁻¹ is much higher in Co–Ni–BrLDH catalyst than Ag/AgBr and activated carbon.	(Fan et al., 2012)

Adsorption	tetracycline	metal hydroxides; LDH	Rxn time =4 min pH=12 Uv visspectra=30 mg L ⁻¹	Decomposition yield: 99.8% Under optimized conditions, 99.5% removal efficiency can be achieved within 4 minutes due to a strong electrostatic interaction and the H bond between the contaminant factor and the positively charged surface of the MMHs.	(Panplado et al., 2019)
visible light Photocatalytic	Tetracycline (TC)	LDH-Ag ₂ O/Ag	Temp. = 80 °C Time= 12 h Wavelength= 400 nm. TC initial concentration = 40 mg L ⁻¹	absorbance 356 nm wavelength. LDH-Ag ₁₀ Photocatalyst proved the strongest absorption of all LDH-Ag ₂ O/Ag composites.	(Chen et al., 2019)
Photocatalytic removal	tetracycline	Cu-Fe/LDH@BiOI _{1.5} composite Photocatalyst		The highest degradation was achieved with 1:10 Cu-Fe/LDH@BiOI _{1.5} composite with 73% in 75 minutes. Other combinations showed lower removal, including Cu-Fe LDH and pure BiOI _{1.5} .	(Zhu et al., 2021)

Foto-Fenton	tetracycline hydrochloride (TC-HCl)	2D/2D FeNi-layered double hydroxide/bimetal-organic frameworks nanosheets (FeNi-LDH/BMNSs) Photocatalyst	After hydrothermal reaction at 110 °C for 20 h, the FeNi-LDH/BMNSs composite can be obtained	The FeNi-LDH/BMNSs + H ₂ O ₂ +Vis the reaction showed perfect TC-HCl degradation rate of 95.76% in 60 minutes under optimum conditions. Also, high TC-HCl removal rates (over 80%) were obtained over a wide pH range. After four reuses, a TOC defradation rate of 48.98%	(Wu et al.,2021)
Fenton-like and Photo-Fenton-like methods.	dye removal	Fe ₃ O ₄ /LDH composite	a cobalt and chromium LDH was prepared by co-precipitation at variable pH at a molar ratio of 3:1 in the presence and absence of magnetite.	The adsorption and oxidation processes using Fe ₃ O ₄ /LDH composite worked with much higher yield than pure LDH.	(Gonçalves et al.,2019)
Fenton-like removal	antibiotic sulfatiazole (STZ)	copper-modified MgFe-CO ₃ LDH		The specific area and decay kinetics of the material increased with the addition of layered copper element. It achieved complete removal of the STZ after 90 minutes.	(Serge et al., 2021)



Fenton-like removal	nitrobenzene	Co-Fe LDH	initial concentration of 50 mg/L nitrobenzene, pH = 2.7, $[H_2O_2]_0 = 500$ mg/L, catalyst dosage = 1 g/L'. Co-Fe LDH	nitrobenzene oxidation is a radical-mediated process confirmed by the addition of T-butanol. Iron leaching is only 12.47 mg/L, even at pH 2.7.	(Bai et al.,2017)
Adsorption and Photocatalytic oxidation	tetracycline	magnetic graphene oxide/ZnO	Temp. =90°C Time =6h the initial antibiotic concentration=100 mg L ⁻¹	The adsorption kinetics of the pollutant is compatible with the second-order kinetic model. The maximum adsorption capacity of the pollutant is 1590.28 mg/g at pH 6.0.	(Qiao et al.,2020)

4.0 EXPERIMENTAL

The experimental work can be examined in four steps:

- ▶ 1. Preparation of the layered double hydroxide(LDH) catalysts
 - ▶ 1.1 Preparation of Fe-Cu LDH catalyst,
 - ▶ 1.2 Preparation of Fe-Ni LDH catalyst,
 - ▶ 1.3 Preparation of Fe-Co LDH catalyst
- ▶ 2. Characterization of the Catalysts
 - ▶ 2.1 Scanning Electron Microscopy Analysis (SEM)
 - ▶ 2.2 X-Ray Photoelectron Spectroscopy Analysis (XPS)
 - ▶ 2.3 X-Ray Diffraction Analysis (XRD)
 - ▶ 2.4 Brunner-Emmett-Teller Surface Area Analysis (BET)
- ▶ 3. Application of advanced oxidation methods
 - ▶ 3.1 Selection of catalyst and determination of operating conditions
 - ▶ 3.2 Photo Fenton-Like Oxidation
 - ▶ a. Catalyst Screening
 - ▶ b. Parametric Study
 - ▶ c. Scavenger Effects
 - ▶ d. Reusability Test
 - ▶ e. Toxicity Test
 - ▶ 3.3 Catalytic Wet Air Oxidation
 - ▶ a. Catalyst Screening
 - ▶ b. Parametric Study
 - ▶ c. Reusability Test
 - ▶ d. Toxicity Test
- ▶ 4. Derivation of kinetic models for purification of target veterinary antibiotic

4.1 Properties of Pharmaceutical Wastewater

In this study, synthetic OTC-HCl wastewater was prepared and used in the laboratory environment. The literature data shows that the average OTC-HCl concentration of real wastewater effluent is 50 ppm (Carson et al., 2002) and hence in this study as initial concentration 50 ppm is used. The characteristics of wastewater used in this study are given in Table 4.1.

Table 4.1: Characteristics of OTC-HCl WasteWater

Water Parameter	Concentration ppm	pH	Dissolved O ₂ , mg/L	Conductivity mS/cm	Turbidity NTU
OTC-HCl Wastewater	50	4	0.004	36	0.3

4.2 Preparation of the Layered Double Hydroxide (LDH) Catalysts:

Fe-Cu LDH, Fe-Ni LDH, Fe-Co LDH catalysts were prepared and their performances were tested in CWAO and PFLO methods. The preparation steps of the catalyst used are given in Figures 4.1-4.3 below.

4.2.1 Fe-Cu LDH Catalysts Preparation

General procedure of preparation of Fe-Cu LDH by co-precipitation method is given below (Mikami et al., 2016 ; Khataee et al., 2019):

- Iron(III) Nitrate Nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Copper (II) Nitrate Trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) are dissolved in distilled water at 1:3 mole ratio.
- after stirring for 30 min, NaOH solution (2 N) is added dropwise to the aqueous phase to raise the pH of solution to 10 and mixed for an additional 30 minutes.
- formation of precipitation is observed
- the precipitate is aged at 60°C room temperature for 10 hours and is filtered out
- then is aged at 80°C for 8 hours

These steps are shown in Figure 4.1.

4.2.2 Fe-Ni LDH Catalysts Preparation

General procedure of preparation of Fe-Ni LDH by co-precipitation method is given below (Mikami et al., 2016 ; Khataee et al., 2019):

- Iron(III) Nitrate Nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Nickel (II) Nitrate Trihydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in distilled water at 1:3 mole ratio.
- after stirring for 30 min, NaOH solution (2 N) is added dropwise to the aqueous phase to raise the pH of solution to 10 and mixed for an additional 30 minutes.
- formation of precipitation is observed
- the precipitate is aged at 60°C room temperature for 10 hours and is filtered out
- then is aged at 80°C for 8 hours

These steps are shown in Figure 4.2.

4.2.3 Fe-Co LDH Catalysts Preparation

General procedure of preparation of Fe-Co LDH by co-precipitation method is given below (Mikami et al., 2016 ; Khataee et al., 2019):

- Iron(III) Nitrate Nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Cobalt (II) Nitrate Trihydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) are dissolved in distilled water at 1:3 mole ratio.
- after stirring for 30 min, NaOH solution (2 N) is added dropwise to the aqueous phase to raise the pH of solution to 10 and mixed for an additional 30 minutes.
- formation of precipitation is observed
- the precipitate is aged at 60°C room temperature for 10 hours and is filtered out
- then is aged at 80°C for 8 hours

These steps are shown in Figure 4.3

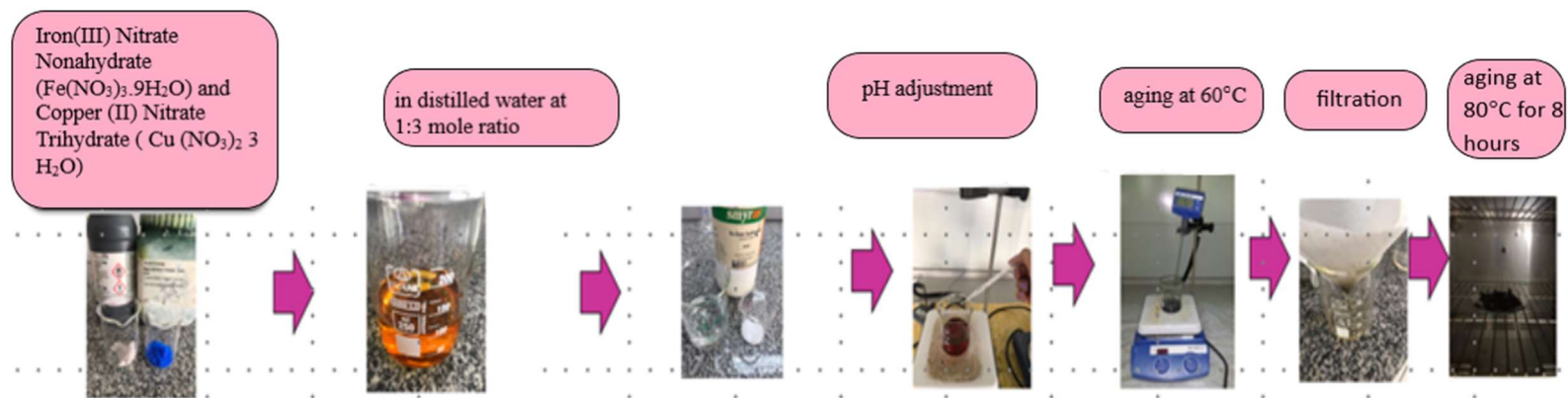


Figure 4.1: Steps in preparation of Fe-Cu LDH Catalyst

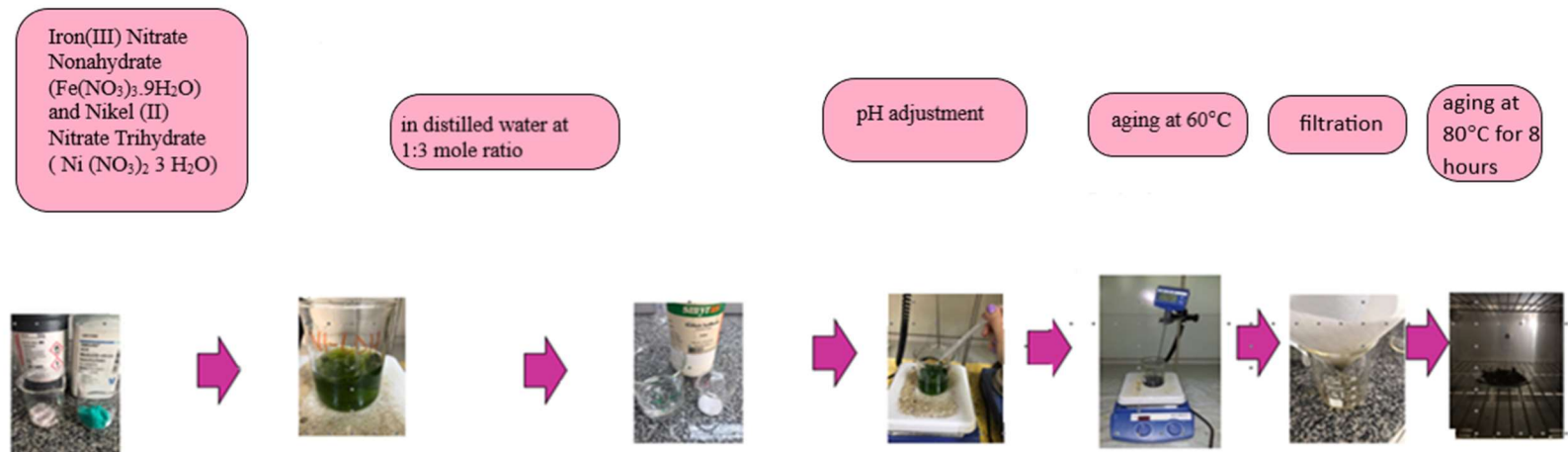


Figure 4.2: Steps in preparation of Fe-Ni LDH Catalyst

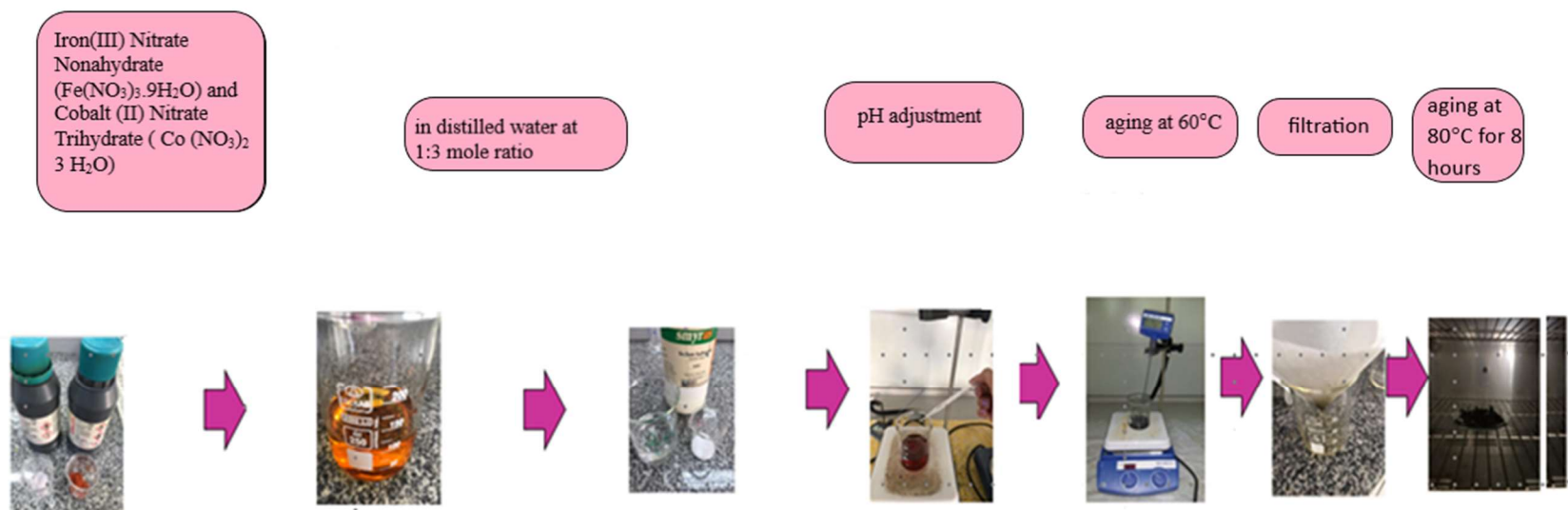


Figure 4.3: Steps in preparation of Fe-Co LDH Catalyst

4.3 Characterization

The characterization study was carried out in order to investigate the characteristic properties of different catalysts (Cu-Fe LDH, Ni-Fe LDH, Co-Fe LDH). In this context, Scanning Electron Microscopy (SEM) , X-ray Diffraction (XRD), X-Ray Photoelectron Spectrometer (XPS) Analysis Brunauer–Emmett–Teller (BET) analyses were performed.

- SEM Analysis Conditions:

All prepared catalysts were coated with gold and palladium and the analysis was performed via Thermo Scientific Apreo S device for two different magnifications (50000 and 100000) under high vacuum. This analysis was performed in EGE-MATAL (Ege University Test and Analysis Application and Research Center).

- XRD Analysis Conditions:

The phases of the catalysts were investigated with a Philips X'Pert Pro X-Ray Diffractometer at İzmir Institute of Technology Materials Research Center. The patterns of the catalysts were examined in the range at $2\theta=5-90^\circ$ angles and search match analysis was performed by a Panalytical Empyrean XRD with $\text{CuK}\alpha$ radiation in the region of 2θ between $10-90^\circ$.

- X-Ray Photoelectron Spectrometer (XPS) Analysis Conditions:

X-ray photoelectron spectroscopy (XPS) measurements were performed by Thermo Scientific K-Alpha in EGE-MATAL.

- BET Analysis Conditions:

The specific surface area and pore size distribution measurements were performed on a Mikromeritics Gemini V analyzer using BET function in Centers for Material Research, İzmir Institute of Technology. Pre-heating process was applied for all prepared catalysts at 350°C for 3 hours and then, specific surface area of the catalysts were evaluated.

4.4. Application of Advanced Oxidation Processes

4.4.1. Photo Fenton-Like Oxidation

4.4.1.1. Experimental Set-up and Procedure

Photo Fenton-Like Oxidation (PFLO) studies were performed in 250mL beakers using UV light or visible light sources. In this study, 80 W perforated lamp preferred as the visible light source. As the UV light sources, 2 unit, 6 Watt UV-C lamps with a wavelength of 254 nm were preferred. Experiments were carried out in a 250 mL beaker using 200 ml of pharmaceutical wastewater with magnetic stirrer. The initial pH of the wastewater is 4. 0.1 HCl or NaOH solutions were used to adjust the pH to the required value. The solution was prepared at determined concentration and different amounts of hydrogen peroxide and different amounts of catalyst were added in each experiment. The reaction was lasted for 90 min. to the solution for 90 min. (30 min. on the dark side, 60 min. in the presence of light). Samples were analyzed at the specified time intervals. The experimental setup is given in Figure 4.4.



Figure 4.4: Experimental set up of PFLO

4.4.1.2. Experimental Plan

In order to determine the best selective catalyst for PFLO studies, the following screening tests were performed (Figure 4.5):

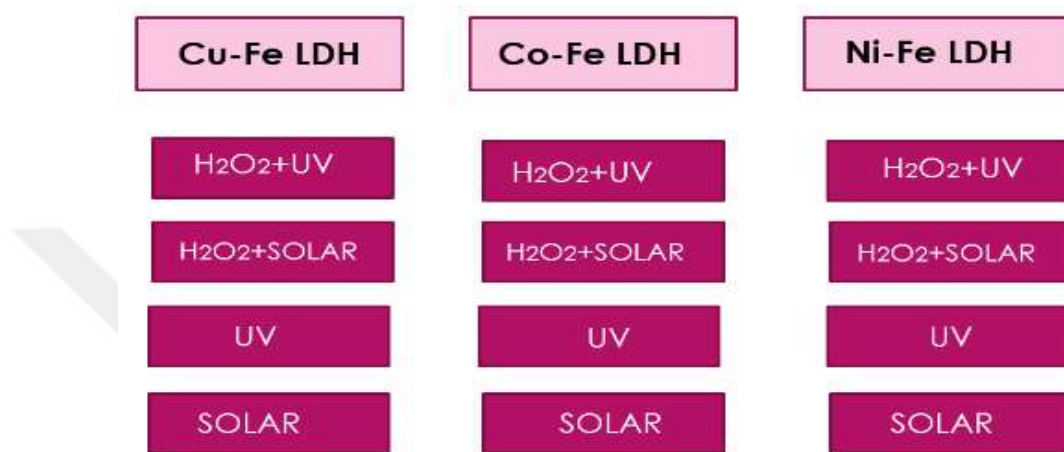


Figure 4.5: Catalyst Selection Experiments for PFLO

As shown in Figure 4.5, the performances of the three different catalysts (Fe-Cu LDH , Fe-Co LDH , Fe-Ni LDH) were tested with two different lights UV light and Solar light (Visible light) at the following conditions:

Operating conditions: H₂O₂= 1mM, OTC-HCl =50 ppm, Catalyst loading=0.5 g/L, pH=4.

The most suitable catalyst was determined by the results of the stated experiments.

To optimize the experimental conditions for the PFLO of OTC-HCl, a statistical approach was applied using the Box-Behnken Design (BBD) model. This design expert software allowed the set of experiments to be developed. Three factors of three levels pH (X_1), catalyst loading (g/L) (X_2) and initial H_2O_2 concentration (ppm) (X_3) were used to determine the model coefficients in quadratic terms (Table 4.2). The chosen levels of the independent variables were based on literature reports (Mikami et al., 2016; Khataee et al., 2019). Three replicates were performed at the central point. The experimental response was the removal of OTC-HCl.

Table 4.2 :Independent factors and levels used for Box-Behnken design

Coded Factor	Factor	Coded Level		
		-1	0	+1
X_1	pH	4	7	10
X_2	catalyst loading (g/L)	0.5	1.5	2
X_3	H_2O_2 concentration (mM)	0	1	2

The proposed reactions conditions are tabulated in Table 4.3:

Table 4.3: Parametric study experimental plan for PFLO

Experiment No	pH	Catalyst Loading	Hydrogen-Peroxide Concentration
1	4	0.5	1
2	10	0.5	1
3	4	1.5	1
4	10	1.5	1
5	4	1	0
6	10	1	0
7	4	1	2
8	10	1	2
9	7	0.5	0
10	7	1.5	0
11	7	0.5	2
12	7	1.5	2
13	7	1	1
14	7	1	1
15	7	1	1

4.4.1.2.1 Scavenger Effect

To determine role of active radicals on PFLO of OTC-HCl over most selective catalyst, methanol and isopropyl alcohol were used as scavengers.

The effect of radical scavengers was searched in order to determine which radical is more effective in the optimum reaction conditions determined as a result of the optimization studies. Methanol and isopropyl alcohol were used as scavengers. Scavengers were previously used to capture hydroxyl radicals generated in the reaction medium. Catch performances were compared by loading different doses. The ratio of the initial concentration of the HO scavenger to the H₂O₂ concentration was determined as 20.

4.4.2. Catalytic Wet Air Oxidation

4.4.2.1. Experimental Set-up and Procedure

The catalytic wet air oxidation experiments were performed in high pressure autoclave type stainless steel reactor (500 mL) that is shown in Figure 4.6 below. For a typical run following procedure is applied:

- pH adjustment is performed for wastewater according to experiment conditions (if required)
- 300 mL of oxytetracycline hydrochloride solution is charged into reactor and catalyst is added.
- the temperature and agitation speed are adjusted.
- cold water circulator is switched on to keep temperature at the set temperature.
- Samples are taken by help of sample valve.
- Analysis are realized.



Figure 4.6: Catalytic wet air oxidation experimental set-up

4.4.2.2. Experiments

In order to determine the best selective catalyst for CWAQ studies, the following screening tests were performed (Figure 4.7):

As shown in Figure 4.7, the performances of the three different catalysts (Fe-Cu LDH, Fe-Co LDH, Fe-Ni LDH) were tested.

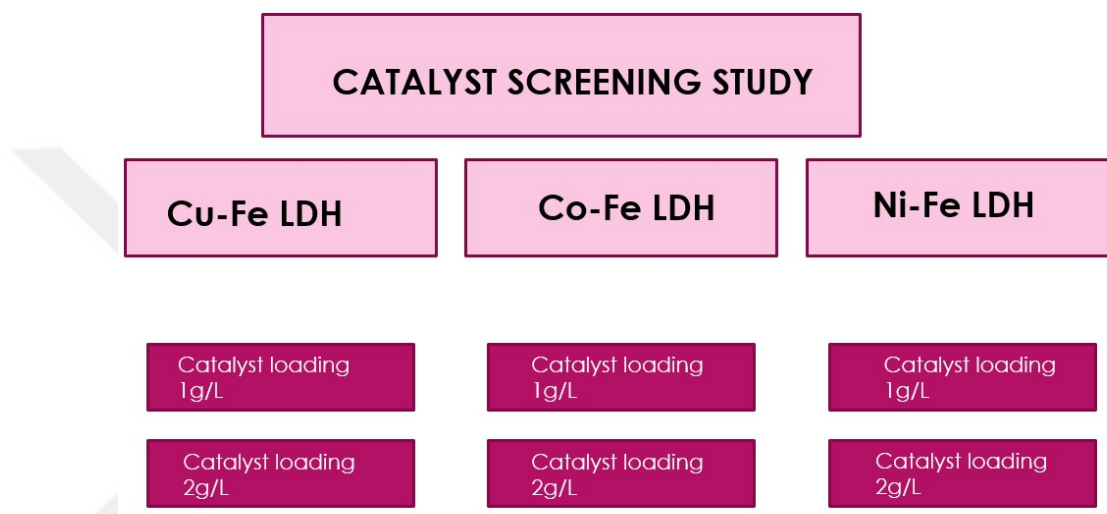


Figure 4.7: Catalyst Screening Study

Catalyst screening experiments were realized with 300 mL aqueous solution of 50 ppm oxytetracycline different amounts of catalyst loading (1g/L and 2g/L) under constant pH (pH=4), temperature (T=50°C) and pressure (P=1atm) conditions. Selection was made with different amounts of catalyst loadings. The most suitable catalyst was selected with the experiments. By using the selected catalyst, a parametric experimental plan was made considering the Box-Behnken design of the Minitab program.

The conditions of the CWAQ method were optimized using the response methodology for 3 variables (n = 3) which are temperature (X₁), pH (X₂) and catalyst loading (X₃) (given in Table 4.4).

Table 4.4: Independent factors and levels used for Box-Behnken design

Coded Factor	Factor	Coded Level		
		-1	0	+1
X₁	Temperature (°C)	30	50	70
X₂	pH	4	7	10
X₃	Catalyst Loading (g/L)	0.5	1.25	2

The proposed reactions conditions are tabulated in Table 4.5

Table 4.5: Parametric study experimental scheme for CWAO

Experiment No	Temperature (°C)	pH	Catalyst Loading (g/L)
1	50	7	1.25
2	30	10	1.25
3	70	7	0.5
4	30	4	1.25
5	50	7	1.25
6	30	7	2
7	70	10	1.25
8	30	7	0.5
9	50	4	2
10	50	7	1.25
11	50	4	0.5
12	70	7	2
13	50	10	0.5
14	70	4	1.25
15	50	10	2

4.5. Analysis

4.5.1 UV-VIS Spectrophotometer

In this study, the process performance was evaluated by considering oxytetracycline hydrochloride concentration values. UV-VIS Spectrophotometer (Thermo Genesys 10S) was used to measure the concentration of polluting water. The oxytetracycline solution had two strong ultraviolet absorption peaks near 275 and 355 nm (Nchima et al., 2017).

Figure 4.8 depicts the oxytetracycline absorption spectrum, with maximum absorption at about 275 nm attributed to the absorption of the chromophore formed by the hydroxyl groups of the molecule's A ring. The maximum at about 354 nm. During this study, the absorbance at 275 nm was considered.

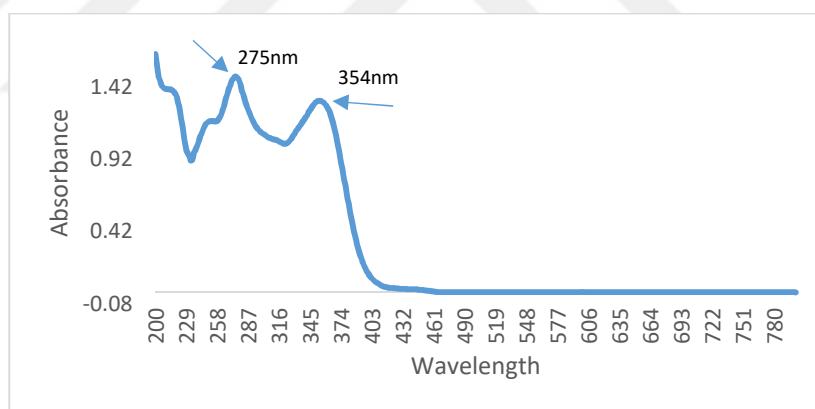


Figure 4.8: UV-vis absorption spectrum of OTC

Efficiency are calculated using the following equation:

$$Removal \% = \frac{C_0 - C_f}{C_0} \times 100$$

C_0 : initial concentrations C_f : final concentrations



Figure 4.9: UV Spectrophotometer

The calibration curve used to determine the concentrations is plotted in Figure 4.10.

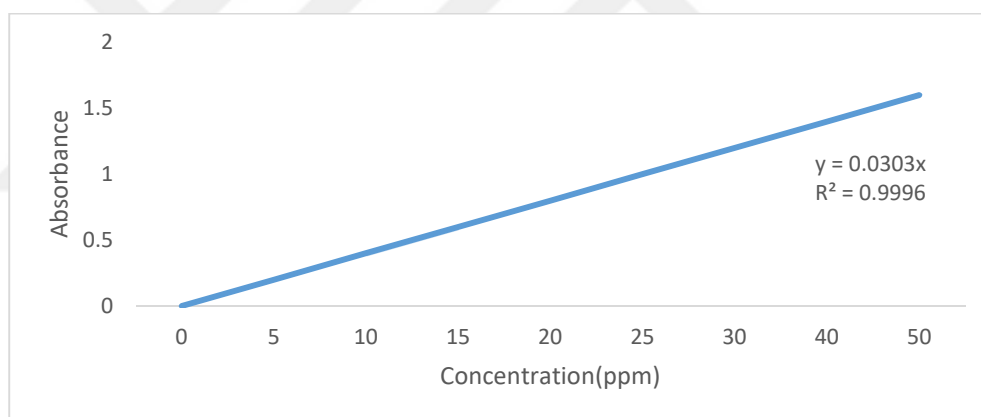


Figure 4.10: Calibration curve of OTC-HCl for UV-VIS spectrophotometer

4.5.2 Toxicity Test

In order to examine the presence of toxic elements, toxicity tests were applied by measuring the root length of the seeds germinated in the waste water resulting from CWAO and PFLO processes. 5 mL of liquid sample per petri dish was added on 15-20 seeds placed on two layers of filter paper and left for 3 days. After 3 days, root lengths were measured and the parameter was calculated from this equation:

$$\text{Growth Inhibition} = \frac{L_0 - L_i}{L_0} \times 100$$

5.0 RESULTS AND DISCUSSION

5.1. Characterization of Catalysts

5.1.1. Scanning Electron Microscopy Analysis (SEM-EDX)

The morphological characteristics of Cu-Fe LDH, Co-Fe LDH, Ni-Fe LDH catalysts in fresh and used forms were measured by SEM images and are shown in Figures 5.1-5.6, respectively. The catalysts were examined by SEM analysis in the range of scale bar: 500nm (0.5 μ m) -1 μ m-2 μ m.

All of the prepared samples have the typical layered structure of LDH. On the SEM images, some aggregated and rounded particles with planar/lamellar structure may be observed

The outer surface of the Cu-Fe LDH catalyst consists of pentagonal and hexagon-like spaces partition separate and wall. Micrographs of the catalysts show they are almost homogeneous and they have leaf like structures.

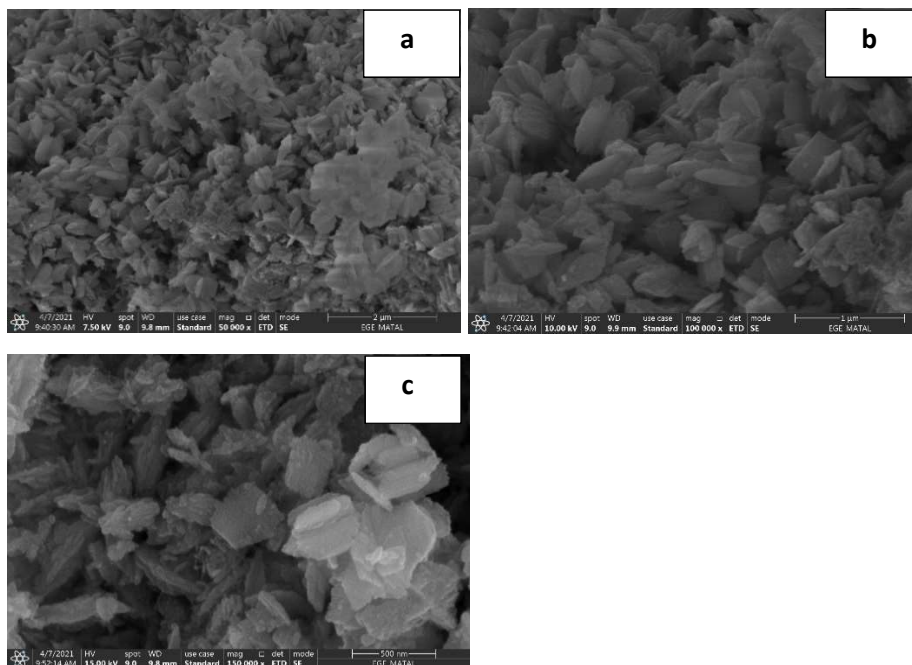


Figure 5.1: SEM images of Cu-Fe-LDH fresh catalyst at various (a)2 μ m(b)1 μ m(c) 500(0.5 μ m)nm

According to the Figure 5.2, the surface structure of Ni-Fe LDH catalyst has a homogeneous structure containing small particles. The pores on the catalyst surface are shown as rough texture. Generally the samples present aggregates of poorly defined shapes. the Ni-Fe-LDH consists of thin layers and coacervates which is the typical product by the co-precipitation method.

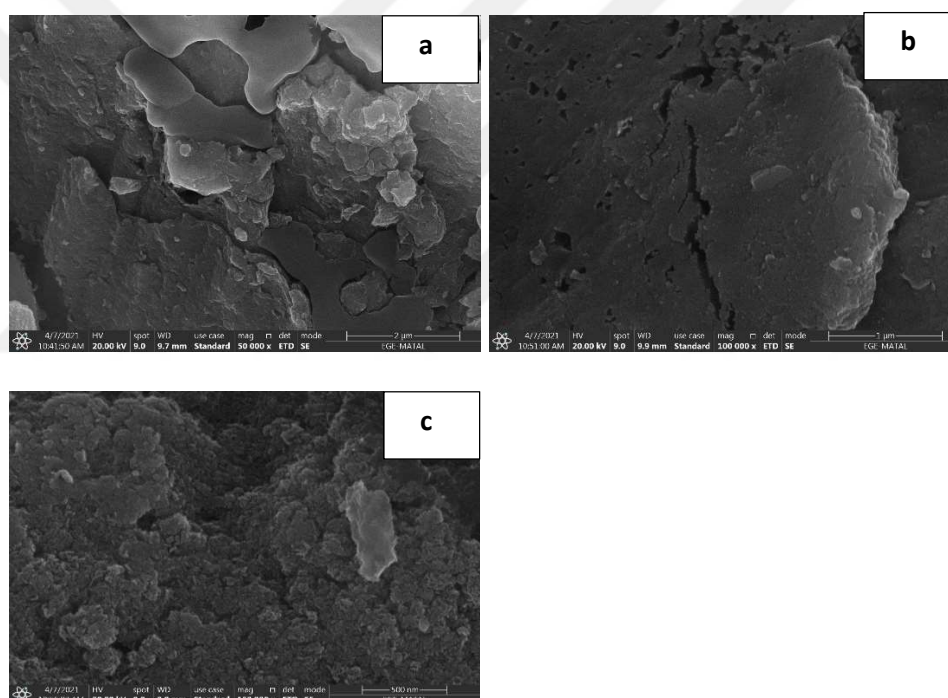


Figure 5.2: SEM images of Ni-Fe LDH fresh catalyst at various (a) 2μm (b) 1μm (c) 0.5μm

The SEM of Co-Fe-LDH shows elliptical plate-like particles (Figure 5.3) supports the formation of LDH in the CoFe bimetallic compound. In general the plate-like particles are aggregated and seems to be piled.

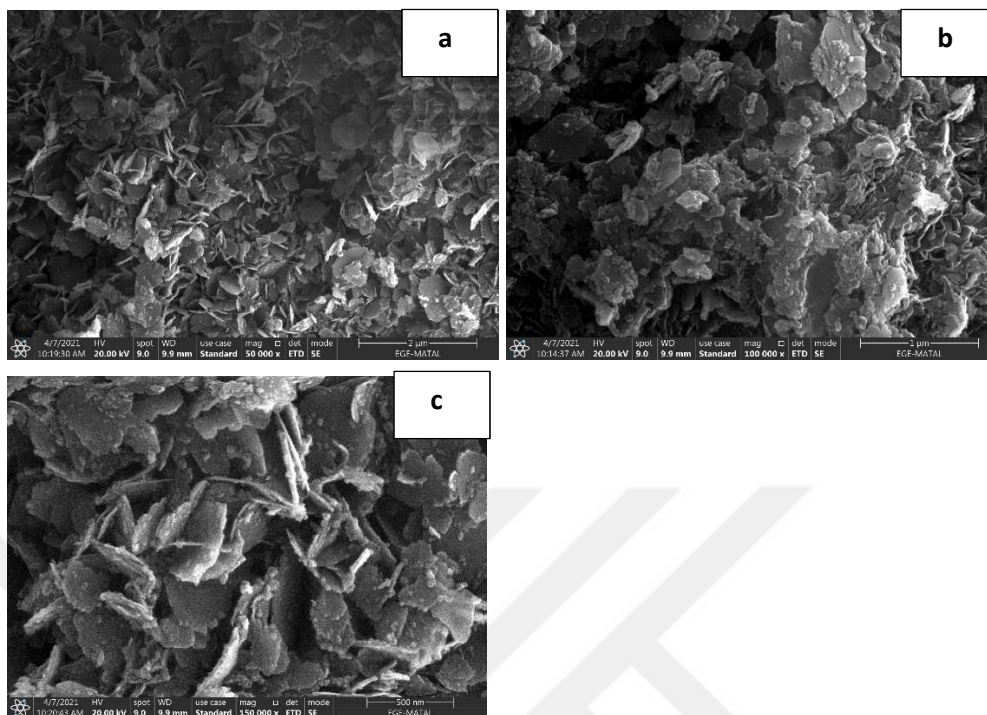


Figure 5.3: SEM images of Co-Fe LDH fresh catalyst at various (a) 2 μm (b) 1 μm (c) 0.5 μm

According to SEM micrographs of the used catalysts, no significant differences were found in the catalyst samples. SEM micrographs of the re-used catalysts are given in the Figures 5.4 - 5.6 below.

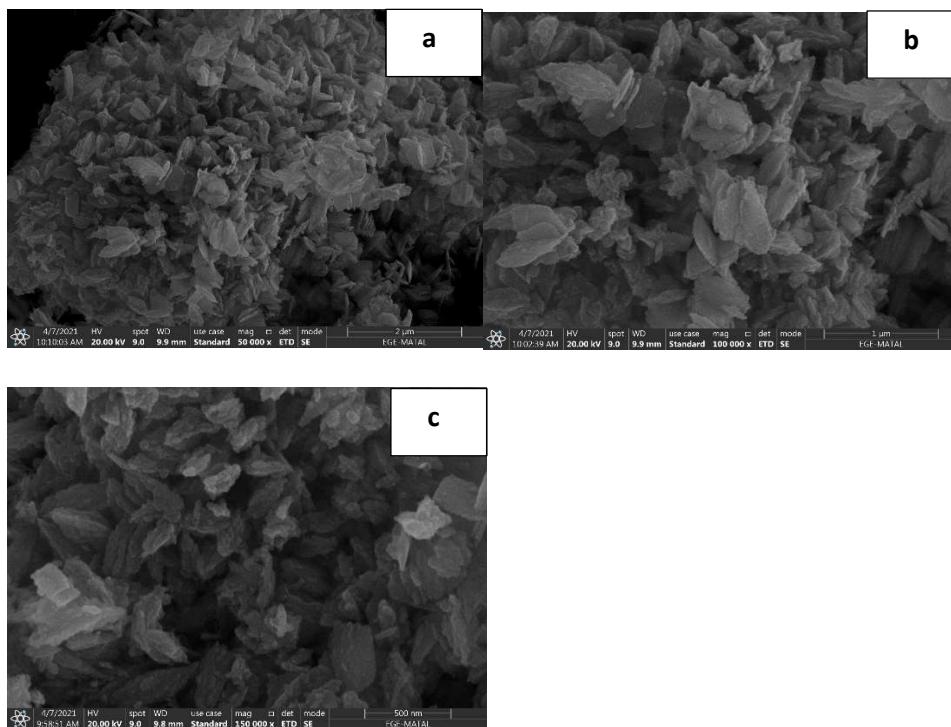


Figure 5.4: SEM images of Cu-Fe LDH 2nd use catalyst at various (a) 2 μm (b) 1 μm (c) 0.5 μm

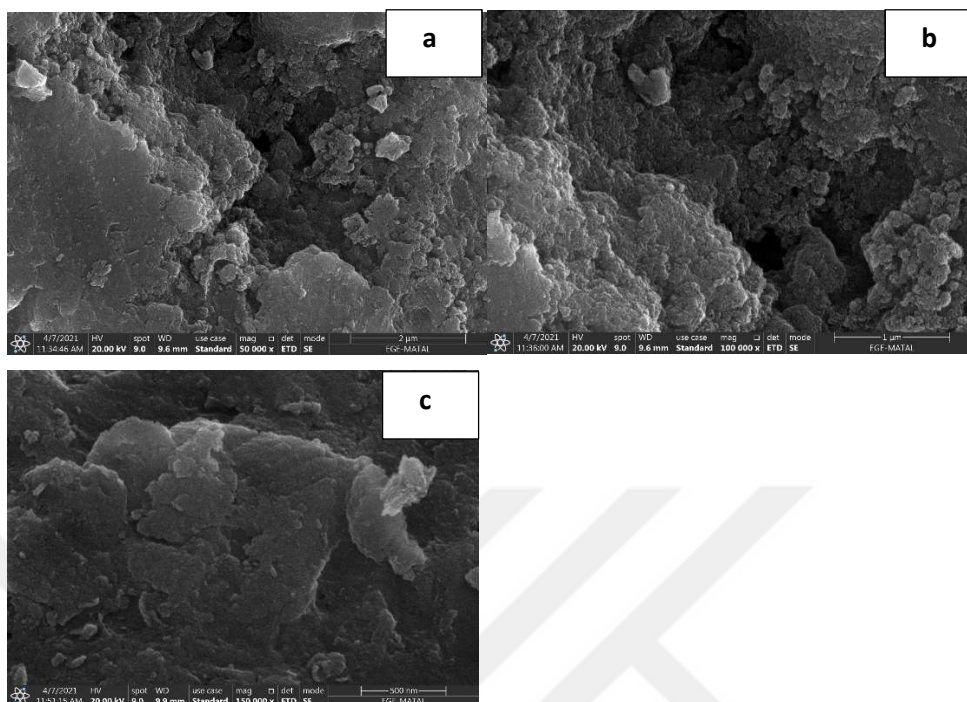


Figure 5.5: SEM images of Ni-Fe-LDH 2nd use catalyst at various (a) 2 μm (b) 1 μm (c) 0.5 μm

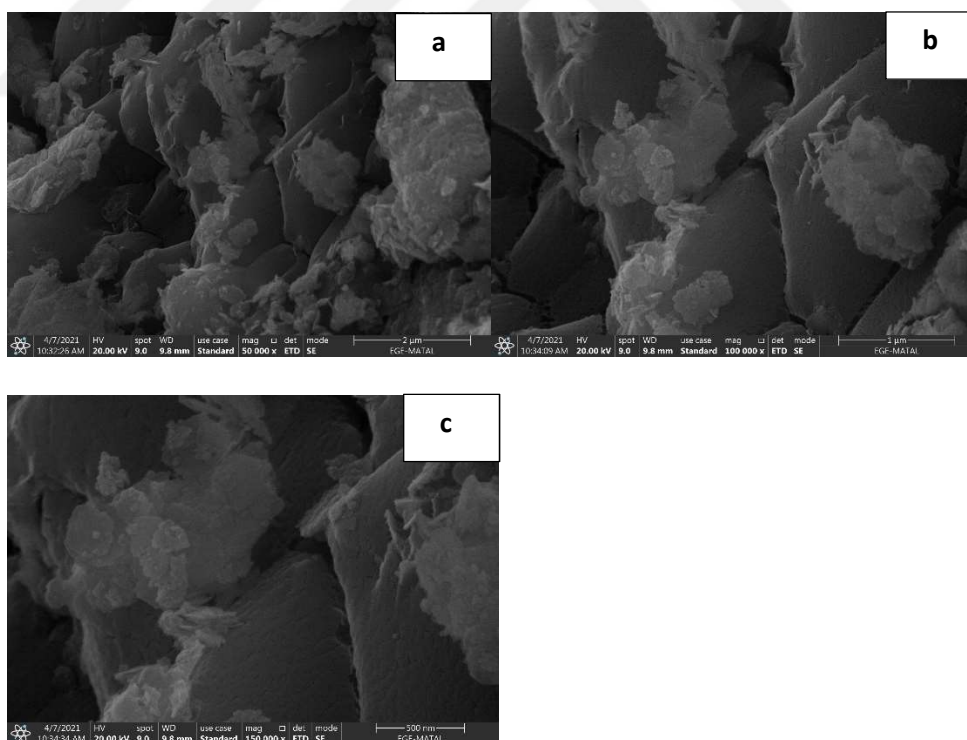


Figure 5.6: SEM images of Co-Fe-LDH 2nd use catalyst at various (a) 2 μm (b) 1 μm (c) 0.5 μm

The results of the elemental analysis of Cu-Fe LDH by EDS are shown in Figure 5.7 and Table 5.1.

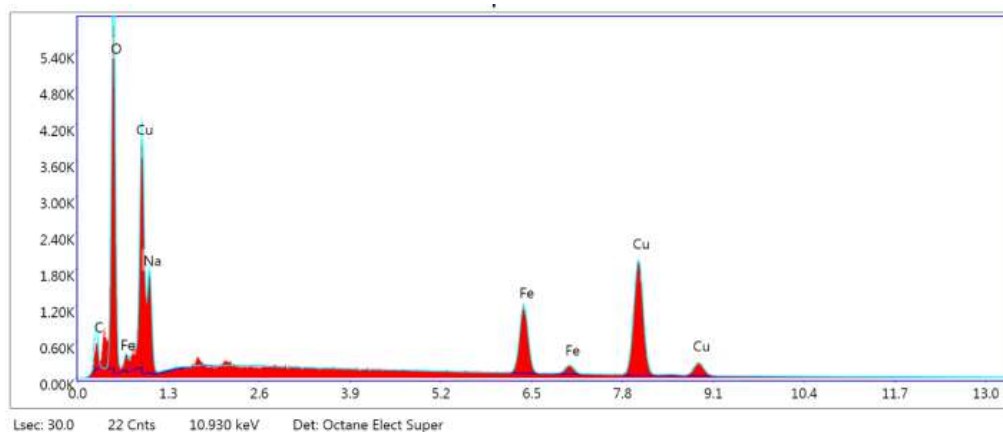


Figure 5.7: The elemental analysis of Cu-Fe LDH by EDS.

Table 5.1: Elemental distribution elements on Cu-Fe LDH catalyst surface

Element	Weight (%)	Atomic (%)
C K	11.54	23.57
O K	27.67	42.44
Na K	14.58	15.56
Fe K	10.94	4.81
Cu K	35.27	13.62

The elements found in the EDS analysis of the Cu-Fe LDH catalyst were confirmed to be C, O, Na, Fe, Cu. Quantitative analysis in Table 5.1 showed that Cu and Fe wt% contents are 35 and 10, respectively.

Elemental distribution elements on Cu-Fe LDH catalyst surface shows that the molar ratio of Cu/Fe is 3.07. This value is in good agreement with the value of 3, which is the ratio that was aimed for when preparing the corresponding LDH catalyst.

The elemental analysis of Co-Fe LDH catalyst are shown in Figure 5.8 and Table 5.2.

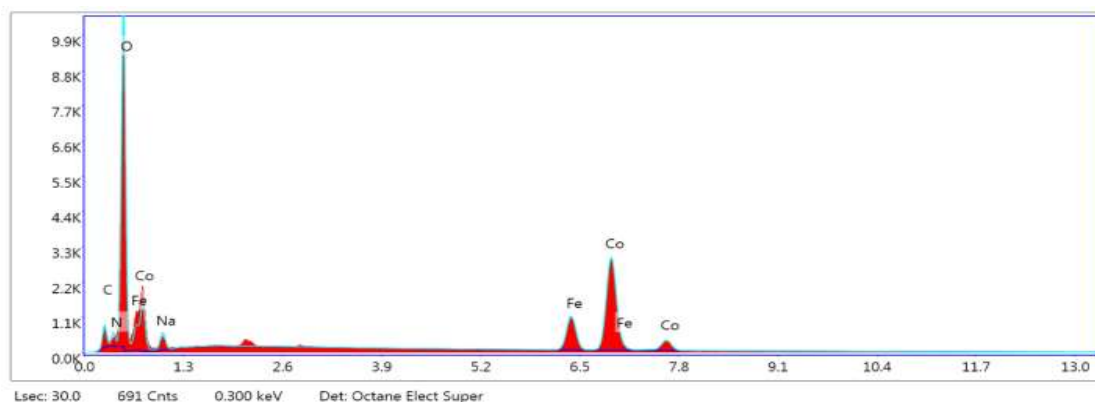


Figure 5.8: The elemental analysis of Co-Fe LDH by EDS.

Elemental distribution elements on Co-Fe LDH catalyst surface shows that the molar ratio of Co/Fe is 4. This ratio is slightly higher than the target corresponding 3 molar ratio.

Table 5.2: Elemental distribution elements on Co-Fe LDH catalyst surface

Element	Weight %	Atomic %
C K	11.63	22.67
N K	2.55	4.26
O K	34.80	50.93
Na K	2.67	2.72
Fe K	9.23	3.87
Co K	39.12	15.55

The elemental analysis of Ni -Fe LDH by EDS is shown in Figure 5.9 and Table 5.3.

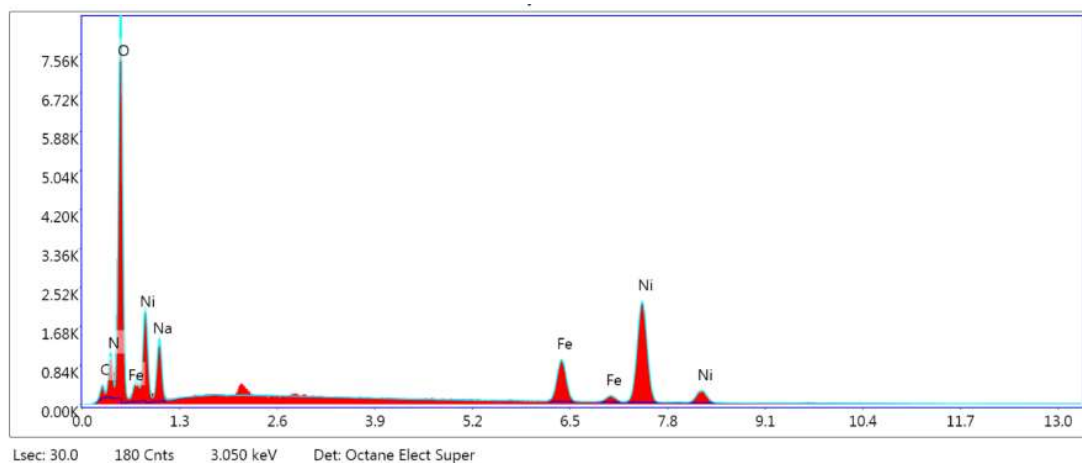


Figure 5.9: The elemental analysis of Ni -Fe LDH by EDS.

Table 5.3: Elemental distribution elements on Ni-Fe LDH catalyst surface

Element	Weight %	Atomic %
C K	4.02	7.68
N K	7.55	12.36
O K	36.40	52.19
Na K	11.97	11.95
Fe K	8.61	3.54
Ni K	31.45	12.29

The elements found in the EDS analysis of Ni-Fe LDH catalyst were confirmed to be C, O, Na, Fe, Ni. Quantitative analysis in Table 5.3 showed that there are Ni (31 wt%), Fe (wt%) in the Ni-Fe-LDH catalyst structure. This elemental distribution on Ni-Fe LDH catalyst surface shows that the molar ratio of Co/Fe is 3.47.

5.1.2. X-ray diffraction analysis (XRD)

X-ray diffraction (XRD) analysis was used to investigate the composition and structural parameters of Cu-Fe LDH, Ni-Fe LDH and Co-Fe LDH catalysts. XRD patterns of catalysts can be investigated in Figure 5.10.

The XRD patterns of LDH catalysts generally show the characteristic peaks of hydrotalcite-like compounds, sharp, high intensity peaks at lower 2θ values and low intensity peaks at higher 2θ values.

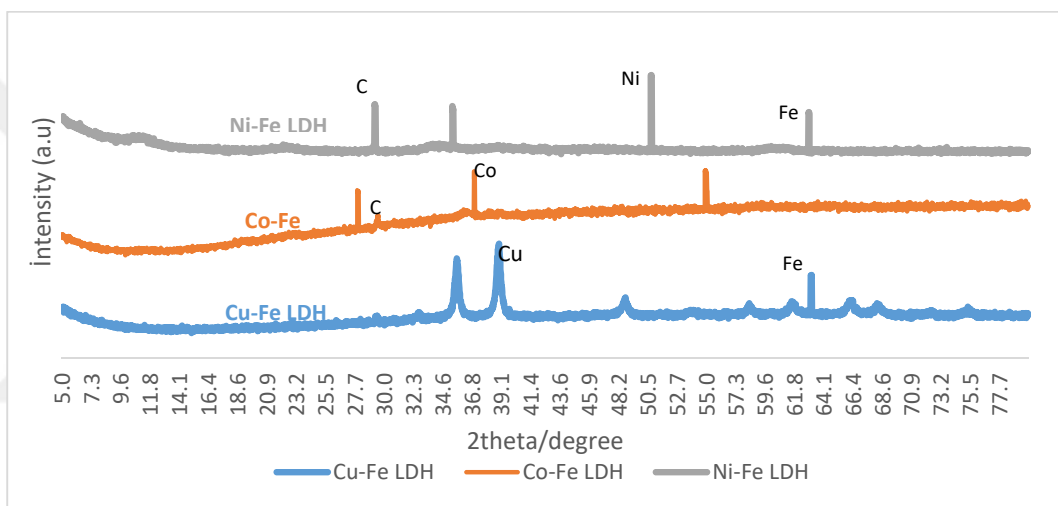


Figure 5.10 : XRD patterns of the catalysts

The diffraction peaks at 27.1° , 29.5° , 36.1° , 55.2° are indexed into (006), (105), (015) and (110) planes of CoFe-LDH (Arif et al., 2019).

As shown in Figure 5.10, Cu-Fe LDH displayed several sharp diffraction peaks at the two theta angles of 35.9° , 38.9° , 48.5° , 58.0° , 61.8° , 63.2° , 66.1° , 68.2° , 75.2° . The XRD pattern showed that Cu-Fe-LDH was well crystallized with a typical layered structure.

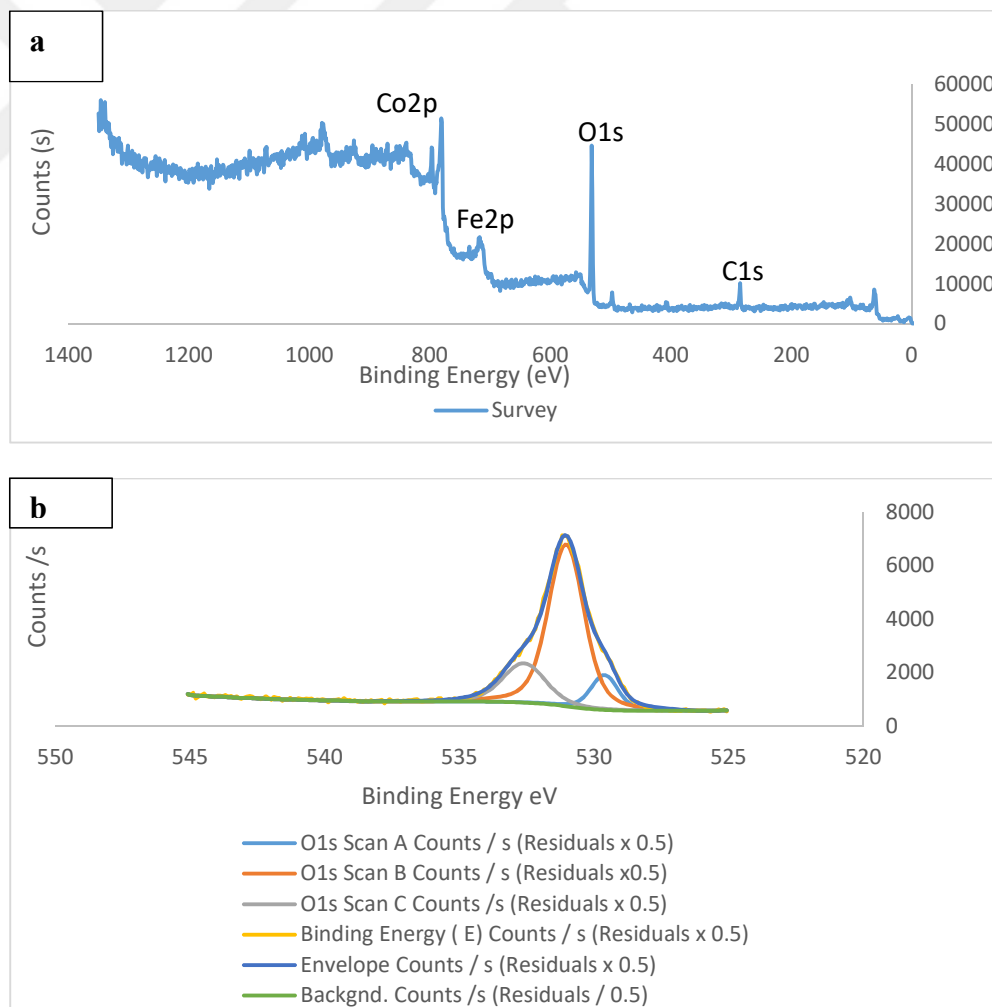
In the study of Liu et al., the results of XRD evaluation for Cu-Fe LDH catalyst are similar (Liu et.al, 2020).

Well-defined peaks at 11.6° , 29.3° , 35.5° and 50.8° are assigned to the planes of (003), (006) (015), (110) of the Ni-Fe LDH, respectively, confirming the formation of LDH crystals.

5.1.3. X-ray Photoelectron spectroscopy analysis (XPS)

XPS tests were performed in MATAL using the Thermo Scientific K-AlpHa analyzer. XPS analysis was used to investigate the surface chemical states of the catalysts. In order to determine the elements and their valences, the binding energy values were analyzed for Cu-Fe LDH, Ni-Fe LDH and Co-Fe LDH catalysts with the help of XPS.

Cu, Fe, Ni, Co, N, O, C elements were found in XPS analysis for three different catalysts. It was defined as Cu 2p scan, Fe 2p scan, Ni 2p scan, Co 2p scan, O 1s scan, C 1s scan.



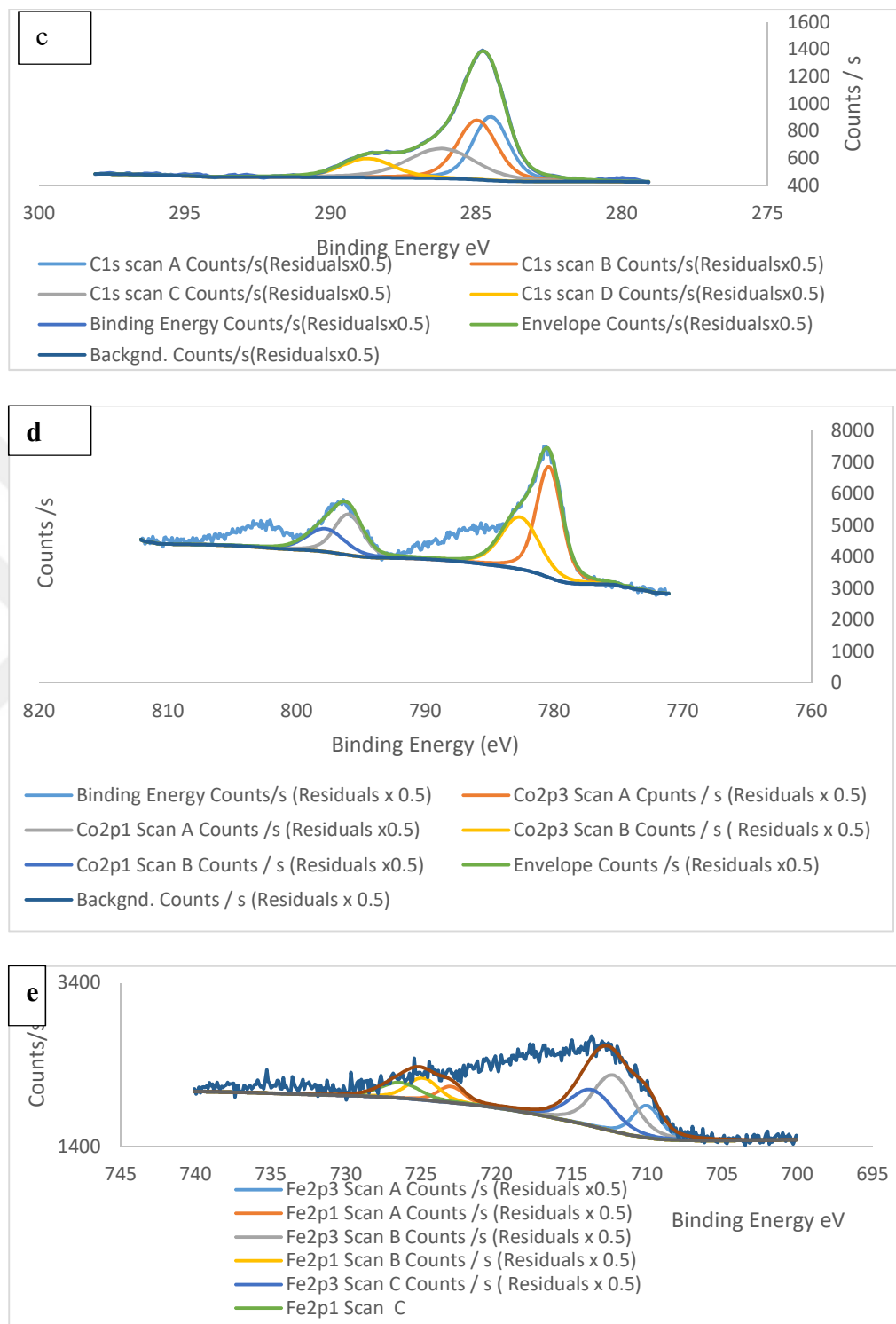
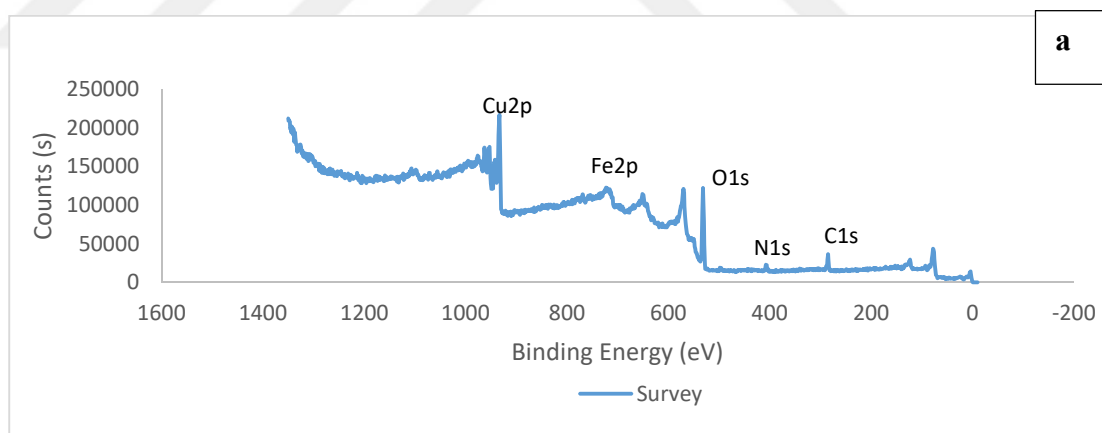


Figure 5.11: XPS spectra of Co-Fe LDH (a) Survey (b) O Scan (c) C scan (d) Co scan (e) Fe scan

The C 1s spectrum in Figure 5.11 has peaks at 288.78, 286.18, 284.98, 284.48, 284.88, 284.78 eV. The C1s spectrum typically has C-C, C-O-C and O-C=O components. The C-C bond exists at a binding energy of 284.8 eV. The peaks seen at 284.78 eV and 284.88 eV can be associated with the presence of CC bonding. The C-O-C bond is seen at 286 eV. The peak of scan C at 286.18 eV can be interpreted as the presence of the C-O-C bond. The O-C=O bond appears at 288.5eV. The peak of C1s scan D is 288.78 eV. This peak can be interpreted as the presence of O-C=O bond (://xpssimplified.com/periodictable.php, 2019).

The O 1s spectrum has peaks at 532.58 eV, 531.08 eV, 531.08 eV 530.98 eV, 529.58 eV. C=O bond is seen at 531.5-532 eV. The peak seen at 531.08 eV indicates the presence of a C=O bond. The Fe 2p spectrum has peaks at 726.58, 724.98, 723.08, 713.88, 713.68, 712.38, 710.08 eV. A peak of about 709.6 eV is expected in the presence of Fe-O bonding. The peak observed at 710.08 eV indicates the presence of Fe-O bonding (Xiao et al., 2020; Bastami et al., 2017).



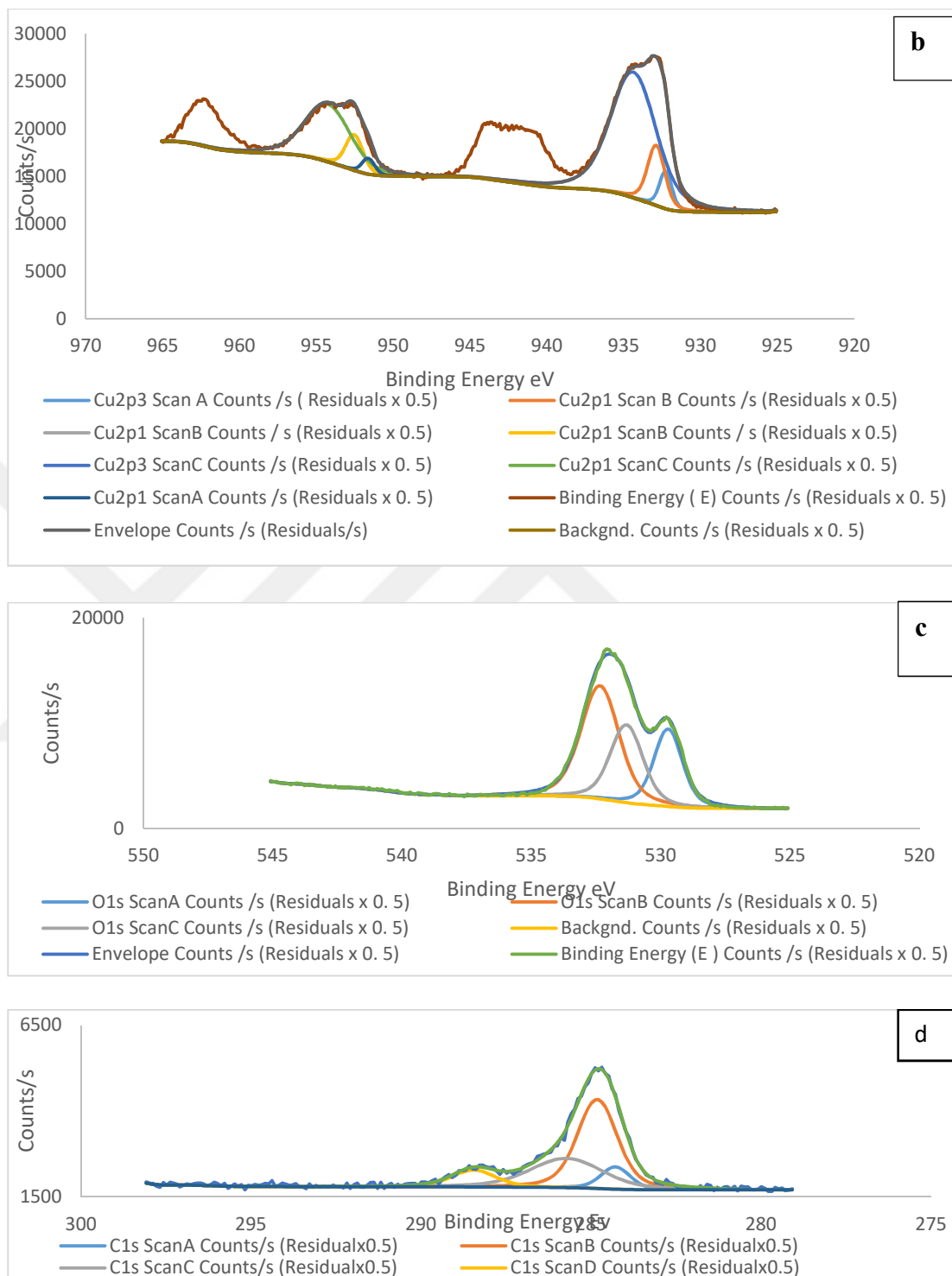
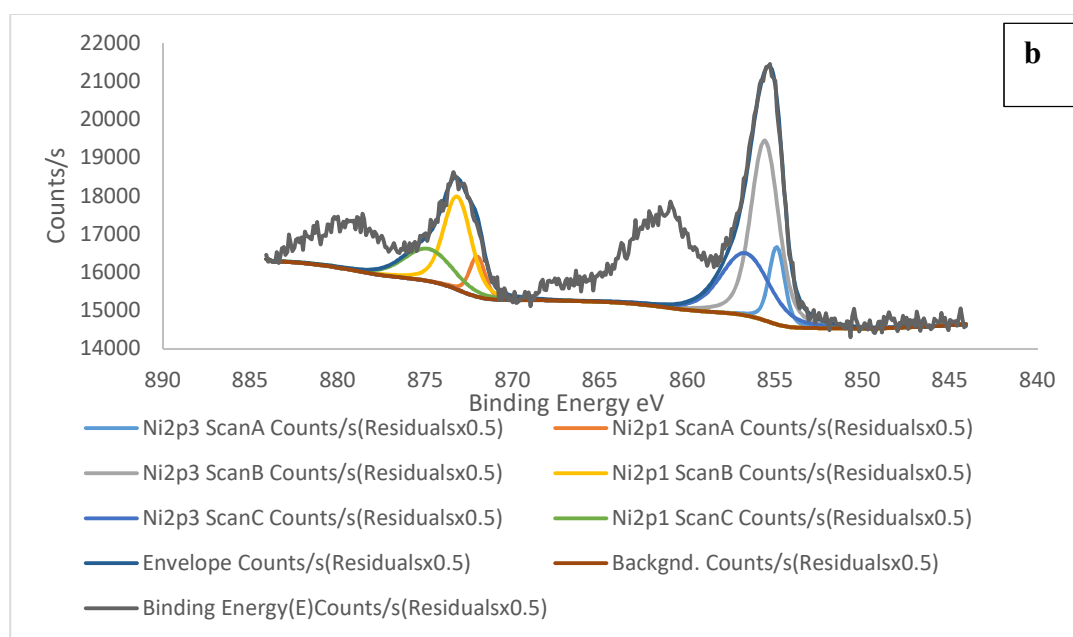
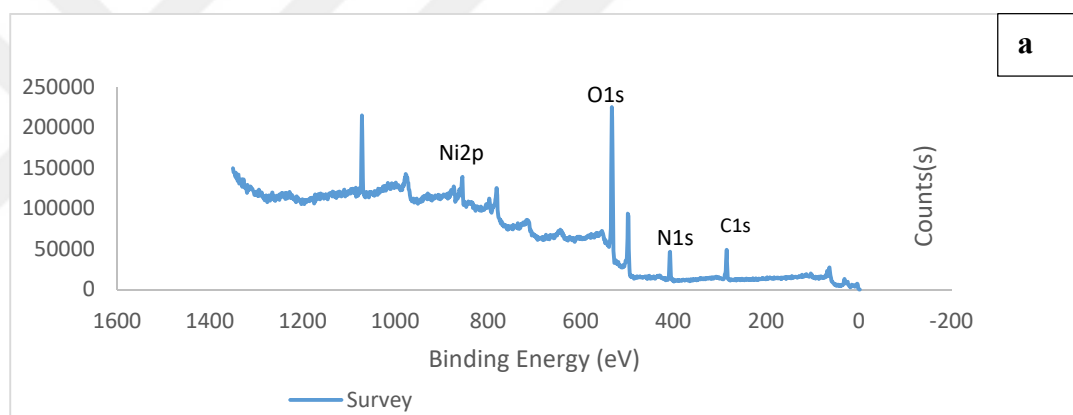


Figure 5.12: XPS spectra of Cu-Fe LDH (a) Survey (b) Cu Scan (c) O scan (d) C scan

The Cu 2p spectrum in Figure 5.12 has peaks at 954.48, 952.58, 934.48, 933.08, 932.88 eV. The Cu-O bond peaks at 933 eV. The peak observed at 933.08 eV can be interpreted as the formation of the Cu-O phase. The peak value of 934.48 eV is

interpreted as Cu 2p^{3/2} binding energies, and the peak value of 954.48 eV is interpreted as Cu 2p^{1/2} binding energies and indicates the presence of Cu²⁺ element. In the studies in the literature, the peaks for copper are given as 934.9 eV and 954.5 eV (Palas et al., 2019; Fan et al., 2010). The overlapping of the peaks confirms the study.

O1s spectrum gave peaks at 532.18, 532.08, 531.38, 529.68 eV. The peak seen at 531.18 eV indicates the presence of a metal C=O bond. In the C 1s spectrum, there are peaks at 288.58, 285.78, 284.78, 284.68, 284.38 eV. Peaks around 284.4 eV indicate C-C bonding. The peak seen at 285.78 eV indicates the presence of C-O-C bond. The peak seen at 288.58 eV can be interpreted as containing the C-O-C bond (<https://xpssimplified.com/periodictable.php>, 2019).



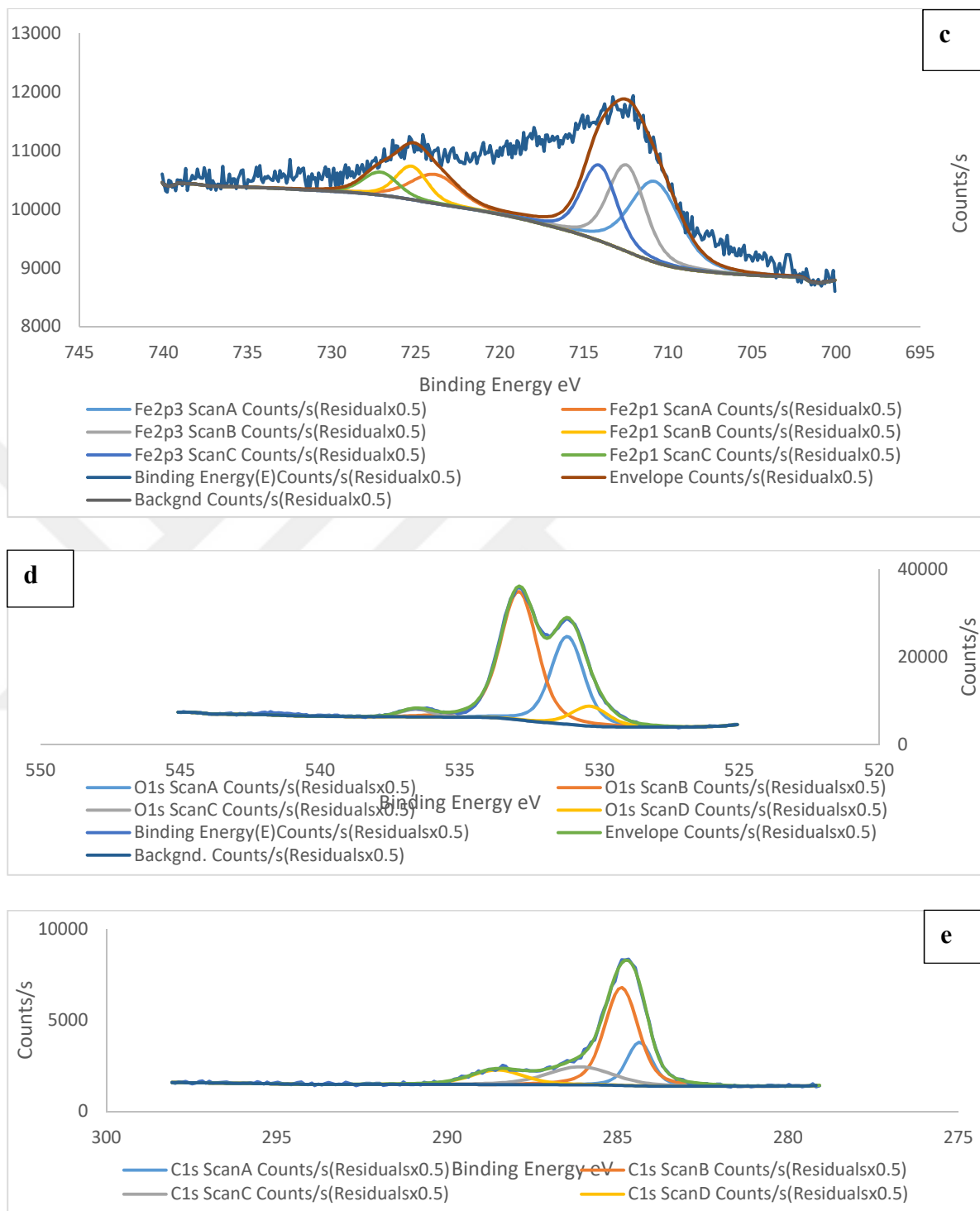


Figure 5.13 : XPS spectra of Ni-Fe LDH (a) Survey (b) Ni Scan (c) Fe scan (d) O scan (e) C scan

In the Ni 2p spectrum, the peaks are at 872.08, 856.78, 855.58, 855.28, 854.88 eV points. The peak seen at 854.88 eV can be interpreted as the presence of Ni-O bond. Ni-O bonding gives a peak at approximately 853.7 eV. The peak seen at 855.28 eV can be interpreted as the presence of Ni(OH)₂, this group is observed at about 855.6 eV (Kumar et al., 2022).

Fe 2p spectrum has peaks at 727.18, 725.28, 723.98, 714.18, 712.48, 710.88 eV. Fe 2p^{3/2} The peak seen at 710.88 eV is interpreted as the presence of Fe₂O₃. Fe₂O₃ peaks at about 710.8 eV. The binding energy of 723.98 eV appeared at the Fe 2p^{1/2} peak. These peaks confirm that iron exists in the +3 oxidation state. The O 1s spectrum has peaks at 541.98, 537.18, 536.58, 532.88, 531.18, 530.38 eV. The peak seen at 530.38 eV indicates the presence of metal oxides. The peak seen at 531.18 eV can be interpreted as the presence of C=O bond. There are peaks at 288.58, 286.08, 284.88, 284.38 eV points in the C1s spectrum. The peak seen at 284.38 eV indicates the presence of C-C bond (<https://xpssimplified.com/periodictable.php>, 2019).

5.1.4. BrunauerEmmett-Teller Analysis (BET)

BET results of Cu-Fe LDH, Ni-Fe LDH and Co-Fe LDH catalysts are shown in Table 5.4.

Table 5.4: Surface area and pore size analysis results for Cu-Fe LDH, Ni-Fe LDH and Co-Fe LDH catalysts

Property	Cu-Fe LDH	Ni-Fe LDH	Co-Fe LDH
BET Surface Area, m²/g	35.65	2.55	22.63
Pore Volume, cm³/g	0.134	0.125	0.164
Pore Size, Å	150.62	336.19	289.1

The results of the measurements of the surface areas of the LDH-structured catalysts show that the specific surface areas in this study are in good agreement with literature data. For example, surface area of 192 m²/g, pore volume of 0.5546 cm³/g and an average pore diameter of 41.7 Å were observed for Cu-Co-Fe LDH catalyst in literature (Lu et al., 2020).

In another study, the surface area, the pore volume and the average pore diameter for Ni-Fe LDH catalyst were determined as 82.04 m²/g, 0.242 cm³/g, 117.8 Å, respectively (Wang et al., 2021).

The results of N₂ adsorption, desorption tests of the catalysts are shown in Figure 5.14.

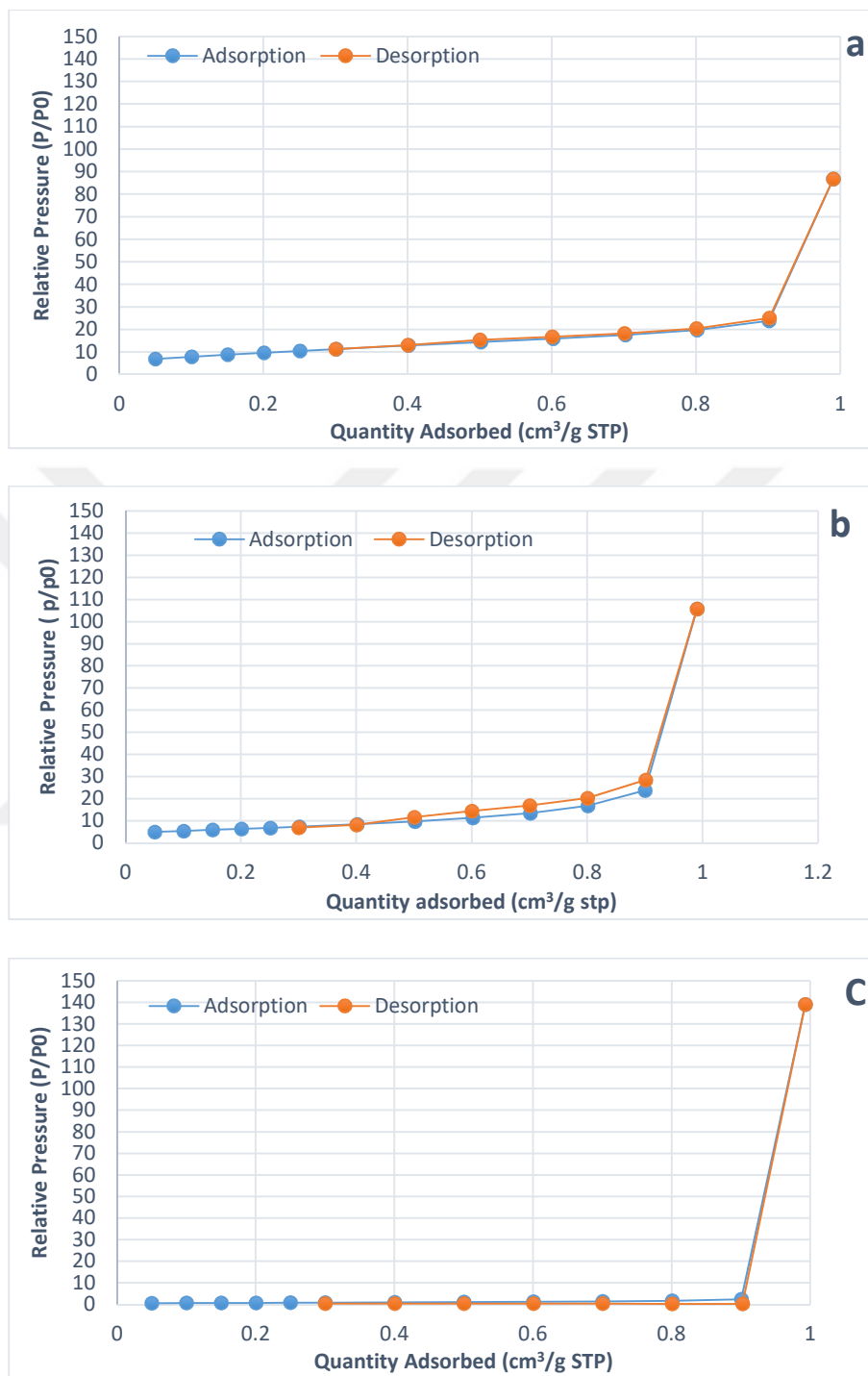


Figure 5.14 :N₂ adsorption/desorption isotherm of (a)Cu-FeLDH,(b)Co-FeLDH and (c)Ni-FeLDH

The N₂ adsorption-desorption isotherms of the three catalysts show similar typical type-III properties and support BET surface area analyses.

As state by the IUPAC classification of the isotherm, the N₂ adsorption isotherm within the three catalysts is similar to the Type-III isotherm showing multilayer structures. Type-III isotherm is convex with respect to the relative pressure axis throughout the entire range. For each catalyst, the P/P₀ value difference between adsorption and desorption was found to be <0, which tells microporous volume is relatively less. Based on IUPAC (International Union of Pure and Applied Chemistry) classification, the resemblance of H₃ type hysteresis loop reveals the existence of flat particles or slit-shaped pores (Tagliazucca et al.,2013; Liu et al., 2019).



5.2 Results of Photo-Fenton-like oxidation experiments

5.2.1 Catalyst screening

The performance of Photo Fenton-like oxidation removal of veterinary antibiotics of oxytetracycline wastewater was compared with three different double-layer catalysts (Cu-Fe LDH, Co-Fe LDH and Ni-Fe LDH). The reactions were carried out under isothermal condition in 250 mL glass-beakers using 2 different types of light sources (UV cabinet and visible light cabinet) with the help of a magnetic stirrer.

Catalyst efficiency was tested for three different catalysts (Cu-Fe LDH, Co-Fe LDH and Ni-Fe LDH) separately using two different cabinets. These tests were performed in absence of H_2O_2 at the original pH value ($\text{pH} = 4$) and the catalyst loading was 1.0 g/L for one and a half hours (30 minutes in the dark, 60 minutes in the presence of light).

In Table 5.5, the results of the examination of the photocatalytic performances of the catalysts through the removal of oxytetracycline solution under UV and visible light irradiation are given. By the results also the synergistic effect in the removal by addition of hydrogen peroxide to ultraviolet light or visible light can be investigated.

Table 5.5: Catalyst Screening experiments results

Oxytetracycline Removal (%)				
	UV Light	UV Light+ H_2O_2	Visible Light	Visible Light+ H_2O_2
Cu-Fe LDH	39.7	66.4	31.7	47.4
Co-Fe LDH	39.4	50.6	44.2	46.6
Ni-Fe LDH	32.1	40.1	42.8	49.5

Both light sources were able to remove the oxytetracycline from aqueous solution with a removal percentage between approximately 30-40% and addition of hydrogen peroxide had a considerable effect under both light sources. Cu-Fe LDH catalyst seems to be more effective with UV irradiation than the visible light where as the other two catalysts performances were better in visible light irradiation condition. It is decided to work with visible light source since solar spectrum has higher visible light spectrum when compared to UV light. The both Co-Fe LDH and Ni-Fe LDH catalysts under visible light showed similar efficiency and addition of hydrogen peroxide was more effective with Ni-Fe LDH. As mention before, prior to the Photocatalytic oxidation, the solutions were shaken in the dark medium for approximately 30 minutes to achieve the adsorption equilibrium of oxytetracycline on the catalysts surface. As seen in Figure 5.15, Ni-Fe LDH, catalyst seems to be more effective in potocatalytic oxidation (~35%).

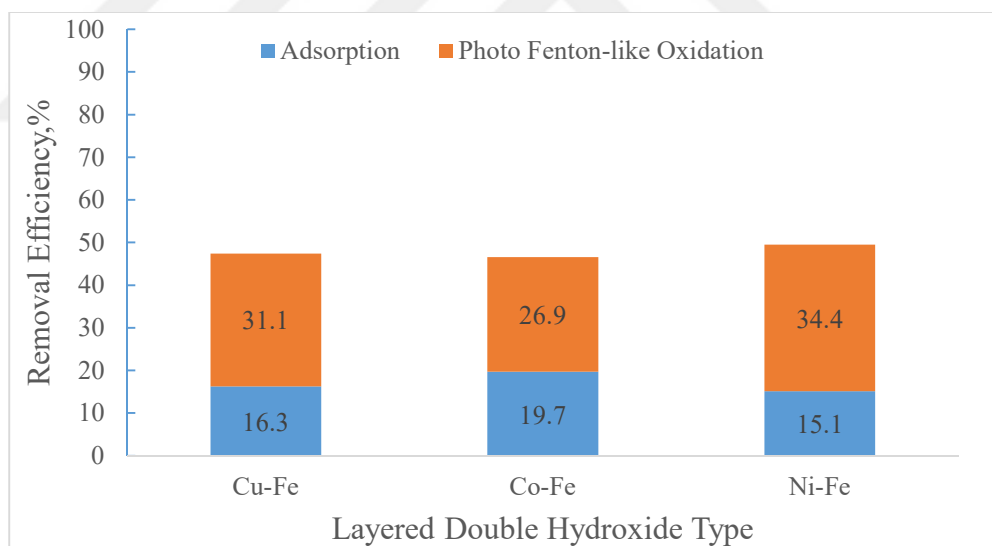


Figure 5.15: Results of Catalyst Screening Experiments

(no H_2O_2 $pH = 4$), catalyst loading 1,0 g/L, visible light)

Since the highest removal in the visible region was observed with Ni-Fe LDH catalyst, it was decided to continue with this catalyst in the optimization studies.

5.2.2. Parametric Study for Photo Fenton-like Oxidation

As a result of the catalyst screening experiments, Ni-Fe LDH, which provides the most effective removal as a catalyst, was used in parametric study. In this part of the study, the experiments were continued with 30 minutes of darkness and the remaining 60 minutes with the light on. The experimental plans of the parametric studies were formed using the Minitab17 program and the Box-Behnken design as a response surface method. The response surface methodology was applied to determine the effect of process variables the removal with a confidence level of 95% . The BoxeBehnken design method was used to find the combination of variables and optimize the experimental conditions study the effects of the four process variables, catalyst loading (0.5-1.5 g/L), H₂O₂ concentration (0-2 mM) and pH (4-10)were examined.

Because of this the experiments carried out the parametric experiment, maximum removal as achieved with 68%. The followings conditions are recommended for the maximum removal: pH 5, hydrogen peroxide concentration 1.5 mM and catalyst load 1.5 g/L. To assess the individual and interactive effects of independent variables pareto plot, surface and contour charts in which the variables influence and the interaction between two independent factors is shown were investigated.

5.2.2.1 The effect of catalyst loading and pH

In Figure 5.16, the effect of catalyst loading and pH for removal was evaluated. Maximum removal was achieved at pH 7 at all catalyst loading values. For example, when pH is increased from pH = 4 to pH = 7 at 1 g/L, removal increased from 49% to 56%. However, It can be concluded that the catalyst is more effective at neutral conditions. with the rise in the pH value from 7 to 10, a marked decrease is observed in the removal. Increasing the catalyst loading had a positive effect on removal efficiency since an increase in catalyst loading increases the available active sites. This effect is more considerable at neutral and basic conditions.

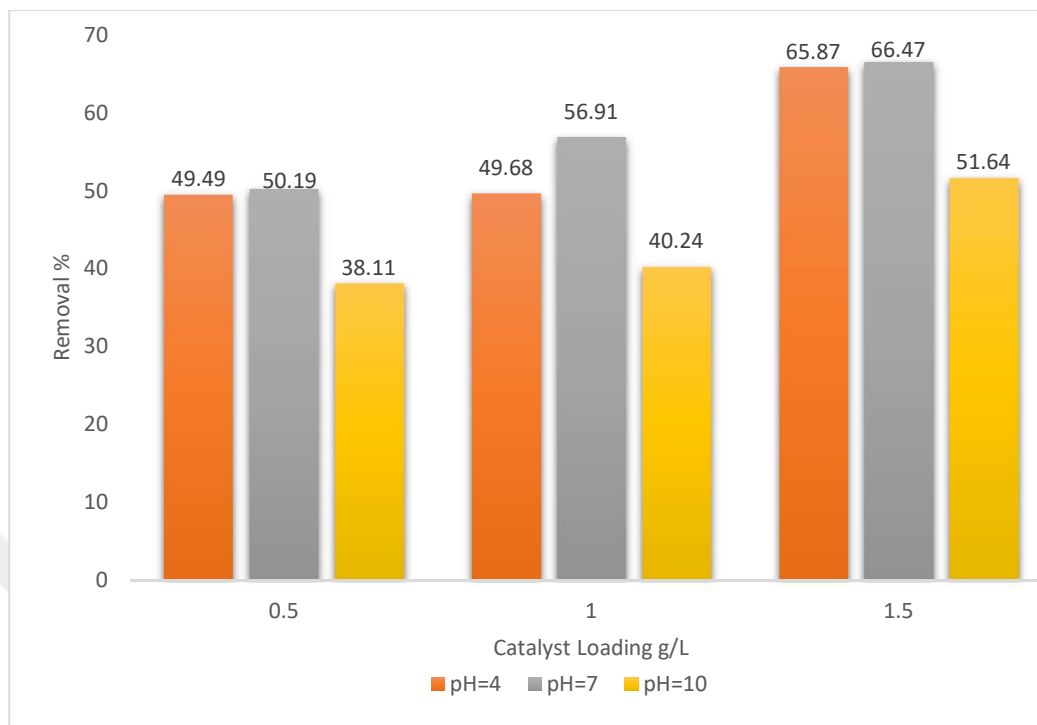


Figure 5.16: The effect of catalyst loading and pH
($[C]_0=50$ ppm, visible light, 90 min, room temperature)

As shown in Figure 5.17, the obtained results showed that the removal efficiency increased gradually as the initial pH increased from 4 to 7 to reach its maximum level, increasing the pH value further more caused a decrease in the removal. For example, when the catalyst loading was 1 g/L and the pH was 4, the removal was 49%. However, when the pH was increased to 7, the removal increased to ~57% where as at pH this value decreased to 40%, It is clear from this that low (pH=4) or high (pH=10) pH values have a negative effect on removal, while pH=7 results in maximum removal.

The removal percentage was found to increase with increasing the catalyst loading until reaching the optimal dosage of 1.5 g/L. For a constant pH value, for example, when pH=4, catalyst loading was tested at different loads. While the catalyst loading was 0.5 g/L, removal 49% was observed. Removal (65%) was obtained at the catalyst loading 1.5 g/L. However, removal decreased as the catalyst loading was urther increased. In the surface graph given, the catalyst loading was 1.5 g/L, and the maximum removal was reached at pH=7.

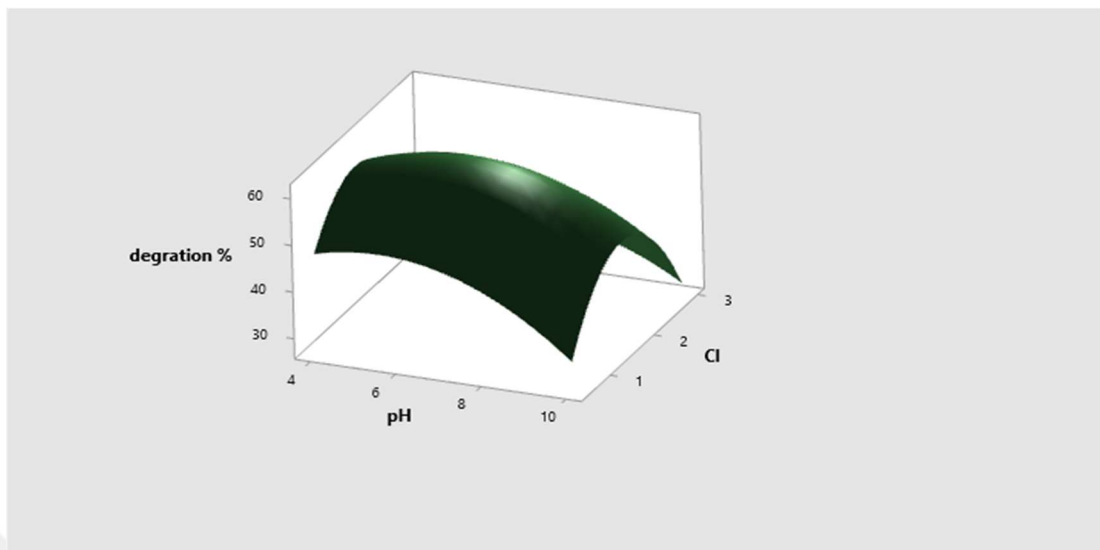


Figure 5.17: Effect of catalyst loading and pH on Surface diagram
($[C]_0=50$ ppm, $H_2O_2=1$ mM, visible light, 90min)

5.2.2.2 Effect of catalyst loading and the H_2O_2 loading

As can be seen in the Figure 5.18, catalyst loading and hydrogen peroxide loading experiments were carried out and the results are evaluated. Two different hydrogen peroxide loadings (1mM, 2mM) were tested for 0.5g/L, 1g/L and 1.5g/L catalyst loadings. In addition a set without addition of H_2O_2 was performed.

Adding hydrogen peroxide to the medium was more effective when the catalyst loading was lower. For example at low catalyst loading value (0.5 g/L), the removal was approximately 40% in the absence of hydrogen peroxide. While addition of 1 mM hydrogen peroxide, the removal reached approximately 50%. But at higher loading values (for exaple at 1.5 g/L), this addition just increased the removal approximately from 64% to 66%.

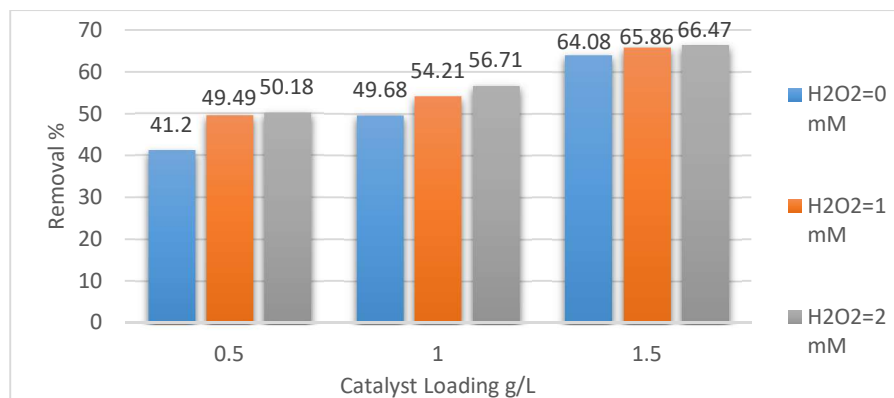


Figure 5.18: Removal results with different hydrogen peroxide concentration

($[C]_0=50$ ppm, visible light, 90 min, room temperature)

The data presented in Figure 5.19 describe, interaction between the catalyst loading and H_2O_2 concentration.

As shown in the Figure 5.19, degradation percentage gradually increased when both catalyst loading the hydrogen peroxide loading increase. However this trend of degradation percentage changed (decreased) when catalyst loading increased beyond the optimum level. According to the experimental results, these two parameters are effective in the removal based on the p-value ($p = 0.220$). The hydrogen peroxide loading did not affect the removal as much as the catalyst loading. Catalyst loading is a more effective parameter in oxytetracycline hydrochlorine removal than hydrogen peroxide loading.

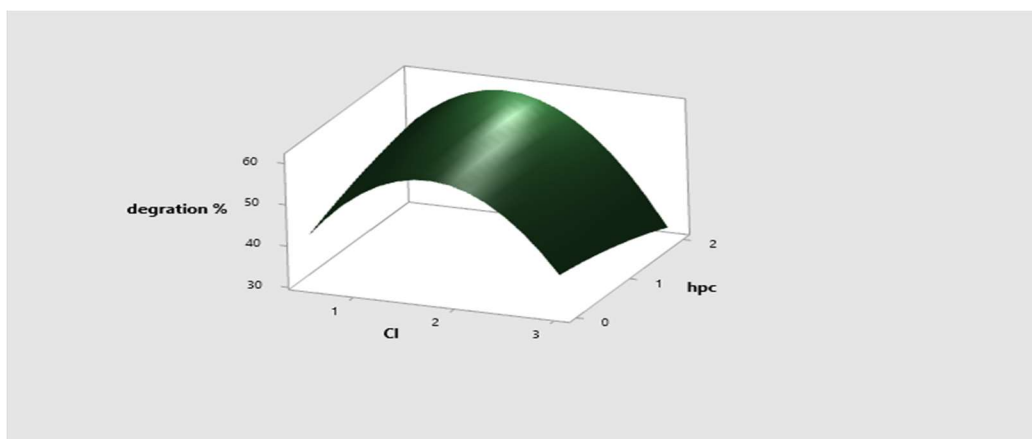


Figure 5.19: Effect of catalyst loading and H_2O_2 loading on Surface diagram

($[C]_0=50$ ppm, visible light, $pH=7$, 90 min, room temperature)

5.2.2.3 Effect of pH and H₂O₂ loading

When the results of parametric experiments were investigated, it was concluded that increasing the amount of H₂O₂ significantly increases photocatalytic removal. The reason for this situation is that the addition of H₂O₂ with the catalyst creates hydroxyl radicals. The pH value of the waste water used is approximately 4. pH has an important effect in catalytic reactions. It affects the structure of the pollutant molecule and the catalyst surface charge. As a result of the experiments, it was concluded that it works with the highest efficiency at neutral pH.

As can be seen in the graph in the Figure 5.20, H₂O₂ loading increased the removal in all pH values. The highest removal (66.47%) was achieved using parameters pH =7, H₂O₂ load = 2mM.

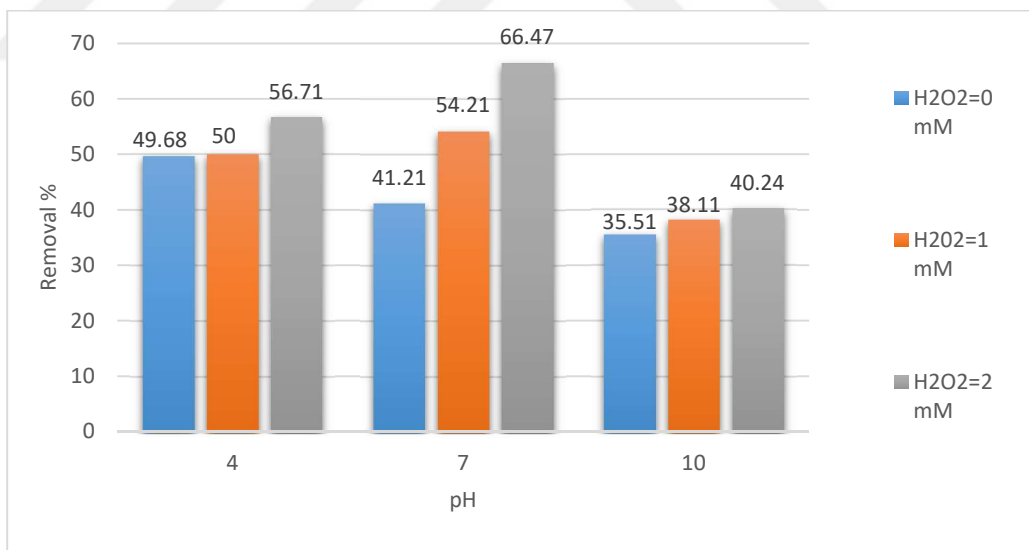


Figure 5.20: Effect of H₂O₂ loading and pH

($[C]_0=50$ ppm, visible light, 90 min, room temperature)

From Figure 5.21, which illustrates the surface plot of the pH and H₂O₂ loading, the range of optimum value of the removal is related to both pH and H₂O₂ loading. The optimum pH sharply affects the removal performance.

As shown in Figure 5.21, the highest removal was obtained when using pH = 5 and H₂O₂ loading = 2mM. It was observed that when the amount of H₂O₂ was increased at constant pH value, the removal increased.

Even when loading H₂O₂, removal at pH = 5 is above 50%. When the H₂O₂ loading is 2mM, the removal increases to around 65%. However, the changes in the pH by keeping the H₂O₂ loading constant are quite effective. For example, when the H₂O₂ loading is constant 2mM, the removal at pH = 10 is around 40%, for pH = 5 the removal is around 65%. Accordingly, the change in pH value is a more effective parameter on removal.

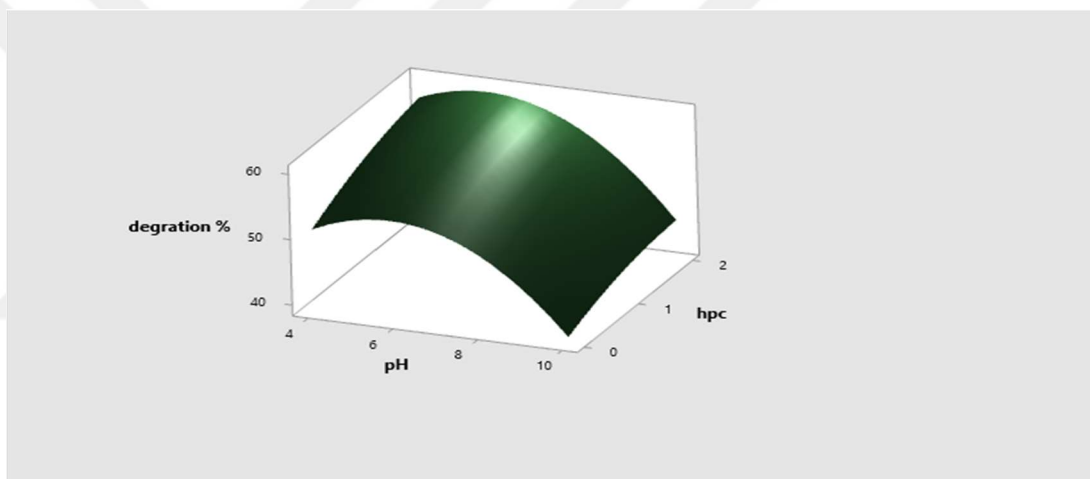


Figure 5.21: Effect of pH and H₂O₂ loading on Surface diagram

([C]_o=50 ppm, visible light, 90 min, room temperature)

As seen in the pareto chart in the Figure 5.22, the most effective parameter is the catalyst loading and the second most effective parameter is the pH value.

Using an estimate Lenth method, Minitab marks the limit at which effects are considered significant. The default severity (alpha=0.05) is used. To illustrate this result, a separate value plot of the paired differences and a 95% confidence interval for the mean of the differences is displayed.

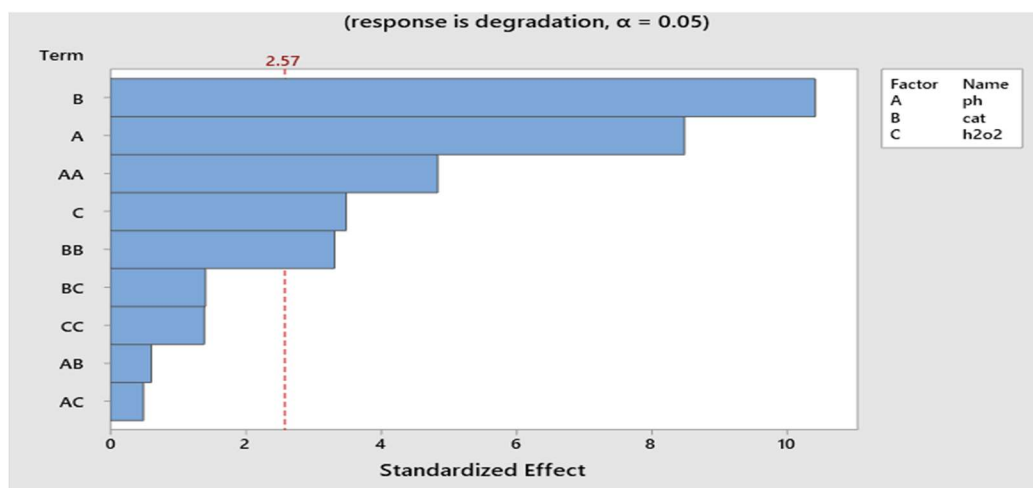


Figure 5.22: Pareto Chart of the Standardized Effect for Photo-Fenton Oxidation

5.2.3 Response optimization

The reaction surface method predicts the conditions under which the highest removal will be achieved. For the highest oxytetracycline hydrochloride degradation ($\sim 66\%$) the optimum values of the parameters may be as follows: Catalyst loading = 1.5g/L, H_2O_2 concentration = 1.5mM, pH=5

Figure 5.23 shows the optimum condition of OTC-HCl with Ni-Fe LDH catalyst in the PFLO method.

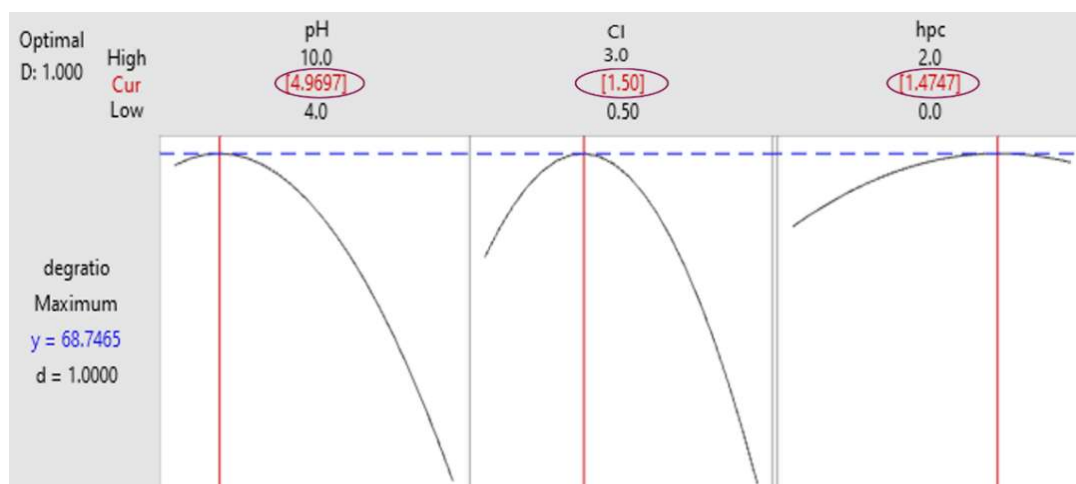


Figure 5.23: Optimum conditions for parameters

($[C]_0 = 50$ ppm, visible light, 90 min, room temperature)

For model validation under the optimum conditions determined, a set of experiment is performed and the removal efficiency was found to be 67% (Figure 5.24) that is very close to the predicted value.

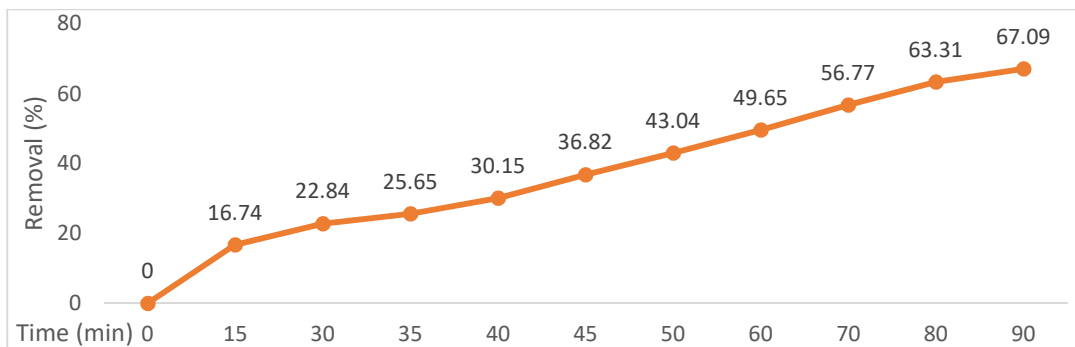


Figure 5.24: Optimum condition experiment result

As a result, 67% OTC-HCl removal was obtained by PFLO method with Ni-Fe LDH.

5.2.4. Scavenger effect

OTC-HCl removal by Photocatalytic oxidation method is affected by hydroxyl radicals. When the HO scavenger is added to the reaction, the radicals tend to reaction with the scavenger rather than the pollutant of interest. It has a negative effect on the removal of the target pollutant.

In order to see the effect show the effect of hydroxyl radicals in the PFLO process, hydroxyl radicals were evaluated with appropriate quenchers. OTC-HCl removal was achieved under optimum conditions by adding methanol and isopropanol separately. Separate studies were performed for isopropanol and methanol, and the results are presented in Figure 5.25.

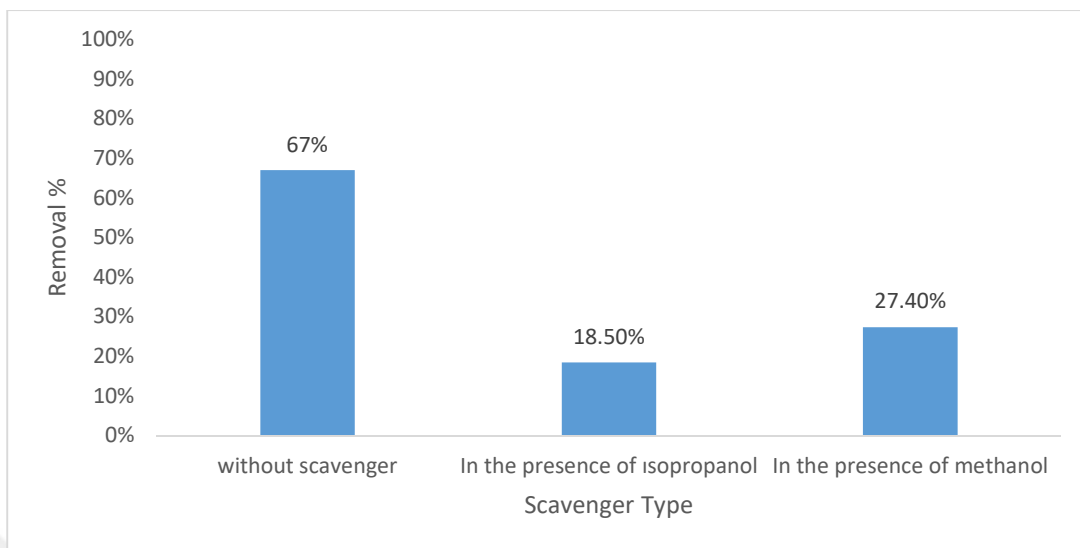


Figure 5.25: Hydroxyl radical scavenger effect on PFLO process

(Radical scavenger conc. : $30\mu\text{m}$)

As can be seen in Figure 5.25, removal yields were observed to be quite low in the presence of methanol and isopropanol (Removal decreased to 27.4% with the addition of methanol. It decreased to 18.5% with the addition of isopropanol). The reason for this is that hydroxyl radicals are mainly involved in the decomposition reactions and are much more effective.

5.2.5 Reusability tests

Evaluation of reusability has become very important for the stability, practical applicability and economic objectives of catalysts. The reusability of Ni-Fe LDH catalyst was investigated with Photo Fenton Like Oxidation method with two replications under optimum conditions. Ni-Fe LDH catalyst was recovered by filtration after fresh use under optimum conditions, rinsed with distilled water and dried with a dryer.

The removal efficiency decreased to 48% in the second replicate. This is a little bit low when compared to the results obtained with fresh catalyst. This decrease indicated that the reusability of the catalyst was not good.

5.2.6 Toxicity tests for OTC-HCL with PFLO

Photographs of seeds grown in untreated and treated OTC-HCl solutions are given in Figure 5.26. Toxicity data in terms of growth inhibition and relative root growth are given in Table 5.6. Each growing root length is shown in Figure 5.26 in different environments.



Figure 5.26: Seeds growing after 72 hours of toxicity tests

Table 5.6: Results of toxicity analysis for the PFLO of OTC-HCL

Mean Length of the Cress Roots Growing after 72 hours, [μm]		
Pure Water	OTC-HCl Solution	Treated OTC-HCl Solution
37.13	14.66	19.46

Data of toxicity tests measured after 72 hours:

Growth inhibition in untreated OTC-HCl solution, % (GI),

$$(37.13-14.66)/37.13*100 = 60.51\%$$

Growth inhibition in treated acetaminophen solution, %,

$$(37.13-19.46)/37.13*100 = 47.59\%$$

Relative Root Growth in untreated OTC-HCl solution, %,

$$(14.66/37.13)*100 = 39.5\%$$

Relative Root Growth in treated OTC-HCl solution, %,

$$(19.46/37.13)*100 = 52.4\%$$

The variation in root length of water-grown cress seeds and purified OTC-HCl solution is shown in Figure 5.27. The mean root length in water is 37.13 μm , in OTC-HCl solution 14.53 μm , and in purified OTC-HCl solution 19.46 μm in average root length.

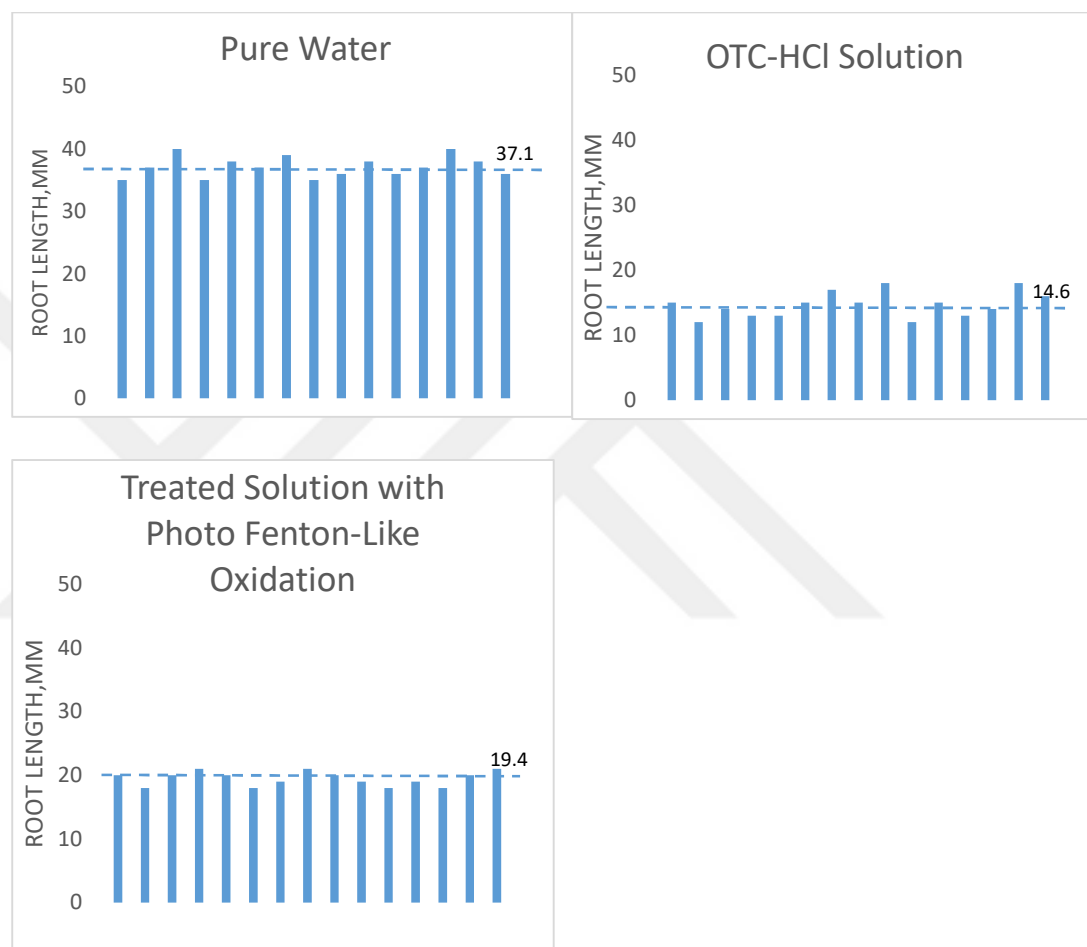


Figure 5.27: Treated OTC-HCl solutions and water-grown seed root lengths for the PFLO method

After PFL oxidation treatment, growth inhibition decreased from 60.5% to 47.5%. It can be concluded that this purification method is not very effective in reducing toxicity. The reason for this can be explained by the lack of full mineralization under optimum PFLO and the presence of end products.

5.3 Results of CWAO Experiments

5.3.1 Catalyst screening

Catalyst screening experiments with catalyst loading of 1g/L and 2g/L catalyst loading in the presence of Ni-Fe LDH, Co-Fe LDH and Cu-Fe LDH catalysts using 300 ml 50 ppm wastewater at original pH value (pH = 4) 1 bar of pressure at 50 ° C for 1.5 hours. Table 5.7 provides the results of catalyst loading studies of oxytetracycline solution by catalytic wet air oxidation.

Table 5.7: Catalyst screening experiments results

Oxytetracycline Removal (%)		
	catalyst loading of 1 g/L	catalyst loading of 2 g/L
Cu –Fe LDH	70.1	60
Co –Fe LDH	41.3	59
Ni –Fe LDH	27.4	48.45

All of the three catalysts had an effect on the degradation of oxytetracycline from solution. But Cu-Fe LDH catalyst showed higher performance when compared with the other catalysts: But removal decreases when catalyst loading increases.

As a result of the catalyst screening experiments, Cu-Fe LDH catalyst was chosen for parametric study. Parametric study was performed with this catalyst.

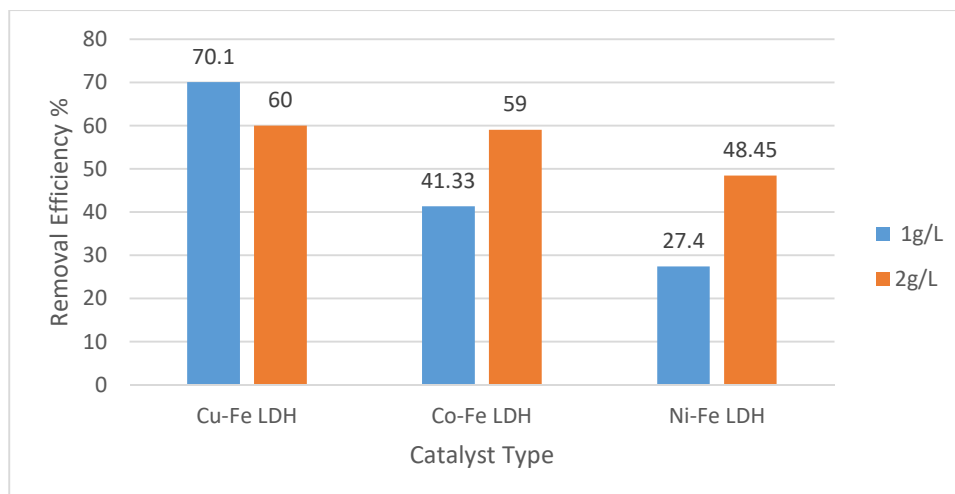


Figure 5.28: Layered Double Hydroxide Type vs Removal Efficiency Chart for Catalytic Wet Air Oxidation

5.3.2 Parametric Study of CWAO

As a result of the catalysts screening experiments, Cu-Fe LDH, which provides the most effective removal, was used as a catalyst in the parametric study. In this part of the study, the experiments were continued for 105 minutes. Experimental plans of parametric studies were planned using Minitab17 program and Box-Behnken design as response surface method. Response surface methodology was applied with 95% confidence level to determine the effect of process variables. The best degradation efficiency (92%) was measured in experiments and was predicted at pH 7, temperature 70 °C and catalyst loading of 0.5 g/L.

5.3.2.1 Effect of pH and catalyst loading

Percentage removals at different pH and catalyst loading values are given in Figure 5.29. The maximum removal was achieved at catalyst loading of 0.5 g/L at all pH values. According to the results seen in the figure, it may be concluded that the catalyst loading is a more effective parameter than pH, and catalyst loading 0.5 g/L is the optimal loading amount. It can be concluded that the catalyst is more effective in neutral conditions.

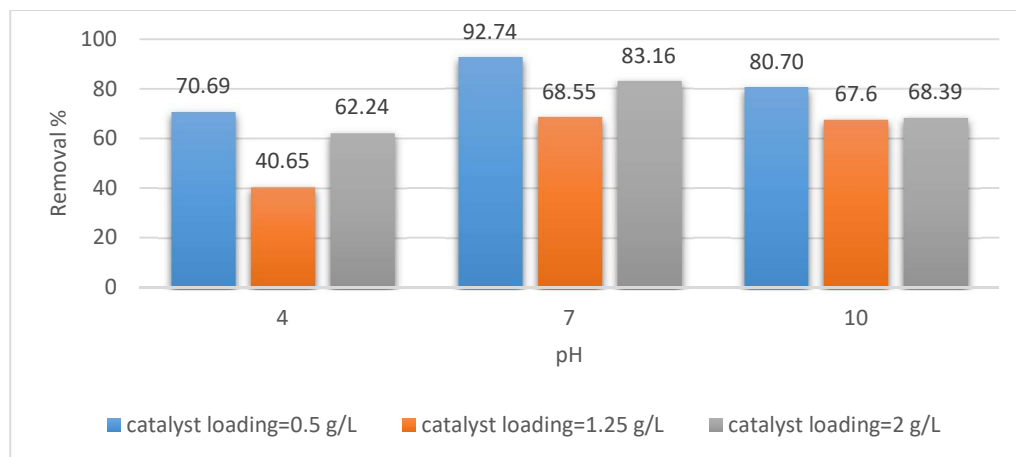


Figure 5.29: Percentage removals at different pH and catalyst loading values

If the surface plot obtained at 50°C (Figure 5.30) is investigated fixing the catalyst loading at 0.5 g/L, the highest removal was obtained at pH =7. Reducing the pH value to 4, removal gave the lowest result (40%) for that catalyst loading. When it was raised to pH = 10 again, removal increased again (62%), but still the highest removal (70%) was reached at pH = 7. Also, when the pH = 10 was taken constant, when the catalyst loading was considered the highest removal was observed, when the catalyst loading was increased from 0.5 g/L the degradation decreased (80% to 68%). In the given surface graph, the catalyst load was 0.5 g/L while maximum removal value was reached at pH=7.

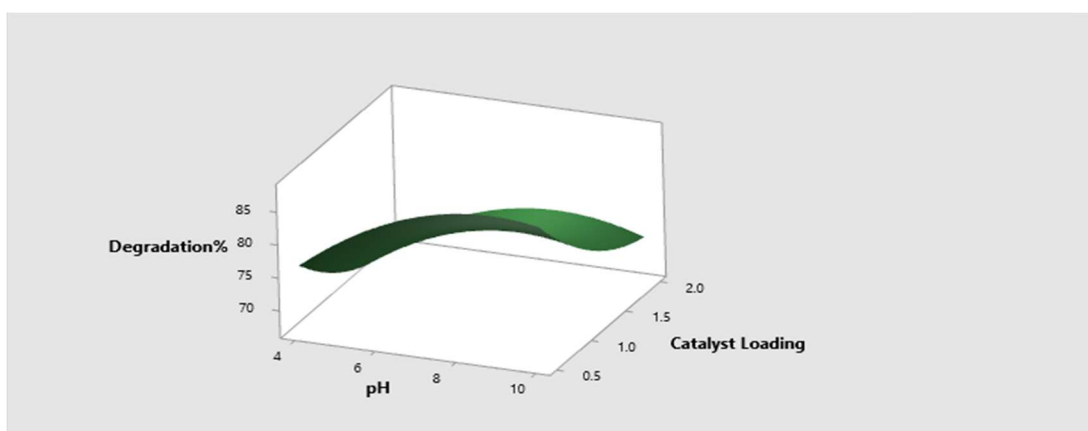


Figure 5.30: Surface diagram - Effect of catalyst loading and pH

($[C]_0=50$ ppm, 105 min, temperature 50°C)

5.3.2.2 Effect of temperature and catalyst loading

In Figure 5.31, interactive impact of catalyst loading and temperature parameters is evaluated. Nine different experiments were performed for catalyst loadings of 0.5 g/L, 1.25 g/L and 2 g/L at 30°C, 50°C and 70°C. Maximum removal was achieved at 0.5g/L catalyst loading at all temperatures. For example, when the catalyst loading is increased from 0.5 g/L to 1.25 g/L at 30°C, the removal drops from 66% to 40%. To give another example, when the catalyst loading is increased from 0.5 g/L to 2 g/L at 70°C, the removal decreases from 92% to 83%. According to this graph, temperature is an effective parameter. The highest removal was obtained with 92% at 70°C and 0.5 g/L conditions.

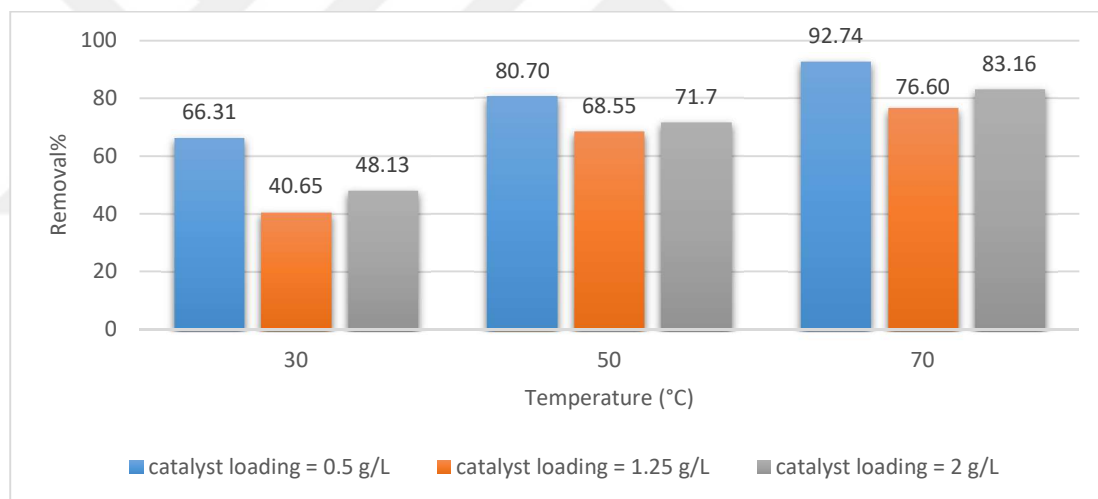


Figure 5.31: Percentage removals at different temperature and catalyst loading values

In Figure 5.32, the interactive effect between T and catalyst loading can be investigated. Temperature is more effective since sharper decline in removal occurs when the temperature decreased. catalyst loading is not effective as much as T. As an example, at 0.5g/L catalyst loading, removal at 30°C is around 65%, but at 70°C removal is about 90%. Similarly, at 1.25 g/L catalyst loading, removal is 40% at 30°C and about 70% at 50°C.

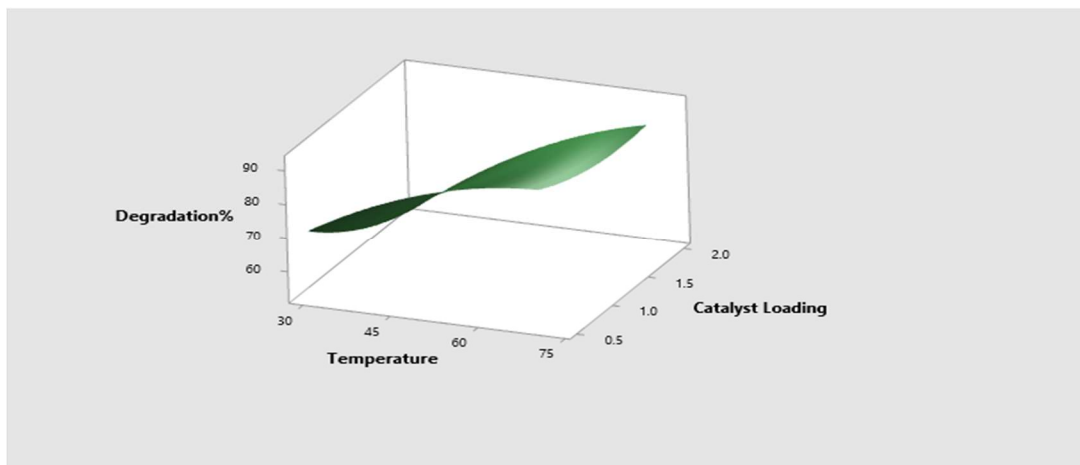


Figure 5.32: Effect of temperature and catalyst loading on Surface diagram
($[C]_0=50$ ppm, 105 min, temperature pH=7)

5.3.2.3 Effect of T and the pH

In Figure 5.33, the interactive impact of T and pH parameters was evaluated. Experiments were performed for pH=4.7 and 10 and at temperatures of 30°, 50° and 70°C. At all temperatures, the removal is minimum at pH=4. As the temperature increases, the removal increases at all pH. The highest removal was obtained at pH =7 and temperature of 70°C with 92%.

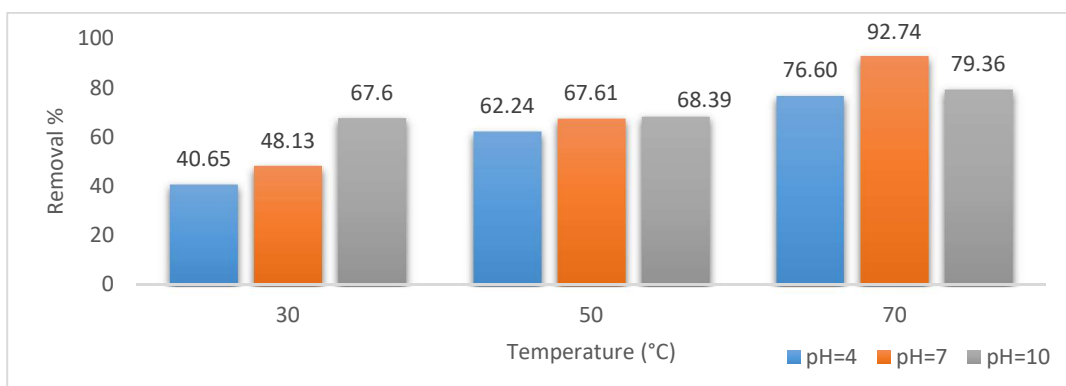


Figure 5.33: Percentage removals at different T and pH

The interaction of pH and temperature is given in Figure 5.34 by surface diagram. Temperature is a more effective parameter on removal than pH. For example, at pH 4 and temperature 30, its removal is around 40% and is at its minimum value. It is clearly seen in the Figure that the removal increases as the temperature increases.

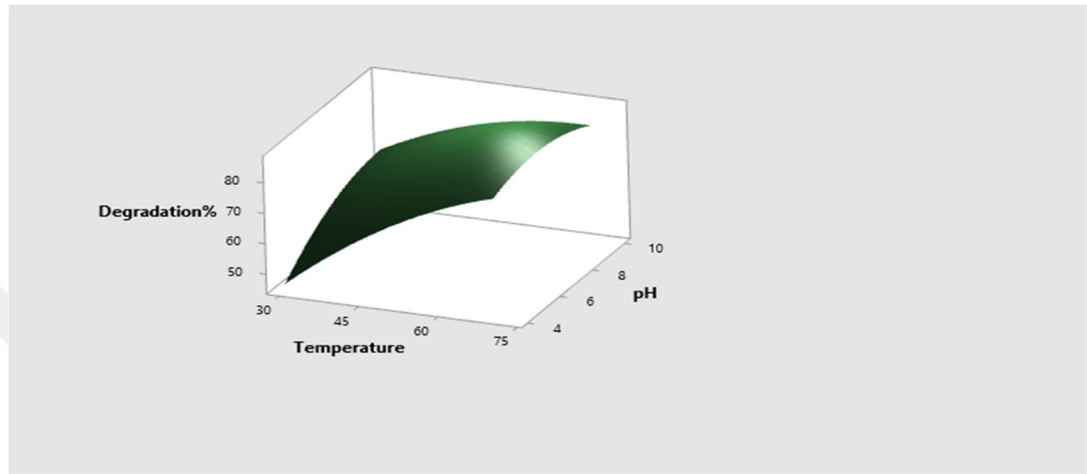


Figure 5.34: Surface diagram - Effect of temperature and pH

As seen in the pareto chart in Figure 5.35, the most effective parameter is temperature and the second most effective parameter is catalyst loading. Among the interactive parameters, the most effective one is temperature-pH (AB).

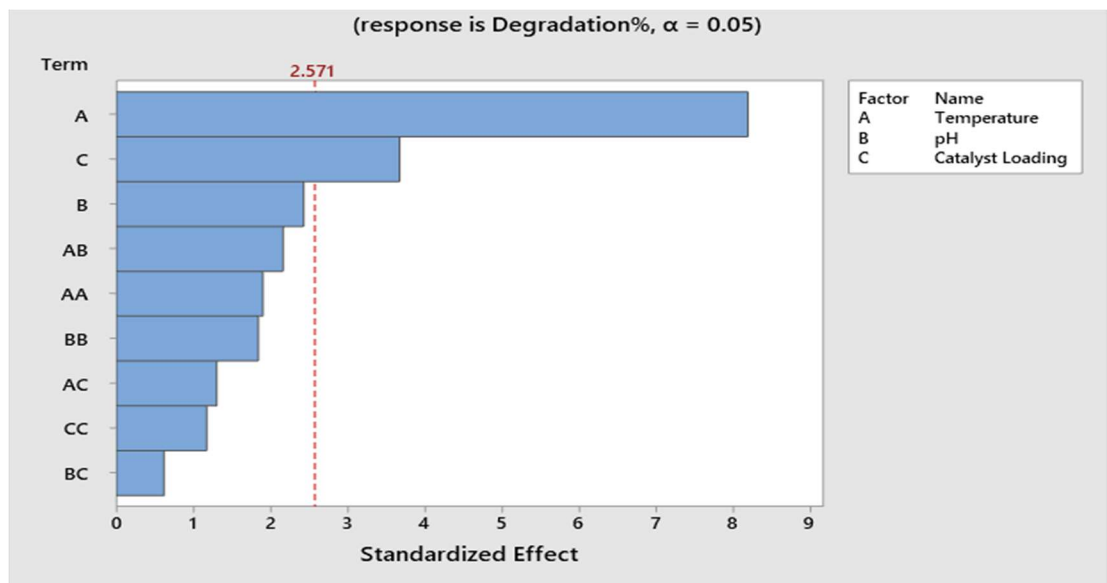


Figure 5.35: Pareto Chart of the Standardized Effect for CWAO

5.3.3 Response optimization

The reaction surface method predicts the conditions under which the highest removal will be achieved. The optimum values of the parameters for the highest oxytetracycline hydrochloride removal (~92%) are determined as follows

Catalyst loading is 0.5 g/L, temperature is 70°C and pH is 7.

Figure 5.36 shows the optimum state of OTC-HCl with Cu-Fe LDH catalyst in the catalytic wet air oxidation method.

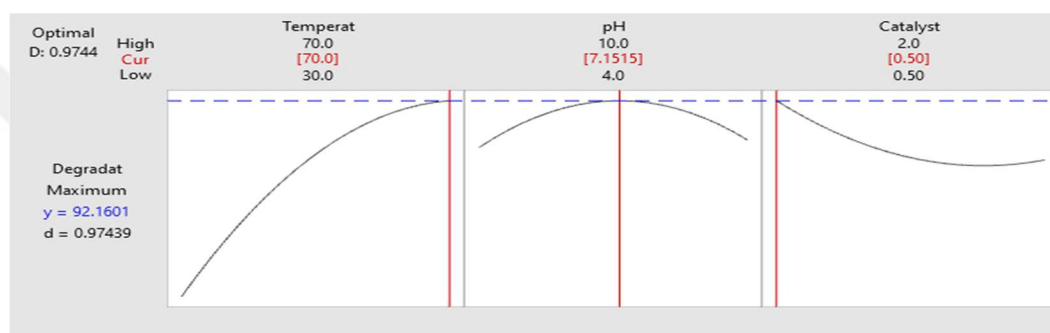


Figure 5.36 : Graphs of Minitab Design of Experiments program result

For this optimum condition, the experiment was set up and time-dependent removal was shown as in Figure 5.37.

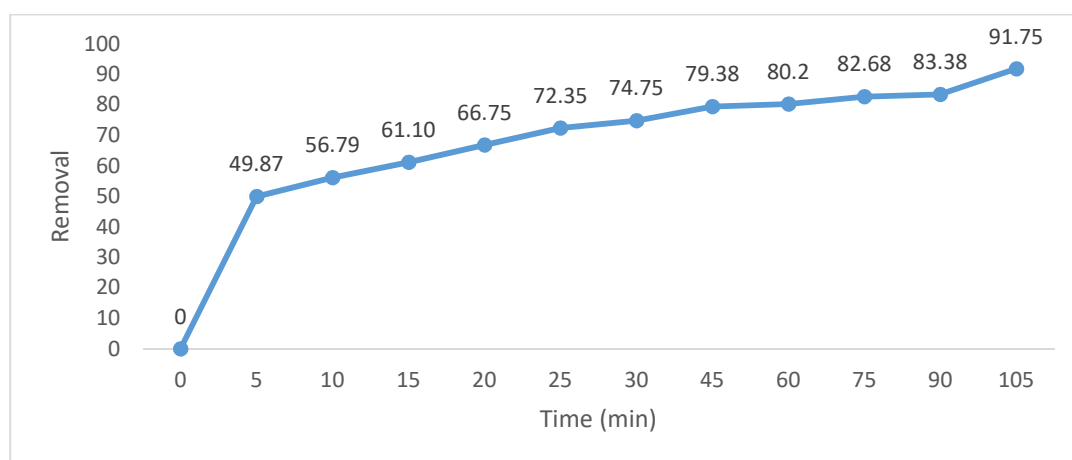


Figure 5.37 : Optimum condition experiment result

As a result, it is recommended to apply CWAO with 92% OTC-HCl removal by CWAO method in the presence of Cu-Fe LDH.

5.3.4 Reusability tests

Catalyst reusability is very important. It is desirable to use the catalyst repeatedly for cost reduction and a greener world vision. To assess reusability, the Cu-Fe LDH catalyst was collected by filtration through filter paper after reuse. The accumulated catalysts were rinsed with pure water and dried in an oven. Under the optimum conditions two replicates were conducted. The removal efficiency decreased to 27% in the second replicate. This is a little bit low when compared to the results obtained with fresh catalyst. This decrease indicated that the reusability of the catalyst was not good.

5.3.5 Toxicity tests for OTC-HCl with CWAO

Toxicity analysis was performed for OTC-HCl solution purified by CWAO method under optimum reaction conditions with Cu-Fe LDH catalyst. The variation in root length of water-grown cress seeds and purified OTC-HCl solution is shown in Figure 5.38. Average root length in water was 37.13 μm , mean root length in OTC-HCl solution was 14.53 μm , and mean root length in purified OTC-HCl solution was 23.73 μm .

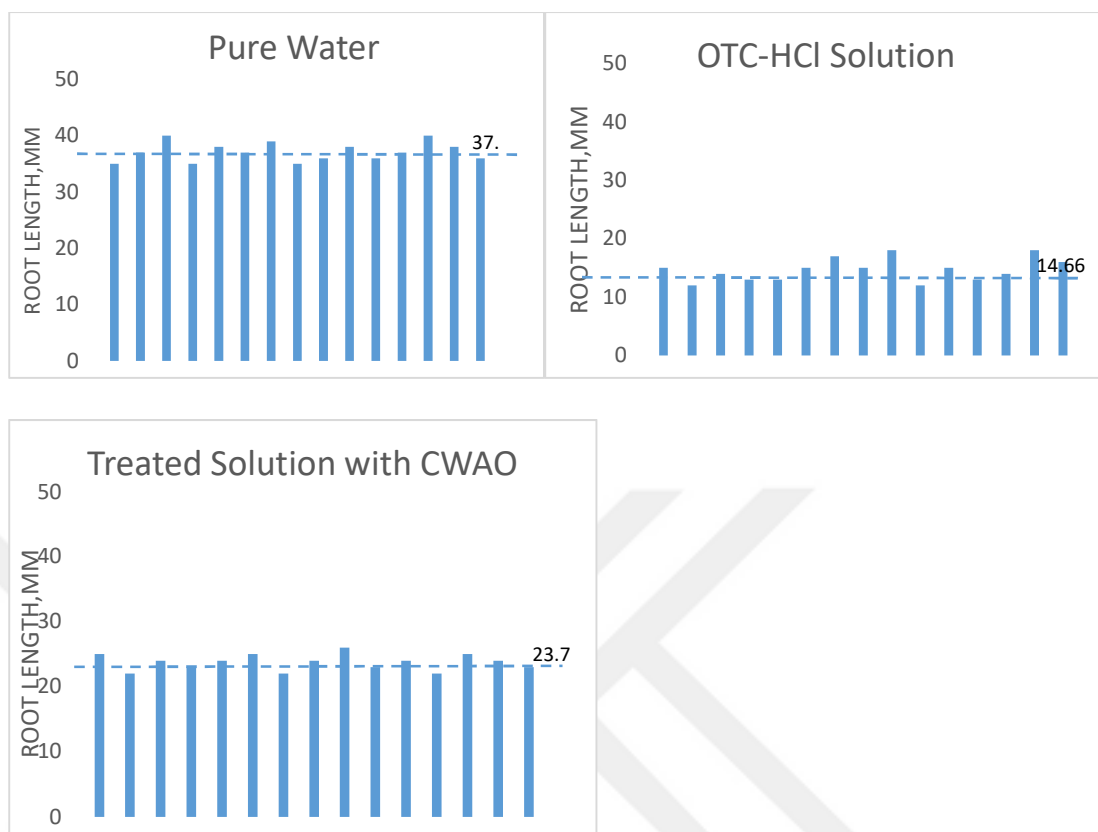


Figure 5.38 :Treated OTC-HCl solutions and water-grown seed root lengths for the CWAQ method

Based on the results,

% in the treated OTC-HCl solution, Growth inhibition,

$$((37.13-23.73)/37.13)*100 = 36.09\%$$

% in the treated OTC-HCl solution, Relative Root Growth,

$$(23.73/37.13)*100 = 63.91\%$$

The growth inhibition value was calculated as (36.09%). The lack of complete removal due to the end product remaining under optimum reaction conditions may explain the growth inhibition in the treated OTC-HCl solution. Growth inhibition for seed growing in the treated dye solution was 23.7% in a study with the CWAQ method (Palas et al., 2017).

5.4 Kinetic Study

5.4.1 Kinetic Study for Photo-Fenton Like Oxidation Method

The kinetic study was carried out with the best promising catalyst at the optimum conditions (pH=5, 1.5 g/L catalyst loading, 1.5mM H₂O₂ concentration) at three different temperatures as 25 °C, 35 °C and 45 °C. A kinetic model was determined for the degradation. Reaction rate constants and activation energy were determined according to these data. The collected kinetic data are given in Table 5.8:

Table 5.8: Kinetic Study Results of PFLO in the presence of Ni-Fe LDH

	25 °C	35°C	45°C
Time (min)	C (ppm)	C (ppm)	C (ppm)
0	50.33283	50.33283	50.33283
15	45.99954	44.66622	43.3329
30	43.3329	41.33292	39.33294
35	42.23291	39.56627	38.36628
40	40.69959	37.1663	35.73298
45	36.73297	32.39968	31.39969
50	32.39968	28.56638	26.9664
60	30.03303	26.19974	25.06642
70	28.39972	23.16644	21.49979
80	24.13309	19.16648	18.06649
90	23.26643	19.66647	17.43316

C: Concentration

Power-Law Based Kinetic Expressions are tested.

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

- ☐ Heterogeneous reaction follows Power law mechanism
- ☐ Surface reaction is dependent on just Oxytetracycline Hydrochloride concentration (C) to the first order or second order

Single Step Model

The kinetic behaviour of the Oxytetracycline Hydrochloride containing wastewater degradation was studied with first order and second order kinetics.

$$-\frac{d[C]}{dt} = k_n [C]^n$$

where; C: Oxytetracycline Hydrochloride concentration [C], t: reaction time,

k_n : kinetic rate constant,

First-order kinetic model equation:

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

$$\ln \left(\frac{C_0}{C} \right) = k_1 * t$$

where, $[C]_0$, is the initial : Oxytetracycline Hydrochloride concentration, $k_1(\text{min}^{-1})$ is the first order reaction rate constant.

Plotting $\ln \left(\frac{C_0}{C} \right)$ vs reaction time, the slope will give the reaction rate constant (Figure 5.39).

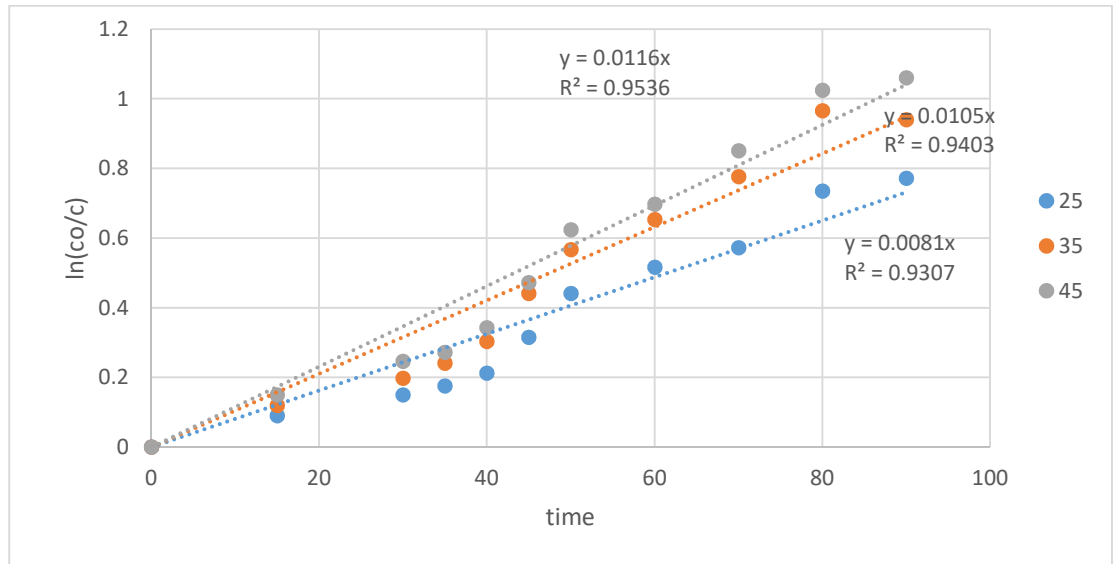


Figure 5.39: The 1st order reaction kinetics

Second-order kinetic model

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

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

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

Plotting $1/C - 1/C_0$ vs reaction time, the slope will give the reaction rate constant (Figure 5.40).

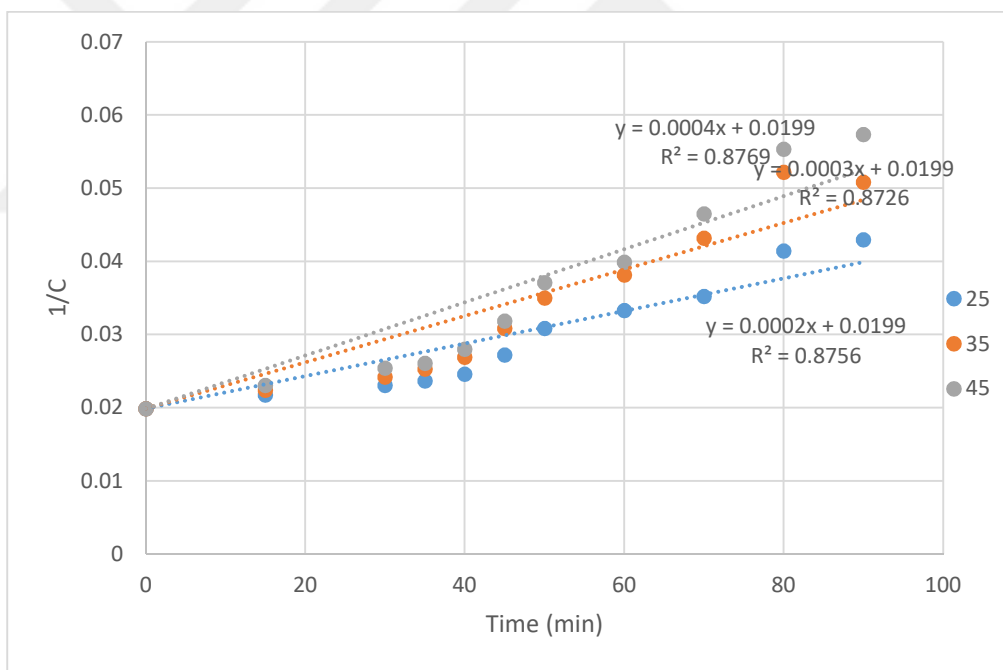


Figure 5.40 : The 2nd order reaction kinetics

Table 5.9 shows the rate constants calculated from the 1st and 2nd order reaction models.

Table 5.9: Regression coefficients and rate constants for 1st and 2nd order reactions

	1 st Order		2 nd Order	
	Rate Constant [min ⁻¹]	Regression Coefficient, R ²	Rate Constant [L/(mg.min)]	Regression Coefficient, R ²
25°C	0.0081	0.9307	0.0002	0.8756
35°C	0.0105	0.9403	0.0003	0.8726
45°C	0.0116	0.9536	0.0004	0.8769

When the regression coefficients are examined, 1st order kinetics shows a better fit.

The activation energy and the pre-exponential factor are also calculated according to the linearized form of the Arrhenius equation using the first order kinetic rate constants.

$$k = Ae^{\left(-\frac{E}{RT}\right)} \rightarrow \ln k = \ln A - \frac{E}{RT}$$

where A is the pre-exponential (frequency) factor [min⁻¹], E is the activation energy [J/mol], R is the ideal gas constant (R=8.314 J/mol.K), and T is the reaction temperature [K]. In Figure 5.41, the Arrhenius plot is presented.

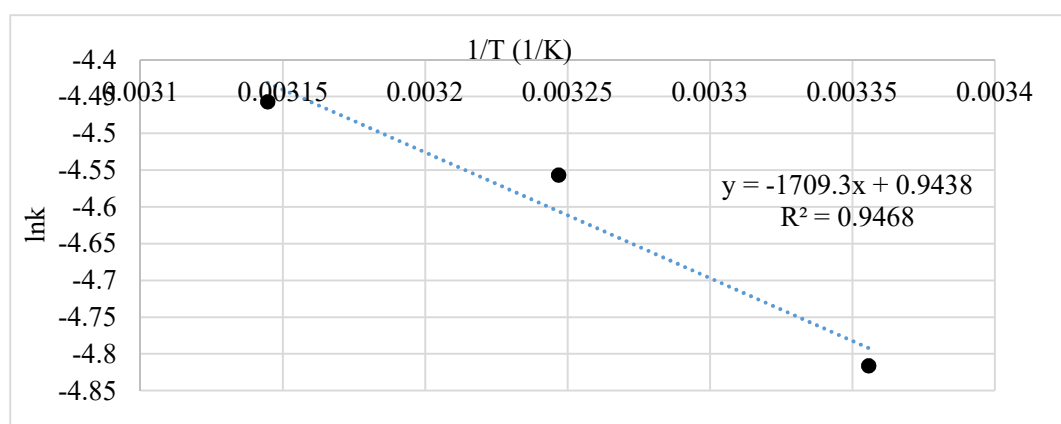


Figure 5.41: Arrhenius Plot

Activation energy and the pre-exponential factor are evaluated as 14.21 kJ/mol and 2.58 L.mol⁻¹min⁻¹

5.4.2 Kinetic Study for CWA0 Method

Kinetic studies were applied under optimum conditions (pH=7, 0.5 g/L catalyst loading,). Temperature values of 30°C, 50°C and 70°C were selected to perform kinetic studies. The data are shown in Table 5.10.

Table 5.10: Kinetic study results of CWA0 in the presence of Cu-Fe LDH

	30°C	50°C	70°C
Time (min)	C(ppm)	C(ppm)	C(ppm)
0	50.33283	50.33283	50.33283
5	26.6664	23.99976	21.66645
10	23.833095	21.399786	19.9998
15	21.833115	19.066476	17.33316
20	19.166475	17.033163	15.733176
25	17.499825	15.533178	13.733196
30	15.833175	13.599864	11.799882
45	15.166515	11.799882	10.133232
60	12.433209	10.366563	8.399916
75	10.799892	8.833245	6.833265
90	10.033233	7.366593	5.499945
105	8.66658	6.99993	4.266624

C:Concentration

Figure 5.42 shows the 1st order reaction rate constants and regression coefficients.

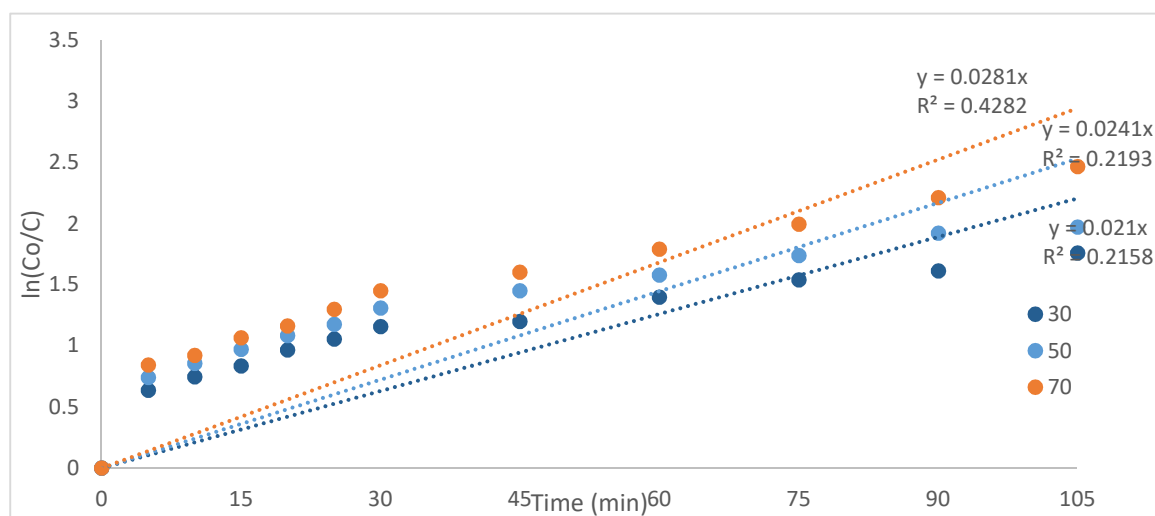


Figure 5.42. The 1st order reaction kinetics

Figure 5.43 shows the 2nd order reaction rate constants and regression coefficients.

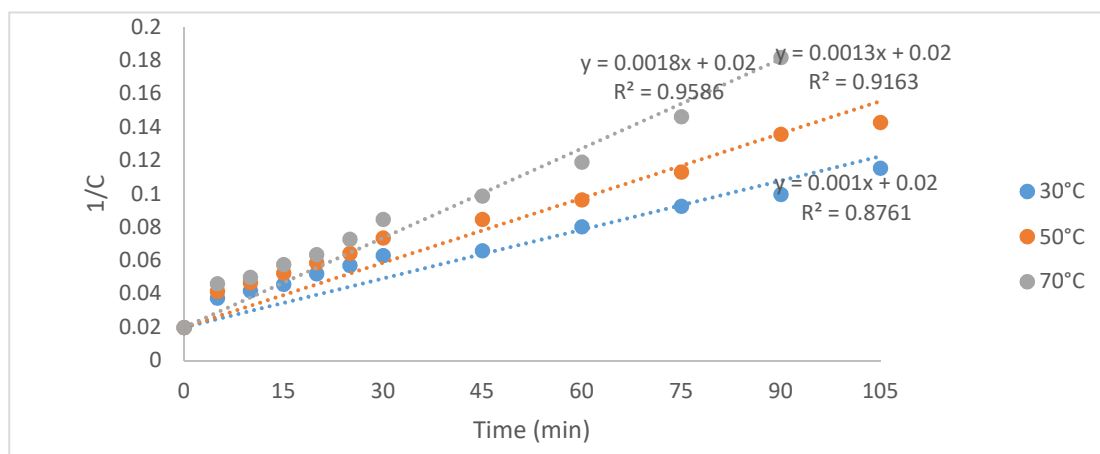


Figure 5.43 The 2nd order reaction kinetics

Table 5.11 : Regression coefficients and rate constants for 1st and 2nd order reactions

	1 st Order		2 nd Order	
	Rate Constant [min ⁻¹]	Regression Coefficient, R ²	Rate Constant [L/(mg.min)]	Regression Coefficient, R ²
30°C	0.021	0.2158	0.001	0.8761
50°C	0.0241	0.2193	0.0013	0.9163
70°C	0.0281	0.4282	0.0018	0.9586

When the regression coefficients are examined, the 2nd order kinetic is more compatible.

Two Step Model

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.

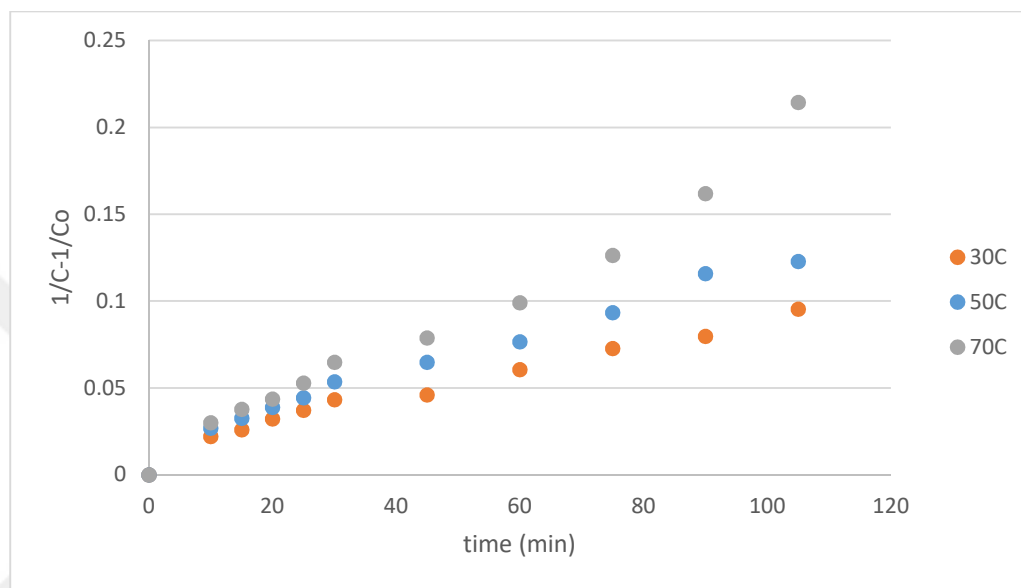


Figure 5.44: Second order kinetic plot in two steps at various temperatures

As seen in Figure, 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 second order reaction kinetics :

According to the results collected the reaction rate constants for both steps were calculated for 30, 50 and 70 °C temperatures and showed in following Table 5.12:

Table 5.12: Results of kinetic model

Temperature (°C)	k _{Fast} (L/(mg.min))	k _{Slow} (L/(mg.min))	R ² _{Fast}	R ² _{Slow}
30	0.0015	0.0006	0.96	0.93
50	0.0019	0.0009	0.94	0.98
70	0.0022	0.0017	0.94	0.93

Arrhenius constant and activation energies for fast and slow steps are calculated and showed in following Table 5.13:

Table 5.13: Arrhenius constant and Activation energies for fast and slow step

	Fast Step	Slow Step
E (J/mole)	8302	22365.49
A (L/(mg.min))	0.04	4.1
R ²	0.99	0.97

According to calculated parameters from linearized form of Arrhenius equation activation energy for fast step was approximately 8.3 kJ/mole (R²=0.99) and for slow step 22.4 kJ/mole (R²=0.97) as expected.

6.0 CONCLUSIONS

In this thesis, Photo Fenton-like oxidation and Catalytic Wet Air oxidation of wastewater containing veterinary antibiotic (oxytetracycline HCl) were applied and double-layered hydroxide (LDH) was applied. And the performances of the two methods were compared.

Photo-Fenton-Like Oxidation

- The performance of Photo Fenton-like oxidation removal of veterinary antibiotics of oxytetracycline wastewater was compared with three different double-layer catalysts (Cu-Fe LDH, Co-Fe LDH and Ni-Fe LDH). The most selective catalyst was determined as Ni-Fe LDH catalyst.
- 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 oxytetracycline.
- Applying the Minitab Design of Experiment program and considering all the parametric studies results, the optimum reaction conditions were determined as Catalyst loading =1.5g/L, H₂O₂ concentration = 1.5mM, pH=5 in the presence Ni-Fe LDH catalyst using visible light source. The degradation efficiencies were evaluated as around 68% at these optimum conditions.
- Kinetic studies were performed at these optimum conditions and it is found that the system fits first order one step kinetic model.

Catalytic Wet Air Oxidation

- The performance of Catalytic Wet Air oxidation of oxytetracycline wastewater was compared with three different double-layer catalysts(Cu-Fe LDH, Co-Fe LDH and Ni-Fe LDH). The most selective catalyst was determined as Cu-Fe LDH catalyst.

- For catalytic wet air oxidation, the parametric study conditions were designed in the presence of Cu-Fe LDH to specify the optimum conditions to get maximum efficiency for 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 0.5 g/L Cu-Fe LDH catalyst loading, at pH 7 and at temperature of 70°C. At these conditions the removal percentage was around 92%.
- 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 oxytetracycline by CWAO process follows two steps second order order reaction.

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