REMOVAL OF CHLORIDAZON HERBICIDE FROM WASTEWATERS USING
FE/H_2O_2, UV/H_2O_2 AND UV/FE/H_2O_2

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ABSTRACT

REMOVAL OF CHLORIDAZON HERBICIDE FROM WASTEWATERS USING FE/H$_2$O$_2$, UV/ H$_2$O$_2$ AND UV/FE/ H$_2$O$_2$

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Chloridazon (5 -amino-4- chloro-2-phenyl-3(2H)-pyridazinon), also named as Pyrazon and classified as organochlorine pesticides, is widely used during sugar beets cultivation. Chloridazon (CLZ) being a pesticide with a high solubility in water is likely to end up in surface and groundwater bodies because of its high mobility in soil. Due to its toxic properties, it may cause serious problems on human health and ecological cycle. In the present study, the removal of CLZ herbicide from water was investigated by means of Advanced Oxidation Processes (AOP's), namely UV/H$_2$O$_2$, Fe/H$_2$O$_2$ (Fenton) and UV/Fe/H$_2$O$_2$ (Photo-Fenton). The effect of operational parameters such as initial CLZ concentration, H$_2$O$_2$ concentration, Fe concentration, pH and temperature were sought. It was observed that CLZ completely disappeared within 1 h by the Fenton and UV/H$_2$O$_2$ processes while in the Photo-Fenton processes approximately 100% disappearance was observed in 20 minutes, under optimum conditions. The optimum conditions were determined as 20 mg/L H$_2$O$_2$, 20 mg/L initial CLZ, pH 3 and 20°C for UV/H$_2$O$_2$ process; 7.5 mg/L Fe^{2+}, 50 mg/L H$_2$O$_2$, 40 mg/L initial CLZ, pH 3 and 20°C for Fenton process, and 5 mg/L Fe^{2+}, 50 mg/L H$_2$O$_2$, 60 mg/L initial CLZ, pH 3 and 20°C for Photo-Fenton process. Desphenyl CLZ, Pyridazine-3,4,5-trione, Oxaluric acid and 5-hydroxyhydantion were identified as

CLZ degradation by-products. Accordingly, degradation pathway was proposed for each process. The reaction kinetics of CLZ followed pseudo-first-order kinetics in case of UV/H_2O_2 while BMG (Behnajady-Modirdhahla-Ghanbery) kinetic model was followed in case of Fenton and Photo-Fenton processes.

Keywords: Chloridazon Removal, Advanced Oxidation Processes, Fenton, Photo-Fenton, UV/H2O2, Kinetics, By-products

ÖZ

KLORİDAZON HERBİSİTİNİN FE/ H_2O_2, UV/ H_2O_2 VE UV/FE/ H_2O_2 İLE ATIKSULARDAN GİDERİMİ

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Pirazon adıyla bilinen Kloridazon herbisiti, organoklorlu bileşikler olarak sınıflandırılmakta ve şeker pancarı üretiminde yaygın olarak kullanılmaktadır. Suda yüksek çözünürlüğe sahip olan Kloridazon (CLZ) herbisitinin, topraktaki yüksek mobilitesi nedeniyle yerüstü ve yeraltı sularına ulaşması yüksek olasıklıktadır. Toksik özelliklere sahip olması nedeniyle de insan sağlığı ve ekolojik döngü üzerinde ciddi problemler yaratması söz konusudur. Yapılan bu çalışmada, CLZ herbisitinin İleri Oksidasyon Proseslerinden Fe/ H_2O_2 (Fenton), UV/ H_2O_2 ve UV/Fe/ H_2O_2 (Foto Fenton) prosesleri ile sudan giderimi araştırılmıştır. Her bir proses için H_2O_2, Fe^{+2}, başlangıç CLZ konsantrasyonu, sıcaklık ve pH parametrelerinin etkisi incelenmiştir. UV/H_2O_2, Fenton ve Foto-Fenton prosesleri için optimum şartlar, sırasıyla, 20 mg/L H_2O_2, 20 mg/L initial CLZ, pH 3 and 20°C; 7.5 mg/L Fe^{2+}, 50 mg/L H_2O_2, 40 mg/L initial CLZ, pH 3 and 20°C; 5 mg/L Fe^{2+}, 50 mg/L H_2O_2, 60 mg/L initial CLZ, pH 3 and 20°C olarak belirlenmiştir. CLZ degradasyon yan ürünleri olarak Desphenyl CLZ, Pyridazine-3,4,5-trione, Oxaluric acid ve 5-hydroxyhydantion tespit edilmiştir. Buna bağlı olarak, her bir proses için degradasyon mekanizması da önerilmiştir. CLZ'nin reaksiyon kinetiği Fenton ve Foto-Fenton proseslerinde BMG (Behnajady-

Modirdhahla-Ghanbery) modelini takip ederken, UV/H$_2$O$_2$ prosesinde psödo birinci derece kinetiğini takip etmiştir.

Anahtar Kelimeler: Kloridazon Arıtımı, İleri Oksidasyon Prosesleri, Fenton, Foto-Fenton, UV/H2O2, Kinetik, Yan Ürünler

To My Lovely Husband and Family

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LIST OF ABBREVIATIONS

AOP	Advanced Oxidation Processes
AA-EQS	Annual Average EQS
BMG	Behnajady-Modirdhahla-Ghanbery
CLZ	Chloridazon
DPC	Desphenyl Chloridazon
EQS	Environmental Quality Standards
GWD	Groundwater Directive
HPLC	High Pressure Liquid Chromotography
Koc	Organic Carbon-Water Partitioning Coefficient
Kow	Octanol/Water Partition Coefficient
LC/MS/MS	Liquid Chromatography-Mass Spectrometry System
MAC-EQS	Maximum EQS
Me-DPC	Methyl-desphenyl-Chloridazon
MLR	Multiple Linear Regression
SWQR	Surface Water Quality Regulation of Turkey
TBGW	Turkish Regulation on Protection of Groundwater against Pollution and Deterioration
TV	Threshold Value
WFD	Water Framework Directive

CHAPTER 1

INTRODUCTION

1.1. General

Depending on the world population growth, the nutritional needs are also increasing. Increase in agriculture demands lead to the excessive use of agrochemicals in order to improve the yield and prevent the loss in products. Pesticides, rank first in the category of micropollutants due to excessive and widespread uses, are the chemicals used to destroy weeds and insects that damage plants and to prevent plant diseases. Although the goal is to increase yield of agricultural products, it is now evident that there are so many harmful effects on environment and human health. Depending on their categories and half-life for each pesticide; it is possible for them to persist, accumulate and transport in soil and water for many years. Some pesticides and their by-products can remain stable in nature. These toxic, low-biodegradable and water soluble chemicals can cause serious environmental pollution due to infiltration to surface and ground water. Especially, water resources close to agricultural areas contain pesticide residues and the consumption of these resources may have serious risks to humans. Also, direct discharges from industries either producing or using the pesticides can cause their elevated levels to be encountered in water courses. The risk has led to regulate the pollution control around the world and important steps have been taken to prevent damages in future. In this respect, EU Water Framework Directive 2000/60/EC (WFD) aims to achieve a good status in ground and surface waters in Europe. A water body which is in good status must meet Environmental Quality Standards (EQS) for priority pollutants which are listed in Annex of WFD. This list includes metals, pesticides, polycyclic aromatic hydrocarbons, organochlorine compounds and endocrine-disruptors and other organic compounds. In addition to the

priority pollutants, there are river basin specific pollutants to be determined by EU member states, for which EQS values should be defined as well. In accordance with these, Turkey, as a EU candidate country, has determined 250 specific pollutants and their EQS values. Priority and specific pollutants are listed in the Surface Water Quality Regulation of Turkey (SWQR) (Official Gazette, 10/08/2016 No: 29797). In this list, it can be evidently seen that pesticides take a major part.

Pesticides are divided into groups such as herbicides, insecticides and fungicides according to their target species. Considering the active compounds, they are also defined as aniline derivatives, carbamates, organochlorines, organophosphates, triazine (Prieto Garcia et al., 2012).

Herbicides, the most widely used group in the field of agriculture, are used to grow, control and kill plants (bushes, weeds, etc.). Nowadays, almost all herbicides in the agricultural market contain organic matter. They are claimed to be the most common pesticides found in water resources. These chemicals found in water resources may cause physiological effects such as mutagenic, carcinogenic and xenobiotic on human health. That is why the removal of herbicides from water has gained importance, recently (Bensalah., 2011).

Chloridazon (5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone) is a chemical belongs to the pyrazinone family of the herbicide group. It is used before and after the planting the sugar beets to combat the broad leaved weeds of beet cultivars as a barrier to photosynthesis. This chemical, commercially named as Pyrazon, is widely used in sugar beets production in all over the world as well as in our country. Chloridazon (CLZ) can easily be transported in various media owing to its high organic carbon-water partitioning coefficient (Koc) and low octanol-water partitioning coefficient (Kow) and therefore it has high potential to enter the surface and groundwater (Buttiglieri et al., 2009). In SWQR, CLZ is listed as specific pollutant for Turkey and relevant EQS values are set. For inland waters, annual average EQS (i.e. AA-EQS)

and maximum EQS (i.e. MAC-EQS) are set as 6 μg/L, whereas for coastal and transitional waters, AA-EQS and MAC-EQS values are set as 0.01 μg/L and 0.1 μg/L, respectively. The pesticides removal from water is possible with physical, chemical and biological methods. Previous studies show that the pesticides can be degraded in high and low rates via these methods. Biological processes are known as non-effective method for the pesticide removal mostly due to its high toxicity and biological persistence (Vilar et al., 2012). An aerobic biodegradation half-life of up to 152 days (anaerobic metabolism of 307-607 days depending on soil texture) suggests that biodegradation is not an important environmental fate process in soil (EPA, 2005) and hence, its biological treatment is not likely effective (Smith and Meggitt, 1970; Castillo and Torstensson, 2007). Further, it is reported in the literature that CLZ biodegrades into polar and water soluble metabolites (Loos et al.,2010). Some chemical and physical methods such as coagulation (Jia et al., 2006) adsorption (Gupta et al., 2006), are the processes not preferred in pesticide removal because they do not always provide high removal efficiencies and produce too much sludge (Samet et al., 2012) (in case of coagulation) or destruction of rejected or adsorbed pesticides is required (in case of adsorption) (Baldauf, 1993). Further, besides being costly (Al Hattab, 2012) these methods do not mineralize the pesticides, just phase conversion takes place (Baldauf, 1993).

Nowadays, the most popular method for wastewater containing pesticides is Advanced Oxidation Processes (AOP). AOPs are defined as the processes which involves the generation of radicals (highly reactive oxidizing species) that are able to attack and degrade organic substances. The advantage of AOPs over all chemical and biological processes is that they do not transfer pollutants from one phase to the other (as in chemical precipitation and adsorption) or do not produce high amounts of sludge (Andreozzi et al., 1999). Photolysis, UV/H_2O_2, Fenton, Fenton-like, Photo-Fenton, ozonation processes are the most preferred AOPs. They have been proven to be suitable for the degradation of low-biodegradability pollutants with a comparable cost

to the well-established conventional treatment methods such as adsorption. In this respect, several AOPs have been proposed for the treatment of wastewaters bearing various pesticides. For example; TiO2 mediated photocatalysis for Aldrin (Bandala et al., 2002; Ormad et al., 2010), Alachlor (Farré et al., 2005; Ormad et al., 2010), Atrazin (Ormad et al., 2010; Campanella and Vitaliano, 2007), Carbaryl (Gelover et al., 2004), Chlorpyrifos (Ormad et al., 2010), Endrin (Ormad et al., 2010), Endosulfan (Ormad et al., 2010), Imidachloprid (Sharma et al., 2009), homogeneous photocatalysis (Fenton and Fenton-like processes) for Alachlor, Atrazine, Diuron (Farre et al., 2005; Pérez et al., 2006), Carbaryl (Kong and Lemley, 2006; Wang et al., 2003), DDT (Barbusiński and Filipek, 2001; Boussahel et al., 2007); ozonation for Butachlor, Acetochlor, Propachlor (Acero et al., 2003), Atrazine (Ma and Graham, 2000), Propane (Nuhn et al., 1995) etc. Although Literature contains enormous number of studies on pesticide removal from waters, researchers are still interested in the subject since the results obtained are highly dependent on the pesticide type due to the diverse and complex molecular structures of pesticides.

Among the studied pesticides, CLZ which is one of the widely used pesticides in our country took a very small place in the literature. In a few study, adsorption (González-Pradas et al., 2005), photolysis with titanium dioxide (Khan et al., 2012) and ozonation (Schatz, 2012) have been applied for this pesticide removal but the removal efficiencies attained are quite variable, ranging from %5 to %100. Besides being in limited numbers, they are not fully detailed studies, except the one by Azaari et al. (2016) who investigated the possible by-products of CLZ degradation during photolysis with titanium dioxide. Moreover, no detailed or complete kinetics study regarding the degradation of CLZ via AOPs such as Fenton Oxidation, Photo-Fenton Oxidation and UV/H_2O_2 are available in the literature. Therefore, this study intends to fill this gap in the Literature.

1.2. Aim and Scope

In the present study, the degradation of CLZ in water by AOPs, namely, UV/H_2O_2, Fenton and Photo-Fenton processes were investigated. To this purpose, the effects of operational parameters, such as temperature, pH, H_2O_2, Fe and initial CLZ concentrations were sought. In this respect, series of batch experiments were performed within the specified ranges of these parameters to allow a systematic parametric study. As different than Fenton process experimentations, experiments with UV/H_2O_2 and Photo-Fenton were conducted in batch reactors where UV light source is integrated to the assembly. Performance of the aforementioned processes were compared toward the CLZ removal efficiency. CLZ concentrations were followed using HPLC. CLZ removal kinetics were also examined for each treatment application and kinetic model analysis were performed. The results obtained were confirmed by statistical analysis using Multiple Regression analysis. Additionally, the possible by-products formation was searched with the help of LC/MS/MS.

CHAPTER 2

LITERATURE REVIEW AND BACKGROUND

2.1. Pesticides

The productivity of agriculture depends on such factors as water, soil, quality of seeds, fertilizer resources and the use of pesticides. However, the most important factor among them stands for the pesticides. Although pesticides are used for protecting agricultural products from insects, weeds and various diseases, environmental damage is inevitable if these chemicals are applied carelessly. At this point, the occurrence and fate of pesticides in water resources, their possible effects on living organisms and the relevant mitigation measures need to be addressed in detail.

2.2. Environmental Fate of Pesticides

The use of pesticide in nature causes to leave residues in the environment. The four main possible compartments are water, air, earth and living beings to observe these residues. Estimated transport mechanisms may occur in physical, chemical and biological ways such as adsorption, precipitation and evaporation in physically; chemical oxidation, photolysis and hydrolysis in chemically; microbial degradation as biological processes. Besides, some parameters have been introduced to understand the mechanism of the pesticide release. These parameters consist of half-life, soil sorption coefficient, water solubility and vapor pressure (Kerle et al., 2007). The decomposition of chemical to be carried in each compartment occurs as a function of the relevant physico-chemical properties. Pesticide properties (solubility in water, tendency to adsorb soil and pesticide persistence) and soil characteristics (clay, sand and organic matter) are important in determining the transport of chemicals over the

environment. These transport and dispersions depend on the formulation of pesticides (chemical properties), type of application, geographical conditions as well as the frequency of its use, climatic conditions, product variety, planting, the soil and weather conditions (Bermúdez-Couso et al., 2013).

Pesticides are generally disintegrated into CO_2, water, ammonia and mineral salts. In addition, they are degraded into some chemicals known as transformation products or degradation products (Somasundaram and Coats, 1990). Even if they are found ng/L or µg/L concentration in aqueous media, it has a potential to create a risk on human health and environment. That's why, the issue of pesticide degradation should be detailed seriously. Degradation mechanism may occur with biotic and/or abiotic factors in environment. While biotic factors are associated with microorganism and/or plants, abiotic factors are correlated with photochemical reactions (Fenner et al., 2013). Heat and light are two primary abiotic factors involved in degradation mechanism. pH may also be considered as important factor for some pesticides; because some of them may exhibit sensitivity to pH (Coats, 1991). Due to the presence of different active substances, the effect of the pH value on the pesticides may vary depending on the molecular structure of the target organic substances (Ku et al., 2000). While some pesticides remain stable in the acidic environment, there are also pesticides that can be easily degraded by hydrolysis in an alkaline environment. Matsumura and Murti (1983) reported that microorganisms, a biotic factor, is known to be important for pesticide breakdown. They classified the mechanism as enzymatic and nonenzymetic. Nonenzymatic factors are known as the factors by which microbes may contribute to the degradation due to the physical factors such as pH, UV light. To put forward more explicitly, these factors can promote the chemical reactions in various ways. For instance, the microbes can absorb the energy from light and transmit it to the pesticide molecule. However, enzymatic reactions stand clearly for the microbial activity during the degradation. If microbes cannot utilize the energy from pesticides, microbial activities may occur via enzyme and/ enzyme with substrate,

known as incidental mechanism. But, if pesticides are utilized as an energy source by the microbe then degradation becomes possible via the process known as catabolism.

With all these degradation mechanisms, it can be inferred that the formation of by-products may be emerged easily in any way. Even some by products are in low concentration in natural environment, numerous of them should be taken into consideration due to the different toxic properties for each, some being more toxic than the parent compound.

2.2.1. Fate of Pesticides in Air

The fate of pesticides in the air can be affected by the application method of the pesticides, vapor loss caused by application after planting or wind erosion events in the soil. Other influencing factors are the physico-chemical properties of the pesticides, the amount used, the nature of the crop and soil characteristics. Sometimes, more than half of the amount applied may enter into the atmosphere within a few days (Van Dijk et al.,1999). Pesticides and their possible by-products can be transported long distances and can reach to the water courses via wet or dry deposition. Also, possible exposure of human beings to the pesticides may occur via inhalation. All these will lead to serious risks when considering the extent of environmental pollution created and the resulting damage (Tiryaki and Temur, 2010).

2.2.2. Fate of Pesticides in Water Courses

Pesticides have high potential for critically contaminating water sources and transporting them to the hydrosphere. These chemicals can reach the rivers, ponds and ocean via diffuse and/or point sources in the form of drainage, leakage, surface and subsurface flows, soil erosion and spraying on fields. In contrast to diffused sources, point pollution sources have a definite location and may include operational or

accidental spills, overflow from drainage, railways or parking lots on urban impervious surfaces (Reichenberger et al., 2007).

Recently, emergence of pesticide pollutants in waters such as drinking water, groundwater and surface waters has been addressed in detail (Luo et al., 2014). The pesticides pollution in water depends not only on their chemical structure but also the nature of the aquatic environment. When the chemical properties of pesticides are considered, persistency should be taken into consideration as a critical factor. If a pesticide has high persistency in aquatic environment, it presents a great danger. Because, in the long run, it may get accumulated within various components. As an evidence of this occurrence, accumulation of pesticide residues observed in the bodies of fishes can be given (Edwards, 1977). The toxic properties of a pesticide seem to be more critical compared to its persistency. That is, pesticides which have low persistence but show toxic properties are attracting more attention in recent years. Such chemicals can be dangerous for aquatic life forms such as fishes, invertebrates and plants even if they are found in low concentrations. When all these effects are considered, it is necessary to take these transport processes into account and their interactions to assess the groundwater and surface water risks to be encountered.

2.2.3. Occurence of Pesticides in Water Courses Around the World

It is inevitable that the surface and especially the ground water is polluted by pesticides near agricultural areas. If water consumed by people is considered, it is of concern for public health (Herrero-Hernández et al., 2013). The presence of such chemicals in water sources is now regarded as the most important environmental problem and substantial regulations related to this problem have been established. Studies show that there is a monitoring network to identify pesticide residues around the World against the pollution problem. Table 2.1 presents average values of some pesticides detected in various environments. As seen from this table, a wide range of occurrence is present.

Table 2.1 Occurrence of Pesticides in Water Courses Around the World

Pesticide	Maximum Concentration (ng/L)	Reference
Atrazine	50.7 (in Black Sea Region)	Orlikowska et al., (2015)
Terbutyhylazine	1111 (in Baltic Coast)	
Bentazone	221 (in Baltic Sea)	
Diuron	107 (in Baltic Sea)	
Fluometuron	12717 (in Spain)	Herrero-Hernández et al., (2013)
Diazinon	2807 (in Spain)	
Myclobutanil	7208 (in Spain)	
Bentazone	10550 (in Austria)	Loos et al., (2010)
N,N- Dimethylsulfamid	52000 (in Germany)	
Chloridazon-desphenyl	13000 (in Germany)	
Carbamazepine	390 (in Austria)	
Bisphenol A	2299 (in US states)	
Diuron	279 (in groundwater)	
Terbutryn	276 (in Switzerland)	Morasch, (2013)
Isoproturon	4565 (in Switzerland)	
Mecoprop	933(in Switzerland)	
Irgarol	2103 (in Switzerland)	

Pesticide	Maximum Concentration (ng/L)	Reference
Terbutryn	276 (in Switzerland)	
Propiconazole	63 (in Switzerland)	

2.3. Treatment Alternatives for Pesticides

Several alternatives have been considered by the researchers toward the pesticides removal from waters. One of these alternatives is an adsorption process in which various adsorbents such as pulp ash (Gupta et al., 2002), active carbon produced from rubber (Hamadi et al., 2004) palm kernel, oil shale ash (Al-Qodah et al., 2007), chestnut Shell (Memon et al., 2007), walnut Shell (Memon et al., 2008) watermelon bark (Memon et al., 2008), coconut Shell (Ignatowicz, 2011) and Cellulose/Grafen Composite (Zhang et al., 2015) have been tested. Removal efficiencies reported are between 90-99% in these studies. For example, Gupta et al. (2006) used fertilizer (carbon slurry) and steel industrial (blast furnace slag, dust, sludge) wastes as adsorbents for the removal of 2,4-D and carbofuran pesticides. The most efficient adsorbent was determined carbon slurry; because, pesticides are adsorbed about 70-80% on the adsorbent. Memon et al. (2008) investigated the removal of methyl parathion by using watermelon shell as adsorbent and reported about 99% removal efficiency at pH 6. Salman et al. (2011) studied adsorption on 2,4-dichlor bophenoxyacetic acid (2,4-D) and bentazone removal by using banana stalk activated carbon as an adsorbent. They reported that the pesticides removal efficiency decreases when the initial concentration of the contaminant is increased. Gupta et al. (2011) used waste rubber tires as adsorbents to remove methoxychlor, methyl parathion and atrazine and removal efficiency %91, %71, %82 for the pesticides was taken, respectively. In these studies, researchers claimed that adsorption process is cost-effective since the adsorbents used were produced from the natural wastes.

Another alternative to remove the pesticides from water courses is biological treatment. There are several studies about biological remediation for pesticide removal based on bioaugmentation, natural attenuation and biostimulation (Marican and Durán-Lara, 2018). Studies reveal that microorganisms are capable of degrading pesticides (Singh et al., 2006; Mir-Tutusaus et al., 2014; Deng et al., 2015). However, the environmental factors such as pH, temperature, concentration of pesticide, nutrients affect the remediation negatively (Anwar et al., 2009). Feakin et al. (1994) claimed that biological methods are not preferable due to the toxic and complex nature of the insecticides. Similarly, Zhang and Pagilla (2010) reported that conventional biological treatment is not possible because these chemicals are resistant to biodegradation and are toxic to microbial cultures when present in high concentrations in water.

Recently, several studies put forward that AOPs are the most efficient method for the treatment of wastewaters containing pesticides. AOPs rely on the formation of hydroxyl radicals with high oxidant properties and provide efficient treatment. Some of these processes include Ozonation, Fenton, Fenton-like, Photo-Fenton, UV / H_2O_2, titanium dioxide and combinations with O_3 / H_2O_2. Arnold et al. (1996) achieved complete degradation of Alachlor pesticide by Fenton processes at 25^0C (C_0=26.4mg/L, Fe^{2+}= 295 mg/L, H_2O_2= 170 mg/L, pH=2.5). Pignatello and Sun (1995) succeed complete mineralization of 28.4 mg/L Metelachlor by Photo-Fenton processes with 340 mg/L H_2O_2 and 55.8 mg/L Fe^{3+}. Huston and Pignatello (1999) investigated the degradation of 38 mg/L Aldicarb by Photo-Fenton processes. They observed that complete degradation of Aldicarb and 62% reduction in TOC is possible in 2 hours. In addition to all, the formation of nitrate and sulfate is observed after the reaction. Teixeira et al. (2005) conducted Photo-Fenton, UV/H_2O_2 and Fenton processes experiments on wastewater containing fungicides and insecticides and reported that Photo-Fenton is the best method for the removal at Fe and H_2O_2 concentration ranging between 0.5-2.8 mmol/L and 10-500 mmol/L, respectively. Mitsika et al. (2013) investigated the effectiveness of Fenton and Fenton-like

processes on the treatment of Acetamiprid-containing wastewaters under different operational conditions. Finally, they found that 5 mg/L acetamiprid is completely degraded approximately in 10 min at conditions of pH=2.9, $Fe^{2+}:H_2O_2 = 3mg*L^{-1}/40mg*L^{-1}$. In addition to these studies, Gozzi et al. (2012) applied Fenton, Photo-Fenton and Ozonation separately to degrade the chlorimuron-ethyl herbicide and reported that the highest yield (85%) was attained in 90 minutes with Photo-Fenton application. The removal of the paraquat herbicide was searched by Santos et al. (2011) with the Fenton process and the results proved that it is completely removed under the conditions of T = 30°C, $[Fe^{2+}] = 5.0 \times 10^{-4}$ M, $[H_2O_2] = 1.6 \times 10^{-2}$ M, and pH = 3.0, for [Paraquat] = 100 mg/L. They stated that there occurred 40% mineralization within 4 hours based on the results obtained from TOC analysis.

Some scientists have proven that ozonation is effective in pesticide removal (Ikehata and Gamal El-Din, 2005; Chen et al., 2013; Cruz-Alcalde et al., 2017). Roche and Prados (1995) indicated that malathion was eliminated by the combination of Ozone and Hydrogen peroxide (O_3/ H_2O_2). In addition, literature studies on combined chemical, physical and biological processes put forward that such methods have also potential to degrade pollutants. For example, Tepuš et al. (2009) used adsorption resins, nanofiltration (NF) and reverse osmosis (RO) membranes for the removal of pesticides (atrazine, deethylatrazine and deisopropylatrazine) and nitrates from groundwater. Their results showed that adsorption resins are successful for pesticide removal but not for nitrate removal. Reverse osmosis rejects all compounds whereas nanofiltration provides removal of Atrazine only. Zhang and Pagilla (2010) applied NF and Photo-Fenton processes to treat industrial wastewaters containing malathion, and indicated that the combined processes are more efficient when it is compared with the both process conducted separately. Yahiaoui et al. (2011) achieved approximately 95% removal of metrubizine by using an electrochemical reactor with UV oxidation.

2.4. Advanced Oxidation Processes (AOPs)

Although AOPs involve different processes, the only common goal is to produce hydroxyl radicals (OH•). These radicals are an exceptional type of oxidant and known as the best one (2.8V) after the Fluorine oxidant. The versatility of AOPs is supported by offering different options for the production of OH• and by establishing specific treatment requirements (Andreozzi, 1999). Various types of AOPs are based on the formation of OH• through chemical reactions such as photochemical or electrochemical reactions. AOPs have recently got attention for wastewater treatment and many researchers have applied these processes in their work (Oturan and Aaron, 2014).

2.4.1. Fenton Processes

The Fenton process, known as the oldest of the AOPs, was first tested by Fenton in 1894 to oxidize tartaric acid. This method has also been applied by other researchers until today. This process is applied to pollutant degradation based on OH• formed by the mixture of hydrogen peroxide (H_2O_2) and iron salts (Fe^{2+}) (see reaction 1) (Basturk and Karatas, 2014; Sruthi et al., 2018). H_2O_2 and Fe^{2+} are known as cheap, easy to handle, safe and environmentally safe chemicals. The high performance of the Fenton process has the advantages of being easy to degrade pollutants in room conditions and not being toxics. With this advantage, it is applied in the treatment of olive mill wastewater, pulp mill wastewater, pesticide wastewater and dye wastewater and so high yields were obtained after the treatment. However, they have some disadvantages as well. Operational cost, being effective only at low pH, formation of excessive amount of sludge and difficulty in recovery of catalysts are the main disadvantages for the Fenton process. To overcome these disadvantages, researchers have studied on variables such as catalysts. Fenton processes have recently been divided into groups, and applied in order to increase the efficiency of wastewater treatment. These are

Photo-Fenton, Electro-Fenton, Cavitation- Fenton and Microwave Fenton processes (Wang et al., 2016).

2.4.2. Photo-Fenton Processes

Photo-Fenton processes are applied to provide energy sources to reduce the catalysts loading that are active in the Fenton and/or increase the activity of the catalyst by using UV or visible light sources. Like classical Fenton, the most efficient results are obtained at pH 3. It is one of the most preferred AOPs to produce more OH• and to degrade organic pollutants with higher efficiency when it is compared with classical Fenton (Wang et al., 2016).

Based on a variety of photo reactions, OH• are generated by photo-reduction of metal ions and initiate the decay process. Photo-Fenton reaction has many advantages when compared with classical Fenton reaction;

- Compared to classic Fenton, OH• formation occurs rapidly with the help of photons, so the degradation occurs faster.
- Operational cost is low; because this process requires less chemical use.

While the sludge formation is low in Photo-Fenton, the classic Fenton forms the opposite of this situation and produces a large amount of sludge. This sludge production is known to lead to increased cost; because the sludge produced needs treatment (Ameta et al., 2018).

2.4.3. UV/H2O2 Processes

Another treatment process is UV/ H_2O_2 among AOPs. The process is based on the addition of H_2O_2 into the reactor in the presence of UV light source, and the formation of OH• is observed like for the Fenton and Photo-Fenton processes. OH• formation is

caused by the decomposition of H_2O_2 with UV radiation. These oxidants subsequently degrade the target pollutants, as noted for the other processes. The influencing parameters include peroxide dose, UV lamp type and its density, reactor contact time, pH and temperature (Chang et al., 2010). Effects of these parameters are explained in detail in Section 2.3.5.

2.4.4. The Mechanism of Fenton, Photo-Fenton and UV/H2O2

The hydroxyl radicals ($OH\bullet$) formed with help of H_2O_2 and Fe^{2+} have a crucial effect on this processes. Due to having strong oxidizing properties, $OH\bullet$ is the main factor for the degradation of organic and inorganic compounds (Pignatello et al., 2006).

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH\bullet \quad ...(1)$$
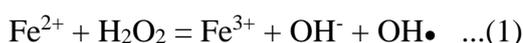
Equation 1 is the main reaction for the Fenton's oxidation and shows the oxidation of Fe^{2+} to Fe^{3+} to decompose H_2O_2 into $OH\bullet$. However, it is important to understand the whole process through other steps involved, as below.

$$Fe^{3+} + H_2O_2 = Fe^{2+} + H^+ + O_2H\bullet \quad (2)$$

$$Fe^{2+} + OH\bullet = Fe^{3+} + OH^- \quad (3)$$

$$Fe^{2+} + O_2H\bullet = Fe^{3+} + HO_2^- \quad (4)$$

$$Fe^{3+} + O_2H\bullet = Fe^{2+} + H^+ \quad (5)$$
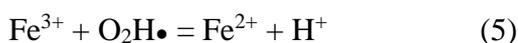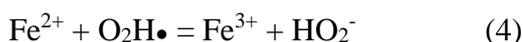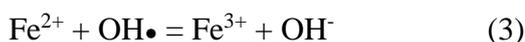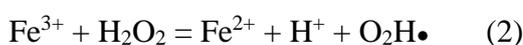
Equation (2) to (5) represent the rate limiting steps in the Fenton's reactions. H_2O_2 is consumed and the Fe^{2+} is recovered from Fe^{3+} during the reaction. Other possible steps in the process of Fenton are radical-radical and reaction of radicals with H_2O_2 as presented below (Eq. 6-9).

$$OH\bullet + OH\bullet = H_2O_2 \quad (6)$$

$$OH\bullet + H_2O_2 = O_2H\bullet + H_2O \quad (7)$$

17

$$O_2H\bullet + O_2H\bullet = H_2O_2 + O_2 \quad (8)$$

$$OH\bullet + O_2H\bullet = H_2O + O_2 \quad (9)$$
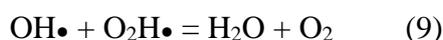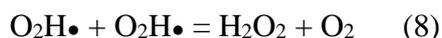
All these reactions clearly show how complex the Fenton's reaction is. The formation of $OH\bullet$ occurs in initiation reaction (Eq. 1). However, $OH\bullet$ can also be consumed by Fe^{2+}, H_2O_2 and hydroperoxyl ($O_2H\bullet$). Also, it can react with itself as seen in Eq. 6. All these equations demonstrate that H_2O_2 can be both radical producer or a consumer (Babuponnusami and Muthukumar, 2014).

$OH\bullet$ have the ability to degrade organic matter (RH) effectively. The mechanism are shown in the following reactions (Lucas and Peres, 2006).

$$RH + OH\bullet = R\bullet + H_2O \quad (10)$$

$$R\bullet + Fe^{3+} = R^+ + Fe^{2+} \quad (11)$$

$$R^+ + H_2O = ROH + H^+ \quad (12)$$
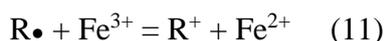
Contrary to Fenton's reaction, the degradation of contaminants is more in the Photo-Fenton reaction. In this reaction, UV irradiation contributes to the formation of $OH\bullet$ by photolysis of Fe^{3+} complex ions and H_2O_2 as shown in Eq. (13). In the presence of H_2O_2, the regenerated Fe^{2+} from the photolysis of Fe^{3+} species is oxidized by H_2O_2 and produces new $OH\bullet$. Thus, the oxidation of organic compounds will accelerate (Badawy et al., 2006).

$$Fe^{3+} + H_2O_2 + hv = Fe^{2+} + H^+ + OH\bullet \quad (13)$$
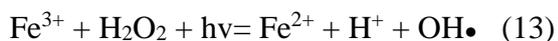
H_2O_2 can be decomposed by UV radiation absorbed in wavelengths ranging from 200 nm to 300 nm and gives a homolytic mass of O-O bond of the H_2O_2 molecule. This situation may contribute to the decomposition of H_2O_2 as secondary reactions (Oturan and Aaron, 2014). The following reactions give stepwise initiation, propagation and termination reactions of UV/ H_2O_2 (Eq.14-20).

$$H_2O_2 + hv = 2OH\bullet \quad .(14)$$

$$OH\bullet + H_2O_2 = HO_2\bullet + H_2O \qquad (15)$$

$$HO_2\bullet + H_2O_2 = OH\bullet + H_2O + O_2 \quad (16)$$

$$OH\bullet + HO_2^- = HO_2\bullet + OH^- \qquad (17)$$

$$2HO_2\bullet = H_2O_2 + O_2 \qquad (18)$$

$$HO_2\bullet + OH\bullet = H_2O + O_2 \qquad (19)$$

$$2OH\bullet = H_2O_2 \qquad (20)$$
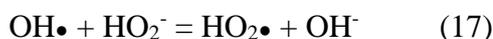
2.4.5. Factors affecting the Fenton, Photo-Fenton and UV/H2O2 Processes

The way and time of decay of the pollutants vary according to the active compounds in the environment. The most efficient conditions must be established for the degradation of each active compound. Parameters created at the beginning such as pH, temperature, should be examined firstly. Besides that, the amount of H_2O_2, the catalysts (Fe^{2+}, depending on the catalyst used) and the initial concentration of contaminants must be determined for each contaminant. Mentioned parameters are the main items affecting the UV/H_2O_2, Fenton and Photo-Fenton reactions. Therefore, the systematic explanation and analysis of each parameter should be done to get best and certain results.

2.4.5.1. Effect of pH

Optimum pH is one of the most important parameters in Fenton and Photo-Fenton processes and generally shows high performance in the range of 3-4 (Neyens and Baeyens, 2003). There may be positive and negative effects on pollutant degradation when the pH is lower or higher than optimum pH (Pouran et al., 2015). Tang and Huang (1996) figured it out how degradation of 2,4 dichlorophenol is affected at higher and lower pH conditions. Low pH has adverse effects on efficiency as well as

on reactions. On the contrary, at high pH, decrease in the formation of OH•, scavenging of H_2O_2, formation of ferric hydroxides complexes and reaction of OH• themselves may be observed (Babuponnusami and Muthukumar, 2014). However, if the pH is above 3, formation of $Fe(OH)_3$ is observed with a low catalytic property (Hashemian, 2013). In accordance with these expectations, Yang et al. (2014) noted that the most efficient removals are obtained at pH 3 in the wastewater containing dye, and the yield is clearly reduced as the pH is increased. Conversely, Xu et al. (2014) proved that dye wastewater is treated efficiently at low pH with a different catalyst. Also, Zhang et al. (2005) and Hermosilla et al. (2009) obtained the highest yield at pH 2.5 in the case of leachate treatment; but they stated that it does not show huge differences at pH between 2 and 4. Supportively, Katsumata et al. (2005) examined the importance of pH in the removal of linuron pesticide by applying Photo-Fenton and stated that the best results were attained at pH 4.

However, there are some contrary findings in the literature regarding the effect of pH. As an example, You et al. (2011) pointed out that they had the highest yield at pH 6 in the Fenton-like process, applied to alcohol wastewater. Similarly, Huang et al. (2013) tried a different catalyst for the degradation of aniline, and they achieved the best results at pH 4-6.

2.4.5.2. Effects of H2O2

The amount of H_2O_2 is an important source for the formation of OH• which affects the oxidation yield. Because as the amount of H_2O_2 increases, the formation of OH• will increase and this will increase the degradation efficiency of the pollutant (Tamimi et al., 2008). However, if too much peroxide is present, it will react with OH• and cause OH_2• which has a low oxidant property (Ramirez et al., 2007).

Javier et al. (2002) pointed out to the importance of the amount of H_2O_2 in applying Fenton process to carbofuran pesticide which belongs to carbamate family. Nieto et

al. (2011) reported that the optimal H_2O_2 value for olive mill wastewater was 100 g/dm³ and the organic matter was removed by 90%. Similarly, in a study conducted toward the treatment of olive mill wastewater by Photo-Fenton, García and Hodaifa (2017) reported that they obtained 90% COD and TOC removal when H_2O_2 concentration was at least 8 g/L. Another study conducted with the UV/ H_2O_2 process applied to the synthetic wastewater containing Rhodamine B dye revealed that optimum value for H_2O_2 is 1.67 mM at neutral conditions where 73% decolorization was attained (AlHamedi et al., 2009).

2.4.5.3. Effects of Fe2+

The amount of catalyst has an important effect on the degradation of pollutants via AOPs. As in the case of H_2O_2, there is an optimum value for the Fe amount. When Fe is added in excess, the reaction in Eq. 3 takes place. The excess amount of catalyst will begin to deplete the OH•. In addition to this effect, it will also add to the overall cost of process not only due to the cost of Fe as a chemical but also excessive amounts of sludge formation which will lead to the extra cost for the sludge treatment. The excess amount of catalyst Fe will cause excessive amounts of sludge formation. Therefore, the need for the sludge treatment process brings extra cost (Wang et al., 2016).

Samet et al. (2012) reported that 90% COD removal in wastewater containing Chlorpyrifos pesticide was achieved with 120 mg/min H_2O_2 and 5mM Fe^{2+} in acidic medium with Fenton process and also they claimed that it could be eliminated within 50% less time in the solar Photo-Fenton process. Moreover, Mitsika et al. (2013) investigated the degradation of Acetamiprid pesticide with Fenton and Fenton-like processes by minimizing the iron concentration and shortening the reaction time, and so far they determined the optimum Fe $^{(+2)}$ value as 3 mg/L. At the end of the experiment they succeed to degrade Acetamiprid completely with the ratio of 3 mg/L Fe^{+2} :40 mg/L H_2O_2 in 10 minutes. Değermenci et al. (2014) studied the effect of Fe^{+2}

concentration between 0.32 and 1.92 g/L for cosmetic wastewater treatment and the optimum value was found to be 1.61 g/L. When this value was exceeded, the COD removal increased from 88% to 90%. Barbusiński and Majewski (2003) have used 60 and 50 mg/dm^3 H_2O_2 and zero valent iron (Fe^0) as a catalyst respectively for the synthetic wastewater containing 100 mg/dm^3 acid red 18 dye in Fenton process and have completely decolorized the wastewater. On the other hand, some researchers emphasize that there are various catalysts that can be used instead of Fe containing catalysts. Hydrated hematite, Magnetite, catalysts including copper and manganese are other examples for catalysts used in Fenton-like processes (Balci et al., 2009; Mendez-Arriaga and Almanza, 2014; Kalal et al., 2014; Avetta et al., 2015).

2.4.5.4. Effects of Contaminant Concentration

Contaminant concentration is one of the important parameter that affect the overall degradation mechanism in AOP's. In many studies, it is stated that if the contaminant concentration is increased, the removal rate will decrease (Lucas and Peres, 2006; Tamimi et al., 2008). They reported that if the contaminant concentration is increased, there will be increment in the contaminant molecules. However, it will not affect the formation of OH•. That's why, degradation rate decreases. For Photo-Fenton or UV/H_2O_2 processes, the removal of the contaminant occurs slowly in higher concentrations (Zhang and Pagilla, 2010). Modirshahla et al. (2007) claimed that the increased dye molecules absorb the light and photons will never reach the catalyst surface. At this point, it is inevitable that the removal efficiency decreases. Daneshvar et al. (2008) explained this occurrence with inner filter effects.

2.4.5.5. Effects of Temperature

As known, in chemical reactions, an increase in the temperature generally leads to an increase in the reaction rates (Munoz et al., 2014). The reason for the increment is explained with the efficient consumption of H_2O_2 in Fenton reactions (Zazo et al.,

2011). Benitez et al. (1999) investigated the effect of temperature on the Fenton reaction during the experiments conducted for the degradation of 2,4,6-Trichlorophenol and found that an increase in temperature results in an increase in the rate constant. Nevertheless, applying a process at 20^0C was considered more logical way in order to reduce the energy consumption. In accordance with this fact, researchers generally prefer to study around 25^oC, aiming less energy consumption (Deng and Englehardt, 2006; Hermosilla et al.,2009).

2.4.6. Degradation Kinetics of AOPs

During AOPs, degradation kinetics of contaminants is known to follow bimolecular kinetics and hence can be principally described by second-order reaction kinetics (Yuan et al., 2009). Therefore, the reaction kinetics of contaminants with AOPs can be expressed with the Equation 21.

$$\frac{dC}{dt} = k_2 * (C) * (O) \qquad (21)$$

where;

k_2   : Second-order rate constant (volume/(mass × time))

[C]   : Contaminant concentration (mass/volume)

[O]   : Oxidant/radical concentration (mass/volume)

However, when the oxidant concentration in the water solution is excess compared to that of contaminant, the reaction rate depends mainly on contaminant concentration, so follows the pseudo first-order kinetics, as well (Sharpless and Linden, 2003; Sun et al., 2007; Oancea and Meltzer, 2014 ; Lopez-Lopez et al., 2015). Then, the reaction kinetics can be simply expressed by Equation 22.

$$\frac{dC}{dt} = k_1 * (C) \qquad (22)$$

where;

k_1 : Pseudo first-order rate constant (time^{-1}) = k_2 (O)

When Equation [22] is integrated, the following equations [23] and [24] are obtained:

$$Ct = Co*e^{-k_1 t} \qquad (23)$$

$$\ln \frac{Ct}{Co} = -k_1 * t \qquad (24)$$

Another kinetic model, called as Behnajady-Modirdhahla-Ghanbery (BMG) kinetic model, was also proposed by Behnajady et al. (2007) to describe about the oxidation of organics by Fenton process. They state that BMG model is simpler and more accurate to forecast the Fenton process. Conversely, Park et al. 2017 claimed that the pseudo-first-order kinetic model can adequately interpret the rapid degradation but not the retarded degradation whereas BMG model well describes both rapid initial degradation and retarded degradation phases.

BMG model is as given in Equation 25 below;

$$\frac{Ct}{Co} = 1 - [t/(m+bt)] \qquad (25)$$

In linearized form:

$$t/[1-(Ct/Co)] = m + bt \qquad (26)$$

The constants m and b are constants for the oxidation capacities and reaction kinetics, respectively. According to the equation, the slope and the intercept m and b constants can be obtained from the time dependent t / [1- (Ct-Co)] graph (Park et al., 2017). The importance of these constants, m and b, has been put forward with the studies done and the available equations. These constants can also be determined from the derivation of the main equation of BMG kinetic model (Eq. 25) ;

$$\frac{dC/Co}{dt} = \frac{-m}{(m+bt)^2} \qquad (27)$$

If t is close to zero, then the equation given below can be derived;

$$\frac{dC/C_0}{dt} = -\frac{1}{m} \qquad (28)$$

And this equation is defined as the first yield of contaminant removal in the process. Thus, a high $1/m$ indicates that the initial degradation rate of contaminant is high. If the time, t, is long and close to infinity, the following equation (Eq. 29) is derived and the constant b is called the theoretical maximum contaminant removal. This indicates the maximum oxidation capacity for Fenton and Photo-Fenton processes at the end of the reaction (Behnajady et al., 2007; Arat and Biçer, 2015; Zhang et al., 2016 ; Xu et al., 2018).

$$\frac{1}{b} = 1 - \frac{C_{t\to\infty}}{C_0} \qquad (29)$$

2.5. Chloridazon (CLZ)

CLZ (Figure 2.1) is an active compound of Pyramin, used for controlling sugar beet and beet root weeds for more than 20 years (Lingens et al., 1985). It is utilized as a selective systematic herbicide that inhibits photosynthesis. This pesticide, which has many commercial names in Europe, has been put on market by the Germans with the name of Pyramin WG (URL1).
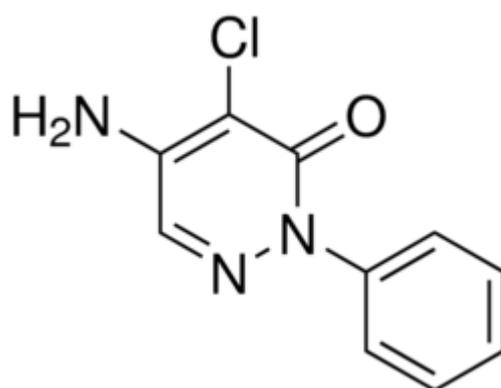
Figure 2.1. Chemical structure of CLZ (URL 2)

2.5.1. The physical and chemical properties of CLZ

Physical and chemical properties of CLZ are presented in Table 2.2.

Table 2.2. Physical Properties of CLZ (EFSA, 2009)

Name of Properties	Details
Chemical Name	Chloridazon (5-amino-4-chloro-2-phenyl-3(2H)-pyradizonone)
Synonym	Pyrazon
Molecular Formula	$C_{10}H_8ClN_3O$
CAS number	1698-60-8
Appearance	Crystalline, Colorless
Molecular Weight (g/mol)	221.6
Water Solubility (mg/L)	422
Density (g/cm^3)	1.54
Log Kow	1.2
Koc	89-340
Dissociation Constant -pKa	3.38
Vapor Pressure	$4.50*10^{-7}$ mmHg at 20ºC
Half-life (days)	105

According to the report published by EFSA, CLZ is a chemical with low biodegradability (EFSA Scientific Report, 2007). In accordance, Capri et al. (1995) described it as a type of pesticide with high persistency. Further, Khan et al. (2012) claimed that this pesticide, which has a high soil mobility, is likely to pass into the water. Log Kow (Octanol-Water Partitioning Coefficient) value points to the possibility to leach to groundwater as micropollutants with a Kow value below 1.5 have a high probability of staying in liquid phase (Dougherty et al., 2010).

CLZ is known to be mobile in some soils (Fernández-Pérez et al., 2011). Reported Koc (Organic Carbon-Water Partitioning Coefficient) values of CLZ are between 89-340 (Tomlin, 2004). According to Cohen (1990), in classification, this Koc value indicates that CLZ have high mobility in soil.

2.5.2. Environmental Fate of CLZ

CLZ is mobile in various soil types and it shows persistency in soil and water (EPA, 2005). The photolysis half-life in the soil is 69 days whereas half-life in aerobic soil is between 90 and 152 days. In anaerobic conditions, the half-life is 307-607 days. The degradation time of CLZ in water was determined to be 12.5 days by photolysis. However, this pesticide has proven to be stable at pH 5 and 7; no degradation will occur. In the EFSA report, experiments were carried out at pH 7 and temperature 25°C, and the results show that CLZ can break down when photolysis is present and the half-life falls from 76 to 22 between March and June.

Considering the properties mentioned above, it is possible that CLZ can be transported from soil to surface and/or groundwater. And, it is in the category of pollutants that may cause pollution in water resources (EPA, 2005).

2.5.3. CLZ in Water Courses

CLZ can move in various soil types and therefore it has potential to enter surface and groundwater (Buttiglieri et al., 2009). There are very few scientific reports on its occurrence and fate in surface and groundwaters. Table 2.3 presents CLZ and its two by-products, desphenyl-Chloridazon (DPC) and methyl-desphenyl-Chloridazon (Me-DPC), detected in water resources at different locations.

Table 2.3. Occurrence of CLZ in Water Sources at Different Locations

Pesticide and Locations	Maximum	Reference
CLZ in Germany inland water	890	Buttiglieri et al. (2009)
DPC in Germany	9500	
Me-DPC in Germany	140	
Netherlands	720	Oskam et al. (1993)
Chile	1380	Barra et al. (1995)
In Mediterranean Sea	1.6	Orlikowska et al. (2015)
In Black Sea	4.9	
Baltic Sea	7.4	
Estauries Baltic Coast	126	
Cossaux	18	Morasch, (2013)
Moulinet	48	
Feurtille	1937	

Pesticide and Locations	Maximum	Reference
Me-DPC in EU	1200	Loos et al. (2010)

2.5.4. Removal methods for CLZ from Water Sources

In this section, literature studies on the removal of CLZ from water are summarized. As seen below, removal methods of adsorption, catalytic photodegradation and biodegradation have been studied.

In the adsorption studies carried out by using natural and ammonium kerolite (Socías-Viciana et al., 2006; Ureña-Amate et al., 2008) and sepiolite (González-Pradas et al., 2005), treated with heat and acid, were used. Socías-Viciana et al. (2006) found that ammonium kerolite is more effective than the natural kerolite adsorbent and the best results were attained at 40ºC. González-Pradas et al. (2005) and Ureña-Amate et al. (2008) have shown that CLZ removal is possible at 60.9-88.3% depending on the conditions. These studies revealed that heated adsorbents are more effective than the adsorbents treated with acid. Further details on these adsorption studies are provided in Table 2.4.

Regarding the biological treatability of CLZ, Buttiglieri et al. (2009) used aerated fixed bed bioreactor and they found that CLZ is completely transformed to the by-product DPC. Chromatographic measurements revealed that CLZ was below the LOD value of 0.05 µg/L. They claimed that CLZ did not pose any treat for the environment as it will be removed almost completely but by-product formed is resistant in further degradation.

Fouad and Mohamed (2011) proved that it is possible to remove CLZ with photodegradation in the presence of Coreshell Magnetic Nanocomposites (Fe_3O_4 @ Au and Fe3O4), and Fe_3O_4 @ Au catalyst is found more efficient because gold has a

plasmonic phenomenon to accelerate the degradation processes. It was seen that if the amount of catalyst increases, the degradation rate will also increase. In the experiments, two different light sources were used to observe its effect and UV lamp is proven to be more effective than the sun-light. The relevant results are shown in detail in Table 2.4.

In another study, Khan et al. (2012) examined the mechanism of decomposition of CLZ and Metribuzin pesticides in water by photocatalysis with titanium dioxide. They observed that CLZ is removed at high yield (62%) under acidic conditions in the presence of UV. They also examined the effect of type of catalyst, pH, concentration of catalyst, pesticide and effect of electron acceptors for each pesticide.

Recently, Azaari et al. (2016) investigated the removal of CLZ by applying UV/ H_2O_2 and UV/TiO_2. The study generally focused on the by-products formation and degradation pathway followed. Both experiment lead to the same products, so they went on with UV/TiO_2, and they identified 7 different by-products named as P1 to P7 in the presence of TiO_2.

Summary of these literature studies is provided in Table 2.4. As seen from this table, a few studies have been conducted on the CLZ removal from water courses. Besides being in limited numbers, they are not fully detailed studies, except the one by Azaari et al. (2016) who investigated the possible by-products of CLZ degradation. Moreover, the removal efficiencies attained are quite variable.

Table 2.4. Different Degradation Methods for CLZ Removal

Method	Conditions	Initial CLZ Conc.	Removal, %	Adsorption capacity, mg/kg	By-products	Kinetic Study	Reference
Adsorption	Adsorbent: 0.5 g Kerolite and 2.0 g Bentonite Observed at 25ºC in 24 h	$45*10^{-4}$ cmol/dm^3	17.1% (Bentonite) 85.1% (Kerolite)	0.072 cmol/kg (Bentonite) 1.30 cmol/kg (Kerolite)	No	No	Gonzlez-Pradas et al. (2000)
	Adsorbent: 0.25 g Sepiolite Adsorbents heated at 110, 200, 400, 600ºC	10.30 mg/L	(S-600):60,9% (S-1.0):5.08%	(S-600):164 mg/kg (S-1.0):2.89 mg/kg	No	No	González-Pradas et al. (2005)

Method	Conditions	Initial CLZ Conc.	Removal, %	Adsorption capacity, mg/kg	By-products	Kinetic Study	Reference
Adsorption	Acid-treated adsorbents with H_2SO_4 at two different concentration 0.25 and 1M						
	Adsorbent: 0.25 g ammonium and natural kerolite 10, 25 and 40^0C at stable pH in 24 h Analysis by HPLC	$3.83*10^{-5}$ to $11.5*10^{-3}$ mol/L	---	$9.6*10^2$ mol/kg	No	No	Socías-Viciana et al. (2006)
	Adsorbent: 0.25 g Kerolite Adsorbents heated at 110, 200, 400, 600^oC	1-200 mg/L	(K-0.5):52.8% (K-600):88.3%	(K-0.5):184.7 mg/kg (K-600):2253 mg/kg	No	No	Ureña-Amate et al. (2008)

Method	Conditions	Initial CLZ Conc.	Removal, %	Adsorption capacity, mg/kg	By-products	Kinetic Study	Reference
	Acid-treated adsorbents with H_2SO_4 at two different concentration 0.25 and 0.5M						
Aerated fixed bed bioreactor	Microorganisms derived from water phase Microorganisms circulated with flow rate 16ml/min in closed loop Kept in dark condition	1 mg/L 10 µg/L	<LOD	---	Yes	Yes	Buttiglieri et al. (2009)
Photo-degradation	Nanoparticles of Fe_3O_4 and coreshell Fe_3O_4 @ Au is used as a catalyst	20 mg/L	80% when 10^{-4} M	---	No	No	Fouad and Mohamed (2011)

Method	Conditions	Initial CLZ Conc.	Removal, %	Adsorption capacity, mg/kg	By-products	Kinetic Study	Reference
	Effect of UV and sun light, different irradiation time and different concentration of catalysts on degradation of CLZ		Fe_3O_4 @ Au is used.				
AOP	Using TiO2 photocatalyst for the degradation of CLZ and Metribuzin	0.18mM	62% CLZ removal at acidic conditions	---	No	Yes	Khan et al. (2012)
	UV/ H_2O_2 and UV/ TiO_2	$5*10^{-5}$ mol/L	---	---	Yes	No	Azaari et al. (2016)

2.6. Legislation on Pesticide Pollution Control

Due to widespread use of pesticides for agricultural purposes, their residues are likely to be found in surface and groundwater sources. Physical and chemical factors of each pesticide is an important factor that determines their fate in water (Matthews, 1998). Depending on their chemical stability in nature, they can be degraded in water and can form by products (Krieger, 2010). In addition to the active ingredients, these by-products are mostly classified as toxic substances and their effects on humans are still under discussion.

Due to occurrence of such chemicals in the water, some regulations were in force both in Europe and our country, namely, Ground Water Directive (GWD) (2006/118/EC) (European Union, 2006), and Water Framework Directives (WFD) (2000/60/EC) (EC, 2000).

In EU WFD 2000/60/EC, it is aimed to keep the water bodies in "good water status". Good status is the status to be attained in a water body in terms of both chemical and ecological means. A water body which is in good status requires to meet Environmental Quality Standards (EQS) for 45 priority substances (including several pesticides), as given in Annex X of WFD. In addition to the priority substances list, EU Member States and candidate countries have listed their river basin specific pollutants. Specific pollutants are of regional or local importance, which impart risks either on river basin or national level. EU Member States and candidate countries are supposed to identify their specific pollutants, to provide EQS values for them and then to monitor in water courses toward maintaining the good water status (Loos et al., 2009). Turkey, being an EU candidate country, has determined its country specific pollutants and is on the way to determine the river-basin specific ones. Currently, 250 specific pollutants (including various pesticides) have been identified and the relevant EQS values have been determined. These specific pollutants and 45 priority pollutants are listed in Surface Water Quality Regulation (SWQR) (Official Gazette, 10/08/2016 No: 29797).

The EU Groundwater Directive (GWD) (2006/118/EC) requests the Member States to derive appropriate threshold values (TVs) for several potentially harmful pollutants in order to assess the chemical status of groundwater bodies. Turkish Regulation on Protection of Groundwater against Pollution and Deterioration (TBGW) (Official Gazette 29363, 22/05/2015) takes the GWD and the WFD as the basis and aims to maintain and to restore the good status in groundwater bodies in Turkey. Currently, for the common groundwater pollutants of nitrates and pesticides, quality standards have been set by TBGW at the national level in Turkey. The quality standards set for nitrates and for active substances in pesticides are 50 mg/L and 0.1 µg/L, respectively. The quality standard for the sum of all individual pesticides (including their relevant metabolites, degradation and reaction products), is 0.1 µg/L. Determination of river basin specific TVs for the specific pollutants is on the way.

CHAPTER 3

MATERIALS AND METHODS

3.1. Pesticide Studied

A pesticide, CLZ is used in this study. This pesticide is obtained commercially from the product named Pyrazon which contains 65% of CLZ as an active compound. Physico-chemical properties of CLZ are as presented in Section 2.4.1.

3.2. Synthetic Wastewater

Since there is no CLZ containing wastewater readily available to use in the study, experiments were performed using synthetic water which was prepared by injecting the desired amounts of CLZ from its stock solution into the ultra-pure water. Stock solution was prepared by adding 153.8 mg of CLZ to 1 L of ultra-pure water to yield a 100 mg/L of stock solution. From this solution, desired concentrations were prepared via appropriate dilutions. The concentration ranges studied (20-60 mg/L) are beyond the levels likely to be found in real domestic wastewaters (possibly at μg/L level). The reason for this lies behind two facts. One is that when studied at very low concentrations, real removal efficiency may not be determined as the effluent at the end of treatment might have an undetectable concentration in HPLC. The other one is to make the possible degradation by-products to be observable as the by-product concentrations will be higher when higher influent pesticide is used. Also, this level of CLZ could be possible to observe in the discharges of industries producing this pesticide. So, this concentration range could represent such wastewaters. Nevertheless, much higher CLZ concentration (i.e. >60 mg/L) were not studied, though the CLZ solubility in water is around 400 mg/L, because it would not be

realistic to observe such high concentration in water courses, even in industrial wastewaters, in real life.

3.3. Chemicals

The chemicals used in this study are HPLC grade acetonitrile (Merck, >99.9% Purity), standard of Chloridazon (Sigma-Aldrich, ≥97% purity), sodium hydroxide (Sigma Aldrich, >99.9% Purity), sulphiric acid (Sigma Aldrich, >99.9% Purity), Iron sulphate heptahydrate (Sigma Aldrich, >99.9% Purity), Hydrogen Peroxide (Sigma Aldrich, >30% Purity), Sodium Sulphite (Tekkim, >98%), Potassium Iodade (Tekkim), Potassium triiodide (Tekkim).

3.4. Experimental Set-up

A cylindrical glass reactor presented in Figure 3.1 is used as a reaction chamber for the Fenton oxidation experimentations. This reactor is 6 cm in width, 26 cm in length, with total volume of 1 L. A magnetic stirrer is placed into the reactor, which provides a mixing rate of 600 rpm to allow for homogeneous mixture. The reactor is also connected to the cooling circulator to provide a water circulation via the pipes at upper and sub entrances of the reactor to keep the water temperature at the desired level. The whole set-up is shown in Figure 3.1.

Figure 3.1. Experimental Set-up used for Fenton Oxidation

During Photo-Fenton and UV/H_2O_2 experimentations, as different than the Fenton oxidation, a UV lamp which is held in a 3 cm quartz bulb is placed in the center of the reactor as shown in Figure 3.2. The UV lamp is kept outside the reactor on for 15 minutes to reach a balance before it is placed into quartz bulb. Following each experiment, the reactor and the quartz tube was washed carefully using the distilled water in order not to carry any contamination to the next experimentation.

Figure 3.2. Experimental set-up used for Photo-Fenton and UV/ H_2O_2 Oxidation

3.5. Experimental Method

3.5.1. Experiments with UV/ H2O2

For the experiments with UV/ H_2O_2, the experimental set-up shown in Figure 3.2 was used. A total of 16 experiments were carried out under 4 different experimental sets as presented in Table 3.1. As seen from this table, effects of pH, H_2O_2 concentration, initial CLZ concentration and temperature, on the performance of UV/H_2O_2 treatment were examined under the experimental sets of 1, 2, 3 and 4, respectively. After the desired amount of stock solution was poured into the reactor, and homogenous mixture was provided by means of magnetic stirrer. In the next step, 1 M NaOH or H_2SO_4

solutions was used while adjusting the pH. To measure the pH value, WTW Multi 3620 IDS device was used. Just right after the pH adjustment, H_2O_2 concentration was maintained in the reactor as presented in the experimental plan, through evacuation with a pipe into the reactor. Once the H_2O_2 was added, the UV lamp was put into the quartz tube. Prior to this, as also previously stated, UV lamp was allowed to stand for 15 minutes to reach a balance. As soon as the lamp was turned on, the experiment was started. The samples were taken at specific time intervals and the necessary measurements were performed. Some experiments have been done in duplicate and average of the measurements were reported. These data were indicated with error bars on the relevant figures, where possible. The reason for the lacking cases was the financial limitations to perform CLZ measurements via HPLC.

Prior to all these experiments, two sets of preliminary experiments were performed in order to see the performance of UV and H_2O_2, separately, so as to serve as a baseline. To this purpose, in the first set, H_2O_2 only (i.e. in the absence of UV light), and in the second set, UV light only (i.e. in the absence of H_2O_2) were applied. In the former one, two H_2O_2 concentrations (25 and 250 mg/L) were applied to the solution containing approximately 10 mg/L of CLZ. In the later one, solution containing 5 mg/L CLZ was subjected to UV light exposure at 4 different pH conditions (pH 3, 5, 7, 9).

Table 3.1. Experimental Sets for UV/ H_2O_2 Treatment

Experimental Set Number - Name	pH	H_2O_2 (mg/L)	Initial CLZ (mg/L)	Temperature (^oC)
1- Effect of pH	2	20	20	20
	3	20	20	20
	4	20	20	20
	5	20	20	20
2 - Effect of H_2O_2	3	5	20	20

Experimental Set Number - Name	pH	H₂O₂ (mg/L)	Initial CLZ (mg/L)	Temperature (°C)
	3	10	20	20
	3	20	20	20
	3	40	20	20
3 - Effect of CLZ	3	20	10	20
	3	20	20	20
	3	20	30	20
	3	20	40	20
4 – Effect of Temperature	3	20	20	10
	3	20	20	20
	3	20	20	30
	3	20	20	40

3.5.2. Fenton Experiments

Like for the experiments with UV/ H_2O_2, the effects of operational parameters, namely, pH, H_2O_2 concentration, initial CLZ concentration, Fe^{2+} concentration and temperature, that will affect the CLZ removal. The experimental plan followed for the Fenton's treatment is given in Table 3.2. The optimum operational condition was seeked by varying the values of operational parameters, while keeping the others constant.

During the experimentations, following the reactor was connected to the cooling circulator to keep the temperature constant, the pH was adjusted. Once the pH was adjusted, the catalyst iron sulphate heptahydrate is added in the form of a liquid solution. Then after, H_2O_2 was added and the experiment was started. The samples were taken at regular time intervals and their CLZ contents were measured. Here, it should be importantly mentioned that the reaction was quenched by adding sodium sulphite into the sample vessel, as also stated by Bensalah et al. (2011).

Table 3.2. Experimental Sets for Fenton Treatment

Experimental Set Number - Name	pH	H_2O_2 (mg/L)	Initial CLZ (mg/L)	Fe^{+2} (mg/L)	Temperature (^oC)
1- Effect of pH	2	100	40	5	20
	3	100	40	5	20
	4	100	40	5	20
	5	100	40	5	20
2 - Effect of Fe^{+2}	3	100	40	2.5	20
	3	100	40	5.0	20
	3	100	40	7.5	20
	3	100	40	10	20
3 - Effect of H_2O_2	3	10	40	5	20
	3	20	40	5	20
	3	50	40	5	20
	3	100	40	5	20
	3	200	40	5	20
4 - Effect of CLZ Concentration	3	50	10	5	20
	3	50	20	5	20
	3	50	40	5	20
	3	50	60	5	20
5 – Effect of Temperature	3	50	40	5	10
	3	50	40	5	20
	3	50	40	5	30
	3	50	40	5	40

3.5.3. Photo-Fenton Experiments

Photo-Fenton experiments were conducted within the experimental plan given in Table 3.3 in order to determine optimum conditions for the removal of CLZ, as done in the other processes. All the operations performed were in the same manner as with Fenton process, except the integration of the UV lamp to the assembly during the Photo-Fenton process. Like for the Fenton process, reactions in the samples taken were immediately quenched using sodium, prior to the CLZ measurements.

Table 3.3. Experimental Sets for Photo-Fenton Treatment

Experimental Set Number - Name	pH	H_2O_2 (mg/L)	Initial CLZ (mg/L)	Fe^{+2} (mg/L)	Temperature (^oC)
1- Effect of pH	2	50	40	5	20
	3	50	40	5	20
	4	50	40	5	20
2 - Effect of Fe^{+2}	3	50	40	2.5	20
	3	50	40	5.0	20
	3	50	40	7.5	20
3 - Effect of H_2O_2	3	10	40	5	20
	3	20	40	5	20
	3	50	40	5	20
4 - Effect of CLZ Concentration	3	50	20	5	20
	3	50	40	5	20
	3	50	60	5	20
5 – Effect of Temperature	3	50	40	5	20
	3	50	40	5	30
	3	50	40	5	40

3.5.4. Quenching the Fenton and Photo-Fenton Reactions

Degradation of pesticides occurs very fast during the Fenton processes (Üstün et al., 2010). Therefore, it is crucial to quench the reaction immediately after taking the sample prior to the analysis for CLZ. Here, the goal is to stop the formation of OH• (by preventing the reaction between Fe and H_2O_2), just right after the sampling, not to lead to erroneously low CLZ measurements.

In order to quench the reactions, researchers have applied different methods. Some researchers followed the way to draw the pH of samples to the range of 9-10 using NaOH (Arslan-Alaton and Dogruel 2004; Wu et al., 2010; Masomboon et al., 2011), while others used sodium (Na_2SO_3) to quench the reactions (Mohanty and Wei, 1993; Oliveira et al., 2006; Bensalah et al., 2011).

In this study, firstly, pH increment method was tried with the addition of NaOH. However, the amount of NaOH to be added per sample was determined to be 1 ml, which would lead to a dilution in the sample taken. Hence, this method was not preferred. Secondly, addition of 0.1 g Na_2SO_3 to each sample taken was tried. In order to determine whether Na_2SO_3 is effective, each sample taken was stored at $4\,^{\circ}C$ for 1 day and its CLZ content was measured again on the next day, and it was seen that results of samples taken on previous day was almost same. So, it was proven that more accurate data would be obtained by means of Na_2SO_3. However, it should be noted that when adding Na_2SO_3 to samples it will interfere some measurements such as COD and TOC. Thus, it can only be used to measure the concentration of specific pollutants.

3.6. Analytical Methods

3.6.1. CLZ Measurement

Samples taken at specific time intervals during the experiment were analyzed by HPLC (Shimadzu, LC-20A prominence). It is equipped with HPLC C18 column (4.6 mm x 250 mm), CBM 20A system controller, LC-20A solvent delivery unit, SIL 20A Auto-sampler and 225 nm UV-VIS detector (190-800 nm). Retention time for CLZ was determined as 5.33 min, but each sample was allowed to stand for 9 minutes in the HPLC device to be able to see possible by-products. Ultra-pure water and acetonitrile mobile phases were used at 65% and 35% rates, respectively, at a constant flow rate of 1 ml/min for CLZ analysis in HPLC. The injection volume of samples was 20 μL. The HPLC device used is shown in Figure 3.3.
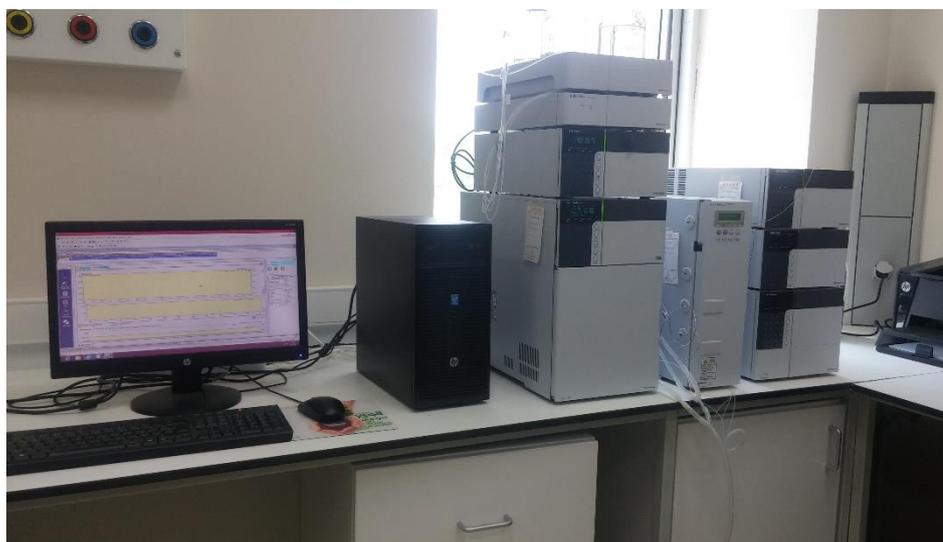
Figure 3.3. HPLC device used

3.6.1.1. Method for CLZ Analysis in HPLC

It is important to establish the method before starting the analysis for HPLC. Therefore, it is necessary to carry out a detailed study by searching mobile phases utilization rates, flow rates and wavelength for CLZ analysis. The literature review and the methods applied are given in Table 3.4.

Table 3.4. Applied Methods for CLZ Analysis in HPLC

Mobile Phases	Ratio for Phases	Flow Rate	Column	UV (nm)	Reference
Acetonitrile-Water mix	35:65	---	C18 (150mm x 3.9 mm)	229	Socías-Viciana et al. (2006)
Acetonitrile-Water mix	35:65	1 mL/min	C18 (150mm x 3.9 mm)	230	Fernández-Pérez et al. (2010)
Acetonitrile-Water mix	35:65	1 mL/min	C18 (150mmx 3.9 mm)	230	Flores Céspedes et al. (2013)
Methanol	100 %	---	C18 (250 mm x 10 mm)	228	Barra et al. (1995)

The best results were obtained at 225 nm at a flow rate of 1ml/min with a mixture of Acetonitrile-Ultra pure water 35:65 with the column C-18. Screen-shuts for the calibration curve prepared and the CLZ peak observed in HPLC, are presented Figure B1 and B2 in Appendix B, respectively.

Figure 3.4 LC/MS/MS device

In the study, Liquid Chromatography-Mass Spectrometry System (LC/MS/MS) device was used for the analysis of degradation by-products of CLZ, if any, after the processes applied. A brief information on LC/MS/MS is available in Appendix B. A Shimadzu-branded (Triple Quadrupole) LC / MS 8030 plus (Liquid Chromatography-tandem mass spectrometer) was used (Figure 3.4). The final LC/MS/MS conditions were; flow rate 0,3 mL/min, temperature 40 ºC, pressure 100 bar, injection volume 0,3 µL and 1 min analysis period in positive mode for each analysis. Methanol (5mM), Ammonium Format (5mM) and water were used as mobile phases. For these analysis, a service was taken from the Central Research Laboratory of the Kastamonu University.

3.6.2. UV light intensity with Chemical Actinometer

In order to measure the light intensity, where UV light application is involved, KI/KIO_3 Actinometer Method was used. This method is reported in the literature as a useful and easy method for low pressure lamps. The basic reaction taking place is given below (Bolton et al., 2011).

$$8I^- + IO_3^- + 3H_2O + hv \rightarrow 3I_3^- + 6OH^- \quad (30)$$
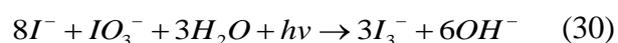
According to the method, 600 ml of the KI/KIO$_3$ Actinometer stock solution were prepared with the chemicals (59.74 g KI, 12.4 g KIO$_3$ and 2.28 g Na$_2$B$_4$O$_7$.10H$_2$O) weighed and added to the 600 ml distilled water. The prepared solution is 0.6M in KI, 0.1M in KIO$_3$ and 0.01 M in Na$_2$B$_4$O$_7$.10H$_2$O. This solution was put into the reactor and samples were taken at specific time intervals. The samples taken were analyzed in the spectrophotometer at 352 nm with a molar extinction coefficient of I$_3^-$ 27600 M^{-1}cm^{-1} and Figure 3.5 was obtained. The slope of the line in this graph indicates the amount of I$_3^-$ formed per unit time. Measurements were conducted in duplicate and arithmetic averages were taken. Errors during the measurements were less than 5%.

Then, photon flux (I$_o$) is calculated by the following equation 31 (Li et al., 2012)

$$I_0 = C_{tri} * V * \frac{1}{\Phi_{tri}} * \frac{1}{t} \qquad (31)$$

Where; I$_o$ is photon flux (Einstein/s), V is volume (L), Φtri is quantum yield (moles/Einstein) and t is time (s). Φtri was calculated according to Equation 32 and was found as 0.67 moles/Einstein. C_{tri}/t was the slope given in Figure 3.5.

$$\Phi tri = (0.71 \pm 0.02) + (0.0099 \pm 0.0004)(t - 24) \quad \text{(at 253.7 nm, 20}^0\text{C)} \qquad (32)$$

Where; t is the temperature of the solution.

With all these given data's, I$_0$ was calculated as 1.9912 μEinstein/s. This value is the photon flux that 10 W lamp distributes to the solution at 253.7 nm. The intensity of light falling to the average area was found by dividing the photon flux by the cross sectional area of the reactor. The reactor with 6 cm diameter has a cross sectional area of 28.2 cm^2. Therefore, the average light intensity per area was calculated as 7.06 x 10^{-8} Einstein/cm^2.s.
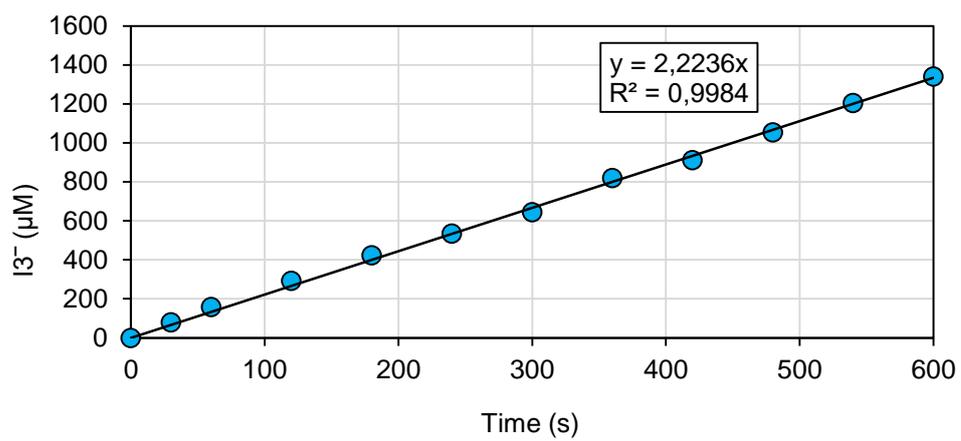
Figure 3.5. Formation of I_3^- in time with KI/KIO$_3$ Actinometer

CHAPTER 4

RESULTS AND DISCUSSION

In this study, UV/H_2O_2, Fenton, UV/Fenton processes and parameters affecting these processes were examined and optimum conditions were established for each process. With the results obtained, the removal of CLZ was investigated with respect to the parameters studied and kinetic analysis was performed for each. The results obtained and the relevant discussions are provided in the following sections.

4.1. CLZ Treatment by UV/H2O2 Process

4.1.1. Preliminary study

Before investigating the treatment of CLZ by UV/H_2O_2, two preliminary experimentations were performed in order to see the effectiveness of UV and H_2O_2 applications separately. It was intended to see their individual performances and also, such study would give an idea about the parameter values to investigate during the combined application of UV and H_2O_2, i.e. UV/ H_2O_2. Results obtained from the experimentations with UV alone and H_2O_2 alone are presented in Figure 4.1 and Table 4.1, respectively.

As seen from Figure 4.1, when the wastewater containing 5 mg/L CLZ was tested under UV lamp for the range of pH 3-9, CLZ removal showed a variation depending on pH. The highest removal (96%) was observed at pH 9, whereas the removals were similar (54, 60 and 67% at pH 3, 5 and 7, respectively). So, it was seen that the removal of CLZ increases with the increment in pH, which is more pronounced at pH 9. The reason for this can be attributed to that the water is decomposed into more OH• over

time at higher pHs by the effect of UV. In a way, pH 9, though quite a high value, was not excluded and it was decided to work within the pH range of 2-9 during the subsequent experimentations with UV/H_2O_2 (Sec 4.1.2).
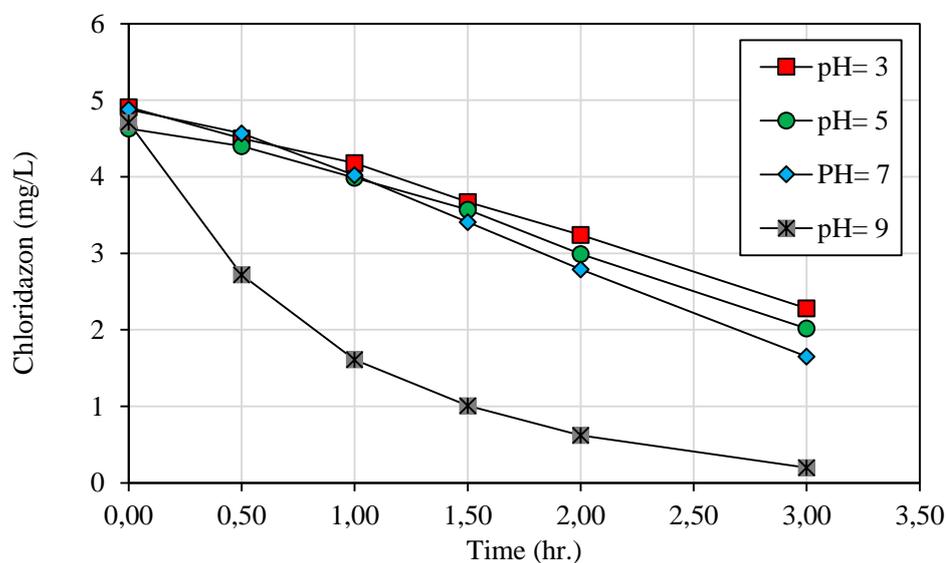
Figure 4.1. CLZ removal at different pH with the presence of UV light

Table 4.1. Only effect of H_2O_2 on CLZ removal in the absence of UV light

T (h)	25 mg/L H_2O_2 HPLC - CLZ(mg/L)	250 mg/L H_2O_2 HPLC - CLZ(mg/L)
0	9,896	9,86
2	9,871	9,81
24	9,849	9,78

Regarding the sole effect of H_2O_2, 25 mg/L and 250 mg/L H_2O_2 were added to the wastewater containing 10 mg/L CLZ in the absence of UV lamp and the effect was observed for 24 h. As seen in Table 4.1, H_2O_2 itself does not appear to have any effect on CLZ removal over time.

4.1.2. Effect of pH

To determine the effect of pH on the CLZ removal performance of the UV/ H_2O_2 process, a series of experiments were performed under different initial pH condition, namely, pH 2, 3, 4, 5, 7 and 9. During these runs, temperature, initial CLZ concentration and H_2O_2 concentration were kept constant at 20 ℃, 20 mg/L and 20 mg/L, respectively. The change in the concentration of CLZ within 1 hour is given in Figure 4.2.

When Figure 4.2 is examined, there is no significant change in CLZ concentration at different pH. The removal of CLZ is given in Figure 4.2b and it shows that the best result is taken at pH 3 with 99.99%. The efficiency increases when the pH increase from 2 to 3, but it is seen that efficiency decreases as pH increases. It is observed that the rate of degradation of CLZ decreases with increasing pH. Previous studies, conducted pH range 2-11 show two reasons for the decrease in CLZ removal. Firstly, decrease in OH radical formation can be observed due to the reaction between OH• and OH⁻in alkaline solutions. This reaction will form O⁻ that has lower oxidation capacity. Secondly, the deprotonation of H_2O_2 will result in the formation of hydroperoxide ions. These will react with H_2O_2, causing water and oxygen to be released. Therefore, the amount of OH• produced by H_2O_2 will decrease (Aleboyeh et al., 2005; Qiao et al., 2005; Liu et al., 2015). During these experimentations, the experiment toward the effect of pH was performed firstly (i.e. Experimental Set 1) and it was seen that pH value of 3 resulted in the highest CLZ removal with respect to removal rate and it seems to be compatible with the results obtained in other studies done with UV/ H_2O_2 (Muruganandham and Swaminathan, 2004b; Ghodbane and Hamdaoui, 2010; Liu et al. 2015). So, in the rest of experimentations, pH was kept constant at 3.
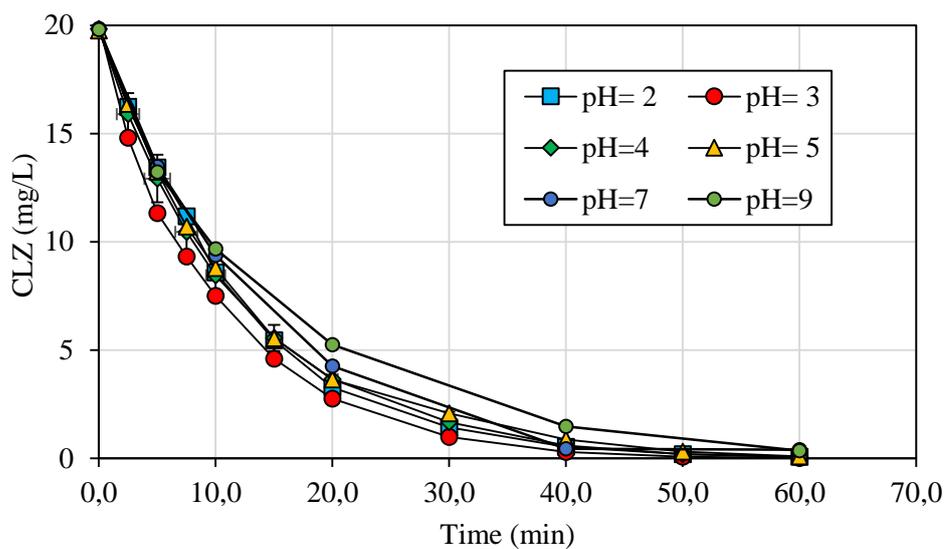
(a)
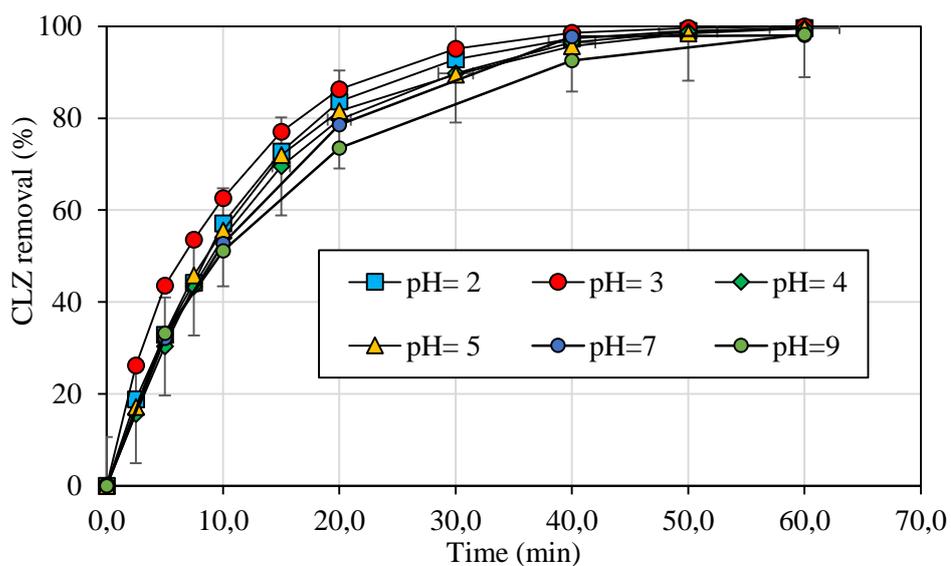
(b)

Figure 4.2. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by UV/H_2O_2 for different pH (CLZ=20 mg/L, H_2O_2 =20 mg/L, T=20°C)

4.1.3. Effect of H2O2 Concentration

As noted previously in Section 2.3.5.2, the importance of H_2O_2 is evident in UV/ H_2O_2 AOP. H_2O_2 is known to be the main source of $OH\bullet$, which play an important role in the degradation of pollutants. Therefore, effect of H_2O_2 concentration was sought. To this purpose, experiments were carried out at a constant pH of 3 and a constant temperature of 20°C when the initial CLZ concentration was 20 mg/L. The concentration of H_2O_2 was changed between 5-40 mg/L and the variation of CLZ was followed. The results obtained are shown in Figure 4.3a. The corresponding removal percentages can be depicted from Figure 4.3b.

As can be seen in Figure 4.3b, the highest CLZ removal was achieved at the H_2O_2 concentration of 40 mg/L; more than 99% removal was attained at the end of 30 min. The corresponding CLZ removals for the H_2O_2 concentrations of 5, 10 and 20 mg/L were 59, 75 and 95%, These were increased to 83, 95 and >99%, respectively, at the end of 60 min.

Although the best results were obtained at 40 mg/L H_2O_2, the rest of parametric experiments were performed at a constant concentration of 20 mg/L H_2O_2, as quite comparable CLZ removals were attained at these two concentrations (as >99% and >95%, respectively) at the end of 30 min (Fig. 4.3b). Also, this choice would allow for more clear assessment of the other parametric results since more gradual decline in CLZ did occur as compared to the case with 40 mg/L H_2O_2. Moreover, if the cost of chemical use in practice is also taken into consideration, working with 20 mg/L H_2O_2 would be a feasible option. This value further proves to be advantageous because it is lower than the concentration of H_2O_2 used (56-1600 mg/L) in other studies with UV/ H_2O_2 processes (Aleboyeh et al., 2005; X. R. Xu et al., 2009; Chelme-Ayala et al., 2010).
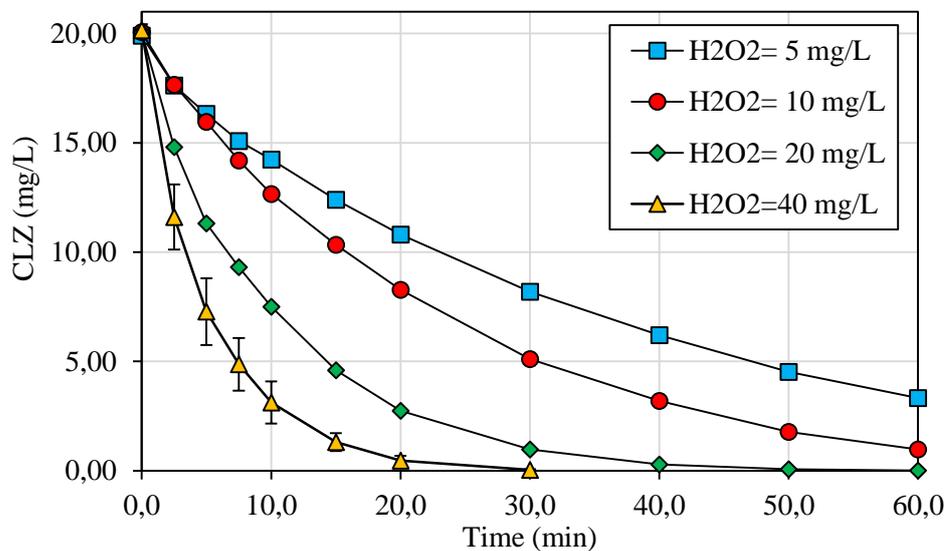
(a)
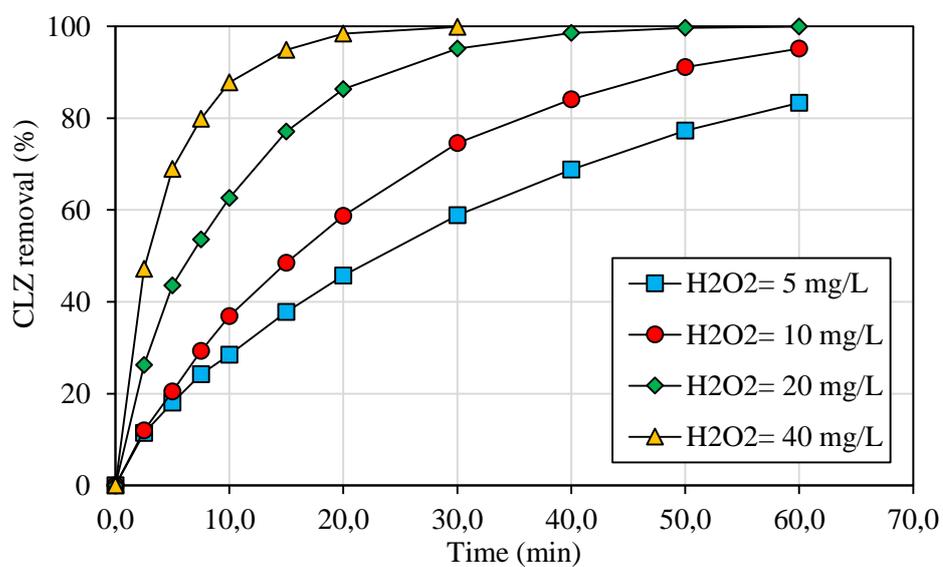
(b)

Figure 4.3. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by UV/H_2O_2 for different H_2O_2 concentrations (İnitial CLZ=20 mg/L, T=20°C, pH=3)

4.1.4. Effect of Initial CLZ Concentration

From past to present studies, initial CLZ concentration generally have been studied between 2-250 mg/L (Socías-Viciana et al., 2006; Flores Céspedes et al., 2013). In this study, initial CLZ values were selected between 10 and 40 mg/L, namely 10, 20, 30 and 40 mg/L. Lower concentration (i.e. 5 mg/L) was also tested, but the disappearance of CLZ was so quick, so it was not possible to observe the removal trend. The experiments were performed keeping the other variables constant at 20 mg/L, 3 and 20°C for H_2O_2, pH and temperature, respectively. The results obtained are presented in Figure 4.4a and b.

Figure 4.4b shows that as the CLZ concentration increases, the removal efficiency decreases at a given time. As seen from this figure, 10 mg/L of CLZ completely disappeared within 15 minutes while 82% of 40 mg/L CLZ was removed in 1 hour. In other words, the rate of disappearance decreases as the initial CLZ concentration increases. In literature studies, two different attributions were done to explain about the reason for such observations. One is related to the amount of OH•, which is the active substance in the removal of contaminants, appears to be constant despite the increase of the contaminant concentration (Gao et al., 2009). The other one is that the byproducts are highly reactive to OH• and their attempts to interact with OH• reduce the removal efficiency of the contaminant itself (Daneshvar et al., 2007).
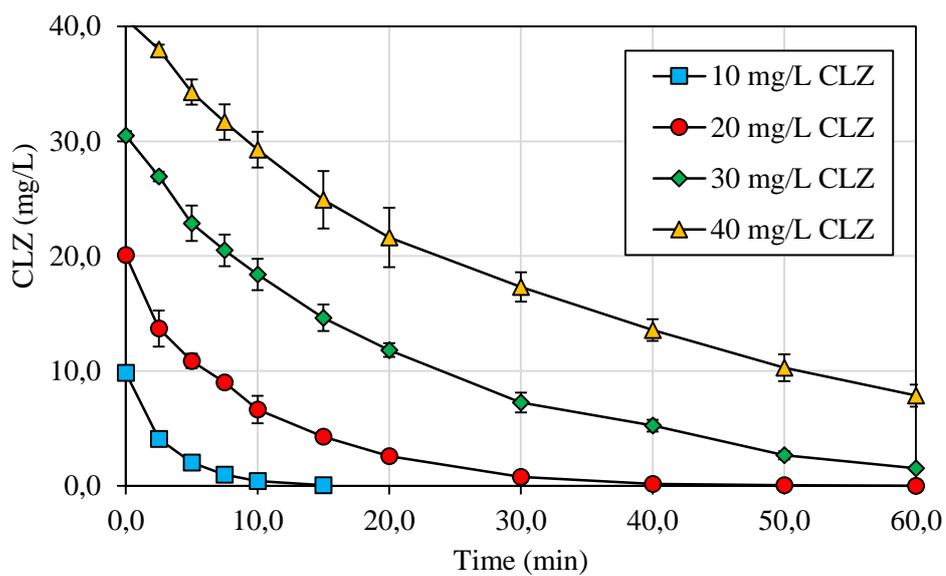
(a)
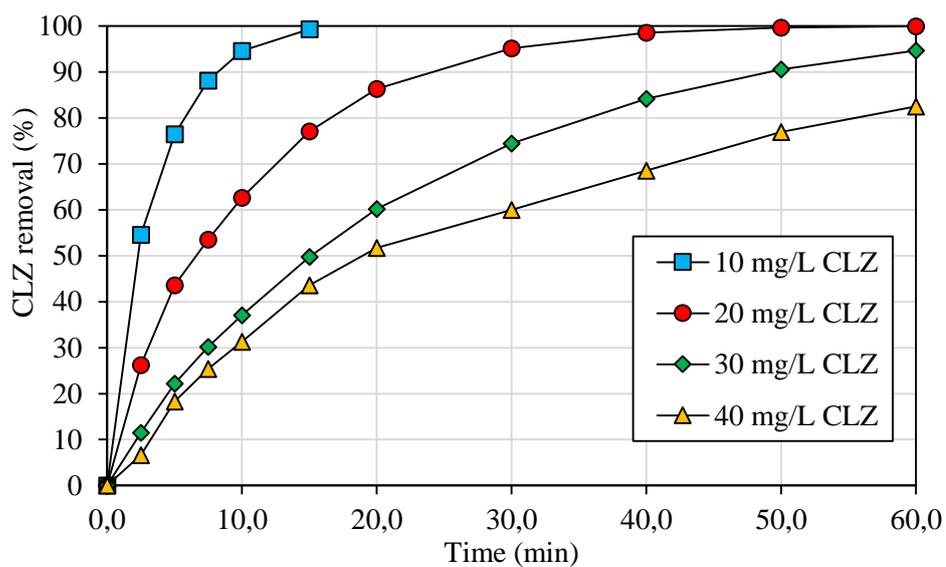
(b)

Figure 4.4. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by UV/H_2O_2 for different initial CLZ concentrations (H_2O_2=20 mg/L, T=20°C, pH=3)

4.1.5. Effect of Temperature

Figure 4.5a and b shows the effect of temperature on CLZ removal efficiency. As can be depicted from the slope of the lines within 10 min (Fig. 4.5a), the initial removal rates increased as the temperature increases. In accordance with this, the lowest efficiency was attained at 10°C while the highest yield was observed at 40°C till up to 20 min. Then after, the removals start getting close to each other; almost complete disappearance of CLZ was observed in 30 min when the temperature was set to 20, 30 and 40°C whereas 98% removal did occur at 10°C in 60 min. So, considering the removal efficiencies attained together with the energy consumption issue, working at 20°C seems feasible.
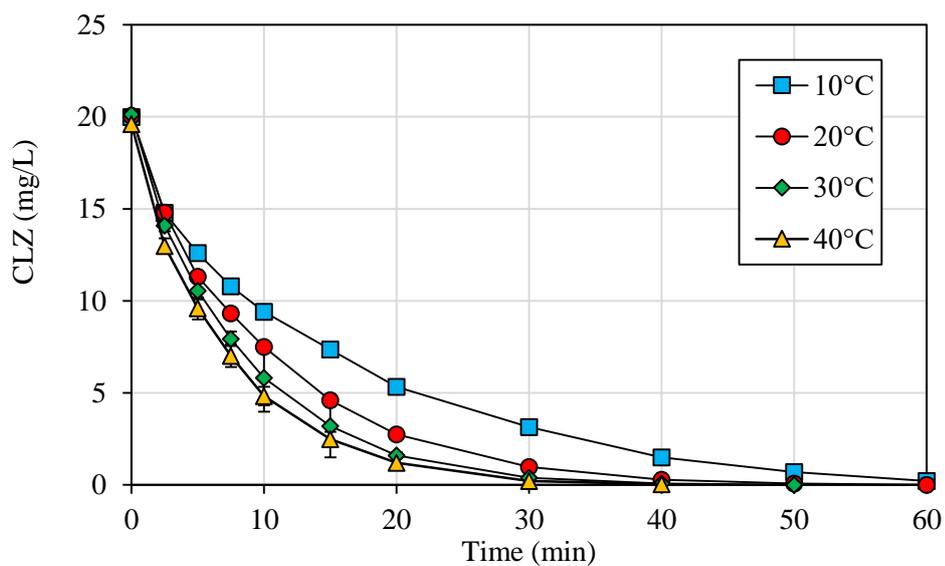
(a)
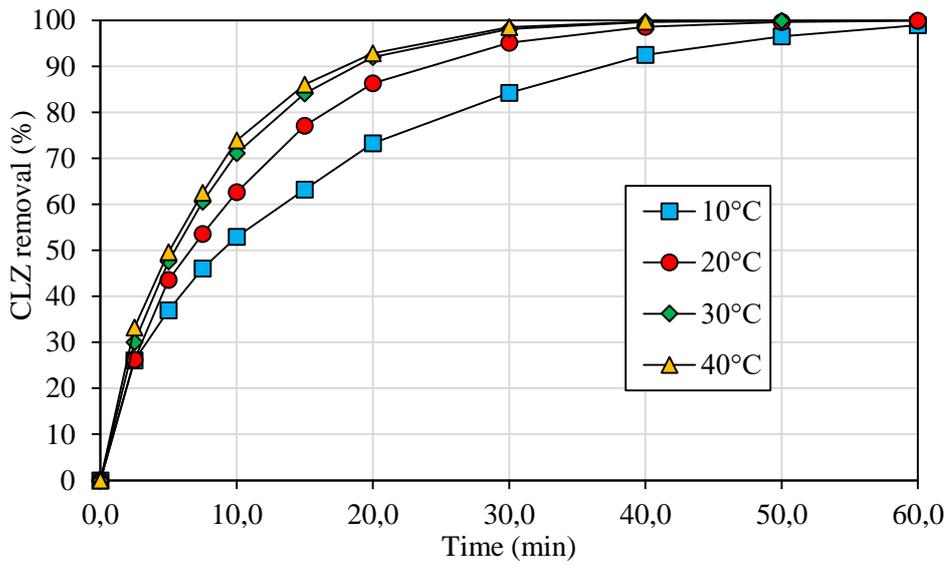
(b)

Figure 4.5. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by UV/H_2O_2 for temperatures (H_2O_2=20 mg/L, pH=3, CLZ=20mg/L)

4.1.6. Reaction Kinetics for UV/H2O2 Experiments

Pseudo first order kinetic model was applied to observe the degradation of the CLZ by UV/ H_2O_2 processes. The results of Pseudo first order kinetic is given in Figure 4.6. Kinetic model constant of k1 and the regression value is also presented in the figure. These analyses belong to the optimum conditions determined for UV/H_2O_2 processes. The kinetic analysis for the other remaining parameters are given in Figure A1–A4, Appendix A.

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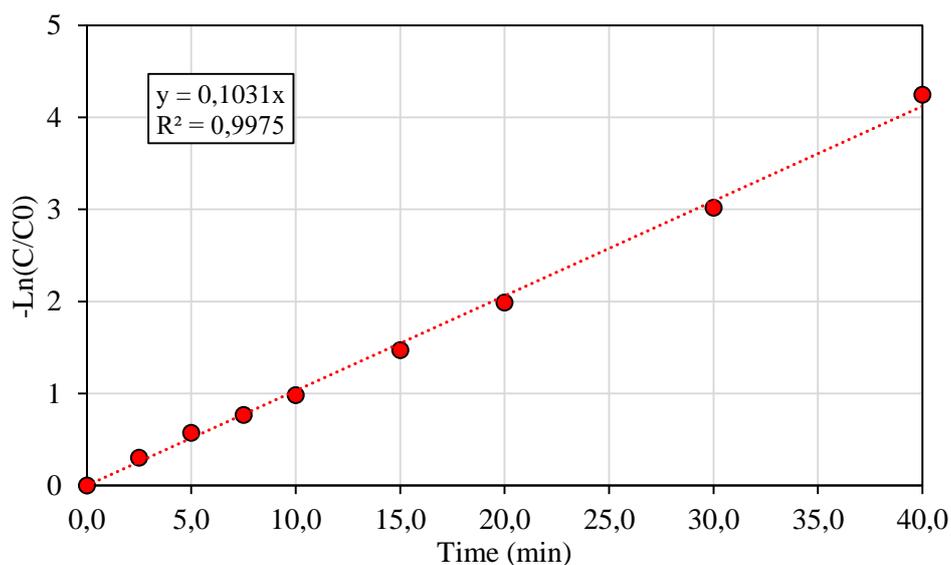
Figure 4.6. Pseudo first order kinetic analysis for CLZ degradation UV/H$_2$O$_2$
processes (T=20°C, H$_2$O$_2$=20mg/L , pH=3 , CLZ=20mg/L)

As shown in Figure, it is seen that the proposed kinetic model fits well (R^2>0.99). This
is all to say, the regression values in the pseudo kinetic model being greater than 0.95
prove that Pseudo kinetic model is perfectly followed and the feasibility of the model
in UV/H$_2$O$_2$ process is clearly demonstrated in Appendix A.

4.2. CLZ Treatment by Fenton Process

4.2.1. Effect of pH

In an attempt to investigate the effect of pH on the CLZ removal performance of the
Fenton process, a series of experiments were performed under different initial pH
conditions, namely, pH 2, 3, 4 and 5. The reason for selecting an acidic pH range lies
behind the fact that more OH• will be formed at lower pH (Neyens and Baeyens, 2003;
Babuponnusami and Muthukumar, 2014; Pouran et al., 2015). Also, formation of

Fe(OH)$_3$ with a low catalytic property is to occur at higher pH values (Hashemian, 2013).

During the experimental runs, temperature, initial concentrations of CLZ, Fe^{2+} and H$_2$O$_2$ were kept constant at 20°C, 40 mg/L, 5 mg/L and 100 mg/L, respectively. Figure 4.7a shows the change in CLZ concentration with time at each pH condition. The corresponding removal efficiencies are provided in Fig.4.7b. Please note that the experiment belonging to pH 3 was performed in duplicate, as indicated with the error bars in Figure 4.7a. Since the variation between these duplicate experiments were very small ($< 3\%$), the experiments for the other pH conditions were not run in duplicate.

As shown in Figure 4.7a and b, the optimum pH value for degradation of CLZ is 3. When the pH was increased from 2 to 3, the initial rate of degradation showed a remarkable increase and when pH was increased to 4, a sharp decrease was observed (Figure 4.7a). It can be depicted from Figure 4.7b that removal efficiency decreases significantly when the pH is increased from 4 to 5. The reason for the inefficiency in the case of pH lower than 3 is the observation of oxoniom ion formation due to the strong proton solubility of H$_2$O$_2$. Unlike this, if pH is greater than 3, formation of ferrous and ferric hydroxides which shows lower catalytic properties compared to Fe^{+2}, reduces the removal efficiency (Sun et al., 2007). As can be seen in Figure 4.7a, at all pH values studied, there seems two phases of CLZ removal; a rapid decrease in CLZ at first (i.e. about within 1-3 min), followed by a gradual decrease. The highest initial removal rate (during the first 3 min) was observed at pH 3. The gradual decline phase was much more slow (almost ceasing down) at pH 2, 4 and 5 than at pH 3. In other words, at pH 3, unlike for other pHs, CLZ removal did continue quite remarkably even in this gradual decline phase. In accordance with all these observations, the highest removal efficiency was achieved at pH 3 as also supported by the literature studies (Arslan-Alaton and Dogruel, 2004; Saritha et al., 2007). At this pH, almost complete disappearance of CLZ ($> 99\%$) was achieved at the end of 60 min (Figure

4.7b). The percent of disappearance was 36, 33 and 5% at pH of 2, 4 and 5, respectively, at the end of experimental time of 60 min.
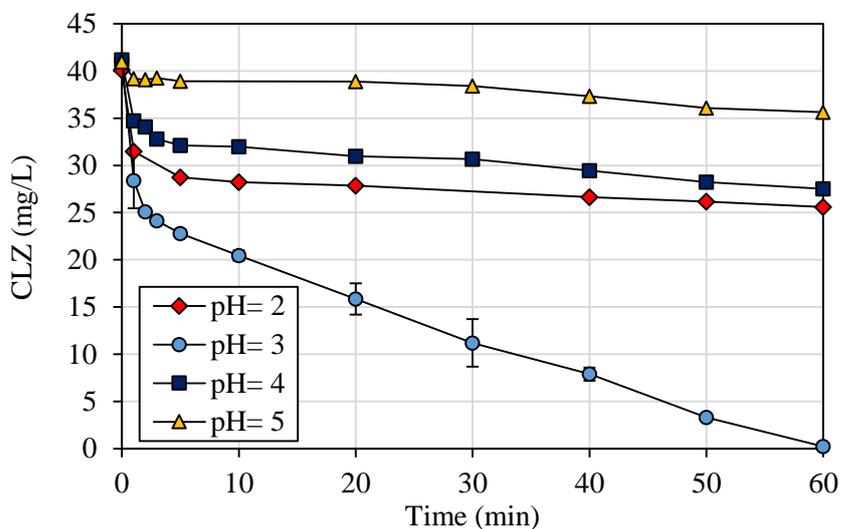
(a)
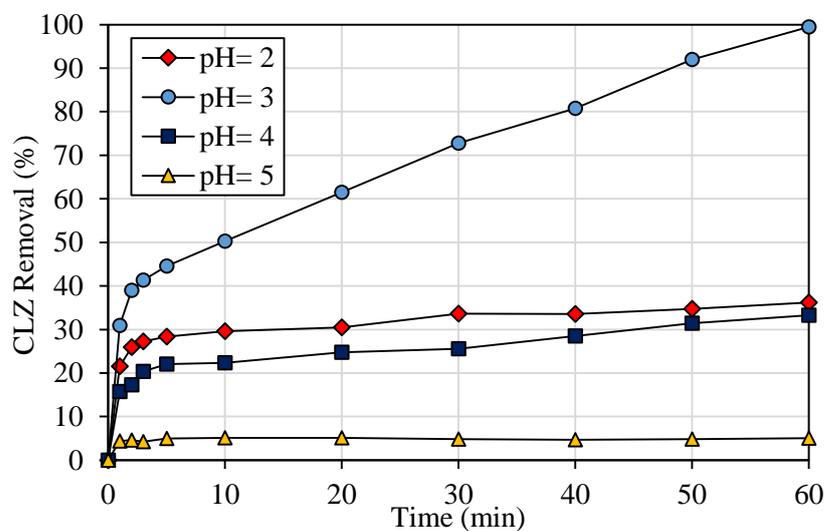
(b)

Figure 4.7. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Fenton Process at different pH (CLZ=40 mg/L, T=20°C, H2O2=100mg/L, Fe^{2+}=5mg/L)

4.2.2. Effect of Fe2+ Concentration

In the classical Fenton Process, Fe containing catalysts are traditionally used as catalyst (Guo et al., 2010; Nieto et al., 2011). The amount of catalyst to be used is an important issue to deal with. So, in this study, experiments were carried out to determine the optimum Fe^{2+} concentration for the removal of CLZ from water. The experiments were performed using Fe^{2+} in the range of 2.5-10 mg/L at a fixed H_2O_2 of 100 mg/L, temperature of 20^oC and pH of 3. The results obtained are shown in Figure 4.8.

Here, it should be noted that the experiment belonging to 10 mg/L Fe^{2+} was performed in duplicate, as indicated with the error bars in Figure 4.8a. Since the variation between these duplicate experiments were very small ($< 2\%$), the experiments for the other Fe^{2+} concentrations were not run in duplicate.

As in the case of experimentations performed at different pH (Sec 4.2.1), the CLZ concentration declined very rapidly at first (i.e. within 1-3 min), but then it ceased down gradually (Figure 4.8a). This gradual decline ended up at the end of 30 min for Fe^{2+} concentrations of 7.5 and 10 mg/L whereas it took 60 min for 5 mg/L Fe^{2+} case. When Fe^{2+} concentration was 2.5 mg/L, CLZ decline was still going on, though very slowly. So, it was evident that as the concentration of Fe^{2+} increases from 2.5 to 10 mg/L, the efficiency of CLZ removal increases. In other words, as the amount of Fe^{2+} increases within the studied range, its catalytic action on the reaction increases. However, literature studies report that although an increased catalyst doses may improve the removal rate, catalyst should not be added in excess due to the possibility of the scavenger effect on the generated radicals. Further, excessive use of catalyst may result in large volume of sludge, in turn increase the need for sludge treatment, eventually leading to higher chemical and treatment cost. Therefore, the concentration of 7.5 mg/L Fe^{2+} seems as optimum. Nevertheless, 5 mg/L Fe^{2+} could also be

considered as optimum as it yielded almost complete CLZ removal though in a longer time.
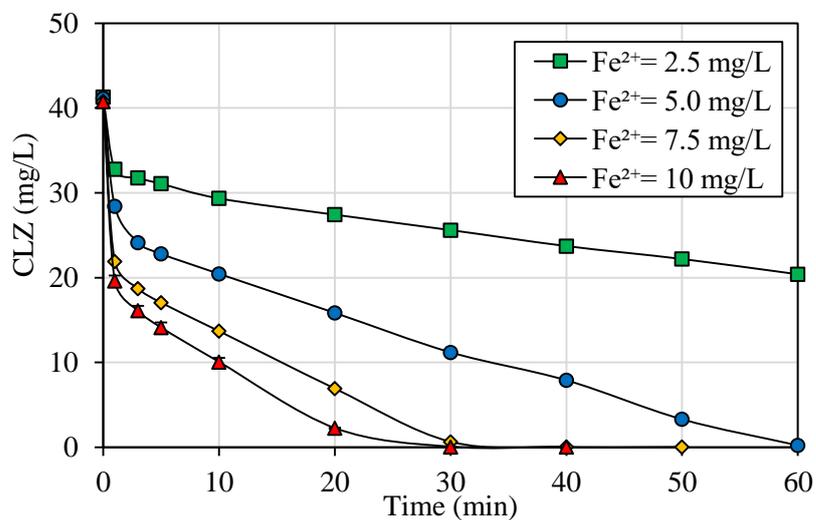
(a)
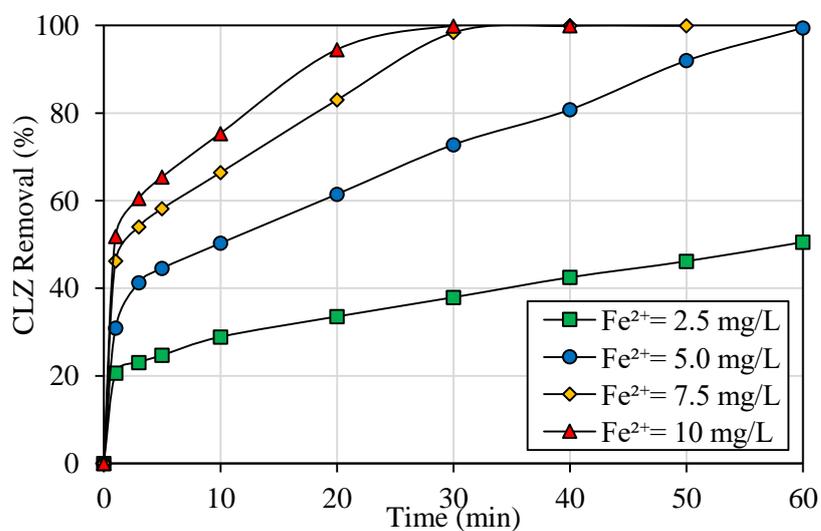
(b)

Figure 4.8. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Fenton Process at different Fe2+ (CLZ=40 mg/L, T=20°C, H_2O_2=100 mg/L, pH=3)

4.2.3. Effect of H2O2 Concentration

To investigate the effect of H_2O_2 on the removal of CLZ by Fenton process, the CLZ removals were followed under the experimental conditions of 40 mg/L initial CLZ, 5 mg/L Fe^{2+} at 20°C and pH 3 while varying the H_2O_2 concentration within the range of 10-200 mg/L. The results obtained are shown in Figure 4.9. An increase in H_2O_2 from 10 to 50 mg/L clearly resulted in the increased removal efficiency of CLZ. Approximately 99% of CLZ was removed within an hour when the H_2O_2 concentration was set to 50 mg/L or higher. As seen from Figure 4.9a and b, the CLZ removals obtained for H_2O_2 concentrations of ≥50 mg/L, the curves almost coincide, indicating that the use of H_2O_2 above 50 mg/L would be in excess. Indeed, when present in excess, H_2O_2 is expected to be converted into water and oxygen, and also to react with OH• (Elmorsi et al., 2010). Therefore, H_2O_2 should not be added in excess.
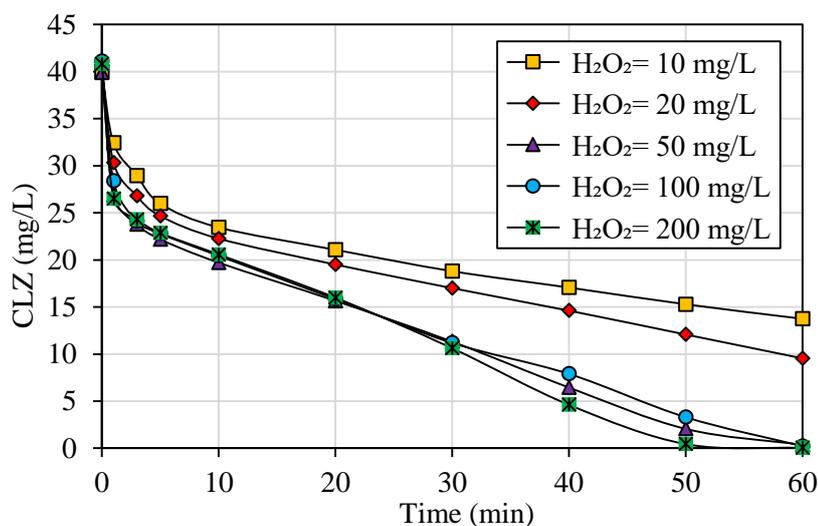
(a)
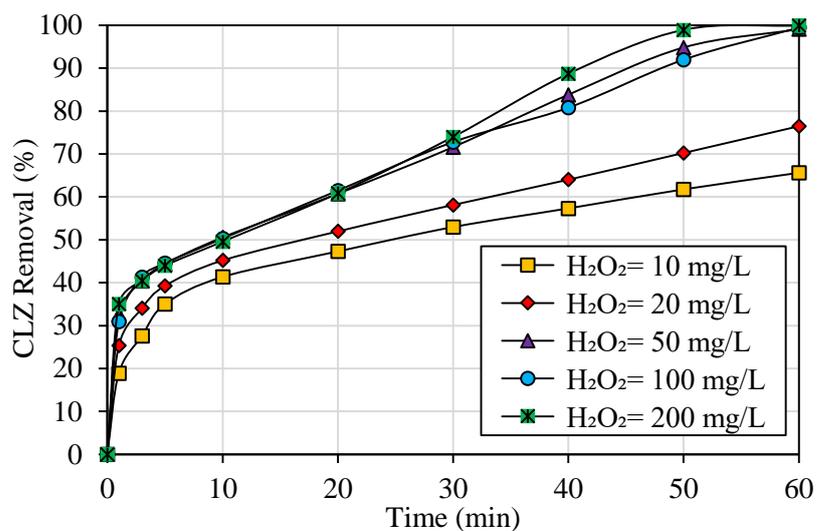
(b)

Figure 4.9. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Fenton process at different H_2O_2 (CLZ=40 mg/L, T=20°C, Fe^{2+}=5 mg/L, pH=3)

4.2.4. Effect of Initial CLZ Concentration

The effect of initial CLZ concentration on CLZ removal by Fenton process was investigated within the concentration range between 10-60 mg/L. The concentration of CLZ less than 10 mg/L was also tested but its disappearance was so quick to allow for monitoring with respect to time. The other experimental conditions were maintained as H_2O_2= 50 mg/L, T=20°C, Fe^{2+}=5 mg/L, pH=3, as to correspond to their optimum values determined above.
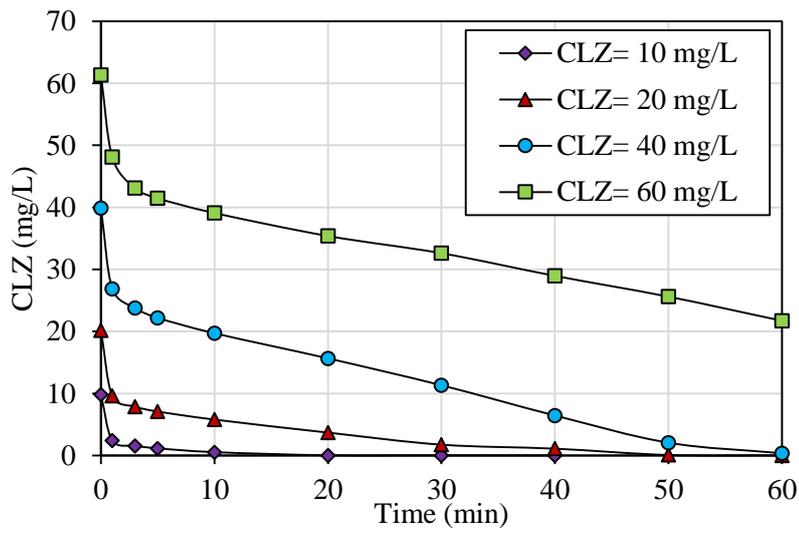
(a)
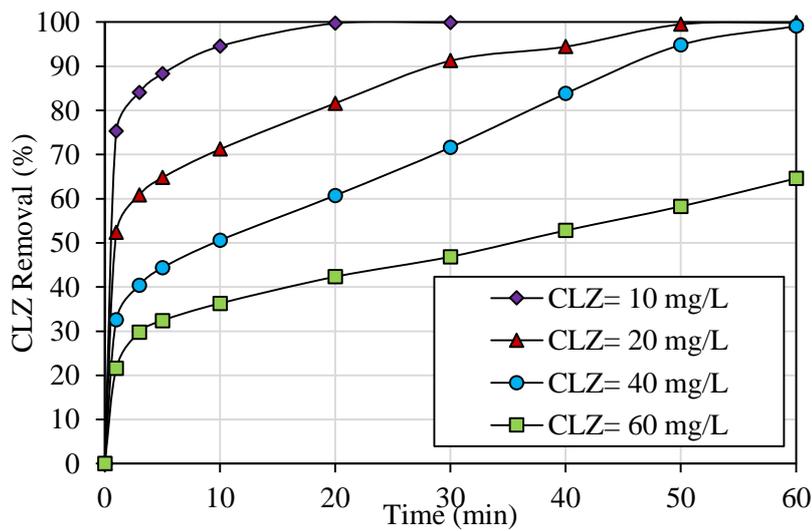
(b)

Figure 4.10. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Fenton process for different initial CLZ concentrations (H_2O_2= 50 mg/L, T=20°C, Fe^{2+}=5 mg/L, pH=3)

The results obtained are provided in Figure 4.10a and b. As shown in this figure, as in the case of experimentations performed previously (Sec 4.2.1, Sec 4.2.2 and Sec 4.2.3), the CLZ concentration declined very rapidly at first, but then it ceased down gradually (Figure 4.10a). This gradual decline ended up at the end of 20 min for CLZ concentration of 10 mg/L whereas it took 60 min for 20 and 40 mg/L CLZ cases. When CLZ concentration was 60 mg/L, CLZ decline was still going on, though very slowly. So, it was evident that as the initial CLZ concentration increases from 10 to 60 mg/L, the CLZ removal efficiency decreases until 40 min. However, at the end of 60 min, the removal performance belonging to the initial CLZ of 10, 20 and 40 mg/L was all same with almost > 99%. The removal efficiency attained for 60 mg/L CLZ was 64% at the end of 60 min, while the removal of CLZ for 10 mg/L CLZ was >99% at the end of 20 min. So, it was clearly seen that when the CLZ concentration increases, the removal efficiency decreases. This was attributed to the fact that there will be no increase in the OH• formed during the reaction when contaminant concentration increases, as also reported by (Modirshahla et al., 2007).

4.2.5. Effect of Temperature

The effect of temperature on CLZ removal was investigated by working at different temperatures, namely, 10, 20, 30 and 40ºC while keeping the other operational parameters constant. The results obtained are shown in Figure 4.11. As seen from this figure, like for the experimentations performed previously (Sec 4.2.1, Sec 4.2.2, Sec 4.2.3 and Sec 4.2.4), the CLZ concentration declined very rapidly at first (within 1-3 min), but then it ceased down gradually (Figure 4.11a). This gradual decline ended up at the end of 20 min for the temperature of 40°C whereas it took 40 and 60 min for 30 and 20°C cases, respectively. When the temperature was 10°C, CLZ decline was still going on, though very slowly. So, it was evident that as the temperature increases from 10 to 40°C, the CLZ removal efficiency increases until 40 min. However, at the end of 60 min, the removal performance belonging to the temperatures of 20, 30 and 40°C was all same with almost > 99.9%. So, it can be said that the increase in temperature

within the studied range has a positive effect on the removal of CLZ. The efficiency rised from %26 to %99.98 while the temperature rises from 10 to 40°C at the end of 60 min. It was also seen that the degradation occurs in a shorter period of time when the temperature rises. So, it can be said that the increase in the formation of OH• with temperature increment which accelerates the Fenton reaction, will increase the efficiency of the CLZ removal, as also reported by S. P. Sun et al. (2009). Fenton applied at room temperature (20-25ºC) should be preferred even though 40ºC of temperature seems to be the most efficient temperature, considering the operating cost.
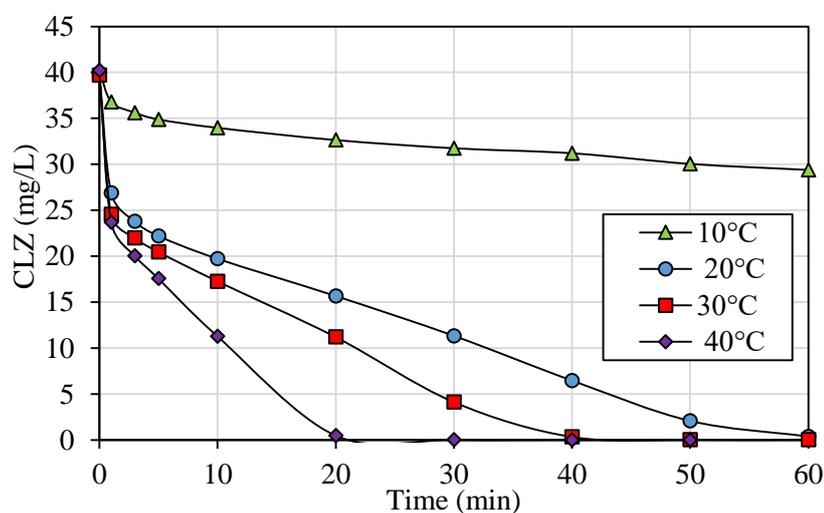
(a)
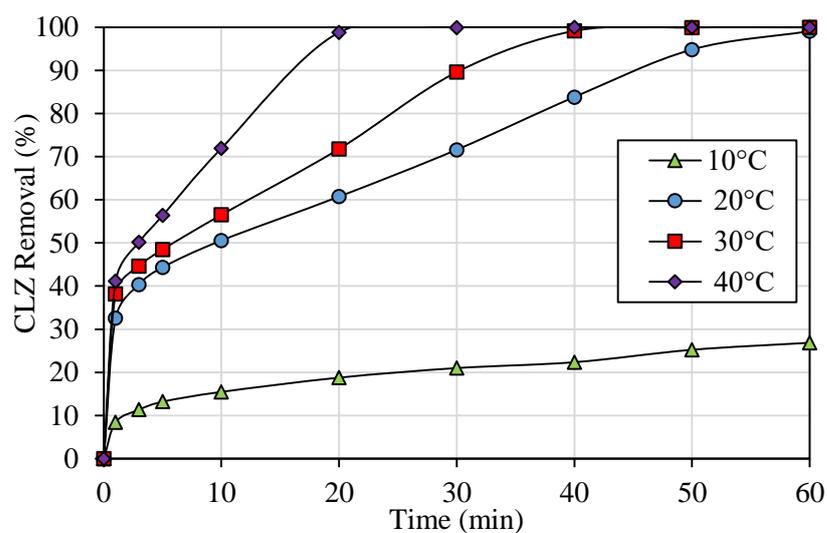
(b)

Figure 4.11. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Fenton process at different temperature (H_2O_2= 50 mg/L, CLZ=40 mg/L, Fe^{2+}=5 mg/L, pH=3)

4.3. CLZ Treatment by Photo-Fenton Process

Following the investigation of CLZ removal by Fenton process, Photo-Fenton process was considered in an attempt to determine the effect of UV light on CLZ removal by Fenton process. To this purpose, parametric investigations were performed for pH, temperature, Fe^{+2} concentration, H_2O_2 concentration and initial CLZ concentration, using the same parameter ranges of Fenton process.

4.3.1. Effect of pH

The effect of pH on Photo-Fenton processes is also very important as in the case of Fenton processes. Because the degradation of existing pollutants in wastewater depends highly on pH, which plays an important role in the formation of OH• (Tamimi

et al., 2008). Hence, firstly the optimum pH value was determined for the CLZ removal in Photo Fenton experiments.

The experiments were carried out at pH values of 2, 3 and 4, keeping the other operational parameters constant (i.e. CLZ=40 mg/L, T=20°C, H_2O_2=50 mg/L, Fe^{2+}=5 mg/L). The effect of pH on CLZ removal is given in Figure 4.12. As shown in this figure, initial degradation of CLZ was so rapid at pH values studied (Figure 4.12a). Within 1 min, almost 30% CLZ removal was attained (Figure 4.12b). Then after, more gradual removal was observed with time.

As it can be depicted from Figure 4.12b, when the pH value was increased from 2 to 3, the efficiency increases but when the pH was increased to 4, it decreases, at a given time until 15 min. This decrease in CLZ removal (i.e. at pH 4) can be attributed to the possibility of precipitation of iron source as ferric hydroxide, as also stated by Ghaly et al. (2001). In addition to this, the oxidation ability of OH• could decrease with increasing pH (Lucas and Peres, 2006).

Figure 4.12b shows that, at the end of 20 min, the effect of pH disappeared as >99% CLZ removal was attained at all pHs studied. When these observations were compared with the results obtained for Fenton process, the positive effect of UV light is evident. In case of Fenton, at pH 3, the required time to reach to about 99% CLZ removal was 60 min (Figure 4.7b) whereas here it took only 10 min. It can be stated that UV irradiation (<300 nm) became a mild way to trigger H_2O_2 decomposition which generates OH• compared to Fenton process, as also evidenced by Ghaly et al. (2001), Shemer et al. (2006) and Rubio et al. (2013).
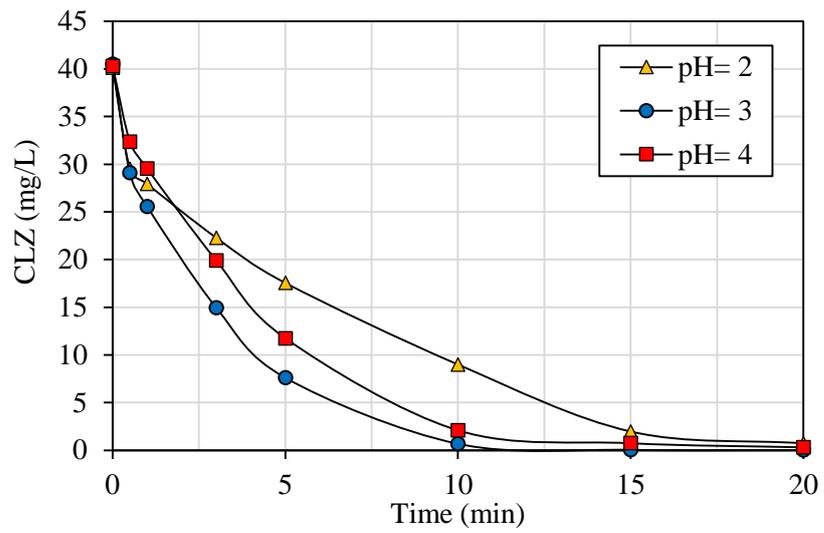
(a)
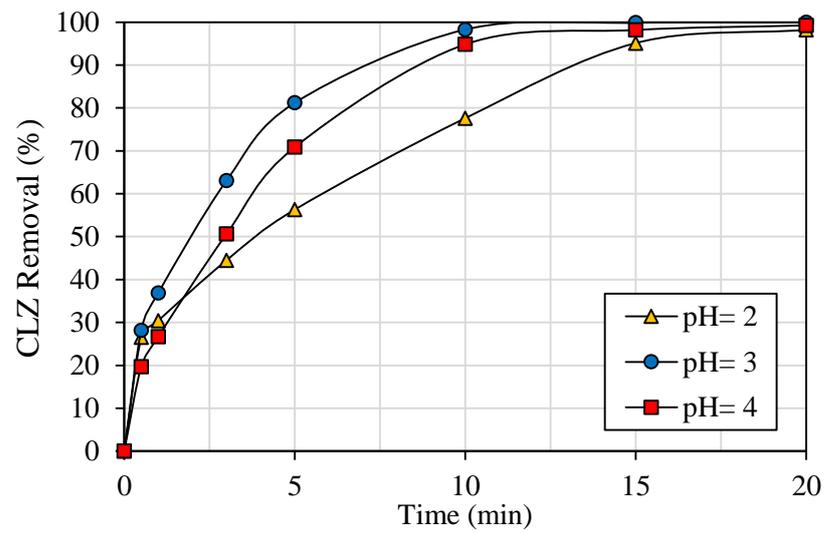
(b)

Figure 4.12. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Photo-Fenton Process at different pH (CLZ=40 mg/L, T=20°C, H_2O_2=50 mg/L, Fe=5 mg/L)

4.3.2. Effect of Fe+2 Concentration

Like for the Fenton process, effect of catalyst (i.e. Fe^{2+}) concentration was investigated on the CLZ removal by Photo-Fenton process. In a way, the effect of UV light as a function of catalyst concentration was sought. To this purpose, experiments were performed at three different Fe^{2+} concentrations, namely, 2.5, 5.0 and 7.5 mg/L. The obtained results are shown in Figure 4.13a and b.

As can be seen in Figure 4.13b, the CLZ removal efficiency increased as the Fe^{2+} concentration increases. However, when the concentration of Fe^{2+} is increased from 5 to 7.5 mg/L, no significant change was observed. This is because, when high amounts of Fe^{2+} used, the formation rate of OH• by the decomposition of H_2O_2 increases and these OH• can also be consumed by the side reactions such as Fe^{3+} (Xu et al., 2009). In addition to all these, if the amount of iron is increased by the increase in OH•, it will cause the formation of Fe^{3+}. This ion will react with the hydroxyl radicals and will form $Fe(OH)_2$. These formed $Fe(OH)_2$ will reduce the effects of the UV source on the degradation of CLZ in Photo-Fenton experiments (Bharadwaj and Saroha, 2015). Moreover, when iron is used in excess, it will create some handicaps in terms of economy and environment. It is important for these processes to determine the optimum iron concentration as it will be expensive to remove or reuse the sludge formed after processes and there will be a huge amount of chemical need. Therefore, the optimum value of Fe^{2+} was chosen as 5 mg/L.
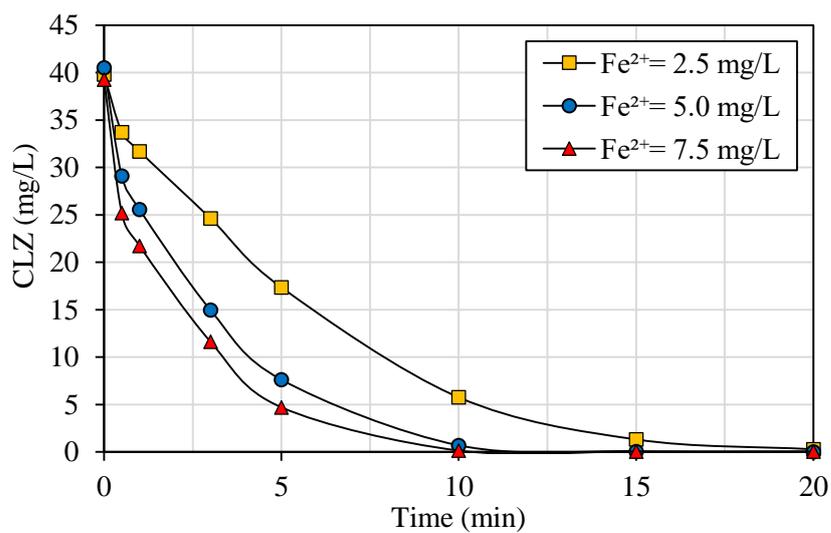
(a)
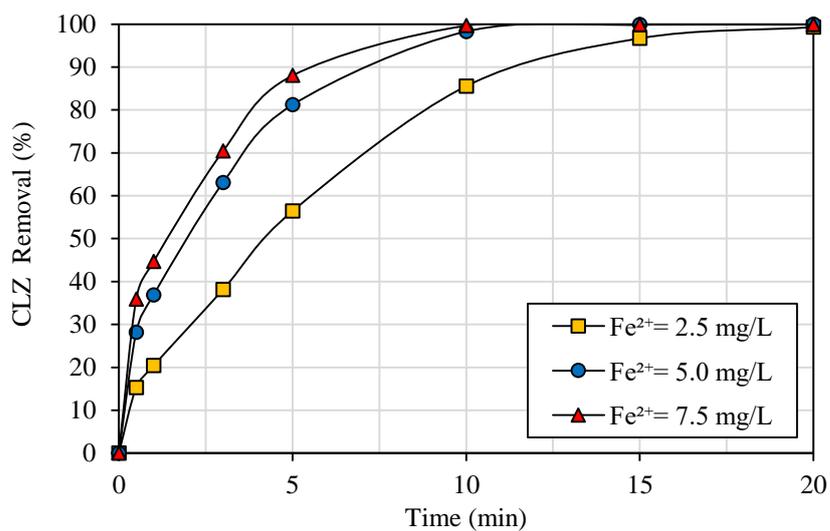
(b)

Figure 4.13. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Photo-Fenton Process for different Fe2+ dosage (CLZ=40 mg/L, T=20°C, H_2O_2=50 mg/L, pH=3)

Figure 4.13b also shows that, at the end of 20 min, all the Fe^{2+} concentrations tested resulted in the same CLZ removal efficiency of >99%. When these observations were compared with the results obtained for Fenton process, the positive effect of UV light is evident. In case of Fenton process, at Fe^{2+} of 5 mg/L, the required time to reach to about 99% CLZ removal was 60 min (Figure 4.8b) whereas here it took only 10 min.

4.3.3. Effect of H2O2 Concentration

Figure 4.14a and b shows the removal of CLZ at different H_2O_2 concentrations (10, 20 and 50 mg/L) in Photo-Fenton process. It can be clearly seen from this figure that the removal efficiency increases when the H_2O_2 increases from 10 to 50 mg/L. The CLZ removal efficiency was 85% at 10 mg/L H_2O_2 at the end of 20 min. while it increased to >99% when 50 mg/L H_2O_2 was used.

Further, if the optimum value for H_2O_2 is exceeded, the H_2O_2 and OH• will react each other and will cause the formation of hydroperoxyl radicals, which has a lower oxidant property. This would mean that there is no contribution to the degradation of the target pollutants (as seen in Eq.15). In addition, OH• can react with each other to form H_2O_2 (Eq.20) (Muruganandham and Swaminathan, 2004a).

When these observations were compared with the results obtained for Fenton process, the positive effect of UV light is evident. In case of Fenton process, at H_2O_2 of 50 mg/L, the required time to reach to about >99% CLZ removal was 60 min (Figure 4.9b) whereas here it took only 10 min.
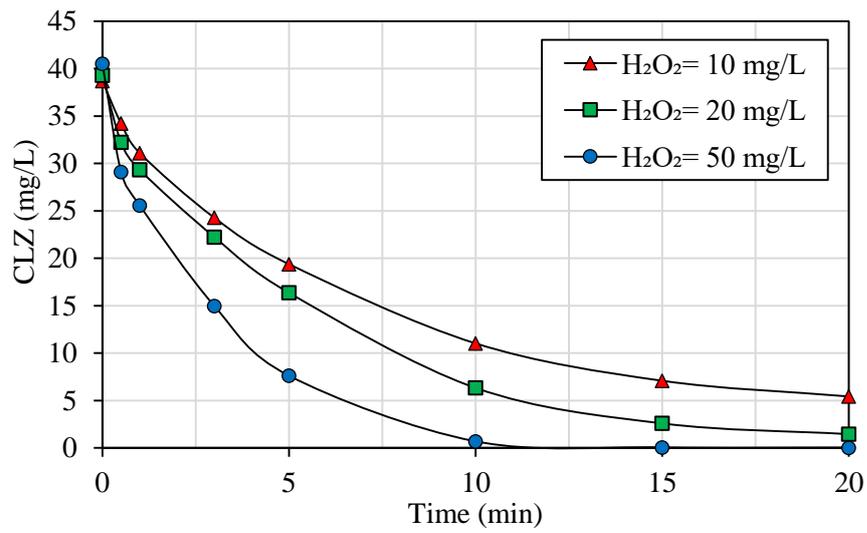
(a)
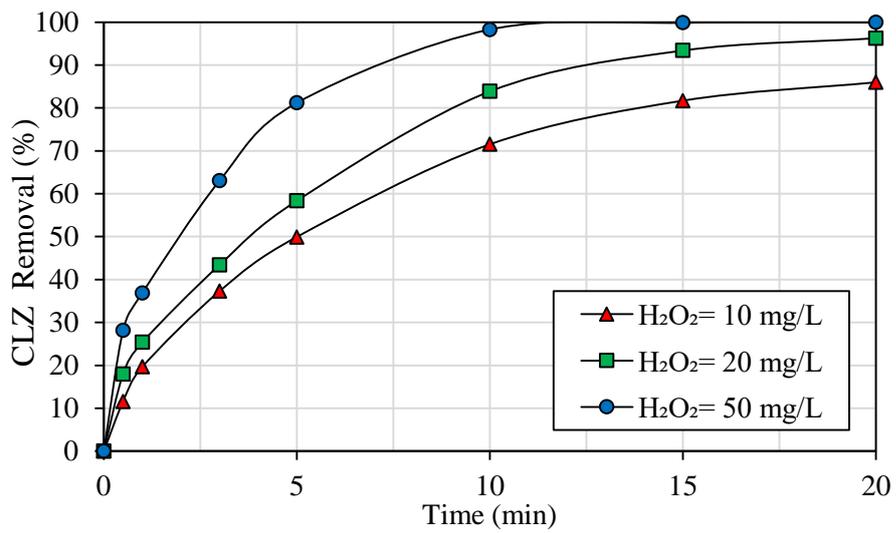
(b)

Figure 4.14. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Photo-Fenton Process at different H_2O_2 dosage (CLZ=40 mg/L, T=20°C, Fe^{2+}=5 mg/L, pH=3)

4.3.4. Effect of initial CLZ Concentration

Figure 4.15 shows the effect of initial CLZ concentration (20, 40 and 60 mg/L) on CLZ removal by the Photo-Fenton process. The other experimental conditions were maintained as $H_2O_2= 50$ mg/L, T=20°C, Fe^{2+}=5 mg/L, pH=3, as to correspond to their optimum values determined above.

It can be seen from Figure 4.15a that, as in the case of experimentations performed previously (Sec 4.3.1, Sec 4.3.2 and Sec 4.3.3), the CLZ concentration declined very rapidly at first, but then it ceased down gradually. This gradual decline ended up at the end of 5 min for CLZ concentration of 20 mg/L whereas it took 10 and 20 min for 40 and 60 mg/L CLZ cases, respectively. The CLZ removal efficiency of >99% was achieved at the end of 5 min when the initial CLZ concentration was 20 mg/L, whereas it was 57 and 81% when initial CLZ was 40 and 60 mg/L, respectively. Since the main factor in the removal of CLZ is the amount of OH• which remains stable as the initial Fe^{2+} and H_2O_2 concentrations are constant during the entire experiments, it is an expected situation to observe the decreasing CLZ removal efficiency while the concentration of CLZ increases.

When compared with the Fenton process, at the CLZ concentration of 20 mg/L, >99% removal was possible at the end of 50 min whereas at the CLZ concentration of 60 mg/L, CLZ removal was only 65% at the end of 60 min. So, the positive effect of UV light is evident.
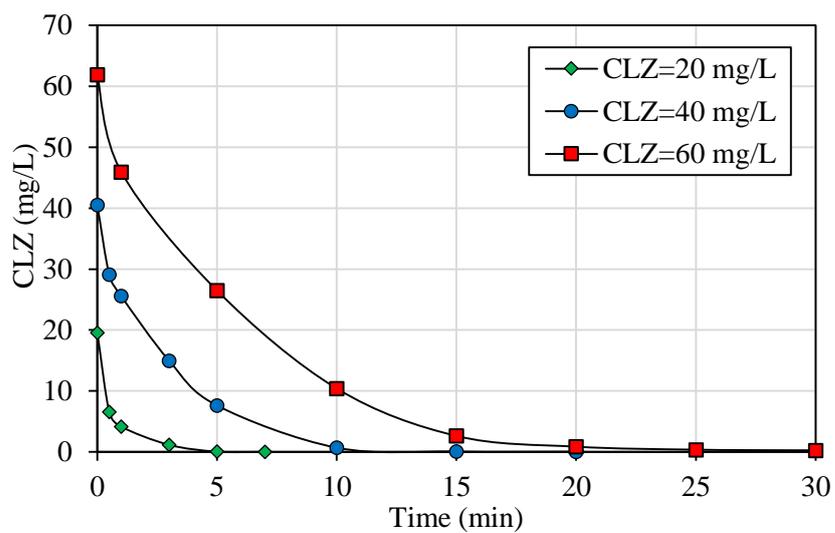
(a)
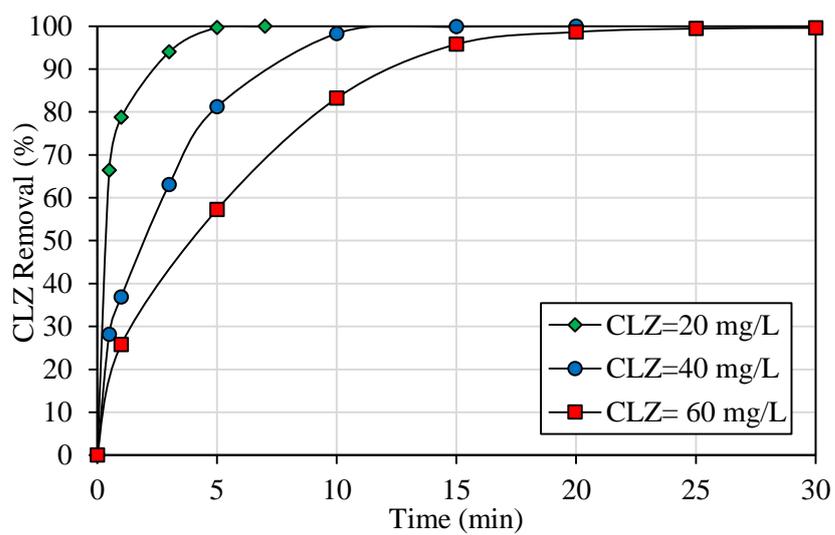
(b)

Figure 4.15. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Photo-Fenton Process at different initial CLZ concentration (T=20°C, H_2O_2=50 mg/L, Fe^{2+}=5 mg/L, pH=3)

4.3.5. Effect of Temperature

Photo-Fenton experiments were carried out at different temperatures (20, 30 and 40ºC) while keeping the other operational parameters constant at CLZ=40 mg/L, Fe^{2+}=5 mg/L, H_2O_2= 50 mg/L, pH=3. The results obtained are shown in Figure 4.16a and b. As the temperature rises from 20°C to 30°C and then to 40ºC, the removal of CLZ increases at a given time of the experimentation during the first 15 min. This trend was more observable at the 5th min of experimentation. Then after the difference between them diminished, reaching to >99% removal at the end of 20 minutes at all temperatures studied (Figure 4.16b). In other words, initial degradation rate of CLZ gets higher as the temperature increases from 20 to 40°C (Figure 4.16a).

When compared with the findings of Fenton process, the stimulatory effect of UV light application is evident in case of Photo-Fenton process. For example, it took 60 min to achieve >99% CLZ removal at the temperature of 20°C in Fenton process (Figure 4.11b) while it took 20 min at the same temperature in Photo-Fenton process. Similarly, at 40°C, >99% CLZ removal was attained at the end of 20 and 10 min in Fenton and Photo-Fenton process, respectively.
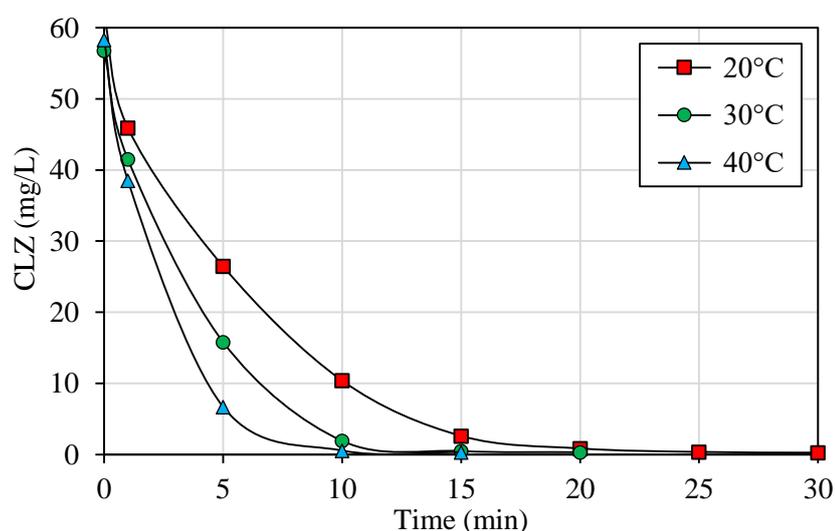
(a)
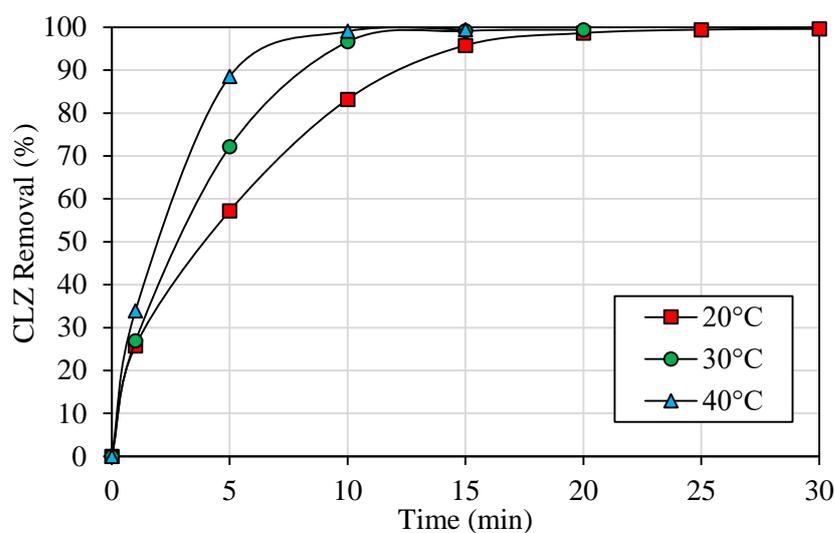
(b)

Figure 4.16. Time course variation of (a) CLZ concentration (b) CLZ removal efficiency by Photo-Fenton Process at different temperature (CLZ=40 mg/L, Fe2+=5 mg/L, H_2O_2= 50 mg/L, pH=3)

4.4. Reaction Kinetics for Fenton and Photo-Fenton Experiments

Pseudo first order kinetics and Behnajady-Modirdhahla-Ghanbery (BMG) reaction kinetics (as given in Sec 2.3.6) were applied and compared to observe the degradation of the CLZ by Fenton and Photo-Fenton processes.

The results of pseudo first order kinetics and BMG kinetic models are given in Figure 4.17 and 4.18, respectively. The relevant kinetic constant is provided in Table 4.2. These analyses belong to the optimum conditions determined for Fenton and Photo Fenton processes. The kinetic analysis for the remaining operational conditions are given in Figure A5–A24, Appendix A.
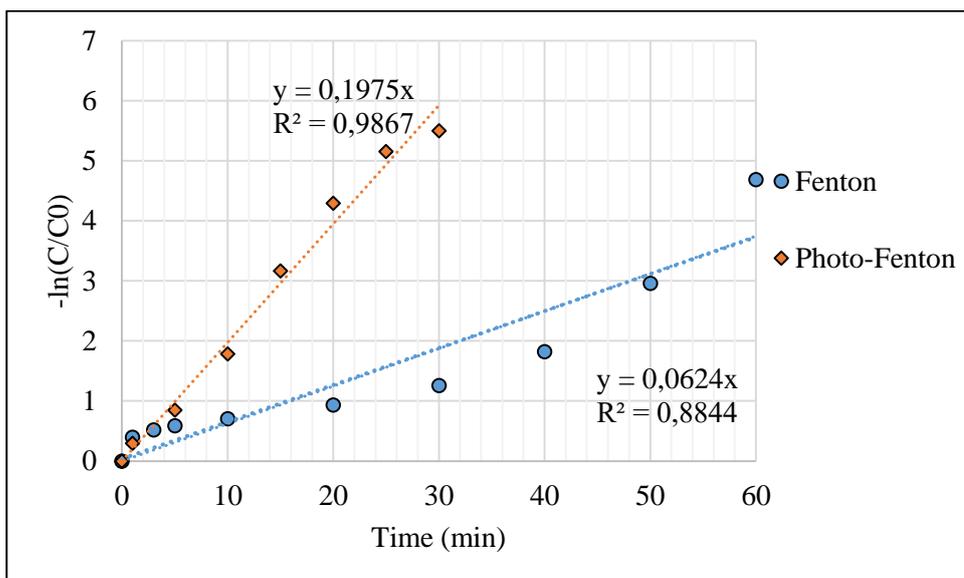
Figure 4.17. Pseudo first order kinetic analysis of CLZ degradation by Fenton and Photo-Fenton processes (pH=3, Fe^{2+}= 5 mg/L, H_2O_2= 50 mg/L, CLZ=40 mg/L, T=20°C for Fenton and pH=3, Fe^{2+}= 5 mg/L, H_2O_2= 50 mg/L, CLZ=60 mg/L, T=20°C for Photo-Fenton)
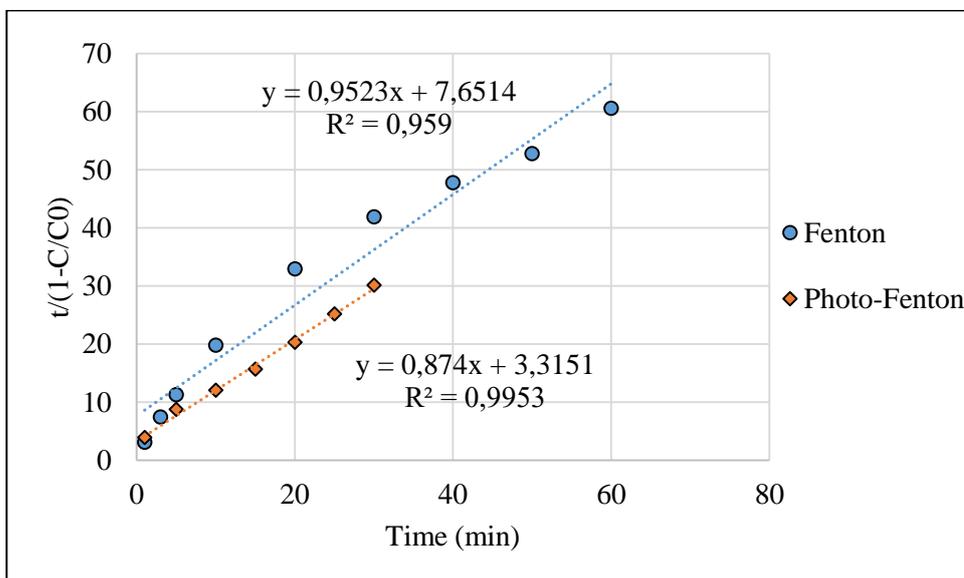
Figure 4.18. BMG kinetic analysis for CLZ degradation by Fenton and Photo-Fenton processes (pH=3, Fe^{2+}=5 mg/L, H_2O_2=50 mg/L, CLZ=40 mg/L, T=20°C for Fenton and pH=3, Fe^{2+}=5 mg/L, H_2O_2=50 mg/L, CLZ=60 mg/L, T=20°C for Photo-Fenton)

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Table 4.2. Pseudo First Order and BMG Kinetic Model Parameters for the
Degradation of CLZ by Fenton and Photo-Fenton Processes

Process	Pseudo First Order		BMG		
	k_1	R^2	m	b	R^2
Fenton	0.0624	0.8844	7.6514	0.9523	0.959
Photo-Fenton	0.1975	0.9867	3.3151	0.874	0.9953

As seen from Table 4.2, compared to pseudo first order kinetics, the BMG kinetic
model gives the higher correlation coefficients, indicating the better fit of BMG model
to the data. The regression values in the BMG model being greater than 0.95 for both
process prove that BMG model is followed perfectly. This finding was all valid for
the other parametric cases as given in Appendix A.

Because of being best fit with BMG kinetic model for the processes, the mathematical
equations are derived according to the correlations of operation parameters (Fe^{2+}/
H_2O_2, pH, Temperature and CLZ concentration) with 1/m and 1/b values as it is done
by Tunç et al. (2012) in their study. The equations are presented in Table 4.3.

Table 4.3. The Correlation Equations for 1/m and 1/b in Fenton and Photo-Fenton
Process

Process	Parameter	Equation	R^2
Fenton	$[Fe^{2+}/H_2O_2]$	$1/m=35.864[Fe^{2+}/H_2O_2]^2+0.233[Fe^{2+}/H_2O_2]+0.05$	0.9897
		$1/b=-211.73[Fe^{2+}/H_2O_2]^2+33.202[Fe^{2+}/H_2O_2]-0.1618$	0.9583

Process	Parameter	Equation	R^2
		$1/m=-0.0592[Fe^{2+}/H_2O_2]^2+0.0097[Fe^{2+}/H_2O_2]+0.1318$	0.9563
		$1/b=1.8834[Fe^{2+}/H_2O_2]^2-1.9162[Fe^{2+}/H_2O_2]+1.1638$	0.9452
	pH	$1/m=-0.0552pH+0.3024$	0.9488
		$1/b = -0.2125pH^2+1.3478pH-1.3899$	0.6297
	CLZ	$1/m=0.0033CLZ^2-0.216CLZ+3.4687$	0.972
		$1/b=-0.001CLZ^2 + 0.0407CLZ+0.6959$	0.9238
	Temperature	$1/m=0.0272e^{0,0653T}$	0.9549
		$1/b = -0.002T^2 + 0.1247T - 0.735$	0.956
Photo-Fenton	$[Fe^{2+}/H_2O_2]$	$1/m=-20.785[Fe^{2+}/H_2O_2]^2 + 10.\ 767[Fe^{2+}/H_2O_2] - 0.248$	1
		$1/b=26.578[Fe^{2+}/H_2O_2]^2-7.305[Fe^{2+}/H_2O_2]+1.5695$	1
		$1/m=4.6179[Fe^{2+}/H_2O_2]^2-3.7751[Fe^{2+}/H_2O_2]+0.9522$	1
		$1/b=-1.6004[Fe^{2+}/H_2O_2]^2+0.8625[Fe^{2+}/H_2O_2]+1.0345$	1
	pH	$1/m= -0.2694\ pH^2+1.642\ pH - 1.8806$	1
		$1/b= 0.0557\ pH^2 - 0.3278\ pH + 1.5864$	1
	CLZ	$1/m=1.0715e^{-0,023CLZ}$	0.9789
		$1/b= -0.0007\ CLZ^2 + 0.0511\ CLZ + 0.3755$	1
	Temperature	$1/m=-0.0056T^2+0.3408\ T-4.1444$	1
		$1/b=-0.0011T^2+0.0716T+0.1053$	1

To interpret the BMG kinetic model, m and b constants should be described clearly. As stated earlier (Sec 2.4.6), $1/m$ and $1/b$ indicates the initial degradation rate of contaminant and the theoretical maximum contaminant removal, respectively. Some

studies set correlations of the affecting operational parameters with $1/m$ and $1/b$ values in the model. While Behnajady et al. (2007) give a correlation of Fe^{2+}/H_2O_2 with the values, Tunç et al. (2012) explain the correlations of all parameters in the experiment with $1/m$ and $1/b$. In our study, the correlations obtained are shown in Figure 4.19.
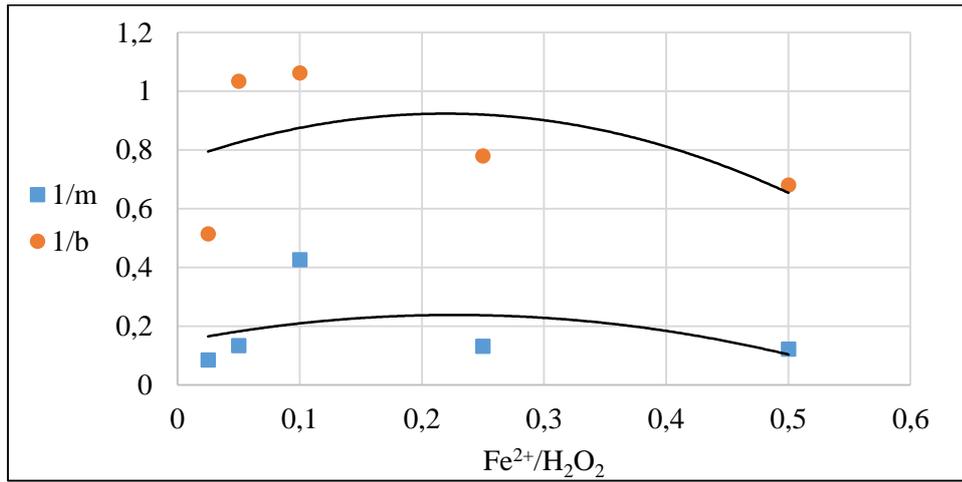
(a)
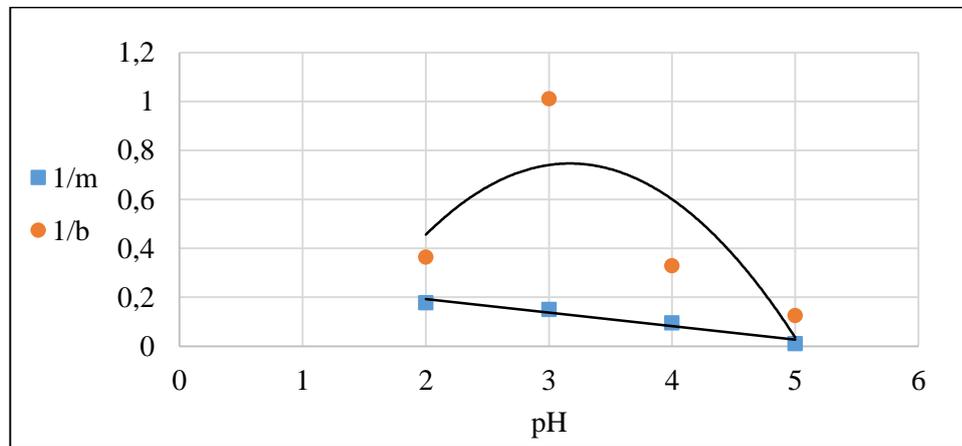
(b)
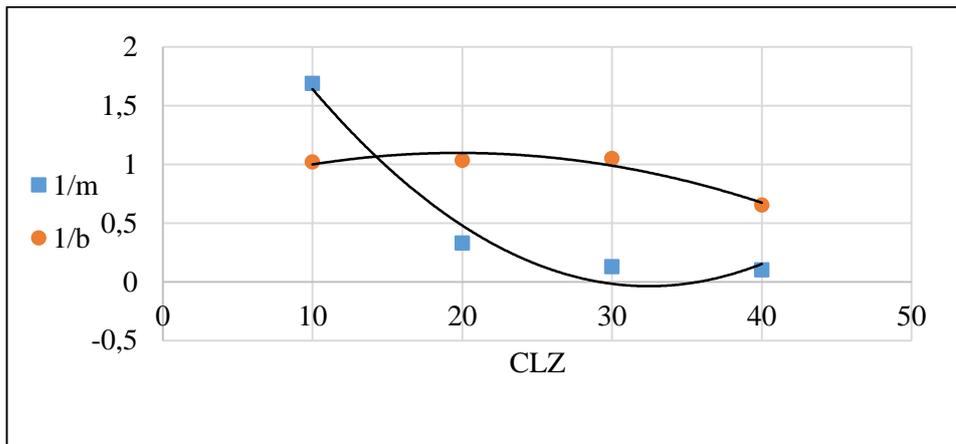
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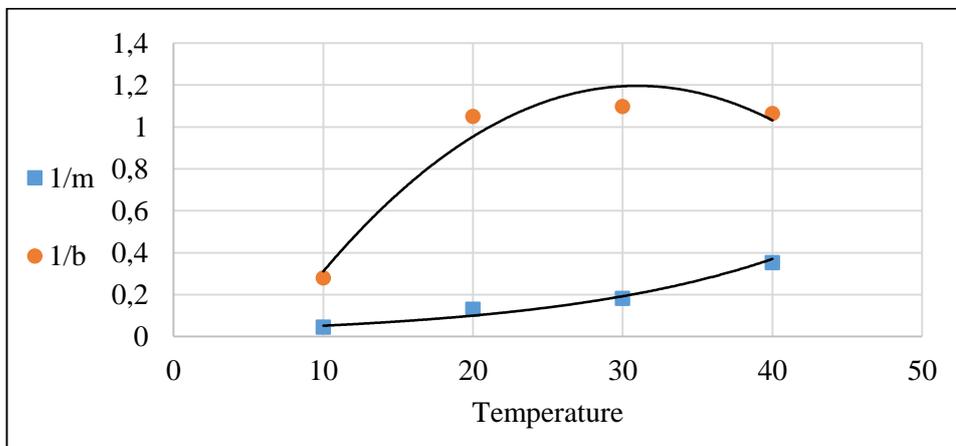
(d)

Figure 4.19. Correlations of Fe^{2+}/H_2O_2, pH, CLZ and Temperature with 1/m and 1/b; (a) Fe^{2+}/H_2O_2 (b) pH (c) CLZ (d) Temperature for Fenton Process

It is seen in Figure 4.19a that 1/m and 1/b values will be at highest level when Fe^{2+}/H_2O_2 ratio is nearly 0.25. For the correlation of pH with 1/m and 1/b, Figure 4.19b show that unlike 1/m, the 1/b shows the maximum for CLZ at pH 3. From Figure 4.19c, 1/m decreases when CLZ concentration is increased. The slightly decrease in 1/b is not taken into consideration. If the temperature is increased, the 1/m and 1/b is also increased (Fig 4.19d).

Fe^{2+}/H_2O_2 correlations with 1/m and 1/b show difference with respect to change in Fe^{2+}/H_2O_2 ratio. 1/b and 1/m slightly decreases with the increase in the ratio. (Fig 4.20a). As seen in Figure 4.20b, while the value of 1/m has reached its highest value,1/b value is seen at the lowest at pH 3. As the CLZ concentration is increased, 1/m decreases and 1 /b increases (Fig 4.20c). As given in Figure 4.20d, 1/m and 1/b show the highest value at 30°C.
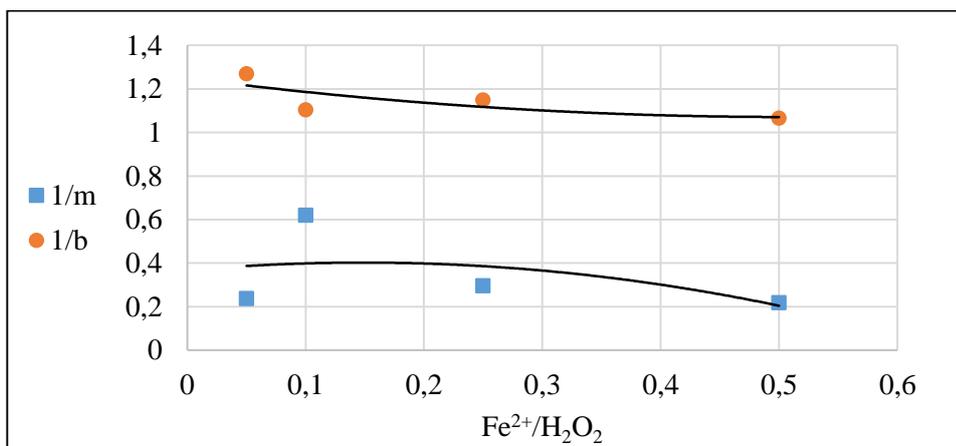
(a)
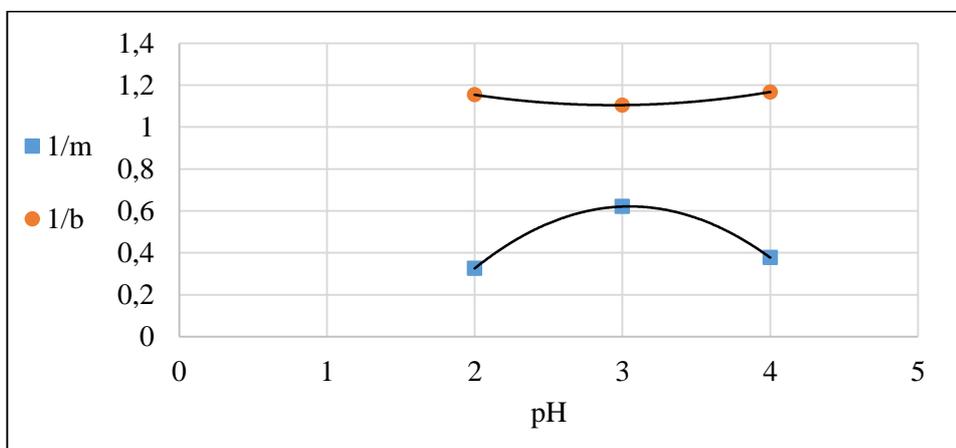
(b)
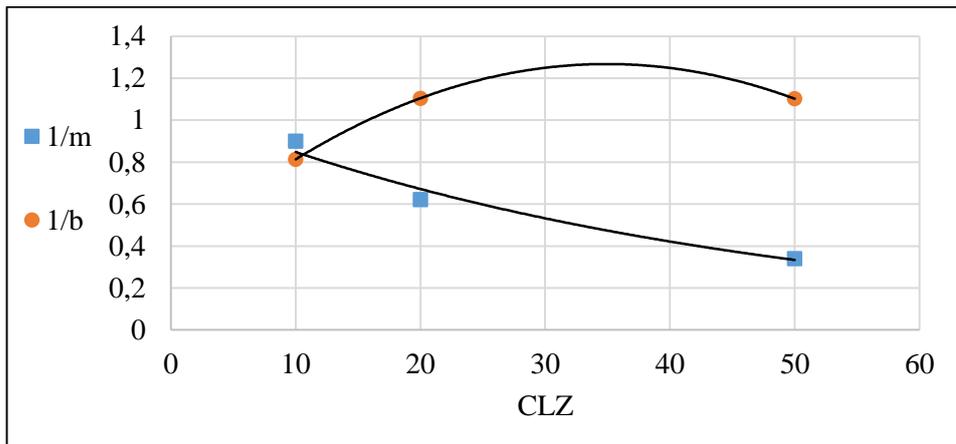
(c)
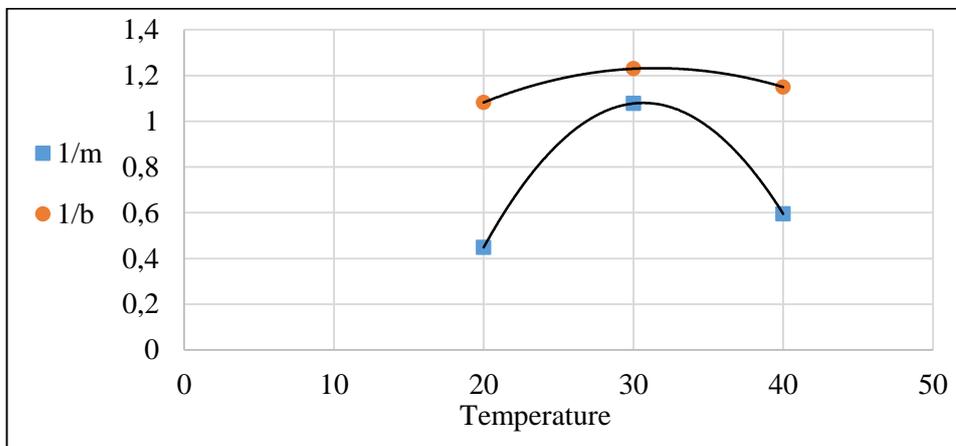
(d)

Figure 4.20. Correlations of Fe^{2+}/H_2O_2, pH, CLZ and Temperature with $1/m$ and $1/b$; (a) Fe^{2+}/H_2O_2 (b) pH (c) CLZ (d) Temperature for Photo-Fenton Process.

4.5. Multiple Linear Regression (MLR) Analysis

The simple linear regression model may be favorable for many situations, but two or more (independent) variables will be needed to explain many models in real life. Regression models with multiple variables are called multiple linear regression (MLR) models (URL3).

MLR models are expressed as;

$$y = a_0 + a_1 X_1 + a_2 X_2 + \ldots + a_n X_n \qquad (33)$$

Where;

Y : dependent variable

a_o : intercept

a_1, a_2, a_3,.a_n : independent variables

X_1, X_2, X_3,.X_n : concentration of independent variables (mg/L)

The purpose of the multiple regression model is to examine the effect of each independent parameter on the dependent variable. There are five independent variables namely CLZ concentration (mg/L), H_2O_2 concentration (mg/L), Fe^{2+} concentration (mg/L), pH and Temperature. CLZ removal (%) is indicated as dependent variable. MLR analysis was performed for each process done in the study by SPSS statistics 22 in this study. After all data is entered into the application at once, the parameters which are effective or ineffective are specified. All results are given in Table 4.4-4.5.

The value of R^2 for UV/H_2O_2, Fenton and Photo-Fenton is 0.812,0.710,0.779, respectively. In other words, five independent variables can explain 81.2% of the change in the dependent variable (CLZ removal) for UV/H_2O_2 process. This value is quite high and satisfactory in research. ANOVA test was significant. The P value is 0.000. Since p value is less than 0.05, it is accepted as significant at 5% significance level. So the regression model is meaningful as a whole.

Table 4.4. The results of MLR analysis

Process	R^2	Sig.ANOVA	Equation
UV/ H_2O_2	0.812	.000	Y=33,639-1.137pH+1.406H_2O_2-1.539CLZ-0.649T+1.329t

Process	R^2	Sig.ANOVA	Equation
Fenton	0.710	.000	$Y=58.179-15.208pH-0.092H_2O_2-1.265CLZ+7.928Fe^{2+}+1.898T+0.671t$
Photo-Fenton	0.779	.000	$Y=-8.551+2.253pH+0.482H_2O_2-1.092CLZ+4.985Fe^{2+}+1.851T+4.044t$

The significance of each parameter is given in Table 4.5. With the p-value given in Table 4.5, it is clear that all parameters except pH are effective in removing CLZ in process UV/H_2O_2. Since the pH parameter has a p value higher than 0.05, its effect on CLZ removal is not considered to be very important. The reason why pH is considered insignificant is that the pH of the 2-9 range in the experiments, does not show much difference although the highest yield is obtained at pH3. As seen in the equations given in Table 4.4, some coefficients were negative. The reason for this is that CLZ has an inverse relationship with the CLZ removal. The analysis of independent variables in the Fenton process shows that the most effective parameters are pH, temperature, CLZ concentration, time and iron concentration. If Temperature increases the degradation of CLZ will also increase. However, the inverse relationship is seen for the CLZ concentration and pH since their coefficient is negative. In other words, if pH increases the CLZ removal will decrease. Since hydrogen peroxide slightly exceeds 5%, it is not considered as a significant parameter to the model. For the Photo-Fenton process, as in UV/H_2O_2, the pH parameter is considered insignificant according to the p-value. The pH range studied in the experiments can be shown as a reason for this. Since there is not much difference between the removal efficiencies according to this range, it is seen that the statistical significance is not normal.

Table 4.5. The significance of each parameter in UV/H_2O_2, Fenton, Photo-Fenton

Process		Correlation						
		pH	H_2O_2 (mg/L)	CLZ (mg/L)	Fe^{2+} (mg/L)	T (^oC)	Time (min)	Constant
UV/H_2O_2		0.120	.000	.000	---	.000	.000	.000
Fenton	p-value	.000	.057	.000	.000	.000	.000	.000
Photo-Fenton	(Sig.)	0.548	.000	.000	.003	.000	.000	0.614

The distribution graph between CLZ removal and predicted values also shows a linear positive relationship for each process applied. The linearity assumption of the regression models of UV/H_2O_2, Fenton and Photo-Fenton are also provided in Figure 4.21.
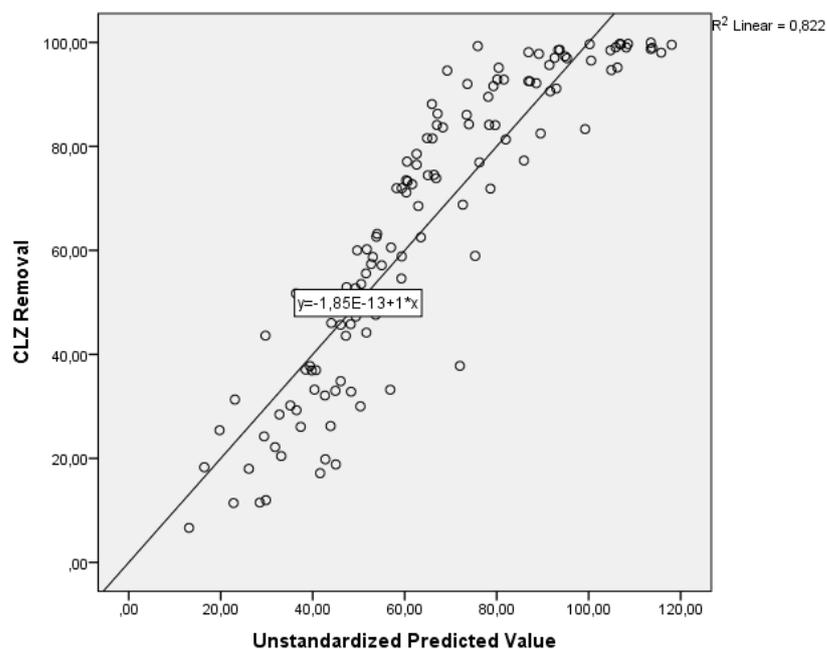
(a)
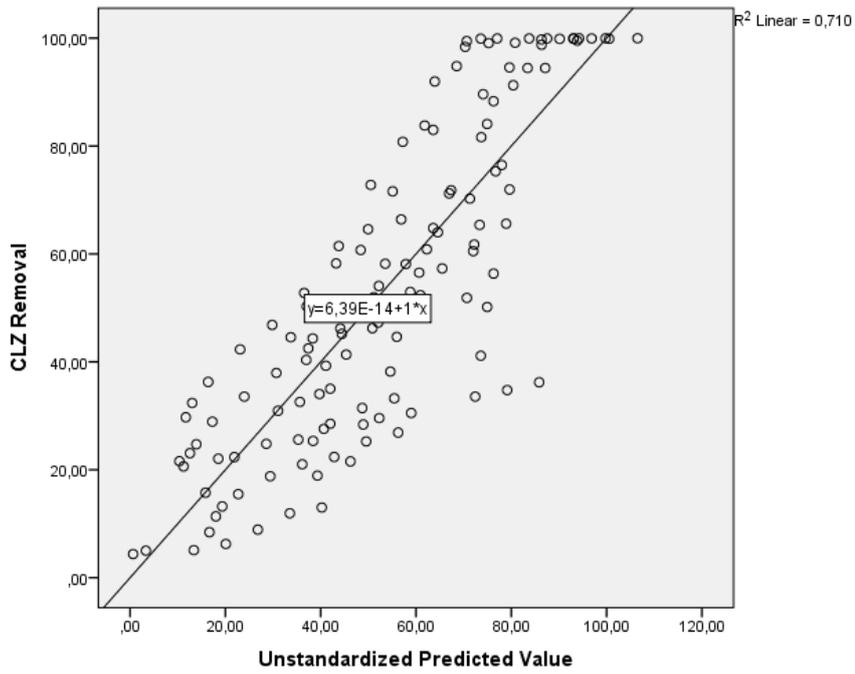
(b)
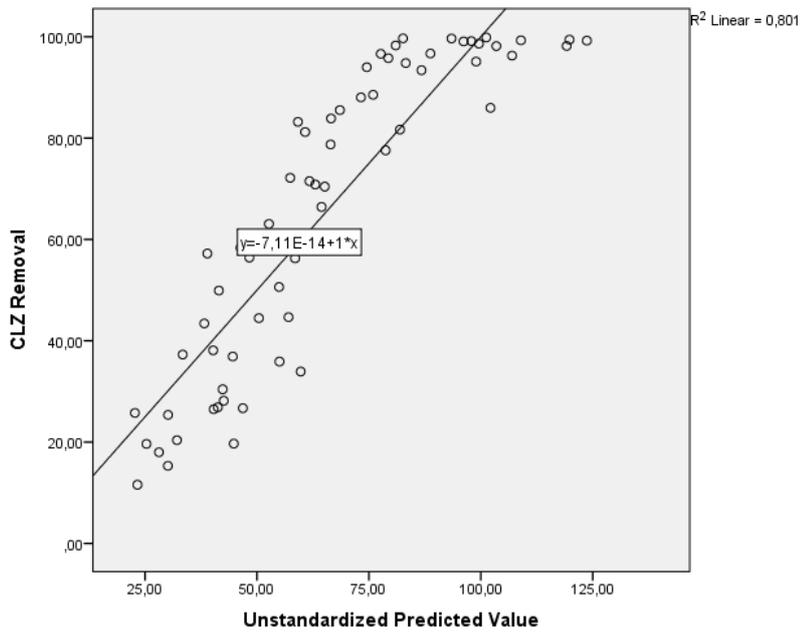
(c)

Figure 4.21. Scatter/Dot for CLZ removal in (a) UV/H_2O_2, (b) Fenton and (c) Photo-Fenton

4.6. Possible By-products formation of CLZ with UV/ H2O2, Fenton and UV/Fenton Processes

As it is known, the widespread use of pesticides in agriculture can cause a serious damage on water resources and the environment with the active substance of pesticides and their by-products. In the literature, desphenyl Chloridazon (DPC) and methyl desphenyl Chloridazon (Me-DPC) are generally observed as by-products of CLZ pesticide degradation (Kowal et al., 2013;Schuhmann et al., 2016; Mbiri et al., 2017). According to EFSA (2007) report, these by- products are more harmful than its active substance, CLZ. However, when determining the possible by-products another important point is to determine the other by products formed with the further degradation of DPC and Me-DPC. Because these intermediates have a potential to damage the environment. Therefore, in the study, the possible by products generated by UV/ H_2O_2, Fenton and Photo-Fenton processes were also investigated. During this analysis, it was inspired from a thesis done by Schatz (2012) on the CLZ removal by ozonation process. In this thesis, Schatz identified the possible by-products of CLZ during ozonation and provided the m/z (mass versus charge) values for the identified products. So, in the present study, these possible by-products were sought, if present, based on the relevant m/z values via LC/MS/MS. The results obtained are presented in the following sub-sections for the processes applied. Prior to these analysis, synthetic wastewater sample containing 1 mg/L CLZ was introduced to the LC/MS/MS to see its peak appearance as well as the impurities, if present, and the spectrum obtained is shown in Figure 4.22.
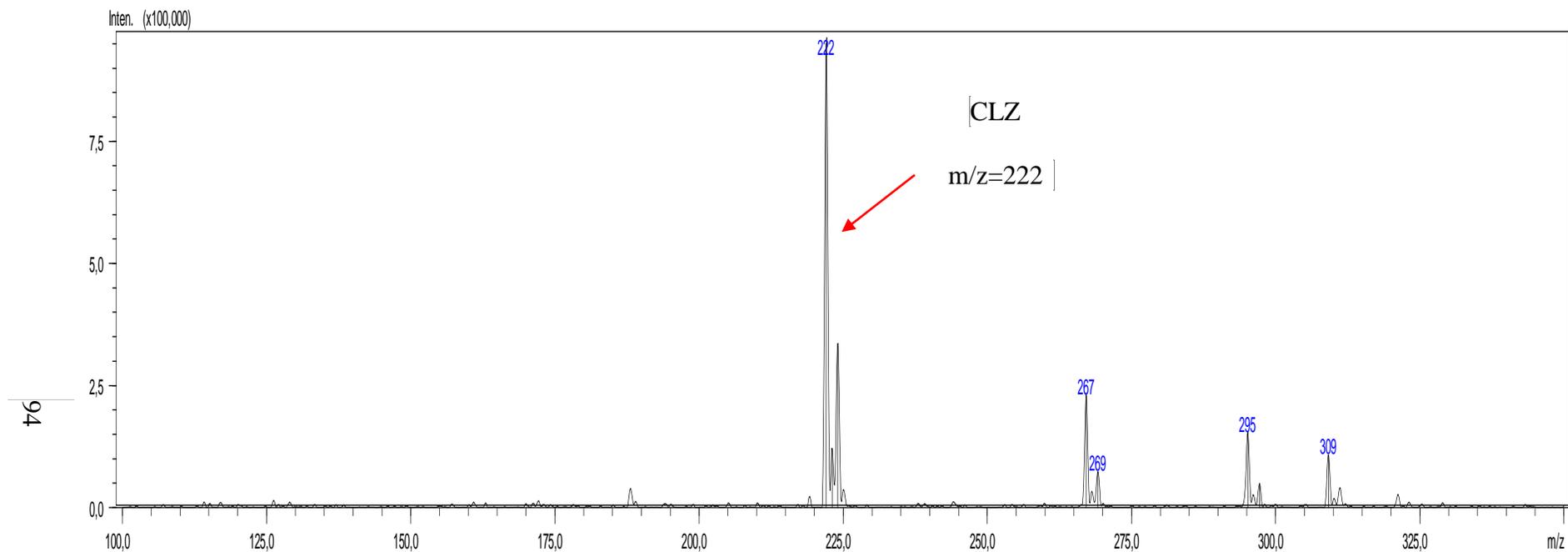
Figure 4.22. LC/MS/MS spectrum of 1 mg/L CLZ (intensity vs m/z)

4.6.1. Possible by-products of CLZ for UV/ H2O2 process

Detection of by-products was performed via using LC/MS/MS device for the optimum conditions determined for degradation of CLZ by UV/ H_2O_2 process. The optimum conditions considered was: T=20°C; H_2O_2=20 mg/L; pH=3; initial CHL=20 mg/L.

The sample taken at the end of the experiment belonging to the above-mentioned optimum conditions was injected to the LC/MS/MS for by-product analysis. The results obtained are shown in Figure 4.23 a and b. When this figure is examined, there seems many by-products formed during process. But, only two of them were proven to be present, namely, DPC and 5-hydroxyhydantion. DPC is definitely formed, because the DPC with an m/z value of 146 is checked with fragment ions and proved to be precisely as DPC considering the data given in Schatz (2012). The other one could be 5-hydroxyhydantion with m/z value of 115. This product is seen in Figure 4.23 with m/z value 134 due to H_2O adding 19 point. It is possibility that 5-hydroxyhydantion is formed from DPC which was formed from CLZ. In Figure 4.24, the possible degradation pathway is given.

It should be noted here that since the standards for these compounds could not be bought, no data for their amount were provided. Nevertheles, it is of sure that CLZ was not degraded completely, but converted to by-products, at least partially, upon application of UV/H_2O_2 process under the conditions mentioned.
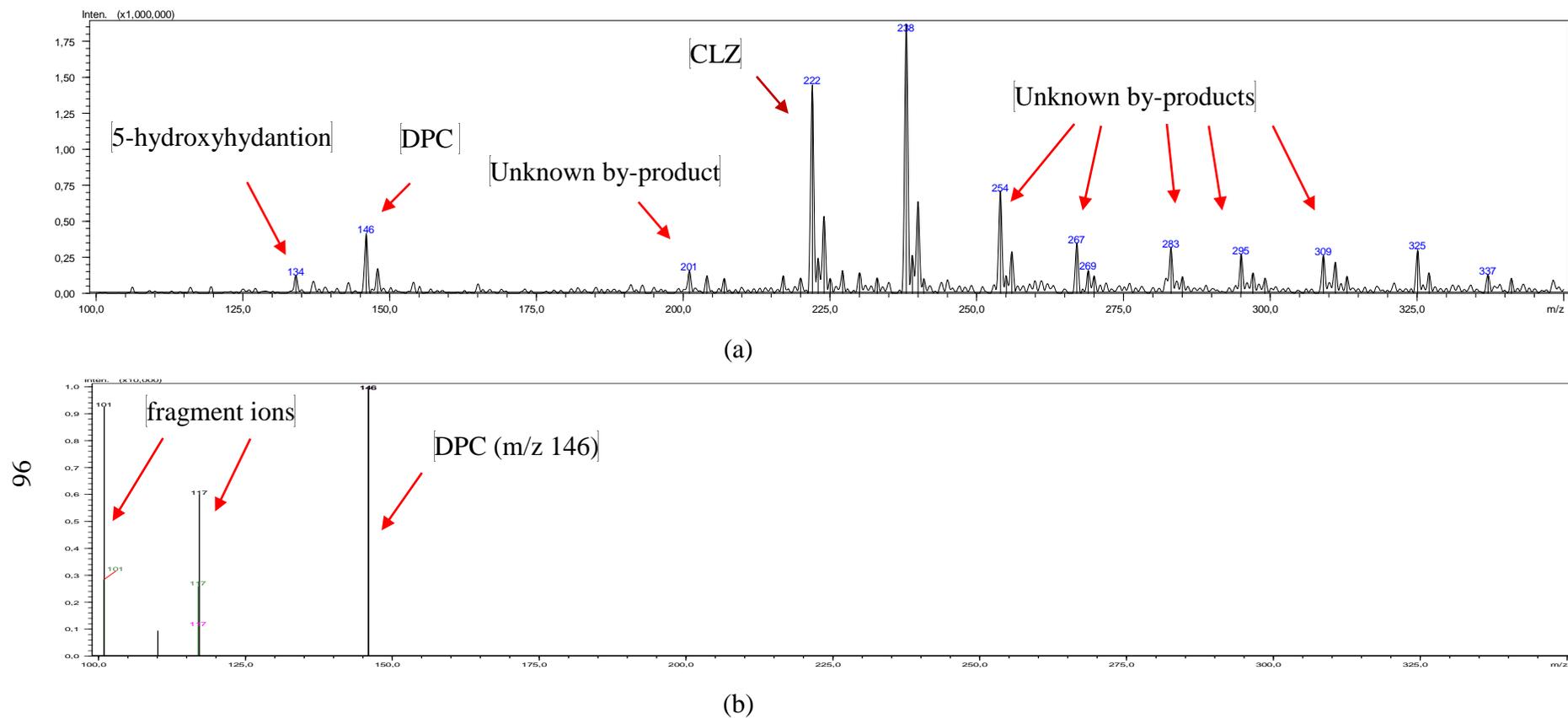
Figure 4.23. (a) LC/MS/MS spectrum of CLZ at the end of UV/H_2O_2 application (T=20°C; H_2O_2=20 mg/L; pH=3; initial CHL=20 mg/L); (b) Fragment ions of DPC (m/z 101 and m/z 117).

CLZ   DPC   5-hydroxyhydantion

Figure 4.24. Proposed degradation pathway for the formation of 5-hydroxyhydantion (Schatz, 2012)

4.6.2. Possible by-products by Fenton and Photo-Fenton processes

For the by-product analysis in the Fenton and Photo-Fenton processes, the conditions considered as optimum were taken into consideration (T=20°C; CLZ=40 mg/L; H_2O_2=50 mg/L; Fe^{2+}=5 mg/L; pH=3 for Fenton and CLZ=60 mg/L; H_2O_2=50 mg/L; Fe^{2+}=5mg/L; pH=3 for Photo-Fenton). The same evaluation was done in these two processes because there was no difference in the m / z values between the samples taken at 1 h for the Fenton and 30 min for the Photo-Fenton processes. Figures 4.25a and b show the results obtained from LC/MS/MS analysis, respectively.

(a)

(b)

(c)

Figure 4.25. LC/MS/MS spectrum of CLZ (a) at the end of Fenton processes
(T=20°C; CLZ=40 mg/L; H_2O_2=50 mg/L-Fe^{2+}=5 mg/L; pH=3); (b) at the end of
Photo-Fenton processes (CLZ=60 mg/L- H_2O_2=50 mg/L- Fe^{2+}=5 mg/L- pH=3); (c)
Fragment ions of Pyradazine-3,4,5-trione (m/z 42 and 56).

CLZ   DPC   Pyridazine-3,4,5-trione
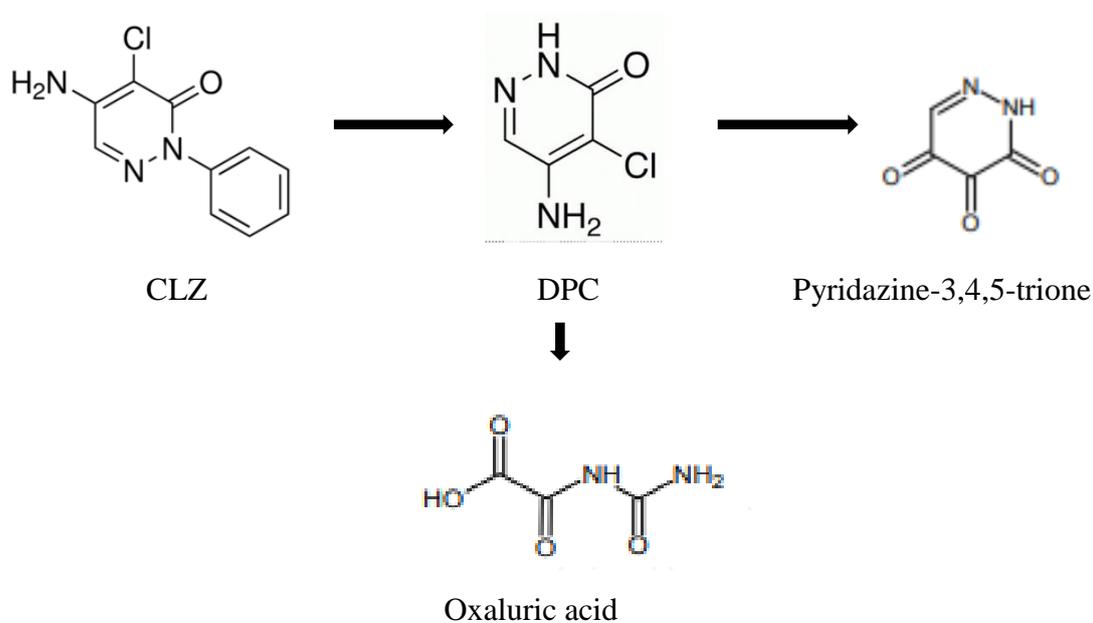
Oxaluric acid

Figure 4.26. Possible degradation pathway for the formation of Pyridazine-3,4,5-
trione and Oxaluric acid (Schatz, 2012).

It was believed that the compound formed during the Fenton and Photo-Fenton
processes upon the degradation of DPC is Pyradazine-3,4,5-trione with an m/z value

of 127. In order to prove it, the fragments ions were checked. As shown in Figure 4.25c, it was proven that the compound is Pyradazine-3,4,5-trione, as helped from the data provided by Schatz (2012). However, since the ammonium format was used as a buffer during the analysis, which binds 33 number to the compound, it was considered that the compound of Oxaluric acid with an m/z value of 165 is formed.

The presence of DPC is thought to come from the compound with an m/z ratio of 165. Because, in the experimental analysis, it is considered that H_2O is bonded to the compound and bring 19 in number to the DPC with an m/z ratio of 146. In this case, the mechanism of degradation pathway would be as given in Figure 4.26.

As in the case of UV/H_2O_2 application, there seems many by-products formed during process. But only two of them became possible to identify. Also, since the standards for these compounds could not be bought, no data for their amount were provided. Nevertheles, it is of sure that CLZ was not degraded completely, but converted to by-products, at least partially, upon application of the Fenton and Photo-Fenton processes under the conditions mentioned.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

It is very important to control the pesticides residues in water since the presence of them in water will create a serious damage then after. In this study, UV/H_2O_2, Fenton and Photo-Fenton processes among AOPs were studied on the removal of CLZ herbicide from water sources. The parameters affecting each process were determined and the optimum values of the parameters, for which the highest CLZ removal was achieved, were indicated. With this determination, the feasibility of these processes for CLZ removal from water has been clearly observed. There is no detailed study for the CLZ removal with AOPs in present studies. The aim is to observe the applicability of these processes in wastewater containing CLZ.

The following conclusions can be drawn from the study:

- CLZ completely disappeared within 1 h, by the Fenton and UV/H_2O_2 processes while in the Photo-Fenton processes approximately 100% disapearance was observed in 20 minutes.
- However, this disappearance of CLZ could not be attributed to the complete degradation as some by-products were observed to be formed at the end of experimentations.
- By-products, namely, DPC, Pyridazine-3,4,5-trione, Oxaluric acid and 5-hydroxyhydantion were identified. There observed some other by-products, but they could not be identified.
- In the UV/H_2O_2 process, the concentration of H_2O_2, CLZ and temperature influenced the removal of CLZ, significantly.

- The effect of pH on Fenton and Photo-Fenton processes was higher compared to UV/H_2O_2 process.
- Photo-Fenton process was superior over Fenton and UV/H_2O_2 process considering the removal efficiencies attained. However, one should consider the economical feasibilities of the processes before deciding to choose as a treatment option. Possible higher sludge production in Fenton Process and additional cost of UV light use in UV/H_2O_2 and Photo-Fenton Processes should be evaluated.

The followings are recommended as future works:

- For the unidentified by-products further studies are recommended. Because they might be more toxic than CLZ and may pose a greater danger to the environment. They should be identified and their removal should be investigated further. Thereby, the study will be only complete as the operational conditions for the complete removal of CLZ will be determined in a way.
- Detailed economic feasibility study is recommended.

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A. KINETICS ANALYSIS FOR CLZ REMOVAL BY UV/H2O2, FENTON AND PHOTO-FENTON PROCESSES

Kinetics Analysis for CLZ Removal by UV/H₂O₂ Process
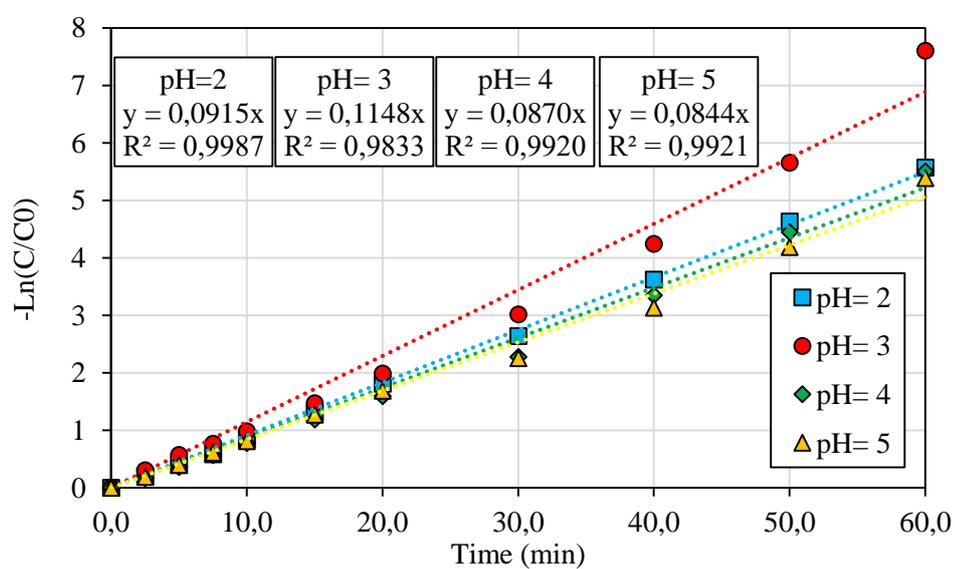
Figure A. 1 .Pseudo First Order analysis for CLZ degradation by UV/H$_2$O$_2$ at different pH
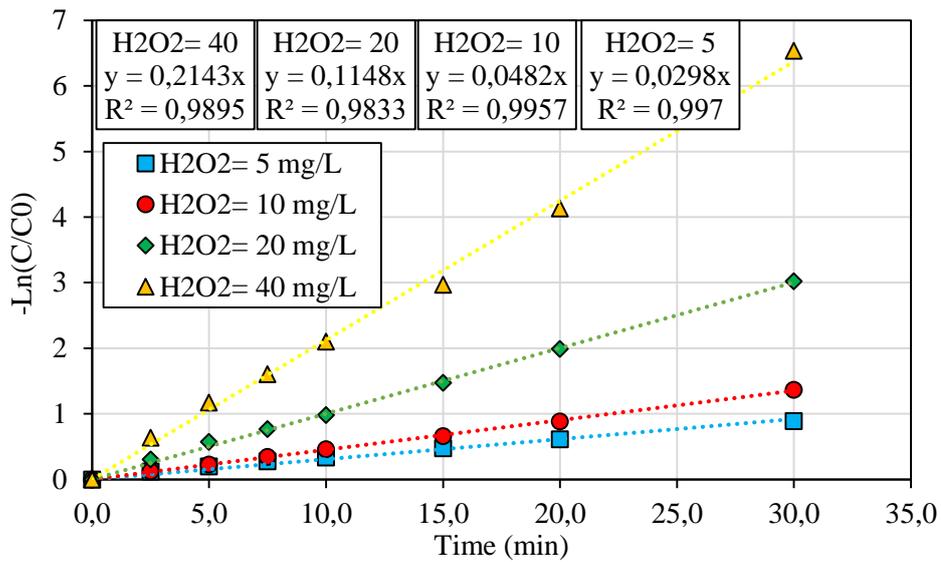
Figure A. 2 .Pseudo First Order analysis for CLZ degradation by UV/H_2O_2 at different H_2O_2 concentration
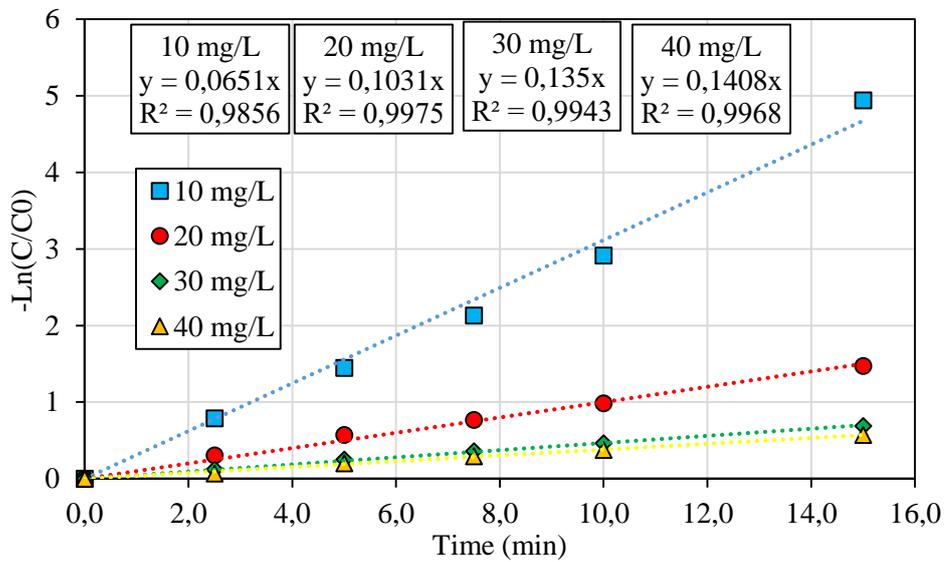
Figure A. 3. Pseudo First Order analysis for CLZ degradation by UV/H_2O_2 at different initial CLZ concentration
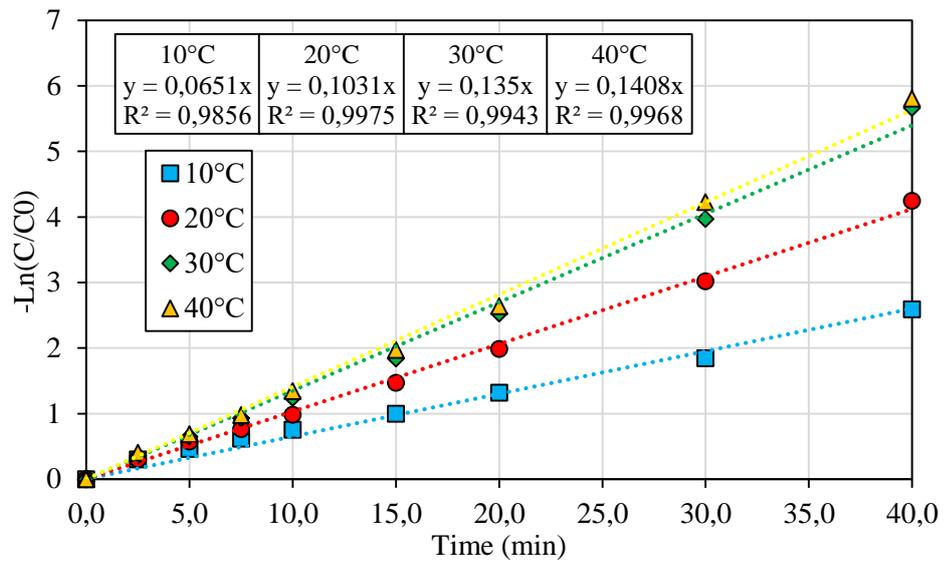
Figure A. 4. Pseudo First Order analysis for CLZ degradation by UV/H_2O_2 at
different Temperature

Kinetics Analysis for CLZ Removal by Fenton Process
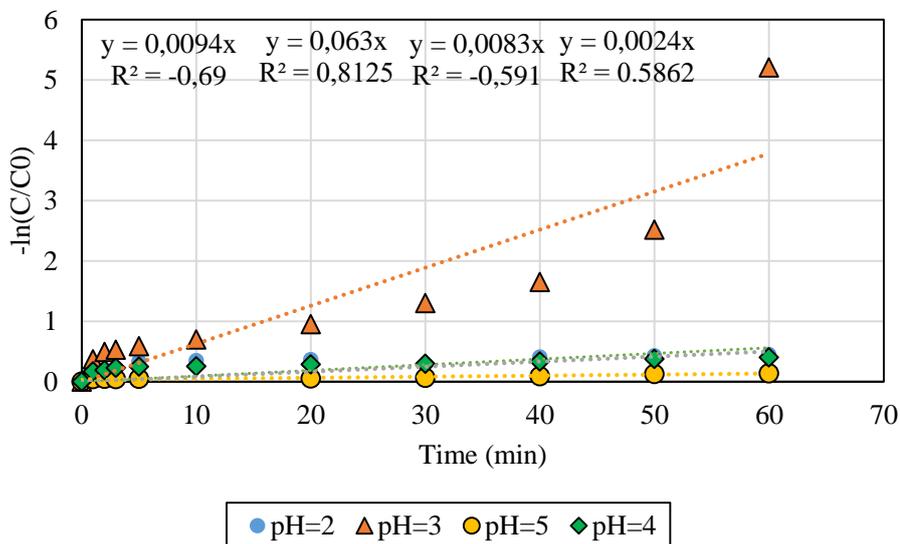
Figure A. 5. Pseudo First Order analysis for CLZ degradation by Fenton at different

pH
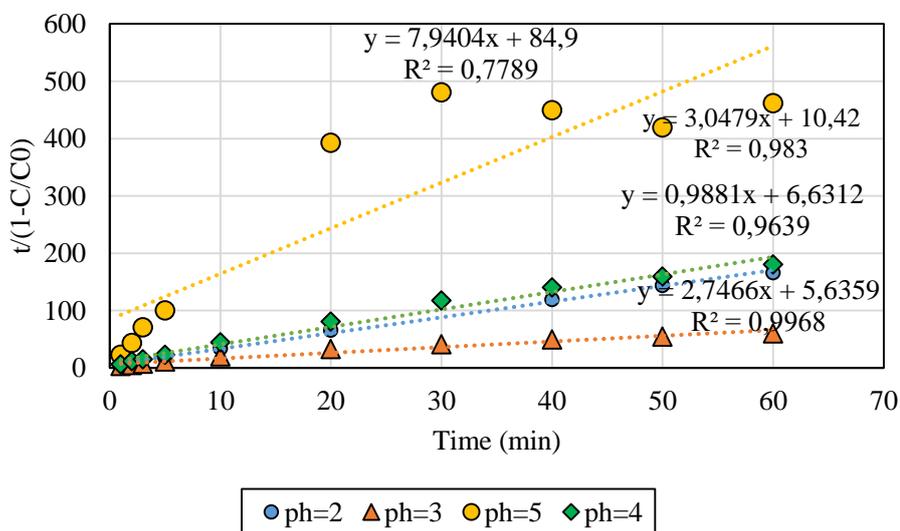
Figure A. 6.BMG kinetic analysis for CLZ degradation by Fenton at different pH
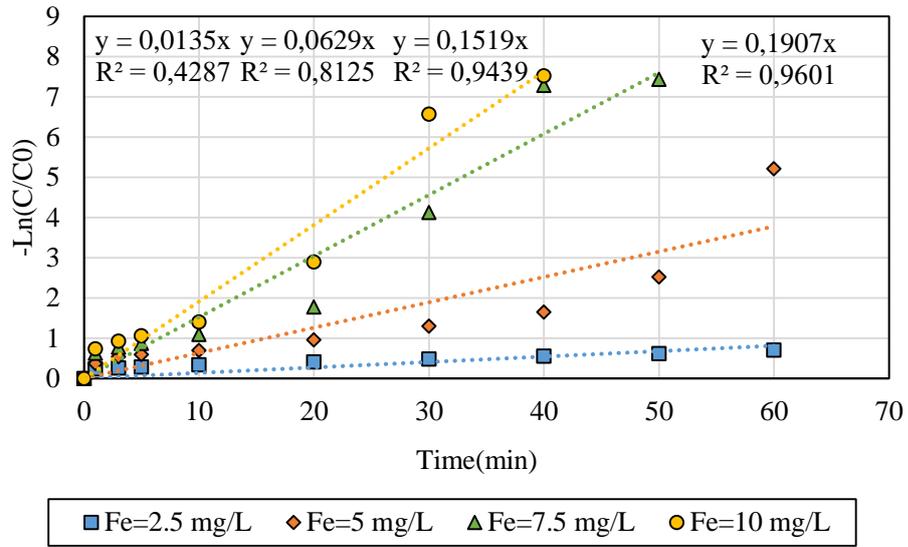
Figure A. 7. Pseudo First Order kinetic analysis for CLZ degradation by Fenton at different Fe^{2+} concentration
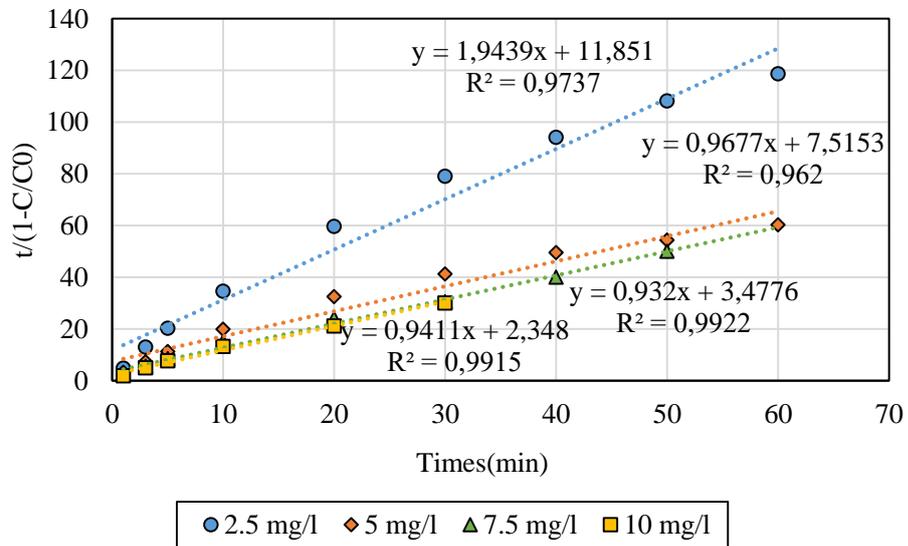
Figure A. 8. BMG kinetic analysis for CLZ degradation by Fenton at different Fe^{2+} concentration
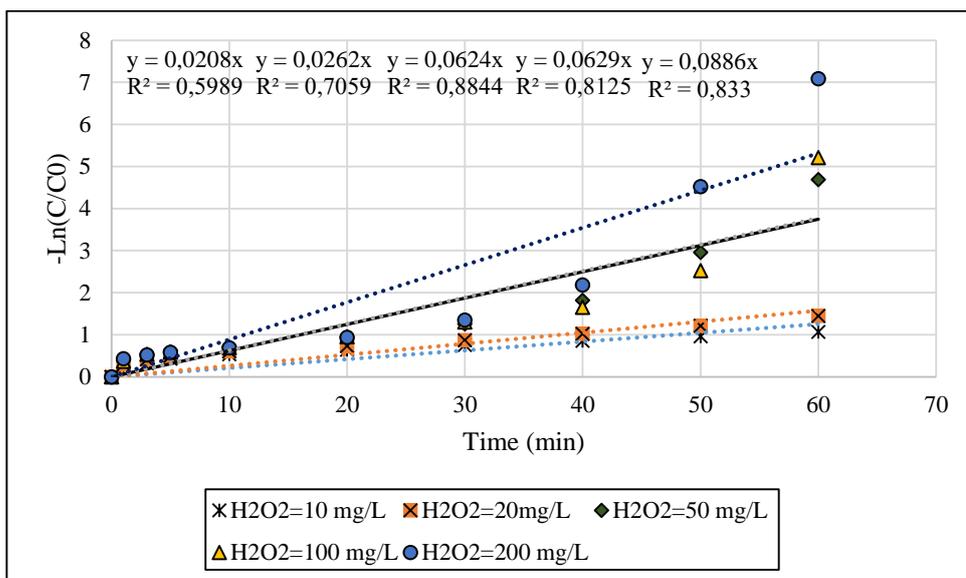
Figure A. 9. Pseudo First Order kinetic analysis for CLZ degradation by Fenton at different H_2O_2 concentration
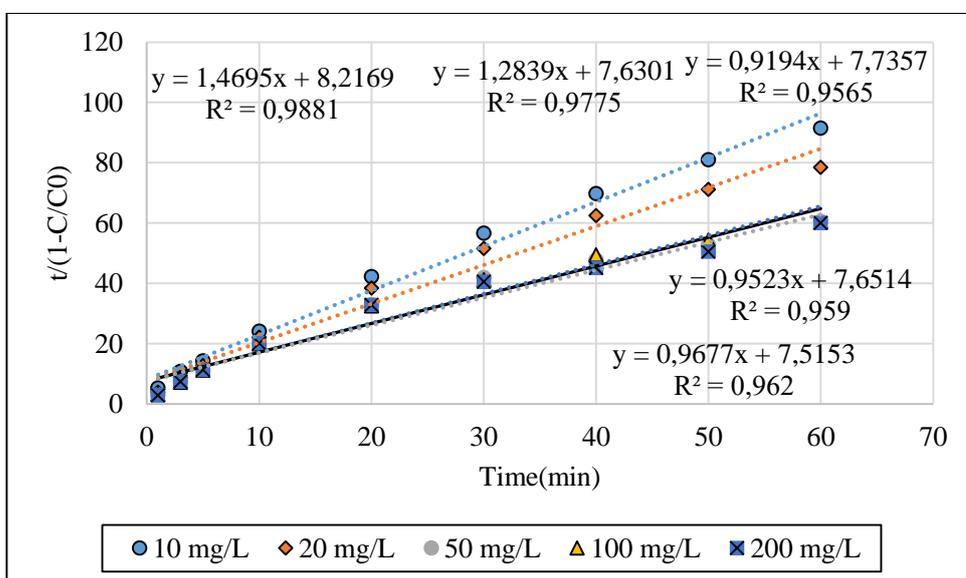
Figure A. 10. BMG kinetic analysis for CLZ degradation by Fenton at different
H2O2 concentration
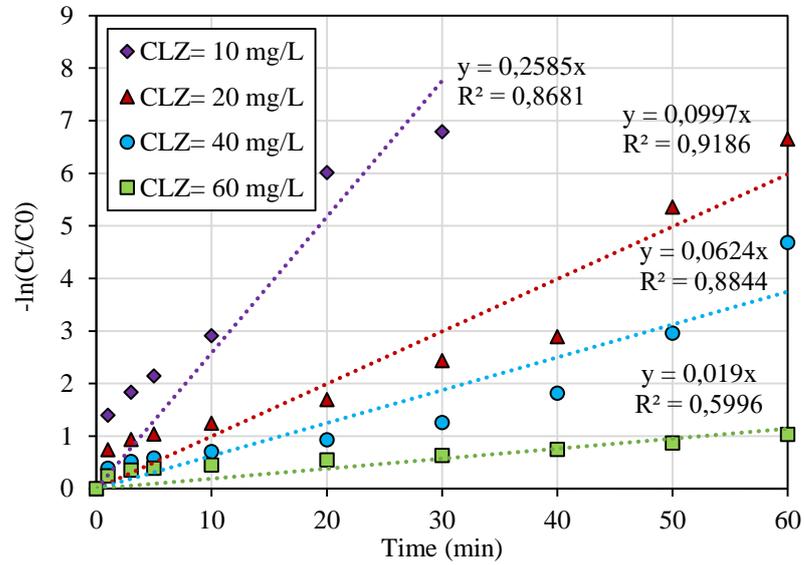
Figure A. 11. Pseudo First Order kinetic analysis for CLZ degradation by Fenton at
different initial CLZ concentration
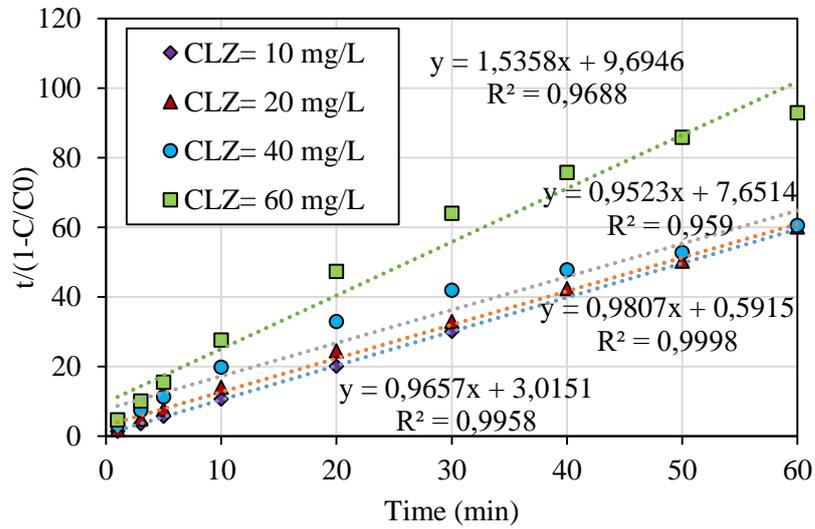
Figure A. 12. BMG kinetic analysis for CLZ degradation by Fenton at different
initial CLZ concentration
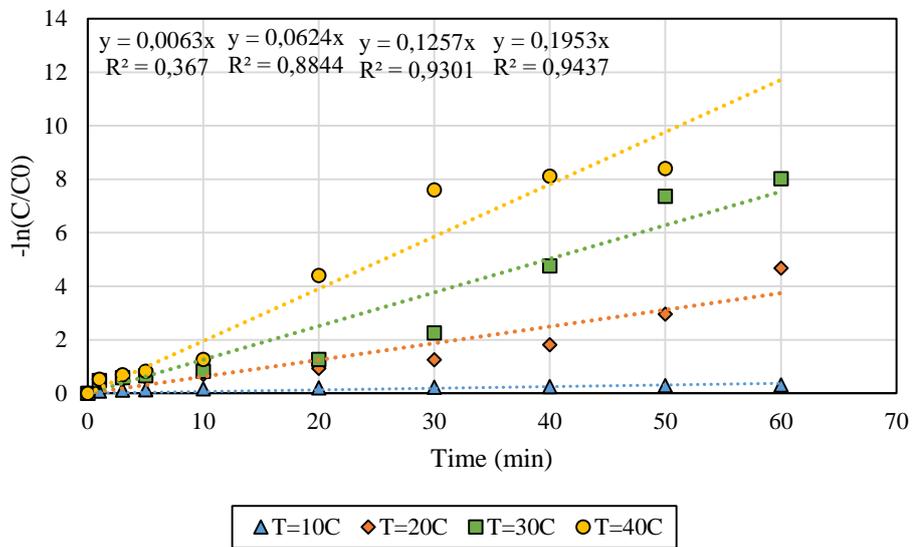
Figure A. 13. Pseudo First Order kinetic analysis for CLZ degradation by Fenton at different Temperature
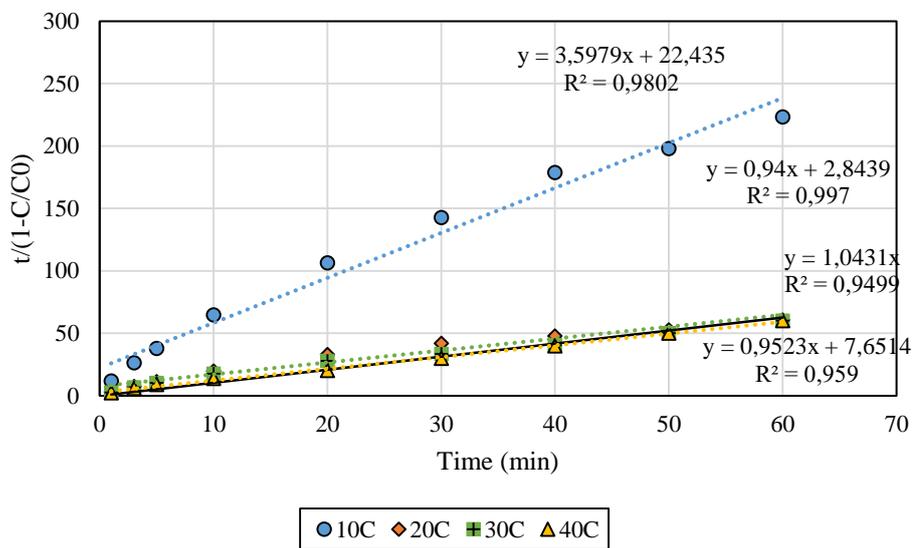
Figure A. 14. BMG kinetic analysis for CLZ degradation by Fenton at different Temperature

Kinetics Analysis for CLZ Removal by Photo-Fenton Process
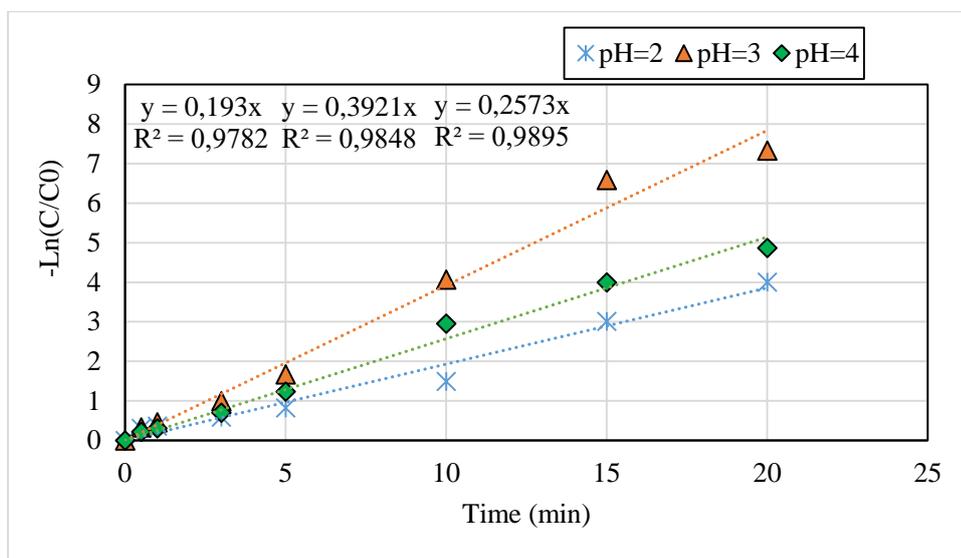
Figure A. 15. Pseudo First Order kinetic analysis for CLZ degradation by Photo-Fenton processes at different pH
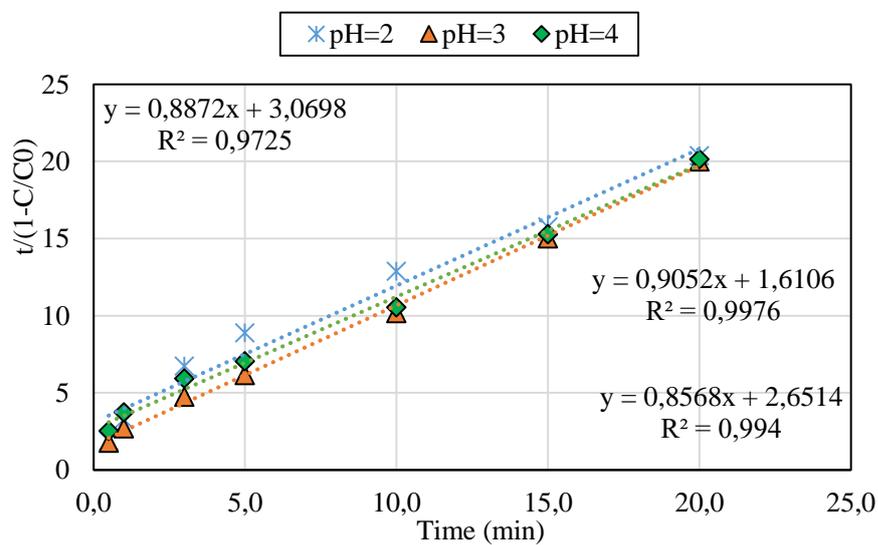
Figure A. 16. BMG kinetic analysis for CLZ degradation by Photo-Fenton at different pH
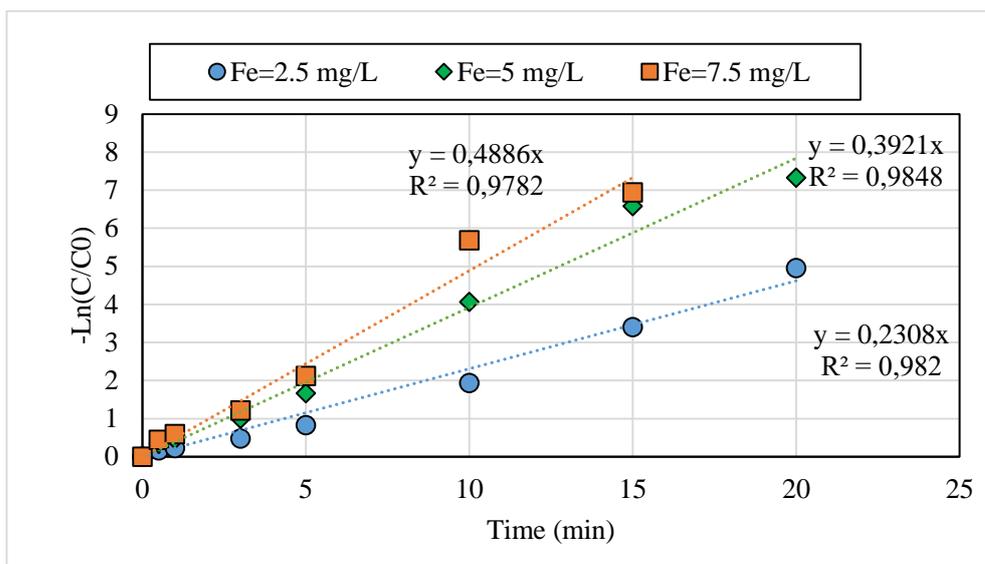
Figure A. 17. Pseudo First Order kinetic analysis for CLZ degradation by Photo-Fenton processes at different Fe^{2+} concentration
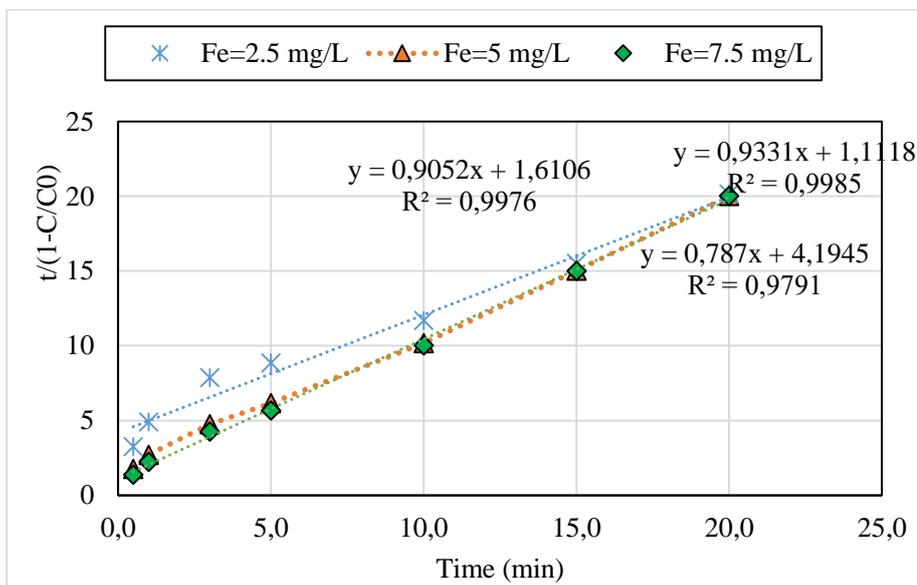
Figure A. 18. BMG kinetic analysis for CLZ degradation by Photo-Fenton at different Fe^{2+} concentration
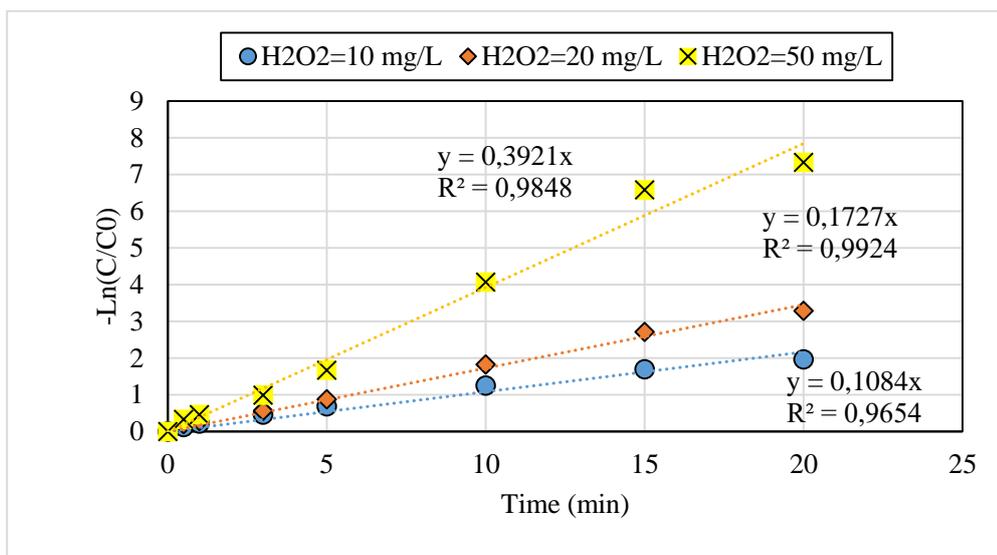
Figure A. 19. Pseudo First Order kinetic analysis for CLZ degradation by Photo-Fenton processes at different H_2O_2 concentration
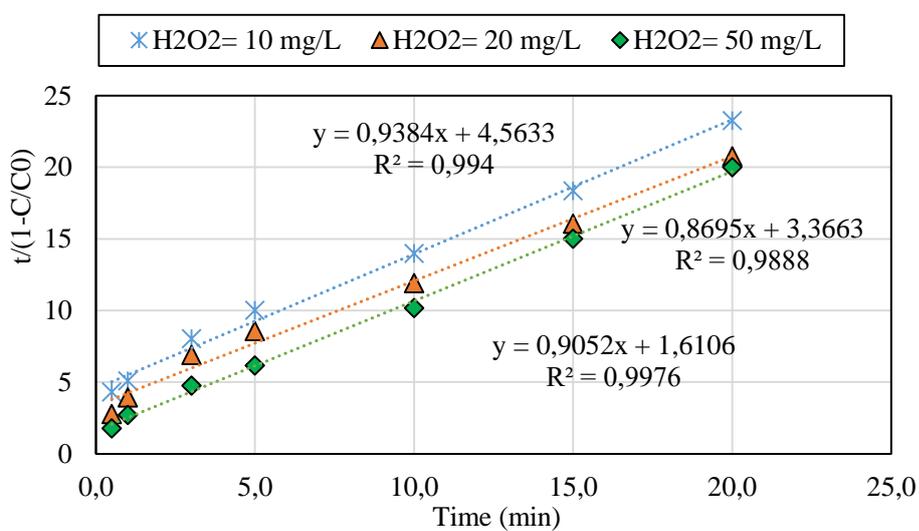
Figure A. 20. BMG kinetic analysis for CLZ degradation by Photo-Fenton at different H_2O_2 concentration
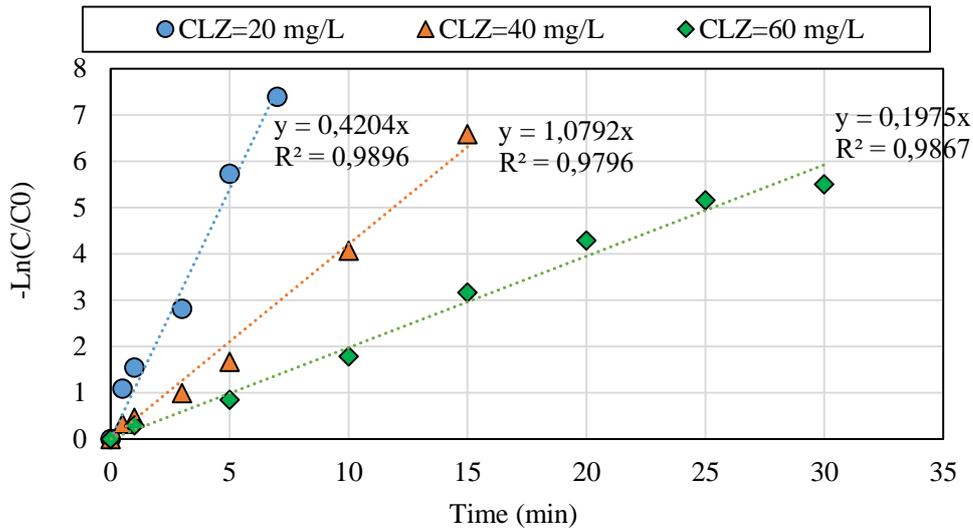
Figure A. 21. Pseudo First Order kinetic analysis for CLZ degradation by Photo-Fenton processes at different initial CLZ concentration
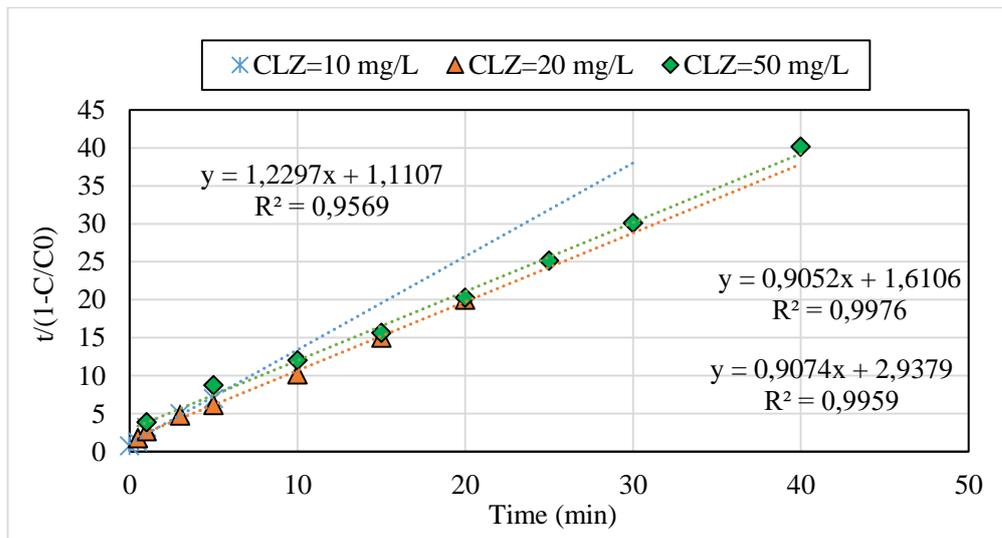
Figure A. 22. BMG kinetic analysis for CLZ degradation at different initial CLZ concentration
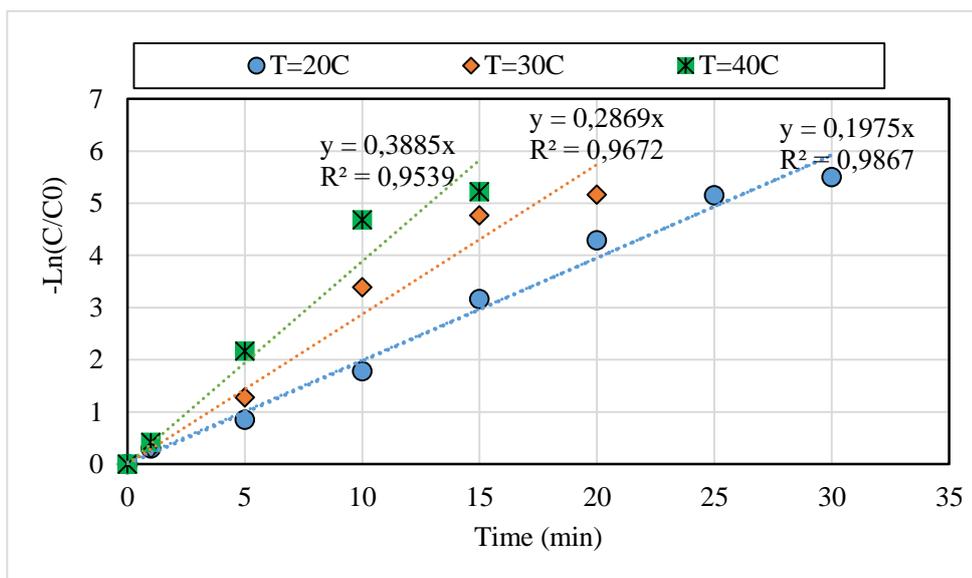
Figure A. 23. Pseudo First Order kinetic analysis for CLZ degradation by Photo-Fenton processes at different Temperature
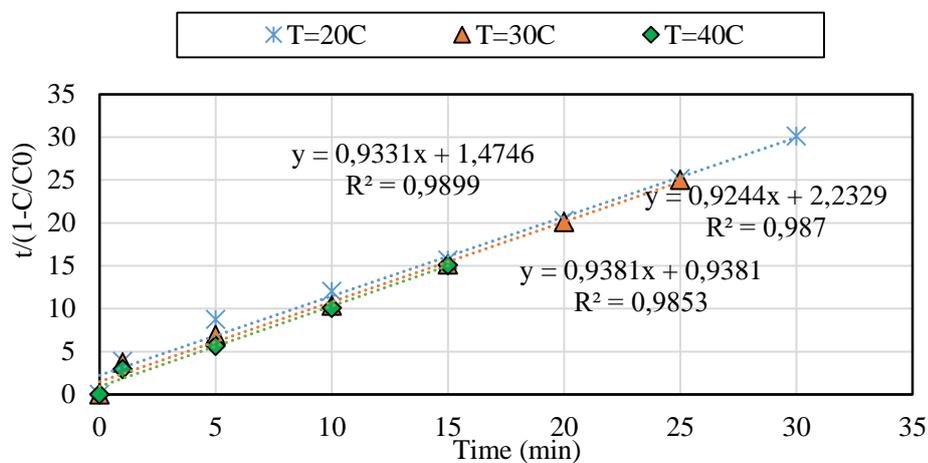
Figure A. 24. BMG kinetic analysis for CLZ degradation by Photo-Fenton at different Temperature

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B. CHROMATOGRAPHIC ANALYSIS

\<Calibration Curve\>

ID#   : 1
Name   : Chlorodizan
Quantitative Method   : External Standard
Function   : f(x)=99458.6*x+915.888
                             Rr1=0.9999982   Rr2=0.9999964
                             MeanRF:100624 RFSD:2734.24   RFRSD:2.7173
FitType   : Linear
ZeroThrough   : Not Through
WeightedRegression   : None
Detector Name   : PDA
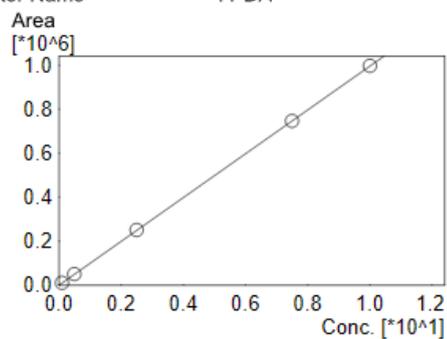
#	Conc (Ratio)	Area	Area
1	0.100	10239.3	10239
		10339.9	10340
2	0.500	51498.4	51498
		49318.7	49319
3	2.500	256586.9	256587
		245157.9	245158
4	7.500	725802.7	725803
		766379.3	766379
5	10.000	1024769.0	1024769
		966762.6	966763

Figure B. 1. Calibration curve in HPLC

Chromatogram
02102017_II1 C:\Users\Hp\Desktop\work\Pestisit\Bıke ULU\02102017_II1.lcd

1   PDA Multi 1 / 225nm 4nm
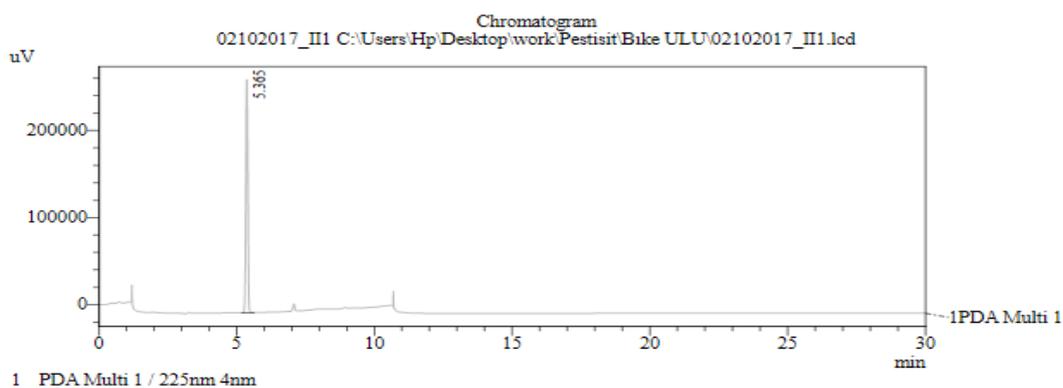
Quantitative Results

PDA ID#	Name	Ret. Time	Conc.	Units
1	chl	5.365	9.910	mg/L

Figure B. 2. An example analysis for CLZ in HPLC

LC/MS/MS

The Liquid Chromatography-Mass Spectrometry System (LC-MS / MS) is a system created by combining chromatography and spectrometry systems. The system consists of liquid chromatography and triple quadrupole. It has two ionization sources. The molecules undergo ionization (gas) to mass spectrometry with the ionization source. The first mass spectrometry is determined by the ratio m / z (mass / charge) of the main ions formed. The resulting ion is broken up with a collision gas (Nitrogen) in the collision cell and the ions formed with breakdown are separated by m / z ratios in the second mass spectrometry. A high sensitivity with fragmentation ions data and strictly qualitative and quantitative analysis can be made.

The LC/MS / MS system is used in the determination of multiple analyses and sensitive quantification of trace amounts of analyses. It is also possible to be used in food analyses such as fruit, milk, meat and so on. Additionally, pesticides and metabolites, hormones, aflatoxin-mycotoxin analyses can be done by LC/MS/MS (URL4).