REMOVAL OF PESTICIDES FROM AQUEOUS SOLUTION BY ELECTROCHEMICAL METHODS

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PhD Dissertation

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ABSTRACT

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The removal efficiency of three pesticides: Bromuconazole, bentazone, and abamectin from model solution using electrocoagulation, electrochemical-Fenton and electro-oxidation processes have been investigated. The effects of operational parameters such as current density, support electrolyte concentration, electrode types and H_2O_2 concentration on the pesticide and COD removal efficiency have been studied. The initial concentration of pesticide was 300, 300, 4.5 mg/L for bromuconazole, bentazone and abamectin respectively. The result showed that the highest removal efficiency of bromuconazole was 92.22% recorded at 20 mA/cm^2 by using electro-oxidation process with energy consumption of 40.91 kWh/m^3. The removal of bromuconazole exhibited a pseudo-second-order reaction with rate constant 0.0009 mg^{-1}Lmin^{-1}. The maximum removal efficiency of bentazone was 91.18% indicated at 20 mA/cm^2 by using electro-oxidation process with energy consumption of 57.63 kWh/m^3. The removal of bentazone exhibited a pseudo-first order reaction with rate constant 0.0462 min^{-1}. The highest removal efficiency of Abamectin was 90.69 % indicated at 20 mA/cm^2 by using electro-oxidation process with energy consumption of 65.37 kWh/m^3. The removal of Abamectin exhibited a pseudo-first order reaction with rate constant 0.0379 min^{-1}. degradation of pesticides with electrochemical methods led to the formation of intermediate species Some of these species were detected by Ion chromatography (IC). The mineralization of pesticides and reduction of their toxicity were also investigated with the Microtox test.

Keywords: Pesticides model wastewater, Electrochemical methods, Intermediate compound, Removal efficiency.

ÖZET

SULU ÇÖZELTİDE PESTİSİTLERİN ELEKTROKİMYASAL YÖNTEMLERLE GİDERİLMESİ

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Danışman: Prof. Dr. Yusuf YAVUZ

Elektrokoagülasyon, elektrokimyasal-Fenton ve elektro-oksidasyon prosesleri kullanarak üç pestisitin (bromokonazl, bentazon ve abamektin) model atık suda giderim verimliliği araştırılmıştır, Akım yoğunluğu, destek elektrolit derişimi, elektrot tipleri ve H_2O_2 derişimi gibi operasyonel parametrelerin pestisit ve KOI giderimi üzerindeki etkileri incelenmiştir. Pestisitin başlangıçtaki konsantrasyonu sırasıyla bromokonazol, bentazone ve abamectin için 300, 300, 4.5 mg/L olmuştur. Sonuç olarak, bromokonazolün en yüksek KOI giderim verimliliği elektro-oksidasyon yönetmi kullanılarak, 20 mA/cm^2'de, 40.91 kWh/m^3 enerji tüketimi ile % 92.22 olarak kaydedilmiştir. Bromokonazolün giderimi, 0.0009 mg^{-1} L.dak^{-1} hız sabiti ile ikinci dereceden tepkime sergilemiştir. Bentazonun maksimum KOI giderim verimliliği, elektro-oksidasyon işlemi kullanılarak 20 mA/cm^2'de, 57.63 kWh/m^3 enerji tüketimi ile % 91.18 olarak belirlenmiştir. Bentazonun giderilmesi, 0.0462 dak^{-1} hız sabitiyle birinci dereceden tepkime sergilemiştir. Abamektin en yüksek giderim verimliliği, elektro-oksidasyon işlemi kullanılarak 20 mA/cm^2'de, 65.37 kWh /m^3 enerji tüketimi ile % 90.69 olarak belirtilmiştir. Abamektin uzaklaştırılması, 0.0379 dak^{-1} hız sabitiyle birinci dereceden tepkime sergilemiştir. Pestisitlerin elektrokimyasal yöntemlerle bozunması, ara türlerin oluşumuna yol açmıştır. Bu türlerin bazıları İyon kromatografisi ile tespit edilmiştir. Pestisitlerin mineralizasyonu ve toksisitelerinin azaltılması da Microtox testi ile incelenmiştir.

Anahtar kelimeler: Atıksu pestisist modeli, Elektrokimyasal metodlar, Ara bileşenlerin, giderim verimliliği.

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MOHAMMED AZEEZ OTHMAN
MAY, 2018

23/05/2018

STATEMENT OF COMPLIANCE WITH ETHICAL PRINCIPLES AND RULES

I hereby truthfully declare that this thesis is an original work prepared by me; that I have behaved in accordance with the scientific ethical principles and rules throughout the stages of preparation, data collection, analysis, and presentation of my work; that I have cited the sources of all the data and information that could be obtained within the scope of this study, and included these sources in the references section; and that this study has been scanned for plagiarism with "scientific plagiarism detection program" used by Anadolu University, and that "it does not have any plagiarism" whatsoever. I also declare that, if a case contrary to my declaration is detected in my work at any time, I hereby express my consent to all the ethical and legal consequences that are involved.

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SYMBOLS AND ABBREVIATIONS

COD	: Chemical Oxygen Demand
BROMU	: Bromuconazole
BEN	: Bentazone
ABA	: Abamectin
ECP	: Electrocoagulation process
EFP	: Electrochemical-Fenton process
EOP	: Electro-oxidation
EPA	: United States Environmental protection agency
UWWT	: Urban waste water treatment plant
USEPA	: United States Environmental Protection Agency
CEC	: Cumulative energy consumption
kWh	: kilo watt hour
mM	: Milli Molar
Krş	: Kuruş
BDD	: Boron Doped diamond
FAS	: Ferrous Ammonium Sulfate
RTI	: Relative Toxicity Index
IC	: Ion Chromatograph

1. INTRODUCTION

The water resources like the rest of the environmental resources on the earth planet are under stress from ever-growing human activities in their desire for fortune. With the development of analytical capabilities, traces of such activities appear intensively in the form of harmful organic pollutants persistent to natural degradation.

During the last years, due to the massive application of pesticides in agriculture, the quantities of these chemical compounds in aqueous media have significantly elevated. Thus, insecticides, herbicides, and Fungicides represent principle contaminants of the aquatic environment, and their existence is of concern because of their potential toxicity to animals as well as to humans.

The main concerned issue is the resistance of such chemical compounds to the available wastewater treatment strategies, which culminates in a lower performance of pollutant removal from water streams. In the modern era, wherein water resources are constantly diminishing simultaneously both population and consumption are increasing, numerous researcher around the world have focused on new options and technologies for the treatment of persistent poisonous organic compounds in the environment. Numerous processes purpose the degradation of organic pollutants that presence in the environment or at least their oxidation to less toxic compounds. The selection of methodology should be based on the factors related particularly to cost and performance, so each method offers advantages as well as limitations.

Electrochemical processes are environmental-pleasant technologies which possess advantages over other technics of smooth implementation and high performance. Among electrochemical technologies, one can cite Electrocoagulation, Electrochemical-Fenton oxidation H_2O_2/Fe^{2+} and Electro-Oxidation process (EOP). Because the oxidation of refractory compounds happens at very high overpotential, the select of the anode material represents the key point.

Within the scope of this study, different electrochemical treatment methods have been chosen for the removal of different pesticides from prepared model solution (Bromuconazole, Bentazone, and Abamectin). These are electro-oxidation process, electrochemical-Fenton process, and electrocoagulation methods process.

In the electrocoagulation working, iron, aluminum, and iron-aluminum (hybrid) electrodes in the form of the parallel plate had been used.

Electrochemical-Fenton is one of the most efficient and promising method for wastewater treatment. During EFP treatment, hydrogen peroxide is catalyzed by ferrous ions to generate hydrogen peroxide. In the study, the different hydrogen peroxide concentrations were added initially.

It is well known that electrochemical-oxidation process using a Boron-Doped Diamond (BDD) electrode represents a promising method for removal of persistent organics. surely, the high oxidation ability of the BDD is due to the electrogeneration of hydroxyl radical (• OH) from the water discharge.

The applicability of electrochemical oxidation of pesticides model water was studied by using parallel plate electrodes of BDD.

In the study, chemical oxygen demand (COD) of the model water were determined. The intermediate compounds of best-obtained degradation results were investigated. Based on the determined reaction, removal efficiency of the pesticides and energy cost of the optimum treatment methods have been evaluated.

The effect of operational parameters such as electrolyte concentration, current density, hydrogen peroxide concentration and electrodes types in pesticide removal efficiency were investigated in a laboratory scale operation.

Keeping in view of thesis subject, this study was also designed to determine toxicities of pesticides at a different stage of treatment.

2. ENVIRONMENTAL POLLUTION AND PESTICIDES

2.1. Water Pollution

Water pollution is a horrible issue, strong enough to drive the world on a road of demolition. Water is a good solvent; most pollutants can easily dissolve in the water and contaminate it. The basic impact of water pollution is immediately suffered by the different organisms that survive in water. On a human level, many humans die every day because of the consumption of infected and polluted water. Water comprises 70% of the Earth’s surface making it one of the most valuable natural resources on our plant. Of this, about 97.5% is salt water and only about 2.5% is fresh water [1]. Regrettably, even this little proportion of fresh water is under extremely large stress because of the rapid increase in population, urbanization and non-sustainable consumption of water in agriculture and industry. World population is exponentially increasing, at the same time fresh water is declining. Many countries suffer from dangerous threats of water deficiency in the last decades, and developing countries struggle with pollution problems due to the absence of suitable management of water [2].

Water pollution is generally induced by humans. As technology, agricultural, and industrial activities increased, water was exposed to many of the problems that affect it due to pollution factors. Industrial, domestic and agricultural wastes are the major pollutants that affect aquatic habitats.

The two main source of water pollution can be noted as a point source and nonpoint sources. The point source indicated the pollutants that release water from belonging to a special identical source and the as example of this may be pollutant released from industries into the water. The nonpoint source refers to the integration of pollutants from a considerable region rather than from identifiable sources such as most of the construction sites.

2.1.1. The problematic of water pollution

Many of the problems that environment is facing in the recent century are concerned about water quantity and water quality issues. It is obvious that the prime public worry in different parts of the world has become chemical pollution of natural water. Chemical pollutants divided into two categories; micropollutants, which relatively occur at the level of a milligram per liter and represent by nutrients such as nitrogen [3] and phosphorous species [4] in addition to natural organic component [5]. Most of the micropollutants exhibit their toxic effects even at a very low concentration, especially if present as mixtures. Within the inorganic pollutants, the challenge in difficulty to assess environmental risk due to their contrasting action under various redox conditions. Inorganic elements do not undergo break down like most of the organic pollutants, the main processes which determine their bioavailability include complexation, oxidation/reduction, precipitation/dissolution reactions, and adsorption. Most of the inorganic elements show different solubility rate in the oxygen availability and under reducing conditions [6]. When dealing with organic pollutants, the major challenge is to overcome with a large number and a great variety of chemicals covering a wide range of physical-chemical properties and reactivities [7]. The sources and impacts of these common classical pollutants are reasonably well understood but designing sustainable treatment technologies for them remains a scientific challenge [8].

2.2. Pesticides Pollution

The globalization problem is increasing competition on the global market for industry and food production. One disadvantage is the rising use of xenobiotic chemicals (compounds which are synthetic products) in the production of food and industry with the dangers of its introduction into the natural environment and/or human. Generally, about 14 million chemicals present, and at least 10,000 of these chemicals are synthesized and manufactured industrially produced. Most of these chemicals are not differentiated with regard to their ecotoxicity or characterized in the term of prominence in the natural environment because of little analytical methods or temporally brief presenting (such as few agricultural pesticides). Pesticides represent a broad range of chemical compounds with different chemical formulations. Increase in the demand for agro-products to control disease and increase productivity has given rise to increases in application and consumption rate of it [9]. Pesticides represent as one of the persistent organic pollutants that took a concern due to their occurrence in different ecosystems. In nature, the residues of pesticide are undergone chemical, physical and biochemical break down process, but due to its stability and water solubility, the pesticide residues preserve in the environment. furthermore, the environmental conditions such as soil properties may also participate in their persistence [10]. The widespread pesticides usage for many years influenced people and the environment adversely due to their persistence and bioaccumulation. Pesticides residues in food as well as in the environment have an effect on the genetic polymorphism, enhance the disease initiation in organisms [11].

2.3. Environmental Fate of Pesticides

The chemo-dynamics of pesticides refers to the understanding the pesticides locomotion, transformation and behavior in addition to their fate in different environment ecology. Increase in need for pesticides uses in different area and subsequent resistance evolution by insects resulted in an increased dosage used for controlling of pesticides which led to the persistence of such pesticides and its metabolite derivatives in the environments due to lack of insufficient degradation. The result of such persistence is pollution of water resources, soil quality change, bioaccumulation, a decrease of biodiversity [12,13]. Residues of different organochlorine pesticides have been detected in sediments and soil [14], seawater and groundwater and other water sources [15].

Several factors direct the fate of pesticides in environmental such as the chemical behavior of pesticides in the environments, pesticides solubility in water, adsorption to the soil, input and removal rate, chemical, physical and microbial degradation rate and on the physical and chemical factors of the environment. The potential risk caused by the pesticides introduction to the environment depends on some factors: pesticides toxic properties, formulation, the amount used, application method and time, and treatment and persistence time in nature. Extravagant and recurrent pesticides application had led to contamination of water, soil, air and food [16,17].

2.4. Classification of Pesticides

Pesticides may be classified in various criteria based on physical properties, against which they are directed, the aim of application, or chemical structure [18]. Insecticides, herbicides, defoliants, desiccants, fungicides, nematicides, avicides, and rodenticides are some of the many kinds of pesticides depending on whether they are designed to kill plants, insects, fungi or rodents respectively. Table 2.1 represent the major classes of pesticides and target pest group [19]. Classification according to chemical nature, most synthetic chemical pesticides fall into the four categories: chlorinated organics, organophosphates, carbamates, and pyrethroids [20].

2.4.1. Non-chemical classification

Table 2.1. *Main classes of pesticides and their target* [20].

Term	Target	Term	Target
Algaecide	Algae	Avicide	Birds
Herbicides	Weeds	Attractant	Attracts insects or birds
Fungicide	Fungi	Miticide	Mites
Nematicide	Nematode	Defoliant	Crop foliage
Piscicide	Fish	Desiccant	Crop plant
Bactericide	Bacteria	Rodenticide	Rodent
Acaricide	Mites, ticks	Molluscicide	Snails, slugs

2.4.2. Chemical classification

2.4.2.1. Chlorinated pesticides

Chlorinated pesticides were manufactured and widely used in the United States throughout the mid part of the 20th century. The most known pesticide in this family is Dichlorodiphenyltrichloroethane (DDT). DDT is a persistent organic pollutant that was ultimately prevented in the United States since 1972. It is considered a probable human carcinogen by the USEPA and can also affect reproductive systems. It is a probable human carcinogen and also affects the endocrine, digestive, and nervous systems [21]. Many organochlorines are also suspected endocrine disruptors. Because of their long half lifetime, over numerous years, it's been forbidden to apply aldrin, dieldrin, and heptachlor in many countries. Organochlorine pesticides lead to a neurotoxic impact in both insect and people. The pesticides toxicity on the human is well notarized, however little data present concerning to their effect on human semen activity. In last years, articles related to a conspicuous decrease in male sperm activity has led to an arguably discussion that environmental pollutants as total and chlorinated hydrocarbons and heavy metals in special may reduce male fertility [22].

2.4.2.2. Organophosphorus pesticides

Organophosphorus pesticides (OPs) represent the type of pesticides that are widely used in agricultural fields because of their relatively high-performance to control different types of pests. These compounds contain a phosphorus atom bound to organic substituents, which may be alkoxy or alkyl groups. Because of their widespread applications, their persistence in the environment leads to serious health and environmental problems [23]. The OPs are extremely toxic as they are potent inhibitors of cholinesterase, an enzyme crucial for the functioning of central and peripheral nervous system [24].

2.4.2.3. Carbamate pesticides

These compounds which mostly insecticides are derived from a carbamic acid and act on insects in a similar way as organophosphate insecticide. Most carbamates are mild cholinesterase inhibitors that cause neurotoxicity in both humans and insects. The persistence of carbamate in environment is usually low, their degradation is usually accelerated by an increasing the alkalinity or the temperature. The digestion of the carbamates in the human body is very rash and will not be stored in the body.

2.4.2.4. Pyrethroid pesticides

The use of pyrethroids pesticides is rising in agriculture and for pest control. Pyrethroids are groups of synthetic organic insecticides which derived from pyrethrin. They have been started to use worldwide since the 1980s due to their low toxicity and high level of effectiveness compared to other types of insecticides, such as organophosphorus and carbamic ester compounds [25]. After introducing to the natural environment, pyrethroids pesticide change among the three phases of solid, liquid, and gas and then introduce to the organisms through food webs.

2.5. Toxicity Due to Pesticides

Intense pesticides application had led to several toxicological impacts on living organisms by direct or indirect exposure to pesticides and its residues. The pesticides negative impact is due to their high toxicity, stability. Among the used pesticides, organochlorine pesticides are more problematic and of serious environmental worry. Toxicity can be defined as the power of a pesticide to make damage or disease to the living organism and is expressed in terms of LD_{50} and LC_{50} values of the pesticides. Based on it, pesticides have been classified as highly toxic, moderately toxic, and slightly nontoxic which are labeled with special symbols. Even if pesticides are labeled slightly toxic or nontoxic, it can be dangerous to humans, other and environment if pesticides are misapplied. World Health Organization classified the pesticides according to hazardous, based on the active ingredients of pesticides to extremely hazardous class (1A), highly hazardous class (1B), and moderately hazardous class (2) and slightly hazardous class 3 active ingredients [26].

2.6. Toxicological Impact of Pesticides

The advantage of pesticides is usually valued in economic terms as the food production is increasing, while risks are measured in terms of people and environmental health. Most active substances of pesticide are toxic. They have been prepared to control living organisms. Therefore, use of pesticides involves expected risks to both peoples who apply them and to those peoples who consume treated products [27]. They can cause damage to health as well as to the surrounding environment, the health impacts include persistent and acute injury to the nervous system, damage in the reproductive organs activity, lung deterioration, and malfunction of the endocrine and immune systems, congenital defects at birth, and cancer [28]. In order to understand the degree of risk associated with uses of pesticides, we have to get knowledge on the determination the hazardous, what factors control the ability for risk [29]. To recognize and decide the intense toxicity of a substance, scientists use a measure termed LD_{50}, that is the lethal dose needed to kill 50 percent of tested animals in vitro (measured as milligrams of poison per kilogram of body weight) [28]

2.7. Direct Impact on Human

Pesticide exposure to the human body occurs directly from agricultural, vocational, and domestic utilization, also it can be transferred indirectly within nutrition. The main exposure pathway of pesticides to the human is within the food webs, air, water, soil, fauna, and flora [30]. Pesticides are spread in the human body by the aid of bloodstream and throughout the skin, urine, and exhaled air [31]. There are four main routes through which pesticides enter the human body: skin, orally, eye, and respiratory system. The pesticides toxicity can vary depending on the place of exposure such as skin, mouth, or respiratory (inhalation). The danger degree of pesticide infection usually directly related to the concentration (dosage) and exposure period in addition to the toxicity of the used chemical [32]. Increasing the incidence of cancer, chronic kidney diseases, immune system suppression, infertility among males and females, disorders of endocrine system, neurological behavioral and neurological disorders, usually among children are related to chronic poisoning by pesticide [33]. Human health risk varies with the scope of exposure. Moderate human health hazards that occur from the pesticides misapplication include headaches, skin rashes, flu, blurred vision but rare, severe human health hazards include blindness paralysis, and even death [34].

2.8. Characteristics of Selected Pesticides

2.8.1. Bromuconazole (BROMU)

2.8.1.1. Definition and uses

Bromuconazole fungicide belongs to the triazole group. it used as a wide-spectrum antifungal agent, that have curative and preventative action, effective against diseases caused by a different fungus such as basidiomycetes, Deuteromycetes, and ascomycetes [35]. Bromuconazole ($C_{13}H_{12}BrC_{12}N_3O$) or 1-[[4-bromo-2-(2, 4 –dichlorophenyl) tetrahydro-2-furanyl] methyl]-1H-1, 2,4-=triazole. CAS-RN/116255-48-2 is a heterocyclic-aliphatic compound [36]. It is Molecular mass is 377.06 g/mole. It has slight alcoholic odor with the pH around the 5. The solubility of pesticide in the water at 20oC is 48 mg/l.

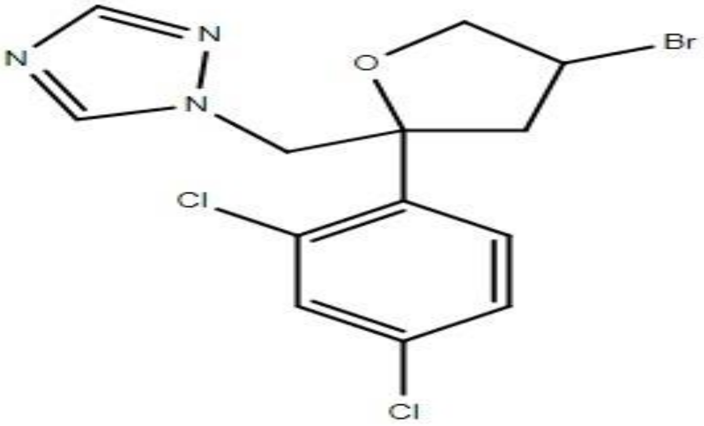

Figure 2.1. *Chemical structure of bromuconazole*

2.8.1.2. Toxicity of Bromuconazole

Despite the widespread use of pesticide in food products such as wheat, barley, and the post-harvest treatment of some fruits, a very little data present about the metabolic fate of this pesticide. Bromuconazole has been classified according to WHO as a class II toxin (moderately poisons). Toxicity by 50% (LD_{50}) for rats and mice, respectively, 365 mg/kg and 1151 mg/kg. bromuconazole also has been seen to be poisonous to birds like mallard and bobwhite at oral LD_{50}>2150 mg/Kg b.w. and to rainbow trout at LC_{50} 1.7mg/L within 94 hours. But it is not poisonous to earthworm and bee. Towards fish such as Bluegill and trout, the toxicity of bromuconazole (LC_{50}) is 3.1 mg/L and 1.7 mg/L, respectively [37]. Bromuconazole not accumulates in tissues and organs and directly metabolized in animals. It is movement is slow in soil but It highly persistent with a half-life of 123-600 days [38].

2.8.2. Bentazone (BEN)

2.8.2.1. Definition and uses

Bentazon (3-(1-methyl ethyl)-1H- 2,1,3-benzothiadiazide-4(3H)-one-2,2-dioxide) is one of the most widely applied selective herbicides in agriculture [39]. Bentazon is post-emergence herbicide belonging to the chemical group of benzothiadiazides applied for the selective control of different types of vegetable and fruit. Its selectivity is based on the ability of crop plants to rapidly metabolize bentazone to 6-OH- and 8-OH- bentazone interacting these with the synthesized sugars, and also acts by interfering with photosynthesis [40].

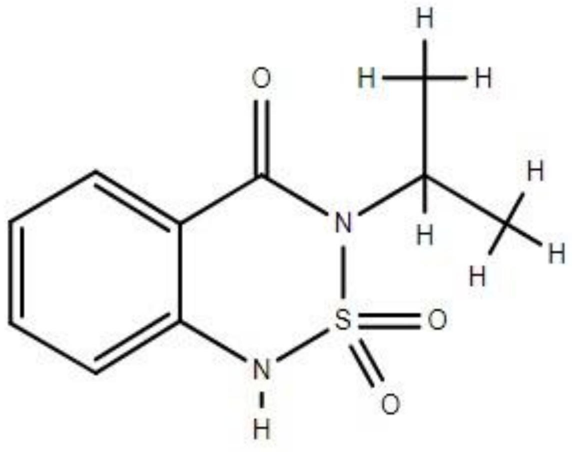

Figure 2.2. *Chemical structure of bentazone*

2.8.2.2. Toxicity of bentazone

Bentazone does not attach to soil particles, it is possibly moving directly through the soil to groundwater, making ecological problems for different resources, such as drinking water [41,42]. World Health Organization (WHO) identified bentazone as moderately toxic (class II) and show 30 µg /L as the maximum acceptable concentration of pesticide in drinking water [43]. Toxicological research shows that the bentazone is poison to some fish and bird species and moderately poison to mammals if taken orally or by dermal exposure [44]. Bentazone exposure shows chronic and acute toxicity in humans, however, deaths have been recorded after a swallow of high doses [45,46]. Bentazone is directly degraded and metabolized by pesticide-resistant plants and also by animals, and formed metabolites, 6-hydroxybentazone, and 8-hydroxybentazone are not as toxic as original compound [47]. Taking into account high water solubility and low soil adsorption characteristics, the major problem may arise in leaching of this chemical under conditions of extreme rainfall [47–48].

2.8.3. Abamectin (ABA)

2.8.3.1. Definition and uses

Abamectin is a white to yellowish crystalline powder. It poses a slight fire hazard if uncovered to heat or flame, a fire and explosion risk in the existence of strong oxidizers [49-50]. Thermal decomposition of the pesticide usually releases hazardous poisonous oxides of carbon. Employee that handling abamectin pesticide must wear goggles in order to prevent contact with the eyes and protective special clothes to deny prolonged skin contact.

Abamectin relates to the avermectins family which are macrocyclic lactones and worldwide used as an antiparasitic agent. It is a mixture of two homologs containing about 80% avermectin B1a and about 20% avermectin B1b [51].

Avermectin B1a (10E,14E,16E,22Z)-(1R,4S,5'S,6S,6'R,8R,12S,13S,20R,21R,24S)-6'-[(S)-sec-butyl]-21,24-dihydroxy-5',11,13,22-tetramethyl-2-oxo-3,7,19trioxatetracyclo [15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene-6-spiro-2'-(5',6'dihydro-2'H-pyran)-12-yl 2,6-dideoxy-4-O-(2,6-dideoxy-3-O-methyl-α-L-arabino-hexopyranosyl)-3-O-methyl-α-L-arabino-hexopyranoside

Avermectin B1b (10E,14E,16E,22Z)-(1R,4S,5'S,6S,6'R,8R,12S,13S,20R,21R,24S)-21,24-dihydroxy-6'-isopropyl-5',11,13,22-tetramethyl-2-oxo-3,7,19-trioxatetracyclo [15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene-6-spiro-2'-(5',6'-dihydro-2'H-pyran)-12-yl2,6-dideoxy-4-O-(2,6-dideoxy-3-O-methyl-α-L-arabino-hexopyranosyl)-3-O- methyl-α-L-arabino-hexopyranoside.

These two components, B1a and B1b, have same biological and toxicological properties [52,53]. Abamectin acts by way of stimulating the discharge of α-aminobutyric acid thus causing paralysis [54]. Abamectin is used as Acaricides and insecticide; to control sucking bugs, soil insects, termites, and some chewing insects [55]. The pesticide highly persistence in environment with hydrolysis half-life of 25 to 48 days. the pesticide tends to the alkaline with the pH around the 8.

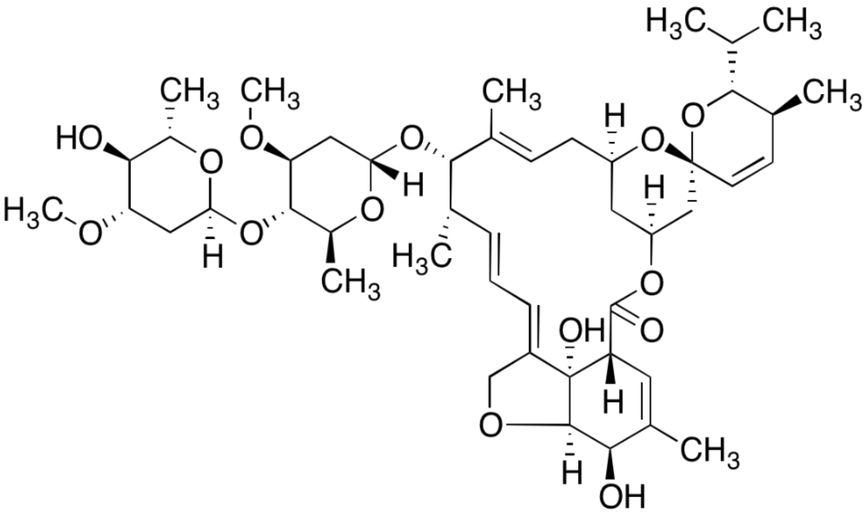

Figure 2.3. *Chemical structure of Abamectin*

2.8.3.2. Toxicity of Abamectin

The application of any chemical as the pesticide led to the exposure of the environment to such chemical. The scope of such exposure relies on the path that follow to apply the chemical, frequency pattern, and the rate, in addition to its persistence in the environment. The persistence of chemicals is specified by its physical and chemical properties, its half-life in water and soil, its photolytic stability, and its ability to bind to soil. These represent the same factors that affect the chemical's bioavailability to organisms. The studies on the environmental toxicity of a compound describe not only the ways that a compound is removed from the environment but also the extent to which it is available to biological organisms. Abamectin is strongly toxic to insects and also seen to be poisonous to mammals. Also its higly toxic to the aquatic invertebrates and fish. Concentrate formulations may cause low to moderate eye irritation and moderate irritation in the skin. Some poisoning symptoms are seen in laboratory animals which include dilation of pupil, convulsions, vomiting, and coma. Abamectin interfering with the insect's nervous system. High doses have to affect mammals, causing some symptoms in the nervous system such as incoordination, excitation, lethargy, tremors, and pupil dilation. Very high doses have brought about dying from breathing failure. Abamectin isn't always effectively absorbed by the skin. Abamectin does not cause allergic skin reactions. The oral LD_{50} for abamectin in mice ranges from 14 mg/kg to greater than 80 mg/kg, and in rats is 10 mg/kg [56].

2.9. Previous Studies on Degradation of Used Pesticides by Different Methods

There are few studies on the treatment of these pesticides. A number of different techniques and methods have been used to remove the present pesticides and each method showed different efficiencies for removal.

2.9.1. Bromuconazole

Avery little scientific studies are found related to the treatment or removal of bromuconazole from aqueous solution.

Crini et al. [57] investigated the removal of bromuconazole from synthetic solutions of five triazole fungicides on activated carbons and cyclodextrin-based adsorbents. They showed that both adsorbents were efficient for the removal of fungicides. The activated carbons showed the highest levels of fungicide removal, but adsorption onto it was non-selective.

2.9.2. Bentazone

Some studies review the technical applicability of different physico–chemical treatments for the removal of bentazone from aqueous solution.

Begum, S. [58] investigated the Field validation of bentazone phytoremediation. He planted trees of (*Salix nigra*) at a density of 2000 trees/hectare in a shallow groundwater plume that contains low levels of bentazone. The extraction and analyzing of roots and stems shows that the 15% of all the plant samples analyzed at the method detection limit of 0.27 mg/kg contained residues of the pesticide. within the range of 0.7mg/kg and 0.32mg/kg, the average bentazone concentration was 0.48mg/kg.

Abdessalem et al. [59] examined the treatment of a mixture containing bentazone by photo-Fenton and electro-Fenton processes. They showed that more than 90% of the total organic compound has been removed within two hours of photo-Fenton treatment at an initial pesticide concentration of 0.125 mM, initial hydrogen peroxide concentration of 100 mM and initial concentration of $Fe^{+3}$of 1mM, whereas the electro-Fenton process needed 8 hours for degradation.

Davezza et al. [60] investigated the photocatalytic degradation of bentazone in soil washing wastes containing alkyl polyoxymethylene surfactants. They demonstrated that the aqueous surfactant solutions had effective action on bentazone removal from the polluted soil. All bentazone removed from waste within one-hour irradiation when working via 1500 mg L^{-1} of suspended TiO_2, while no traces of aromatic residues has been found after two hours.

Mir et al. [61] investigated the photocatalytic degradation of Bentazone in TiO aqueous suspension under different condition. They suggested that TiO2 increase the efficiency of UV/H_2O_2 process for the efficient mineralization of bentazone. They found that Titanium dioxide Degussa P25 was more efficient when compared with other commercially available such as PC500 and Hombikat UV100.

2.9.3. Abamectin

Some of the treatment studies were conducted in order to remove the abamectin. From these studies, Matos et al. [62] validated that the photo-Fenton process been influential in degradation of water and effluents polluted with abamectin, the maximum removal rate of 70% of the pesticides occur at 60 minutes of UV irradiation and 60% mineralization was observed after 180 minutes of reaction.

Jodeh et al. [63] investigated the abamectin adsorption and kinetics in greenhouse soil in Palestine. Results indicate that the highest removal percentage of abamectin has been 7.5 % when the dosage of adsorbent was 3gram. the abamectin removal percentage at pH 12 reach 14.4% while the lower removal percentage recorded at pH7 which recorded 9.1%. Also, temperature effect on soil adsorption was examined within range of 15-47 ^{o}C.

Ghalwa et al. [64] exanimated the removal ability of abamectin from aqueous model solution using the electrocoagulation process (stainless steel (SS) and iron (Fe) electrodes) and studied the effect of some operational parameter such as initial abamectin concentration, pH, current density, support electrolyte concentration and type of electrode, They showed that abamectin and COD removals were 94% and 76.9% by using SS at current density 87.5 mA/cm^2 and were 64.5% and 50%, by using Fe electrodes at 50 mA/cm^2. The initial pesticide concentration was 150 mg/L.

Errami et al. [51] exanimated the anodic oxidation of abamectin pesticide over BDD anodes under the various concentrations of NaCl. The experimental results showed that within optimal experimental conditions of current density 80 mA/ cm^2, 88% of COD has been removed in 2.5 h in the presence of 2g/L of NaCl as supporting electrolyte.

3. WASTEWATER TREATMENT PROCESSES

Toxic compounds are usually persistent chemicals with a high bioaccumulation potential. Many processes aim at the break down of the pollutants in the wastewater or at least their oxidation to less toxic compounds. The selection of process involves factors related mainly to degradation efficiency and cost, so each method has advantages as well as limitations

3.1. Physical Treatment

There are several different methods of water treatment. Physical methods achieve removal of pollutant by use of naturally occurring forces, such as gravity, electrical attraction. Usually, the mechanisms included in physical treatment do not led to the changes in chemical structure of the target pollutant. But only the physical state is changed.

3.1.1. Sedimentation

Sedimentation is usually used to remove the suspended solids from wastewater. Depending on the solid nature found in the suspension sedimentation may be separate in the three main classifications, there are linty, discrete settling and zone settling. In the discrete, the particle keeps its character and does not change in shape, size or density during the process. In linty settling the particles massed within the settling period which lead to change in size and settling rate. Zone settling flocculent suspensions with more initial concentration settles down by gravity. The flocculant forces between particles cause settling down as a mold in which particles keep in a constant status relative to each other as they settle down. [65]

3.1.2. Coagulation

The coagulation is a low-cost, vigorous and environmentally friend method that applied for the treatment of wastewater. Colloids particles are stable do not settle out and will not be removed by traditional physical treatment processes. The reason is that of the large surface-to-volume ratio that results from their tiny size [66].

The hydrophobic colloids have no water affinity and non-stable in the existence of electrolytes. They are easily oversensitive to coagulation. Prevention of agglomeration and settling is due to electrical properties that produce repelling force among the colloids. Stabilizing ions are highly adsorbed to an inner fixed layer that provides a particle charge which changes with the number of adsorbed ions and valency. The diffuse outer layer formed by oppositely charged ions which are caught near the surface via electrostatic forces. [67]

3.2. Biological Treatment

Biological treatment of wastewater is usually the best economical alternative if compared with another treatment process. Variety of factors determines the ability of pollutant to undergo biological degradation such as its concentration, chemical structure and target pollutant [68]. A large number of an organic compound easily breaks down to simpler compound, but other natural and synthetic occur inorganic ones are resistance to natural degradation. For that biological treatment is a cheap and easy to apply for degradation of these compounds [69]. The presence of inhibitory substance or pH can also impact the biological degradation [70]. The biological processes are applied via a different group of organisms. All organisms in the biological treatment must necessarily have their origins from wastewater. The two main types of biological treatment plants are bioremediation and activated sludge.

3.2.1. Bioremediation

Bioremediation takes a special interest among other treatment processes since it is eco-friendly and the only technology that use the plants and microbes to degrade the pollutants insitu. Bioremediation is the use of biodegradation processes to eliminate environmental pollutants from the point where they have been released [71].

Biodegradation includes pesticides or other organic compounds break down to less complex compounds and finally to water and CO_2 and oxides or mineral salts of other elements present by organisms especially microorganisms. The complete degradation of a pollutant into inorganic components is known as biomineralization. Sometimes the break down leads to the formation of less toxic organic compounds, denoted as partial biodegradation. The pesticide thus degraded or/ and transformed by the microorganism is used as a carbon, nitrogen, any other mineral source. For example, Achromobacter xylosoxidans strain CS5 has been able to utilize both endosulfan and endosulfan sulfate as sulfur, carbon and energy source end in complete mineralization of endosulfan by hydrolytic pathway [72]. Having knowledge about pesticide metabolism by the microorganism is important for proceeding bioremediation strategies for polluted water.

3.2.2. Activated sludge treatment

The activated sludge treatment principle is that the mass of activated sludge is kept dynamic in the water by aeration or stirring. regardless of the living biomass, the suspended solids include inorganic and organic particles. Some of the organic particles can be broken down by submitting them to hydrolysis while some others are non-degraded [73].

3.3. Chemical Treatment

Chemicals are used in order to expedite the treatment process. These chemical processes, which induce chemical reactions, and are used alongside physical and biological treatment processes to achieve various water standards.

3.3.1. Ozonation

Ozone is a gas at normal pressure and temperature. The ozone solubility in water depends on the temperature and the ozone partial pressure in the gas phase and has recently been a function of pH. Because of its super oxidation potential, treatment by ozone is vastly applied in drinking water treatment for color removal, odor and taste control, disinfection, reduction of disinfection by-products formation, and also for the effective degradation of several organic pollutants. organic pollutant reacts with Ozone either directly by reaction with molecular ozone or through indirect reactions with free radicals (e.g. $OH^{\cdot}$) formed by the ozone decomposition. The hydroxyl radical formation rate depends on the water characteristic, including pH, alkalinity content, and type of organic matter [74]. Molecular ozone reacts selectively with aromatic systems unsaturated bonds, and amino groups but the reaction with hydroxyl radicals is unselective and faster process.

3.3.2. Wet air oxidation (WAO)

Wet air oxidation is a technique used in organics reduction. This method based on phase reaction that involves breaking down of suspended or dissolved organic matter by oxidation with molecular oxygen in the liquid phase under high temperature and pressure, usually (200–325°C) and 150 atm bar in order to keep the liquid phase. WAO destroys pollutant in wastewater by converting complex organic structures into a simpler compound such as CO_2 and water [75]. Only a few information is present that indicates the efficiency of WAO for pesticides degrading.

3.4. Review Literature of Pesticides Treatment by Different Methods

Yatmaz et al. [76] investigated the degradation of monocrotophos pesticide from aqueous solutions by the different electrochemical process such as direct electrooxidation, indirect electrooxidation, electro-Fenton and electrocoagulation processes. İn direct electro-oxidation Ti electrode was used in order to degrade the monocrotophos from solutions with a different initial concentration (50, 100, 200, 300 mg/L) at 50 and 100 A/m^2. They observed that increasing the initial monocrotophos and supporting electrolyte concentration increases the monocrotophos degradation and decreases the energy consumption. But increasing the current density increases the monocrotophos degradation but also increases the energy consumption. The degradation of 300 mg/L monocrotophos solution by electrocoagulation using iron electrodes (6 g/L NaCl, 6 g/L NaCl) was examined and 78 % removal was obtained. The degradation of 300 mg/L MCP solution (50 A/m^2, 6 g/L NaCl) by the indirect electro-oxidation methods using Ti electrodes with adding 2 mM H_2O_2/min was also investigated and 100 % monocrotophos degradation was obtained. They observed that best method was electro-Fenton process using Fe electrodes and adding 2 mM H_2O_2/min with a current density of (93 A/m^2). The complete degradation occurred in less than 5 mins and was mineralized to the yields of 66 % efficiency at 90 mins.

Fenoll et al. [77] examined the fenamiphos pesticide degradation in leaching water using different mixed-phase titanium dioxide (TiO_2), zinc oxide (ZnO), Tungsten(VI) oxide (WO_3), and tin(IV) oxide (SnO_2) at pilot plant scale under natural sunlight. The time needed for degradation 50% was in the range 1-3 minutes for ZnO and TiO_2. The main intermediates of photolytic were fenamiphos-sulfoxide and fenamiphos sulfone detected during the fenamiphos degradation. The study was showed that zinc oxide is the most effective in catalyzing the degradation of fenamiphos and as well as their metabolites. They observed that the complete disappearance of the studied compounds occurred after 240 mins of illumination in the $ZnO/Na_2S_2O_8$ system.

Vlyssides et al. [78] examined the removal of methyl parathion from aqueous solution by Electrochemical Oxidation. The electrochemical treatment of methyl parathion was investigated by using Ti/Pt as an anode and Stainless Steel (SS) as a cathode, and NaCl as the electrolyte. The treatment was carried out with 6 L of 8% w/w aqueous suspension of methyl parathion pesticides 20 g/L of NaCl. The removal efficiency during electrochemical degradation of a 0.152 M methyl parathion in an electrolytic cell of 6 L with a residence time of 2 hours and current density 0.56 A/cm^2 at 45 °C was about 82%.

Bourgin et al. [79] investigated the imidacloprid pesticide degradation by ozonation. Solutions of 39.0μg/mL imidacloprid were prepared either by Gaucho Blé® seed loading solution dilution or by standard dissolution. Imidacloprid and their oxidation products concentration in both solution measured by HPLC-UV for 100g/m^3 of ozone in the access gas. İn both case no significant difference was seen. Degradation of imidacloprid in both solutions obeys the pseudo-first order reaction with reaction rates (0.129-0.147 min^{-1}), degradation products with the same HPLC retention times were spotted and their concentrations as a function of the treatment duration follow a very similar way. The study of ozone concentration in the access gas from 25 to 100 g/m^3 showed that the imidacloprid pesticide degradation is also a first-order reaction with respect to ozone. The ozonation intermediate products were then collected and identified by ESI (+)-MS.

Babu et al. [80] studied the comparison of electrooxidation, electrocoagulation and electro-Fenton in the removal of pesticides from solution contains methyl parathion, atrazine, and triazophos). İn order to determine the optimum pH condition, the experiments were run out at different pH, at the end of 6 hours of treatment the COD reduced from 1810 to 431 mg/L (pH6), 210 mg/L (pH10), and 341mg/L (pH8) by electrooxidation, electrocoagulation, and electro-Fenton respectively. The results showed that at a constant current density of 5 A dm$^{-2,}$ the highest COD reduction was detected by electrocoagulation at pH10 (88%), followed by electro-Fenton at pH8 (81%) and electrooxidation at pH6 (76%). Furthermore, they have also investigated the current efficiency, energy consumption and the energy cost of degradation.

Behloul et al. [81] examined the removal of the pesticide malathion from aqueous solution using electrocoagulation methods. The effects of some operational parameters such as initial concentration of pesticide, initial pH, salt concentration, the distance between electrodes, and current density on the malathion removal efficiency were studied. The relationship between current density and the supporting electrolyte on electrical energy consumption were also evaluated. The response surface methodology methods showed that the experimental's design not affected by the studied parameter.

Other factors had negative and positive effects. With the optimum currents density of 10 mA/cm^2 and pH6, 40 mg/L initial concentration, 2500 mg/L salt concentration, 27°C temperature and the distance of 2 cm between electrode. Over 90% of malathion pesticide was removed during 10 minutes of electrolysis

Amooey et al. [82] validated the removal of Diazinon by electrocoagulation using aluminum electrode. The effect of several operating parameters such as initial concentration of Diazinon, solution conductivity, current density, pH, and electrolysis duration was investigated on removal efficiency. The obtained results indicated that the removal efficiency of Diazinon significantly affected by on the current density, its initial concentration and electrolysis time. the solution conductivity has no significant effect on removal efficiency. The highest removal efficiency of 89% recorded at Current density (12 mA/cm^2), initial pesticide concentration (60 mg/L), solution conductivity (6.5 mS/cm) and pH 3.

Zhang et al. [83] studied the association between toxic tolerance in green alga Chlamydomonas reinhardtii and degradation and Bioaccumulation of pesticide fluroxypyr. They treated the microalgae with fluroxypyr at 0.05–1.00 mg l^{-1} for 2 days or 0.50 mg l^{-1} for 1–5 days. The growth of Chlamydomonas reinhardtii was activated at low levels of fluroxypyr (0.05–0.5 mg l^{-1}) but the growth inhibited at high dosage (0.75–1.00 mg l^{-1}). The significant accumulation of pesticide by Chlamydomonas reinhardtii was indicated and the accumulated pesticide rapidly break down in the cells. After 5 days more than 57% of cellular pesticides degraded.

Zheng-huang and Bao-feng [84] improved the removal of degradation-resistant pesticide with high salinity by wet air oxidation process. The COD and removal rate of chroma during the process has been investigated. The results showed that the process was affected by temperature, reaction time oxygen partial pressure and the acidity of the reaction system. The COD removal rate of 98.0% and over 99.0% removal rate of chroma were indicated under the following conditions: Oxygen partial pressure of 4.2mPa, temperature 280℃, initial pH of the system 2.0 and reaction time was 150min.

Frangos et al. [85] described the degradation of deethylatrazine pesticide (DEA) by combining UV photolysis with the electrochemical generation of H_2O_2. The E-UV/H_2O_2 process uses a carbon-based cathode to electrochemically produce hydrogen peroxide from O_2 produced from anodic side reactions such as oxidation of water. The generated hydrogen peroxide then undergoes UV254 induced photolysis to yield hydroxyl radical, which can significantly enhance pollutant degradation in the E-UV/H_2O_2 process. By using the air, anodic produced oxygen, and pure oxygen, the deethylatrazine degradation rate by E-UV/H_2O_2 process increased by 148%, and 116%, 205% respectively. As compared to the mathematical total of the individual ratios of the corresponding electrolysis ($k = 0.003\ min^{-1}$) processes and electrolysis ($k = 0.003\ min^{-1}$) UV photolysis ($k = 0.129\ min^{-1}$). Because of their rapid removal rate, the E-UV/H_2O_2 decreased the electrical energy consumption by 90% compared with UV photolysis alone.

Lafi and Al-Qodah [86] studied the pesticide elimination from aqueous media by combining the biological treatment with advanced oxidation process. they investigated that the combination of O3 and UV radiation promotes the degradation of pesticides and no residual of pesticides seen at end of treatment. They observed that 90-100% of Deltamethrin has been removed by a combination of O_3 and O_3/UV during the 210 minutes. They also indicated that 20% of COD reduced if the pH of the solution was more than 4. The pesticide removal and COD obeyed the pseudo-first-order kinetics. The efficiency of biological treatment in removing the bulk chemical oxygen demand from the solution also studied. Biological treatment has been effective when the treated water by O_3/UV fed to a bioreactor. More than 95% of chemical oxygen demand removed after 64 hours of biological process at 25^oC and pH 7.

Chelme-Ayala et al. [87] investigated the oxidation of trifluralin and bromoxynil by ozone and O_3/H_2O_2 in the natural water. They observed that ozonation alone is not efficient in degradation of pesticides since only 50% of degradation achieved. By using combination process O_3/H_2O_2 significant increase in degradation was observed. The O_3 concentration needed to degrade the pesticides was $5*\ 10^{-4}$ M. A biphasic O_3 behavior was also studied. İn relates to the condition of experiments, the ozone degradation rate constant was approximately between $3.2*10^{-3}\ s^{-1}$ to $4.2*10^{-2}\ s^{-1}$ and $7.4*10^{-4}s^{-1}$ to $5.8*10^{-2}\ s^{-1}$ for trifluralin and bromoxynil samples respectively. The microtox toxicity analysis for both pesticides indicated that the toxic effect decrease at the beginning of the treatment, but the significant increase of toxicity indicated at the end of the reaction.

4. ELECTROCHEMICAL TREATMENT TECHNOLOGIES

Industrial and agricultural wastewater treatment in the world day by day constitute a bigger problem. However, the search for lower cost and more efficient methods of treatment in compared to old used methods is under investigation. Parallel to this increase in wastewater, new treatment techniques are emerging day by day. Toxicity degradation needs development of new methods for the treatment of such toxic pollutants in a safe and cost-effective way. Water purification by electrochemical methods has been the subject of rising concern in last year's [88]. In last years, the electrochemical treatment process has been taken a considerable affinity for wastewater treatment due to its environmentally friendly, efficient methods and versatile treatment process. The main critical point that recognizes electrochemical processes from other is the process shape and structure (electrode type, applied current, electrical voltage and process type).

4.1. Electrochemical Treatment Types

Electrochemical treatment processes mainly include three methods. Such systems can work alone or at the same time, few electrochemical methods can be used in combination.

4.1.1. Electrocoagulation (EC)

Electrocoagulation process involves the in-situ pollutant dissolving by generating coagulants electrically [89]. Involve many physical and chemical reaction in which iron or aluminum electrodes form either iron or aluminum ions respectively [90]. The metal ions formation happens at the anode; hydrogen gas set free from the cathode [91]. The electrodes react with the water during the operation phase of the process and form metal hydroxides such as $Al(OH)_3$, $Fe(OH)_2$ and $Fe(OH)_3$. Treatment in the system starts with the formation of metal hydroxides.

When the current is applied to a metal electrode, metal (M) oxidizing to their cation (Mn^+) (Eq 4.1). Jointly, the reduction of water to the hydroxyl ion and hydrogen gas occur (Eq 4.2). Electrocoagulation thus introduces metal cations to the media [92].

$$\mathrm{M} \rightarrow \mathrm{M}^{\mathrm{n}} + \mathrm{ne} \tag{4.1}$$

$$2\mathrm{H_2O} + 2\mathrm{e}^- \rightarrow 2\mathrm{OH}^- + \mathrm{H_2} \tag{4.2}$$

Electrocoagulation usually involves three basic processes [93].

a) Electrolytic reactions at the surface of the electrodes

b) Coagulants formation (metallic ions) in the liquid phase

c) Gathering of the destabilized phases to form flocs.

4.1.1.1. Reaction mechanism of EC

The chemistry of the medium essentially the conductivity, highly affects the EC mechanism. Also, different parameters such as particular size, pH, and the concentration of chemical ingredient affect the EC process [89]. Electrocoagulation is a complex process proceed by chain steps. At the time that the current is passed through the reactor, it must beat the equilibrium potential difference, anode over potential, cathode overpotential and potential drop of the solution. The anode overpotential includes the activation overpotential and concentration potential, also possible passive overpotential generated from the passive film at the anode flat, while the cathode overpotential is fundamentally composed of the concentration overpotential and activation overpotential. Reactions at electrode flat, coagulants formation in aqueous media, soluble or colloidal pollutants adsorption on coagulants.

Aluminum or iron electrodes are generally used in the electrocoagulation process. This is because the adsorption capacity of metallic ions is high, which is why it is a good coagulant [94]. In the iron electrode, two mechanisms have been proposed [95].

4.1.1.2. EC using iron electrodes

The chemical reactions taking place at the anode are given as below.

Mechanism 1:

Anode:
$$4Fe_{(s)} \rightarrow 4Fe+2_{(aq)} + 8e^- \tag{4.3}$$
$$4Fe^{+2}_{(aq)} + 10H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+_{(aq)} \tag{4.4}$$

Cathode:
$$8H^+_{(aq)} + 8e- \rightarrow 4H_{2(g)} \tag{4.5}$$

Overall:
$$4Fe_{(s)} + 10\ H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \tag{4.6}$$

Mechanism 2:

Anode:
$$Fe(s) \rightarrow Fe^{+2}(aq) + 2e^- \tag{4.7}$$
$$Fe^{+2}_{(aq)} + 2OH^-_{\ (aq)} \rightarrow Fe(OH)_{2\ (s)} \tag{4.8}$$

Cathode:
$$2H_2O_{(l)} + 2e- \rightarrow H_{2(g)} + 2OH^-_{\ (aq)}) \tag{4.9}$$

Overall:
$$Fe_{(s)} + 2H_2O_{\ (l)} \rightarrow Fe(OH)_{2\ (s)} + H_{2\ (g)} \tag{4.10}$$

4.1.1.3. EC using aluminum electrodes

The electrochemical reaction occurred at Al anode can be summarized as follows:

Anode: $Al(s) \rightarrow Al3^{+}_{(aq)} + 3e^{-}$ (4.11)

Cathode: $3H_2O_{(l)} + 3e^{-} \rightarrow 3/2\ H_2 + 3OH$ (4.12)

Overall: $Al_{(s)} + 3H_2O_{(l)} \rightarrow Al(OH)_{3(s)} + 3H^{+}$ (4.13)

For the aluminum electrodes, $Al^{3+}{}_{(aq)}$ ions will immediately undergo further spontaneous reaction to generate corresponding hydroxides and polyhydroxides. Due to hydrolysis of Al^{3+}, $Al\ (H_2O)_6{}^{3+}$, $Al\ (H_2O)_5OH^{2+,}$ $Al(H_2O)(OH)^{2+}$ are generated [96].

The large specific area of Aluminum hydroxide then facilitates compound adsorption and traps the colloids [97].

4.1.1.4. Advantages and disadvantages of EC process [98]

4.1.1.4.2. Advantages of EC process

1. Simple handy equipment requirement and it is easy to run.
2. Low operating cost in EC in compared to the other techniques.
3. The electrolytic treatment process controlled simply.
4. There is no need to any chemical. So, there is no potential of secondary pollutants production that caused by adding chemical.
5. The electrocoagulation usually composed of metallic hydroxide or oxide. The sludge formed by the process easily settled down, so Sludge can be produced in very small quantities.
6. Electrocoagulation mass tends to be larger, it contains little bound water, more stable and is more durable to acid, and so, and thus it can be separate faster via filtration.
7. Electrocoagulation generate effluent with less (TDS) content when compared with chemical treatments. In the case of reusing the water, the low TDS level participate to a lower recovery cost.
8. The electrocoagulation process has the benefit of eliminating the little colloidal particles, due to the applied electric field that sets them in faster motion, thereby helping the coagulation.

9. The pollutants in the solution transported to the surface by the gas bubble that produced during the electrolysis. So, it can be easily collected and removed.
10. At the end of electrocoagulation clear, odorless and colorless water formed.
11. Electrocoagulation process deals with a significant change in waste streams with different pollutants.
12. The EC process can be practically applied in rural areas where electricity is not present since a solar panel attached which may be enough to carry out the process.

4.1.1.4.3. Disadvantages of EC process

1. An impermeable insulator oxide film produces on the cathode in some electrocoagulation system.
2. Required the water with high conductivity.
3. In some case the usage of electricity can be so expensive.
4. Due to oxidation, anode want to be replacement because of dissolved in the wastewater by an action of oxidation

4.1.2. Electrochemical- Fenton process (EFP)

In advance oxidation process, oxidation by applying Fenton’s reagent seems to be the best alternative, operative, potent and environmentally friendly methods, a large number of toxicant and organic contaminant used to be treated by this method. The oxidation of organic substance by iron (II) and hydrogen peroxide is termed “Fenton chemistry” and the first who observed by H.J.H. Fenton. Fenton who first described the oxidation of tartaric acid by hydrogen peroxide by the aid of ferrous iron ions. Fenton observed in 1894 that some metals have the properties of oxygen transfer that improve the use of hydrogen peroxide. İn fact, some metals have a strong catalytic power to generate strong reactive hydroxyl radicals (•OH). For the time being, the Fenton's reaction is employed to treat different types of water pollution such as phenols, formaldehyde, pesticides [99].

These methods totally named advanced oxidation processes (AOPs) which comprise the use of hydroxyl radicals (OH•) as the oxidation agent. Fenton process has two ingredients, which is catalytic chemical species such as Fe^{2+}or Fe^{3+} and a chemical oxidant (H_2O_2) which are commonly used for the Fenton’s reaction [100].

AOPs operate with less energy requirement than direct oxidation. AOPs involve in the production of (OH•) in an adequate quantity that affects water purification [101]. The hydroxyl radicals are super-reactive species, that attack all part of organic molecules [100].

4.1.2.1. Theory of Fenton Process

Electrochemical-Fenton is one of best effective, strong and environmentally friendly methods. In the Fenton reaction (OH•) are generated by the reduction of hydrogen peroxide. The degradation mechanism of the organic contaminant by Fenton reaction is given in equations below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + HO^{\cdot} \qquad (4.14)$$

Equation (4.14) is determined as Fenton reaction that denotes the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) ions to convert hydrogen peroxide into hydroxyl radicals. It is deemed as the core of the Fenton chemistry.

$$RH + HO^{\cdot} \rightarrow R^{\cdot} + H_2O \qquad (4.15)$$

Where, RH represent organic contaminant

$$R^{\cdot} + Fe^{2+} \rightarrow R^{+} + Fe^{2+} \qquad (4.16)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^{-} \qquad (4.17)$$

The treatment by the Fenton process show some disadvantages because a large amount of Fe sludge is produced by applying a high concentration of ferrous so that wastewater treatment is been expensive and it requires a large quantity of chemicals. Fenton’s reaction is only worked at narrow pH because iron ions will be settled down at higher pH values and movement of H_2O_2 are difficult [102].

4.1.3. Electro-Oxidation Process (EOP)

EOP is the most widely used process since it allows the degradation of highly toxic waste [103]. It is also named ‘‘electrochemical combustion’’ process because of complete mineralizing of organic pollutants, i.e., oxidized the organic pollutant to CO_2, water, and inorganic salts, by direct reaction with hydroxyl radicals ($\cdot OH$) that electrically generated from water discharge at the anode [104,105].

The electrochemical generation and reactivity of ($\cdot OH$) dependent directly on the nature of the electrode material [106]. Therefore, for the oxygen evolution reaction, a non-active anode is needed for the oxygen evolution reaction, since such type of electrode weakly interacts with (·OH), allowing the direct reaction of organics with radical.

The use of a boron-doped diamond (BDD) in EOP supplies total mineralization with high current efficiency for organics pollutant in wastewater [107]. The BDD anode represents the best non-active electrode which offering such behavior [108,109]. So, it has been suggesting as a perfect anode for degradation of organics by EOP.

4.1.3.1. Theory of EO

Thermodynamically, the electrochemical break down of soluble organic matter in the water must be carried out at low potentials, the thermodynamic potential of water oxidation to molecular oxygen (1.23 V per standard hydrogen electrode (SHE) under standard conditions), as shown in equation (4.18) [110]:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{4.18}$$

In acidic condition, water may be break on the electrode, highly oxidative absorbed hydroxyl radicals produced (Eq 4.19):

$$H_2O + M \rightarrow M\,(^*OH) + H^+ + e^- \tag{4.19}$$

where M indicates the surface of the electrode.

The organic pollutant R can be oxidized on the anode surface by these radical as follows (Eq 4.20):

$$R_{(aq)} + M(^*OH)_{n/2} \rightarrow M + \text{Oxidation products} + n/2\ H^+ + n/2\ e^- \tag{4.20}$$

where *n* denotes to the electron numbers involved in the oxidation reaction of organic pollutant. The reaction of organics (R) with the electrogenerated hydroxyl radicals (Eq 4.20) is in the contest with the side reaction of the anodic drainage of the radicals to oxygen (Eq 4.21):

$$M\,(^*OH) \rightarrow M + 12\ O_2 + H^+ + e^- \tag{4.21}$$

Anodic activity relies on electrodes overpotential for oxygen evolution [88]. For example, platinum electrodes represent lower potential value to oxygen evolution reactions (1.3 V vs SHE), and BDD electrodes (Ti/BDD, 2.7 V vs SHE). This indicates that higher current density with low oxygen evolution side reaction seen on Ti/BDD electrodes during anodic oxidation of hydroxyl radical.

4.1.3.2. The advantage of EO process

Advanced oxidation technique such as electro-oxidation (EO) was recently remarked as alternatives for removal of pollutant from aqueous solution. with a high potential for wastewater containing both bio-degradable and bio-refractory compounds. This process doesn’t produce sludge.

The main advantage of the EO process is that only electrical energy is used in the oxidation of organic contaminant does not need chemicals. İt is known as environmentally friendly since electron itself has been effective, clean and safe reagent. EO is non-selective and can break down many pollutants and treat from microlitres to thousand of liters [111, 112].

EO process can be applied for continuous operation such as in urban wastewater treatment plant (UWWT), especially for applications with low flow rate and water reclamation, since EO process allow disinfection of the reclaimed water.

5. EXPERIMENTAL METHODS

The equipment, materials, and analysis methods are described in this chapter. The experimental works were designed to investigate the effects of different operating parameters on pesticides treatment efficiency and COD.

5.1. Electrocoagulation Methods Using Iron Electrodes

An electrochemical cell consists of a 600 mL glass reactor. All experiments were conducted with 400 mL of the prepared model solution. In this method, six parallel iron electrodes installed, arranged as 3 anodes and 3 cathodes figure (5.1). Electrodes with an immersed area of 83 cm^2 were used. The electrodes were connected to a digital DC power supply. A constant current density of 5, 10 15, and 20 mA/cm^2 was applied as all other experimental systems for comparison. A constant stirring speed of 300 rpm using magnetic stirrer was ensured during the experiment. Experiments were carried out for 80 min at original pH condition and by adding 1, 5 and 10 mM support electrolyte. Samples were drawn at regular intervals of 20 min to estimate the COD reduction efficiency and other analysis.

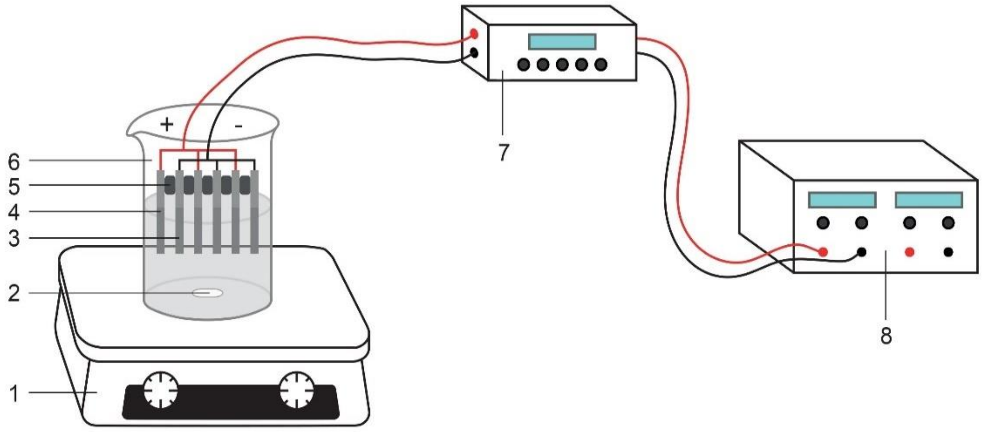

Figure 5.1. *Schematic of experimental electrocoagulation system (1. thermostatic magnetic stirrer, 2. magnet, 3. cathode, 4. anode, 5. Rubber Insulator, 6. beaker, 7. polarity changer, 8. DC power supply)*

5.2. Electrocoagulation Methods Using Aluminum Electrodes

The condition of treatment and withdraw interval period of the samples are the same as other electrochemical process. Each electrode was with the length of 5.5 cm and width of 5 cm, the distance between the two electrodes was 0.5 cm. The support electrode of 10mM was added to the system

5.3. Electrocoagulation Methods Using Hybrid (mixed) Electrodes

A laboratory DC power supply was used for electrolysis. Electrolysis was carried out at room temperature in a cylindrical open glass cell of 600 mL equipped with six electrodes (3 aluminum and 3 iron electrodes) vigorously stirred with a magnetic bar (300 rpm). The working electrodes arranged in series (one aluminum, one iron) with a diameter of 83 cm^2 for both commercially obtained aluminum and iron electrodes.

5.4. Electrochemical-Fenton Methods

The experiment involved electrolyzing 400 mL of the pesticides solution in a 600-mL beaker by adding different concentration of hydrogen peroxide (500,1000,2000,3000 mgH_2O_2/mL initially). The model solution in the reactor was kept stirred with a magnetic stir bar to satisfy the system with air. Sodium sulfate (1mM) was added as the electrolyte in order to improve conductivity in the solution. In order to electrolyze the model solution, six parallel iron electrodes were used. The active surface area of iron electrodes was 83cm^2. Electrolysis was carried out by passing an appropriate amount of constant current for a given length of time.

5.5. Electro-oxidation Methods Using Born Doped Diamond (BDD)

Electrolysis was performed with DC power supplies using two BDD electrodes (one anode and one cathode) with the length of 5 cm and width of 3.7 cm and the distance between two electrodes of 0.5cm. The supporting electrolyte (Na_2SO_4) of 5mM and 10mM was added. The samples were withdrawn at a time interval of 20 min for 80 min. laboratory scale electrochemical reactor shown in figure (5.2).

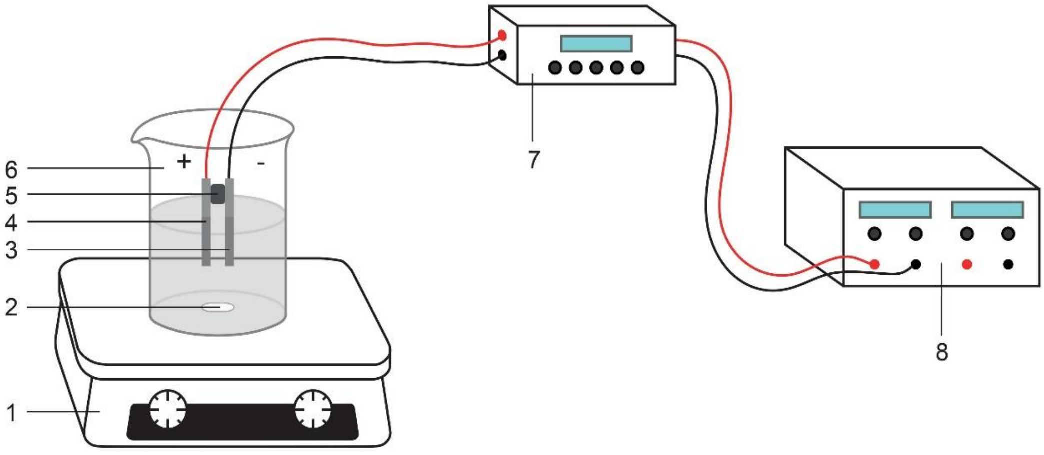

Figure 5.2. *Laboratory scale Electro -oxidation reactor (1. thermostatic magnetic stirrer, 2. magnet, 3. cathode, 4. anode, 5. Rubber Insulator, 6. beaker, 7. polarity changer, 8. DC power supply)*

5.6. Used Electrode Materials

The electrode is the main part of the electrochemical system, the nature of the electrode material strongly affects the efficiency of electrochemical processes for oxidation of organic compounds and for that, in research, different electrodes have been used to find the most effective one toward organic oxidation.

The selection of appropriate electrode is important in electrocoagulation process. The main electrode materials are aluminum and iron. Both electrodes are not expensive, easily obtained and effective materials with most pollutant [113].

Newly, electro-oxidation has taken a large interest in the treatment of wastewater due to the introduction of a new electrode material. Using quality Born doped diamond (BDD) as electrode seems to be an effective method for degrading of organics pollutants up to total mineralization.

High-quality Born doped diamond (BDD) electrodes have some main technologically properties which including inert surface and low adsorption properties, obvious stability to corrosion even in very strong acidic medium, and high O_2- evolution overpotential. During electrolysis, the BDD anode produces a large number of the hydroxyl radicals ($OH^{\cdot}$**)** that adsorbed weakly on their surface, and accordingly, it possesses high reactivity for oxidation of organic, giving it the possibility of effective treatment of polluted water [114,115].

5.7. Used Equipment and Chemical Materials

The pesticide used in the work was bromuconazole, bentazone and abamectin. All model solutions were prepared from the commercially available pesticides having a pesticide concentration is 100g/L, 480 g/L, and 18 g/L respectively.

Analytical grades sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) has been used as electrolytes from Merck. Hydrogen peroxide (H_2O_2, 30% from Merck) was used for the electrochemical-Fenton process. Standard solutions of potassium dichromate ($K_2Cr_2O_7$), silver sulfate (Ag_2SO_4) and sulfuric acid (H_2SO_4) reagent were prepared for COD measuring.

A laboratory digital DC power supply was used for electrolysis. a polarity changer device was used to prevent film layer formed on the electrodes and to allow the electrodes to corrode at the same level.

Table 5.1. *Equipment used during the treatment process*

Name	Model
laboratory digital DC power supply	Statron 3262.3 model (0-300 V and 0-4 A)
a polarity changer device	
Centrifuge	Nüve-Bench Top Centrifuge, NF 800R, Turkey
UV-Vis spectrophotometer	Shimadzu UV-1800
Electronic Balance	Ohaus EP612C Explorer Pro Precision
Tabletop Scan Electron Microscope	TM3030 plus, Hitachi High-Technologies
Microtox model 500	Modern Water Microtox Model 500 Analyzer (120v/220v, 50/60Hz) - AZF50A000/AZF50A002
Laboratory Dryıng Oven	Ecocell EC55 oven—MMM Medcenter

5.8. Procedures and Analysis

5.8.1. pH determination

The pH value of any media can be an indicator of its possible toxicity or corrosivity. It can indicate the efficiency of water treatment. pH can be defined as a measure of the hydrogen ion concentration in the media [116]. The pH level of the samples was confirmed by a commercial pH meter (Orion™ Star A211).

5.8.2. Estimation of chemical oxygen demand (COD) and pesticide concentrations

In order to evaluate the electrochemical treatment, two parameters were measured, the remaining pollutant concentration of best-obtained results and COD Remaining pollutants of (bromuconazole, bentazone, and abamectin) concentration were measured with the UV-visible spectrophotometer at (λmax= 202, 230 and 198 nm respectively).

Chemical oxygen demand (COD) is a vastly applied parameter in controlling the pollution degree in water and managing the quality of effluent [117]. COD is the important parameter that widely used to evaluate the organic content of the wastewater. The COD value indicates the oxygen equivalent of the organic substances that oxidized by ($K_2Cr_2O_7$) in the acidic conditions (H_2SO_4) by using silver sulfate (Ag_2SO_4) as a catalyst. The chemical oxygen demand of samples was determined according to the procedure given by TS 2789 standard (Water quality – Determination of COD). The samples titrated with ferric ammonium sulfate (FAS) which was prior standardized to each measuring to determine the amount of potassium dichromate consumed.

COD removal percentage of taken samples were calculated as follows:

$$\boldsymbol{COD\ removal}\,\% = \frac{(CODo\ - CODt)}{CODo} * 100 \tag{5.1}$$

Where COD_o (initial) and COD_t (any time) of the pesticide treatment and calculated in mg/L.

5.8.3. Determination of energy consumption

The efficiency of pesticides degradation depends on the energy consumption for reduction of organic matter in terms of COD, which represent one of the most important factors in the economics of electrolysis. In order to investigate the effect of the current density on the pesticides degradation within the specific time, different electrode types at the different current densities were used. potential differences were recorded at specific time intervals during the experiments performed and this data was used in energy consumption and cost determination. Electrical energy consumption calculated as follow:

$$\boldsymbol{Energy\ Consumption}\ (KWh/m^3) = \frac{V * I * t}{Vol.} \tag{5.2}$$

Where

V= potential different (V)

I= current density (A)

t= Time interval (h)

Vol.= volume of sample in the reactor (m^3)

In order to determine the energy cost for the treatments, the data has been taken from energy market requlatory.

5.8.4. Ion chromatography analysis (IC)

Analyzing and determination of trace elements in the presence of high levels of ions can be a big challenge. Ion chromatography is the technique that used for analyzing ions present in water samples [118].

The concentration of ammonium and nitrate ions released during electrolysis of pesticides was measured by IC (Dionex-10 supplied with a conductivity detector). A cationic (IonPac® CS12A-Dionex) and anionic (IonPac® AS14-Dionex) exchanger columns were used for nitrate and ammonium ions respectively. The injections volume was 25µL. The mobile phase and regenerant solutions were 20 mM methane sulfonic acid (Fluka, 70%) with a flow rate of 0.85 ml min^{-1} and 100 mM tetrabutylammonium hydroxide (Aldrich, 40%) in the cation analysis, respectively. On the other hand, 30 mM sodium hydroxide (Fluka, 99%) with a flow rate of 0.80 ml min^{-1} and 22 mM H_2SO_4 (Across, 98%) was used in the anion analysis as mobile phase and regenerant, respectively. Calibration curves were obtained using pure parameters of the corresponding ions.

5.8.5. Toxicity determination

The toxicity of samples was investigated using a Microtox® M500 Toxicity Analyzer and the test organism was lyophilized bacteria known as Vibrio fischeri NRRL B-11177 strain. Toxicity determination followed the manufacturer's procedures (Azur Environmental, Carlsbad, USA) [119]. Freeze-dried bacteria, diluent (2% NaCl) and reconstruction solution were obtained from Microbics Corporation (Carlsbad, USA).

The results of toxicity were expressed as effective concentration EC_{50}, which is known as effective concentration of a toxic substance that reduces the intensity of light emission by 50% (reduction in the light emission by bacteria) in 5 min,15 mins of contact at an incubation temperature of 15^{o}C [120]. The inhibition of the luminescence, compared with a non-toxic control in order to obtain the inhibition percentage, and has been calculated with the Microtox data calculation software (version 1.18) after incubation times of 5min and 15 mins.

In order to indicate the variation in toxicity, the toxicity results of the samples are also expressed as relative toxicity index (RTI) according to the equation below: [121,122]

$$\boldsymbol{RTI} = \frac{\%\, EC_{50}\, at\ (t_0)}{\%\, EC_{50}\ (t)} \qquad (5.3)$$

where % EC_{50} (t_0) and % EC_{50} (t) are the 5, 15 min sample Microtox toxicity at times 0 and t.

Toxicity categorizing on the basis of percentage which produce 50% of light reduction towards Microtox and allows comparison of toxicity among different samples as follows [122,123]: % EC_{50} ≤25 = highly toxic; 25–50 = moderately toxic; 51–75 = toxic; >75 = slightly toxic; >100 = non-toxic.

5.8.6. Scanning electron microscopy with energy-dispersive spectroscopy

Scanning Electron Microscopes (SEM) scan the samples with a focused electron beam and deliver images with information about the samples' topography and structure. To assess the surface structure of the sludges and electrodes samples, a small sample of each film (approximately 10 × 10 mm) was mounted on a scanning electron microscopy (SEM) stub. The Hitachi TM3030 SEM at 15 kV was employed to image and identify compositional of sludge formed after electrochemical treatment process.

The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions. The elemental distribution scan of elements found on the surface of the samples was performed using scan energy dispersive X-ray spectroscopy (EDS) with SwiftED3000 module oxford instruments that attach to the SEM.

6. RESULTS

6.1. Bromuconazole

The effect of current density, electrolyte concentration, and electrode type on the degradation of Bromuconazole and COD was investigated at four different current densities. The reactions were carried out for 80 min using electrochemical methods. The initial concentration of bromuconazole was 300 mg.L^{-1}, The temperature at the beginning was about 20-25 ^{o}C, while during electrolysis period a significant increase in temperature determined (28-33^{o}C).

6.1.1. Electrocoagulation methods using iron electrodes

Table 6.1. *300 mg/L bromuconazole containing solution (EC-Fe, i=5mA/cm2, 1mM* Na_2SO_4*, pH= 5.18)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	24.5	1182	0.0	0.0	0.0	0.0	0.0
20	24.3	496.47	58.00	0.00340	8.50	8.50	208.16
40	24.1	469.50	60.28	0.00337	8.43	16.92	414.61
60	23.9	458.85	61.18	0.00334	8.36	25.28	619.35
80	23.8	417.53	64.68	0.00333	8.32	33.60	823.23
Sludge amount (gram)= 1,88							

Table 6.2. *300 mg/L bromuconazole containing solution (EC-Fe, i=10mA/cm^2, 1mM* Na_2SO_4*, pH= 5.18)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	30.5	1218.46	0.0	0.0	0.0	0.0	0.0
20	27.4	457.69	62.44	0.00757	18.93	18.93	463.85
40	27.2	447.51	63.27	0.00752	18.79	37.73	924.31
60	27.2	422.34	65.34	0.00752	18.79	56.52	1384.78
80	27	409.89	66.36	0.00746	18.66	75.18	1841.86
Sludge amount (gram)=2.14							

Table 6.3. *300 mg/L bromuconazole containing solution (EC-Fe, i=15mA/cm^2, 1mM* Na_2SO_4*, pH= 5.18)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	33.5	1197.32	0.0	0.0	0.0	0.0	0.0
20	31	392.57	67.21	0.01280	32.00	32.00	784.03
40	30.8	367.33	69.32	0.01272	31.79	63.80	1563.00
60	30.5	331.67	72.30	0.01259	31.49	95.28	2334.39
80	30.7	304.88	74.54	0.01268	31.69	126.97	3110.83
Sludge amount (gram)=2.54							

Table 6.4. *300 mg/L bromuconazole containing solution (EC-Fe, i=20mA/cm^2, 1mM Na_2SO_4, pH= 5.18)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	35.3	1100	0.0	0.0	0.0	0.0	0.0
20	34.7	320.33	70.88	0.01918	47.95	47.95	1174.86
40	34.6	309.71	71.84	0.01913	47.82	95.77	2346.34
60	34.4	284.85	74.10	0.01902	47.54	143.31	3511.05
80	34.3	266.48	75.77	0.01896	47.40	190.71	4672.37
Sludge amount (gram)=2.88							

Table 6.5. *300 mg/L bromuconazole containing solution (EC-Fe, i=5mA/cm^2, 5mM Na_2SO_4, pH= 5.07)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	22.6	1023	0.0	0.0	0.0	0.0	0.0
20	20.3	341.48	66.62	0.00284	7.10	7.10	173.89
40	20.1	325.21	68.21	0.00281	7.03	14.13	346.08
60	20	302.69	70.41	0.00280	6.99	21.12	517.41
80	20	297.52	70.92	0.00280	6.99	28.11	688.74
Sludge amount (gram)=2.25							

Table 6.6. *300 mg/L bromuconazole containing solution (EC-Fe, i=10mA/cm^2, 5mM Na_2SO_4, pH= 5.07)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	25.3	1082	0.0	0.0	0.0	0.0	0.0
20	23.2	341.48	68.44	0.00641	16.03	16.03	392.75
40	23.2	322.51	70.19	0.00641	16.03	32.06	785.50
60	23	313.12	71.06	0.00636	15.89	47.95	1174.86
80	22.8	291.89	73.02	0.00630	15.75	63.71	1560.84
Sludge amount (gram)=2.4							

Table 6.7. *300 mg/L bromuconazole containing solution (EC-Fe, i=15mA/cm^2, 5mM Na_2SO_4, pH= 5.07)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	30.4	1069.34	0.0	0.0	0.0	0.0	0.0
20	27.4	305.17	71.46	0.01131	28.29	28.29	692.98
40	27.3	280.32	73.79	0.01127	28.18	56.47	1383.43
60	27.1	251.36	76.49	0.01119	27.98	84.44	2068.83
80	27.1	238.41	77.70	0.01119	27.98	112.42	2754.22
Sludge amount (gram)=2.68							

Table 6.8. *300 mg/L bromuconazole containing solution (EC-Fe, i=20mA/cm^2, 5 mM Na$_2$SO$_4$, pH= 5.07)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	33.3	1211.69	0.0	0.0	0.0	0.0	0.0
20	31.1	298.17	75.39	0.01719	42.98	42.98	1052.97
40	30.9	272.14	77.54	0.01708	42.70	85.68	2099.18
60	30.6	243.87	79.87	0.01692	42.29	127.97	3135.23
80	30.5	231.49	80.90	0.01686	42.15	170.12	4167.89
Sludge amount (gram)=2.94							

Table 6.9. *300 mg/L bromuconazole containing solution (EC-Fe, i=5mA/cm^2, 10mM Na$_2$SO$_4$, pH= 4.97)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	16.6	1045.18	0.0	0.0	0.0	0.0	0.0
20	14.1	319.28	69.45	0.00197	4.93	4.93	120.78
40	13.9	300.50	71.25	0.00194	4.86	9.79	119.07
60	13.9	291.11	72.15	0.00194	4.86	14.65	119.07
80	13.8	272.33	73.94	0.00193	4.83	19.48	118.21
Sludge amount (gram)=2.77							

Table 6.10. *300 mg/L bromuconazole containing solution (EC-Fe, i=10mA/cm^2, 10mM Na$_2$SO$_4$, pH= 4.97)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.6	1057.56	0.0	0.0	0.0	0.0	0.0
20	18.3	313.54	70.35	0.00506	12.64	12.64	309.79
40	18.2	290.28	72.55	0.00503	12.58	25.22	308.10
60	18	272.01	74.28	0.00498	12.44	37.66	304.72
80	17.9	255.75	75.82	0.00495	12.37	50.03	303.02
Sludge amount (gram)= 2.89							

Table 6.11. *300 mg/L bromuconazole containing solution (EC-Fe, i=15mA/cm^2, 10mM Na$_2$SO$_4$, pH= 4.97)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	26.9	1138.77	0.0	0.0	0.0	0.0	0.0
20	24.8	294.07	74.18	0.01024	25.60	25.60	627.22
40	24.7	273.68	75.97	0.01020	25.50	51.10	624.69
60	24.5	249.89	78.06	0.01012	25.29	76.39	619.63
80	24.3	237.50	79.14	0.01003	25.08	101.48	614.57
Sludge amount (gram)=3.54							

Table 6.12. *300 mg/L bromuconazole containing solution (EC-Fe, i=20mA/cm^2, 10mM Na_2SO_4, pH= 4.97)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.2	1170.82	0.0	0.0	0.0	0.0	0.0
20	26.3	274.28	76.57	0.01454	36.35	36.35	890.45
40	26.1	251.50	78.52	0.01443	36.07	72.41	883.68
60	26.1	222.11	81.03	0.01443	36.07	108.48	883.68
80	26.2	218.33	81.35	0.01448	36.21	144.69	887.07
Sludge amount (gram)=3.58							

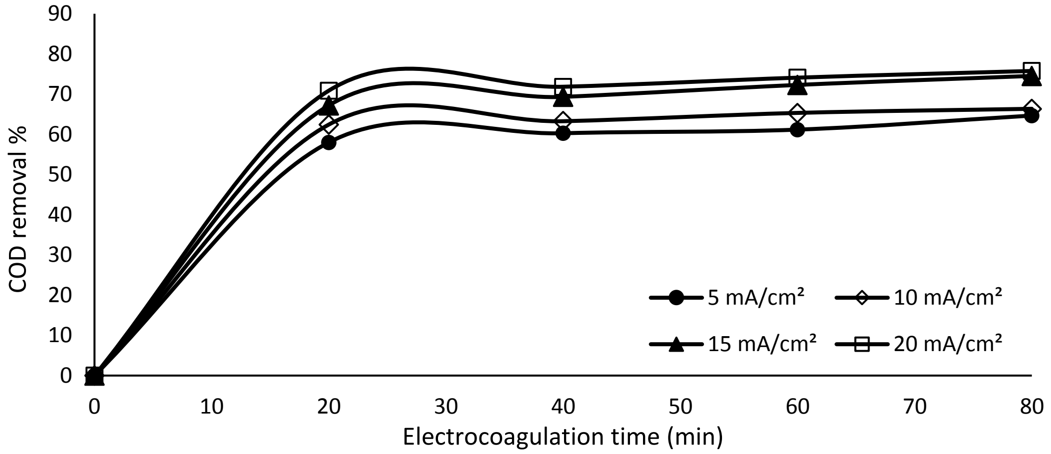

Figure 6.1. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, pH= 5.18)*

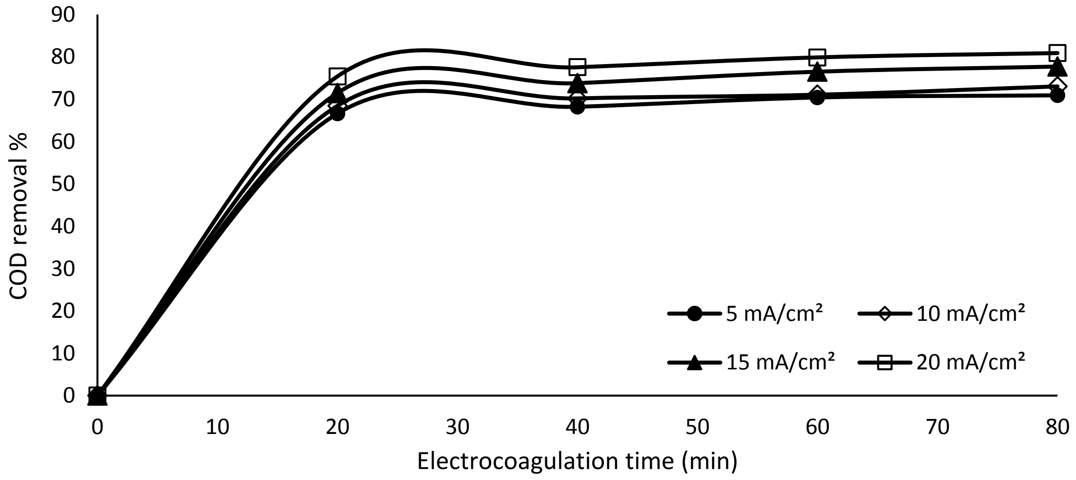

Figure 6.2. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 5mM Na_2SO_4, pH= 5.07)*

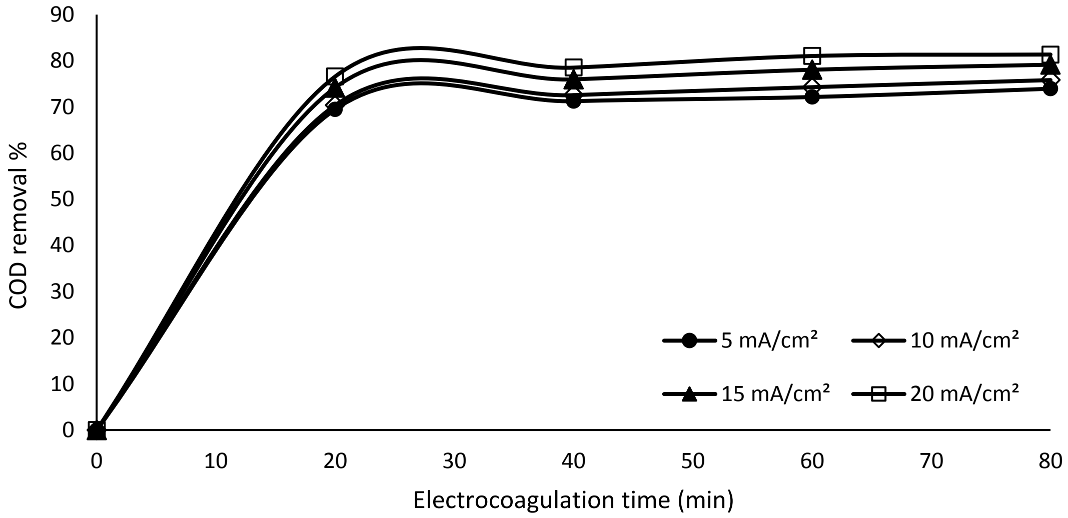

Figure 6.3. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 10mM* Na_2SO_4*, pH= 4.97)*

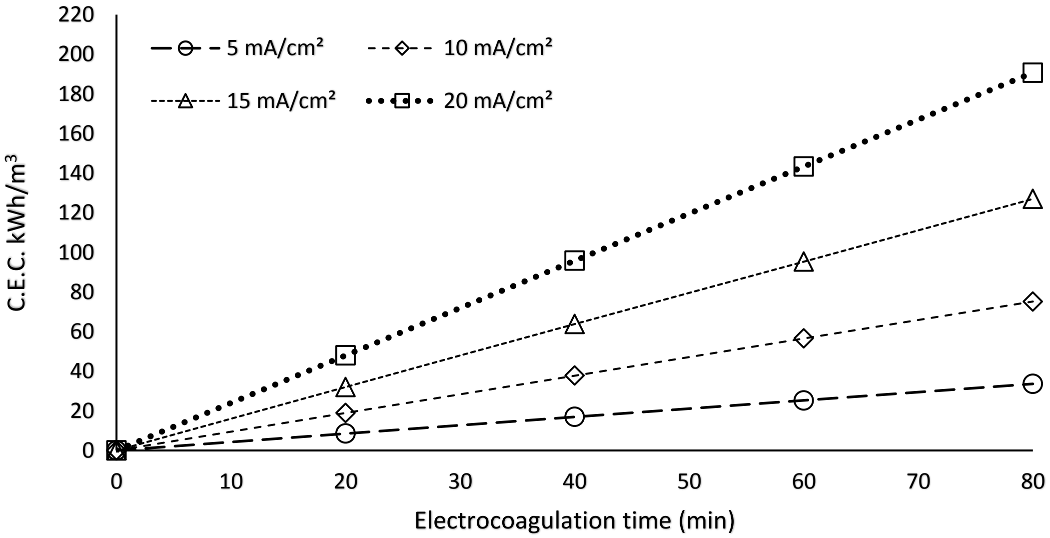

Figure 6.4. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 1mM* Na_2SO_4*, pH= 5.18).*

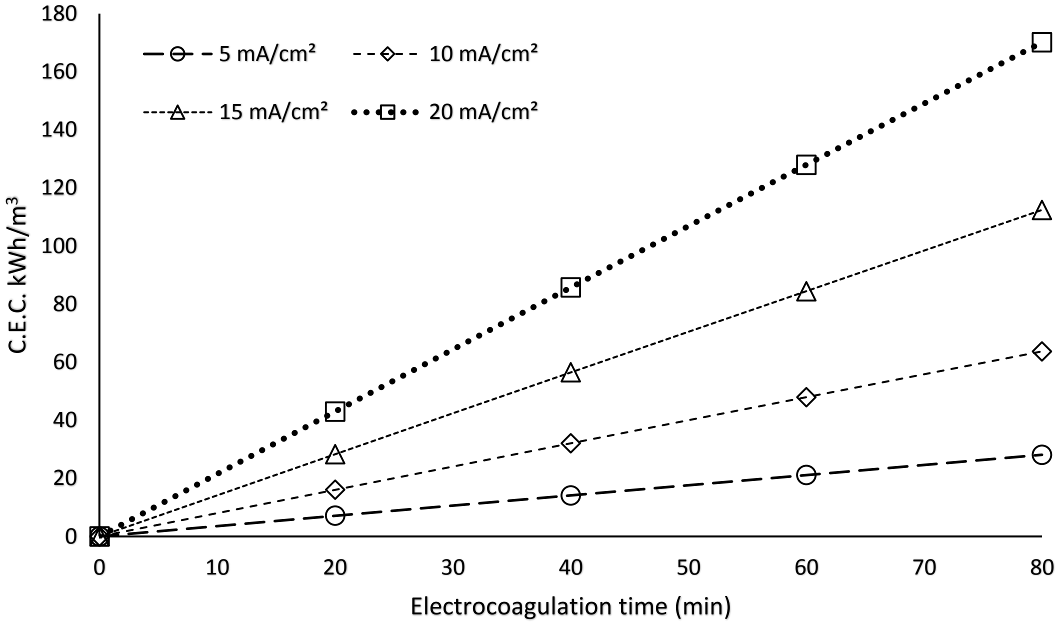

Figure 6.5. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 5mM Na_2SO_4, pH= 5.07)*

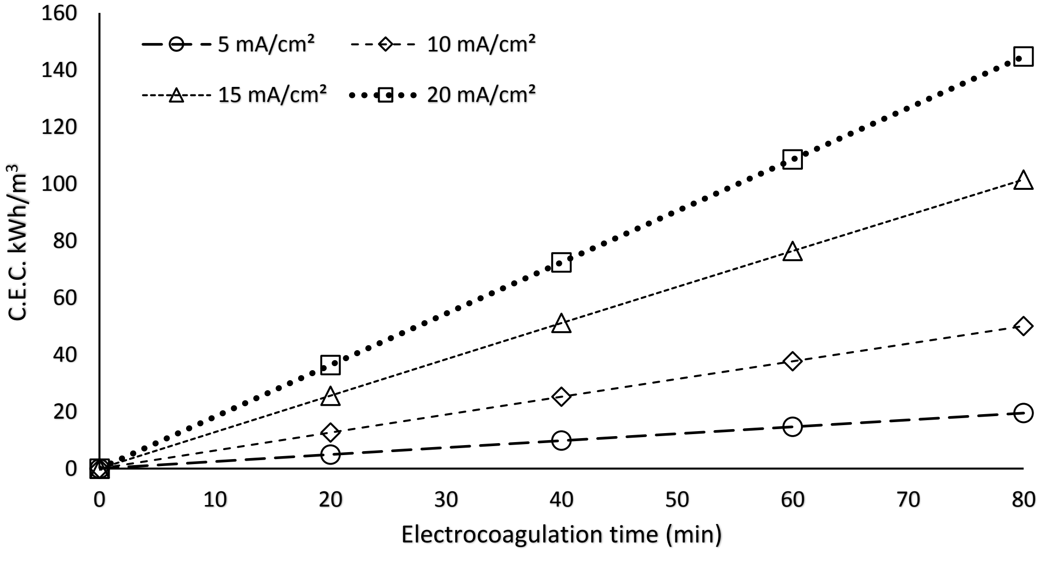

Figure 6.6. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bromuconazole, 10mM Na_2SO_4, pH= 4.97)*

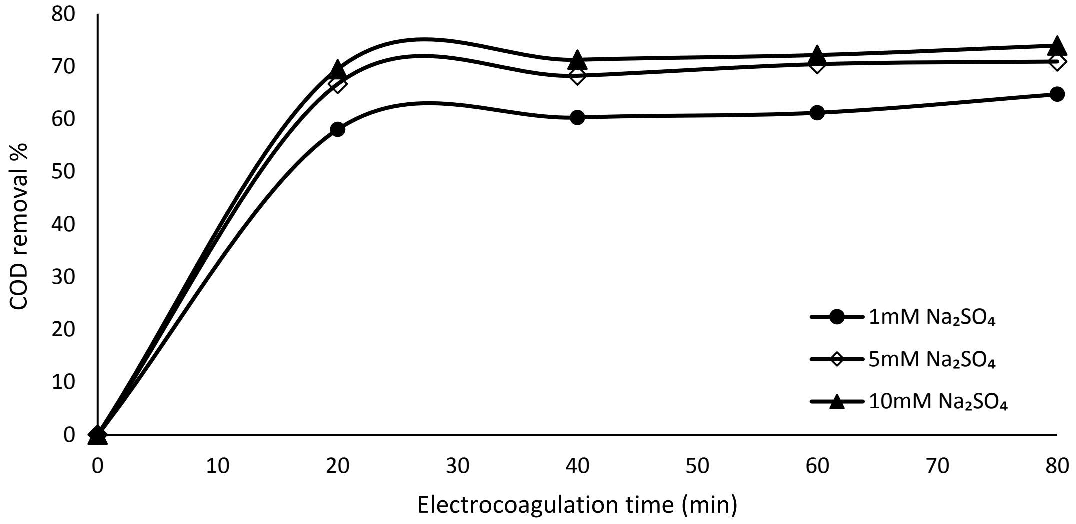

Figure 6.7. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 5mA/cm^2)*

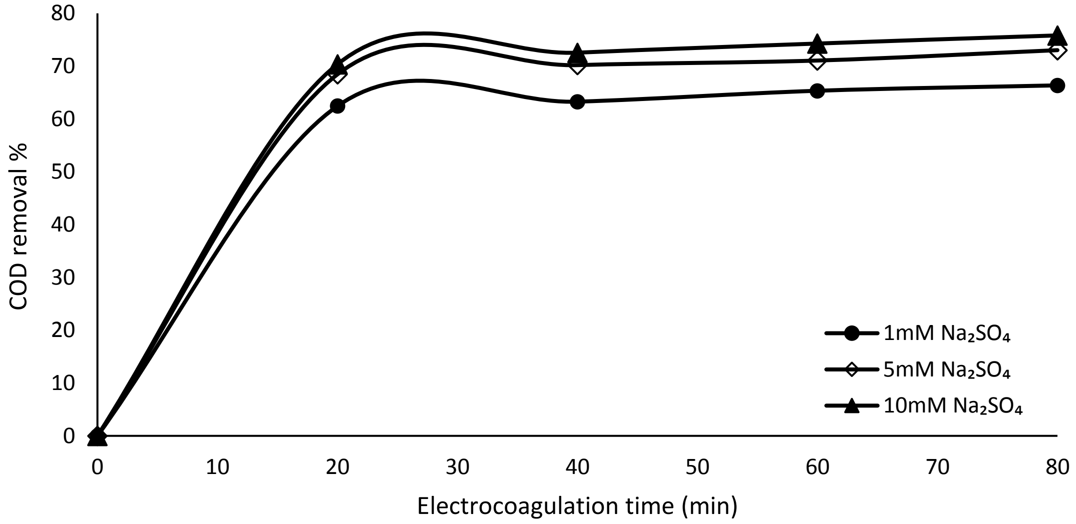

Figure 6.8. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 10mA/cm^2)*

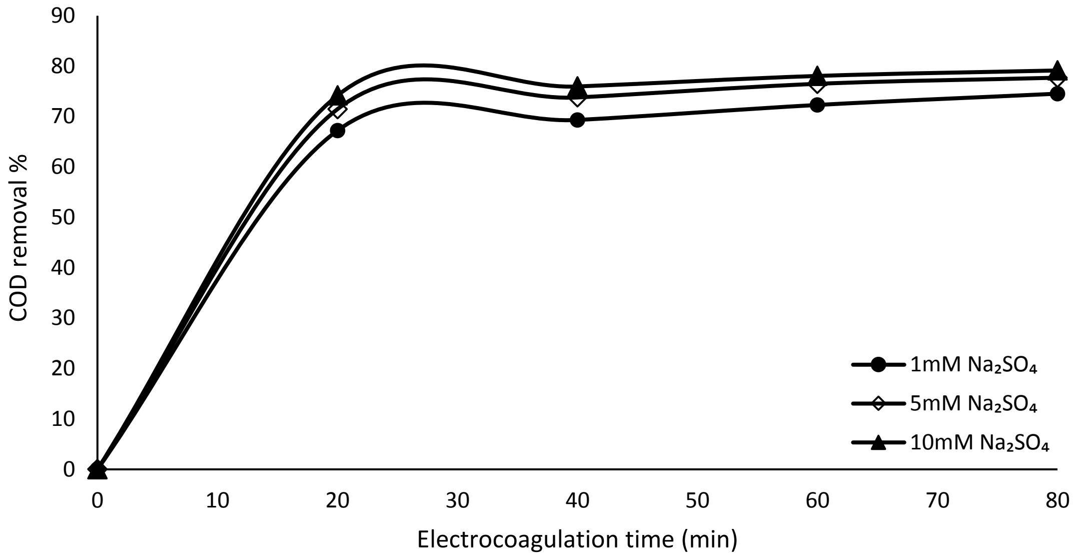

Figure 6.9. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 15mA/cm^2)*

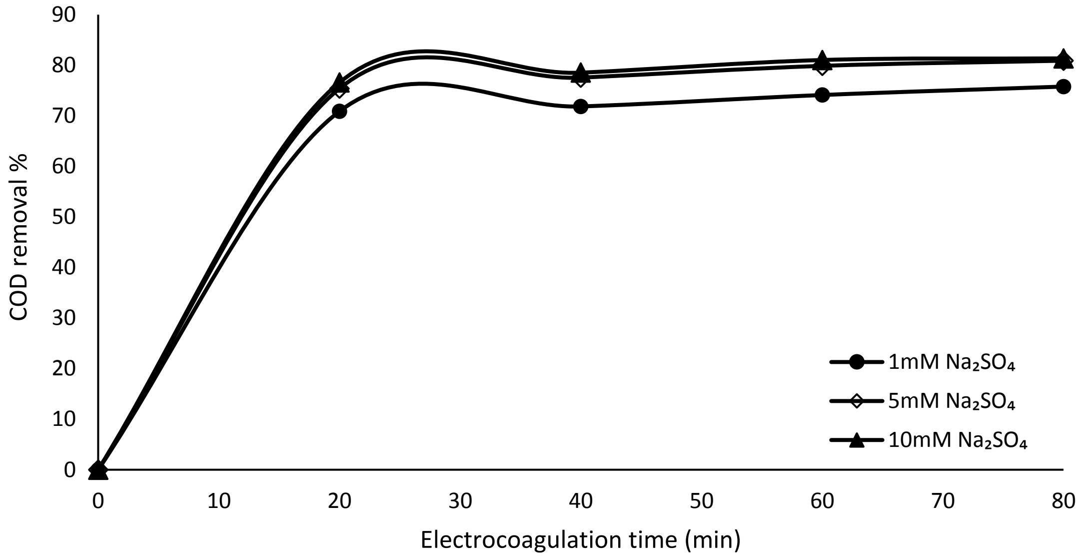

Figure 6.10. *Variation of COD removal over the time depending on support electrolyte concentration (EC Fe, Co= 300 mg/L bromuconazole, 20mA/cm^2)*

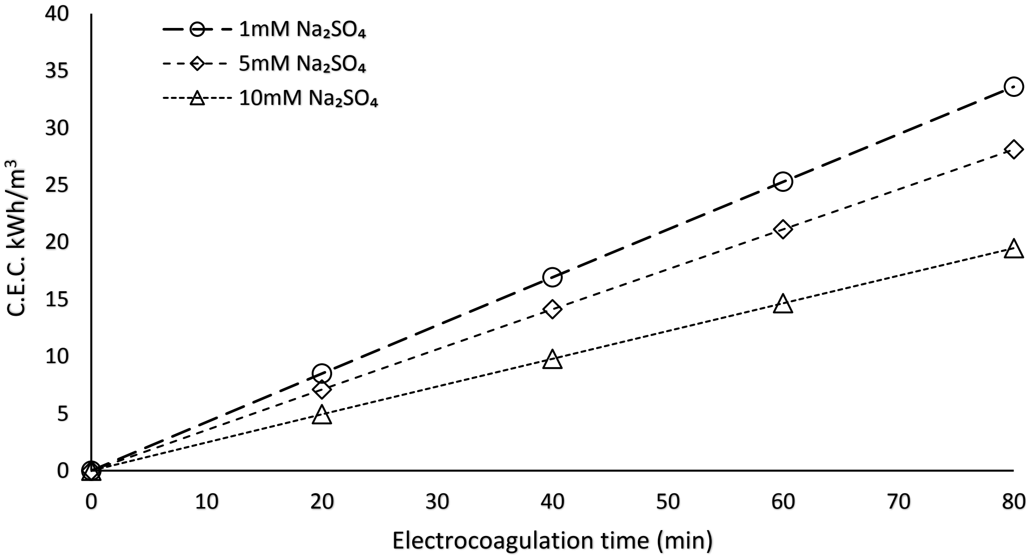

Figure 6.11. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 5mA/cm^2)*

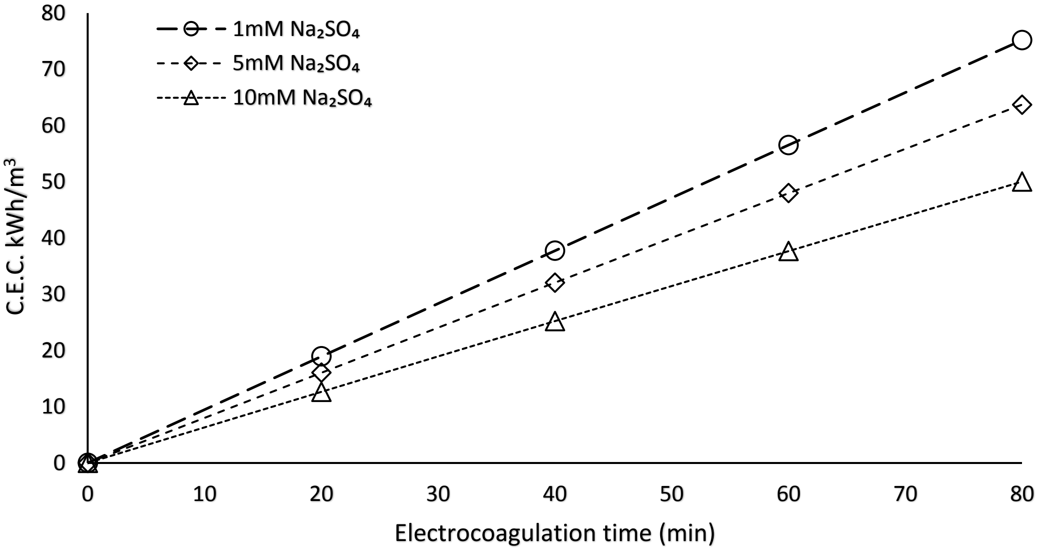

Figure 6.12. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 10mA/cm^2)*

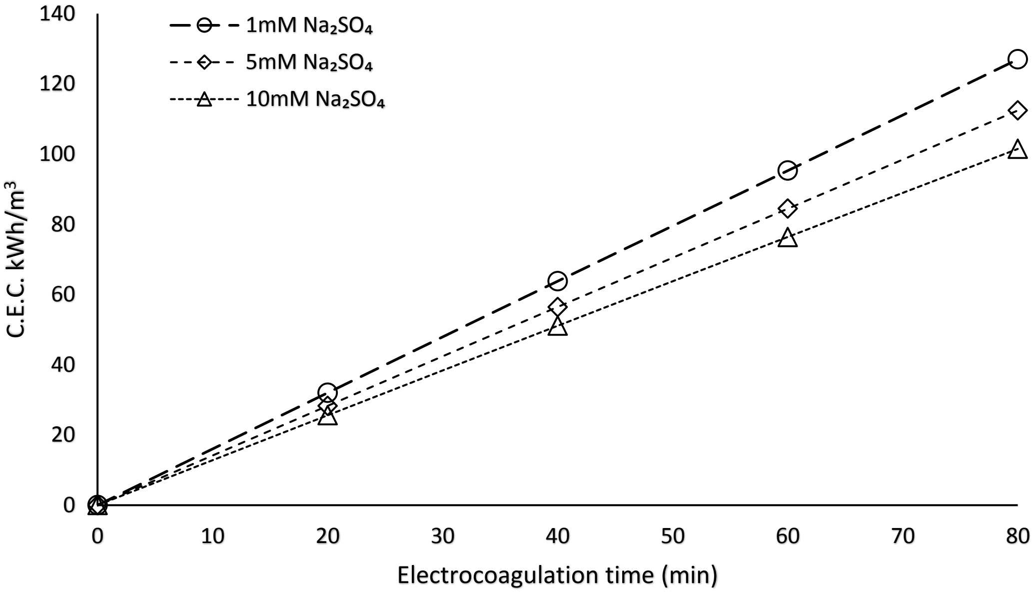

Figure 6.13. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 15mA/cm^2)*

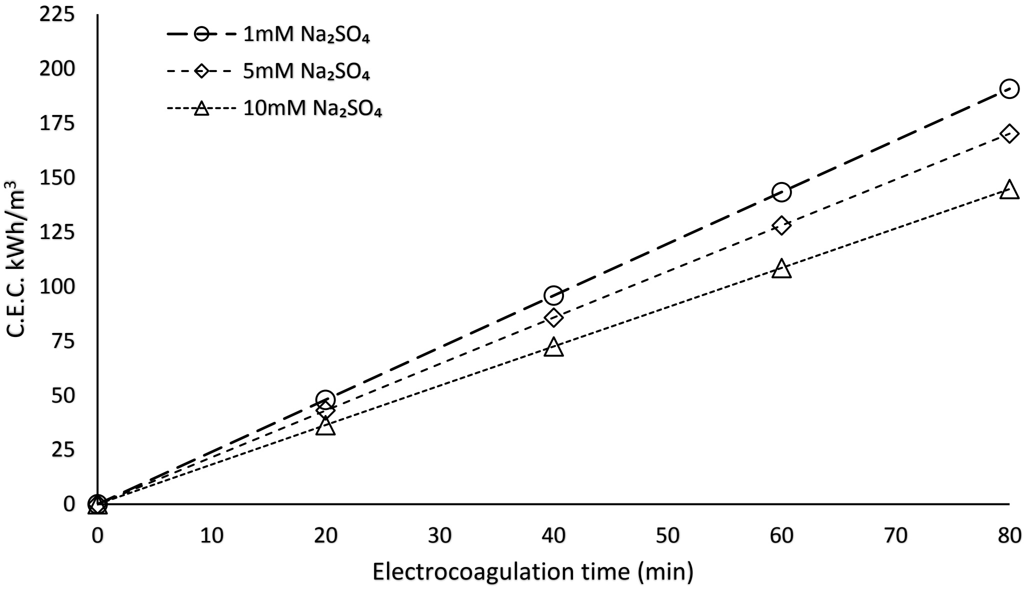

Figure 6.14. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bromuconazole, 20mA/cm^2)*

6.1.2. Electrocoagulation methods using aluminum electrodes

Table 6.13. *300 mg/L Bromuconazole containing solution (EC-Al, i=5mA/cm^2, 10mM Na_2SO_4, pH= 4.91)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	25.2	1142.64	0.0	0.0	0.0	0.0	0.0
20	20.4	391.38	65.75	0.00285	7.13	7.13	174.75
40	20.2	368.75	67.73	0.00283	7.06	14.20	173.04
60	20	346.78	69.65	0.00280	6.99	21.19	171.32
80	20.1	336.26	70.57	0.00281	7.03	28.22	172.18
Sludge amount (gram)= 1.57							

Table 6.14. *300 mg/L Bromuconazole containing solution (EC-Al, i=10mA/cm^2, 10mM Na_2SO_4, pH= 4.91)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	30	1142.64	0.0	0.0	0.0	0.0	0.0
20	25.4	358.75	68.60	0.00702	17.55	17.55	429.99
40	25.1	335.23	70.66	0.00694	17.34	34.89	424.91
60	25	315.32	72.40	0.00691	17.27	52.17	423.22
80	24.8	292.61	74.39	0.00685	17.14	69.30	419.83
Sludge amount (gram)=1.71							

Table 6.15. *300 mg/L Bromuconazole containing solution (EC-Al, i=15mA/cm^2, 10mM Na_2SO_4, pH= 4.91)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	38	1142.64	0.0	0.0	0.0	0.0	0.0
20	32.1	318.75	72.10	0.01325	33.14	33.14	811.85
40	31.7	296.78	74.03	0.01309	32.72	65.86	801.73
60	30.8	276.26	75.82	0.01272	31.79	97.66	778.97
80	30.5	264.32	76.87	0.01259	31.49	129.14	771.38
Sludge amount (gram)= 1.98							

Table 6.16. *300 mg/L Bromuconazole containing solution (EC-Al, i=20mA/cm^2, 10mM Na_2SO_4, pH= 4.91)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	40.3	1142.64	0.0	0.0	0.0	0.0	0.0
20	35.7	288.75	74.73	0.01973	49.34	49.34	1208.72
40	35.5	269.23	76.44	0.01962	49.06	98.39	1201.95
60	34.9	255.32	77.66	0.01929	48.23	146.62	1181.63
80	34.6	242.61	78.77	0.01913	47.82	194.44	1171.47
Sludge amount (gram)= 1.87							

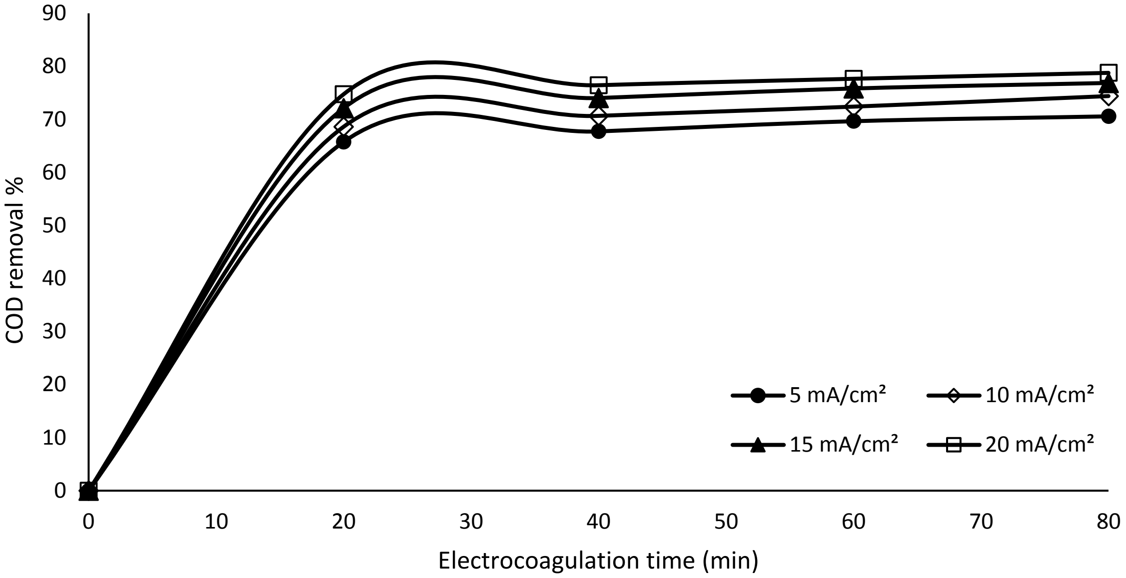

Figure 6.15. *Variation of COD removal over the time depending on current density (EC-Al, Co= 300 mg/L bromuconazole, 10 mM Na_2SO_4, pH= 4.91)*

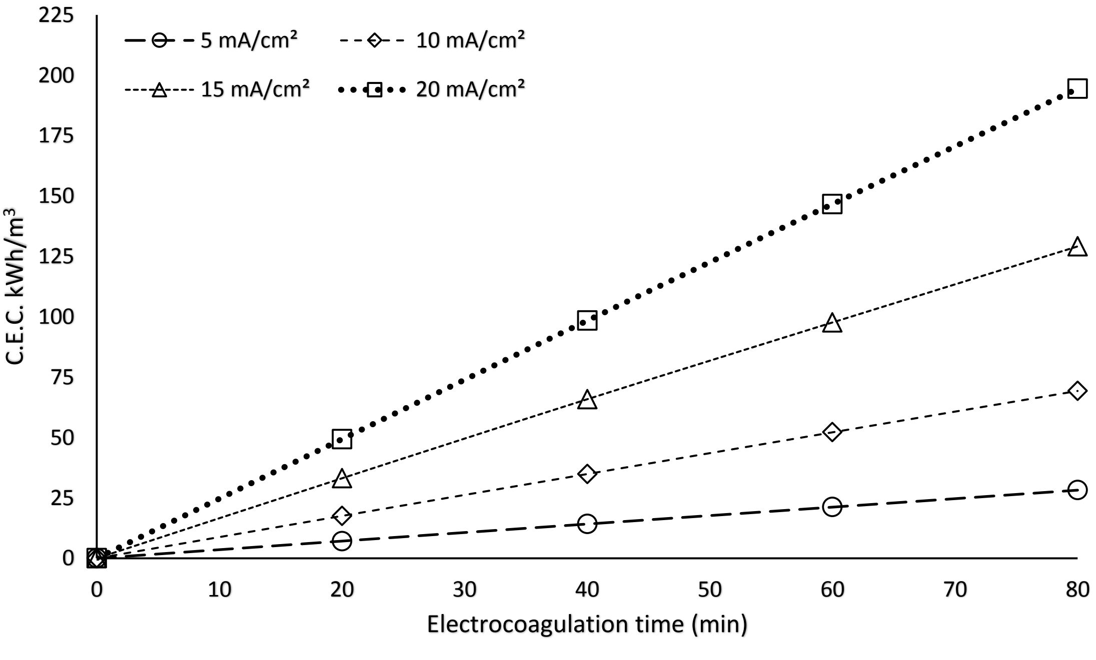

Figure 6.16. *Variation of energy consumption over the time depending on current density (EC-Al, Co= 300 mg/L bromuconazole, 10 mM Na_2SO_4, pH= 4.91)*

6.1.3. Electrocoagulation methods using hybrid (mixed) electrodes

Table 6.17. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=5mA/cm^2, 1mM Na_2SO_4, pH= 5.11)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.5	1192.34	0.0	0.0	0.0	0.0	0.0
20	21.7	408.73	65.72	0.00303	7.59	7.59	185.89
40	21.5	408.73	65.72	0.00301	7.52	15.10	184.17
60	21.3	372.79	68.73	0.00298	7.45	22.55	182.46
80	21.2	347.81	70.83	0.00297	7.41	29.97	181.60
Sludge amount (gram)=1.73							

Table 6.18. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=10mA/cm^2, 1mM Na_2SO_4, pH= 5.11)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	30.8	1192.34	0.0	0.0	0.0	0.0	0.0
20	28.6	378.39	68.26	0.00790	19.76	19.76	484.16
40	28.4	373.1	68.71	0.00785	19.62	39.39	480.78
60	28.1	339.25	71.55	0.00777	19.42	58.80	475.70
80	28	311.92	73.84	0.00774	19.35	78.15	474.00
Sludge amount (gram)=1.87							

Table 6.19. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=15mA/cm^2, 1mM Na_2SO_4, pH= 5.11)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.5	1192.34	0.0	0.0	0.0	0.0	0.0
20	32.9	349.43	70.69	0.01359	33.96	33.96	832.08
40	32.7	339.25	71.55	0.01350	33.76	67.72	827.02
60	32.2	321.97	73.00	0.01330	33.24	100.96	814.38
80	32.2	291.92	75.52	0.01330	33.24	134.20	814.38
Sludge amount (gram)=1.92							

Table 6.20. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=20mA/cm^2, 1mM Na_2SO_4, pH= 5.11)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	39.2	1192.34	0.0	0.0	0.0	0.0	0.0
20	35.5	301.23	74.74	0.01962	49.06	49.06	1201.95
40	35.2	293.17	75.41	0.01946	48.64	97.70	1191.79
60	35.1	274.97	76.94	0.01940	48.51	146.21	1188.40
80	35	253.17	78.77	0.01935	48.37	194.58	1185.02
Sludge amount (gram)= 2.2							

Table 6.21. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=5mA/cm^2, 5mM Na_2SO_4, pH= 5.29)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.1	1175.44	0.0	0.0	0.0	0.0	0.0
20	18.4	339.71	71.10	0.00257	6.43	6.43	157.62
40	18.2	309.34	73.68	0.00255	6.36	12.80	155.90
60	17.9	289.16	75.40	0.00250	6.26	19.06	153.33
80	17.7	269.16	77.10	0.00248	6.19	25.24	151.62
Sludge amount (gram)= 1.83							

Table 6.22. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=10mA/cm^2, 5mM Na_2SO_4, pH= 5.29)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	24.4	1175.44	0.0	0.0	0.0	0.0	0.0
20	21.5	318.56	72.90	0.00594	14.86	14.86	363.97
40	21.2	287.56	75.54	0.00586	14.65	29.50	358.89
60	21	266.23	77.35	0.00580	14.51	44.02	355.50
80	20.9	246.43	79.04	0.00578	14.44	58.46	353.81
Sludge amount (gram)=2.47							

Table 6.23. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=15mA/cm^2, 5mM Na_2SO_4, pH= 5.29)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	31.4	1175.44	0.0	0.0	0.0	0.0	0.0
20	26.2	305.25	74.03	0.01082	27.05	27.05	662.63
40	26.1	273.77	76.71	0.01078	26.94	53.99	660.10
60	26	257.25	78.11	0.01074	26.84	80.83	657.57
80	26.1	233.77	80.11	0.01078	26.94	107.77	660.10
Sludge amount (gram)=2.56							

Table 6.24. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=20mA/cm^2, 5mM Na_2SO_4, pH= 5.29)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	33.1	1175.44	0.0	0.0	0.0	0.0	0.0
20	31.2	251.54	78.60	0.01725	43.12	43.12	1056.36
40	31.1	230.52	80.39	0.01719	42.98	86.10	1052.97
60	30.8	217.71	81.48	0.01703	42.56	128.66	1042.81
80	30.6	202.32	82.79	0.01692	42.29	170.95	1036.04
Sludge amount (gram)=2.73							

Table 6.25. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=5mA/cm^2, 10mM Na_2SO_4, pH= 5.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	12.3	1208.72	0.0	0.0	0.0	0.0	0.0
20	11.9	354.74	70.65	0.00166	4.16	4.16	101.94
40	11.4	312.56	74.14	0.00159	3.99	8.15	97.65
60	11.1	296.74	75.45	0.00155	3.88	12.03	95.08
80	10.9	283.56	76.54	0.00152	3.81	15.84	93.37
Sludge amount (gram)= 2.47							

Table 6.26. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=10mA/cm^2, 10mM Na_2SO_4, pH= 5.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	19.5	1229.56	0.0	0.0	0.0	0.0	0.0
20	15.8	330.57	73.11	0.00437	10.92	10.92	267.47
40	15.5	293.34	76.14	0.00428	10.71	21.63	262.39
60	15.3	274.56	77.67	0.00423	10.57	32.20	259.01
80	15.1	252.23	79.49	0.00417	10.43	42.63	255.62
Sludge amount (gram)= 2.86							

Table 6.27. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=15mA/cm^2, 10mM Na_2SO_4, pH= 5.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	22.9	1229.56	0.0	0.0	0.0	0.0	0.0
20	20.9	300.25	75.58	0.00863	21.58	21.58	528.58
40	20.7	269.64	78.07	0.00855	21.37	42.94	523.53
60	20.5	255.25	79.24	0.00846	21.16	64.11	518.47
80	20.3	231.77	81.15	0.00838	20.96	85.06	513.41
Sludge amount (gram)=2.65							

Table 6.28. *300 mg/L bromuconazole containing solution (EC-Fe-Al, i=20mA/cm^2, 10mM Na_2SO_4, pH= 5.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	26.9	1208.72	0.0	0.0	0.0	0.0	0.0
20	24.9	248.79	79.42	0.01376	34.41	34.41	843.05
40	24.7	226.42	81.27	0.01365	34.13	68.54	836.28
60	24.5	213.38	82.35	0.01354	33.86	102.40	829.51
80	24.3	204.52	83.08	0.01343	33.58	135.98	822.74
Sludge amount (gram)= 3.18							

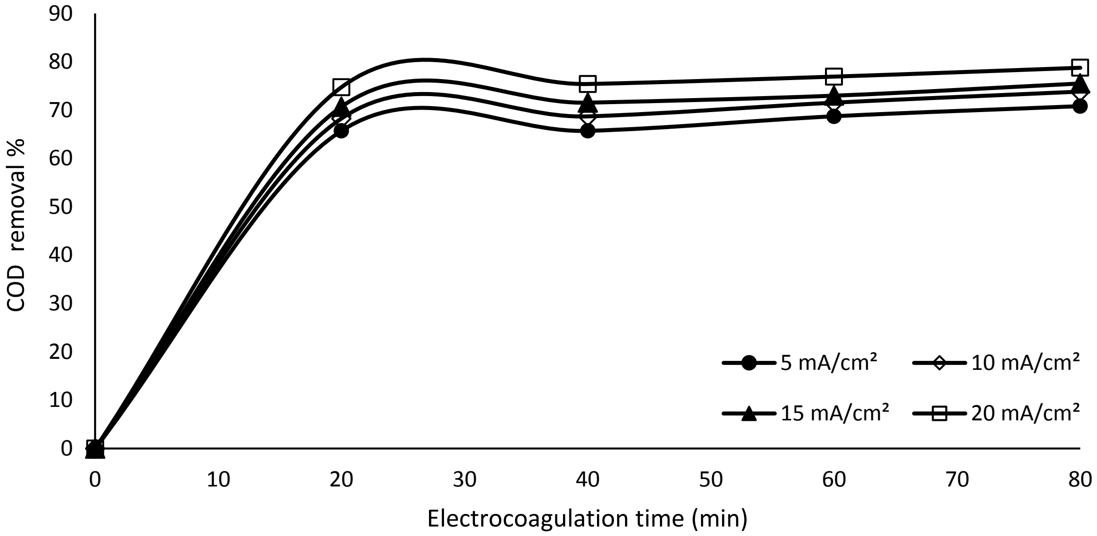

Figure 6.17. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 1mM* Na_2SO_4*, pH= 5.11)*

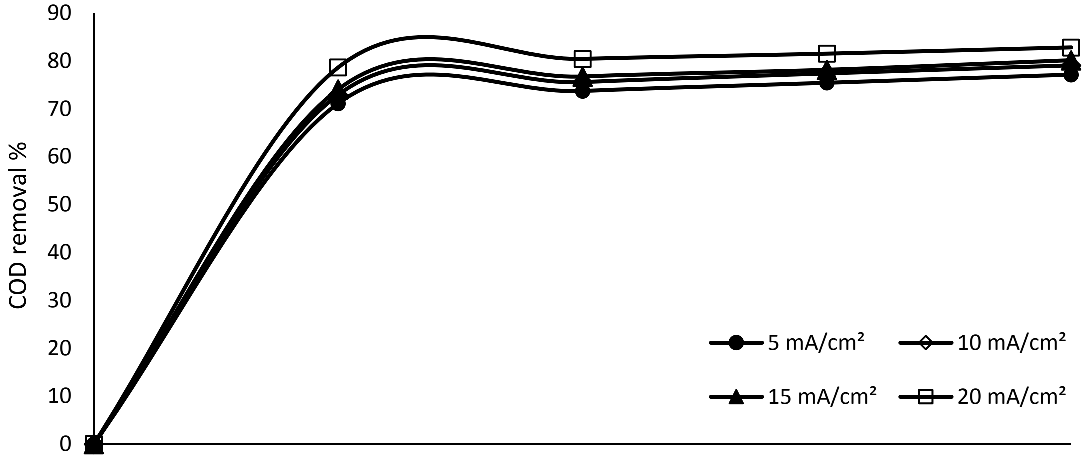

Figure 6.18. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 5mM* Na_2SO_4*, pH= 5.29)*

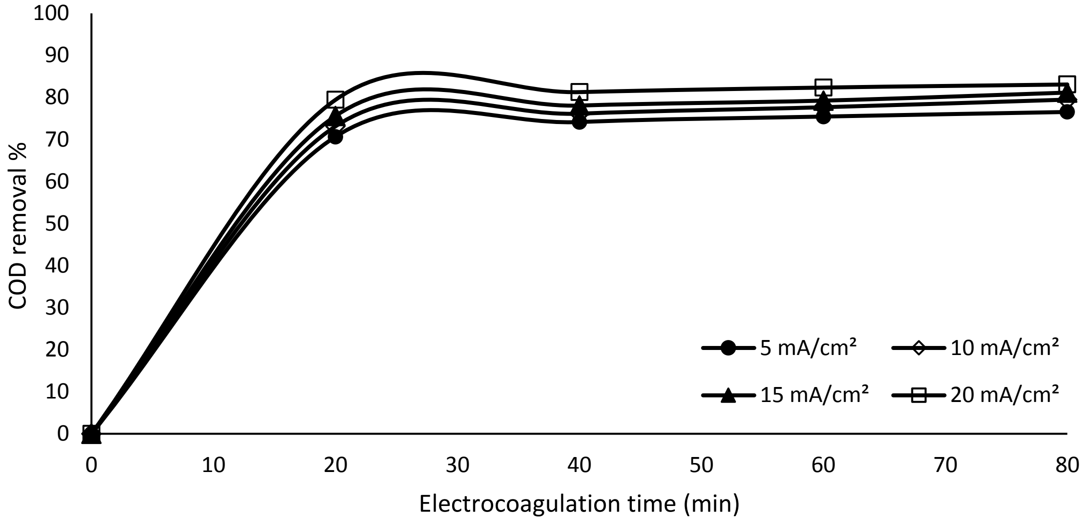

Figure 6.19. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 10 mM Na_2SO_4, pH= 5.2)*

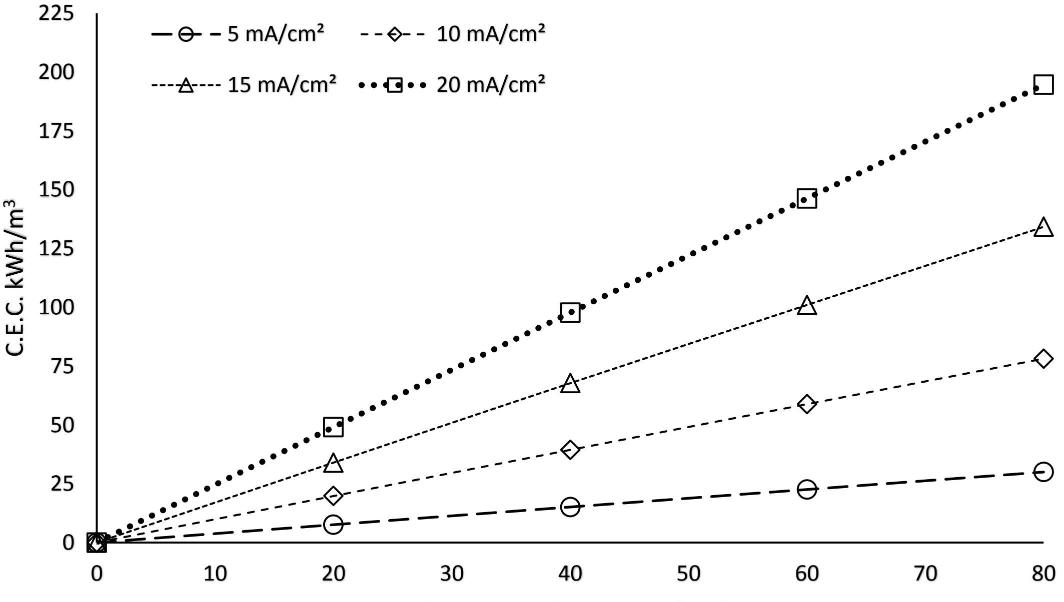

Figure 6.20. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, pH= 5.11)*

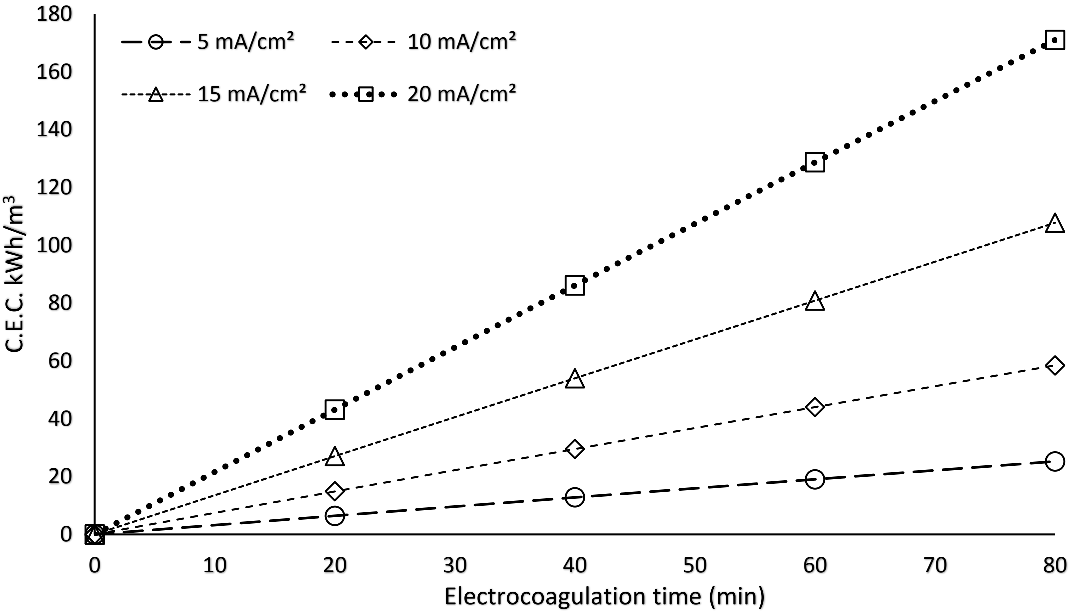

Figure 6.21. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 5mM Na_2SO_4, pH= 5.29)*

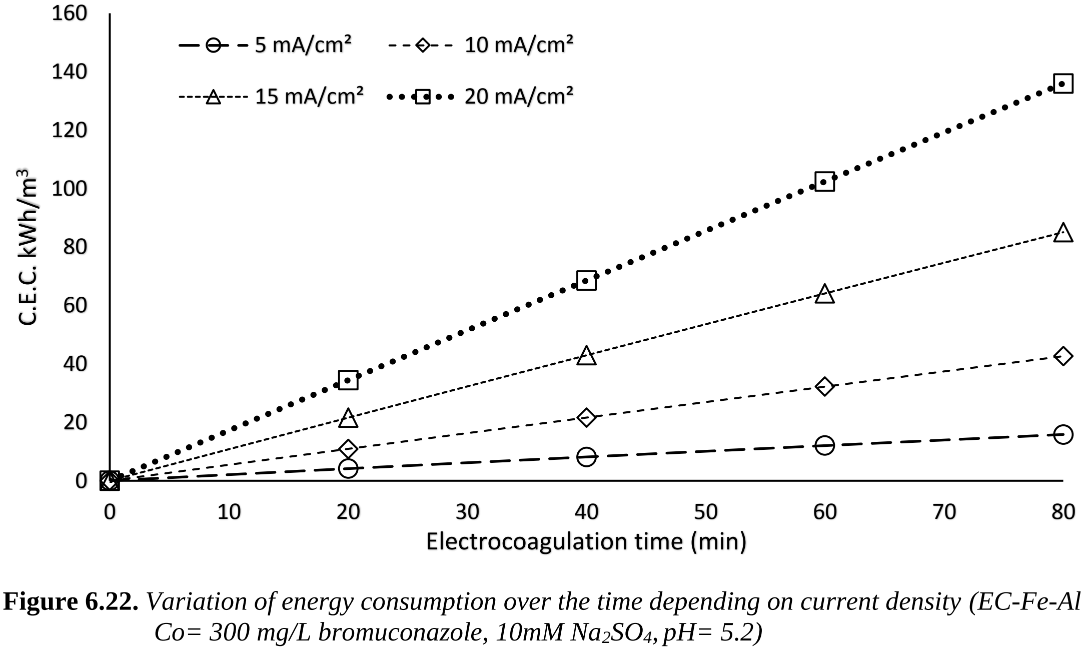

Figure 6.22. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bromuconazole, 10mM Na_2SO_4, pH= 5.2)*

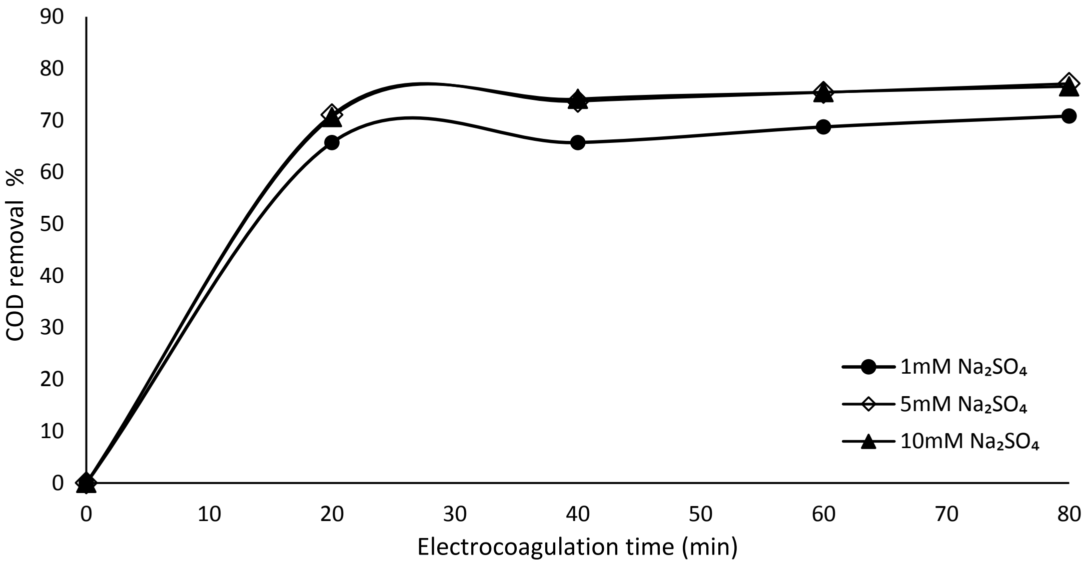

Figure 6.23. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 5mA/cm^2)*

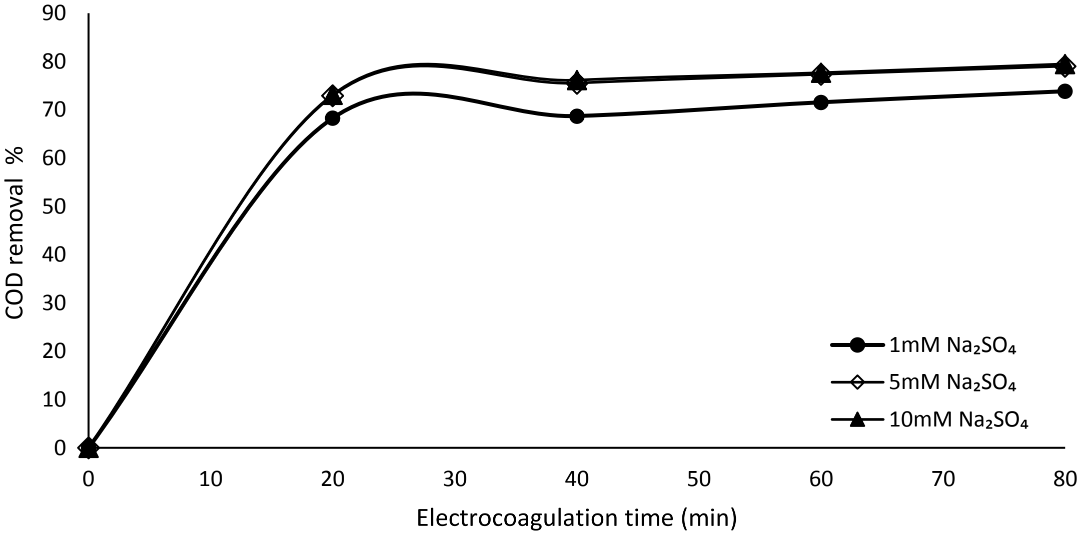

Figure 6.24. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 10 mA/cm^2)*

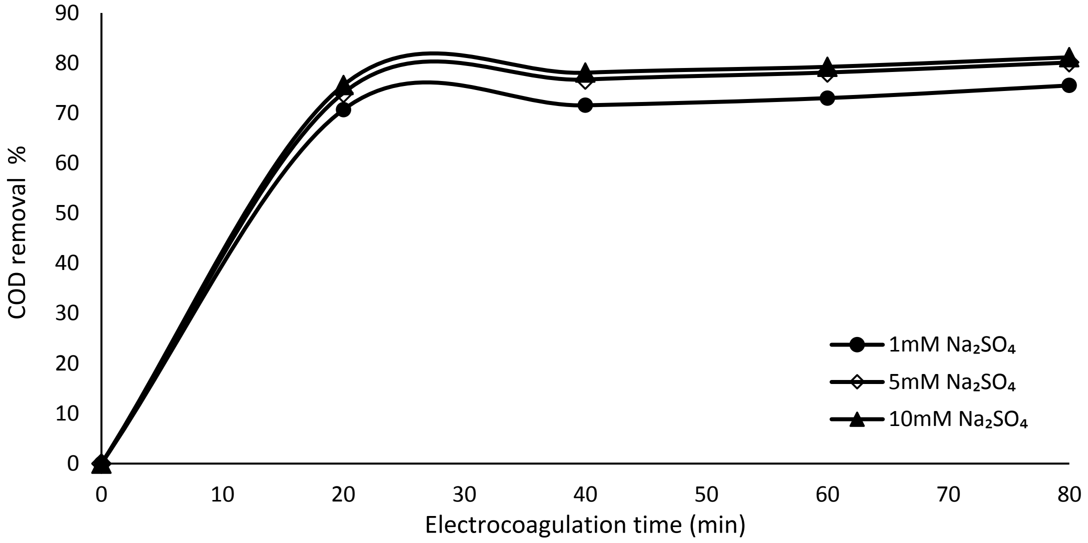

Figure 6.25. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 15mA/cm^2)*

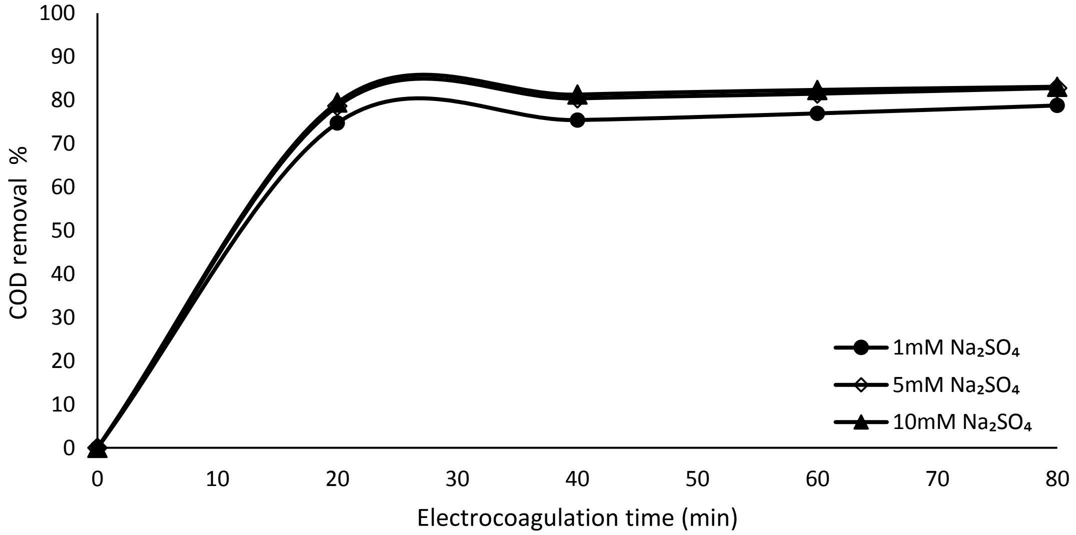

Figure 6.26. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 20mA/cm^2)*

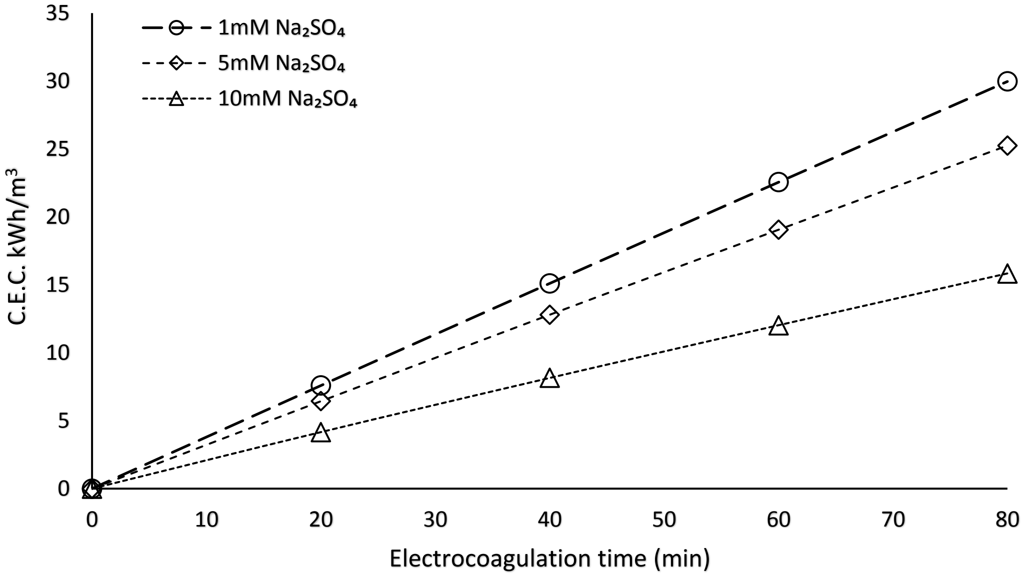

Figure 6.27. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 5mA/cm^2)*

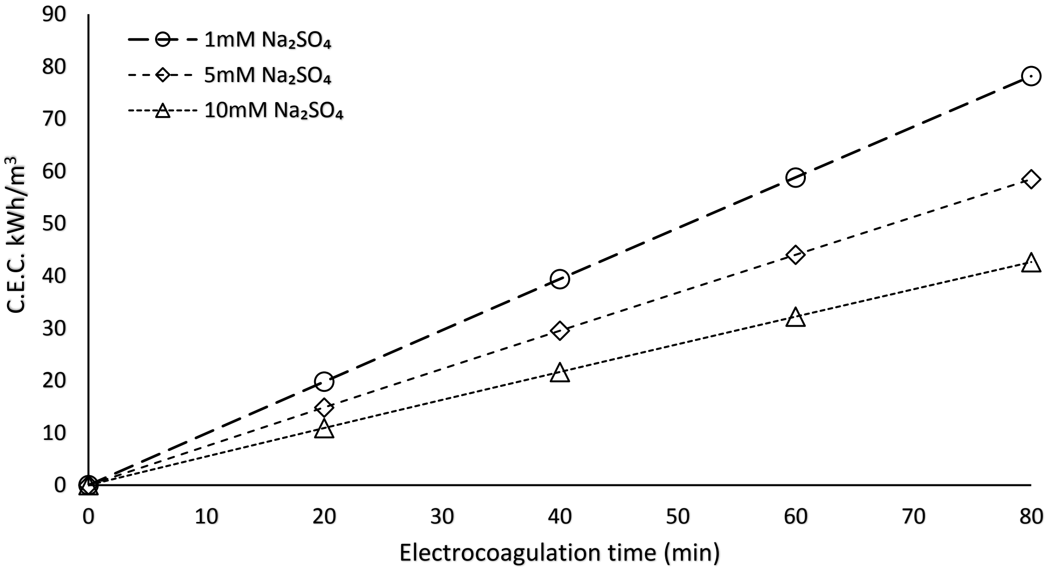

Figure 6.28. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 10mA/cm^2)*

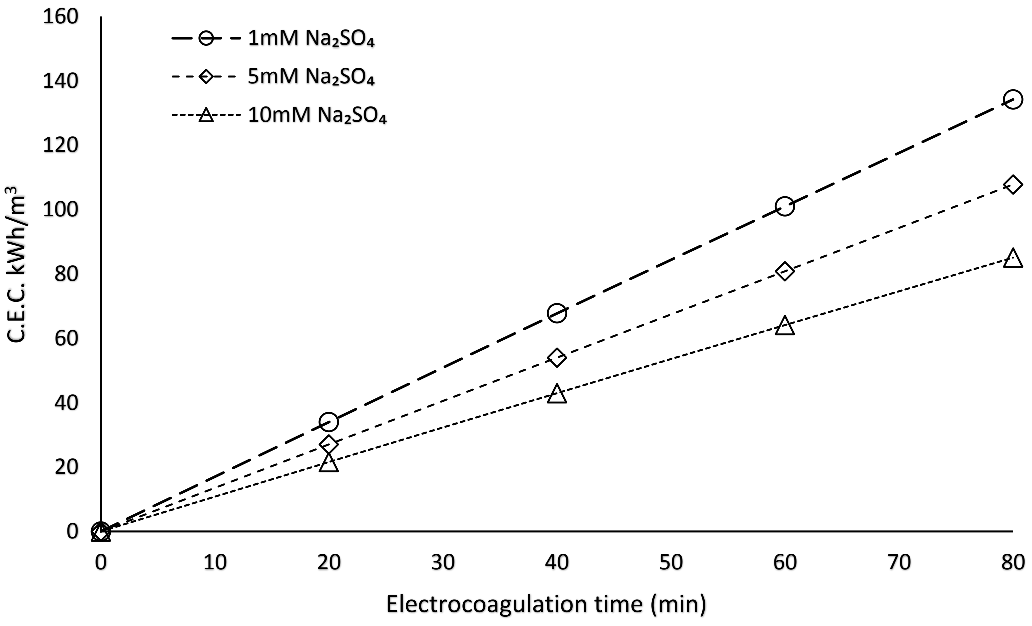

Figure 6.29. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 15mA/cm^2)*

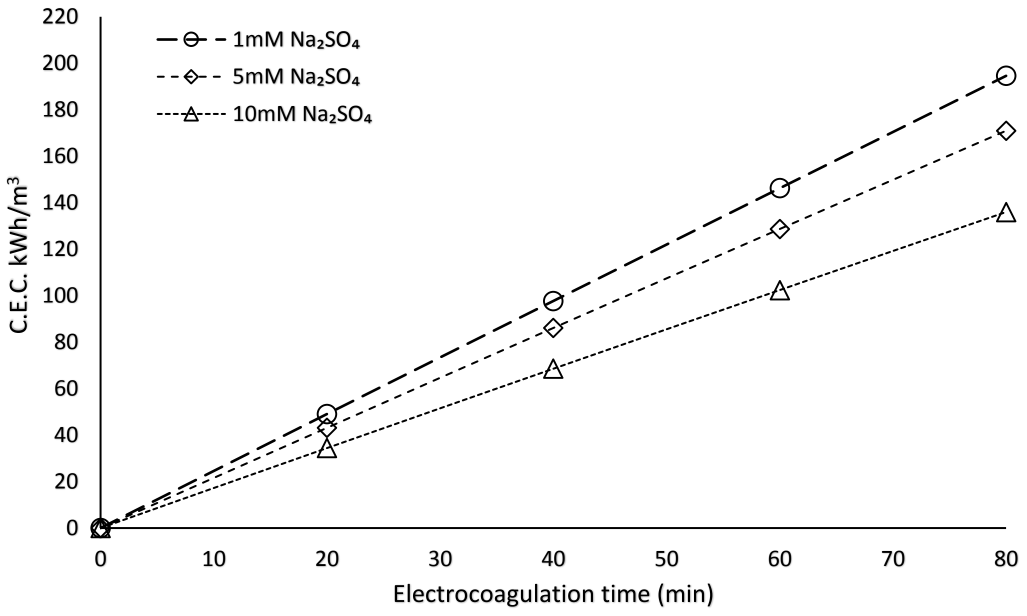

Figure 6.30. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bromuconazole, 20mA/cm^2)*

6.1.4. Electrochemical-Fenton methods

Table 6.29. *300 mg/L bromuconazole containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/L, pH= 4.9)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	24.3	1192.18	0.0	0.0	0.0	0.0	0.0
20	21.3	505.9	57.57	0.00298	7.45	7.45	182.46
40	21.1	467.47	60.79	0.00295	7.38	14.83	180.75
60	20.4	438.68	63.20	0.00285	7.13	21.96	174.75
80	20.5	420.47	64.73	0.00287	7.17	29.13	175.61
Sludge amount (gram)= 0.83							

Table 6.30. *300 mg/L bromuconazole containing solution (EF, i=10 mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/L, pH= 4.9)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	30.8	1196.23	0.0	0.0	0.0	0.0	0.0
20	28.7	467.45	60.79	0.00793	19.83	19.83	485.85
40	28.4	431.69	63.79	0.00785	19.62	39.45	480.78
60	27.9	396.99	66.70	0.00771	19.28	58.73	472.31
80	27.9	372.37	68.77	0.00771	19.28	78.01	472.31
Sludge amount (gram)= 0.74							

Table 6.31. *300 mg/L bromuconazole containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/L, pH= 4.9)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	35.2	1240.33	0.0	0.0	0.0	0.0	0.0
20	32.5	451.62	63.59	0.01342	33.55	33.55	821.96
40	32.3	427.2	65.56	0.01334	33.34	66.89	816.91
60	32.1	385.51	68.92	0.01325	33.14	100.03	811.85
80	31.8	369.12	70.24	0.01313	32.83	132.86	804.26
Sludge amount (gram)= 0.87							

Table 6.32. *300 mg/L bromuconazole containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/L, pH= 4.9)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	36.6	1240.33	0.0	0.0	0.0	0.0	0.0
20	35.2	428.35	65.46	0.01946	48.64	48.64	1191.79
40	35	389.61	68.59	0.01935	48.37	97.01	1185.02
60	34.8	365.8	70.51	0.01924	48.09	145.10	1178.25
80	34.9	337.8	72.77	0.01929	48.23	193.33	1181.63
Sludge amount (gram)= 0.89							

Table 6.33. *300 mg/L bromuconazole containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/L, pH= 4.98)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	22	1217.88	0.0	0.0	0.0	0.0	0.0
20	20.6	382.29	68.61	0.00288	7.20	7.20	176.47
40	20.6	352.74	71.04	0.00288	7.20	14.41	176.47
60	20.4	339.15	72.15	0.00285	7.13	21.54	174.76
80	20.3	314.45	74.18	0.00284	7.10	28.64	173.90
Sludge amount (gram)= 0.93							

Table 6.34. *300 mg/L bromuconazole containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/L, pH= 4.98)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.5	1275.98	0.00	0.0	0.0	0.0	0.0
20	26.6	342.29	71.89	0.00735	18.38	18.38	450.31
40	26.5	316.72	73.99	0.00732	18.31	36.69	448.62
60	26.1	289.46	76.23	0.00721	18.03	54.73	441.84
80	26.1	279.50	77.05	0.00721	18.03	72.76	441.84
Sludge amount (gram)= 0.9							

Table 6.35. *300 mg/L bromuconazole containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/L, pH= 4.98)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.2	1175.98	0.0	0.0	0.0	0.0	0.0
20	30.1	312.45	73.43	0.01243	31.07	31.07	761.26
40	30.1	279.66	76.22	0.01243	31.07	62.14	761.26
60	30	249.15	78.81	0.01239	30.97	93.11	758.74
80	29.8	230.23	80.42	0.01231	30.76	123.88	753.68
Sludge amount (gram)= 1.09							

Table 6.36. *300 mg/L bromuconazole containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/L, pH= 4.98)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	35.8	1094.86	0.0	0.0	0.0	0.0	0.0
20	35.5	267.86	75.53	0.01962	49.06	49.06	1201.95
40	35.2	220.72	79.84	0.01946	48.64	97.70	1191.79
60	35	198.46	81.87	0.01935	48.37	146.07	1185.02
80	34.9	179.50	83.61	0.01929	48.23	194.30	1181.63
Sludge amount (gram)= 0.93							

Table 6.37. *300 mg/L bromuconazole containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/L, pH= 5.05)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.4	1194.86	0.0	0.0	0.0	0.0	0.0
20	19.8	349.61	70.74	0.00277	6.92	6.92	169.62
40	19.6	305.37	74.44	0.00274	6.85	13.78	167.90
60	19.4	282.56	76.35	0.00271	6.78	20.56	166.19
80	19.3	262.15	78.06	0.00270	6.75	27.31	165.33
Sludge amount (gram)= 0.98							

Table 6.38. *300 mg/L bromuconazole containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/L, pH= 5.05)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	26.8	1154.31	0.0	0.0	0.0	0.0	0.0
20	25.2	305.81	73.51	0.00697	17.41	17.41	426.61
40	25	271.34	76.49	0.00691	17.27	34.69	423.22
60	24.8	246.22	78.67	0.00685	17.14	51.82	419.84
80	24.8	226.54	80.37	0.00685	17.14	68.96	419.84
Sludge amount (gram)= 1.12							

Table 6.39. *300 mg/L bromuconazole containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/L, pH= 5.05)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	30.1	1154.31	0.0	0.0	0.0	0.0	0.0
20	28.8	257.57	77.69	0.01189	29.73	29.73	728.39
40	28.7	244.69	78.80	0.01185	29.63	59.36	725.86
60	28.5	221.94	80.77	0.01177	29.42	88.78	720.80
80	28.7	190.36	83.51	0.01185	29.63	118.40	725.86
Sludge amount (gram)= 1.1							

Table 6.40. *300 mg/L bromuconazole containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/L, pH= 5.05)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	34.6	1204.52	0.0	0.0	0.0	0.0	0.0
20	34.2	250.47	79.21	0.01891	47.26	47.26	1157.94
40	34.1	232.36	80.71	0.01885	47.12	94.39	1154.55
60	33.9	207.15	82.80	0.01874	46.85	141.24	1147.78
80	33.9	180.79	84.99	0.01874	46.85	188.08	1147.78
Sludge amount (gram)= 1.19							

Table 6.41. *300 mg/L bromuconazole containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/L, pH= 5.1)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.1	1196.23	0.0	0.0	0.0	0.0	0.0
20	18.7	293.75	75.44	0.00262	6.54	6.54	160.19
40	18.5	272.55	77.22	0.00259	6.47	13.01	318.67
60	18.4	249.12	79.17	0.00257	6.43	19.44	476.29
80	18.1	222.81	81.37	0.00253	6.33	25.77	631.35
Sludge amount (gram)= 0.89							

Table 6.42. *300 mg/L bromuconazole containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/L, pH= 5.1)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	25.5	1196.23	0.00	0.0	0.0	0.0	0.0
20	23.5	272.55	77.22	0.00650	16.24	16.24	397.83
40	23.3	244.64	79.55	0.00644	16.10	32.34	792.27
60	23	227.89	80.95	0.00636	15.89	48.23	1181.64
80	23	208.72	82.55	0.00636	15.89	64.12	1571.00
Sludge amount (gram)= 1.33							

Table 6.43. *300 mg/L bromuconazole containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/L, pH= 5.1)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.4	1219.26	0.00	0.0	0.0	0.0	0.0
20	27.8	247.41	79.71	0.01148	28.70	28.70	703.10
40	27.5	232.27	80.95	0.01136	28.39	57.09	1398.61
60	27.4	210.80	82.71	0.01131	28.29	85.37	2091.59
80	27.5	185.93	84.75	0.01136	28.39	113.76	2787.11
Sludge amount (gram)= 1.21							

Table 6.44. *300 mg/L bromuconazole containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/L, pH= 5.1)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	33.7	1219.26	0.00	0.0	0.0	0.0	0.0
20	33.3	228.22	81.28	0.01841	46.02	46.02	1127.46
40	33.1	207.34	82.99	0.01830	45.74	91.76	2248.16
60	33	178.57	85.35	0.01824	45.60	137.37	3365.46
80	32.8	152.39	87.50	0.01813	45.33	182.69	4476.00
Sludge amount (gram)= 1.39							

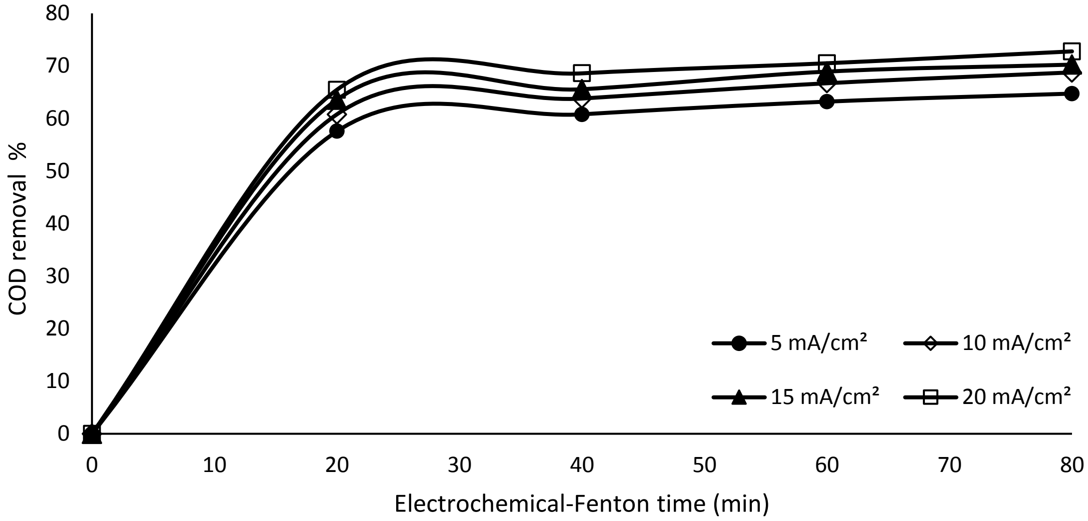

Figure 6.31. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 500mg H_2O_2/L, pH= 4.9)*

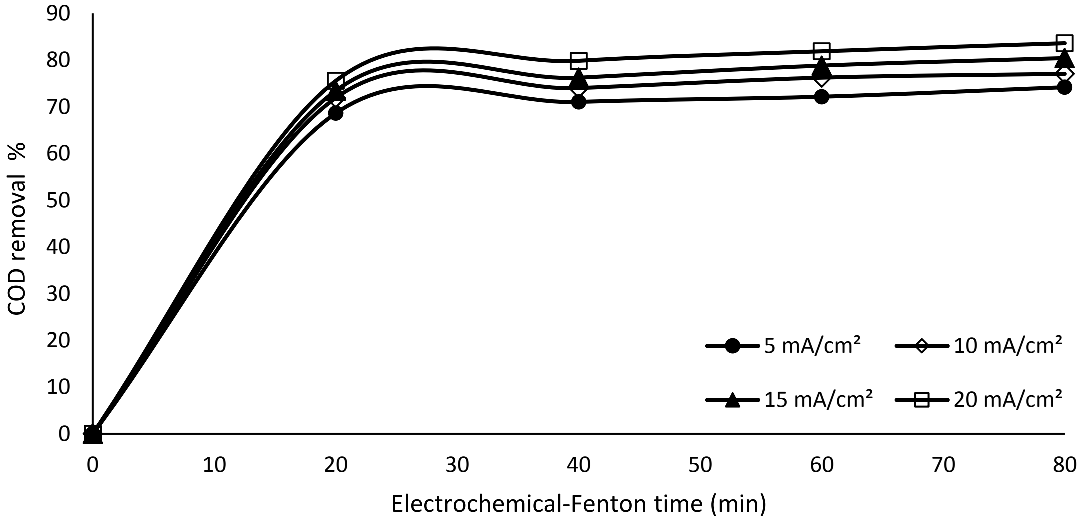

Figure 6.32. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 1000mg H_2O_2/L, pH= 4.98)*

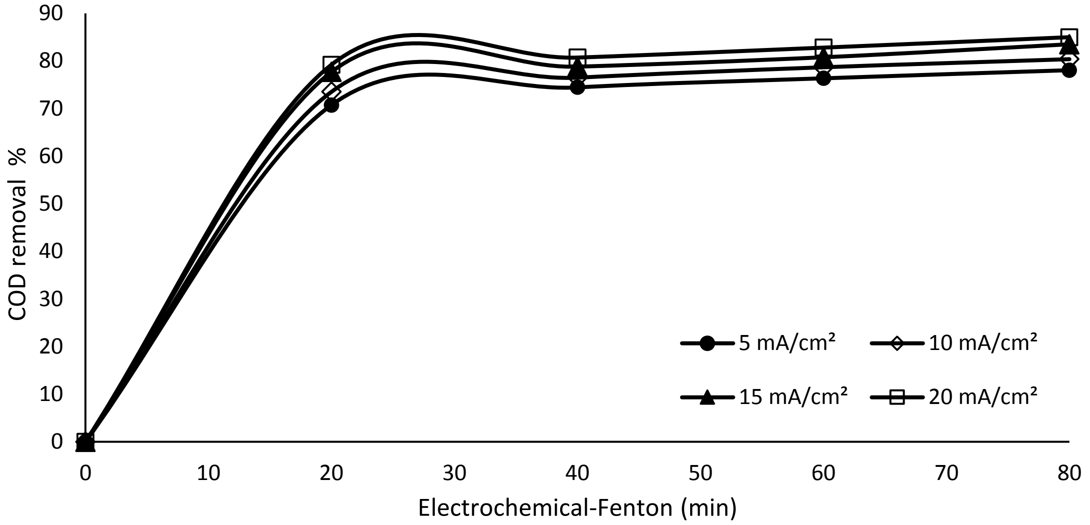

Figure 6.33. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 2000mg H_2O_2/L, pH= 5.05)*

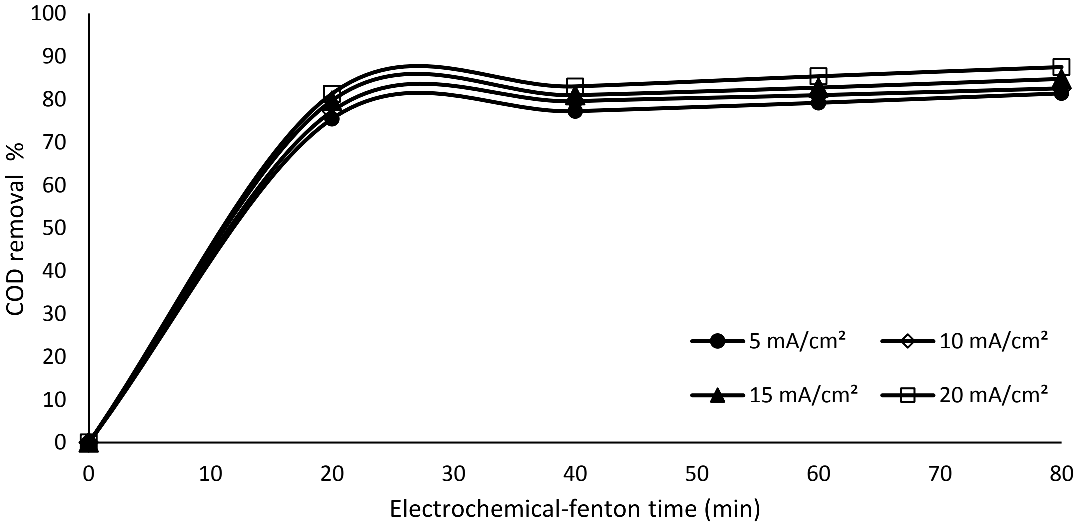

Figure 6.34. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 3000mg H_2O_2/L, pH= 5.1)*

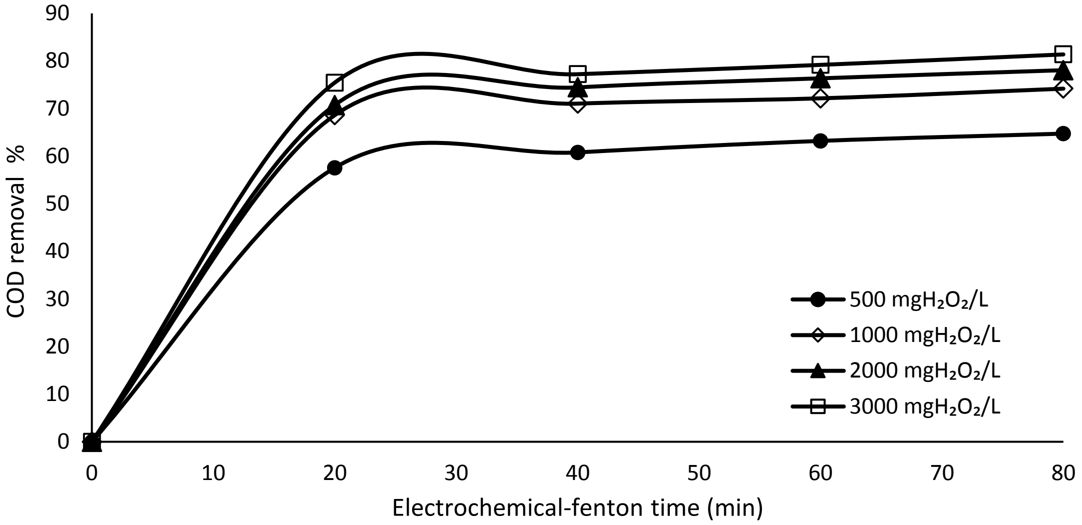

Figure 6.35. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, i=5mA/cm^2, 1mM Na_2SO_4)*

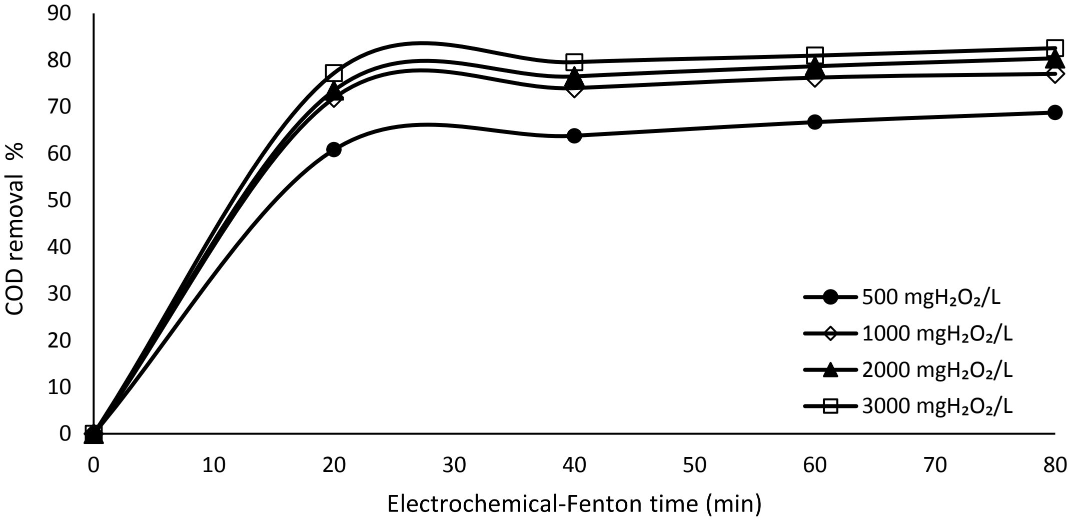

Figure 6.36. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, i=10mA/cm^2, 1mM Na_2SO_4)*

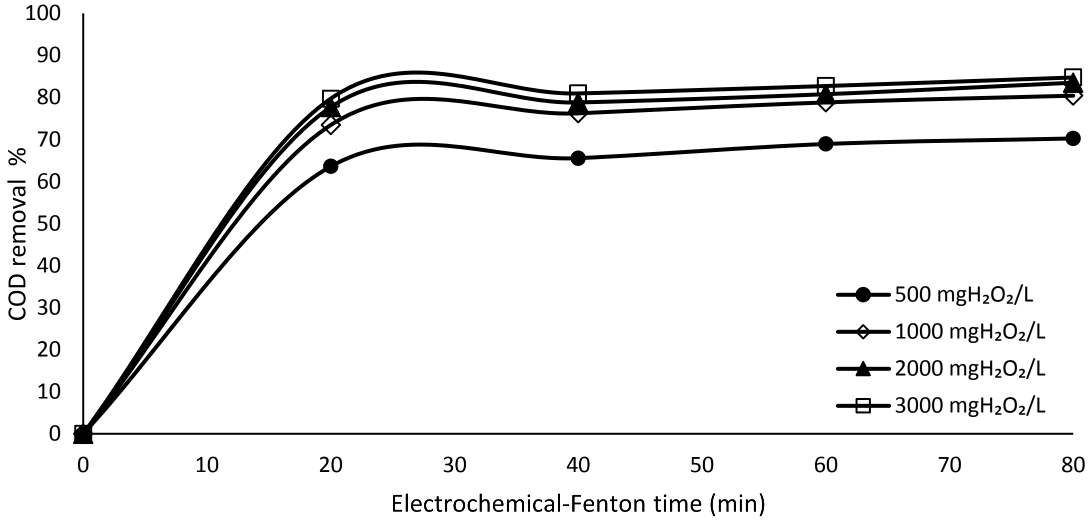

Figure 6.37. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, i=15mA/cm^2, 1mM Na_2SO_4)*

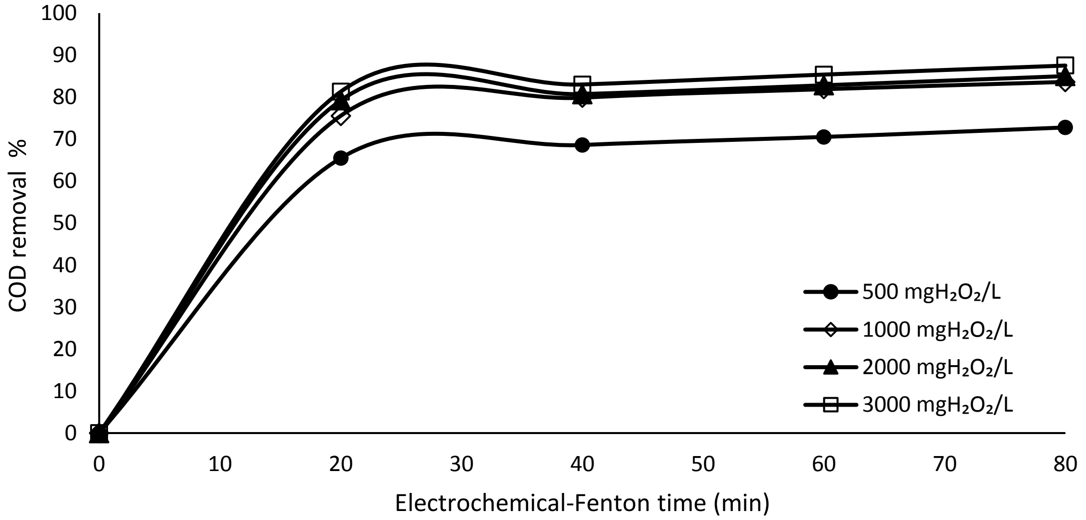

Figure 6.38. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, i=20mA/cm^2, 1mM Na_2SO_4)*

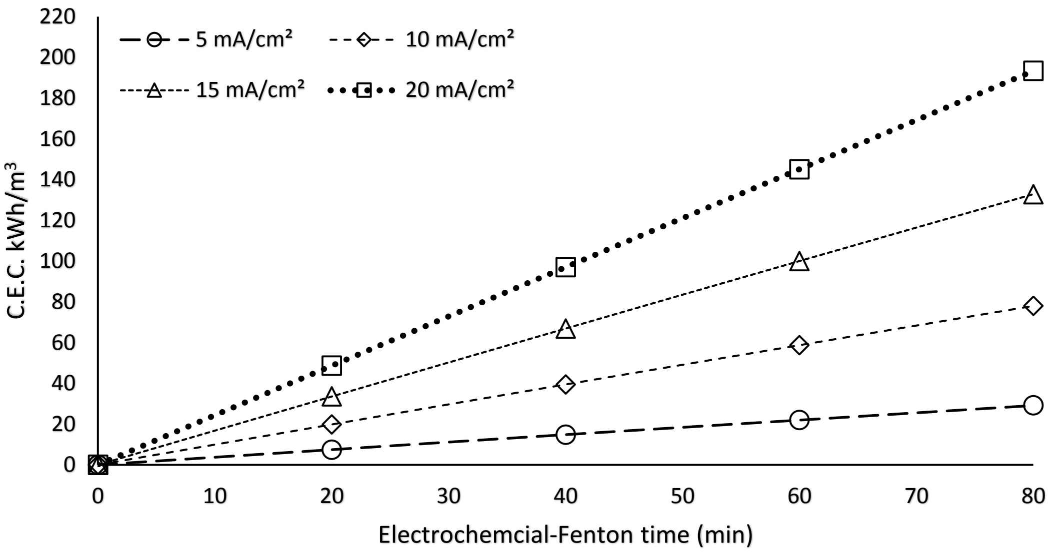

Figure 6.39. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 500 mg H_2O_2/L, pH= 4.9)*

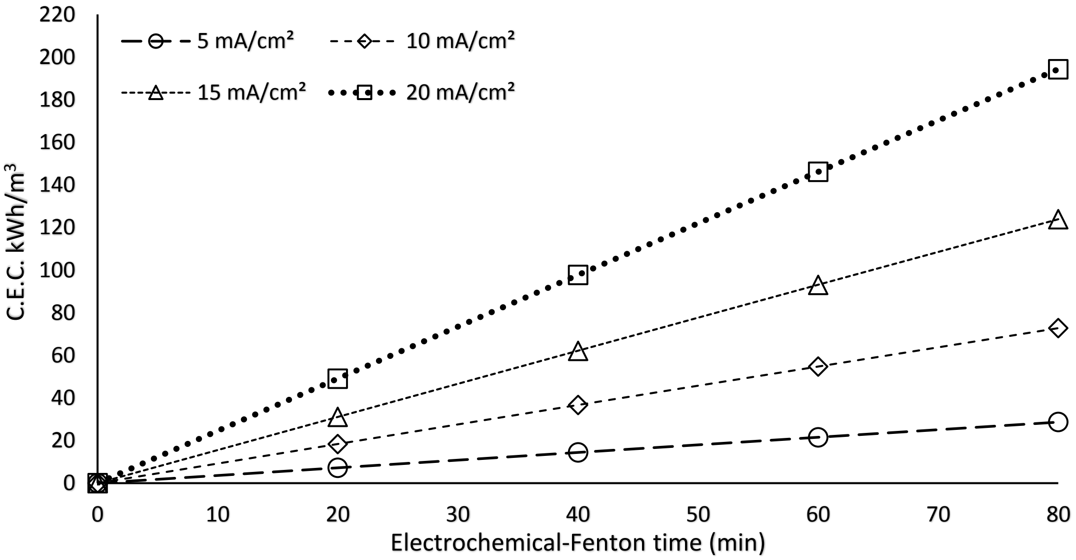

Figure 6.40. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 1000 mg H_2O_2/L, pH= 4.98)*

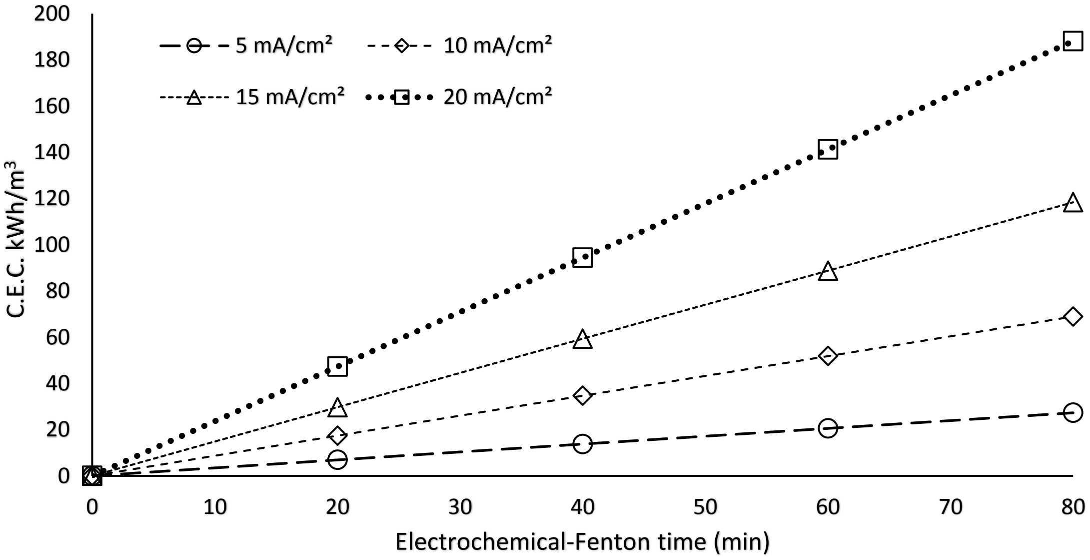

Figure 6.41. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 2000 mg H_2O_2/L, pH= 5.05)*

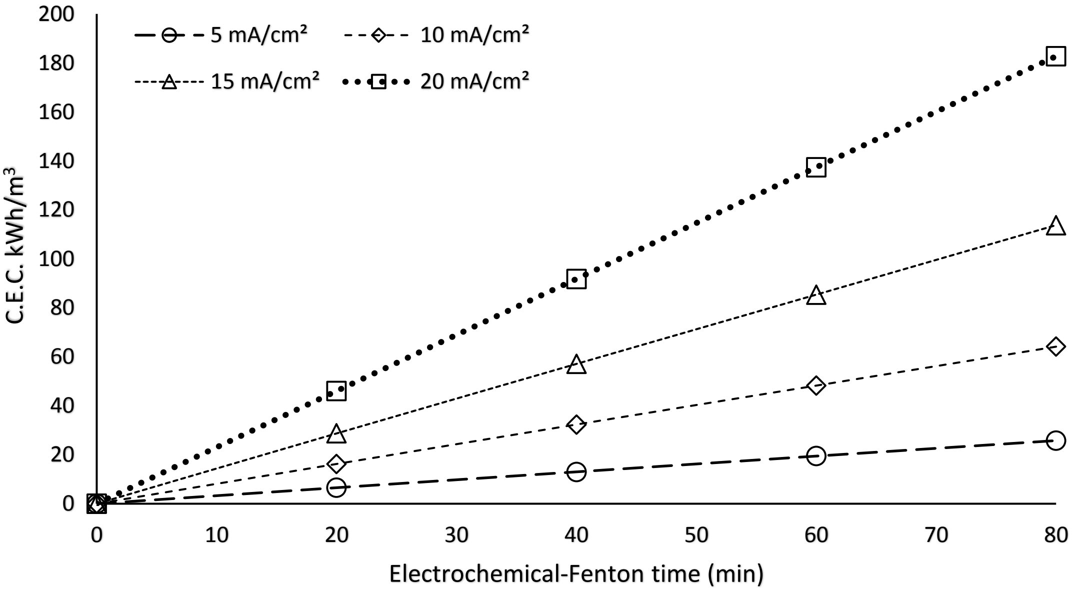

Figure 6.42. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, 3000 mg H_2O_2/L, pH= 5.1)*

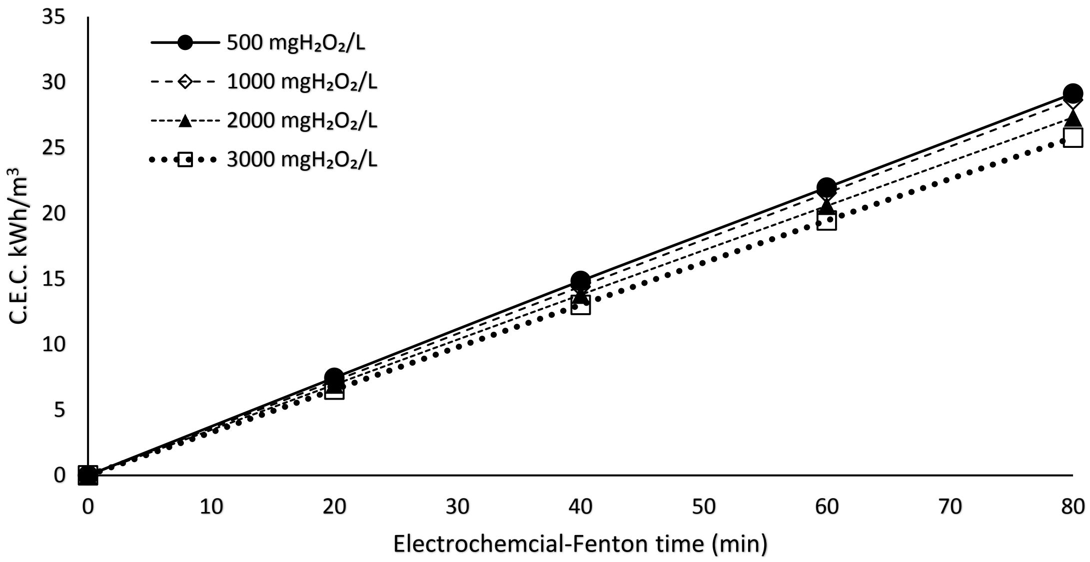

Figure 6.43. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, i=5 mA/cm^2)*

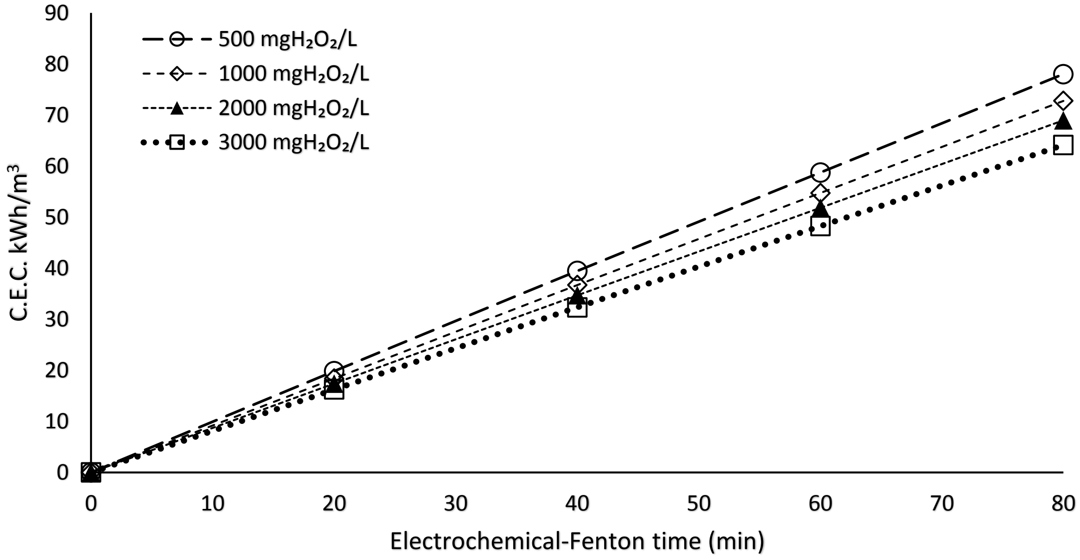

Figure 6.44. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, i=10 mA/cm^2)*

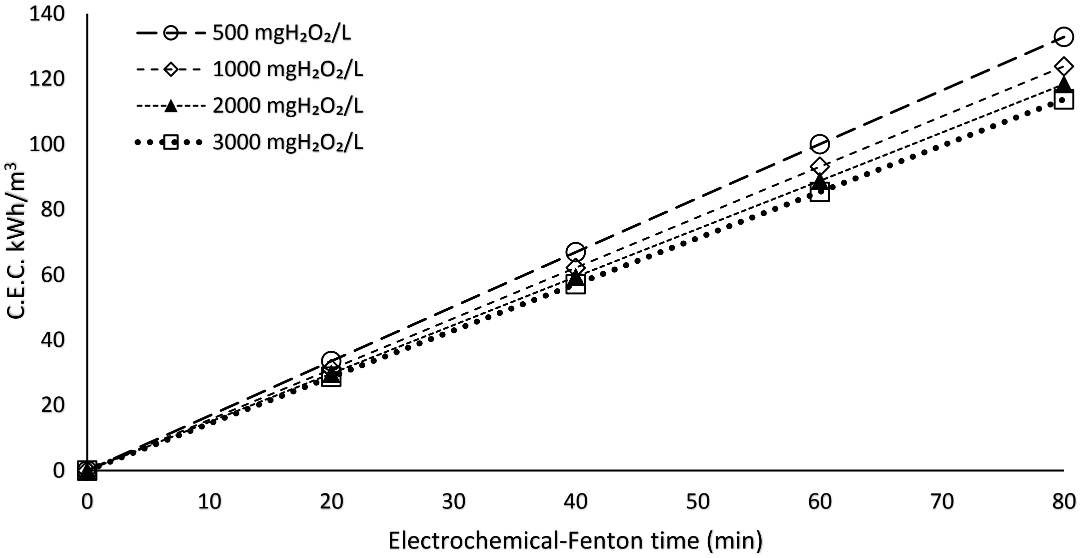

Figure 6.45. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, i=15mA/cm^2)*

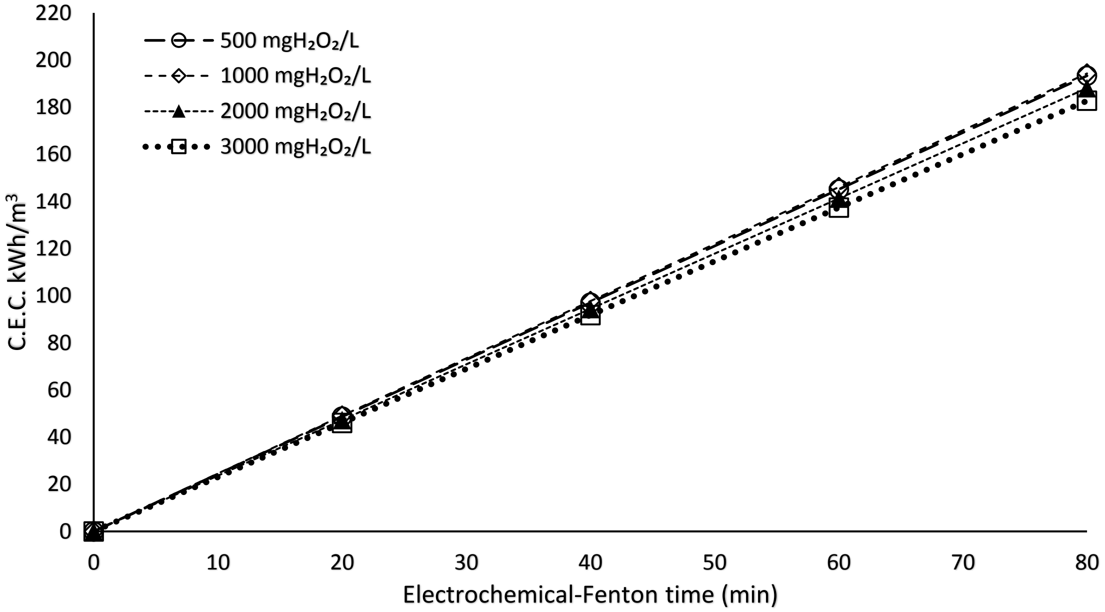

Figure 6.46. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L bromuconazole, 1mM Na_2SO_4, i=20mA/cm^2)*

6.1.5. Electro-oxidation methods using a boron-doped diamond (BDD)

Table 6.45. *300 mg/L bromuconazole containing solution (EO, i=5mA/cm^2, 5mM Na_2SO_4, pH= 4.71)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	5.7	1162.74	0.0	0.0	0.0	0.0	0.0
20	5.4	317.35	72.71	0.00076	1.89	1.89	46.25
40	5.3	296.19	74.53	0.00074	1.85	3.74	45.40
60	5.4	275.23	76.33	0.00076	1.89	5.63	46.25
80	5.1	264.46	77.26	0.00071	1.78	7.41	43.68

Table 6.46. *300 mg/L bromuconazole containing solution (EO, i=10mA/cm^2, 5mM Na_2SO_4, pH= 4.71)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	7.7	1162.74	0.0	0.0	0.0	0.0	0.0
20	7.5	298.57	74.32	0.00207	5.18	5.18	126.96
40	7.5	274.34	76.41	0.00207	5.18	10.36	126.96
60	7.3	260.23	77.62	0.00202	5.04	15.41	123.58
80	7.1	242.25	79.17	0.00196	4.91	20.31	120.19

Table 6.47. *300 mg/L bromuconazole containing solution (EO, i=15mA/cm^2, 5mM Na_2SO_4, pH= 4.71)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	9.2	1162.74	0.0	0.0	0.0	0.0	0.0
20	8.6	239.30	79.42	0.00355	8.88	8.88	217.50
40	8.5	218.14	81.24	0.00351	8.77	17.65	214.97
60	8.3	196.99	83.06	0.00343	8.57	26.22	209.91
80	8.3	183.52	84.22	0.00343	8.57	34.79	209.91

Table 6.48. *300 mg/L bromuconazole containing solution (EO, i=20mA/cm^2, 5mM Na_2SO_4, pH= 4.71)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.4	1162.74	0.0	0.0	0.0	0.0	0.0
20	10	220.00	81.08	0.00553	13.82	13.82	338.57
40	10.1	198.31	82.94	0.00558	13.96	27.78	341.96
60	9.9	185.96	84.01	0.00547	13.68	41.46	335.19
80	9.8	162.17	86.05	0.00542	13.54	55.00	331.80

Table 6.49. *300 mg/L bromuconazole containing solution (EO, i=5mA/cm^2, 10mM Na_2SO_4, pH= 4.87)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	2.6	1183.4	0.0	0.0	0.0	0.0	0.0
20	2.6	271.37	77.05	0.00036	0.91	0.91	22.27
40	2.4	254.21	78.50	0.00034	0.84	1.75	20.55
60	2.4	227.96	80.72	0.00034	0.84	2.59	20.55
80	2.3	198.34	83.23	0.00032	0.80	3.39	19.70

Table 6.50. *300 mg/L bromuconazole containing solution (EO, i=10mA/cm^2, 10mM Na_2SO_4, pH= 4.87)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	4.8	1183.4	0.0	0.0	0.0	0.0	0.0
20	4.8	216.64	81.68	0.00133	3.32	3.32	81.25
40	4.8	186.82	84.20	0.00133	3.32	6.63	81.25
60	4.6	168.12	85.78	0.00127	3.18	9.81	77.87
80	4.5	156.41	86.77	0.00124	3.11	12.92	76.17

Table 6.51. *300 mg/L bromuconazole containing solution (EO, i=15mA/cm^2, 10mM Na_2SO_4, pH= 4.87)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	6.9	1183.4	0.0	0.0	0.0	0.0	0.0
20	6.9	180.36	84.75	0.00285	7.12	7.12	174.51
40	6.6	158.44	86.60	0.00273	6.81	13.94	166.92
60	6.7	140.44	88.12	0.00277	6.92	20.85	169.45
80	6.7	119.57	89.89	0.00277	6.92	27.77	169.45

Table 6.52. *300 mg/L bromuconazole containing solution (EO, i=20mA/cm2, 10mM Na2SO4, pH= 8.42*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	7.6	1183.4	0.0	0.0	0.0	0.0	0.0
20	7.6	143.25	87.88	0.00420	10.50	10.50	257.31
40	7.3	126.87	89.27	0.00404	10.09	20.59	247.16
60	7.4	113.25	90.42	0.00409	10.23	30.82	250.54
80	7.3	92.00	92.22	0.00404	10.09	40.91	247.16

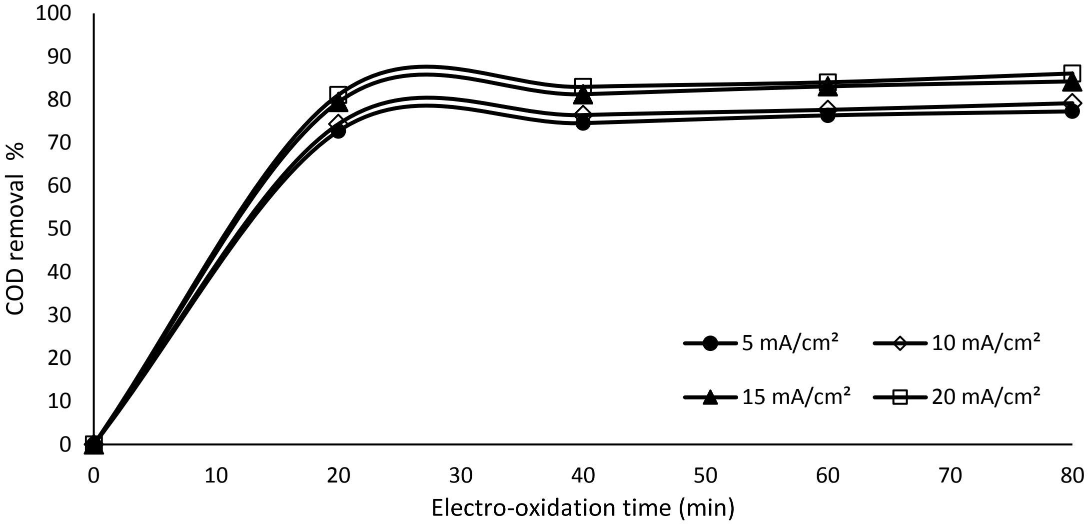

Figure 6.47. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bromuconazole, 5mM* Na_2SO_4*, pH= 4.71)*

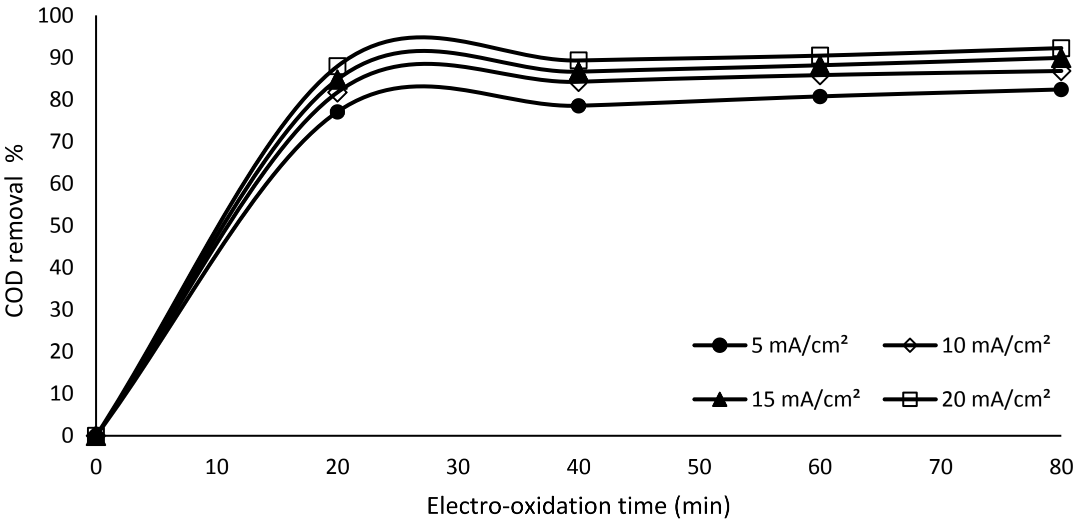

Figure 6.48. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bromuconazole, 10 mM* Na_2SO_4*, pH= 4.87)*

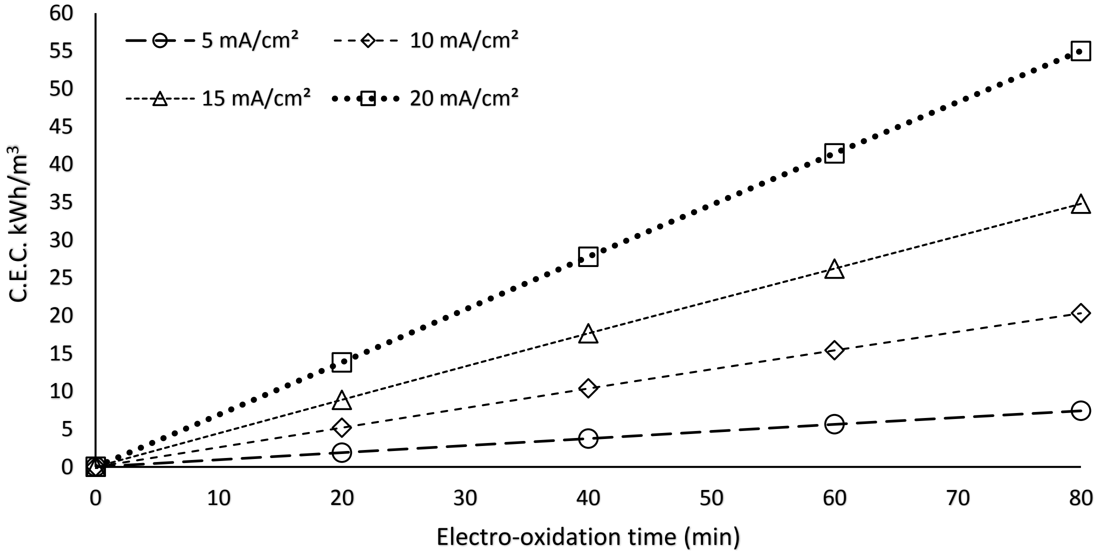

Figure 6.49. *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bromuconazole, 5mM* Na_2SO_4*, pH= 4.71)*

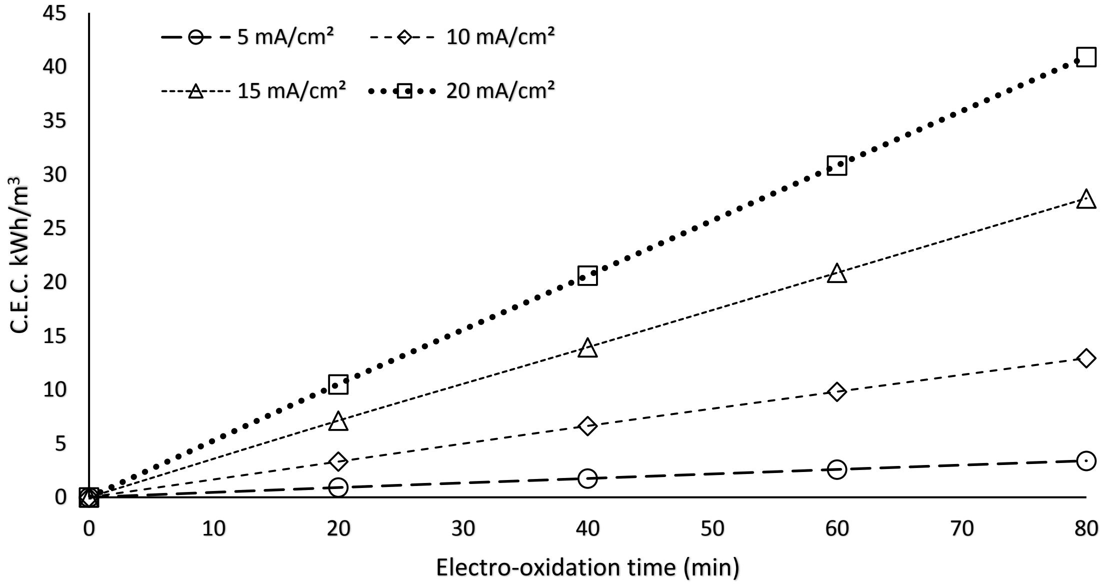

Figure 6.50. *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bromuconazole, 10 mM* Na_2SO_4*, pH= 4.87)*

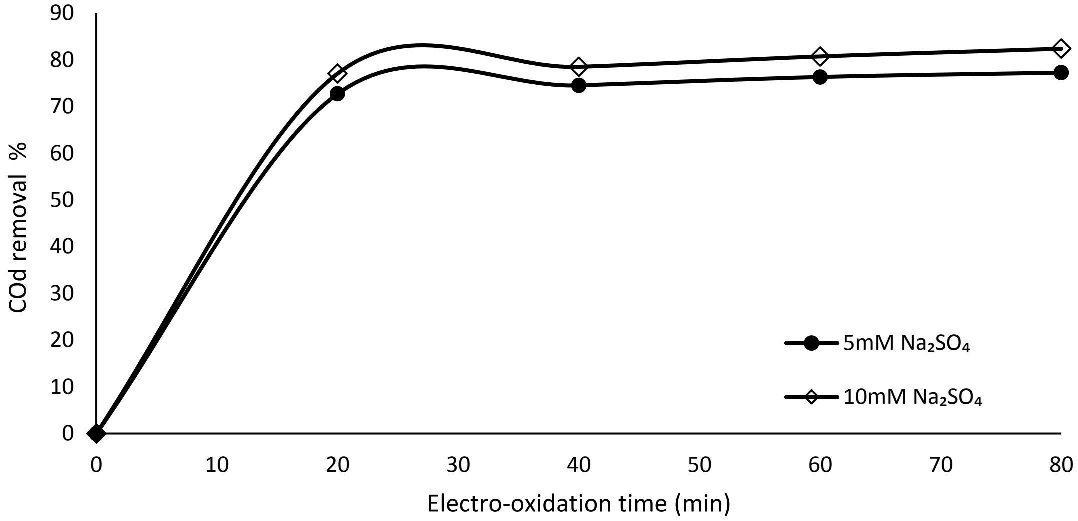

Figure 6.51. *Variation of COD removal over the time depending on support electrolyte concentration (EO. Co= 300 mg/L bromuconazole, 5mA/cm^2)*

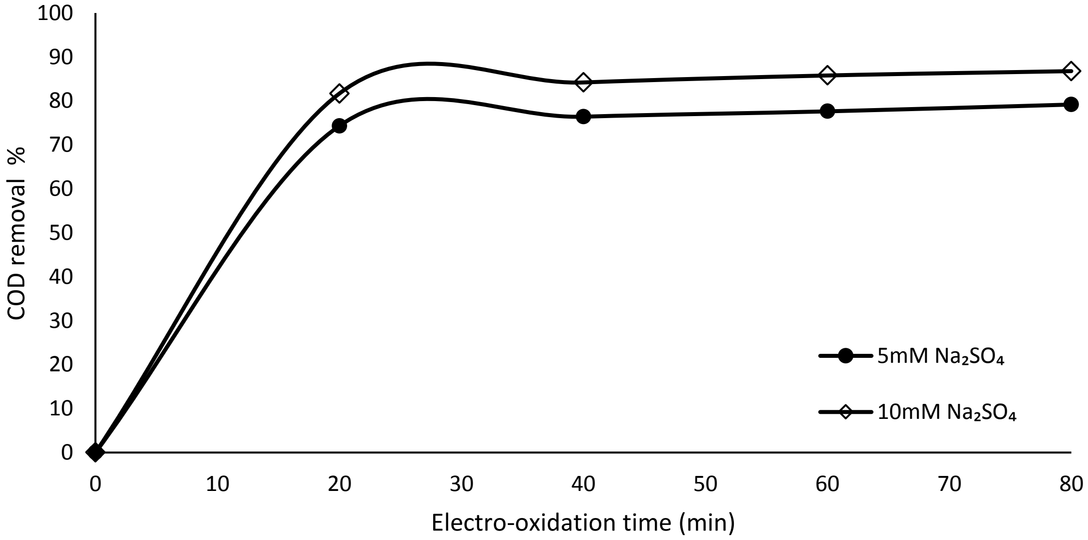

Figure 6.52. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 10 mA/cm^2)*

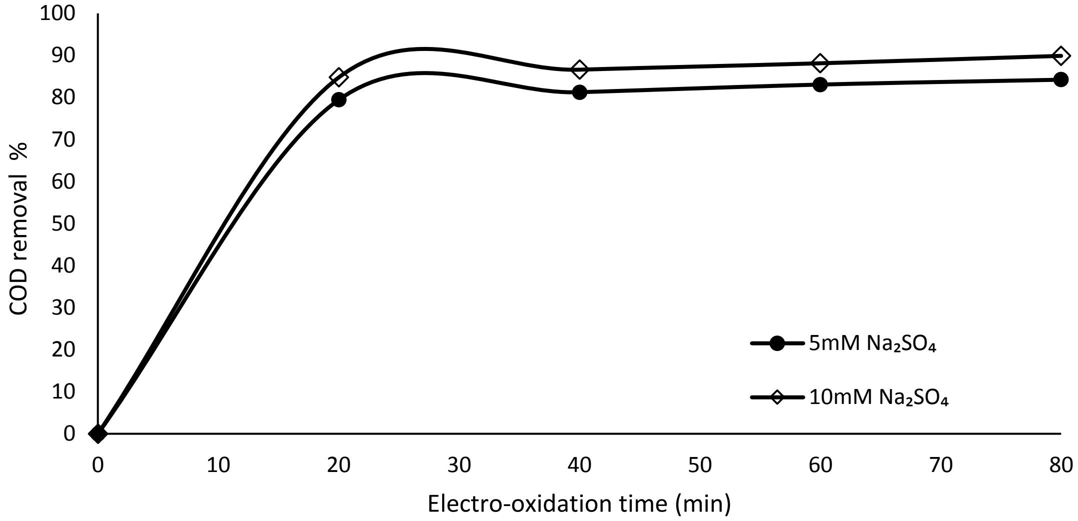

Figure 6.53. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 15 mA/cm^2)*

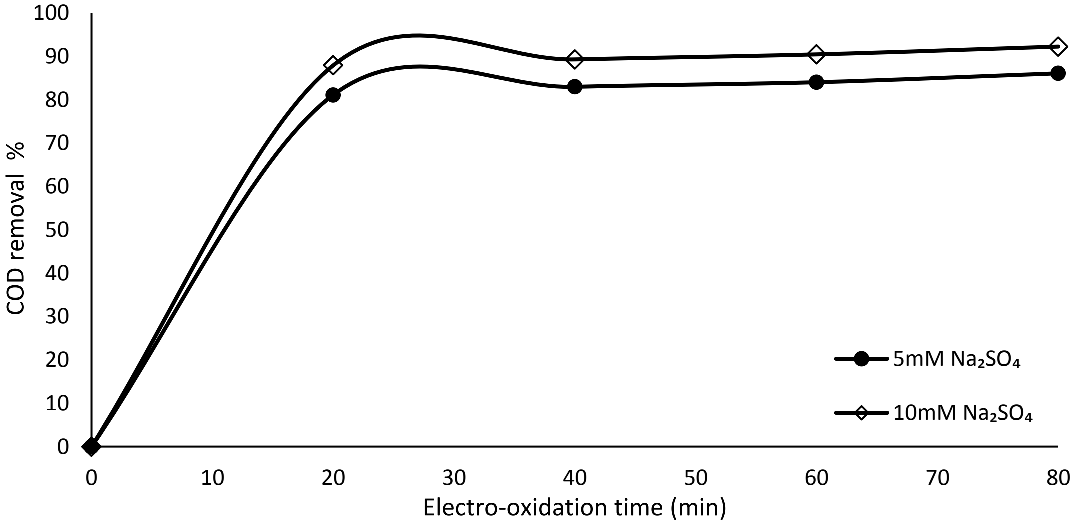

Figure 6.54. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 20 mA/cm^2)*

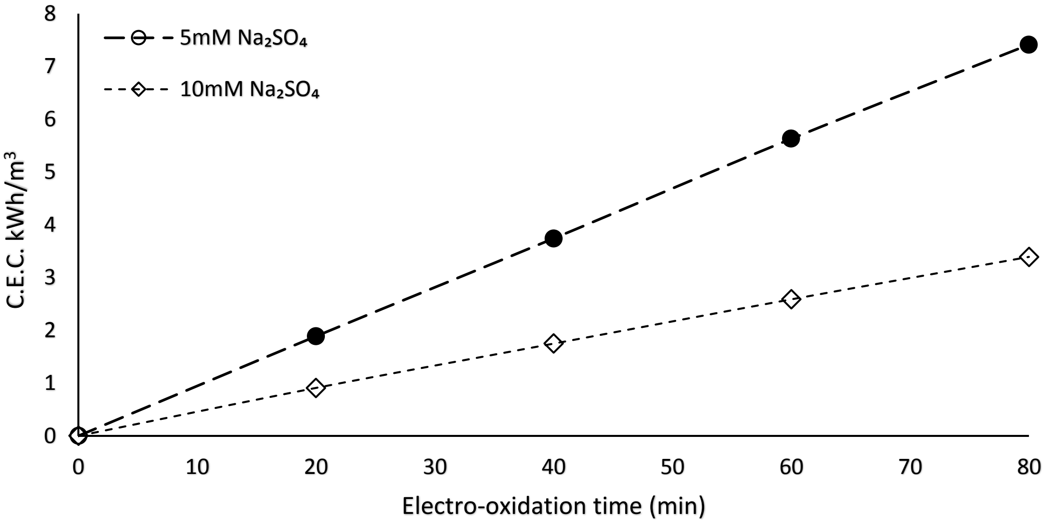

Figure 6.55. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 5mA/cm^2)*

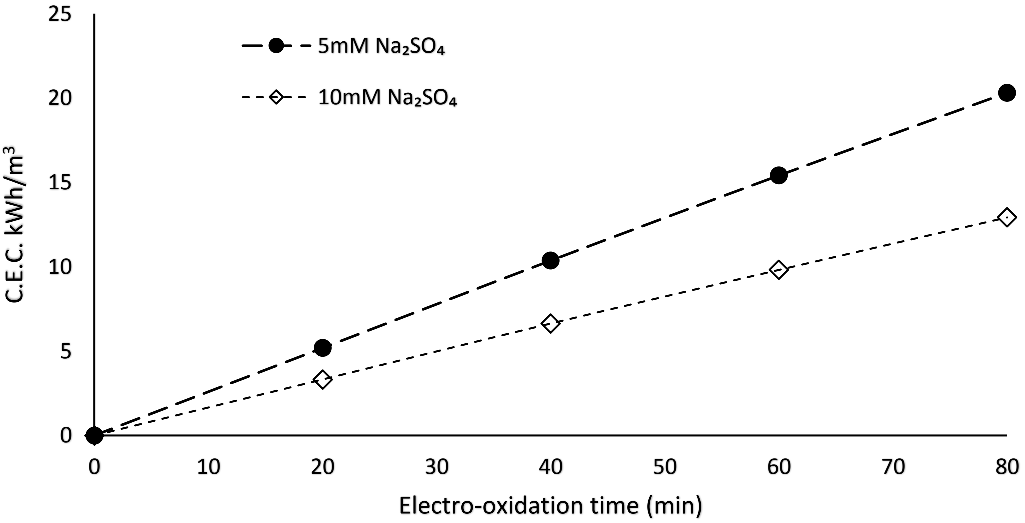

Figure 6.56. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 10 mA/cm^2)*

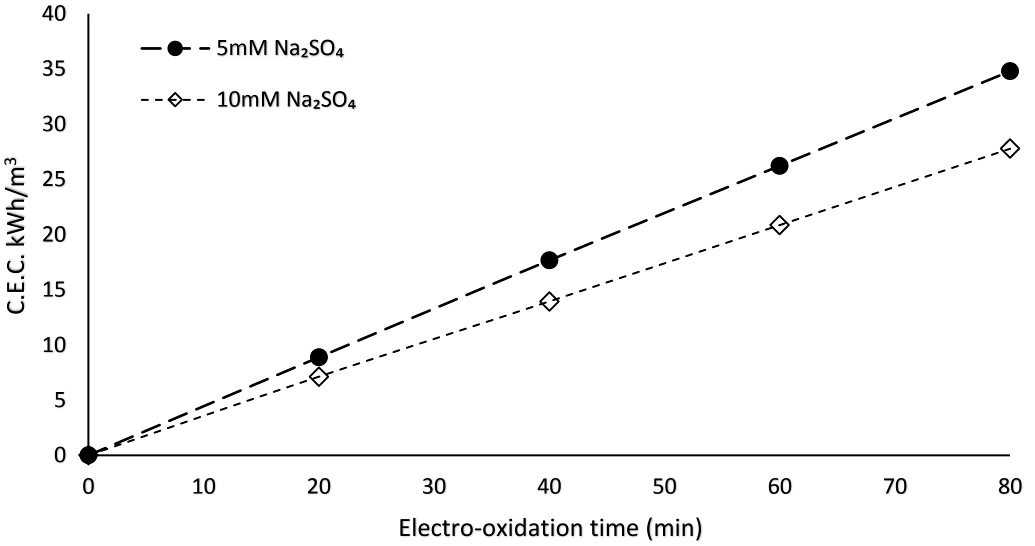

Figure 6.57. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 15mA/cm^2)*

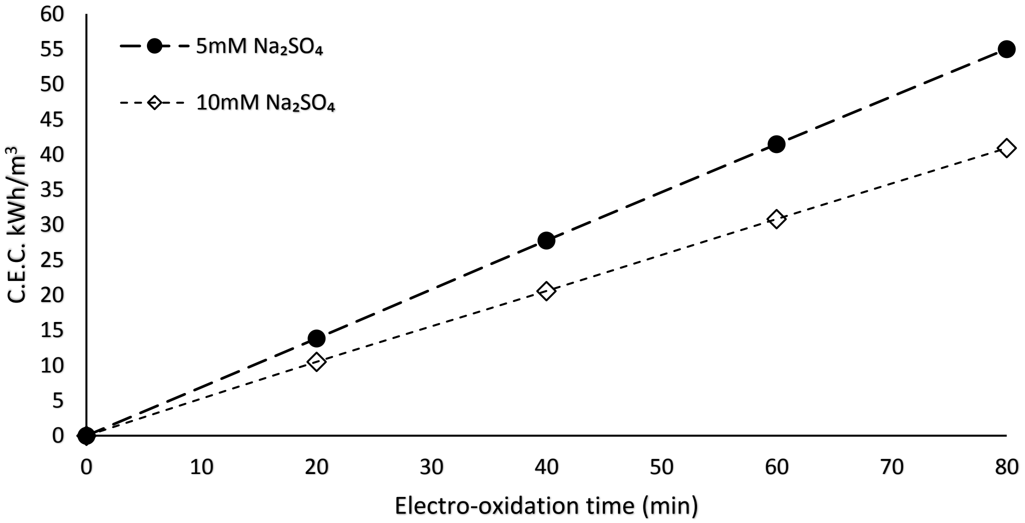

Figure 6.58. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bromuconazole, 20mA/cm^2)*

6.1.6. Ion chromatography (IC)

Released inorganic ions during different electrochemical methods were identified by ion chromatography (IC). samples were collected from model solutions at different electrolysis times for best-obtained result for each treatment methods.

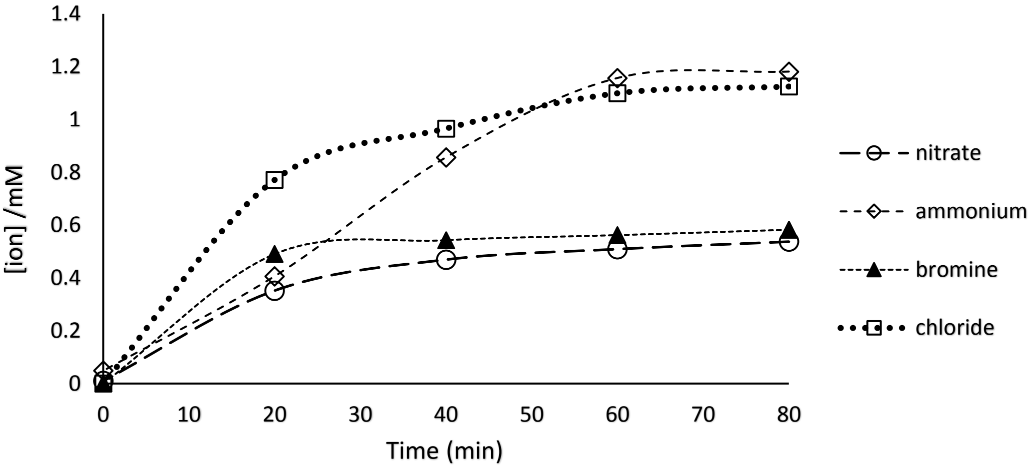

Figure 6.59. *Inorganic ions concentrations over the time during electrocoagulation of bromuconazole solution measured by IC (Co= 300 mg/l, 10 mM Na_2SO_4, 20 mA/cm^2).*

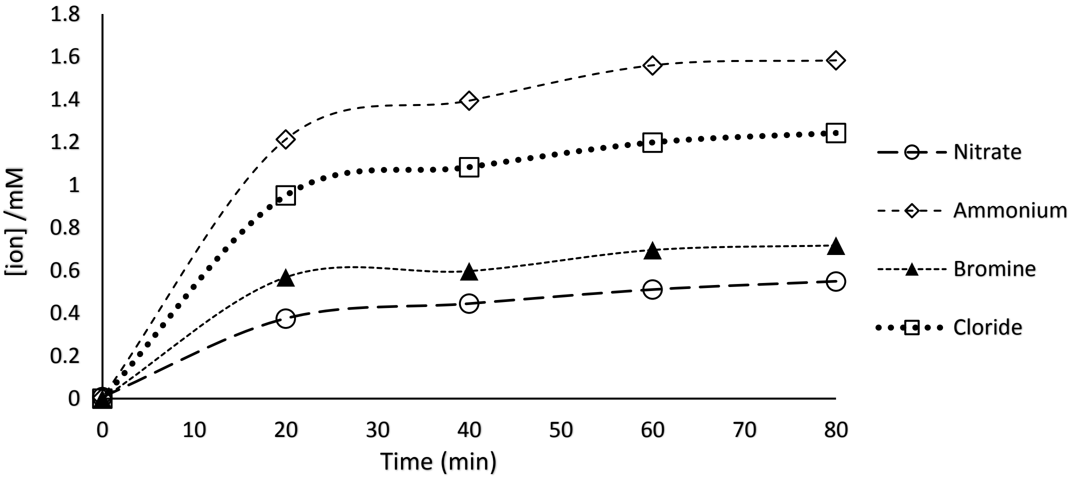

Figure 6.60. *Inorganic ions concentrations over the time during electrochemical-Fenton of bromuconazole solution measured by IC (Co= 300 mg/l, 1 mM Na_2SO_4, 3000 mg H_2O_2/L 20 mA/cm^2).*

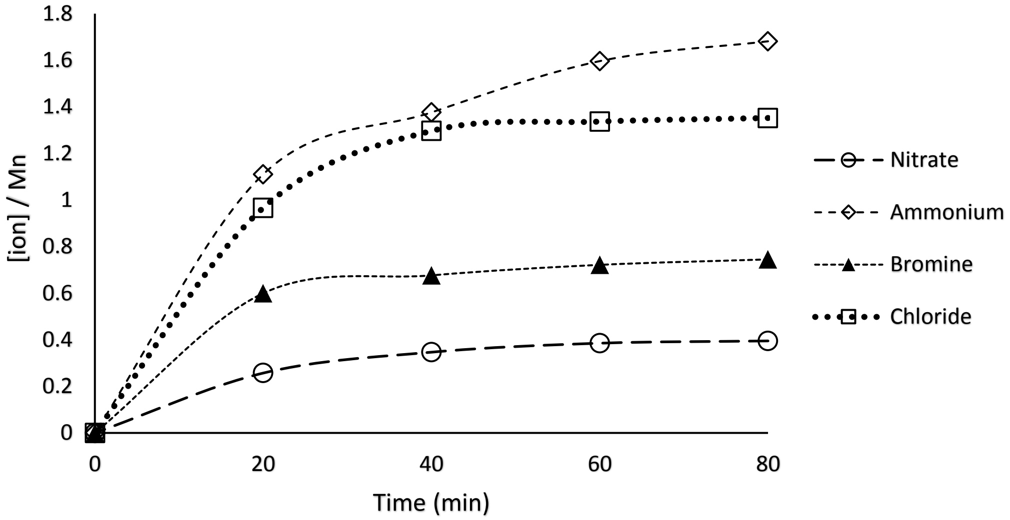

Figure 6.61. *Inorganic ions concentrations over the time during electro-oxidation of bromuconazole solution measured by IC (Co= 300 mg/l, 10 mM Na_2SO_4, 20 mA/cm^2).*

6.1.7. Toxicity determination

Toxicity determination is crucial point in assessing environmental contamination. The toxicity of best-obtained result from each treatment methods was evaluated on samples collected from model solutions at different electrolysis times. Toxicity measurements were done by means of the Microtox assays, based on determining the luminescence inhibition of the bacteria V. fischeri.

Table 6.53. *Microtox toxicity of bromuconazole as a function of different treatment methods in term of EC_{50}.*

Treatment technique	Treatment Time (min)	% EC_{50} (5min)	Toxicity degree	% EC_{50} (15min)	Toxicity degree
ECP	0	19	Hight toxic	24	High toxic
	40	41	moderate toxic	49	moderate toxic
	80	42	moderate toxic	53	Toxic
EFP	0	22	High toxic	31	moderate toxic
	40	47	moderate toxic	56	Toxic
	80	54	Toxic	69	Toxic
EOP	0	19	High toxic	24	High toxic
	40	57	Toxic	60	Toxic
	80	69	Toxic	86	Slight toxic

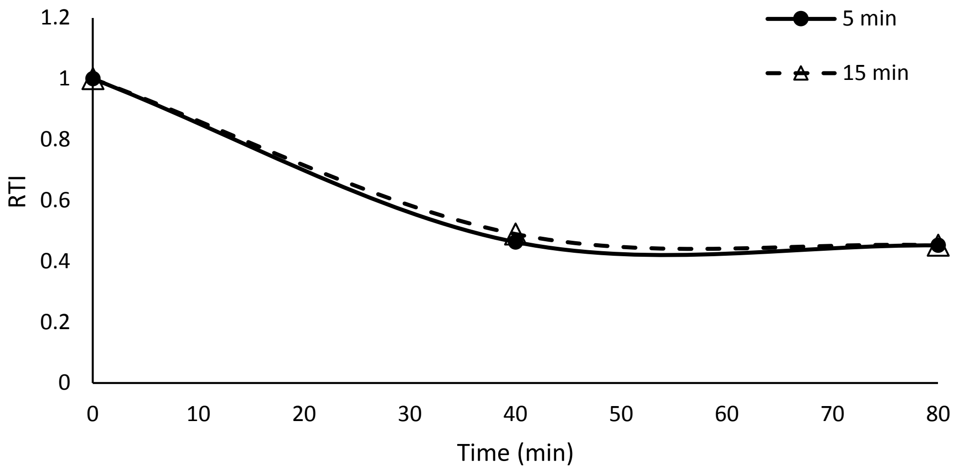

Figure 6.62. *Variation of 5th and 15th mins toxicity of bromuconazole by electrocoagulation with the time.*

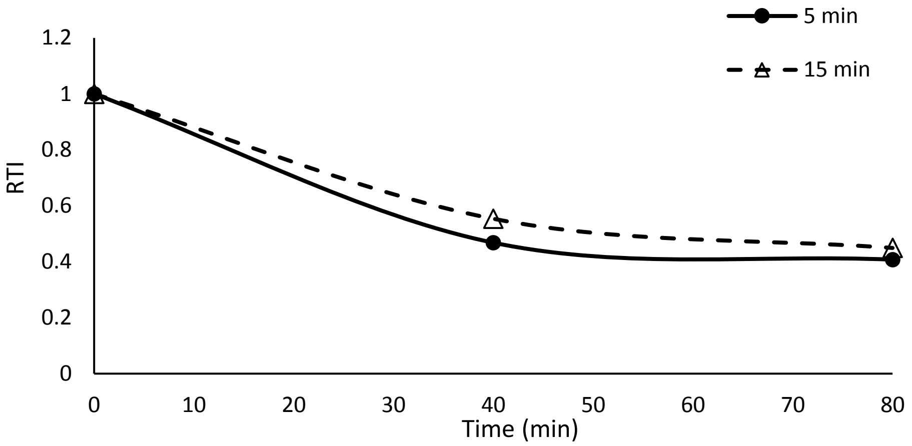

Figure 6.63. *Variation of 5th and 15th mins toxicity of bromuconazole by electrochemical-Fenton with the time.*

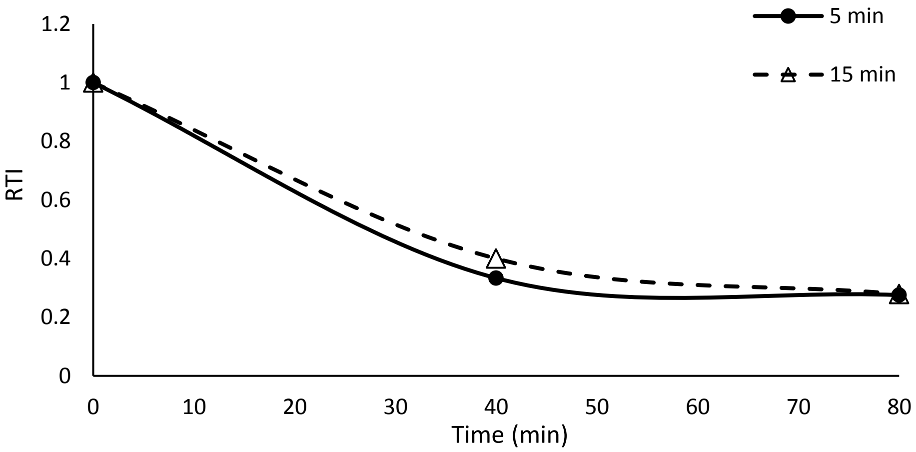

Figure 6.64. *Variation of 5th and 15th mins toxicity of bromuconazole by electro-oxidation with the time.*

6.1.8. Kinetic studies

The significance of kinetics study is that it gives knowledge about the mechanisms of chemical reactions. In addition to being of real scientific interest, knowledge the mechanisms of reaction are of important use in order to decide the most effective way that makes the reaction occur.

The concentration of pesticide was decreased to (49.5, 26.3, 18.3, 12.3 mg/L) at (20, 40, 60, 80 mins) respectively by electro-oxidation process. A kinetic analysis showed that the removal of bromuconazole by an electro-oxidation treatment technique using BDD followed second-order kinetics model. The lines in plot indicate a good correlation of experimental data with the kinetic models for removal rates. The calculated constant (k) values from the plot of figure 6.65 were 0.0009 mg^{-1}Lmin^{-1}with a correlation coefficient of (.9894) according to the equation 6.2, and as can be seen, the calculated 1/C-1/C$_o$ from above equation agree with the experimental data.

$$-\frac{d[Bromuconazole]}{dt} = \mathrm{K}[Bromuconazole]^2 \qquad (6.1)$$

İn which their integration gives, for [Abamectin]= [Abamectin]$_o$ at t= 0:

$$\frac{1}{C} - \frac{1}{Co} = \mathrm{k}t \qquad (6.2)$$

where C$_0$ and C represent pesticide concentration (mg/L) at the beginning and after electrolysis time, respectively. k (mg^{-1}Lmin^{-1}) is the rate constant and t indicate the electrolysis time (min). The temperature during electrolysis period was 30 ^{o}C

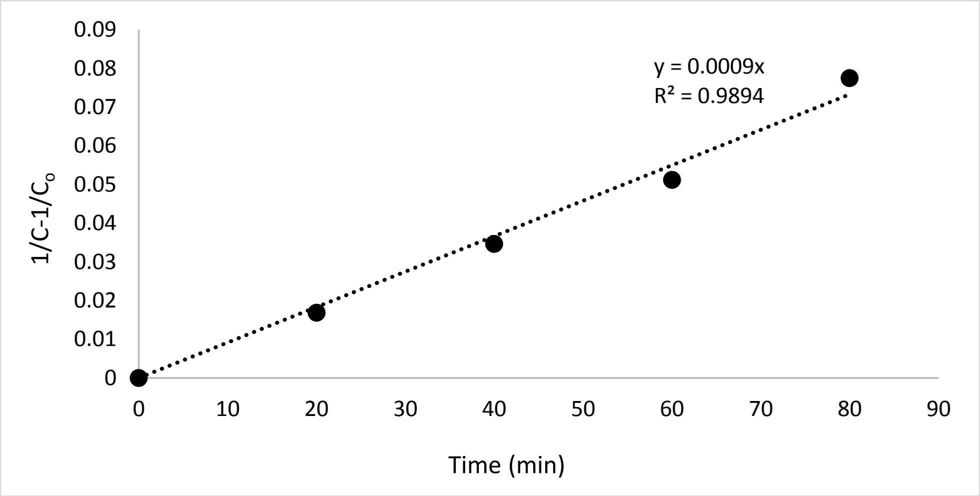

Figure 6.65. *Relation between 1/C-1/C$_o$ against the time for bromuconazole removal using BDD electrodes (Co= 300mg/L, i=20mA/cm^2, 10mM Na$_2$SO$_4$, pH= 4.87)*

6.2. Bentazone

A series of experiments were carried out to evaluate the removal efficiency of bentazone by different electrochemical techniques. The model solution was prepared by distilled water. The experiments were carried out for 80 min with initial pesticide concentration of 300mg.L^{-1}, different electrolyte concentrations were used.

6.2.1. Electrocoagulation methods using iron electrodes

Table 6.54. *300 mg/L bentazone containing solution (EC-Fe, i=5mA/cm^2, 1mM Na_2SO_4, pH= 6.53)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	18.1	534.64	0.0	0.0	0.0	0.0	0.0
20	17.3	238.35	55.42	0.00242	6.05	6.05	148.19
40	16.8	218.25	59.18	0.00235	5.87	11.92	143.91
60	16.5	210.13	60.70	0.00231	5.77	17.69	141.34
80	16.3	201.23	62.36	0.00228	5.70	23.39	139.63
Sludge amount (gram)=1.98							

Table 6.55. *300 mg/L bentazone containing solution (EC-Fe, i=10mA/cm^2, 1mM Na_2SO_4, pH= 6.53)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	30.3	534.64	0.0	0.0	0.0	0.0	0.0
20	23.4	218.15	59.20	0.00647	16.17	16.17	396.13
40	23.1	200.92	62.42	0.00638	15.96	32.13	391.05
60	22.8	189.32	64.59	0.00630	15.75	47.88	385.97
80	22.7	180.47	66.24	0.00627	15.69	63.57	384.28
Sludge amount (gram)=2.32							

Table 6.56. *300 mg/L bentazone containing solution (EC-Fe, i=15mA/cm^2, 1mM Na_2SO_4, pH= 6.53)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	33.8	534.64	0.0	0.0	0.0	0.0	0.0
20	29.7	198.31	62.91	0.01226	30.66	30.66	751.15
40	29.4	179.47	66.43	0.01214	30.35	61.01	743.56
60	29	168.46	68.49	0.01197	29.94	90.95	733.44
80	28.8	160.72	69.94	0.01189	29.73	120.68	728.39
Sludge amount (gram)= 2.44							

Table 6.57. *300 mg/L bentazone containing solution (EC-Fe, i=20mA/cm^2, 1mM Na_2SO_4, pH= 6.53)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	36.3	534.64	0.0	0.0	0.0	0.0	0.0
20	32.9	184.31	65.53	0.01819	45.47	45.47	1113.92
40	32.4	160.78	69.93	0.01791	44.78	90.24	1096.99
60	32.1	153.17	71.35	0.01774	44.36	134.60	1086.83
80	32.1	145.68	72.75	0.01774	44.36	178.96	1086.83
Sludge amount (gram)= 2.48							

Table 6.58. *300 mg/L bentazone containing solution (EC-Fe, i=5mA/cm^2, 5mM Na_2SO_4, pH= 6.17)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	14.8	544.35	0.0	0.0	0.0	0.0	0.0
20	12.2	196.86	63.84	0.00171	4.27	4.27	104.51
40	12	177.36	67.42	0.00168	4.20	8.46	102.79
60	11.9	163.59	69.95	0.00166	4.16	12.62	101.94
80	11.7	152.64	71.96	0.00164	4.09	16.71	100.22
Sludge amount (gram)=2.42							

Table 6.59. *300 mg/L bentazone containing solution (EC-Fe, i=10mA/cm^2, 5mM Na_2SO_4, pH= 6.17)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.7	544.35	0.0	0.0	0.0	0.0	0.0
20	18.5	177.52	67.39	0.00511	12.78	12.78	313.18
40	17.7	160.63	70.49	0.00489	12.23	25.01	299.64
60	17.4	148.48	72.72	0.00481	12.02	37.04	294.56
80	17.6	138.64	74.53	0.00486	12.16	49.20	297.94
Sludge amount (gram)=2.64							

Table 6.60. *300 mg/L bentazone containing solution (EC-Fe, i=15mA/cm^2, 5mM Na_2SO_4, pH= 6.17)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	29.5	544.35	0.0	0.0	0.0	0.0	0.0
20	22.8	158.35	70.91	0.00941	23.54	23.54	576.64
40	22.5	146.35	73.11	0.00929	23.23	46.76	569.05
60	22.8	129.72	76.17	0.00941	23.54	70.30	576.64
80	23	120.87	77.80	0.00950	23.74	94.04	581.70
Sludge amount (gram)= 3.1							

Table 6.61. *300 mg/L bentazone containing solution (EC-Fe, i=20mA/cm^2, 5mM Na_2SO_4, pH= 6.17)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	35.4	544.35	0.0	0.0	0.0	0.0	0.0
20	28.6	142.43	73.83	0.01581	39.52	39.52	968.33
40	25.7	133.47	75.48	0.01421	35.52	75.04	870.14
60	25.5	117.65	78.39	0.01410	35.24	110.28	863.37
80	25.9	108.95	79.99	0.01432	35.79	146.07	876.91
Sludge amount (gram)= 3.43							

Table 6.62. *300 mg/L bentazone containing solution (EC-Fe, i=5mA/cm^2, 10 mM Na_2SO_4, pH= 6.68)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	8.5	544.35	0.0	0.0	0.0	0.0	0.0
20	7.8	190.72	64.96	0.00109	2.73	2.73	66.81
40	7.6	172.82	68.25	0.00106	2.66	5.38	65.10
60	7.5	159.47	70.70	0.00105	2.62	8.01	64.24
80	7.3	150.51	72.35	0.00102	2.55	10.56	62.53
Sludge amount (gram)= 2.75							

Table 6.63. *300 mg/L bentazone containing solution (EC-Fe, i=10mA/cm^2, 10mM Na_2SO_4, pH= 6.68)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.1	544.35	0.0	0.0	0.0	0.0	0.0
20	9.8	166.52	69.41	0.00271	6.77	6.77	165.90
40	9.3	154.32	71.65	0.00257	6.43	13.20	157.43
60	9.1	144.36	73.48	0.00252	6.29	19.49	154.05
80	9.1	135.78	75.06	0.00252	6.29	25.77	154.05
Sludge amount (gram)= 3.37							

Table 6.64. *300 mg/L bentazone containing solution (EC-Fe, i=15mA/cm^2, 10mM Na_2SO_4, pH= 6.68)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.0	544.35	0.0	0.0	0.0	0.0	0.0
20	16.8	147.56	72.89	0.00694	17.34	17.34	424.89
40	14.8	131.85	75.78	0.00611	15.28	32.62	374.31
60	14.5	117.73	78.37	0.00599	14.97	47.59	366.72
80	15.2	108.95	79.99	0.00628	15.69	63.28	384.42
Sludge amount (gram)= 3.74							

Table 6.65. *300 mg/L bentazone containing solution (EC-Fe, i=20mA/cm^2, 10mM Na_2SO_4, pH= 6.68)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	29.5	544.35	0.0	0.0	0.0	0.0	0.0
20	22.8	128.71	76.36	0.01260	31.51	31.51	771.95
40	21.3	114.56	78.95	0.01177	29.44	60.94	721.17
60	21.1	102.42	81.18	0.01166	29.16	90.10	714.39
80	19.4	93.17	82.88	0.01072	26.81	116.91	656.84
Sludge amount (gram)= 4.1							

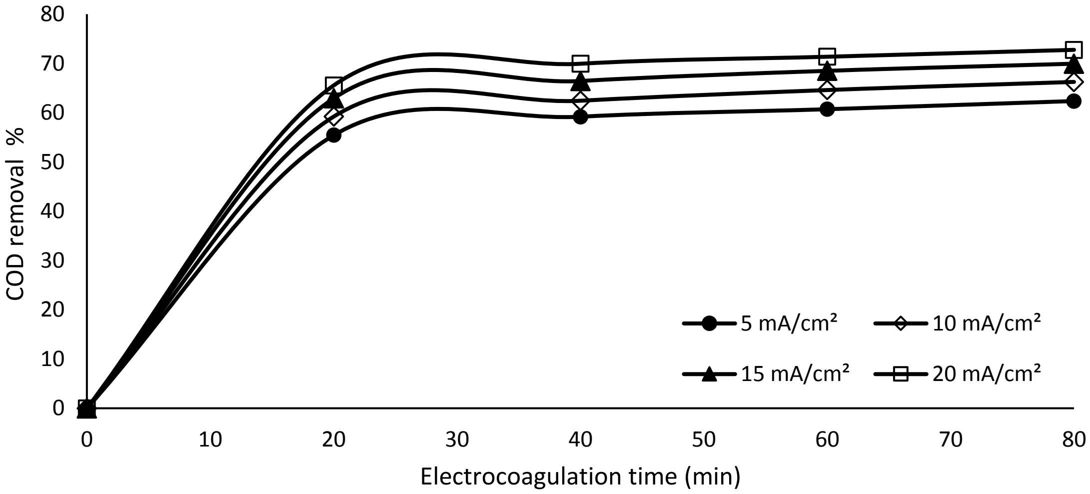

Figure 6.66. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 1mM Na_2SO_4, pH= 6.53)*

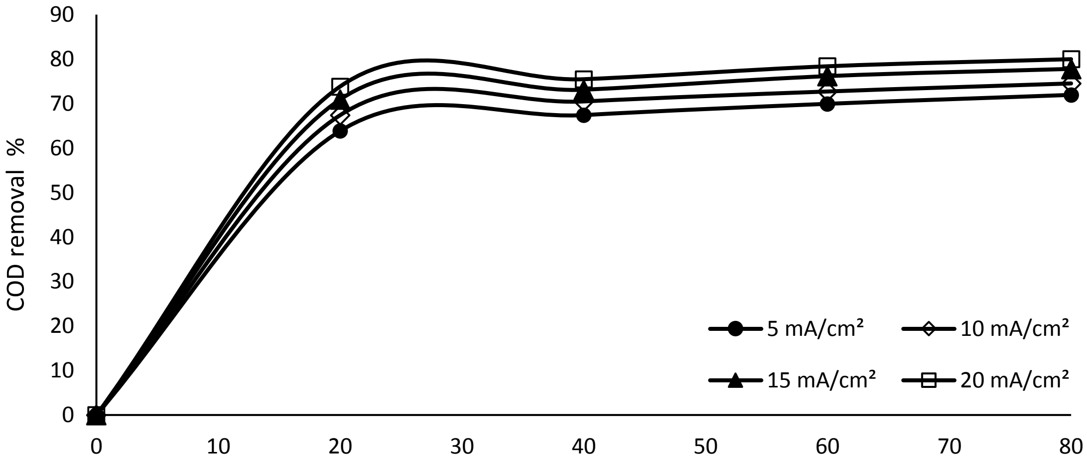

Figure 6.67. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 5mM Na_2SO_4, pH= 6.17)*

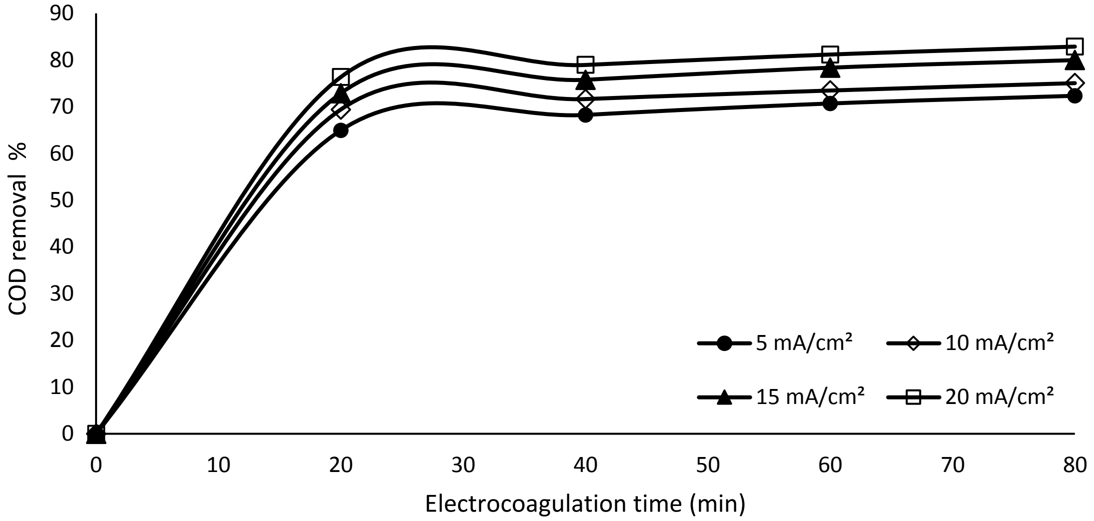

Figure 6.68. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 10mM Na_2SO_4, pH= 6.68)*

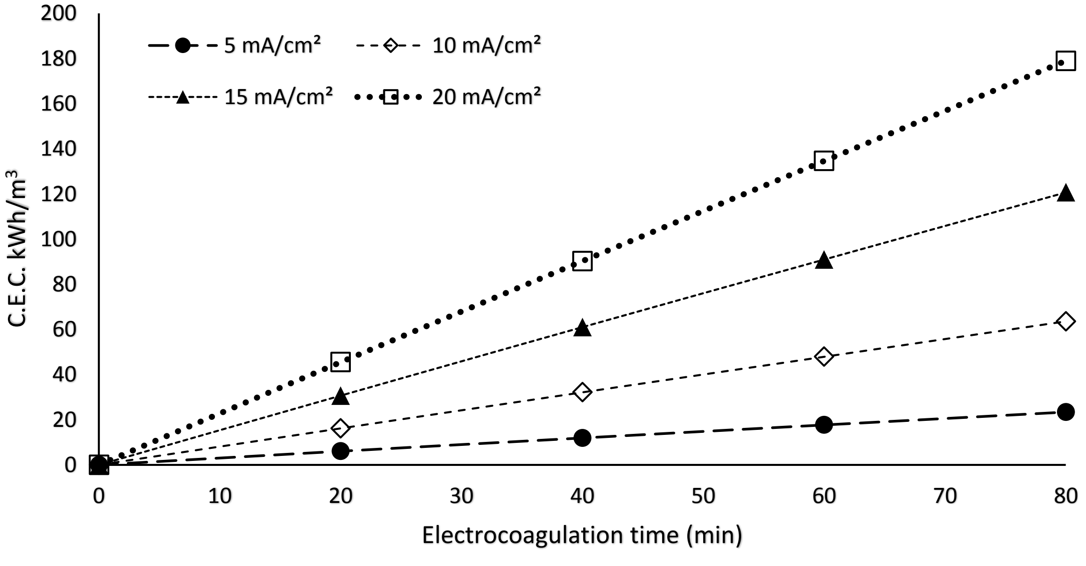

Figure 6.69. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 1mM Na_2SO_4, pH= 6.53)*

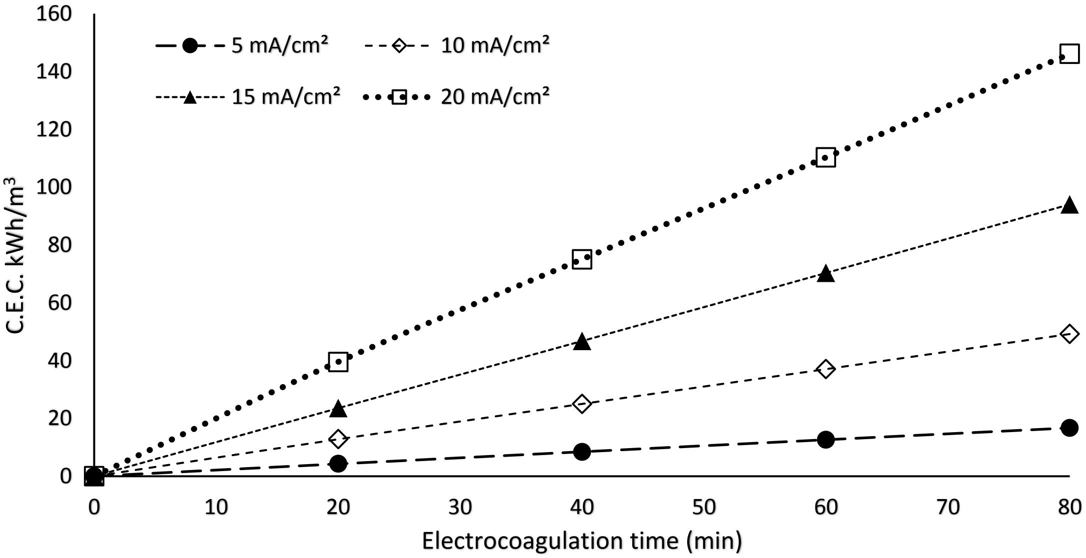

Figure 6.70. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 5mM* Na_2SO_4*, pH= 6.17)*

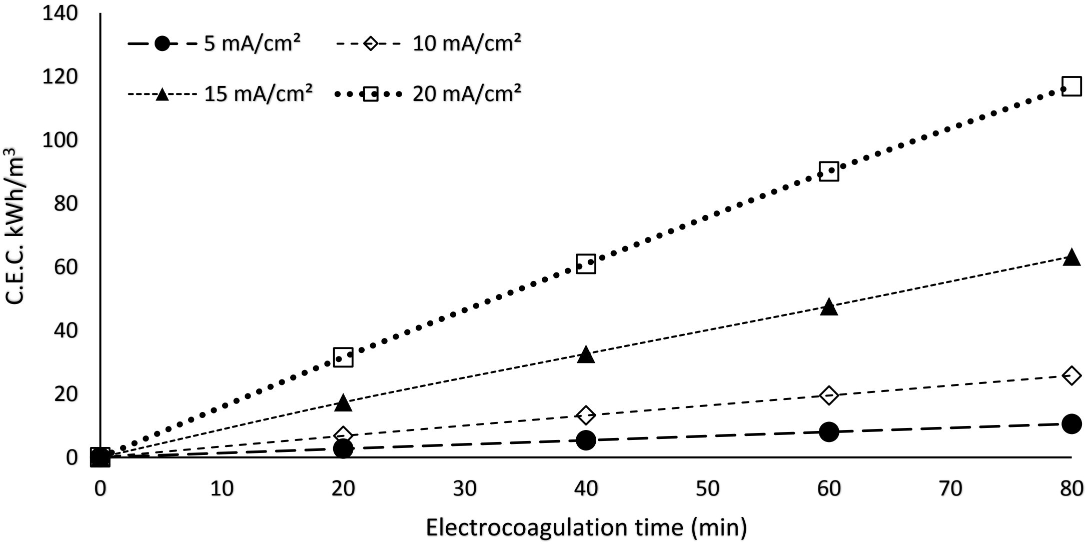

Figure 6.71. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 300 mg/L bentazone, 10mM* Na_2SO_4*, pH= 6.68)*

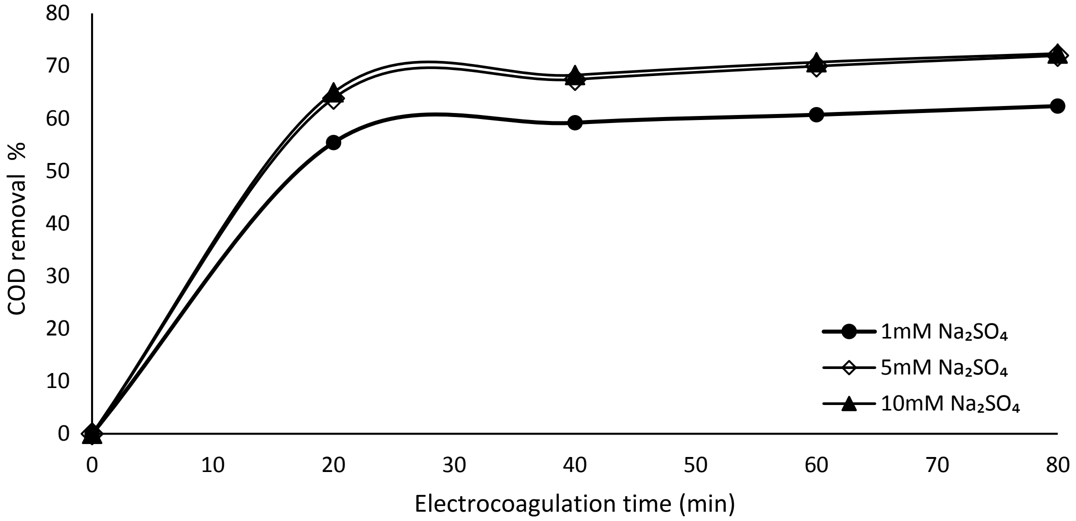

Figure 6.72. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 5mA/cm^2)*

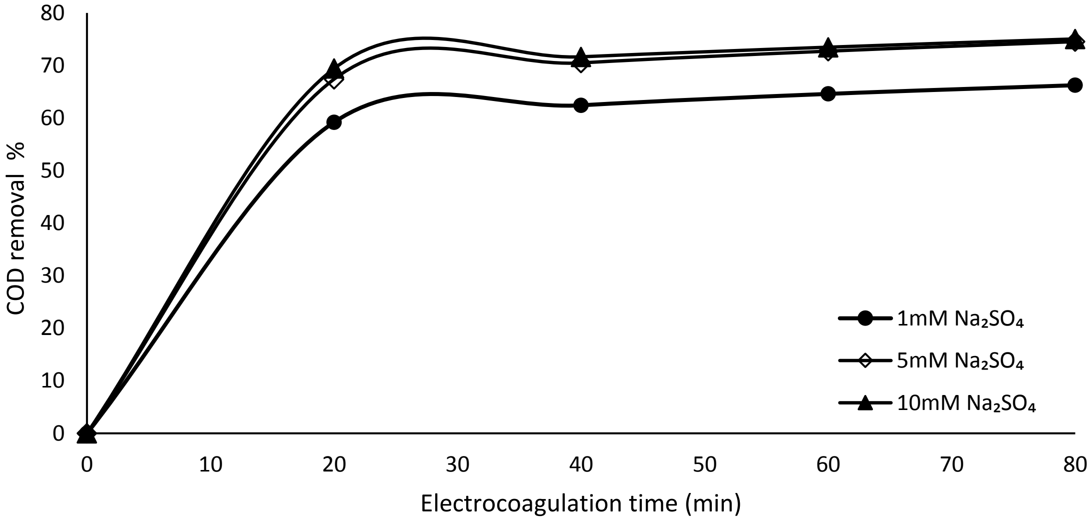

Figure 6.73. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 10 mA/cm^2)*

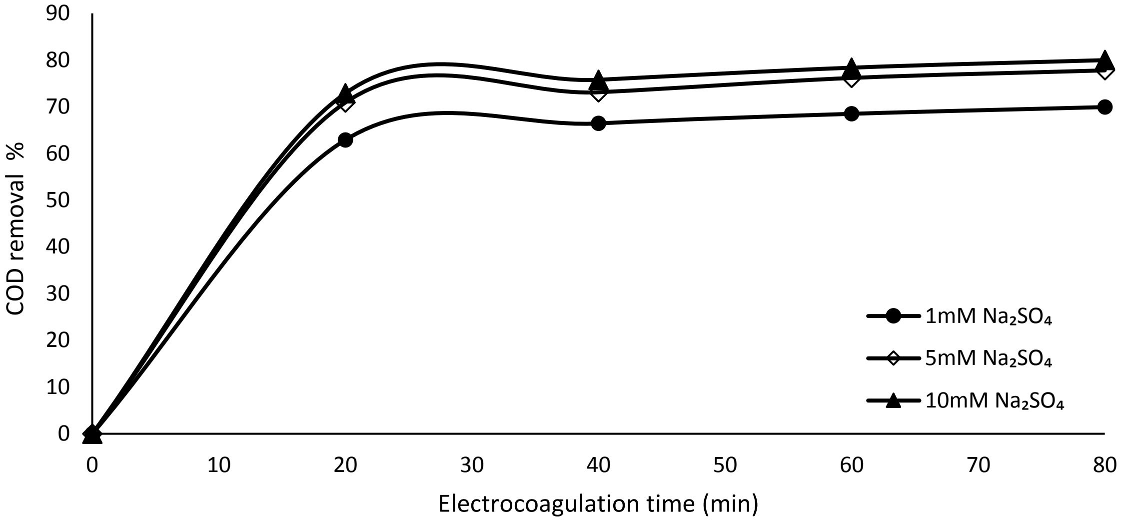

Figure 6.74. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 15 mA/cm^2)*

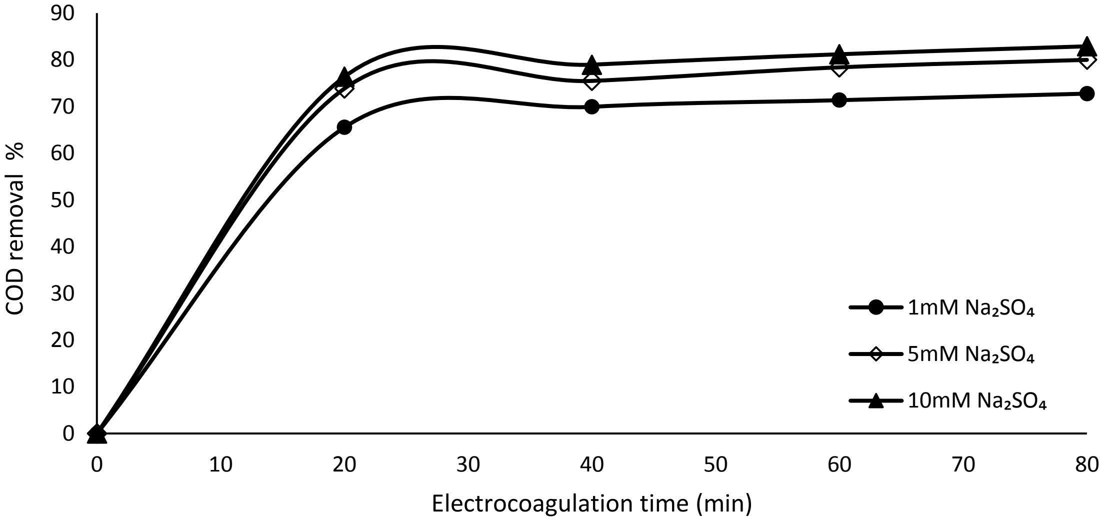

Figure 6.75. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 20 mA/cm^2)*

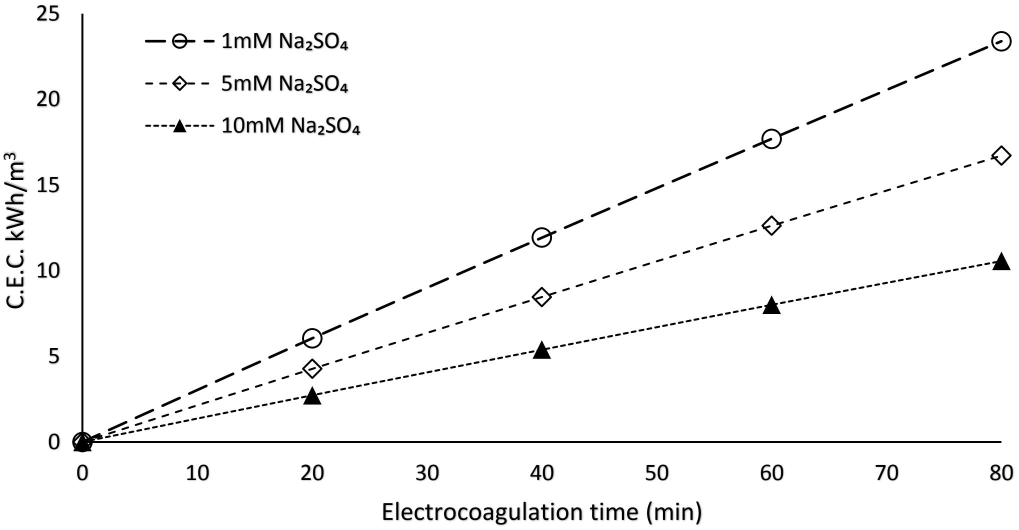

Figure 6.76. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 5mA/cm^2)*

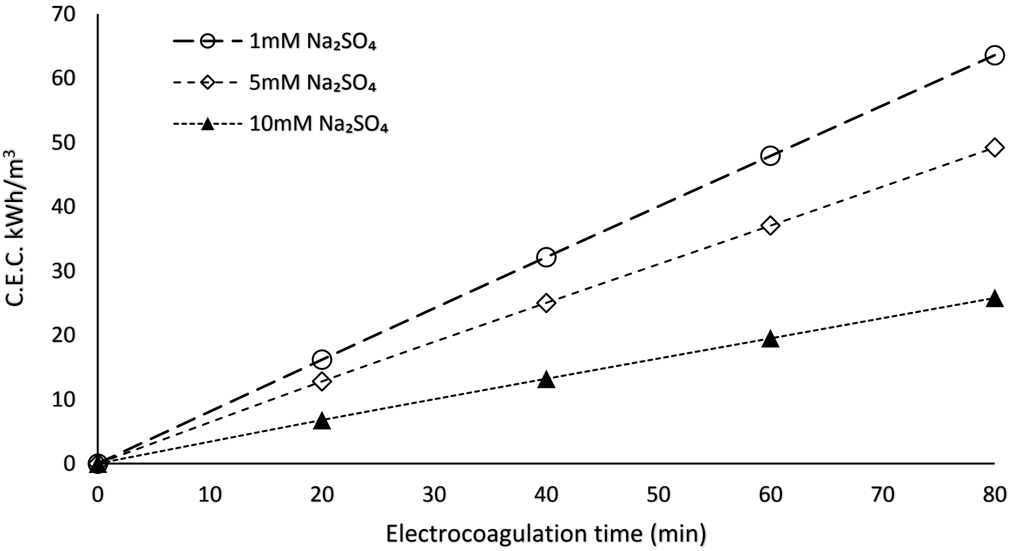

Figure 6.77. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 10 mA/cm^2)*

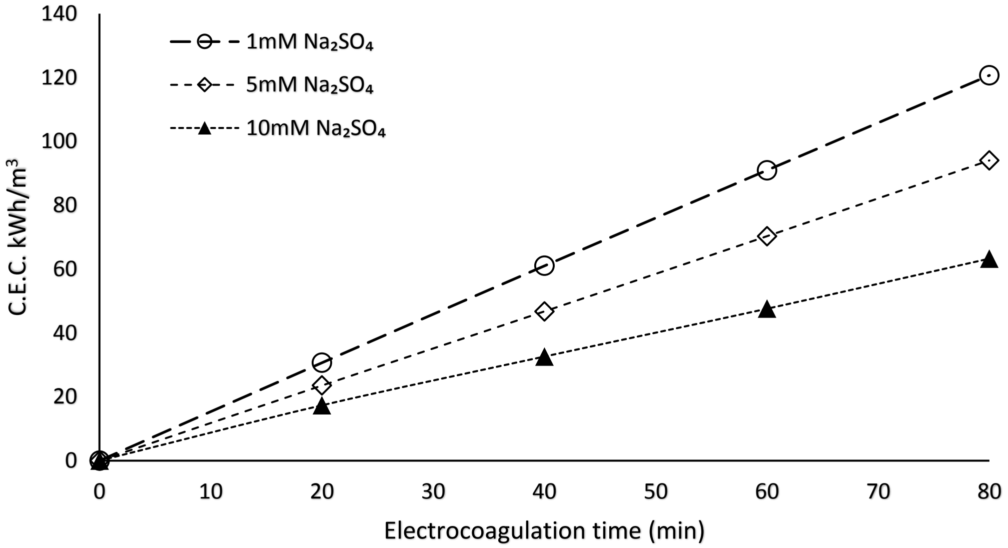

Figure 6.78. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 15mA/cm^2).*

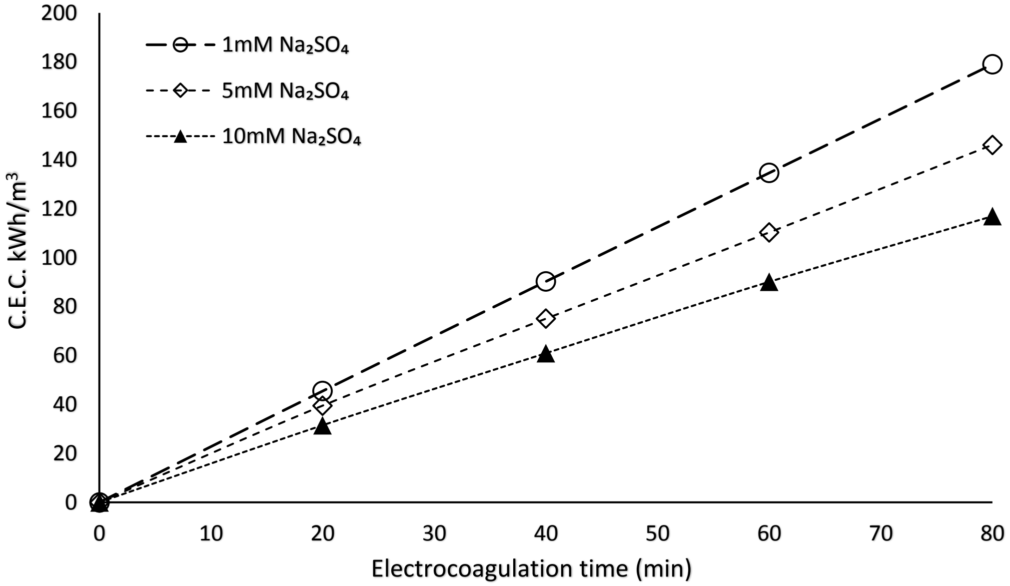

Figure 6.79. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 300 mg/L bentazone, 20mA/cm^2).*

6.2.2. Electrocoagulation methods using aluminum electrodes

Table 6.66. *300 mg/L bentazone containing solution (EC-Al, i=5mA/cm^2, 10mM Na$_2$SO$_4$, pH= 6.47).*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	29.4	568.82	0.0	0.0	0.0	0.0	0.0
20	27.5	280.24	50.73	0.00385	0.00	0.00	235.57
40	26.1	262.45	53.86	0.00365	9.62	9.62	223.58
60	26.3	243.7	57.16	0.00368	9.13	18.74	225.29
80	25.8	234.22	58.82	0.00361	9.20	27.94	221.01
Sludge amount (gram)= 1.73							

Table 6.67. *300 mg/L bentazone containing solution (EC-Al, i=10mA/cm^2, 10mM Na$_2$SO$_4$, pH= 6.47).*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	39.2	568.82	0.0	0.0	0.0	0.0	0.0
20	38.8	254.23	55.31	0.01072	26.81	26.81	656.84
40	37.5	238.74	58.03	0.01036	25.91	52.72	634.83
60	37.6	223.58	60.69	0.01039	25.98	78.70	636.52
80	36.8	210.37	63.02	0.01017	25.43	104.13	622.98
Sludge amount (gram)= 1.69							

Table 6.68. *300 mg/L bentazone containing solution (EC-Al, i=15mA/cm^2, 10mM Na$_2$SO$_4$, pH= 6.47)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	48.2	568.82	0.0	0.0	0.0	0.0	0.0
20	39.8	230.33	59.51	0.01643	41.09	41.09	1006.59
40	39.7	198.35	65.13	0.01639	40.98	82.07	1004.06
60	38.4	182.75	67.87	0.01586	39.64	121.71	971.18
80	38.1	171.72	69.81	0.01573	39.33	161.04	963.60
Sludge amount (gram)= 1.82							

Table 6.69. *300 mg/L bentazone containing solution (EC-Al, i=20mA/cm^2, 10mM Na$_2$SO$_4$, pH= 6.47)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	47.8	568.82	0.0	0.0	0.0	0.0	0.0
20	42.8	210.28	63.03	0.02366	59.15	59.15	1449.11
40	41.9	173.35	69.52	0.02316	57.90	117.05	1418.64
60	39.7	161.89	71.54	0.02195	54.86	171.91	1344.15
80	40.8	149.72	73.68	0.02255	56.38	228.30	1381.39
Sludge amount (gram)=1.98							

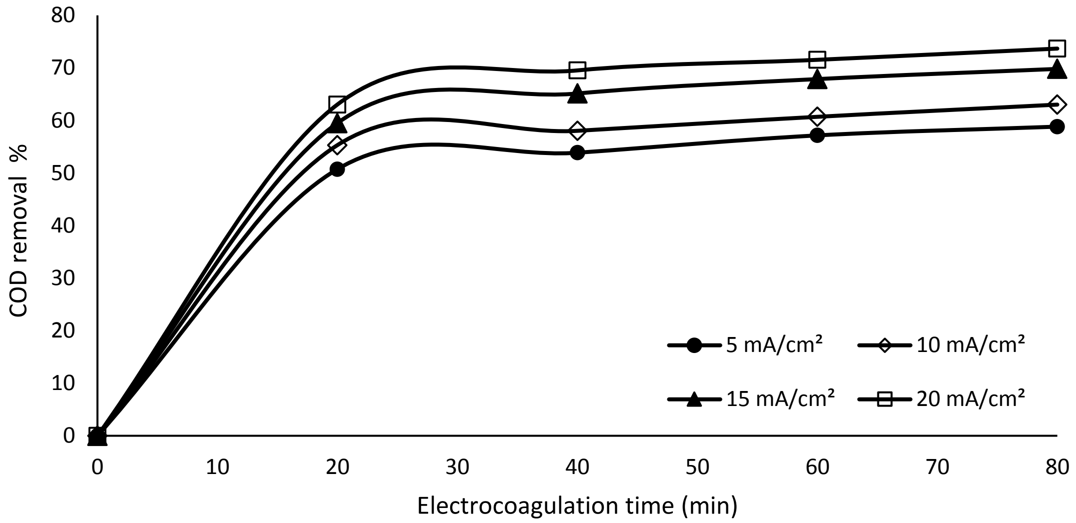

Figure 6.80. *Variation of COD removal over the time depending on current density (EC-Al, Co= 300 mg/L bentazone,10 mM Na_2SO_4, pH= 6.47)*

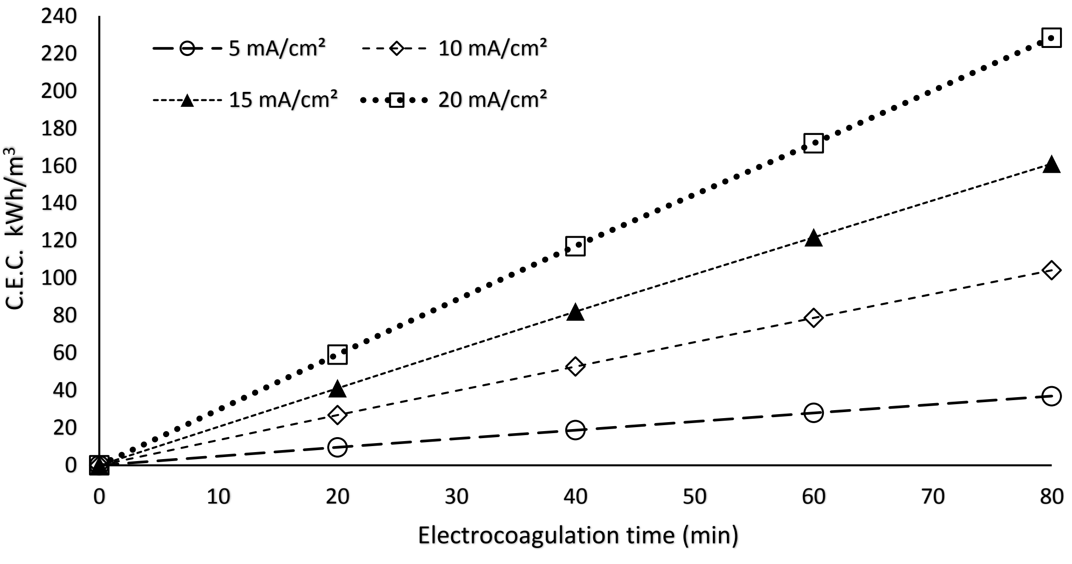

Figure 6.81. *Variation of energy consumption over the time depending on current density (EC-Al, Co= 300 mg/L bentazone,10mM Na_2SO_4, pH= 6.47)*

6.2.3. Electrocoagulation methods using hybrid (mixed) electrodes

Table 6.70. *300 mg/L bentazone containing solution (EC-Fe-Al, i=5mA/cm^2, 1mM Na_2SO_4, pH= 6.8)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	25.7	563.24	0.0	0.0	0.0	0.0	0.0
20	19.5	214.34	61.95	0.00273	6.82	6.82	167.04
40	19.1	203.21	63.92	0.00267	6.68	13.50	163.61
60	18.7	192.46	65.83	0.00262	6.54	20.03	160.19
80	18.7	179.71	68.09	0.00262	6.54	26.57	160.19
Sludge amount (gram)= 1.61							

Table 6.71. *300 mg/L bentazone containing solution (EC-Fe-Al, i=10mA/cm^2, 1mM Na_2SO_4, pH= 6.8)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.4	563.24	0.0	0.0	0.0	0.0	0.0
20	25.6	200.36	64.43	0.00708	17.69	17.69	433.37
40	25.6	189.42	66.37	0.00708	17.69	35.38	433.37
60	24.9	177.37	68.51	0.00688	17.21	52.58	421.52
80	25.0	164.49	70.80	0.00691	17.27	69.86	423.22
Sludge amount (gram)= 1.82							

Table 6.72. *300 mg/L bentazone containing solution (EC-Fe-Al, i=15mA/cm^2, 1mM Na_2SO_4, pH= 6.8)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.7	563.24	0.0	0.0	0.0	0.0	0.0
20	29.2	182.93	67.52	0.01206	30.14	30.14	738.50
40	29.2	165.75	70.57	0.01206	30.14	60.29	738.50
60	29.0	156.32	72.25	0.01197	29.94	90.22	733.44
80	28.9	152.32	72.96	0.01193	29.83	120.06	730.92
Sludge amount (gram)=2.08							

Table 6.73. *300 mg/L bentazone containing solution (EC-Fe-Al, i=20mA/cm^2, 1mM Na_2SO_4, pH= 6.8)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	38.4	563.24	0.0	0.0	0.0	0.0	0.0
20	34.8	170.93	69.65	0.01924	48.09	48.09	1178.251
40	34.2	158.7	71.82	0.01891	47.26	95.35	1157.936
60	34.2	149.72	73.42	0.01891	47.26	142.62	1157.936
80	34.1	142.35	74.73	0.01885	47.12	189.74	1154.55
Sludge amount (gram)=2.38							

Table 6.74. *300 mg/L bentazone containing solution (EC-Fe-Al, i=5mA/cm^2, 5mM Na$_2$SO$_4$, pH= 6.5)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	22.1	568.82	0.0	0.0	0.0	0.0	0.0
20	16.3	203.74	64.18	0.00228	5.70	5.70	139.63
40	16.1	193.11	66.05	0.00225	5.63	11.33	137.91
60	15	180.46	68.27	0.00210	5.24	16.57	128.49
80	15.7	162.71	71.40	0.00220	5.49	22.06	134.49
Sludge amount (gram)= 2.86							

Table 6.75. *300 mg/L bentazone containing solution (EC-Fe-Al, i=10mA/cm^2, 5mM Na$_2$SO$_4$, pH= 6.5)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	23.4	568.82	0.0	0.0	0.0	0.0	0.0
20	21.1	185.21	67.44	0.00583	14.58	14.58	357.19
40	20.8	174.46	69.33	0.00575	14.37	28.95	352.12
60	20.7	164.71	71.04	0.00572	14.30	43.26	350.42
80	20.5	150.71	73.50	0.00567	14.16	57.42	347.04
Sludge amount (gram)=3.15							

Table 6.76. *300 mg/L bentazone containing solution (EC-Fe-Al, i=15mA/cm^2, 5mM Na$_2$SO$_4$, pH= 6.5)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	29.5	568.82	0.0	0.0	0.0	0.0	0.0
20	26.2	175.57	69.13	0.01082	27.05	27.05	662.63
40	25.9	159.51	71.96	0.01069	26.74	53.78	655.04
60	25.4	150.83	73.48	0.01049	26.22	80.00	642.40
80	25.1	140.64	75.28	0.01036	25.91	105.91	634.81
Sludge amount (gram)=3.61							

Table 6.77. *300 mg/L bentazone containing solution (EC-Fe-Al, i=20mA/cm^2, 5mM Na$_2$SO$_4$, pH= 6.5)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	33.7	568.82	0.0	0.0	0.0	0.0	0.0
20	30.5	160.23	71.83	0.01686	42.15	42.15	1032.66
40	29.9	150.64	73.52	0.01653	41.32	83.47	1012.34
60	30.2	139.57	75.46	0.01669	41.73	125.20	1022.50
80	30.2	127.57	77.57	0.01669	41.73	166.94	1022.50
Sludge amount (gram)=3.84							

Table 6.78. *300 mg/L bentazone containing solution (EC-Fe-Al, i=5mA/cm^2, 10mM Na_2SO_4, pH= 6.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	14.5	548.22	0.0	0.0	0.0	0.0	0.0
20	11.5	179.71	67.22	0.00161	4.02	4.02	98.51
40	11.3	150.74	72.50	0.00158	3.95	7.97	96.80
60	11.1	141.72	74.15	0.00155	3.88	11.85	95.087
80	11.2	134.42	75.48	0.00157	3.92	15.77	95.94
Sludge amount (gram)=3.54							

Table 6.79. *300 mg/L bentazone containing solution (EC-Fe-Al, i=10mA/cm^2, 10mM Na_2SO_4, pH= 6.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.8	548.22	0.0	0.0	0.0	0.0	0.0
20	16.4	150.45	72.56	0.00453	11.33	11.33	277.63
40	16.2	142.45	74.02	0.00448	11.19	22.53	274.24
60	16	135.71	75.25	0.00442	11.06	33.58	270.86
80	16.1	128.76	76.51	0.00445	11.12	44.71	272.55
Sludge amount (gram)=3.82							

Table 6.80. *300 mg/L bentazone containing solution (EC-Fe-Al, i=15mA/cm^2, 10mM Na_2SO_4, pH= 6.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	24.7	548.22	0.0	0.0	0.0	0.0	0.0
20	20.5	140.58	74.36	0.00846	21.16	21.16	518.47
40	20.2	128.59	76.54	0.00834	20.85	42.01	510.88
60	20.1	120.23	78.07	0.00830	20.75	62.76	508.35
80	20.1	116.23	78.80	0.00830	20.75	83.51	508.35
Sludge amount (gram)=4.1							

Table 6.81. *300 mg/L bentazone containing solution (EC-Fe-Al, i=20mA/cm^2, 10mM Na_2SO_4, pH= 6.2)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	27.3	548.22	0.0	0.0	0.0	0.0	0.0
20	25.4	130.83	76.14	0.01404	35.10	35.10	859.98
40	25.1	116.61	78.73	0.01387	34.69	69.79	849.83
60	25.1	106.67	80.54	0.01387	34.69	104.48	849.83
80	25	102.12	81.37	0.01382	34.55	139.02	846.44
Sludge amount (gram)=3.91							

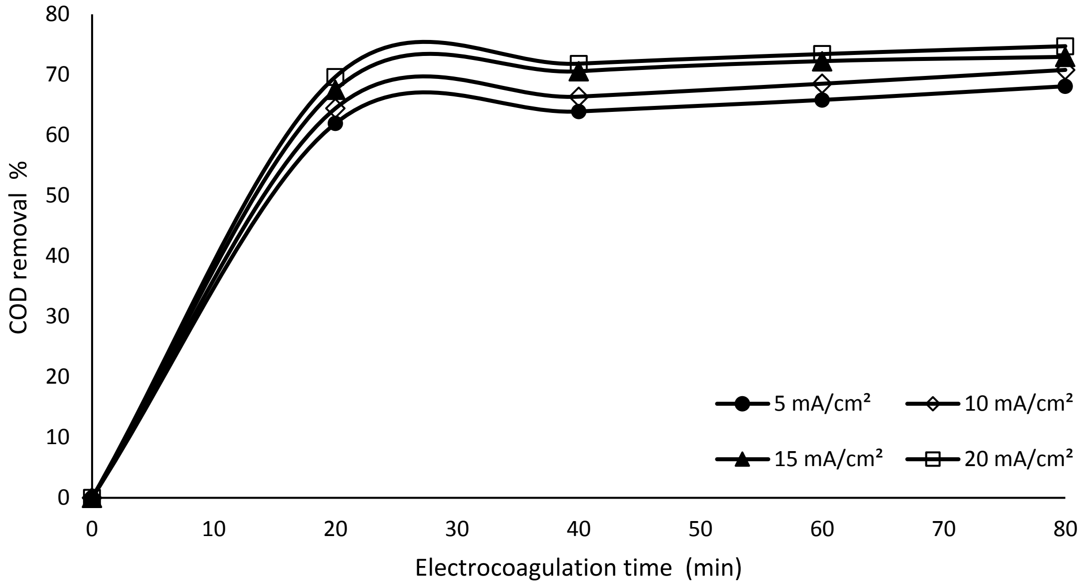

Figure 6.82. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 1mM Na_2SO_4, pH= 6.8)*

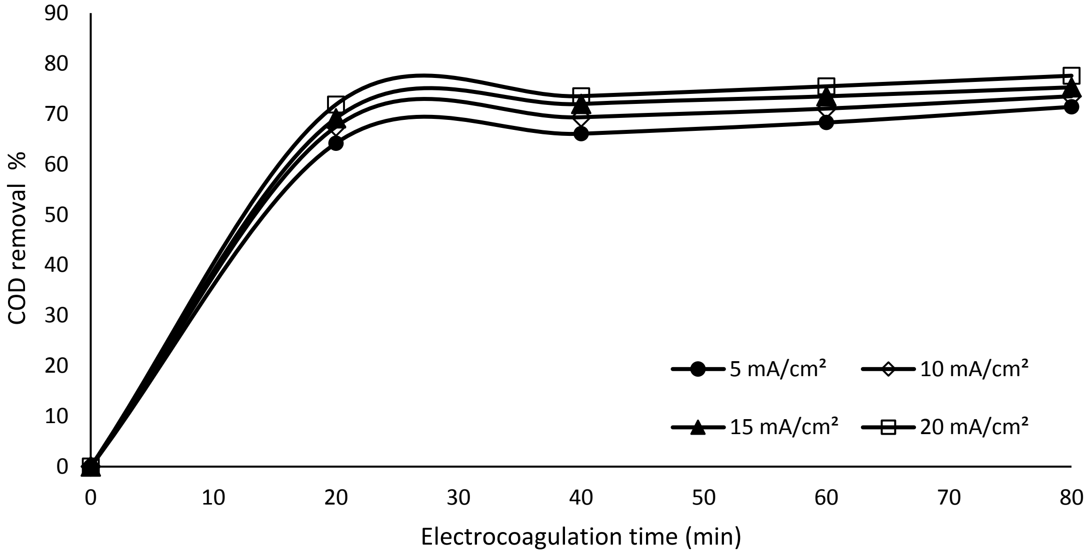

Figure 6.83. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 5 mM Na_2SO4, pH= 6.5)*

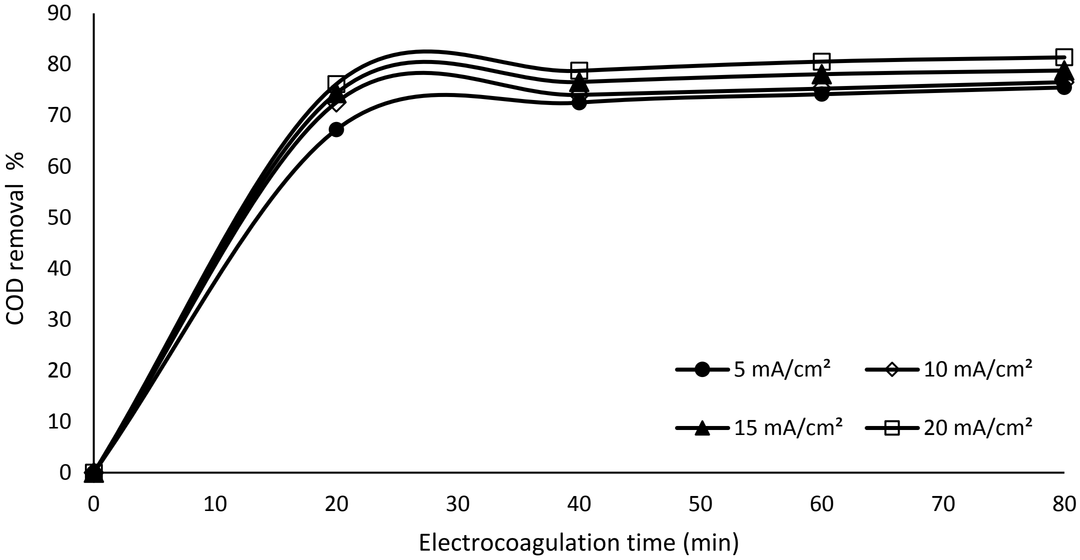

Figure 6.84. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 10 mM* Na_2SO4*, pH= 6.2)*

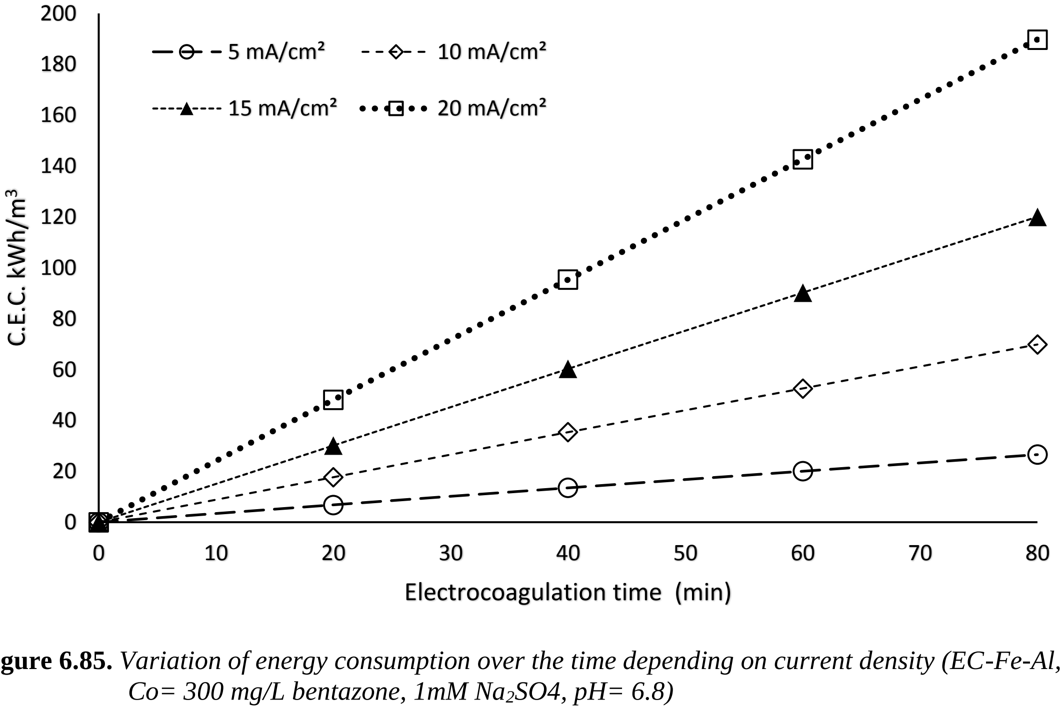

Figure 6.85. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 1mM* Na_2SO4*, pH= 6.8)*

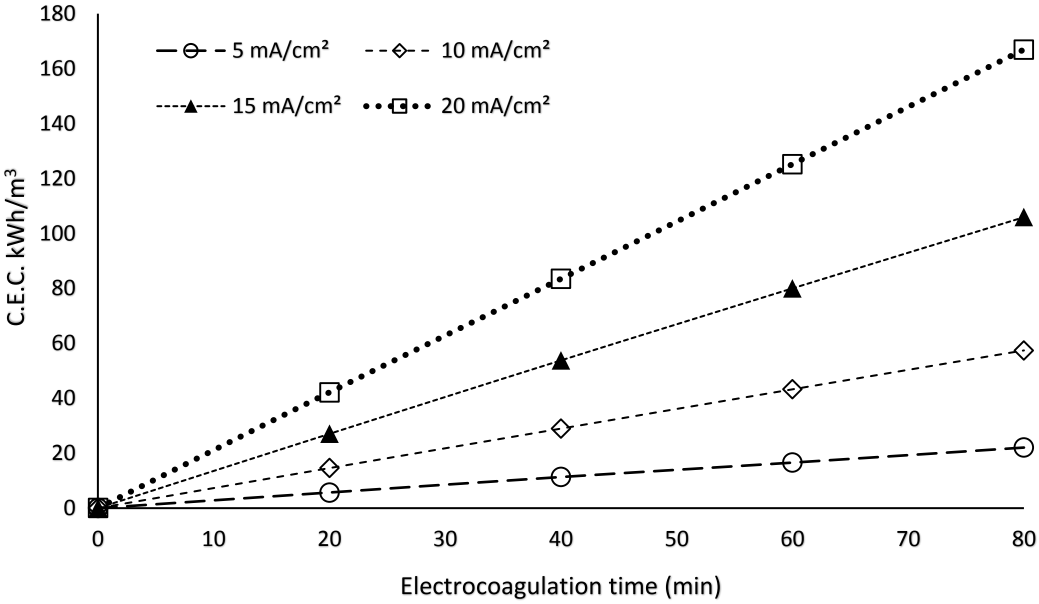

Figure 6.86. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 5mM Na_2SO4, pH= 6.5)*

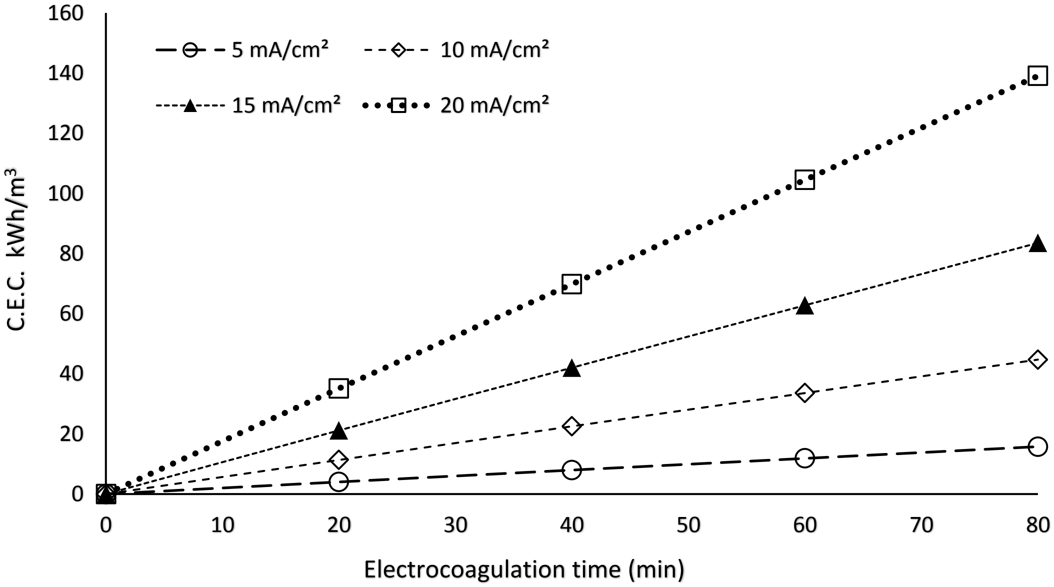

Figure 6.87. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 300 mg/L bentazone, 10 mM Na_2SO4, pH= 6.2)*

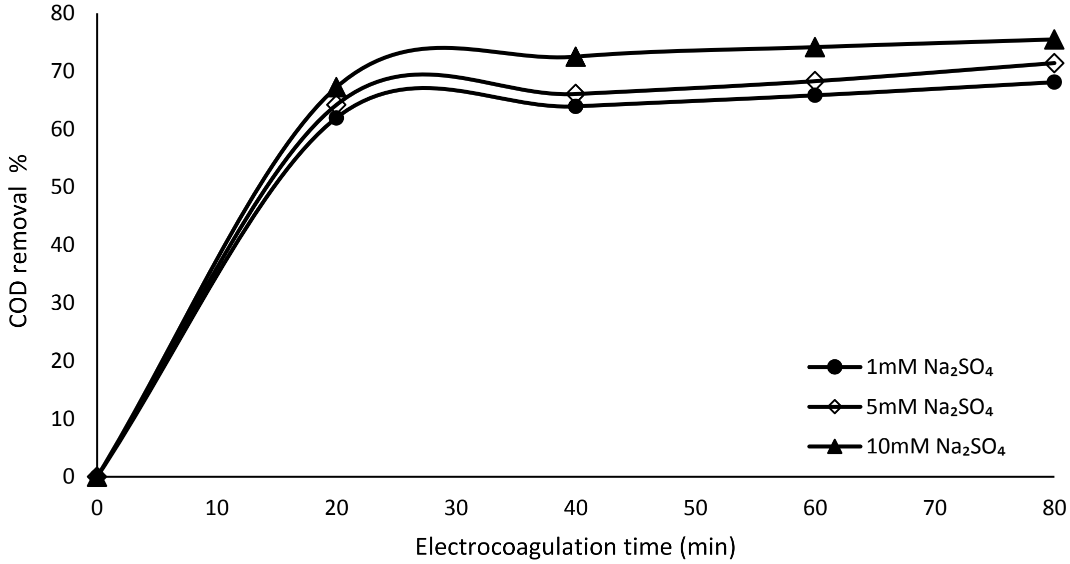

Figure 6.88. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 5mA/cm^2).*

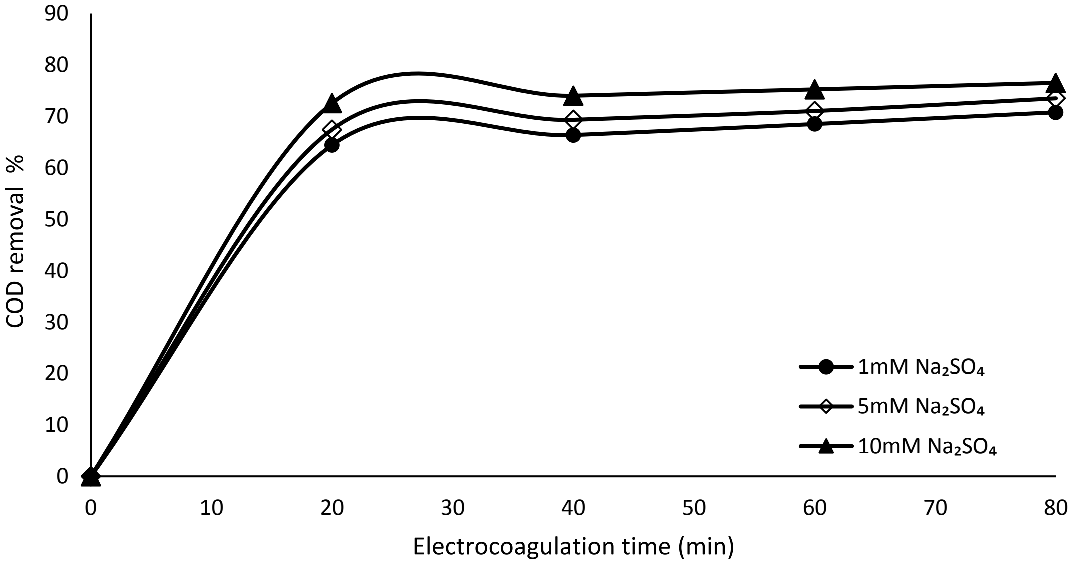

Figure 6.89. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 10 mA/cm^2).*

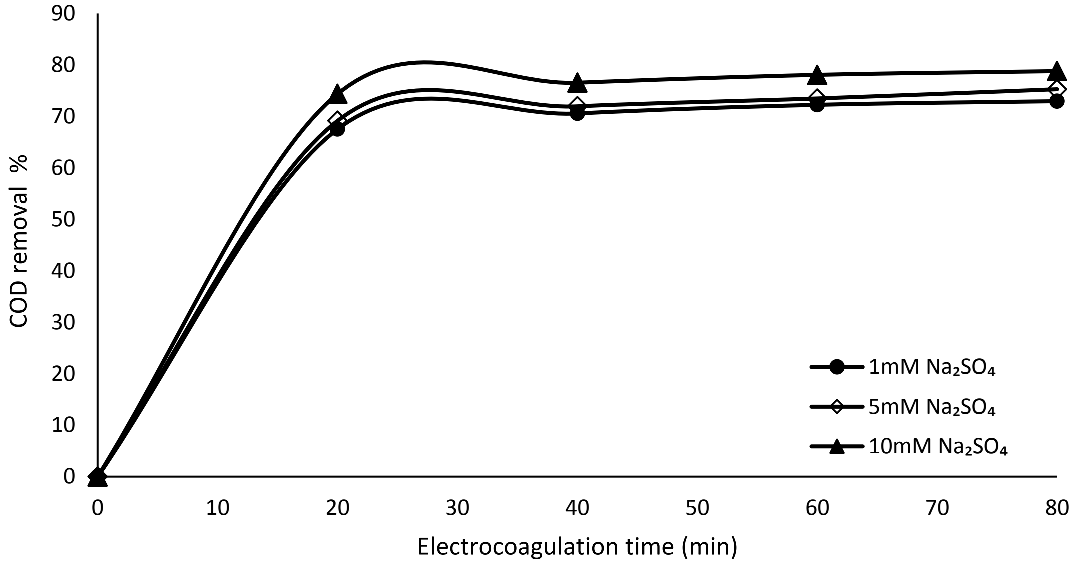

Figure 6 90. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 15mA/cm^2)*

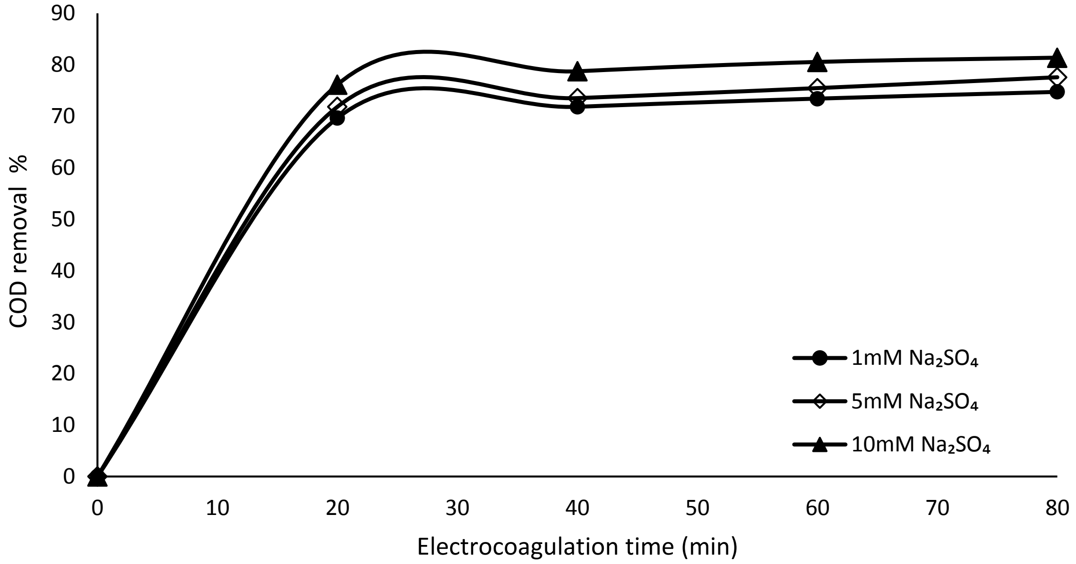

Figure 6.91. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 20 mA/cm^2)*

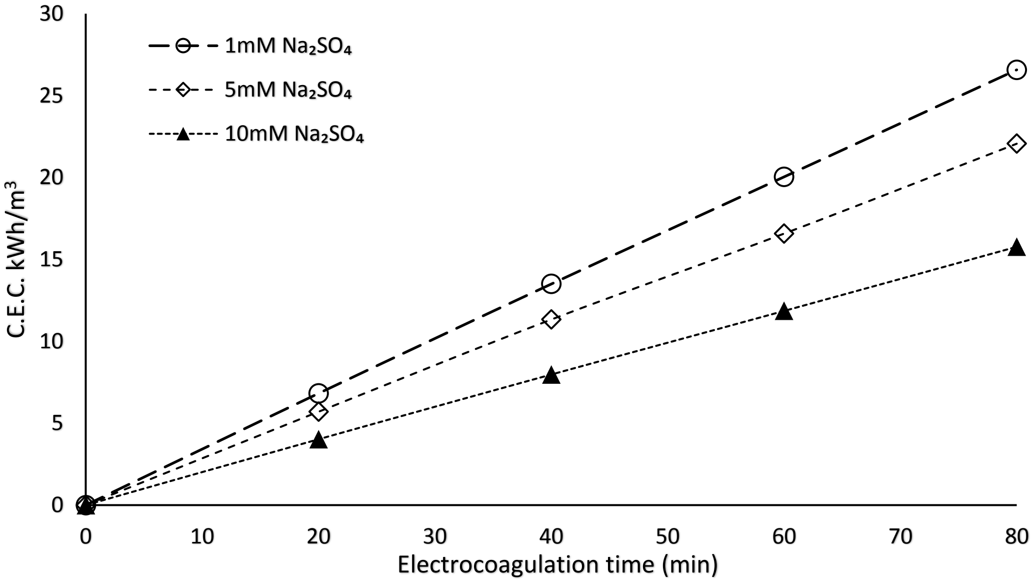

Figure 6.92. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 5mA/cm^2)*

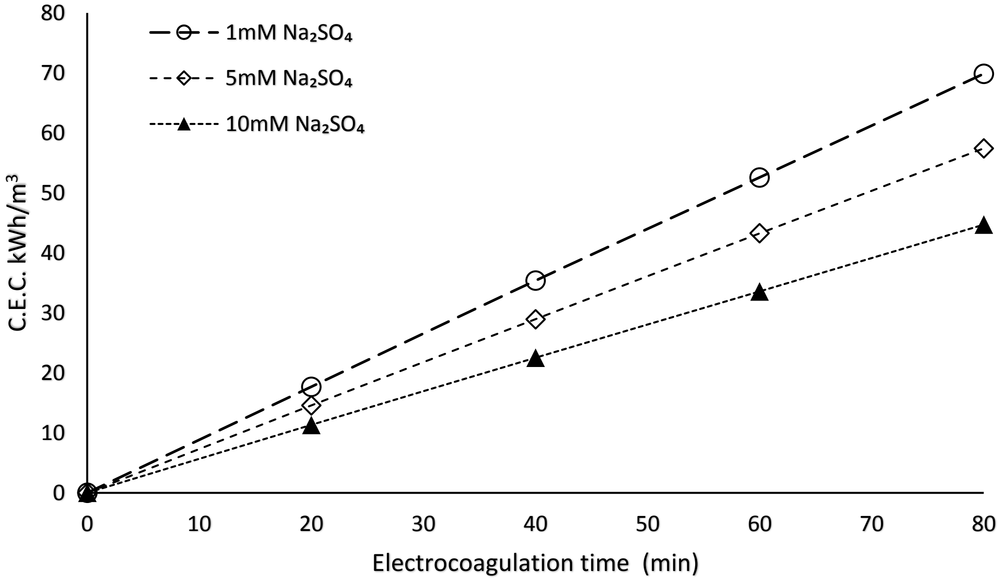

Figure 6.93. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 10 mA/cm^2)*

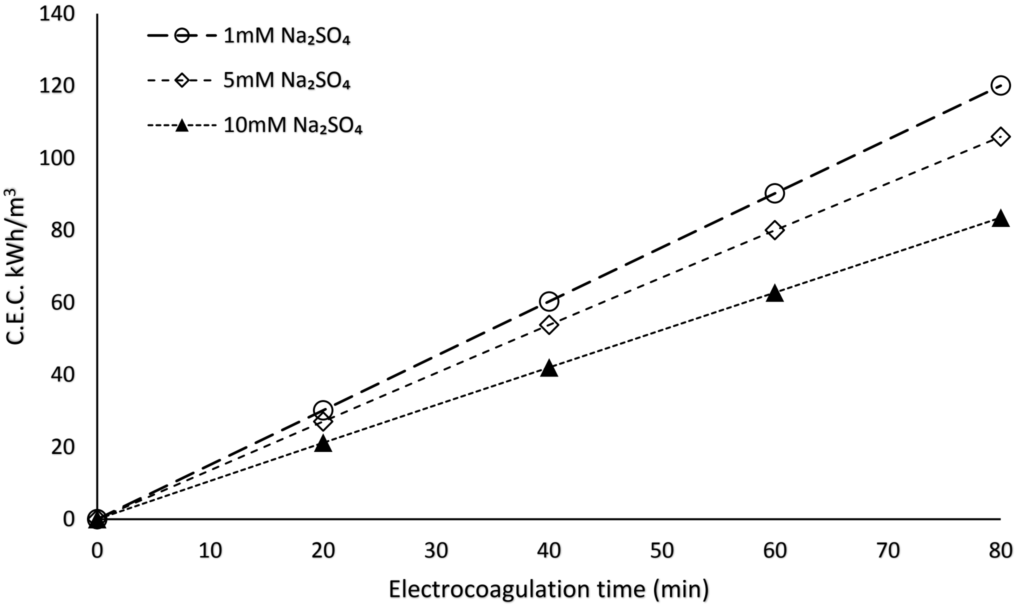

Figure 6.94. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 15 mA/cm^2)*

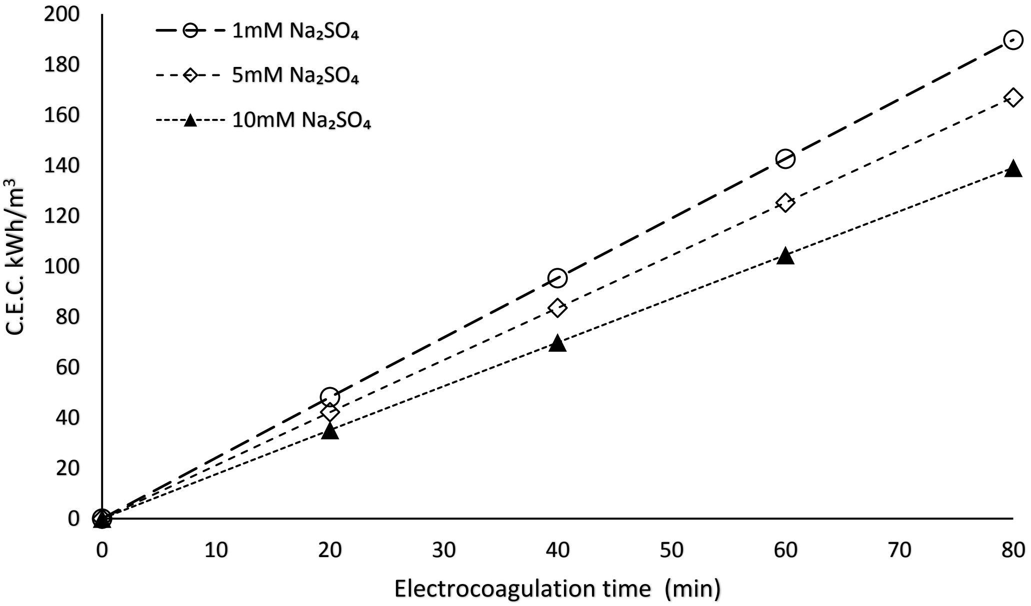

Figure 6.95. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 300 mg/L bentazone, 20 mA/cm^2)*

6.2.4. Electrochemical-Fenton methods

Table 6.82. *300 mg/L bentazone containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 6.57)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	17.6	568.82	0.0	0.0	0.0	0.0	0.0
20	15.5	176.19	69.03	0.00217	5.42	5.42	132.77
40	15.3	164.36	71.11	0.00214	5.35	10.77	131.06
60	15.1	155.69	72.63	0.00211	5.28	16.05	129.35
80	14.9	148.57	73.88	0.00208	5.21	21.26	127.63
Sludge amount (gram)= 1.22							

Table 6.83. *300 mg/L bentazone containing solution (EF, i=10 mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH=6.57)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.3	568.82	0.0	0.0	0.0	0.0	0.0
20	20.1	167.36	70.58	0.00556	13.89	13.89	340.27
40	19.8	160.85	71.72	0.00547	13.68	27.57	335.19
60	19.6	150.85	73.48	0.00542	13.54	41.11	331.80
80	19.4	139.32	75.51	0.00536	13.40	54.52	328.42
Sludge amount (gram)=1.41							

Table 6.84. *300 mg/L bentazone containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 6.57)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	26.9	568.82	0.0	0.0	0.0	0.0	0.0
20	25.3	147.69	74.04	0.01045	26.12	26.12	639.87
40	25.1	138.02	75.74	0.01036	25.91	25.91	634.81
60	25	125.18	77.99	0.01032	25.81	25.81	632.28
80	25	109.35	80.78	0.01032	25.81	25.81	632.28
Sludge amount (gram)=1.06							

Table 6.85. *300 mg/L bentazone containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 6.57)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.4	568.82	0.0	0.0	0.0	0.0	0.0
20	30	140.35	75.33	0.01658	41.46	41.46	1015.73
40	29.8	123.88	78.22	0.01647	41.18	41.18	1008.96
60	29.7	110.72	80.54	0.01642	41.04	41.04	1005.57
80	29.4	96.46	83.04	0.01625	40.63	40.63	995.41
Sludge amount (gram)= 1.18							

Table 6.86. *300 mg/L bentazone containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 6.76)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	16.1	544.68	0.0	0.0	0.0	0.0	0.0
20	14.3	150.72	72.33	0.00200	5.00	5.00	122.49
40	14.1	140.54	74.20	0.00197	4.93	9.93	120.78
60	13.9	132.32	75.71	0.00194	4.86	14.79	119.07
80	13.7	124.97	77.06	0.00192	4.79	19.58	117.36
Sludge amount (gram)= 0.97							

Table 6.87. *300 mg/L bentazone containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 1000mg H_2O_2/l, pH= 6.76)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	19.3	544.68	0.0	0.0	0.0	0.0	0.0
20	18.3	143.69	73.62	0.00506	12.64	12.64	309.79
40	18.1	138.42	74.59	0.00500	12.51	25.15	306.41
60	18.1	125.85	76.89	0.00500	12.51	37.66	306.41
80	18	117.21	78.48	0.00498	12.44	50.10	304.72
Sludge amount (gram)= 1.24							

Table 6.88. *300 mg/L bentazone containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 6.76)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	24.9	544.68	0.0	0.0	0.0	0.0	0.0
20	23.4	128.85	76.34	0.00966	24.16	24.16	591.81
40	23.2	110.72	79.67	0.00958	23.95	48.11	586.75
60	23.1	99.37	81.76	0.00954	23.85	71.95	584.23
80	23.2	90.37	83.41	0.00958	23.95	95.90	586.75
Sludge amount (gram)= 1.44							

Table 6.89. *300 mg/L bentazone containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 6.76)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	31.3	544.68	0.0	0.0	0.0	0.0	0.0
20	27.6	112.72	79.31	0.01526	38.14	38.14	934.47
40	27	102.13	81.25	0.01493	37.31	75.45	914.15
60	27.1	94.72	82.61	0.01498	37.45	112.91	917.54
80	27.1	83.13	84.74	0.01498	37.45	150.36	917.54
Sludge amount (gram)= 1.58							

Table 6.90. *300 mg/L bentazone containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 6.39).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	13.9	534.34	0.0	0.0	0.0	0.0	0.0
20	12.9	124.32	75.64	0.00180	4.51	4.51	110.50
40	12.2	111.29	78.05	0.00171	4.27	4.27	104.51
60	11.6	99.56	80.21	0.00162	4.06	4.06	99.37
80	11.4	87.17	82.50	0.00159	3.99	3.99	97.65
Sludge amount (gram)=1.36							

Table 6.91. *300 mg/L bentazone containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 6.39).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	19.4	534.34	0.0	0.0	0.0	0.0	0.0
20	16.2	116.46	77.09	0.00448	11.19	11.19	274.24
40	15.7	104.18	79.36	0.00434	10.85	10.85	265.78
60	15.5	93.36	81.35	0.00428	10.71	10.71	262.39
80	15.2	80.69	83.69	0.00420	10.50	10.50	257.31
Sludge amount (gram)=1.34							

Table 6.92. *300 mg/L bentazone containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 2000mg H_2O_2/l, pH= 6.39).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.2	534.34	0.0	0.0	0.0	0.0	0.0
20	19.5	102.97	80.73	0.00805	20.13	20.13	493.18
40	19.3	90.18	83.12	0.00797	19.92	40.05	488.12
60	19.1	82.67	84.53	0.00789	19.72	59.77	483.06
80	18.9	70.26	86.85	0.00780	19.51	79.28	478.00
Sludge amount (gram)=1.69							

Table 6.93. *300 mg/L bentazone containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 2000mg H_2O_2/l, pH= 6.39).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	30.2	534.34	0.0	0.0	0.0	0.0	0.0
20	25.1	88.96	83.35	0.01387	34.69	34.69	849.83
40	25	81.54	84.74	0.01382	34.55	69.24	846.44
60	25.1	74.47	86.06	0.01387	34.69	103.92	849.83
80	24.9	60.12	88.75	0.01376	34.41	138.33	843.05
Sludge amount (gram)=1.41							

Table 6.94. *300 mg/L bentazone containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/l, pH= 6.56).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	12.7	532.47	0.0	0.0	0.0	0.0	0.0
20	10.7	138.21	74.04	0.00150	3.74	3.74	91.66
40	10.6	123.93	76.73	0.00148	3.71	7.45	90.80
60	10.5	115.33	78.34	0.00147	3.67	11.12	89.94
80	10.6	103.11	80.64	0.00148	3.71	14.83	90.80
Sludge amount (gram)= 1.28							

Table 6.95. *300 mg/L bentazone containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4. 3000 mg H_2O_2/l, pH= 6.56).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	17.4	532.47	0.0	0.0	0.0	0.0	0.0
20	14.3	129.99	75.59	0.00395	9.88	9.88	242.08
40	14.1	118.52	77.74	0.00390	9.74	19.62	238.69
60	14	110.64	79.22	0.00387	9.67	29.30	237.00
80	14	98.18	81.56	0.00387	9.67	38.97	237.00
Sludge amount (gram)= 1.48							

Table 6.96. *300 mg/L bentazone containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4. 3000 mg H_2O_2/l, pH= 6.56).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.1	532.47	0.0	0.0	0.0	0.0	0.0
20	17.3	105.52	80.18	0.00714	17.86	17.86	437.54
40	17.1	92.64	82.60	0.00706	17.65	35.51	432.48
60	16.8	86.37	83.78	0.00694	17.34	52.85	424.89
80	16.9	74.93	85.93	0.00698	17.45	70.30	427.42
Sludge amount (gram)=1.23							

Table 6.97. *300 mg/L bentazone containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4. 3000 mg H_2O_2/l, pH= 6.56).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	29.9	532.47	0.0	0.0	0.0	0.0	0.0
20	23	90.52	83.00	0.01271	31.78	31.78	778.72
40	22.8	86.64	83.73	0.01260	31.51	63.29	771.95
60	22.6	75.37	85.85	0.01249	31.23	94.53	765.18
80	22.3	66.93	87.43	0.01233	30.82	125.34	755.02
Sludge amount (gram)=1.61							

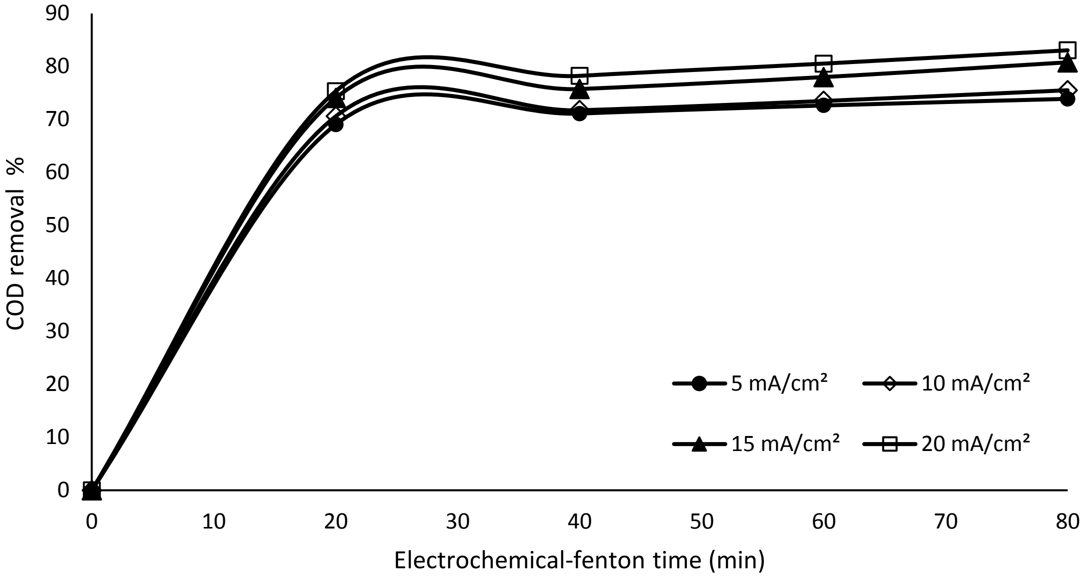

Figure 6.96. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bentazone, 1mM Na_2SO_4, 500mg H_2O_2/L, pH= 6.57)*

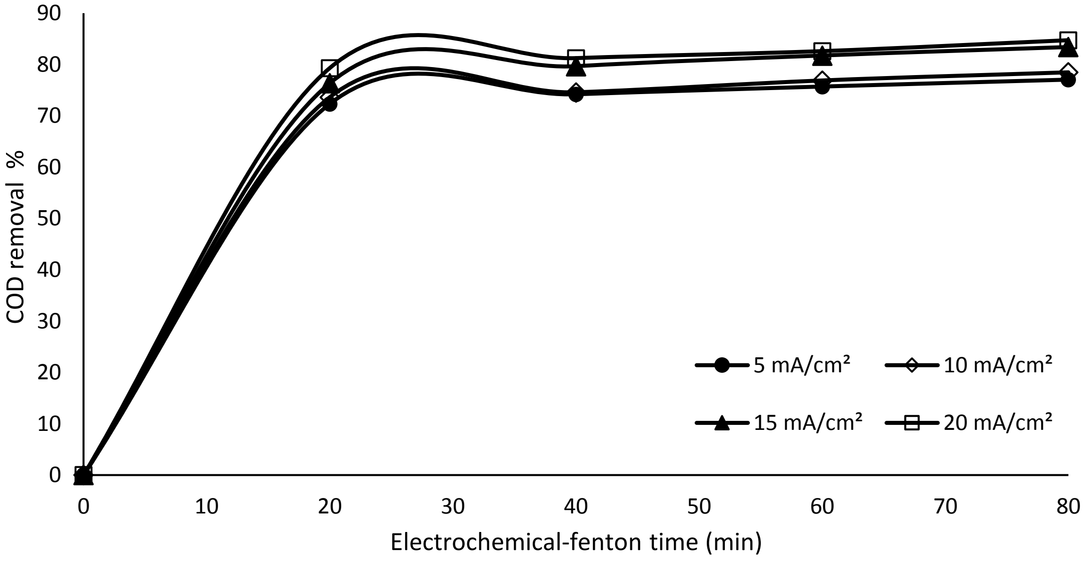

Figure 6.97. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L bentazone, 1mM Na_2SO_4, 1000mg H_2O_2/L, pH= 6.76)*

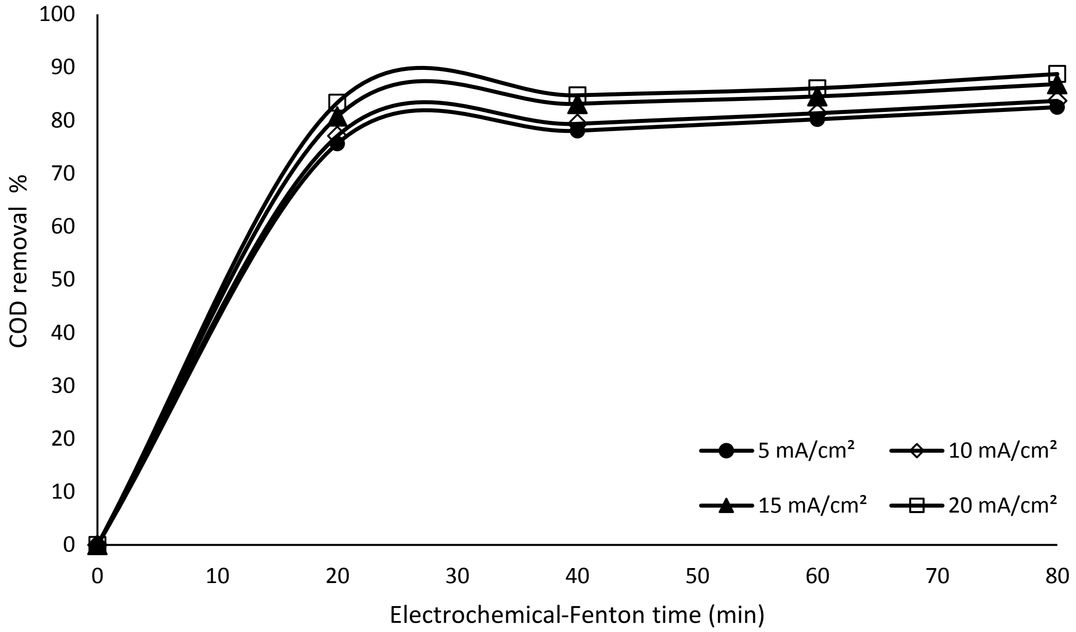

Figure 6.98. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 2000mg H_2O_2/L, pH= 6.39)*

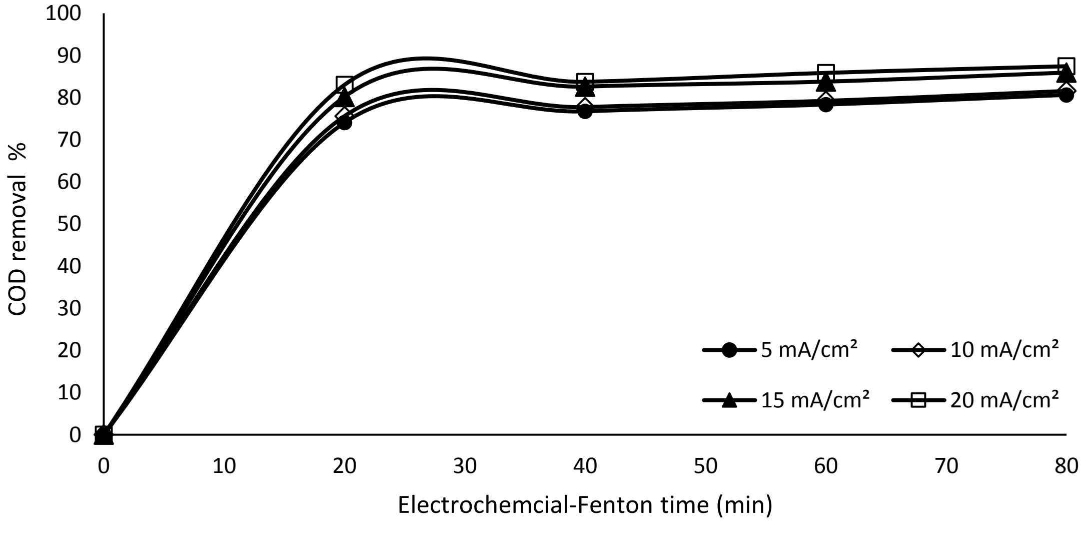

Figure 6.99. *Variation of COD removal over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 3000mg H_2O_2/L, pH= 6.56)*

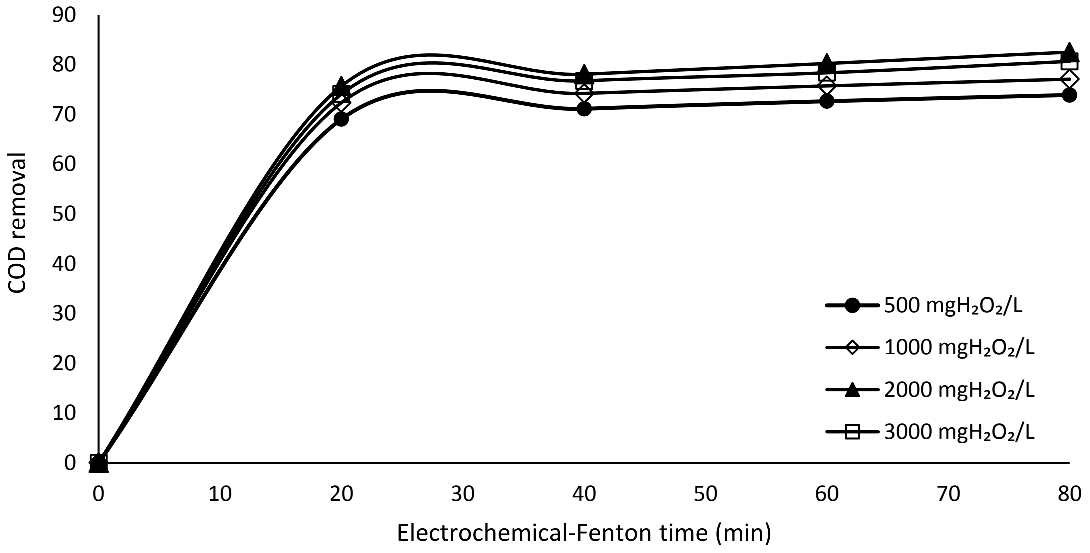

Figure 6.100. *Variation of COD removal over the time depending on* H_2O_2 *concentration (EF, Co= 300 mg/L Bentazone,* $i=5mA/cm^2$*, 1mM* Na_2SO_4*)*

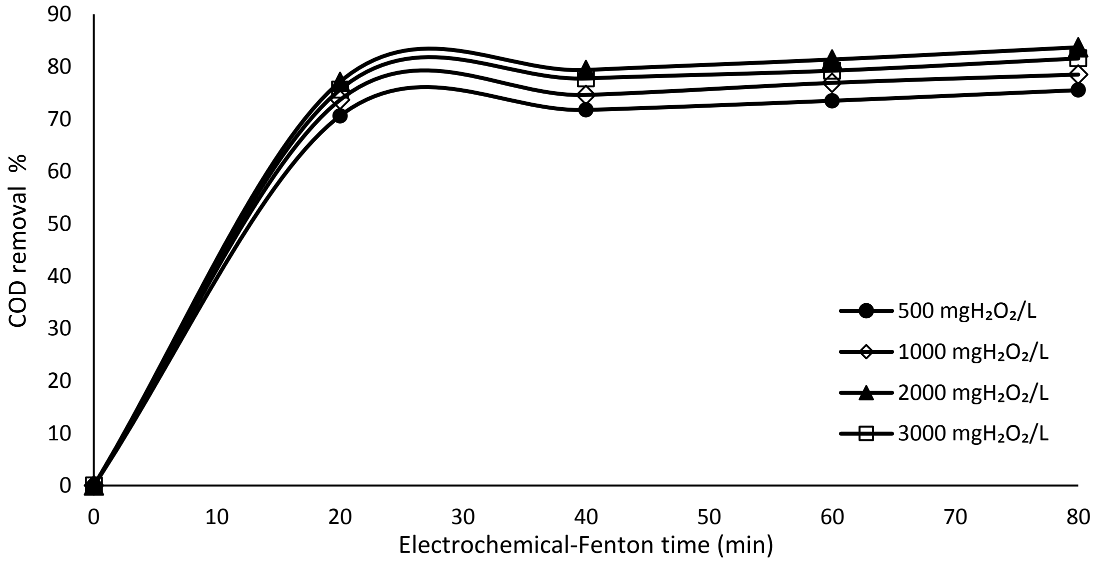

Figure 6.101. *Variation of COD removal over the time depending on* H_2O_2 *concentration (EF, Co= 300 mg/L Bentazone,* $i=10mA/cm^2$*, 1mM* Na_2SO_4*)*

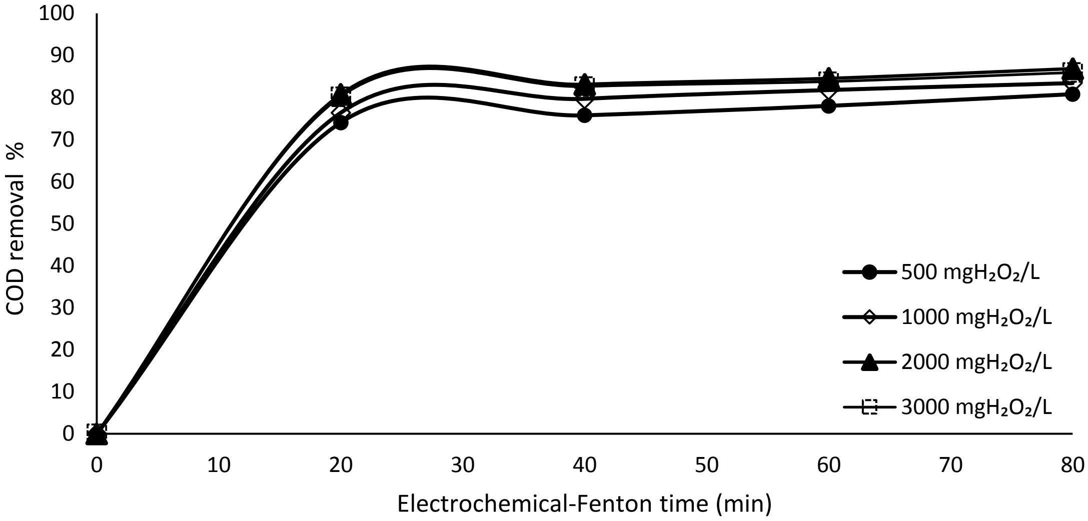

Figure 6.102. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L Bentazone, i=15mA/cm^2, 1mM Na_2SO_4)*

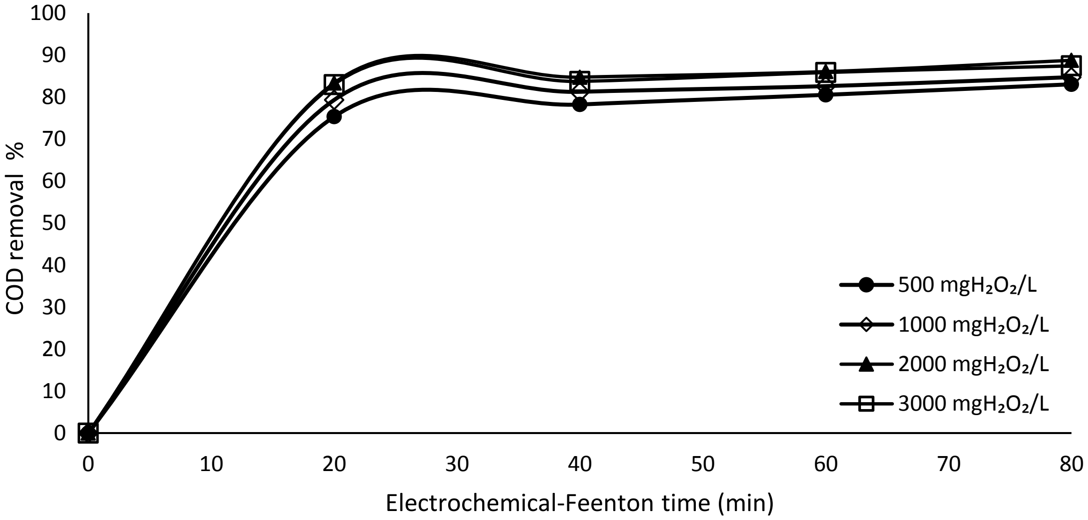

Figure 6.103. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L Bentazone, i=20mA/cm^2, 1mM Na_2SO_4)*

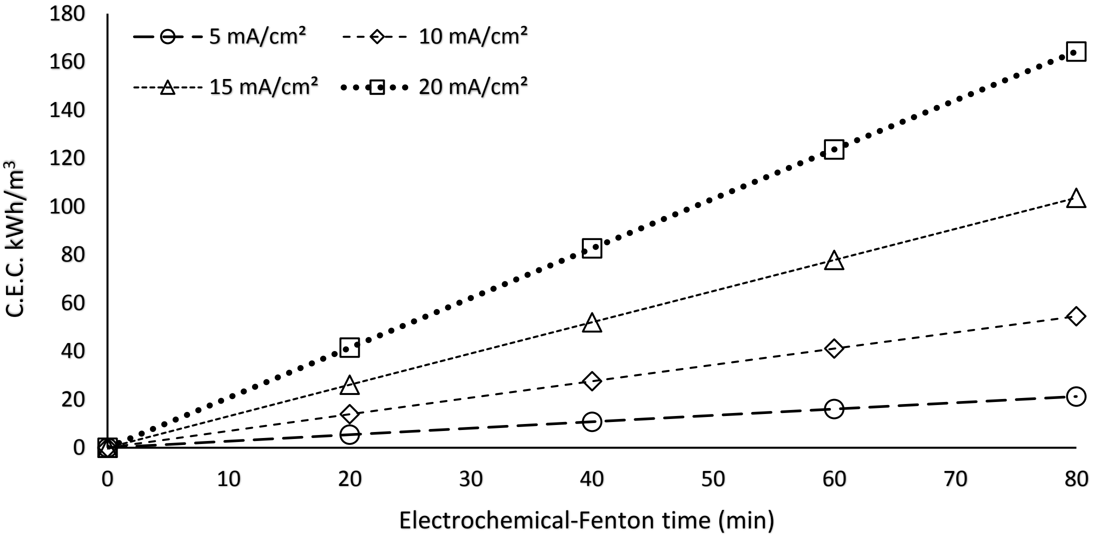

Figure 6.104. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 500mg H_2O_2/L, pH= 6.57)*

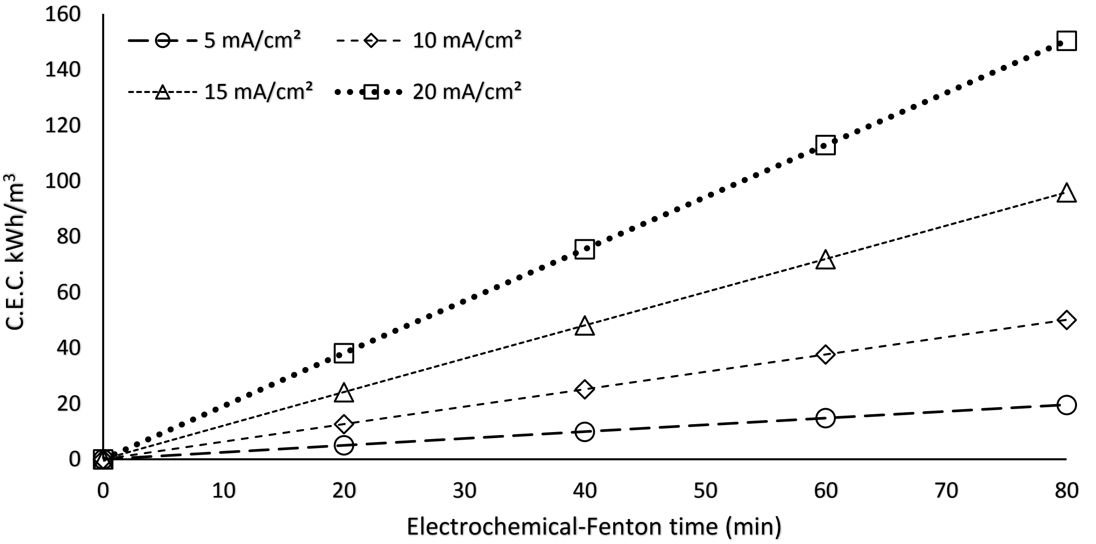

Figure 6.105. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 1000mg H_2O_2/L, pH= 6.76)*

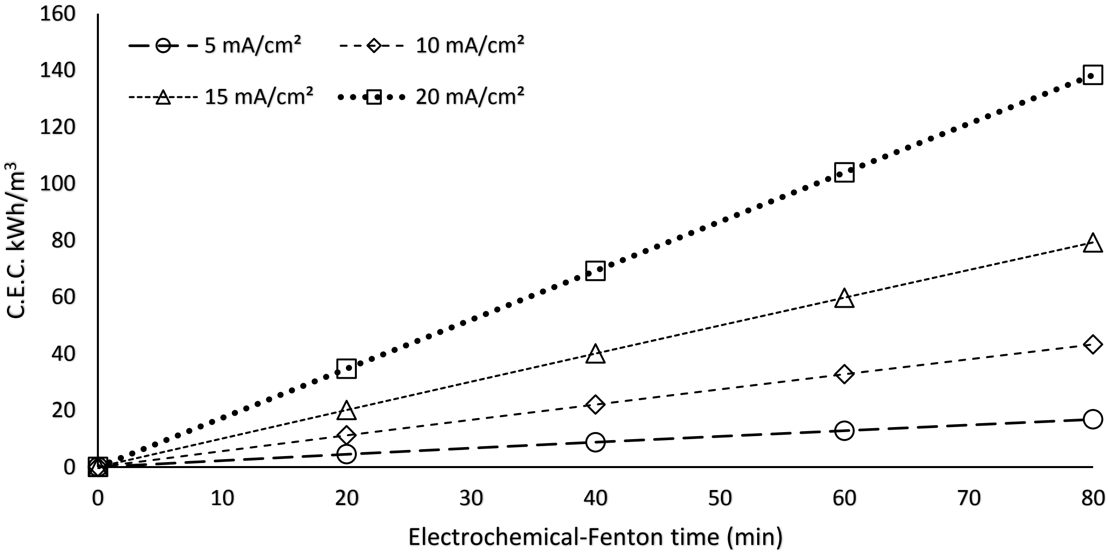

Figure 6.106. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 2000mg H_2O_2/L, pH= 6.39)*

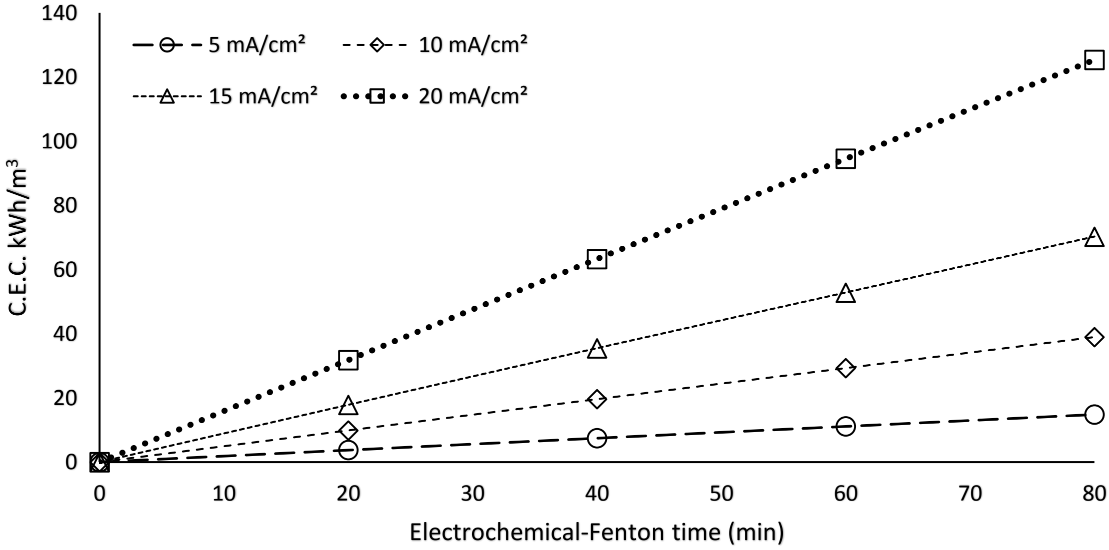

Figure 6.107. *Variation of energy consumption over the time depending on current density (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, 3000mg H_2O_2/L, pH= 6.56)*

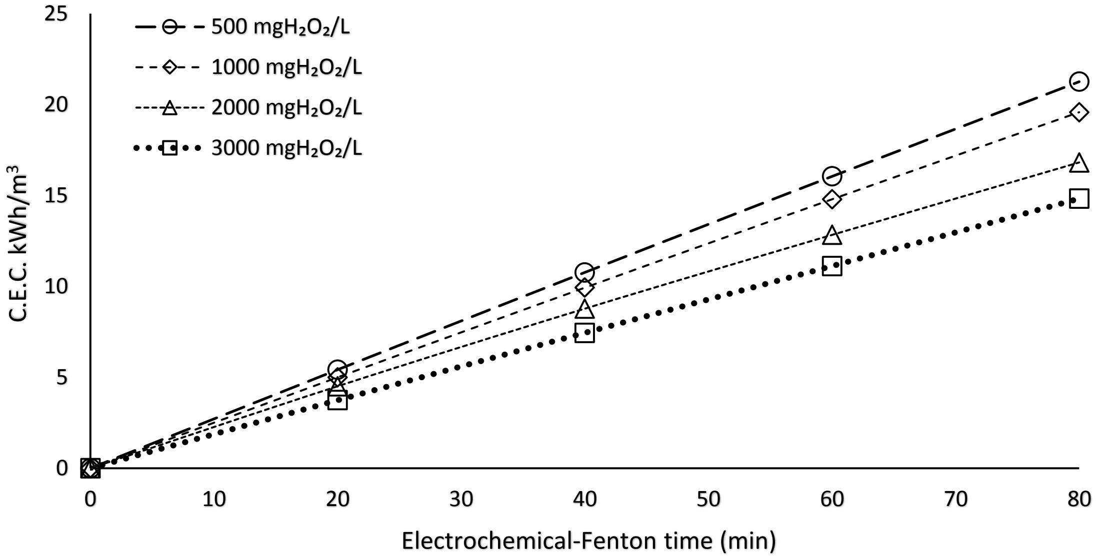

Figure 6.108. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, i=5mA/cm^2)*

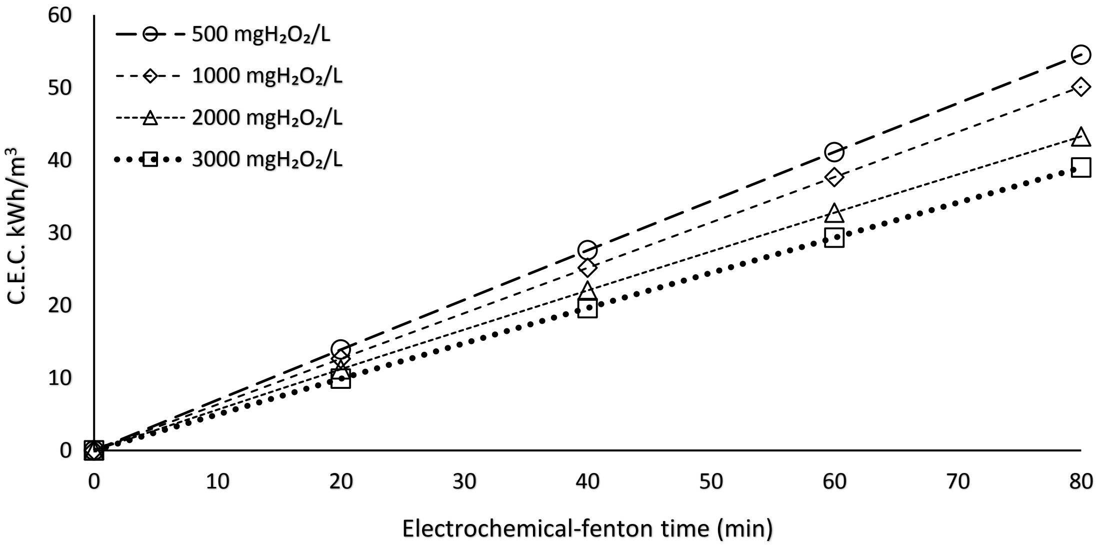

Figure 6.109. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 300 mg/L Bentazone, 1mM Na_2SO_4, i=10mA/cm^2)*

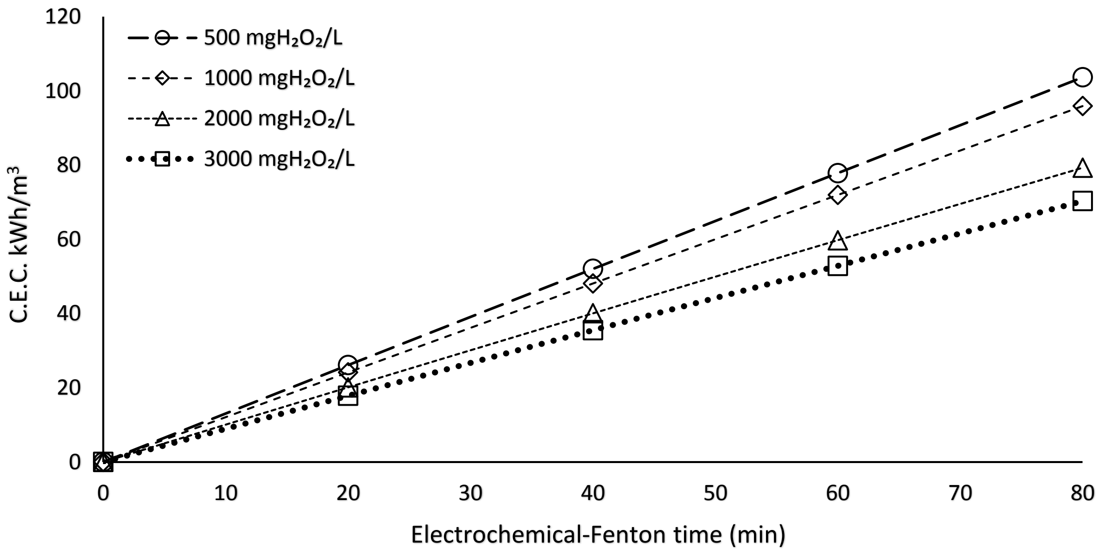

Figure 6.110. *Variation of energy consumption over the time depending on* H_2O_2 *concentration (EF, Co= 300 mg/L Bentazone, 1mM* Na_2SO_4*, i=15mA/cm*^{2}*).*

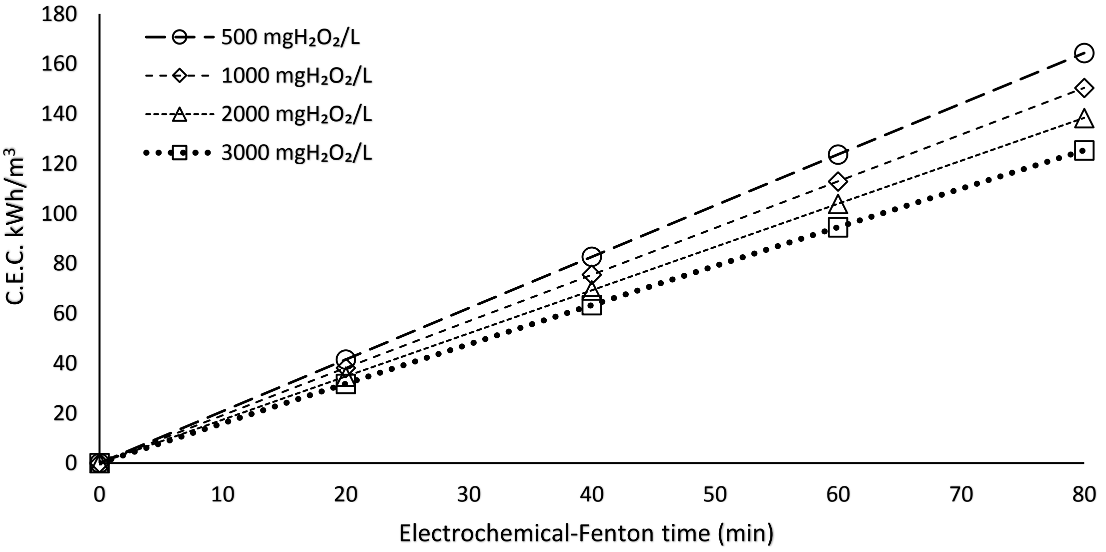

Figure 6.111. *Variation of energy consumption over the time depending on* H_2O_2 *concentration (EF, Co= 300 mg/L Bentazone, 1mM* Na_2SO_4*, i=20mA/cm*^{2}*).*

6.2.5. Electro-oxidation methods using a boron-doped diamond (BDD)

Table 6.98. *300 mg/L bentazone containing solution (EO, i=5mA/cm^2, 5mM Na_2SO_4, pH= 6.43)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	6.5	539.58	0.0	0.0	0.0	0.0	0.0
20	6.8	180.65	66.52	0.00095	2.38	2.38	58.25
40	6.9	159.64	70.41	0.00097	2.41	4.79	59.11
60	6.9	134.57	75.06	0.00097	2.41	7.20	59.11
80	6.8	122.56	77.29	0.00095	2.38	9.58	58.25

Table 6.99. *300 mg/L bentazone containing solution (EO, i=10mA/cm^2, 5mM Na_2SO_4, pH= 6.43)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	8.5	539.58	0.0	0.0	0.0	0.0	0.0
20	8.5	160.25	70.30	0.00235	5.87	5.87	143.90
40	8.3	140.84	73.90	0.00229	5.74	11.61	140.51
60	8.2	114.40	78.80	0.00227	5.67	17.27	138.82
80	8.3	102.37	81.03	0.00229	5.74	23.01	140.51

Table 6.100. 300 *mg/L bentazone containing solution (EO, i=15mA/cm^2, 5mM Na_2SO_4, pH= 6.43)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.9	539.58	0.0	0.0	0.0	0.0	0.0
20	10.1	144.79	73.17	0.00417	10.43	10.43	255.44
40	10.2	125.34	76.77	0.00421	10.53	20.96	257.97
60	10.2	105.19	80.50	0.00421	10.53	31.49	257.97
80	10.3	86.44	83.98	0.00425	10.63	42.12	260.50

Table 6.101. *300 mg/L bentazone containing solution (EO, i=20mA/cm^2, 5mM Na_2SO_4, pH= 6.43)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	13.2	539.58	0.0	0.0	0.0	0.0	0.0
20	12.8	133.82	75.20	0.00708	17.69	17.69	433.38
40	12.5	101.23	81.24	0.00691	17.27	34.96	423.222
60	12.2	86.69	83.93	0.00674	16.86	51.82	413.065
80	12.1	75.47	86.01	0.00669	16.72	68.54	409.679

Table 6.102. *300 mg/L bentazone containing solution (EO, i=5mA/cm^2, 10mM Na_2SO_4, pH= 6.31)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	4.5	557.28	0.0	0.0	0.0	0.0	0.0
20	4.3	160.25	71.24	0.00060	1.50	1.50	36.84
40	4.3	130.64	76.56	0.00060	1.50	3.01	36.84
60	4.3	118.78	78.69	0.00060	1.50	4.51	36.84
80	4.2	106.41	80.91	0.00059	1.47	5.98	35.98

Table 6.103. *300 mg/L bentazone containing solution (EO, i=10mA/cm^2, 10mM Na_2SO_4, pH= 6.31)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	6.1	557.28	0.0	0.0	0.0	0.0	0.0
20	6.1	139.87	74.90	0.00169	4.21	4.21	103.27
40	6.1	114.69	79.42	0.00169	4.21	8.43	103.27
60	5.9	97.18	82.56	0.00163	4.08	12.51	99.88
80	6	81.61	85.36	0.00166	4.15	16.65	101.57

Table 6.104. *300 mg/L bentazone containing solution (EO, i=15mA/cm^2, 10mM Na_2SO_4, pH= 6.31)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	8	557.28	0.0	0.0	0.0	0.0	0.0
20	7.9	112.56	79.80	0.00326	8.16	8.16	199.80
40	7.9	96.88	82.62	0.00326	8.16	16.31	199.80
60	8	82.67	85.17	0.00330	8.26	24.57	202.33
80	7.8	66.32	88.10	0.00322	8.05	32.62	197.27

Table 6.105. *300 mg/L bentazone containing solution (EO, i=20mA/cm^2, 10mM Na_2SO_4, pH= 6.31)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.6	557.28	0.0	0.0	0.0	0.0	0.0
20	10.5	94.74	83.00	0.00580	14.51	14.51	355.51
40	10.6	75.99	86.36	0.00586	14.65	29.16	358.89
60	10.3	61.10	89.04	0.00569	14.23	43.39	348.74
80	10.3	49.17	91.18	0.00569	14.23	57.63	348.74

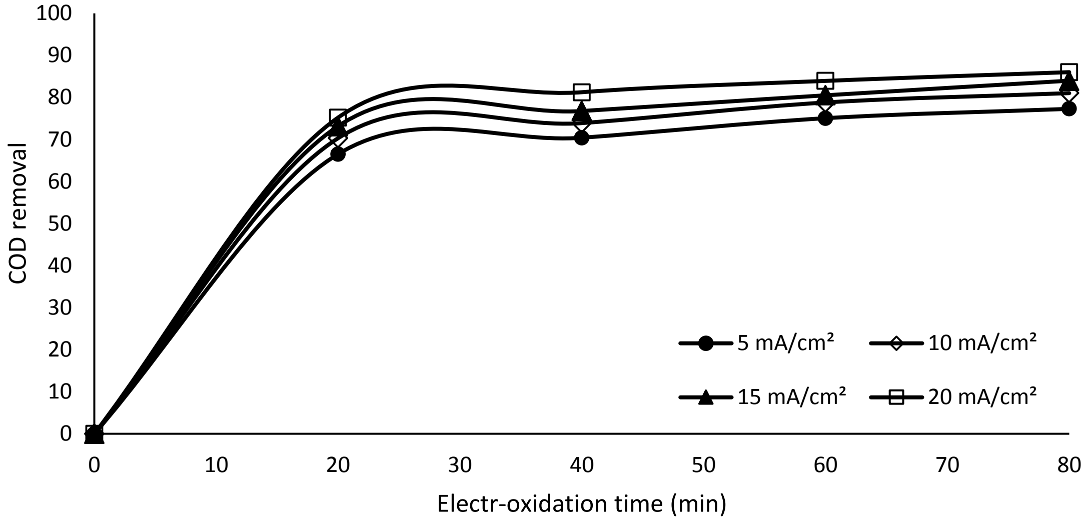

Figure 6.112. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bentazone, 5mM Na_2SO_4, pH= 6.43)*

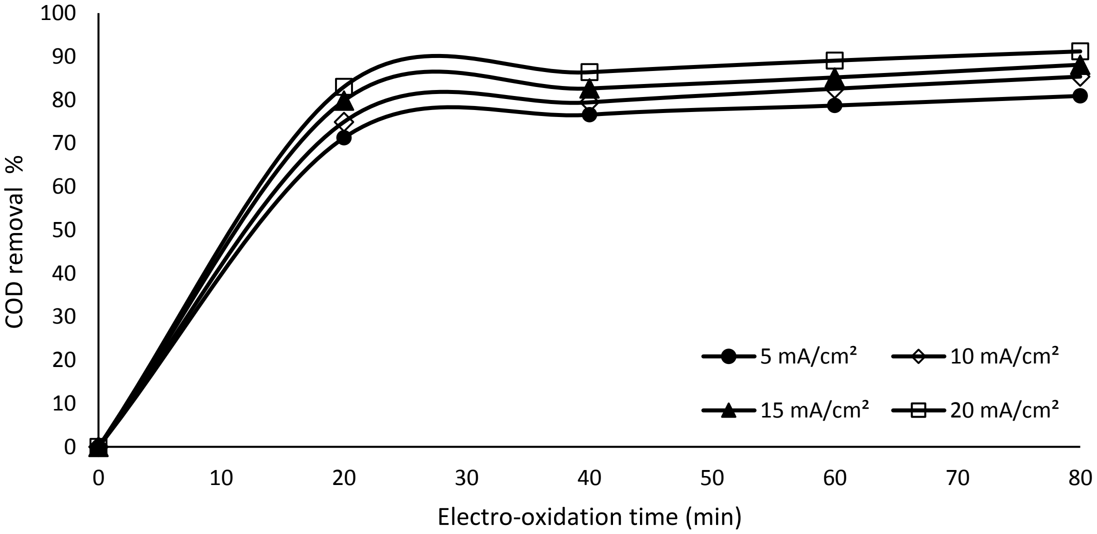

Figure 6.113. *Variation of COD removal over the time depending on current density (EO, Co= 300 mg/L bentazone, 10mM Na_2SO_4, pH= 6.31)*

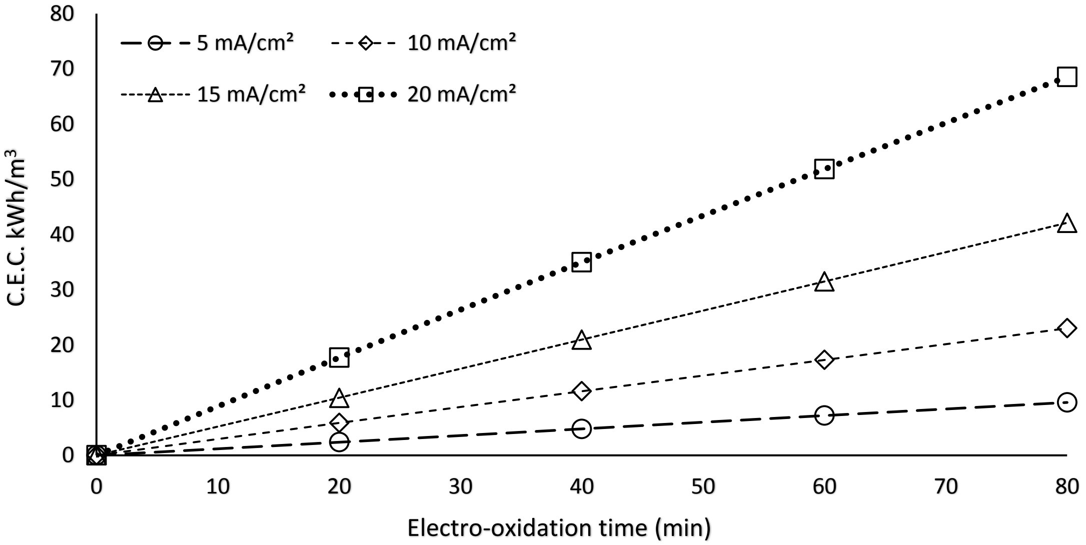

Figure 6.114. *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bentazone, 5mM* Na_2SO_4*, pH= 6.43)*

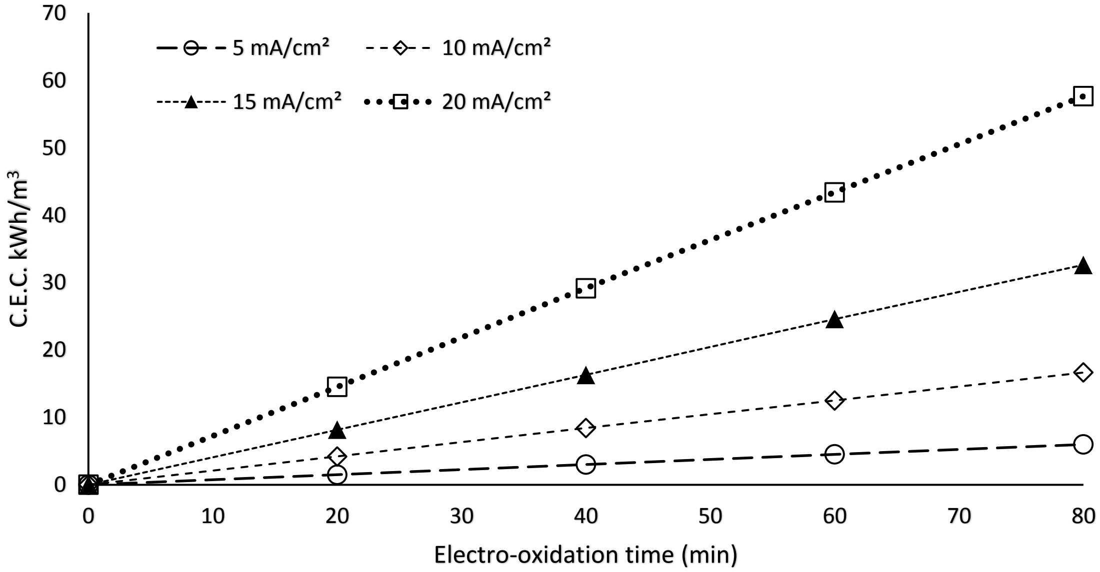

Figure 6.115. *Variation of energy consumption over the time depending on current density (EO, Co= 300 mg/L bentazone, 10 mM* Na_2SO_4*, pH= 6.31)*

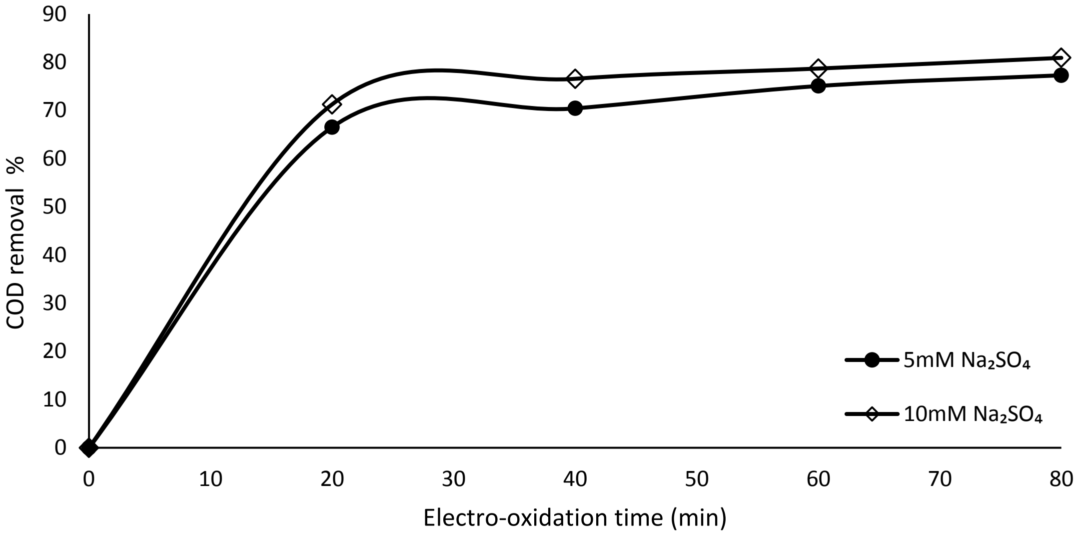

Figure 6.116. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bentazone, 5mA/cm^2)*

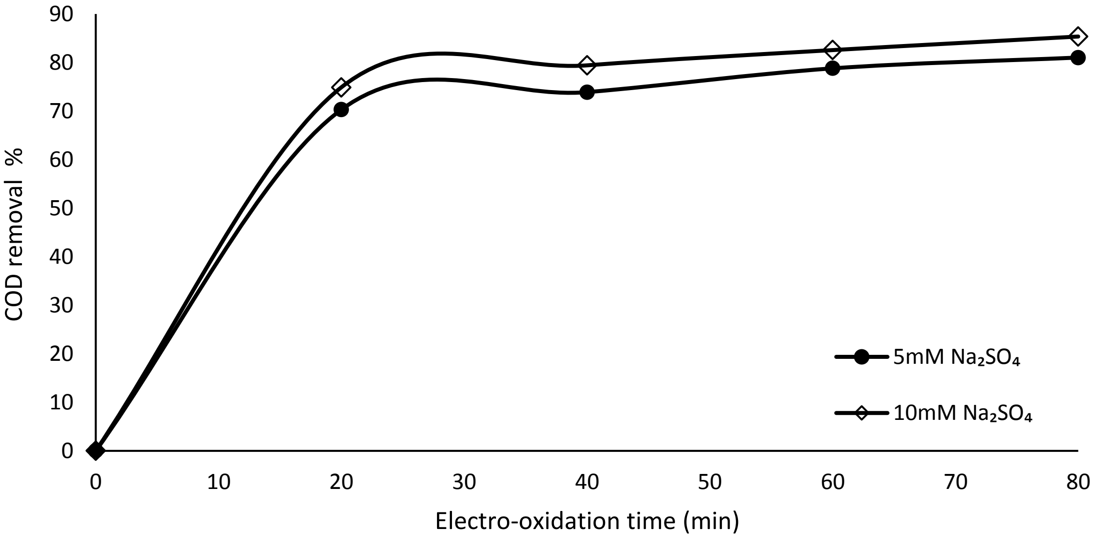

Figure 6 117. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bentazone, 10 mA/cm^2)*

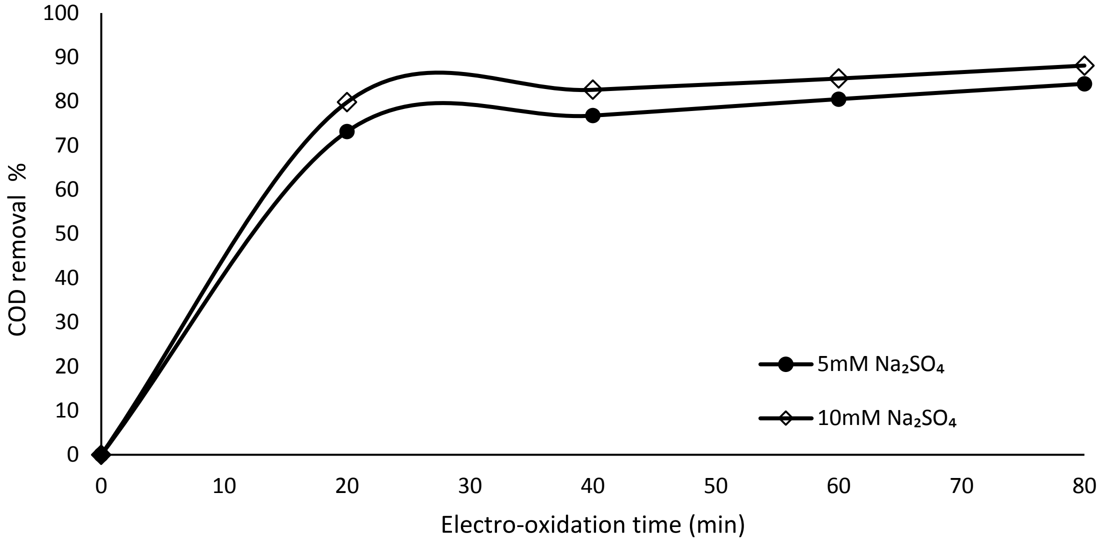

Figure 6.118. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bentazone, 15 mA/cm^2)*

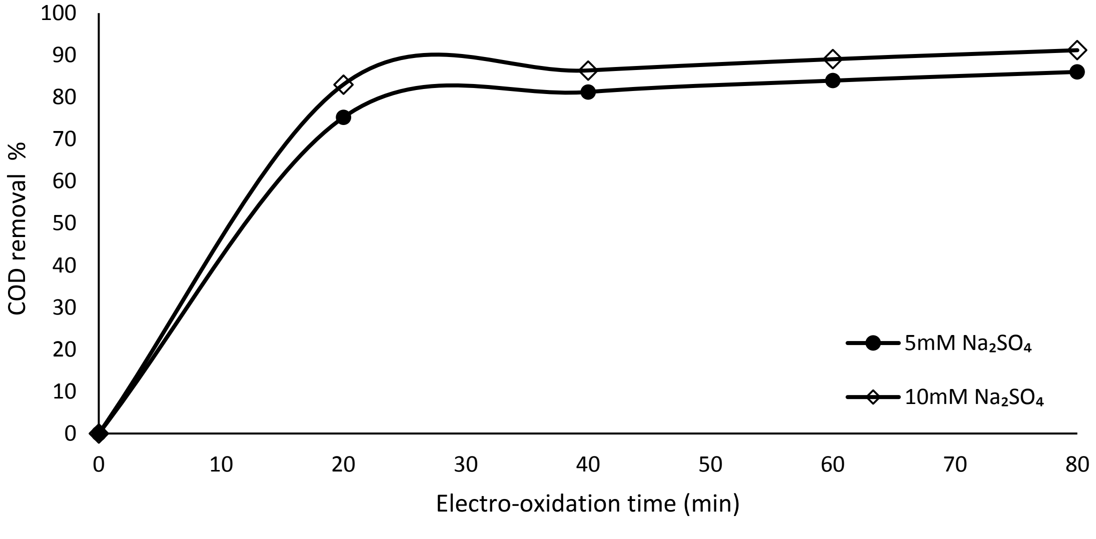

Figure 6.119. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 300 mg/L bentazone, 20 mA/cm^2)*

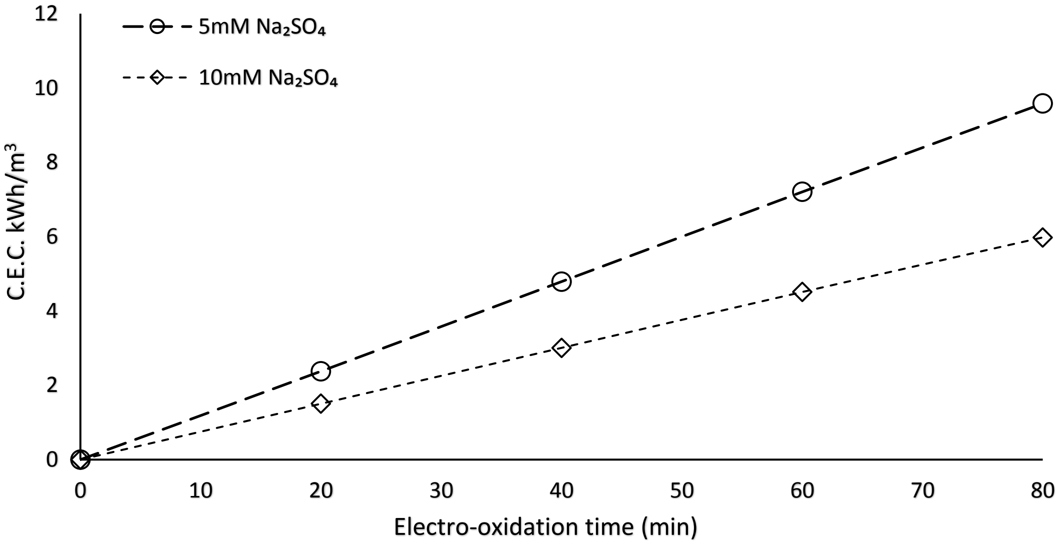

Figure 6.120. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bentazone, 5mA/cm^2)*

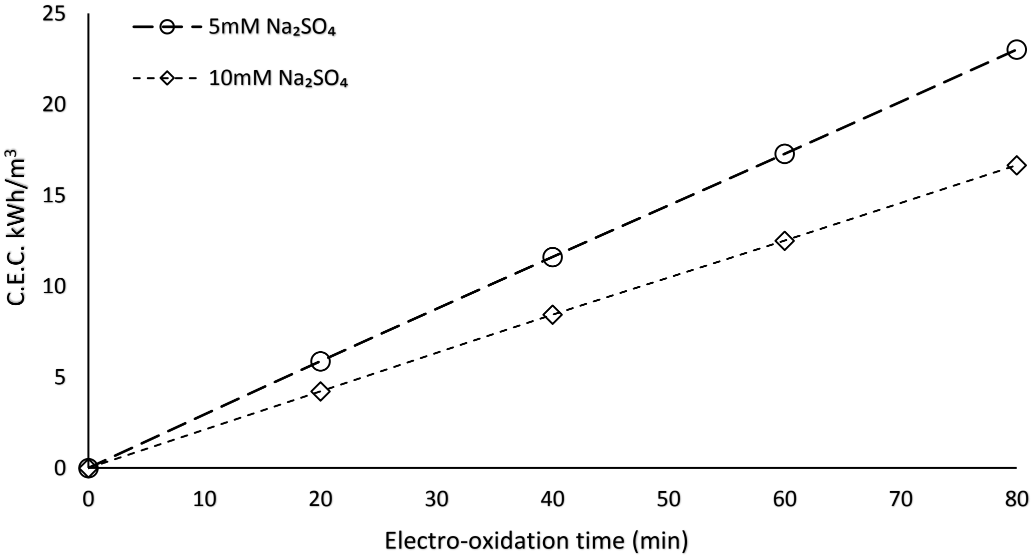

Figure 6.121. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bentazone, 10 mA/cm^2)*

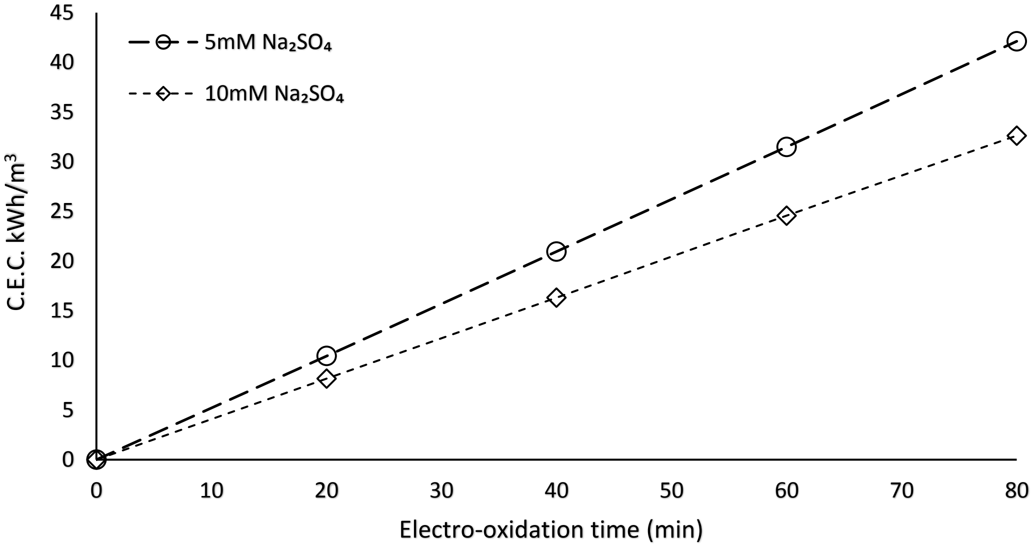

Figure 6.122. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bentazone, 15mA/cm^2)*

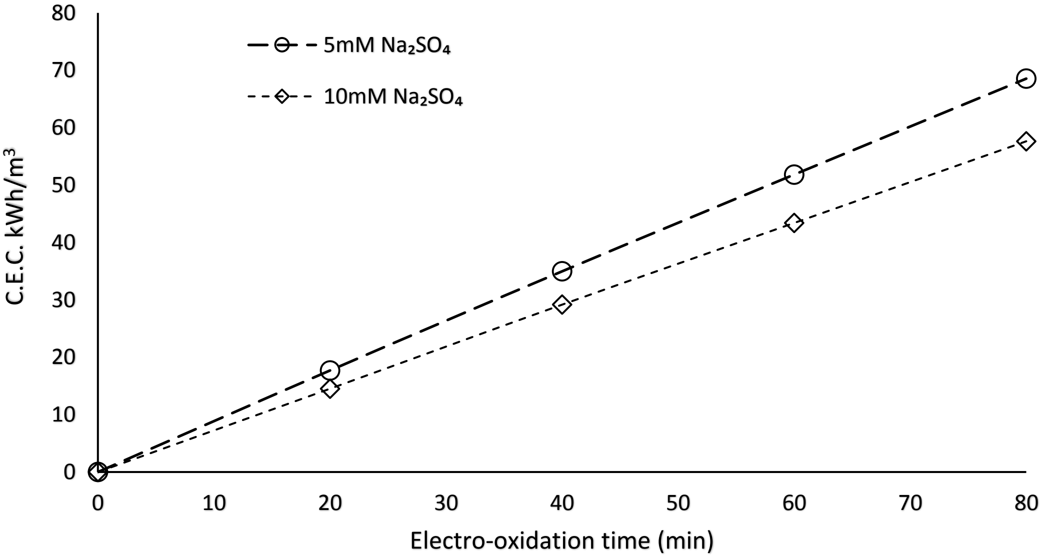

Figure 6.123. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 300 mg/L bentazone, 20mA/cm^2)*

6.2.6. Ion chromatography (IC)

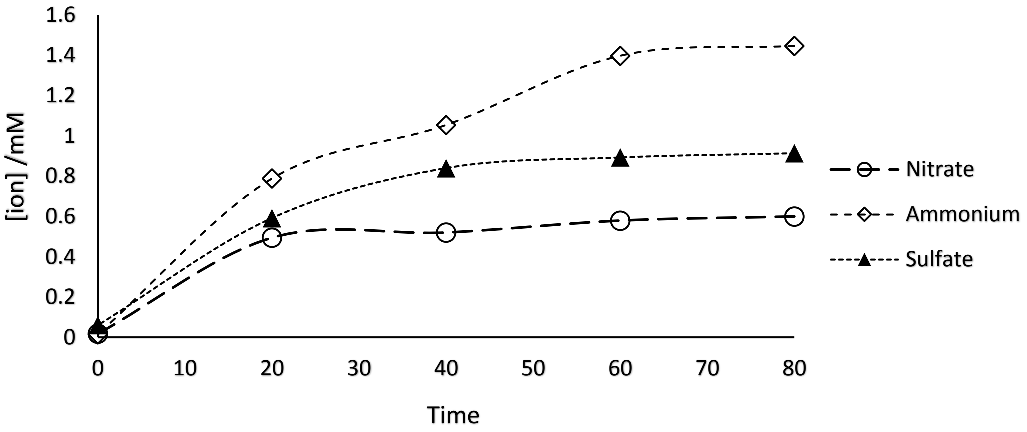

Figure 6.124. *Inorganic ions Concentration over the time during electrocoagulation of bentazone solution measured by IC (EC, Co= 300 mg/l, 10 mM NaCl, 20 mA/cm^2)*

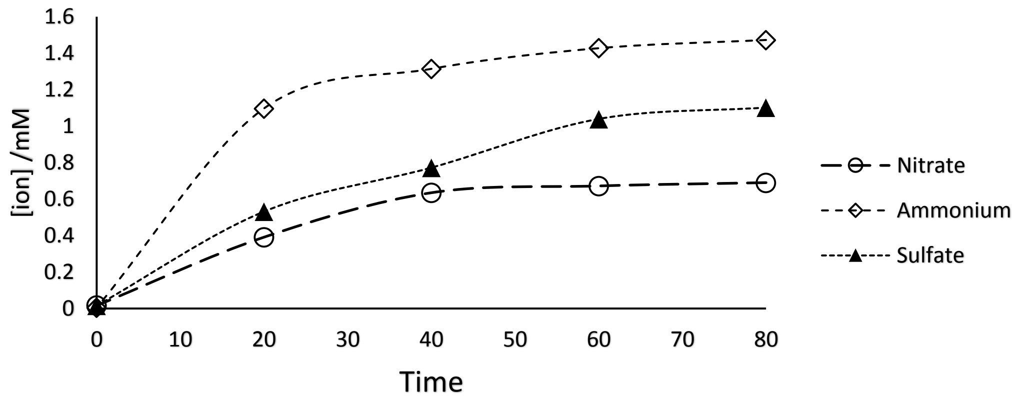

Figure 6.125. *Inorganic ions Concentration over the time during electrochemical-Fenton of bentazone solution measured by IC (EF, Co= 300 mg/l, 1 mM NaCl, 2000mg H_2O_2/l, 20 mA/cm^2)*

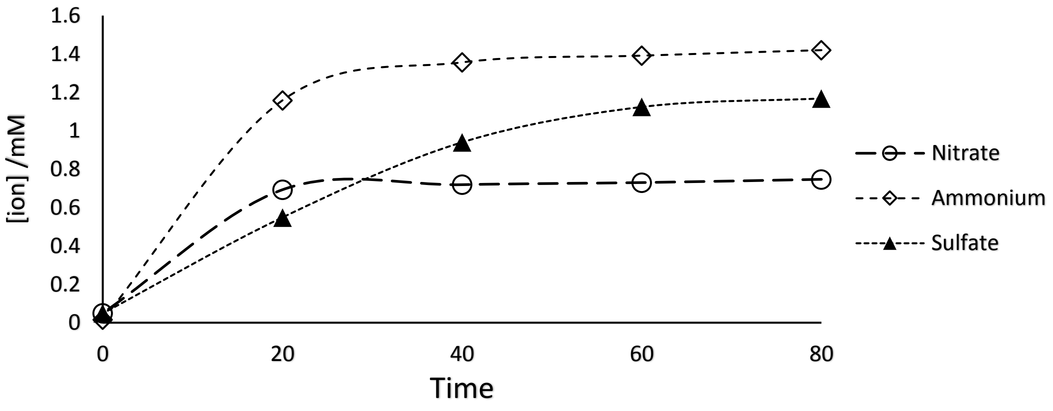

Figure 6.126. *Inorganic ions Concentration over the time during electro-oxidation of bentazone solution measured by IC (EO, Co= 300 mg/l, 10 mM NaCl, 20 mA/cm^2)*

6.2.7. Toxicity determination

Table 6.106. *Microtox toxicity of bentazone as a function of different treatment methods in term of* EC_{50}.

Treatment technique	**Treatment Time (min)**	**% EC_{50} (5min)**	**Toxicity degree**	**% EC_{50} (15min)**	**Toxicity degree**
ECP	0	25	Moderate toxic	32	Moderate toxic
	40	59	Toxic	68	Toxic
	80	62	Toxic	75	Toxic
EFP	0	31	Moderate toxic	39	Moderate toxic
	40	62	Toxic	68	Toxic
	80	77	Slight toxic	94	Slight toxic
EOP	0	27	Moderate toxic	33	Moderate toxic
	40	71	toxic	71	Slight toxic
	80	81	Slight toxic	94	Slight toxic

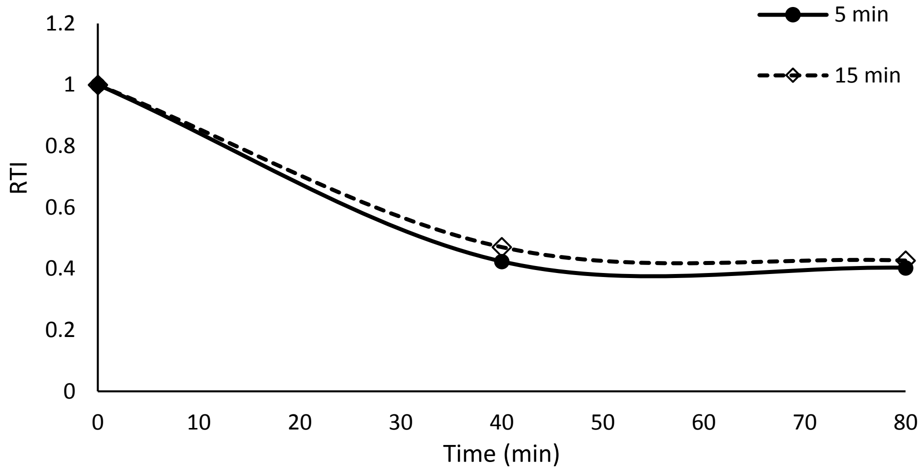

Figure 6.127. *Variation of 5th and 15th mins toxicity of bentazone by electrocoagulation with the time.*

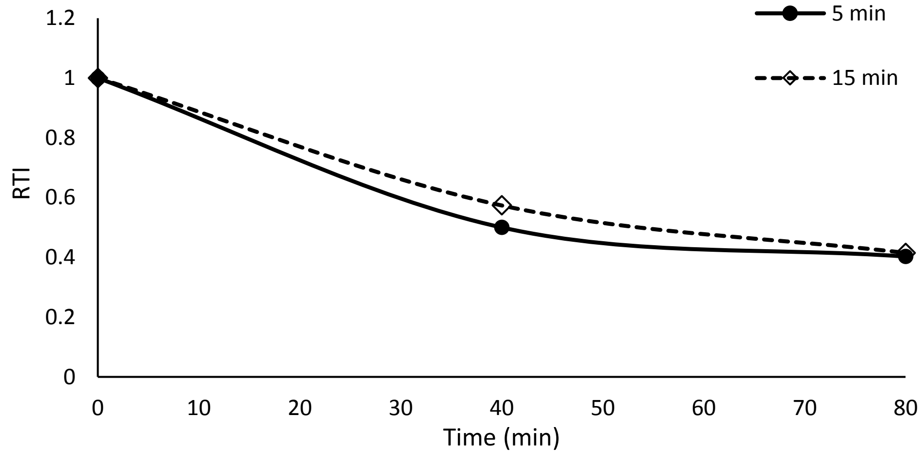

Figure 6.128. *Variation of 5th and 15th mins toxicity of bentazone by electrochemical-Fenton with the time.*

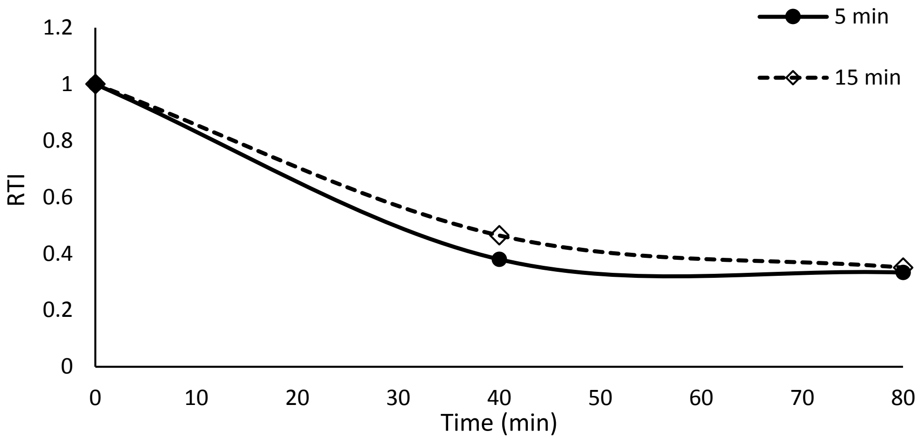

Figure 6.129. *Variation of 5th and 15th mins toxicity of bentazone by electro-oxidation with the time.*

6.2.8. Kinetic studies

Essential understanding of the reaction kinetics and mechanism are important in designing system and improving the catalytic chemical processes. The mechanism of chemical reaction consists of a set of primary processes which clarifies the way that overall reaction progress. major parameters in kinetics studies of chemical reaction represent the chemical reaction rate. The concentration of bentazone was decreased to (81.14, 49.35, 18.34 and 8.1mg/l) at (20, 40, 60, 80 mins) respectively during electro-oxidation process. Figure 6.130 showed that bentazone removal efficiency by electro-oxidation using boron-doped diamond exhibited pseudo first order with perfect correlation coefficients (0.9797) according to equation 6.10. The rate constants values at optimum condition and reaction time were 0.0462 min^{-1}. The reaction rates are very susceptible to the temperature, usually increase quickly by increasing temperature. The temperature of the reactor was 27°C during the experiment.

$$-\frac{d[Bentazone]}{dt} = \mathrm{K}[Bentazone] \tag{6.3}$$

Rearrange to give:

$$\frac{d[Bentazone]}{[Bentazone]} = -\mathrm{Kdt} \tag{6.4}$$

Integrate both side of the equation:

$$\int_{[c_0]}^{[c]} \frac{d[Bentazone]}{[Bentazone]} = -k \int_{[t_0]}^{[t]} dt \tag{6.5}$$

(6.6)

$$\int_{[c_0]}^{[c]} \frac{1}{[Bentazone]} d[Bentazone] = -k \int_{[t_0]}^{[t]} dt$$

Recall from calculus that:

$$\int \frac{1}{x} = \ln(x) \tag{6.7}$$

$$\ln[Bentazone] \Big|_{[c]_0}^{[c]_t} = -kt \Big|_0^t \tag{6.8}$$

$$\ln[Bentazone]_0 - ln\,[Bentazone]_t = \mathrm{K}t \tag{6.9}$$

Now, recall from the laws of logarithms that

$$ln \frac{[Bentazone]o}{[Bentazone]t} = \mathrm{k}t \tag{6.10}$$

In which k is the pseudo-second-order rate constant.

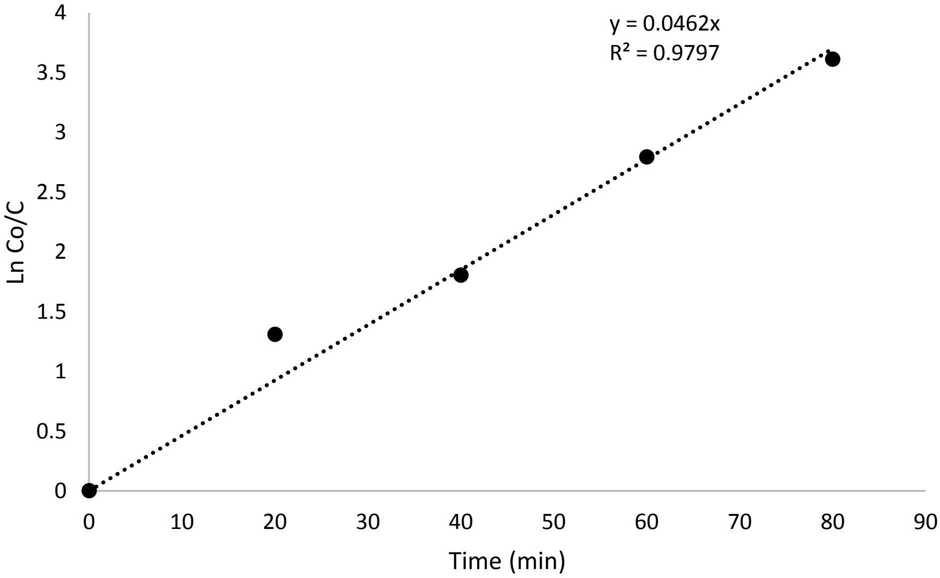

Figure 6.130. *Relation between Ln Co/C against the time for bentazone removal using BDD electrodes (Co= 300mg/L, i=20mA/cm^2, 10mM Na_2SO_4, pH= 8.63)*

6.3. Abamectin

6.3.1. Electrocoagulation methods using iron electrodes

Table 6.107. *4.5 mg/L abamectin containing solution (EC-Fe, i=5mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.5	583.52	0.0	0.0	0.0	0.0	0.0
20	18.7	244.37	58.12	0.00262	6.54	6.54	160.19
40	18.6	229.56	60.66	0.00260	6.50	13.04	159.33
60	18.4	218.84	62.50	0.00257	6.43	19.48	157.62
80	18.3	204.52	64.95	0.00256	6.40	25.87	156.76
Sludge amount (gram)= 1.96							

Table 6.108. *4.5 mg/L abamectin containing solution (EC-Fe, i=10mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	22.2	583.52	0.0	0.0	0.0	0.0	0.0
20	20.4	234.47	59.82	0.00564	14.10	14.10	345.34
40	20.2	222.15	61.93	0.00558	13.96	28.05	341.96
60	20.3	210.29	63.96	0.00561	14.03	42.08	343.65
80	20.1	199.72	65.77	0.00556	13.89	55.97	340.27
Sludge amount (gram)= 2.33							

Table 6.109. *4.5 mg/*L *abamectin containing solution (EC-Fe, i=15mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.8	583.52	0.0	0.0	0.0	0.0	0.0
20	24.5	214.85	63.18	0.01012	25.29	25.29	619.63
40	24.1	214.85	63.18	0.00995	24.88	50.17	609.52
60	23.8	200.69	65.61	0.00983	24.57	74.74	601.93
80	23.8	189.85	67.46	0.00983	24.57	99.31	601.93
Sludge amount (gram)=2.51							

Table 6.110. *4.5 mg/*L *abamectin containing solution (EC-Fe, i=20 mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	34.3	583.52	0.0	0.0	0.0	0.0	0.0
20	28.8	203.56	65.12	0.01592	39.80	39.80	975.10
40	28.5	197.63	66.13	0.01575	39.39	79.19	964.94
60	28.3	186.97	67.96	0.01564	39.11	118.29	958.17
80	28.1	172.54	70.43	0.01553	38.83	157.13	951.40
Sludge amount (gram)=2.77							

Table 6.111. *4.5 mg/*L *abamectin containing solution (EC-Fe, i=5mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	18.8	566.34	0.0	0.0	0.0	0.0	0.0
20	14.2	204.85	63.83	0.00199	4.97	4.97	121.64
40	14	191.26	66.23	0.00196	4.90	9.86	119.93
60	13.8	176.14	68.90	0.00193	4.83	14.69	118.21
80	13.9	162.67	71.28	0.00194	4.86	19.55	119.07
Sludge amount (gram)=2.28							

Table 6.112. *4.5 mg/*L *abamectin containing solution (EC-Fe, i=10mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	21.5	566.34	0.0	0.0	0.0	0.0	0.0
20	17	197.44	65.14	0.00470	11.75	11.75	287.79
40	16.8	184.85	67.36	0.00464	11.61	23.35	284.40
60	16.6	163.92	71.06	0.00459	11.47	34.83	281.01
80	16.4	150.53	73.42	0.00453	11.33	46.16	277.63
Sludge amount (gram)=2.47							

Table 6.113. *4.5 mg/L abamectin containing solution (EC-Fe, i=15mA/cm$_2$, 5mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	23.4	566.34	0.0	0.0	0.0	0.0	0.0
20	20.6	182.69	67.74	0.00851	21.27	21.27	521.00
40	20.4	166.18	70.66	0.00842	21.06	42.32	515.94
60	20.2	149.45	73.61	0.00834	20.85	63.18	510.88
80	20.1	140.21	75.24	0.00830	20.75	83.93	508.35
Sludge amount (gram)=2.53							

Table 6.114. *4.5 mg/L abamectin containing solution (EC-Fe, i=20mA/cm$_2$, 5mM Na$_2$SO$_4$, pH= 8.32)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	29.7	566.34	0.0	0.0	0.0	0.0	0.0
20	26.3	180.56	68.12	0.01454	36.35	36.35	890.4595
40	26.1	161.27	71.52	0.01443	36.07	72.41	883.6879
60	25.8	144.32	74.52	0.01426	35.65	108.07	873.5306
80	25.5	128.71	77.27	0.01410	35.24	143.31	863.3733
Sludge amount (gram)=2.93							

Table 6.115. *4.5 mg/L abamectin containing solution (EC-Fe, i=5mA/cm^2, 10mM Na$_2$SO$_4$, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	13.3	573.67	0.0	0.0	0.0	0.0	0.0
20	10.8	199.64	65.20	0.00151	3.78	3.78	92.51
40	10.5	190.36	66.82	0.00147	3.67	7.45	89.94
60	10.6	173.64	69.73	0.00148	3.71	11.15	90.80
80	10.3	163.85	71.44	0.00144	3.60	14.76	88.23
Sludge amount (gram)=2.76							

Table 6.116. *4.5 mg/L abamectin containing solution (EC-Fe, i=10mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	15.7	573.67	0.0	0.0	0.0	0.0	0.0
20	12.4	209.44	63.49	0.00343	8.57	8.57	209.91
40	12.2	188.75	67.10	0.00337	8.43	17.00	206.53
60	12	160.17	72.08	0.00332	8.29	25.29	203.14
80	12.2	150.83	73.71	0.00337	8.43	33.72	206.53
Sludge amount (gram)=3.17							

Table 6.117. *4.5 mg/L abamectin containing solution (EC-Fe, i=15mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	20.4	573.67	0.0	0.0	0.0	0.0	0.0
20	17.2	177.89	68.99	0.00710	17.76	17.76	435.01
40	17	169.96	70.37	0.00702	17.55	35.30	429.95
60	17.1	148.55	74.11	0.00706	17.65	52.96	432.48
80	16.9	137.31	76.06	0.00698	17.45	70.40	427.42
Sludge amount (gram)=3.35							

Table 6.118. *4.5 mg/L abamectin containing solution (EC-Fe, i=20 mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	29.2	573.67	0.0	0.0	0.0	0.0	0.0
20	21.1	167.17	70.86	0.01166	29.16	29.16	714.39
40	21	154.55	73.06	0.01161	29.02	58.18	711.01
60	20.8	137.41	76.05	0.01150	28.74	86.92	704.24
80	20.7	120.15	79.06	0.01144	28.61	115.53	700.85
Sludge amount (gram)=3.81							

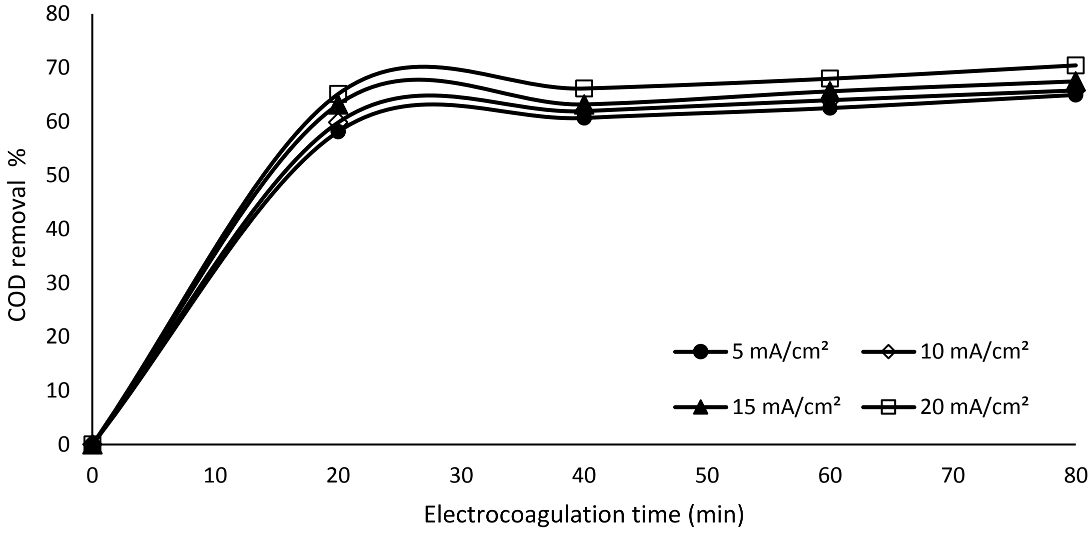

Figure 6.131. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, pH= 8.32)*

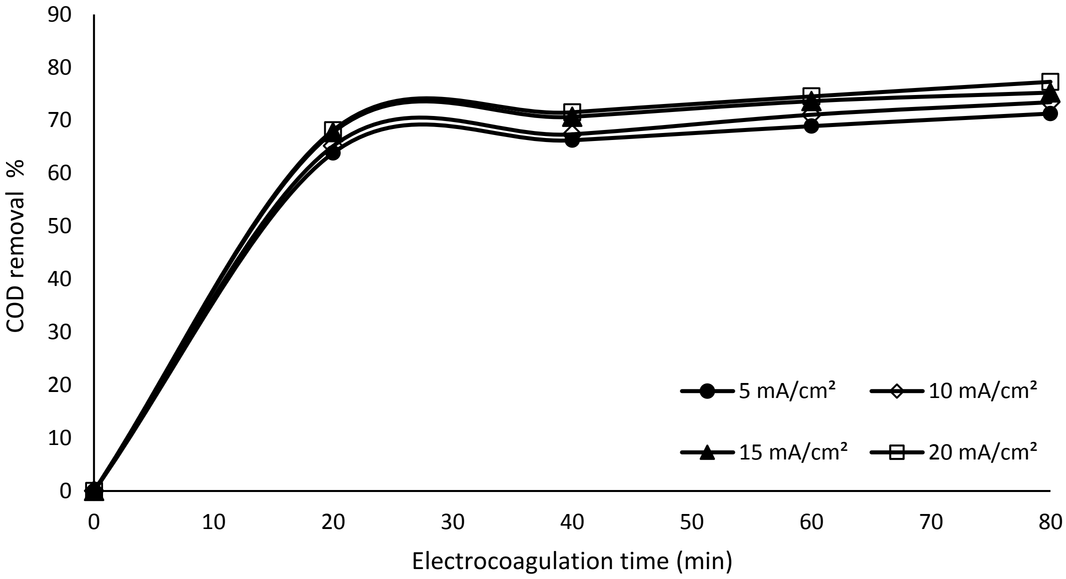

Figure 6.132. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin, 5mM* Na_2SO_4*, pH= 8.32)*

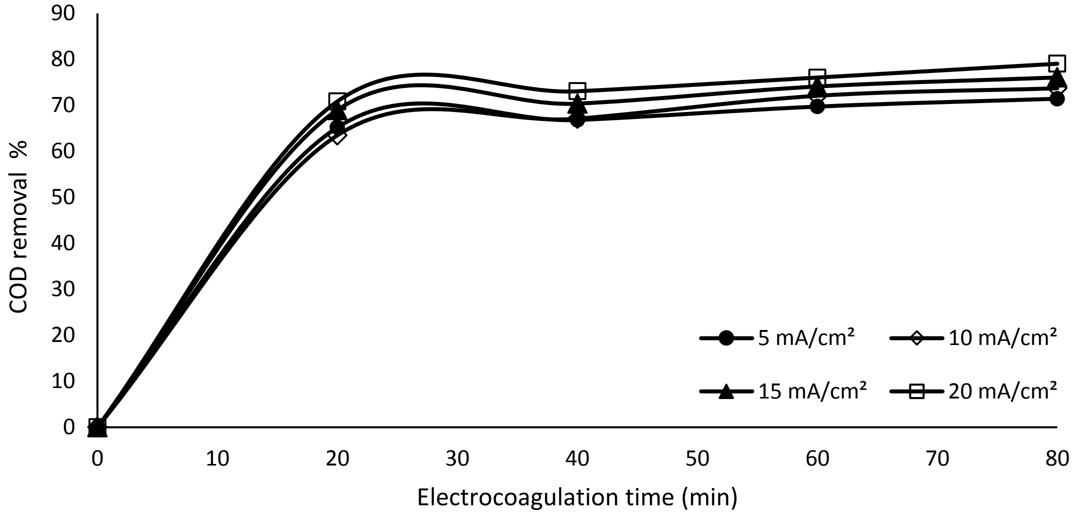

Figure 6.133. *Variation of COD removal over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin, 10mM Na_2SO_4, pH= 8.38)*

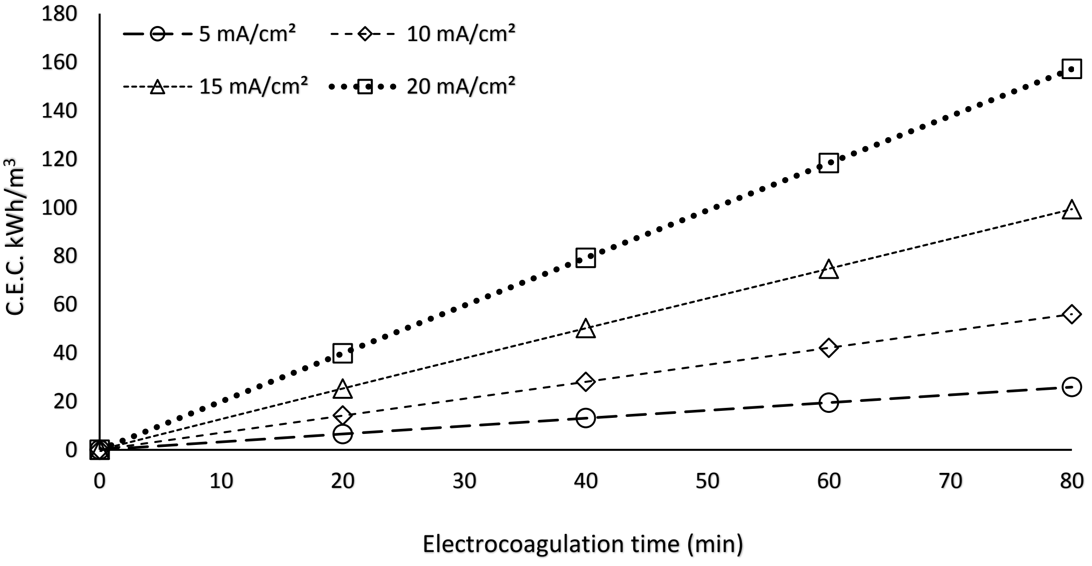

Figure 6.134. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, pH= 8.32)*

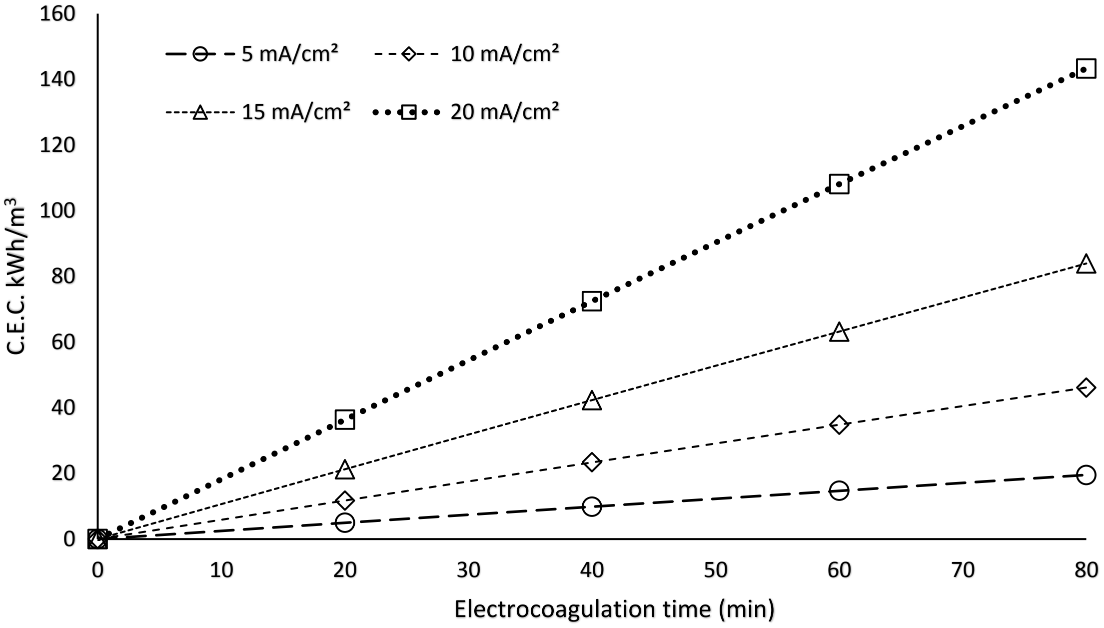

Figure 6.135. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin, 5mM Na_2SO_4, pH= 8.32)*

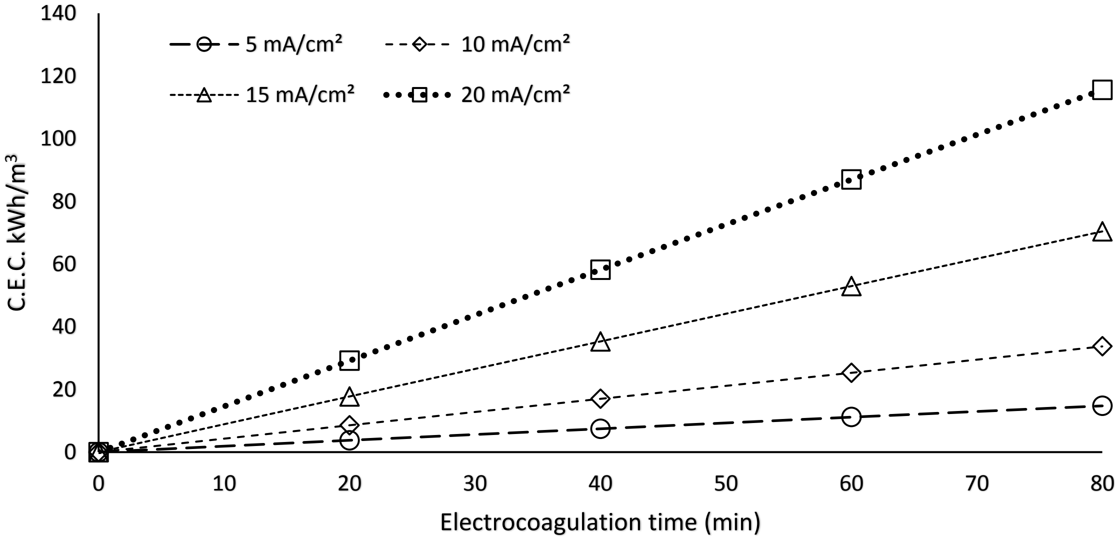

Figure 6.136. *Variation of energy consumption over the time depending on current density (EC-Fe, Co= 4.5 mg/L abamectin,* 10*mM Na_2SO_4, pH= 8.38)*

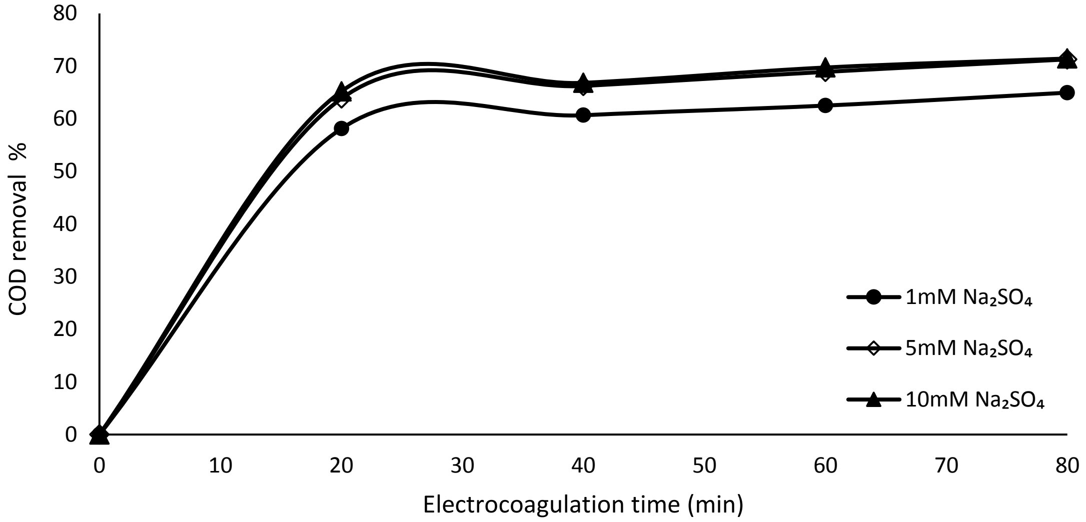

Figure 6.137. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 5 mA/cm^2)*

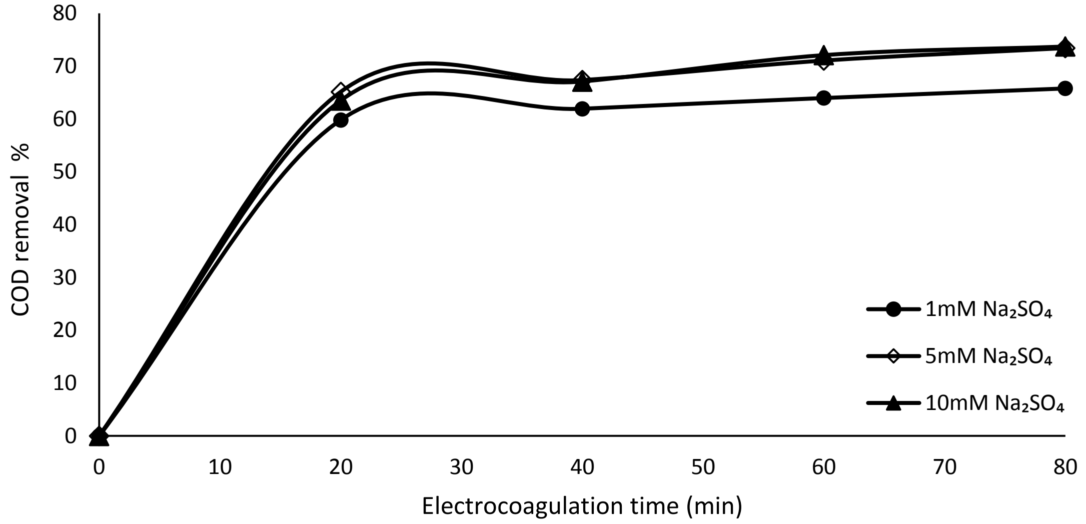

Figure 6.138. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 10 mA/cm^2)*

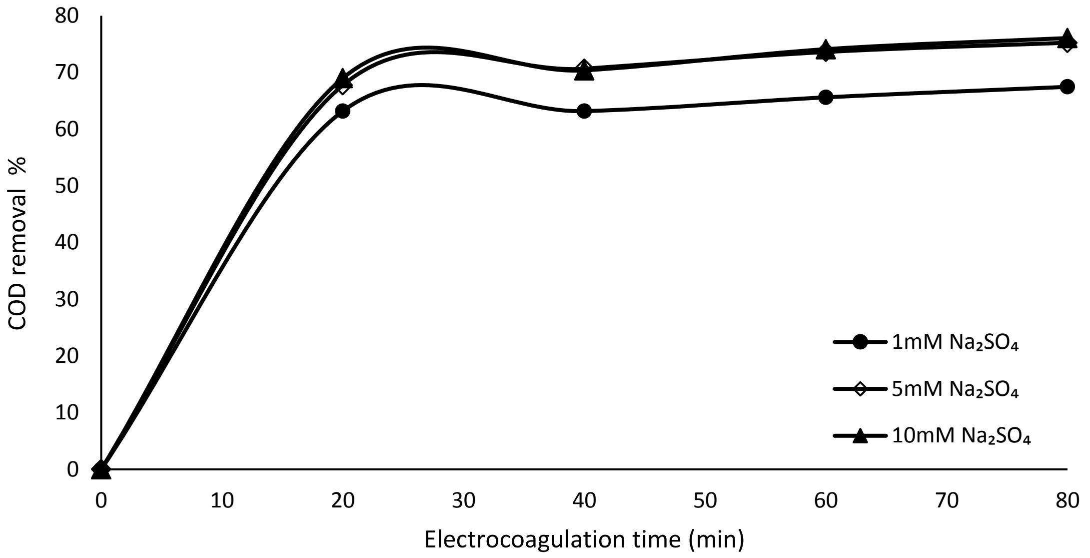

Figure 6.139. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 15mA/cm^2)*

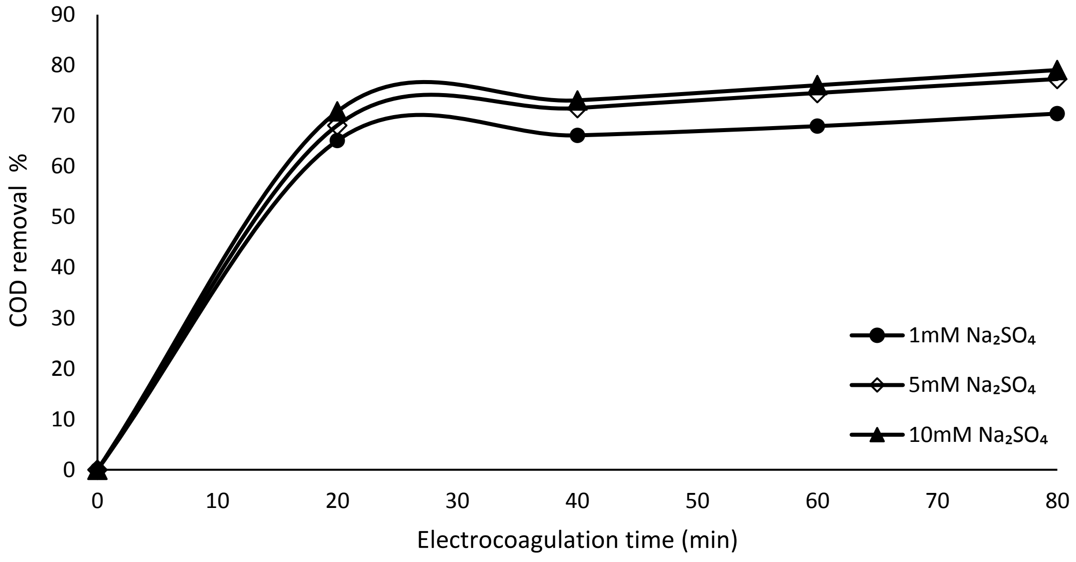

Figure 6.140. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 20 mA/cm^2)*

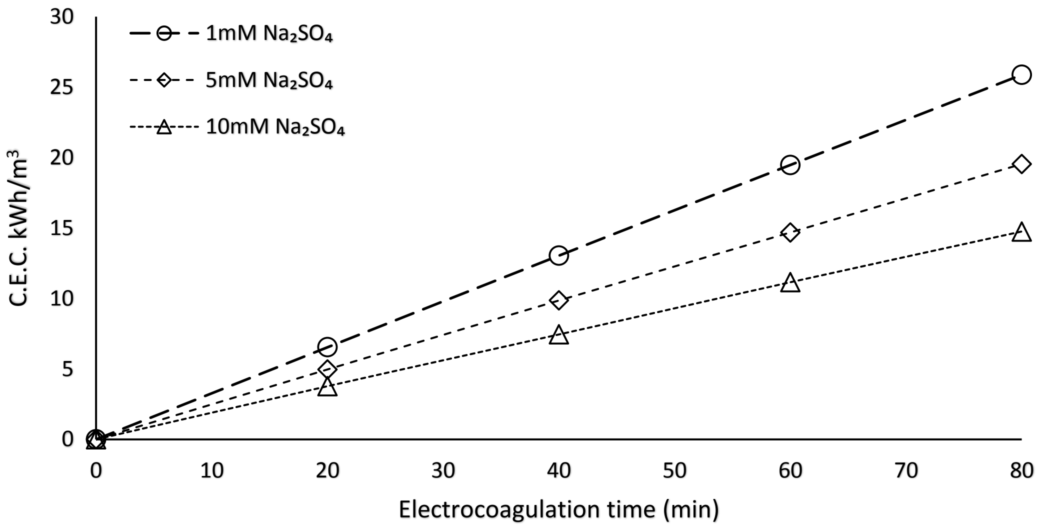

Figure 6.141. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 5mA/cm^2)*

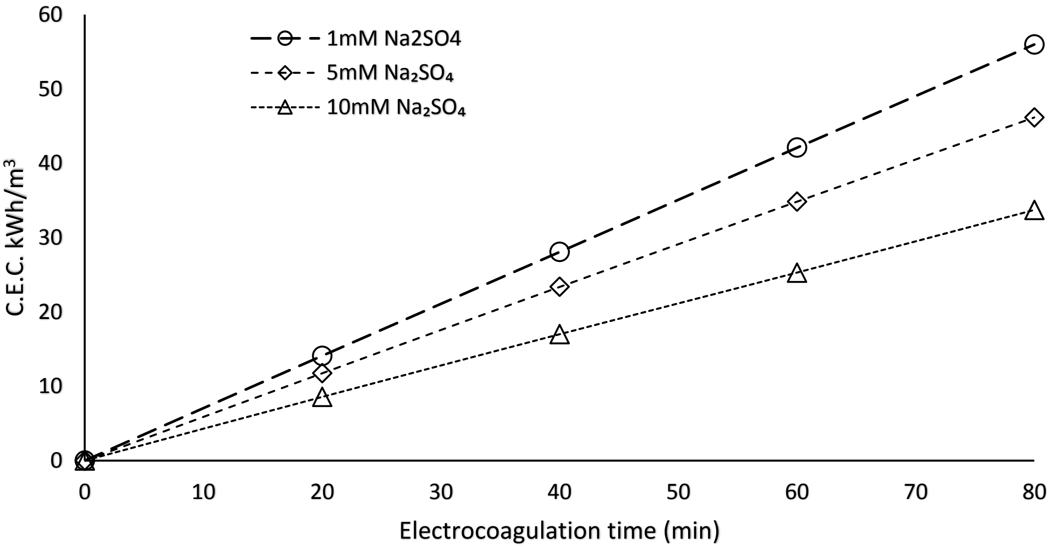

Figure 6.142. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 10mA/cm^2)*

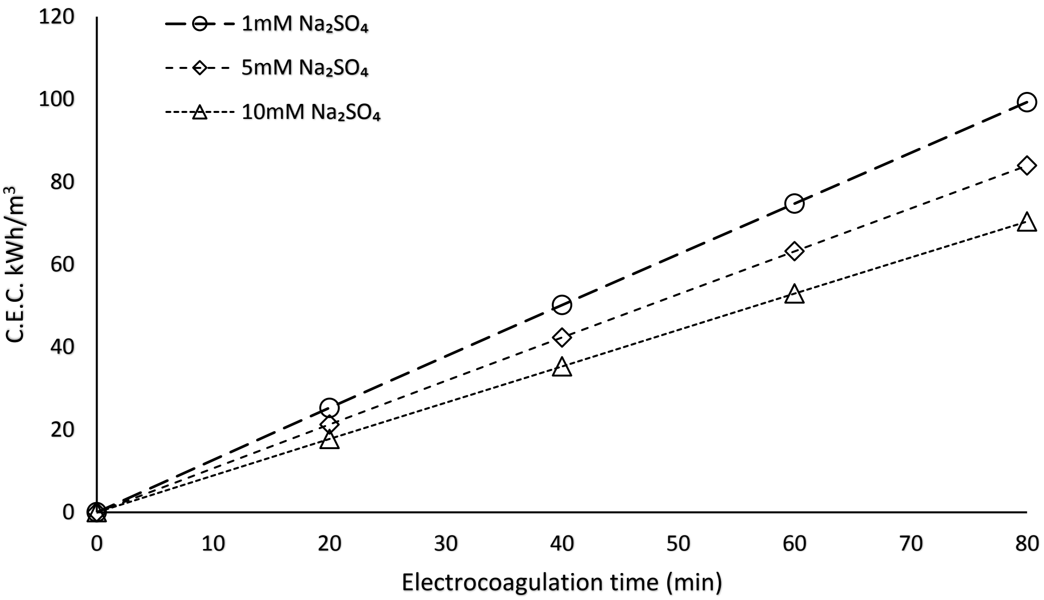

Figure 6.143. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 15mA/cm^2)*

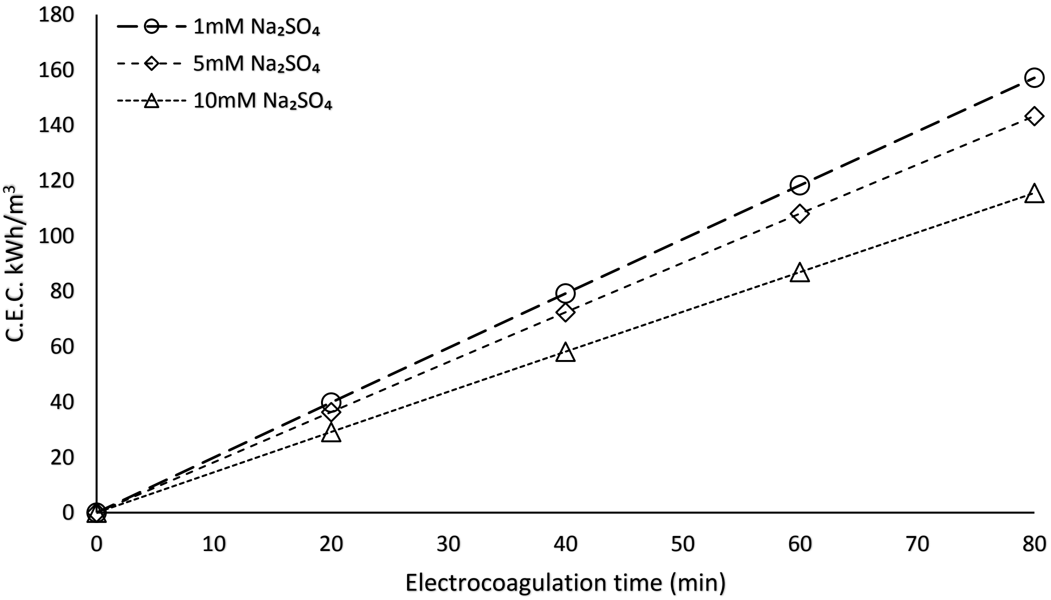

Figure 6.144. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe, Co= 4.5 mg/L abamectin, 20 mA/cm^2)*

6.3.2. Electrocoagulation methods using aluminum electrodes

Table 6.119. *4.5 mg/L abamectin containing solution (EC-Al, i=5mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.7	534.87	0.0	0.0	0.0	0.0	0.0
20	27.5	212.41	60.29	0.00385	9.62	9.62	235.57
40	26.3	204.59	61.75	0.00368	9.20	18.81	225.29
60	26.1	196.23	63.31	0.00365	9.13	27.94	223.58
80	25.4	190.41	64.40	0.00355	8.88	36.82	217.58
Sludge amount (gram)=1.16							

Table 6.120. 4*.5 mg/L abamectin containing solution (EC-Al, i=10mA/cm^2, 10mM Na_2SO_4, pH= 8.38).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	36.8	534.87	0.0	0.0	0.0	0.0	0.0
20	32.7	190.41	64.40	0.00904	22.59	22.59	553.57
40	32.2	176.59	66.98	0.00890	22.25	44.84	545.11
60	32.2	164.23	69.30	0.00890	22.25	67.09	545.11
80	31.5	158.41	70.38	0.00871	21.77	88.86	533.26
Sludge amount (gram)=1.21							

Table 6.121. *4.5 mg/L abamectin containing solution (EC-Al, i=15mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	53.5	534.87	0.0	0.0	0.0	0.0	0.0
20	35.3	179.34	66.47	0.01458	36.44	36.44	892.78
40	34.9	163.81	69.37	0.01441	36.03	72.47	882.66
60	34.6	153.81	71.24	0.01429	35.72	108.19	875.08
80	34.1	149.81	71.99	0.01408	35.20	143.39	862.43
Sludge amount (gram)=1.53							

Table 6.122. *4.5 mg/L abamectin containing solution (EC-Al, i=20mA/cm^2, 10mM Na_2SO_4, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	59	534.87	0.0	0.0	0.0	0.0	0.0
20	37.8	166.50	68.87	0.02090	52.24	52.24	1279.82
40	37.6	154.23	71.16	0.02078	51.96	104.20	1273.05
60	35.8	142.43	73.37	0.01979	49.47	153.67	1212.10
80	34.2	132.52	75.22	0.01891	47.26	200.94	1157.93
Sludge amount (gram)=1.6							

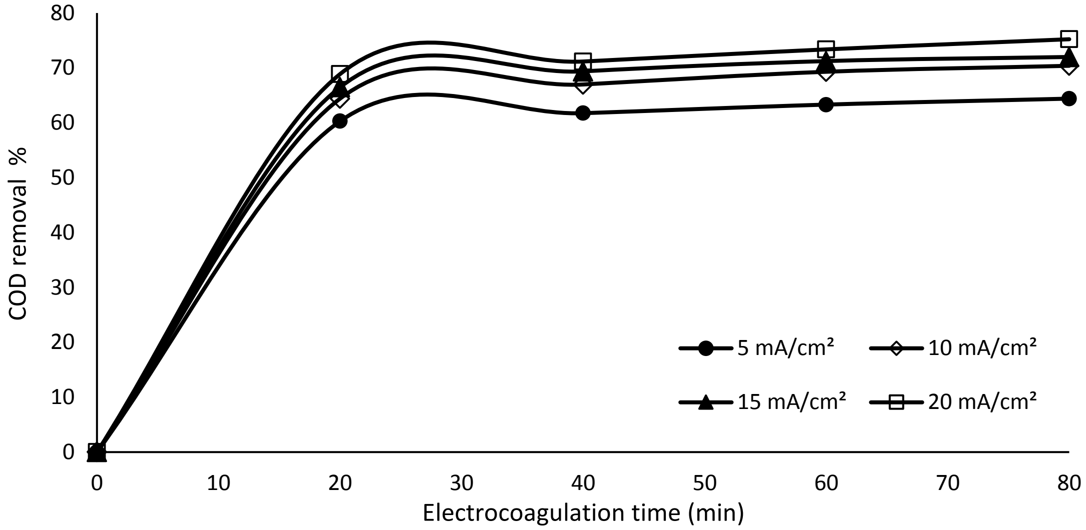

Figure 6.145. *Variation of COD removal over time depending on current density (EC-Al, Co= 4.5 mg/L abamectin,10 mM Na_2SO_4, pH= 8.38)*

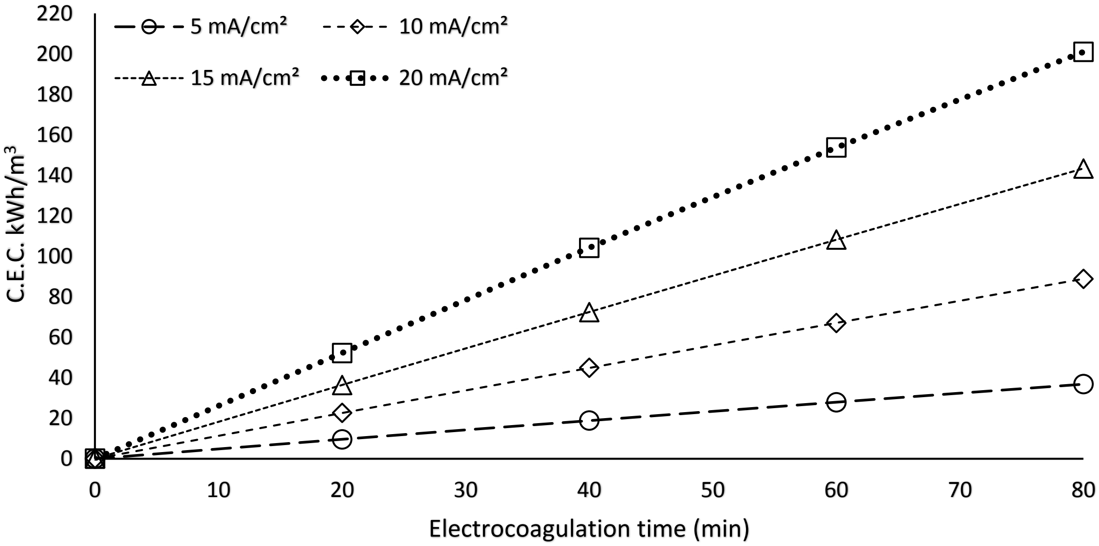

Figure 6.146. *Variation of energy consumption over time depending on current density (EC-Al, Co= 4.5 mg/L abamectin,10 mM Na_2SO_4, pH= 8.38)*

6.3.3. Electrocoagulation methods using hybrid (mixed) electrodes

Table 6.123. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=5mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	26.5	537.5	0.0	0.0	0.0	0.0	0.0
20	22.5	215.57	59.89	0.00315	7.87	7.87	192.74
40	22.1	207.14	61.46	0.00309	7.73	15.59	189.31
60	22.1	197.69	63.22	0.00309	7.73	23.32	189.31
80	22	189.12	64.81	0.00308	7.69	31.01	188.46
Sludge amount (gram)=1.69							

Table 6.124. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=10mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.3	537.5	0.0	0.0	0.0	0.0	0.0
20	26.3	208.17	61.27	0.00727	18.17	18.17	445.22
40	25.9	200.65	62.67	0.00716	17.90	36.07	438.45
60	25.6	191.14	64.44	0.00708	17.69	53.76	433.37
80	25.6	186.63	65.28	0.00708	17.69	71.45	433.37
Sludge amount (gram)=1.85							

Table 6.125. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=15mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.1	537.5	0.0	0.0	0.0	0.0	0.0
20	31.4	198.26	63.11	0.01297	32.41	32.41	794.14
40	31.1	193.57	63.99	0.01284	32.10	64.52	786.56
60	31	186.88	65.23	0.01280	32.00	96.52	784.03
80	29.8	178.19	66.85	0.01231	30.76	127.28	753.68
Sludge amount (gram)=1.91							

Table 6.126. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=20mA/cm^2, 1mM Na$_2$SO$_4$, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	37.4	537.5	0.0	0.0	0.0	0.0	0.0
20	35.1	193.34	64.03	0.01940	48.51	48.51	1188.40
40	35	184.23	65.72	0.01935	48.37	96.87	1185.02
60	34.8	179.41	66.62	0.01924	48.09	144.97	1178.25
80	34.7	170.19	68.34	0.01918	47.95	192.92	1174.86
Sludge amount (gram)=2.18							

Table 6.127. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=5mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.29)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	24.4	564.47	0.0	0.0	0.0	0.0	0.0
20	17.5	212.57	62.34	0.00245	6.12	6.12	149.91
40	17.2	203.14	64.01	0.00241	6.01	12.13	147.34
60	16.9	196.69	65.15	0.00236	5.91	18.04	144.77
80	16.6	187.12	66.85	0.00232	5.80	23.85	142.20
Sludge amount (gram)=1.87							

Table 6.128. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=10mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.29)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	29.4	564.47	0.0	0.0	0.0	0.0	0.0
20	21.7	194.82	65.49	0.00600	14.99	14.99	367.35
40	21.5	186.93	66.88	0.00594	14.86	29.85	363.97
60	21.2	173.24	69.31	0.00586	14.65	44.50	358.89
80	20.7	167.28	70.37	0.00572	14.30	58.80	350.42
Sludge amount (gram)=2.24							

Table 6.129. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=15mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.29)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	30.1	564.47	0.0	0.0	0.0	0.0	0.0
20	25.5	178.31	68.41	0.01053	26.32	26.32	644.92
40	25.2	168.97	70.07	0.01041	26.01	52.34	637.34
60	25.2	157.45	72.11	0.01041	26.01	78.35	637.34
80	25	150.77	73.29	0.01032	25.81	104.16	632.28
Sludge amount (gram)=2.47							

Table 6.130. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=20mA/cm^2, 5mM Na$_2$SO$_4$, pH= 8.29)*

Time (min)	**Voltage (V)**	**COD (mg/L)**	**COD removal (%)**	**Energy consumption (kWh/400 mL)**	**Energy consumption (kWh/m^3)**	**Cumulative energy consumption (kWh/m^3)**	**Energy cost (Krş/m^3)**
0	35.9	564.47	0.0	0.0	0.0	0.0	0.0
20	28.4	162.36	71.24	0.01570	39.25	39.25	961.56
40	28.2	154.75	72.58	0.01559	38.97	78.22	954.78
60	28	143.46	74.59	0.01548	38.69	116.91	948.01
80	28.1	139.11	75.36	0.01553	38.83	155.75	951.40
Sludge amount (gram)=2.82							

Table 6.131. *4.5 mg/L abamectin containing solution (EC-Fe-Al. i=5mA/cm^2, 10mM Na_2SO_4, pH= 8.36).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	22.8	534.25	0.0	0.0	0.0	0.0	0.0
20	14.5	158.14	70.40	0.00203	5.07	5.07	124.21
40	14.1	152.14	71.52	0.00197	4.93	10.00	120.78
60	14.0	148.52	72.20	0.00196	4.90	14.90	119.93
80	14.1	138.52	74.07	0.00197	4.93	19.83	120.78
Sludge amount (gram)=2.47							

Table 6.132. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=10mA/cm^2, 10mM Na_2SO_4, pH=8.36).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	23.7	534.25	0.0	0.0	0.0	0.0	0.0
20	18.7	134.32	74.86	0.00517	12.92	12.92	316.57
40	18.5	129.24	75.81	0.00511	12.78	25.70	313.18
60	18.6	123.35	76.91	0.00514	12.85	38.56	314.87
80	18.4	114.28	78.61	0.00509	12.71	51.27	311.49
Sludge amount (gram)=2.52							

Table 6.133. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=15mA/cm^2, 10mM Na_2SO_4, pH= 8.36)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	28.4	534.25	0.0	0.0	0.0	0.0	0.0
20	22.2	117.34	78.04	0.00917	22.92	22.92	561.46
40	22	115.89	78.31	0.00908	22.71	45.63	556.40
60	21.9	109.29	79.54	0.00904	22.61	68.24	553.88
80	22.8	94.34	82.34	0.00941	23.54	91.77	576.64
Sludge amount (gram)=2.85							

Table 6.134. *4.5 mg/L abamectin containing solution (EC-Fe-Al, i=20mA/cm^2, 10mM Na_2SO_4, pH= 8.36)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	32.8	534.25	0.0	0.0	0.0	0.0	0.0
20	25	100.86	81.12	0.01382	34.55	34.55	846.44
40	24.9	97.23	81.80	0.01376	34.41	68.96	843.05
60	24.7	97.23	81.80	0.01365	34.13	103.09	836.28
80	24.6	87.65	83.59	0.01360	34.00	137.09	832.90
Sludge amount (gram)=3.13							

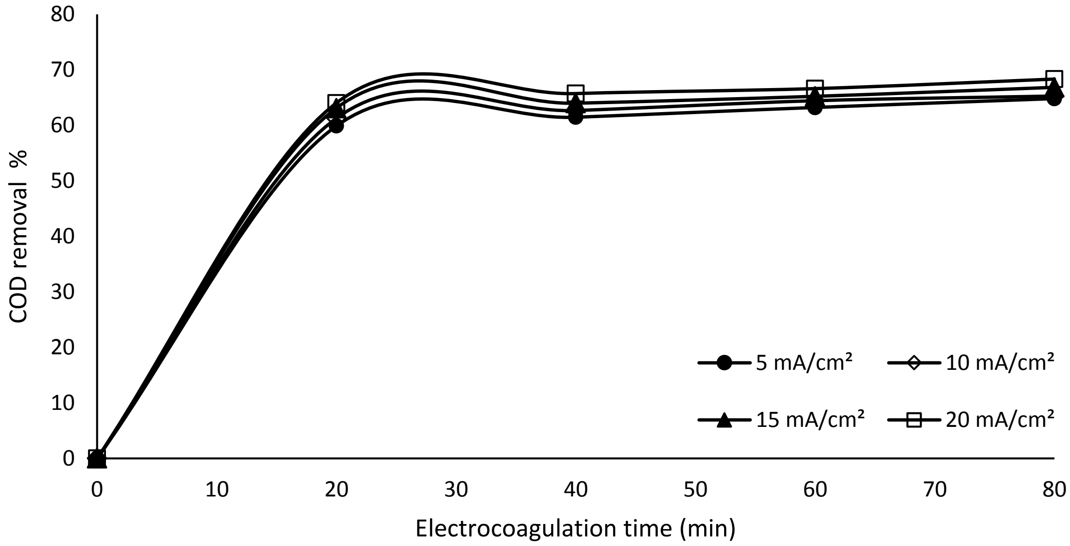

Figure 6.147. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, pH= 8.24)*

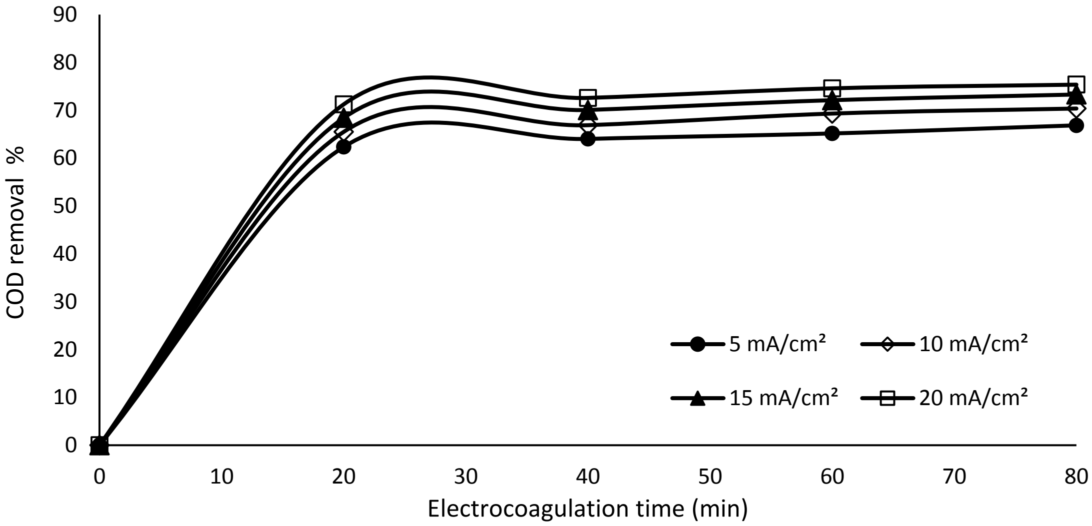

Figure 6.148. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 5mM Na_2SO_4, pH= 8.29)*

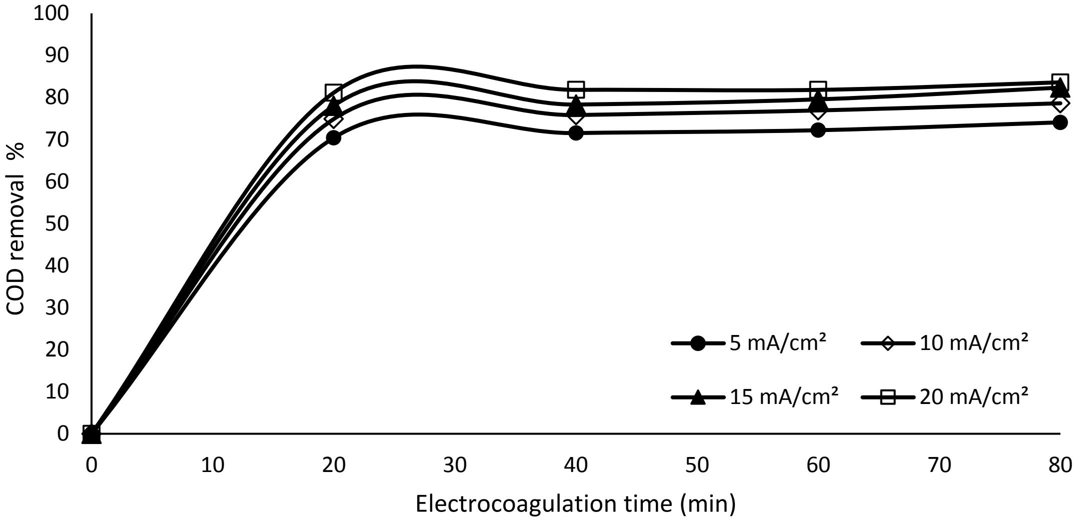

Figure 6.149. *Variation of COD removal over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 10 mM* Na_2SO_4*, pH= 8.36)*

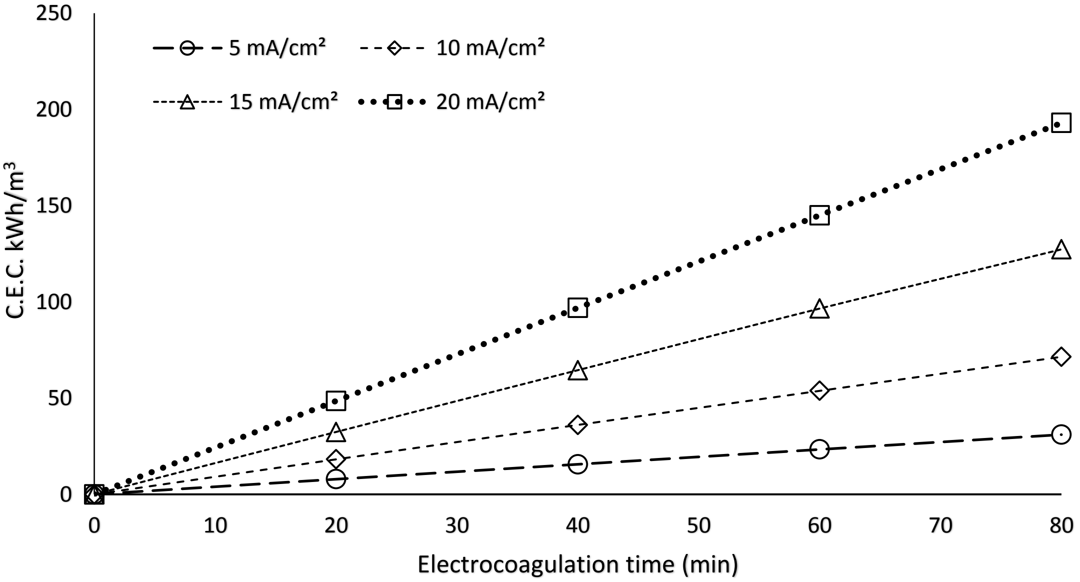

Figure 6.150. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, pH= 8.24)*

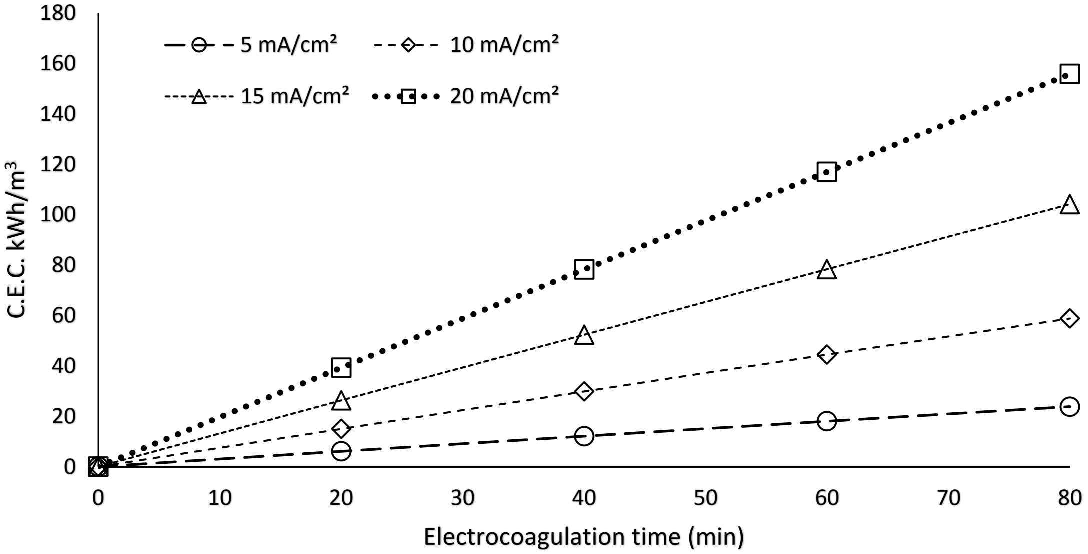

Figure 6.151. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 5mM* Na_2So_4*, pH= 8.29)*

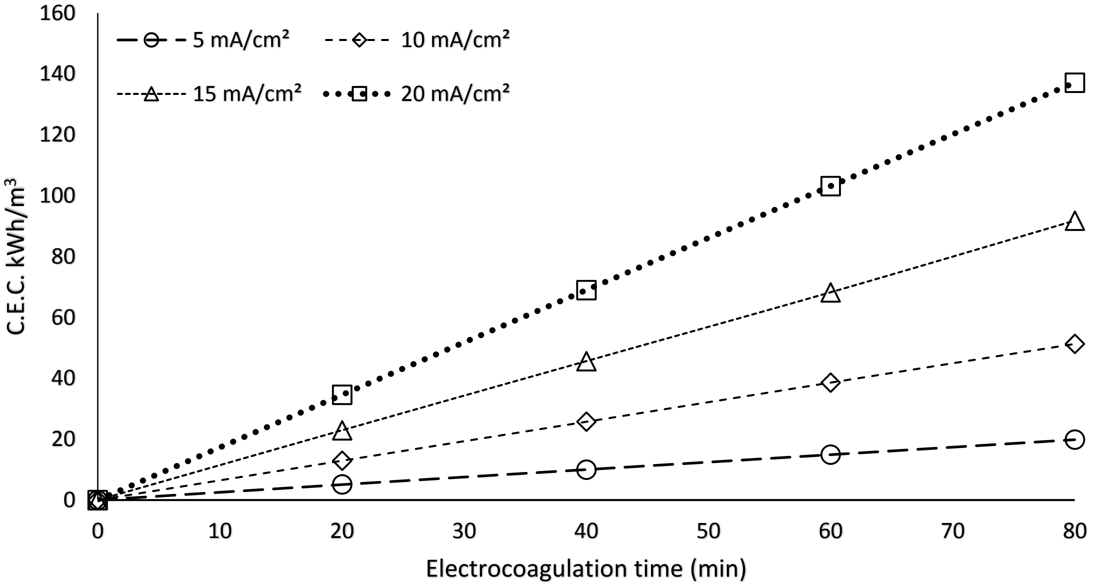

Figure 6.152. *Variation of energy consumption over the time depending on current density (EC-Fe-Al, Co= 4.5 mg/L abamectin, 10mM* Na_2So_4*, pH= 8.36)*

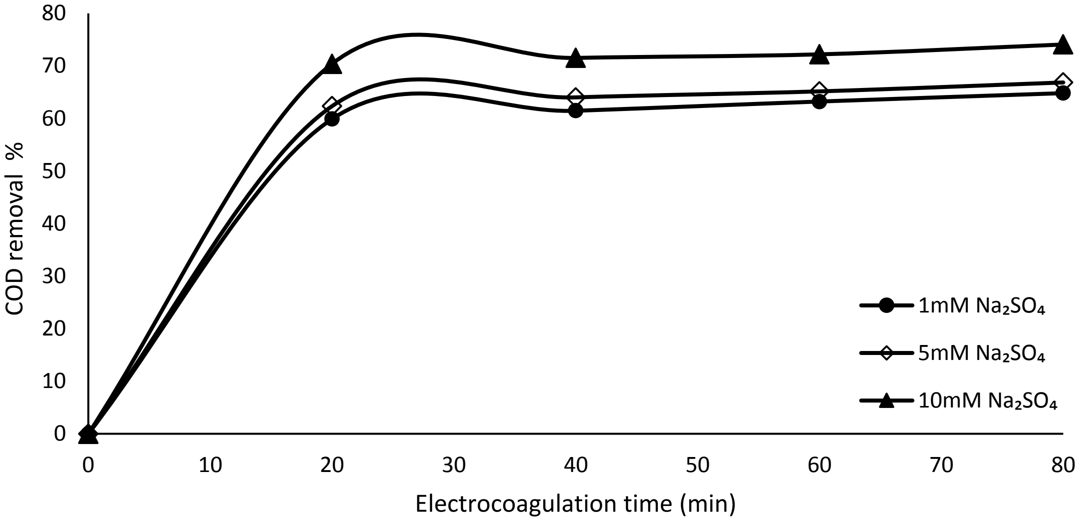

Figure 6.153. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 5mA/cm^2)*

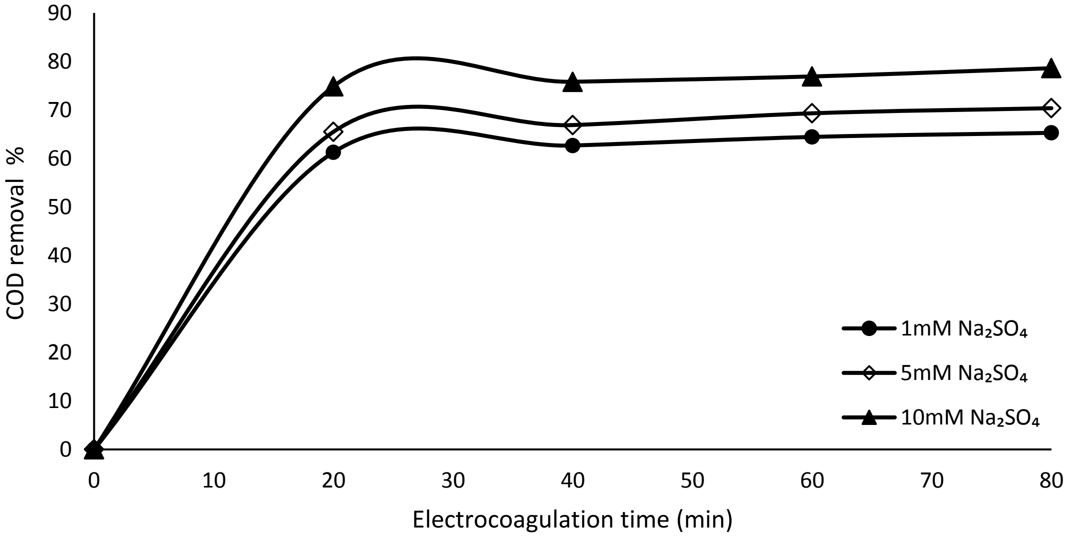

Figure 6.154. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 10 mA/cm^2)*

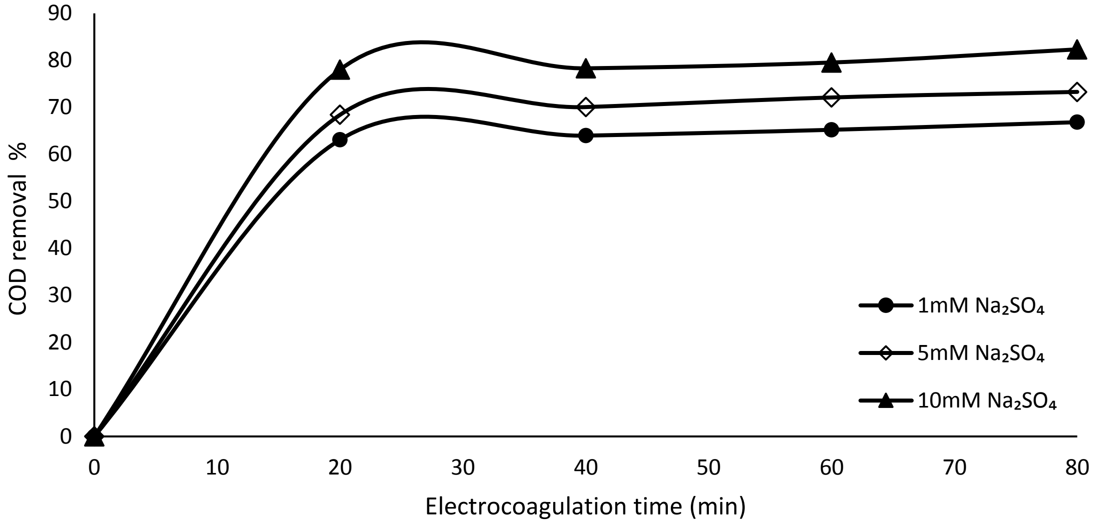

Figure 6.155. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 15mA/cm^2)*

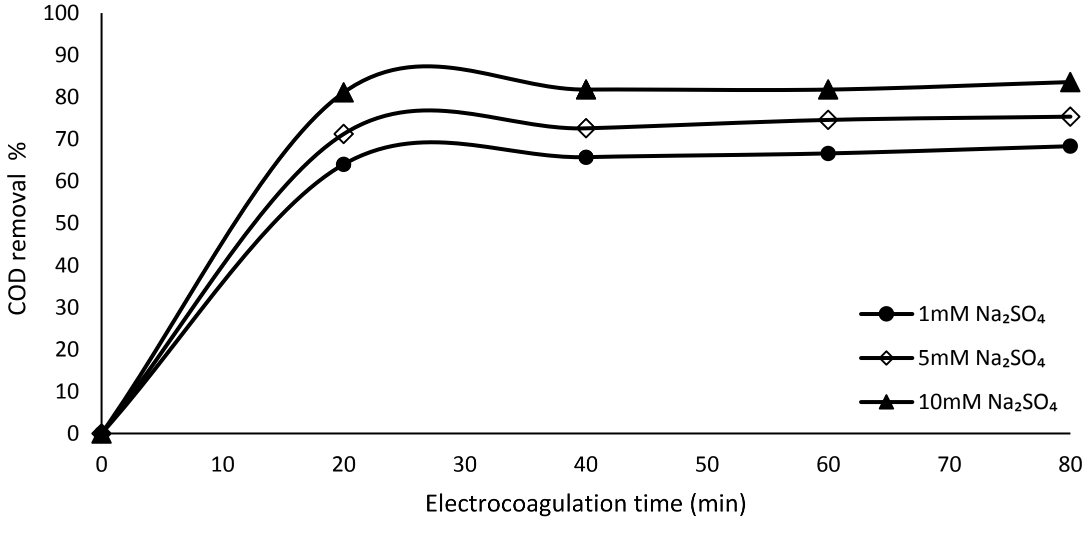

Figure 6.156. *Variation of COD removal over the time depending on support electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 20mA/cm^2)*

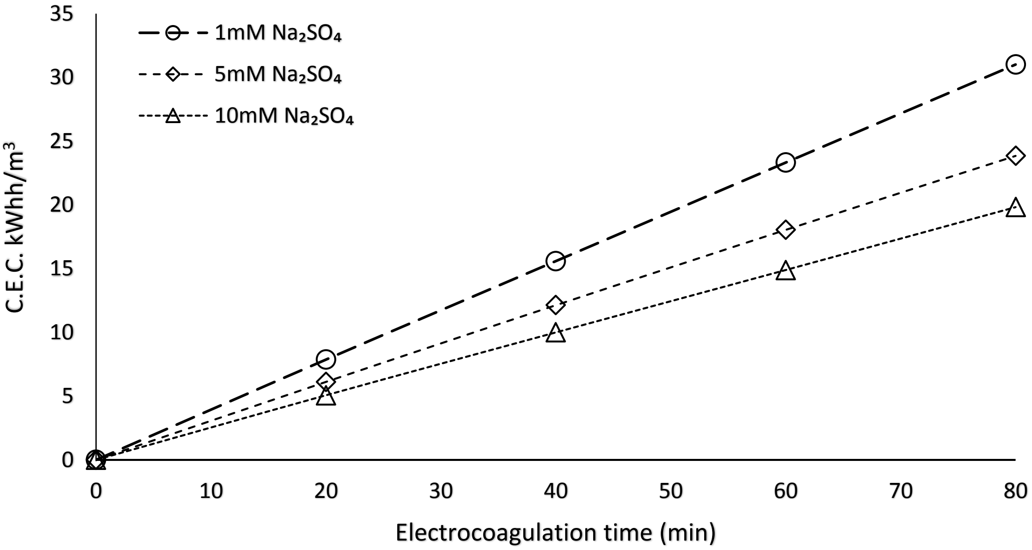

Figure 6.157. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 5mA/cm^2)*

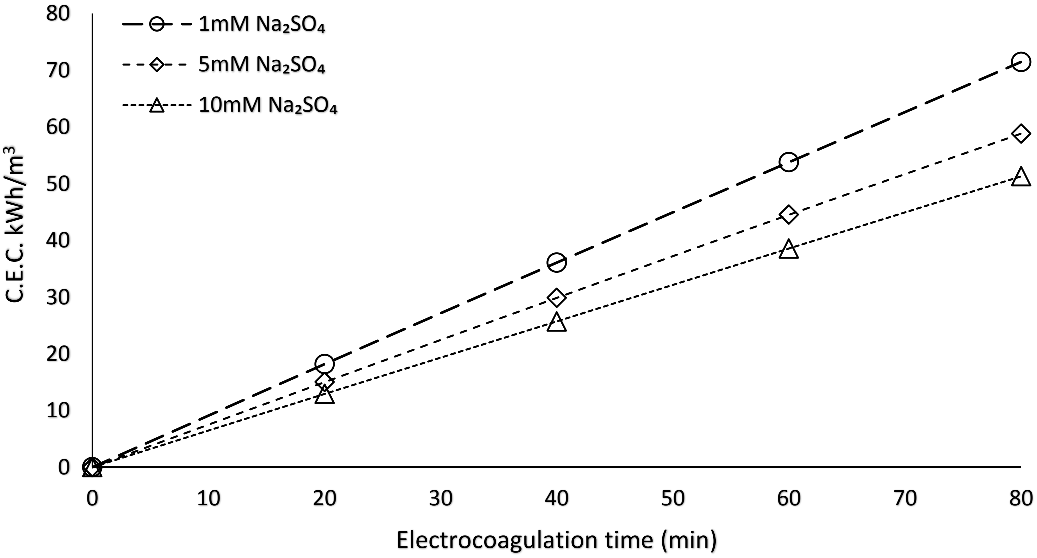

Figure 6.158. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 10mA/cm^2)*

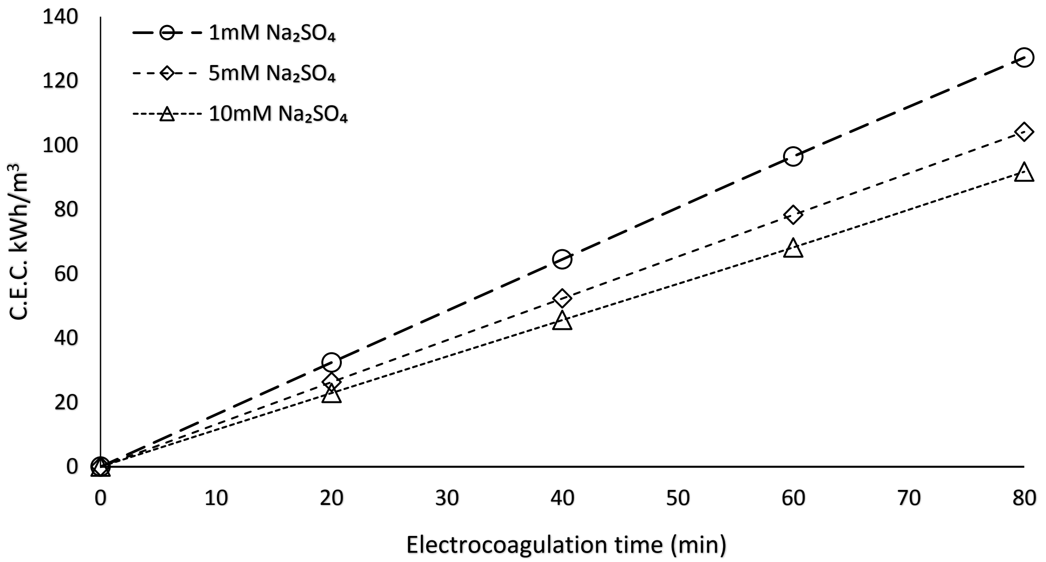

Figure 6.159. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 15mA/cm^2).*

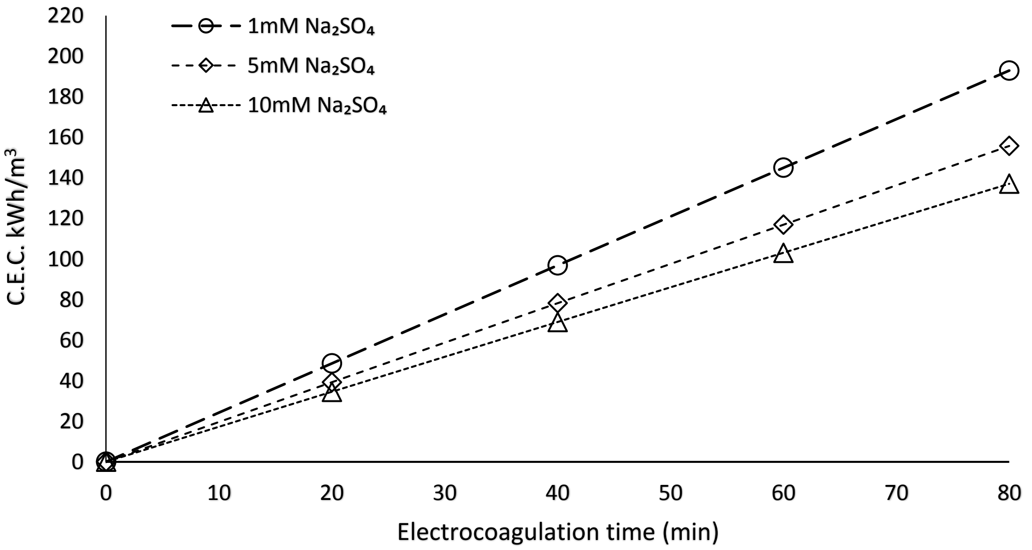

Figure 6.160. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EC-Fe-Al, Co= 4.5 mg/L abamectin, 20mA/cm^2)*

6.3.4. Electrochemical-Fenton methods

Table 6.135. *4.5 mg/l abamectin containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 8.34)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	25.3	552.68	0.0	0.0	0.0	0.0	0.0
20	20.9	241.42	56.32	0.00292	7.31	7.31	179.03
40	20.7	229.54	58.47	0.00290	7.24	14.55	177.32
60	20.5	218.28	60.51	0.00287	7.17	21.71	175.61
80	20.3	203.32	63.21	0.00284	7.10	28.81	173.89
Sludge amount (gram)= 0.96							

Table 6.136. *4.5 mg/l abamectin containing solution (EF, i=10 mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 8.34)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	27.1	552.68	0.0	0.0	0.0	0.0	0.0
20	22.5	227.31	58.87	0.00622	15.55	15.55	380.90
40	22.3	211.79	61.68	0.00616	15.41	30.96	377.51
60	22.1	199.19	63.96	0.00611	15.27	46.23	374.12
80	22	187.66	66.05	0.00608	15.20	61.43	372.43
Sludge amount (gram)= 1.1							

Table 6.137. *4.5 mg/l abamectin containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 8.34)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	32.3	552.68	0.0	0.0	0.0	0.0	0.0
20	24.8	218.75	60.42	0.01024	25.60	25.60	627.22
40	24.5	198.63	64.06	0.01012	25.29	50.89	619.63
60	24.3	187.56	66.06	0.01003	25.08	75.98	614.57
80	24.3	179.97	67.44	0.01003	25.08	101.06	614.57
Sludge amount (gram)= 1.08							

Table 6.138. *4.5 mg/l abamectin containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 500 mg H_2O_2/l, pH= 8.34)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	35.7	209.63	62.07	0.0	0.0	0.0	0.0
20	27.4	209.63	62.07	0.01515	37.87	37.87	927.70
40	27.1	193.31	65.02	0.01498	37.45	75.32	917.54
60	26.9	186.44	66.27	0.01487	37.17	112.49	910.77
80	26.9	177.87	67.82	0.01487	37.17	149.67	910.77
Sludge amount (gram)= 1.26							

Table 6.139. *4.5 mg/l abamectin containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 8.15)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	21.8	543.22	0.0	0.0	0.0	0.0	0.0
20	18.3	233.72	56.98	0.00256	6.40	6.40	156.76
40	18.1	218.96	59.69	0.00253	6.33	12.73	155.05
60	18.0	205.74	62.13	0.00252	6.29	19.02	154.19
80	18.1	198.28	63.50	0.00253	6.33	25.35	155.05
Sludge amount (gram)= 0.95							

Table 6. 140. *4.5 mg/l abamectin containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 8.15)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	28.7	543.22	0.0	0.0	0.0	0.0	0.0
20	21.5	217.72	59.92	0.00594	14.86	14.86	363.97
40	21.3	198.96	63.37	0.00589	14.72	29.57	360.58
60	21.3	189.74	65.07	0.00589	14.72	44.29	360.58
80	21.1	182.28	66.44	0.00583	14.58	58.87	357.19
Sludge amount (gram)= 1.28							

Table 6.141. *4.5 mg/l abamectin containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 8.15)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	31.7	543.22	0.0	0.0	0.0	0.0	0.0
20	23.8	209.33	61.46	0.00983	24.57	24.57	601.93
40	23.6	190.66	64.90	0.00974	24.36	48.93	596.87
60	23.1	180.64	66.75	0.00954	23.85	72.78	584.23
80	23.2	172.61	68.22	0.00958	23.95	96.73	586.75
Sludge amount (gram)= 1.14							

Table 6.142. *4.5 mg/l abamectin containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 1000 mg H_2O_2/l, pH= 8.15)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	33.5	543.22	0.0	0.0	0.0	0.0	0.0
20	25.1	200.51	63.09	0.01387	34.69	34.69	849.83
40	25	180.91	66.70	0.01382	34.55	69.24	846.44
60	24.8	177.66	67.30	0.01371	34.27	103.51	839.67
80	24.6	169.43	68.81	0.01360	34.00	137.50	832.90
Sludge amount (gram)= 1.32							

Table 6.143. *4.5 mg/l abamectin containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	22.8	542.05	0.0	0.0	0.0	0.0	0.0
20	17.6	227.64	58.00	0.00246	6.15	6.15	150.76
40	17.4	213.43	60.63	0.00243	6.08	12.24	149.05
60	17.1	197.38	63.59	0.00239	5.98	18.22	146.48
80	16.9	192.67	64.46	0.00236	5.91	24.13	144.77
Sludge amount (gram)= 0.86							

Table 6. 144. *4.5 mg/l abamectin containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	24.1	542.05	0.0	0.0	0.0	0.0	0.0
20	20	214.72	60.39	0.00553	13.82	13.82	338.57
40	19.8	197.96	63.48	0.00547	13.68	27.50	335.19
60	19.5	186.24	65.64	0.00539	13.47	40.97	330.11
80	19.4	177.28	67.29	0.00536	13.40	54.38	328.42
Sludge amount (gram)= 1.26							

Table 6.145. *4.5 mg/l abamectin containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	28.2	542.05	0.0	0.0	0.0	0.0	0.0
20	22.6	201.66	62.80	0.00933	23.33	23.33	571.58
40	22.3	188.64	65.20	0.00921	23.02	46.35	563.99
60	22.1	176.61	67.42	0.00913	22.81	69.16	558.93
80	22.1	168.12	68.98	0.00913	22.81	91.98	558.93
Sludge amount (gram)= 1.33							

Table 6.146. *4.5 mg/l abamectin containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 2000 mg H_2O_2/l, pH= 8.24)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	27.7	558.34	0.0	0.0	0.0	0.0	0.0
20	24.5	203.51	63.55	0.01354	33.86	33.86	829.51
40	24.4	184.91	66.88	0.01349	33.72	67.58	826.12
60	24.1	176.66	68.36	0.01332	33.30	100.88	815.97
80	24	164.43	70.55	0.01327	33.17	134.05	812.58
Sludge amount (gram)= 1.42							

Table 6.147. *4.5 mg/l abamectin containing solution (EF, i=5mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/l, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	20	521.25	0.0	0.0	0.0	0.0	0.0
20	15.7	175.63	66.31	0.00220	5.49	5.49	134.49
40	15.5	165.95	68.16	0.00217	5.42	10.91	132.77
60	15.3	158.26	69.64	0.00214	5.35	16.26	131.06
80	15.1	144.54	72.27	0.00211	5.28	21.54	129.35
Sludge amount (gram)= 1.17							

Table 6.148. *4.5 mg/l abamectin containing solution (EF, i=10mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/l, pH= 8.38)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	23.7	521.25	0.0	0.0	0.0	0.0	0.0
20	17.5	154.23	70.41	0.00484	12.09	12.09	296.2555
40	17.5	142.37	72.69	0.00484	12.09	24.18	296.2555
60	17.3	134.96	74.11	0.00478	11.95	36.14	292.8698
80	17.2	124.96	76.03	0.00475	11.88	48.02	291.1769
Sludge amount (gram)= 1.31							

Table 6.149. *4.5 mg/l abamectin containing solution (EF, i=15mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/l, pH= 8.38).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	25.3	537.42	0.0	0.0	0.0	0.0	0.0
20	20.7	157.69	70.66	0.00855	21.37	21.37	523.53
40	20.4	145.33	72.96	0.00842	21.06	42.43	515.94
60	20.2	130.12	75.79	0.00834	20.85	63.28	510.88
80	20.1	121.23	77.44	0.00830	20.75	84.03	508.35
Sludge amount (gram)= 1.48							

Table 6.150. *4.5 mg/l abamectin containing solution (EF, i=20mA/cm^2, 1mM Na_2SO_4, 3000 mg H_2O_2/l, pH= 8.38).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (Kwh/400 mL)	Energy consumption (Kwh/m^3)	Cumulative energy consumption (Kwh/m^3)	Energy cost (Krş/m^3)
0	27.8	537.42	0.0	0.0	0.0	0.0	0.0
20	22.4	146.37	72.76	0.01238	30.96	30.96	758.41
40	22.2	138.46	74.24	0.01227	30.68	61.63	751.64
60	22	125.67	76.62	0.01216	30.40	92.04	744.87
80	22.1	119.12	77.83	0.01222	30.54	122.58	748.25
Sludge amount (gram)= 1.61							

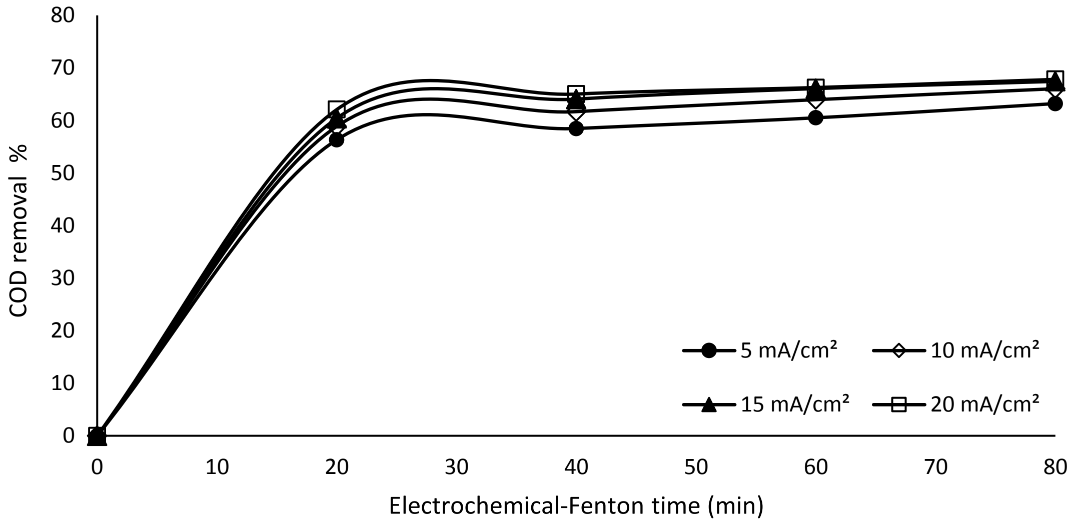

Figure 6.161. *Variation of COD removal over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, 500mg H_2O_2/L, pH= 8.34).*

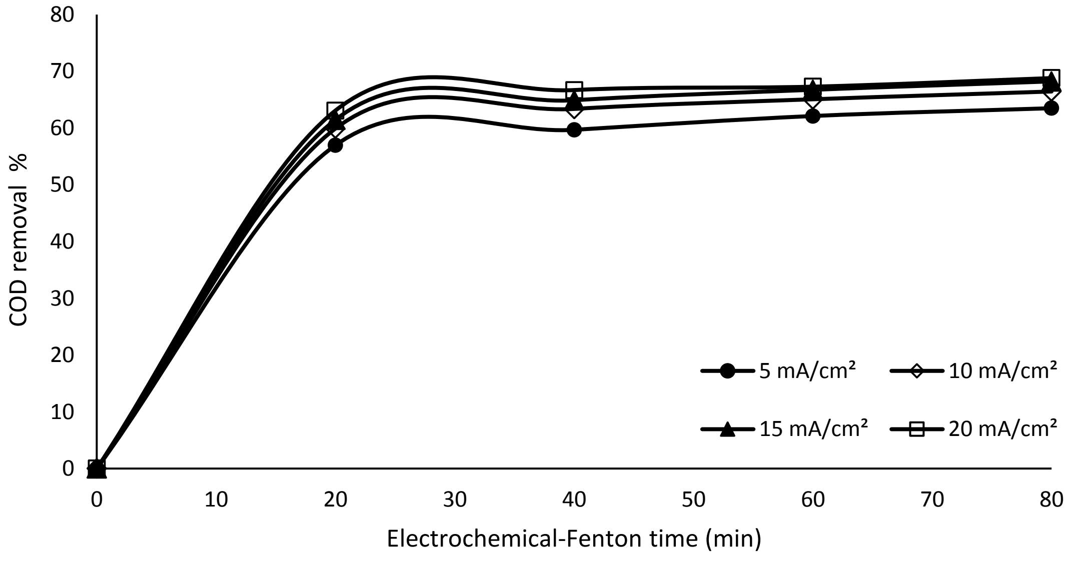

Figure 6.162. *Variation of COD removal over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, 1000mg H_2O_2/L, pH= 8.15).*

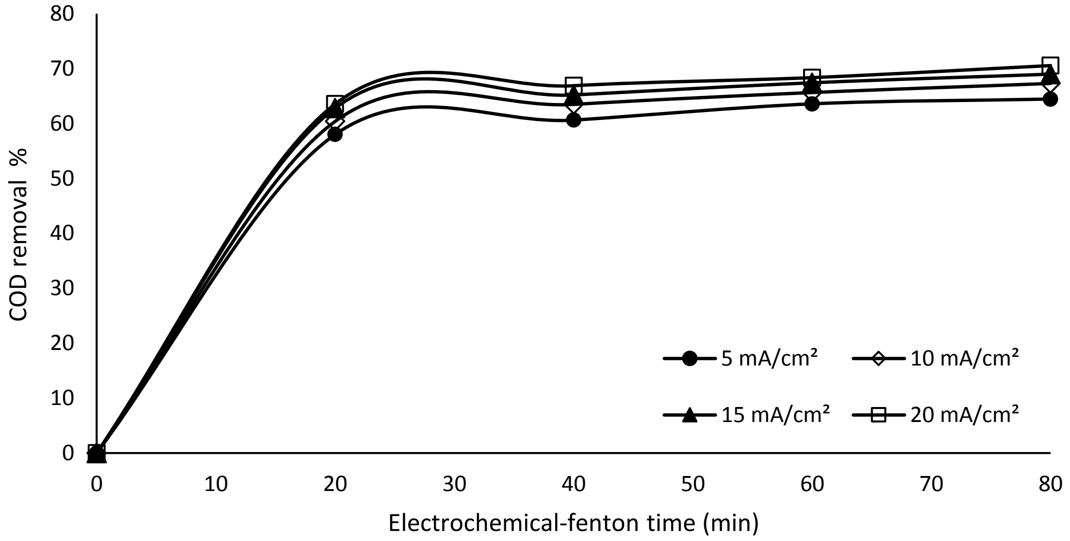

Figure 6.163. *Variation of COD removal over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, 2000mg* H_2O_2*/L, pH= 8.24).*

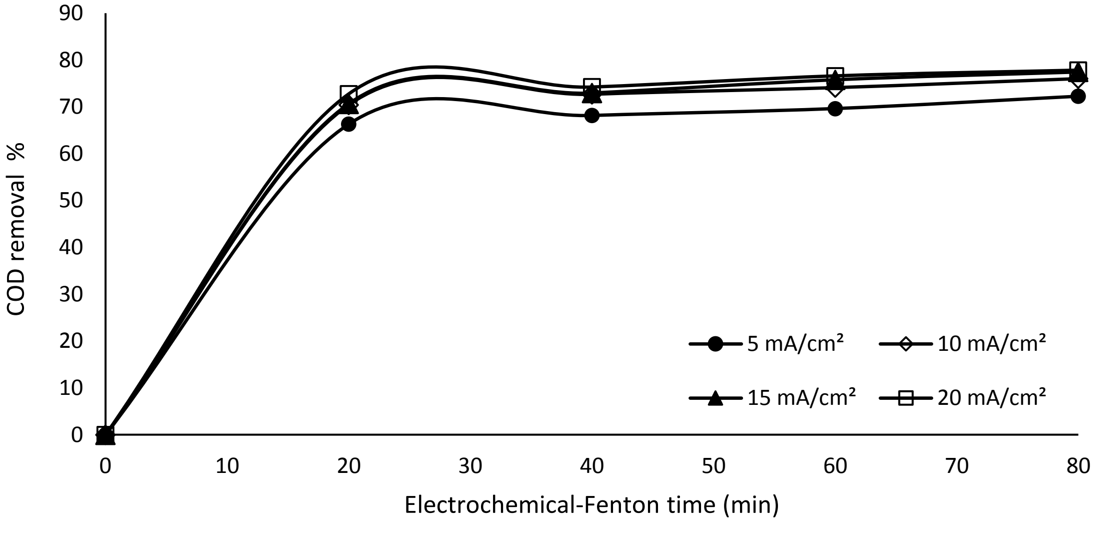

Figure 6.164. *Variation of COD removal over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, 3000mg* H_2O_2*/L, pH= 8.38)*

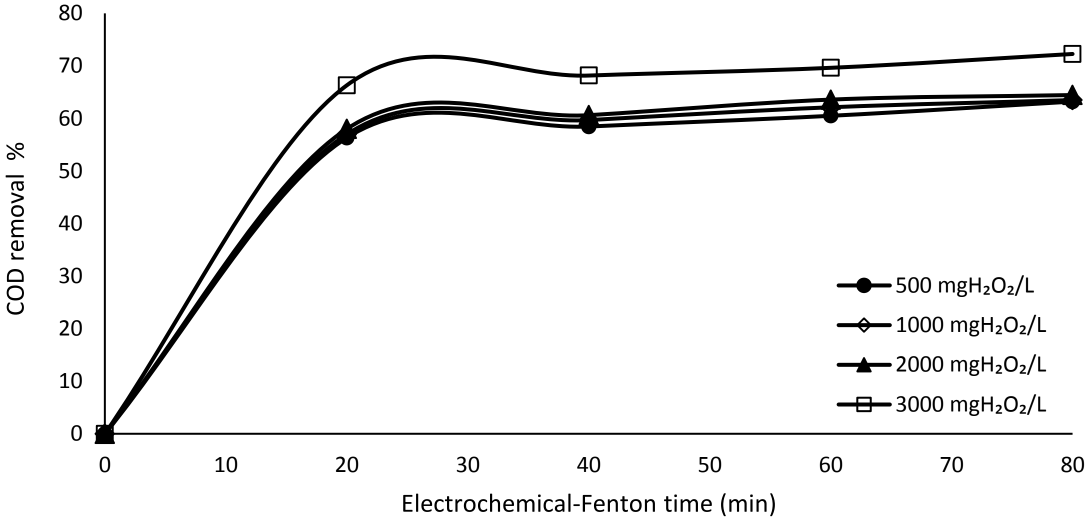

Figure 6.165. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, i=5mA/cm^2, 1mM Na_2SO_4)*

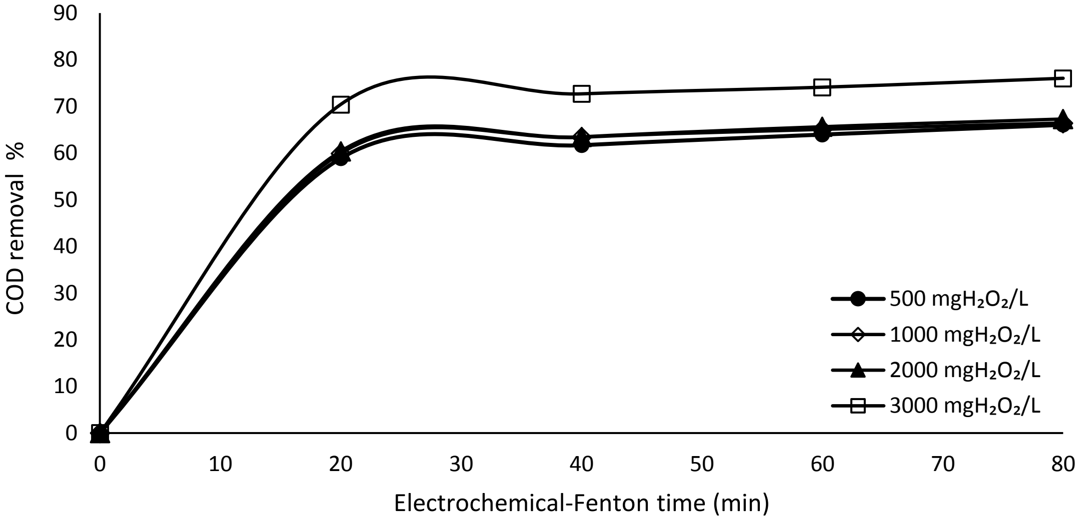

Figure 6.166. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, i=10mA/cm^2, 1mM Na_2SO_4)*

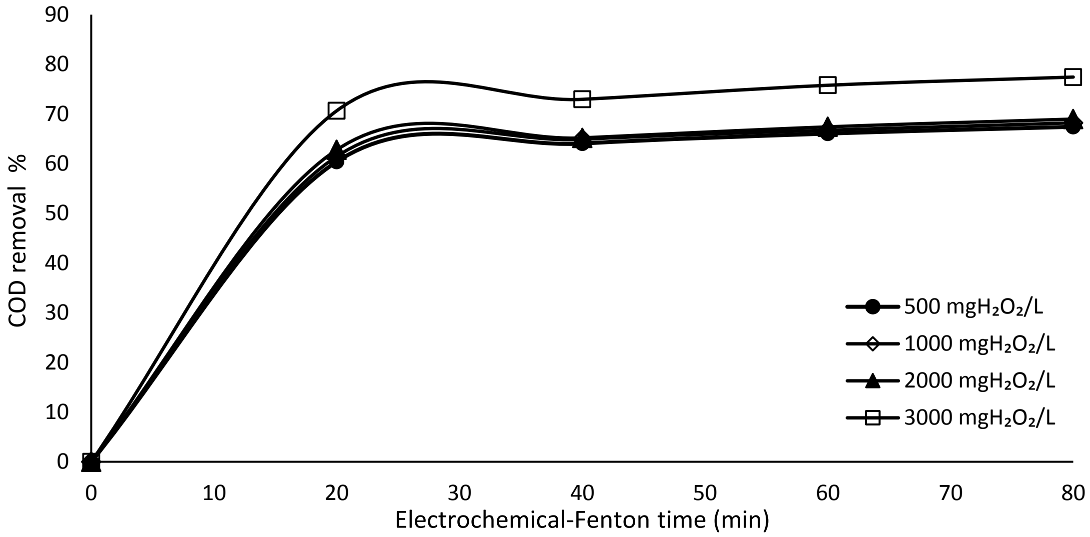

Figure 6.167. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, i=15mA/cm^2, 1mM Na_2SO_4)*

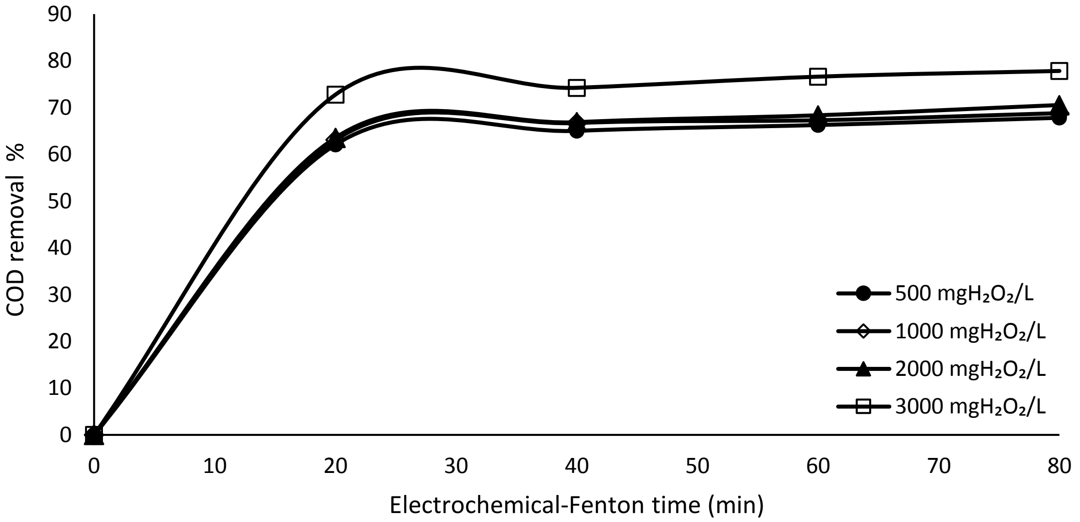

Figure 6.168. *Variation of COD removal over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, i=20mA/cm^2, 1mM Na_2SO_4)*

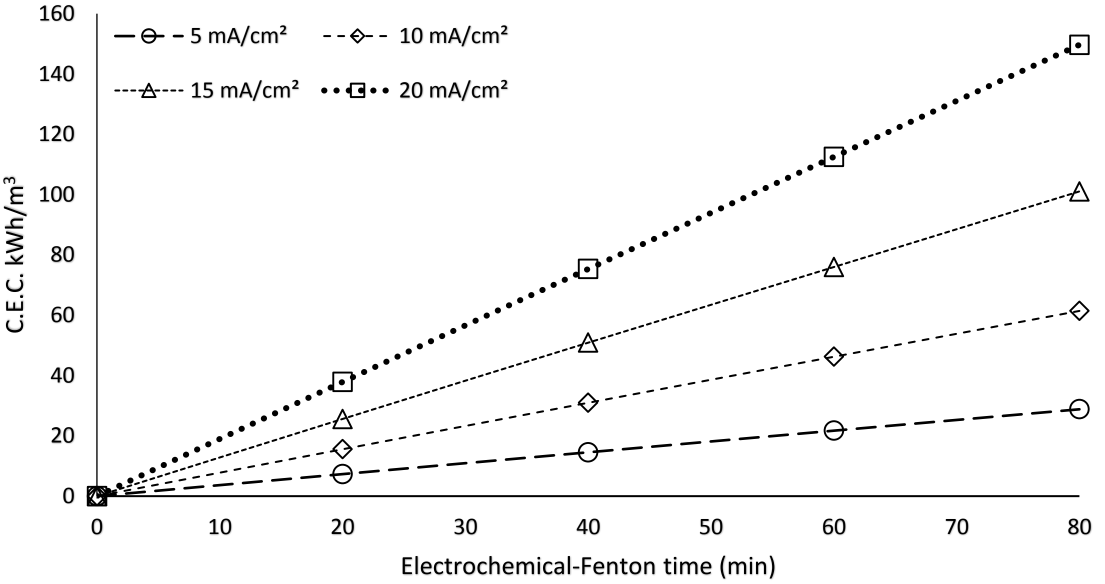

Figure 6.169. *Variation of energy consumption over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, 500mg* H_2O_2*/L, pH= 8.34)*

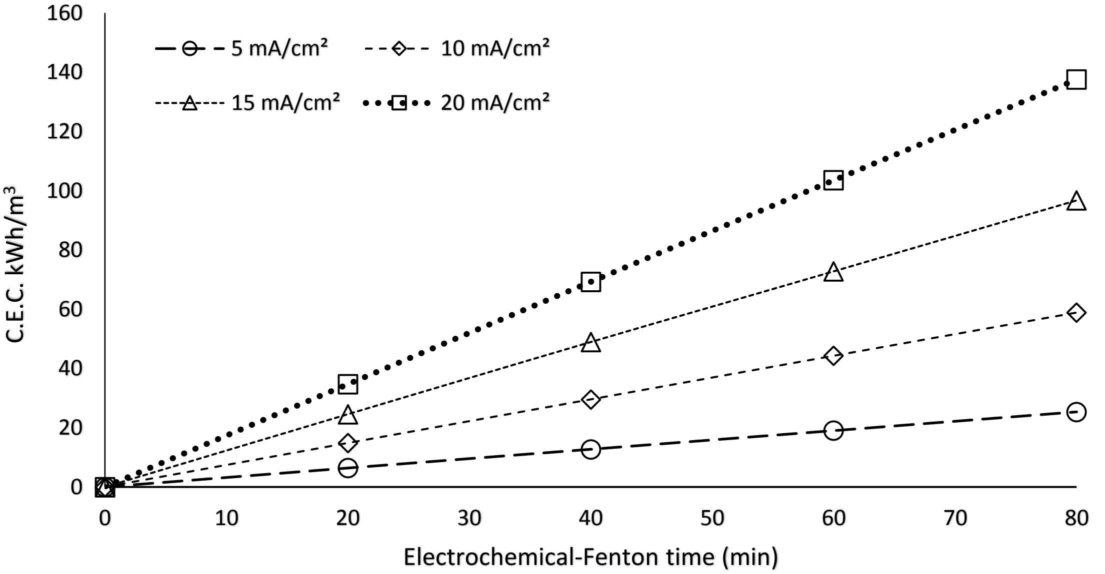

Figure 6.170. *Variation of energy consumption over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, 1000mg* H_2O_2*/L, pH= 8.15)*

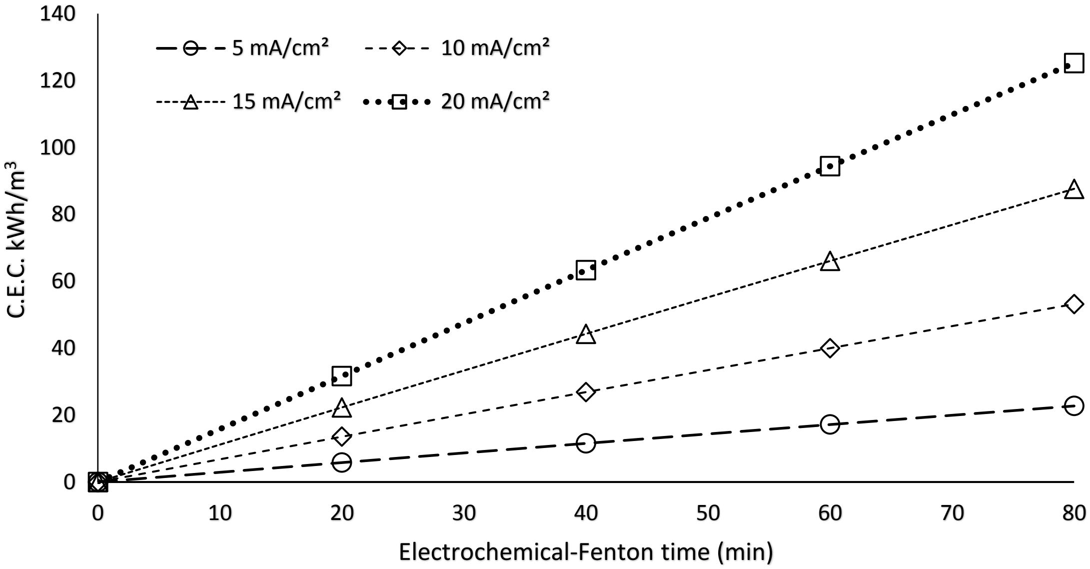

Figure 6.171. *Variation of energy consumption over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, 2000mg H_2O_2/L, pH= 8.24)*

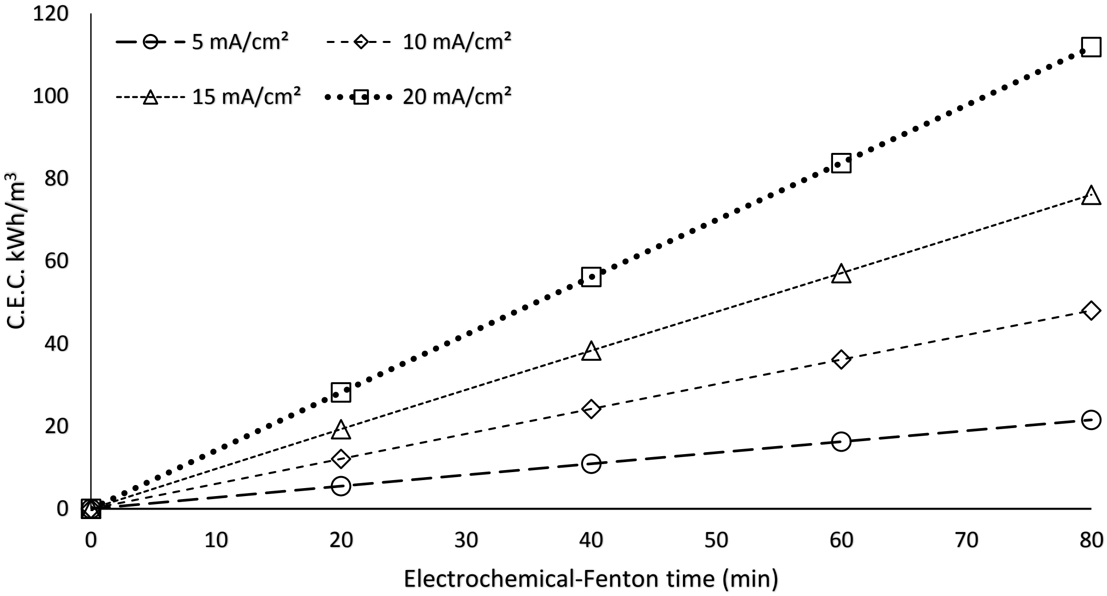

Figure 6.172. *Variation of energy consumption over the time depending on current density (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, 3000mg H_2O_2/L, pH= 8.38)*

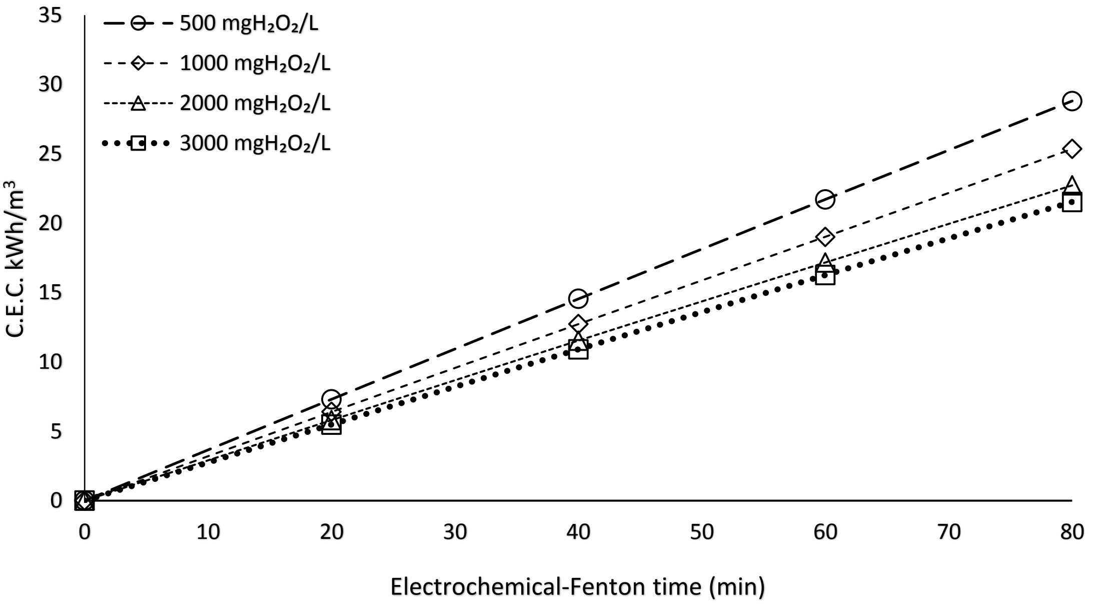

Figure 6.173. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, i=5mA/cm^2)*

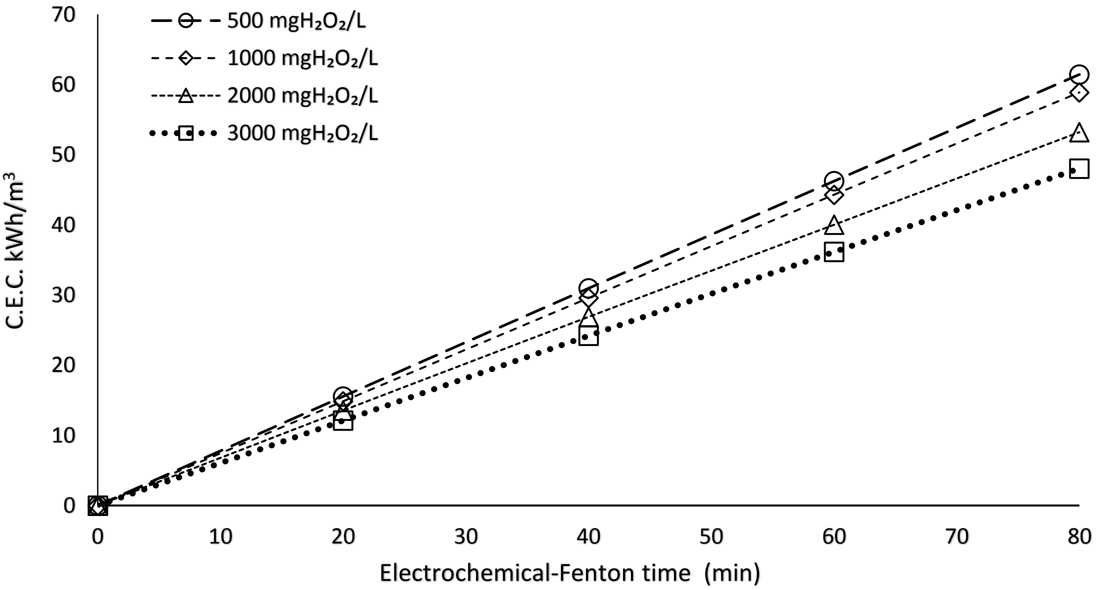

Figure 6.174. *Variation of energy consumption over the time depending on H_2O_2 concentration (EF, Co= 4.5 mg/L abamectin, 1mM Na_2SO_4, i=10mA/cm^2)*

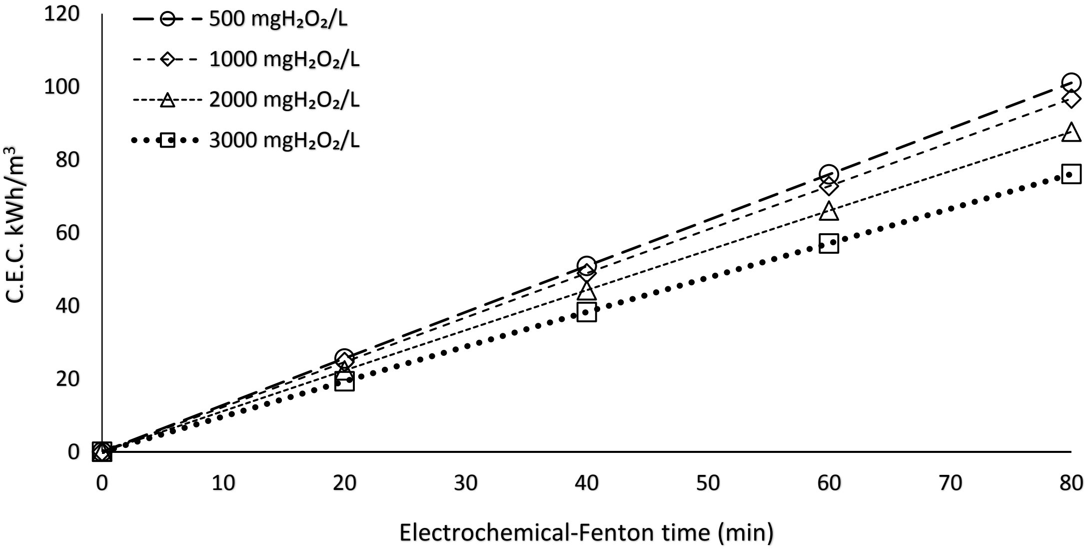

Figure 6.175. *Variation of energy consumption over the time depending on* H_2O_2 *concentration (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, i=15mA/cm*^{2}*)*

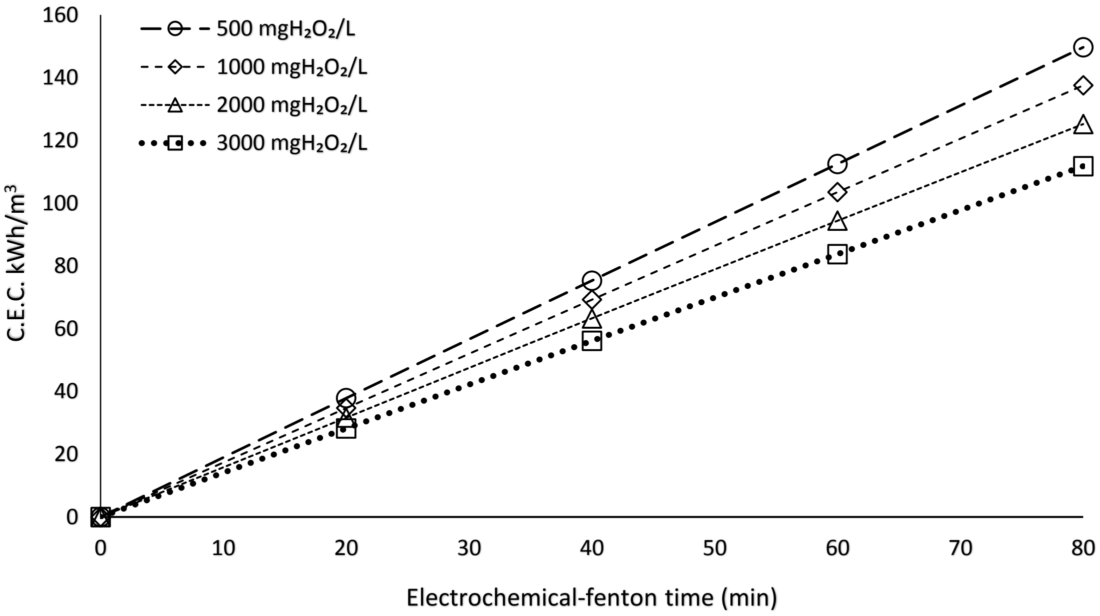

Figure 6.176. *Variation of energy consumption over the time depending on* H_2O_2 *concentration (EF, Co= 4.5 mg/L abamectin, 1mM* Na_2SO_4*, i=20mA/cm*^{2}*)*

6.3.5. Electro-oxidation methods using born doped diamond (BDD)

Table 6.151. *4.5 mg/L Abamectin containing solution (EO, i=5mA/cm^2, 5mM Na_2SO_4, pH= 8.47)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	8	548.32	0.0	0.0	0.0	0.0	0.0
20	8.4	143.71	73.79	0.00117	2.94	2.94	71.95
40	8.2	131.71	75.98	0.00115	2.87	5.80	70.24
60	8.1	127.65	76.72	0.00113	2.83	8.64	69.38
80	8.2	114.42	79.13	0.00115	2.87	11.50	70.24

Table 6.152. *4.5 mg/l Abamectin containing solution (EO, i=10mA/cm^2, 5mM Na_2SO_4, pH= 8.47)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.5	548.32	0.00	0.0	0.0	0.0	0.0
20	10.8	135.94	75.21	0.00299	7.46	7.46	182.83
40	10.7	120.55	78.01	0.00296	7.39	14.86	181.13
60	10.7	109.36	80.06	0.00296	7.39	22.25	181.13
80	10.7	94.51	82.76	0.00296	7.39	29.64	181.13

Table 6.153. *4.5 mg/l Abamectin containing solution (EO, i=15mA/cm^2, 5mM Na_2SO_4, pH= 8.47)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	14.7	548.32	0	0.0	0.0	0.0	0.0
20	14.2	121.87	77.77	0.00586	14.66	14.66	359.13
40	13.9	110.16	79.91	0.00574	14.35	29.01	351.55
60	13.9	101.24	81.54	0.00574	14.35	43.36	351.54
80	13.7	80.51	85.32	0.00566	14.14	57.50	346.49

Table 6.154. *4.5 mg/l Abamectin containing solution (EO, i=20mA/cm^2, 5mM Na_2SO_4, pH= 8.47)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	19	548.32	0	0.0	0.0	0.0	0.0
20	16.6	116.47	78.76	0.00918	22.94	22.94	562.03
40	16.2	104.16	81.00	0.00896	22.39	45.33	548.49
60	15.9	90.54	83.49	0.00879	21.97	67.30	538.33
80	15.7	71.21	87.01	0.00868	21.70	89.00	531.56

Table 6.155. *4.5 mg/l Abamectin containing solution (EO, i=5mA/cm^2, 10mM Na_2SO_4, pH= 8.63)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	5.2	543.89	0.0	0.0	0.0	0.0	0.0
20	5.3	120.41	77.86	0.00074	1.85	1.85	45.40
40	5.3	114.14	79.01	0.00074	1.85	3.71	45.40
60	5.3	102.37	81.18	0.00074	1.85	5.56	45.40
80	5.4	92.38	83.01	0.00076	1.89	7.45	46.25

Table 6.156. *4.5 mg/l Abamectin containing solution (EO, i=10mA/cm^2, 10mM Na_2SO_4, pH= 8.63)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	8.9	543.89	0.0	0.0	0.0	0.0	0.0
20	8.4	110.54	79.68	0.00232	5.80	5.80	142.2027
40	8.5	96.36	82.28	0.00235	5.87	11.68	143.8955
60	8.5	86.67	84.06	0.00235	5.87	17.55	143.8955
80	8.6	76.16	86.00	0.00238	5.94	23.49	145.5884

Table 6.157. *4.5 mg/l Abamectin containing solution (EO. i=15mA/cm^2, 10mM Na_2SO_4, pH= 8.63)*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	10.5	543.89	0.0	0.0	0.0	0.0	0.0
20	10.6	98.30	81.93	0.00438	10.94	10.94	268.08
40	10.7	82.75	84.79	0.00442	11.05	21.99	270.61
60	10.5	66.91	87.70	0.00434	10.84	32.83	265.55
80	10.4	60.21	88.93	0.00429	10.74	43.56	263.03

Table 6.158. *4.5 mg/l Abamectin containing solution (EO, i=20mA/cm^2, 10mM Na_2SO_4, pH= 8.63).*

Time (min)	Voltage (V)	COD (mg/L)	COD removal (%)	Energy consumption (kWh/400 mL)	Energy consumption (kWh/m^3)	Cumulative energy consumption (kWh/m^3)	Energy cost (Krş/m^3)
0	12.4	543.89	0.0	0.0	0.0	0.0	0.0
20	12.2	91.19	83.23	0.00674	16.86	16.86	413.06
40	11.6	75.50	86.12	0.00641	16.03	32.89	392.75
60	11.9	57.48	89.43	0.00658	16.45	49.34	402.90
80	11.6	50.63	90.69	0.00641	16.03	65.37	392.75

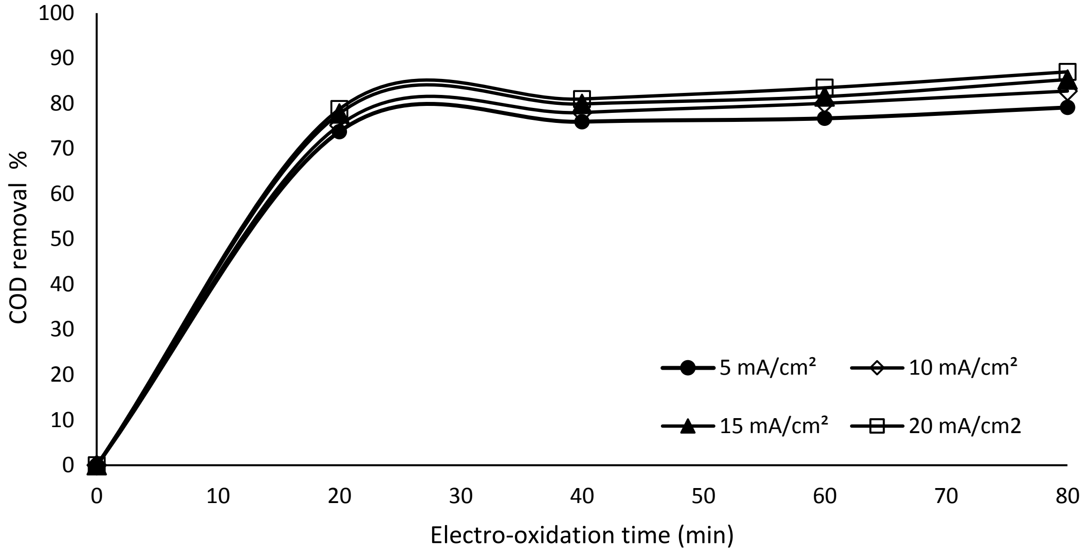

Figure 6.177. *Variation of COD removal over the time depending on current density (EO, Co= 4.5 mg/l Abamectin, 5mM Na_2SO_4, pH= 8.47)*

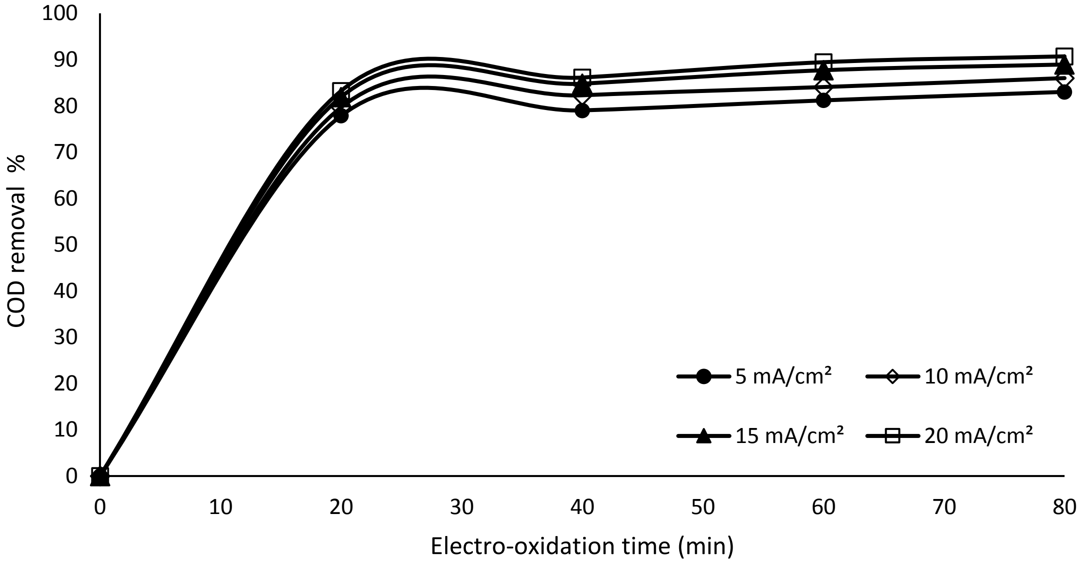

Figure 6.178. *Variation of COD removal over the time depending on current density (EO, Co= 4.5 mg/l Abamectin, 10 mM Na_2SO_4, pH= 8.63)*

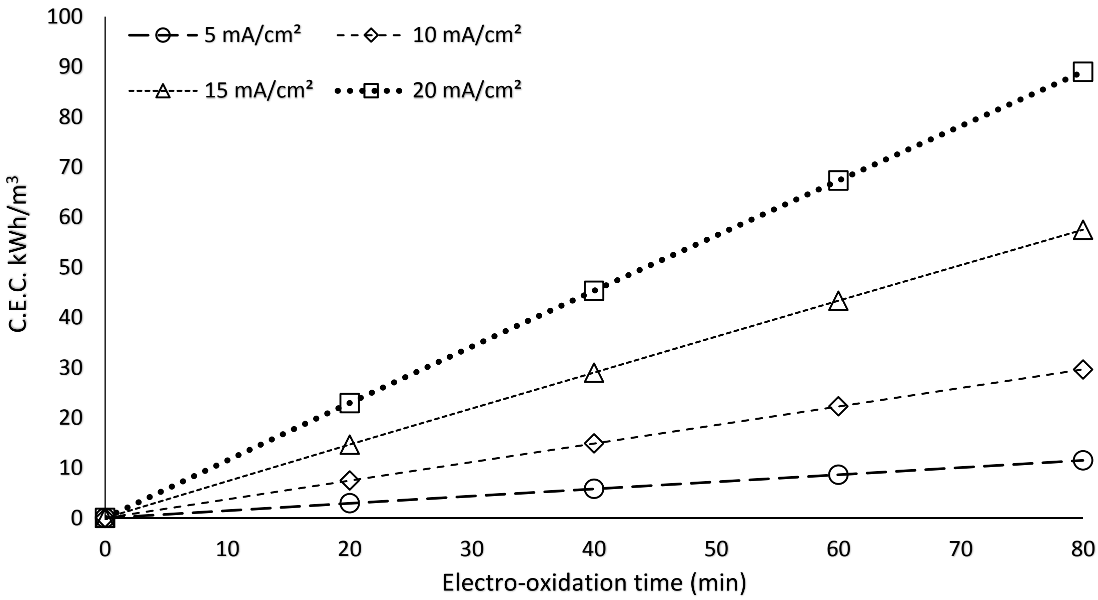

Figure 6.179. *Variation of energy consumption over the time depending on current density (EO, Co= 4.5 mg/l Abamectin, 5mM Na_2SO_4, pH= 8.47)*

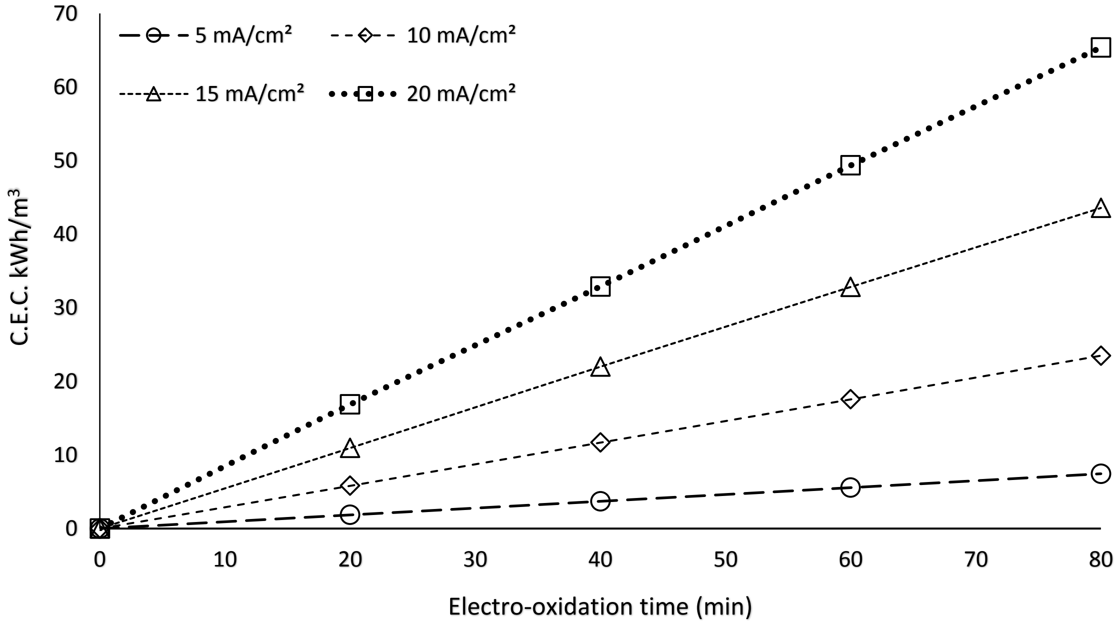

Figure 6.180. *Variation of energy consumption over the time depending on current density (EO, Co= 4.5 mg/l Abamectin, 10 mM Na_2SO_4, pH= 8.63)*

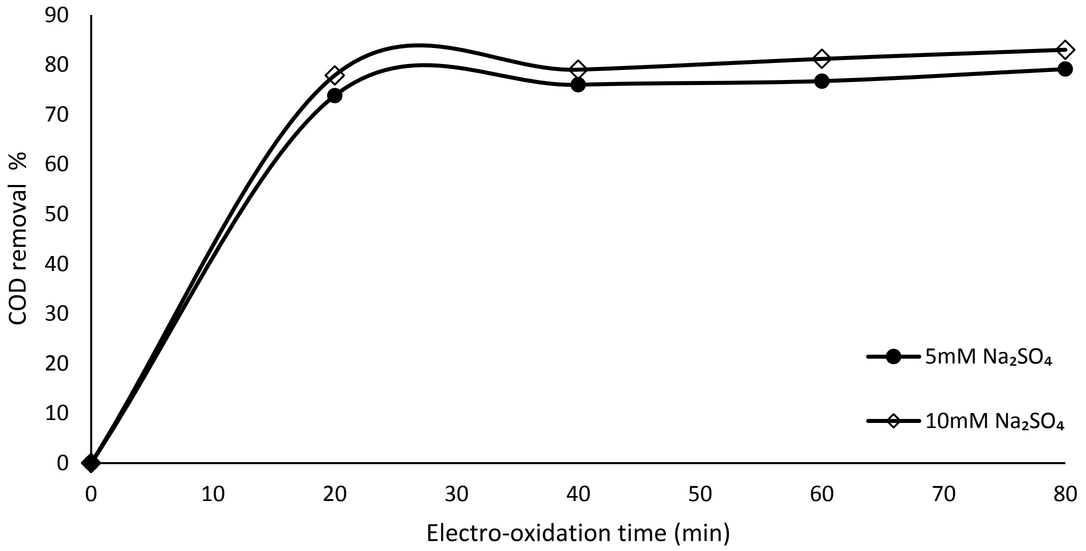

Figure 6.181. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 5mA/cm^2)*

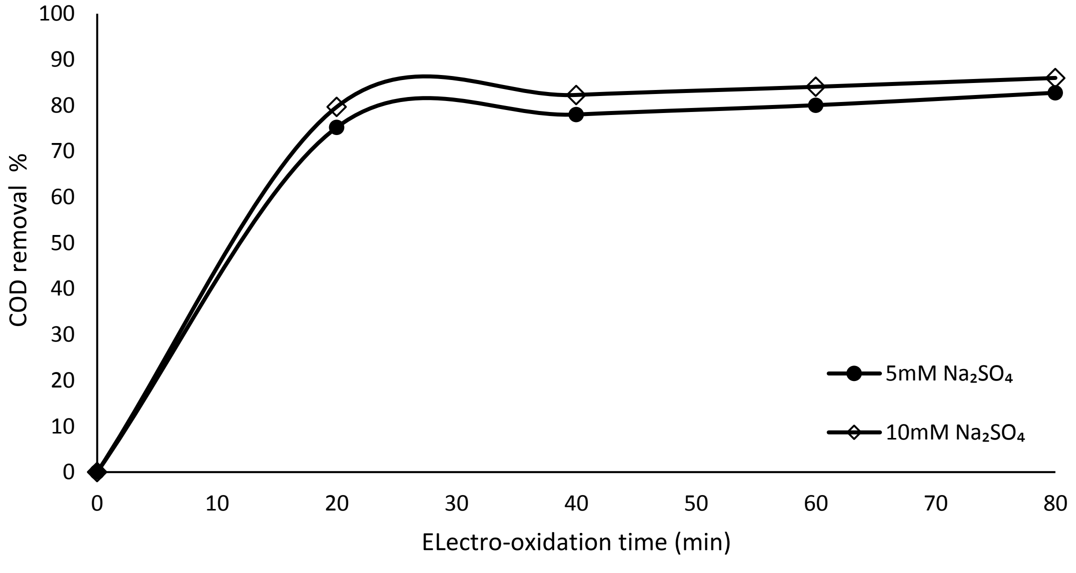

Figure 6.182. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 10 mA/cm^2)*

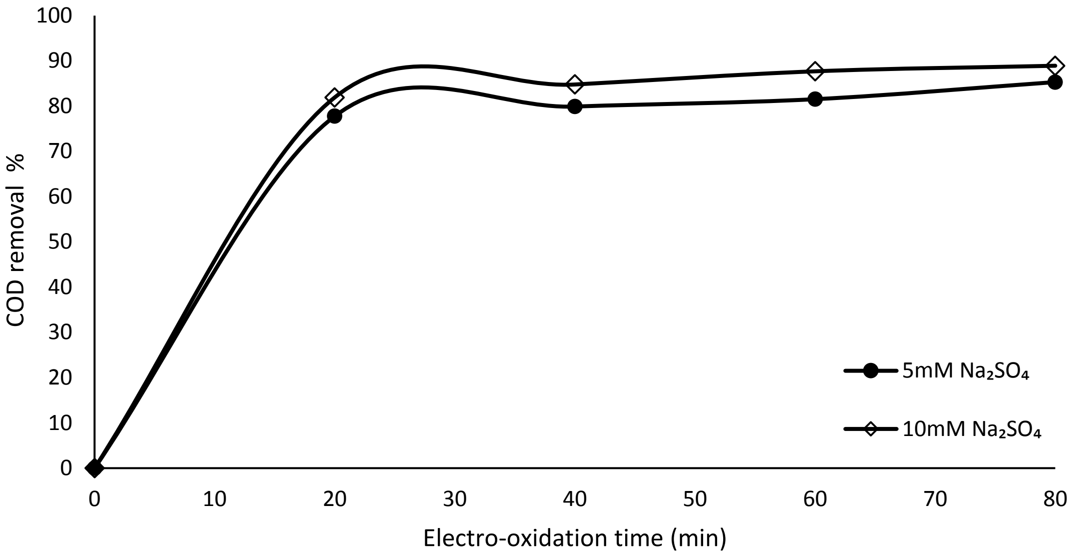

Figure 6.183. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 15 mA/cm²)*

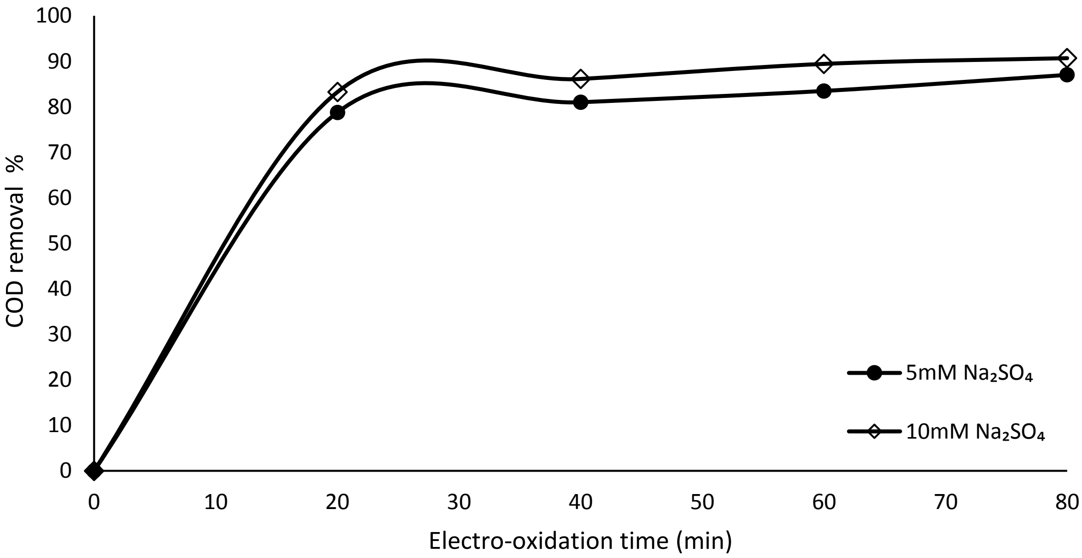

Figure 6.184. *Variation of COD removal over the time depending on support electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 20 mA/cm²)*

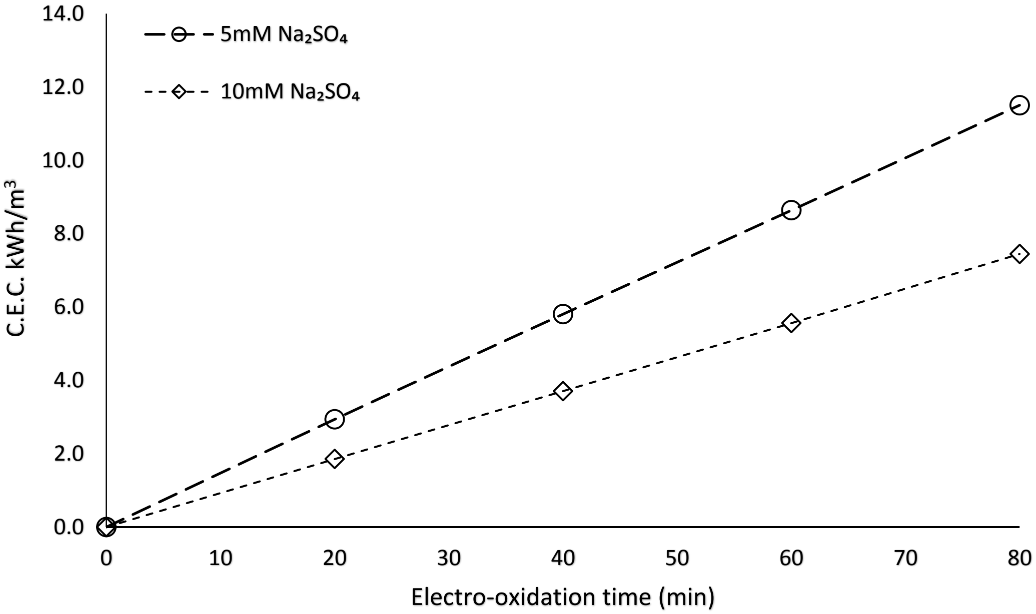

Figure 6.185. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 5mA/cm^2)*

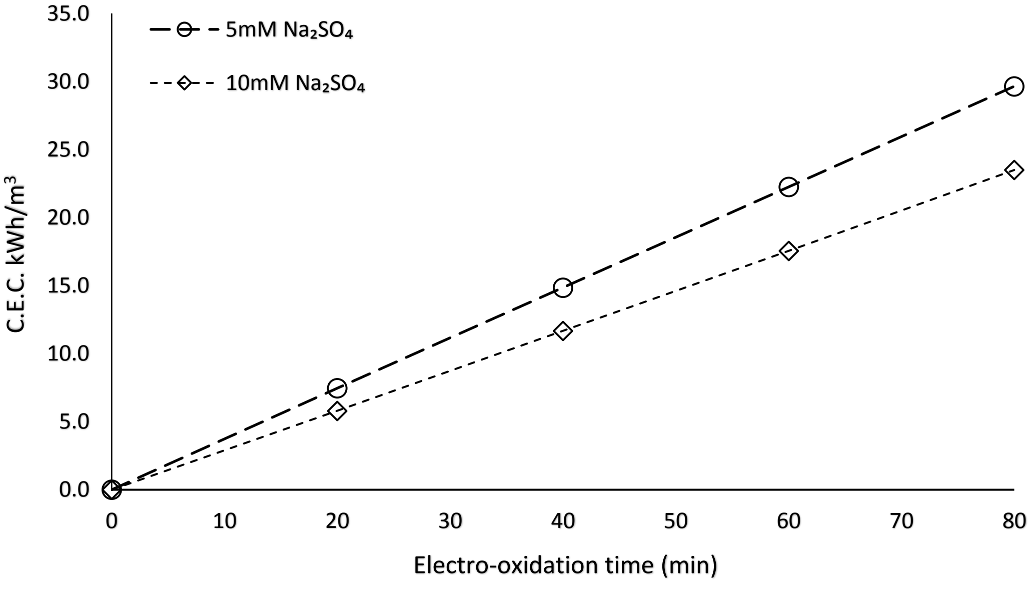

Figure 6.186. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 10 mA/cm^2)*

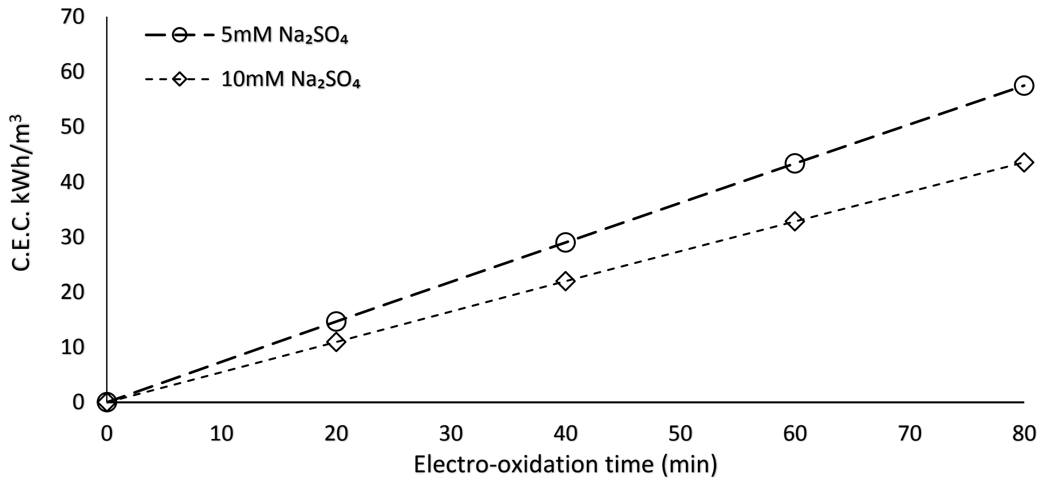

Figure 6.187. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 15mA/cm^2)*

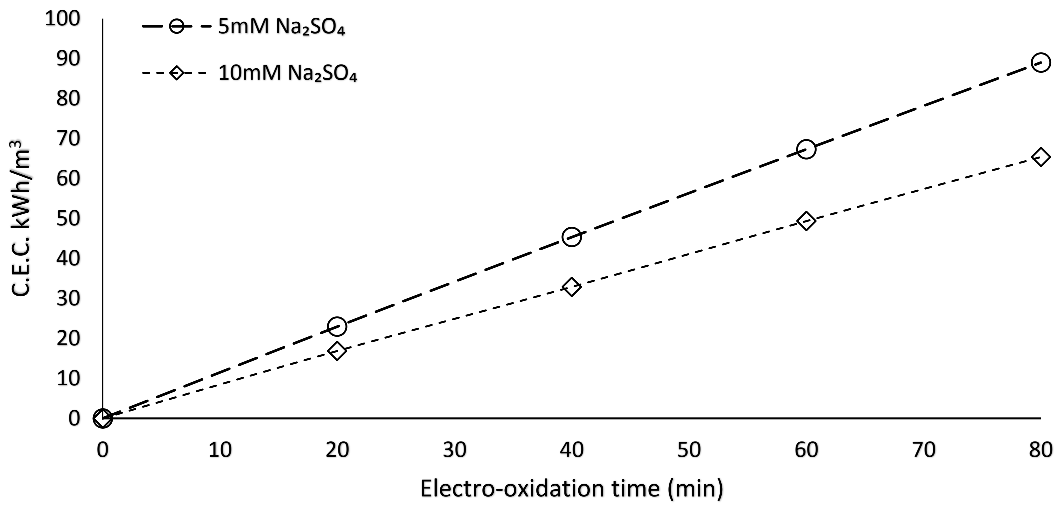

Figure 6.188. *Variation of energy consumption over the time depending on supporting electrolyte concentration (EO, Co= 4.5 mg/l Abamectin, 20mA/cm^2).*

6.3.6. Toxicity determination

Table 6.159. *Microtox toxicity of abamectin as a function of different treatment methods in term of EC$_{50}$.*

Treatment technique	**Treatment Time (min)**	**% EC$_{50}$ (5min)**	**Toxicity degree**	**% EC$_{50}$ (15min)**	**Toxicity degree**
ECP	0	16	High toxic	21	High toxic
	40	46	Moderate toxic	49	Moderate toxic
	80	54	Toxic	70	Toxic
EFP	0	21	High toxic	24	High toxic
	40	58	Toxic	64	Toxic
	80	65	Toxic	72	Toxic
EOP	0	20	High toxic	24	High toxic
	40	58	Toxic	62	Toxic
	80	77	Slight toxic	87	Slight toxic

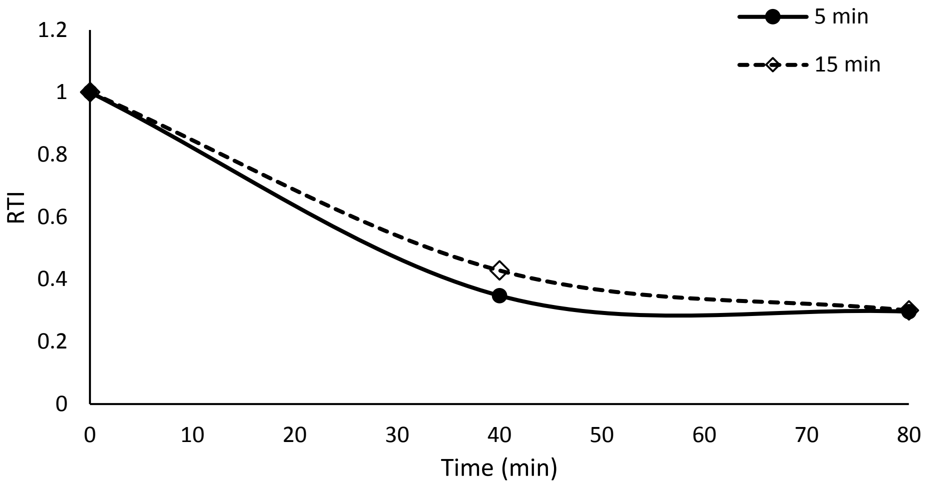

Figure 6.189. *Variation of 5th and 15th mins toxicity of abamectin by electrocoagulation with the time.*

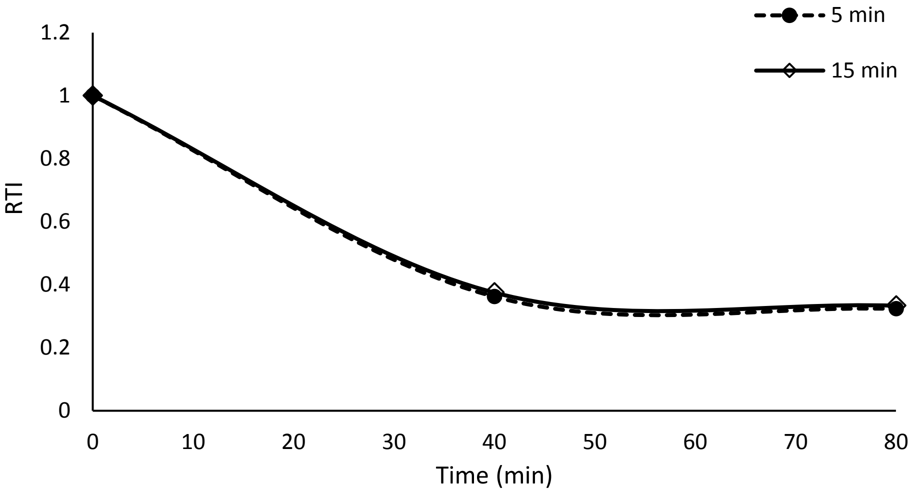

Figure 6.190. *Variation of 5th and 15th mins toxicity of abamectin by electrochemical-Fenton with the time.*

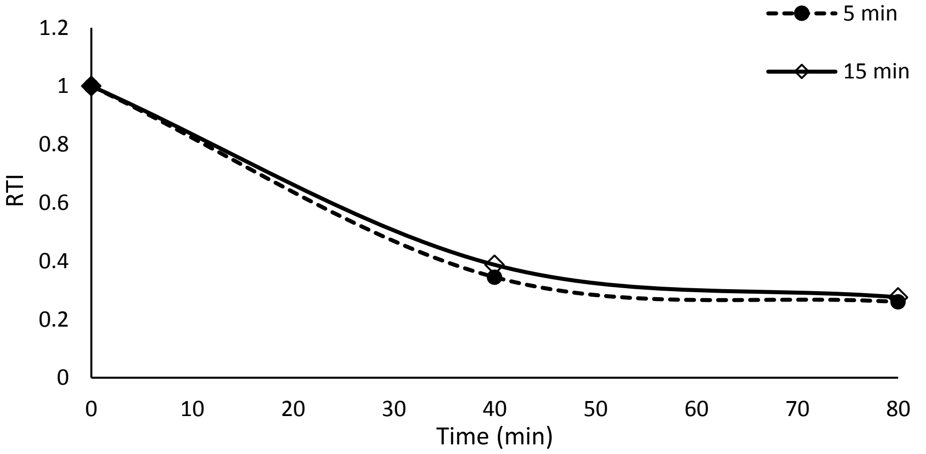

Figure 6.191. *Variation of 5th and 15th mins toxicity of abamectin by electro-oxidation with the time.*

6.3.7. Kinetic studies

Kinetics studies play an important role in determining the order of reaction and the rate constant of the treatment removal. rate constant is critical in the design of treatment units. It is very critical to determine the reaction rates type for the treatment process. Reaction Rate shows the rates at which concentration of reactant change in the unit of time. The concentration of abamectin was (1.81, 1.17, 0.51, and 0.19 mg/L) at (20, 40, 60, 80 mins) respectively during the electro-oxidation. Figures 6.192 represent the removal efficiency of abamectin exhibited pseudo first order with perfect correlation coefficients (0.9865) for BDD electrodes according to equation 6.12. The rate constants values at optimum condition and reaction time were 0.0379 min^{-1}. The temperature of the system was about 28°C during the electrolysis.

$$-\frac{d[Abamectin]}{dt} = k[Abamectin] \qquad (6.11)$$

İn which their integration gives, for [Abamectin]= $[\text{Abamectin}]_o$ at t= 0:

$$\ln\frac{[Abamectin]o}{[Abamectin]t} = kt \qquad (6.12)$$

In which k is the pseudo-first-order rate constant.

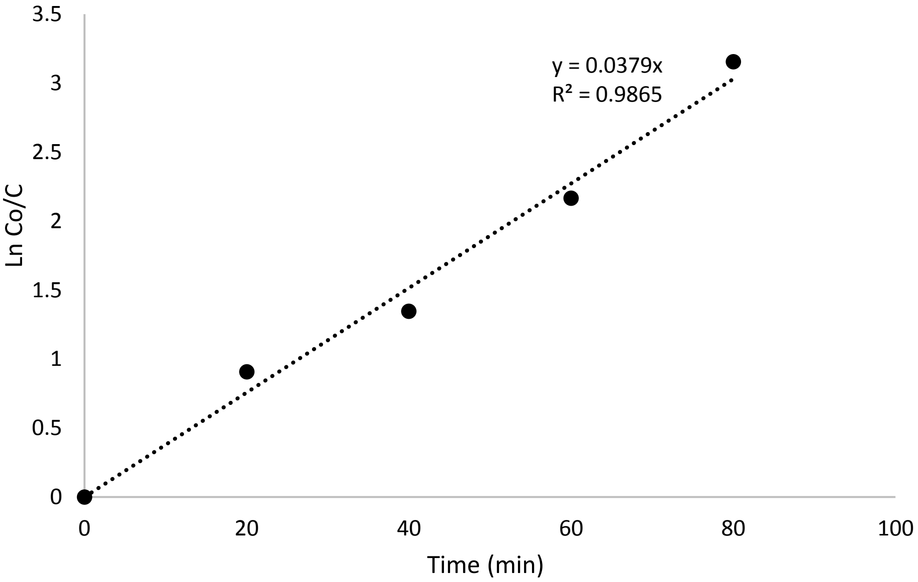

Figure 6.192. *Relation between Ln Co/C against the time for abamectin removal using BDD electrodes (Co= 4.5mg/L, i=20mA/cm^2, 10mM Na_2SO_4, pH= 8.63)*

7. DISCUSSION

7.1. Bromuconazole

The removal efficiencies of pesticide bromuconazole from aqueous solution were examined by electrocoagulation using different electrodes. The effects of current density and concentration of supporting electrolyte were investigated on removal efficiency of the pesticides and COD. It was observed that these factors significantly affected the treatment of bromuconazole from aqueous solution.

7.1.1. Electrocoagulation methods using iron electrodes

The performance of electrocoagulation with an iron electrode for removal of bromuconazole was investigated. Parameters such as current density and support electrolytes were investigated in an attempt to achieve a higher removal efficiency. The solution of 300mg/L of pesticides were prepared. The pH of the model solution was ~ 5.

During pesticide electrolysis with electrocoagulation using iron electrode, the solution in the reactor becomes green and gas bubbles appeared at the cathode. After a while, the solution becomes clear and a green and yellowish orange sludge are formed. The formation of green and yellow colors can be attributed to ferrous and ferric hydroxide.

As the current density increased, the removal efficiency of bromuconazole and COD improved as is shown in figures 6.1- 6.3. This is due to the generated amount of metal hydroxide which is directly related to the applied current density. By increasing the current density, the ion production efficiency on the cathode as well as anode increases. Accordingly, there is an increase in floc formation in the solution that improves the efficiency of pesticides removal. The increase of bubbles and coagulant generation rate result in increasing amount of H_2 bubbles and the decrease in their size with increasing current density leading to the faster removal of pesticides [124].

It was also indicated that an increase in current density resulted in an increase of solution turbidity. This may be because higher current density results in an increase in anodic dissolution which in turn improves the flocculation.

In addition, the results in figures 6.4-6.6 revealed that the increased current density resulted in higher energy consumption. At the maximum removal efficiency, the energy consumption and energy cost were 144,69 kWh/m^{3}and 887,07 Krş/m^3 respectively.

The figures 6.7- 6.10 shows the variation of removal efficiency and COD over the time by testing different support electrolyte concentrations. The removal efficiency of bromuconazole and COD enhanced at higher supporting electrolyte concentrations, so that the maximum COD removal was 81,35 % at a current density of 20mA/cm^2 and supporting electrolyte of 10 mM Na_2SO_4 respectively. As shown in the figures, the optimum supporting electrolyte concentration was 5mM and above this concentration, no significant increase in COD removal efficiency was observed. By increasing the concentration of electrolyte at a constant voltage, the solution conductivity increased, and resistance decreased which means the amount of passing current and the amount of producing metallic hydroxide increased. This resulted in a reduction of oxide layer and enhanced the electrode anodic dissolution and pesticide degradation efficiency [125].

The energy consumption decreased by increasing the supporting electrolytes concentration at different current densities, as shown in figure 6.11- 6.14. The minimum values for energy consumption were recorded at 10mM supporting electrolyte concentration. The addition of supporting electrolyte resulted in less power consumption because of enhanced solution conductivity [126].

7.1.2. Electrocoagulation methods using aluminum electrodes

The formation of the floc was observed shortly after the start of the experiment. The hydrogen produced at the cathode swiped the formed flocs toward the surface of the reactor as white clay. The aluminum electrode consumed and eroded. The electro-dissolution of anode resulted in the formation of flocs and water reduction at the cathode that continuously generated in the solution.

The removal efficiency and COD of bromuconazole in aqueous solution using electrocoagulation method by aluminum electrodes were investigated. It was observed that the increase of current density significantly affected the removal efficiency rate as shown in the figure 6.15. This could be due to the (Cl^-) ions that released from pesticide structures. It destroyed any oxide film that formed on the anode surface that could decrease the rate of anode dissolution. This effect finally resulted in the increased amount of $Al(OH)_3$ in the reactor which improved the removal efficiency. The optimum COD removal efficiency for electrocoagulation using aluminum electrode was 77,74% obtained at the 15mA/cm^2 current density.

According to the figure 6.16, the energy consumption was increased by increasing the current density. Despite the lower removal efficiency compared to that recorded with the iron electrodes, the energy consumption is also higher than that of the iron electrodes.

The energy consumption and energy cost of maximum removal efficiency was 194,44 kWh/m^3 and 1171,47krş/m^3 as shown in table 6.16. The highest COD removal of 78,77 % was recorded at the end of electrolysis with a current density and support electrolyte of 20 mA/cm^2, 10 mM Na_2SO_4 as shown in the table 6.16. The energy consumption and efficiencies values indicate the superior in the performance of iron electrodes over aluminum electrodes in the treatment of bromuconazole pesticides.

7.1.3. Electrocoagulation methods using hybrid (mixed) electrodes

Electrocoagulation includes generation of coagulants in in-situ by dissolution of iron and Aluminum electrodes electrically. The generation of ions takes place at the anode, while at the cathode H_2 production take place along with hydroxyl release. Removal of bromuconazole from model solution by electrocoagulation process using a combination of six aluminum and the iron electrode was investigated. The initial concentration of pesticides was 300 mg/L, the temperature was about 26 ^oC, the pH was ~5. The effect of current density and support electrolytes on removal efficiency has been evaluated.

The current density is the parameter that controlling the reaction rate of the electrochemical process. It also controls the rate of coagulant and bubbles formation. In order to evaluate the effect of current density on bromuconazole removal efficiency in the reactor, experiments with different current densities were carried out. Figure 6.17-6.19 showed the COD removal efficiency of pesticide in the reactor as a function of treatment time at the different current densities. The removal rate of pesticide and COD increased by increasing the current density. The increasing of current density results in an increase in ion production efficiency at anode and cathode. This is because, by increasing current density, the anodic dissolution extension (Faraday law) results in the formation of a high quantity of metal hydroxide complex that improves removal efficiency of pesticides.

The increase of current density during the treatment time associated with metal hydroxide generation. As the removal efficiency rate increased by increasing current density, the amount of sludge formed was also increased.

Different concentration of Na_2SO_4 was added as a supporting electrolyte to improve the conductivity of the solution since the conductivity of model solution was low. Figure 6.23-6.26 showed that the increase in the amount of Na_2SO_4 to 5mM results in increasing removal efficiency dramatically while at 10 mM no significant difference in removal efficiency recorded. Which indicates that the optimum support electrolyte concentration was 5mM.

The figure 6.27-6.30 reported the energy consumption as a function of operating time at the supporting electrolyte concentration. The results showed that energy consumption inversely proportional to the Na_2SO_4 concentration. The energy consumption and energy cost at optimum removal efficiency of 82,79 % were 170,95 kWh/$m^3$and 1036,04 Krş/m^3 respectively as shown in table 6.24.

7.1.4. Electrochemical-Fenton methods

Organic pollutants oxidation in the electrochemical-Fenton system is directly related to the amount of hydrogen peroxide radicals produced by the Fenton's reaction [127]. The removal efficiency of pesticide bromuconazole has been investigated by adding 500, 1000, 2000, and 3000 mgH_2O_2/L of hydrogen peroxide to the reactor at different current densities. As shown in the figures 6.31- 6.34, the removal efficiency of pesticides and COD directly proportional to current density. The removal efficiency increases by increasing the current density [128].

According to the figure 6.35-6.38, the COD removal efficiency increased significantly by increasing hydrogen peroxide concentration. Hydrogen peroxide concentration is an important factor of EFP, increasing their concentration dosage result in increasing of hydroxyl radical that in turn increase the removal efficiency [129]. It was reported from figures that the optimum hydrogen peroxide solution was 1000mgH_2O_2/L and no significant removal observed by increasing above this concentration. The highest COD removal percentage was 84,99% and 87,50 % recorded at 20mA/cm^2 with an H_2O_2 concentration of 2000, and 3000 mgH_2O_2/L respectively at 80 minutes of treatment as seen in tables 6.40 and 6.44. This is because of the combined impact of ferrous which neutralize the charge of colloidal particles in the reactor and decrease their solubility, also responsible for $^{\cdot}OH$ and HOCl formation.

The effect of hydrogen peroxide concentration on energy consumption was also investigated and according to the figures 6.43-6.46 the energy consumption slightly decreased by increasing the hydrogen peroxide at 1mM supporting electrolyte.

7.1.5. Electro-oxidation methods using a boron-doped diamond (BDD)

The electro-oxidation using boron-doped diamond seen to be the most promising technique for removal of pollutant because of their oxidation ability and electro-generation of hydroxyl radical. The degradation of bromuconazole model solutions by BDD electrode has been studied within 5, 10, 15, and 20 mA/cm^2 at two different concentration of supporting electrolytes (5 mM and 10 mM Na_2SO_4).

The COD removal efficiency was improved by increasing the current density. A significant increase was seen in removal efficiency by increasing the current density during 80 minutes of treatment as in figures 6.47, 6.48. The highest reduction in COD observed during first 20 minutes of electrolysis in all experiments. The electro-oxidation of pesticide occur heterogeneously, taken into account the transporting of pollutant to the surface of electrodes and after that be oxidized. At the beginning the COD concentration was large, and the rate of reduction was submitted to current control. For this reason, the rapid decreases in COD removal percentage were seen during first 20 minutes of electrolysis.

The second most critical variable influencing the bromuconazole removal is the supporting electrolyte dosage. This parameter showed positive effect within the whole interval of experiments as in figures 6.51- 6.54. This fact can be proved right by considering two factors. First, the increased salt concentration increases the conductivity of the solution. Secondly, the formation of oxidizing species such as peroxydisulfate ($S_2O_8^{2-}$) is also preferred by the increase of SO_4 ions (in the case of using Na_2SO_4 as support electrolyte) in the solution [130]. The highest COD removal percentage was 92.22%, recorded at 20 mA/cm^2 current density and 10mM supporting electrolyte in the 80 minutes of treatment as shown in the table 6.52.

The results also showed that when the experiments were carried out with 5mM support electrolyte concentration, the effective current density was 15mA/cm^2. while at

10 mM, the optimum current density was 10mA/cm^2. This indicated the simultaneous effect of current density and support electrolytes on the pesticide removal efficiency.

Figures 6.49, 6.50 shows the energy consumption along the electrochemical oxidation treatment processes. The energy demand for electrolysis is measured in kilowatt-hours per cubic meter. The energy consumption rate was increased linearly with increasing of current density, Whereas it's reversely propositional to supporting electrolyte concentration and showed a significant decrease by increasing of Na_2SO_4 concentration as in the figures 6.55-6.58.

7.1.6. Analysis of inorganic ions degradation of bromuconazole by ion chromatography

The ions chromatography is a process that separates ions and polar molecules based on their affinity to the ion exchanger which allow monitoring the inorganic ions result from the degradation of bromuconazole. The variation of inorganic ions concentration during electrolysis by different electrochemical methods are present in figures 6.59-6.61. The results show the amount of NH_4^+ and NO_3^- released during electrolysis and indicate that most of the nitrogen was converted to ammonium ions during the electrolysis process, the concentration of ammonium ions is twice of nitrate ions. İn EFP and EOP, the ammonium formation was rapid within the first 20 minutes of electrolysis but in electrocoagulation, it's gradually increased. The total concentration of ammonium and nitrate at the end of EFP and EOP was closed to amino group amount in bromuconazole.

During first 20 minutes of electrolysis, a large amount of Cl^- was released. While its concentration is lower than its amount in the organic structure of pesticide. This because of two facts: first, some amount of chloride was settled down in sludge in ECP and EFP. the second, participate in the formation of some intermediate compounds. The concentration of released bromine reached 91% and 94% of initial organic bromine at the end of electrolysis by EFP and EOP respectively. However, in electrocoagulation, some of the bromine was settled down in the sludge.

7.1.7. Microtox assay and toxicity assessment

Microtox bioassay tests were used to evaluate the toxicity of model solution of the bromuconazole treated in the electrochemical reactor for given times including the time zero under best experimental conditions. The results illustrated as the relative toxicity index values versus reaction time presented in Figure 6.62-6.64. According to the ratings, toxicities of pesticide in model solution were reduced to more agreeable levels when compared to the toxicities of the initial solution were taken into consideration. The three electrochemical technique showed high performance to decrease the toxicity of highly toxic pesticide but was not at a required and expected level. This can be explained due to the chloride ions that released from pesticide to the solution. Availability of the chloride (Cl^-) ions in the water can cause the formation of DBPs which are suspected carcinogenic compounds [131].

The % EC50 (5min) of initial toxicity was reduced to 42%, 54% and 69 % for ECP, EFP, and EOP respectively after 80 minutes of the electrolysis. However, the %EC50 (15mins) exhibited the reduction of initial concentration by 53%, 69%, and 86% for ECP, EFP, and EOP respectively for same electrolysis time as seen in the table 6.53.

7.1.8. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS)

A tabletop SEM Hitachi TM3030 was used for imaging particle sizes and distribution. The sludge formed after electrolysis of bromuconazole was examined using SEM, the results of which are shown in Figure appx 1.1and 1.3. at 800x and 2.0kx. In electrocoagulation process, the floc formation was much more than that of the electrochemical-Fenton process, since in EFP the structure of organic matters breaks down into much more smaller molecules. Also, in EFP some of the carbons mineralized to carbon dioxide, so the final sludge formed was less.

The sample region studied with SEM can also be analyzed to indicate the particular elements that by utilizing (EDS). EDS provides information about the chemical composition of the sample and also provides extra data about the particularity that are seen in the SEM graphs. The EDS spectrum of the sludge of bromuconazole degraded with ECP and EFP showed in figure appx 1.2 and 1.4.

Typically, in electrocoagulation, the sludge contains (Cl) ions in a small amount and are likely to be pesticide residues. A small amount of S and Na also observed which is come as a result of supporting electrolytes (Na_2SO_4) addition. The elemental maps showed that the distributions of Fe in ECP and EFP practically identical, and the area enriched with this element roughly coincides with the particle boundaries.

7.2. Bentazone

The different electrochemical treatment methods of bentazone in model solutions have been investigated. The rate of mineralization has been estimated by the measurement of global parameters such as removal efficiency and chemical oxygen demand. The effect of operating factors such as current density, nature of electrode, hydrogen peroxide concentration, and support electrolytes concentration has been studied on the efficiency of bentazone removal.

7.2.1. Electrocoagulation methods using iron electrodes

The removal efficiency of bentazone and COD by electrocoagulation was studied at four different current densities. The reactions were carried out for 80 minutes using six parallel iron electrodes. The effect of current density and supporting electrolyte has been investigated.

Significant COD removal efficiency was noted within the 80 minutes by increasing the current density at different support electrolyte concentrations of Na_2SO_4 as seen in figures 6.66-6.68. The amount of current density determines the rate of coagulant production and control the size and rate of the bubble formation, and therefore affects the flocs growth [88].

The effect of supporting electrolyte concentration on COD removal efficiency of solutions have been investigated with initial pesticide concentrations of 300 mg/L, and supporting electrolyte concentrations of 1mM, 5mM, and 10 mM Na_2SO_4. As shown in Figures 6.72-6.75, the optimum Na_2SO_4 concentration was 5mM and non-significant removal indicated by increasing the supporting electrolyte above this optimum concentration. The 5mM of supporting electrolyte was an optimum concentration for a solution with 100 mg/L natural organic matter, while the favorable concentration was 10 mM for the solution of organic matters with a concentration more than 100 mg/L [131]. As shown in the table 6.65, the maximum COD removal percentage was 82.88% and was observed at 20 mA/cm^2.

Electrical energy consumption is a major economical parameter in EC process as all other electrochemical processes. According to the figures 6.76-6.79, the increase of supporting electrolyte resulted in decrease of the energy consumption. And by taking the energy consumption into consideration, the best COD removal efficiency was 79.99%

recorded at 15mA/cm^2 with total energy consumption of 63.28 kWh/m^3 as represented in table 6.64. also, iron electrodes released a higher quantity of Fe ions into the reactor and they formed a higher quantity of sludge.

The electrocoagulation of bentazone using iron electrodes shows better removal efficiency than the aluminum electrodes. This difference in removal efficiency can be explained by high affinity of iron(III) hydroxide to the pollutant in compare to aluminum hydroxide. A number of mole of ferrous (Fe^{2+}) electrically generated during treatment is more than (Al^{3+}), then more ferrous and ferric hydroxide is generated [97].

7.2.2. Electrocoagulation methods using aluminum electrodes

Effect of current density on COD removal efficiency by electrocoagulation using two parallel aluminum electrodes was investigated with an initial bentazone concentration of 300mg/l and 10 mM support electrolytes. Figure 6.80 depicts the effect of current density on removal efficiency and COD, for aluminum electrode materials with an operating time of 80 min. It was found that removal rate has increased by increasing current density. The large surface area of aluminum hydroxide encourages adsorption of the soluble organic compound and traps colloids [132]. On the other side, the reaction at the cathode is critically important due to the producing of gas bubbles which raise the particles of the pollutant to the surface by the flotation process. An additional benefit of gas bubbles producing is facilitating pollutant particles and coagulant collisions [133].

According to the figure 6.81, The energy consumption and energy cost is always a linear function of the current density. The energy consumption has increased by the increase of current density. Remarkable high voltage and energy consumption value reached to 228.3 kWh/m^3 at 20mA/cm^2 has been recorded which gave maximum COD removal of 73.68% as in the table 6.69.

The COD removal efficiency and energy consumption values showed the low performance of aluminum in compare to iron as electrode materials. This is because of the low electrical conductivity of model solution which was ~22µS/cm and Oxide film formation on the surface of aluminum electrodes leads to decrease of system efficiency to remove the pesticide. Insulating coat of alumina (Al_2O_3) usually produced on the surface of aluminum electrodes, that lead to increase energy consumption and in turn decrease the treatment efficiency [134].

7.2.3. Electrocoagulation methods using hybrid (mixed) electrodes

The effect of electrocoagulation process using Fe-Al hybrid electrodes in the removal of bentazone pesticide from model solution (300 mg/L) at the different current density and electrolytes concentration was optimized and followed by successful scale-up experiments. The experiments carried out at about 30 ^{o}C.

The relationship between current density and COD removal efficiency was investigated at (5, 10, 15, and 20mA/cm^2). Experimental results at different current densities indicated the increase in the removal efficiency by increasing the current density, and this clearly seen when the current density increased to 15 and 20 mA/cm^2 as shown in the figure 6.82-6.84. By applying high current densities, the scope of anodic dissolution rises, in turn, the number of hydroxy-cationic complexes rises too, that results in an increase of the removal of chemical oxygen demand [135]. The observed percentages of COD removal were lower than that determined by the other electrochemical methods, this may be due to the covered film that formed on the surface of aluminum electrodes. But it is interesting to note that the averaged COD before and after electrocoagulation were significantly different and reached to 81,37 % at 20mA/cm^2 table 6.81. The removal of COD electrocoagulation could be assigned to the elimination of suspended solids and to settling down of dissolved organic molecules [136].

The effect of support electrolytes was also studied in the process. A sample of the model solution was treated by using Al-Fe electrodes. Addition of Na_2SO_4 led to increase of the anode consumption, the sludge amount and volume increased noticeably. As the Na_2SO_4 dosage increases, the deterioration of sludge settling rate and the sludge amount increases. Also, the appreciable increase of COD removal seen by increases the supporting electrolyte. The optimum supporting electrolytes concentration was 5mM. On the other hand, the figures 6.92-6.95 showed that adding supporting electrolytes enhances the conductivity and reduces the energy consumption. The supporting electrolyte rise conductivity of the solution, in turn, it affects the produced current and energy consumption of the process [137].

7.2.4. Electrochemical-Fenton methods

Bentazone pesticide removal efficiency was examined as a function of current density. The optimum COD removal efficiency (88,75%) recorded at the end of the treatment was higher than those measured by electrocoagulation processes. The removal efficiency increased with current density and this clearly indicated at 15mA/cm^2 as in figures 6.95-6.98. This can be interpreted by the increasing of current density induce the formation of a large amount of charge, that enhances degradation and removal. In addition, increasing in current density also induce metal dissolution and hydroxyl radicals (HO•) generation.

In order to obtain the maximum effectiveness of the electrochemical-Fenton process, the hydrogen peroxide concentration is critical. The anode diffuse iron ions, that catalyzes the formation of hydroxyl radical (HO•). Different concentrations of H_2O_2 (500,1000, 2000, 3000 mg H_2O_2/L) has been used during treatment and an optimal concentration (2000 mgH_2O_2/L) was obtained as shown in figures 6.100- 6.103. Up the optimum hydrogen peroxide concentration, the decrease in the removal efficiencies was recorded. This is generally because the increased addition of hydrogen peroxide to reactor suppressed the hydrogen peroxide radical by reacting with it to form water and hydroperoxyl radical ($HO_2\cdot$), in turn, the hydroperoxyl radical react with each other and from water and O_2 and compete for the reaction of abamectin with hydroxyl radical. The increased amount of hydrogen peroxide shows the scavenging impact on hydroxyl radicals [138].

The table 6.93 showed the energy consumption and energy cost at optimum removal efficiency was (138,33 kWh/m^3) and (843,05 Krş/m^3) respectively at 20mA/cm^2.

The increase of pH value has been recorded at end of the treatment. This can be due to the electrochemically produced iron at the anode.

7.2.5. Electro-oxidation methods using a boron-doped diamond (BDD)

The feasibility of the electro-oxidation methods provided with BDD electrodes for the treatment of bentazone pesticide was evaluated. The current density is the main factor since it controls the amounts of reactive oxygen species and other electrogenerated oxidants that have the ability to destroy pollutant.

The influence of the applied current density and support electrolytes in the removal of pesticides has been determined. The result obtained from figure 6.112, 6.113 clearly showed that current density is the variable exerting the most remarkable influence on the COD removal efficiency of bentazone. This fact can be explained by taking into account the formation of the highly reactive hydroxyl radical which directly influenced by the current density and other oxidizing species like peroxodisulfate, (if Na_2SO_4 is used as in this work) can also be competitively formed with reactive oxygen.

The increase of support electrolytes directly affected the removal efficiency of bentazone and COD as shown in figure 6.116- 6.119. the maximum COD removal was 86.01% and 91.18% at 20mA/cm^2 for 5mM and 10 mM Na_2SO_4 respectively table 6.101, 6.105.

The electrochemical oxidation technical feasibility is usually assessed in terms of removal percentage of contaminants; however, economic feasibility is assessed by energy consumption. Effect of supporting electrolyte dosage on energy consumption has been investigated. The reverse relationship was observed between support electrolytes and energy consumption, by increasing the Na_2SO_4 the energy consumption decreased. The electro-oxidation process showed low energy consumption in comparison to other electrochemical treatment process. The maximum energy consumption of 68.54 kWh/m^3 was recorded at 20mA/cm^2 and 5mM Na_2SO_4 supporting electrolyte concentrations.

However, the energy cost for highest removal efficiency by electro-oxidation treatment of (348,74Krş/m^3) recorded at the optimal current density of 20 mA/cm^2 was half than that recorded while applying Fenton's oxidation process at a same current density which was (843,05 Krş/m^3).

7.2.6. Analysis of inorganic ions degradation of bentazone by ion chromatography

Ionic species separate differently depending on species type and size. The ions chromatography is a process that provides quantitative analysis of inorganic ions from a complex mixture. The variation of inorganic ions concentration during electrolysis by different electrochemical methods are present in figures 6.124-6.126. At the end of electrolysis by EFP and EOP, the amount of released sulfate (SO_4^{-2}) was about 84% and 94%. Some of the sulfates were settled in the sludge.

The results showed that the concentration of NH_4^+ increase rapidly at the end of electrolysis which indicated that most of the nitrogen was converted to ammonium. İn EFP and EOP, the ammonium formation was fast within the first 20 minutes of electrolysis but in electrocoagulation, the gradual increase was observed that indicate a rapid break down of pesticide. After 20 minutes nonsignificant increase was indicated.

The total concentration of ammonium and nitrate at the end of electrolysis is near to the stoichiometric amount of amino group in the bentazone structure.

7.2.7. Microtox assay and toxicity assessment

Toxicity assays depended on bioluminescence in V. fisheri are used for routine screening and primary evaluation of bentazone pesticide model solution or as part of more detailed environmental assessments. In the study, the luminescence test was selected as a sensitive and reproducible screening method to evaluate the toxicity during the treatment. To investigate variation in toxicity, the percentage inhibition data obtained in optimum experimental condition for each electrochemical method were changed to the relative toxicity index (RTI). The results illustrated as the RTI values versus reaction time are presented in Figure 6.127- 6.129. A decrease of relative toxicity index values during the electrolysis reflects the disappearance of the toxic compounds. Initial toxicity EC50 (5min) was reduced by 62%, 77% and 81% after 80 minutes of the treatment for ECP, EFP, and EOP. Whereas, the EC50 (15mins) values were reduced by 75%, 94, and 94% for 80 minutes of electrolysis as shown in the table 6.106. the EFP and EOP showed the ability to decrease the toxicity to slight toxic degree according to category given by [122,123]. This happens at the same time as COD reduced.

7.2.8. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS)

Morphological characteristics of the sludge formed at the end of bentazone electrolysis were observed by scanning electron microscopy Hitachi TM3030. SEM examination gives us an idea about surface structure; whether it is amorphous or crystalline. Floc density and size significantly affects the performance of solid separation processes from solution. Dense and large flocs have high sedimentation speeds and not hardly dewatered. Sludge obtained after ECP and EFP treatment at optimum operating conditions. According to the figure appx 1.5 and 1.7, In ECP the flocs produced from iron-based chemical coagulants and appear as amorphous fractal structures. The high removal rate of an organic pollutant due to the continuous production of ferrous minimize sludge formation. The Sem image indicated the presence of much higher floc in ECP-generating sludge in compared to EFP- genearating sludge. This due to the formation of carbon dioxide as a result of carbons mineralization.

Elemental composition of the specific particles was measured using (EDS) to verify the chemistry of the particles. The objective of the analysis was to indicate the quantity and distribution of elements formed after electrolysis and settled as sludge The EDS spectrum of sludge formed as a result of electrolysis shown in figure appx 1.6 and 1.8. the iron element was recognized well and its distribution in both ECP and EFP was identical. in addition, the presence of sodium (Na) and sulfate (S) was not surprising since the used supporting electrolyte was Na_2SO_4.

Element compositions (in weight percent) for ECP- and EFP-generated sludge through EDX analysis is given in Table appx 1.3, 1.4. It was found that the weight percent of Fe was higher in ECP generated sludge. And the weight percentage of oxygen is higher in the EFP generating sludge.

7.3. Abamectin

7.3.1. Electrocoagulation methods using iron electrodes

The coagulant concentration rate determined by current density. This parameter has a significant effect on the pesticides removal efficiency. The impact of the current density on the COD removal percentage during electrolysis processes with the iron electrodes is shown in figures 6.131- 6.133. The operating conditions of the electrocoagulation process were 4.5 mg/L initial concentration of the abamectin, time of electrolysis was 80 min. and temperature of ~30˚C. The plot of figures showed that the removal efficiency of the abamectin increased with the increase of the current density up to 20 mA/cm^2.

Generally, Na_2SO_4 is added as support electrolyte to increase the conductivity in electrocoagulation process. the wastewater conductivity adjusted to required levels by adding a suitable concentration of support electrolytes [139]. The effect of Na_2SO_4 concentration on the COD removal efficiency of abamectin is shown in figures 6.137-6.140. By increasing Na_2SO_4 concentration in model solution, the conductivity and the current density increased. The generated higher ionic strength result in an increase in current density at the equivalent cell voltage, the voltage of the reactor decreases with increasing of conductivity at steady current density. Thus, the voltage required for gaining a particular current density will be reduced and as the result, the consumed electrical energy will reduce. As observed from table 6.114, the COD removal efficiency of abamectin during electrolysis process increased up to 77,27% when 5mM Na_2SO_4 added as a supporting electrolyte. It was noticed that increasing the conductivity of the solution over 5mM has not a remarkable effect on the removal percentage, but only the energy consumption decreased. According to obtained results, the optimum support electrolyte concentration is 5mM Na_2SO_4. The energy consumption and energy cost for the optimum obtained result were 143.31kWh/m^3 and 863,3733 Krş/m^3 indicated at 20 mA/cm^2 and 5mM supporting electrolyte.

7.3.2. Electrocoagulation methods using aluminum electrodes

Electrocoagulation method with aluminum electrodes. The performance of electrocoagulation process was investigated for COD reduction and energy consumption. The effects of the key operating condition such as current density were investigated to evaluate the electrode performance. Electrocoagulation treatment by aluminum was carried at a different current density (5, 10, 15, 20 mA/cm^2). The variation of removal efficiency with current density is shown in figure 6.145. It was recorded that maximum COD removal efficiency was 75,22 % at 80 mA/cm^2 at the end of treatment (80 mins) table 6.122. the low removal efficiency due to the fact that the electrode is blocked by a solid deposit which inhibits the aluminum dissolution and also may be due to the high temperature of the reactor during the electrolysis process. As the temperature of reactor became more than 300 K, the considerable increase in movement of produced ions seen in which their chance to aggregate and form metallic hydroxide decrease [140].

As shown in the figure 6.146, the energy consumption maximum of optimum COD removal was 200,94 kWh/m^3 recorded at 20 mA/cm^2. It is observed that the more energy was consumed by aluminum electrode as compared to energy consumed by other electrocoagulation methods for maximum COD removal efficiency. The energy consumption is lower with iron than other electrodes [141].

7.3.3. Electrocoagulation methods using hybrid (mixed) electrodes

The efficiency of a hybrid system composed of iron and aluminum electrodes was investigated for remove of abamectin from model solution. The behavior of the hybrid electrodes depends on both iron and aluminum individual properties against pollutants. Under optimum conditions, the effect of current density and electrolyte concentration were studied.

Current density is one of the critical variables that affected the electrochemical treatment process [142]. In order to determine the effect of current density with the hybrid anode, the following density was applied: 5, 10, 15 and 20 mA/cm^2. The results from table 6.123-6.126 revealed that no significant differences in removal efficiency values were observed by increasing the current density of 1mM support electrolytes. This is because of the low electrical conductivity of model solution which was ~22 µS/cm and the added amount of support electrolytes was not enough to improve the appropriate conductivities. This also can be proved by the high voltage and energy consumption during the treatment process. By elevating of current density at 5mM and 10mM support electrolyte, the result showed a significant effect on COD removal efficiency. The maximum COD removal efficiency was 83,59 % recorded at 20mA/cm^2 within 80 min of treatment as in table 6.133.

In order to evaluate the effect of support electrolyte on COD removal efficiency and to increase the conductivity, Na_2SO_4 was added to the system. Variation of COD removal percentage with Na_2SO_4 concentration is shown in figures 6.153-6.156. The increasing of support electrolyte concentration resulted in an increase of COD removal efficiency and this significantly appeared at 10 mM concentration. This indicates that the electrocoagulation system using hybrid electrodes reached to the steady and optimum state at 15mA/cm^2 and 10 mM Na_2SO_4

On the other hand, the figures 6.149-6.151 indicate that increase of current density resulted in increasing of energy consumption. At the optimum removal efficiency, the energy consumption was 91,77 kWh/m^3. By taking the present electric price in turkey into the account, the energy cost of electrocoagulation at optimum COD removal efficiency was 576,64 krş/m^3 table 6.130.

7.3.4. Electrochemical-Fenton methods

In the EFP the degradation of the pesticides takes place by an attack of hydroxyl radicals that are formed from the reaction of H_2O_2 with ferrous iron that electrochemically generated anodes. The study was done to achieve degradation of the pesticides by optimizing reagent concentrations. The effect of current density on removal efficiency was investigated at 5, 10, 15, and 20mA/cm^2. Results from figures 6.161-6.164 indicates clearly that removal rate increased by increasing current density. This indicate that electrochemically generation of ferrous increased by increasing current density. Ferrous generation percentage is proportional to the applied current density, however at high current density its gradual decreases as the electrolysis proceed.

The Fenton electrochemical system efficiency is promoted by adding a sufficient amount of hydrogen peroxide. The effect of hydrogen peroxide dosage studied at four different concentration. The result from figures 6.165-6.168 shows a slight increase in removal efficiency at a low concentration of hydrogen peroxide, while the significant increase in removal efficiency was at 3000 mgH_2O_2/L. The removal efficiency of pollutant increases with increase in hydrogen peroxide dosage, and this increase due to the hydrogen radical dosage the formed from the addition of hydrogen peroxide [143].

As reported from figures 6.169- 6.172, the current density is directly proportional to energy consumption, by increasing the current density the energy consumption increased too. the maximum removal efficiency was 77,83 % recorded at 20mA/cm^2 and 3000 mgH_2O_2/L. The energy consumption was 122,58kWh/m^3 as seen in the table 6.150. By taking into consideration the electric price, the energy cost at maximum removal efficiency was 748,25 Krş/m^3.

Comparing with the removal efficiency, energy consumption, and energy cost of other used electrochemical system, the electrochemical Fenton reaction is not efficient for degradation of abamectin. this may be due to the high pH value of the model solution and the electrochemically formed ferrous ion take place in different competing reactions that decrease its concentration in the solution such as oxidized to ferric ions by Fenton reaction, entering the reaction with hydroxyl radical and reaction with RO_2.

7.3.5. Electro-oxidation methods using a boron-doped diamond (BDD)

The electrochemical oxidation of pesticide abamectin which is one of potentially dangerous pesticide was studied by (BDD) electrodes. The influence of some operating parameters, such as current density and the supporting electrolyte was investigated.

The current density is an important parameter that influences kinetic of the electrolysis and also processes economics. İts equal to the ratio between the current applied and electrode surface area. So the current density changed by changing the surface area of electrodes and/or the current. So, as the current density increases, the improves in abamectin degradation rate investigated by the rise of the hydroxyl radical production rate as shown in figures 6.177,6.178.

According to the figures 6.179, 6.180, the increase in current density resulted in an increase of energy consumption. consequently, increase in energy cost of the system. The table 6.158 showed that at the maximum COD removal percentage of 90,69 % recorded at 20mA/cm^2 and 10mM for current density and electrolytes concentration respectively. The energy consumption and energy cost was 65,37kWh/m^3 and 392,75 Krş/m^3 respectively.

The addition of support electrolytes rise the conductivity and lessons the resistance and thus, reduces the energy cost of the electrochemical process. Figures 6.181-6.184 showed the influence of Na_2SO_4 on COD removal efficiency with two different electrolyte concentration. It can be seen that the removal efficiency increases by increasing electrolyte concentration. In fact, BDD oxidation of aqueous solutions containing sodium sulfate promotes the formation of persulfates, which the very strong oxidant that has high reduction potentials [144]. The figure 6.185-6.188 indicate that the energy consumption inversely proportional to the concentration of support electrolytes.

The electro-oxidation system using BDD showed the higher pesticide and COD removal percentage for abamectin in compare to other electrochemical treatment methods. But still, the removal value is below the expected percentage. This may be due to the high pH value of a model solution that enhances the formation polymeric intermediate of the hydroxyl that reduce the degradation.

7.3.6. Microtox assay and toxicity assessment

The toxicity assessment of the abamectin is the important point in evaluating the possibility of electrochemical technique in degradation process of pesticide. The Microtox® bacterial assay was used to determine 5 min and 15 mins EC50 values for abamectin degradation during the electrolysis process. Relative toxicity indices were determined based on the EC50 values at 5 and 15 minutes. According to the results presented in figure 6.189-6.191. The reduction of toxicity of model solution to more agreeable levels is indicated when the toxicities of the initial solution were taken into consideration. The toxicities of pesticide during electrolysis investigated and are expressed as EC50 (%) values as in the in table 6.159. The used electrochemical technique differed greatly in their ability to reduce the toxicity. Higher % EC50 values indicate low toxicity. The toxicity of EC50 (5min) was reduced by 54%, 65 % and 77% after 80 minutes of electrolysis for ECP. EFP, and EOP respectively. However, the toxicity results at EC50 (15 mins) were 70%, 72%, and 87% for ECP, EFP, and EOP respectively.

7.3.7. Scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS)

The properties of sludge formed at end of electrolysis were studied by SEM-EDS in order to obtain additional information about the efficiency of each electrochemical treatment and composition of sludge. Likely to the bromuconazole and bentazone, the Sem image showed that the EC system produced more iron per unit power and the floc had a faster growth rate compared to EFP as in figure appx 1.9 and 1.11.

The SEM images studies can be examined in the presence of particular elements by EDS. energy-dispersive spectra and X-ray element maps were obtained using a TM3030 plus, Hitachi Scanning Electron Microscope with an operating potential of 15 kV. As expected the Fe had identical distribution and enriched with this element in both ECP and EFP as shown in figure appx1.10 and 1.12. The composition of the element in weight percent for ECP- and EFP-generated sludge through EDX analysis is given in Table appx 1.5, 1.6. It was found that the weight percent of C was higher in ECP generated sludge. And the weight percentage of oxygen is higher in the EFP generating sludge.

7.4. Scanning electron microscopy and elementary analysis of electrodes

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were carried out on a Hitachi 3030 plus model instrument. The SEM micrographs of iron and aluminum electrode are shown in Figures appx 1.13 and 1.15. the iron electrode is porous and loose in compared to aluminum electrode. So, the Fe electrode has a larger effective area than the Al electrode, which is in favor of the activity of electrode. The porosity increases the surface area proportional to dissolve the amount of metals. The support electrolyte ions found more surface available to react, so they may affect the energy consumption of process. In the EDS spectrum of the aluminum, the presence of small amount of Cl observed as in the figure appx 1.16. This is because of the film coat that formed on the anode and results in a reduction of anode dissolution.

8. CONCLUSION AND RECOMMENDATION

The electrochemical treatment can efficiently remove pesticides by using different techniques. The observations show the significance of selecting optimum degradation parameter in order to get high removal rates that are critically essential for any practical applications of electrochemical process. The present study attempted to investigate and compare the applicability of three electrochemical technique in the treatment of bromuconazole, bentazone and abamectin pesticides in model wastewater. The effects of current density, type of electrode, hydrogen peroxide concentration and support electrolyte concentration were investigated on removal efficiency and COD.

In general, the electrochemical technique is an effective, fast, and clean process to remove pesticides from solution. The treating of bromuconazole, bentazone and abamectin pesticides in aqueous solution was affected by current density, electrode type, hydrogen peroxide and supporting electrolyte concentration.

It was noted that these variables significantly influence the bromuconazole pesticide removal efficiency. The electro-oxidation treatment methods showed superiority in COD removal efficiency on the other electrochemical methods. the maximum removal efficiency of 92,22% was obtained at 20 mA/cm^2 and 10 mM Na_2SO_4 as a supporting electrolyte. The energy consumption and energy cost were 40,91 kWh/m^{3}and 247,16 Krş/m^3 respectively. The electrochemical-Fenton process also showed high removal rate of 87,50% recorded at 20 mA/m^2 and 3000 mg H_2O_2/L but the energy consumption and energy cost were significantly higher which was 182,69 kWh/m^3 and 4476,00 Krş/m^3 respectively.

The removal of bentazone pesticides in aqueous solution was affected by current density, type of electrode, supporting electrolyte and hydrogen peroxide concentration. The results of bentazone degradation by electrochemical methods indicated that the electro-oxidation gave highest removal efficiency and COD in compare to other techniques. The best removal efficiency of 91,18 % was obtained at 20mA/cm^2 and 10mM for current density and support electrolyte respectively. The energy consumption and energy cost of maximum obtained result were 57,63 kWh/m^3 and 348,74 Krş/m^3 respectively.

The results showed that the removal of abamectin pesticides was more effective by using the electro-oxidation technique. The highest COD removal rate was 90,69% with low energy consumption and energy cost which was 65,37 kWh/m^3 and 392,75 Krş/m^2. The effects of operational factors on removal efficiency and energy cost clearly indicated.

Under the conditions of the study, the pesticides depletion processes were described abivously by "pseudo first-order reaction, except bromuconazole, for which a pseudo second-order rate law was more convenient.

The electrochemical techniques showed significantly high efficiency in reducing the toxicity of the pesticides in compared to the initial toxicity. But because the formation of some intermediate compound during the electrolysis of bromuconazole degradation, the reduction of toxicity is less than other pesticides at the end of treatment.

The results of ion exchanger chromatography showed the releasing of different inorganic ions from heteroatoms structure of bromuconazole and bentazone which was Cl^-, NH_4^+, NO_3^- SO_4^{-2} and Br. The concentration of released inorganic ions were closed to their stoichiometric amount in the pesticides.

Much practice is needed to improve and develop more accurate processes for designing the kinetics of pesticides in the wastewater. Advanced electrochemical processes for wastewater applications either using electrocoagulation, electrochemical-Fenton or electro-oxidation will advantageously complete in the market, in overcoming one of the major challenges which are the treatment cost of the process, there is need of the future research that must lead to the decrease the treatment cost. Future study must also investigate the impact of such technologies in combination with other inexpensive and effective process such as biological treatment processes for degradation of recalcitrant compounds. Where each technique by itself may not be effective enough for the degradation of toxic compounds.

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APPENDIX 1- SEM IMAGES AND ELEMENTARY ANALYSIS

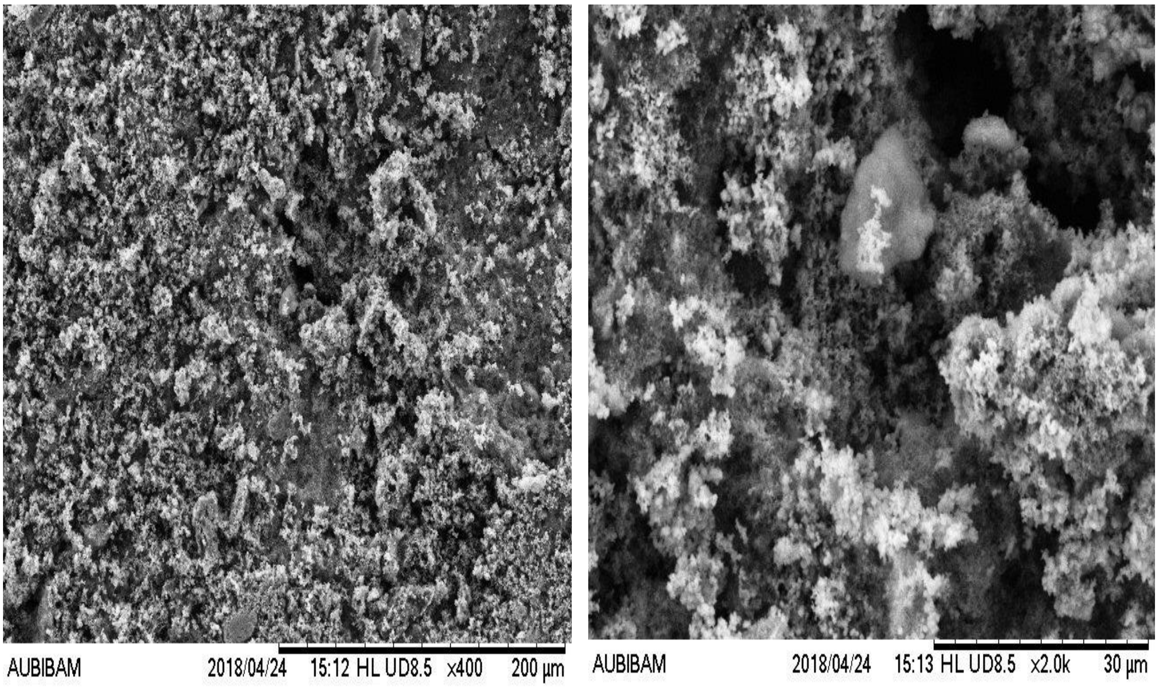

Figure appx 1.1. *Scanning electron microscope images of sludge formed at the end of electrocoagulation of bromuconazole (at 400x and 2.0Kx)*

Table appx 1.1. *Elementary analysis of sludge formed at the end of electrocoagulation of bromuconazole*

Element	Weight %	Atomic %
O	22,93	42,88
Fe	66,87	35,83
Cl	0,24	0,20
C	6,99	17,42
N	1,16	2,49
Br	1,09	0,41
Na	0,25	0,33
S	0,46	0,43
Total	100,00	100,00

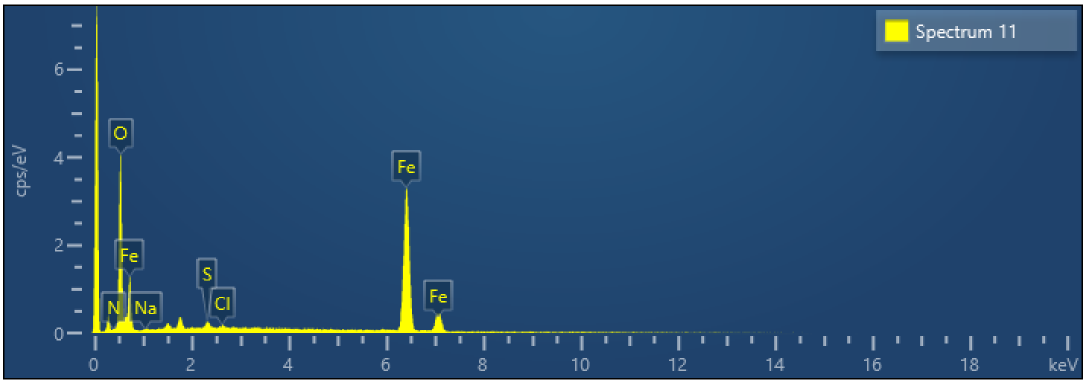

Figure appx 1. 2. *EDS spectrum of sludge formed at the end of electrocoagulation of bromuconazole*

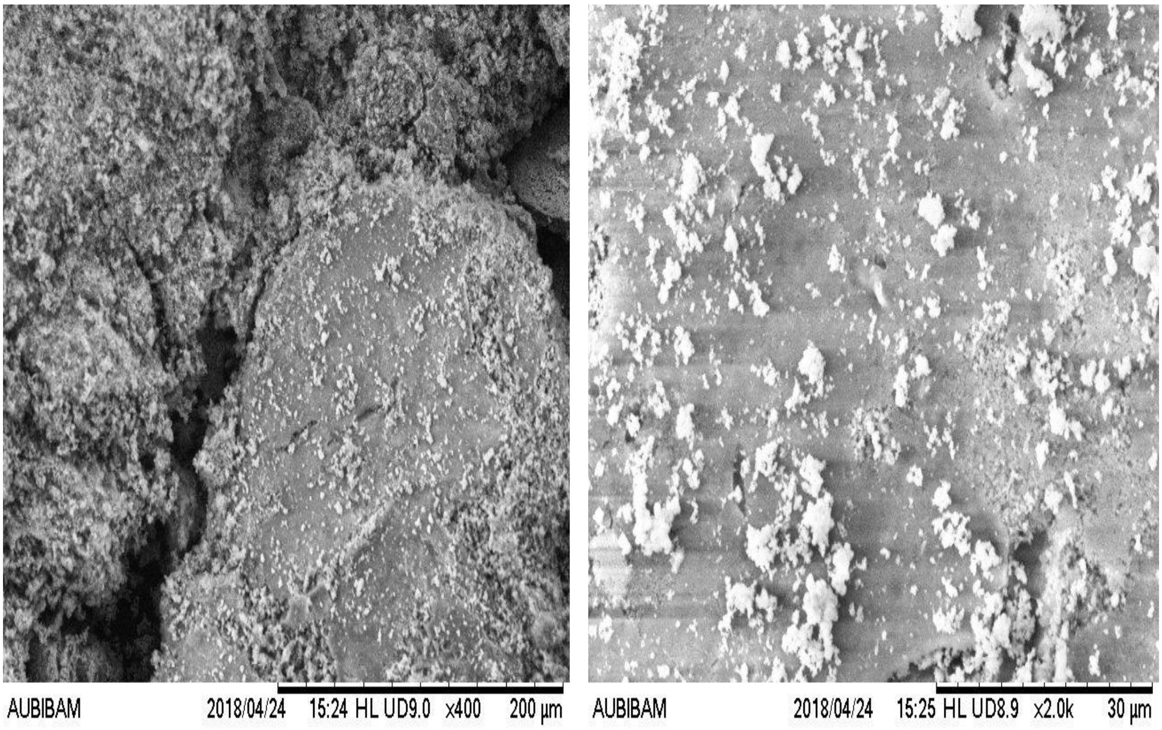

Figure appx 1.3. *Scanning electron microscope images of sludge formed at the end of electrocchemical-fenton of bromuconazole (at 400x and 2.0Kx)*

Table appx 1.2. *Elementary analysis of sludge formed at the end of electrochemical-Fenton of bromuconazole*

Element	Weight %	Atomic %
C	16,39	30,58
O	31,97	44,79
Fe	45,69	18,34
Cl	2,19	1,39
Na	0,62	0,61
S	0,81	0,56
N	2,34	3,74
Total	100,00	100,00

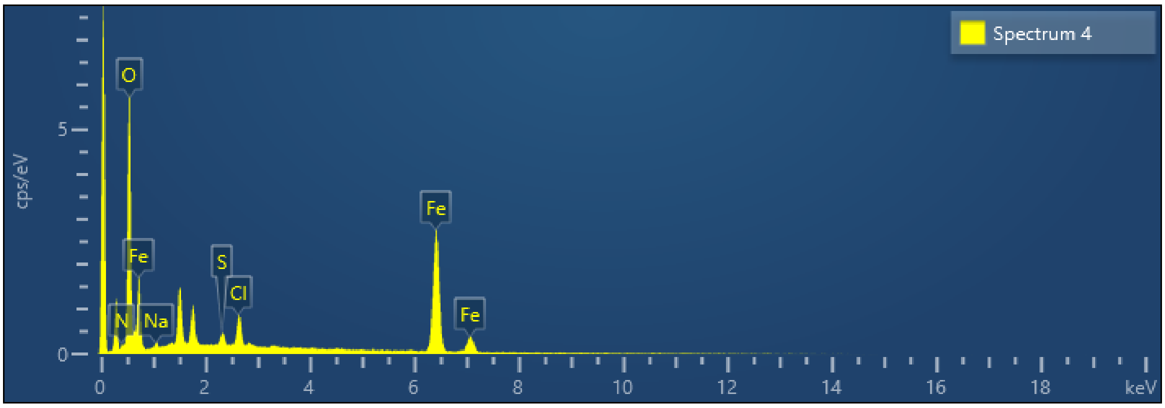

Figure appx 1.4. *EDS spectrum* of *sludge formed at the end of electrochemical-Fenton of bromuconazole.*

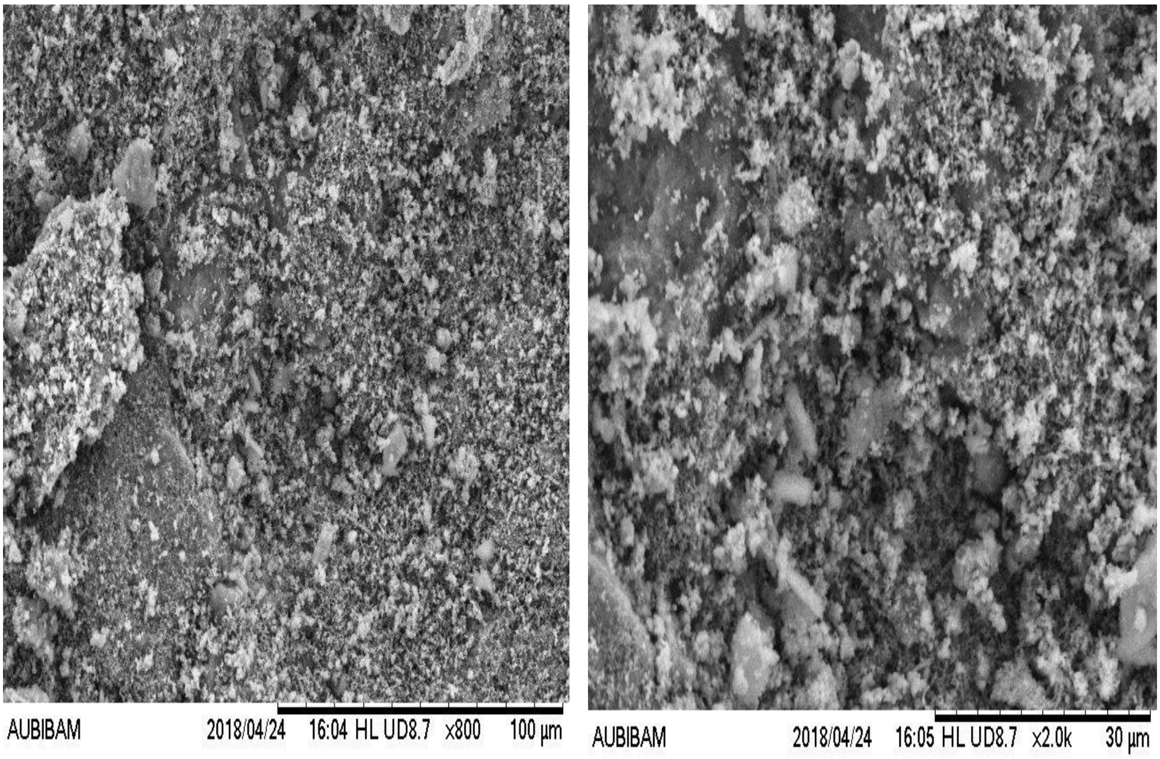

Figure appx 1.5. *Scanning electron microscope images of sludge formed at the end of electrocoagulation of bentazone (at 400x and 2.0Kx)*

Table appx 1.3. *Elementary analysis of sludge formed at the end of electrocoagulation of bentazone*

Element	Weight %	Atomic %
O	13,23	28,48
Fe	77,73	47,92
C	7,16	20,53
Na	0,63	0,95
S	0,67	0,72
N	0,56	1,39
Total	100,00	100,00

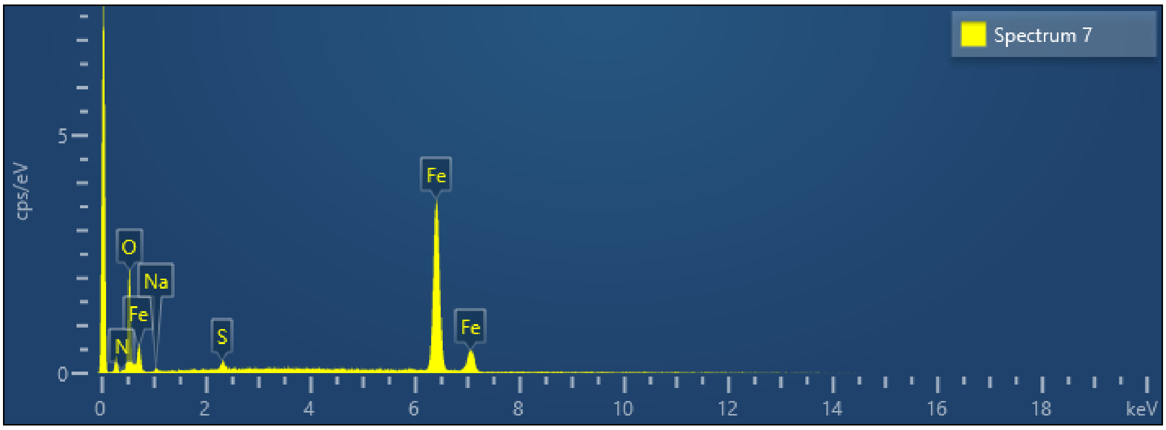

Figure appx 1.6. *EDS spectrum of sludge formed at the end of electrocoagulation of bentazone*

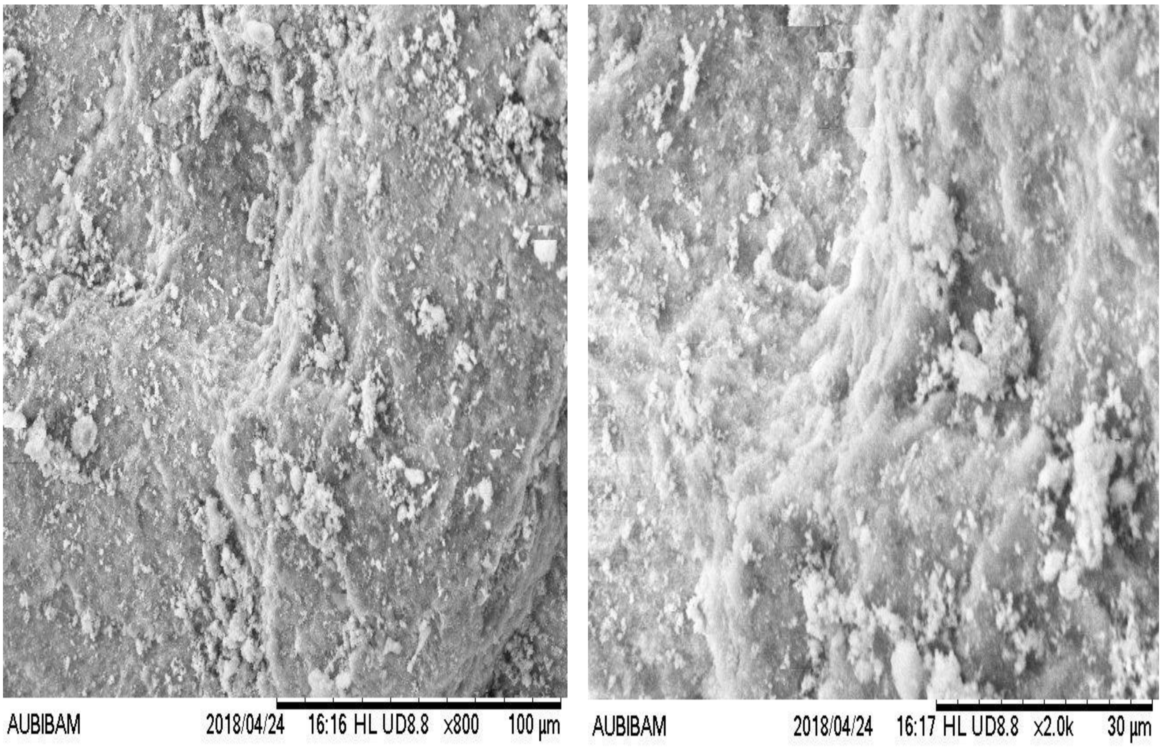

Figure appx 1.7. *Scanning electron microscope images of sludge formed at the end of electrochemical-Fenton of bentazone (at 400x and 2.0Kx)*

Table appx 1.4. *Elementary analysis of sludge formed at the end of electrochemical-Fenton of bentazone*

Element	**Weight %**	**Atomic %**
C	17,87	33,70
O	30,99	43,86
Fe	49,46	20,05
N	1,27	2,06
S	0,23	0,17
Na	0,17	0,17
Total	100,00	100,00

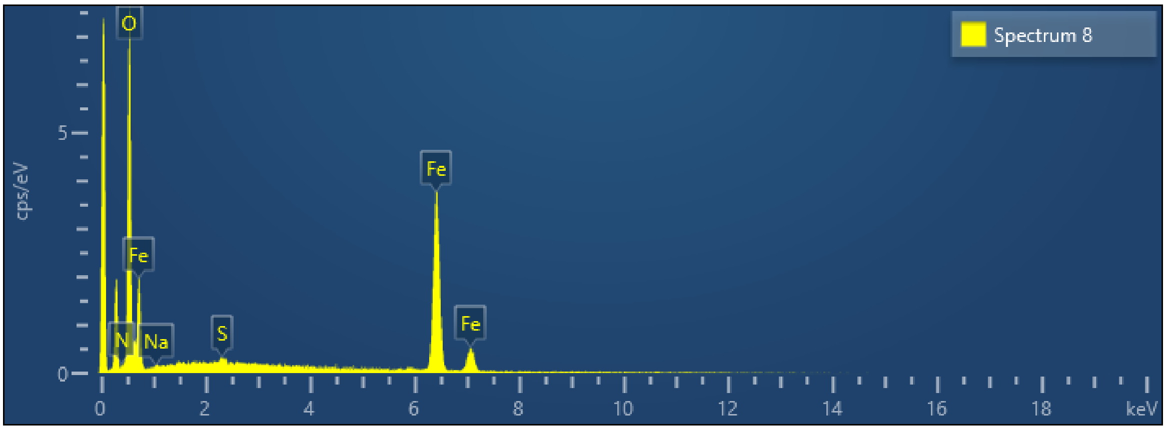

Figure appx 1.8. *EDS spectrum* of *sludge formed at the end of electrochemical-Fenton of bentazone.*

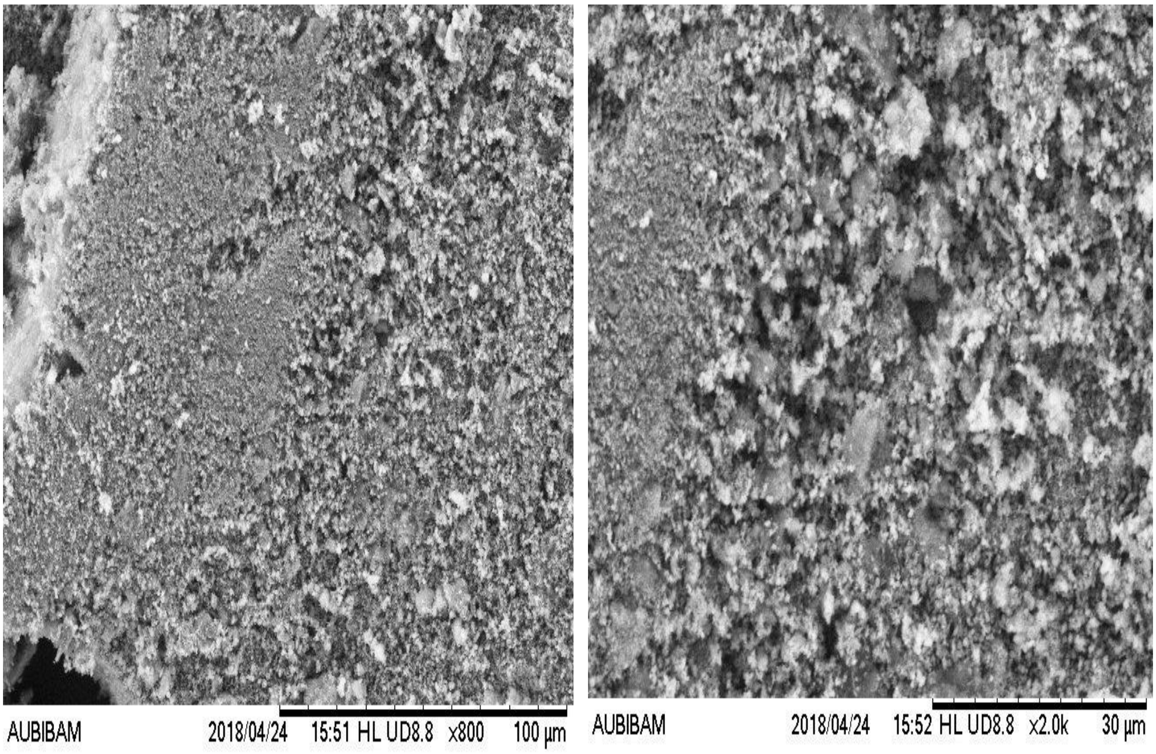

Figure appx 1.9. *Scanning electron microscope images of sludge formed at the end of electrocoagulation of abamectin (at 400x and 2.0Kx).*

Table appx 1.5. *Elementary analysis of sludge formed at the end of electrocoagulation of abamectin.*

Element	**Weight %**	**Atomic %**
C	12,55	27,36
O	26,75	43,78
Fe	59,96	28,11
S	0,24	0,20
Na	0,49	0,56
Total	100,00	100,00

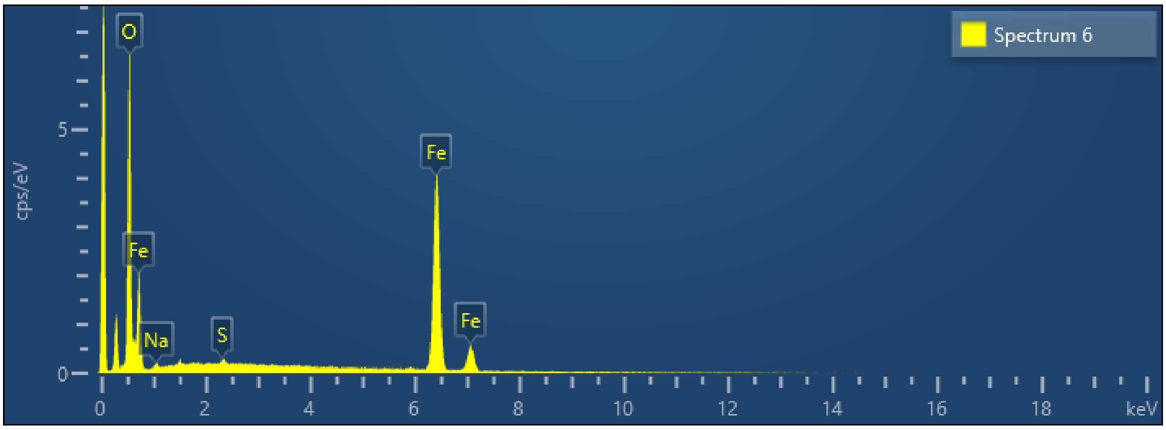

Figure appx 1.10. *EDS spectrum* of *sludge formed at the end of electrocoagulation of Abamectin.*

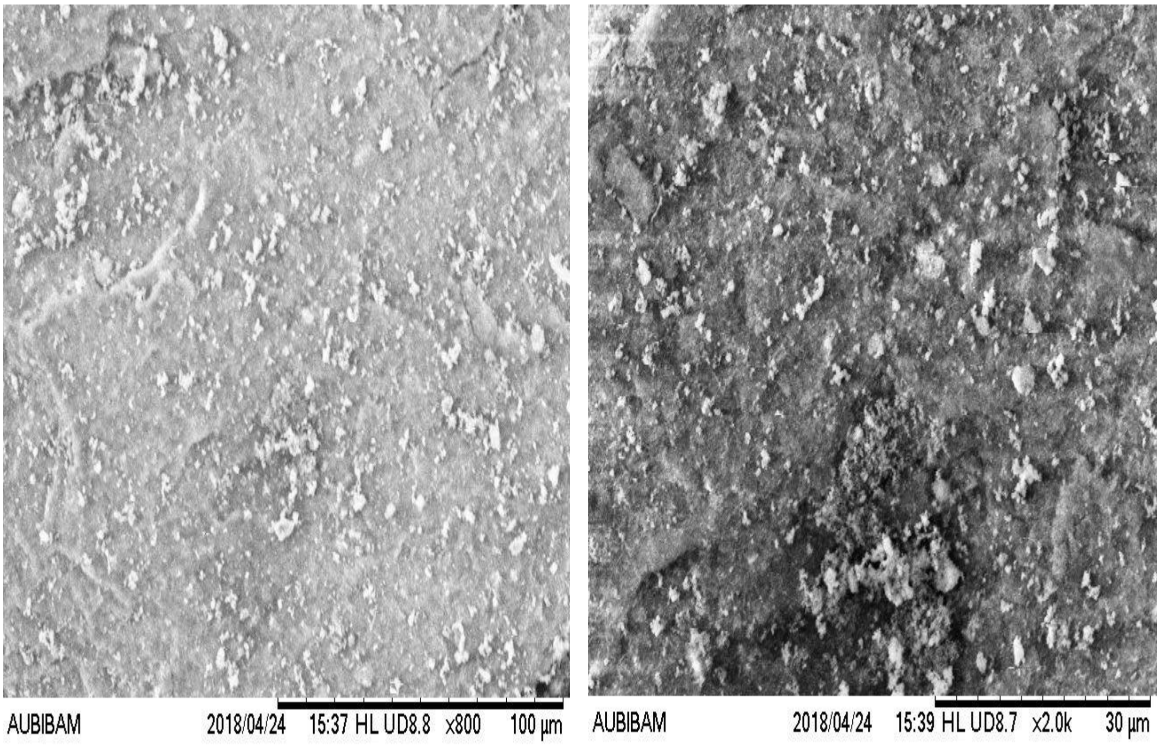

Figure appx 1.11. *Scanning electron microscope images of sludge formed at the end of electrochemical-Fenton of abamectin (at 400x and 2.0Kx).*

Table appx 1.6. *Elementary analysis of sludge formed at the end of electrochemical-Fenton of abamectin*

Element	**Weight %**	**Atomic %**
O	31,02	54,18
Fe	62,64	31,34
Na	0,02	0.02
C	6,15	14,30
S	0,18	0,15
Total	100,00	100,00

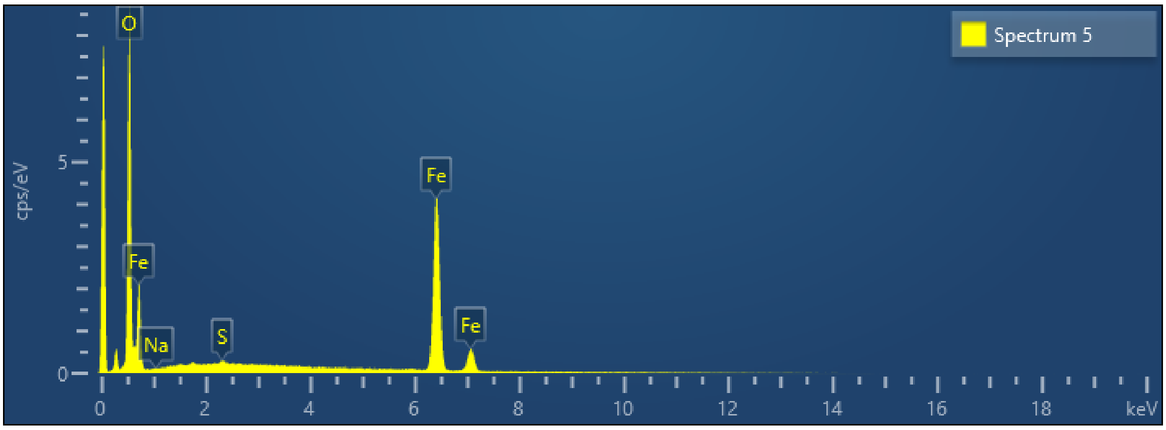

Figure appx 1.12. *EDS spectrum of sludge formed at the end of electrochemical-Fenton of Abamectin.*

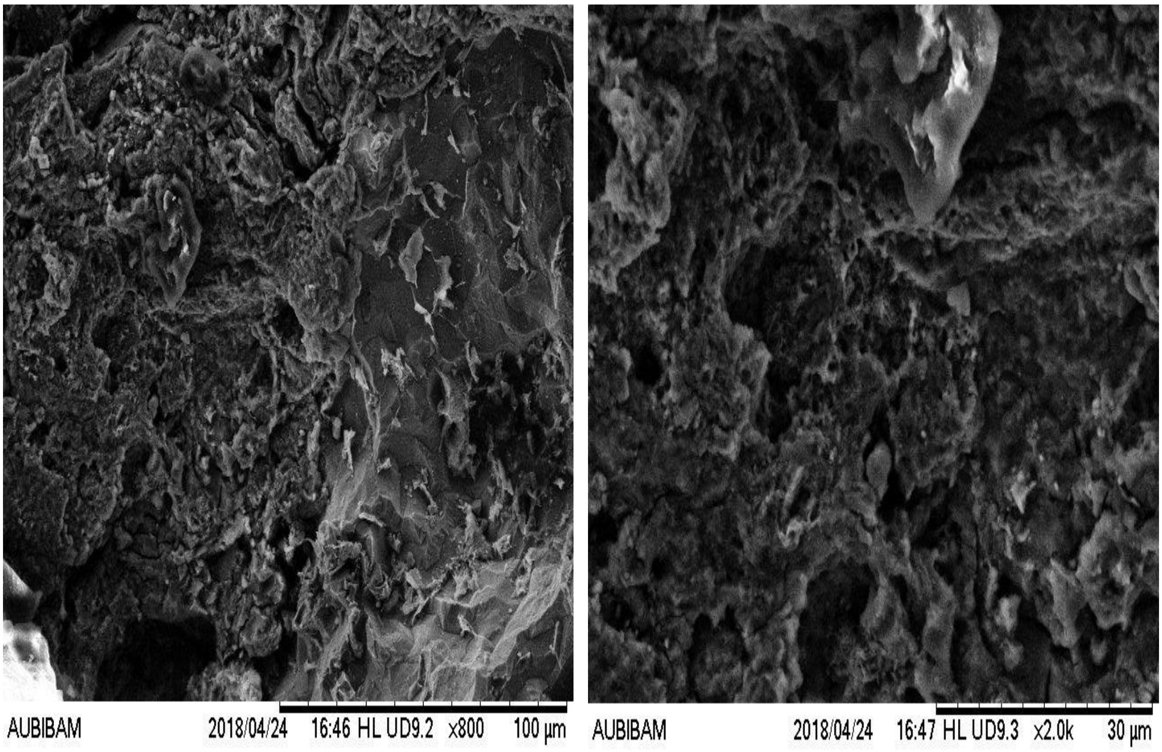

Figure appx 1.13. *Scanning electron microscope images of iron electrodes(at 400x and 2.0Kx).*

Table appx 1.7. *Elementary analysis of iron electrode*

Element	Weight %	Atomic %
C	10,64	24,32
O	25,92	44,48
Fe	63,44	31,19
Total	100,00	100,00

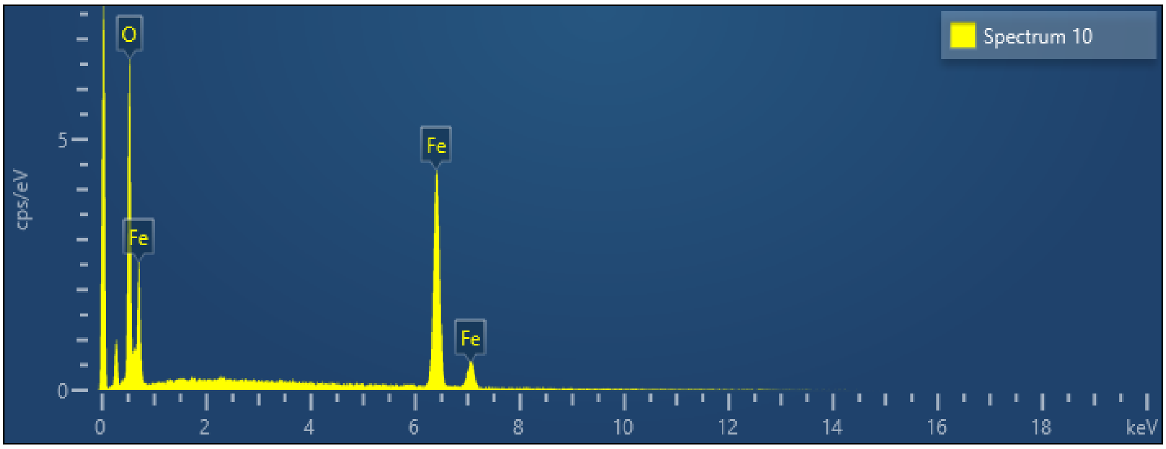

Figure appx 1. 14. *EDS spectrum of iron (Fe) electrode surface.*

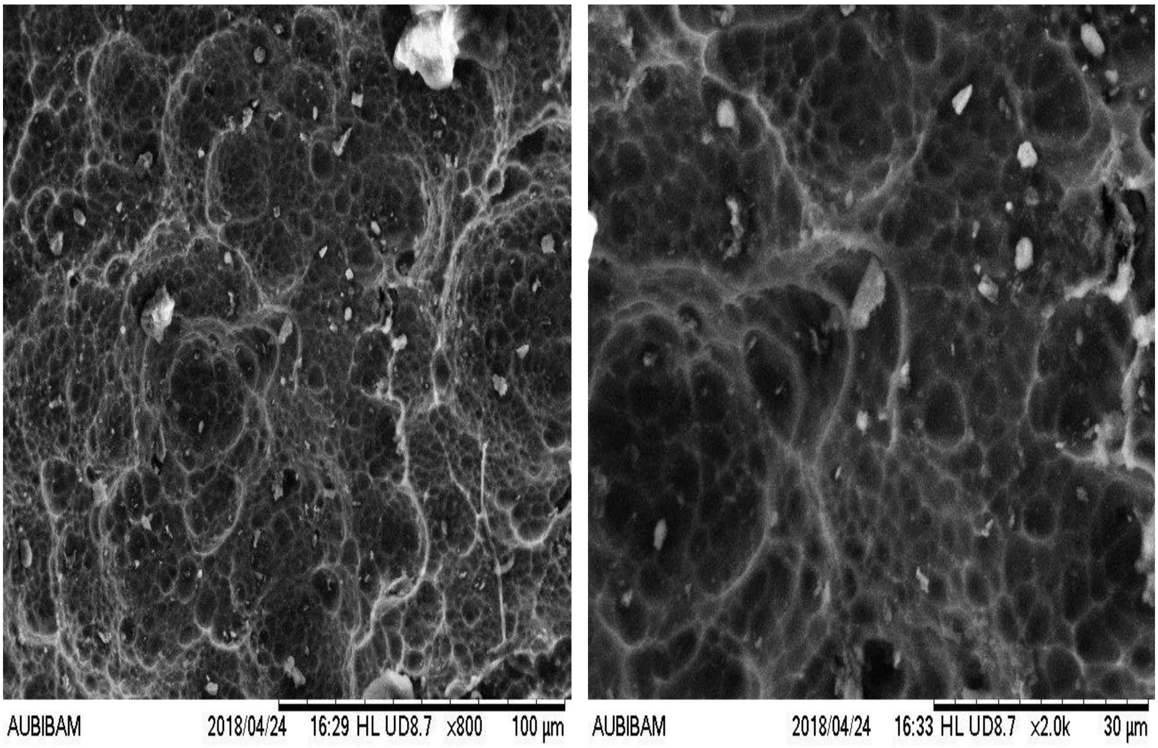

Figure appx 1.15. *Scanning electron microscope images of Aluminum electrodes(at 400x and 2.0Kx).*

Table appx 1.8. *Elementary analysis of Aluminum electrode*

Element	**Weight %**	**Atomic %**
O	10,06	10,76
Al	48,04	30,48
C	40,87	58,25
Cl	0,81	0,39
S	0,21	0,11
Total	100,00	100,00

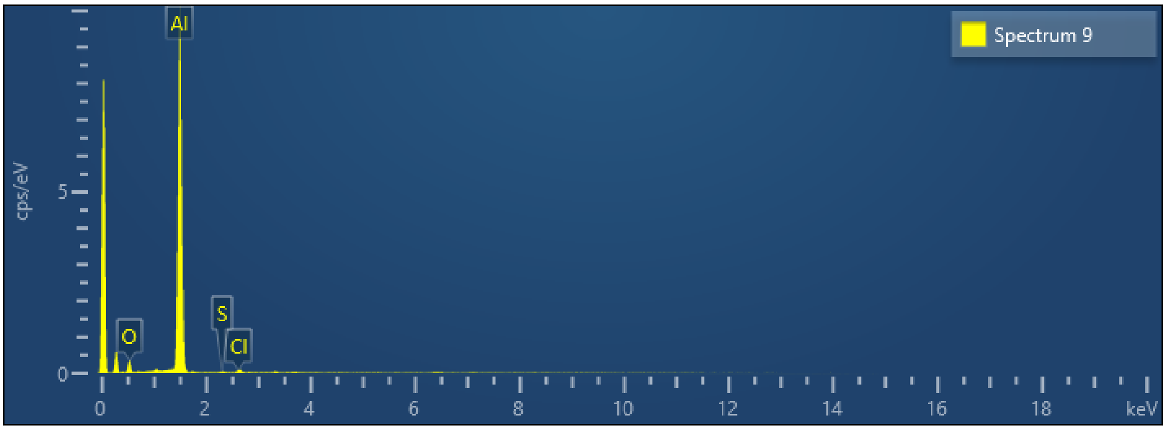

Figure appx 1.16. *EDS spectrum of aluminum (Al) electrode surface.*

APPENDIX 2- CALIBRATION CURVE

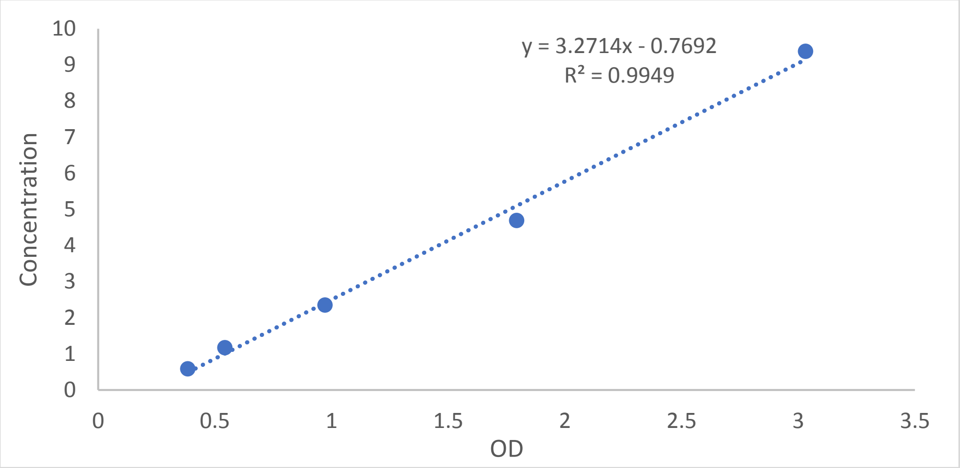

Figure appx 1.17. *Calibration curve for bromuconazole concentration vs OD*

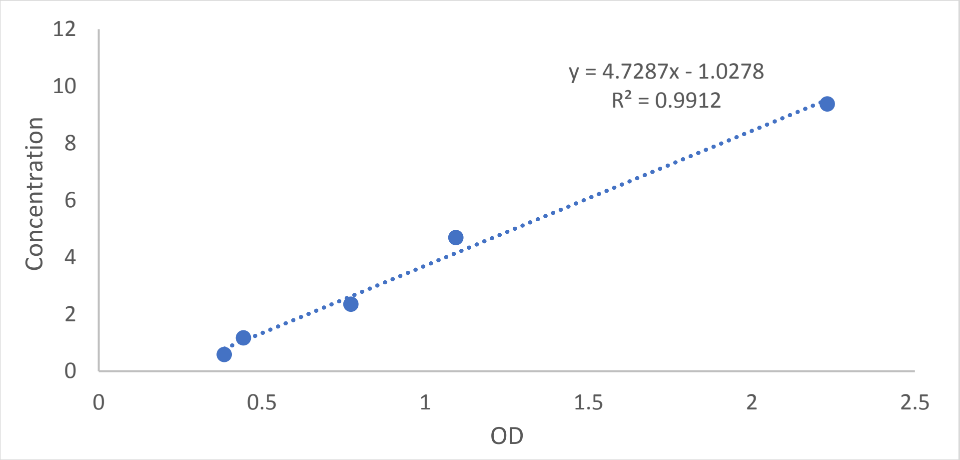

Figure appx 1.18. *Calibration curve for Bentazone concentration vs OD*

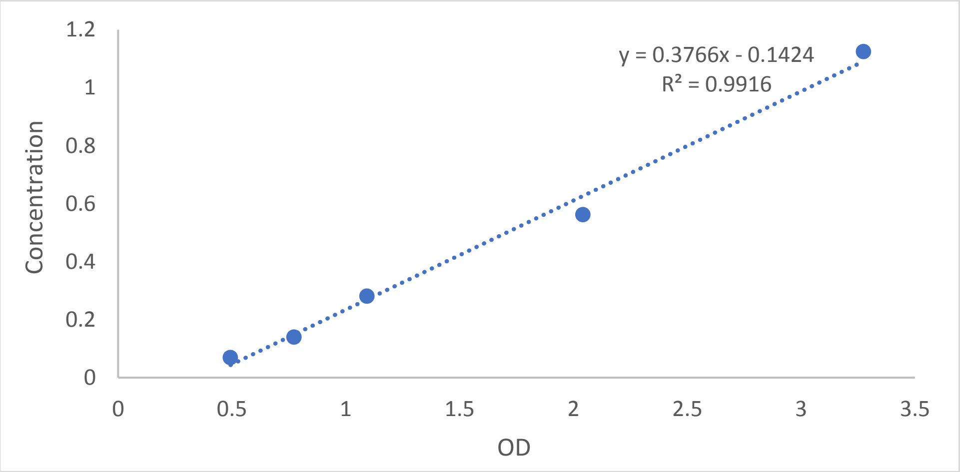

Figure appx 1.19. *Calibration curve for Abamectin concentration vs OD*

APPENDIX 3- EXAMPLE CALCULATIONS

In example calculations, the data from Table 6.12 were used. In the electrocoagulation treatment with iron electrodes, the solution with initial pesticide concentration of 300mg.L^{-1}. The current density of 20mA/cm^2 and the 10mM Na_2SO_4 as a supporting electrolyte were used. The sample was taken at 80 min.

Current Density Calculation

The iron electrode has 3.5cm length and 3.2 widths. As 3.5 cm of electrodes immersed in sample water, the active area accounted as follows:

Since each electrode has two surfaces:

3,2*3.5*2= 22,4 cm^2

We have 3 active anodes so

3*22,4=67,2 cm^2

Each electrode side surface area:

(3,5*2+3,2) *0,5=5,1cm^2

For three anodes:

3*5,1=15,3 cm^2

Now the whole active area equal to:

67,2+15,3= 82,5cm^2

The active surface area of the electrodes was determined and its 83cm^2. Current density defined as the amount of electric current flowing per unit cross-sectional area of a material in mA/cm^2. And calculated by given below:

1000*I/100= 10*I   where I is the current intensity

Energy Consumption Calculation

The energy consumption calculated by equation (5.2).

$$\text{Energy Consumption } (\text{KWh/m}^3) = \frac{\text{V} * \text{I} * \text{t}}{\text{Vol.}}$$

Since the experiment was conducted with 400 ml of prepared model solution:

$$\text{Energy Consumption } = \frac{(26.2 * 1.66 * 20/60)/1000}{0.0004} = 36{,}21\text{kWh/m}^3$$

Removal Efficiency Calculation

The removal efficiency was calculated according to equation (5.1).

$$\boldsymbol{COD\ removal}\ \% = \frac{(CODo\ - CODt)}{CODo} * 100$$

$$\boldsymbol{COD\ removal}\ \% = \frac{(1170{,}82 - 227{,}33)}{1170{,}82} * 100 = 80{,}58\ \%$$