

**COMPARATIVE METHOD BETWEEN ELECTROCOAGULATION AND
OZONOLYSIS FOR SULPHIDE REMOVAL**

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**BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG**

**COMPARATIVE METHOD BETWEEN ELECTROCOAGULATION AND
OZONOLYSIS FOR SULPHIDE REMOVAL**

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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UNIVERSITI MALAYSIA PAHANG**

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Dedicated to my family and friends.

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ABSTRACT

Sulphide is one of the example of contaminants contains in industries and give harmful effect to human, plant, and environment. High amount of sulphide content contributed to corrosion of pipe in industries. In this research, it was intended to develop the new technologies by using comparison between Ozonolysis and Electrocoagulation (EC) method that will give the highest percentage of Sulphide removal. The experiment was carried out in batch reactor and conducted under galvanostatic regime at current 1A and the voltage supply was 30V. Both of methods were run in 0.8L of sample solutions which were stock sulphide and sample from MTBE companies. Concentrations of both samples at influent were varied at (50,100,150 and 200) ppm. EC process involved Iron electrodes where arrangements of electrodes monopolar-parallel (M-P) and bipolar-parallel (B-P) were investigated in this research. By weighing both the electrode before and after electrocoagulation and based on Faraday's law, weight of precipitated were determined. Ozone injection during ozonolysis was 10% for all trials. Solutions had been used in both method were taken at regular times at (3, 6, 9, 12, and 15 minutes) to measure Sulphide removal while (15, 30, 45, and 60 minutes) for COD removal. Then, percentage of Sulphide removal was calculated and efficiency of COD removal was evaluated. In ozonolysis, 98.97% of sulphide removal had achieved by using sample from MTBE, while only 48.48% sulphide removal used in stock sulphide. The arrangement of B-P electrode had achieved 77.57% and 84.87% of Sulphide and COD removal, while in monopolar only 40% and 78.64% of Sulphide and COD removal respectively. In conclusion, sample from MTBE gave the high quality in removal of Sulphide in ozonolysis treatment, and B-P arrangement was the best position to determine the highest percentage of Sulphide removal in electrocoagulation.

ABSTRAK

Sulfida adalah salah satu contoh bahan tercemar yang terdapat didalam industri dan memberikan kesan bahaya terhadap manusia, tumbuhan, dan persekitaran. Kandungan Sulfida yang tinggi menyumbang kepada penghakisan paip di dalam industry. Dalam kajian ini, ia bertujuan untuk membangunkan teknologi baru dengan menggunakan perbandingan kaedah Ozonolysis dan Electrocoagulation (EC) yang akan memberi peratusan tertinggi terhadap penyingkiran Sulfida. Eksperimen telah dijalankan dalam reaktor kelompok dan telah dijalankan di bawah rejim galvanostatic pada nilai arus elektrik pada 1A dan voltan yang digunakan adalah 30V. Kedua dua kaedah ini dijalankan dengan menggunakan 0.8L sampel larutan dimana sampel stok larutan Sulfida dan sampel air sisa daripada kilang MTBE telah digunakan dalam eksperimen ini. Kepekatan kedua dua sampel pada influen dipelbagaiakan pada (50,100,150 and 200) ppm. Proses EC melibatkan elektrod besi di mana kedudukan elektrod iaitu monopolar-selari dan bipolar selari dikaji dalam projek ini. Dengan menimbang elektrod sebelum dan selepas EC dan berdasarkan undang-undang Faraday, berat mendakan yang terhasil dalam larutan dikaji. Suntikan ozon dalam ozonolysis adalah 10% untuk semua percubaan. Larutan yang digunakan dalam kedua dua kaedah diambil pada masa yang tetap iaitu pada jangka masa (3, 6, 9, 12, dan 15) minit untuk mengukur penyingkiran Sulfida manakala (15, 30, 45, dan 60) minit untuk penyingkiran COD. Kemudian, peratusan penyingkiran Sulfida dikira dan ketetapan penyingkiran COD juga dinilai. Dalam ozonolysis, sebanyak 98.97% penyingkiran Sulfida telah dicapai apabila larutan yang digunakan adalah sampel daripada syarikat MTBE, manakala hanya 48.48% penyingkiran sulfide dicapai apabila larutan sulfide digunakan. Kedudukan bipolar-selari, masing masing mencapai 77.57% dan 84.87% penyingkiran sulfide dan COD, sementara dalam monopolar-selari hanya 40% dan 78.64% penyingkiran sulfide dan COD. Secara keseluruhan, sampel daripada syarikat MTBE memberikan kualiti yang paling terbaik dalam penyingkiran Sulfida, sementara pula dalam EC, kedudukan bipolar-selari adalah yang terbaik dalam menentukan peratusan yang tertinggi untuk penyingkiran sulfide dan COD.

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LIST OF SYMBOLS

A	Ampere
<i>I</i>	Current
V	Voltage

LIST OF ABBREVIATIONS

EC	Electrocoagulation
OH ⁻	Hydroxyl ions

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Water is one of the most important substances on earth. All the living things and non-living things need water to continue their daily life (Clayton, 2006). Largest percentage composition in our body is water. In fact, nobody can survive for more than a few days without drinking water because it is one of our basic needs and necessities (Greening Earth Society, 2011). Of the approximately $1.4 \times 10^6 \text{ km}^3$ of water in this planet, which is about 70% of the planet, the percentage of salt water in this large amount is 97.5%. The remaining 2.5% is fresh water with 99% of this amount frozen in the icecaps or combined as soil moisture. As the world became more industrial, it contributes to the water pollution including sea and river also can affect the source of the portable human in daily life. This issues is a serious problem to the entire world, because it can threatens the health and human beings, plants, animals, and give high risk to the environment.

Global populations are expected to exceed nine billion by 2050. Urban populations may rise nearly twice as fast, projected to nearly double from current 3.4 billion to 6.4 billion by 2050, with numbers of people living is rising even faster, from 1.0 to 1.4 billion in just a decade. Over a fifth of the global total, 1.6 billion people are expected to live by the coast by 2015. Inadequate infrastructure and management systems for the increasing volume of wastewater that they produce are at the heart of the wastewater crisis. (Corcoran, 2010). Generally, wastewater can be simplified as the waste that comes from human daily life. There are several sectors in Industrial Wastewater that have been published to the government. For an example, Petrochemical Wastewater (PCWW), Municipal Wastewater (MWW), Pulp and Paper Industry,

Petroleum Refinery and etc. Nowadays, treatment of industrial wastewater becomes a problem of major concern. PCWW consists of high concentration of aromatic petroleum hydrocarbons, some non - degradable, and high toxicity that give harmful effect to surroundings, (M.T.Jafarzadeh, 2011). Therefore, Sulphide is the one of the example of contaminant that contains in PCWW which is colorless, foul smelling, highly toxic and corrosive besides it will give an odor smells like rotten eggs.

All living and non-living things will get hemorrhage and death when they get exposed until maximum eight hours to the concentrations greater than 100ppm. They also will be fatal when exposed to concentration above 600ppm and will be highly stresses when concentration is 50ppm (M.K Amosa, 2010). The presence of Sulphide ion combines with hydrogen ions will form dissolved hydrogen sulphide and hydrosulphide ion depending on pH. Sulphides will directly attacks on metals including iron that can cause blistering and embrittlement of ductile iron pipe. Besides, extensive damage to electrical contacts and circuit also will occur on lower concentration of hydrogen sulphides. Therefore, in this project, performance of removal Sulphides will be determined by using comparison between EC with Ozonolysis.

1.2 Motivation

Sulphide becomes the hot topic in industrial wastewater because it gives high impact to industries. The larger problem occur in chemical industries is corrosion. When metals are exposed to an aggressive environment or to atmosphere effects tend to reverse to the lesser energy state of ore. All these processes are enhanced by the aggressive conditions that sometimes can be found in the industry, high temperature and pressure or corrosive environments. Therefore, corrosion may imply a lot of economic costs in the productive system. (R. Leiva-García, 2014). According to NACE (2002), the cost of corrosion in USA could be established in 276 million of dollars per year.

Besides, in Beneath Melbourne's northern industries, they have faced with sulphide problem in wastewater and it's shown that the average amount of hydrogen sulphide was found to be 18 ppm. The sewer pipe lifespan was estimated to be 147

years and this could threaten public health if this gas is accidentally released to the above ground environment and inhaled by the people surroundings (Marleni, 2013). Based on (Hessel et al) submitted a questionnaire about health effects from hydrogen sulfide exposure to 175 oil and gas workers in Alberta, Canada, a known region of sour gas. Of the 175 workers, one third reported having been exposed to H₂S, and 14 workers (8%) experienced knockdown, 47 a term for the loss of consciousness due to inhaling high concentrations of hydrogen sulfide (Hessel, 1997).

Hydrogen sulphide can exists in equilibrium with bisulfide (HS⁻) and Sulphide (S²⁻) in aqueous solution and can form H₂S gas when it's volatile (Levent Altas, 2008). Therefore, it is quite important to develop and use techniques that can allow determining and monitoring the corrosion of the metals. Therefore, an effective wastewater treatment which is composed by combination of unit operations and unit process design to reduce the certain constituents of wastewater to an acceptable level was determined. So, Ozonolysis and Electrocoagulation process was applied to remove COD, sulphides in Petrochemical Wastewater (PCWW) by using sacrificial anodes made of Iron.

1.3 Problem Statement

The problems of this research were the acute toxicity of inhaled hydrogen sulphides can give high effect to the human respiratory, cardiac and nervous system. Sulphides give harmful effect to people and surroundings because it has high contamination in the wastewater that provides one the greatest health challenges restricting development and increasing poverty through costs to health care and lost labour productivity. Almost 900 million people still do not have access to safe water to continue their daily life. Every year, at least 1.8 million children below five years old were died due to water related disease, accounting for around 17 per cent of deaths in this age group. Worldwide some 2.2 million people die each year from diarrhoeal disease. Poor hygiene and unsafe water is responsible for around 88 per cent of all diarrhoeal incidents (Corcoran, 2010).

Besides, Sulphides that contain in wastewater very dangerous to the aquatic life due to the acidic condition and there will be insufficient oxygen to them in advance, they will be suffocate and safety hazards to sewer employees due to the high toxicity of the gaseous hydrogen sulfide. It will give high difficulty to the aquatic life to continue their respiratory system. Hydrogen Sulphides under low-pH condition also can promote corrosion of piping system in the industries and it will form deposited on the anode electrode. H₂S has properties of weak acid that have low pH and can promote corrosion and it will give poisoning of catalysts used by the downstream refinery sector. In a few cases, H₂S may be removed by deterioration of asbestos cement pipe.

1.4 Objectives

The Objective of this research is to study performance of sulphide removal using comparison between Electrocoagulation and Ozonolysis in stock sulphide solution and actual petrochemical wastewater from sample at MTBE

1.5 Scopes of Study

To achieve the objectives; the scopes of this research are:

1. To determine the quality of stock solution and actual petrochemical wastewater.
2. To determine the percentage of sulphide removal after Ozonolysis and Electrocoagulation.
3. To identify the arrangement of Iron electrodes (monopolar and bipolar) used in the electrocoagulation that give high percentage removal of Sulphide.
4. To determine pH value in the dissolution on the anode and cathode during treatment process.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This research presents the experimental study about the efficiency of Sulphide removal using comparison between treatments of electrocoagulation with ozonolysis. It will involve some parameters such as COD, pH value, and concentration of both solutions. The efficiency will depend on the percentage removal of COD and percentage of Sulphide by after doing process. Besides that, through the experiment, the most effective water quality energy consumption for Electrocoagulation (EC) process will be identified. More than that, this research also study about the effect of electrocoagulation to pH of the sample. During the EC process, pH of solution should be in range 11-13pH to ensure that there is only Sulphide ion is present. The conventional wastewater treatment widely used nowadays over all the worlds includes physical, chemical, and biological treatment in order to remove suspended solids, biodegradable organic matters and etc. EC which is classified as the physicochemical treatment method is selected depends on the process condition itself. Definitely, each method have their own advantages and disadvantages but the process condition must be considered first to choose the best method. Comparison between EC with ozonolysis is the best chosen method nowadays in order to remove Sulphide in industrial wastewater.

2.2 Introduction

This chapter presents information regarding the basics of wastewater treatment by using comparison between EC and ozonolysis in order to remove the inorganic material in the industrial. Besides, the parameter study in this research also will explain in this chapter. First section will present definition of wastewater and their treatment. Furthermore, treatment of Sulphide by using EC and Ozonolysis will explained more detailed. Generally, wastewater can be defined as the waste that comes from domestic sewage such as from kitchen, bathroom, laundry, and toilets. Besides, sources of wastewater also can be liquid that have been discharge from commercial and industrial premises, and chemical manufacturers. All of this wastewater contains many constituents such as pathogens, organic, inorganic, toxins and etc. (Mickova, 2015). For an example, waste that comes from Petrochemical wastewater contains high contamination of inorganic substance such as Sulphides which are very harmful to people, environment and surroundings. (Sergio A. Martinez-Delgadillo, 2014).

This issue cannot simply take an action because it will disturb our population or next generation. Therefore, treatment of wastewater need take an action. Treatment of wastewater can be classified into two which are by conventional method and another one is advanced wastewater treatment. Conventional treatment method can be group into three, which are by physical, chemical and biological method (Mickova, 2014).

Firstly, physical method of wastewater is the process when there is no chemical or biological is added into reaction. It is totally about the physical phenomena that are used to treat or improve the quality of wastewater. The examples of the process are sedimentation, screening, filtration, degasification and etc. (Sen, 2015). Mostly, all of this process comes from primary treatment whereby it is the first waste that comes from industrial sectors. Secondly, chemical method is includes the using of chemical into the process in order to improve the quality of water. The examples of the process are chlorination, ozonation, coagulation, adsorption, and ion exchange. Ozone known as strong oxidizing agent that widely use in oxidizing disinfection process. Besides, coagulation is the process where the chemical is added and through the reactions it will form insoluble products that can be easily removed from wastewater by using physical methods. Thirdly is by using biological method whereby this method is using

microorganisms to degrade the natural organic waste resulting in dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD).

On the other side, advance treatment wastewater is the advanced method when the conventional treatment cannot counter the problem, therefore advance treatment will settle it down. Advanced treatment method will include the use of electricity and it had been practiced in the second part of 20th century. For an example, if the substances or metal that cannot be degradable or remove from the wastewater, it will solve by using advanced process such as electrocoagulation, electro-flocculation, electro-disinfection electro-reduction and etc. In this research, it will be more focus on comparison between EC processes with Ozonolysis to remove Sulphide which are very high contamination in our industrial wastewater.

Table 2-1: Advantages and disadvantages of the treatment

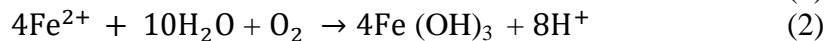
Treatment	Advantages	Disadvantages
Conventional treatment	<ul style="list-style-type: none"> - Great adaptability of microorganism 	<ul style="list-style-type: none"> - Time consuming - Require extensive land and demand determination of method for further use of neutralization
Advanced treatment	<ul style="list-style-type: none"> - Process does not require additional consumption of chemicals, because it only involves the movement of electrons to stimulate the reactions. - Easy to handles - Environmental friendly 	

2.3 Electrocoagulation

EC is a simple and efficient method to remove the flocculating agent generated by electro-oxidation of sacrificial anode electrodes (Edris Bazrafshan, 2012). They develop the electrocoagulation process involved two types of electrodes which is Aluminium and Iron, (Mickova, 2015). On the other hand, EC is based on the in situ formation of the coagulant as the sacrificial anode corrodes due to an applied current. Fe or Al is dissolved from the anode generating corresponding metal ions, which almost immediately hydrolyse to polymeric iron or aluminium hydroxide (Kabdashy, 2012). In definition, EC is the application of electrical potential across electrodes placed in a moving solution to be treated.

The additional benefit of EC compared to chemical coagulation is the electrical current moves through the solution and promotes several other mechanisms that influence removal of species from solution. (Shammas, 2010). This process is non-chemical, electrical means of removing suspended solids, colloidal material, and sparingly soluble salts as well as other dissolved solids from waters and wastewaters. In fact, there are several benefits of EC relative to chemical coagulation. One of the benefits is EC removes many species that chemical coagulation cannot remove furthermore the coagulants are produced via electrodes. More than that, EC produces cleaner water with less sludge. (G.Mousavi, 2011). EC also has no temperature effect; it can be used in a wide range of temperature. Besides that, EC requires no toxic chemical safety requirements and is efficient in killing virus and cysts as well as coliform bacteria (Mickley, 2004). The reaction that happens at the cathode and anode during the EC process is shown in the equation below:

Anode: (Fe²⁺)



Cathode:



Overall:



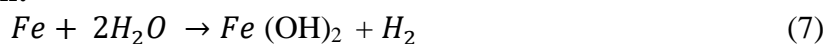
Anode: (Fe³⁺)



Cathode:



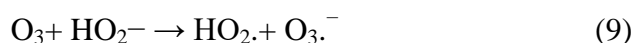
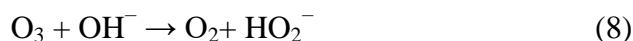
Overall:



In this type of process, EC current is used where electrode plates are sacrificed, which means dissolve into solution and causing increased high metal concentrations that end up as oxide precipitates (Murat Eyvaz, 2014). In general, EC process has three main stages. The first one is coagulants forming due to anode electrical oxidation. The next step is destabilizing pollutants and suspended substances and emulsion breaking. Lastly, the instable particles combine and form floc. (M.Malakootian, 2009). Moreover, the other advantage of EC is the adsorption rate of produced hydroxides by this process is 100 times as much as hydroxides produced through chemical processes and they do not produce secondary pollutants (Murat Eyvaz, 2014).

2.4 Ozonolysis

Ozonation implies the use of ozone in the treatment of wastewater. Ozone is a strong oxidizing agent that oxidizes organic pollutants via two pathways: direct oxidation with ozone molecules and the generation of free-radical intermediates, such as the •OH radical, which is a powerful, effective, and non-selective oxidizing agent (M. Hern´andez-Ortega, 2010). In advanced, Ozonation process can be done when there is fluctuation happened in the flow rate. Moreover, this process also requires transfer of O₃ molecules from gas phase to liquid phase. Therefore, mass transfer will be limiting step and it will reduce the efficiency and will increase operating costs. One of the aims of ozone application in wastewater treatment is to remove toxic inorganic substances and this mainly involves the removal of cyanide (CN⁻) mostly associated with metal processing and electronics industry wastewaters. Nitrite (NO₂⁻) and sulphide (H₂S or S₂⁻) react quickly with ozone and therefore their removal is sometimes carried out using ozonation (Lisa Avery, 2010). The decomposition of ozone in water to form hydroxyl radicals occurs through the following mechanism (Roberto Andreatti, 1999), where hydroxide ions initiate the reaction (Eqs 8-14):





According to reactions (8) and (9) the initiation of ozone decomposition can be artificially accelerated by increasing the pH value. Side reaction (Eq 14) is a fast process and plays an important role in waters with low dissolved organic carbon and alkalinity since it can reduce the oxidative capacity of the system: (Murat Eyvaz1, 2014). Ozone injection in water treatment has been used for disinfection, as well as oxidation of sulphide and other constituents in water. Contactor basins typically have been used for ozone dissolution in water using a fine bubble diffusion system. In the past, ozone generators produced ozone concentrations on the order of 5 percent or less. In recent years, ozone generators are capable of producing ozone concentrations on the order of 8 to 11 percent or more from oxygen gas without requiring excessive power. This higher concentration allows the use of venturi injectors to dissolve ozone effectively in water without the need for the diffusers and detention time provided by contactors. Furthermore, it was found that pressurized contact of ozone using venturi injectors provided more rapid, consistent oxidation of sulfide ion at lower applied ozone dosages than fine bubble diffusion. Use ozone for sulfide removal to minimize detention time for ozone oxidation. Maintain sulfide residual leaving the ozone treatment process. If ozone is not used as the primary disinfectant, there is no need to maintain an ozone residual. The complete oxidation of sulfide to sulfate occurs in three seconds, whereas the half-life of ozone is approximately 18 to 20 minutes (Curtis Kunihiro, 2008).

Table 2-2:Advantages and Disadvantages of EC and Ozonolysis

Process	Advantages	Disadvantages
Electrocoagulation	<ul style="list-style-type: none"> - Involves movement of electrons - Coagulants are produced via electrode - Will enhance the removal of substances from the solution - High efficiency removal compared with chemical coagulation - Less amount of sludge will produces - Easy to handle and low cost of maintenance - Lower operating cost - Use no chemicals as coagulating agents. These are generated during the electrolysis process by electro-dissolution of a sacrificial anode made of aluminum or iron. 	<ul style="list-style-type: none"> - The sacrificial electrodes needs to be replace periodically because it were dissolved and hence lost into the wastewater streams as a result of oxidation. - Impermeable oxide film may be formed at the cathode, hence it will leading to the efficiency loss
Ozonolysis	<ul style="list-style-type: none"> - Reduce amount of sludge production - increases the oxidation of pollutants that are dissolved in the solution and that cannot be eliminated via electrocoagulation 	<ul style="list-style-type: none"> - high cost of equipment and maintenance,

2.5 Previous Work on Electrocoagulation

Generally, electrocoagulation (EC) famously known used to treat water and wastewaters or in exact way, reduced matters in that water. There has been a lot of study in electrocoagulation field. The treatment of wastewater by EC was increasingly practiced in the 20th century, but with limited success and popularity. Since EC is an effective process in order to remove any suspended particles, organic compounds, oils, and heavy metals, many type of sector industries have been used EC to enhance their treatment of wastewater. The example of industries that have been used this EC were Petroleum Refinery wastewater, Tannery wastewater, Municipal wastewater, and etc.

In the Textile wastewater, it consume large amount of water and produces color wastewater. Generally, textile industries used more than 10,000 dyes and pigments for dyeing natural and synthetic fibers. In this research, the researcher had studied about the efficiency of EC treatment process by using Aluminium electrodes acts as an anode in order to treat synthetic wastewater containing Reactive Red198 (RR198). The parameters that been controlled in this experiment such as voltage, time of reaction, electrode connection mode, initial dye concentration, electrolyte concentration, and inter electrode distance on dye removal efficiency (W.Balla, 2010). In addition, the researcher also determined the value of electrical energy consumption, electrode consumption, and operating cost at optimum condition of EC process. The results showed that 98.6% and 84% dye and COD were removed respectively. Electrode consumption, energy consumption and operating cost were 0.052 kg/m³, 1.303kWh/m³ and 1.144 RM/m³, respectively. It can be concluded that electrocoagulation process by aluminum electrode is very efficient and clean process for reactive dye removal from colored wastewater. (Arash Dalvand, 2011).

For the last decades, EC has been optimized to minimize electrical power consumption and minimize removal of heavy metals, heavy metals, dye and colour. (A.Dalvand, 2011) . One of the studies is in vegetable oil refinery, where Aluminium acts as anode electrodes in the process EC. Within this study, it can be concluded value of COD removal was 98.9% for 90 minutes. Current density was 35mA/cm², energy consumption was 42kWh/kg for COD removed. (Tezcan Un, 2009). In the tannery wastewater, the authors more considered on COD,Sulphide and oil-grease removals.

The value of COD, Sulphide and oil-grease removal was 82%, 90% and 96% respectively. The optimum parameters that have been used in this experiment were 35mA/cm² for electrical current, pH value for the wastewater was maintained at pH of 3, and time for retention time was recorded for 10 minutes electrolysis time. At the end of experiment, value of energy consumption was 42kWh/kg for COD removed, 0.524kWh/kg for Sulphide removed and 0.00018kWh/kg for oil-grease removed. (Şengil, Kulaç, & Özacar, 2009).

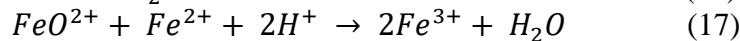
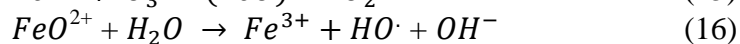
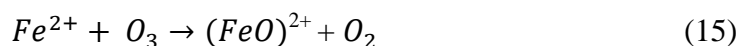
In the previous work on EC process, they have a researcher have been studied on the efficiency of EC and factors that give lower energy consumption in order to remove turbidity in the Petrochemical Wastewater (PCWW). PCWW produce large amount of wastewater from their manufacturing process like desalting, hydrocracking, hydroskimming, and vapour condensate. (Tobiszewski, 2012). Moreover, PCWW has organic compounds that have poor biodegradability and need to be treated by using efficient technologies (Zhang, 2011). In this study, the experiments were achieved 97.43% efficiency maximum turbidity removal. (Saidat Olanipekun Giwa, 2012).

There are many researchers that studied on the electrode materials. They want to identify the type of electrochemical reactions that will enhance the EC process. Generally, EC consist of two electrodes, which are anode and cathode. In the Paper Mill Wastewater, it has been use two type of different electrodes which are Aluminium (Al) and Iron (Fe) acts as anode and cathode respectively (R.Katal, 2011). Different types of electrodes used in the EC process will give impact to the performance of EC reactor, especially at the anode electrode, which it is determines the types of cations produces into the solution (I.Alill, 2012).

During the EC process, Al will dissolve to the Al (III), whereas Fe will dissolve either as Fe (II) or Fe (III). (S.Chaturvedi, 2013). Fe (III) shows a better coagulant compared with Fe (II) because it has lower solubility of hydroxide and has higher positive charge. In the other works, the researchers have found that by using Al electrodes is becomes superior compared to Fe, but on the other side Al electrode is more expensive. Iron dissolution in sulfide aqueous solutions results mainly in iron sulfide that precipitates in the pH range of 5-7 (Zaharia, 2006). Before sedimentation, it was noticed that the treated solutions with mild steel anode are black colored due to the FeS formed (Marius Sebastian Secula, 2012). EC process produces coagulants such as

iron or aluminium (Al) hydroxides having a considerable sorption capacity by anodic dissolution and also pollutants are removed simultaneously by deposition on cathode electrode or by flotation due to the hydrogen gas produced at the cathode (Kara S, 2013). Besides, the previous research also had studied on the Sulphides removal by using two types of anode materials (Al, mild steel). The objectives in this study were to investigate the relation to anodic solution, efficiency removal and energy consumption needed in the EC process. The results shown when mild steel used as anode, it will give the higher removal efficiency of Sulphide ion, lower energy consumption, and lower electrical operating costs compared to Al anodes. (M.Secula, 2012). Al anodes will give higher advantages on the removal of Zn (II), Cu (II), Cr (VI), and Ni (II). (I.Heidmann, 2008).

In addition to the improvement coming from the addition of the effects of the separated single treatment technology, the combined process involves an increased hydroxide radical production because transition metal ions (Fe^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} , Ag^{+} , and Zn^{2+}) work as catalysts in the homogeneous liquid phase for the degradation of organic pollutant in wastewater. During the combined process, the metal ion established the rate of reaction in the degradation system and the efficiency of ozone application. The most accepted mechanisms for which the metal ions accelerate the decomposition of ozone to generate hydroxyl radical are shown in (15)–(17). The Fe^{2+} cation is used as example in the well-known Fenton process. This mechanism helps to explain the synergistic effect of the combination of both technologies and the resulting high efficiencies (C. E. Barrera-Díaz, G. Roa-Morales, P. B. Hernández, C. M., 2014).



To explain why there is no 100% of COD removal, it is necessary to remember that degradation processes that involved oxidants, despite their high reactivity and low selectivity, normally also produce refractory final products analysis in the costs for an actual successful application is necessary..

CHAPTER 3

METHODOLOGY

3.1 Preparation of stock sulphide solution

Each molecule of Sodium Sulphide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) contains one mole of Sulphide S^{2-} element:

Molecular weight of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O} = 240.18 \text{ g/mol}$

Atomic weight of $\text{S}^{2-} = 32 \text{ g/mol}$

$$\frac{1,000\text{mg S}^{2-}}{\text{L}} \times \frac{1\text{g S}^{2-}}{1,000\text{mgS}^{2-}} \times \frac{1\text{ mol S}^{2-}}{32\text{g S}^{2-}} \times \frac{1\text{mol Na}_2\text{S}\cdot 9\text{H}_2\text{O}}{1\text{ mol S}^{2-}} \times \frac{240.18\text{g Na}_2\text{S}\cdot 9\text{H}_2\text{O}}{1\text{ mol Na}_2\text{S}\cdot 9\text{H}_2\text{O}} \times \frac{100\text{g Na}_2\text{S}\cdot 9\text{H}_2\text{O}}{99.5\text{g Na}_2\text{S}\cdot 9\text{H}_2\text{O}}$$

$$\frac{24018000}{3184000} = 7.5433 \text{ g Sulphide powder}$$

To prepare stock solution it required to weight 7.5433g of Sulphide powder and dissolve it in 1L of Deionized water. pH value and Sulphide content of this dissolution was measured first to ensure that there is no hydrogen sulphide produced when this solution react under electrocoagulation process and ozonolysis. pH value for stock solution was estimate under pH 11-13 and Sulphide content was in range 1000mg/L.

3.2 Determination of Water Quality

pH and COD of the stock solution and sample wastewater from MTBE was measured before and after the experiment.

3.3 Electrochemical Reactor Setup

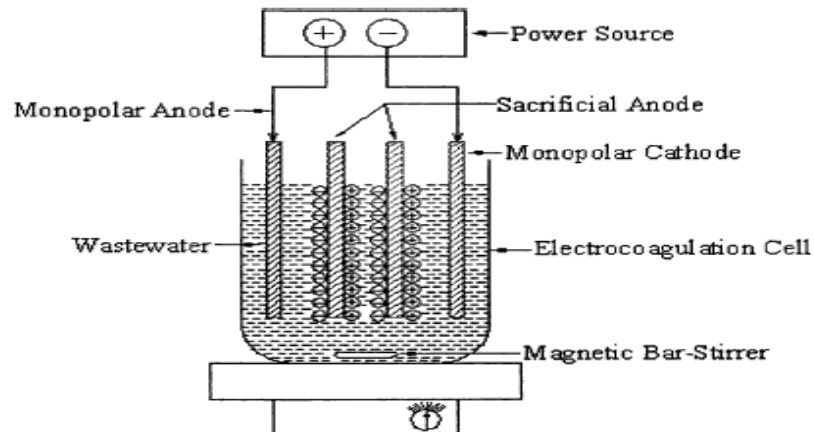


Figure 3-1: Arrangement of bipolar - parallel electrode (Mollah M, 2001)

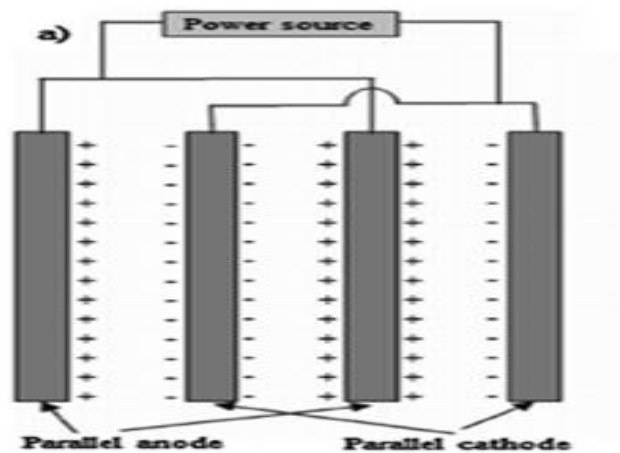


Figure 3-2: Arrangement of monopolar – parallel electrode (Mollah M, 2001)

- 1) Fig. 1.0; Bipolar electrode in parallel connections (BP-P): As shown in the sacrificial electrodes are placed between the two parallel electrodes without any electrical connection. Only the two monopolar electrodes are connected to the electric power source with no interconnections between the sacrificial electrodes. When an electric current is passed through the two electrodes, the neutral sides of the conductive plate will be transformed to charged sides, which have opposite charge compared to the parallel side beside it.

2) Fig. 1.1; anodes and cathodes are in parallel connection (Monopolar electrodes in parallel connections (MP-P)) :

- The current is divided between all the electrodes in relation to the resistance of the individual cells.
- The parallel connection needs a lower potential difference compared with serial connections.

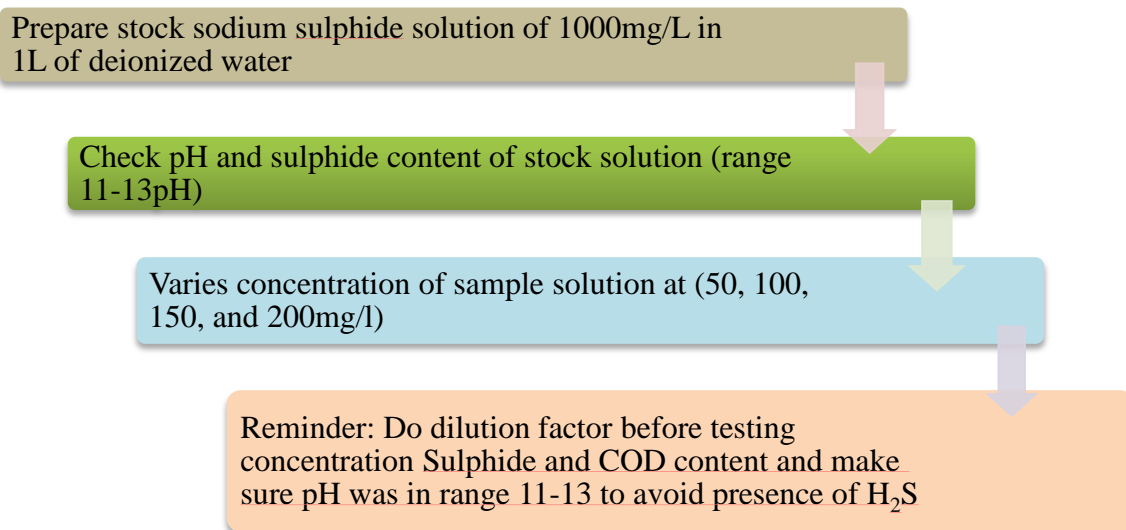
Generally, in the simplest form, Electrocoagulation (EC) reactor may be made up of an electrolytic cell with one anode and one cathode. Anode electrodes will undergo oxidation, thus, the electrode will electrochemically corrodes when the material was connected to an external power source. While cathode will undergo reduction process and produced hydrogen bubbles at the electrode. But, this arrangement is not suitable for wastewater treatment, because for a workable rate of metal dissolution, the use of electrodes with large surface area is required. (Mollah M, 2001). In this research, arrangement of electrodes for monopolar and bipolar in parallel connection has been chosen to identify the percentage removal of sulphide and COD were shown in Figure 1.0 (a) and Figure 1.0 (b) above.

In the monopolar parallel arrangement, a conductive plate was placed in between two electrodes having opposite charges. In this experiment, same conductive plates which are iron electrodes were used. In bipolar mode, a conductive plate is neither connected to other electrodes nor to the DC power supply. However, without any electrical connection, the two neutral sides of the plate transform to charged sides which have an opposite charge compared to the parallel beside the electrode. This plate is commonly called the bipolar electrode. Arrangement of conductive plate may be in series or parallel.

The EC process was carried out using an electrochemical reactor operating in batch mode. The reactor was conducted in the capacity of 1.0L but only 0.8 L was used in all trials. (Gonzalez-Rivas C. E., 2015). The corresponding experiments were carried out with an arrangement of two parallel monopolar Fe electrodes. Each electrode was 5.0×4.0 cm with a surface area of 20 cm². Current of 1.0 A was supplied into each of experiments. The distances between electrodes were 0.8cm. 30V of DC power source was supplied to the system. Samples were taken at regular intervals to determine COD and Sulphide removal.

3.4 Procedure Electrocoagulation

3.4.1 Before electrocoagulation (stock sulphide and sample from MTBE)



Stock sulphide solution of 1000mg/L was prepared before start doing the experiment. (Section 3.5). Then, pH of stock solution was checked by using pH meter and Sulphide content inside the solution also was measured. Sulphide content was determined by using Sulphide Reagent 1 and Sulphide Reagent 2. Further step please refer in Appendix. In order to prevent the presence of Hydrogen Sulphide (H₂S), make sure Sulphide content must be in range 1000mg/L (Buyukgungor, 2008) and pH of stock solution must be in range pH 11-13. If the pH of Sulphide content was less than pH of 6, (Tech Bulletin: Overview of H₂S) then hydrogen sulfide is mainly in the H₂S form which is very dangerous to human.

After prepared stock solution, concentration was varies at concentration 50, 100, 150, and 200 mg/L (Weisheng, 2011) before entering a reactor capacity of 1.0L. Calculation amount of volume to take from stock solution in order to prepare sample of solution of 0.8L (Rivas, 2015) was determined by using specific formula as shown in (Section 3.5).

3.4.2 Calculation to prepare sample of solution

Mass Of Sodium Sulphide Powder

$$\frac{1,000\text{mg } S^{2-}}{L} \times \frac{1\text{g } S^{2-}}{1,000\text{mg } S^{2-}} \times \frac{1\text{ mol } S^{2-}}{32\text{g } S^{2-}} \times \frac{1\text{mol } Na_2S \cdot 9H_2O}{1\text{ mol } S^{2-}} \times \frac{240.18\text{g } Na_2S \cdot 9H_2O}{1\text{ mol } Na_2S \cdot 9H_2O} \times \frac{100\text{g } Na_2S \cdot 9H_2O}{99.5\text{g } Na_2S \cdot 9H_2O}$$
$$\frac{24018000}{3184000} = 7.5433 \text{ g Sulphide powder in 1L of DI water}$$

$$\text{pH} = 12.32, S^{2-} = 1129 \text{ (ppm)}$$

$M_1V_1 = M_2V_2$, where

M_1 = concentration of Stock Sulphide from 1L of stock solution (ppm)

V_1 = volume of stock sulphide solutions to entered the EC reactor (mL)

M_2 = Concentration of Sulphide (ppm)

V_2 = Volume of sample to entered the reactor (800mL)

Calculation:

1) At 50 ppm

$$M_1V_1 = M_2V_2$$

$$(1129)(V_1) = (50)(1000\text{ml})$$

$$V_1 = 44.29 \text{ mL} + 755.71 \text{ mL DI water}$$

2) At 100 ppm

$$M_1V_1 = M_2V_2$$

$$(1129)(V_1) = (100)(1000\text{ml})$$

$$V_1 = 88.57 \text{ mL} + 711.43 \text{ mL DI water}$$

3) AT 150 ppm

$$M_1V_1 = M_2V_2$$

$$(1129)(V_1) = (150)(1000)$$

$$V_1 = 132.86 \text{ mL} + 667.14 \text{ mL DI water}$$

4) At 200 ppm

$$M_1V_1 = M_2V_2$$

$$(1129)(V_1) = (200)(1000)$$

$$V_1 = 177.18 \text{ mL} + 622.82 \text{ mL DI water}$$

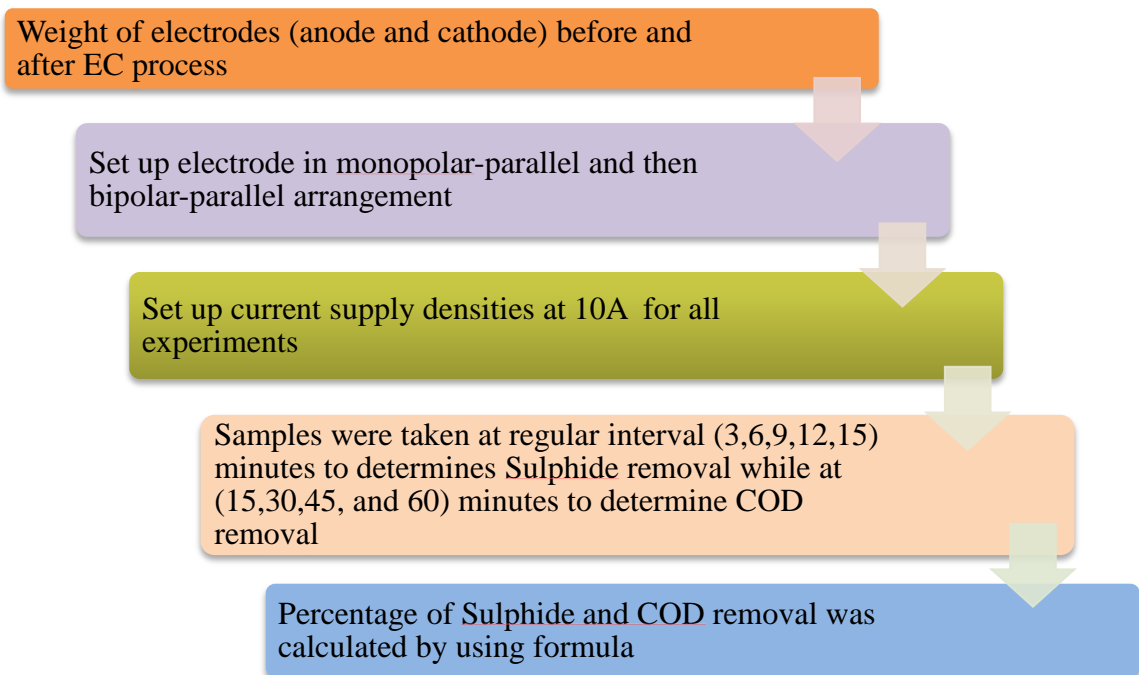
3.4.3 MTBE samples

Sample from MTBE companies was used in both treatments of electrocoagulation and Ozonolysis, Sulphide content inside the wastewater was carried out by methylene blue spectrophotometric method. (FENG Jing-wei, 2007).

3.4.4 Sulphide solution

Sample of sulphide solution was prepared by using the stock sulphide solution that had been prepared. By varied the concentration of sulphide at influent which were at (50,100,150, and 200) mg/L, (Gao Xiaohua, 2011), the volume of sulphide solution were took out from the stock sulphide and then diluting into deionized water to complete the solution at 0.8L of sample (Gonzalez-Rivas, 2015) as shown in the Section 3.5.

3.4.5 During Electrocoagulation



* dilution factor was constant at 1000.

* sample solutions refers to stock sulphide and sample from MTBE.

* filter the solution after treatment of EC and weight the amount of precipitation that corrodes during the process.

*all the experiment must be work in fume hood area.

Both of electrode at anode and cathode were weighed before entered into the reactor of EC. After that, arrangement of electrode was set up in monopolar- parallel as shown in Figure 1.0(a). Then, current supply to the reactor was set at 10A and the voltage supply was 30V. Let the sample undergo the reaction process inside the reactor for 1 hour. The sample were taken at regular interval which were at (3,6,9,12,and 15) minutes in order to determine the Sulphide removal during the EC process. Then, the sample continued taken at another times which were at (15,30,45, and 60) minutes in order to determine the COD removal.

After the reaction complete at 1 hour, both the electrodes were took out from the reactor and weighed again. Besides, sample solution from the reactor also was proceeding to the filtration process. From the filtration process, the amount of deposited that occurred during the process was determined. The percentage removal of Sulphide and COD removal was calculated by using formula at Section 3.6. The step was repeated by changed the arrangement of electrode from monoolar-paraller to bipolar-parallel.

3.4.6 Formula used to determine percentage of sulphide and COD removal

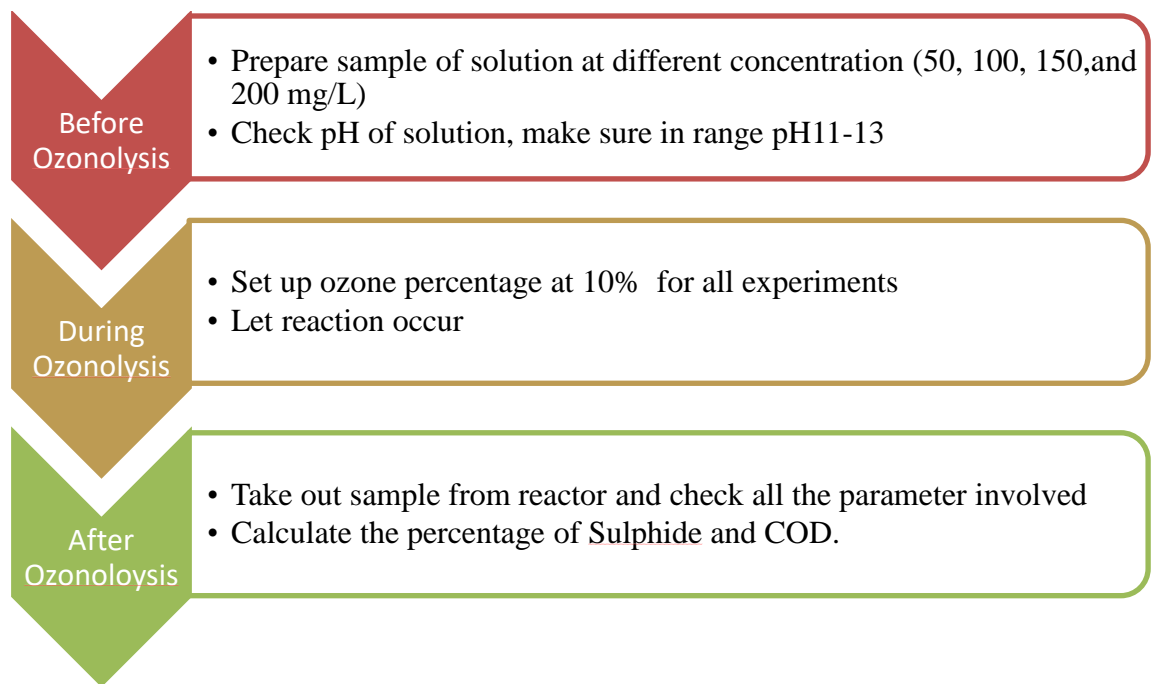
3.4.7 Percentage of sulphide removal

$$\frac{S^{2-} \text{ concentration at influent} - S^{2-} \text{ concentration at effluent}}{S^{2-} \text{ concentration at influent}} \times 100$$

3.4.8 Percentage of COD removal

$$\frac{\text{Influent COD} - \text{Effluent COD}}{\text{Influent COD}} \times 100$$

3.5 Procedure of Ozonolysis



Sample of solution were prepared at different concentration which were at (50,100,150, and 200) mg/L. More details at Section 3.5. pH of all the sample solution were checked before undergo Ozonolysis treatment. Then, the sample were entered the reactor capacity of 1L. Percentage of ozone was setup at 10% for all the trials of experiment. (Lebrecht, 2015). The reaction of Ozone inside he reactor was let for 1 hour. The sample were taken at regular interval which were at (3,6,9,12, and 15) minutes to determine the percentage of sulphide removal while (15,30,45, and 60) minutes to determine the COD removal. The set up were repeated for the other sample of MTBE at different concentration.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Ozonolysis by using sulphide solution (constant t=12 min)

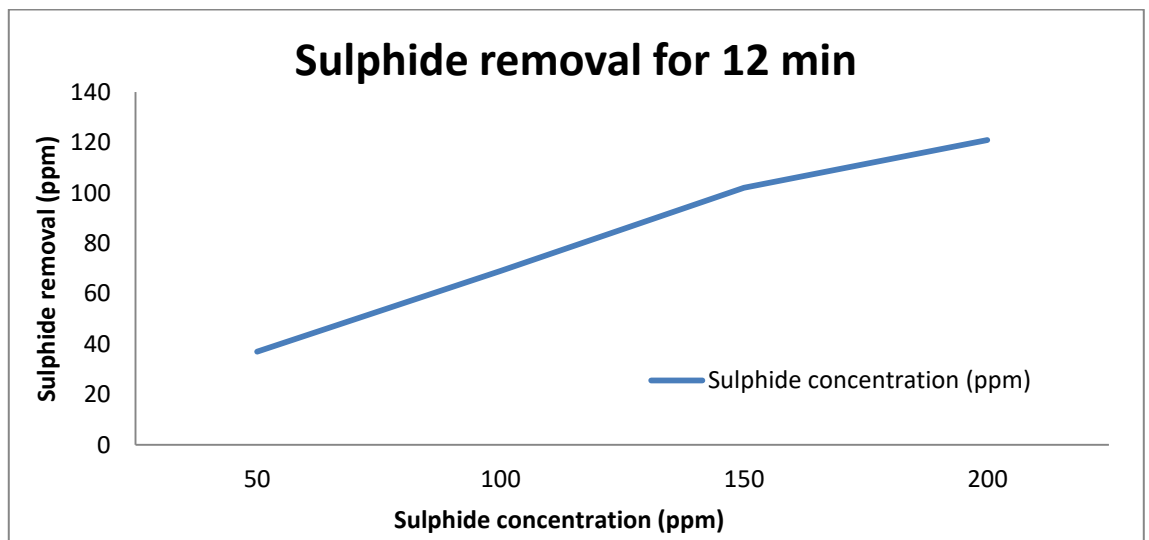


Figure 4-1: Sulphide removal at constant time (12min) after Ozonolysis

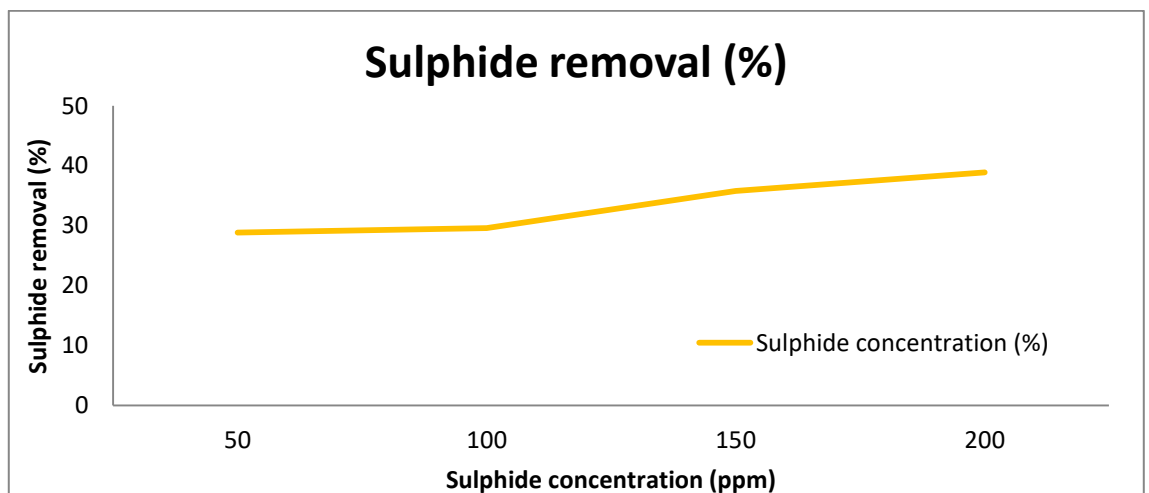


Figure 4-2: Sulphide removal (%) at constant time (12min) after Ozonolysis

From the Figure 4-3: above, it shows the trend of sulphide concentration (ppm) at different concentration (50,100,150, and 200) ppm while the times were constant at 12 minutes for all the trials. Sulphide solution at differents concentrations were used in Ozonolysis treatment. It shows that the graphs of sulphide removal were increased with increasing of the concentration of sulphide. Thus, the percentage of sulphide removal in Figure 4-4 shows increments of Sulphide removal from 28.85% to 38.89%.

4.2 Ozonolysis using sulphide solution at difference residence time

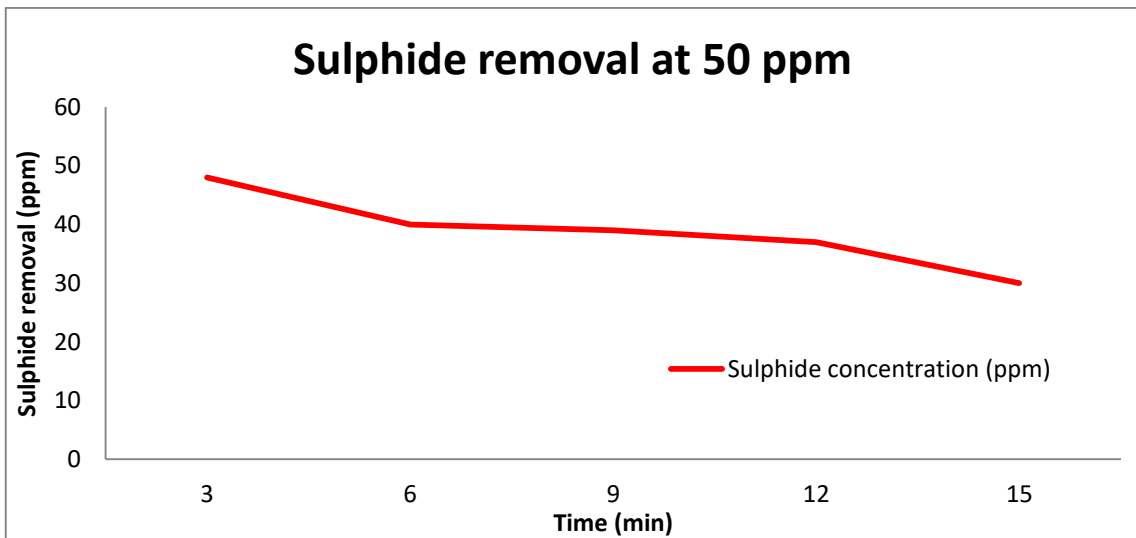


Figure 4-5: Sulphide removal at 50 ppm using sulphide solution after ozonolysis

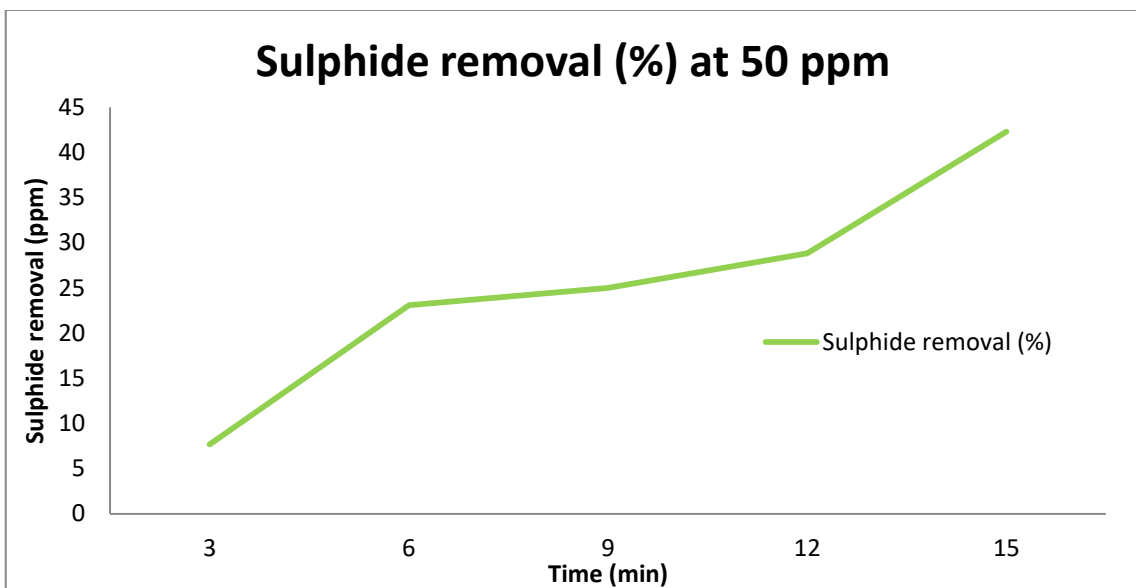


Figure 4-6: Sulphide removal (%) at 50 ppm using sulphide solution after ozonolysis

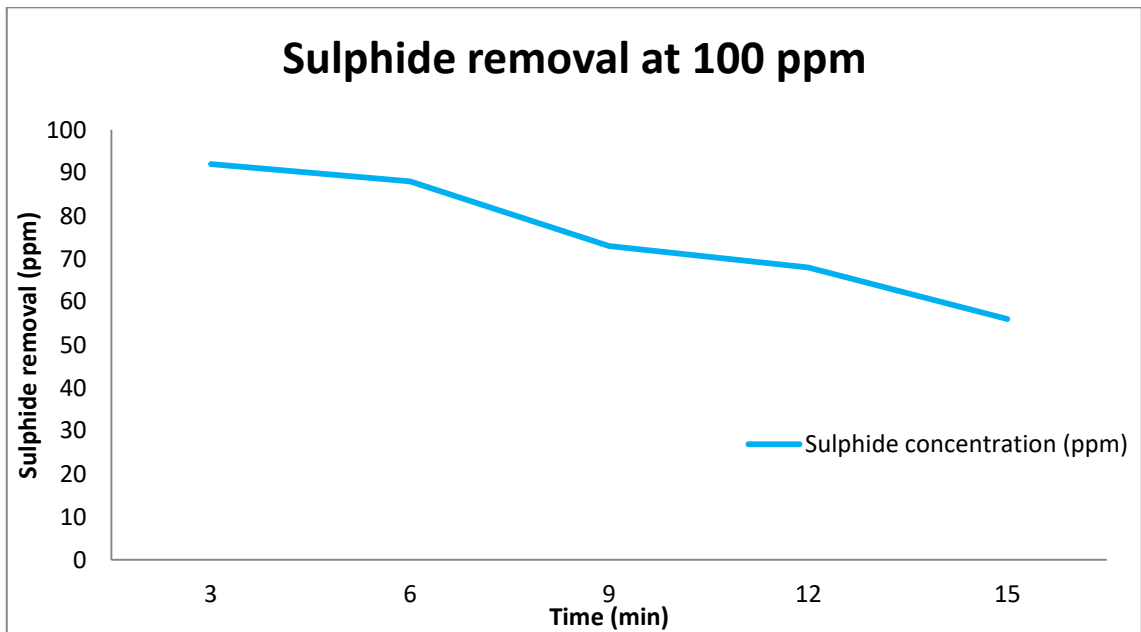


Figure 4-7: Sulphide removal at 100 ppm using sulphide solution after ozonolysis

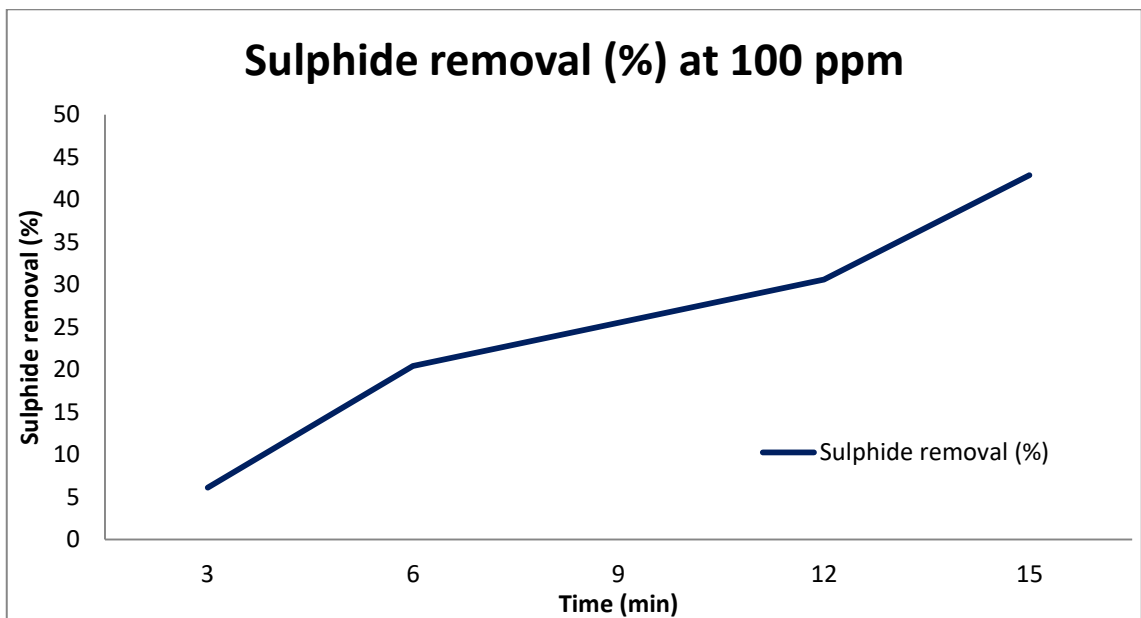


Figure 4-8: Sulphide removal (%) at 100 ppm using sulphide solution after ozonolysis

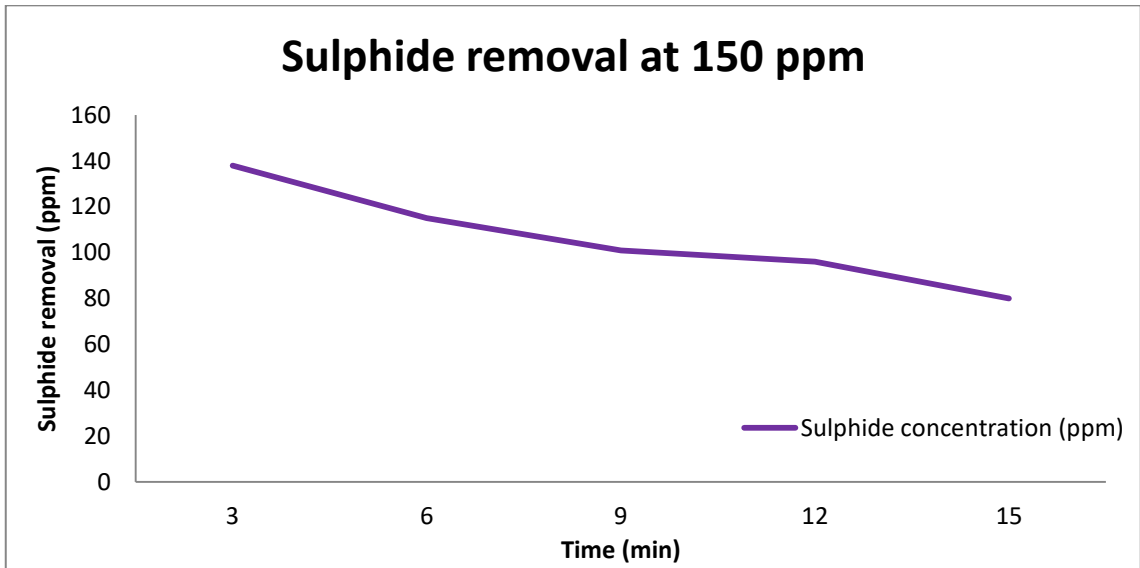


Figure 4-9: Sulphide removal at 150 ppm using sulphide solution after ozonolysis

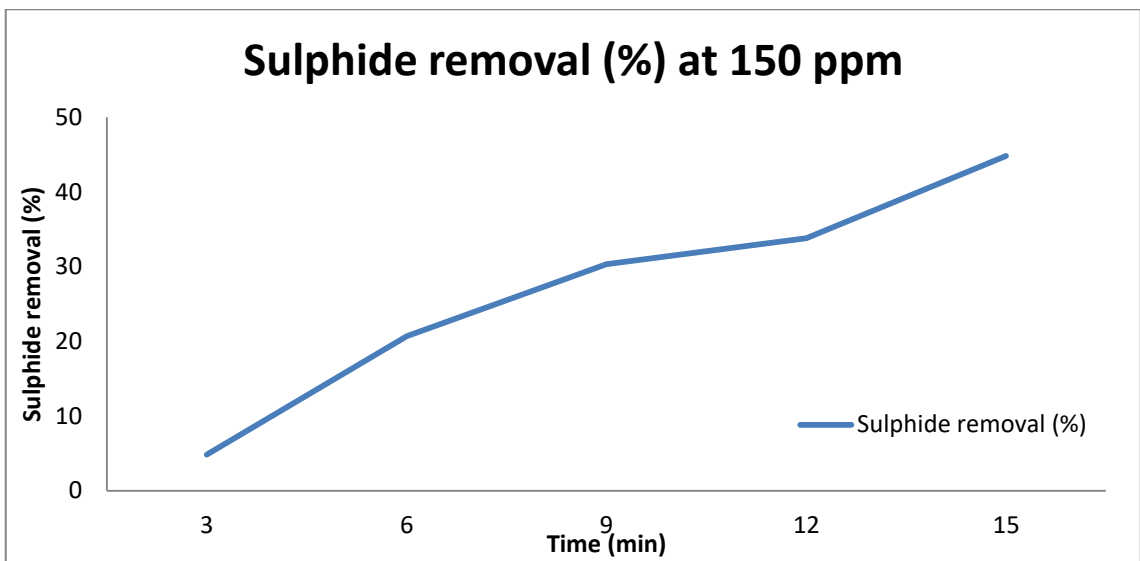


Figure 4-10: Sulphide removal (%) at 150 ppm using sulphide solution after ozonolysis

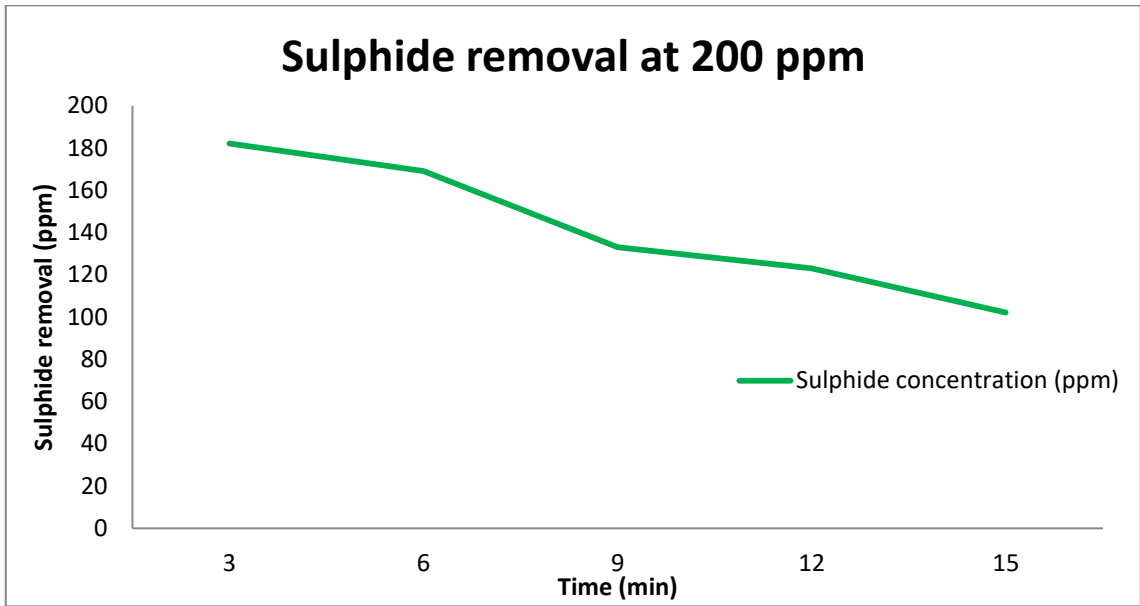


Figure 4-11: Sulphide removal at 150 ppm using sulphide solution after ozonolysis

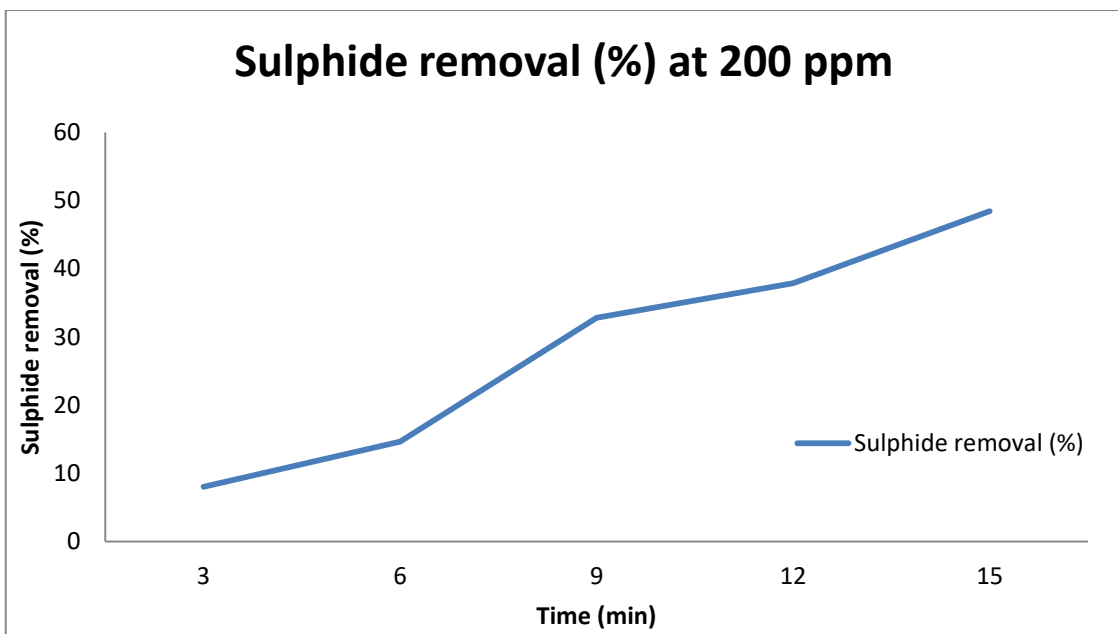


Figure 4-12: Sulphide removal (%) at 200 ppm using sulphide solution after ozonolysis

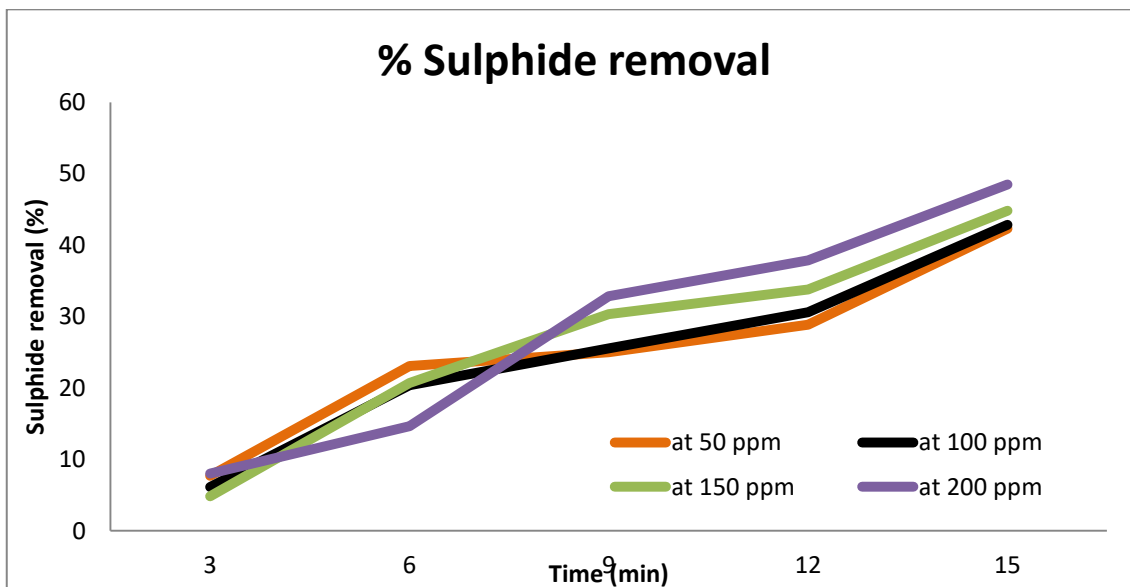


Figure 4-13: Sulphide removal (%) in overall concentration (ppm) using sulphide solution after ozonolysis

From the Figure 4-14, Figure 4-15, Figure 4-16, and Figure 4-17, it shows the reduction of sulphide after Ozonolysis treatment at different concentration within 15 minutes. After 3 minutes of reaction, the percentage in Figure 4-18, Figure 4-19, Figure 4-20, and Figure 4-21 shows the removal of Sulphide for all concentration does not exceed 10% of removal. After reaction completed within 15 minutes, at 50 ppm the percentage of removal was increased from 7.69% reached up until 42.31%. At 100 ppm, percentage of sulphide removal was from 6.12% up to 42.86% of removal. Same goes at 150 ppm and 200 ppm, the percentage removal increased until 44.83% and 48.48% respectively. From Figure 4-22, the trend shows that increased of concentration will increase the percentage removal of sulphide. The highest percentage removal when used stock sulphide as the sample solution inside the treatment of ozonolysis will give only 48.48% of sulphide removal at 200 ppm. The removal does not exceed 50% of removal.

4.3 Ozonolysis by using sample wastewater from MTBE (constant t=12min)

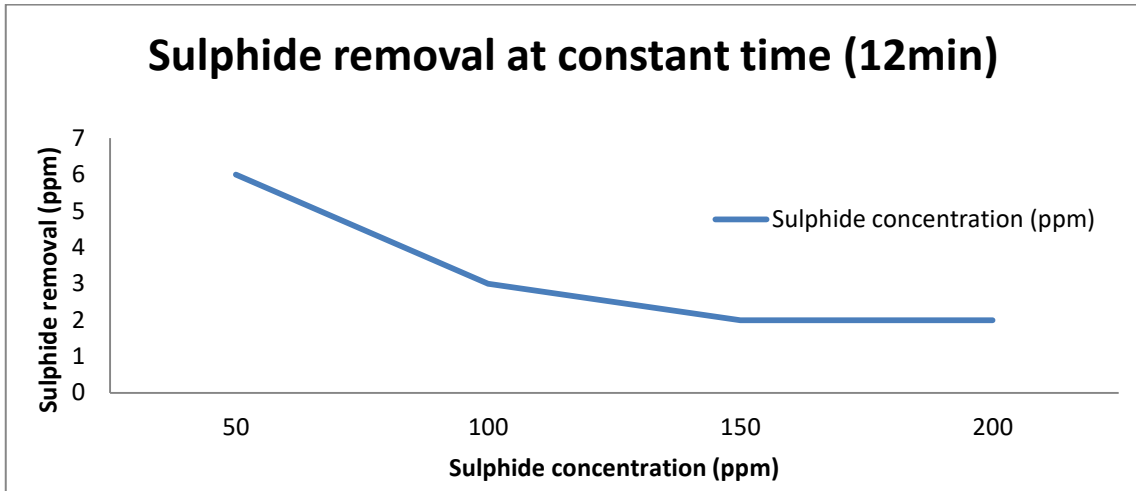


Figure 4-23: Sulphide removal (ppm) at constant time (12min) after Ozonolysis treatment by using sample from MTBE

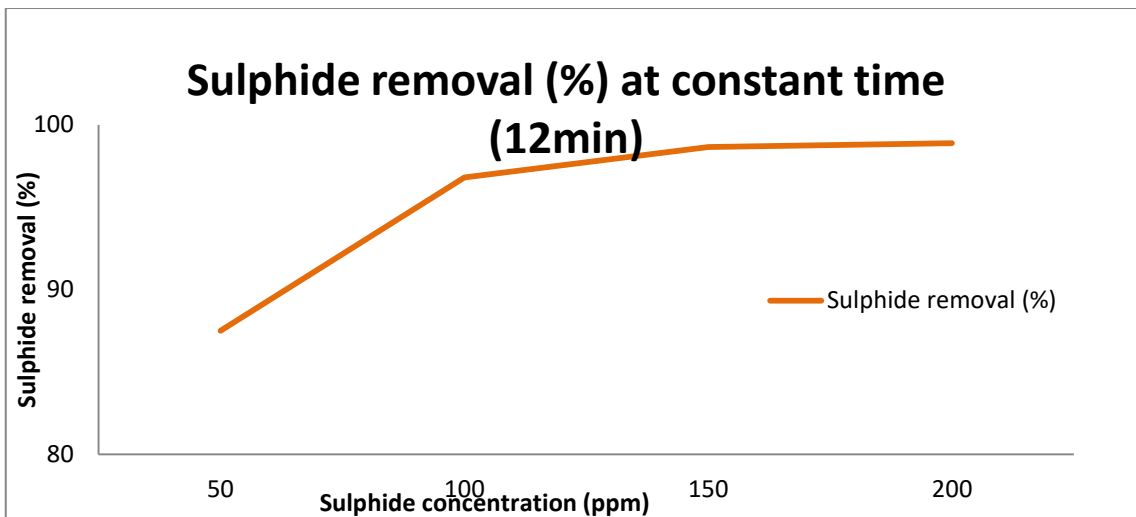


Figure 4-24: Sulphide removal (%) at constant time (12min) after Ozonolysis treatment by using sample from MTBE

From the Figure 4-25 above, it shows the trend of sulphide concentration (ppm) at different concentration (50,100,150, and 200) ppm while the times were constant at 12 minutes for all the trials. Sample from MTBE at different concentrations were used in Ozonolysis treatment. From the Figure 4-26, it shows that the graphs of sulphide removal were increased with increasing of the concentration of sulphide. In the process, 10% of Oxygen was injected to increase the efficiency of the treatment, thus it leads to the higher percentage removal of Sulphides which were from 87.50 % to 98.89% and it almost achieved to 100% of removal as shown in Figure 4-13.

4.4 Ozonolysis by using sample wastewater from MTBE at different residence t

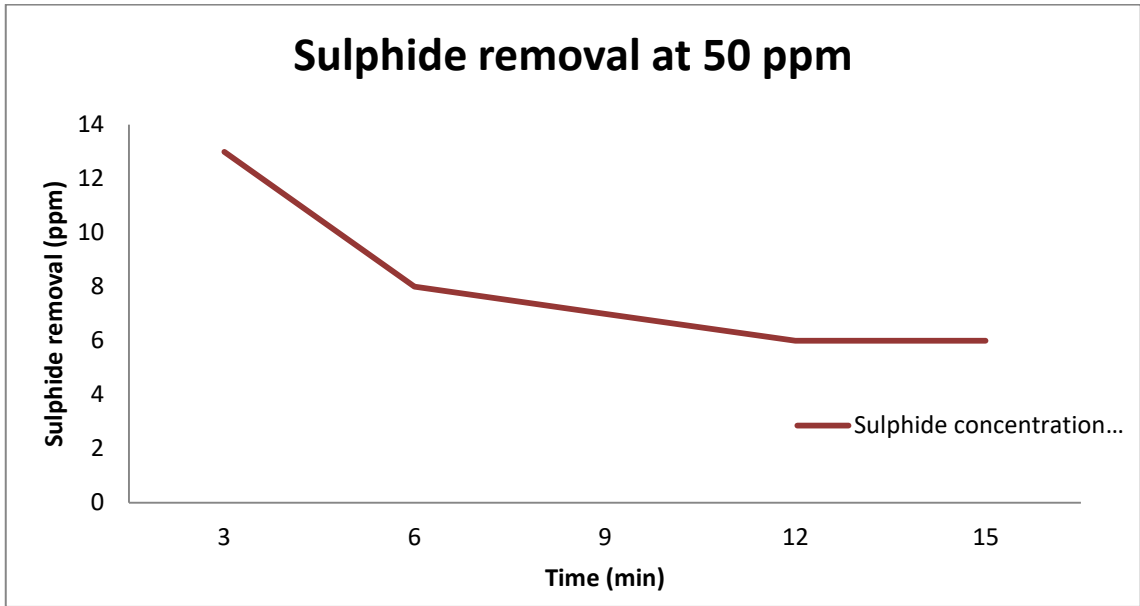


Figure 4-27: Sulphide removal at 50 ppm using sample from MTBE after Ozonolysis treatment

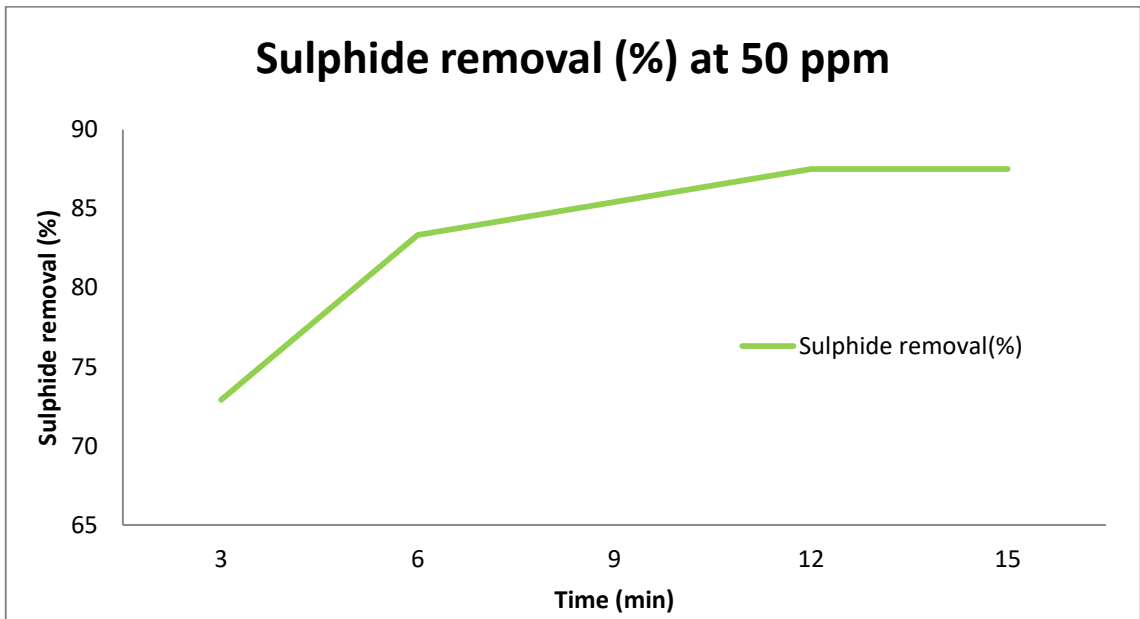


Figure 4-28: Sulphide removal (%) at 50 ppm using sample from MTBE after Ozonolysis treatment

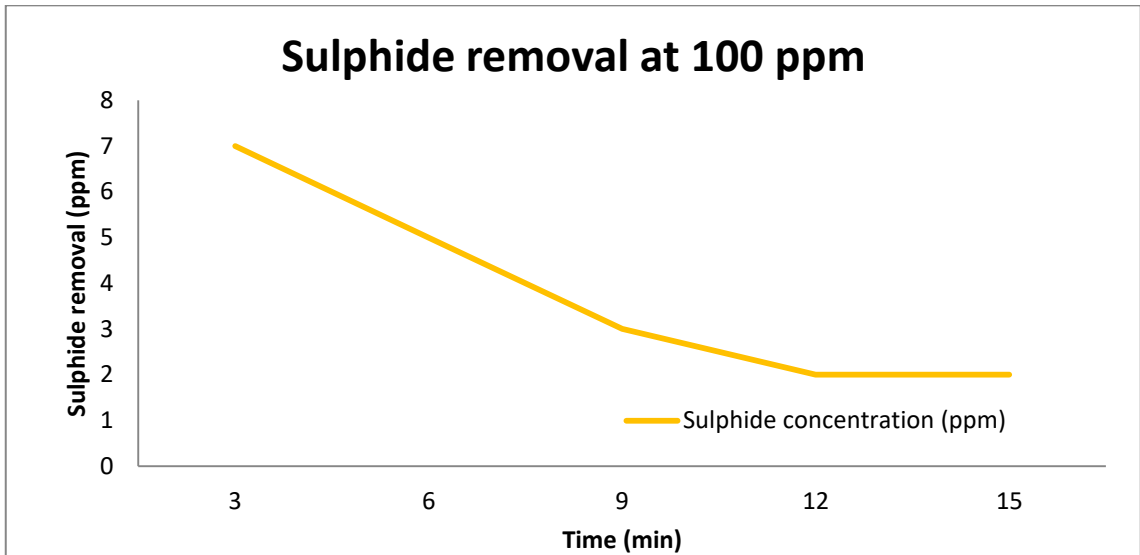


Figure 4-29: Sulphide removal at 100 ppm using sample from MTBE after Ozonolysis treatment

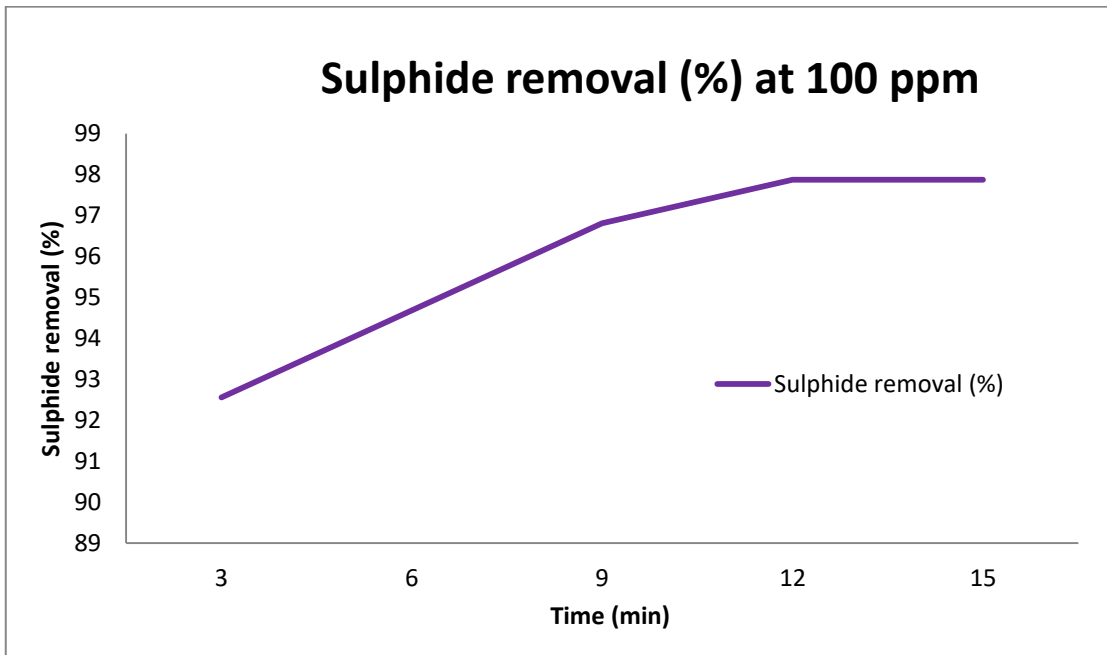


Figure 4-30: Sulphide removal (%) at 100 ppm using sample from MTBE after Ozonolysis treatment

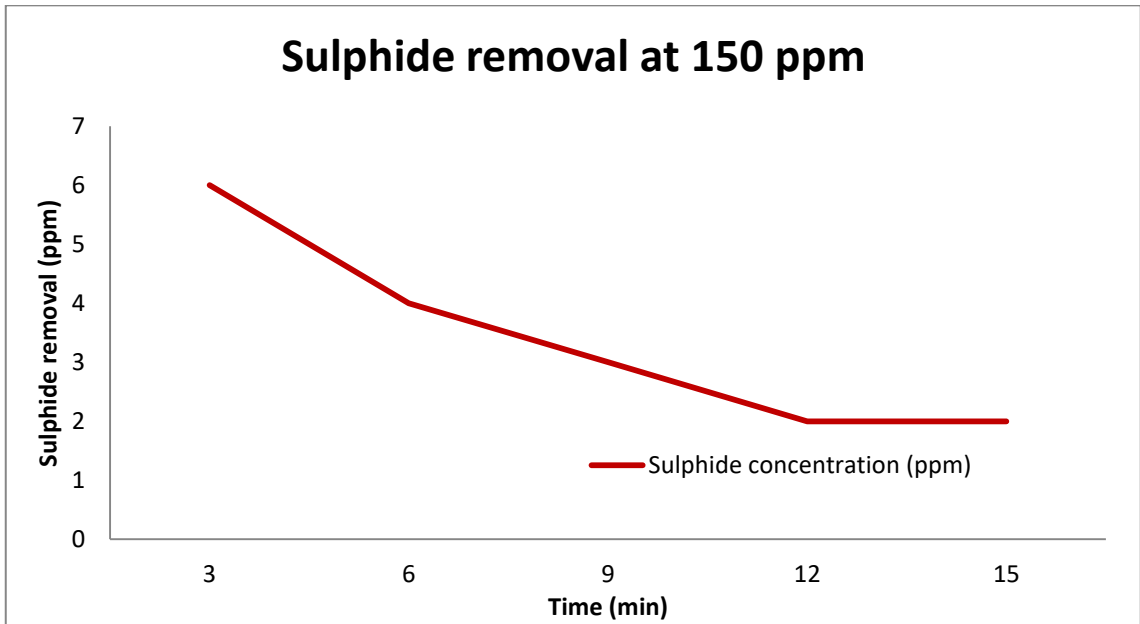


Figure 4-31: Sulphide removal at 150 ppm using sample from MTBE after Ozonolysis treatment

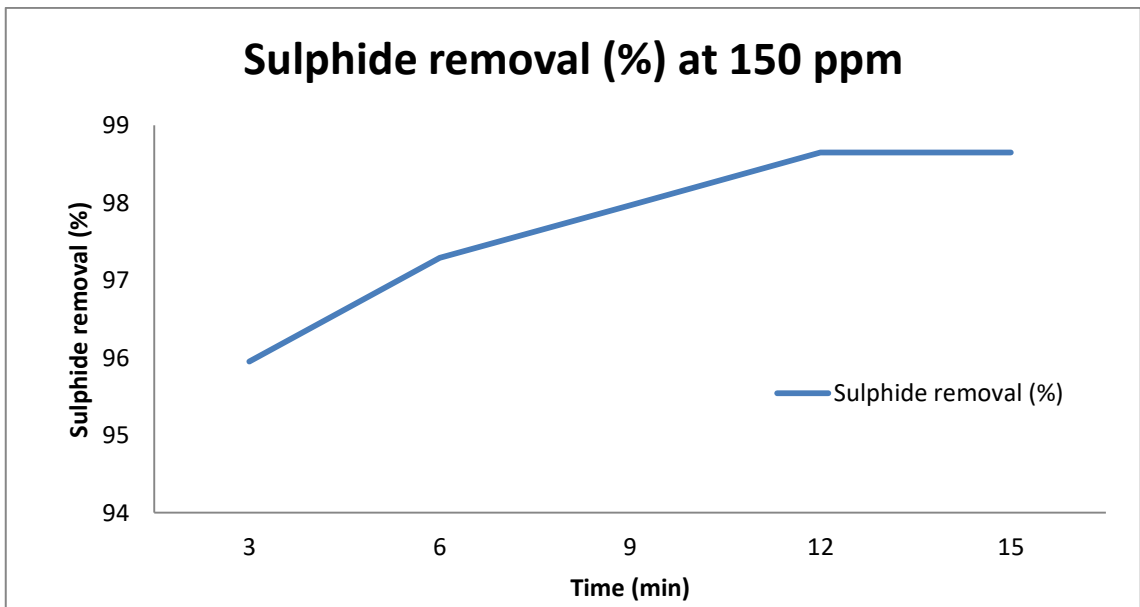


Figure 4-32: Sulphide removal (%) at 150 ppm using sample from MTBE after Ozonolysis treatment

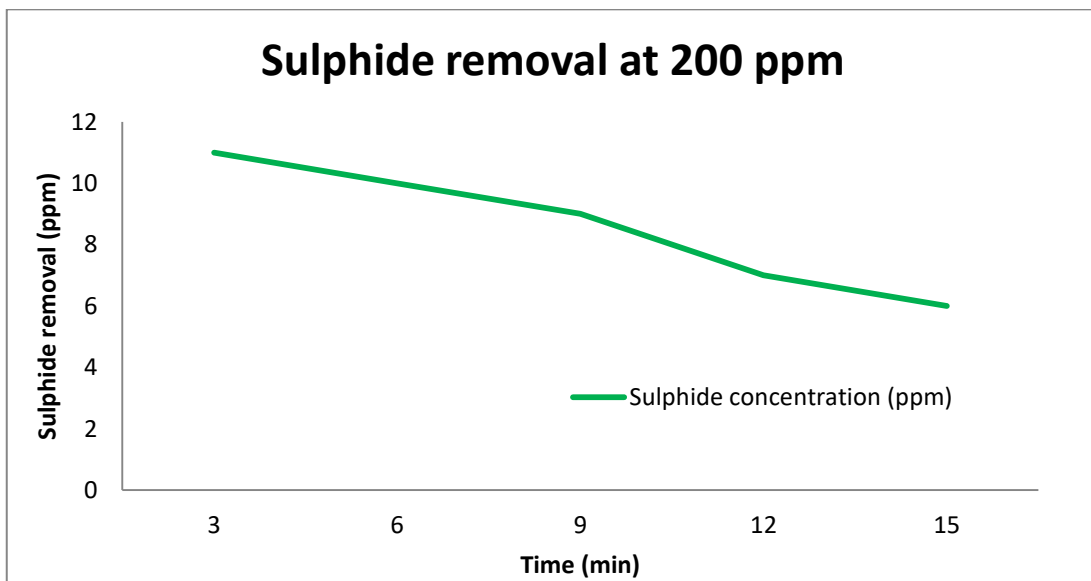


Figure 4-33: Sulphide removal at 200 ppm using sample from MTBE after Ozonolysis treatment

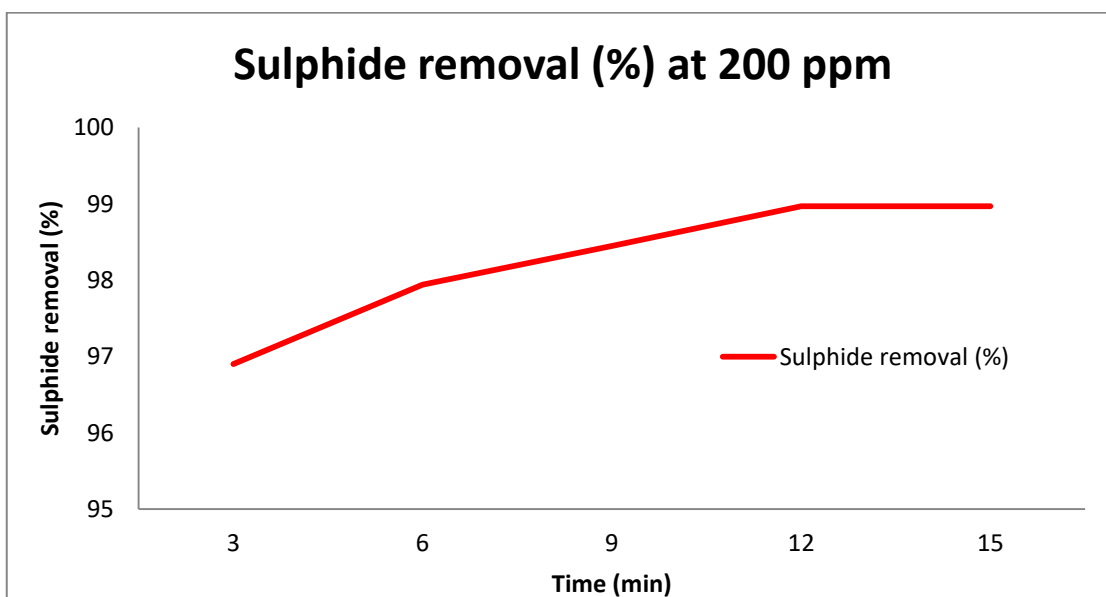


Figure 4-34: Sulphide removal (%) at 200 ppm using sample from MTBE after Ozonolysis treatment

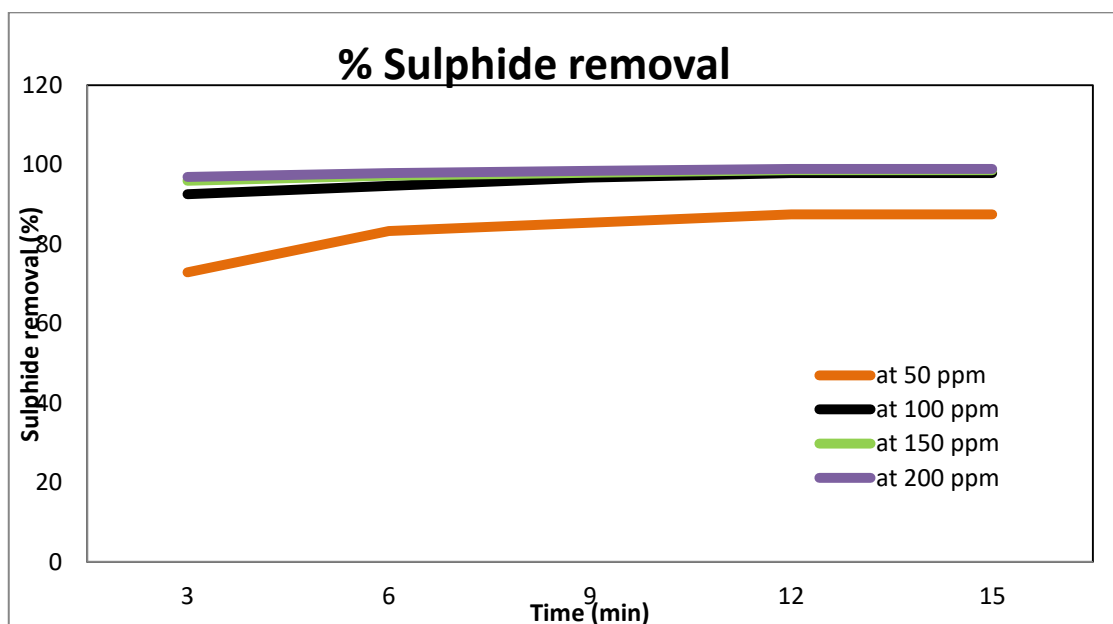
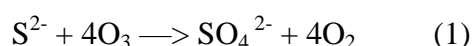


Figure 4-35: Sulphide removal (%) at overall concentration (ppm) using sample from MTBE after Ozonolysis treatment

From the Figure 4-36, Figure 4-37, Figure 4-38, and Figure 4-39 it shows the reduction of sulphide after Ozonolysis treatment at different concentration within 15 minutes. At 50 ppm until 200ppm, the reductions of sulphide were constant after 12 minutes of reactions. During ozone treatment, the reaction of ozone with simple oxidizable ions such as S^{2-} to form oxyanions such as SO_3^{2-} and SO_4^{2-} (Overbeck, 2010). The reaction of ozone with sulphide ion during treatment as shown in equation 1 below:



Ozone reacts rapidly with organic compound that have multiple bonds (C=C, N=N) and with ions such as S^{2-} to form oxyanions such as SO_3^{2-} and SO_4^{2-} . It does not react rapidly with singly bonded organic structures such as C-O or C-C. (R.L Crawford, T.F.Hess, and Paszczynski, 2008). After 3 minutes of reaction, the percentage removals of Sulphide for all concentration as shown in Figure 4-40, Figure 4-41, Figure 4-42, and Figure 4-43 were exceeds 70% of removal. After reaction completed within 15 minutes, at 50 ppm the percentage of removal was increased rapidly from 72.92% reached up until 88%. At 100 ppm, percentage of sulphide removal was from 92.56% up to 97.87% of removal. Same goes at 150ppm and 200 ppm, the percentage removal increased

dramatically until 98.65% and 98.97% respectively. From Figure 4-44 , the trend shows that increased of concentration will increase the percentage removal of sulphide. The highest percentage removal when used sample from MTBE inside the treatment of ozonolysis will give the highest percentage removal at 98.97% which were almost 100% removal.

In conclusion, in Ozonolysis, it shows that the best quality of sample was sample from MTBE compared than sulphide solution itself. Both of the samples were run at same condition, where is the ozone injection was 10%, the volume of the samples were 0.8L and the time for the running experiment were constant within 15 minutes to determine the sulphide removal. From the results had obtained, at 200ppm, it shows that only 48.48% of sulphide removal was achieved when using the sulphide solution compared than sample from MTBE, it can achieved 98.97% of sulphide removal where is the value had almost reached 100% of removal.

4.5 Ozonolysis by using sample wastewater from MTBE (COD removal)

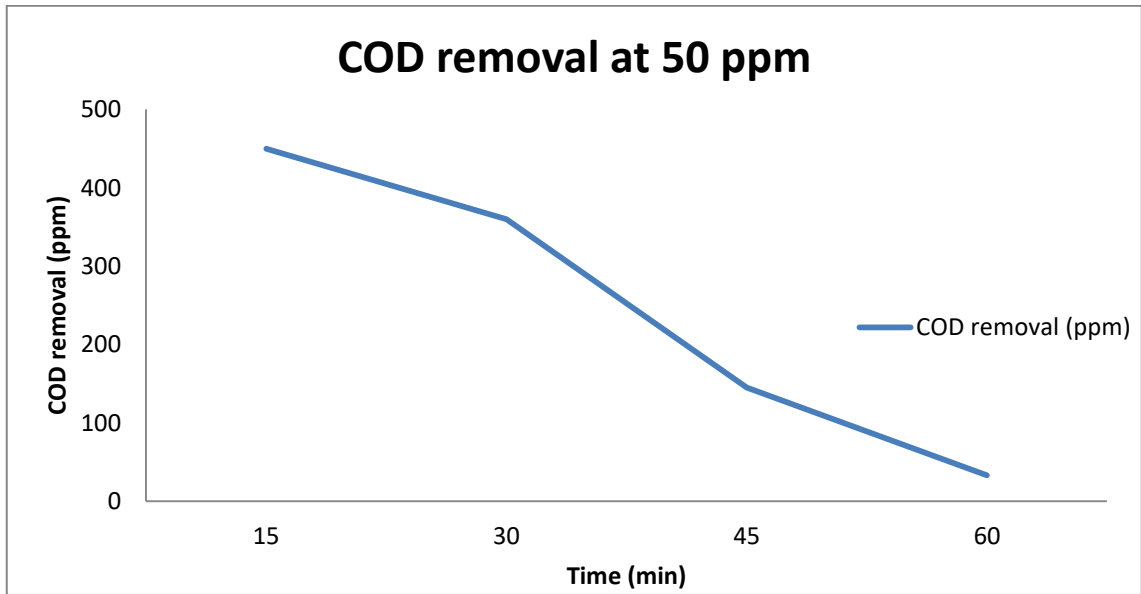


Figure 4-45: COD removal at 50 ppm using sample from MTBE after Ozonolysis treatment

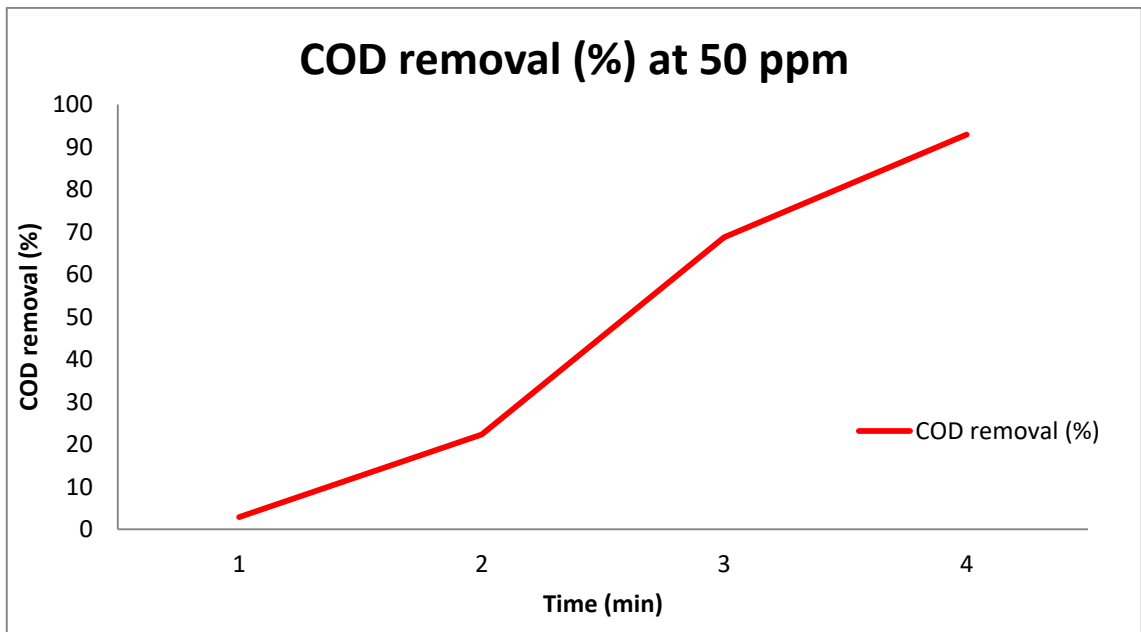


Figure 4-46: COD removal (%) at 50 ppm using sample from MTBE after Ozonolysis treatment

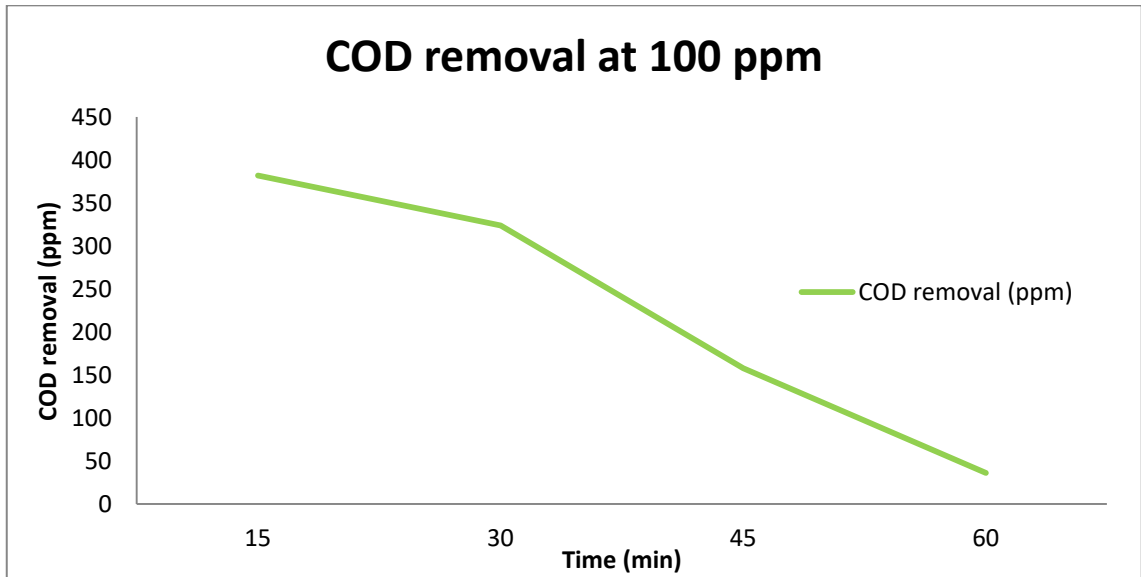


Figure 4-47: COD removal at 100 ppm using sample from MTBE after Ozonolysis treatment

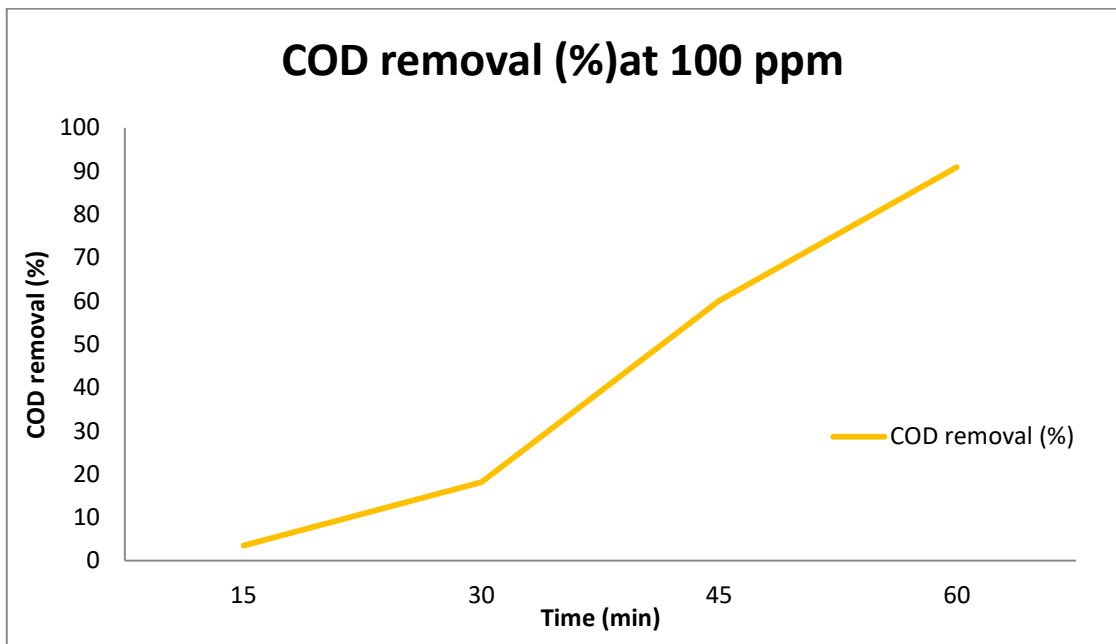


Figure 4-48: COD removal (%) at 100 ppm using sample from MTBE after Ozonolysis treatment

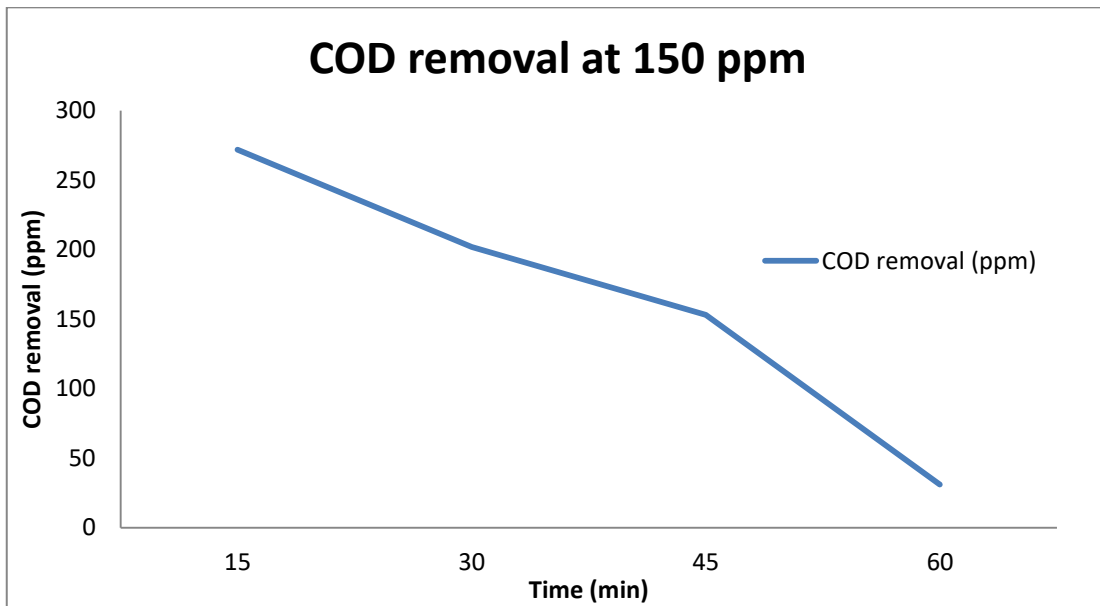


Figure 4-49: COD removal at 150 ppm using sample from MTBE after Ozonolysis treatment

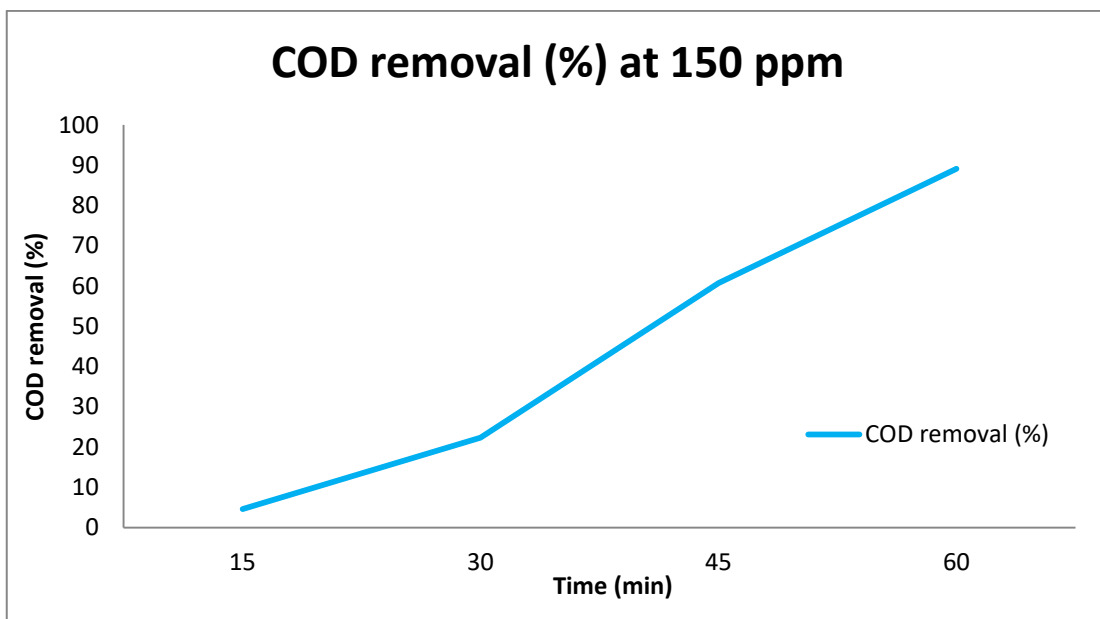


Figure 4-50: COD removal (%) at 150 ppm using sample from MTBE after Ozonolysis treatment

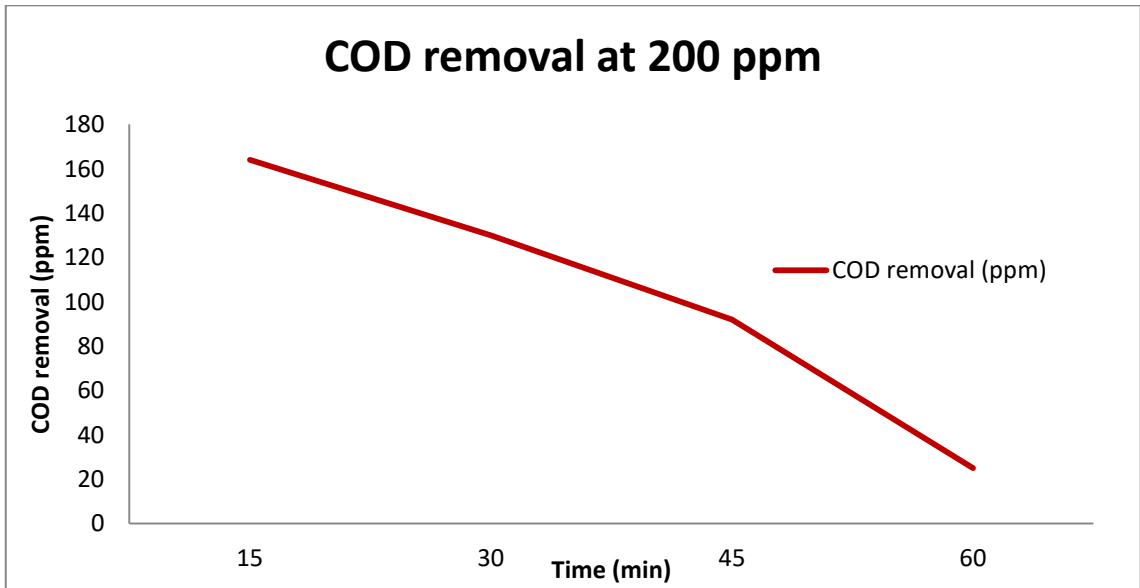


Figure 4-51: COD removal at 200 ppm using sample from MTBE after Ozonolysis treatment

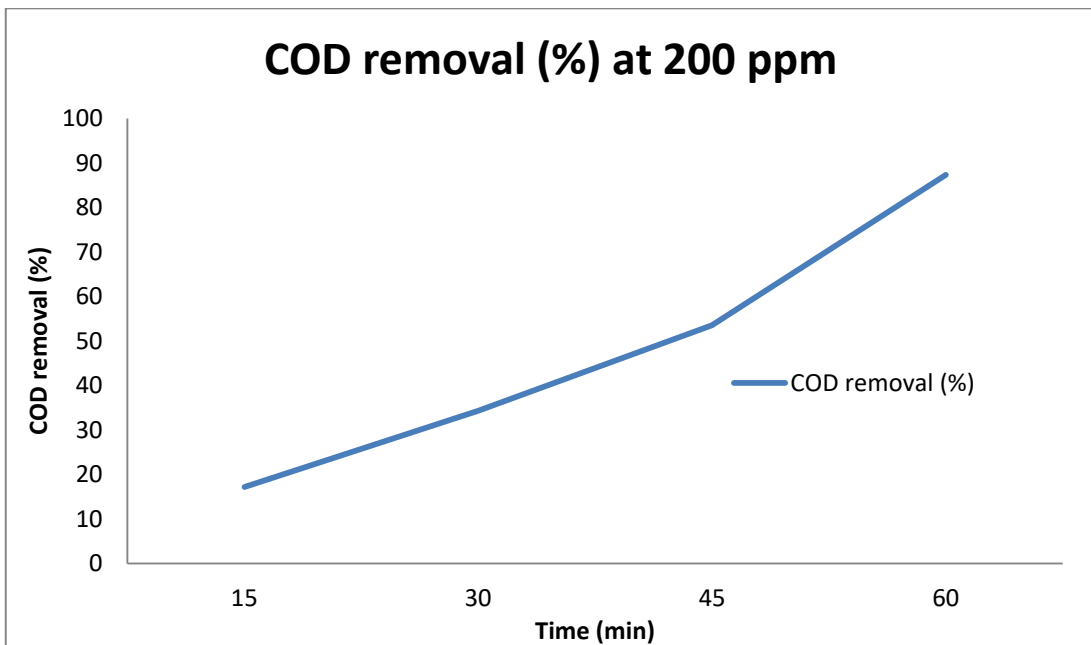


Figure 4-52: COD removal (%) at 200 ppm using sample from MTBE after Ozonolysis treatment

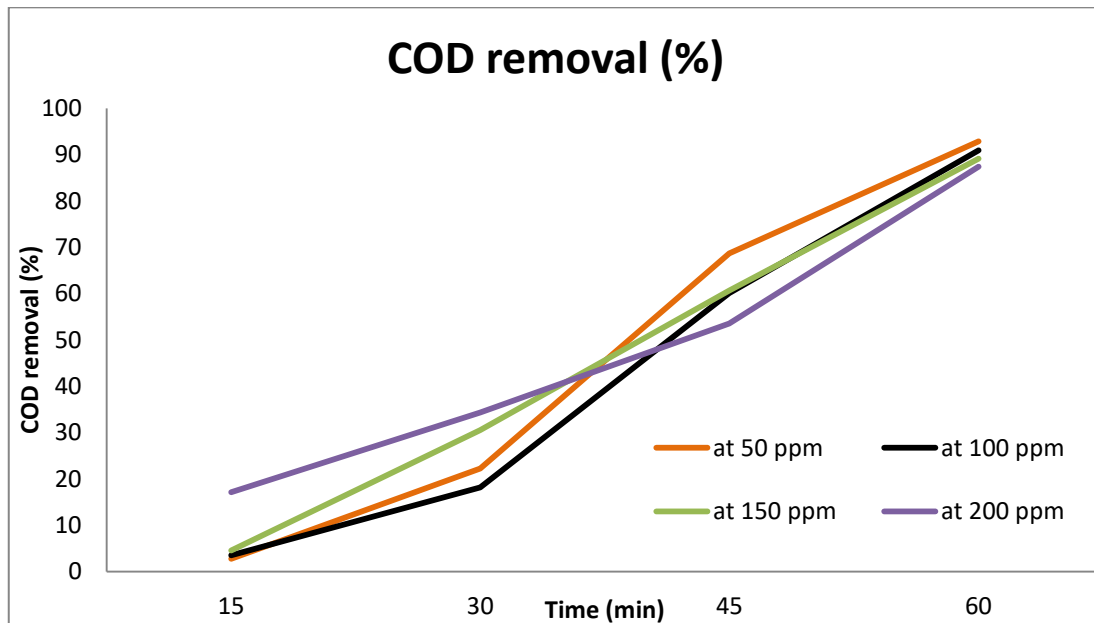


Figure 4-53: COD removal (%) at overall concentration (ppm) using sample from MTBE after Ozonolysis treatment

From the Figure 4-54, Figure 4-55, Figure 4-56, and Figure 4-57, it shows the trends of COD removal at different concentration which were at (50, 100, 150, and 150) ppm. All the concentration undergo treatment of ozonolysis, and the samples were tooks after 15 minutes for 1 hour to determine COD removal. At 50ppm, the pH was increased from 6.45pH to 7.99pH after the process. During 30 minutes of reaction, at 50ppm, percentage removal of COD as shown in Figure 6.1 was 22.25%. From the (Dogruel, S. Genceli, E.A, Babuna, F.G, and Orhon.D, 2006), percentage of COD removal was 20% after 30 minutes of reaction. From Figure 4-58, when compared at all the concentration, it can be concluded that within 30 minutes of reaction, percentage of COD removal were in range 20%30% of removal. Besides, when increased the concentration at influent, the trends for COD removal for complete 1 hour of reaction, has slightly decreased from 92.87% to 87.37% to the high concentrated of solution. In alkaline conditions, ozone decomposition leads to the formation of °OH-radicals, the combinations of radicals and molecules effects of ozone is efficient and economical. It shows the reduction of COD can achieved up to 60% .

4.6 Electrocoagulation reaction process

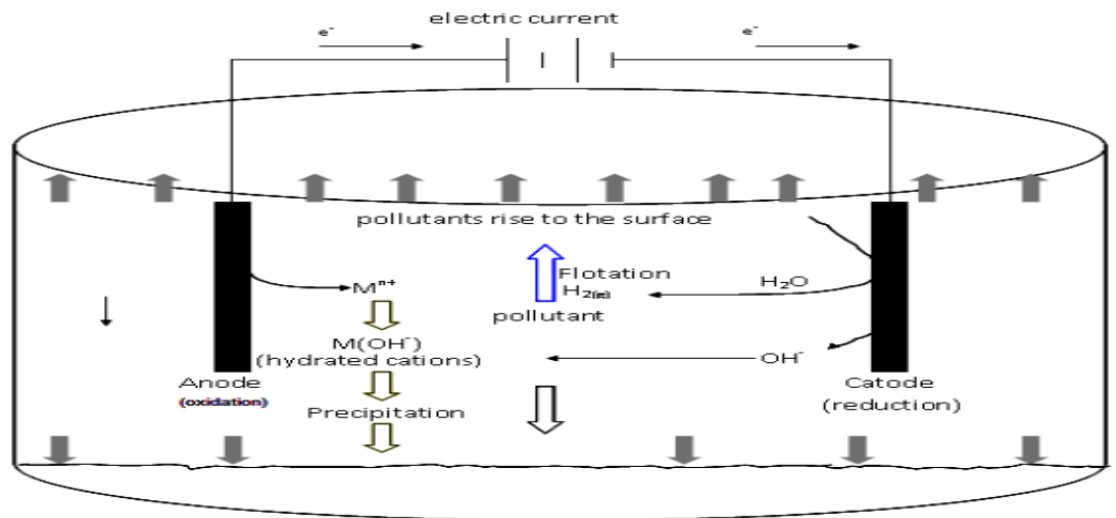


Figure 4-59: Schematic diagram of an electrocoagulation cell with two electrodes.

(Mollah M Y A et al, 2004)

4.7 Electrocoagulation by using sample from MTBE (Monopolar – Parallel for sulphide removal)

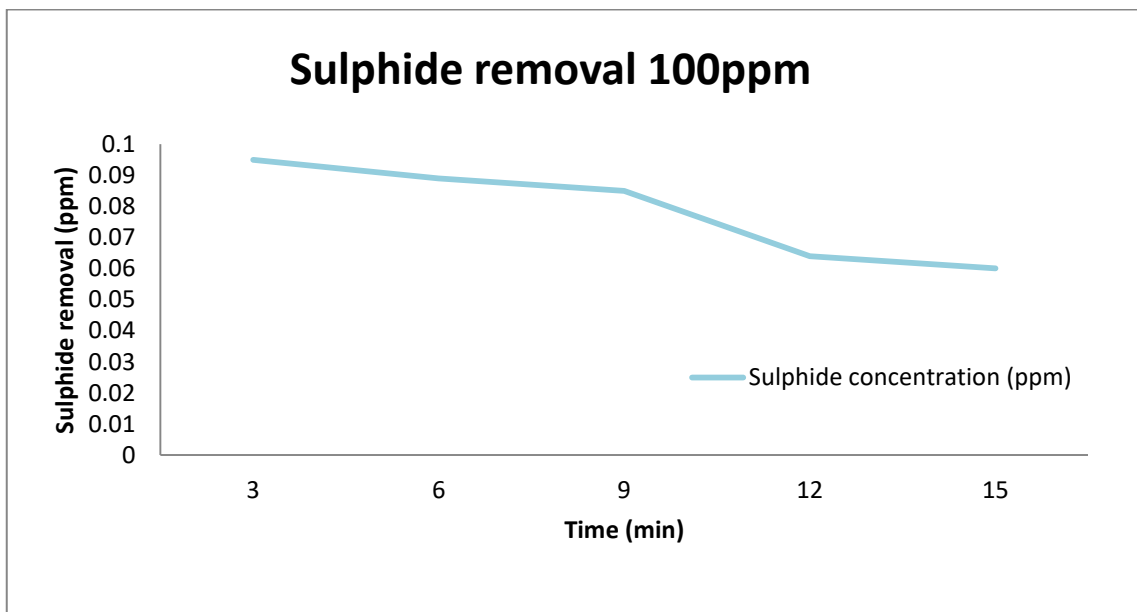


Figure 4-60: Sulphide removal by using sample from MTBE after EC (monopolar)

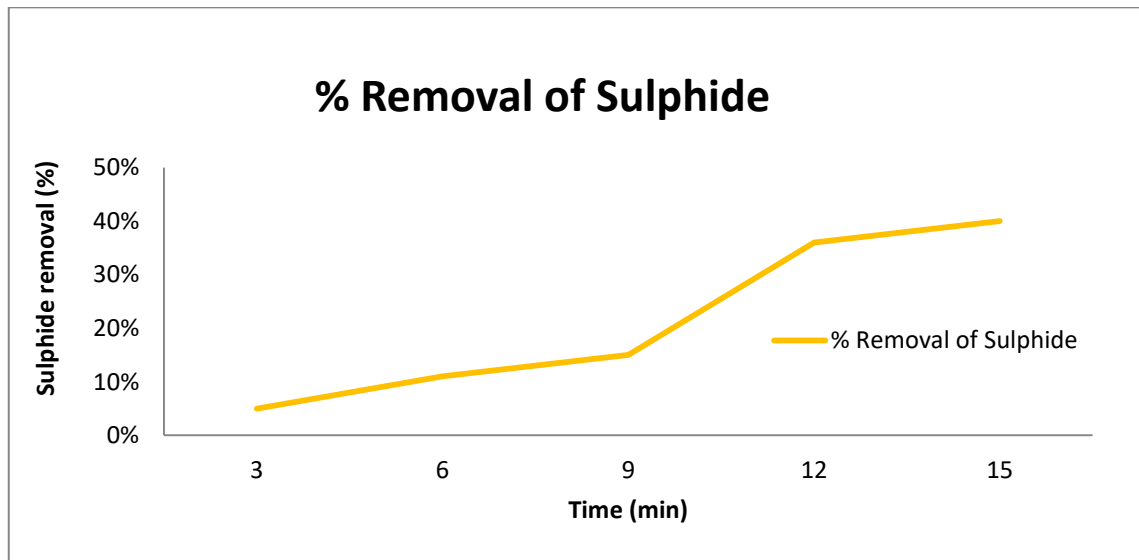
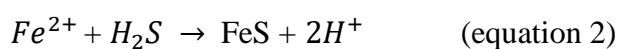


Figure 4-61: Sulphide removal (%) using sample from MTBE after EC (monopolar)

From the Figure 4-62 and Figure 4-63 above, the trend shows the reduction and percentage of sulphide inside the MTBE solution after EC treatment. pH of sample was 7.85 before treatment of EC and it was in the neutral region. The initial pH must be in the neutral region in order to perform the EC treatment. When the initial pH were in the acidic region, therefore pH were increased rapidly such that the value was greater than 8-9 pH at the end of reaction (Dermentzis, 2016).

After treatment of EC, pH sample from MTBE solutions were increased slightly from 7.10 to 7.85 within 15 minutes. pH of the effluent slightly changes when the initial pH values was in the range of 6-8 pH due to the effect of pH buffering during the treatment. Major contribution of increased in pH were formation of $Fe(OH)_2$ at the anode electrode under the alkaline conditions. (Chen,2004). Moreover, at the cathode, finest and smallest bubbles were formed at the neutral condition (Kabdashi, I.Arslan-Alaton, T.Olmez-Hanci and O.Tunay., 2012). The pH of samples were not changed markedly because of the cathodically produced OH^- ions combines with the anodically produced Fe^{2+} and Fe^{3+} ions and precipitate as insoluble metal hydroxide (Dermentzis, 2016). The reaction equation of the precipitation as shown in equation below:



4.8 Electrocoagulation by using sample from MTBE (Bipolar – Parallel for Sulphide removal)

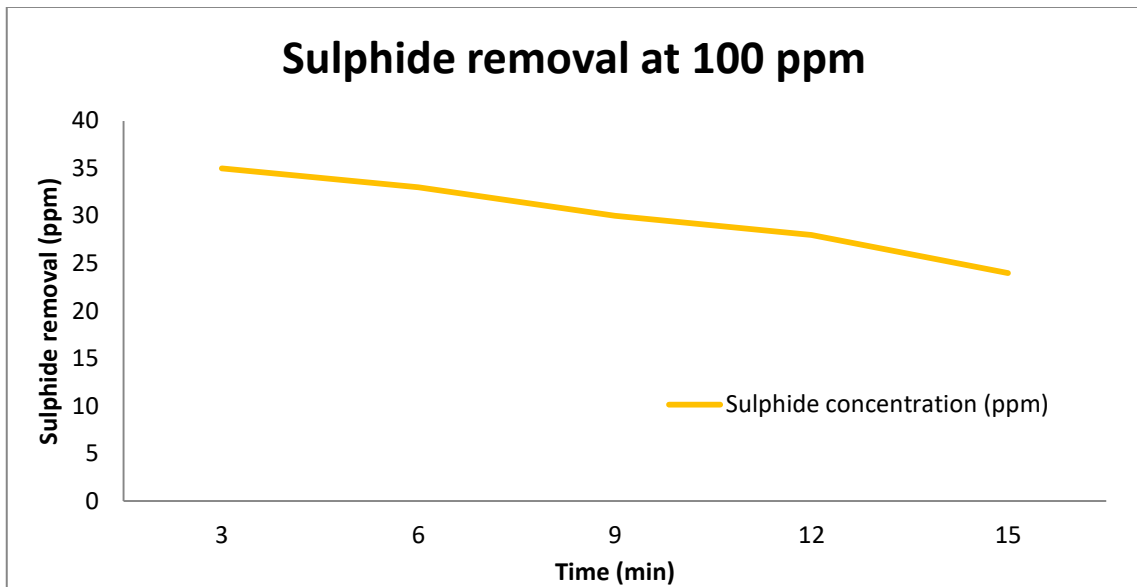


Figure 4-64: Sulphide removal by using sample from MTBE after EC (bipolar)

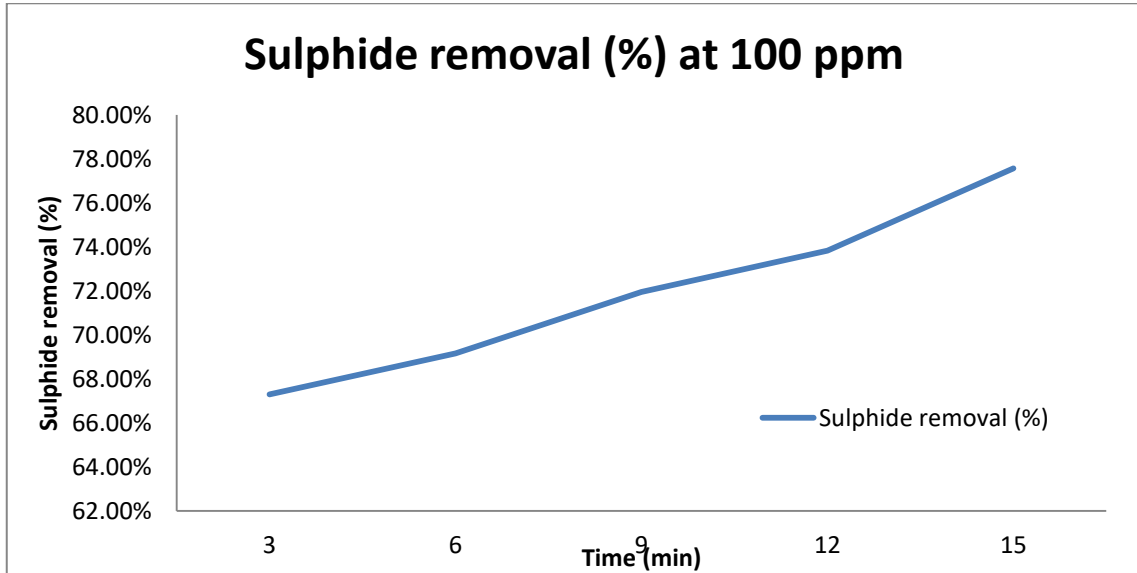
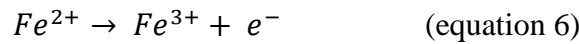
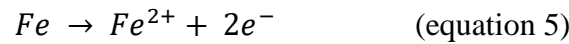


Figure 4-65: Sulphide removal (%) using sample from MTBE after EC (bipolar)

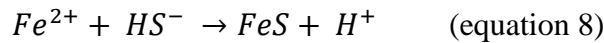
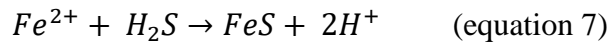
From the Figure 4-66 above, it shows Sulphide concentration of the sample of MTBE solution after EC treatment by arrangement of electrode in bipolar condition. Initially, sulphide concentration was 100ppm. After undergo EC treatment for 15 minutes, the concentration of sulphide was decreases from 100ppm to 24 ppm.

Therefore, the percentage of sulphide removal as shown in Figure 4-67 in bipolar arrangement is increases from 67.29% to 77.57%. Larger percentage removals of sulphide were affected by sacrificial of iron electrodes that were refer to bipolar arrangement of electrode (Sengil I.A, Kulac.S, Ocazar.M, 2009).

During the treatment, the color of the solution became pale after electrocoagulation. The colority changes during electrocoagulation treatment are shown in Figure below. Depending on the pH, sulfide exists as H_2S , HS^- and S^{2-} . Because of the dissolving of the metal on the surface of the electrodes, in the case of Iron electrodes, Fe^{2+} was released into the liquor (equation 5) and converted to Fe^{3+} partly for the oxidation of the electrode or in the circumstance of oxidation (equation 6).



As a result of the reaction between Fe^{2+} , Fe^{3+} and H_2S , HS^- , S^{2-} species, black color FeS precipitate which was insoluble appeared and the color of the liquor became dark quickly, the concentration of sulfide dropped rapidly (equation 7, 8, 9) (Muruganathan et al., 2004a).



Furthermore, sulfide could be also partially oxidized by Fe^{3+} . Precipitates of ferric hydroxides formed were converted to FeS by sulfide ions by reductive dissolution mechanism (Poulton et al., 2002). According to the literature (Muruganathan M, Raju G B, Prabhakar S., 2004), the species pyrite, marcasite, elemental sulfur and FeS_2 could also be detected.

4.9 Electrocoagulation by using sample from MTBE (Monopolar – Parallel for COD removal)

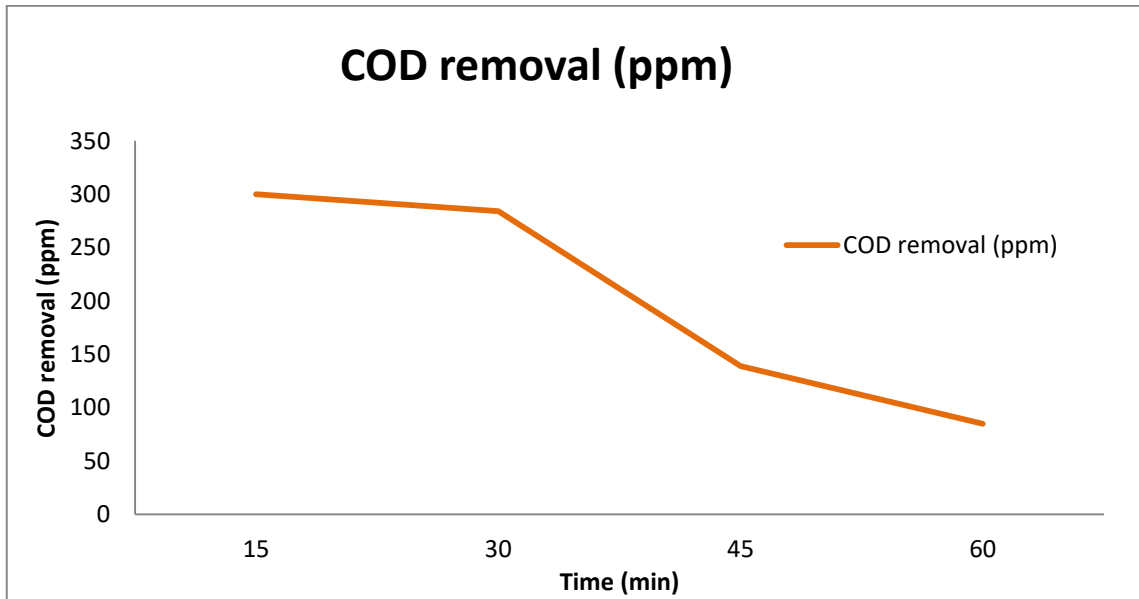


Figure 4-68: COD removal (ppm) by using sample from MTBE after EC

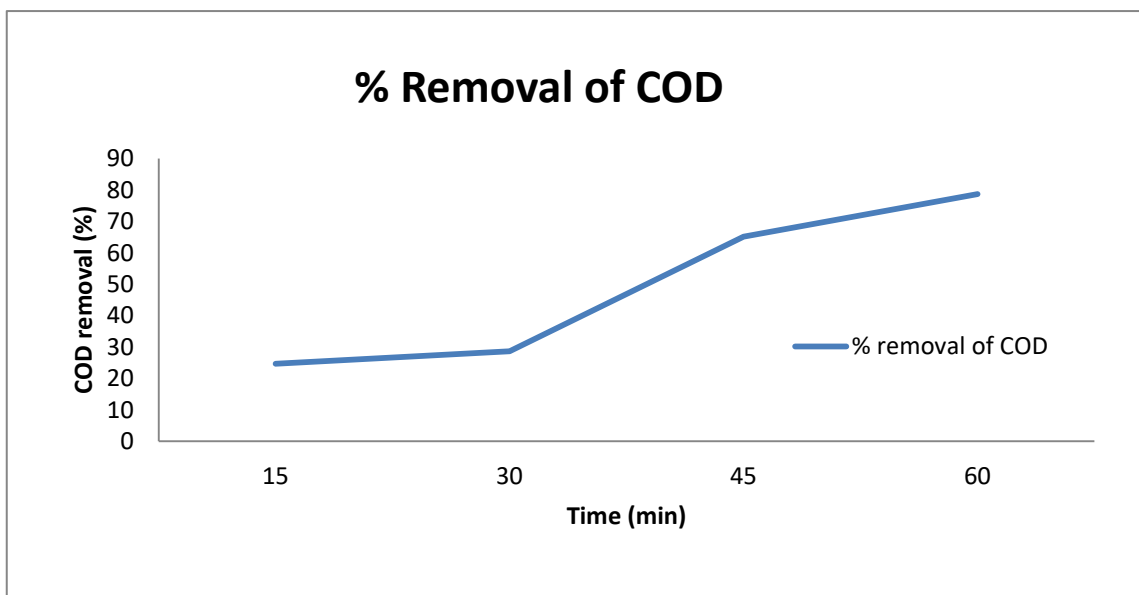


Figure 4-69: COD removal (%) by using sample from MTBE after EC treatment

Table 4-1: Mass of electrode (Monopolar - Parralel)

Type of electrode	Mass before EC (g)	Mass after EC (g)	Mass loss (g)
Anode	255.7	225.0	0.7
Cathode	221.1	221.1	0.0



Picture 1: Weight of corrodes or deposited inside the solution = 7.021 g

From the Figure 4-70 above, COD value is determined in the 100ppm concentration of the sulphide. COD value at the influent was at 398 ppm. After the EC treatments for 1 hour, COD value were decreased rapidly from 398ppm to 85 ppm, thus it shows that the percentages of COD removal as shown Figure 4-71 were increased from 24.62% to 78.64%. During 30 minutes of reaction, COD removal was increased slowly from 24.62% to 28.64%. At this time, production of OH⁻ was lower. After 1 hour, the COD removal had achieved the maximum reduction where is at 78.64%, compared from the (Abbas, 2013), the maximum COD removal was obtained at 77.3%. Based on the table above, it shows the mass of electrode for both anode and cathode before and after the EC process. it can be concluded that, only 0.7 g weight loss of electrode and the amount of deposited (Picture 1) inside the solution after filtration process was 7.021g.

4.10 Electrocoagulation by using sample from MTBE (Bipolar – Parallel for COD removal)

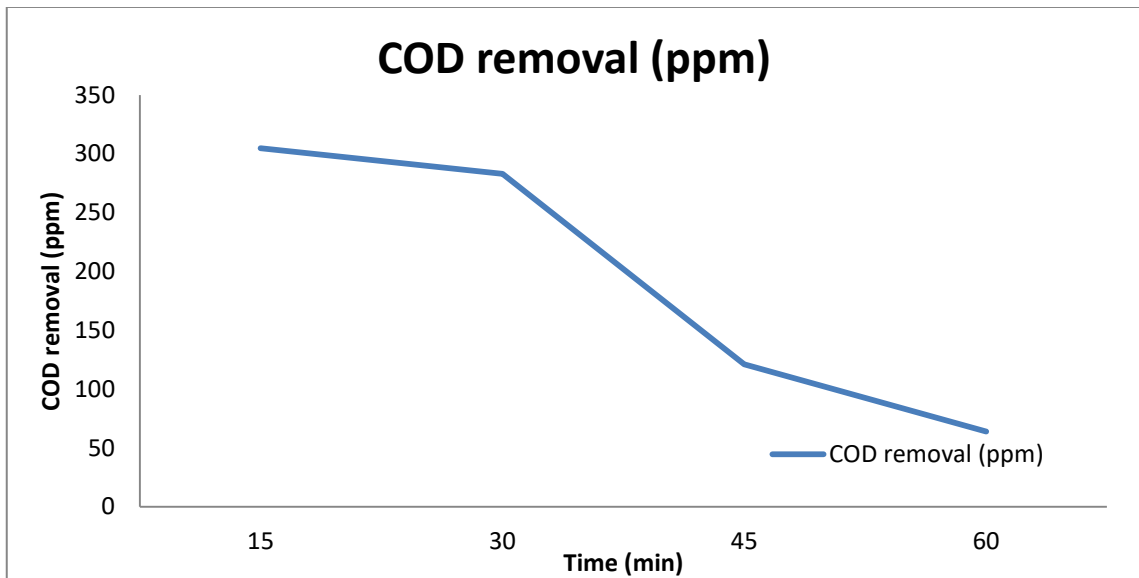


Figure 4-72: COD removal (ppm) using sample from MTBE after EC (bipolar)

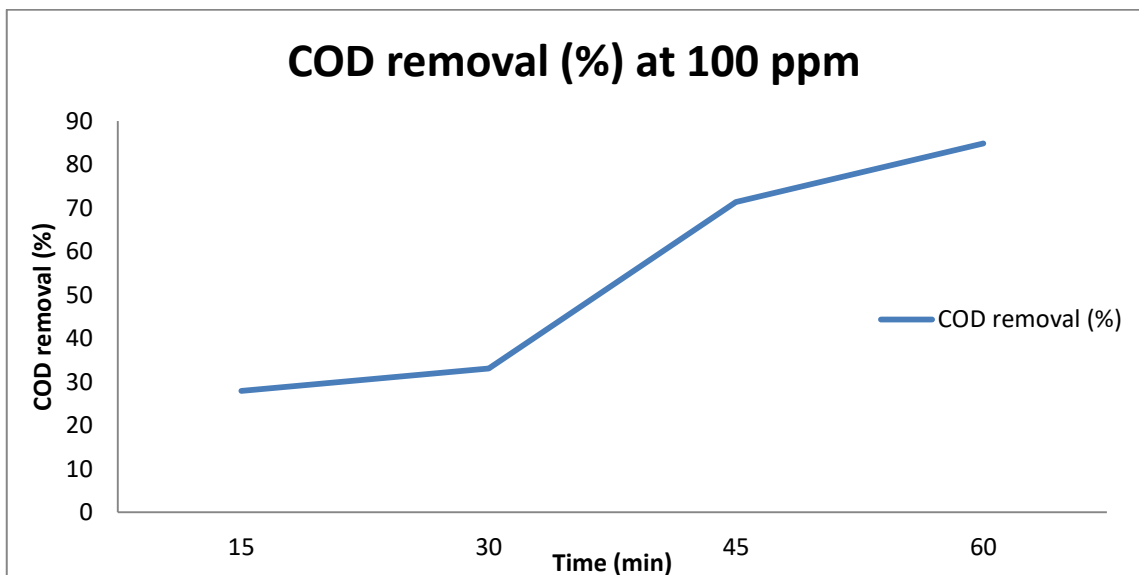


Figure 4-73: COD removal (%) using sample from MTBE after EC (bipolar)

Table 4-2: Mass of electrode (Bipolar - Parallel)

Type of electrode	Mass before EC (g)	Mass after EC (g)	Mass loss (g)
Anode	255.0	223.9	1.1
Cathode	221.1	221.1	0.0



Picture 2: Weight of corrodes or deposited inside the solution = 10.883g

From the Figure 4-74 above, it shows the trend of percentage removal of COD by using EC treatment in bipolar arrangements was increased time to time. Initially, before treatment of EC, value of COD was 424ppm, and its shows reduction when increased of time where is the value of COD reduced to 64 ppm. Thus, its shows the percentage removal of COD at the final treatment for 1 hour was reached 84.87% Figure 4-75. From (Abbas, 2013), the maximum COD removal value is 77.3% was obtained with Iron electrodes. Iron (Fe^{2+} or Fe^{3+}) reacted with metallic hydroxides (OH^-) in solution to produce $\text{Fe}(\text{OH})_2$. $\text{Fe}(\text{OH})_2$ have large surface areas that are beneficial for rapid adsorption of organic compounds and trapping of colloidal particles. The gas bubbles (H_2 and O_2) produced at the cathode and anode enhanced the removal efficiency in EC processes. (Asselin, 2008). From the result had obtained, the mass loss of electrode was 1.1g and the amount of precipitation by using bipolar electrode was 10.822g. The EC technique has been observed to be more effective for the removal of COD than the conventional coagulation and sedimentation processes.

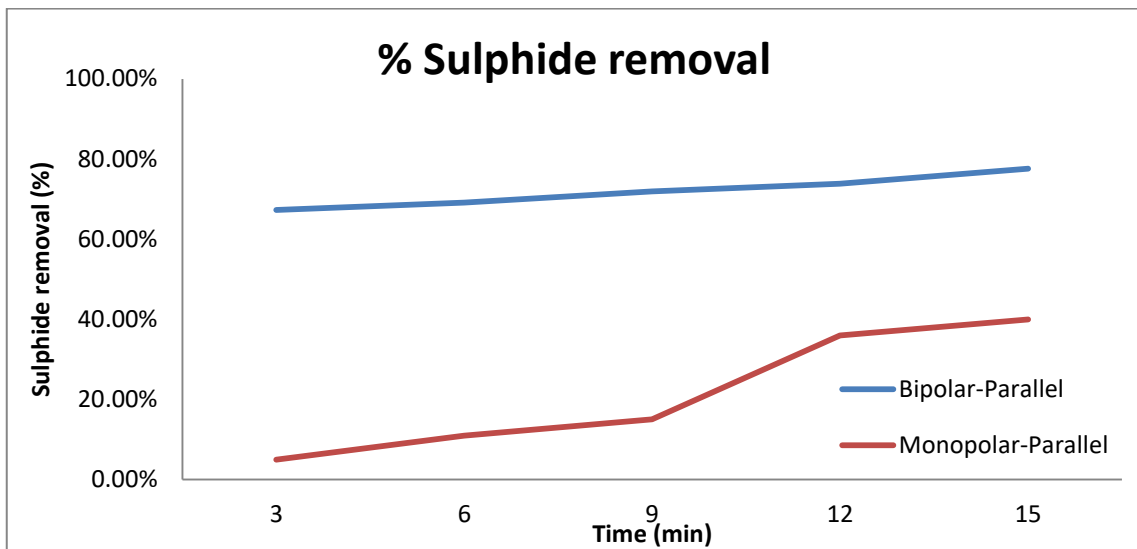


Figure 4-76: Sulphide removal (%) in EC treatment for monopolar and bipolar arrangement

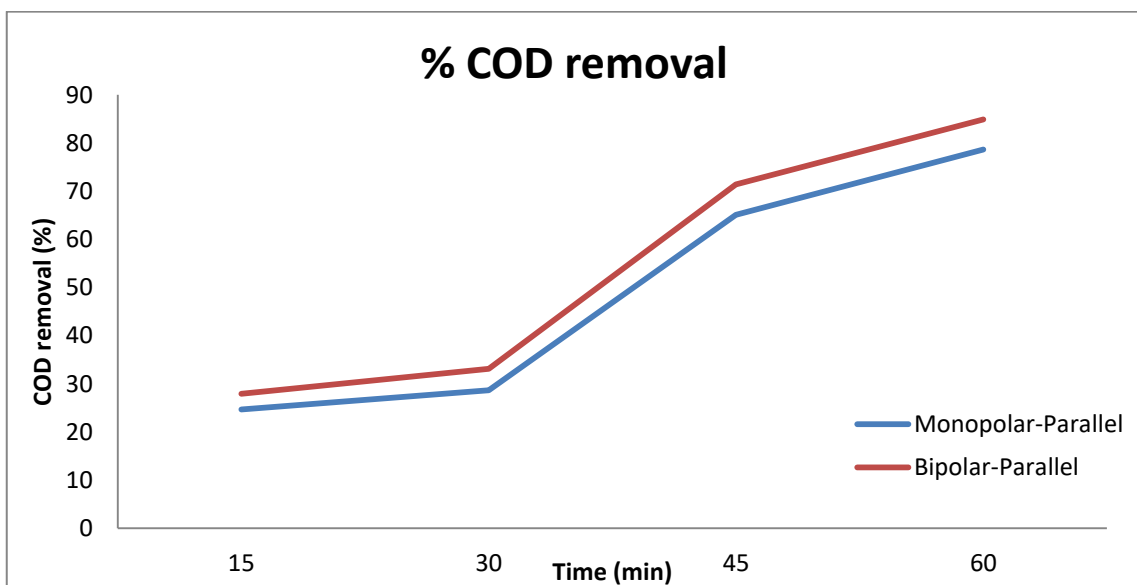


Figure 4-77: COD removal (%) in EC treatment for monopolar and bipolar arrangement

In conclusion, the arrangement of electrode in bipolar arrangements shows the best condition to conduct the experiment of Electrocoagulation. From the result had obtained, refer to Figure 4-78 it shows that the percentage removal of sulphide had achieved 77.57% compared to monopolar arrangement, only 40% of sulphide can be removed. It is because, in the bipolar arrangement, it has sacrificial electrode that consist of iron electrode, that contributed to the production of hydroxide ions that gives

effect to the higher of pH, large amount of Ferrous Sulphide obtained and lastly, large amount of precipitate that can be formed inside the dissolution. In terms of COD removal, compared to journal that had obtained, (Abbas, 2013), the maximum value of COD removal was 77.3%. In this experiment, from Figure 4-79, both of the arrangement does not give large difference, since the highest percentage of COD removal for both were 78.64% and 84.87% respectively.

In the journal, the current used was at 0.6A, while in this experiment, instead of 0.6A, the current used was at 1.0A. It can be concluded that, the higher the current supply, the higher the COD removal can be obtained (Dermentzis, 2016). In terms of mass loss of electrode, in the bipolar arrangement, it shows the higher removal of weight loss which are 1.1g compared than monopolar only 0.7g. Besides, the amount of precipitation inside the solution of MTBE during EC in bipolar arrangement also show the larger amount which is 10.883g compared than monopolar only 7.012g. it can be summarized that, bipolar arrangement has high efficiency on EC process. Therefore, EC technique has been observed to be more effective for the removal of COD than the conventional coagulation and sedimentation processes. (A. K. Chopra, Arun Kumar Sharma*, 2013)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, the best quality of sample was proved by the sample from MTBE compared to the sulphide solution. In ozonolysis treatment, sample from MTBE shows the higher efficiency in the removal of Sulphide where it had achieved until 97.87% compared than sulphide solution only 42.86% of removal. Both of samples were conducted at the same injection of ozone which were 10% and the time interval within 15 minutes. In terms of COD removal, sample from MTBE shows 90.91% of removal within 60 minutes of reaction. To explain why there is no 100% of COD removal, it is necessary to remember that degradation process that involved oxidants, despite their high reactivity and low selectivity, normally also produce refractory final products (Gonzalez-Rivas, 2015).

In electrocoagulation process, bipolar arrangements show the best type of condition to enhance the removal of Sulphide and COD removal. From the results obtained, it shows that, 77.57% sulphide removal was achieved compared than monopolar only 40% of removal. It is because in the bipolar arrangement, it has sacrificial of iron electrodes that contributed to the high amounts of hydroxyl ions to produce at the cathode, at the same time increased the pH of solution. Besides, the fines and smallest bubbles also were formed at the cathode thus it increased the efficiency to remove the colloidal or coagulant particles from the solution. From , they said the maximum removal of COD was 77.3% at 0.6A. in this experiment, COD removal for both arrangements does not shows large difference where is in monopolar, it had achieved 78.64% while in bipolar was 84.87% at current of 1.0A. Thus, it can be concluded that, increased of current, will increased the COD removal in the EC process.

5.2 Recommendation

There are some precautions need to take in consideration in order to get the best result in the experiment. Before doing the Electrocoagulation treatment, iron electrode at anode and cathode must be rub with sandpaper and rinsed with distilled water in order to enhance the efficiency of the process and avoid the other impurities that will affect the treatment. While doing the EC treatment, make sure that the wire connection at anode and cathode does not touch with others because it will lead to the wire short of the EC generator. The fuse inside the generator will be damage. After the EC treatment, the electrode that had been used must be weight and then enter the oven in order to dried the moisture content, then the electrode was weighed again in order to determine the mass loss of electrode. Besides, the solution must be filtered first in order to identify the amount of precipitate inside the solution. Meanwhile, in ozonolysis treatment, make sure the injection of ozone is not too high. In terms of determination of sulphide content inside the sample solution, the solution of sample will be turn into to colour of light blue to ensure the presence of sulphide after Sulphide Reagent 1 and Sulphide Reagent 2 was added. Overall, the EC treatment and ozonolysis must worked in the fumehood area to avoid pungent smell of rotten egg if hydrogen sulphide was presence. In conclusion, to increase the percentage removal of sulphide in future, hybrid method of Electrocoagulation with Ozonolysis will give the higher removal in shorten time is recommended.

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APPENDIX



Weight Sulphide powder
By using weighing balance



COD value adsorbance by using
Spectrophotometer



Sample solution after adding
Sulphide reagent 1



Color of Sulphide solution after
adding Sulphide Reagent 1 and 2



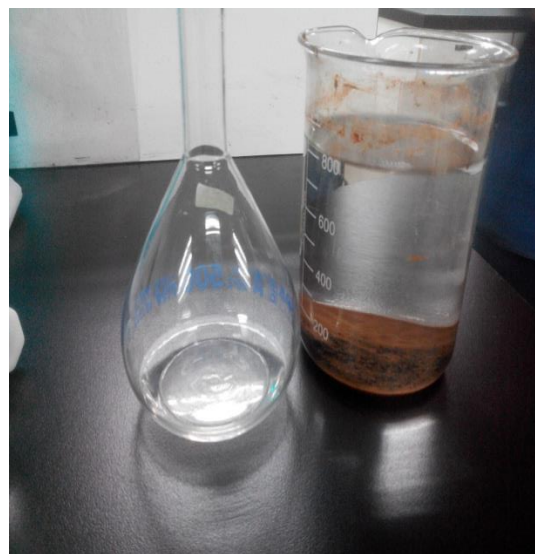
Figure 11.4: pH value determined by using pH meter



Figure 11.5: Weight of anode electrode before EC treatment



Black deposited of FeS on the anode electrode after EC treatment



Precipitation at the bottom of solution after EC treatment 1 hour



Filtration of the sample solution after EC



Sample of MTBE solution before and after EC



Sample take at regular interval time during ozonolysis