

**EFFECT OF CO_3^{2-} , HCO_3^- , and SO_4^{2-} ON THE DEGRADATION
OF PHENOL IN ELECTROCHEMICAL OXIDATION
PROCESS**

BY

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Dedication

To my Family.

*To my brother Sami who has been the
wind beneath my wings until I completed
this work.*

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THESIS ABSTRACT

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TITLE OF STUDY: Effect of CO_3^{2-} , HCO_3^- , and SO_4^{2-} On the Degradation of Phenol in Electrochemical Oxidation Process.

MAJOR FIELD: Environmental Engineering

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Historically, extensive research was conducted in the degradation of phenol using electrochemical oxidation process, which has recently achieved considerable success. However, the process has experienced some difficulties mainly due to the species present in raw water which hinder the degradation process.

The main objectives of this study are to optimize the operational parameters and to investigate the effect of chemical species, present in raw water, on the degradation of phenol using electro-chemical oxidation process. In this study, a lab-scale experimental reactor was used to carry out the electrochemical oxidation of phenol.

The results showed that at 75 ppm of phenol concentration, 45 mA/sq cm current density and 6000 ppm electrolyte (sodium chloride) were found to be the optimum operation parameters. The parameters optimization realized in this study was the main reason behind the success achieved in the phenol removal and removal enhancement in the raw water. The results of this study confirmed that only two species, namely, sodium bicarbonate and magnesium chloride hinder the phenol degradation process. In order to enhance phenol removal, 1% of Hydrogen Peroxide was added. This enhancement is due to the possible effect of the Fenton's reaction (AOP). This resulted in 25 minutes reduction in the process time. The findings of this study are expected to contribute to solving the phenol degradation problem and enhancing the environmental efforts of the removal of the industrial wastewater phenols.

ملخص الرسالة

الاسم : بشري عثمان ابراهيم محمد أحمد
عنوان الرسالة : تأثير الكربونات، البيكربونات، و الكبريتات على ازالة الفينول عن طريق عملية الأكسدة الكهروكيميائية.
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تاريخياً، أجريت العديد من الأبحاث العلمية لإزالة الفينول باستخدام عملية الأكسدة الكهروكيميائية ، والتي حققت نجاحاً كبيراً في الآونة الأخيرة، ولكن مع ذلك النجاح الذي حققته، فإن العملية واجهت بعض الصعوبات أهمها وجود بعض المركبات الكيميائية الأخرى في المياه الخام التي غالباً ما تكون سبباً رئيساً في إعاقة عملية إزالة الفينول.

الأهداف الرئيسية لهذه الدراسة هي تحسين المعايير التشغيلية و بحث تأثير المركبات الكيميائية الموجودة في المياه الخام على عملية أكسدة الفينول باستخدام عملية الأكسدة الكهروكيميائية . في هذه الدراسة ، تم استخدام خلية كهروكيميائية بنطاق مختبري للقيام بعملية الأكسدة الكهروكيميائية للفينول.

أظهرت الدراسة أن المعايير التشغيلية الأمثل لفينول ذي تركيز 75 جزء في المليون هي 45 أمبير / سم مربع لكثافة التيار و 6000 جزء في المليون للمحلول الالكتروليتي (كلوريد الصوديوم). التحسين في المعايير التشغيلية الذي تحقق في هذه الدراسة كان سبباً رئيساً وراء النجاح الذي تحقق في رفع كفاءة عملية إزالة الفينول في المياه الخام . كما أن نتائج هذه الدراسة أكدت أن اثنين فقط من أنواع المركبات الكيميائية الموجودة في المياه الخام وهما بيكربونات الصوديوم ، وكلوريد المغنيسيوم اللذان يعوقان عملية أكسدة الفينول. للتسريع من عملية إزالة الفينول، تمت إضافة 1 ٪ من فوق أكسيد الهيدروجين . مما أدى إلى تخفيض 25 دقيقة من وقت عملية الإزالة وذلك يعود إلى الأثر المحتمل لحدوث تفاعل فنتون كعملية أكسدة متقدمة . ومن المتوقع ان تسهم نتائج هذه الدراسة في حل مشكلة إزالة الفينول، وتعزيز الجهود البيئية لإزالة الفينول من مياه الصرف الصناعي.

ماجستير الهندسة
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CHAPTER 1

INTRODUCTION

The petrochemical industry is facing a major challenge in responding to the political and social imperatives of continuous improvement in environmental requirements. Improvements in the current technologies along with exploration of new technologies and their various combinations are under research for various types of petrochemical effluents with contaminants such as phenols.

Phenol compounds used widely in industry were intentionally or inadvertently released into the environment in large quantities. Widespread contamination of water by phenol has been recognized as an issue of growing importance in recent years, and has been listed as priority pollutant by the U.S. Environmental Protection Agency (EPA) (Lin and Tseng, 1999). Wastewater containing phenols has malodorous odor, high toxicity, bioaccumulation carcinogenic potentials and is of considerable health concern, even at low concentration. As the accumulation of these aromatic compounds in the environment has become a serious problem nowadays, it is very urgent to develop effective method to remove these contaminants from effluents before being discharges to the receiving environment (Cong, Y., Cheng, and Tian, T., 2005).

Many technologies have been investigated for removing and degradation of phenolic compounds in wastewater. These include adsorption (Rengaraj et al., 2002),

biodegradation (Miland et al., 1996), Oxidation (UV/Fe⁺³) (Zhou et al., 2001), extraction by liquid membrane (Lin et al., 2004) and oxidation (Comninellis and Pulgarin, 1991; Tahar and Savall, 1998; Polcaro et al., 1999; Tahar and Savall, 1999; Awad and Abuzaid, 2000; Azni Idris, and Katayon Saed, 2003). Traditional treatment processes such as biological treatments were not very effective for degradation of phenols (Azni Idris, and Katayon Saed, 2003; Xuejun et al., 2005).

Recently, advanced oxidation processes (AOPs) have attracted the attention of many researchers as they can be used to effectively treat wastewater containing phenols (A de Lucas et al., 2008; Zhang and George, 2005). Another common type of treatment methods for degrading phenols is the electrochemical methods, which have been widely studied (Brillas et al., 1995; Tahar and Savall, 1998; Houk et al., 1998; Polcaro et al., 1999; Cong et al., 2004; Siddiqui, 2006).

Electrochemical oxidation has been applied to many kinds of wastewater (Naumczyk et al., 1996; Simonsson, 1997). It is presented as an effective, selective, economical, and clean alternative for dealing with wastewaters bearing high loads of organic compounds such as phenol. By means of electrochemical oxidation, pollutants in wastewater can be completely mineralized by electrolysis using high oxygen over-voltage anodes (Xuejun Chen, Zhemin Shen, Xiaolong Zhu², Yaobo Fan, and Wenhua Wang, 2005).

More research has been undertaken with the aim of gaining a better insight into this process and, consequently, to develop a less expensive application. These researches

concluded that the electrochemical generation of oxidants used for the recovery or treatment of wastewaters from industrial plants by electrochemical oxidation processes is playing an ever increasing role due to their reliable operating conditions and ease of handling (M. Fryda, Th. Matthée, and S. Mulcahy, 2005).

A relevant study was carried out to remove phenol from simulated petrochemical wastewater using electrochemical treatment. The degradation of phenol was found to be acutely affected by the base solvent "raw water" of simulated wastewater as some of the species present in raw water may hinder the degradation process. The study recommended investigating the effect of species present on the raw water and may hinder the conversion of phenol into chlorophenols (Siddiqui, M., A., 2006).

The main objective of this study is to improve the phenol electrochemical degradation process when raw water is used as base solvent in the preparation of the synthetic refinery and petrochemical industry wastewater. This study also aims to investigate techniques to overcome the effect of the chemical species responsible for hindering the degradation of phenol. And finally the operation parameters, which include the phenol concentration, the current density and the electrolyte, were optimized to maintain the optimum phenol removal efficiency in the presence of the hindering species. Up to the knowledge of the investigator, this problem has not yet been investigated. The findings of this study are expected to contribute to solving this problem and enhancing the environmental efforts of the removal of the industrial wastewater phenols.

CHAPTER 2

LITERATURE REVIEW

The first part of this chapter discusses the composition, basic characteristics, uses, health and environmental impact of the phenol and the treatment and analysis methods used for the phenol degradation, detection and quantification in order to establish background information about this pollutant. The rest of the chapter provides a short review and description of the processes investigated in this study.

2.1. PHENOL

The term *phenol* is usually used to describe any compound that contains a hydrocarbon derivative containing an [OH] group bound to an aromatic ring see figure 2.1 (American Chemical Society, 2009). As reported by Arslan et al. 2005, phenols are a class of organic compounds, where phenol C_6H_5OH that is under investigation in this study is the simplest member (Arslan et al., 2005).

2.1.1. BASIC CHARACTERISTICS

Phenol is a white crystalline mass which turns red or pink if exposed to air or light. It has a burning taste and a distinct aromatic, acrid odor. It can be tasted and smelled at levels lower than those that are associated with harmful effects i.e. 0.04

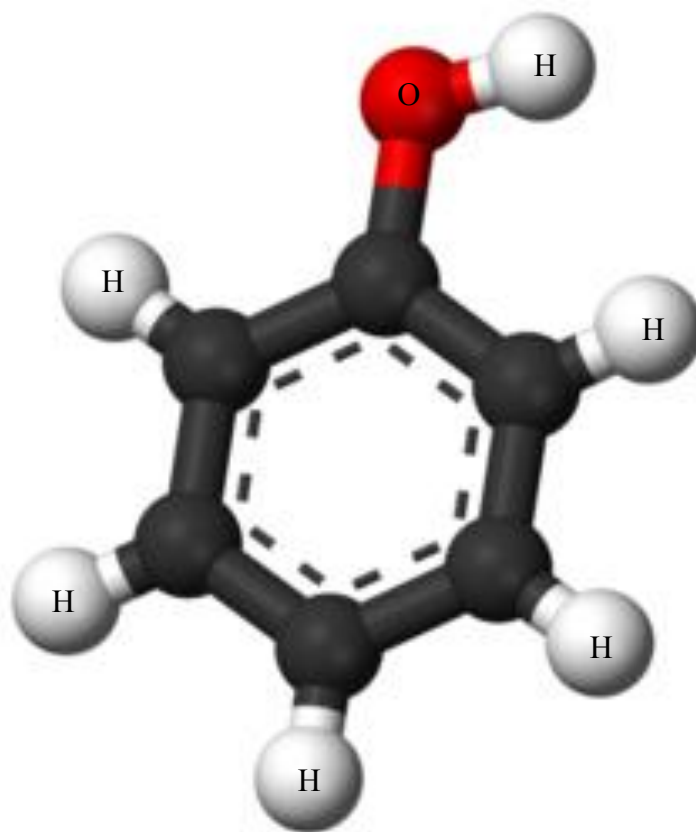


FIGURE 2.1: 3-Dimensional Representation of Phenol Structure

ppm (US Agency for Toxic Substances and Disease Registry, 2009). Its molecular weight is 94.144 g/mol and its melting point and boiling point are 41° C and 182° C respectively. The commercial product is a liquid.

Phenol has a limited solubility in water (8.3 g/100 ml) and it is very soluble in liquid sulfur dioxide, acetic acid, carbon tetrachloride and alcohol, and soluble in chloroform, ether, glycerol, petrolatum, carbon disulfide, volatile and fixed oils, aqueous alkali hydroxides, and acetone. It is slightly soluble in mineral oil. It is almost insoluble in petroleum ether. Phenol is combustible when exposed to heat, flame, or oxidizers and emits toxic fumes when heated. It is incompatible with strong oxidizers and calcium hypochlorite (US Occupational Safety and Health Administration (OSHA), 2009).

It is slightly acidic: the phenol molecule has weak tendencies to lose the H^+ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion $C_6H_5O^-$, also called phenoxide anion. Compared to aliphatic alcohols, phenol shows much higher acidity; it even reacts with aqueous NaOH to lose H^+ , whereas aliphatic alcohols do not. However, many carboxylic acids are more acidic than phenol (John McMurry 2008 and Silva P. J., 2009).

2.1.2. SOURCES OF DISCHARGE

Phenol is found naturally in animal wastes and decomposition of organic wastes and also is obtained from coal tar or crude petroleum. It was first isolated in 1834 from coal tar and this remained the main source of phenol until the First World War. The first synthetic method was then devised and all of the phenol today is manmade (Karl Harrison, 2009).

The primary use of phenol is in the production of phenolic resins, which are used in the plywood, construction, automotive, and appliance industries. Phenol is also used in the production of caprolactam and bisphenol A, which are intermediates in the manufacture of nylon and epoxy resins, respectively. Other uses of phenol include as a slimicide, as a disinfectant, and in medicinal products such as ear and nose drops, throat lozenges, and mouthwashes (US Agency for Toxic Substances and Disease Registry, 1998).

Phenols are frequently found in various industrial effluents and reported in hazardous waste sites. The major sources of phenolic wastes are oil refineries, coal gasification and liquefaction plants, chemical plants, resin and paint industries. 'Phenols' in waste water include phenol and other compounds containing one or more hydroxyl groups attached to an aromatic ring. As little as .005ppm of phenol will impart objectionable taste and odour to drinking water, where it combines with chlorine to form chlorophenols. It is also toxic to fish and

has a high oxygen demand. Following are two examples of the utility of this process.

2.1.3. HEALTH HAZARDS

Inhalation and dermal exposure to phenol is highly irritating to the skin, eyes, and mucous membranes in humans. Symptoms of acute toxicity in humans include irregular breathing, muscle weakness and tremors, loss of coordination, convulsions, coma, and respiratory arrest at lethal doses (Agency for Toxic Substances and Disease Registry (ATSDR 2009). Acute animal tests in rats, mice, and rabbits have shown phenol to have high acute toxicity from oral exposure (U.S. Department of Health and Human Services, 2009).

Phenol is among the list of priority of organic pollutants proposed by the US Environmental Protection Agency "EPA" (Yan et al., 2006). EPA has established a provisional Reference Concentration (RfC) for phenol of 0.006 milligrams per cubic meter (mg/m^3) based on no effects in rats, mice, or monkeys. The provisional RfC is a value that has had some form of Agency review, but it does not appear on IRIS (US Environmental Protection Agency "EPA", 2009).

The World Health Organization (WHO) prescribed 1 $\mu\text{g}/\text{L}$ as the maximum permissible concentration of total phenol in drinking water (Kumaran and Paruchuri, 1996; Nuhoglu and Yalcin, 2005).

Phenol is toxic to aquatic organisms, however Due to scarcity of exposure data, firm conclusions cannot be drawn with regard to the extent of the risk for either aquatic or terrestrial ecosystems (Zhang and George, 2005).

However, in view of the derived environmental concern level for water, it is reasonable to assume that aquatic organisms may be at risk in any surface or sea waters that are contaminated with phenol (World Health Organization, Geneva, 1994). Elimination of phenol is, therefore, a necessity to preserve the environmental quality. Yet, they are considered to be one of the major and most difficult pollutants in wastewater to be removed by water treatment processes.

2.1.4. TREATMENT METHODS

Treatment of wastewater containing high concentration of phenol is difficult with traditional wastewater treatment methods that normally include a biological treatment step. Therefore, the most efficient way to treat phenol is degrading it by a specific method directly at the point of discharge before sending it to common wastewater treatment facility. The methods proved effective for this purpose are Fenton (Chedeville and Bayraktar, 2005), O_3/UV , O_3/H_2O_2 , Wet air oxidation and electrooxidation using Ti/SnO_2-Sb anode (Li et al., 2005).

Extensive research had been conducted to remove phenol and its derivatives. Current treatment processes include carbon adsorption, solvent extraction,

biodegradation, advanced oxidation and electrochemical processes. The selection of proper treatment mainly depends on the treatment efficiency, reliability, ease of control and economics (Dane et al., 2007).

Carbon adsorption and solvent extraction can effectively remove phenol from aqueous solutions, but the high cost of carbon regeneration and extraction solvent hindered the large scale application (Azni et al., 2003).

Advanced oxidation processes (AOPs) include ultraviolet (UV) photolysis (Sun et al., 2006), direct ozonation (Staehelin et al., 1985), high-energy electron irradiation (Nickelson et al., 1993), supercritical oxidation (Krajnc et al., 1997; Thornton et al., 1992), and ultrasonification (Petrier et al., 1994). Over the past decade, another AOP utilizing a pulsed corona discharge in gas or liquid phase has been used in removing and degrading organic contaminants from aqueous solutions (Clements et al., 1987; Joshi et al., 1995) in a laboratory scale experimental setups. All of these advanced oxidation methods suffer high operation cost.

On the other hand, biological treatment methods are not quite effective as anaerobic process cannot effectively remove phenol from the liquid phase (Yan et al., 2007).

Electrochemical methods for water treatment have attracted wide attention and recognized to be advantageous due to high efficiency, easy to control, and low

costs (Zhang and George, 2005). The destruction of phenols using electrochemical methods has been studied (Sathish et al., 2005).

The influence of operational parameters such as temperature, pH, initial substance concentration, current density, and electrode material on the performance of the electrochemical oxidation process was thoroughly investigated (Zhang and George, 2005). Evaluation of reaction products, electrode fouling and current efficiency were also carried out (Zhang and George, 2005).

Recently, Electrochemical Oxidation has been intensively studied for the degradation of phenol in aqueous solutions (Brillas et al., 1995; Tahar and Savall, 1998; Houk et al., 1998; Polcaro et al., 1999; Hayashi et al., 2003; Cong et al., 2004; Siddiqui, 2006).

In recent years, there has been increasing interest in developing electrochemical methods for purifying waters containing organic contaminants (Wang J. and Farrell J, 2004). A relevant study was carried out to remove phenol from simulated petrochemical wastewater using electrochemical treatment (Siddiqui, M., A., 2006). The degradation of phenol was found to be considerably affected by the base solvent of simulated wastewater, the raw water, which contains some species that may hinder the degradation process. The study recommended investigating the effect of species present on the raw tap water and may hinder the conversion of phenol into chlorophenols.

2.2. ELECTROCHEMICAL OXIDATION OF PHENOL

The electrochemical oxidation reactions of hazardous organic species such as phenol are a promising method for wastewater treatment (Houk et al., 1998; Tahar and Savall, 1998; Brillas et al., 1998). Electrochemical oxidation processes are expected to remediate the soluble phase of pollutant, i.e. phenol in the pollutant-matrix dealt in this study.

The method of electrochemical oxidation for treatment of the Phenols contained in wastewater has become a hot focus in recent years because of its better effects than traditional chemical, physical and biological methods. (Hongzhu Ma and Lin Gu, 2006).

The advantages of electrochemical oxidation include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation.

A concise description of some types of electrochemical reactions along with important side reactions expected to influence the removal mechanism, and the use of the stainless steel electrodes in process are discussed in the following sections.

2.2.1 SIMPLE REDOX REACTIONS

A simple redox reaction is one that involves a change in the electrical charge of a charge carrier, usually a simple or complex ion in the solution, by its taking away, an electron from the electrode (reduction), or its giving an electron to the electrode (oxidation). The same carrier may be present in solution in two states of charge.

The higher, more positive charge is called the oxidized state, and the lower, less positive charge is called the reduced state (John et al., 2002).

For example, when ferric and ferrous ions are both present in solution in significant quantity, and when electron exchange with the electrode is sufficiently fast, redox equilibrium is established at the electrode, giving it a well-defined potential, or reversible redox potential (Encyclopædia Britannica, 2009).

2.2.2. REACTIONS THAT PRODUCE GASES

When hydrogen ions in solution react with electrons ejected from a metal, hydrogen atoms are formed at the surface, where they combine among themselves or with other hydrogen ions and electrons to give gaseous hydrogen molecules. If all the reactions are fast enough, an equilibrium is attained between hydrogen ions and gaseous hydrogen (Encyclopædia Britannica, 2009).

A metal in contact with solution at which such a situation exists is called the reversible hydrogen electrode, and its electrical potential is arbitrarily taken to be zero; every other electrode can thus be compared with it as it represents the basis for constituting the hydrogen scale of relative electrode potentials. Similarly, negative hydroxyl ions in solution (OH^-) can be made to give up electrons to a metal and, in a series of reactions; the final one is the formation of gaseous oxygen. Chlorine is another gaseous product; it evolves upon electrochemical

oxidation of chloride ions in concentrated solutions of neutral and acid salts (Petrucci R. H., McCreary T., Scott S. P., 2004).

2.2.3 REACTIONS THAT DEPOSIT AND DISSOLVE METALS

When a metal ion is reduced and discharged as a neutral atom, or species, it tends to build into the metal lattice of the electrode. Thus, metals can be deposited at electrodes. Conversely, if electrons are taken away from the metal electrode by applying positive potentials to it, the metal ions thus formed can cross the double layer of electric charge at the interface, undergo hydration (combination with water), and enter the solution. The metal electrode thus dissolves. Many metals establish well-defined electric potentials when they are in contact with their own ions in solution (Bard, A.J., Inzelt, G., and Scholz F., 2008)

2.2.4 OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

A reaction of the oxidation and reduction of organic compounds can also be done at electrodes. Such reactions, however, are mostly irreversible in the literal sense that they lead to products that cannot easily be converted back into the original substance. Exceptions are some oxygen- and nitrogen-containing compounds (quinones, amines, and nitrous compounds) that can give fairly well-defined reversible potentials (John McMurry, 2008).

2.2.5. STAINLESS STEEL ELECTRODES APPLICABILITY

The electrochemical oxidation technique depends mainly on the type of anode used (Vercesi et al., 1991; Rao et al., 2001) but also on the properties of the wastewater (Rodrigo et.al, 2001; Y.H. Wanga, K.Y. Chana, X.Y. Lib, and S.K. Soc, 2006).

For elimination of phenol from aqueous solutions by electrochemical oxidation at stainless steel oxide electrodes, which is usually used for wastewater treatment, electro-oxidation involves the generation of an in-situ coagulants by electrically dissolving iron ions from electrodes (Chen, 2003).

The metal ions generation takes place at the anode, while hydrogen gas is released from the cathode. The electrodes can be arranged in a mono-polar mode as shown in figure 2.2. The stainless steel electrodes can be in plate or packed forms of scraps such as steel turnings and millings.

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

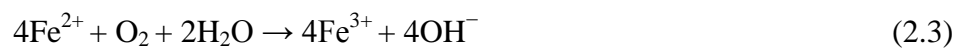
For iron anode:



At alkaline conditions;



At acidic conditions;



In addition, there is oxygen evolution reaction;



The reaction at the cathode is;



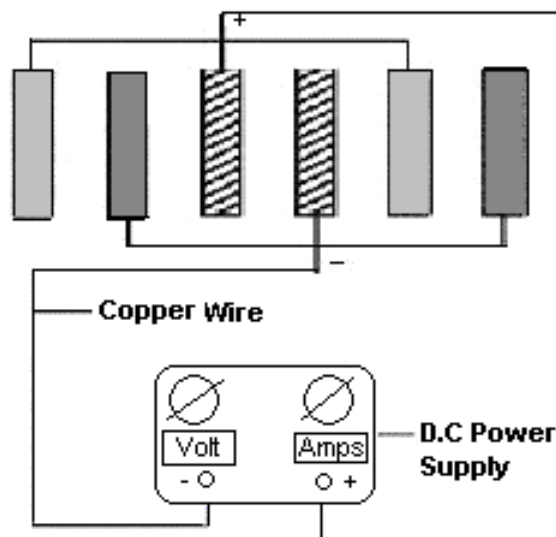


Figure 2.2: Monopolar Electrode Arrangement

2.3. PRESENCE OF CHEMICAL SPECIES IN RAW WATER

The raw water used in this study is of ground water source. Ground waters are usually of higher quality than surface sources. However, they can contain traces of agricultural chemicals and a few may contain toxic chemicals, which occur naturally in some aquifers.

2.3.1. SOURCES OF CHEMICAL SPECIES

Even if the water leaves the source in a relatively clean state, it may get contaminated as it travels through pipes, which could be quite old. It is almost impossible for the water not to become contaminated by something undesirable (Arik A. M, and Philippe G B., 2001).

Also tap water is treated with a large number of chemicals in order to kill bacteria and other microorganisms. In addition, it may contain other undesirable contaminants like toxic metal salts, hormones and pesticides, or it may become contaminated by chemicals or microbes within pipes and storage reservoirs (e.g. lead, and Iron).

2.3.2 TYPES OF CHEMICAL SPECIES

Typically raw tap water contains the following species:

- Chlorine
- Fluorine compounds
- Trihalomethanes (THMs)
- Salts of:
 - Calcium.
 - Sodium.
 - Magnesium.
 - Potassium.
 - Aluminum.
 - Copper.
 - Lead.
 - Arsenic.
 - Mercury.
 - Cadmium.
 - Barium.
- Bicarbonate.
- Nitrates.
- Carbonate.

In general, levels of Ca^{2+} , Mg^{2+} , and Na^+ are higher among groundwater sources than among surface water sources. Tap water sources that contained high levels of Ca^{2+} generally contain high levels of Mg^{2+} but not necessarily high levels of Na^+ (Arik et al., 2001).

2.3.3 EFFECT OF CHEMICAL SPECIES ON THE PROCESS

The total dissolved solids present in raw water causing interference in the redox reactions occurring in the electrochemical oxidation process. Though this fact the complex matrix of total dissolved solids present in raw water has a major role to play in phenol degradation efficiency of the process, but they also possess the requirement of confirmation and explanation of complete removal of phenol with deionized water used as a base solvent (Siddiqui, M., A., 2006).

The higher degradation of phenol in the initial phase that could not continue at later stages was attributed to a reaction taking place at the surface of the cathode that has a significant role in the electrochemical degradation of phenol (Siddiqui, M., A., 2006). It was initially suspected that this hindrance was due to gradual accumulation of high amount of salts present in the raw water used as the base of synthetic wastewater.

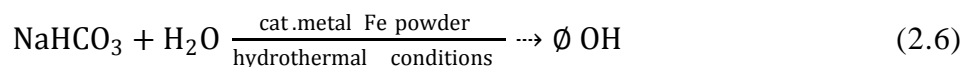
Later, it was found that the relatively higher removal of phenol in the initial stage of experiments, which fails to persist during treatment for longer time periods, is not linked with the coating on the cathode. It may be a complex reaction between chemical species of raw water and the ions released during electrolysis, yielding such results. The exact mechanism responsible for the observed results was proposed for further research. (Siddiqui, M. A., 2006).

In cases where the source of raw water is groundwater, the major cations that can be found are $[\text{Na}^+]$, $[\text{Mg}^{++}]$, and $[\text{Ca}^{++}]$, and the anions are $[\text{SO}_4^{--}]$ and $[\text{HCO}_3^-]$. Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) salts are represented by calcium sulfate and magnesium sulfate, which is usually used in electrochemical processes as additional electrolyte to accelerate the ionization process (Pacheco, M. and Lopes, A., 2007).

Generally, the Sodium (Na^+) species present in raw water are sodium chloride or sodium bicarbonate. Because for pH ranges that occur in natural waters, the alkalinity is usually in the form of the bicarbonate ion, HCO_3^{-1} . In fact, at pH 7.5 or below, the bicarbonate ion is essentially all the alkalinity.

Sodium chloride is often used as electrolyte in a lot of researches which are carried out by using electrochemical process, while sodium bicarbonate might react with water molecules in the presence of iron powder in hydrothermal

conditions as in the following reaction (Hongming Y., Ying M., Chao H., and Shouhua F, American Chemical Society, Organic Letters, 2007).



In addition, bicarbonate is a scavenger with a strong effect, which might work as scavenger for OH[•] radical in the process. For instance, in a solution with a high pH value or an oxidation-process, the presence of scavengers is undesired, since the scavengers react very fast with OH[•] radicals and lower the oxidation capacity.

The scavenging capacity can be defined as follows;

$$K_{\text{OH-DOC}}[\text{DOC}] + K_{\text{OH-HCO}_3^-}[\text{HCO}_3^-] + K_{\text{OH-CO}_3^{2-}}[\text{CO}_3^{2-}]$$

For this kind of processes a low scavenging capacity is required (the bicarbonate concentration is less important), Figure 2.3 illustrates the relation of the carbonate ratio, bicarbonate ratio and pH (Lenntech Advanced Oxidation, 2007).

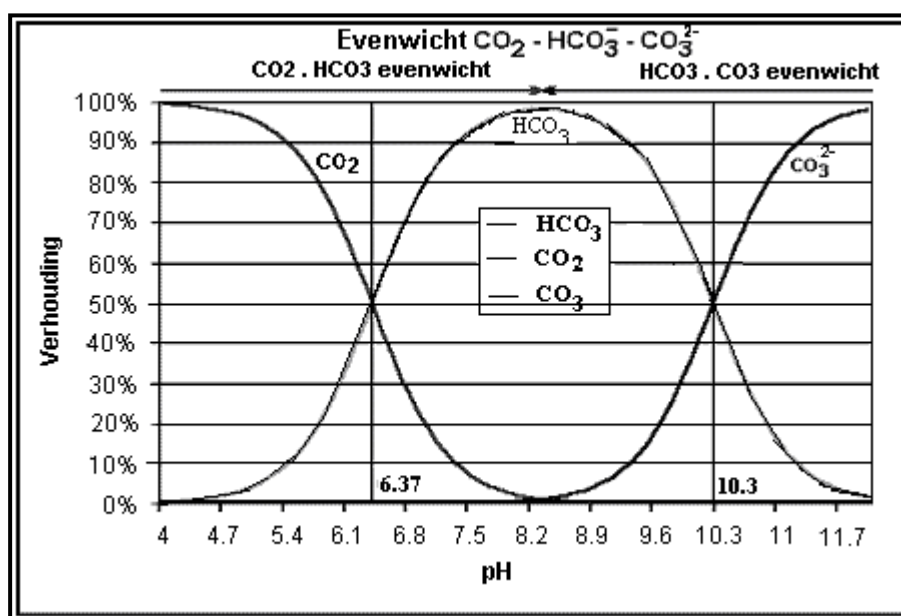


Figure 2.3: Equilibrium carbonate, bicarbonate and carbon dioxide

(After Lenntech Advanced Oxidation, 2007)

CHAPTER 3

Objectives

As discussed in the previous chapter, when electrochemical treatment was used to remove phenol from refinery and petrochemical wastewaters, the degradation of phenol was found to be acutely affected by the types of chemical species present in the wastewater, as some of the chemical species present in raw water hinder the degradation process (Siddiqui, M. A., 2006).

The main objective of this study is to investigate the effect of chemical species, present in raw waters, on the degradation of phenol using electro-chemical oxidation process. The specific objectives are:

- (1) To optimize/study the operational parameters, which include the *current density*, the *phenol concentration* and the *electrolyte* to maintain the optimum phenol removal efficiency in the presence of the hindering species.
- (2) To investigating the effect of CO_3^{2-} , HCO_3^- , and SO_4^{2-} on the hindrance of phenol degradation in the electro-chemical oxidation process.
- (3) To investigate chemical techniques for overcoming the effect of the chemical species responsible for hindering the degradation of phenol.

CHAPTER 4

METHODOLOGY

This chapter discusses the apparatus, materials, methods, and analysis techniques used in this study to carry out the laboratory investigations required to achieve the assigned objectives of this research.

4.1. PREPARATION OF SYNTHETIC WASTEWATER

The typical raw water characteristics mentioned in table 4.1 were used as a reference in this study. The deionized water was used as base solvent to prepare all combinations of phenol and chemical species of the raw water shown in table 4.1.

4.2. LAB-SCALE EXPERIMENTAL SETUP

The experiments of the electrochemical oxidation of phenol were carried out in a reactor made of Pyrex glass (fleaaker) with a volume of 0.5 L and filled with 500 ml solutions containing phenol and 4 g/L NaCl as the electrolyte. Two stainless steel electrodes (100 mm × 40 mm × 2 mm) were used as both anode and cathode.

The electrodes were connected to a DC power supply with galvanostatic operational options for controlling the current density as shown in Figure 4.1. A distance of 30 mm between anode and cathode was maintained for all the experiments in this study.

Table 4.1: Characteristics of raw water at KFUPM (Bld. 26)

Substance or Characteristic	Maximum Concentration Level
Sodium ^a , mg/L	585.62
Potassium ^a , mg/L ^a	47.18
Calcium ^a , mg/L ^a	327.56
Magnesium ^a , mg/L	92.74
Ferrous ^b , mg/L	0.531
Bicarbonate ^a , mg/L	1543.3
Chlorides ^a , mg/L	601.04
Fluoride ^b , mg/L	0.60
Sulfates ^a , mg/L	302
Nitrates ^a , mg/L	2.79
Bromide ^b , mg/L	4.06
pH ^a	7.45
Total Organic Carbon (TOC) ^a	2.908
Total Dissolved Salts (TDS) ^a	3630.0

Sources: ^aLaboratory tests (2009)

^bAfter the Center for Environment & Water, Research Institute, KFUPM (2004)

Note: The Total Alkalinity is represented as bicarbonate [HCO₃⁻] because the pH is less than 7.5.

A stirrer that can be driven by magnetic stirrer apparatus was used to mix the contents during experimental runs. The reaction temperature was monitored with a glass thermometer and was kept homogenous through pre-adjusting magnetic stirrer apparatus before experimentation (Figure 4.1).

4.3. PREPARATION OF ELECTRODES

Commercial AISI 304 stainless steel sheets were used as the electrode material in this study. The electrodes were prepared with dimensions of (100 mm × 40 mm × 2 mm), and were used as both anode and cathode.

4.4 DESIGN OF EXPERIMENTS

There were two phases of experimental design, first phase and second phase intended for optimizing the operational parameters and raw water chemical species investigation respectively.

In the first phase, fifteen experiments with different sittings were performed for optimizing phenol concentration, current density, and electrolyte. With different phenol concentration ranging from 25 mg/L to 500 mg/L, current density 30 mA/cm², electrolyte (NaCl) 2000 mg/L, and contact time 90 minute six experiments were conducted to investigate the optimum phenol concentration.

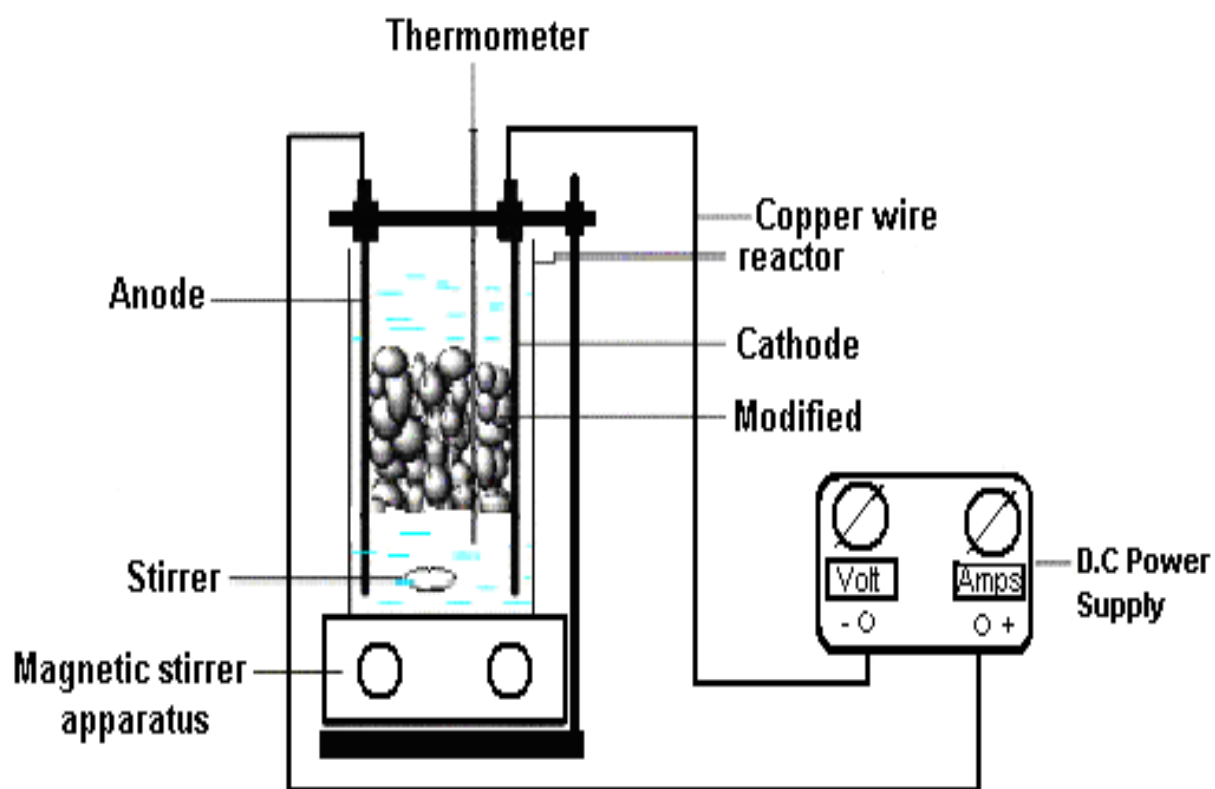


Figure 4.1: Schematic illustration of Experimental
Lab-Scale setup.

More five experiments were performed to determine the optimum current density from five current densities (7.5, 15, 30, 45, and 52.5 mA/cm²) with the optimum phenol concentration, 2000 mg/l NaCl, and 90 minute contact time.

Finally for electrolyte investigation four experiments were performed for sodium chloride concentrations (2000, 4000, 6000 and 8000 mg/L) with the optimum phenol concentration, optimum current density, and contact time 90 minutes. For all experiments in the first phase the sampling intervals used were (0, 2, 5, 15, 10, 20, 30, 45, 60, and 90) minutes. Table 4.2 summarizes the design of experiments adopted for this phase.

In the second phase, fifteen experiments were performed at contact times (2, 5, 10, 15, 20, 30, 45, and 60 minutes). The current density used in experiments was 45 mA/cm². A concentration of 6000 mg/L of Sodium Chloride (NaCl) was added as an electrolyte where deionized water was used as a base solvent, only phenol with a concentration of 75 ppm was used to prepare synthetic wastewater in these experiments, the chemical species were added individually and collectively to the synthetic wastewater. Table 4.3 summarizes the design of experiments adopted for this phase.

TABLE 4.2: Design of Experiments, Phase I

Exp. No.	Phenol (mg/l)	Current Density mA/cm²	Contact Time (min)	NaCl Conc. (mg/l)
PHENOL CONCENTRATION INVESTIGATION				
1	25	30	90	2000
2	50	30	90	2000
3	75	30	90	2000
4	100	30	90	2000
5	250	30	90	2000
6	500	30	90	2000
CURRENT DENSITY INVESTIGATION				
7	75	7.5	90	2000
8	75	15	90	2000
9	75	30	90	2000
10	75	45	90	2000
11	75	52.5	90	2000
ELECTROLYTE INVESTIGATION				
12	75	Optimum	90	2000
13	75	Optimum	90	4000
14	75	Optimum	90	6000
15	75	Optimum	90	8000

TABLE 4.3: Design of Experiments, Phase II

Exp. No.	Phenol (mg/l)	Current Density mA/cm²	Contact Time (min)	CaSO₄ (mg/l)	MgSO₄ (mg/l)	MgCL₂ (mg/l)	NaHCO₃ (mg/l)	NaCl Conc. (mg/l)
INDIVIDUAL CHEMICAL SPECIES INVESTIGATION								
16	75	Opt.	90	350	0	0	0	Opt.
17	75	Opt.	90	0	100	0	0	Opt.
18	75	Opt.	90	0	0	100	0	Opt.
19	75	Opt.	90	0	0	0	1600	Opt.
DUAL CHEMICAL SPECIES INVESTIGATION								
20	75	Opt.	90	350	100	0	0	Opt.
21	75	Opt.	90	350	0	100	0	Opt.
22	75	Opt.	90	350	0	0	1600	Opt.
23	75	Opt.	90	0	100	100	0	Opt.
24	75	Opt.	90	0	100	0	1600	Opt.
25	75	Opt.	90	0	0	100	1600	Opt.
TRIPLE CHEMICAL SPECIES INVESTIGATION								
26	75	Opt.	90	350	100	100	0	Opt.
27	75	Opt.	90	0	100	100	1600	Opt.
28	75	Opt.	90	350	0	100	1600	Opt.
29	75	Opt.	90	350	100	0	1600	Opt.
COLLECTIVE CHEMICAL SPECIES INVESTIGATION								
30	75	Opt.	90	350	100	100	1600	Opt.

4.5. SAMPLE COLLECTION

In the first phase of experiments ten samples were collected over a period of one and half hour at time intervals (0, 2, 5, 10, 15, 20, 30, 45, 60, and 90 minutes). But in the second phase nine samples were collected over a period of one hour at time intervals (0, 2, 5, 10, 15, 20, 30, 45, and 60 minutes).

4.6. TESTING OF CONTAMINANTS

Shimadzu UV-Spectrophotometer was used to detect the concentration of phenol in the samples; also Gas Chromatograph (GC) and Gas Chromatograph-Mass Spectrophotometry (GC-MS) were used at optimum conditions for the detection of phenol and the byproduct of the electrochemical redox reaction. A pH meter and Thermometer were used to measure the pH and the temperature of the samples, respectively.

The following methods and apparatus were used to analyze the treated samples.

4.6.1. UV-SPECTROPHOTOMETER

Shimadzu UV-Spectrophotometer was used to detect the concentration of phenol in the samples. The device was set in quantization mode; calibration curve was generated from standard solutions of phenol and used to calculate the concentrations of phenol in the all samples, the peak at 270 nm was used for this purpose. More details about calibration curve in section 4.7.

4.6.2. GAS CHROMATOGRAPH (GC)

Agilent 6890N GC system (DB1 column) was used to confirm UV spectrophotometer results for the degradation of Phenol. Dichloromethane (10 ml) was used for the extraction of samples, which was replaced with Isopropanol in nitrogen evaporator during the process of concentrating the sample extracts.

4.6.3. GAS CHROMATOGRAPH-MASS SPECTROPHOTOMETRY (GC-MS)

Gas Chromatograph-Mass Spectrophotometry (GC-MS): Agilent's 6890N GC/MS analyzer was used to confirm spectrophotometer results for the degradation of Phenol. The intermediate compounds detected through GC-MS helped to propose a degradation mechanism. Same procedure was used for the extraction of the samples as for GC analysis.

4.6.4. CHEMICAL OXYGEN DEMAND (COD)

Chemical oxygen demand (COD): Method 5220 C, Closed Reflux, Titrimetric method, Standard Methods for the examination of water and wastewater, 19th edition 1995.

4.6.5 INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (ICPMS)

ICPMS is a relatively new technique for the determination of trace elements in solution. It offers better sensitivity than graphite furnace AA with the multi-element speed of ICPOES. Agilent 7500cx ICPMS was used to analyze stainless steel electrodes material, sludge's, and other treated samples for metal.

In a typical application, metals were placed in solution by acid digestion. The solution is sprayed into flowing argon and passed into a torch which is inductively heated to approximately 10,000 °C. At this temperature, the gas and almost everything in it is atomized and ionized, forming a plasma which provides a rich source of both excited and ionized atoms. In ICPMS, positive ions in the plasma are focused down a quadrapole mass spectrometer. By acquiring the mass spectrum of the plasma, data can be obtained for almost the entire periodic table in just minutes with detection limits below 0.1 ug/L for most elements.

4.6.6. PHENOLS-METHOD 604

A 1-L sample is acidified and extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to 2-propanol during concentration to a volume of 10-mL or less. The concentrations of phenols in the extract are measured using a gas chromatography (GC) system equipped with a flame ionization detector (FID).

The method also provides for a derivatization and column chromatography cleanup procedure to aid in the elimination of interferences. Using this approach, the concentrations of phenols in the extract are measured by detecting derivatives using a GC system with an Electron Capture Detector (ECD). This method covers the determination of phenol and certain substituted phenols in wastewater and other waters (see Table 4.4).

This is a flame ionization detector gas chromatographic (FIDGC) method applicable to the determination of the compounds listed below (table 4.4) in municipal and industrial discharges as provided under US EPA 40 CFR Part 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds in table 4.4, compound identifications should be supported by at least one additional qualitative technique.

This method describes analytical conditions for derivatization, cleanup, and electron capture detector gas chromatography (ECDGC) that can be used to confirm measurements made by FIDGC.

Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above (Table 4.4), using the extract produced by this method (US Environmental Protection Agency (EPA), 2009).

TABLE 4.4.: Parameters can be Determined By Phenols-Method 604

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2—Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2

After US EPA, Method Guidance, 2009

4.6.7. PHENOLS-METHOD 625

This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Table 4.4 above may be qualitatively and quantitatively determined using this method. The method may be extended to include other parameters.

This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed above (Table 4.4) in municipal and industrial discharges as provided under 40 CFR Part 136.1 (US Environmental Protection Agency (EPA), 2009).

4.7. STANDARD CURVE FOR PHENOL

Different concentrations of phenol solutions were prepared for calibrating the UV-Vis spectrophotometer. The data are presented in Table A1 in the appendix for the calibration curve of phenol (Figure 4.2), it is seen that the coefficient of determination R^2 is 0.9937, which means the variability of the data is insignificant. This may occur because of the number of dilutions prepared for the standard solution. The equation of the best-fitted line is $Y = 0.0121X + 0.119$. Here Y is the absorbance and X is the concentration of phenol in (mg/l). Chemical oxygen demand COD test also was examined for the same samples (dilutions) to confirm the quality of calibration curve of phenol (Figure 4.3).

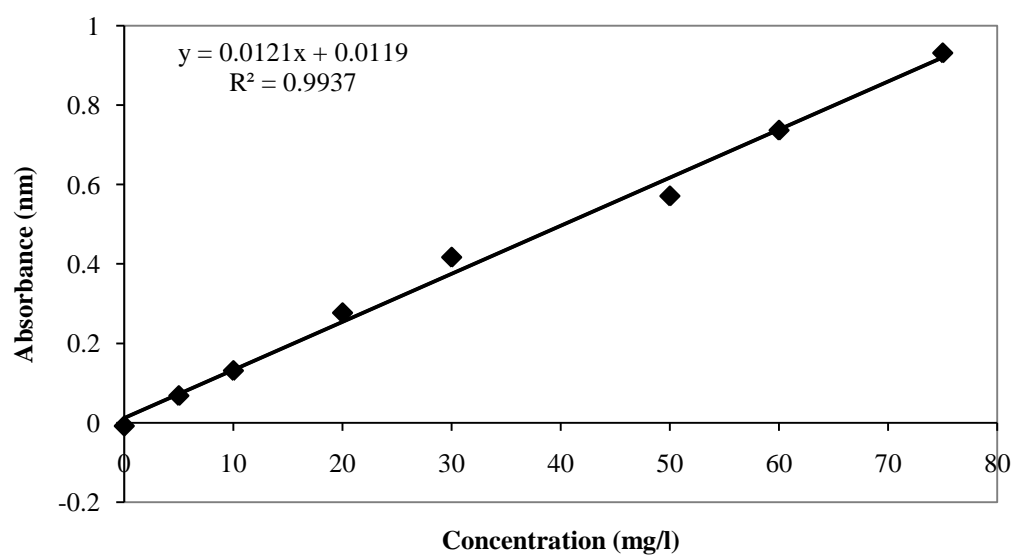


FIGURE 4.2: Standard Curve for Phenol at 270 nm

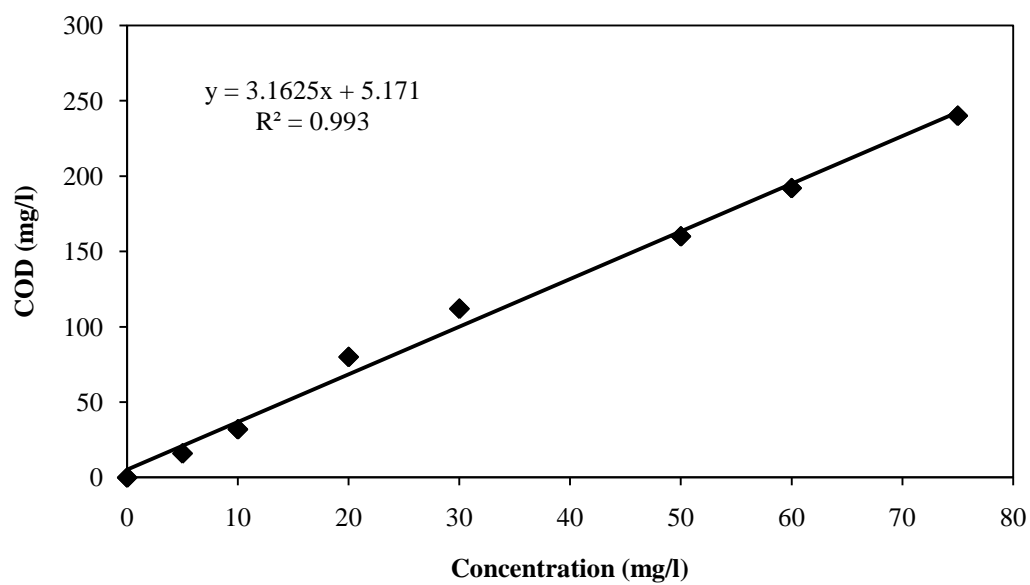


FIGURE 4.3: Chemical Oxygen Demand (COD) Curve for Phenol

CHAPTER 5

RESULTS AND DISCUSSION

5.1. OPERATION PARAMETERS OPTIMIZATION

The electrochemical oxidation process has several operational parameters, which have direct and indirect significant effects on the phenol degradation process. Therefore, this study initially aimed to investigate those parameters to enhance the phenol degradation process by achieving the optimal conditions.

5.1. 1. PHENOL CONCENTRATION

In this investigation, it was proven that the phenol concentration significantly affects the phenol degradation in the electrochemical oxidation process when synthetic refinery and petrochemical wastewater with different phenol concentrations ranging from 25 mg/l to 500 mg/l was used.

In the first experiment using 25 mg/l phenol the concentration of phenol decreased slowly in the first two time intervals (figure 5.1); however, between 10 to 30

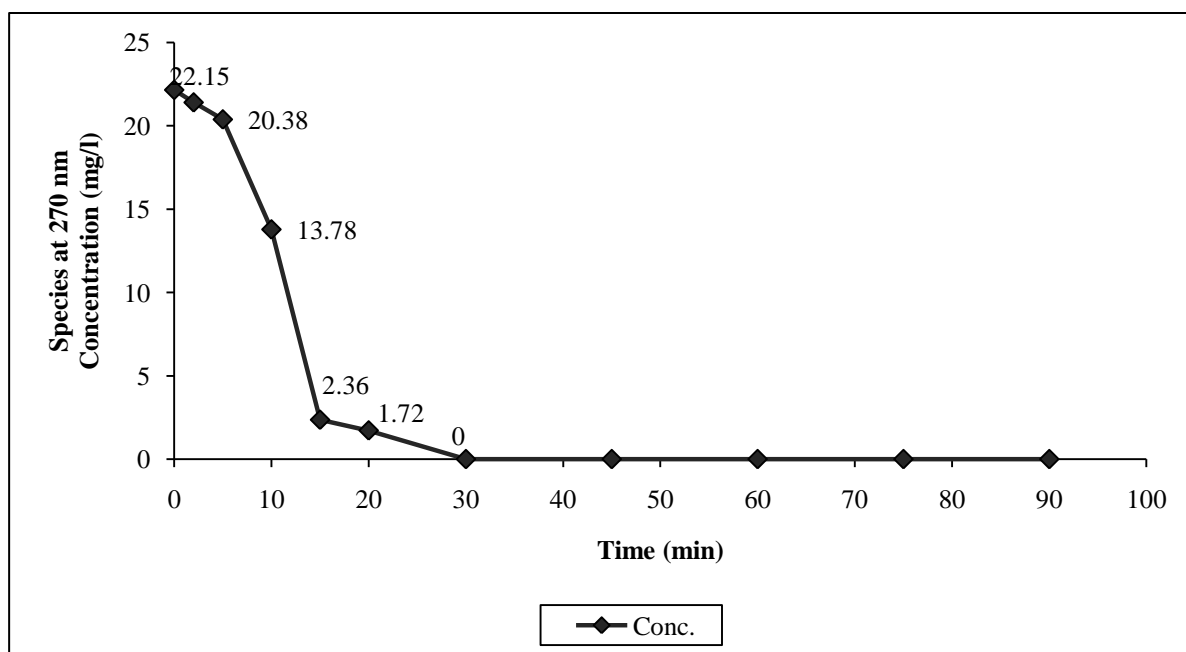


FIGURE 5.1: Effect of Concentration on the Degradation of Phenol at 25 mg/l of phenol and a Current Density of 30 mA/cm²

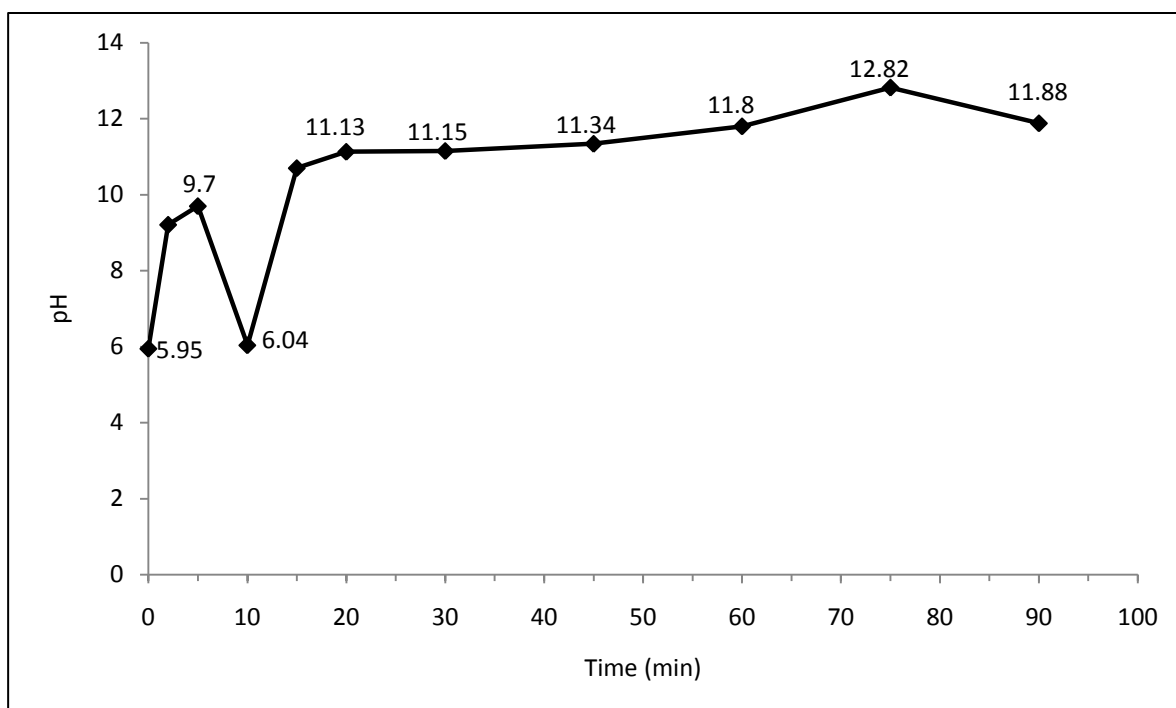


FIGURE 5.2: The pH pattern of Phenol Degradation Process at 25 mg/l of phenol and a Current Density of 30 mA/cm²

minutes it dropped rapidly till it reached zero at the 30 minutes interval. To allow the reaction to reach a static level the experiment was run for 90 minutes.

It is clear from the respective graph that maximum phenol removal is achieved with time. This figure also demonstrates that the concentration reached zero at the 30 minutes interval and remained constant for another 60 minutes. For more details on the experiment data see table A4 in the appendix. The accompanying pH graph in figure 5.2 above shows that the pH values were fluctuating at the first intervals and stayed high after the 20 minutes interval.

This analysis was repeated for another five experiments for concentrations of 50, 75, 100, 250, and 500 mg/l. It was noticed based on these analyses that the total percent of phenol removal was directly proportional to the pH and the detention time and inversely proportional to the phenol concentration. Results obtained from these analyses were used to determine the phenol removal percentage for the six concentrations of phenol. The summary of the results given in Table 5.1 below was used to construct the associated graph (Figure 5.3), which portrays the percentage removal versus phenol concentration within the same contact time (90 minutes).

More data and analysis of phenol concentration and pH for the conducted experiments are attached in the appendix in tables A3, A4, A7, A10, A13 and A16; and Figures A5, A6, A8, A9, A11, A12, A14, A15, A17 and A18.

Table 5.1: Removal Percentage after Phenol Treatment for 90 minutes at 30 mA/cm²**Current Density and Different Concentrations of Phenol**

Concentration (mg/l)	Removal Percentage (%)
25	100.0
50	91.73
75	66.24
100	64.49
250	41.10
500	20.00

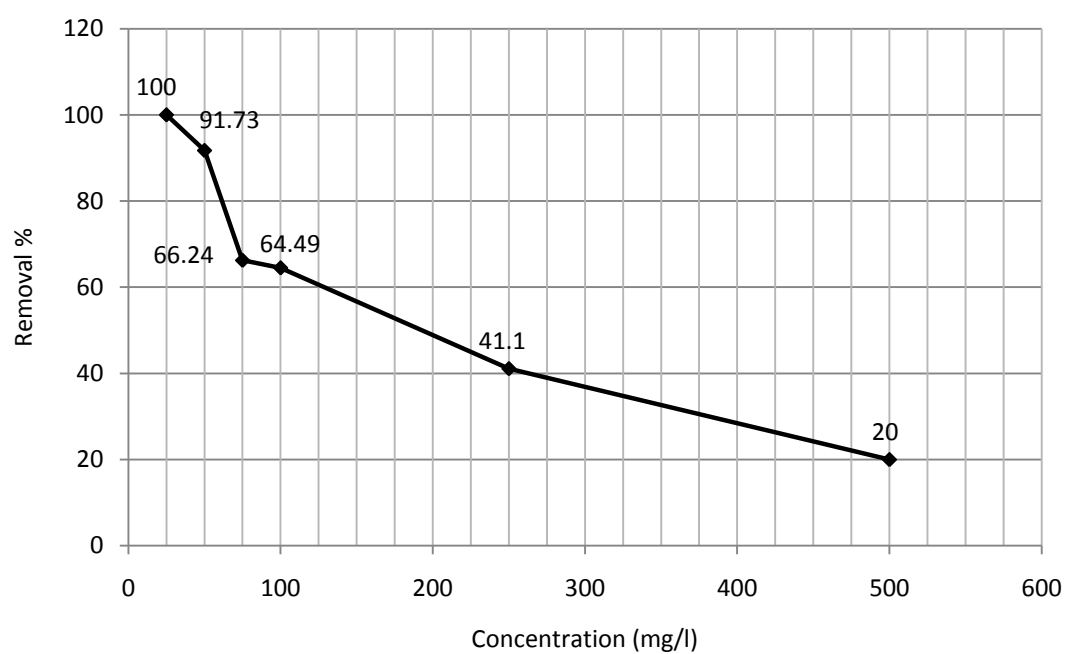


FIGURE 5.3: Removal Percentage vs. Concentration for Phenol after Treatment for 90 minutes at 30 mA/cm² Current Density

5.1.2. ELECTROLYTE CONCENTRATION

Four experiments were carried out to identify the optimum electrolyte concentration for phenol removal. In these experiments, different amounts of sodium chloride; 2000, 4000, 6000 and 8000 mg/l were used with 75 mg/l of phenol concentration, 30 mA/cm² of current density and 90 minutes contact time.

For the aforementioned concentrations of sodium chloride, phenol removal efficiencies of 56.8, 65.2, 83.6 and 54.5 were achieved, respectively (Figures 5.4, 5.5, 5.6, and 5.7). The summary of the results given in the Table 5.2 below was used to construct the associated graph (Figure 5.8), which portrays the percentage removal versus electrolyte concentration within the same detention time. The increase of phenol removal efficiency in the first three experiments is attributed to the fact that when the concentration of the electrolyte increases, the conductivity of the water matrix will in turn increase. This will result in phenol oxidation enhancement. Further increase in the electrolyte concentration results in reduction of the oxidation capacity of the system due to the following reasons:

- Higher energy consumption in the water matrix.
- Formation of solvated ion pairs such as sodium ion (Na⁺) and chloride ion (Cl⁻), where sodium ion has no functional effect as a "free ion" catalyst.

The results indicate that the optimum phenol removal is at concentration of 6000 mg/l (Figure 5.8). The data of phenol concentration and pH for the conducted experiments are attached in the appendix (Tables A19, A20, A21, and A22).

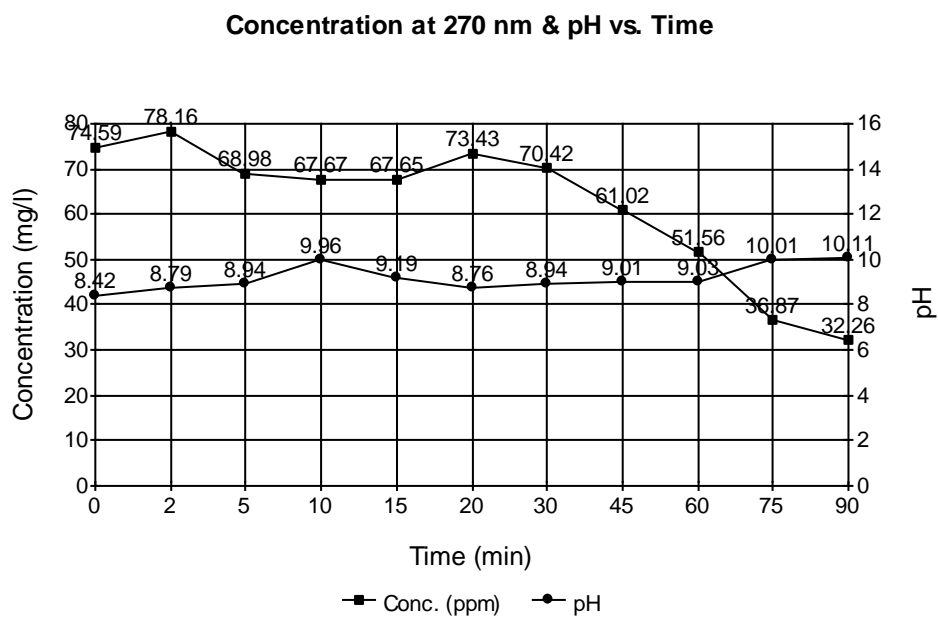


Figure 5.4: Phenol Concentration and pH vs. Contact Time after Electrochemical Treatment at 2 g/L NaCl and 30 mA/cm² Current Density

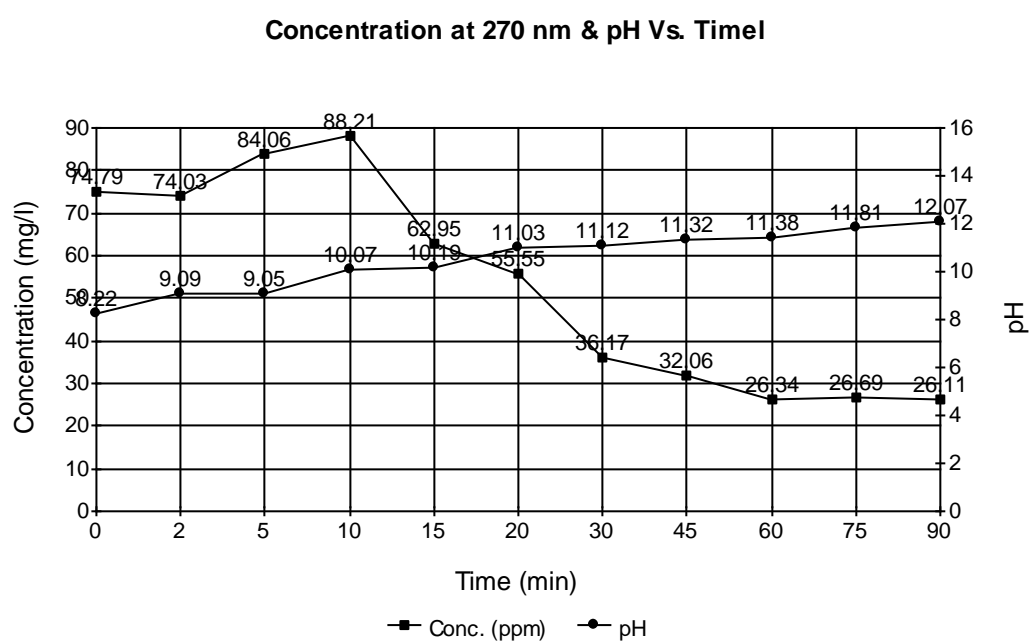


Figure 5.5: Phenol Concentration and pH vs. Contact Time after Electrochemical

Treatment at 4 g/L NaCl and 30 mA/cm² Current Density

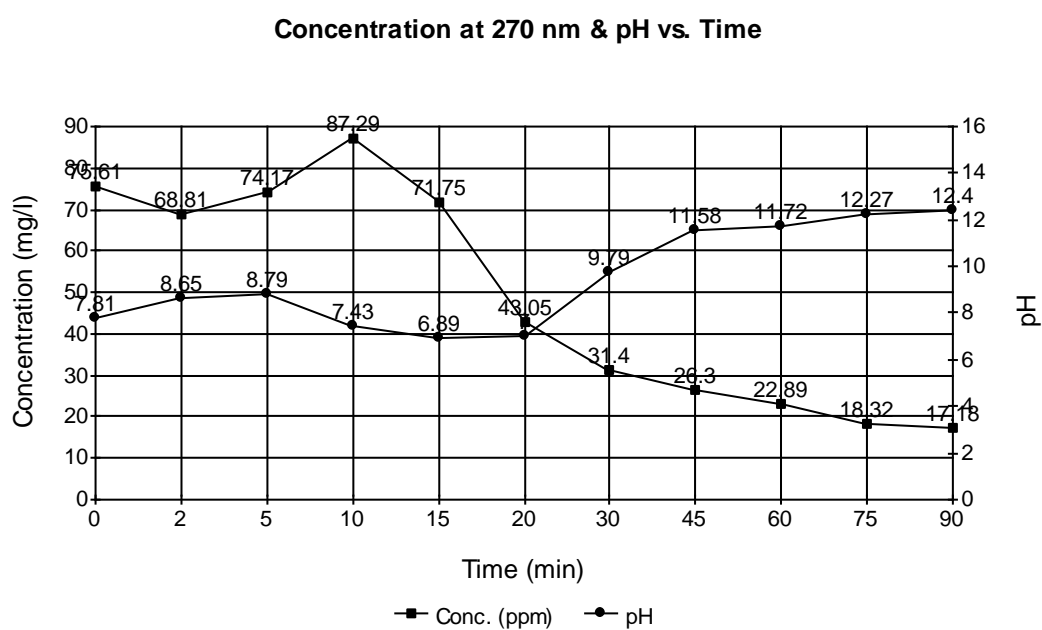


Figure 5.6: Phenol Concentration and pH vs. Contact Time after Electrochemical Treatment at 6 g/L NaCl and 30 mA/cm² Current Density

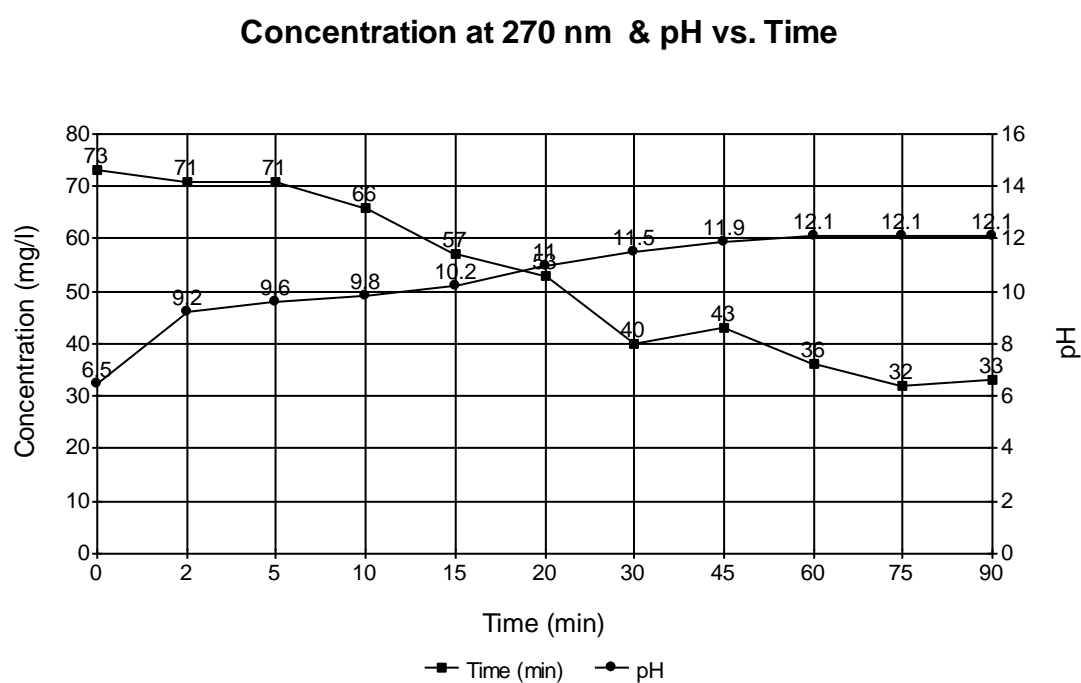


Figure 5.7: Phenol Concentration and pH vs. Contact Time after Electrochemical Treatment at 8 g/L NaCl and 30 mA/cm² Current Density

Table 5.2: Removal Percentage of Phenol after 90 Minutes of Treatment at 30 mA/cm²**Current Density and Different Electrolyte Concentrations**

Sodium Chloride Concentration (g/L)	Removal Percentage (%)
2	56.8
4	65.2
6	83.6
8	54.5

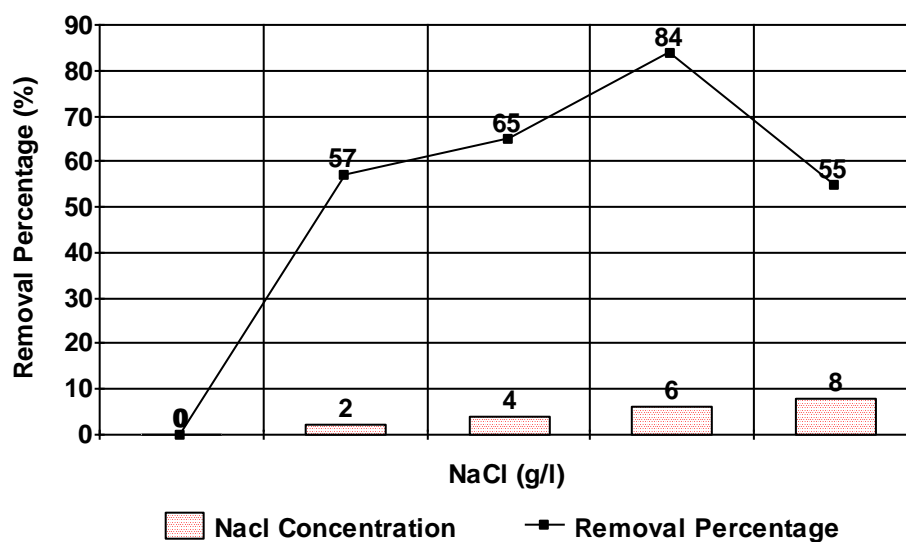


FIGURE 5.8: Phenol Removal Percentage vs. Electrolyte Concentration after 90 Minutes of Treatment at 30 mA/cm² Current Density and 75 ppm Phenol Concentration

5.1.3 CURRENT DENSITY

In this investigation, it was confirmed that the current density considerably affects the phenol degradation process when different current densities were used. Five experiments were performed to identify the optimum current density for phenol removal. During these experiments, the optimum phenol concentration of 75 mg/l and optimum electrolyte 6000 mg/l were used with different current densities ranging from 7.5 mA/cm² to 52.5 mA/cm².

A control experiment was conducted for each test in this investigation (for more details see tables A28 to A37 and figures A29 to A39 in the appendix). Phenol removal efficiencies of 29.44, 45.30, 83.60, 93.85 and 84.22 were realized for 7.5, 15, 30, 45, and 52.5 mA/cm² of current densities, respectively (Figures 5.9 to 5.18).

The results show that the optimum phenol removal was observed at 45 mA/cm² current density (figure 5.19). The figure shows that as the current density increased, phenol oxidation increased till a value of 45 mA/cm² after which phenol oxidation was found to slow down. The increase in phenol oxidation can be attributed to the fact that more current density results in more ionization in the water matrix, which leads to more reactions and consequently, more phenol conversion. Further increase in current density results in slowing down the oxidation process. This may be attributed to the metal transition phenomenon

since active stainless steel electrodes (precipitating electrodes) were used. In this case, metals such as nickel and chromium will migrate from the stainless steel electrodes to the water matrix. This might lead to reduction in the oxidation capacity. The data of phenol concentration and pH of the performed experiments are manifested in tables A23, A24, A25, A26 and A27 in the appendix.

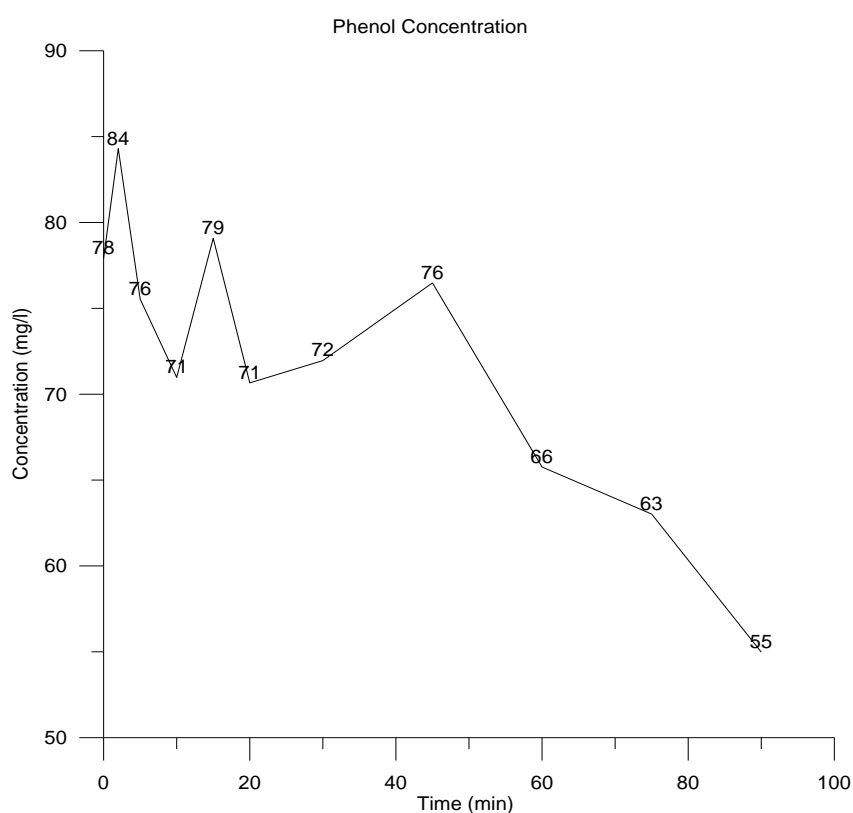


FIGURE 5.9: Phenol Treatment at a Current Density of 7.5 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

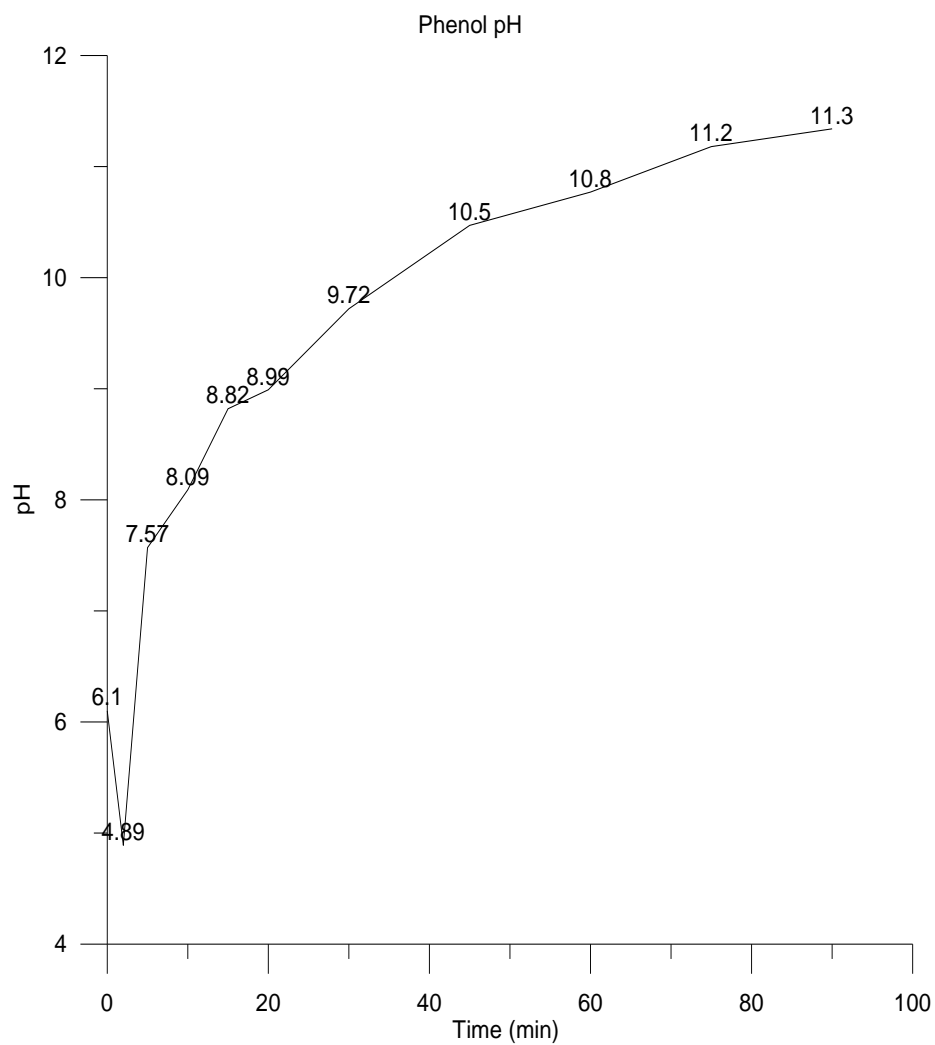


FIGURE 5.10: pH profile During Phenol Treatment at a Current Density of 7.5 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

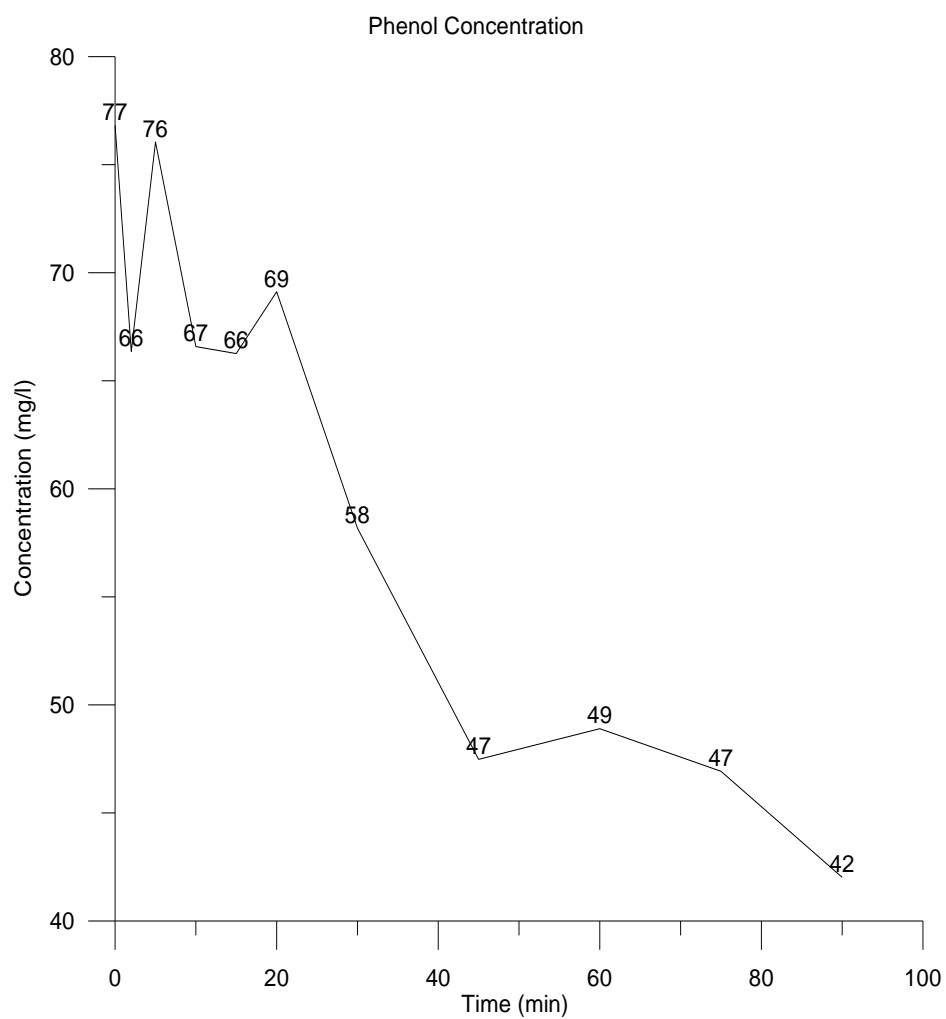


FIGURE 5.11: Phenol Treatment at a Current Density of 15 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

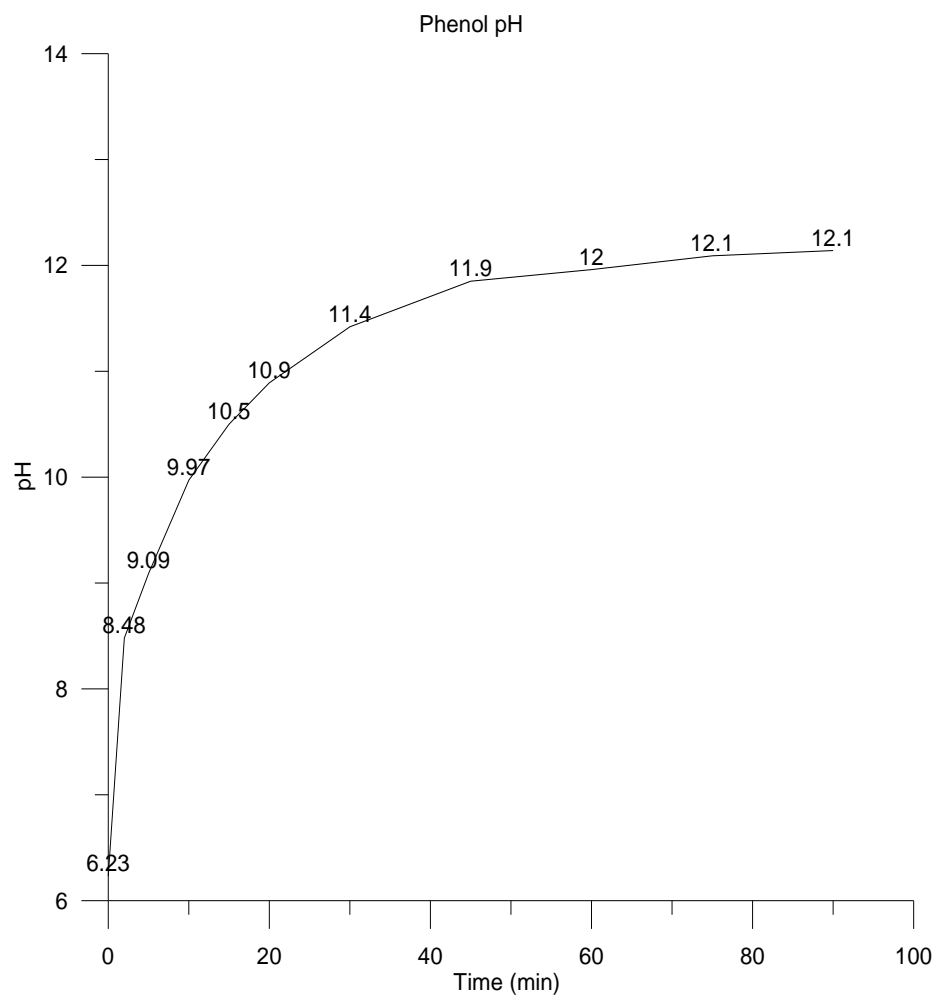


FIGURE 5.12: pH profile During Phenol Treatment at a Current Density of 15 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

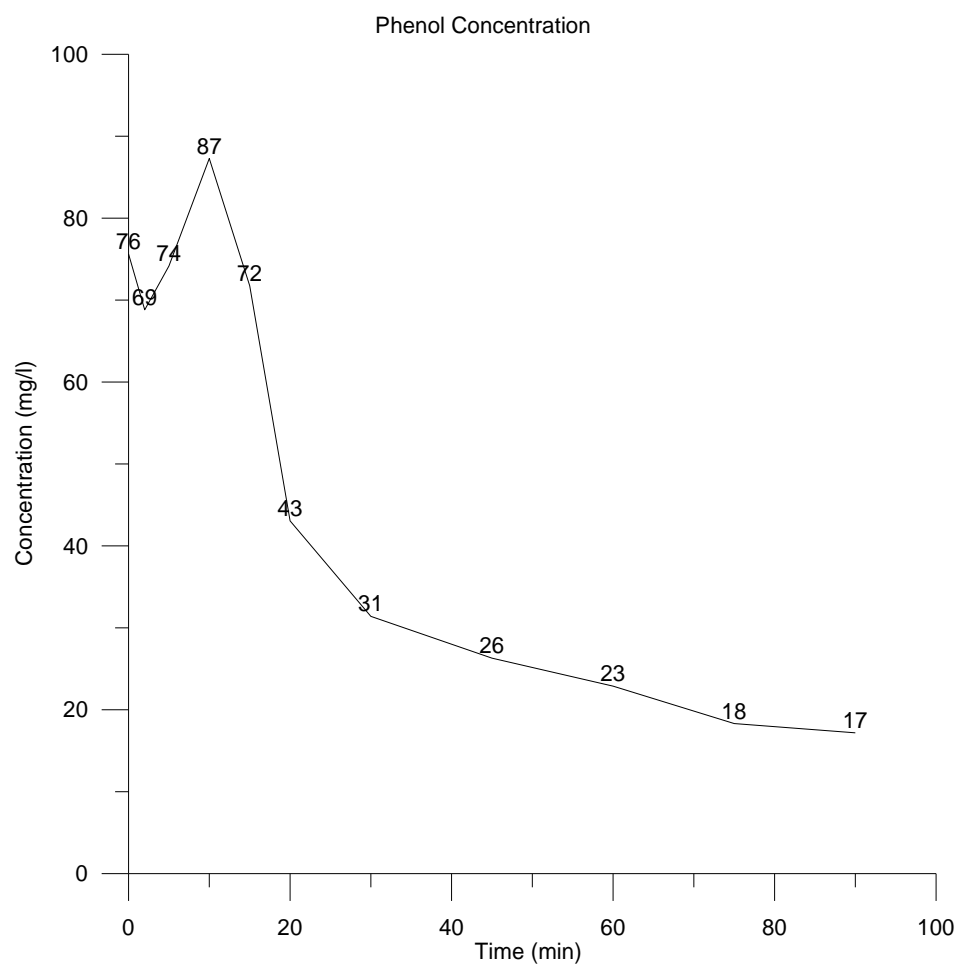


FIGURE 5.13: Phenol Treatment at a Current Density of 30 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

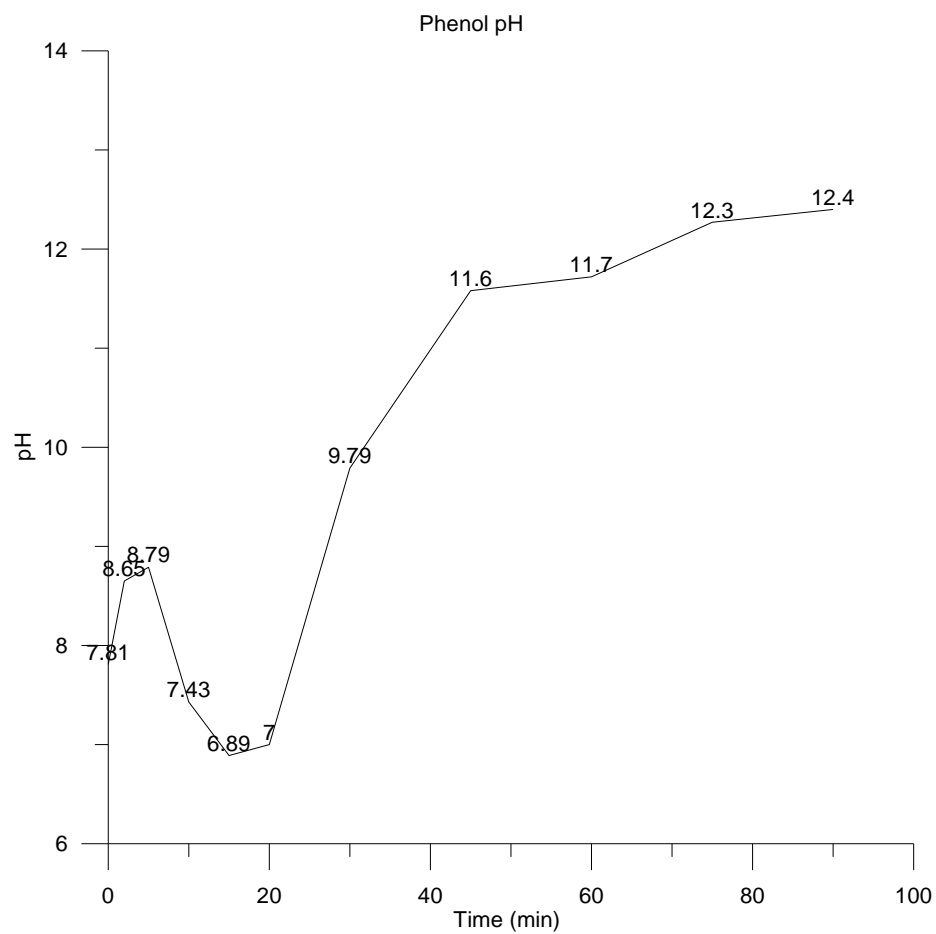


FIGURE 5.14: pH profile During Phenol Treatment at a Current Density of 30 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

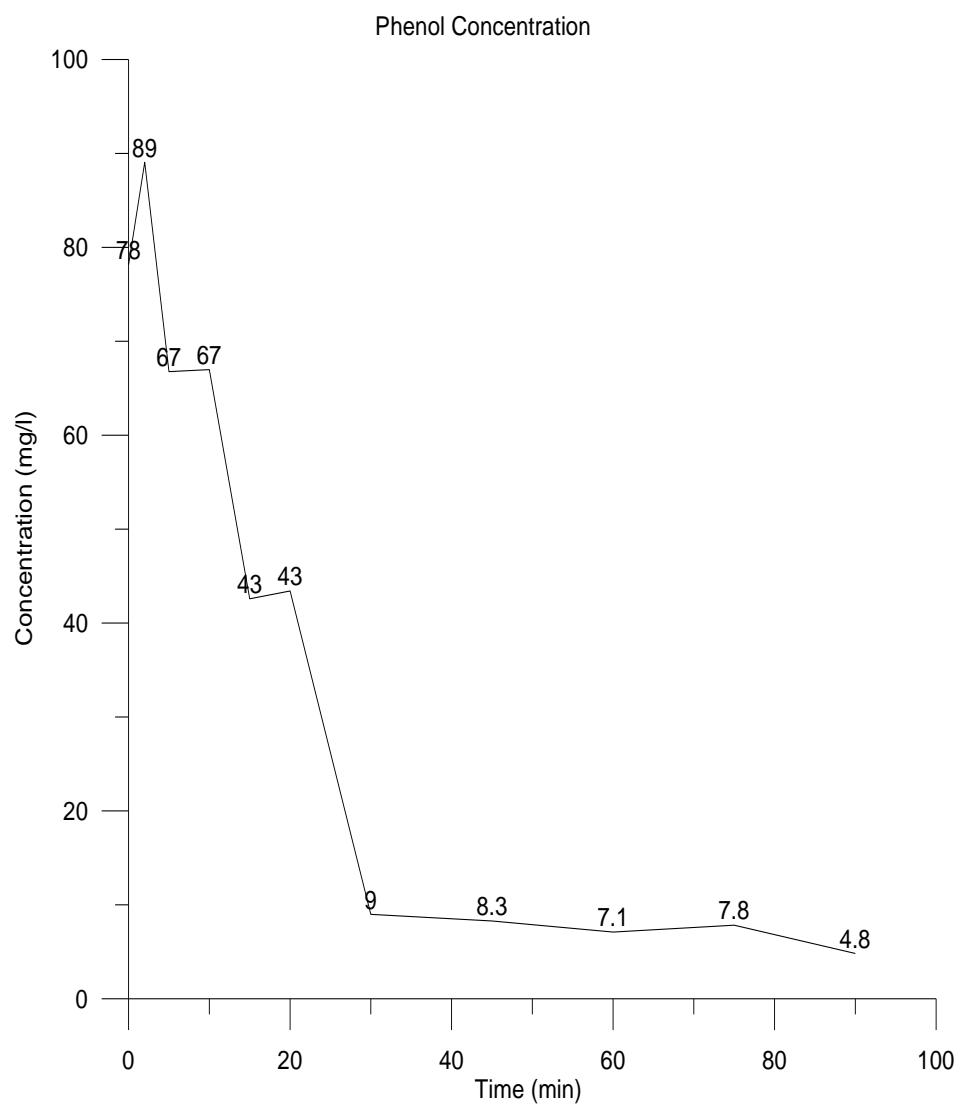


FIGURE 5.15: Phenol Treatment at a Current Density of 45 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

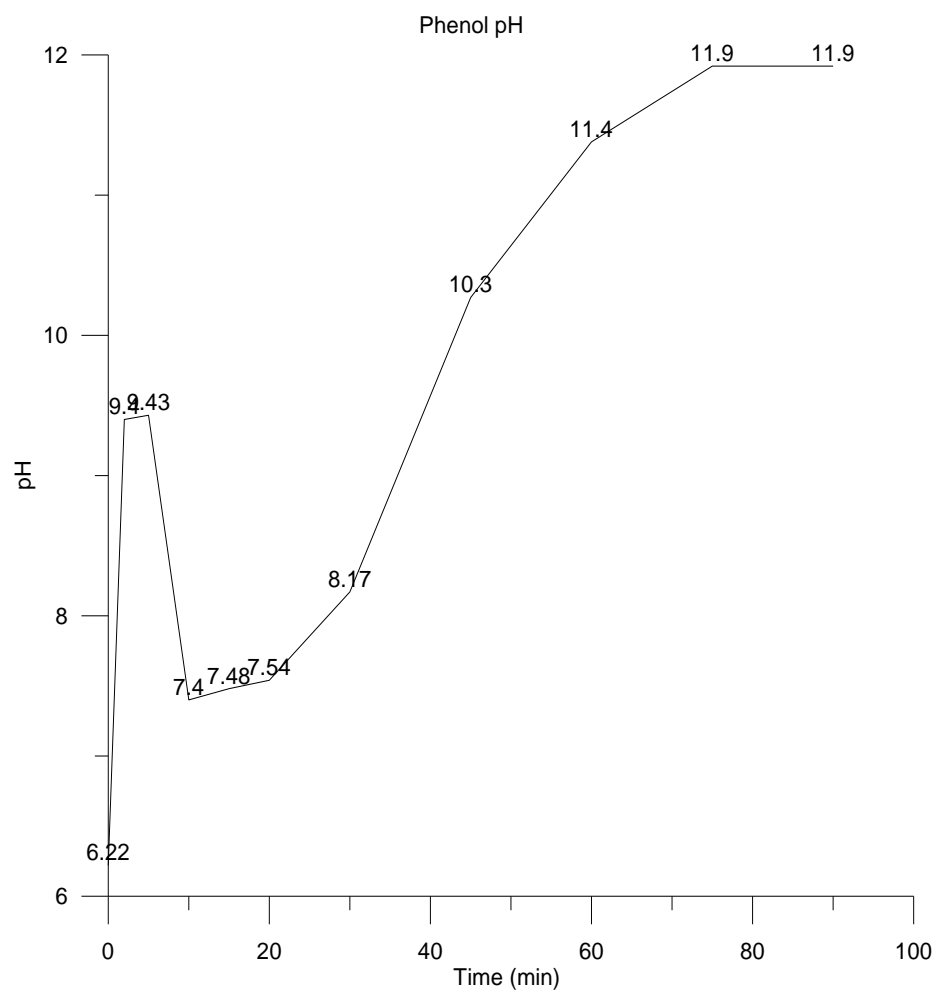


FIGURE 5.16: pH profile During Phenol Treatment at a Current Density of 45 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

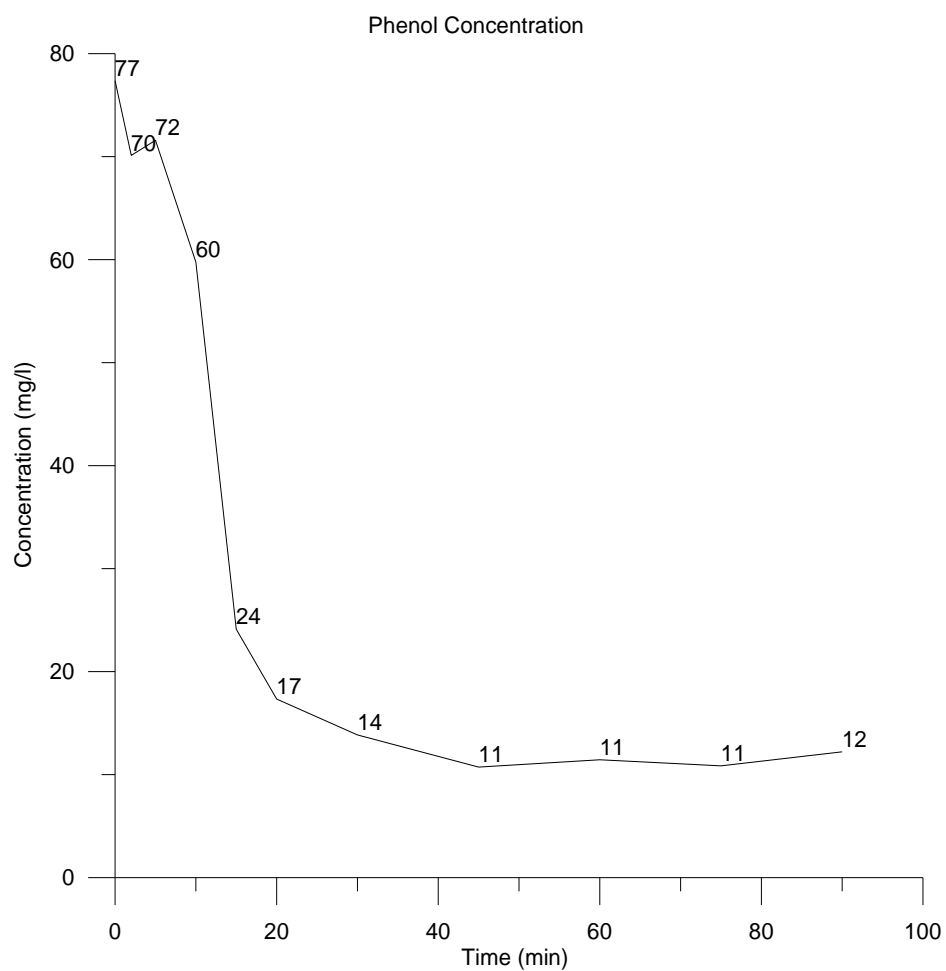


FIGURE 5.17: Phenol Treatment at a Current Density of 52.5 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

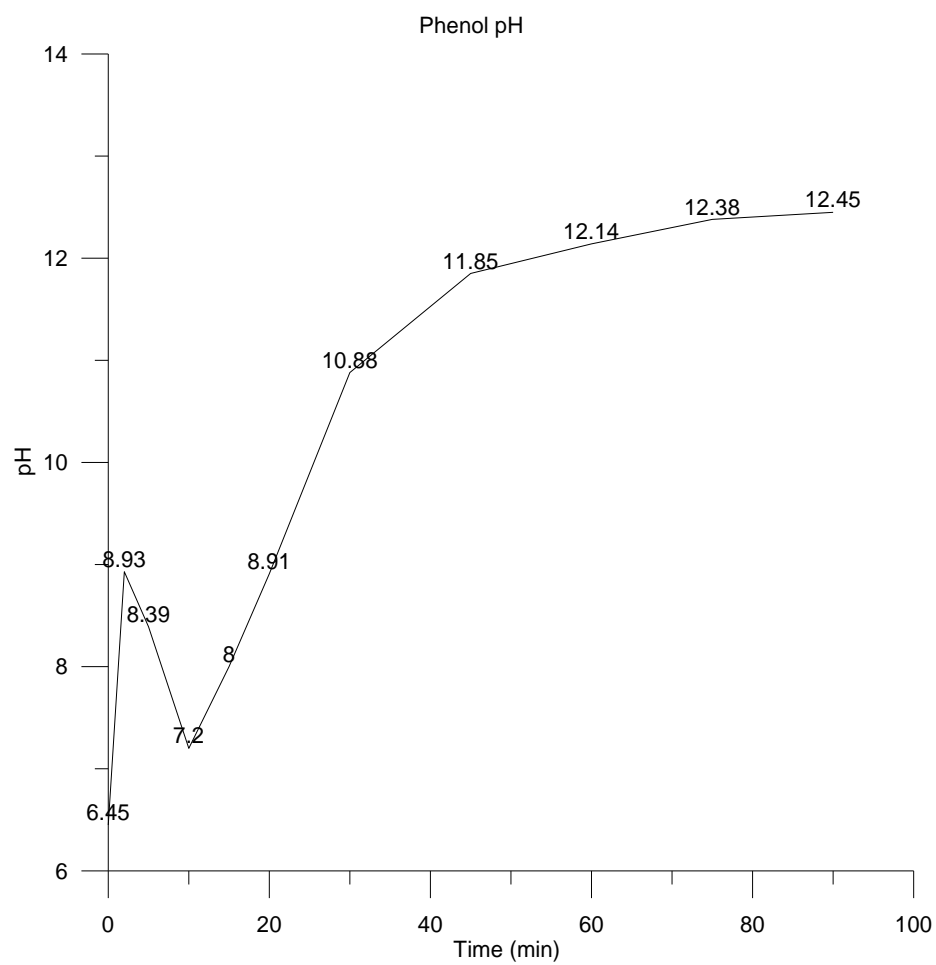


FIGURE 5.18: pH profile During Phenol Treatment at a Current Density of 52.5 mA/cm², Phenol Concentration of 75 mg/l and Optimum Electrolyte Concentration

Table 5.3: Removal Percentage after Phenol Treatment at Optimum Phenol and Electrolyte Concentrations with Different Current Densities:

Current Density (mA/cm²)	Removal Percentage (%)
7.5	29.44
15	45.30
30	83.60
45	93.85
52.5	84.22

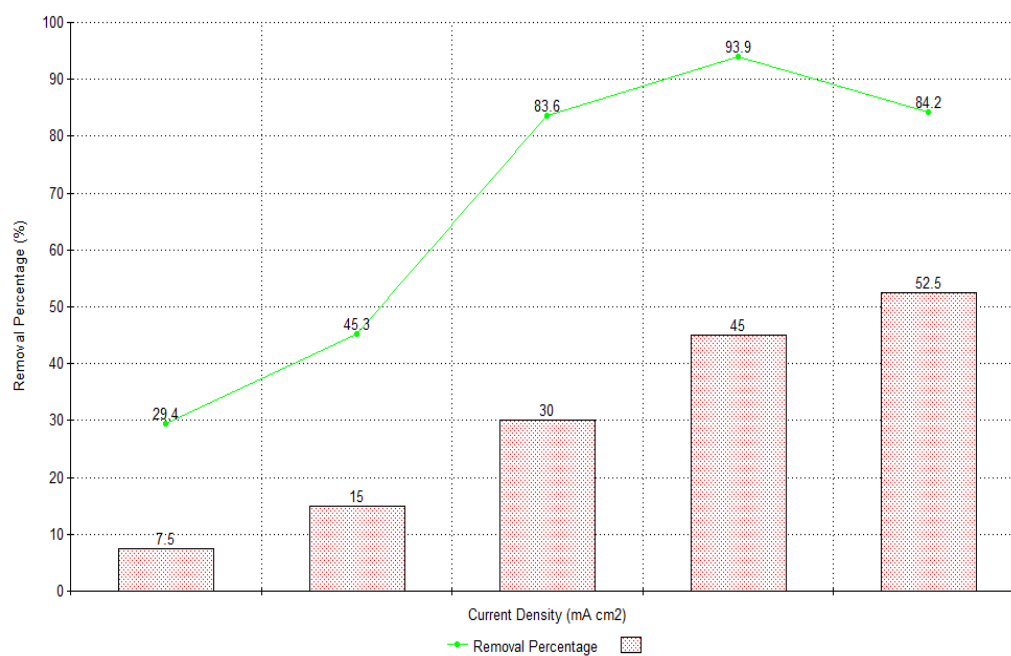


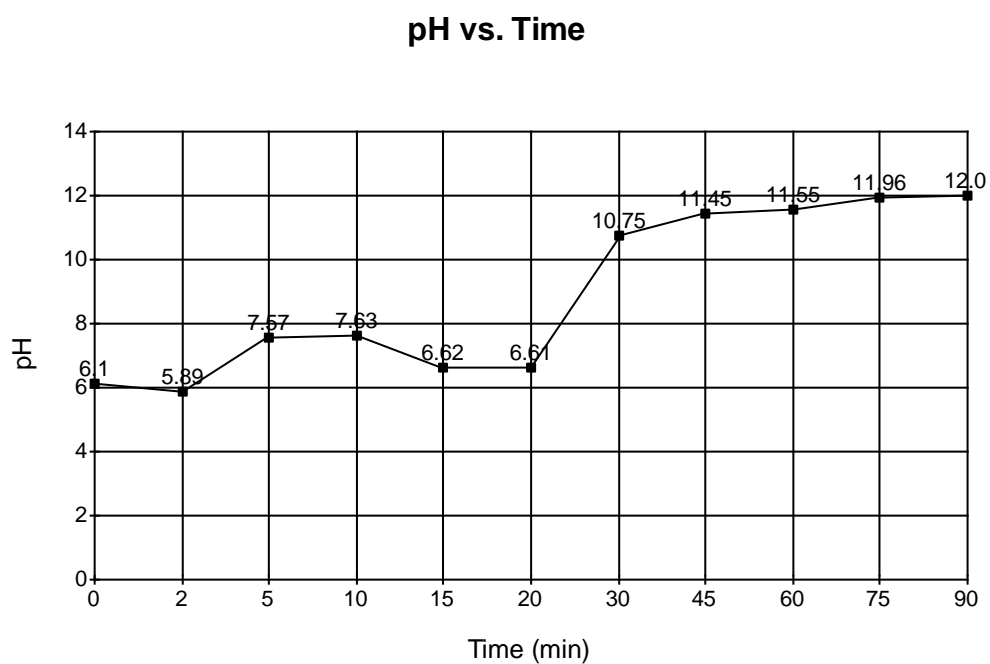
FIGURE 5.19: Removal Percentage after Phenol Treatment at Optimum Phenol and Electrolyte Concentrations with Different Current Densities

5.2. ADDITIONAL PARAMETERS AFFECTING PHENOL DEGRADATION PROCESS

5.2.1. BEHAVIOR OF DEIONIZED WATER

Since the deionized water was used as a base solvent for the phenol preparation, it was necessary to investigate the individual behavior of the deionized water during the electrochemical oxidation process without phenol.

An experiment was carried out for the deionized water alone by setting the optimal operational parameters determined earlier in this study. Figure 5.20 shows pH profile for deionized water after 90 minutes of treatment. In the first 20 minutes of the treatment, it was observed that the pH values did not show any constancy and were not even close to each other. However, after 10 more minutes (at 30 minutes time interval), the pH values significantly increased from 6.61 up to 10.75 and continued to rise till reached 12 at the end of the experiment. Figure 5.21 shows the concentration profile at 270 nm for the deionized water under electrochemical oxidation process at optimum conditions. As shown in this figure, the concentration increased with time till reached the maximum value at 15 minutes. After that, the concentration decreased till reached the minimum value at 30 minutes. Subsequently, the concentration remained steady till the end time of the experiment.



**FIGURE 5.20: pH Profile for Deionized Water under Electrochemical Oxidation
Process at Optimum Conditions**

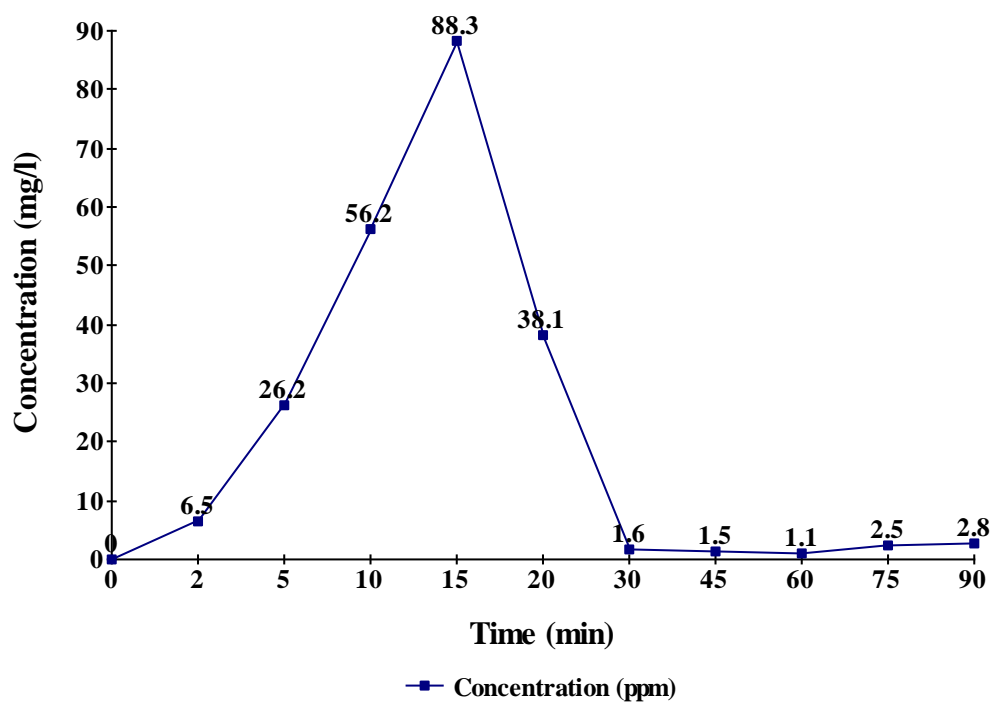


FIGURE 5.21: False Phenol Concentrations Calculated based on Absorbance Readings at 270 nm for Deionized Water

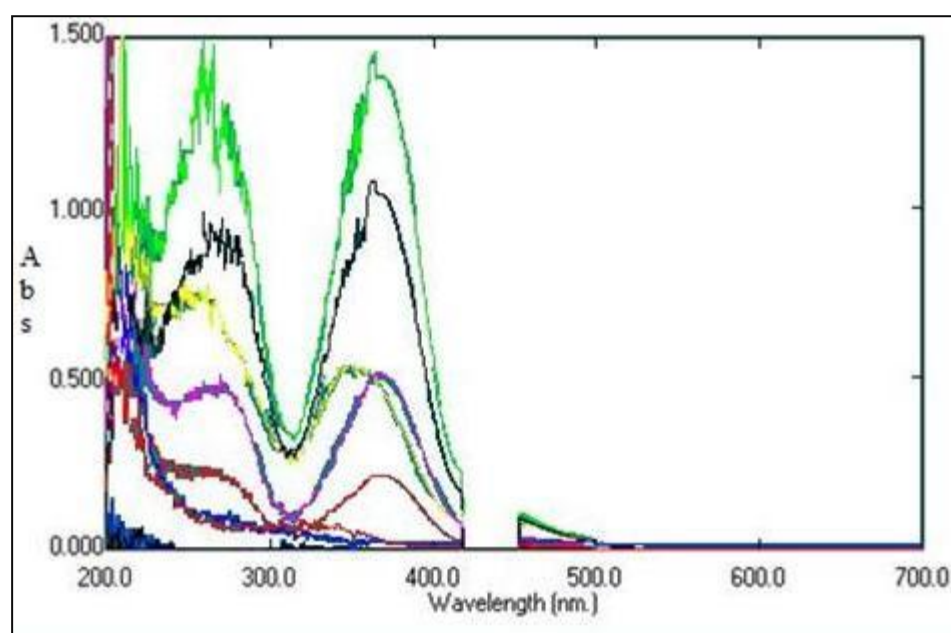


FIGURE 5.22: UV-Spectrophotometer Graph for Deionized Water after Electrochemical Oxidation Process at Optimum Conditions

TABLE 5.4: Metal Analysis for Deionized Water after Electrochemical Oxidation**Process at Optimum Conditions**

Sample No.	Time (min)	Fe 259.941 (ppm)	Cr 267.716 (ppm)	Ni 231.604 (ppm)	Mn 260.569 (ppm)	S 180.731 (ppm)
1	0	0.245	ND*	ND*	ND*	0.362
2	2	0.064	4.64	0.374	0.002	0.936
3	5	0.089	11.1	1.44	0.004	0.726
4	10	0.075	20.2	2.62	0.008	0.845
5	15	0.115	31.4	5.26	0.010	0.443
6	20	0.050	38.0	10.4	0.015	ND*
7	30	0.043	30.2	15.7	0.280	ND*
8	45	0.066	0.017	0.032	0.008	0.233

* ND-not detected

The UV-spectrophotometer apparatus unexpectedly read considerable values of absorbance at 270 nm wavelength, especially during the first phase of the experiment (see figure 5.22 above). The obtained readings for the deionized water could be due to the effect of color as no phenol was added. Since, these readings are obtained at a wavelength similar to that of phenol, a color interfere should be expected. Therefore, it can be concluded that the UV-Spectrophotometer doesn't qualify to quantify the phenol concentrations when precipitating electrodes are used due to color interference. The data of the concentration at 270 nm and pH of the performed experiment are shown in table A40 in the appendix.

The presence of color in the treated sample may be attributed to the metal transition phenomena since active stainless steel electrodes (precipitating electrodes) were used. For further explanation a comprehensive metal analysis was conducted on the treated samples as shown in table 5.4.

5.2.2. STAINLESS STEEL ELECTRODES ANALYSIS

In this study, all the electrochemical oxidation experiments conducted for phenol degradation, the stainless steel electrodes were used as a cathode and anode. Since they are precipitating electrodes, they take part in the reaction within the water matrix. So, it was important to study the composition of the material of the used electrodes. Table 5.5 below presents the metallic composition of the stainless steel electrode along with their concentration in ppm.

TABLE 5.5: Analysis of Stainless Steel Electrodes Used in This Study

Metal	Sample (1)	Sample (2)	Average
Iron, (ppm)	465,616	437,182	451,399
Chromium, (ppm)	124,284	139,219	131,751
Nickel, (ppm)	55,874	69,270	62,572
Molybdenum, (ppm)	1,540	1,443	1,492
Manganese, (ppm)	7,915	7,258	7,587
Silicon, (ppm)	2,440	2,042	2,241
Phosphorus, (ppm)	3,668	3,158	3,413

5.2.3. EFFECT OF pH

To study the effect of pH on the phenol concentration, several experiments were conducted. The effect on the phenol concentration was studied in both alkaline and acidic media. The alkalinity of the media was achieved by adding sodium hydroxide, whereas the acidity was accomplished by adding hydrochloric acid.

In the alkaline state (Table 5.6), it was observed that the phenol concentration at pH 7 slightly decreased from its original value and subsequently remained constant up to pH 10 before considerably decreased reaching 30 ppm at pH 14 (figure 5.23). In acidic state (Table 5.7), there were no big differences observed in the phenol concentration over the range of pH between 1 to 5 (figure 5.24).

To avoid any possible reaction that may occur due to the addition of sodium hydroxide and hydrochloric acid and for further confirmation, pH 4 & pH 10 buffer tablets were used (Table 5.8). The phenol concentration at pH 4 significantly increased and decreased at pH 10 by about 5 ppm from the original concentration (figure 5.25). When the electrolyte, the sodium chloride, was added in the acidic state, the increase in the phenol concentration became less (Figure 5.26). This proves that the phenol concentration decreases in the alkaline media and increases in the acidic media.

TABLE 5.6: Concentration and pH Data of Phenol at Alkaline Condition

No.	Additives	pH_(desired)	pH_(attained)	Absorption (nm)	Conc. (ppm)
0	(Blank)	-	6.59	0.6505	52.78
1	Sodium Chloride	-	6.38	0.6648	53.96
2	Sodium Chloride and Sodium Hydroxide	6	5.92	0.6648	53.96
3	Sodium Chloride and Sodium Hydroxide	7	7.00	0.6057	49.07
4	Sodium Chloride and Sodium Hydroxide	8	8.03	0.6016	48.74
5	Sodium Chloride and Sodium Hydroxide	9	9.02	0.6003	48.63
6	Sodium Chloride and Sodium Hydroxide	10	10.06	0.6211	50.35
7	Sodium Chloride and Sodium Hydroxide	11	11.05	0.4862	39.20
8	Sodium Chloride and Sodium Hydroxide	12	12.00	0.4902	39.53
9	Sodium Chloride and Sodium Hydroxide	13	13.00	0.4332	34.82
10	Sodium Chloride and Sodium Hydroxide	14	14.02	0.3718	29.74

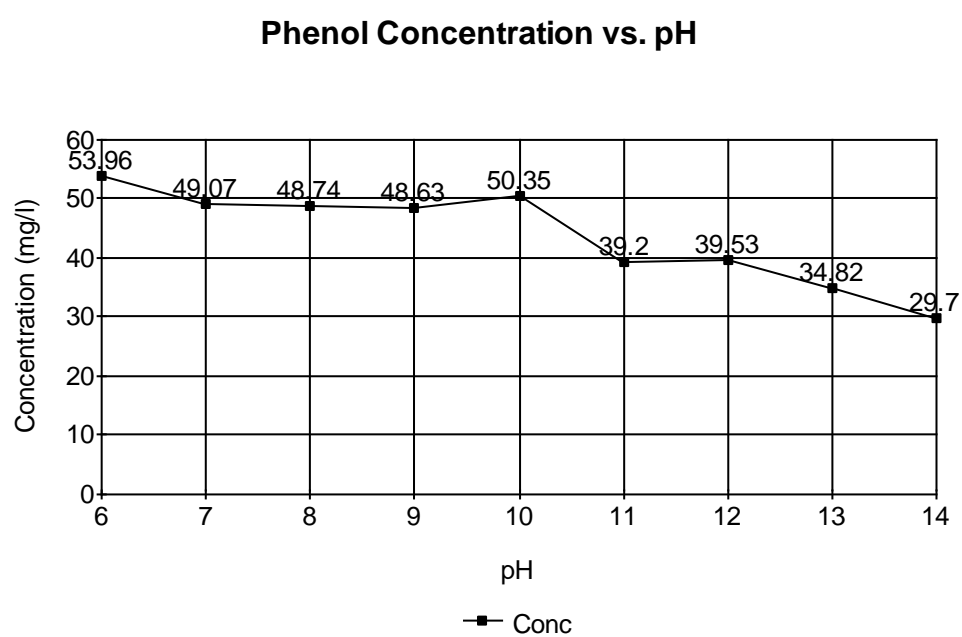


FIGURE 5.23: Phenol Concentration Vs. pH at Alkaline Condition

TABLE 5.7: Concentration and pH Data of Phenol at Acidic Condition

No.	Additives	pH_(desired)	pH_(attained)	Absorption (nm)	Conc. (ppm)
0	(Blank)	-	6.57	0.6511	52.83
1	Sodium Chloride	-	6.33	0.6579	53.39
2	Sodium Chloride and Hydrochloric acid	5	5.04	0.4930	39.76
4	Sodium Chloride and Hydrochloric acid	4	4.02	0.5492	44.40
5	Sodium Chloride and Hydrochloric acid	3	3.07	0.6031	48.86
6	Sodium Chloride and Hydrochloric acid	2	2.02	0.4502	36.22
7	Sodium Chloride and Hydrochloric acid	1	1.03	0.3636	29.07

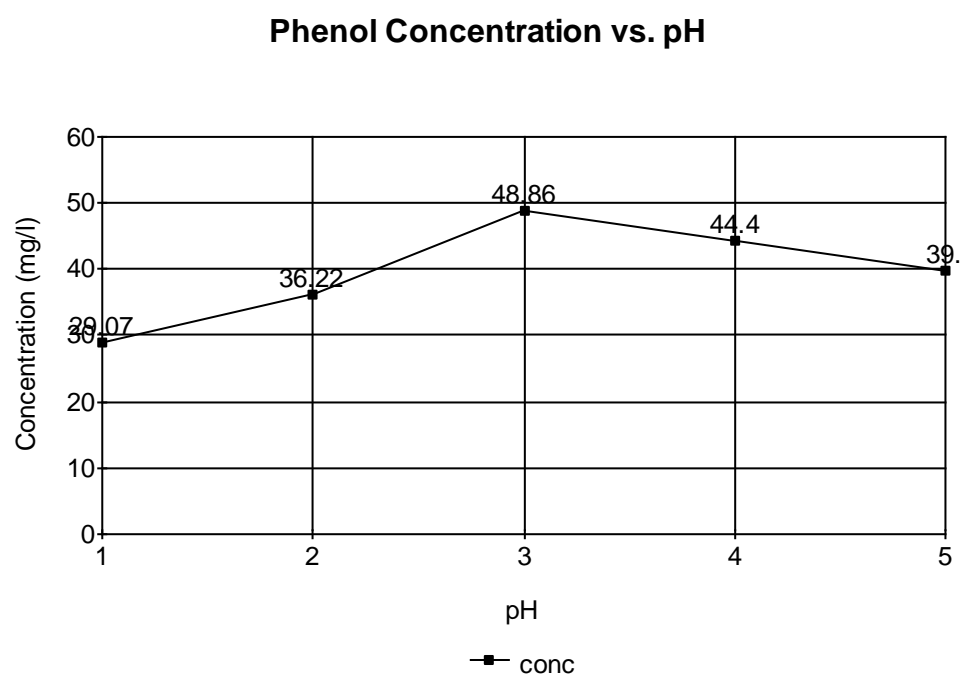
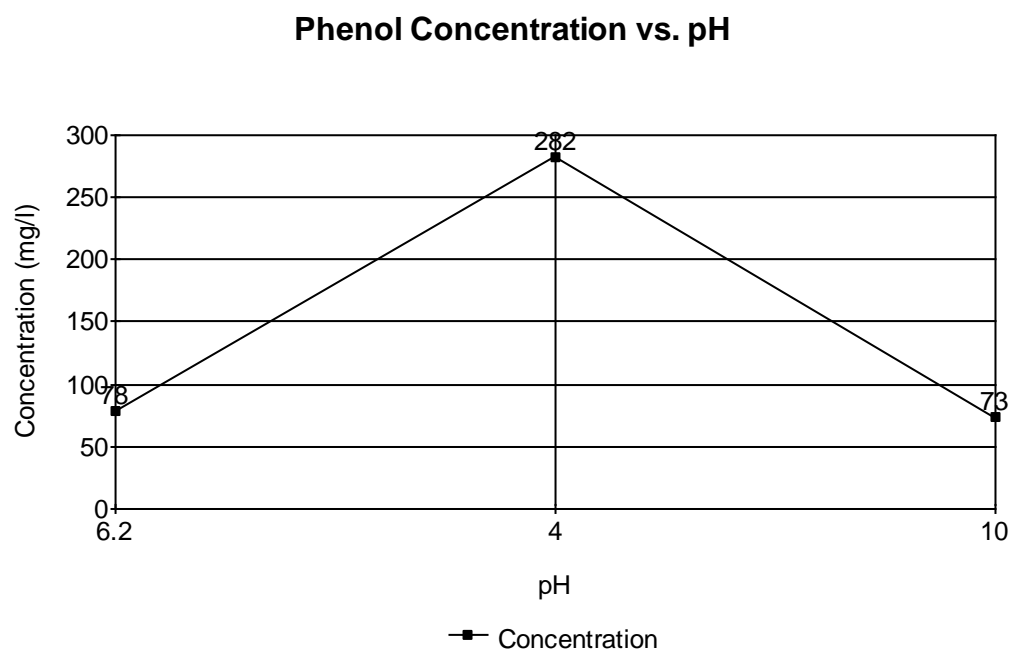


FIGURE 5.24: Phenol Concentration Vs. pH at Acidic Condition

TABLE 5.8: Phenol Concentration and pH Data at Acidic and Alkaline Conditions

No.	Additives	pH_(desired)	pH_(attained)	Absorbance (nm)	Conc. (ppm)
Without Sodium Chloride					
1	Blank	-	6.56	0.9504	77.56
2	pH 4 - buffer (tablet)	4	4.03	3.4291	282.41
3	pH 10 – buffer (tablet)	10	10.04	0.8907	72.63
With Sodium Chloride					
4	Blank	-	5.60	0.9564	78.06
5	pH 4 - buffer (tablet)	4	3.98	2.0483	168.30
6	pH 10 – buffer (tablet)	10	9.95	0.8948	72.97



**FIGURE 5.25: Phenol Concentration Vs. pH at Acidic and Alkaline Conditions
without Sodium Chloride**

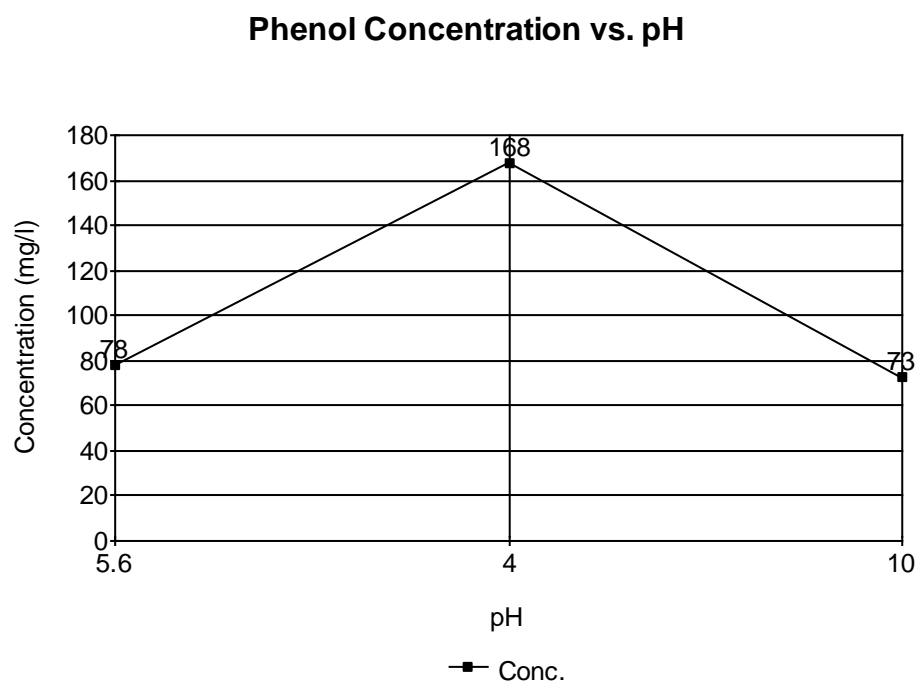


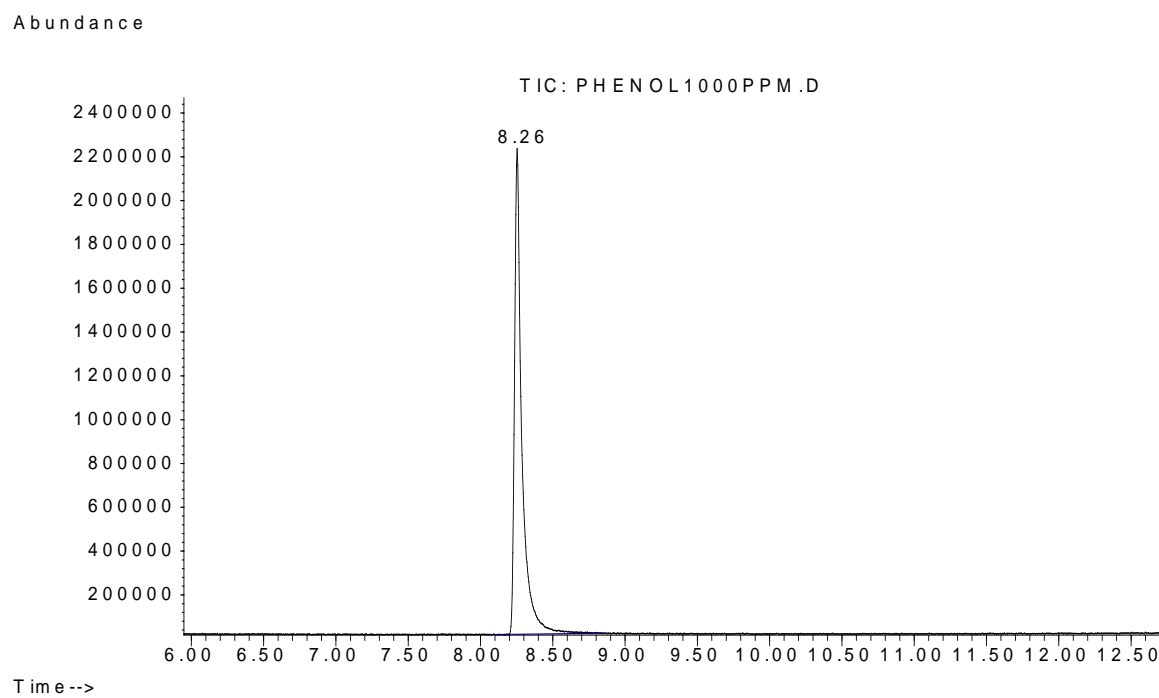
FIGURE 5.26: Phenol Concentration Vs. pH at Acidic and Alkaline Conditions with Sodium Chloride

5.2.4 PHENOL PURITY AND STABILITY UNDER PRE-TREATMENT CONDITIONS

For accuracy, the purity of the used phenol was analyzed using GC-MS to confirm that there are no other impurities associated with the used phenol. GC-MS did not detect any substances other than phenol as shown in figure 5.27 below. This assures the purity of the phenol used in this study.

An experiment was carried out to investigate the stability of the phenol under the pre- treatment conditions (the ambient air, temperature, additives, and the stirring condition, etc.). Figure 5.28 below shows that phenol concentration was fluctuating around a value of about 85 mg/l over a time period of 90 minutes, where obtained readings did not reflect any significant variation in the phenol concentration.

Figure 5.29 shows the behavior of pH over the period of 90 minutes. In the first 2 minutes, it was noticed that there was a little drop in the pH value which may be attributed to the atmospheric carbon monoxide and carbon dioxide dissolved in the phenol solution. After two minutes, the pH values were observed to be consistent with insignificant variation till the end of the 90 minutes. For additional information about phenol concentration and pH see table A41 in the appendix.



No.	Ret. Time	Peak Area	Identification
1	8.255	78382161	Phenol Std.

**Figure 5.27: GC-MS Chromatogram for Phenol with Deionized Water
As a Base Solvent**

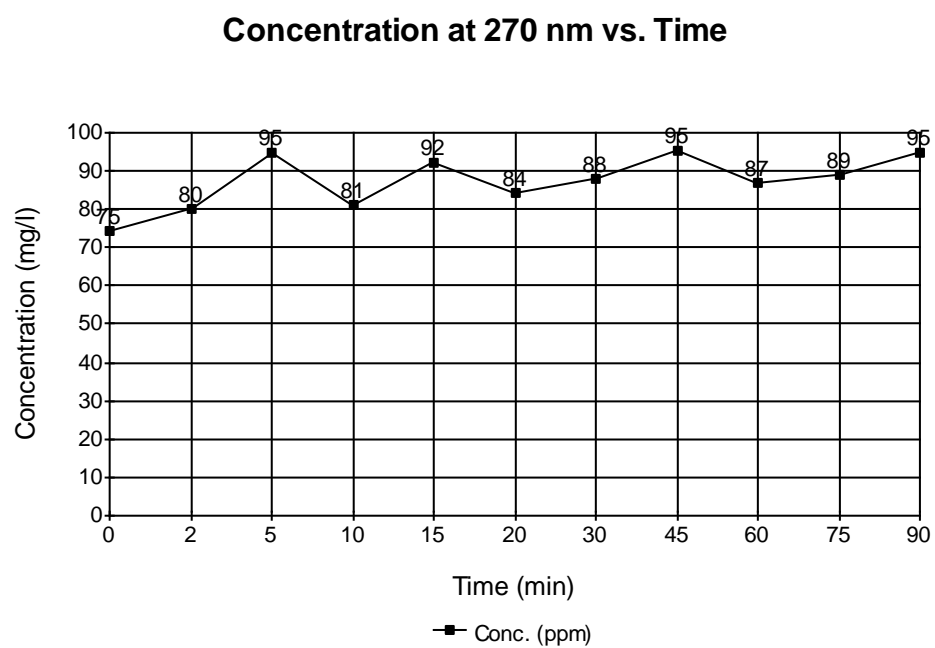


FIGURE 5.28: Phenol Concentration at Pre-treatment Condition

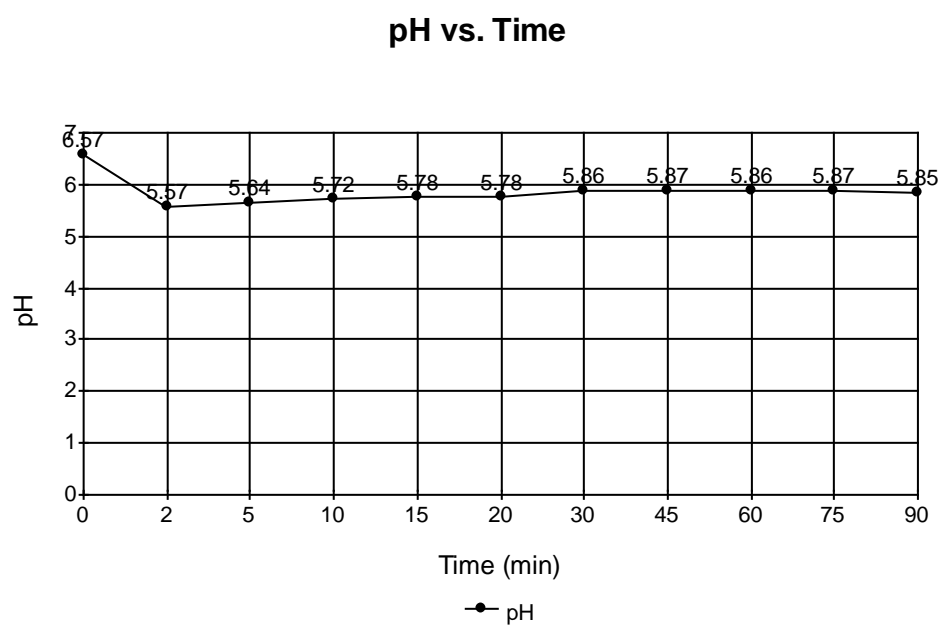


FIGURE 5.29: pH Profile for Phenol at Pre-treatment Condition

5.3. PHENOL ANALYSIS AFTER TREATMENT AT OPTIMUM CONDITIONS

Since the operational parameters (*Electrolyte concentration and Current density*) and other influential parameters (*Section 5.2.*) were set at the optimum conditions, a final experiment was conducted using deionized water as a base solvent for phenol. The concentration of phenol was detected throughout the experiment at time intervals of 0, 2, 5, 10, 20, 30, 45, 60, 75, and 90 minutes.

It can be noted that after the decrease in the phenol concentration by 7 ppm at the first two minutes of treatment, the concentration of phenol reached the highest value observed (87 ppm) at 10 minutes (figure 5.30). Subsequently, a regular decrease in the concentration of phenol was observed with the increase in contact time. However, the removal of phenol didn't exceed 84 percent since the minimum concentration at the end of the experiment was 17 ppm. The results of figure 5.30 are discussed in the subsequent section (5.4).

Figure 5.31 shows that after the increase in pH of the phenol during the first five minutes of the experiment the pH of the phenol reached the lowest observed value (6.89) at 15 minutes. After that a regular increase in the pH of the phenol was observed with the increase in contact time. The maximum pH observed was 12.4 for a contact time of 90 minutes. The results of figure 5.31 are discussed in the subsequent section (5.4). For more details about the phenol concentration and pH values of this experiment see table A42 in the appendix.

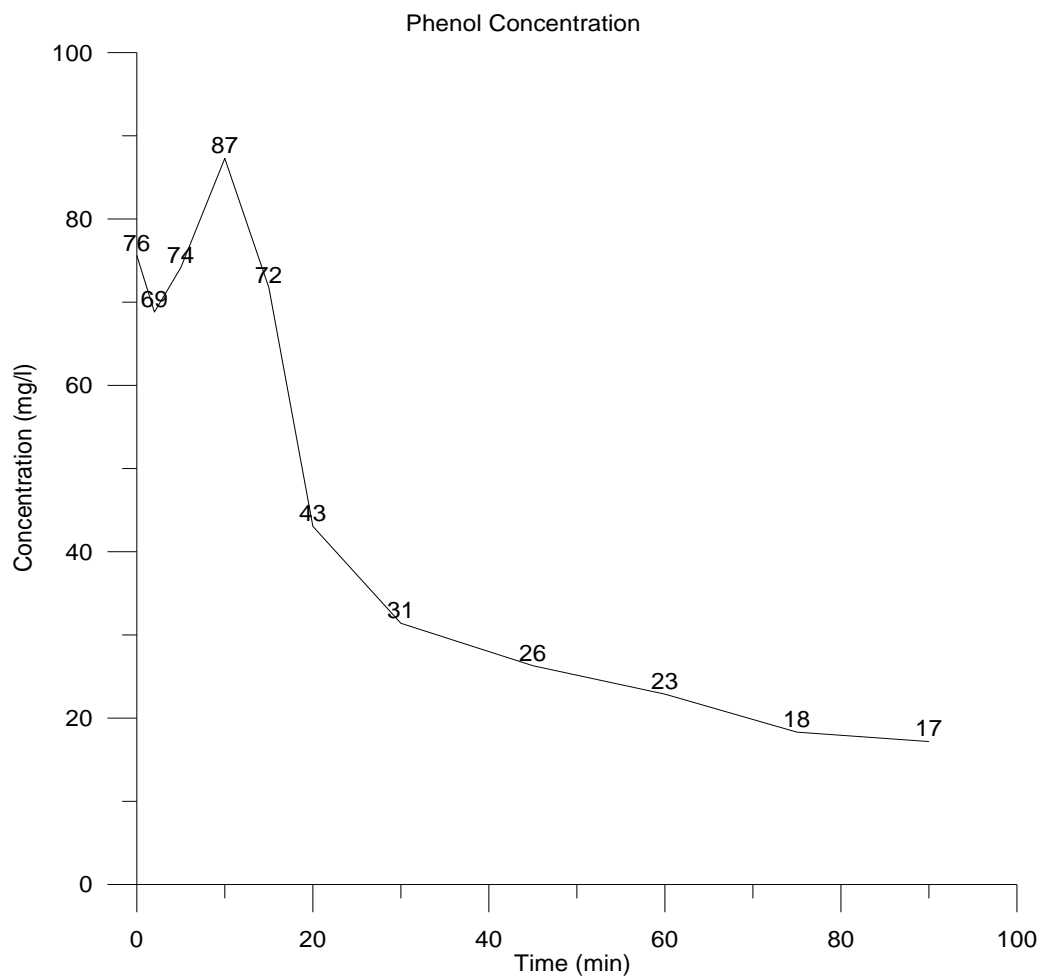


Figure 5.30: Phenol Concentration Profile under Electrochemical Oxidation Treatment at Optimum Conditions

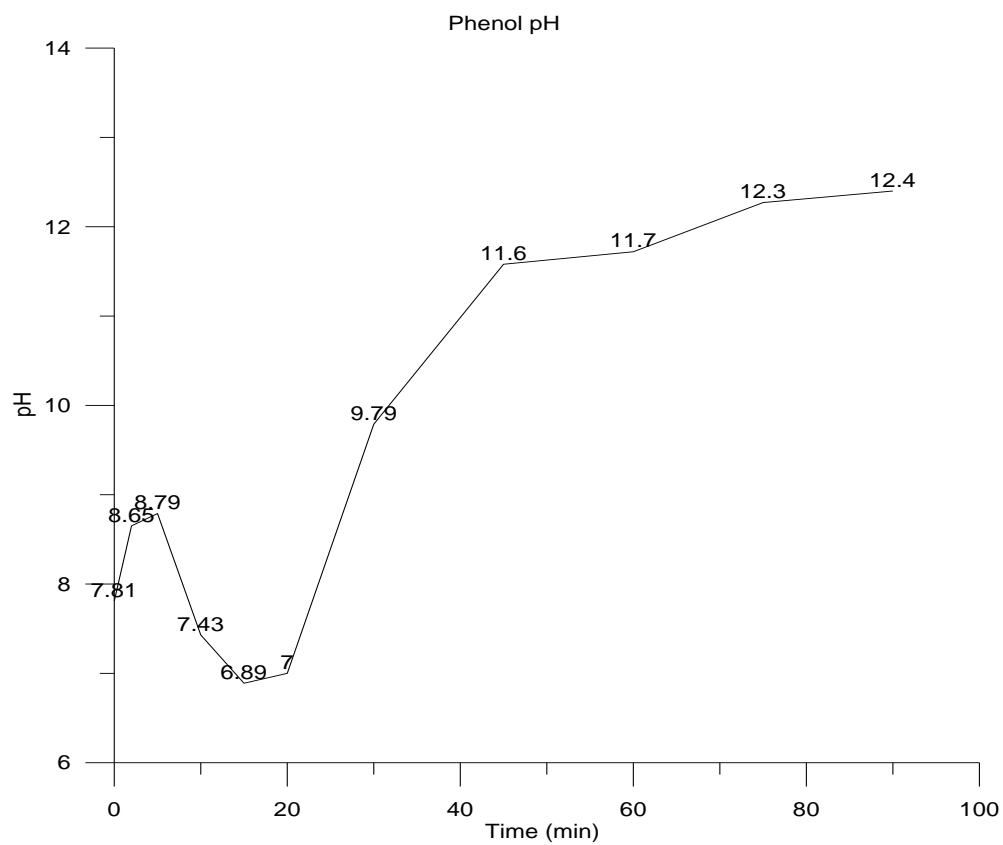


Figure 5.31: pH Profile for Phenol under Electrochemical Oxidation Treatment at Optimum Conditions

5.4. INTERFERENCES IN PHENOL ANALYSIS

As mentioned before in section 5.2.1, the UV-spectrophotometer apparatus reads substantial values of absorbance at 270 nm wavelength, especially during the first phase of the experiment conducted in the absence of phenol using deionized water (see figure 5.22 in section 5.2.1 above). Therefore, the phenol readings should be expected to be interfered with color readings at 270 nm wavelength. Consequently, the obtained readings demonstrated in figure 5.30 in the above section may not indicate the presence of phenol and could be attributed to the effect of color. When this analysis was repeated using Gas Chromatography (GC) and Gas Chromatography-Mass Spectrometry (GC-MS), the obtained results indicate clearly that the phenol degraded within the first two to ten minutes of treatment and completely mineralized at 20 minutes (see figures A43 to A55 in the appendix). This confirms that the UV-Spectrophotometer does not qualify to quantify the phenol due to color interference. Therefore, GC and GC-MS were used for the subsequent analyses of this study to investigate the affect of the raw water chemical species on the phenol degradation process and the possible reaction pathways.

5.5. RAW WATER CHEMICAL SPECIES INVESTIGATION

Fifteen experiments were conducted to investigate the effect of chemical species of the raw water. Different combinations of the chemical species were investigated to identify the species responsible for hindering or delaying the degradation process of the phenol when raw water is used as base solvent. These combinations include individual specie, dual species, triple species and all the species collectively. Calcium sulfate, magnesium

sulfate, magnesium chloride and sodium bicarbonate are the chemical species analyzed in these experiments.

5.5.1. INDIVIDUAL CHEMICAL SPECIES INVESTIGATION

Four experiments were conducted to investigate the four chemical species of the raw water individually using an electrochemical oxidation process set at optimum conditions. As demonstrated in figure 5.32 the calcium sulfate did not hinder or slow down the phenol degradation process as the phenol completely degraded within ten minutes from the start-up of the experiment. The experiment extended to sixty minutes to confirm that no reverse reaction is involved in the process. For more details about the GC Chromatograms of this experiment refer to figures A56 to A59 in the appendix.

When Magnesium sulfate was used as the only raw water specie, the phenol also degraded in ten minutes. The experiment was also extended for another 50 minutes during which the phenol concentration remained zero indicating irreversible reaction (figure 5.33). For more details about this experiment refer to figures A60 to A63 in the appendix.

Based on these results, it was concluded that both calcium sulfate and Magnesium sulfate have no hindering effect on the phenol degradation process as

both calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions work as "free ion" catalysts enhancing the phenol oxidation process.

Magnesium chloride and sodium bicarbonate when investigated individually as raw water chemical species, the phenol degradation during the GC analysis was completely hindered as the phenol disappeared in ten minutes of treatment and reappeared in the magnesium chloride case but ended higher than the original concentration in sodium bicarbonate case. This indicates that the hindrance caused by the magnesium chloride is due to a reverse reaction (figures 5.34 and 35). For further details about these experiments refer to figures A64 to A73 in the appendix.

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- In the sodium bicarbonate case, bicarbonate is a scavenger with a strong effect, which might work as scavenger for OH-radical ($\bullet\text{OH}$) in the process and lower the oxidation capacity. While sodium bicarbonate itself might react with water molecules in the presence of iron powder in hydrothermal conditions to form phenol. Furthermore, after the ionization of phenol hydrogen ion (H^+) may reacts with the bicarbonate ion (HCO_3^-) forming carbonic acid (H_2CO_3), which disintegrates to release carbon dioxide (CO_2) and generate water (H_2O). The phenoxy ion (O^-) reacts with the excess water to regenerate phenol.

—

- In the case of magnesium chloride, aqueous magnesium ion (Mg^{2+}) and chloride ion (Cl^-) are formed. The high concentration of chloride ion (Cl^-) of the electrolyte

leads to a reverse reaction. Hence, magnesium ion (Mg^{2+}) and chloride ion (Cl^-) remain as solvated ion pair where magnesium ion (Mg^{2+}) has no functional effect as a catalyst.

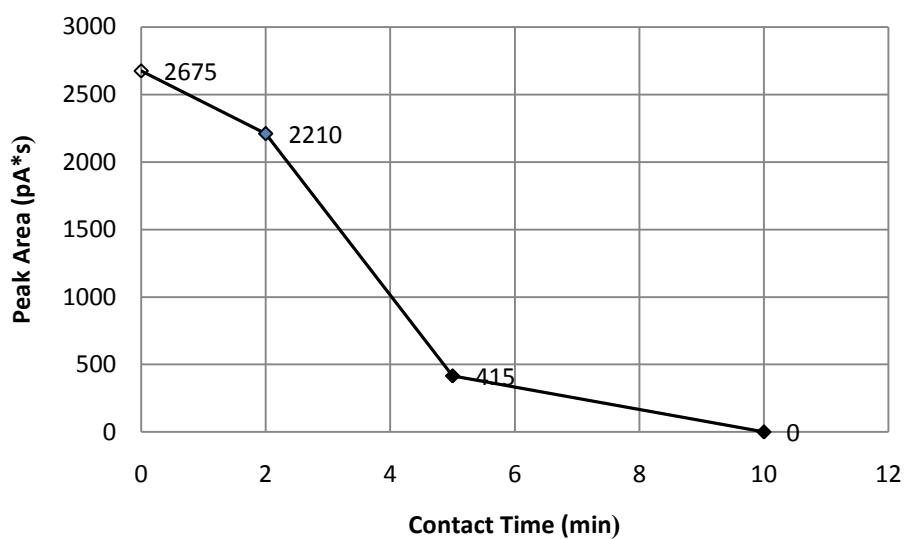


FIGURE 5.32 (a): Peak Area of GC Analysis vs. Contact Time for CaSO_4 Investigation

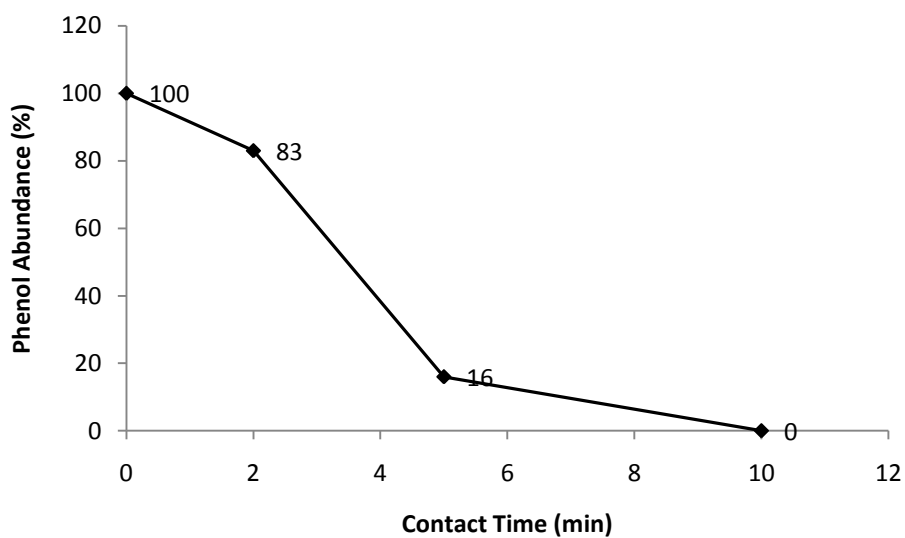


FIGURE 5.32 (b): Phenol Abundance Percentage vs. Contact Time for CaSO_4 Investigation

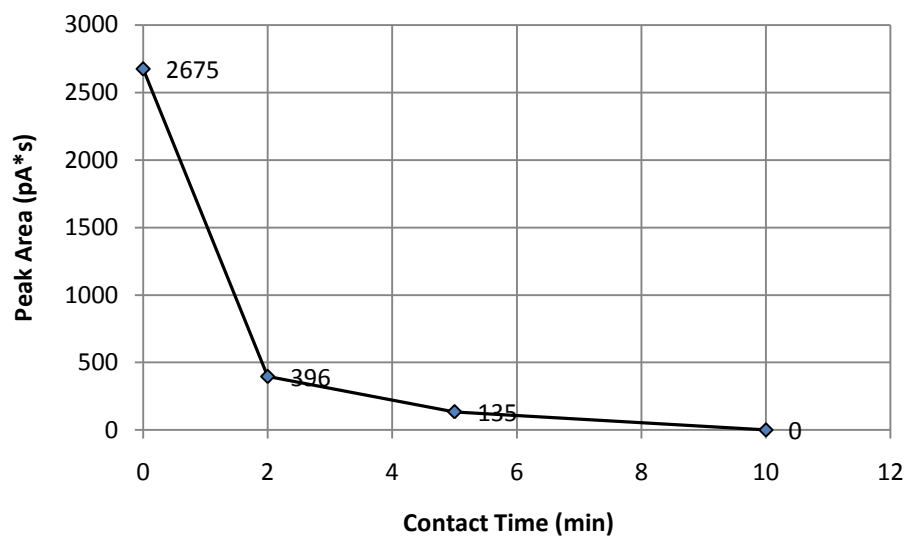


FIGURE 5.33 (a): Peak Area of GC Analysis vs. Contact Time for MgSO₄ Investigation

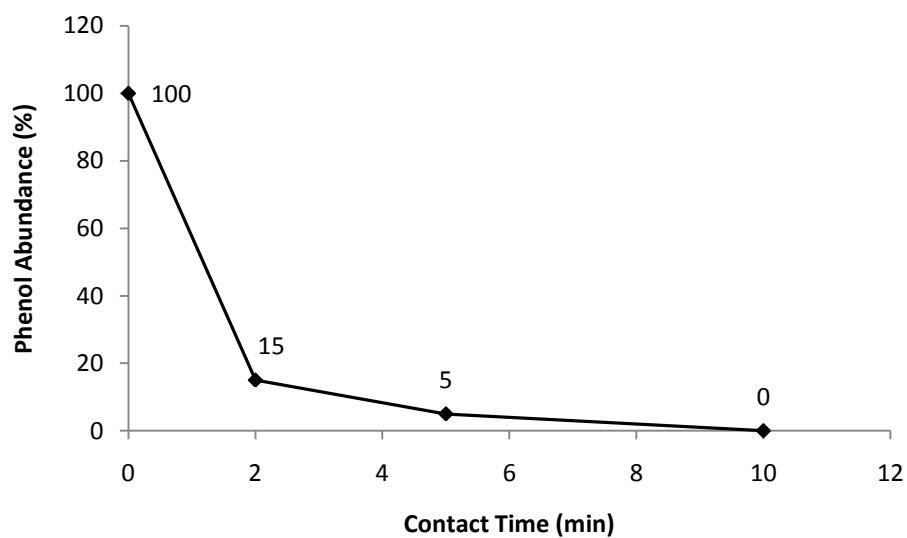


FIGURE 5.33 (b): Phenol Abundance Percentage vs. Contact Time for MgSO₄ Investigation

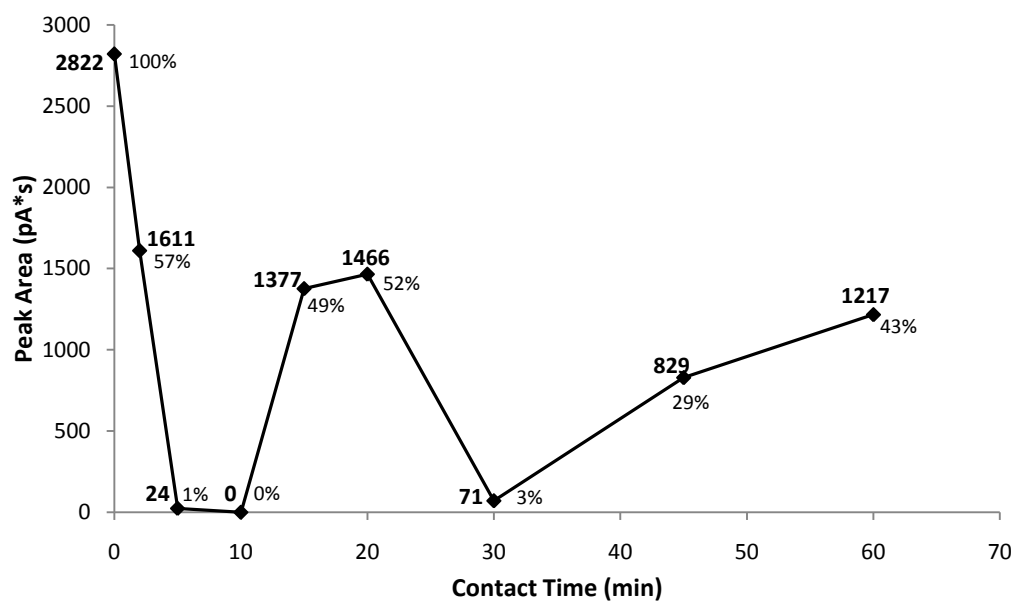


FIGURE 5.34: Peak Area of Phenol and Abundance Percentage vs. Contact Time in MgCl_2 Investigation

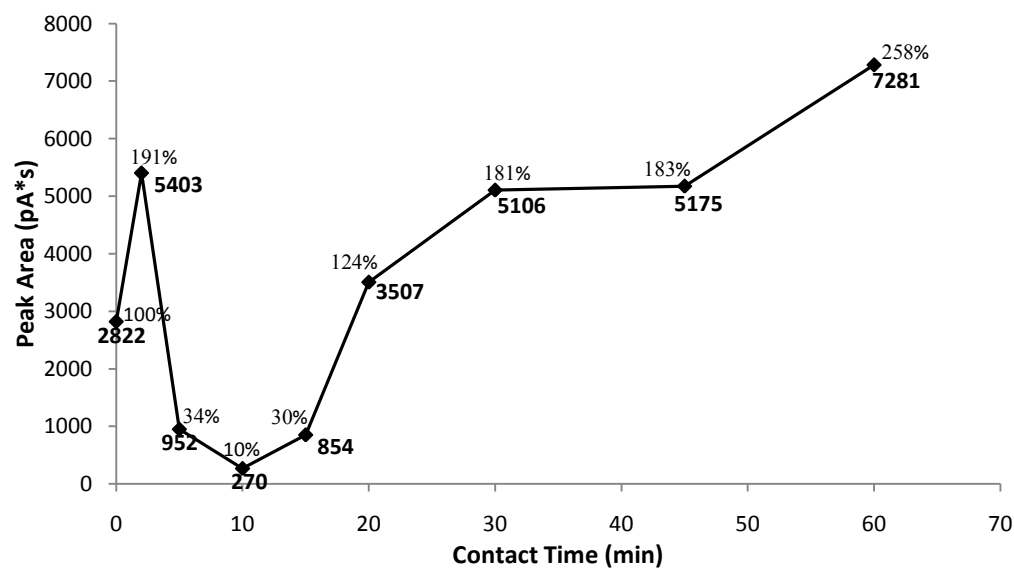


FIGURE 5.35: Peak Area of Phenol and Abundance Percentage vs. Contact Time in NaHCO_3 Investigation

5.5.2 DUAL CHEMICAL SPECIES INVESTIGATION

Dual investigation was performed for the four chemical species of the raw water. Six experiments were carried out to study the effect of chemical species of the raw water on the degradation of phenol using electrochemical oxidation process at optimum conditions.

As the calcium sulfate and magnesium sulfate were used as raw water species, the GC analysis did not show any hindrance to the degradation of phenol as the phenol concentration dropped significantly in the initial two minutes of treatment and no phenol was detected after 10 minutes of treatment. As shown in figures A74 to A78 in the appendix, the phenol concentration remained zero for the rest of the experiment.

When sodium bicarbonate and Magnesium sulfate were used as the only raw water species in the experiment, the phenol was degraded in five minutes as manifested in the GC results.

The experiment was extended to 60 minutes and complete degradation or conversion of phenol was confirmed. For more information about this experiment see figures A79 to A83 in the appendix.

For sodium bicarbonate and calcium sulfate investigation, GC results showed significant removal for phenol in first 5 minutes of treatment, whereas no phenol was detected after 10 minutes. Figures A84 to A88 in the appendix provide further details about these experiments.

In the dual investigation of the effect of sodium bicarbonate and magnesium chloride when used as raw water species, the phenol degradation during the GC analysis was completely hindered as its concentration fluctuated with slight differences throughout the experiment time, and ended almost with its original value. These results confirm the outcome obtained from the individual investigation for both sodium bicarbonate and magnesium chloride in the previous section which indicate that both species play an important role in hindering phenol degradation. For further details about these experiments refer to figures A89 to A92 in the appendix.

The phenol degraded gradually and was completely removed after 15 minutes when calcium sulfate and magnesium chloride were used as the only raw water species in the electrochemical process. Figures A93 to A98 in appendix provide more details about this experiment.

When the effect of both magnesium sulfate and magnesium chloride was investigated using the same method, the phenol concentration dropped significantly after two minutes from the start-up of the process then increased. The

concentration value fluctuated after two minutes and settled to zero after twenty minutes. Refer to figures A99 and A105 in the appendix for more details about this experiment.

As the magnesium chloride unexpectedly showed hindrance when investigated individually, the analyses of the last two experiments were conducted using CG-MS to verify the GC results obtained in the individual investigation of the raw water chemical species.

Table 5.9 summarizes the results of experiments adopted for this investigation.

TABLE 5.9: Effect of Dual Chemical Species on the Phenol Degradation

Dual Combination	Effect on Degradation
NaHCO ₃ and CaSO ₄	Phenol disappeared in 10 minutes of treatment
NaHCO ₃ and MgSO ₄	Phenol disappeared in 5 minutes of treatment
NaHCO ₃ and MgCl ₂	Hindrance
CaSO ₄ and MgSO ₄	Phenol disappeared in 10 minutes of treatment
CaSO ₄ and MgCl ₂	Phenol disappeared in 15 minutes of treatment
MgSO ₄ and MgCl ₂	Phenol disappeared in 20 minutes of treatment

5.5.3 TRIPLE CHEMICAL SPECIES INVESTIGATION

To further investigate the compound effect of the chemical species in the raw water, four experiments were conducted using four combinations of three chemical species.

First, a combination of sodium bicarbonate, calcium sulfate and magnesium sulfate was used as the raw water species in the process. Within five minutes of the process, the phenol concentration dropped considerably and reached zero at ten minutes. Refer to figures A106 to 109 in the appendix for more details about this experiment.

A combination of sodium bicarbonate, calcium sulfate and magnesium chloride was then used as raw water species in the process. It was observed that the phenol degradation was completely hindered by the presence of the combination of these species. This confirmed the conclusion made in the two previous sections that whenever sodium bicarbonate and magnesium chloride exist individually or jointly in the raw water hinder the phenol degradation process. For further details about this experiment, refer to figures A110 to A112 in the appendix.

When a combination of sodium bicarbonate, magnesium sulfate and magnesium chloride and a combination of calcium sulfate, magnesium sulfate and magnesium chloride were used as the raw water chemical species in the last two experiments,

the phenol fully degraded after ten and twenty minutes, respectively. Figures A113 to A122 in the appendix provide further details about these two experiments.

Table 5.10 summarizes the results of experiments adopted for this investigation.

TABLE 5.10: Effect of Triple Chemical Species on the Phenol Degradation

Triple Combination	Effect on Degradation
NaHCO_3 , CaSO_4 , and MgSO_4	Phenol disappeared in 10 minutes of treatment
MgCl_2 , CaSO_4 , and MgSO_4 ,	Phenol disappeared in 20 minutes of treatment
NaHCO_3 , MgSO_4 , and MgCl_2	Phenol disappeared in 10 minutes of treatment
NaHCO_3 , CaSO_4 , and MgCl_2	Hindrance

5.5.4 COLLECTIVE CHEMICAL SPECIES INVESTIGATION

Finally, all the four species were used together as the chemical species of the raw water used as a base solvent in the electrochemical oxidation process. It was noted that the phenol concentration fluctuated during the first thirty minutes of the treatment and totally mineralized at forty five minutes as the GC chromatograph graph does not show any peaks after forty five minutes (figure 5.36). For further details about the GC analysis of this experiment, refer to figures A123 to A131 in the appendix.

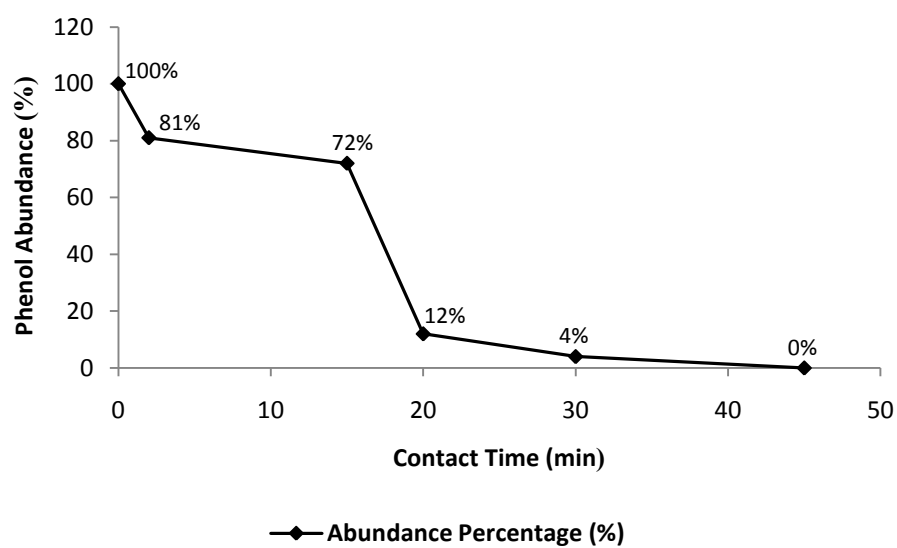
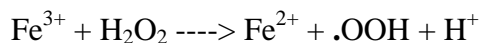
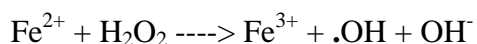


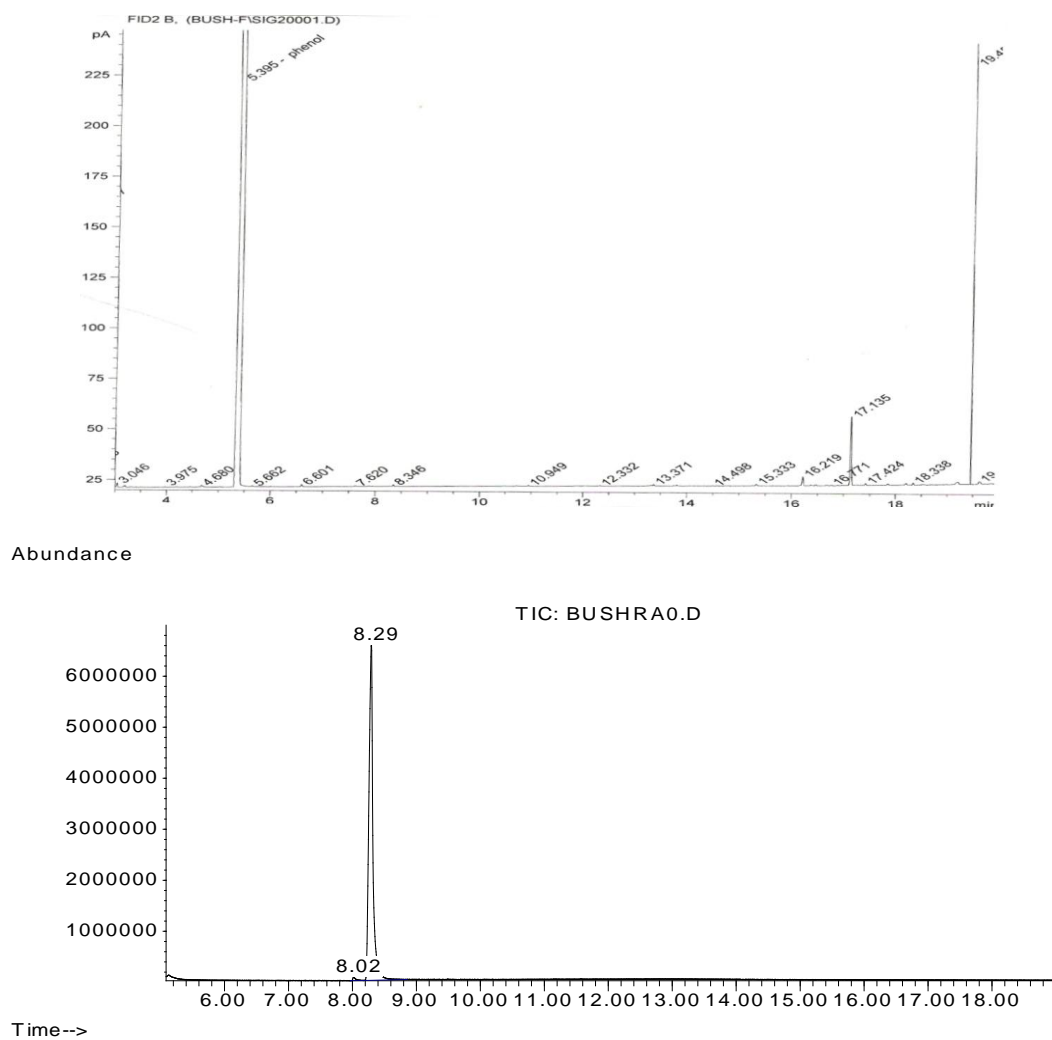
FIGURE 5.36: Phenol Abundance Percentage vs. Contact time

5.6. PHENOL DEGRADATION ENHANCEMENT BY HYDROGEN PEROXIDE

The phenol degradation process in the presence of all the four chemical species was repeated with the addition of hydrogen peroxide as a catalyst. When 1% of hydrogen peroxide was added, the phenol was significantly removed after ten minutes from the start-up of the experiment instead of thirty minutes in the regular case (Figures 5.37 to 5.42). This enhancement is due to the possible effect of the Fenton's reaction of the advance oxidation process (AOP), which resulted in about 20 minute's reduction in the process time. According to Fenton's reaction, iron precipitating from the electrodes reacts with the hydrogen peroxide generating hydroxyl radicals as shown in the following equations:

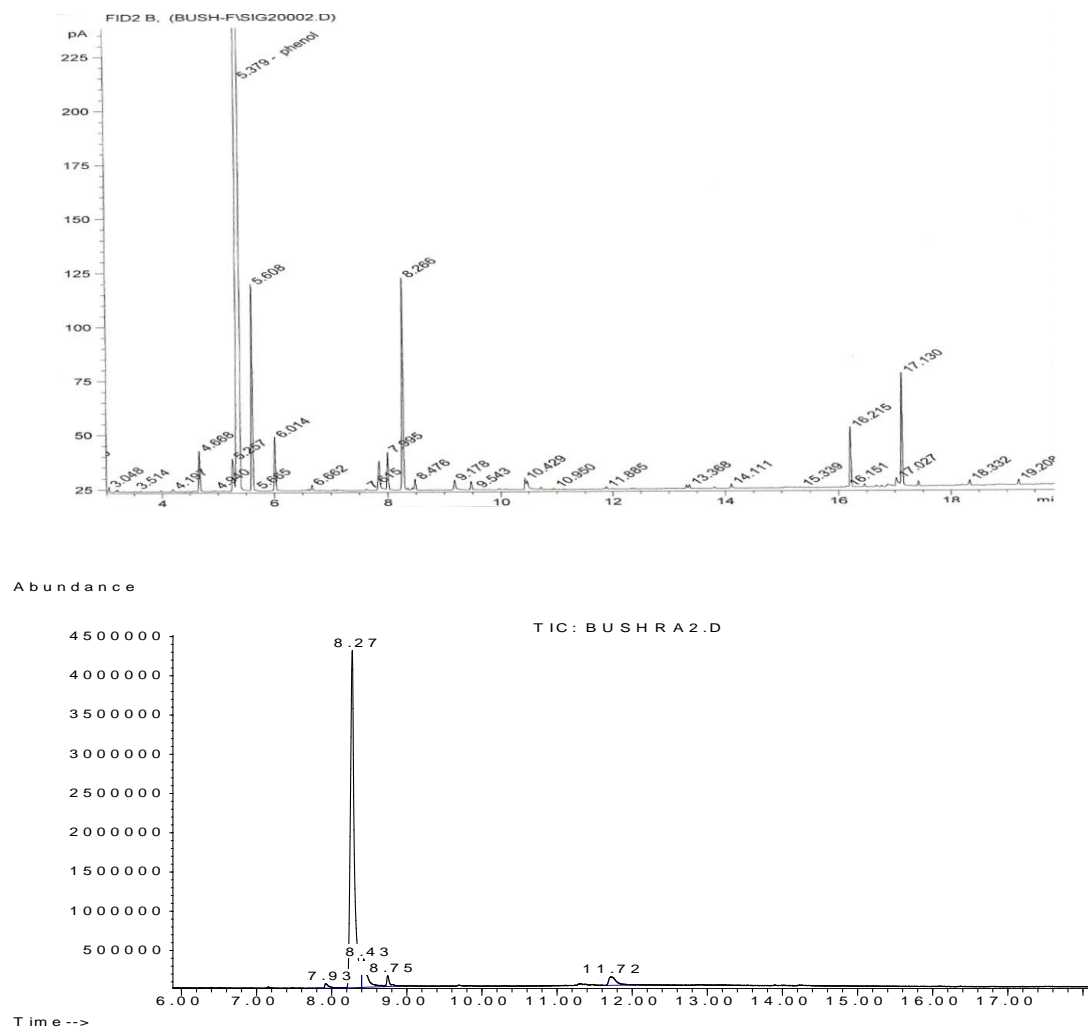


Since it was concluded that in more alkaline medium, more phenol is degraded, the hydrogen peroxide was used to generate enough hydroxide radical to expedite the phenol removal though increasing the alkalinity of the medium and overcoming the effect of the present scavengers such as the bicarbonate radical of the sodium bicarbonate.



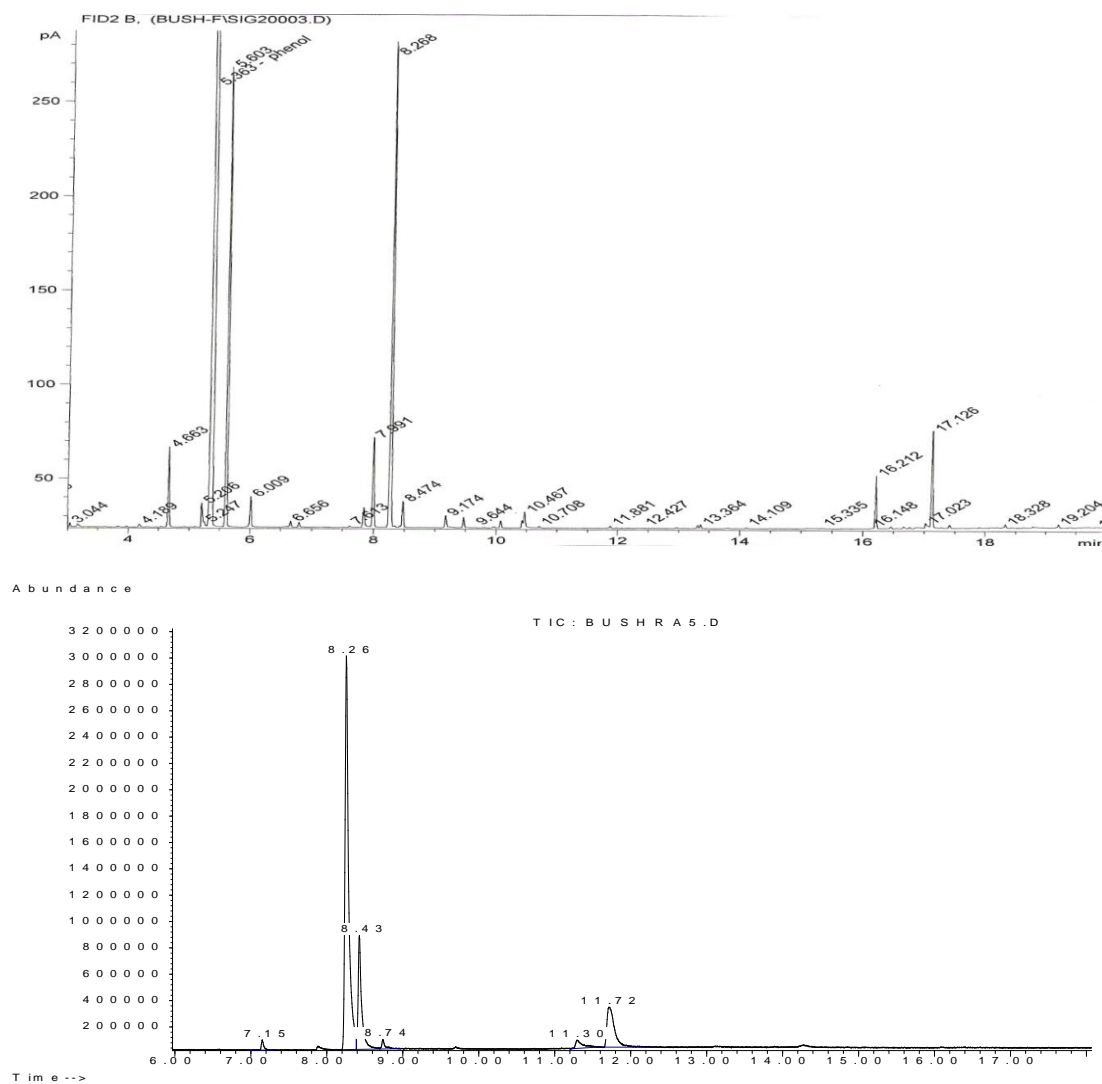
No.	Ret. Time	Peak Area	Identification
1	8.022	2185857	Impurity from solvent
2	8.294	287289391	Phenol

FIGURE 5.37: GC and GC-MS Chromatograms of Sample before Treatment as a Control



No.	Ret. Time	Peak Area	Identification
1	7.926	2331971	Impurity from solvent
2	8.274	153606753	Phenol
3	8.429	16055279	Phenol, 2-Chloro
4	8.748	3878570	Impurity from solvent
5	11.721	7560655	Phenol, 2,6-Dichloro

**Figure 5.38: GC and GC-MS Chromatograms of Samples Treated For 2 Minutes,
With 1% Addition of Hydrogen Peroxide**



No.	Ret. Time	Peak Area	Identification
1	7.152	1679419	p-Benzoquinone
2	8.260	99022887	Phenol
3	8.431	27750578	Phenol, 2-Chloro
4	8.740	2292507	Impurity from solvent
5	11.299	4118849	Phenol, 2,4-Dichloro
6	11.720	21141636	Phenol, 2,6-Dichloro

**Figure 5.39: GC and GC-MS Chromatograms of Samples Treated For 5 Minutes,
With 1% Addition of Hydrogen Peroxide**

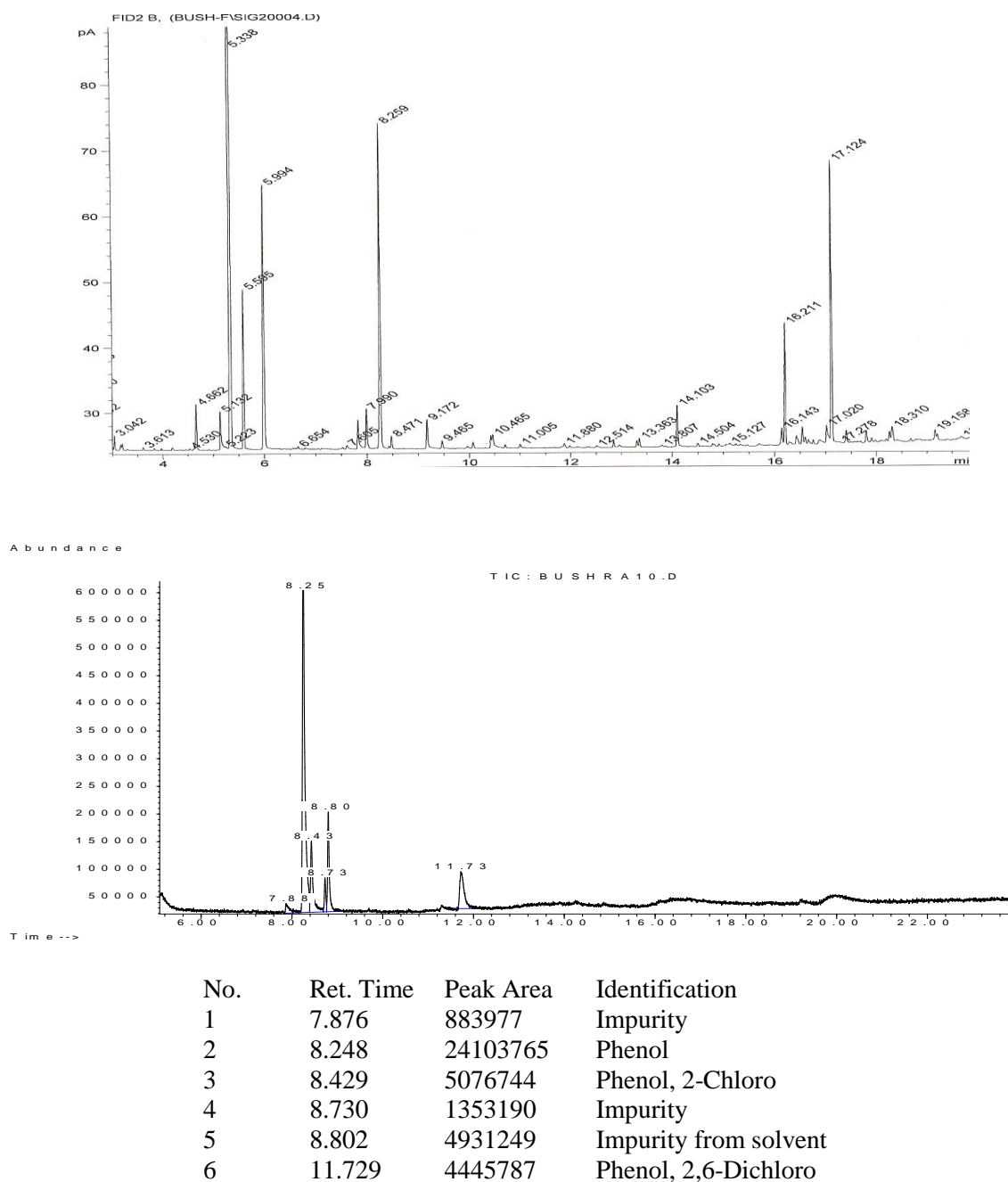
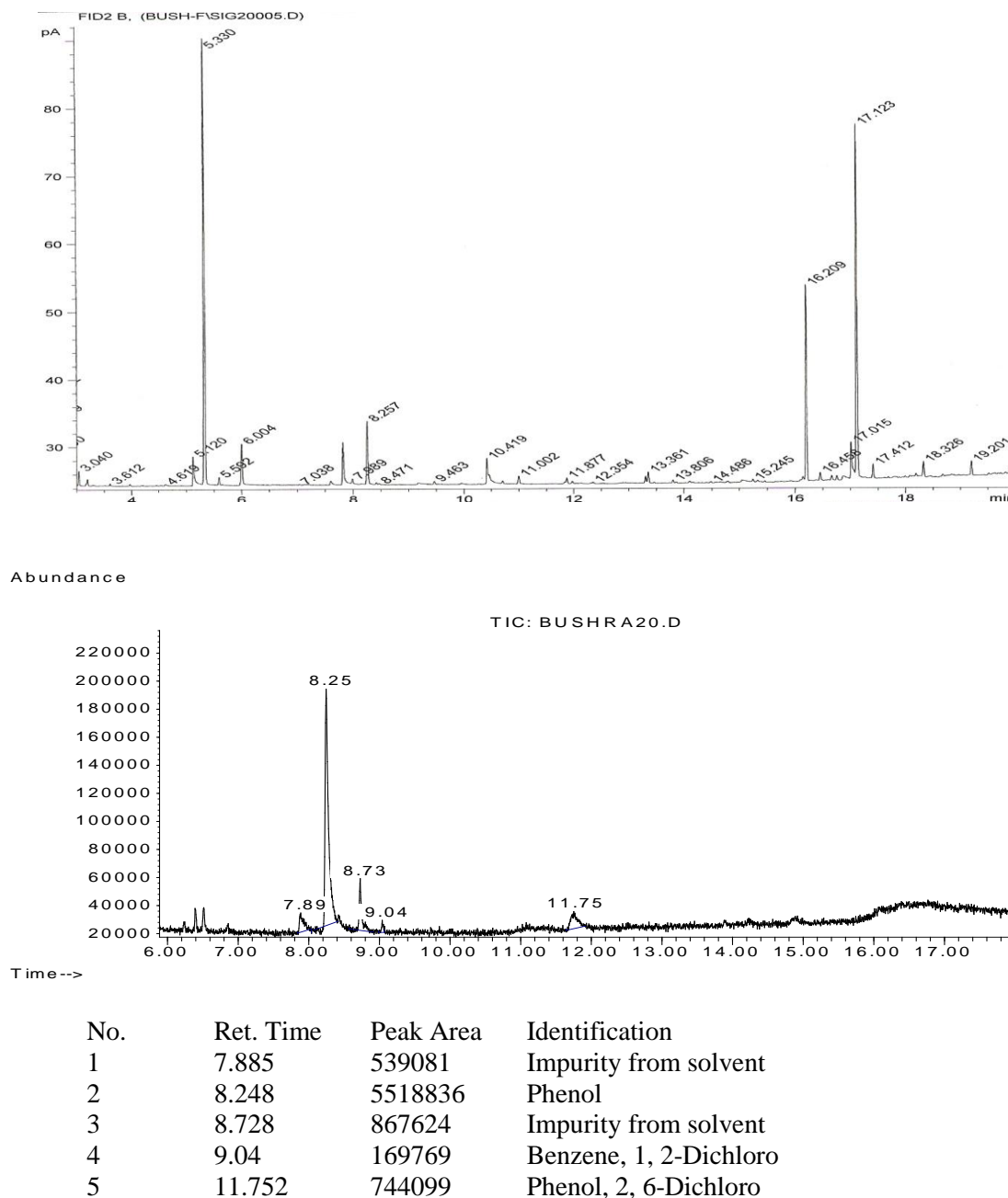


Figure 5.40: GC Chromatogram of Samples Treated For 10 Minutes, With 1% Addition of Hydrogen Peroxide



**Figure 5.41: GC and GC-MS Chromatograms of Samples Treated For 20 Minutes,
With 1% Addition of Hydrogen Peroxide**

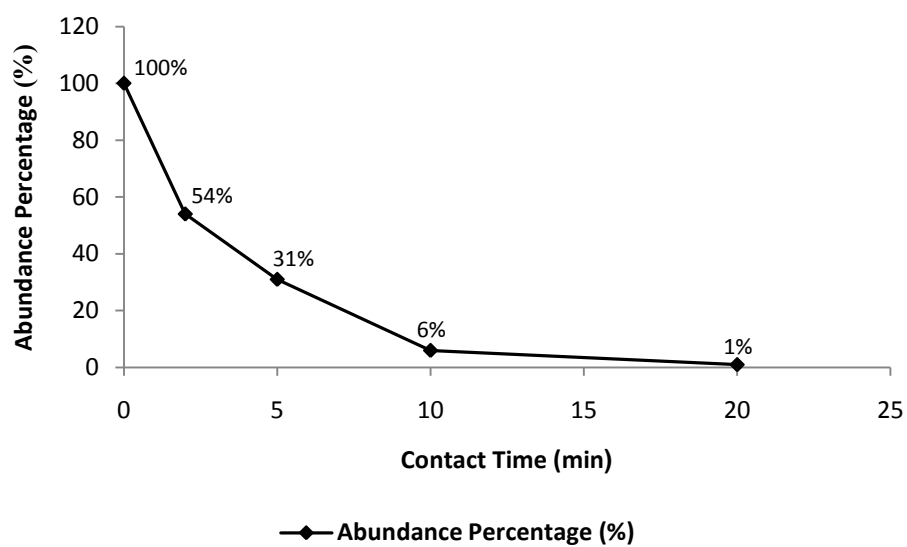


Figure 5.42: Phenol Abundance Percentage vs. Contact Time

CONCLUSIONS & RECOMMENDATIONS

The phenol has always been a major environmental issue and a serious challenge to degrade. The attempts of previous studies, which were based on the standard parameters available in the literature, for phenol removal were hindered in most of the cases by the presence of chemical species that prevent the degradation of the phenol. Therefore, the first goal of this study was to optimize the operational parameters and other parameters affecting the phenol removal through careful and intensive testing, screening and selection process for the different parameters individually and collectively. As a result, 75% phenol concentration, which simulates the phenol concentration in the refinery and petrochemical waste, 45 mA/sq cm current density, and 6000 ppm electrolyte (sodium chloride) were found to be the optimum operation parameters for the phenol degradation process. The optimization analyses also proved that in high (pH) alkalinity medium, more phenol degradation can be achieved.

In addition, the behavior of the deionized water was studied when the commonly used stainless steel electrodes were used as both cathode and anode in the electrochemical oxidation process. It was found that the stainless steel electrodes undergo a metal transition process in which Ni, Cr, and Fe are released into the water matrix giving colors interfering with the spectrophotometer reading of the phenol. This suggests that the UV spectrophotometer, which has been used in most recent phenol removal studies, could give false readings and therefore proper background measurements and precise data

analysis such as digital subtraction are required. Therefore, this study was carried out using GC and GC-MS. Furthermore, the pre-treatment conditions of the phenol were studied to verify its stability. The phenol concentration and pH were examined in the typical pre-treatment conditions and no tangible alterations were recorded.

The parameters optimization realized in this study was the main reason behind the success achieved in the phenol removal in the raw water and removal enhancement in the deionized water compared to previous studies.

After setting all the optimum parameters, fifteen experiments were conducted to investigate the chemical species of the raw water which include calcium sulfate, magnesium sulfate, magnesium chloride and sodium bicarbonate. Different combinations of the chemical species were investigated to identify the species responsible for hindering or delaying the degradation process of the phenol in the raw water used as a synthetic base solvent. These combinations include individual specie, dual species, triple species and all the species collectively. The results of these analyses confirmed that only two species among the investigated ones, namely, sodium bicarbonate and magnesium chloride when present together or individually hindered the phenol degradation in the various experiments conducted which indicate that both species play an important role in hindering or delaying the phenol degradation in general.

To further enhance the phenol removal in the raw water, 1% Hydrogen Peroxide was added to release enough hydroxide radicals in the water matrix to increase the medium alkalinity and overcome the scavenger effect of the bicarbonate radicals. This enhancement is due to the possible effect of the Fenton's reaction as an advance oxidation process (AOP), which resulted in about 20 minute's reduction in the process time.

This study may establish a good basis for further investigations on the total dissolved solids by adding more chemical species, which could be associated with refinery and petrochemical waste in the synthetic raw water used as a base solvent.

Using a different electrolyte salt such as MgSO_4 instead of NaCl is expected to waive the effect of the two hindering species and enhance the removal efficiency. Also the use of different electrodes such as graphite or aluminum electrodes instead of stainless steel electrodes can be investigated. These could help extend this effort toward the practical application of this method in the removal of phenol from live refinery and petrochemical waste.

APPENDIX

TABLE A1: Data of Standard Curve for Phenol at 270 nm:

Concentration (mg/l)	Absorbance (nm)
0	-0.0081
5	0.0681
10	0.1312
20	0.2767
30	0.4166
50	0.5707
60	0.7362
75	0.9308

TABLE A2: Data of Chemical Oxygen Demand (COD) test for Phenol:

No. of sample in replicates	Sample name	Phenol concentration (mg/l)	Volume (ml)	COD (mg/l)
1	1a	0	1.85	0
2	1b	0	1.85	0
3	2a	5	1.8	16
4	2b	5	1.8	16
5	3a	10	1.75	32
6	3b	10	1.75	32
7	4a	20	1.6	80
8	4b	20	1.6	80
9	5a	30	1.5	112
10	5b	30	1.5	112
11	6a	50	1.35	160
12	6b	50	1.35	160
13	7a	60	1.25	192
14	7b	60	1.25	192
15	8a	75	1.1	240
16	8b	75	1.1	240

TABLE A3: pH and Concentration Data for 25 ppm of Phenol after Treatment

No. of sample	Time (min)	Absorption (nm)	Concentration (ppm)	pH
0	0	0.2799	22.15	5.95
1	2	0.2708	21.40	9.21
2	5	0.2585	20.38	9.70
3	10	0.1786	13.78	6.04
4	15	0.0405	2.36	10.70
5	20	0.0327	1.72	11.13
6	30	0.0119	0	11.15
7	45	-0.0076	0	11.34
8	60	-0.0263	0	11.80
9	75	-0.0442	0	12.82
10	90	-0.0619	0	11.88

TABLE A4: pH and Concentration Data for 50 ppm of Phenol after Treatment

No.	Time (min)	Absorption (nm)	Concentration (ppm)	pH
0	0	0.6075	49.22	8.48
1	2	0.6159	49.92	9.21
2	5	0.5563	44.99	9.42
3	10	0.4944	39.88	7.42
4	15	1.0843	88.63	4.34
5	20	0.0862	6.14	11.33
6	30	0.1288	9.66	11.55
7	45	0.0697	4.78	12.12
8	60	0.0443	2.68	12.11
9	75	0.0569	3.72	12.13
10	90	0.0611	4.07	11.91

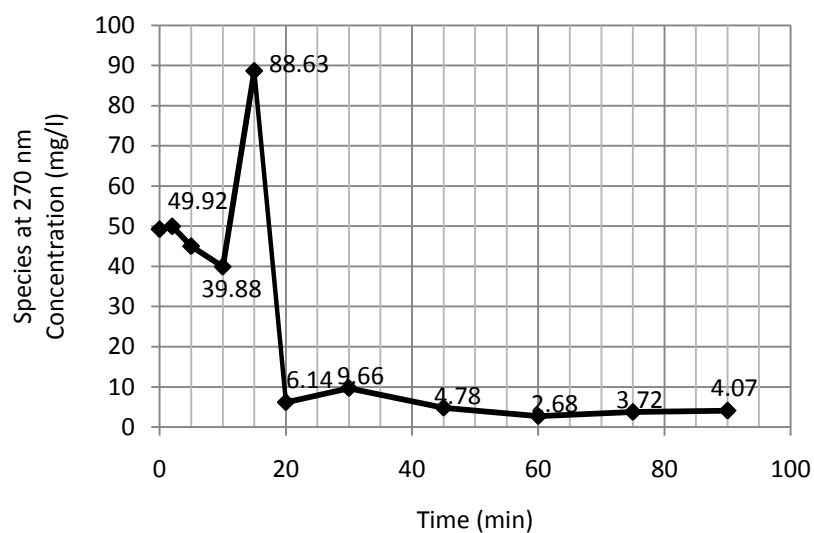


FIGURE A5: Effect of Concentration on the Degradation of Phenol at 50 ppm of phenol and a Current Density of 30 mA/cm²

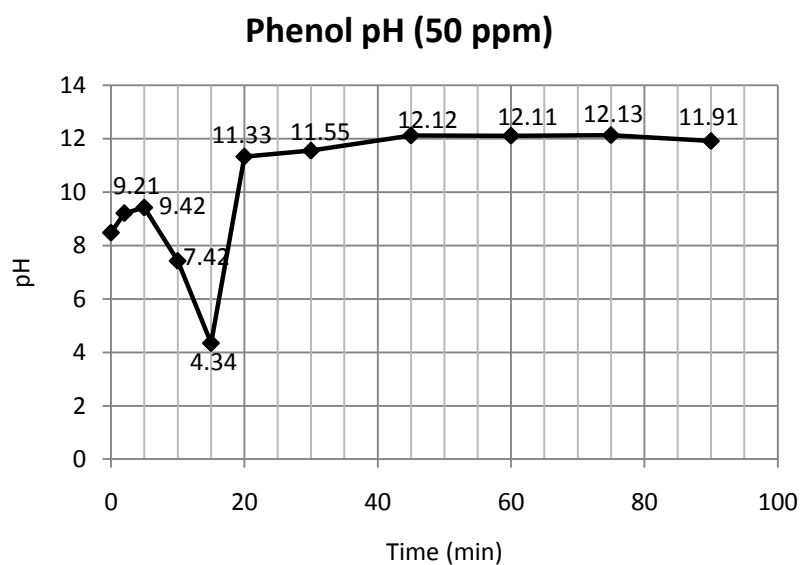


FIGURE A6: The pH pattern on the Phenol Degradation Process at 50 ppm of phenol and a Current Density of 30 mA/cm²

TABLE A7: pH and Concentration Data for 75 ppm of Phenol after Treatment

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9150	74.64	8.46
1	2	0.9202	75.07	9.06
2	5	0.9343	76.23	9.02
3	10	0.9173	74.83	9.11
4	15	0.7610	61.91	9.02
5	20	0.6317	51.22	9.12
6	30	0.3967	31.80	11.10
7	45	0.3265	26.00	11.32
8	60	0.3157	25.11	11.45
9	75	0.3197	25.44	11.64
10	90	0.3168	25.20	11.96

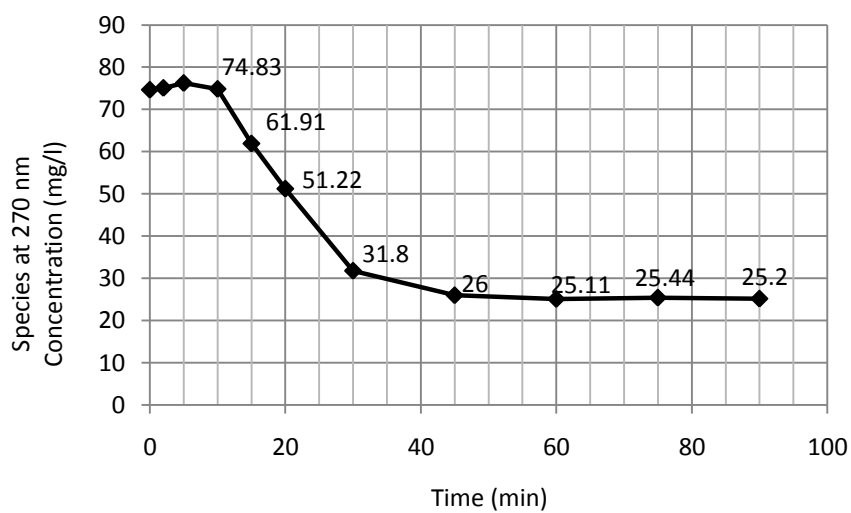


FIGURE A8: Effect of Concentration on the Degradation of Phenol at 75 ppm of phenol and a Current Density of 30 mA/cm²

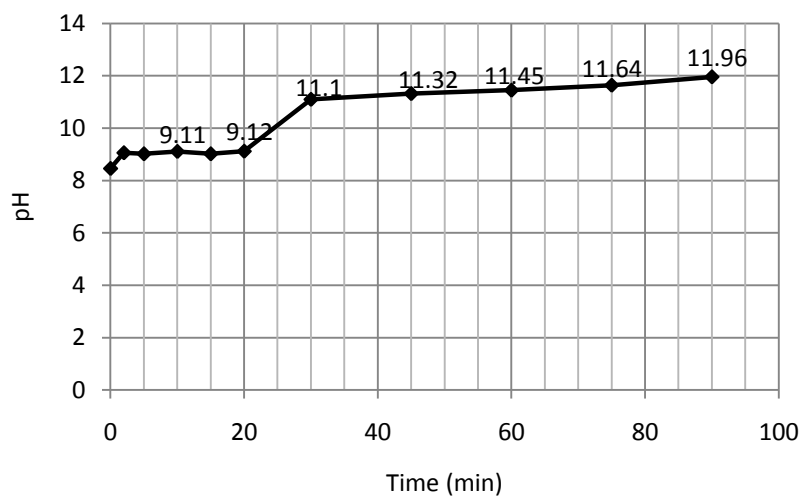


FIGURE A9: The pH pattern on the Phenol Degradation Process at 75 ppm of phenol and a Current Density of 30 mA/cm²

TABLE A10: pH and Concentration Data for 100 ppm of Phenol after Treatment

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.6461	104.83	7.81
1	2	0.6549	106.29	8.82
2	5	0.7364	119.77	9.80
3	10	0.7887	128.41	9.18
4	15	0.6496	105.41	8.21
5	20	0.4506	72.52	8.17
6	30	0.6544	53.10	10.31
7	45	0.5670	45.88	11.16
8	60	0.4451	35.80	11.23
9	75	0.4595	36.99	11.50
10	90	0.4623	37.22	11.63

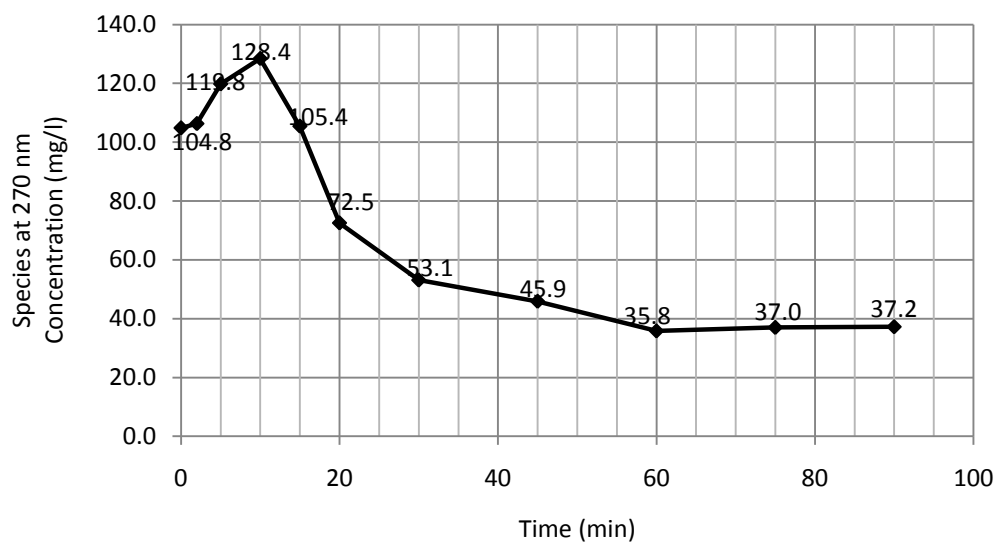


FIGURE A11: Effect of Concentration on the Degradation of Phenol at 100 ppm of phenol and a Current Density of 30 mA/cm²

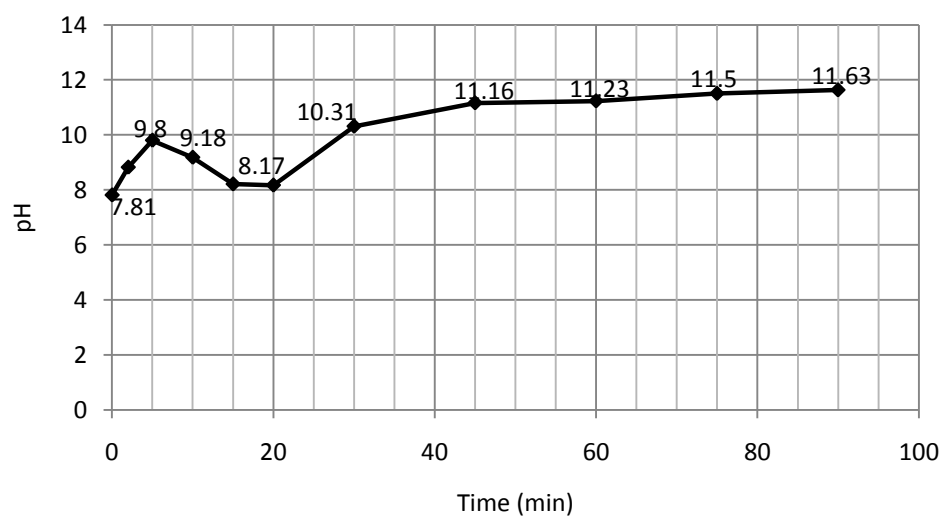


FIGURE A12: The pH pattern on the Phenol Degradation Process at 100 ppm of phenol and a Current Density of 30 mA/cm²

TABLE A13: pH and Concentration Data for 250 ppm of Phenol after Treatment

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.8104	$65.99 \times 4 = 264.0$	7.53
1	2	0.8280	$67.45 \times 4 = 269.8$	8.70
2	5	0.8572	$69.86 \times 4 = 279.4$	9.36
3	10	0.9390	$76.62 \times 4 = 306.5$	10.09
4	15	0.6446	$52.29 \times 4 = 209.2$	10.69
5	20	0.5821	$47.12 \times 4 = 188.5$	9.37
6	30	0.5119	$41.32 \times 4 = 165.3$	11.26
7	45	0.4982	$40.19 \times 4 = 160.8$	11.54
8	60	0.4862	$39.20 \times 4 = 156.8$	11.38
9	75	0.4967	$40.07 \times 4 = 160.3$	11.66
10	90	0.4823	$38.88 \times 4 = 155.5$	11.64

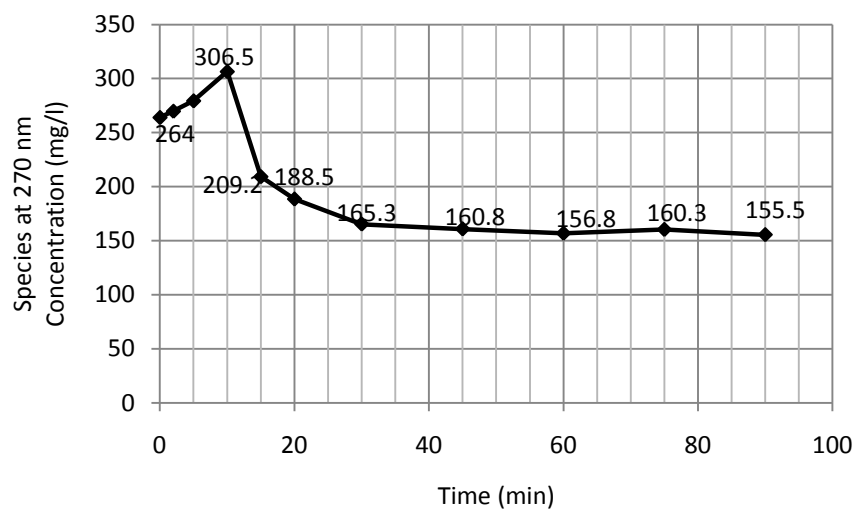


FIGURE A14: Effect of Concentration on the Degradation of Phenol at 250 ppm of phenol and a Current Density of 30 mA/cm²

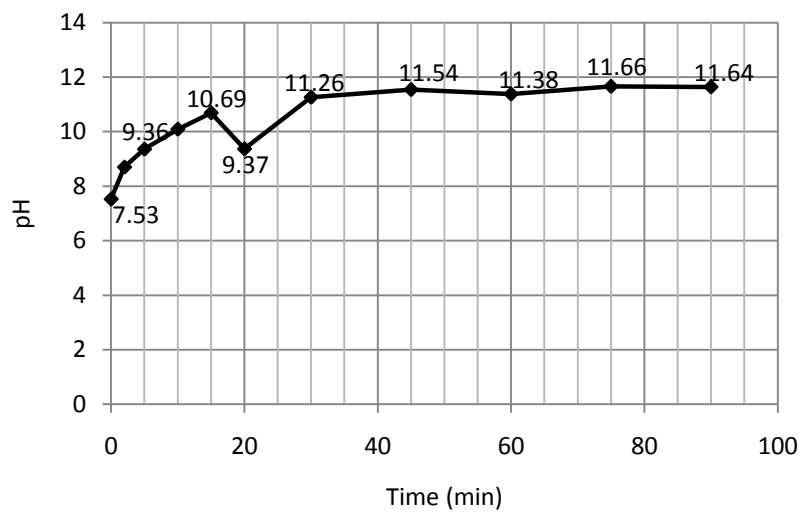


FIGURE A15: The pH pattern on the Phenol Degradation Process at 250 ppm of phenol and a Current Density of 30 mA/cm²

TABLE A16: pH and Concentration Data for 500 ppm of Phenol after Treatment

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.7925	$64.51 \times 8 = 516.1$	7.30
1	2	0.7706	$62.70 \times 8 = 501.6$	8.29
2	5	0.7329	$59.59 \times 8 = 476.8$	8.89
3	10	0.7343	$59.70 \times 8 = 477.6$	10.09
4	15	0.7126	$57.91 \times 8 = 463.3$	10.08
5	20	0.6606	$53.61 \times 8 = 428.9$	10.87
6	30	0.6492	$52.67 \times 8 = 421.3$	11.18
7	45	0.6157	$49.90 \times 8 = 399.2$	11.25
8	60	0.6560	$53.23 \times 8 = 425.9$	11.31
9	75	0.6349	$51.49 \times 8 = 411.9$	11.37
10	90	0.6365	$51.62 \times 8 = 412.9$	11.35

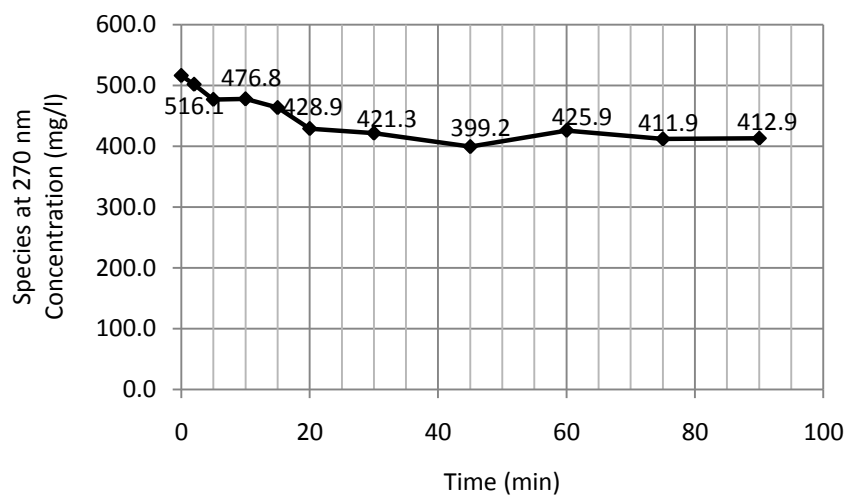


FIGURE A17: Effect of Concentration on the Degradation of Phenol at 500 ppm of phenol and a Current Density of 30 mA/cm²

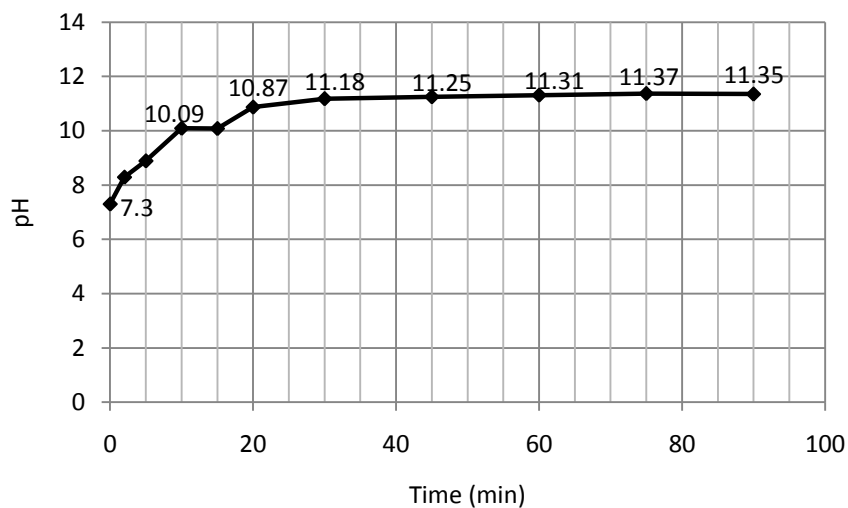


FIGURE A18: The pH pattern on the Phenol Degradation Process at 500 ppm of phenol and a Current Density of 30 mA/cm²

TABLE A19: pH and Concentration Data of Phenol after Electrochemical**Treatment at 2 g/L NaCl and 30 mA/cm² Current Density**

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9144	74.59	8.42
1	2	0.9576	78.16	8.79
2	5	0.8466	68.98	8.94
3	10	0.8307	67.67	9.96
4	15	0.8305	67.65	9.19
5	20	0.9004	73.43	8.76
6	30	0.8640	70.42	8.94
7	45	0.7502	61.02	9.01
8	60	0.6358	51.56	9.03
9	75	0.4580	36.87	10.01
10	90	0.4022	32.26	10.11

TABLE A20: pH and Concentration Data of Phenol after Electrochemical**Treatment at 4 g/L NaCl and 30 mA/cm² Current Density**

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9169	74.79	8.22
1	2	0.9077	74.03	9.09
2	5	1.0290	84.06	9.05
3	10	1.0792	88.21	10.07
4	15	0.7736	62.95	10.19
5	20	0.6841	55.55	11.03
6	30	0.4496	36.17	11.12
7	45	0.3998	32.06	11.32
8	60	0.3306	26.34	11.38
9	75	0.3348	26.69	11.81
10	90	0.3278	26.11	12.07

**TABLE A21: pH and Concentration Data of Phenol after Electrochemical
Treatment at 6 g/L NaCl and 30 mA/cm² Current Density**

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9268	75.61	7.81
1	2	0.8445	68.81	8.65
2	5	0.9093	74.17	8.79
3	10	1.0681	87.29	7.43
4	15	0.8801	71.75	6.89
5	20	0.5328	43.05	7.00
6	30	0.3918	31.40	9.79
7	45	0.3301	26.30	11.58
8	60	0.2889	22.89	11.72
9	75	0.2336	18.32	12.27
10	90	0.2198	17.18	12.40

**TABLE A22: pH and Concentration Data of Phenol after Electrochemical
Treatment at 8 g/L NaCl and 30 mA/cm² Current Density**

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.8970	73.15	6.53
1	2	0.8683	70.78	9.16
2	5	0.8716	71.05	9.60
3	10	0.8123	66.15	9.83
4	15	0.6952	56.47	10.19
5	20	0.6567	53.29	11.01
6	30	0.4999	40.33	11.50
7	45	0.5256	42.45	11.87
8	60	0.4437	35.69	12.05
9	75	0.3995	32.03	12.09
10	90	0.4147	33.29	12.11

TABLE A23: pH and Concentration Data of Phenol after Electrochemical Treatment at Optimum Condition and 7.5 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9547	77.92	6.1
1	2	1.0319	84.30	4.89
2	5	0.9258	75.53	7.57
3	10	0.8708	70.98	8.09
4	15	0.9688	79.08	8.82
5	20	0.8669	70.66	8.99
6	30	0.8826	71.96	9.72
7	45	0.9373	76.48	10.47
8	60	0.8076	65.76	10.77
9	75	0.7744	63.02	11.18
10	90	0.6771	54.98	11.34

TABLE A24: pH and Concentration Data of Phenol after Electrochemical Treatment at Optimum Condition and 15 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9414	76.82	6.23
1	2	0.8149	66.36	8.48
2	5	0.9321	76.05	9.09
3	10	0.8175	66.58	9.97
4	15	0.8137	66.26	10.50
5	20	0.8483	69.12	10.89
6	30	0.7159	58.18	11.42
7	45	0.5864	47.48	11.85
8	60	0.6036	48.90	11.96
9	75	0.5798	46.93	12.09
10	90	0.5203	42.02	12.14

TABLE A25: pH and Concentration Data of Phenol after Electrochemical Treatment at Optimum Condition and 30 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9268	75.61	7.81
1	2	0.8445	68.81	8.65
2	5	0.9093	74.17	8.79
3	10	1.0681	87.29	7.43
4	15	0.8801	71.75	6.89
5	20	0.5328	43.05	7.00
6	30	0.3918	31.40	9.79
7	45	0.3301	26.30	11.58
8	60	0.2889	22.89	11.72
9	75	0.2336	18.32	12.27
10	90	0.2198	17.18	12.40

TABLE A26: pH and Concentration Data of Phenol after Electrochemical Treatment at Optimum Condition and 45 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9575	78.15	6.22
1	2	1.0895	89.06	9.40
2	5	0.8197	66.76	9.43
3	10	0.8223	66.98	7.40
4	15	0.5271	42.58	7.48
5	20	0.5372	43.41	7.54
6	30	0.1207	8.99	8.17
7	45	0.1122	8.29	10.27
8	60	0.0978	7.10	11.38
9	75	0.1066	7.83	11.92
10	90	0.0701	4.81	11.92

TABLE A27: pH and Concentration Data of Phenol after Electrochemical Treatment at Optimum Condition and 52.5 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.9481	77.37	6.45
1	2	0.8604	70.12	8.93
2	5	0.8781	71.59	8.39
3	10	0.7350	59.76	7.20
4	15	0.3037	24.12	8.00
5	20	0.2217	17.34	8.91
6	30	0.1796	13.86	10.88
7	45	0.1418	10.74	11.85
8	60	0.1503	11.44	12.14
9	75	0.1433	10.86	12.38
10	90	0.1597	12.21	12.45

TABLE A28: pH and Concentration Data of Deionized Water after Electrochemical Oxidation Process at Optimum Condition and 7.5 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	-0.0344	0	6.22
1	2	-0.0093	0	4.78
2	5	0.1133	8.38	5.50
3	10	0.1913	14.83	5.49
4	15	0.2181	17.04	5.33
5	20	0.1818	14.04	5.64
6	30	0.0697	4.78	5.34
7	45	0.0087	0	5.24
8	60	0.0088	0	7.96
9	75	0.0126	0.06	9.27
10	90	0.0201	0.68	4.86

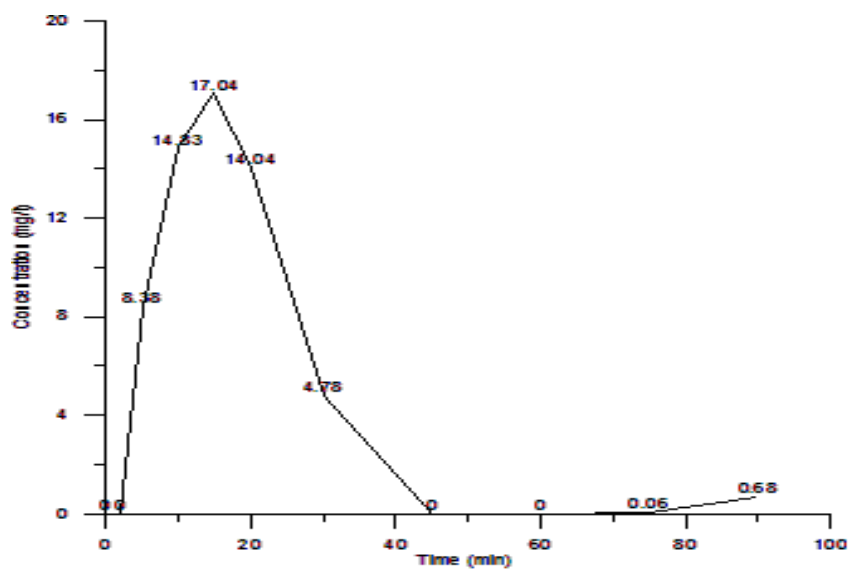


FIGURE A29: Concentration Profile at 270 nm for Deionized Water after Treatment at Optimum Conditions and Current Density of 7.5 mA/cm²

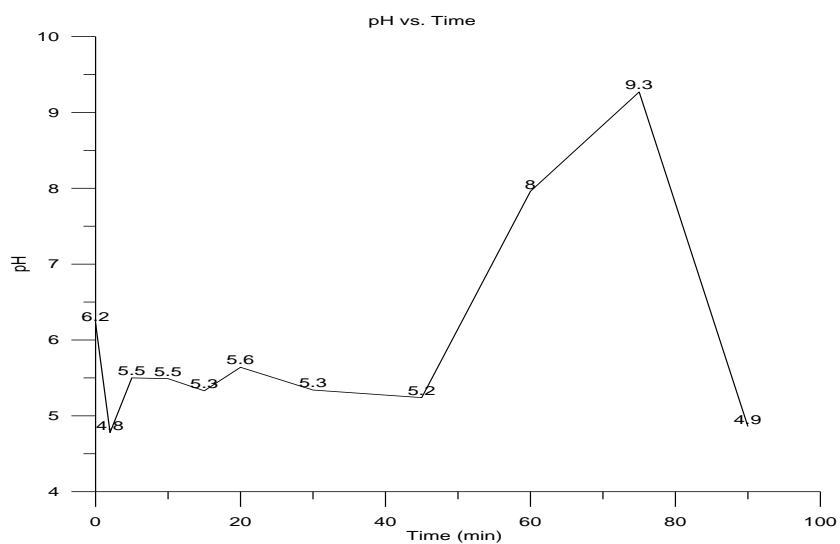


FIGURE A30: pH Profile for Deionized Water after Treatment at Optimum Conditions and Current Density of 7.5 mA/cm²

TABLE A31: pH and Concentration Data of Deionized Water after Electrochemical Oxidation Process at Optimum Condition and 15 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	0.0020	0	6.17
1	2	0.0244	1.03	5.64
2	5	0.0323	1.69	10.14
3	10	0.0242	1.02	10.74
4	15	0.0442	2.67	11.02
5	20	0.0320	1.66	11.21
6	30	0.0239	0.99	11.42
7	45	0.0397	2.30	11.64
8	60	0.0448	2.72	11.42
9	75	0.0471	2.91	11.45
10	90	0.0442	2.67	11.53

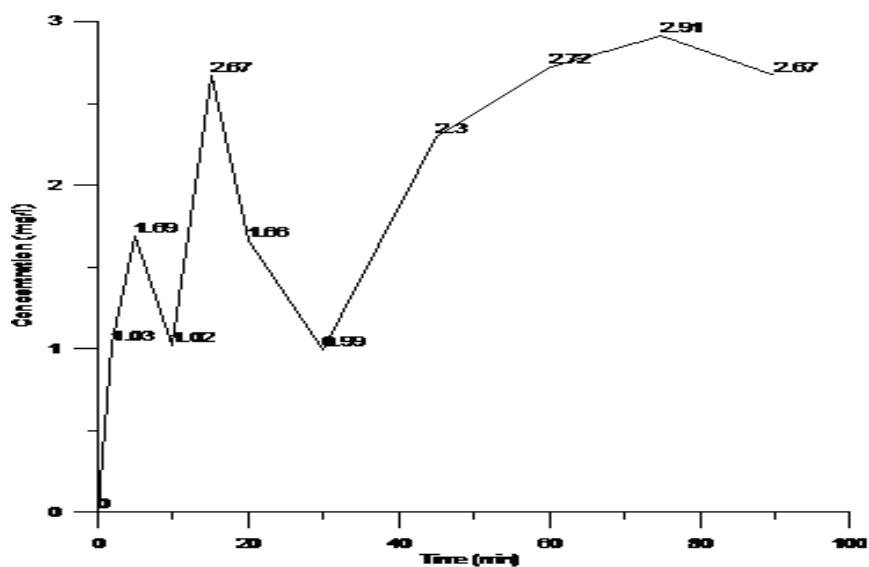


FIGURE A32: Concentration Profile at 270 nm for Deionized Water after Treatment at Optimum Conditions and Current Density of 15 mA/cm²

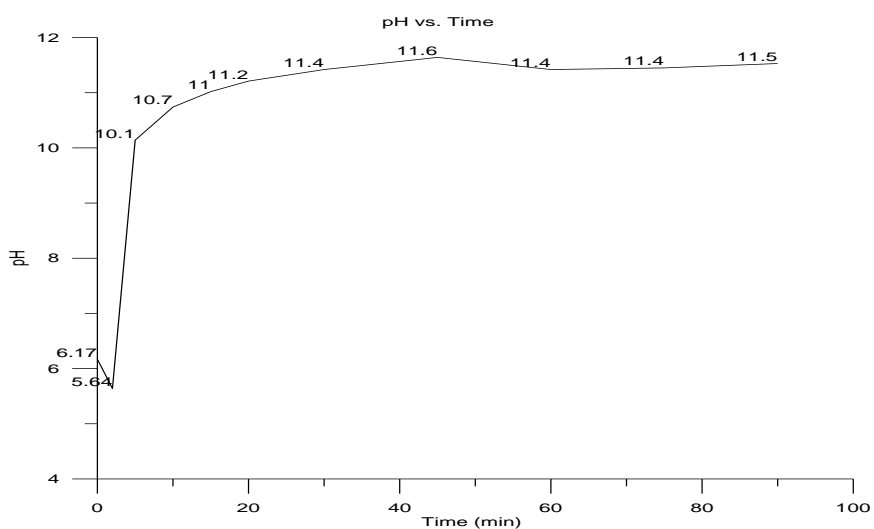


FIGURE A33: pH Profile for Deionized Water under Electrochemical Oxidation Process at Optimum Conditions and Current Density of 15 mA/cm²

TABLE A34: pH and Concentration Data of Deionized Water after Electrochemical Oxidation Process at Optimum Condition and 30 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	-0.0128	0	6.13
1	2	0.2191	17.12	7.33
2	5	0.5092	41.10	7.09
3	10	0.7008	56.93	6.68
4	15	1.0193	83.26	6.46
5	20	1.1567	94.61	6.25
6	30	0.9386	76.59	6.12
7	45	0.0950	6.87	8.33
8	60	0.0731	5.06	11.06
9	75	0.2815	22.28	11.63
10	90	0.1141	8.45	11.75

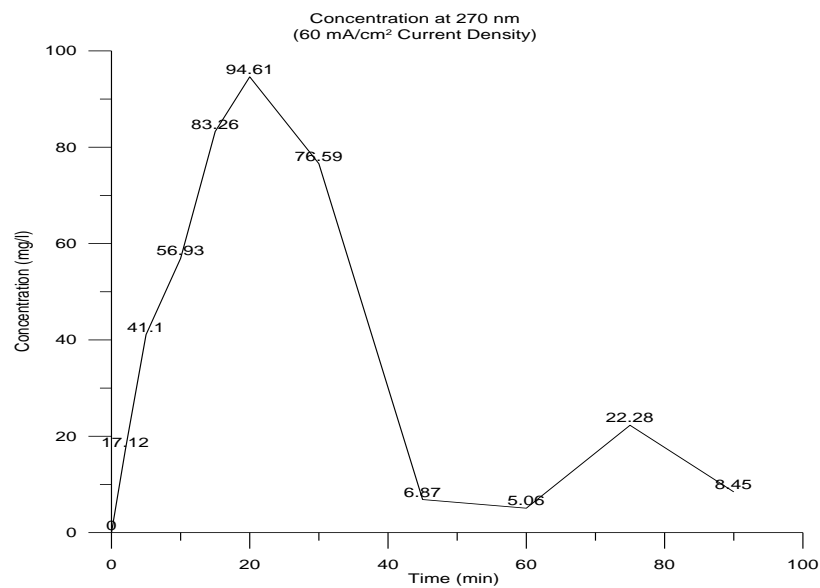


FIGURE A35: Concentration Profile at 270 nm for Deionized Water after Treatment at Optimum Conditions and Current Density of 30 mA/cm²

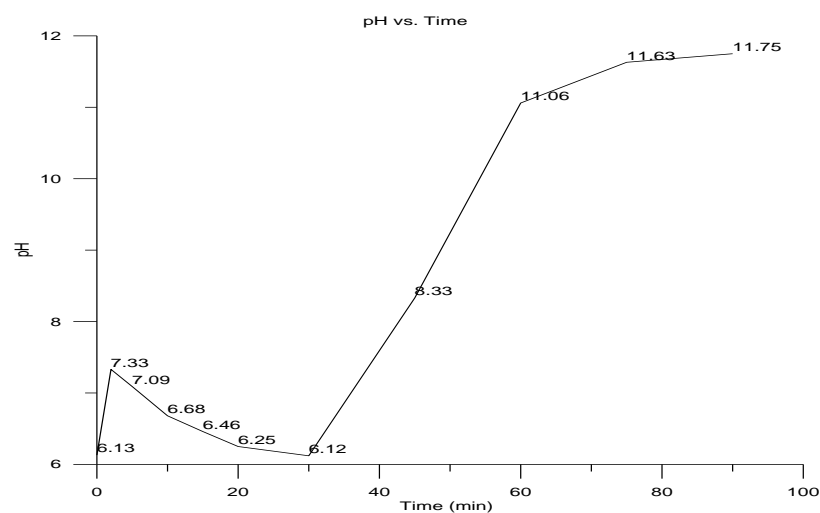


FIGURE A36: pH Profile for Deionized Water after Treatment at Optimum Conditions and Current Density of 30 mA/cm²

TABLE A37: pH and Concentration Data of Deionized Water after Electrochemical Oxidation Process at Optimum Condition and 45 mA/cm² Current Density

No.	Time (min)	Absorption	Conc. (ppm)	pH
0	0	-0.0065	0	6.05
1	2	0.0966	7.00	4.98
2	5	0.0531	3.40	5.35
3	10	0.0621	4.15	6.03
4	15	0.0302	1.51	4.64
5	20	0.0385	2.20	11.55
6	30	0.0503	3.17	11.21
7	45	0.0859	6.12	12.15
8	60	0.0751	5.22	12.26
9	75	0.0107	0	12.34
10	90	0.0144	0.21	12.35

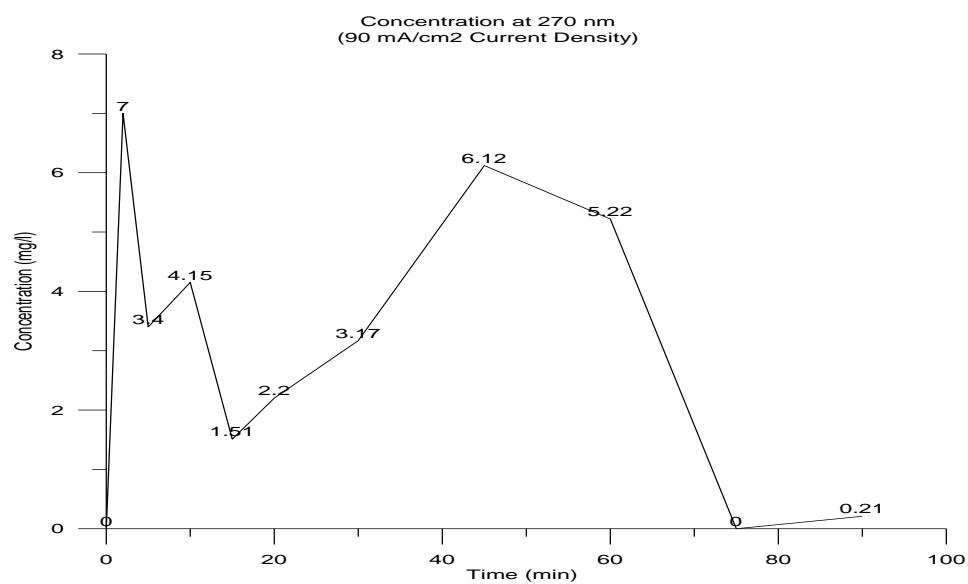


FIGURE A38: Concentration Profile at 270 nm for Deionized Water after Treatment at Optimum Conditions and Current Density of 45 mA/cm²

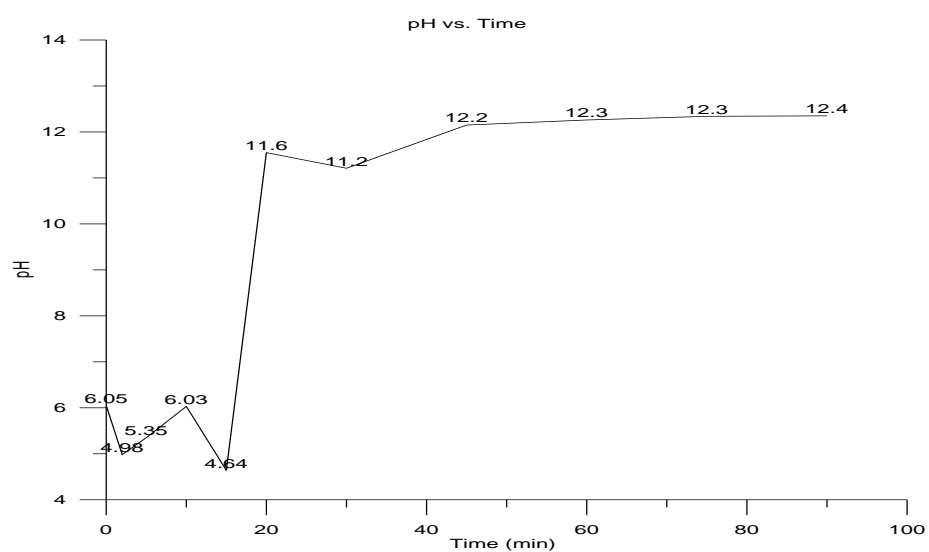


FIGURE A39: pH Profile for Deionized Water under Electrochemical Oxidation Process at Optimum Conditions and Current Density of 45 mA/cm²

**Table A40: Concentration at 270 nm and pH Profile for Deionized Water under
Electrochemical Oxidation Process at Optimum Conditions**

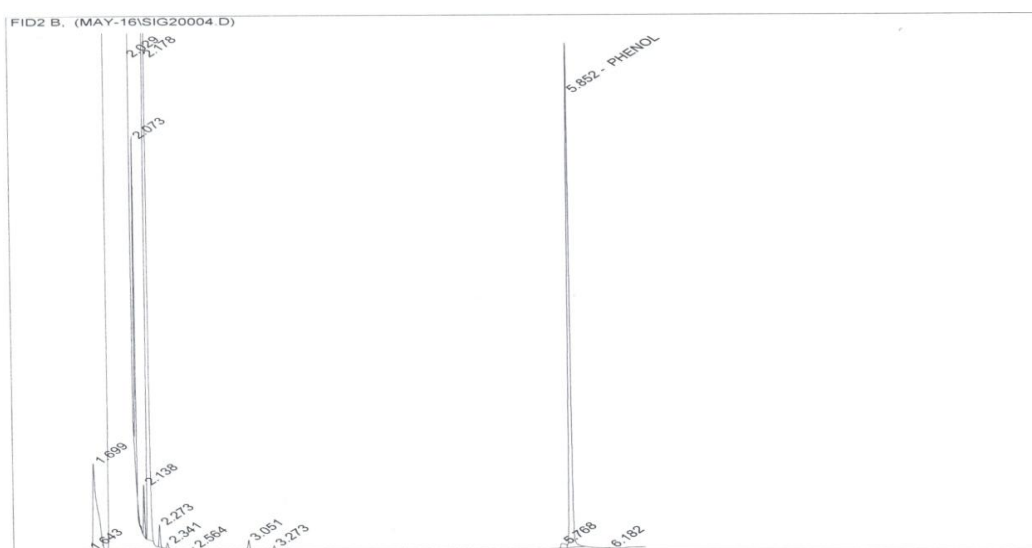
No.	Time (min)	pH	Absorption (nm)	Concentration. (ppm)
0	0	6.10	-0.0184	-2.50
1	2	5.89	0.0912	6.55
2	5	7.57	0.3291	26.21
3	10	7.63	0.6924	56.24
4	15	6.62	1.0804	88.31
5	20	6.61	0.4724	38.06
6	30	10.75	0.0309	1.57
7	45	11.45	0.0305	1.54
8	60	11.55	0.0256	1.13
9	75	11.96	0.0426	2.54
10	90	12.02	0.0453	2.76

Table A41: Phenol Concentration and pH Data at Pre-treatment Conditions

No.	Sampling Time (min)	Absorbance (nm)	Concentration (ppm)	pH
0	0	0.9136	74.52	6.57
1	2	0.9805	80.05	5.57
2	5	1.1603	94.91	5.64
3	10	0.9911	80.93	5.72
4	15	1.1300	92.40	5.78
5	20	1.0338	84.45	5.78
6	30	1.0737	87.75	5.86
7	45	1.1632	95.15	5.87
8	60	1.0651	87.04	5.86
9	75	1.0883	88.96	5.87
10	90	1.1603	94.91	5.85

Table A42: Phenol Concentration and pH Data at Optimum Conditions

No.	Sampling Time (min)	Absorbance (nm)	Concentration (ppm)	pH
0	0	0.9268	75.61	7.81
1	2	0.8445	68.81	8.65
2	5	0.9093	74.17	8.79
3	10	1.0681	87.29	7.43
4	15	0.8801	71.75	6.89
5	20	0.5328	43.05	7.00
6	30	0.3918	31.40	9.79
7	45	0.3301	26.30	11.58
8	60	0.2889	22.89	11.72
9	75	0.2336	18.32	12.27
10	90	0.2198	17.18	12.40

**FIGURE A43: GC Chromatogram of Phenol Sample with Deionized Water before Treatment**

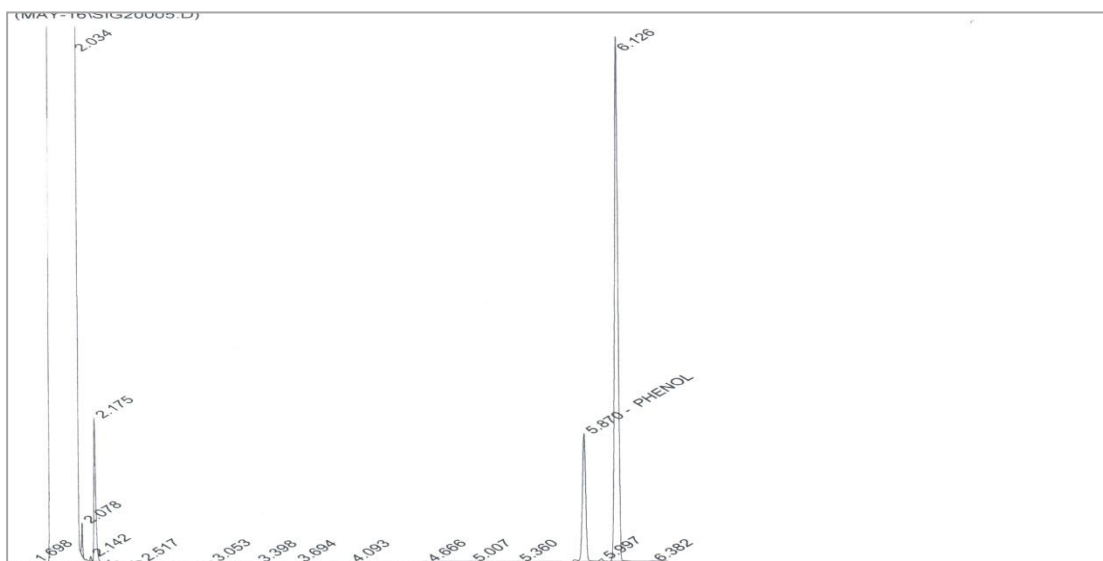


FIGURE A44: GC Chromatogram of Phenol with Deionized Water Sample Treated for 2 Minutes

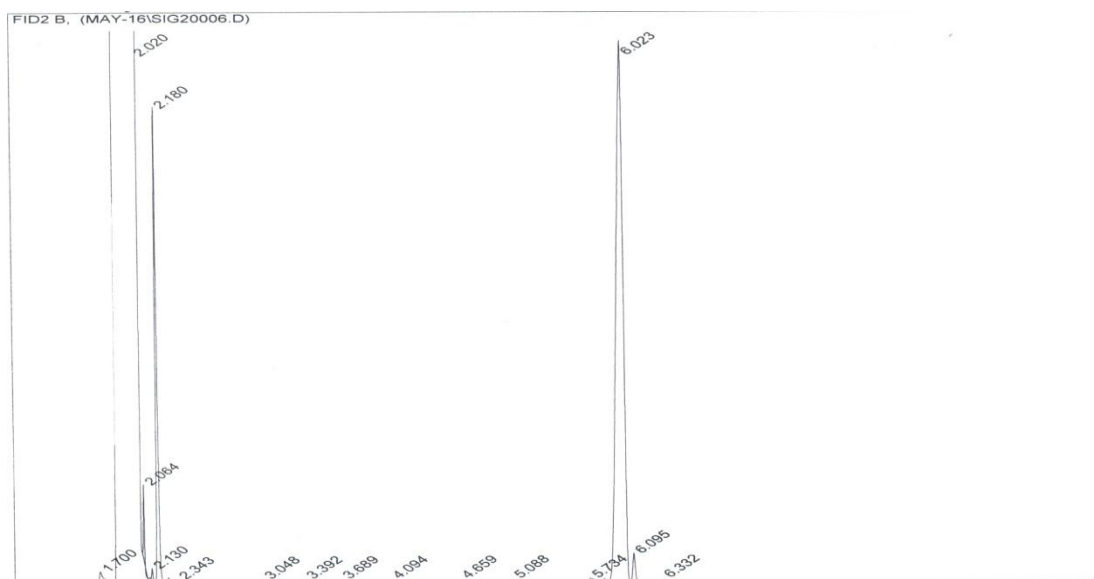


FIGURE A45: GC Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 5 Minutes

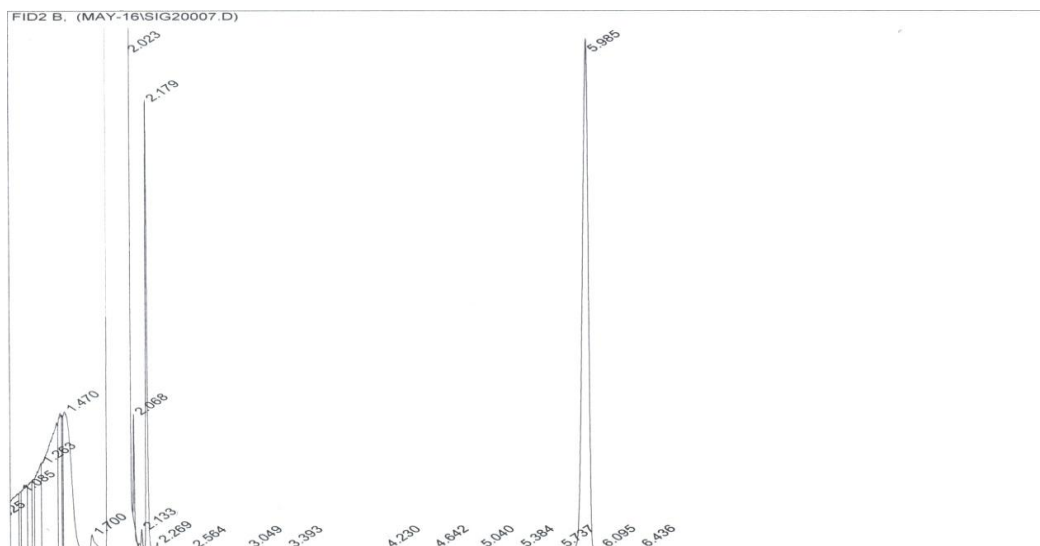


FIGURE A46: GC Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 10 Minutes

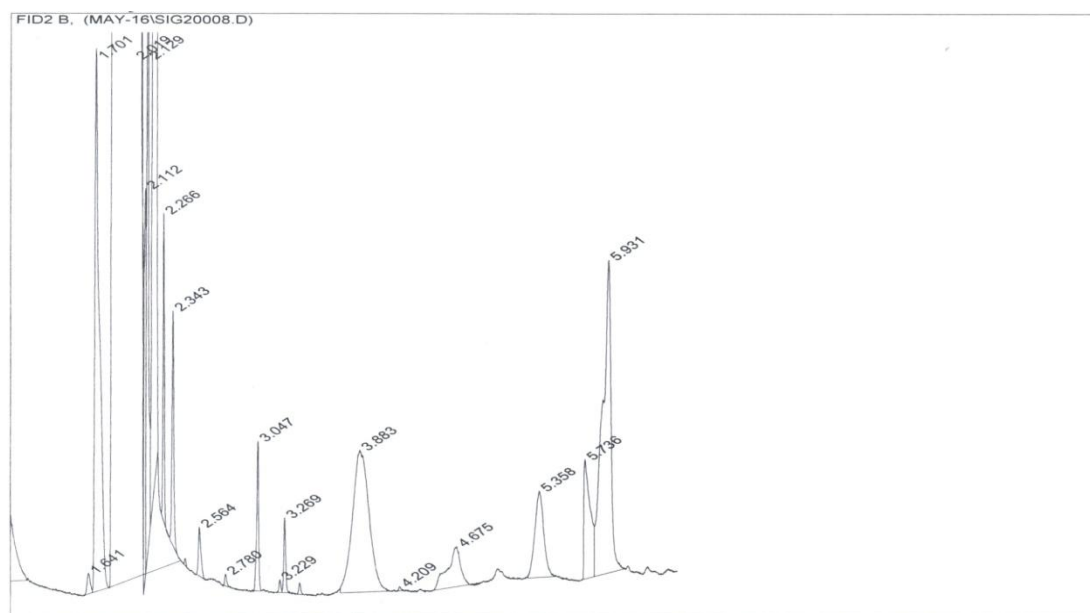


FIGURE A47: GC Chromatogram of Phenol with Deionized Water Sample Treated for 15 Minutes

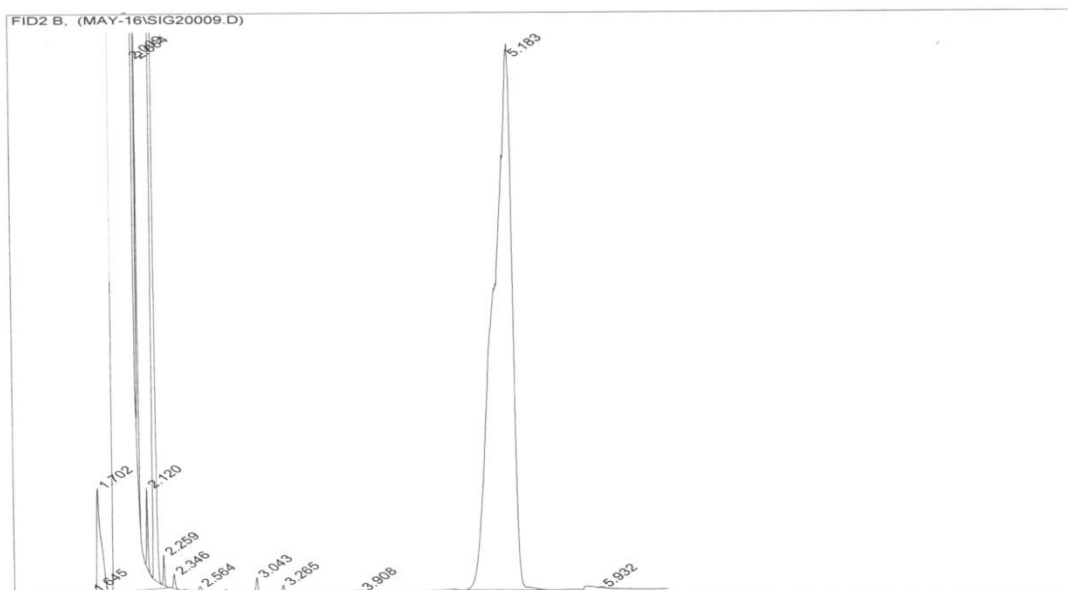


FIGURE A48: GC Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 20 Minutes

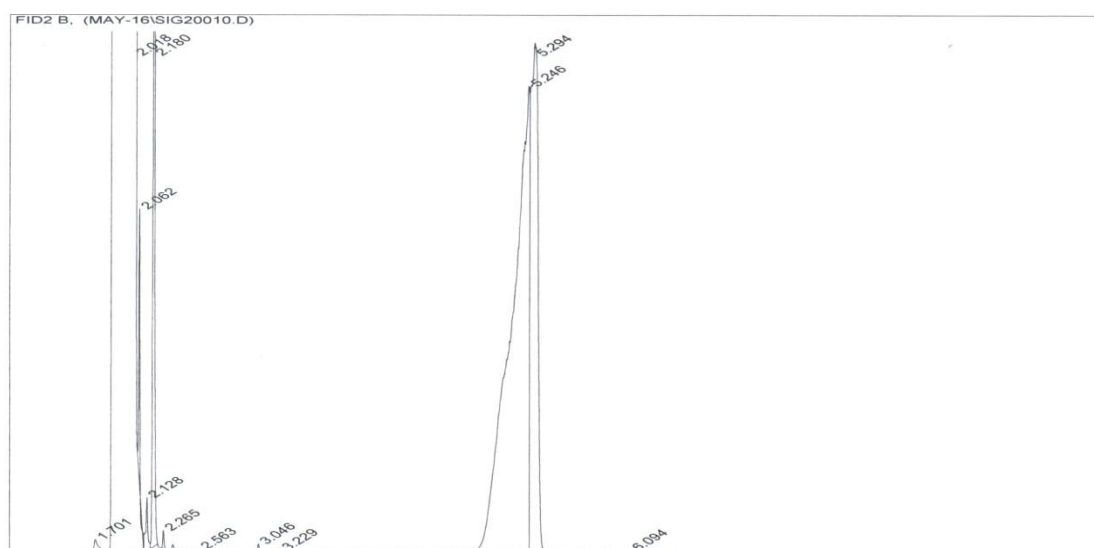


FIGURE A49: GC Chromatogram of Phenol with Deionized Water Sample Treated for 30 Minutes

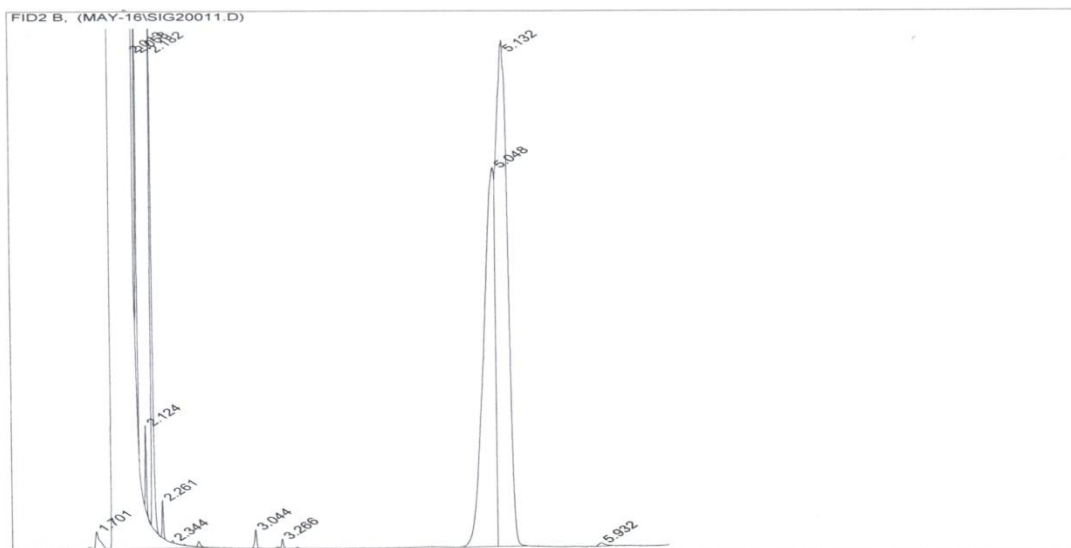


FIGURE A50: GC Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 45 Minutes

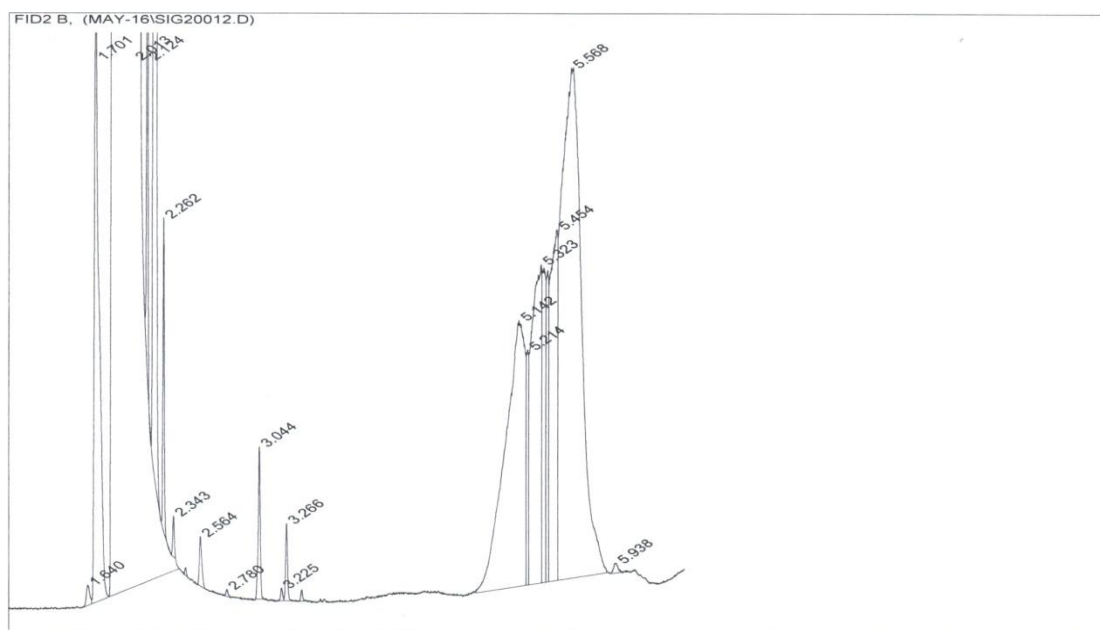


FIGURE A51: GC Chromatogram of Phenol with Deionized Water Sample Treated for 60 Minutes

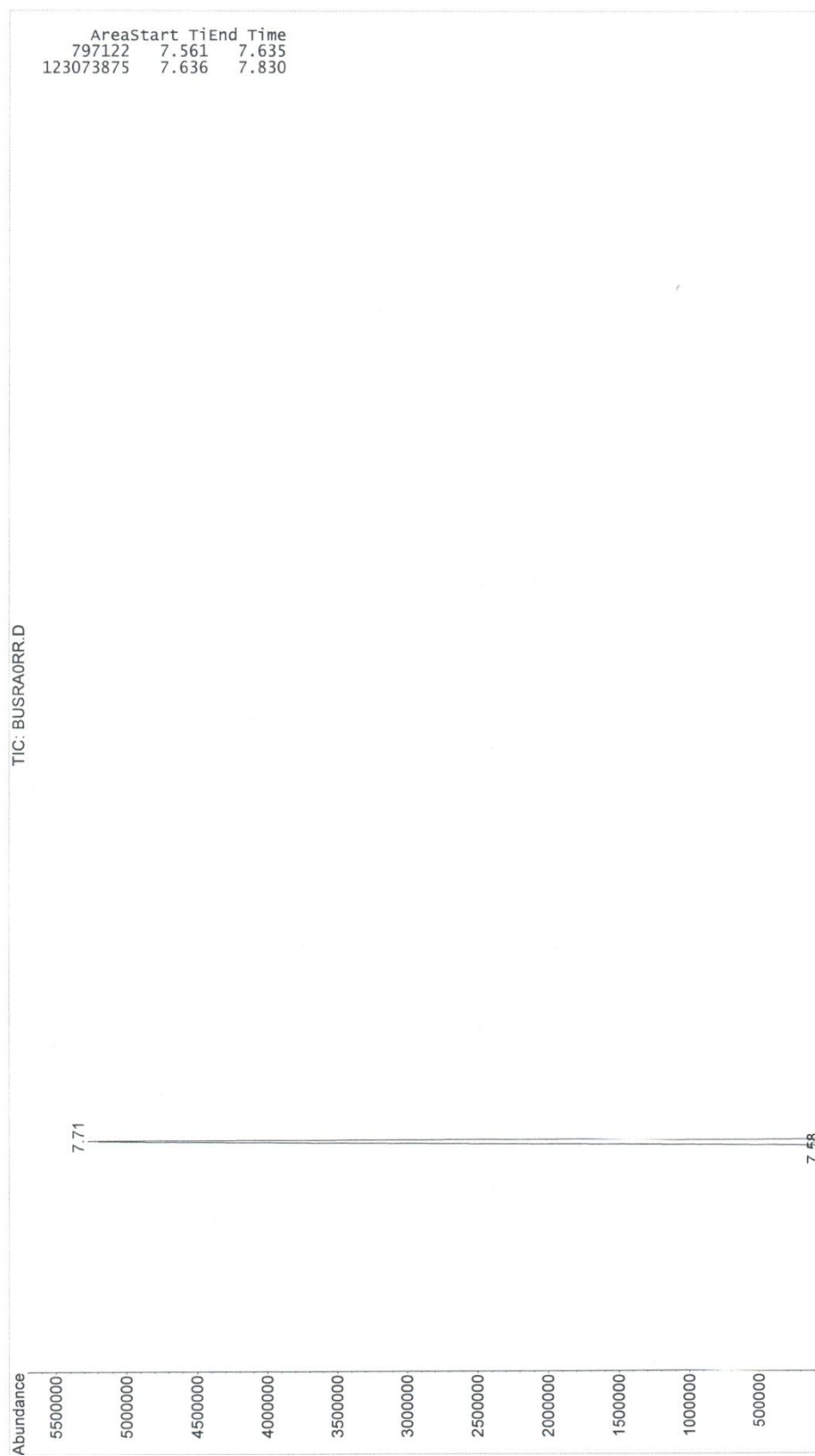


FIGURE A52: GC-MS Chromatogram of Phenol with Deionized Water (as a Base Solvent) Samples before

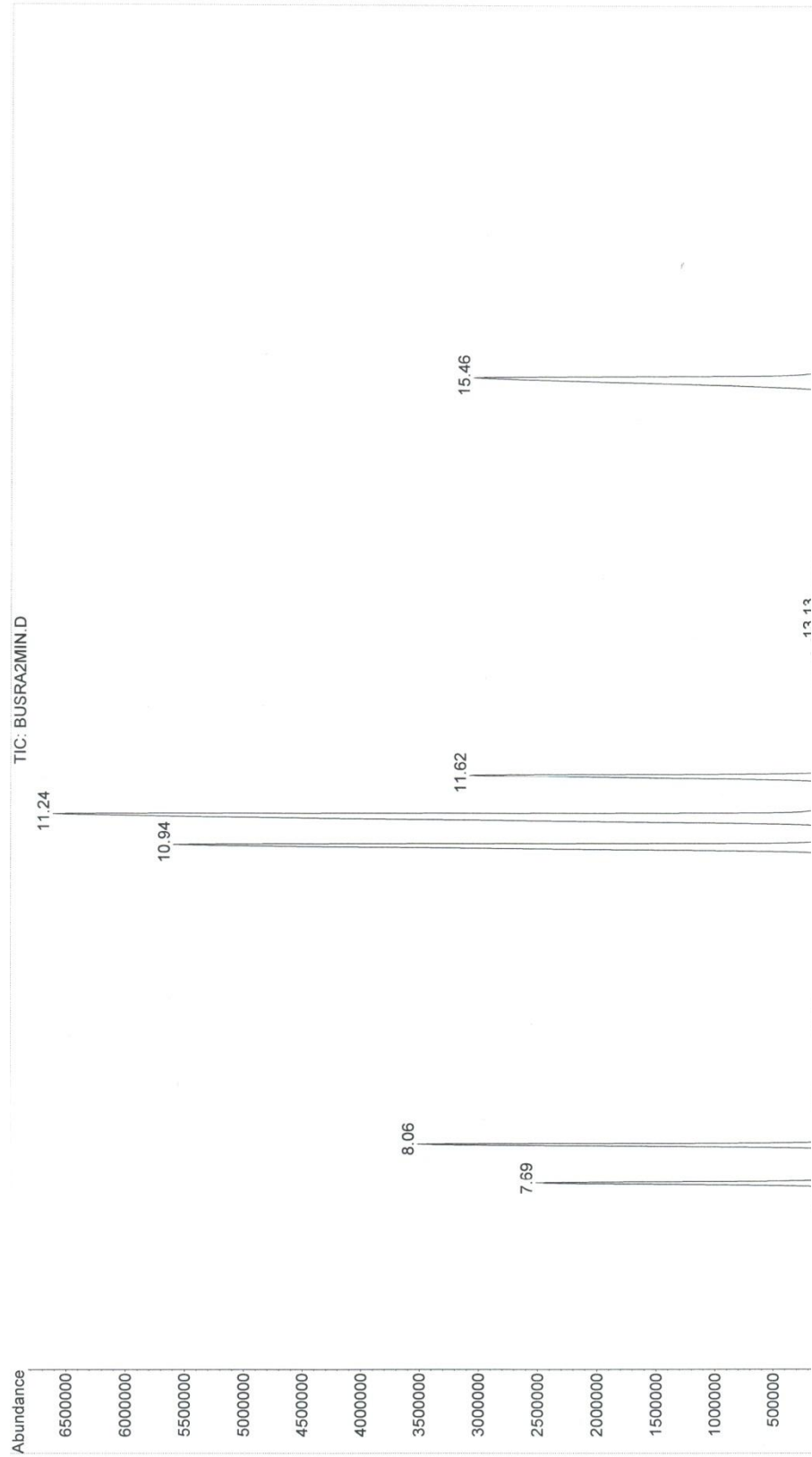


FIGURE A653: GC-MS Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 2 Minutes

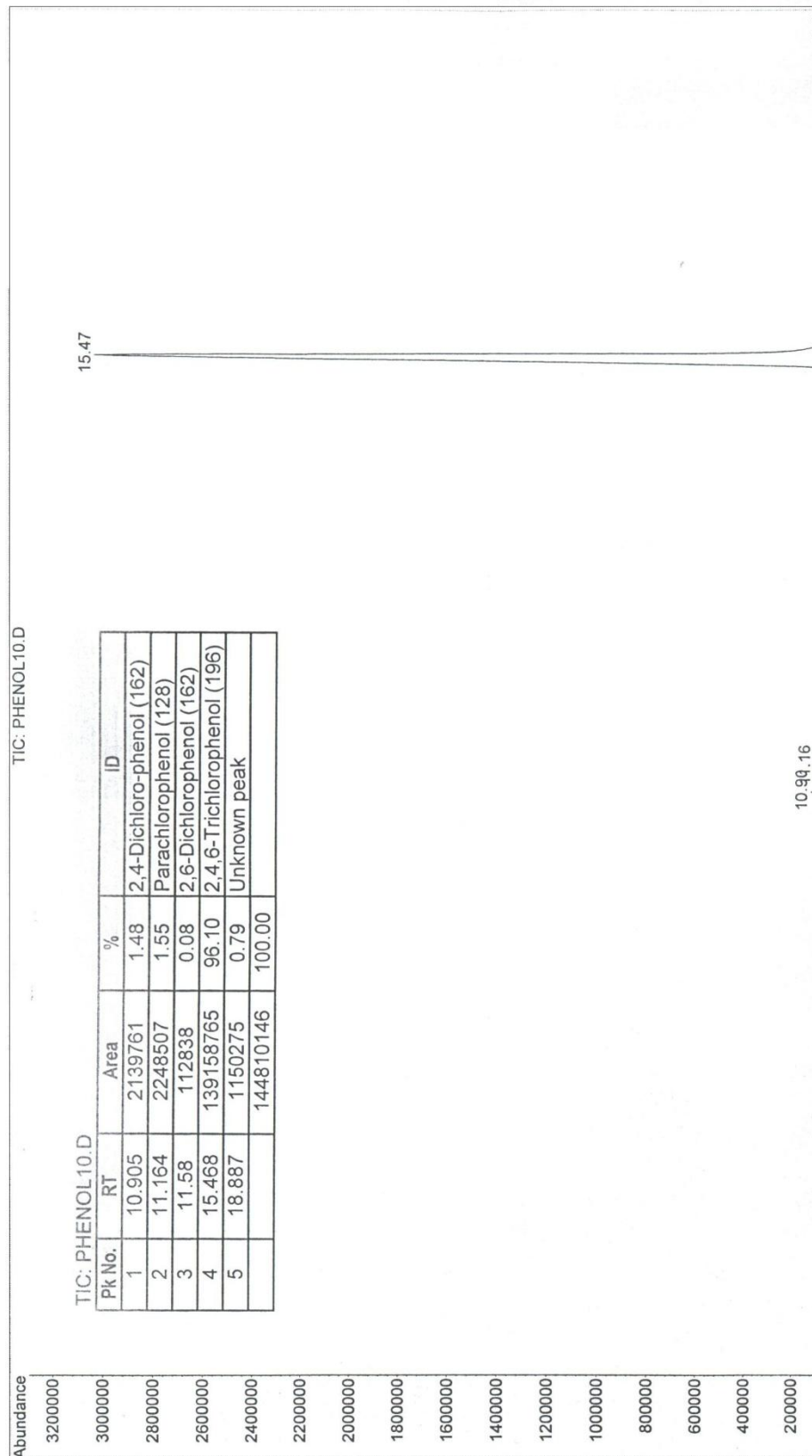


FIGURE A54: GC-MS Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 10 Minutes

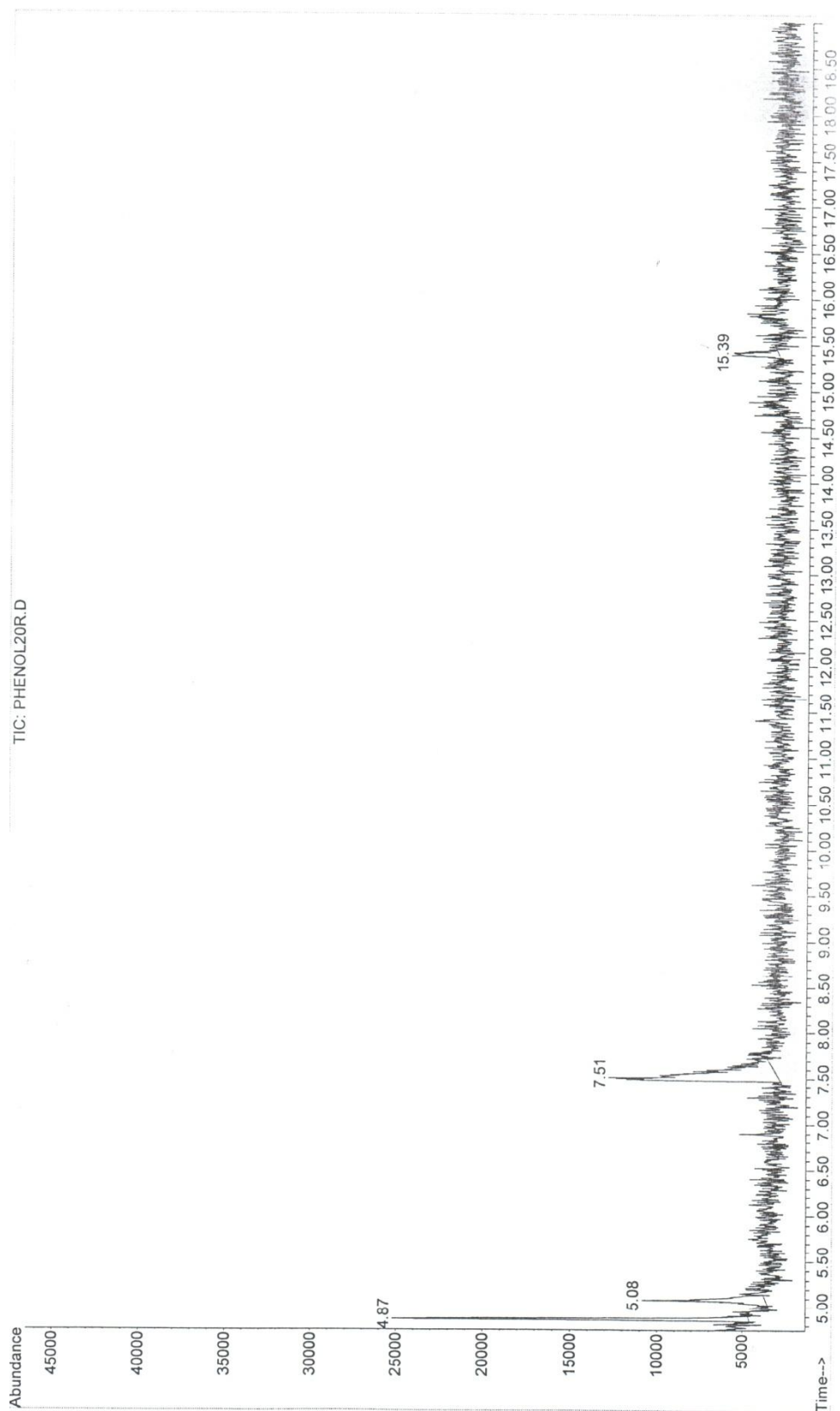


FIGURE A55: GC-MS Chromatogram of Phenol with Deionized Water (as a Base Solvent) Sample Treated for 20 Minutes

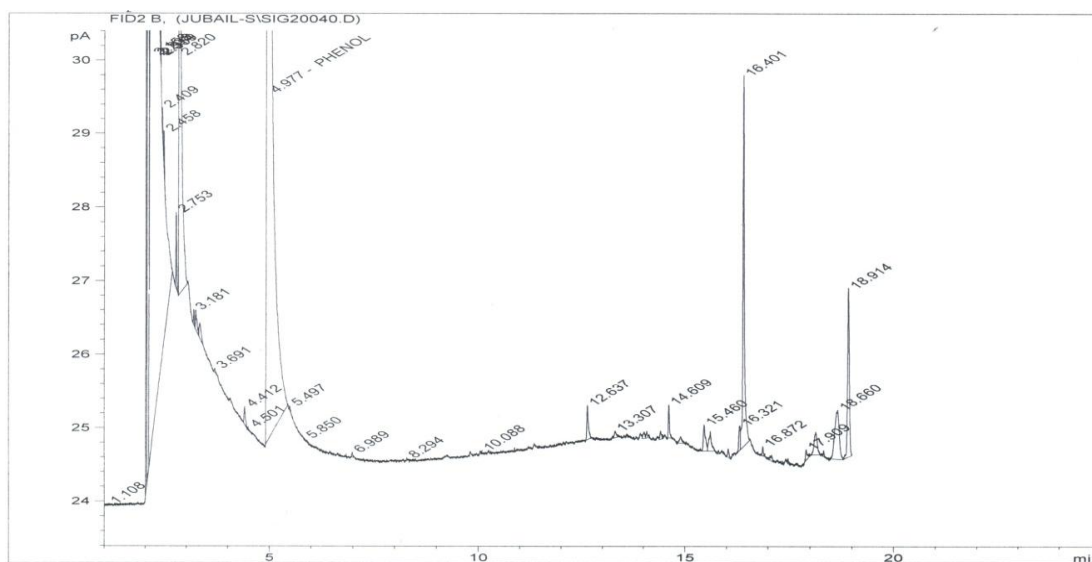


FIGURE A56: GC Chromatogram of Sample before Treatment for CaSO_4 Investigation

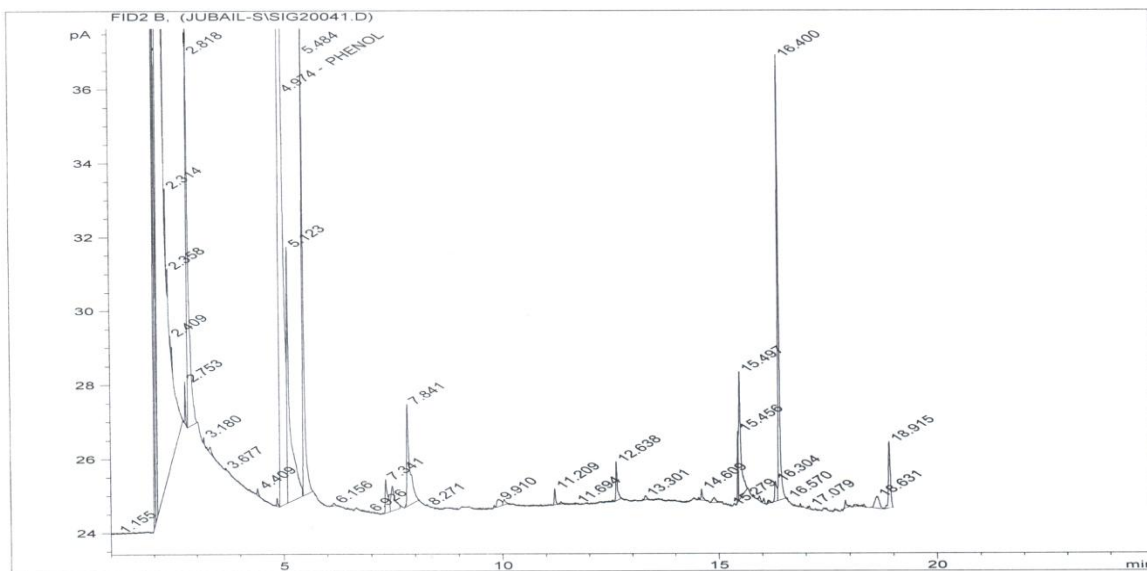


FIGURE A57: GC Chromatogram of Samples Treated for 2 Minutes, in CaSO_4 Investigation

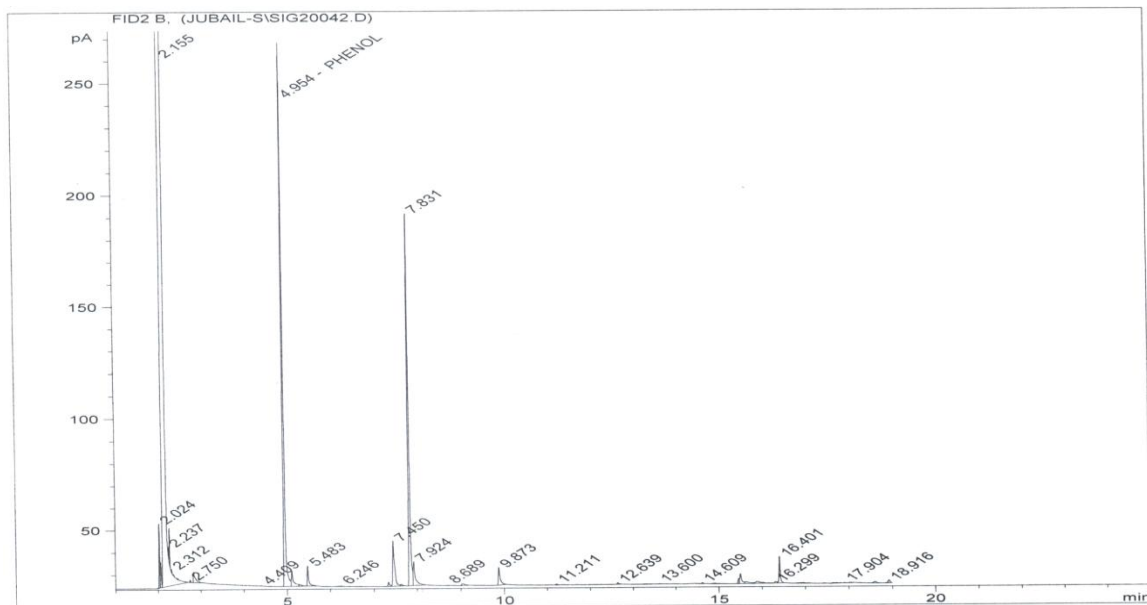


FIGURE A58: GC Chromatogram of Samples Treated for 5 Minutes, in CaSO_4 Investigation

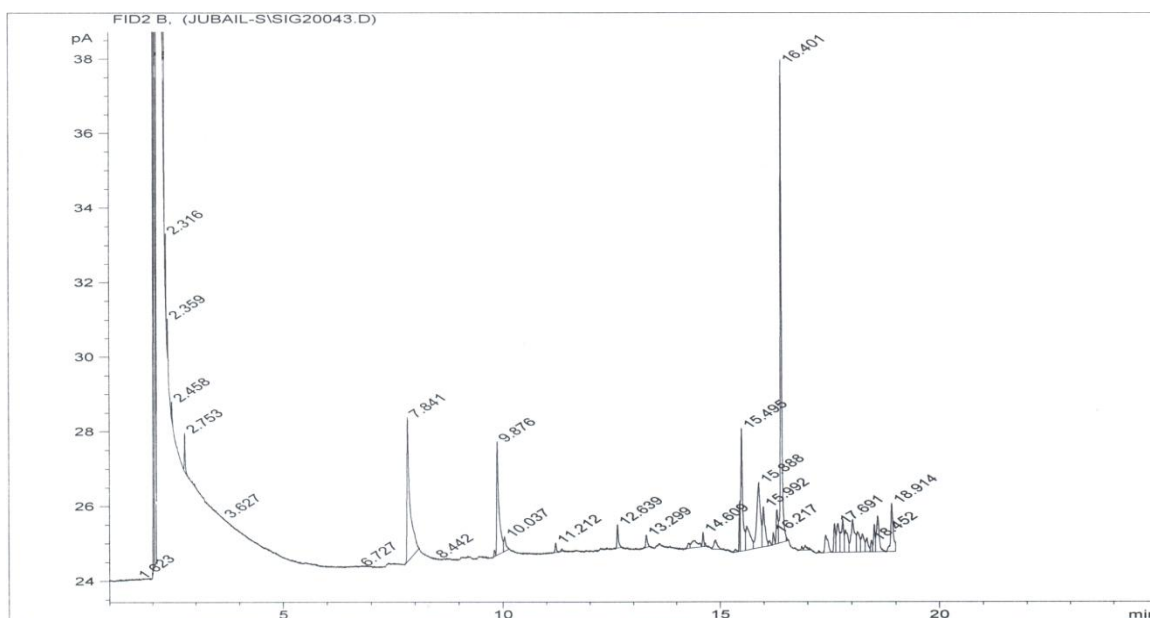


FIGURE A59: GC Chromatogram of Samples Treated for 10 Minutes, in CaSO_4 Investigation

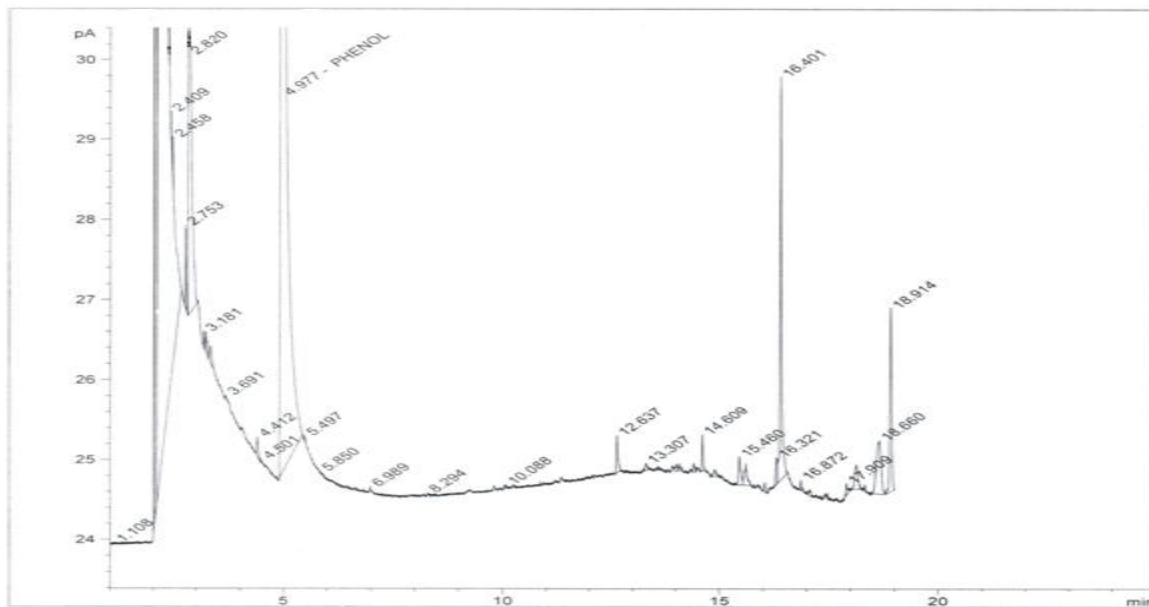


FIGURE A60: GC Chromatogram of Sample before Treatment for MgSO_4 Investigation

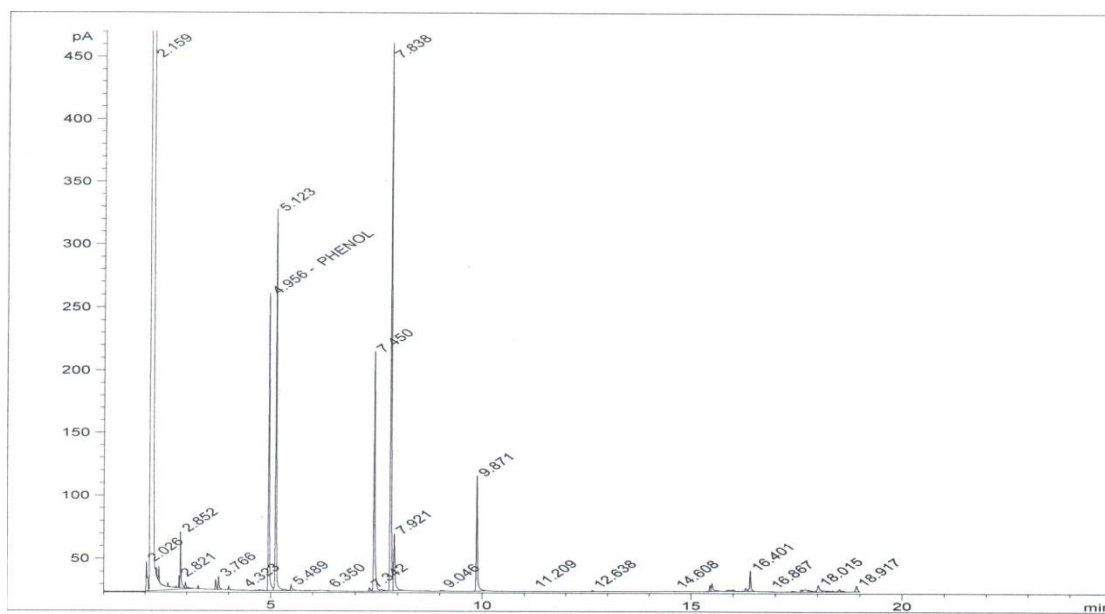


FIGURE A61: GC Chromatogram of Samples Treated for 2 Minutes, in MgSO_4 Investigation

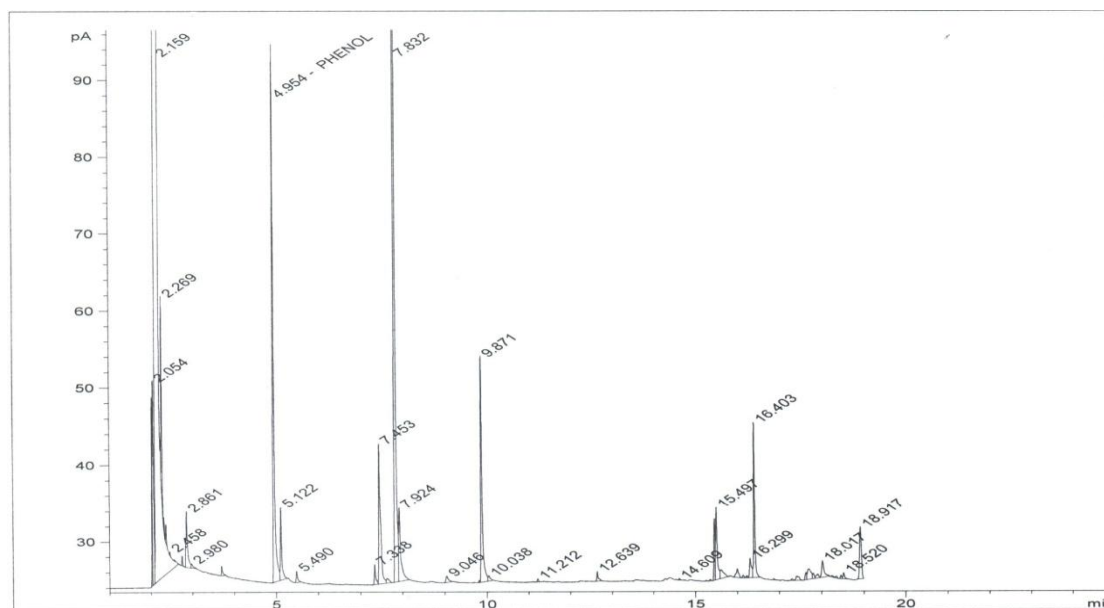


FIGURE A62: GC Chromatogram of Samples Treated for 5 Minutes, in MgSO_4 Investigation

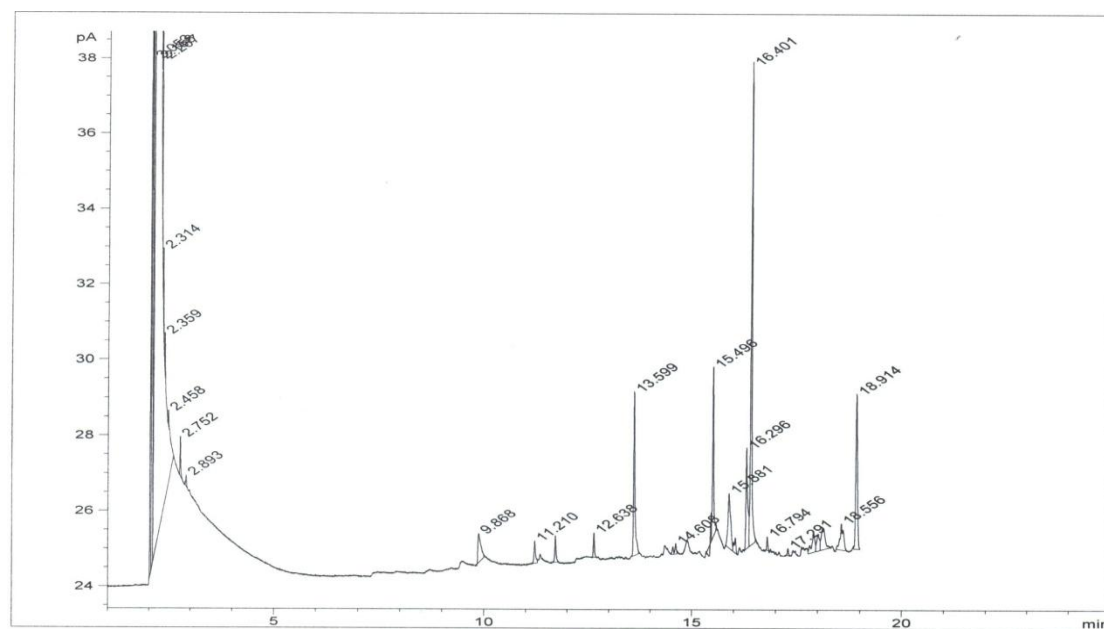


FIGURE A63: GC Chromatogram of Samples Treated for 10 Minutes, in MgSO_4 Investigation

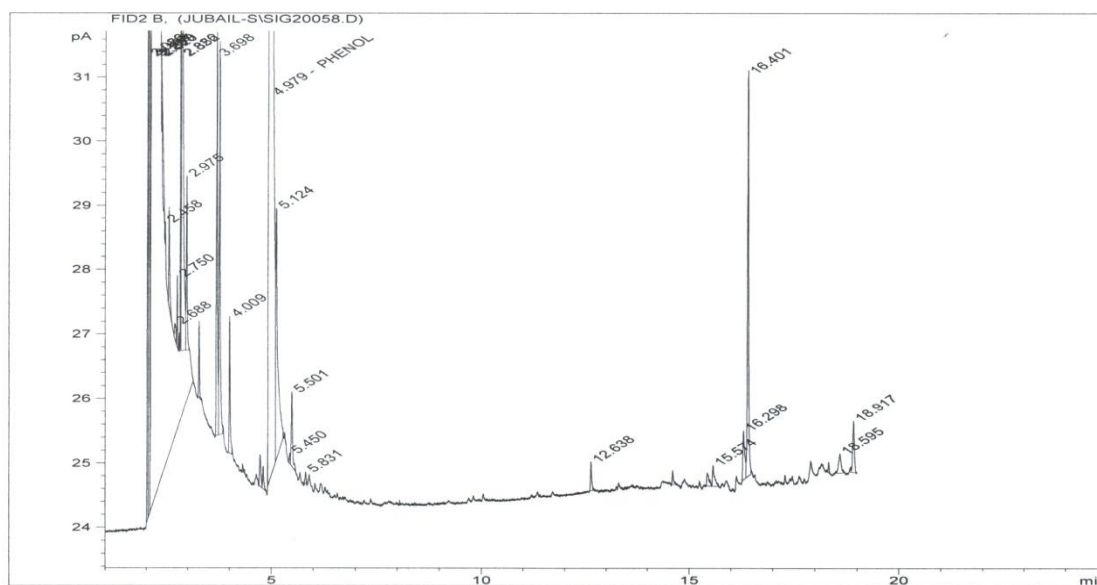


FIGURE A64: GC Chromatogram of Sample before Treatment for MgCl_2 Investigation

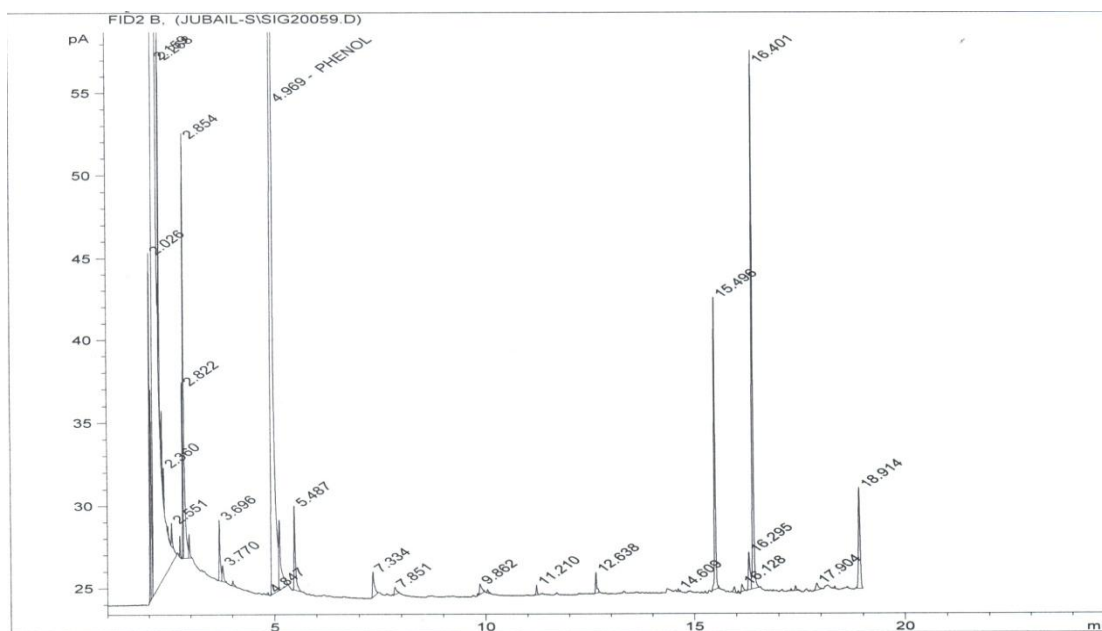


FIGURE A65: GC Chromatogram of Samples Treated for 2 Minutes, in MgCl_2 Investigation

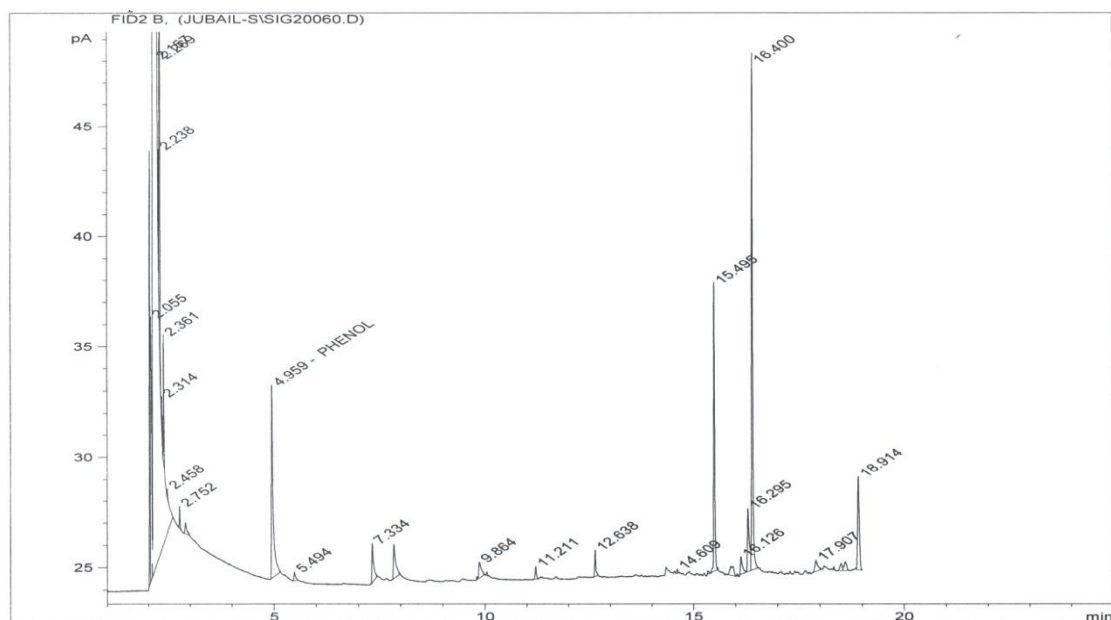


FIGURE A66: GC Chromatogram of Samples Treated for 5 Minutes, in MgCl_2 Investigation

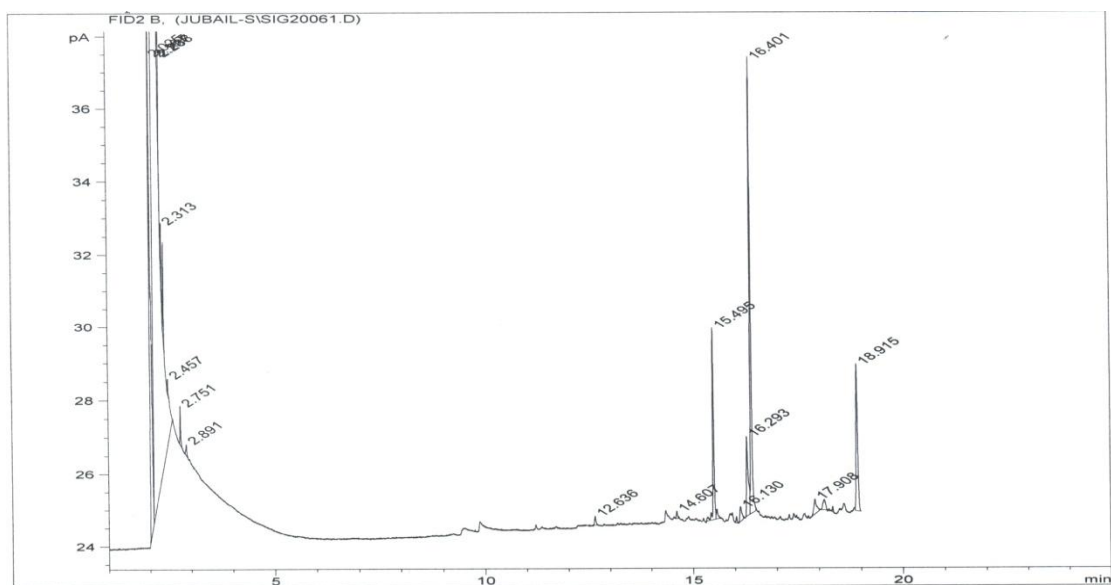


FIGURE A67: GC Chromatogram of Samples Treated for 10 Minutes, in MgCl_2 Investigation

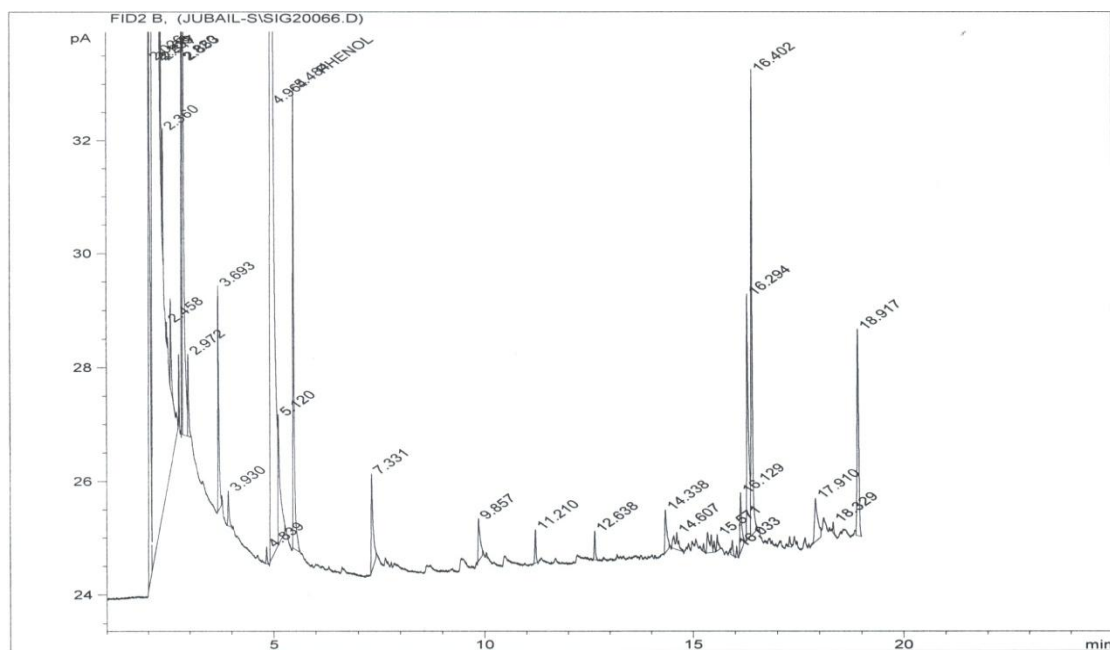


FIGURE A68: GC Chromatogram of Samples Treated for 60 Minutes, in MgCl_2 Investigation

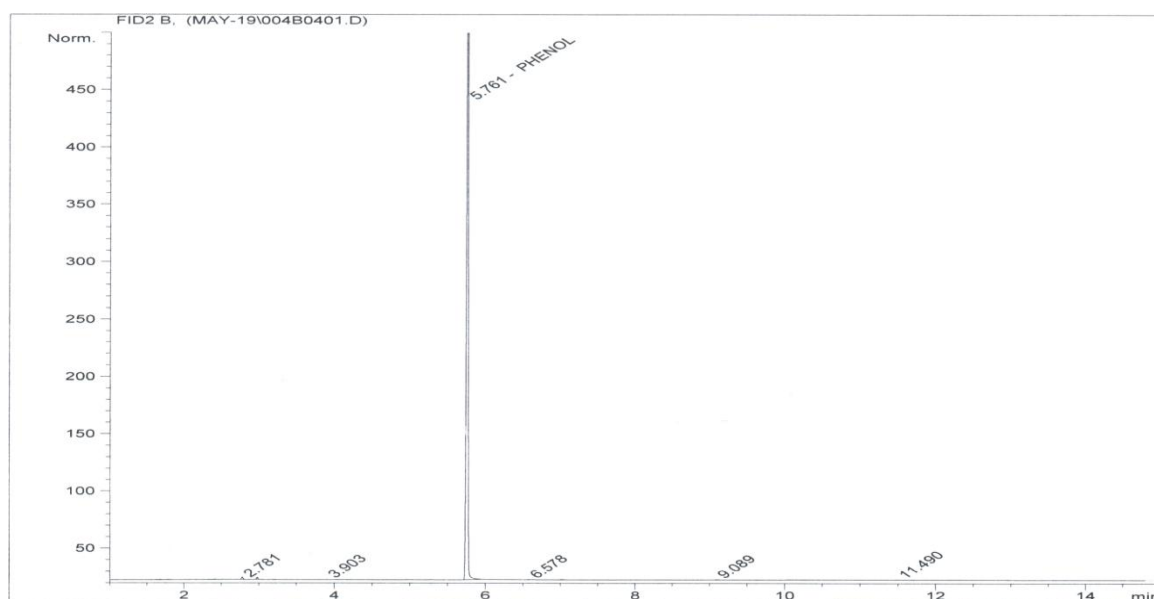


FIGURE A69: GC Chromatogram of Sample before Treatment for NaHCO_3 Investigation

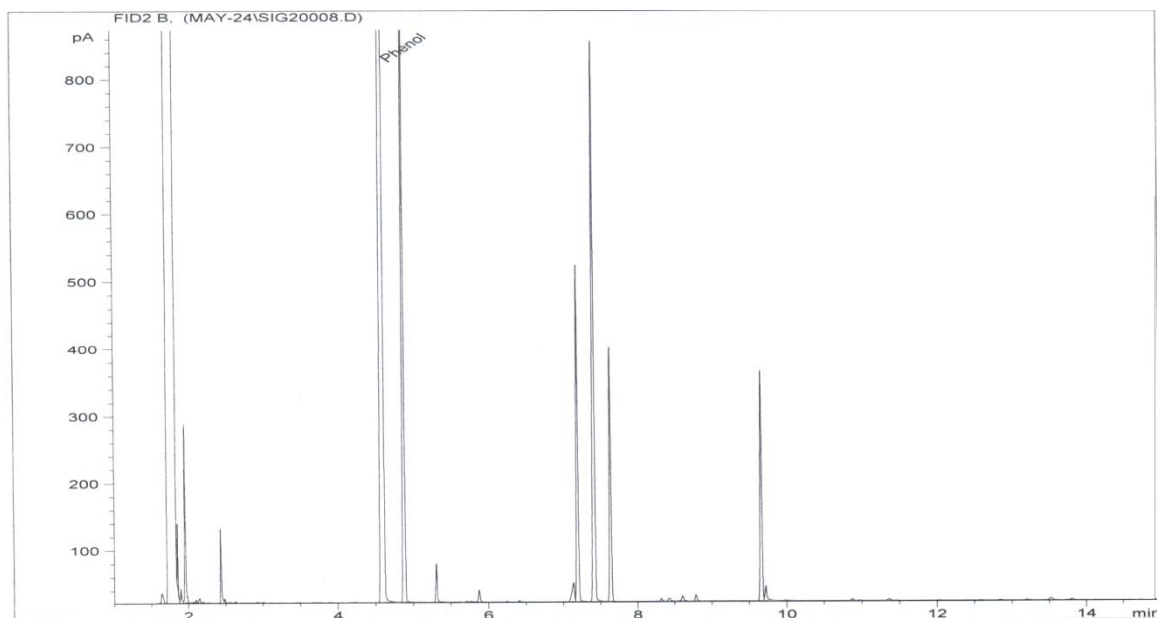


FIGURE A70: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 Investigation

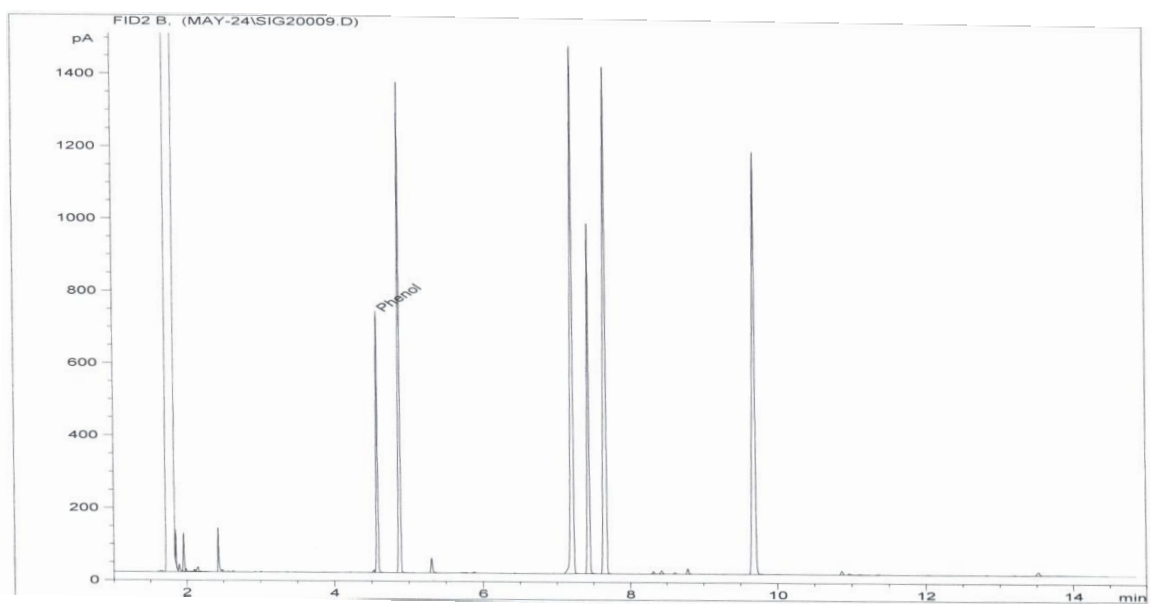


FIGURE A71: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 Investigation

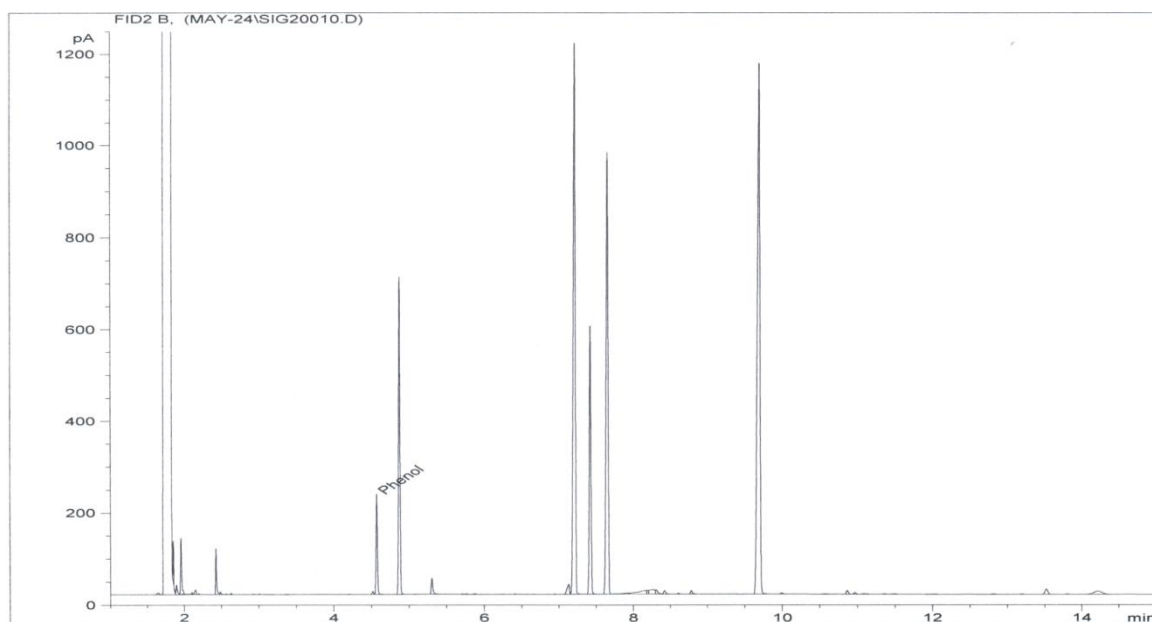


FIGURE A72: GC Chromatogram of Samples Treated for 10 Minutes in NaHCO_3 Investigation

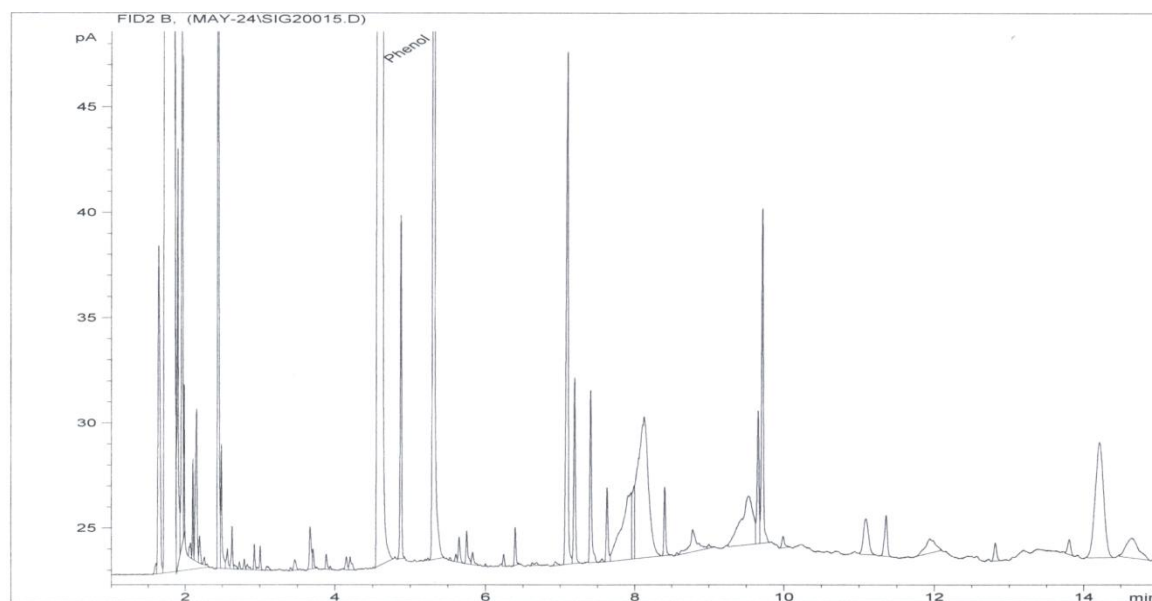


FIGURE A73: GC Chromatogram of Samples Treated for 60 Minutes, in NaHCO_3 Investigation

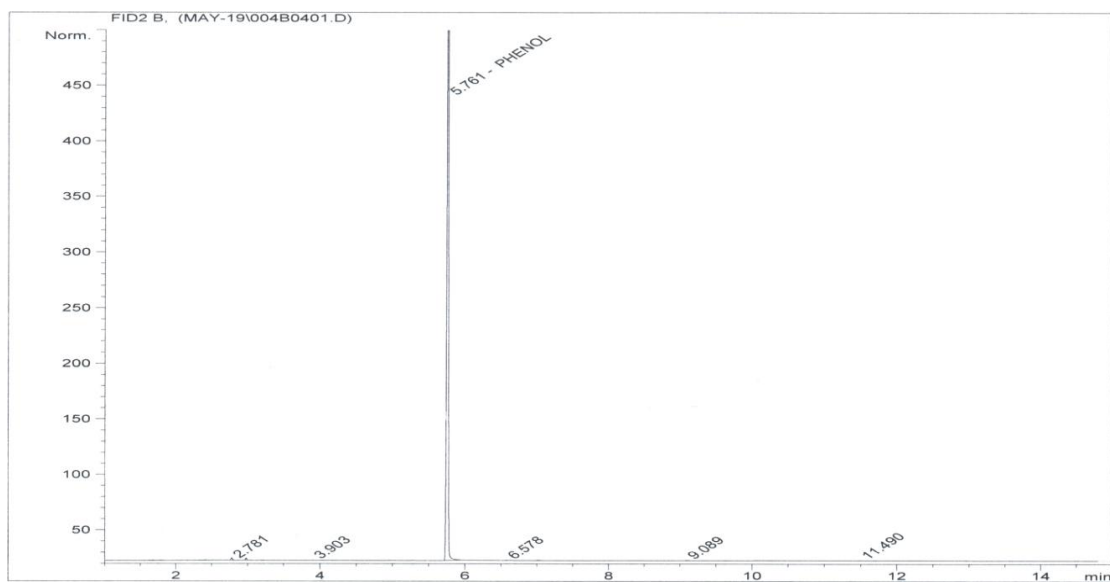


FIGURE A74: GC Chromatogram of Sample before Treatment for CaSO_4 , and MgSO_4 Investigation

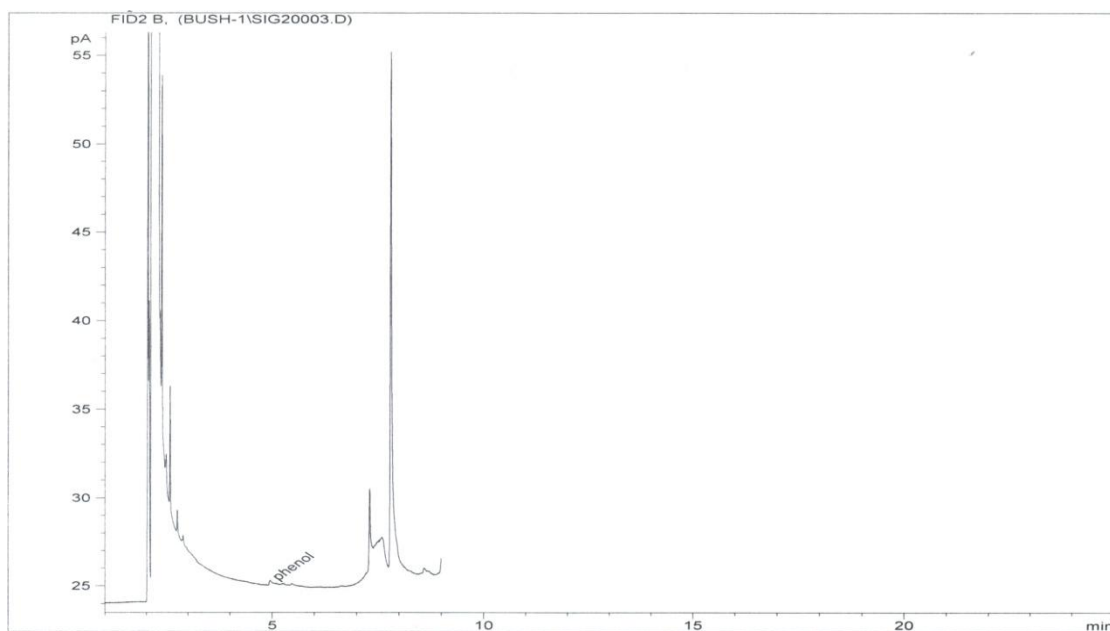


FIGURE A75: GC Chromatogram of Samples Treated for 2 Minutes, in CaSO_4 , and MgSO_4 Investigation

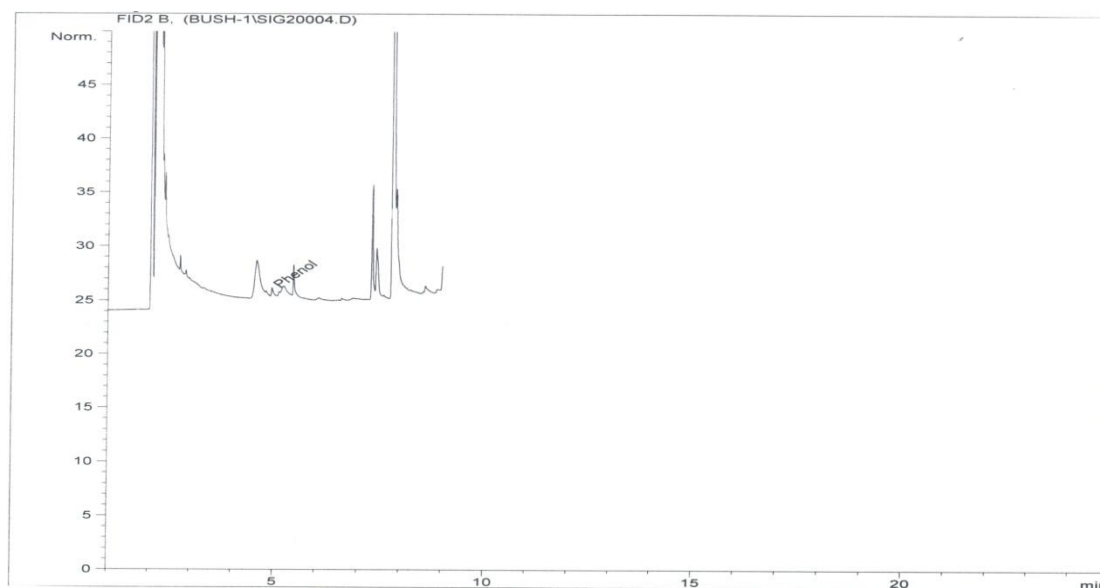


FIGURE A76: GC Chromatogram of Samples Treated for 5 Minutes, in CaSO_4 , and MgSO_4 Investigation

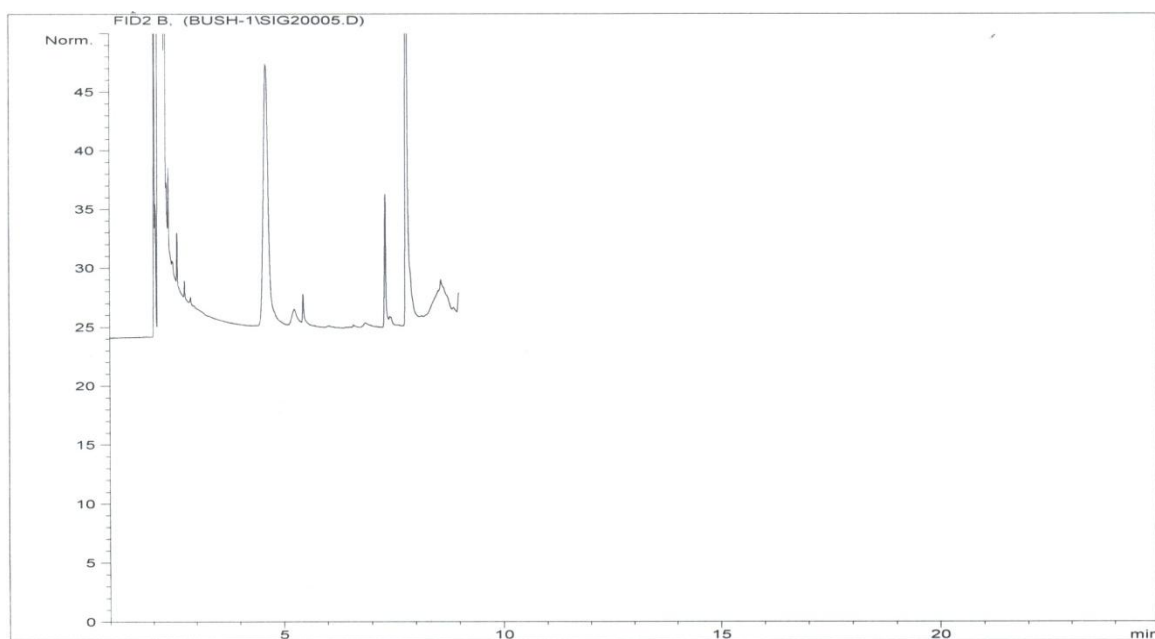


FIGURE A77: GC Chromatogram of Samples Treated for 10 Minutes, in CaSO_4 , and MgSO_4 Investigation

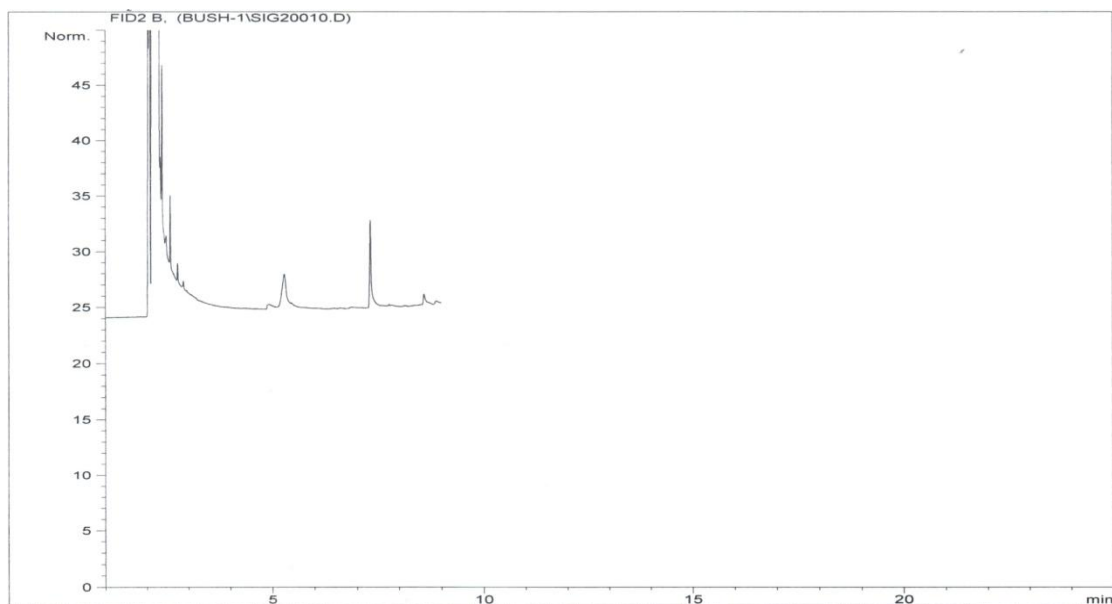


FIGURE A78: GC Chromatogram of Samples Treated for 60 Minutes, in CaSO_4 , and MgSO_4 Investigation

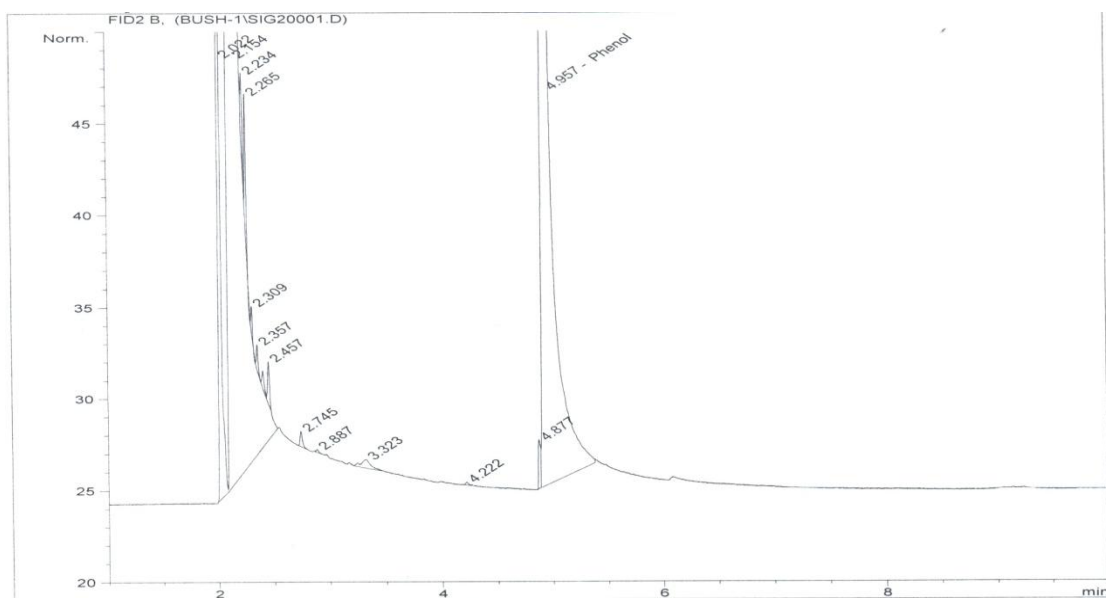


FIGURE A79: GC Chromatogram of Sample before Treatment for NaHCO_3 and MgSO_4 Investigation

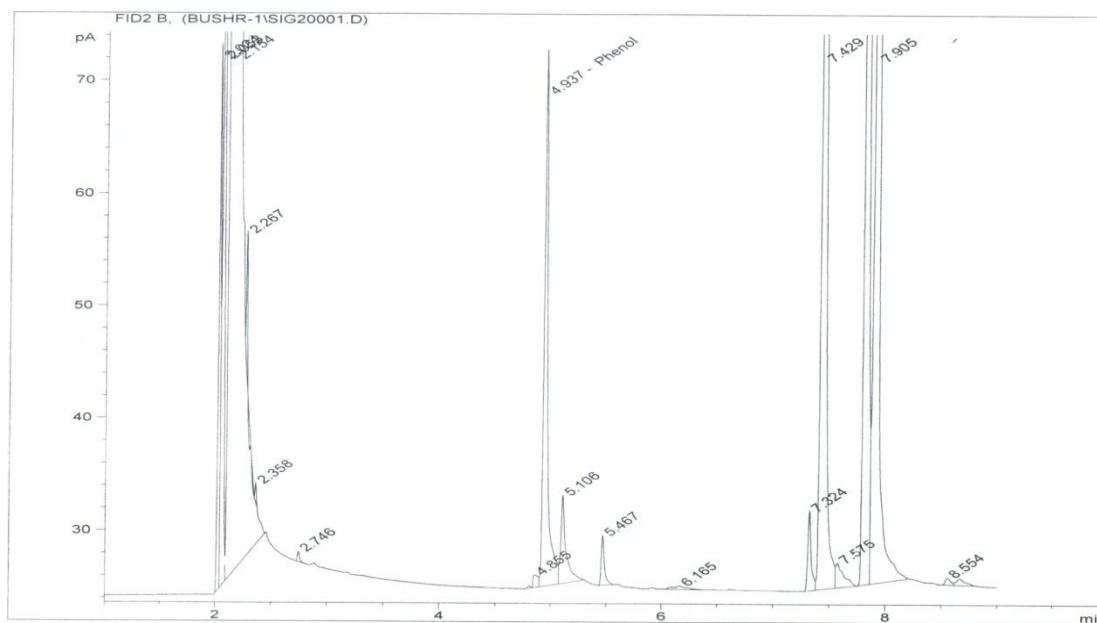


FIGURE A80: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 and MgSO_4 Investigation

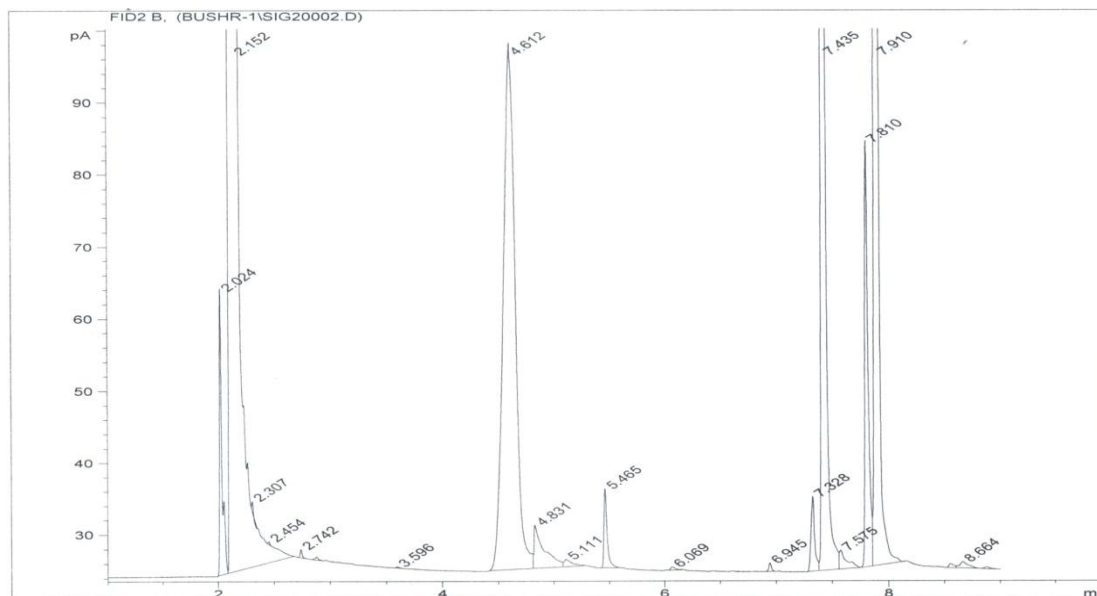


FIGURE A81: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 and MgSO_4 Investigation

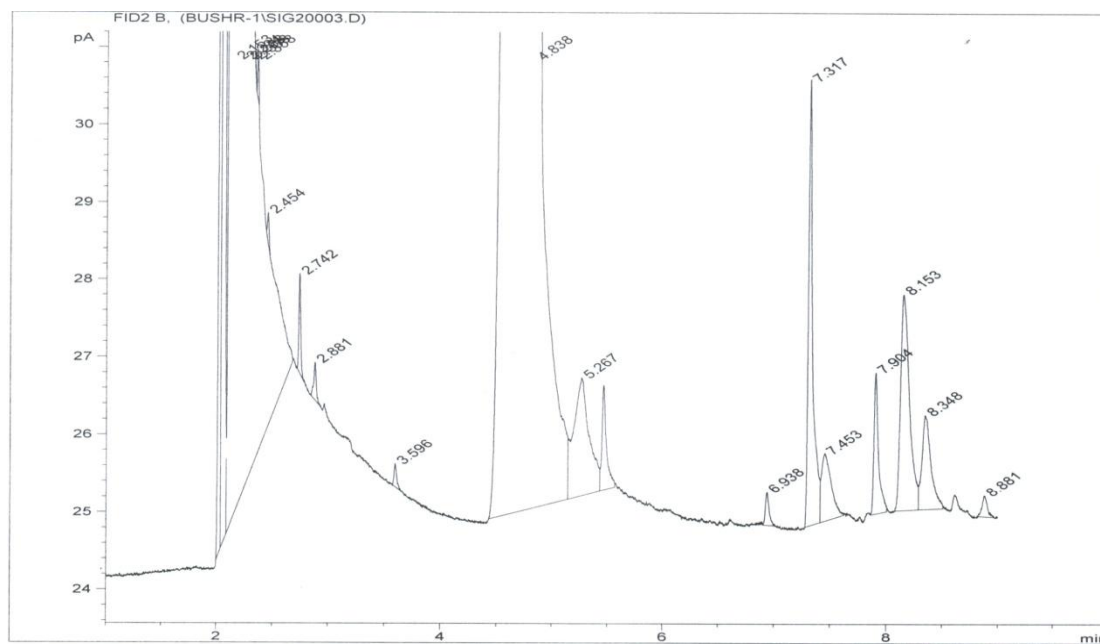


FIGURE A82: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 and MgSO_4 Investigation

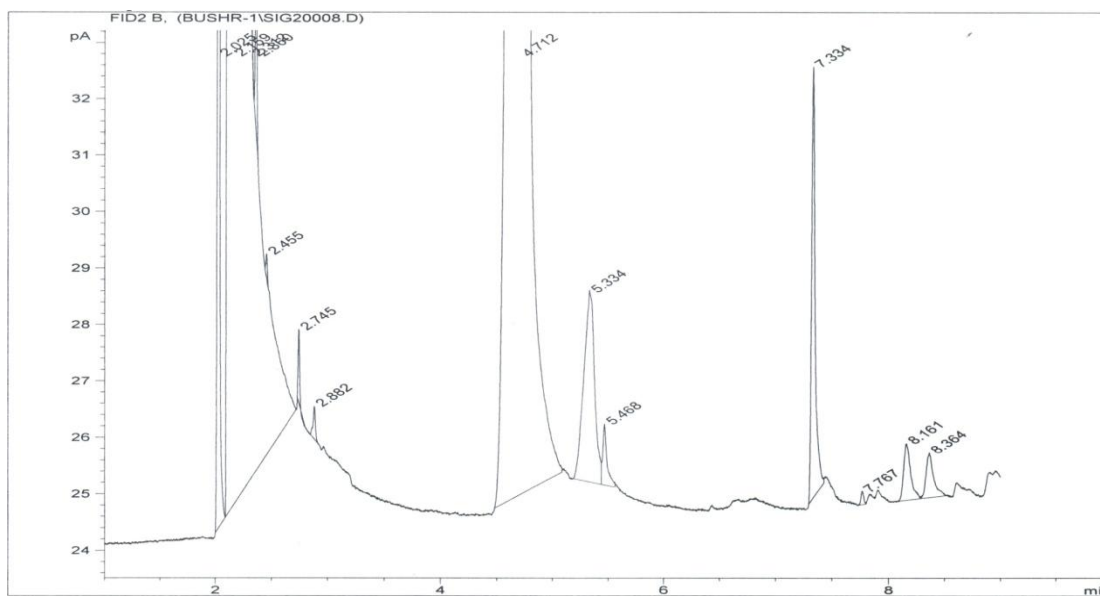


FIGURE A83: GC Chromatogram of Samples Treated for 60 Minutes, in NaHCO_3 and MgSO_4 Investigation

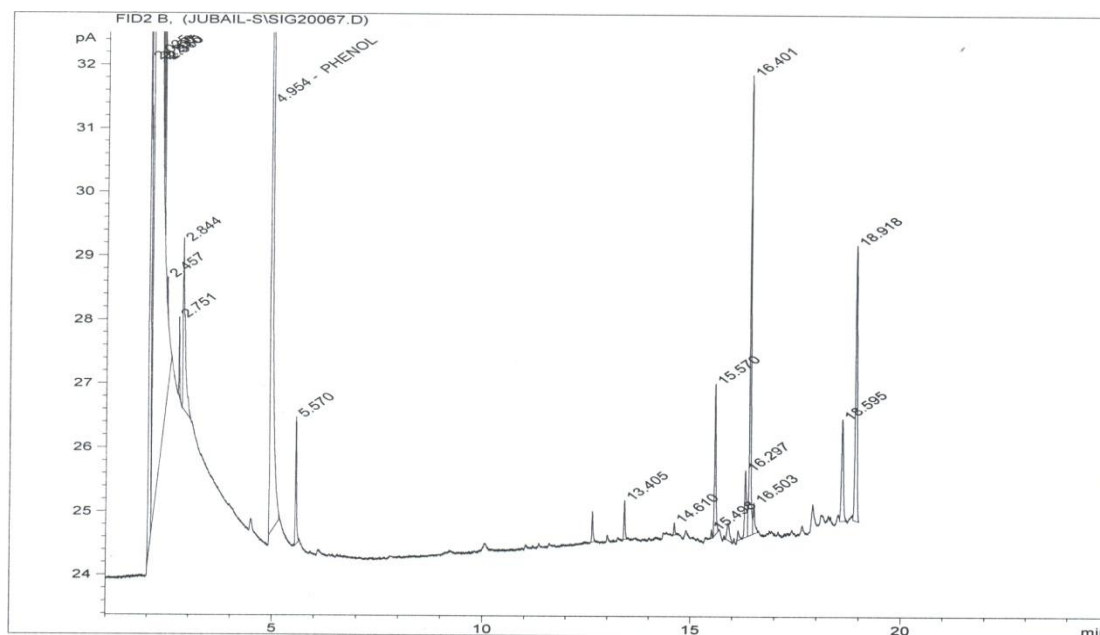


FIGURE A84: GC Chromatogram of Sample before Treatment for NaHCO_3 and CaSO_4 Investigation

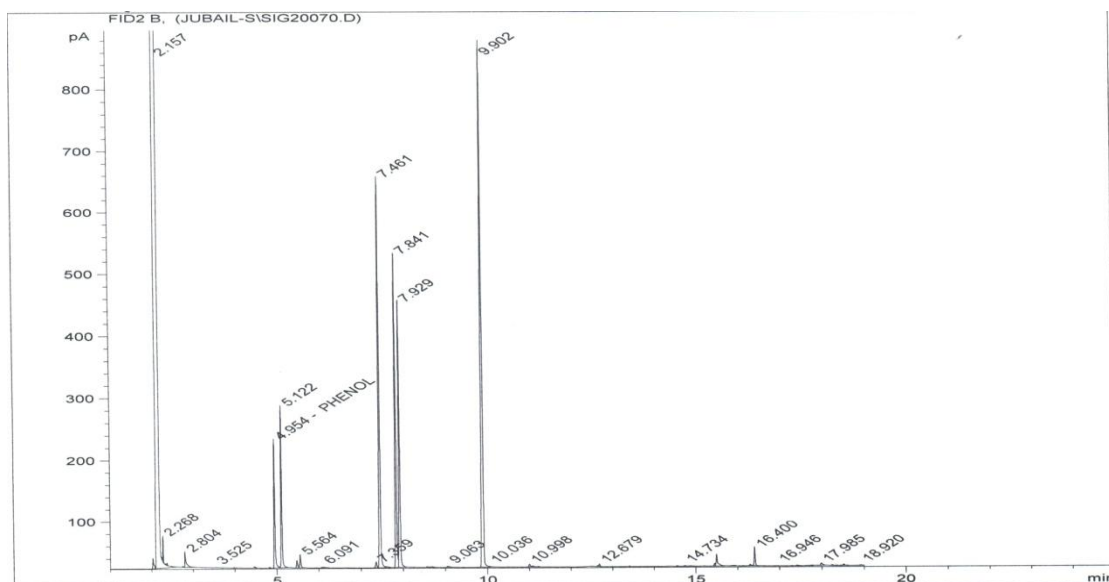


FIGURE A85: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 and CaSO_4 Investigation

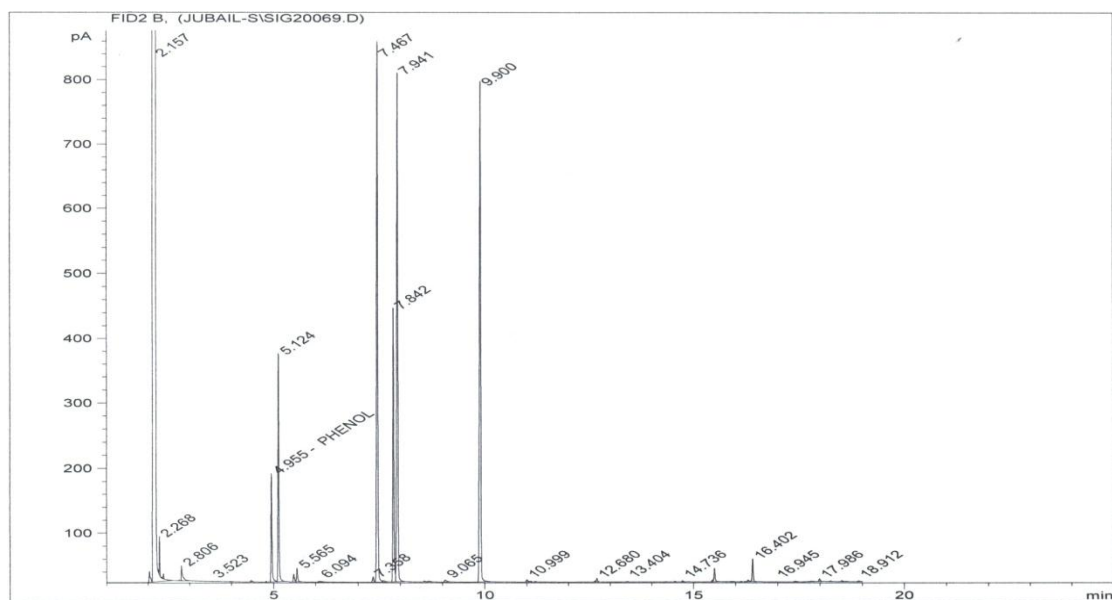


FIGURE A86: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 and CaSO_4 Investigation

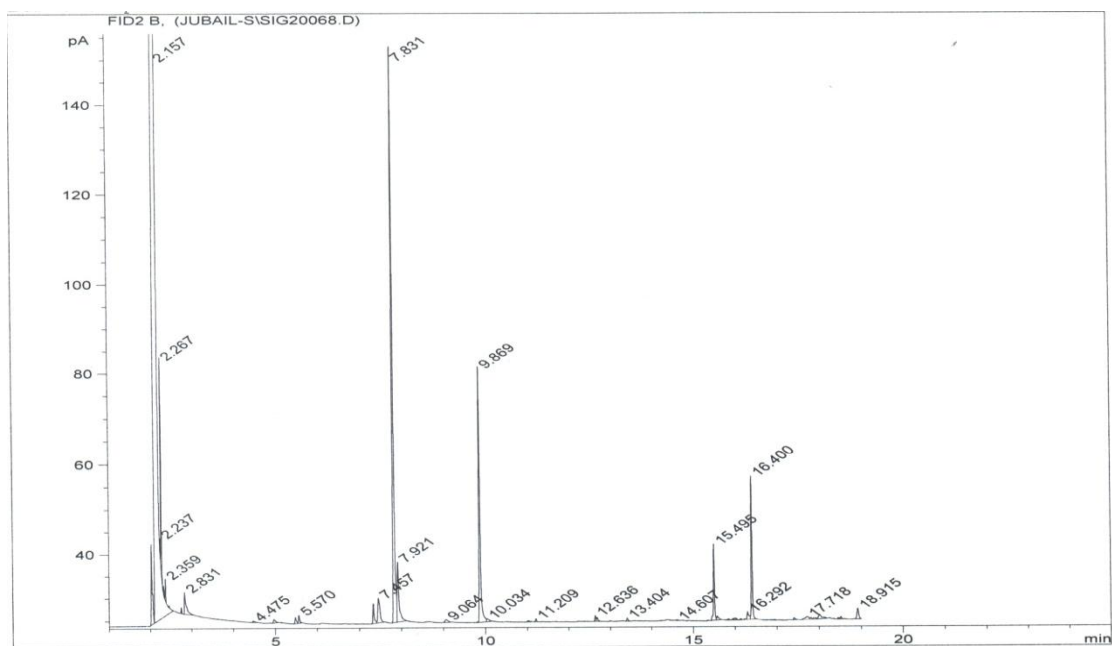


FIGURE A87: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 and CaSO_4 Investigation

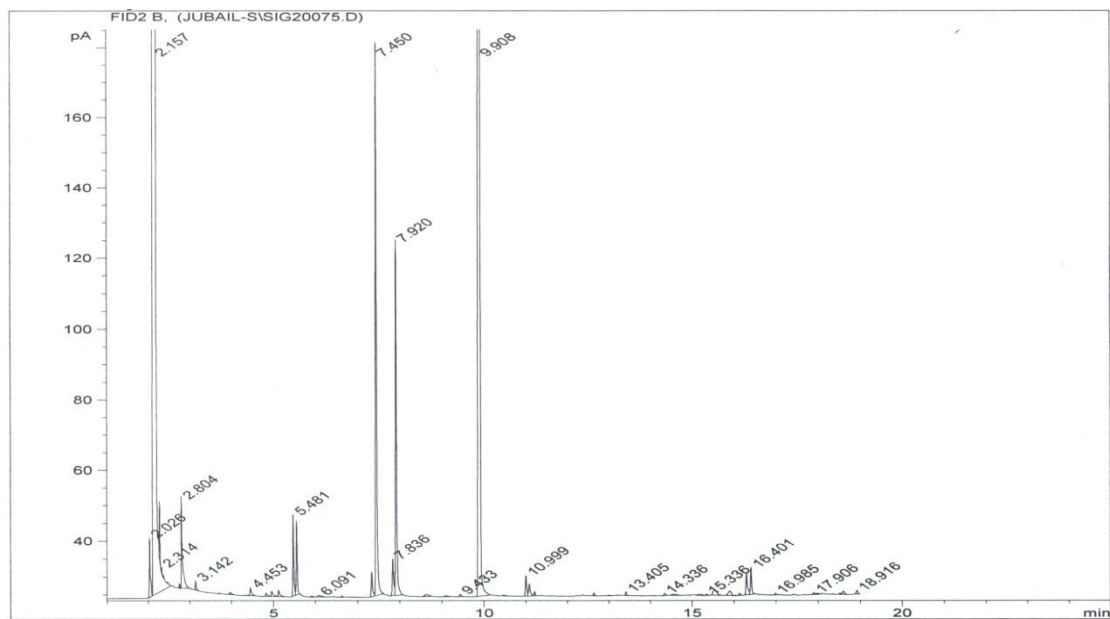


FIGURE A88: GC Chromatogram of Samples Treated for 60 Minutes, in NaHCO_3 and CaSO_4 Investigation

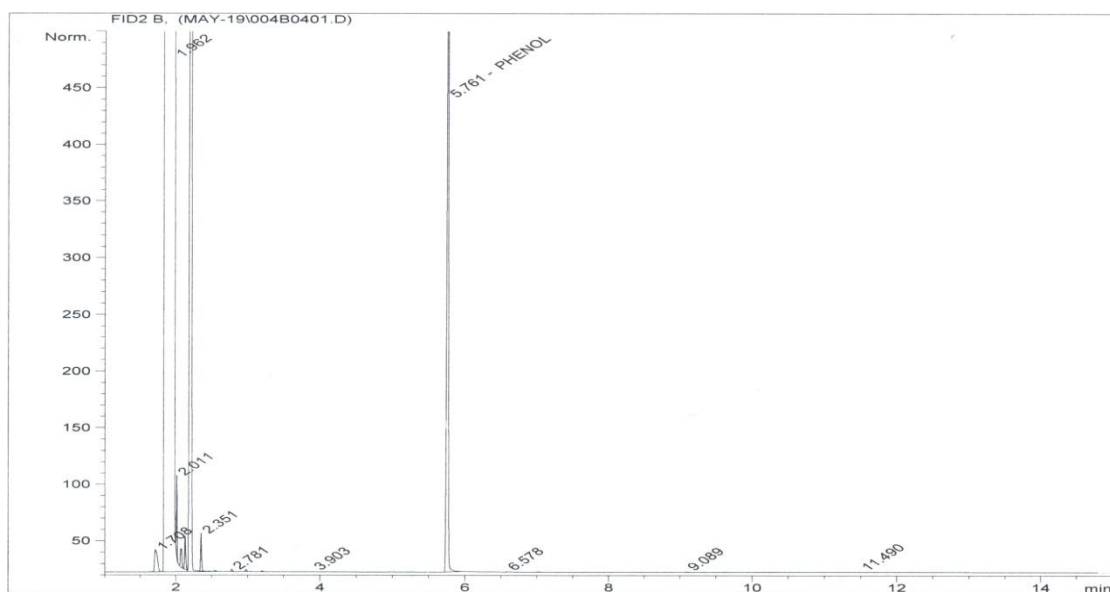


FIGURE A89: GC Chromatogram of Sample before Treatment for NaHCO_3 and MgCl_2 Investigation

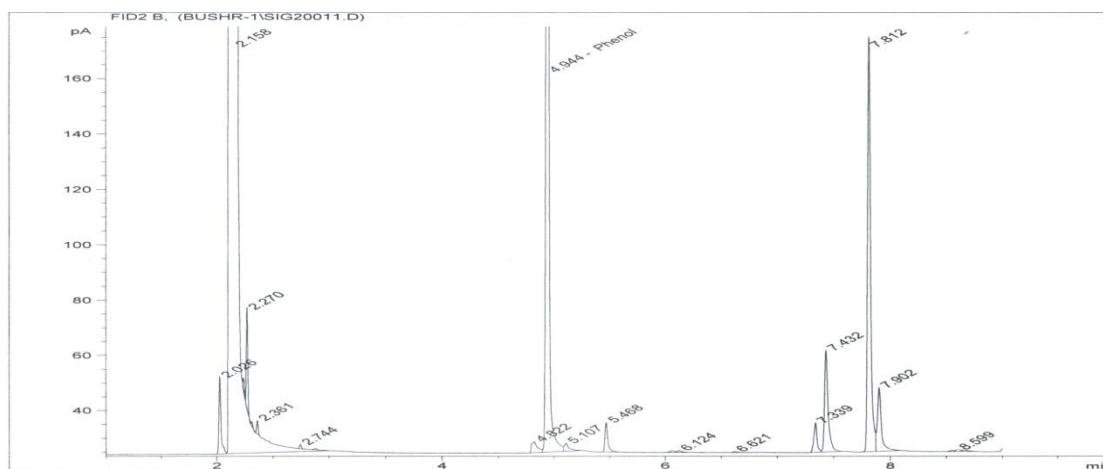


FIGURE A90: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 and MgCl_2 Investigation

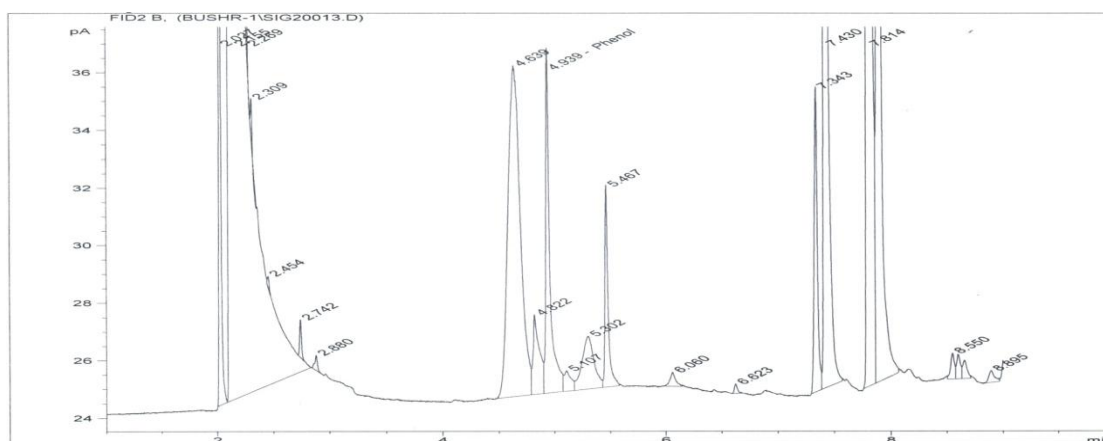


FIGURE A91: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 and MgCl_2 Investigation

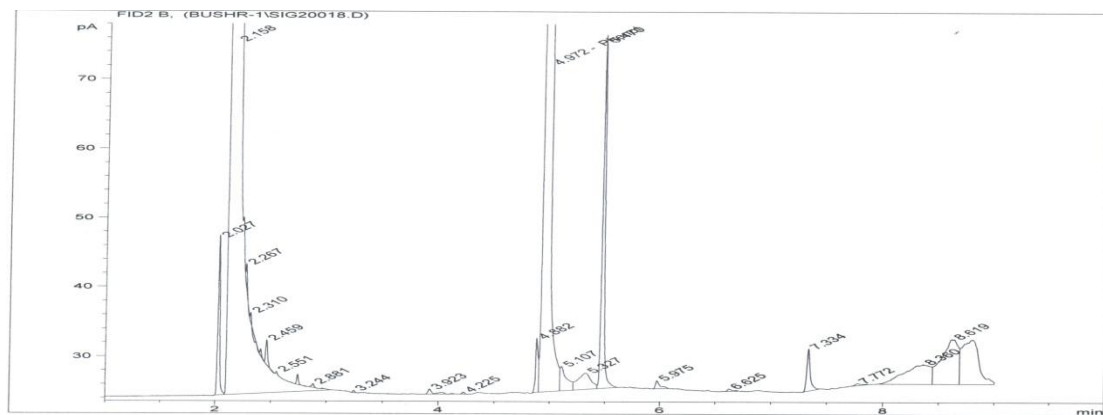


FIGURE A92: GC Chromatogram of Samples Treated for 60 Minutes, in NaHCO_3 and MgCl_2 Investigation

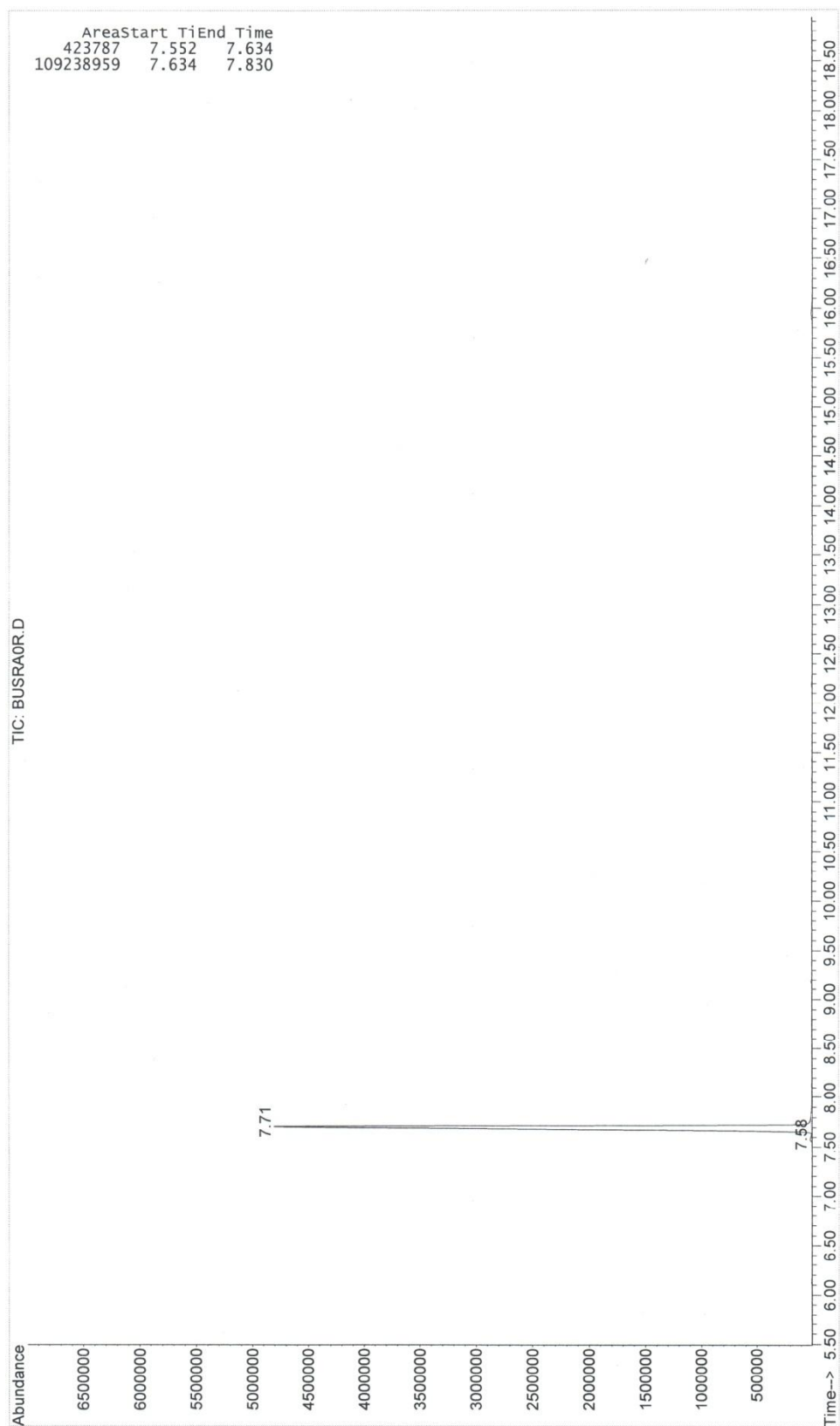


FIGURE A93: GC-MS Chromatogram of Sample before Treatment for CaSO_4 and MgCl_2 Investigation

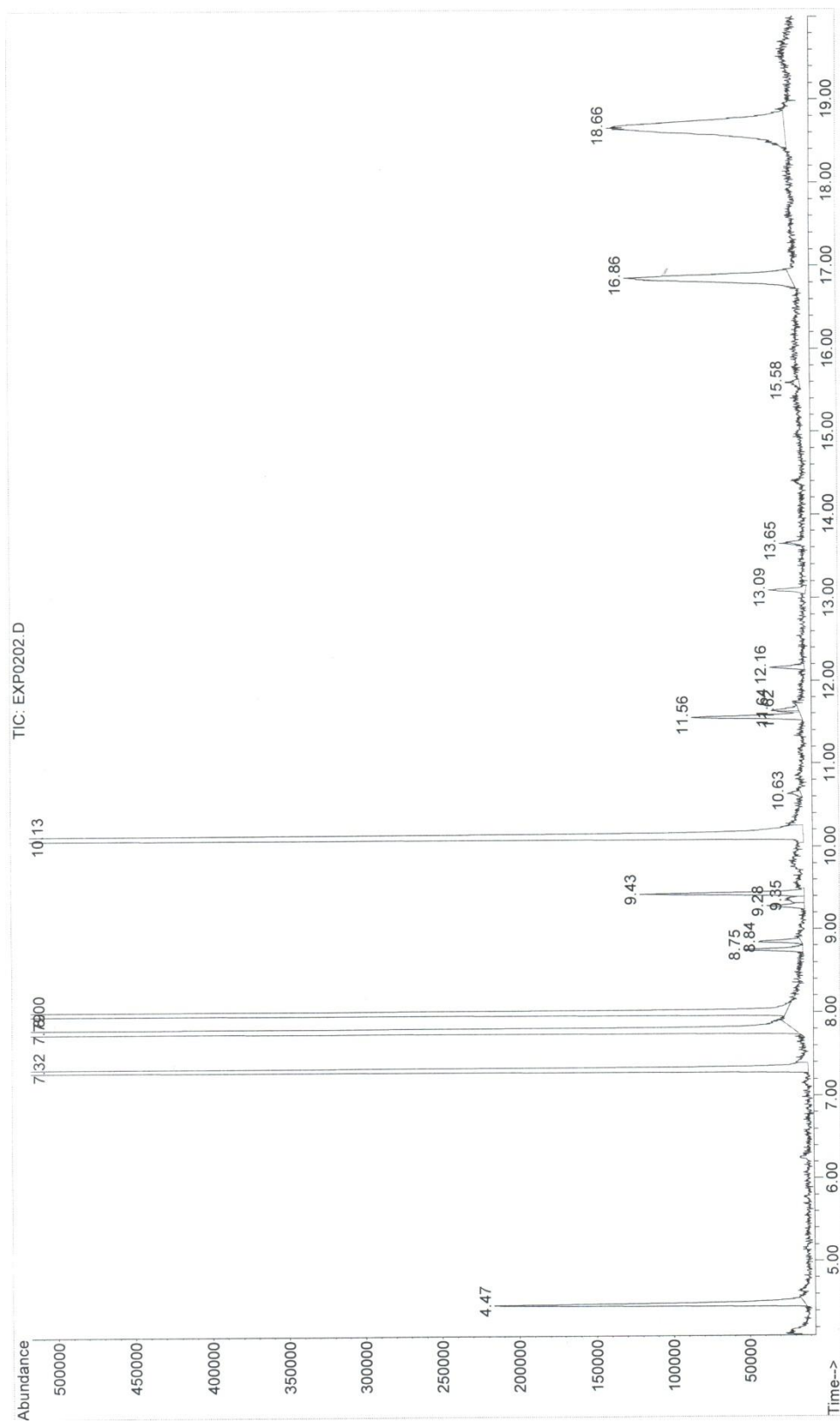


FIGURE A94: GC-MS Chromatogram of Samples Treated for 2 Minutes, in CaSO_4 and MgCl_2 Investigation

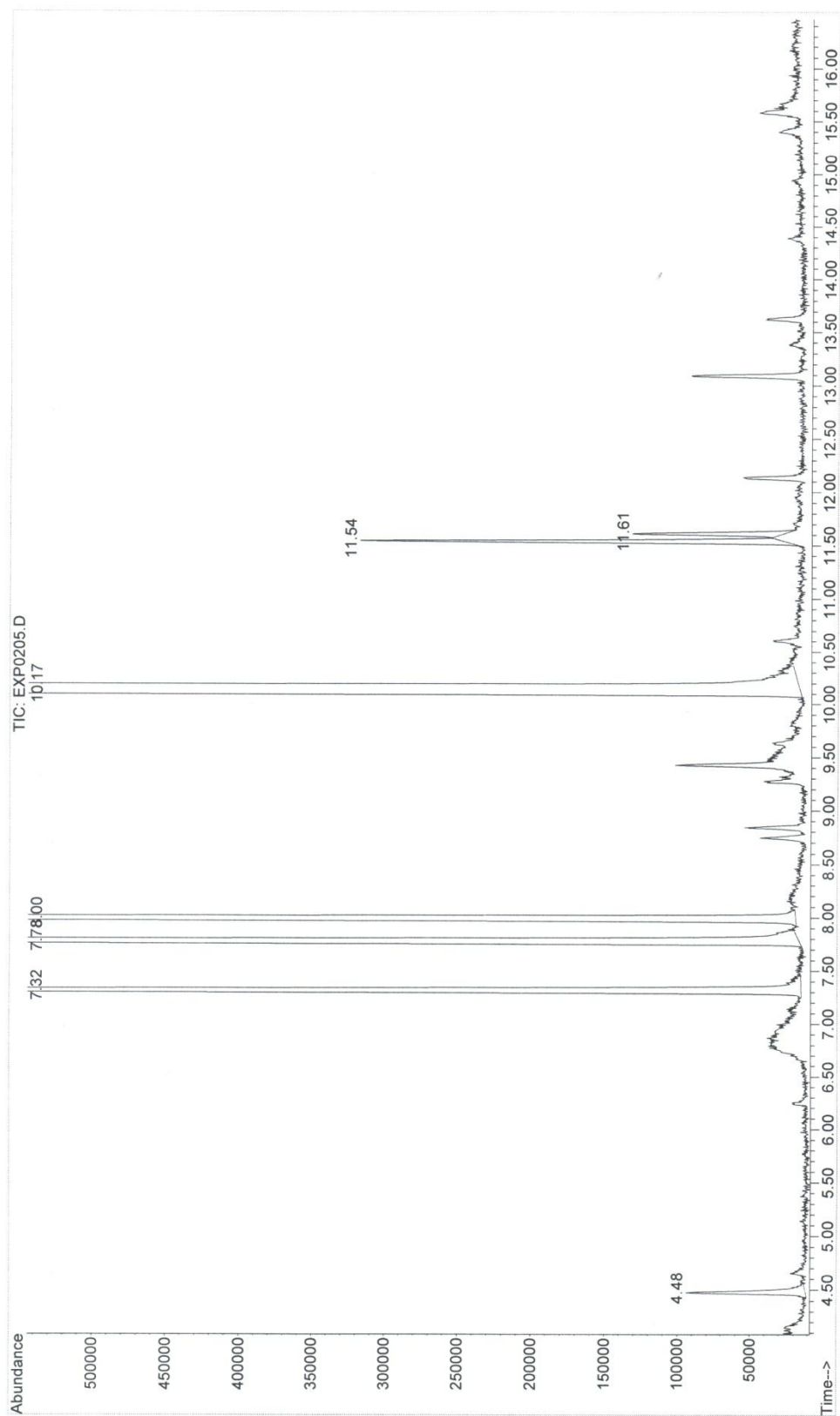


FIGURE A95: GC-MS Chromatogram of Samples Treated for 5 Minutes, in CaSO₄ and MgCl₂ Investigation

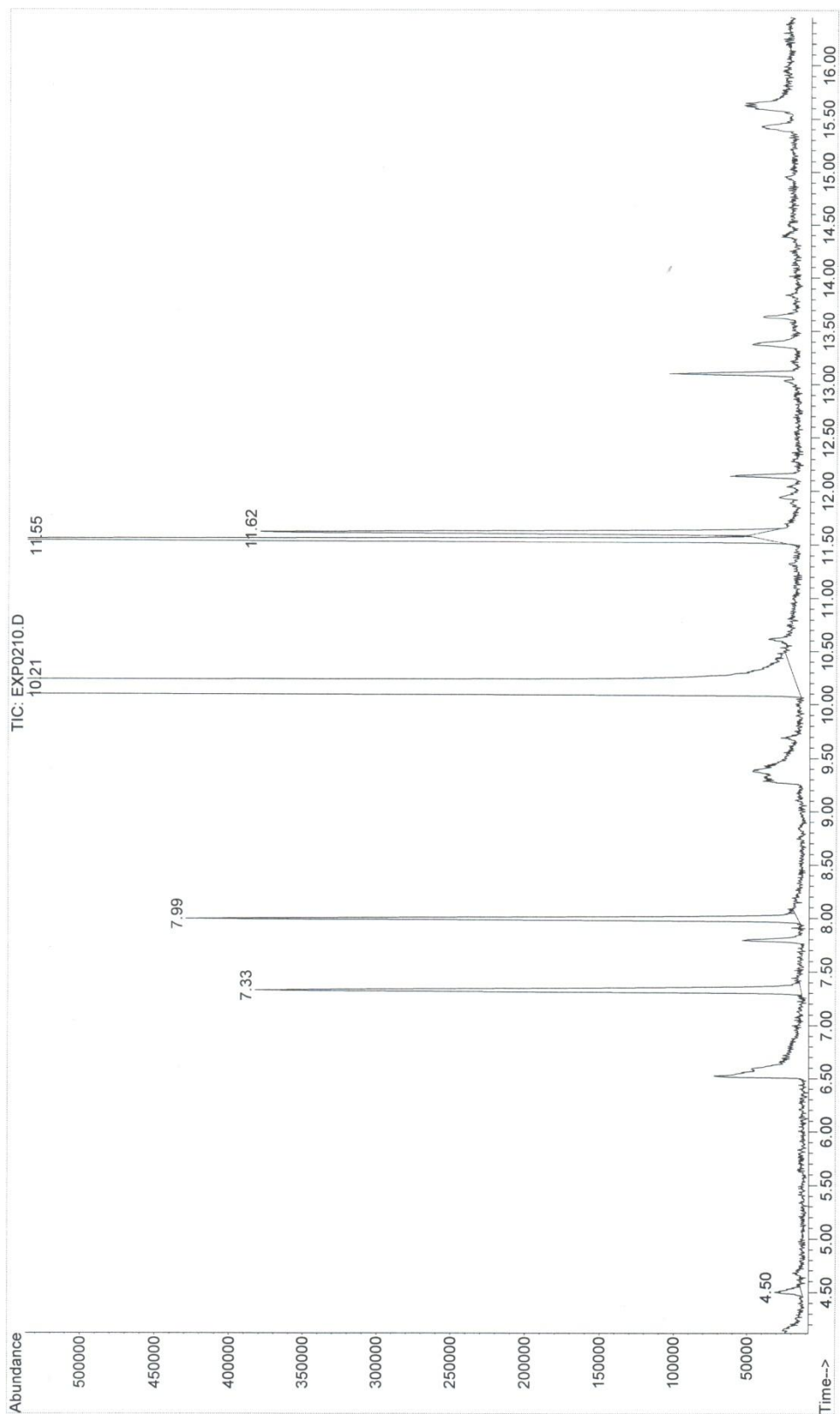


FIGURE A96: GC-MS Chromatogram of Samples Treated for 10 Minutes, in CaSO_4 and MgCl_2 Investigation

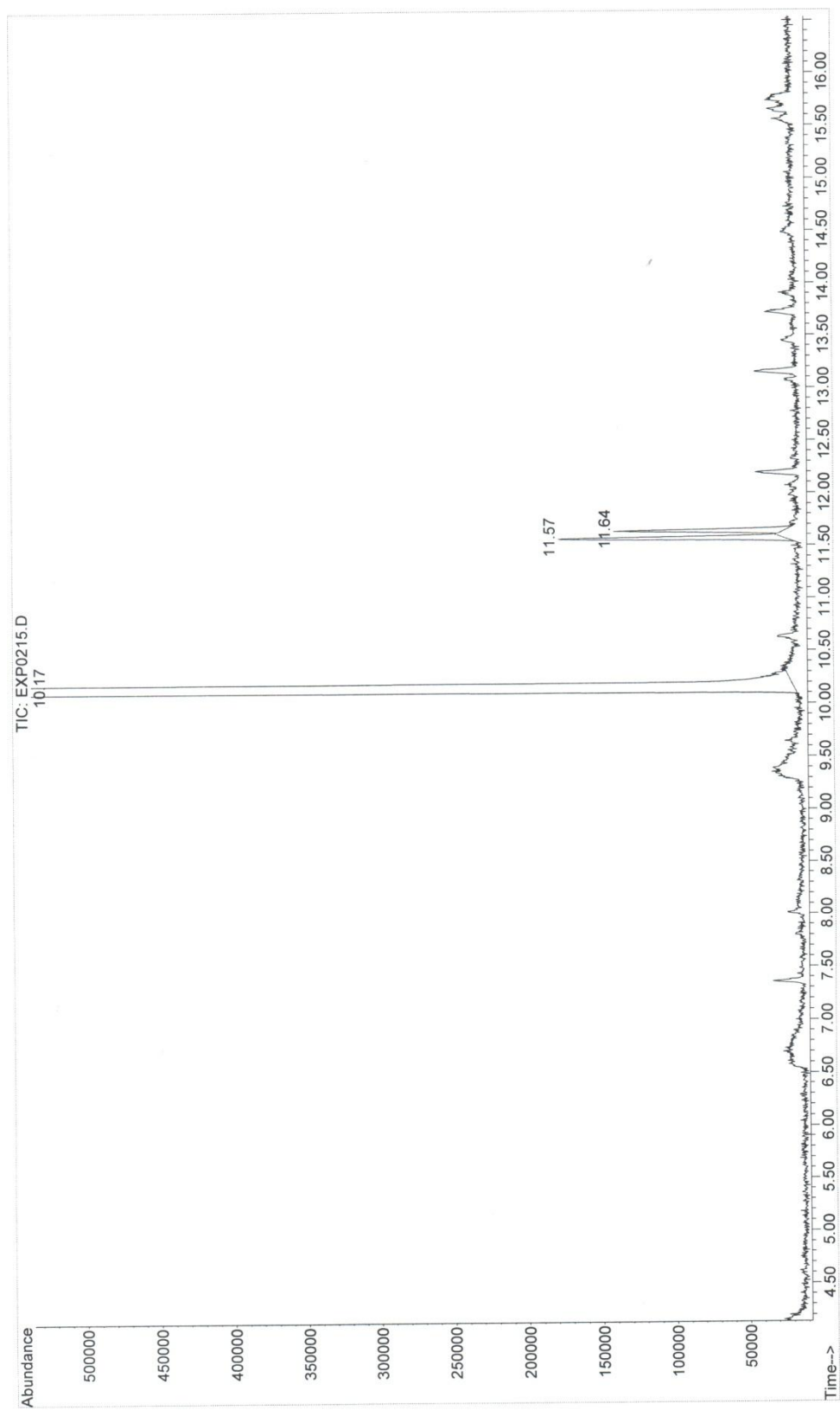


FIGURE A97: GC-MS Chromatogram of Samples Treated for 15 Minutes, in CaSO_4 and MgCl_2 Investigation

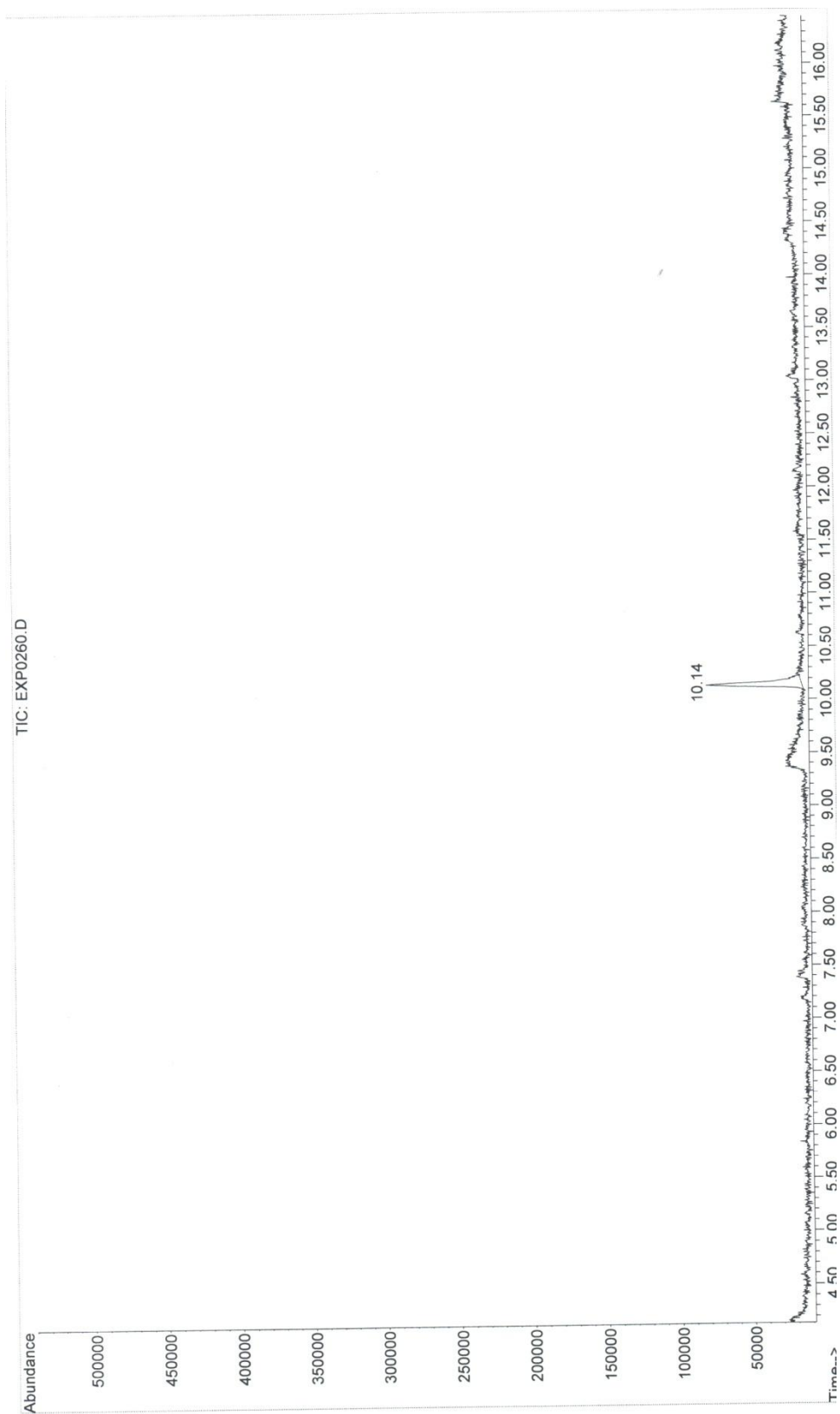


FIGURE A98: GC-MS Chromatogram of Samples Treated for 60 Minutes, in CaSO_4 and MgCl_2 Investigation

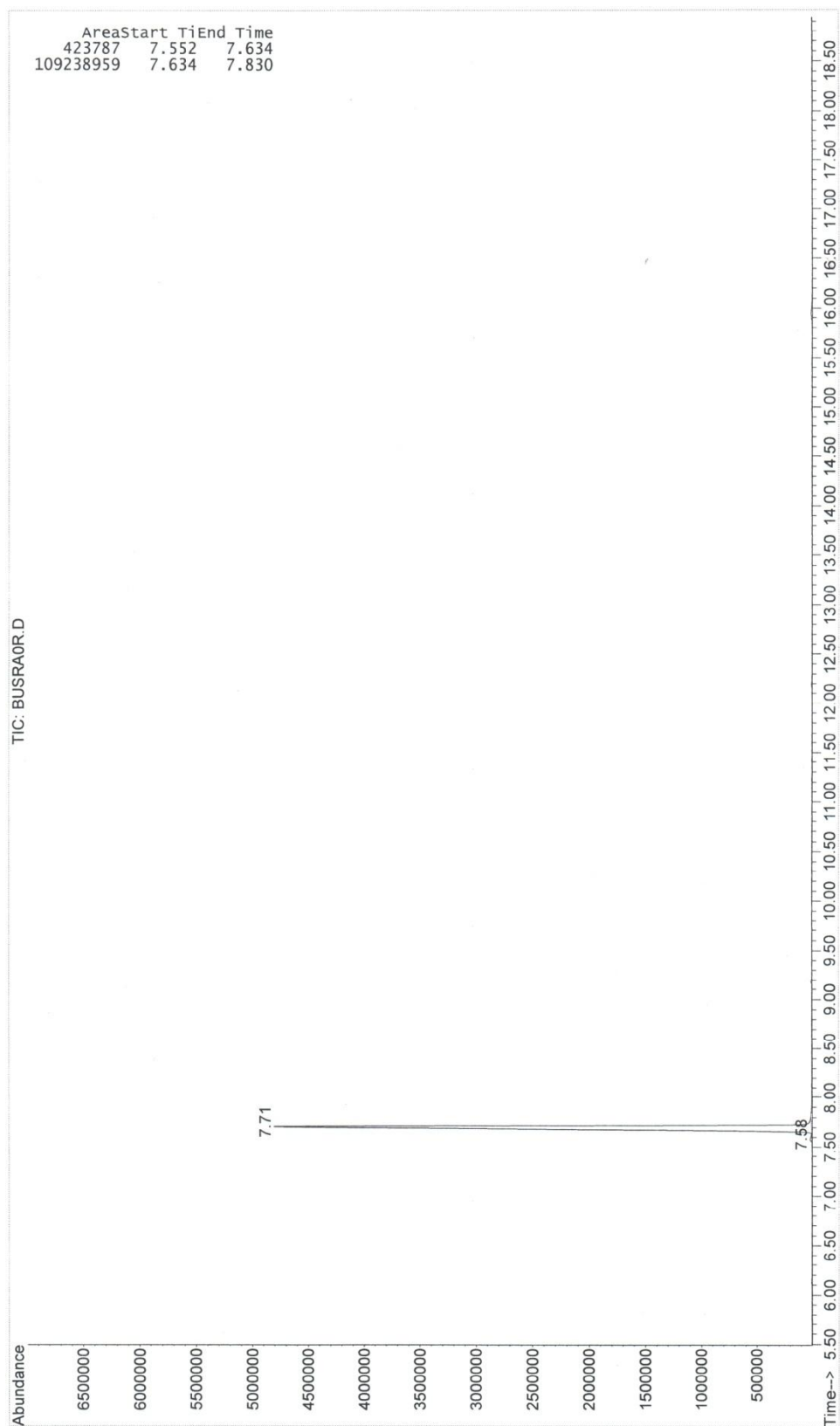


FIGURE A99: GC-MS Chromatogram of Sample before Treatment for MgSO_4 and MgCl_2 Investigation

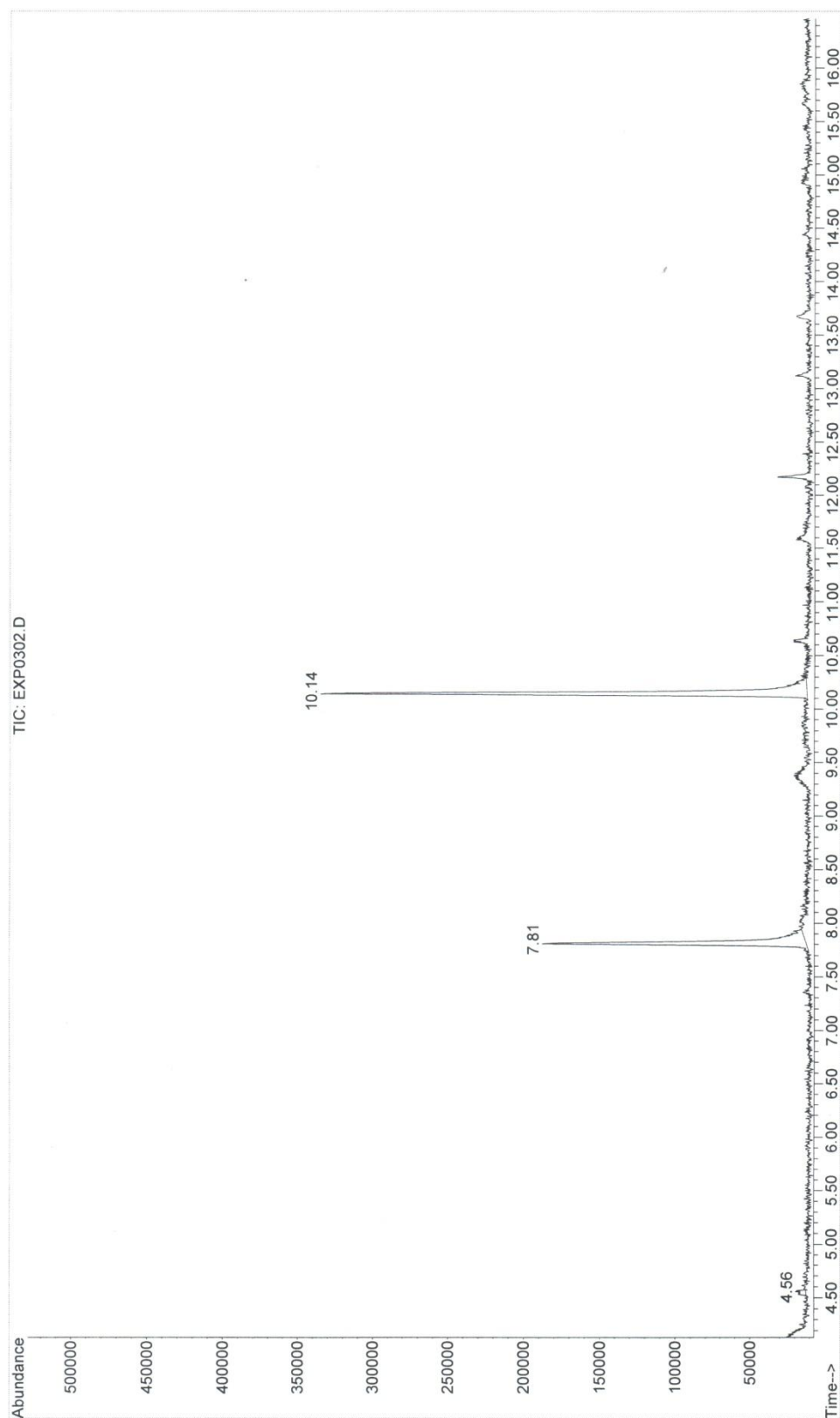


FIGURE A100: GC-MS Chromatogram of Samples Treated for 2 Minutes, in MgSO_4 and MgCl_2 Investigation

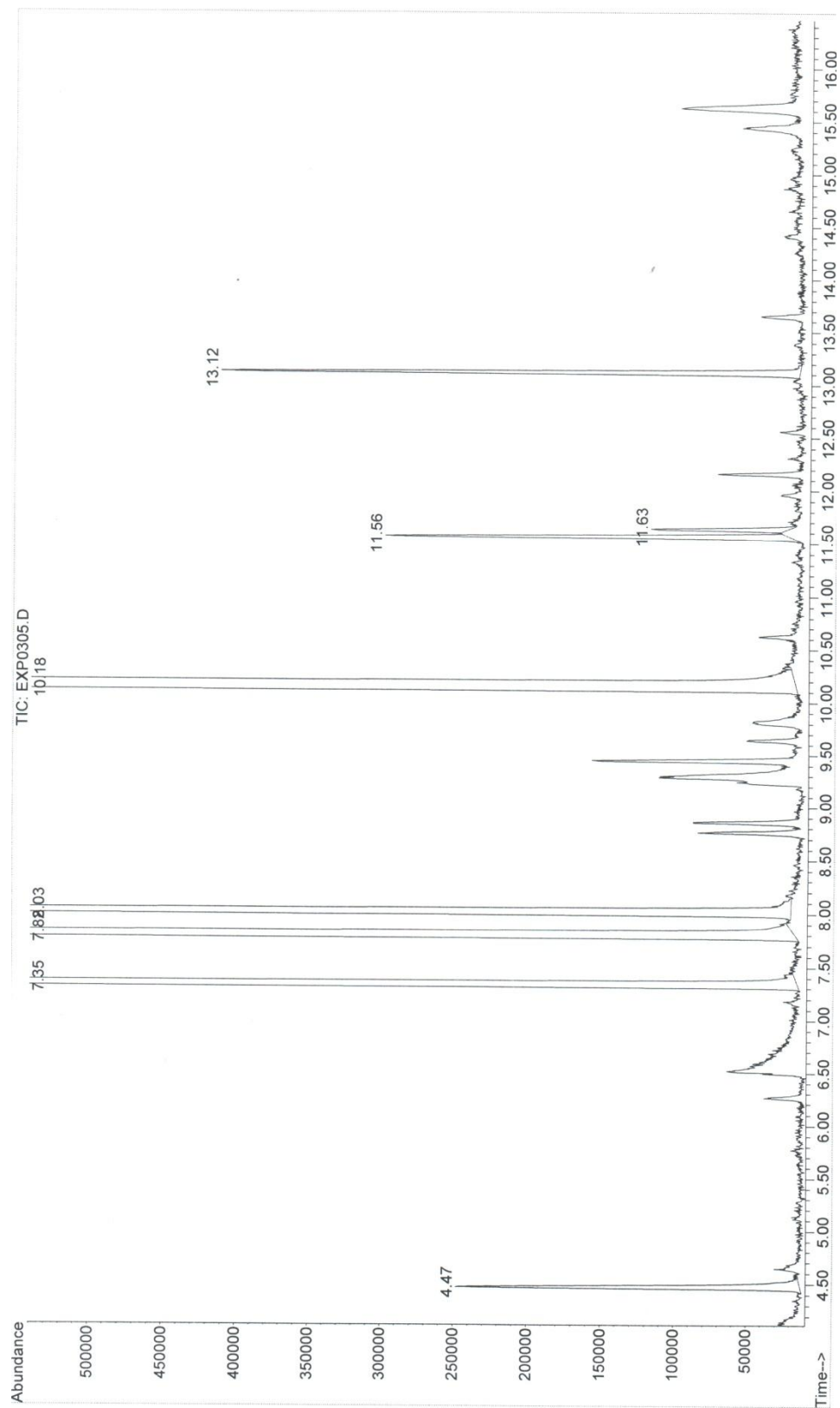


FIGURE A101: GC-MS Chromatogram of Samples Treated for 5 Minutes, in MgSO_4 and MgCl_2 Investigation

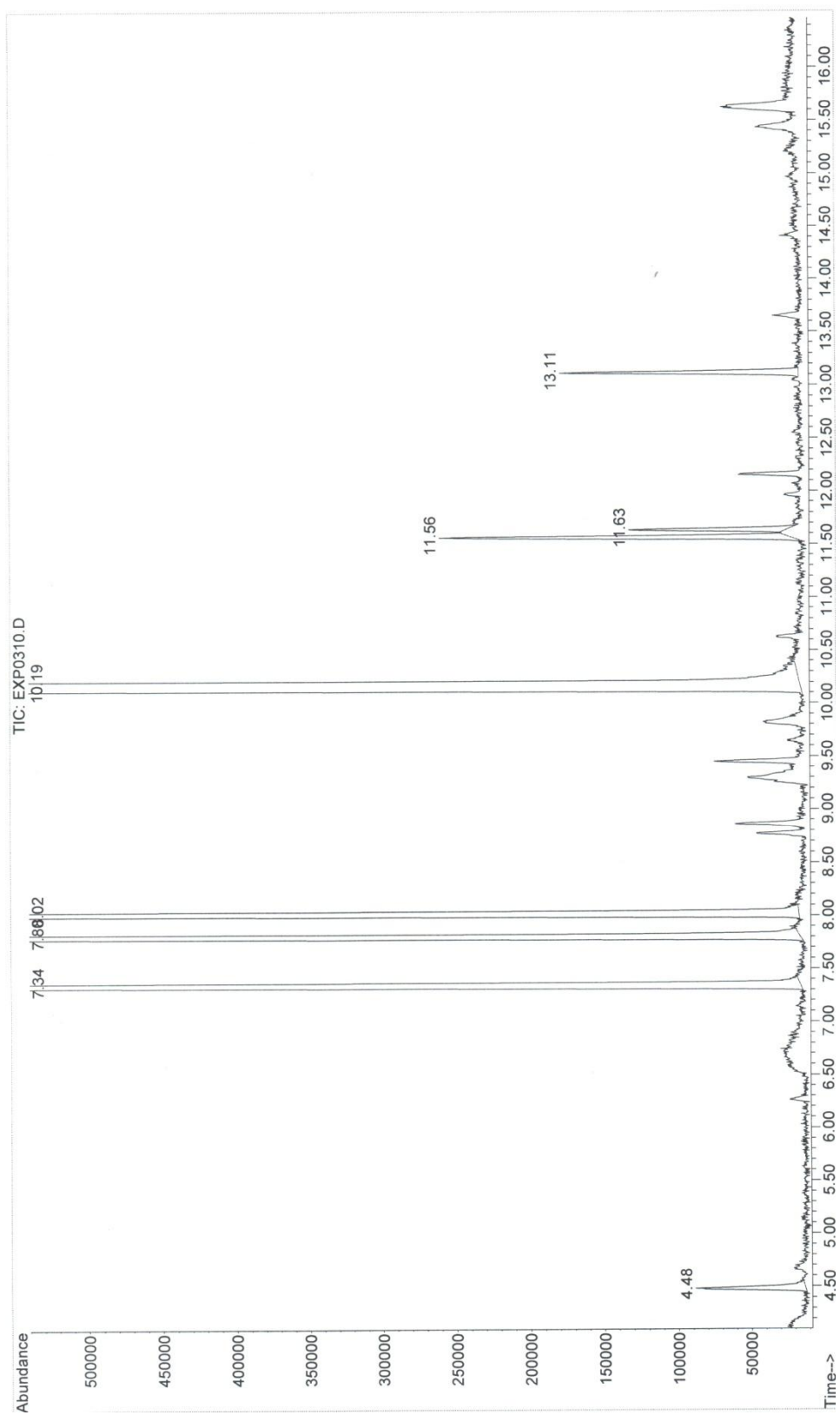


FIGURE A102: GC-MS Chromatogram of Samples Treated for 10 Minutes, in MgSO_4 and MgCl_2 Investigation

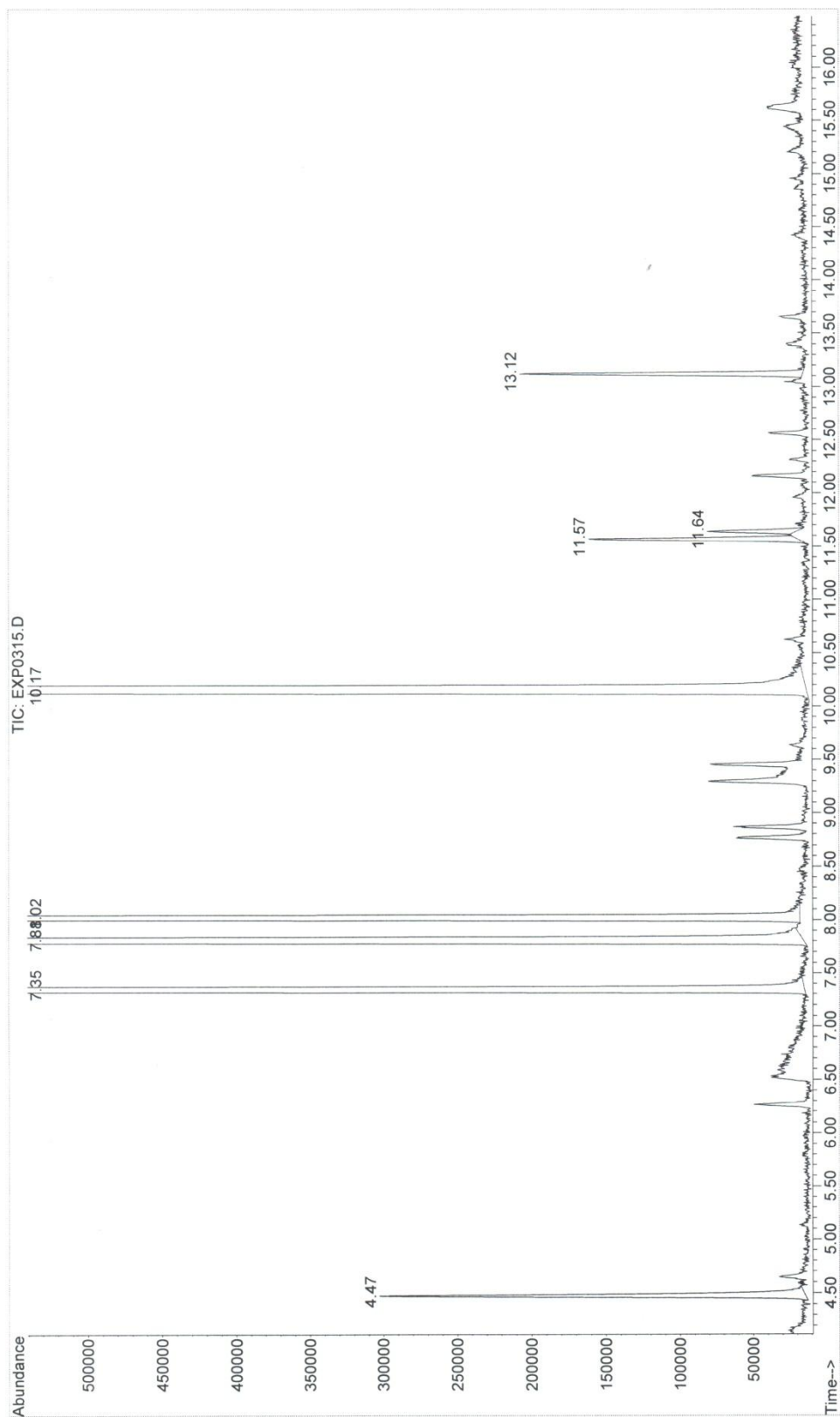


FIGURE A103: GC-MS Chromatogram of Samples Treated for 15 Minutes, in MgSO_4 and MgCl_2 Investigation

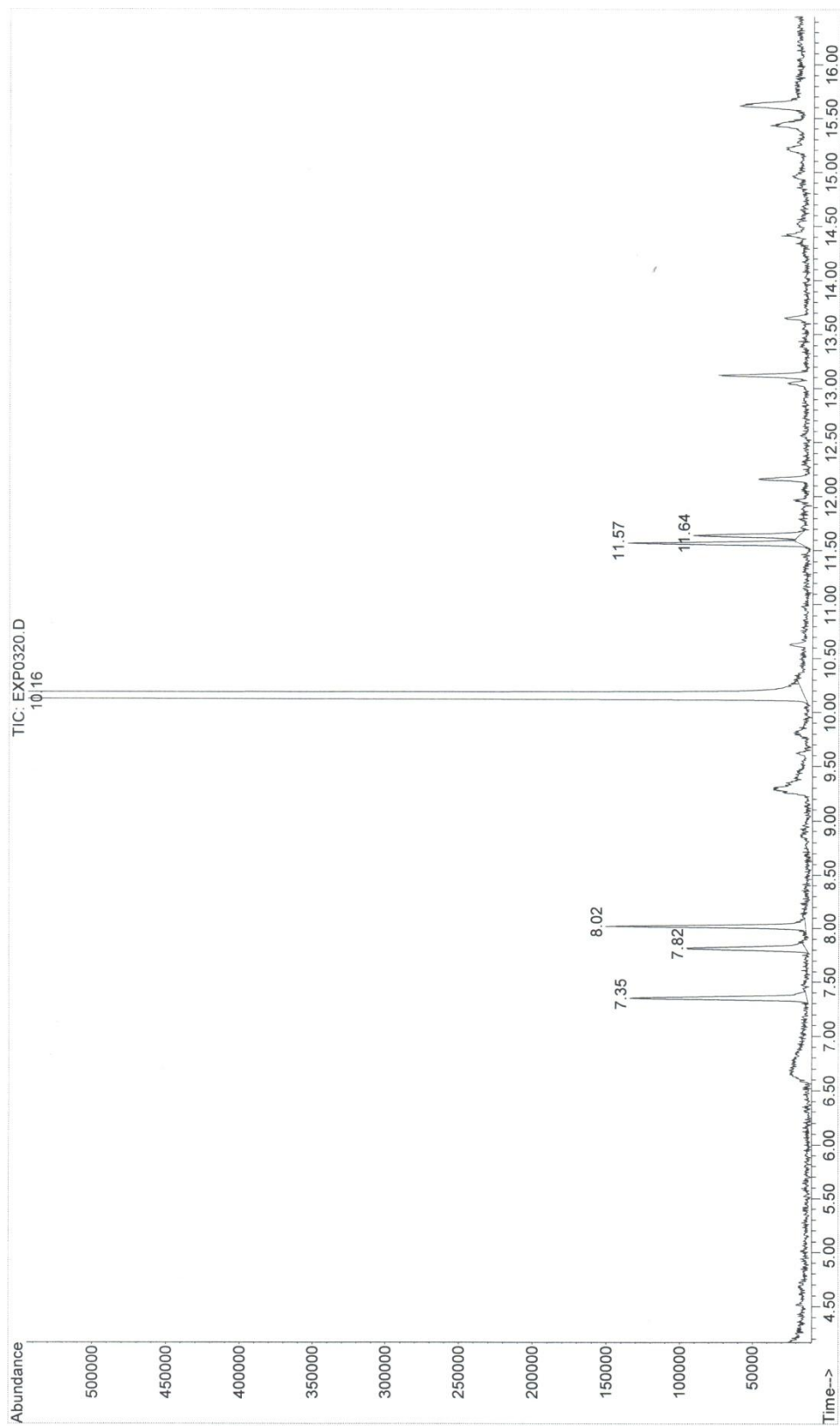


FIGURE A104: GC-MS Chromatogram of Samples Treated for 20 Minutes, in MgSO_4 and MgCl_2 Investigation

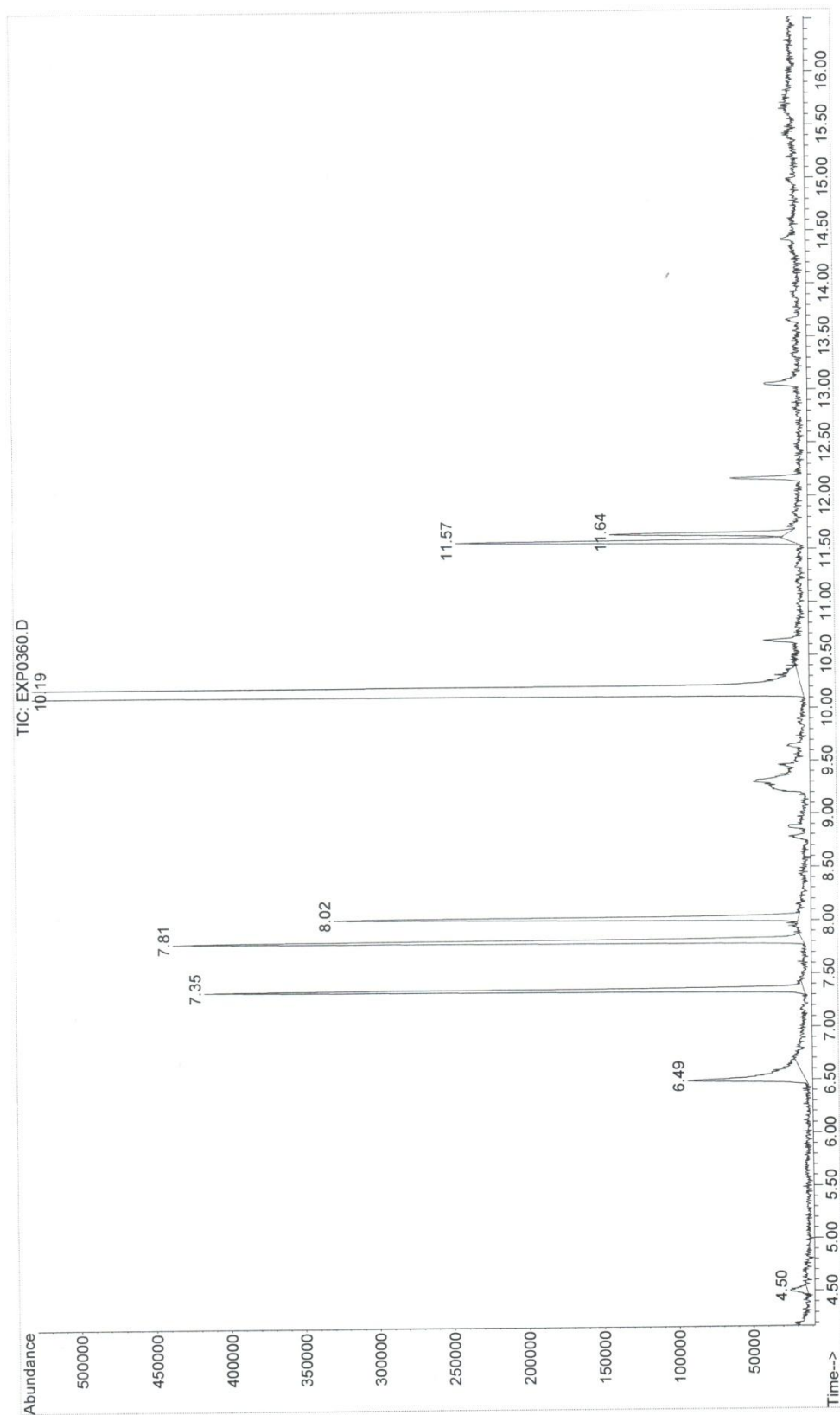


FIGURE A105: GC-MS Chromatogram of Samples Treated for 60 Minutes, in MgSO_4 and MgCl_2 Investigation

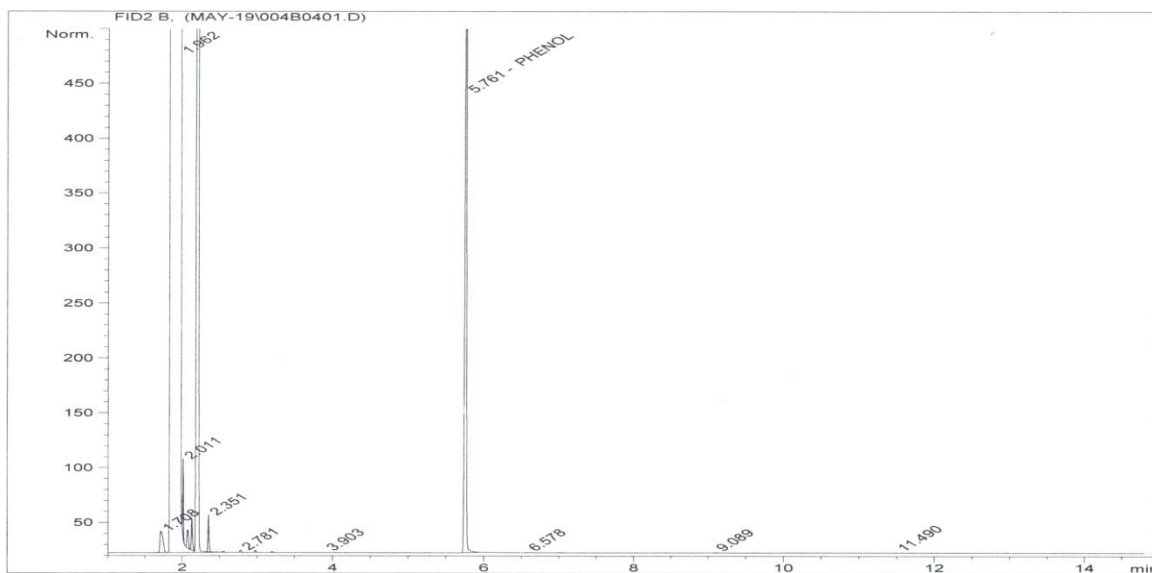


FIGURE A106: GC Chromatogram of Sample before Treatment for NaHCO_3 , CaSO_4 , and MgSO_4 Investigation

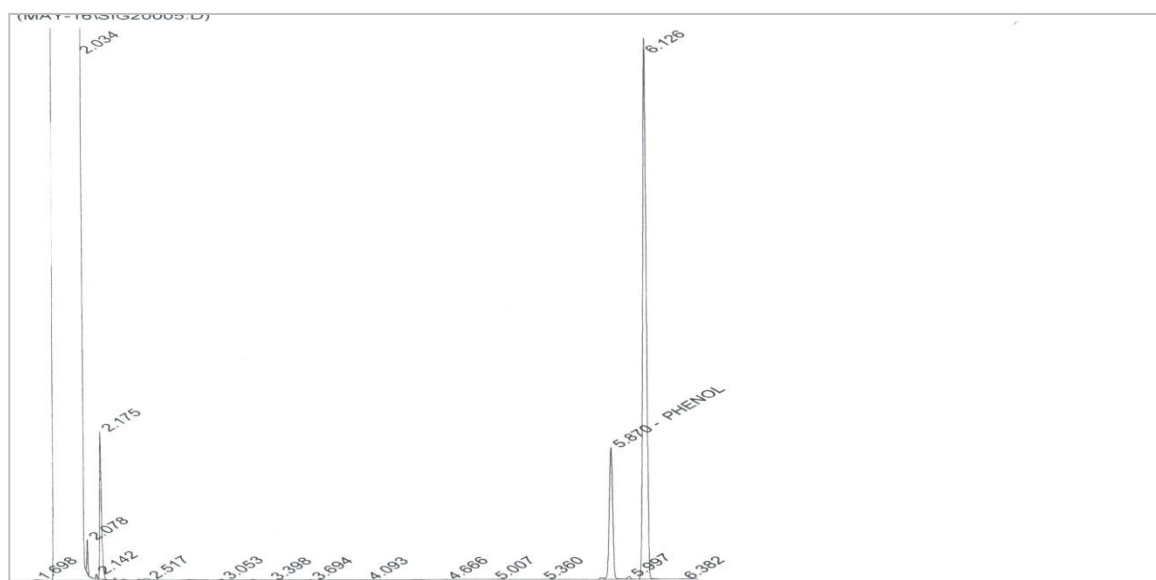


FIGURE A107: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 , CaSO_4 , and MgSO_4 investigation

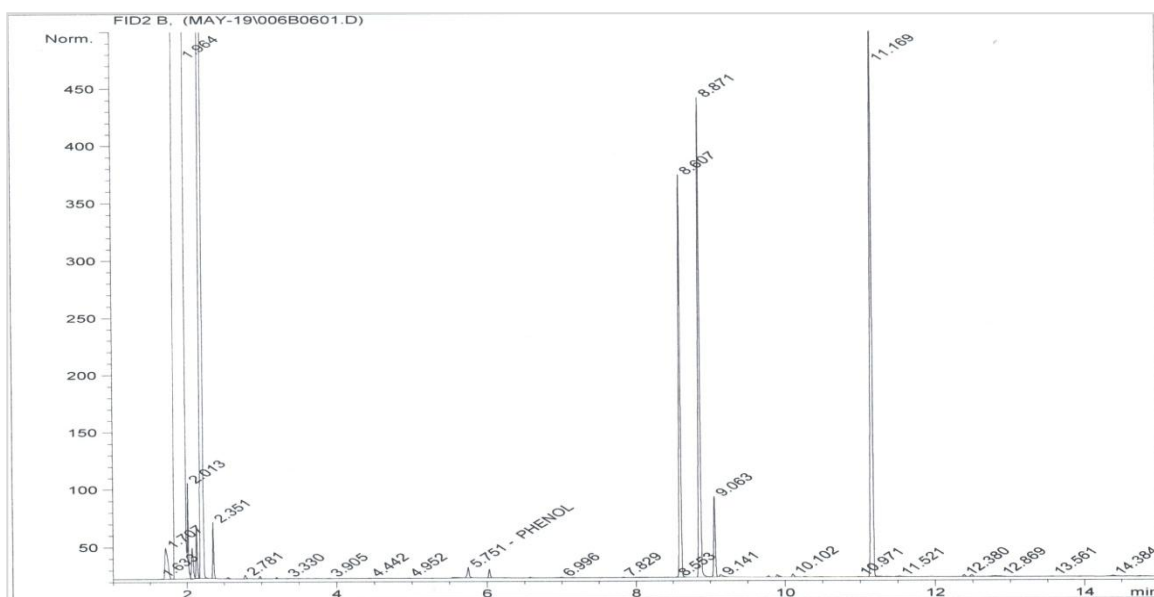


FIGURE A108: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 , CaSO_4 , and MgSO_4 investigation

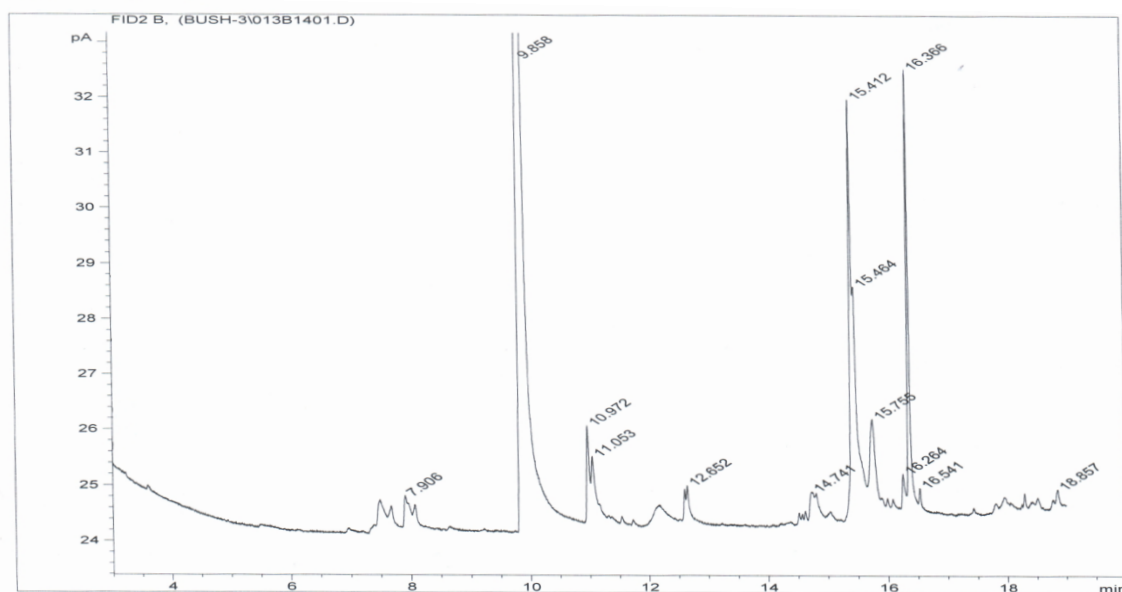


FIGURE A109: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 , CaSO_4 , and MgSO_4 investigation

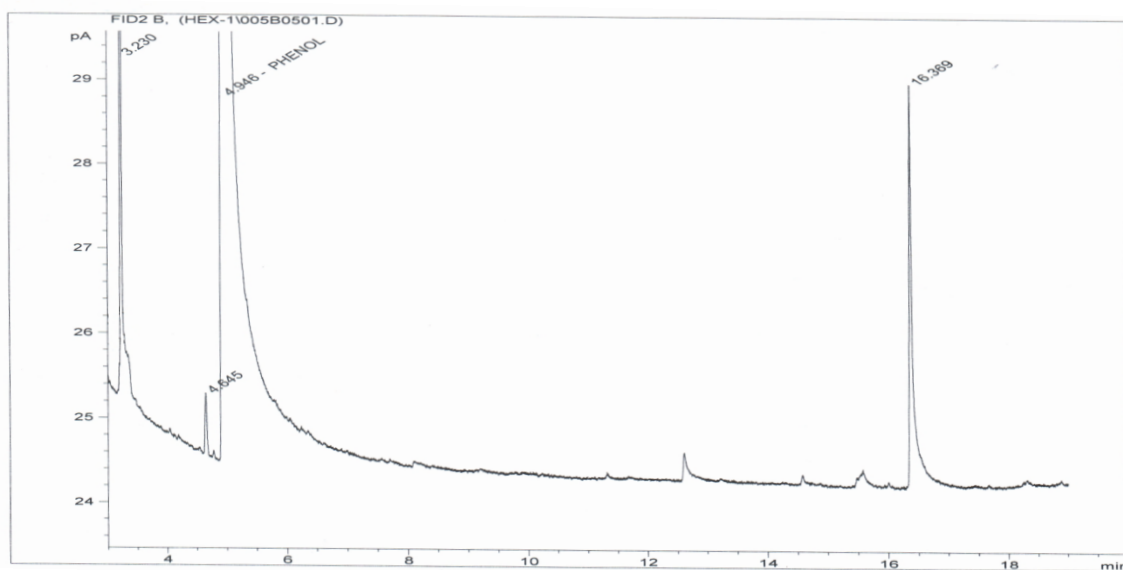


FIGURE A110: GC Chromatogram of Sample before Treatment for NaHCO_3 , CaSO_4 , and MgCl_2 Investigation

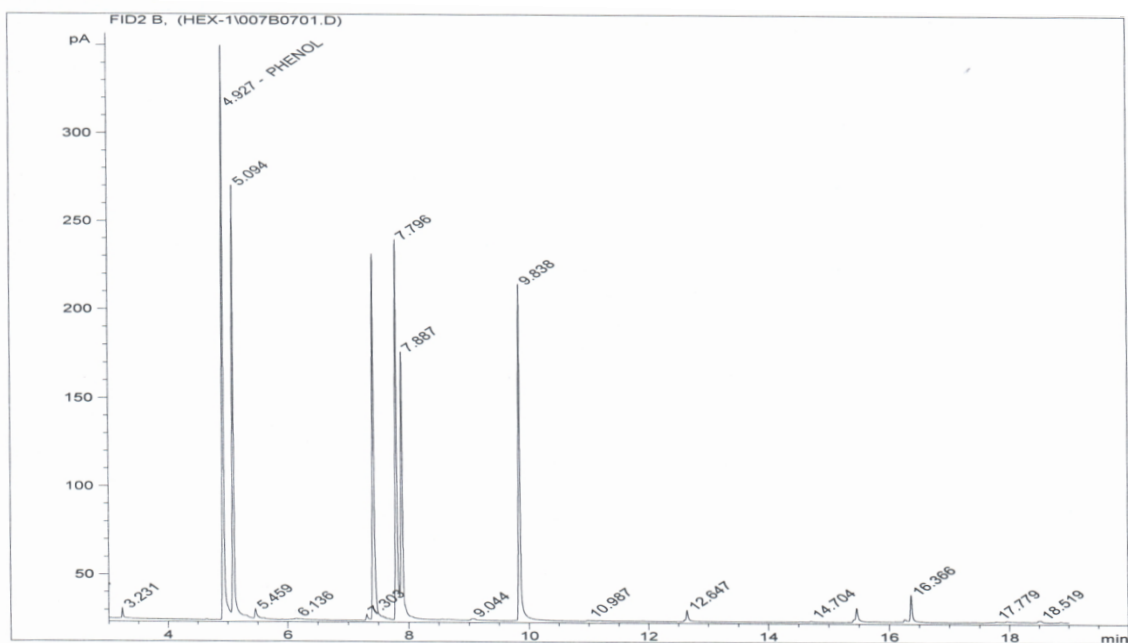


FIGURE A111: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 , CaSO_4 , and MgCl_2 Investigation

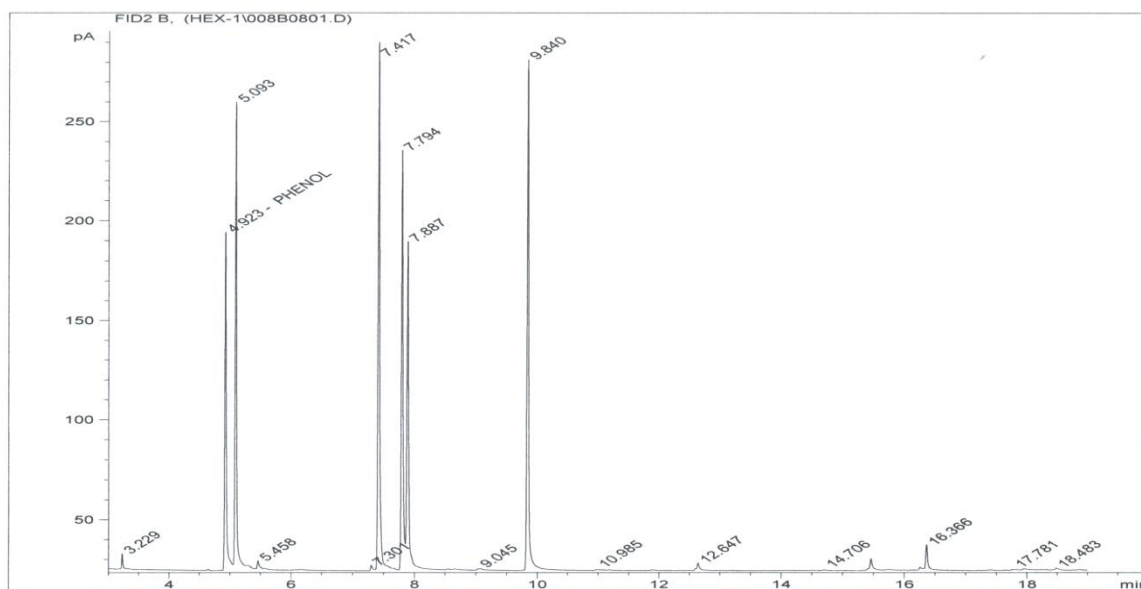


FIGURE A112: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 , CaSO_4 , and MgCl_2 Investigation

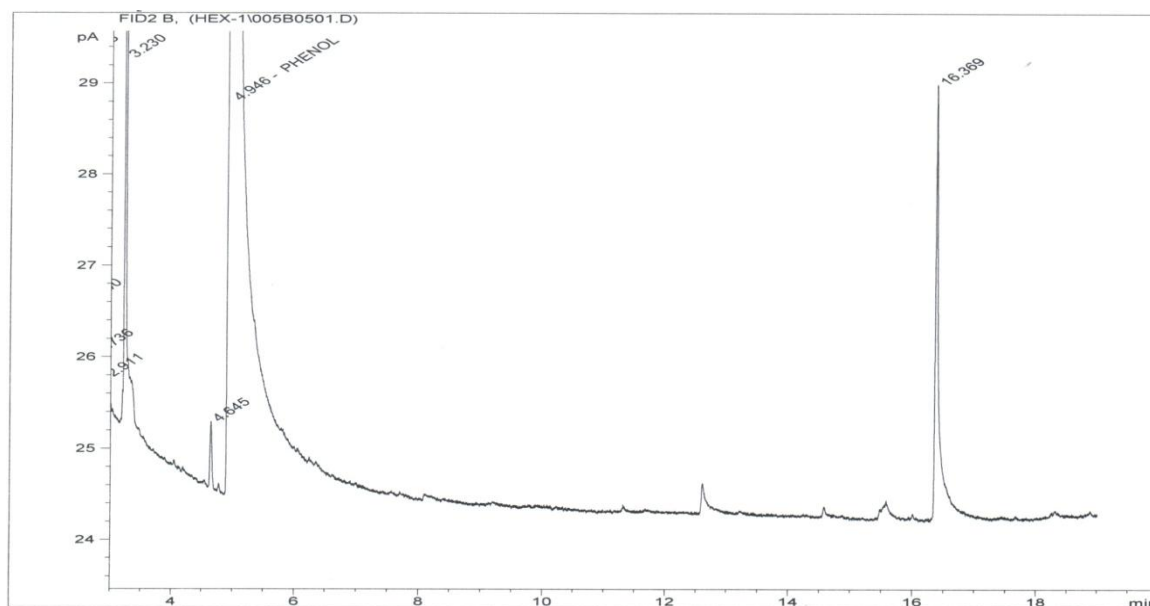


FIGURE A113: GC Chromatogram of Sample before Treatment for NaHCO_3 , MgSO_4 , and MgCl_2 Investigation

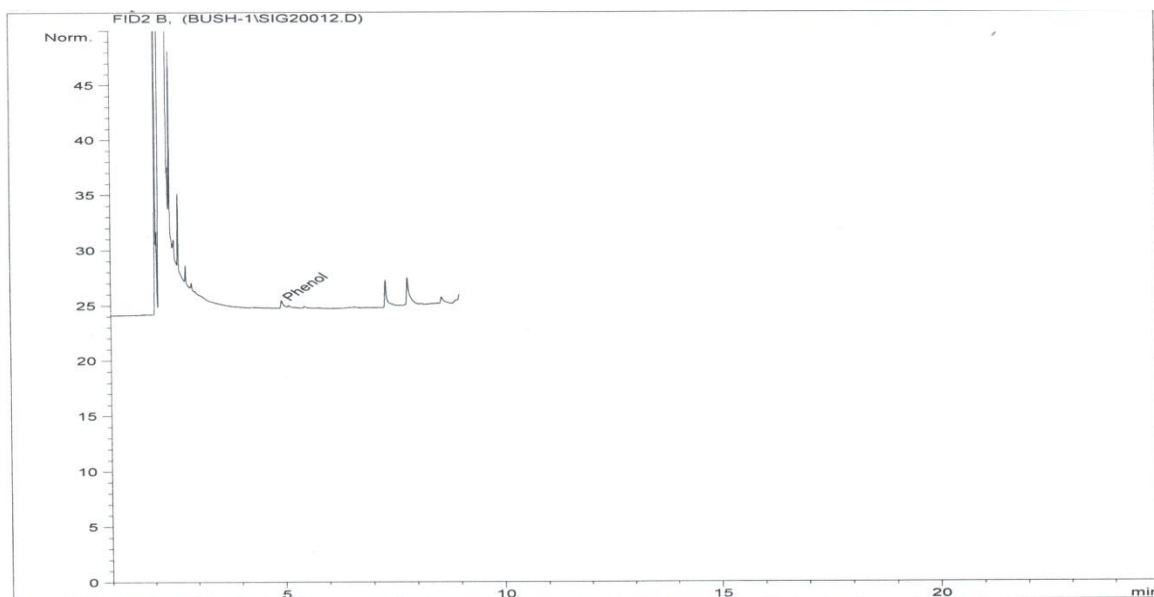


FIGURE A114: GC Chromatogram of Samples Treated for 2 Minutes, in NaHCO_3 , MgSO_4 , and MgCl_2 Investigation

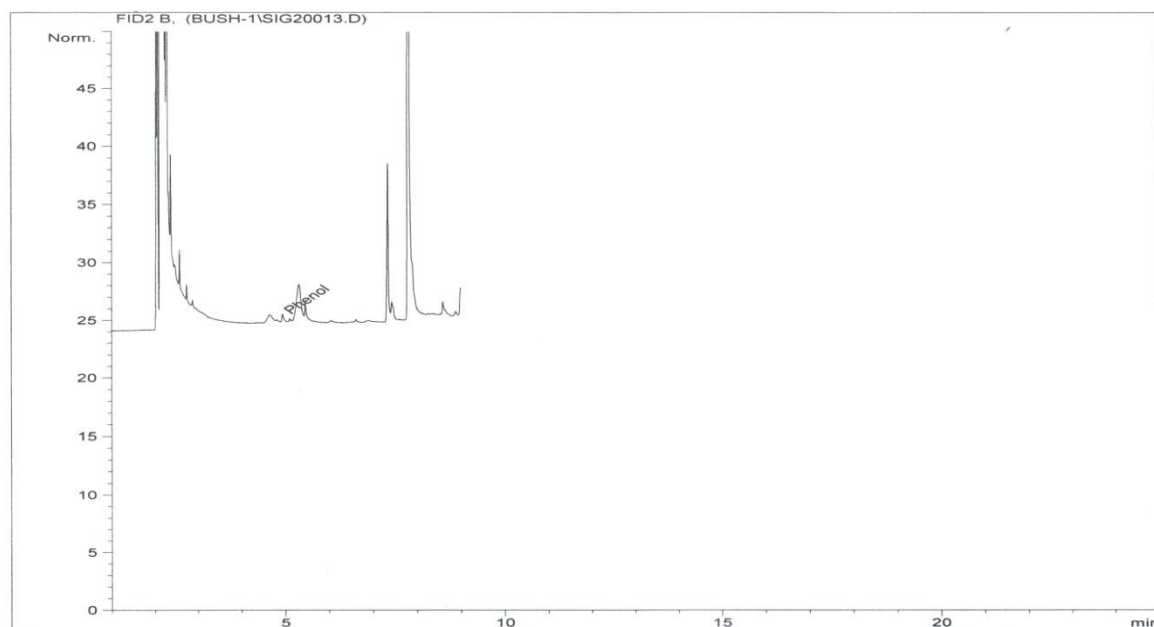


FIGURE A115: GC Chromatogram of Samples Treated for 5 Minutes, in NaHCO_3 , MgSO_4 , and MgCl_2 Investigation

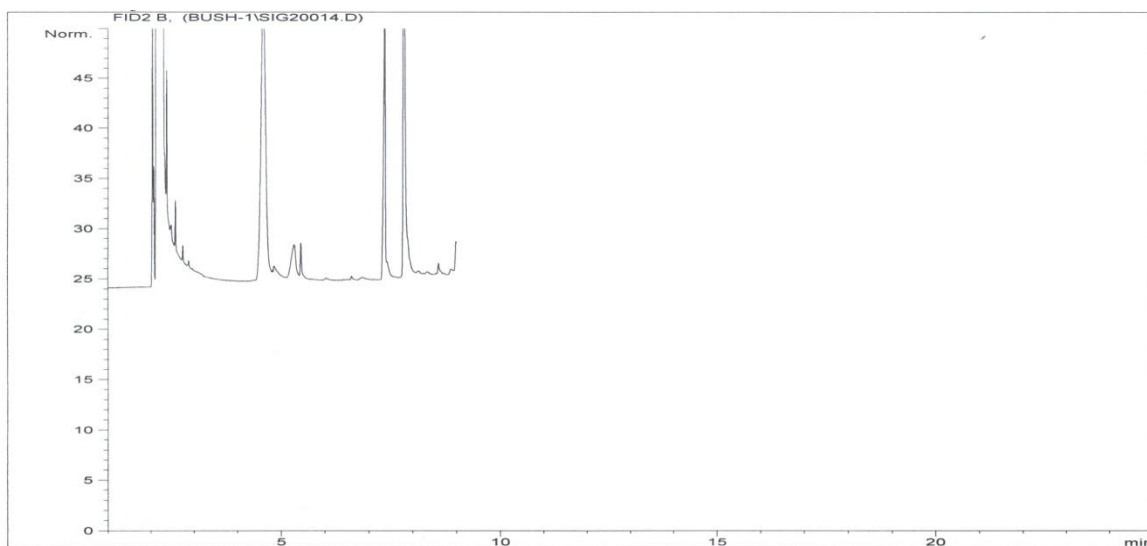


FIGURE A116: GC Chromatogram of Samples Treated for 10 Minutes, in NaHCO_3 , MgSO_4 , and MgCl_2 Investigation

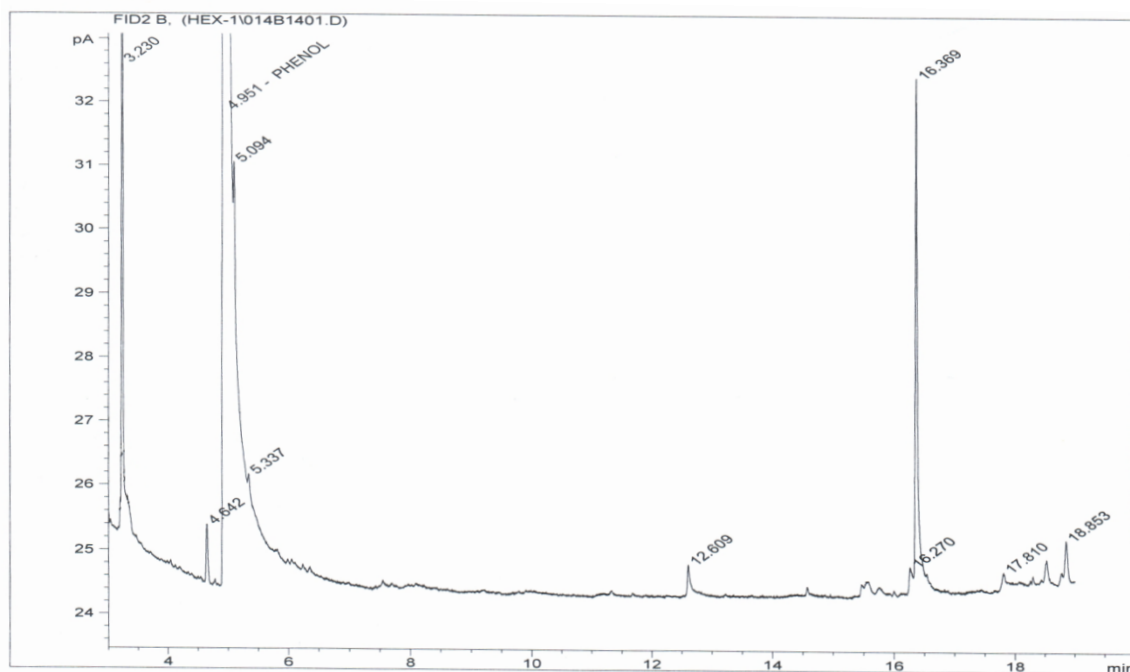


FIGURE A117: GC Chromatogram of Sample before Treatment for CaSO_4 , MgSO_4 , and MgCl_2 Investigation

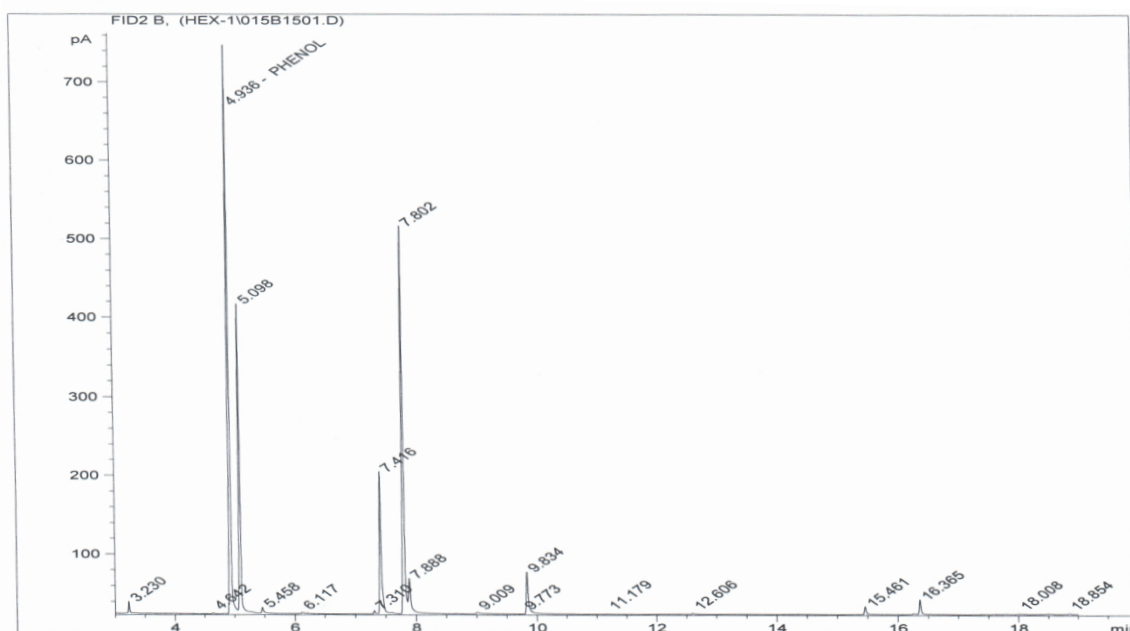


FIGURE A118: GC Chromatogram of Samples Treated for 2 Minutes, in CaSO_4 , MgSO_4 , and MgCl_2 Investigation

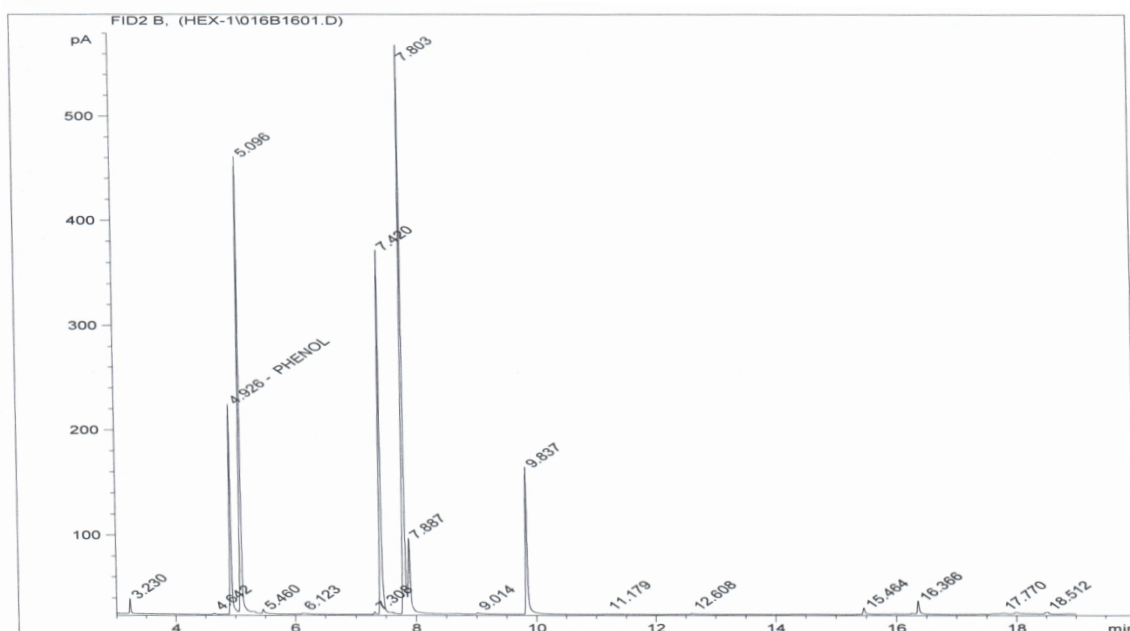


FIGURE A119: GC Chromatogram of Samples Treated for 5 Minutes, in CaSO_4 , MgSO_4 , and MgCl_2 Investigation

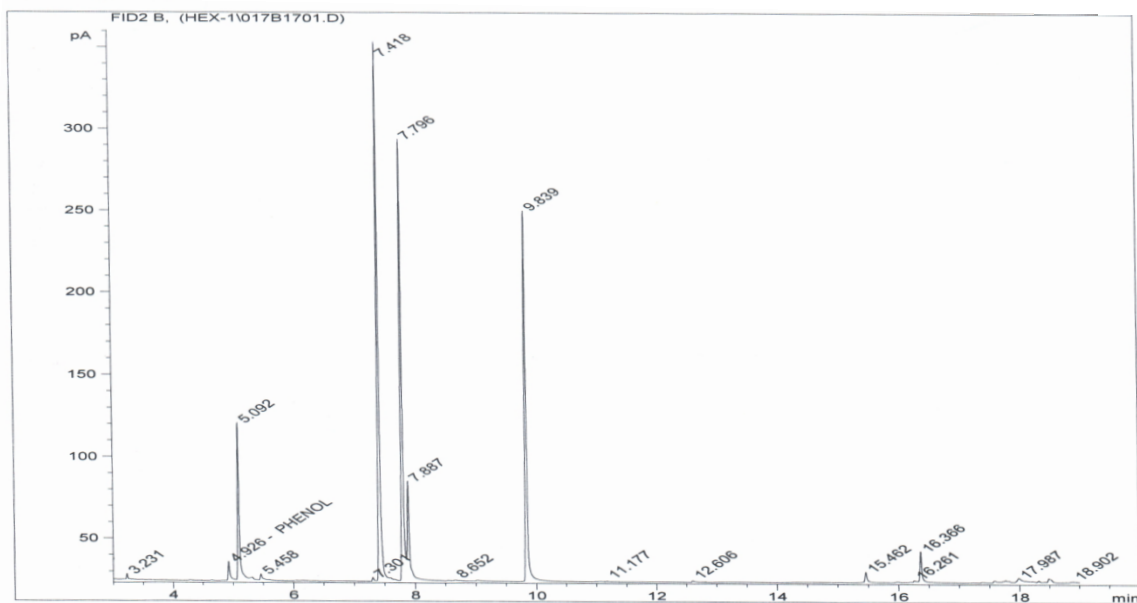


FIGURE A120: GC Chromatogram of Samples Treated for 10 Minutes, in CaSO_4 , MgSO_4 , and MgCl_2 Investigation

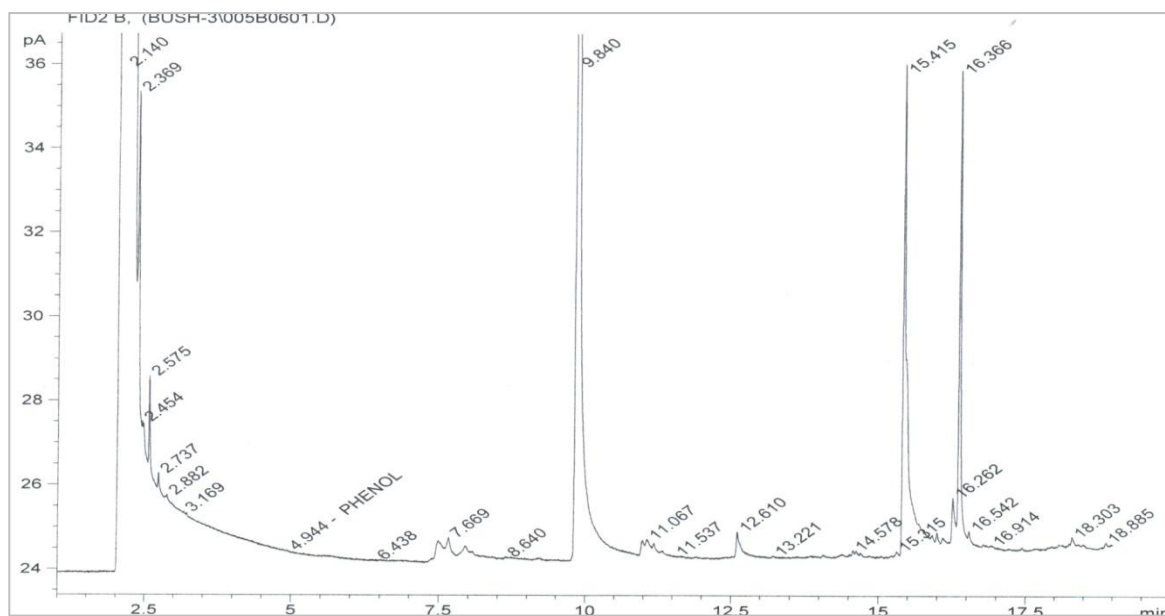


FIGURE A121: GC Chromatogram of Samples Treated for 15 Minutes, in CaSO_4 , MgSO_4 , and MgCl_2 Investigation

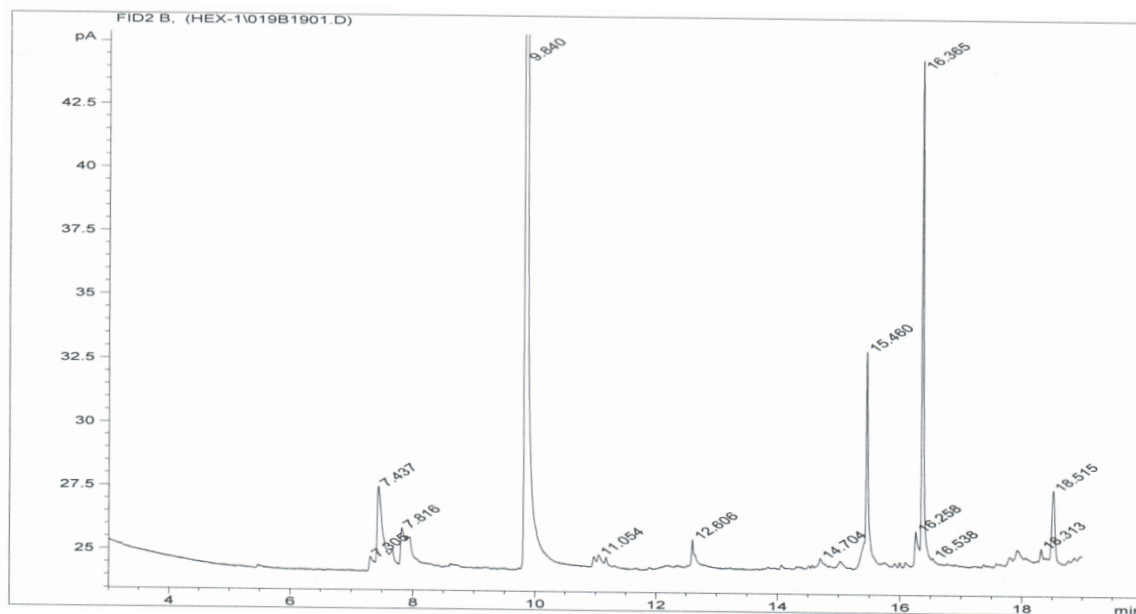


FIGURE A122: GC Chromatogram of Samples Treated for 20 Minutes, in CaSO_4 , MgSO_4 , and MgCl_2 Investigation

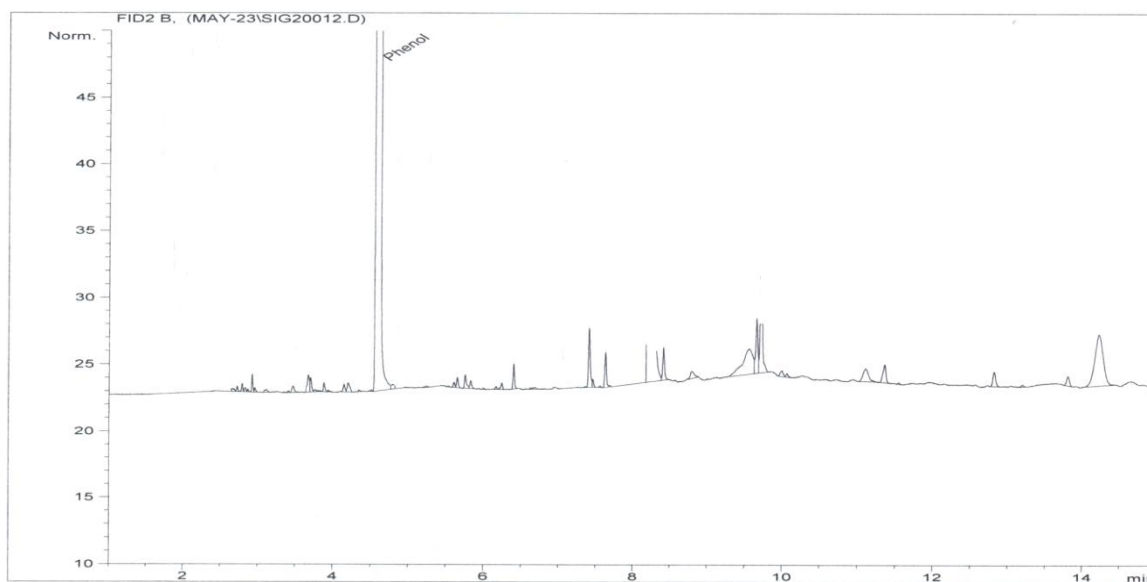


FIGURE A123: GC Chromatogram of Sample before Treatment, for Collective Chemical Species Investigation

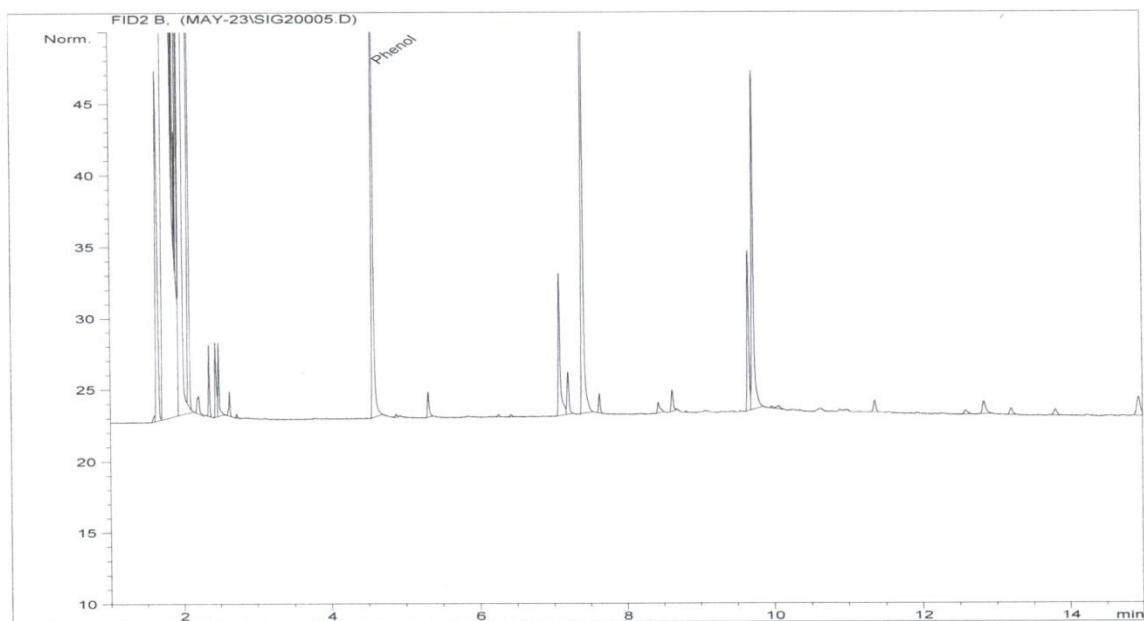


FIGURE A124: GC Chromatogram of Samples Treated for 2 Minutes, in Collective Chemical Species Investigation

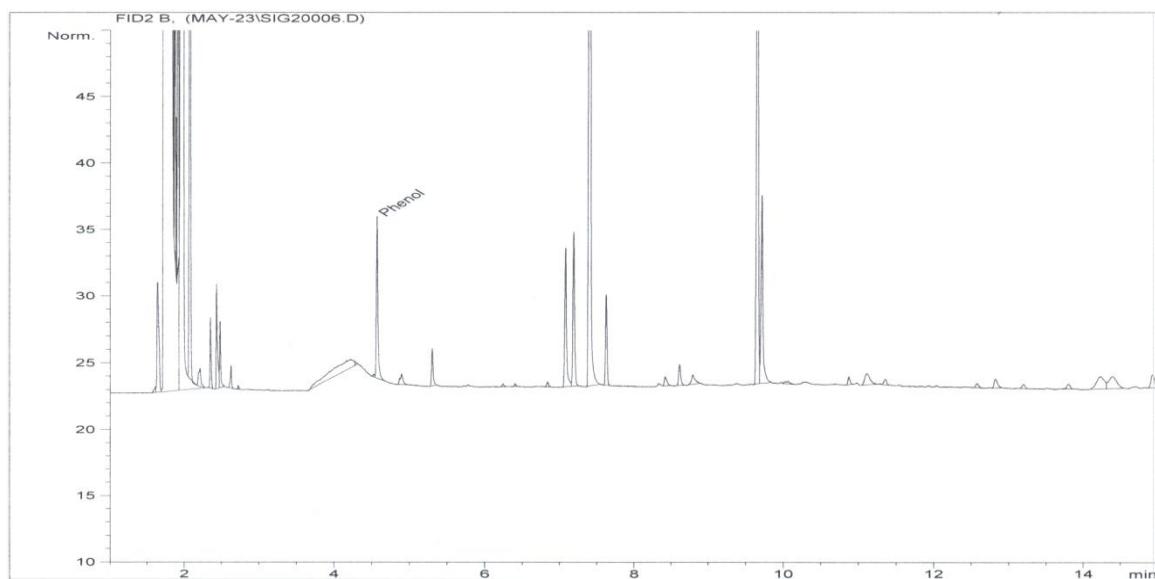


FIGURE A125: GC Chromatogram of Samples Treated for 5 Minutes, in Collective Chemical Species Investigation

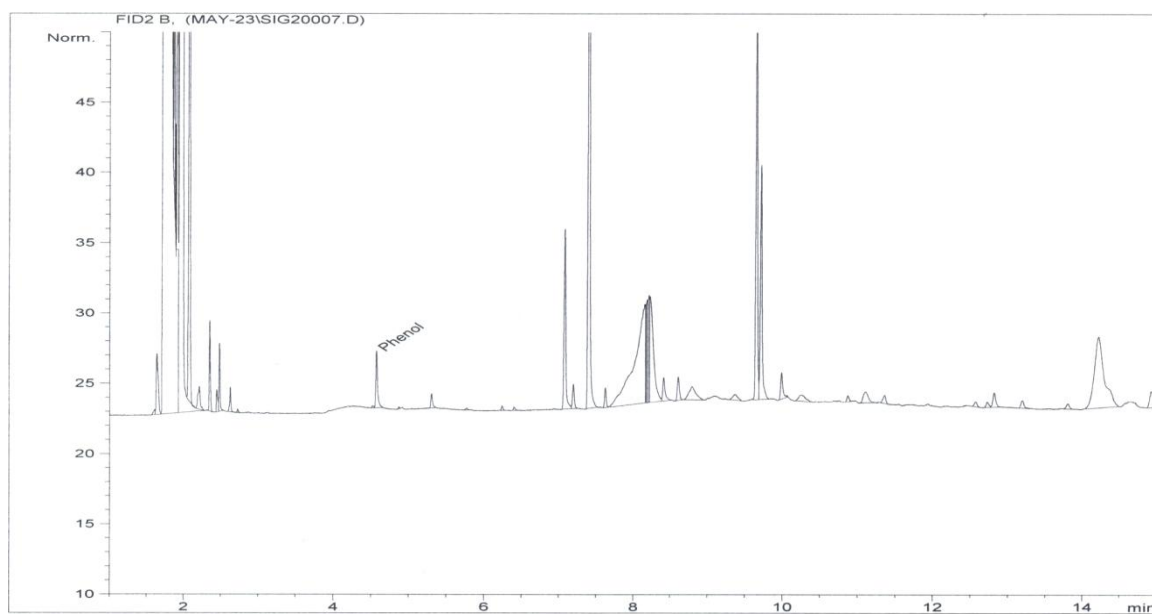


FIGURE A126: GC Chromatogram of Samples Treated for 10 Minutes, in Collective Chemical Species Investigation

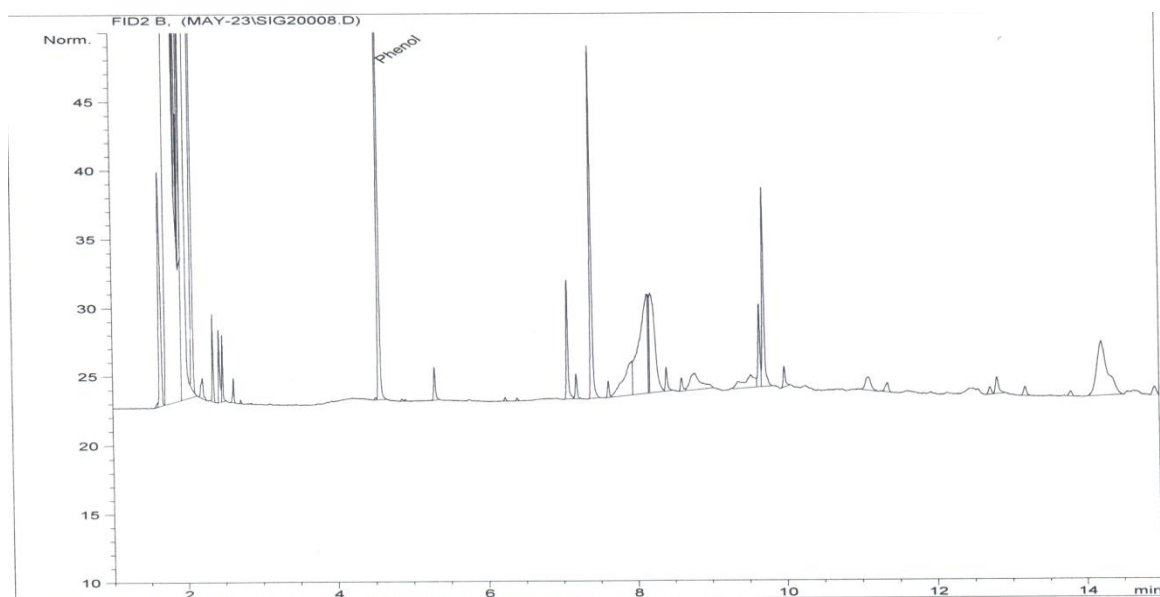


FIGURE A127: GC Chromatogram of Samples Treated for 15 Minutes, in Collective Chemical Species Investigation

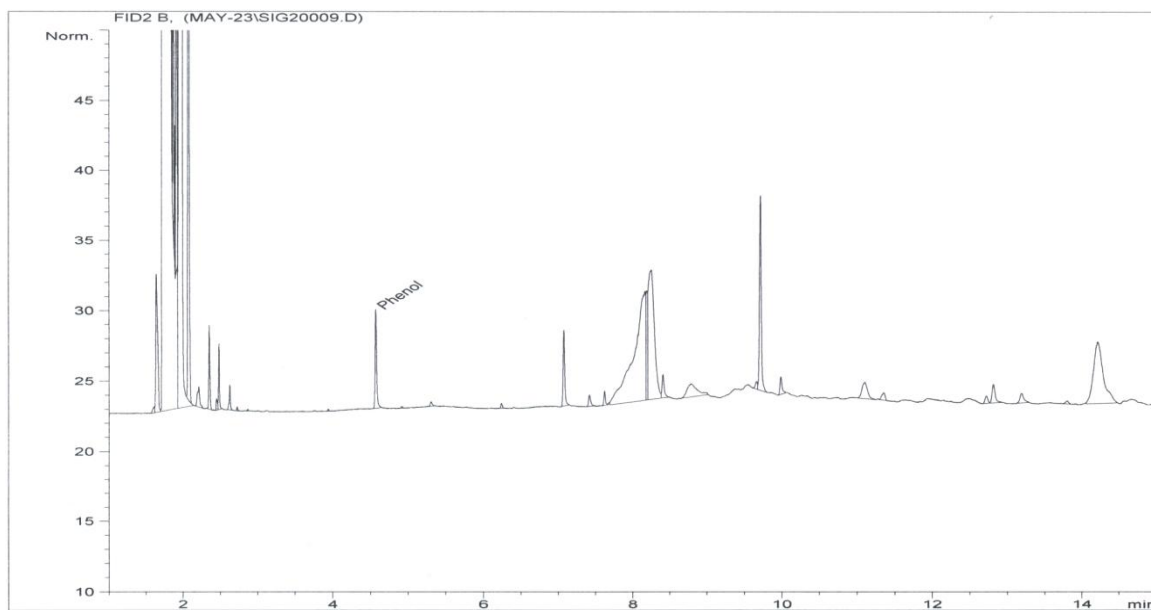


FIGURE A128: GC Chromatogram of Samples Treated for 20 Minutes, in Collective Chemical Species Investigation

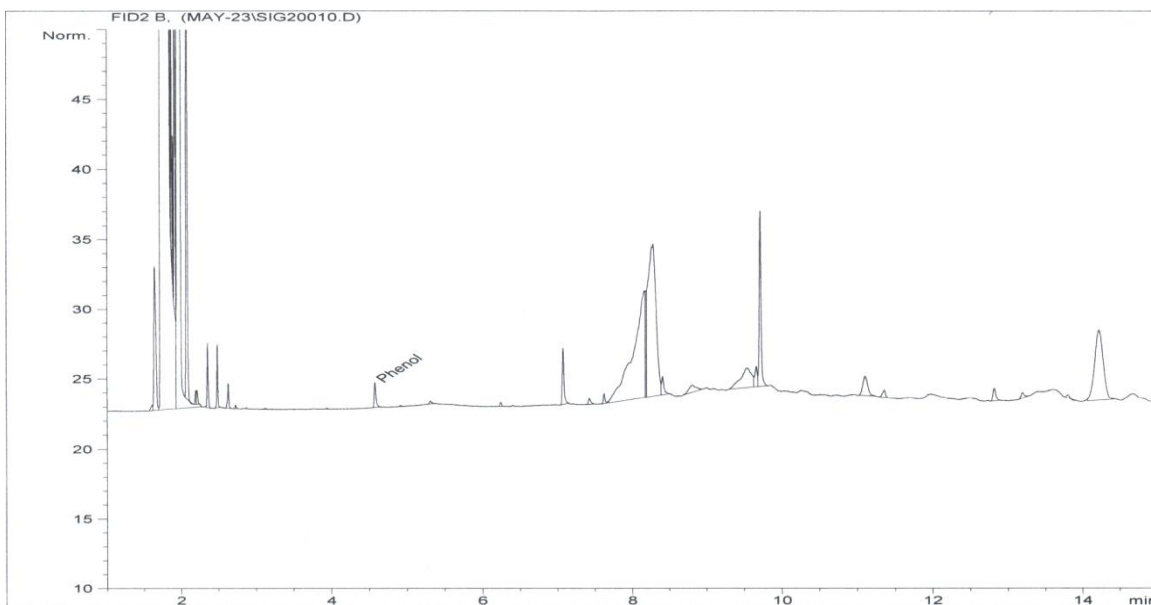


FIGURE A129: GC Chromatogram of Samples Treated for 30 Minutes, in Collective Chemical Species Investigation

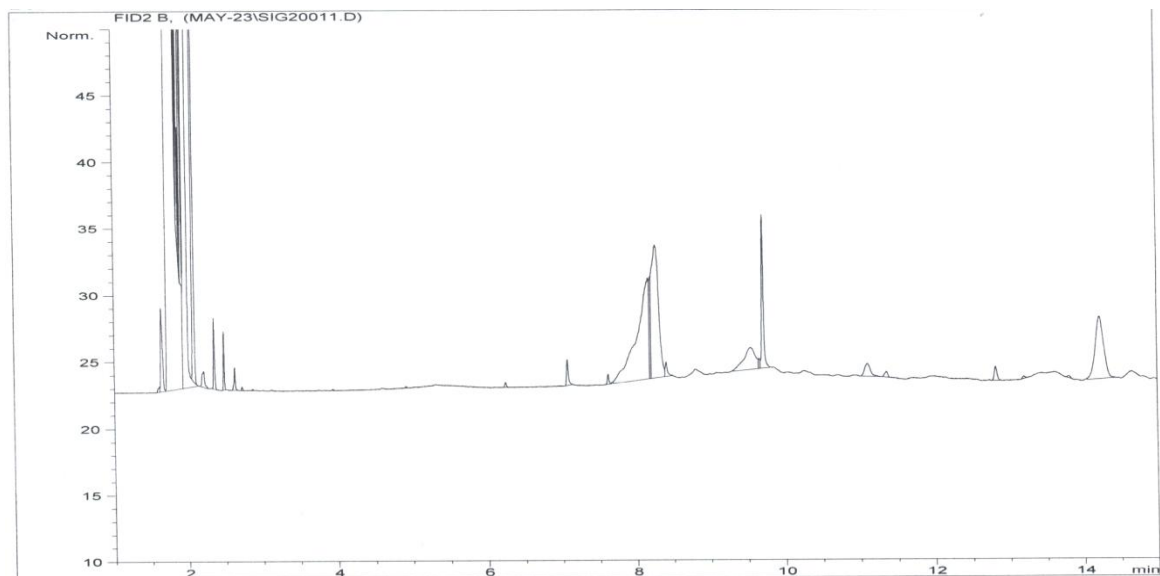


FIGURE A130: GC Chromatogram of Samples Treated for 45 Minutes, in Collective Chemical Species Investigation

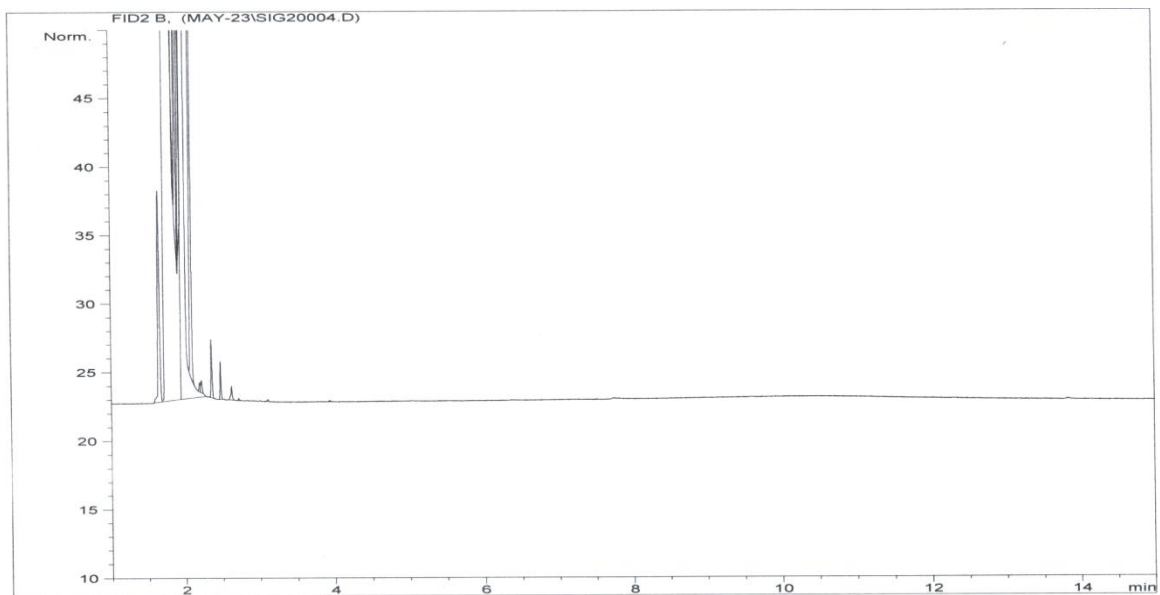


FIGURE A131: GC Chromatogram of Samples Treated for 60 Minutes, in Collective Chemical Species Investigation

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VITA

EDUCATION

Master of Science in Civil Engineering

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PROFESSIONAL EXPERIENCE

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September 2006 up to date

Work Experience:

- Carried out extensive lab research involving experiments and analysis for petrochemical industry wastewater treatment by using Electrochemical Oxidation Process.
- Prepared several technical reports and presentations during the course work.
- Member of analysis team of a project carried out to recycle petroleum fly ash in western province of Saudi Arabia.
- Assisted in laboratory and grading courses work.
- Helped out in researches & projects by gathering information's, conducting experiments, and analyzing results.

Laboratory Experience:

Use of advanced lab equipment such as:

- UV-Spectrophotometers
- Gas Chromatograph (GC)
- Gas Chromatography-Mass Spectrometry (GC-MS)
- TOC Analyzer
- Oil Analyzer

Expertise in water quality tests & standard analytical methods such as;

- Toxicity Characteristic Leaching Procedure (TCLP).
- Extraction Procedure Toxicity (EP Tox) Test
- Phenol Extraction Procedure.
- Multiple Tube Test Procedure.
- Chemical Oxygen Demand (COD).
- Biochemical oxygen demand (BOD).
- Total Suspended Solids (TSS).
- Total Dissolved Solids (TDS)
- *Others.*

Operate & Design Reactors such as:

- Electro-chemical Oxidation Process Reactors.
- Anaerobic membrane bioreactors (AnMBR).

Research & Publications:

- **Bushra, O. I.**, and Al-Malack, M. H., (2009). Water Quality Management: A case study, Wadi Al-arj, Al-Ta'if Area, The International Conference on Water Conservation in Arid Regions (ICWCAR'09), October 12 – 14, 2009.
- **Bushra, O. I.**, Al-Malack, M. H., and Bukhari, A. A., (2009). Hindrance of Phenol Degradation in Electrochemical Oxidation Process. (Accepted)
- **Bushra, O. I.**, Al-Malack, M. H., and Bukhari, A. A., (2009). Effect of Chemical Raw Water Species on the Degradation of Phenol in Electrochemical Oxidation Process. (In progress)

Conferences:

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