

Liquid Phase Oxidation of Phenols in Industrial Wastewater Using an Adsorbent – Catalyst Matrix

by

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Certification

I hereby declare that this submission is my own work toward the PhD and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the University, except where due acknowledgement has been made in the text.

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Abstract

Phenols constitute an important class of toxic organic compounds found in most refinery waste water streams. Due to its refractory nature towards conventional waste water treatment methods it requires a much more severe conditions to effect meaningful oxidation. Catalytic Wet Air Oxidation (CWAO), the most promising treatment method for phenol abatement currently has a high operation cost due largely to the absence of a suitable cost effective catalyst. The current study has investigated the use of the spent Fluidized Catalytic Cracking (FCC) catalyst as a suitable cost effective catalyst for the CWAO process and identified the appropriate operating conditions for its usage in this regard.

The spent FCC catalyst has been proven to be a good adsorbent of phenol, a property not found in the fresh catalyst. Its performance as phenol adsorbent compared with activated carbon has been found to be about 16.62% that of activated carbon. It was found out that particles were agglomerated with a d_{25} for the fresh and spent catalyst being 48 μm and 68 μm respectively against a d_{50} of 68 μm and 88 μm respectively. The pore volume had also increased from 0.4 cm^3/g to 0.9 cm^3/g . The spent FCC unlike the fresh catalyst was found to contain Ni, V, Cu, Fe and Sr which are potential catalyst.

The spent catalyst was impregnated with varying amounts of CuO , Fe_2O_3 and MnO_2 and tested for phenol oxidation using various amounts of H_2O_2 as radical initiator. It was however found out that the spent catalyst impregnated with 0.97% Fe_2O_3 was a very effective catalyst for the catalytic wet air oxidation of phenol using 1 vol. % H_2O_2 as a

radical initiator and a relatively low air pressure of 0.4 cm Hg (533 Pa) gauge and temperature of 50°C. The results were then tested with refinery stripped sour water with about 100% mineralization.

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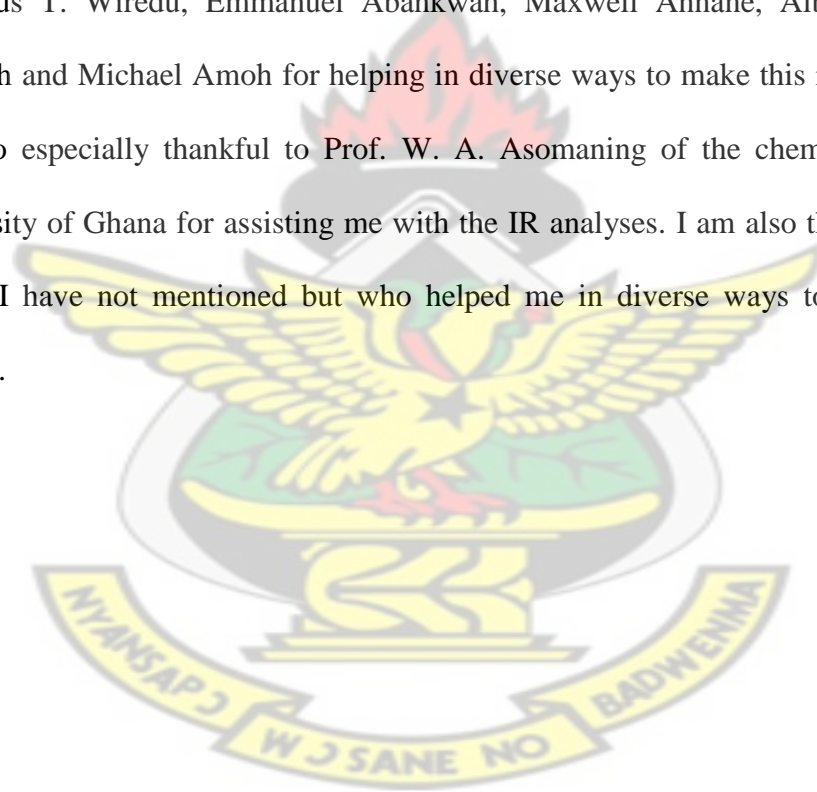
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Chapter 1

Introduction

1.1 Background

Phenols are highly important, well-known and widely used compounds in different fields of the chemical industry. This group of compounds finds application in the manufacture of plastics and plasticizers, phenolic resins, epoxy resins, explosives, drugs, colors and detergents. Different substituted phenols are also included in the manufacture of herbicides, insecticides, algacides, bactericides, molluscicides and fungicides (Nguyen, *et al.*, 2003).

Widespread use of phenols, often in large-scale production, leads to their unavoidable appearance in the environment. Large amounts of phenols also are generated from lignin degradation in paper production. In addition nitrophenols are formed photochemically in the atmosphere from vehicle exhausts. Phenols can also be formed by degradation of organophosphorous insecticides and chlorophenoxyacetic acids (Glezer, 2003).

Phenols are very potent protoplasmic poison, and as such they destroy any tissues they come into contact with (Wallace, 1998). They also act as a local anaesthetic so that upon contact with the skin no pain is felt. However, by the time pain is felt serious skin burns and absorption through the skin may have occurred. Phenol absorption through the skin is very rapid and would ultimately lead to death. Contact with the eye also leads to blindness.

Because phenol is a protoplasmic poison it finds use naturally in plant tissues as an antibacterial agent. In water bodies phenol poses serious threats to aquatic life. Phenol also has the ability to impart a negative taste to fish even at levels of 0.1 ppm in water bodies.

The appearance of phenols in surface water or groundwater leads to formation of more toxic chlorinated phenols during water disinfection processes. The pyrolysis of polychlorinated phenols may result in the formation of polychlorodibenzofurans (PCDF) and polychlorodibenzodioxins (PCDD) which are considerably more toxic than the original phenols. These poly-chlorinated phenols exhibit estrogen-like properties, are carcinogenic and result a in decrease in males' sperm count (Glezer, 2003).

1.2 Statement of Problem

In most processing industries a large majority of the wastewater discharged contains aromatic compounds of which about 23% are phenolic in nature (Suarez-Ojeda, *et al.*, 2004). This situation is mainly due to phenol's high solubility in water. These phenols when discharged into the environment end up in surface waters, like lakes and rivers, as well as underground water and as a result pollute them.

Due to phenol's toxicity, it is important to treat waste water containing phenols to bring their concentrations to levels prescribed by law before they are discharged into the environment. Ghana's Environmental Protection Agency, EPA has a maximum phenol discharge concentration of 2 ppm for wastewater.

Mishra, *et al.*, 1995, have reported several methods by which this goal can be achieved.

They include:

1. Catalytic Wet Air Oxidation process (CWAO) or its advanced form known as Supper Critical Wet Air Oxidation Process (SCWAO)
2. Photo Oxidation also known as Advanced Oxidation Processes
3. Electrochemical Oxidation
4. Biological Oxidation
5. Incineration (*if phenol concentration is very high*).

The underlining principle for all these methods is oxidation of the phenols. In a typical petroleum refinery, where cresol (*o*-,*m*-,*p*- cresol) feature prominently in the discharged waste water, incineration would not be very practical as the phenol concentrations in the wastewater streams are not very high (between 600 ppm - 2500 ppm). Of the above listed methods, the most favored treatment method is the Catalytic Wet Air Oxidation. However, this method has not seen wide scale industrial application due largely to the high cost of operation involved, (Santos *et al.*, 2007). Although the use of biological treatment is generally cheaper than all the methods known, it fails when the phenol concentration in the wastewater is higher.

1.3 Objective

The primary objective of this study is to investigate and propose a catalytic wet air oxidation treatment method that uses relatively cheaper inputs and therefore more economical.

To achieve the main objective the following specific objectives were considered:

1. To investigate the properties of the spent fluidized catalytic cracking (FCC) process catalyst and its use as an adsorbent to remove phenols from refinery waste water.
2. To investigate whether the spent FCC catalyst could be applied as a catalyst that facilitates the liquid phase oxidation of phenol in industrial waste water.
3. To investigate if the properties of the spent FCC catalyst could be enhanced to improve its efficiency in the liquid phase oxidation of phenol.
4. To determine the optimum conditions for the liquid phase oxidation of phenols catalyzed by the spent FCC catalyst.

1.4 Justification

The ultimate goal of this study is to provide a cost effective method by which petroleum refineries can ensure that the wastewater they discharge contains phenol within the acceptable levels prescribed by law. In addition the use of the spent FCC catalyst would also provide a further source of income to the petroleum refineries since until now it was simply discarded at landfill sites.

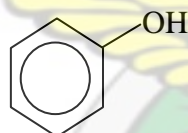
Chapter 2

Literature Review

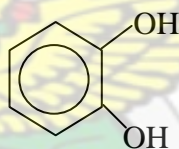
2.1 Phenols

2.1.1 Introduction

Phenols refer to a group of aromatic compounds in which there is at least a hydroxyl group (OH) directly attached to a carbon atom in a benzene ring (Kaftory, 2003). They are classified as monohydric, dihydric, trihydric phenols, and so on, accordingly as they contain one, two and three hydroxyl groups. The simplest member of this group is also referred to as phenol.



Phenol



Catechol

Phenols constitute, among others, an important class of antioxidants that inhibit the oxidative degradation of organic materials including a large number of biological aerobic organisms and commercial products. In the human blood plasma, α -tocopherol, well-known as a component of vitamin E, has been proven to be the most efficient phenol derivative to date to trap the damaging peroxy radicals ($\text{ROO}\cdot$) (Glezer, 2003).

Phenol is an important starting material for numerous intermediates and final products. It is formed during petroleum cracking. Phenol occurs as a component of natural products and some organisms. For example, it is a component of lignin, from which it can be liberated by hydrolysis. Lignin is a complex biopolymer that accounts for 20–30% of the dry weight of

wood. Phenol can also be found as a metabolic product in the mammalian urine, pine needles and oil from tobacco leaves. Abundant natural substances such as thymol and carvacrol are also derivatives of phenols. (Nguyen *et al.*, 2003).

2.1.2 Properties of phenols

By their nature, phenols are also alcohols due to the OH group they contain, but they differ in many ways from normal aliphatic alcohols. For instance they are more acidic than normal aliphatic alcohols (Wallace, 1998). The hydroxyl group of phenol determines its acidity whereas the benzene ring characterizes its basicity. Phenols owe their reactivity to their ability to scavenge radicals by hydrogen or electron transfer in much faster processes than radical attacks on an organic substrate (Steenken and Neta, 2003).

Phenol has a low melting point. It crystallizes in colourless prisms and has a characteristic, slightly pungent odor. In the molten state, it is a clear, colourless, mobile liquid. In the temperature range $T < 68.4^{\circ}\text{C}$, its miscibility with water is limited; above this temperature it is completely miscible. The melting and solidification points of phenol are quite substantially lowered by water. Phenol is readily soluble in most organic solvents (aromatic hydrocarbons, alcohols, ketones, ethers, acids, halogenated hydrocarbons etc.) and somewhat less soluble in aliphatic hydrocarbons. Phenol forms azeotropic mixtures with water and other substances.

In contrast to aliphatic alcohols, phenol forms salts with aqueous alkali hydroxide solutions, (Nguyen, *et al.*, 2003). At room temperature, phenol can be liberated from the salts even with carbon dioxide. At temperatures near the boiling point of phenol, it can displace carboxylic acids, e.g. acetic acid, from their salts, and then phenolates are formed.

The contribution of ortho- and para-quinonoid resonance structures allows electrophilic substitution reactions such as chlorination, sulphonation, nitration, nitrosation and mercuration. The introduction of two or three nitro groups into the benzene ring can only be achieved indirectly because of the sensitivity of phenol towards oxidation. Nitrosation in the para position can be carried out even at ice bath temperature. Phenol readily reacts with carbonyl compounds in the presence of acid or basic catalysts (Nguyen, *et al.*, 2003).

With oxidizing agents, phenol readily forms a free radical which can dimerize to form diphenols or can be oxidized to form hydroxybenzenes and quinones. Since phenol radicals are relatively stable, phenol is a suitable radical scavenger and can also be used as an oxidation inhibitor. Such a property can also be undesirable, e.g. the autoxidation of cumene can be inhibited by small quantities of phenol (Nguyen, *et al.*, 2003). This refractory nature of phenols toward oxidation makes it an important pollutant in wastewater.

2.1.3 Production

Phenol is one of the most versatile and important industrial organic chemicals. Until World War II, phenol was essentially a natural coal-tar product. Eventually, synthetic methods replaced extraction from natural sources because its consumption had risen significantly (Nguyen, *et al.*, 2003). Currently, only small quantities of phenol are obtained from coal tar. Higher quantities are formed in coking or low-temperature carbonization of wood, brown coal or hard coal and in oil cracking.

Several industrial processes have been developed for the synthetic production of phenol (Wallace, 1998).

These include:

1. Sulphonation of benzene and production of phenol by heating the benzenesulphonate in molten alkali hydroxide.
2. Chlorination of benzene and alkaline hydrolysis of the chlorobenzene.
3. Chlorination of benzene and catalytic saponification by Cu in the steam hydrolysis of the chlorobenzene, (Raschig process, Raschig–Hooker, Gulf oxychlorination).
4. Alkylation of benzene with propene to isopropylbenzene (cumene), oxidation of cumene to the corresponding tert-hydroperoxide and cleavage to phenol and acetone (Hook process).
5. Toluene oxidation to benzoic acid and subsequent oxidizing decarboxylation to phenol (Dow process).
6. Dehydrogenation of cyclohexanol–cyclohexanone mixtures.

Among these processes, only the Hook process and the toluene oxidation are important industrially. The other processes were discarded for economic reasons. In the Hook process acetone is formed as a by-product. This has not, however, hindered the expansion of this process, because there is a market for acetone. New processing plants predominantly use the cumene process. The cumene process is based on the oxidation of cumene by oxygen to cumene hydroperoxide which undergoes acidic cleavage to produce phenol and acetone. The cumene oxidation is the predominant process used industrially due to the availability of raw materials and the non-corrosive nature of the reaction involved.

2.1.4 Usage

Phenol was first used as a disinfectant in 1865 by the British surgeon Joseph Lister at Glasgow University, Scotland, for sterilizing wounds, surgical dressings and instruments. But it was not until his death (47 years after) that it became accepted as such (Nguyen *et al.*, 2003). Dilute solutions of phenol are useful antiseptics, despite its frightening side effect which include kidney damage, toxic fumes as well as being a co-carcinogen. In the first half of the past century, a bottle of antiseptic chlorophenols was a common attribute as a medicine in many homes. Its solution was used for bathing cuts, cleaning grazes, rinsing the mouth and gargling to cure sore throats. Nevertheless, it was revealed that its solution likely contains dioxins. Consequently, phenol has only limited use in pharmaceuticals today because of its toxicity.

Commercially, however, phenol is used in the production of phenolic resins (plastics) which are important components of such items as appliance knobs, handles and housings of washing machine agitators and electrical devices. One example of its commercial usage is the phenol-formaldehyde polymer or phenol-formaldehyde resin called Bakelite (Formica, Micarta). A phenol derivative, phenolphthalein is prepared by the reaction of phenol with phthalic anhydride in the presence of sulphuric acid and used as an indicator for acidity or alkalinity. 2,4-Dichlorophenol and 2,4,6-Trichlorophenol are stronger antiseptic than phenol but are less soluble in water than it is.

2,4-Dichlorophenoxyacetic acid (2,4-D), acts as a growth hormone (Nguyen *et al.*, 2003) which makes it particularly effective as a weed killer against broad-leaf weeds, even in a tiny drop. It is actually a superb selective weed killer for lawns and grain crops because it does not affect grass and cereals. It is also sometimes used to trick plants into flowering.

Phenols from peat smoke are included in the flavours of Scotch whisky to dry the malt.

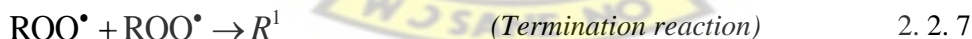
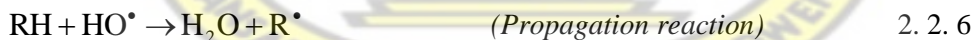
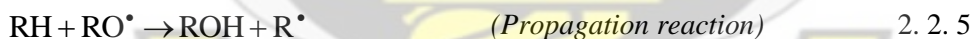
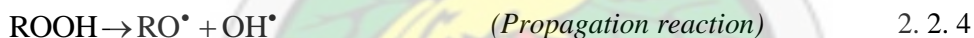
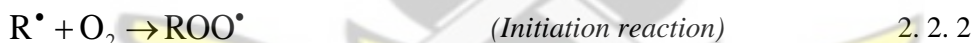
2.1.5 Toxicity

Phenol occurs in normal metabolism and is harmless in small quantities according to present knowledge, but it is definitely toxic in high concentrations. It can be absorbed through the skin, by inhalation and by swallowing. The typical main absorption route is the skin, through which phenol is reabsorbed relatively quickly, simultaneously causing caustic burns on the area of skin affected (Wallace, 1998; Nair *et al.*, 2008).

Besides the corrosive effect, phenol can also cause sensitization of the skin in some cases. Resorptive poisoning by larger quantities of phenol (which is possible even over small affected areas of skin) rapidly leads to paralysis of the central nervous system with collapse and a severe drop in body temperature. Contact with the eye can lead to blindness, (Wallace, 1998). On skin contamination, local anesthesia sets in after an initial painful irritation of the area of affected skin, creating an underestimation of a possible resorptive poisoning. If phenol penetrates deep into the tissue, this can lead to phenol gangrene through damage to blood vessels, (Nair *et al.*, 2008). The effect of phenol on the central nervous system is sudden collapse and loss of consciousness. This is the same for humans and animals. Most of the phenol absorbed by the body is excreted in the urine as phenol and/or its metabolites. Only smaller quantities are excreted with faeces or exhaled.

2.2 An Overview of The Chemistry of Organic Oxidation Reactions

In the study of the oxidation of phenols, it is important to review the general chemistry of the oxidation of organic compounds. Typically, oxidation reactions of organic compounds through free radical mechanism, involves an initiation reaction, a propagation reaction and a termination reaction. The initiation reaction provides a starting radical species, the propagation reaction produces an intermediate product as well as more radicals to sustain the reaction and the termination reaction results in the formation of final products and the destruction of all unused radicals. This scheme of reactions can be depicted by the following series of reactions:



where R is an alkyl group or a phenyl group and In^\bullet is the initiator radical and R^1 is the non-radical product formed.

The above series of reactions are known collectively as the hydroperoxide cycle (Hobbs, 1998).

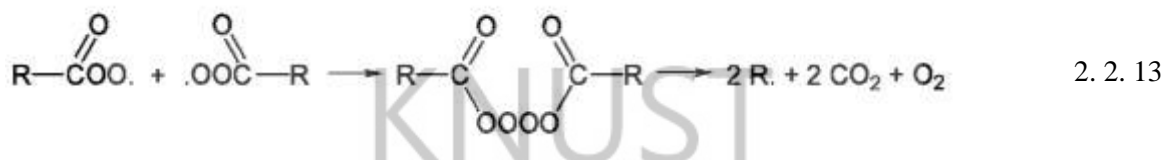
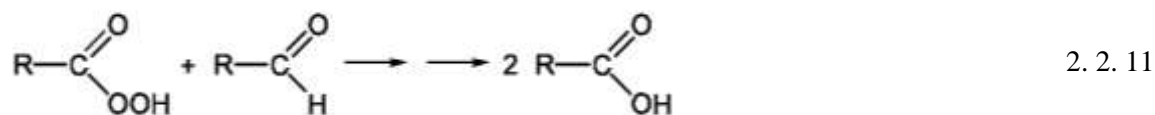
$$\begin{array}{c}
 \begin{array}{ccc}
 \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R} + \text{R} \cdot \\ | \\ \text{H} \end{array} & \xrightarrow{\quad} & \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R} + \text{RH} \\ | \\ \cdot \end{array} \\
 & \swarrow \text{O}_2 \text{ Path II} & \downarrow \text{O}_2 \\
 \text{HOO} \cdot + \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R} \cdot & & \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R} \\ | \\ \text{O} \cdot \end{array} \\
 & \nwarrow \text{RH Path I} & \uparrow \\
 \text{R} \cdot + \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R} \\ | \\ \text{OOH} \end{array} & \xleftarrow{\quad} & \begin{array}{c} \text{OH} \\ | \\ \text{R}-\text{C}-\text{R} \\ | \\ \text{O} \cdot \end{array} \\
 & \searrow & \\
 & \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R} + \text{HOOH} &
 \end{array}
 \end{array}$$

2.2.9

$$R-\overset{\overset{O}{\parallel}}{C}-H + R\cdot \longrightarrow RH + R-\overset{\overset{O}{\parallel}}{C}\cdot \xrightarrow{O_2} R-\overset{\overset{O}{\parallel}}{C}-OO\cdot$$

2.2.9





Equations 2.2.12 and 2.2.13 generally occur at high temperatures and are usually not the desired products if the oxidation is not expected to go to completion. Consequently, for reactions 2.2.12 and 2.2.13 to occur under moderate or lower temperatures a suitable catalyst would have to be incorporated into the reaction medium. In the case of phenols, relatively high temperatures have been reported (Mishra *et al.*, 1995). It is the proposal of the current study to investigate conditions for complete oxidation under low temperatures.

2.2.1 Radical Initiation Reactions

A radical initiation reaction results when a molecule decomposes into radicals by homolytic splitting of usually the weakest bond of the molecule or molecular combinations (Denisov, *et al.*, 2003). Homolytic splitting becomes increasingly difficult to occur with increasing bond dissociation energy (BDE) of the atomic bond within the molecule. The factors that affect the BDE include the following.

1. The type of atoms involved in the bond.
2. The type of atoms that surround the bond being split

3. A π -bond in the α position

The π -bond position affects the BDE because it stabilizes the formed radical by its interaction with the unpaired π -electrons of the benzene ring. For example, the C-C bond in $\text{CH}_3\text{CH}_2\text{-CH}_2\text{CH}_3$ has a BDE of 364 kJmol^{-1} but the same bond in $\text{CH}_3\text{CH}_2\text{-CH}_2\text{Ph}$ has a BDE of 318 kJmol^{-1} . (where *Ph* is a phenyl group)

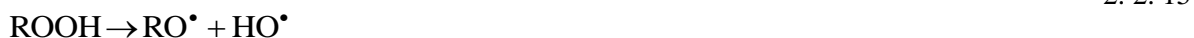
Even though the radical initiation generally starts with the splitting of the weakest bond within the molecule, in some cases several bonds within the molecule split simultaneously.

Once the radicals are created they can react with the reactant to produce more radicals or recombine to form other products. When this radical reaction results in the complete decomposition of the initiator molecules, the effectiveness of the initiator molecule as a radical initiators is decreased.

According to Denisov *et al.*, (2003), dialkylperoxides (ROOR), hydroperoxides (ROOH) as well as molecular oxygen can be used to initiate free radical reactions as follows:



Initiation is a result of homolytic splitting of the O-O bond.



In the case of molecular oxygen the reaction is facilitated in the presence of polar solutions due to the polar nature of the transition state:



Radicals can also be generated by ions in the presence of peroxides:



In this case the ions act as electrons donors while the peroxides act as electron acceptors, splitting into a radical and an OH^- ion. Generally transition metal ions (M^{n+}) catalyze the decomposition of hydrogen peroxides as follows.



Although an initiator molecule may be present in a reaction medium it does not necessarily mean it would spontaneously decompose into a radical and start the reaction, it may have to be triggered to start. This can be achieved by one of three main ways (Denisov, *et al.*, 2003). These are:

1. Photolysis (photosensitization)
2. Thermolysis

3. Redox reactions

2.2.2 Photolysis or Photosensitization

When an electromagnetic radiation is applied to a molecule, depending on the wave length of the radiation, the molecule may absorb it or it may not have any effect on it, (Denisov *et al.*, 2003). If the molecule absorbs the radiation it may become excited. Most organic compounds would absorb electromagnetic radiation with wave lengths within the UV range, particularly, between 200-300 nm for aromatic compounds. The fate of the excited molecule could be any of the following:

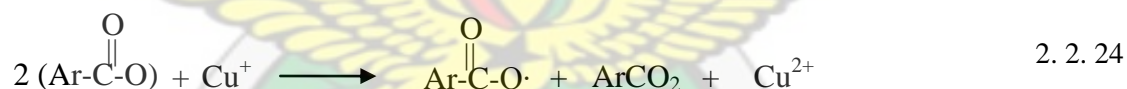
- The excited molecule could cleave into two more stable molecules or radicals in order to become stabilized. This is known as *photolysis*.
- The excited molecule could return to the ground state by releasing all its energy in one step to a nearby molecule which becomes excited in the process. This process is known as *photosensitization*. Molecules that behave like this are referred to as *photosensitizers*.
- The excited molecule could return to the ground state by releasing its energy to another molecule which does not become excited and thus quench the excitation.
- The excited molecule could simply return to the ground state by gradually releasing its energy, usually in the form of light, to the environment.

2.2.3 Thermolysis

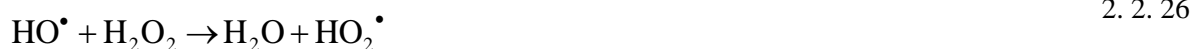
Thermolysis refers to thermally induced fission of a radical initiator. This can occur both in the liquid and gas phase. Bonds with low bond dissociation energies (BDE) frequently require much lower temperatures to cleave while much higher temperatures are required to cleave very strong bonds like C-C bonds. The thermal cracking of hydrocarbons is a typical thermolysis reaction.

2.2.4 Redox Reactions

A radical could be created by an electron transfer from a transition metal ion (redox reaction) to an organic compound, such as in the decomposition of acyl peroxides catalyzed by copper (I).



Fenton's reagent, which is simply a solution of FeSO_4 and H_2O_2 is a reagent which can be used to initiate a radical reaction based on a redox reaction:



2 .2.5 Propagation Reactions

The initiation reaction is an endothermic reaction and so the self sustenance of the reaction is largely dependent on the propagation reactions. The products formed from these reactions determine the ultimate direction of the termination reactions and hence the final products formed. The factors that influence the path along which these reactions follow include the following.

1. Cage Effect
2. Presence of Transition metal cations

2 .2.6 Cage Effect

When a radical initiator molecule decomposes in the gas phase, the formed radicals immediately fly apart in different directions. However, in the liquid phase the formed radicals exist side by side for a certain time, surrounded by solvent molecules which by the action of intermolecular forces create a “cage” around the pair of radicals (Cage Effect). The cage effect is not only limited to liquid phase reactions but also occurs in the gas phase as well, however its effect is not as pronounced in the gas phase as it is in the liquid phase. Lying side by side each other, the probability that the formed radicals would recombine to form the initiator molecule back or other products becomes increased. If the recombination of the radicals results in the formation of the initiator molecule it reduces the extent of the reaction since the radicals get deactivated as a result of the recombination. In the gas phase the formed radicals lie very far apart from each other, reducing the cage effect significantly. In the gas phase the probability of formed radical recombining is usually very low (*between 0.1 - 2.0%*) (Denisov *et al.*, 2003).

The cage effect is not altogether very detrimental but can be used to control the kind of products formed. For example, in the photolysis of azomethane in the gas phase in the presence of propane (RH) the ratio $\frac{[C_2H_6]}{[N_2]}$ is 0.015 with the main reaction path being as follows:



or 2.2.30



On the other hand, if the same reaction is carried out in the liquid phase the ratio $\frac{[C_2H_6]}{[N_2]}$ becomes 0.65 due to the recombination of the methyl radical pair in the cage and the main reaction follows the path:



Thus if the desired product from the photolysis of the azomethane is C_2H_6 , due to the cage effect, higher yields would be obtained if it is conducted in the liquid phase.

The severity of the cage effect depends on the following factors:

- **Viscosity**: A highly viscous solvent significantly impedes the mobility of the formed radicals in the solvent and hence in general the more viscous a solvent is the more pronounced the cage effect will be.
- **Pressure**: For incompressible fluids pressure increases have very little impact on caging but for compressible fluids increasing pressure increases the viscosity of the solvent and hence increases the cage effect.
- **Spin Multiplicity Effect**: This affects radicals generated by either photolysis or photosensitization. For radical to recombine to form the initiator molecules they must be in the singlet state. Thus if the formed radical is in the triplet state recombination can only occur if it drops to the singlet state. However triplet-to-singlet drops are usually improbable because the triplet state radicals are more stable than singlet state radicals. Thus the more triplet state radicals are formed the less pronounced the cage effect will be. This implies that depending on the photosensitizer used, the cage effect could be controlled.

2.2.7 Presence of Transition Metal Cations

The presence of a transition metal cation in the reaction medium has two negating effects, (Denisov, *et al.*, 2003). That is, they can be used to propagate a radical reaction as well as terminate it. Transition metal cations catalyze the decomposition of the alky peroxides as well as hydroperoxides formed during the propagation reaction. In addition, they react with the intermediate products formed during the propagation reaction to produce more radicals.



Oxygen oxidizes the transition metal ions (*usually in the lower valence state*) generating hydroperoxyl radicals, hydroxyl radicals or superoxide ions in the process. An example is the production of hydroxyl radicals and superoxide ions by reaction of oxygen with Fe^{2+}



Thus under those circumstances the presence of the transition metal ions ensures that there is a constant supply of radicals to sustain the reaction.

On the contrary, if hydroperoxyl radicals propagate the chain oxidation of a substrate, transition metal ions retard the process after some time by a cyclic chain termination reaction as follows:



Thus under this circumstance the presence of the transition metal ions can be used to prevent the reaction from going to completion or *running away*.

2.2.8 Other factors

Initiators are introduced into the reaction medium generally, in very small amounts because they usually have long chain lengths, (Denisov *et al.*, 2003). When the radicals formed attack the initiator molecules they facilitate the decomposition of initiator molecules which ultimately enhances the oxidation reaction (Denisov, 1981). If the heat released during this reaction is not enough to compensate for the heat taken up during the initiation as well as the propagation reactions, the reaction could come to an abrupt end if there is no external source of heat. Thus the self sustenance of the oxidation reaction depends largely on the amount of heat released during the propagation reactions. In liquid phase reactions this heat can also be taken up by the solvent and which causes the temperature of the solution to rise. If the solvent is equally susceptible to oxidation it could end up being oxidized. In addition the heat released could also vaporize the solvent which could also affect the overall reaction. In this regard the pressure of the reaction environment is usually raised to prevent the solvent from vaporizing. But pressure increases also increase the cage effect which usually prevents the oxidation from going to completion. If complete oxidation is not desired, which is usually the case, pressure increases enhances the reaction.

In situations where the reaction is to be conducted under near atmospheric conditions and/or the organic compound (phenol) concentration is not high in the solvent, a suitable catalyst and adsorbent would be required.

2.3 Phenol Oxidation

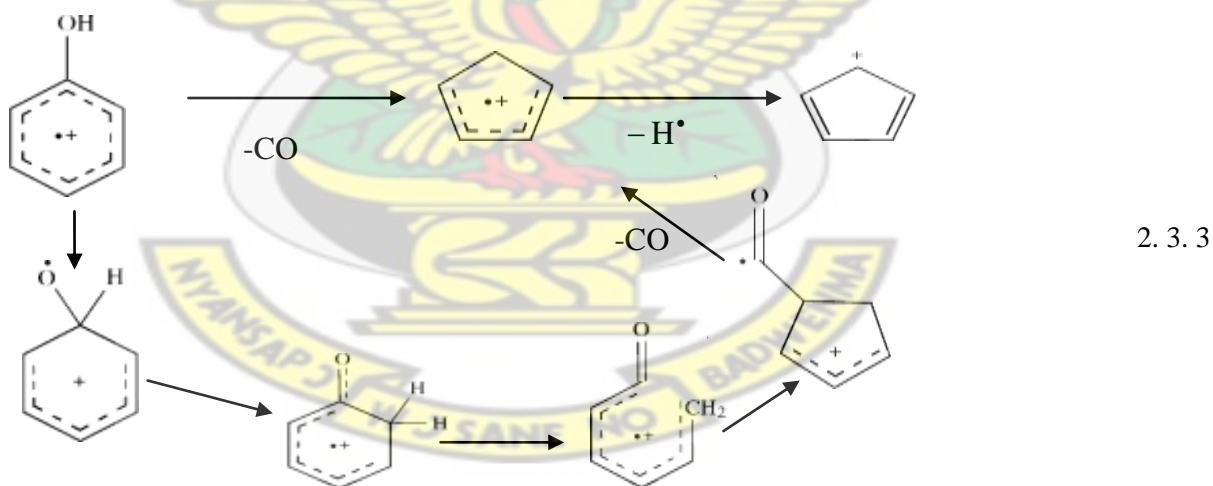
Phenol oxidation can take place in the vapour/gas or in the liquid phase. The oxidation of phenols proceeds by hydrogen atom abstraction from the phenolic OH group as shown below (Rivas, *et al.*, 1998; Steenken and Neta, 2003):



or by electron transfer to an acceptor with sufficiently high electron affinity as shown below:



where **A** is any atom or molecule capable of accepting an electron or hydrogen atom and Ph is a phenyl group. In the gas-phase the reaction may proceed as follows (Kuck, 2003):



2.3.2 Liquid Phase Oxidation of Phenols

The liquid phase oxidation of phenols using dioxygen (*molecular oxygen*) can be catalyzed by transition metal compounds in the presence of hydrogen peroxides, hydroperoxides or alky peroxides which may be incorporated directly into the reaction medium or may be

formed during the course of the reaction (Denisov, *et al.*, 2003). Some of the metal species that have been used as catalysts include Cu^{2+} , Fe^{2+} , CuO , ZnO , Ru and Ce (Mishra, *et al.*, 1995; Chang, *et al.*, 1995; Debellefontaine, *et al.*, 1996).

The reaction mechanism of a variety of metalloenzymes, selective oxidations of phenols catalyzed by transition metal complexes capable of activating oxygen have long been investigated (Yamamura, 2003). As a result, many efforts have been made to prepare efficient metal complexes by a combination of metals and new ligands (Yamamura, 2003).

2.3.3 Oxidation of Phenols by Metal Ions

Phenol oxidation is known to be catalysed by cuprous chloride in the presence of nitrogen-containing compounds such as pyridine, oximes and others under an oxygen atmosphere (Yamamura, 2003). Lead oxide (PbO_2) has been used as an oxidant in sterically hindered phenoxyl radicals. Silver oxide (Ag_2O) or manganese oxide (MnO_2) can also be used in this regard (Huysmans and Waters, 1966). Unsubstituted phenoxyl radicals can be produced by oxidation with Ce^{4+} in aqueous solution at low pH. Substituted phenoxyl radicals including semiquinones, phenol radical cations and oxypyrones can also be produced by using Ce^{4+} in aqueous solutions as well. In basic solution also $[\text{Fe}(\text{CN})_6]^{3-}$ can be used to oxidize phenols. The reaction probably proceeds by the production of the phenolates (Steenken and Neta, 2003).

Ti^{2+} and Ag^{2+} have been found to react with 4-methoxyphenol and 3,5-dimethoxyphenol by 100% electron transfer, whereas with TiOH^+ the efficiency of electron transfer is only 75%, (Steenken and Neta, 2003). The ease of oxidation increases considerably in going from the neutral phenols to the phenolates; even the weak oxidants $\text{Ti}(\text{OH})_2$ and $\text{Ag}(\text{OH})_2$ are able to

oxidize the phenolates with 100% yield to give the corresponding phenoxyl radicals. The oxidizability of phenols increases as you go from phenol to the dihydroxybenzenes. Hydroquinone and resorcinol are oxidized with 100% yield not only by Ti^{2+} but also by the weaker oxidant TiOH^+ . Catechol forms a complex with Ti^{2+} , which has the same structure as that produced by the reaction of ortho-semiquinone radical with Ti^+ or by reaction of ortho-benzoquinone with Ti^0 . The rate constants for reaction of the Ti^{2+} and Ag^{2+} species are between $10^8 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Phenol is also oxidized by ferrate (V) ions and ferrate (VI) ions. It has been suggested that ferrate (VI) ions oxidize phenol by a one-electron transfer mechanism ($k = 10^7 \text{ M}^{-1} \text{ s}^{-1}$) whereas ferrate (V) ions oxidize it by a two-electron transfer mechanism ($k = 3.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

2.3.4 Oxidation of Phenols by Free Radicals

A number of free radicals could be used in the oxidation of phenols. These include halogen and pseudo-halogen dimer radical anions, aminyl radical, nitrogen radicals, oxygen-centered radicals, hydroxyl radicals and oxide radicals (Steenken and Neta, 2003). The halogen and pseudo-halogen dimer radical anions, $\text{X}_2^{\bullet-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$), react efficiently with phenols and phenolate ions to give the corresponding phenoxyl radicals.



The aminyl radical ($^{\bullet}\text{NH}_2$) is also able to produce phenoxyl radicals from substituted phenolates. The rate constants for this reaction ($k = 3.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for phenolate) increase strongly with increasing electron-donating power of the substituent to give a Hammett reaction constant (ρ) of -3.3, from which it can be concluded that the reaction

proceeds by electron transfer. The Hammett constant is derived from an equation which describes a linear free-energy relationship relating reaction rates and equilibrium constants for many reactions involving benzoic acid derivatives with meta- and para- substituents to each other with just two parameters: a substituent constant and a reaction constant. The value $\rho = -3.3$ is more than twice that determined for the oxidation of substituted phenols by $\text{Cl}_2^{\bullet-}$ or of phenolates by $\text{Br}_2^{\bullet-}$ or $(\text{SCN})_2^{\bullet-}$. This increased selectivity of the aminyl radical ($^{\bullet}\text{NH}_2$) radical is in line with its lower reactivity. The radical N_3^{\bullet} produced in the reaction of N_3^- with $^{\bullet}\text{OH}$, gives the phenoxyl-type radical on reaction with phenols and phenolate ions, whereby N_3^{\bullet} shows very little tendency to perform hydrogen-abstraction reactions from C-H bonds additionally present.

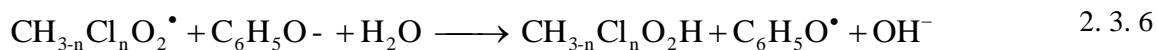
A large number of oxygen-centered radicals react with phenols to yield phenoxyl radicals. Whereas $^{\bullet}\text{OH}$, the simplest of the oxygen-centered radicals, reacts mainly by an addition/elimination mechanism, most of the other radicals seem to produce phenoxyl radicals via hydrogen or electron transfer. The oxide radical, $\text{O}^{\bullet-}$, the conjugate base of the $^{\bullet}\text{OH}$ radical, also has been proposed to react with phenolate by electron transfer. In the reaction of $(\text{CH}_3)_3\text{CO}^{\bullet}$ with p-substituted phenols to yield phenoxyl radicals a large kinetic isotope effect has been observed, i.e. $\frac{k_{\text{H}}}{k_{\text{D}}} = 3-5$, which means that in the transition

state an O-H bond is broken as in a hydrogen abstraction reaction. The kinetic isotope effect (KIE) is the ratio of reaction rates of two different isotopically labeled molecules in a chemical reaction. It is also called "isotope fractionation". k_{H} and k_{D} are reaction rate constants using hydrogen and deuterium respectively. It has been noted that there is also an increase in the rate constant with increasing electron-donating power of the substituent

(Hammett constant, $\rho = 0.9$) , which indicates that there is charge separation in the transition state with partial positive and negative charge on the aromatic ring and on *t*-butoxyl, respectively. As compared to *tert*-butoxyl radical, peroxy radicals RO_2^\bullet react more slowly with phenols. These reactivity differences can be related to differences in the O–H bond dissociation energies which are 440 kJ mol^{-1} for RO–H but only 360 kJ mol^{-1} for ROO–H;



These reactions do not depend on the nature of ROO \cdot (for a particular phenol) but are quite sensitive to the nature of the phenol. For example, for reaction of a peroxy radical from styrene with phenol $k = 5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, for reaction with 2,5-di-*tert*-butyl-4-methylphenol $k = 1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, for 2,3,5,6-tetramethyl-4-methoxyphenol $k = 2.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and for α -tocopherol (Vitamin E) $k = 2.35 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. An explanation for this trend has been given in terms of PhO–H bond strengths and of stereo-electronic factors that determine the stabilization of the phenoxyl radical (Steenken & Neta, 2003). As expected for a hydrogen abstraction mechanism, this reaction exhibits a large kinetic isotope effect ($\frac{k_{\text{H}}}{k_{\text{D}}} = 4 - 11$). Alkylperoxy radicals substituted at the α -position by halogens show a higher reactivity with respect to oxidation of phenolates.

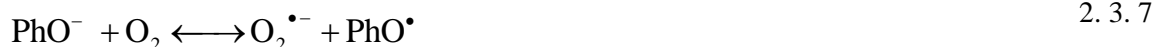


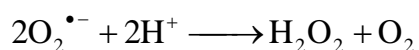
The rate constant increases from $1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for $n = 1$ to $2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $n = 3$, due to the withdrawal of electron density from the reaction center by the electronegative halogens (Steenken and Neta, 2003).

In general, the rate constants for oxidation by methylperoxyl radicals substituted at the α -position with various groups are greatly dependent on the electron-withdrawing power of these groups. The rate constants for halogenated peroxy radicals are highly influenced also by the solvent; variations of nearly two orders of magnitude have been observed for the reaction with Trolox-C (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, a Vitamin E analogue). In addition the rate constant generally increases with solvent polarity. Rate constants for the reactions of chlorinated methylperoxyl radicals with Trolox-C in aqueous solutions have been measured as a function of temperature and the activation energies were found to be 6.4 kJ mol^{-1} for $\text{CH}_2\text{ClO}_2^\bullet$ and 17 kJ mol^{-1} for the dichloro- and trichloromethylperoxyl (Steenken and Neta, 2003).

2.3.5 Formation of Phenoxyl Radicals from Phenols by Reaction with O_2 and/or $\text{O}_2^{\bullet-}$ (Autoxidation)

Autoxidation is the formation of phenoxyl or alkoxyl radicals from the reaction between organic compounds and oxygen or oxygen centered radicals with or without the assistance of a catalyst. The autoxidation of phenols is slow in neutral and, especially, in acid solution but becomes very noticeable in alkaline solutions (Steenken and Neta, 2003). This base catalysis of phenol oxidation is due to the conversion of the neutral phenols to the phenolate ions, which are more easily oxidized by the oxidant than their conjugate acids.





2. 3. 9

The use of soluble metal catalysts such as Cu^{2+} (CuSO_4) though effective in catalysing the phenol oxidation also has the potential to increase the metal ion concentration of the treated phenol solution above acceptable levels. Consequently when such catalysts are used they are usually immobilized on suitable supports by impregnating them with their oxides. In the case of zeolites the metal cation can be incorporated into the zeolite structure as well, (Mishra, *et al.*, 1995).

2 .3.6 Technologies for the Liquid Phase Oxidation of Phenols in Wastewater

The technologies for the liquid phase oxidation of phenols in wastewater can be classified into four broad categories. These include;

1. Catalytic Wet Air Oxidation and Super Critical Wet Air Oxidation
2. Photo-Oxidation (Advanced Oxidation Process, AOP)
3. Biological Oxidation using enzymes
4. Electrochemical Oxidation

Of the above methods the Catalytic Wet Air Oxidation process is the most favoured (Prasad, *et al.*, 2007) .

2.3.7 Catalytic Wet Air Oxidation (CWAO)

Catalytic wet air oxidation (CWAO) process refers to a group of oxidation processes in which the primary reaction is an autoxidation of the organic compound. The CWAO process usually requires the use of oxygen partial pressures of about 2 - 14 bars , which is about 10- 67 bars of air (Mishra, *et al.*, 1995; Debellefontaine, *et al.*, 1996; Suarez-Ojeda, *et al.*, 2004; Santos, *et al.*, 2007). The reaction temperature used is between 100 °C and 320 °C. An adsorbent may or may not be used. Rivas, *et al.*, (1998) have presented an exhaustive reaction mechanism of the CWAO process. Shende and Mahajani (1997) as well as Debellefontaine, *et al.*, (1996), simplified the series of reactions involved in the CWAO process as follows:

- Transfer of oxygen from the bulk gas phase to the bulk liquid phase.
- Instantaneous saturation of the interface with respect to the solute gas.
- Chemical reaction at the interface.
- The desorption of the gaseous products.

During the CWAO process the organic compound in this case the phenol, degrades to low molecular weight compounds and finally to highly refractory low molecular weight carboxylic acids. Suarez-Ojeda, *et al.* (2004) as well as several other researchers according Mishra, *et al.*(1995) have confirmed this trend. For many of these studies the objective have been to combine CWAO with Biological treatment methods because CWAO process on its own does not usually result in complete mineralization as doing that may require severe operation conditions. Shende & Mahajani (1997) reported the use of a homogenous catalyst in the form of CuSO_4 to completely mineralize the formed refractory carboxylic acids. In their work pure oxygen was used at a pressure of 0.345 – 1.388 MPa and

temperatures of between 215 – 235 °C. Like other CWAO processes, they propose the use of a homogenous catalyst which itself could lead to another environmental hazard as these catalysts dissolve in the wastewater and are discharged along with it. For the effluent from such treatment units to meet environmental standards, they would have to be treated to recover most, if not all of the dissolved metals. The economic implications of such treatment processes is clear. In the work of Suarez-Ojeda, *et al.* (2004) however, no catalyst was employed, instead, a packed column of activated carbon was used. The oxygen pressure used was 2 bars and the temperature used was 140°C. The results showed a marginal mineralization but the main products were low molecular weight carboxylic acids. Heterogenous catalysts, such as CuO also react with the carboxylic acids formed during the CWAO process, and hence leach Cu²⁺ into solution (Mishra, *et al.*, 1995).

Oxidation of phenols under milder conditions of temperature (≤ 100°C) in the presence of catalyst such as MnO₂ results in low extent of reaction and the products formed are oxidative coupled products (Mishra, *et al.*, 1995).

The rate of oxidation of phenol increases with increasing alkalinity, indicated by increase in the concentration of the phenolate ion, (Mishra, *et al.*, 1995). In addition there is a significant length of induction period before the oxidation actually commences. The length of induction period has been found to depend on the concentration of the phenol, the concentration of oxygen, the temperature and the type of phenol being oxidized. (Suarez-Ojeda, *et al.*, 2004) reported an induction period of 8 h. After this induction period, oxidation proceeds considerably fast until a steady state is reached. Several researchers have also observed that under certain conditions of temperature, this steady state period is followed by a third step during which the rate of oxidation is considerably slowed down (Mishra, *et al.*, 1995). This slow down has been attributed to the presence of carboxylic

acids or the low molecular weight products formed, which are resistant to further oxidation.

Many catalyst systems have been developed for the liquid phase oxidation of phenols (Mishra, *et al.*, 1995). They include:

- Sodium Peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$)
- Manganese Dioxide (MnO_2)
- Iron(III) Oxide (Fe_2O_3)
- Cu-Fe-Bi-K system
- Cu/C
- Mn/Ce
- Noble metals (Pt, Ru, Rh, Ir, Pd) : Of the noble metals Ru showed the best catalytic effect while Pt and Rh were better than homogeneous copper catalyst.
- Copper(II) Oxide and Zinc(II) Oxide (CuO/ZnO)
- Sodium sulphite (Na_2SO_3) and Cu^{2+} : in which case complete destruction of phenol could be achieved in 15-18 min for a 100mg/L phenol solution using an oxygen partial pressure of 2.5 bar (0.25 MPa).
- $\text{H}_2\text{O}_2/\text{Fe}^{2+}$
- Pt/ Al_2O_3

A Mn/Ce system have been proved to be the best catalyst system for the complete oxidation of phenols. (Mishra, *et al.*, 1995)

The selectivity (α), the ratio of the rate of acetic acid formation to CO_2 formation, has been found to be 0.15 for phenol and 0.37 - 0.96 for 2-chlorophenol (Mishra, *et al.*, 1995). The

values of α for 2-chlorophenol has been found to depend on the temperature of the reaction medium.

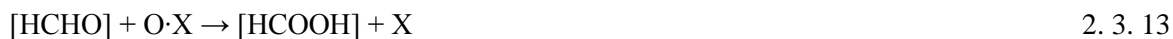
The greatest limitation of this treatment method apart from the initial cost of equipment, is the refractory nature of acetic acid. Acetic acid is the predominant carboxylic acid formed during this process. Due to its refractory nature complete mineralization requires very severe reaction conditions of temperature (225°C-300°C) and pressure (oxygen partial pressures of 3.5 - 120.8 bar). Accordingly, several catalyst systems have been developed. They include:

- CuSO_4 , CuNO_3 (homogeneous catalyst)
- Cu, Pd, CoO/ZnO (13:165), Cu:Mn:La Oxides (4:2:1) supported on a spinel support (48.5% ZnO and 51.5% Al_2O_3), Copper chromite, iron oxide, Co:Bi (5:1) complex oxides, Ru/Ce and Mn/Ce. (Heterogeneous transition metal catalyst).

Of the various catalyst systems studied the multicomponent systems such as Co:Bi, Cu:Co, Cu:Co:Bi Ru/Ce and Mn/Ce systems were considerably more active. The Co:Bi (5:1) have been found to be the best amongst them.

The oxidation of acetic acid to CO_2 and H_2O over FeO catalyst has been proposed to proceed through the formation of intermediate products, namely formic acid (HCOOH) and methanaldehyde (HCHO) (Mishra, *et al.*, 1995). Accordingly, the following reaction mechanism have been proposed for its decomposition





where X indicates a vacant catalyst site and O·X indicates an oxidized site (oxygen atom trapped on a catalyst site).

Contrary to acetic acid, propionic acid as well as higher molecular weight carboxylic acids are much easier to oxidize. Their oxidation to CO₂ and H₂O have been proposed to proceed along two main paths. The first is that, they are oxidized directly to CO₂ and H₂O and the second path is that they are oxidized to acetic acid via acetaldehyde as intermediate product. This revelation implies that with the appropriate choice of catalyst and operation conditions their decomposition can be directed. What remains to be found out is the stable low cost catalyst to achieve this feat under very mild operating conditions of temperature and pressure.

In terms of energy, the CWAO process can be self sustaining by designing the system such that the out going effluent exchange their heat with the incoming wastewater. Under some circumstances electricity can be generated from the out going effluent before ultimately discharging it.

2.3.8 Super Critical Wet Air Oxidation (SCWAO)

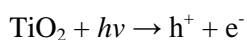
Super Critical Wet Air Oxidation (SCWAO) is an extension of the CWAO process and they differ primarily in the operating condition used. SCWAO is oxidation using molecular oxygen or oxygen containing gases in the presence of water at / above its critical point (Matjaz and Janez, 1997), that is, temperatures and pressures greater or equal to 374°C and 22.1 MPa respectively. Under such conditions the reaction rates are significantly increased, due largely to the fact that under such conditions the organic compound and the oxygen are mixed into a single homogeneous phase. In addition, under such conditions water becomes increasingly non polar and hence inorganic compounds become insoluble in it and as a result precipitate out of it, while organic compounds become more soluble in it. During SCWAO complete mineralization is easily achieved and usually a catalyst is not required. The only draw back of this treatment method is cost of equipment. In terms of energy it is completely self sustaining and can even be used to generate electricity.

2.3.9 Photo-Oxidation (Advanced Oxidation Process, AOP)

As mentioned earlier (*see Section 2.2.1*), one of the means by which a radical reaction can be initiated is by irradiating the reactants with UV radiation. This is the underlining principle behind photo-oxidation. The natural means by which most hazardous compounds are degraded in the environment is by this means. However, this process is naturally very slow and so has to be sped up.

Photocatalytic reactions occur when charge separations are induced in a large band-gap semiconductor by excitation with UV-band-gap radiations. This excitation results in the

creation of an oxidizing site, a “hole”, and a reducing site, an “electron”. (Serrano & Lasa, 1997)

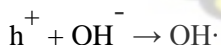


2. 3. 16

This photogenerated electron-hole ($\text{e}^- - \text{h}^+$) pair can then be captured by compounds which are adsorbed on the surface of the photocatalyst. The hole formed can be filled by an electron transferred either from the adsorbed organic compound, in this case the phenol, or from an adsorbed water molecule. In the latter case, hydroxyl radicals are formed as follows:

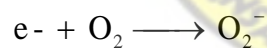


2. 3. 17

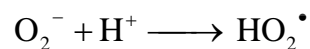


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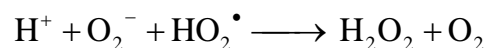
In addition, several other radicals may be produced by the electron formed as follows:



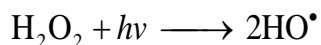
2. 3. 19



2. 3. 20



2. 3. 21



TiO₂ in the anatase phase is predominantly used as the photosensitizer, (Kraft, *et al.*, 2003). This is because, not only is it a good photosensitizer (because of its large band-gap), but has the ability to adsorb both oxygen and the phenols on its surface, thus facilitating the oxidation reaction. Molecular oxygen (air) is the main oxidant used for these processes (Laoufi, *et al.*, 2007). The use of H₂O₂ as oxidant have also been reported by Asim, *et al.*(1997)

The presence of transition metal ions such as Ag⁺, Cr₂O₇²⁻, Cu²⁺, Fe²⁺ have been reported to facilitate the photo degradation of phenols possibly by trapping the photogenerated electrons and preventing them from recombining with the photogenerated holes (Rideh, *et al.*, 1997) . In this regard, Fenton's reagent is sometimes incorporated into the reaction medium to speed up the process. Like the CWAO process, there is a significant induction period required for the reaction to commence. Laoufi, *et al.* (2007), recorded an induction period of 4 h. As would be expected, the rate of the reaction depends on the phenol concentration, the light intensity as well as the catalyst loading (the amount of TiO₂ used). Additionally, the rate of reaction varies inversely with pH (Laoufi, *et al.*, 2007) . The impact of temperature increase was found not to be very significant for these reactions because although temperature increases result in an increase in the rate constant, there is a corresponding decrease in the adsorption capacity of the TiO₂ (Rideh, *et al.*, 1997). With regards to the final and intermediate products formed, the lack of a thorough reaction mechanism for these reactions has made it difficult to determine. That notwithstanding, several researchers have reported a considerable reduction in the COD (chemical oxygen

demand) of the solution treated. The major drawback of this treatment method has been its efficiency. Serrano & Lasa (1997), have put its ideal efficiency at 28.9%.

2.3.10 Biological Oxidation

According to the principle of microbial infallibility, no natural organic compound is totally resistant to biodegradation provided that the environmental conditions are favourable. Consequently though phenol is very toxic to most bacteria at even very low concentrations, given enough time and the appropriate conditions, they can be degraded by some bacteria. Phenol is known to be degraded by phenol degrading bacteria, fungi or the uses of enzymes (artificial or natural). The bacteria used include *micrococcus spp*, *Nocardia spp*, *Athrobacter spp* (Tibbles & Baecker, 1989), *Bacillus spp*, *Pseudomonas spp*, *Acinetobacter spp* and *Achromobacter spp* (Nair, *et al.*, 2008). The fungi used include *Fusarium spp*, *Phanerocheate chrysosporium*, *Corious ersicolor*, *Ralstonia spp*, and *Streptomyces spp* (Nair, *et al.*, 2008). According to Tibbles and Baecker (1989) the mesophilic phenol-degrading bacteria required about 18 weeks to reduce a 650 ppm phenol containing leachate to 7-13 ppm. It has also been found that the bacteria, *Klebsiella oxytoca* can degrade a 100 ppm phenol solution to 25 ppm in 72 h or 3 days.

The use of enzymes to oxidize phenols is fast gaining popularity as phenol is very toxic to many bacteria. Most of these phenol-degrading bacteria break phenols down by the use of enzymes they produce. Biological oxidation using bacteria is the least expensive of the treatment methods because these bacteria can be easily cultured from sewage sludge. A non exhaustive list of microorganisms known to degrade or oxidize phenols as well as enzymes is presented in Table 2.3.2 and Table 2.3.2

Table 2. 3.1 Microorganisms in the biodegradation of phenolic compounds (Nair, *et al.*, 2008)

Type of phenol	Microorganisms	Type of phenol	Microorganisms
Chloro phenol	<i>Achromobacter sp</i>	Phenol	<i>Ochromonas danica</i>
Phenol	<i>Acinetobacter calcoaceticus</i>	Phenol	<i>Phanerocheate chrysosporium</i>
Phenol	<i>Acinetobacter johnsonii</i>	Phenol	<i>Phormidium valderianum</i>
Phenol	Aerobic consortium	Phenol	<i>Pleurotus ostreatus</i>
Phenol	<i>Agaricus bisporus</i>	2-chlorophenol	<i>Pseudomanas putida</i>
Phenol	<i>Alcaligenes sp</i>	Phenol	<i>Pseudomonas flurorescens</i>
Phenol	<i>Bacillus brevis</i>	Phenol	<i>Pseudomonas pictorium</i>
Phenol	<i>Bacillus stearothermophilus</i>	Phenol	<i>Pseudomonas putida</i>
Phenol	<i>Chalara paradoxa</i>	Chloro phenol	<i>Pseudomonas putida</i>
4. Nonyl phenol	<i>Clavariopsis aquatica</i>	Dichlorophenol	<i>Pseudomonas putida</i>
Phenol	<i>Coprinus cinereus</i>	Phenol	<i>Ralstonia eutropha</i>
Bisphenol A	<i>Coprinus cinereus</i>	Phenol	<i>Rhizoctonia praticola</i>
Phenol	<i>Coriolus versicolor</i>	Phenol	<i>Rhodococcus erythropolis</i>
Phenol	<i>Fusarium sp</i>	Phenol	<i>Sphingomonas chlorophenolica</i>
Penta, chlorophenol	<i>Lentinula edodes</i>	Pentachlorophenol	<i>Streptomyces setonii</i>
Pentachlorophenol	<i>Lentinus bisporous</i>	Phenol	<i>Termitomyces albuminosus</i>
2, 4-dichloro phenol	Mixed culture	Phenol	<i>Trametes trogii</i>
Phenol	Mixed Fungi	Phenol	<i>Trichosporon cutaneum</i>
Phenol, Nitrophenol	<i>Nocardioides</i>		

Table 2. 3.2 Enzymes involved in the biodegradation of phenolic compounds (Nair, *et al.*, 2008)

Type of Phenol	Enzyme	Type of Phenol	Enzyme
Phenol	<i>Catechol 1,2oxygenase</i>	Phenol	<i>Laccase</i>
Phenol	<i>Catechol 2,3 dioxygenase</i>	Bis phenol	<i>Peroxidase</i>
Phenol	<i>Horse radish peroxidase</i>	Lignophenols	<i>Peroxidase</i>
Methoxyphenol	<i>Laccase</i>	Phenol	<i>Peroxidase</i>
		Phenol	<i>Phenol hydroxylase</i>

Type of Phenol	Enzyme
Phenol	<i>Phenol Oxidase</i>
Phenol	<i>Polyphenol Oxidase</i>

Type of Phenol	Enzyme
Phenol	<i>Tyrosinase</i>

The mechanism of biodegradation may be simplified by the following steps:

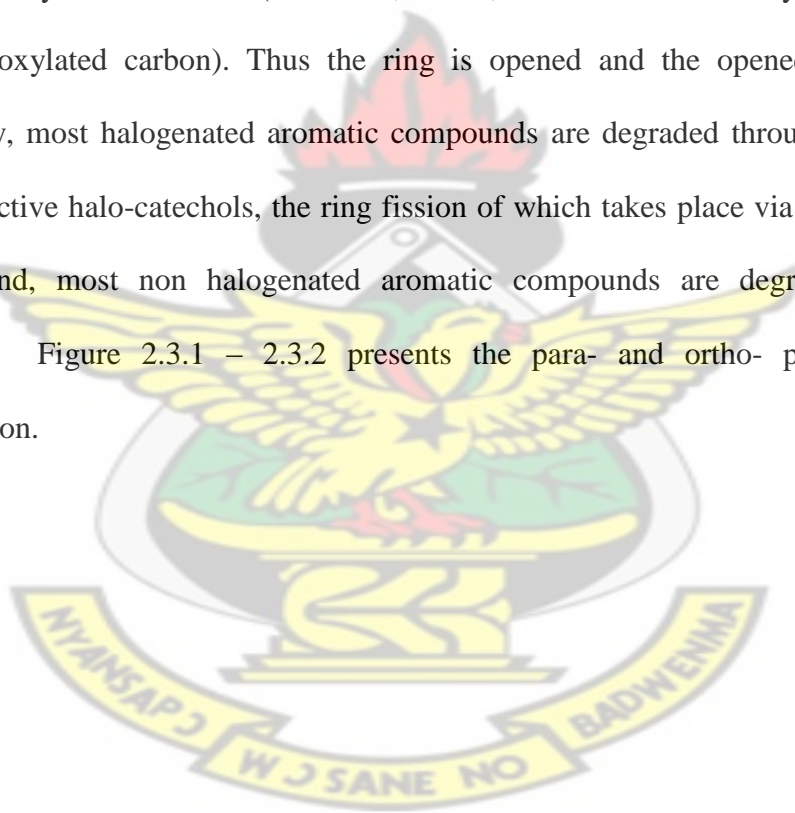
1. Attachment of the microbe to the aromatic ring
2. Activation of the aromatic ring by introduction of hydroxyl groups
3. Enzymatic ring cleavage or fission
4. Transformation of the fission products

The critical step in the oxidation of aromatic compounds is the destruction of the resonance structure by hydroxylation and fission of the benzoid ring which is achieved by *dioxygenase*-catalysed reactions in the aerobic systems (Nair, *et al.*, 2008). Based on the substrate that is attacked by the ring cleaving enzyme *dioxygenase*, the oxidation of the aromatic compound can be grouped as catechol pathway, gentisate pathway, and proto catechaute pathway. In all these pathways, the ring activation by the introduction of hydroxyl groups is followed by the enzymatic ring cleavage. The ring fission products, then undergo transformations leading to the general metabolic pathways of the organisms. Most of the aromatic catabolic pathways converge at catechol. Catechols are formed as intermediates from a vast range of substituted and nonsubstituted mono and poly aromatic compounds.

Aerobically, phenol also is first converted to catechol, and subsequently degraded via ortho- or meta- fission to intermediate of products. The initial ring fission is catalysed by an ortho cleaving enzyme, catechol 1, 2 *dioxygenase* or by a meta cleaving enzyme catechol 2, 3 *dioxygenase*, where the product of ring fission is a cis-muconic acid for the former and 2-

hydro cis muconic semi-aldehyde for the latter. *Streptomyces setonii* (ATCC 39116) degrade aromatic compounds such as phenol or benzoate via an ortho cleavage pathway using catechol 1,2-dioxygenase.

A bacterial strain, *Serratia plymuthica* is able to tolerate phenol up to a concentration of 1050 mg/L. In this case phenol was degraded through ortho pathway and the crude extract showed the presence of ring cleaving enzyme catechol 1, 2-dioxygenase. Catechols are cleaved either by ortho-fission (intra-diol, that is, carbon bond between two hydroxyl groups) or by a meta-fission (extra diol, that is, between one of the hydroxyl groups and a non-hydroxylated carbon). Thus the ring is opened and the opened ring is degraded. Generally, most halogenated aromatic compounds are degraded through the formation of the respective halo-catechols, the ring fission of which takes place via ortho-mode. On the other hand, most non halogenated aromatic compounds are degraded through meta pathway. Figure 2.3.1 – 2.3.2 presents the para- and ortho- pathways of phenol degradation.



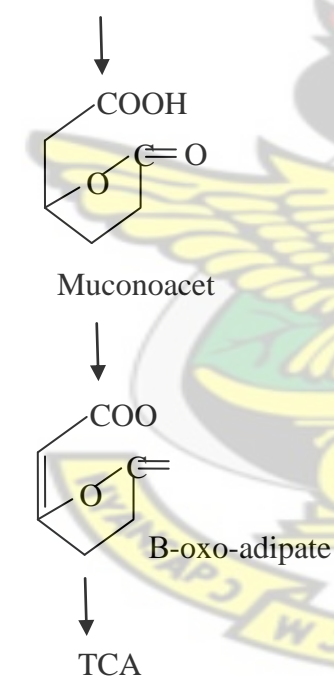
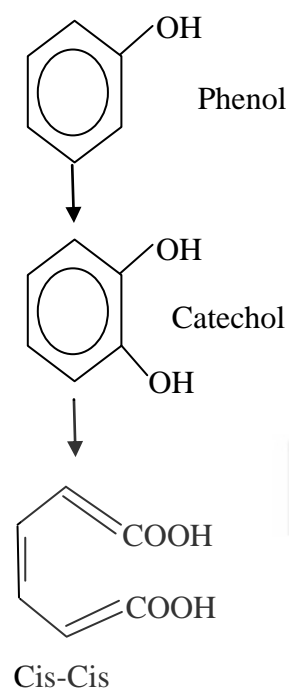


Figure 2. 3. 1 Meta Pathway of phenol degradation

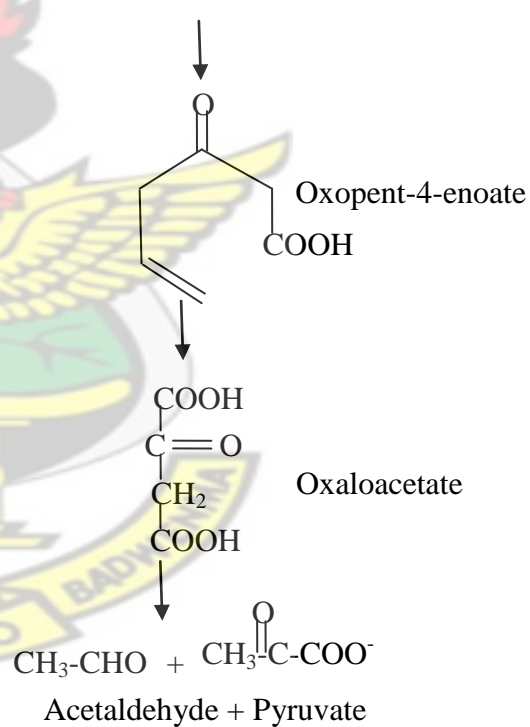
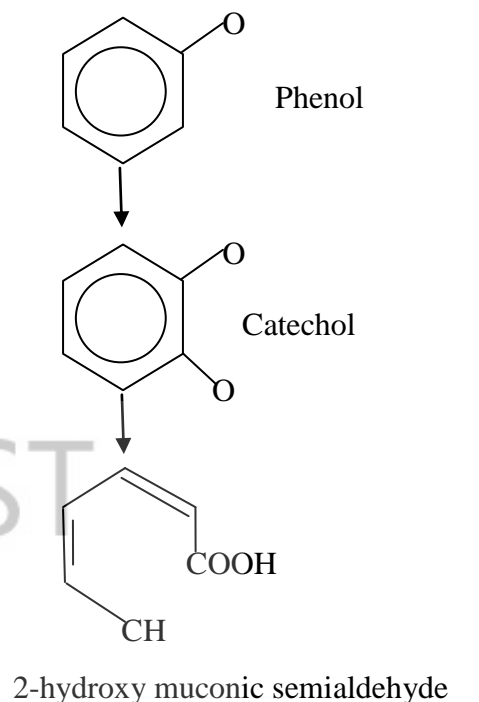


Figure 2. 3. 2 Ortho Pathway of phenol biodegradation

The mechanism of degradation of aromatic compounds is generally dependent on the nature of the organic compound, its solubility, and nature of the organism, type of the enzyme and also by the external factors affecting biodegradation (Nair *et al.*, 2008). In some cases, through the action of *monooxygenase*, aromatic compounds may be converted into gentisic acid. The fission of this compound occurs between the hydroxyl and carboxyl groups, that is, meta fission. It has been shown in some cases that chloroaromatic compounds such as 4-chlorobenzoate, 4-chlorophenol and others may get dechlorinated during the hydroxylation resulting in the formation of 4-hydroxy benzoates (4-HBA).

4 HBA on further hydroxylation will be converted to protocatechuate acid (3,4-dihydroxy benzoic acid), which may be cleaved either through ortho or meta mode.

Several external factors can limit the rate of biodegradation of organic compounds. These factors may include temperature, pH, oxygen content, substrate concentration and physical properties of contaminants. Each of these factors has to be optimized for the selected organism to achieve maximum degradation of the organic compound of choice. Unfortunately for industrial wastewater this optimization is almost impossible because most of these factors fluctuate so badly. These fluctuations could lead to lower phenol degradation or to the destruction of most of these bacteria. These in addition to the slow nature of biological oxidation are the major limitations associated with this method of phenol oxidation. Usually biological oxidation alone does not result in complete mineralization, unless given sufficiently long period.

2.3.11 Electrochemical Oxidation

Electrochemical oxidation of organic compounds involves the use of an electrolytic cell to facilitate the oxidation of the compound. The relevant reactions occur at the anode which is usually made of graphite (carbon) although the use of oxide anodes is becoming popular, (Allen, 1995)

Depending on the type of electrolyte used and the applied voltage, several radicals as well as oxidizing species may be produced which ultimately lead to the oxidation of the organic compound. Example, when chloride containing compounds are used as electrolytes, hypochlorite is produced at the anode which in turn oxidizes the organic compound. However, the use of chloride containing electrolytes also presents another environmental problem. Under such conditions, chlorophenols, which may be more toxic than the original phenols may even be produced if the applied voltage is strong enough. Despite the limitation associated with the use of chloride containing electrolytes, they are still used because the concentration of the organic compound in the wastewater is not very high and so with a well stirred reactor, the formed hypochlorite can move from the surface of the anode into the bulk solution to effect the oxidation of more dissolved organic compounds (Allen, 1995; Uğurlu, *et al.*, 2006). The electrolytes used include magnesium chloride, calcium chloride, potassium chloride and sodium chloride. Magnesium chloride gives the best result whiles sodium chloride gives the least results according to Allen (1995).

Air is sometimes admitted into the system to facilitate the oxidation (Uğurlu, *et al.*, 2006). Better results are achieved when hydrogen peroxide or hydroperoxide is used instead of air. The use of activated carbon slurry as a working electrode in a three-phase three-dimensional reactor, has also been suggested for waste water with low phenol

concentration. In this case, the activated carbon adsorbs the phenols (Uğurlu, *et al.*, 2006) and thus concentrates them on its surface. The concentration of electrolyte used for these reactions does not really affect the rate at which the reaction proceeds but rather reduces the over voltage required to accomplish the reaction. The rate of the reaction rather increases with increase in the acidity of the solution.

Electrochemical oxidation of phenols usually does not result in complete mineralization. Aside this limitation, the use of electrolytes makes this oxidation method not very environmentally friendly.

In the forgoing studies, there is little evidence in the literature about the complete mineralization or break down of phenols into carbon dioxide and water.

2 . 4 Adsorption of Phenols from Aqueous Solutions

To achieve a significant adsorptive capacity an adsorbent must have a high specific area, which implies a highly porous structure with very small micropores. In addition it must have a preferential affinity or selectivity for the adsorbate. The selectivity of the asorbent during a physical adsorption is largely equilibrium dependent.

According to the literature, of the many different type of adsorbents there are, only two of them can be effective in concentrating dissolved organic compounds from dilute aqueous solutions. These are activated carbon (Buscaa, *et al.*, 2008) and silicalites (*low aluminmun zeolite*) (Ruthven, 1998). These adsorbents are useful in this regard because of their

hydrophobic nature. It must also be noted that activated carbon can be made very hydrophilic by introducing surface oxide groups on it.

2.4.1 Characteristics of Activated Carbon

Activated carbon is a predominantly amorphous solid that has an extraordinarily large internal surface area and pore volume (Baker, *et al.*, 1998). These unique characteristics are responsible for its adsorptive properties which are exploited in many different liquid- and gas phase applications. Through the choice of precursor, method of activation and control of processing conditions, the adsorptive properties of the products are tailored for various applications.

The structure of activated carbon is best described as a twisted network of defective carbon layer planes, cross-linked by aliphatic bridging groups. X-ray diffraction patterns of activated carbon reveal that it is nongraphitic, remaining amorphous because the randomly cross-linked network inhibits reordering of the structure even when heated at 3000°C. This property of activated carbon contributes to its most unique feature, namely, the highly developed and accessible internal pore structure.

Typical commercial activated carbon has a surface area ranging between 500-2000 m²/g, even though higher surface areas of between 3500-5000 m²/g are possible. (Baker, *et al.*, 1998)

Adsorption by activated carbon is not only dependent on the internal surface area and pore size distribution but also on the surface chemistry of the activated carbon. Functional groups are formed on the surface of the activated carbon during activation by interaction of

free radical on the carbon surface with atoms such as oxygen and nitrogen, both from within the precursors and from the atmosphere. The functional groups render the surface of the activated carbon chemically reactive and influence its adsorptive properties. Activated carbon is generally considered to exhibit a low affinity for water, which is important with respect to the adsorption of gases in the presence of moisture. However functional groups on the carbon surface can interact with water, rendering the carbon surface more hydrophilic. The electrokinetic properties of an activated carbon comes in handy when it is used as a catalyst support as it contributes to its reactivity.

Activated carbon for use in liquid-phase application differs from gas-phase carbons primarily in pore size distribution. Liquid phase carbons have significantly more pore volume in the macropore range, which permits liquid to diffuse more rapidly into the mesopores and micropores. The larger pores also promote greater adsorption of large molecules, either impurities or products, in many liquid-phase applications.

Activated carbon used for liquid-phase applications are usually in the form of powder, granules or shaped forms. The average size of the powdered carbon particles is between 15-25 μm . Granular or shaped carbon particle size is usually between 0.3-3.0 mm. A significant factor in choosing between powdered and non-powdered activated carbon is the degree of purification required in the adsorption application.

2.4.2 Characteristic of Zeolites

Zeolites are by far the best stable molecular sieves. There are 34 known natural zeolites and about 100 zeolites which do not have natural counterparts (Gates, *et al.*, 1979, K \ddot{u} hl &

Kresge, 1998). Of this large number of zeolites only a few have commercial application; they are mostly synthetic zeolites and synthetic analogous of natural zeolites.

Zeolites refer to a group of aluminosilicate crystals in which the basic unit is a tetrahedron of oxygen surrounding either an aluminum or silicon cation.



Figure 2. 4. 1 Basic units of zeolite

Each silicon ion has its +4 charge balanced by a tetrahedral oxygen (*each contributing an electron*) thus, the silica tetrahedra are therefore electrically neutral. Each alumina tetrahedron has a residual charge of -1 since the trivalent aluminum ion is bonded to four oxygen anions each contributing an electron. Therefore each aluminum tetrahedron requires a +1 charge from a cation in the structure to maintain electrical neutrality. These cations are usually sodium in the zeolite as it is initially prepared, but can be readily be replaced by ions exchange. Ion exchange represents the most direct and useful method for the alteration of zeolite properties.

The silica and the alumina tetrahedra are combined into more complicated secondary units, which form the building blocks of the framework zeolite crystal structures. The unit cell of zeolite can be simplified as $M_{j/n}(AlO_2)_j(SiO_2)_y \cdot zH_2O$ where M represents the exchangeable

cation and j , y , and z are integers. The n is the oxidation state of the exchangeable cation. The catalytic as well as the adsorptive properties of zeolites can be controlled by altering these values. When the ratio $\frac{y}{j}$ increases, the zeolite becomes more stable as well as become more hydrophobic (Crittenden & Thomas, 1998).

The tetrahedra are arranged so that zeolites have an open framework structure, which defines a pore structure with a high surface area. This surface area is different from that of amorphous solids such as silica-alumina in that it is a true part of the crystalline solid and not the area of termination of the primary particles of the solid. Therefore the chemistry of the zeolite surface is determined uniquely by the properties of the crystalline solid, which is a major advantage in elucidating the catalytic chemistry.

In all zeolites pore diameters are determined by free aperture resulting from 4-, 6-, 8-, 10- or 12-membered rings of oxygen atoms and these have maximum values calculated to be 2.6 Å, 3.6 Å, 4.2 Å, 6.3 Å and 7.4 Å respectively.

Only zeolites with 8- and 12-membered oxygen have found major catalytic applications (Gates, *et al.*, 1979). The smaller apertures place unacceptable size limitations on the molecules to be adsorbed. The zeolites of industrial importance are zeolites A, X, Y, erionite and synthetic mordenite.

Zeolites are high capacity, selective adsorbents capable of separating molecules based on the size and the shape of the molecules relative to the size and geometry of the main apertures of the structure. They adsorb molecules, in particular those with a permanent dipole moment which show other interaction effects, with selectivity that is not found in

other solid adsorbents. Separation may be based on the molecular-sieve effect or may involve the preferential or selective adsorption of one molecular species over another. These separations are governed by several factors. These include the following:

1. The basic framework structure, or topology of the zeolite
2. The specific location of the exchanged cation in the structure
3. The number of exchanged cations per unit cell
4. The charge on the exchanged cation
5. The size of the exchanged cations.

Thus by controlling the exchanged cation the selectivity of the zeolite in a given separation can be tailored.

2.4.3 Adsorption of Phenols from Wastewater

Activated carbon is the most widely used adsorbent for this purpose due to its high capacity (Buscaa, *et al.*, 2008). However, activated carbon is considerably expensive and its regeneration is also very expensive, (Lin & Juang, 2009). These limitations associated with it make it economically not the first choice for wastewater treatment industrially.

As a result various materials have been considered as adsorbent for the adsorption of phenols from wastewater. Lin and Juang (2009) have provided a comprehensive lists of the various materials that have been tested. The list includes various activated carbons, synthetic resins, coal adsorbent or chars, red mud, bagase fly ash, coal fly ash, waste sludge adsorbents and various clay or metallic adsorbents. They also evaluated the various

adsorbents for specific phenol derivatives. However the theory of adsorption for these materials has not been presented.

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Chapter 3

Materials and Methods

3.1 Materials

One of the objectives of this study was to identify or develop an adsorbent - catalyst matrix (*i.e., an adsorbent with catalytic properties*) which would be suitable for oxidizing phenols in the liquid phase.

The adsorbents considered for the study include the spent and fresh catalyst from the *fluidized catalytic cracking* (FCC) process and granulated activated carbon. The spent catalyst for all the experiments conducted was obtained from the RFCC (Residual Fuel Catalytic Cracker) plant of Tema Oil Refinery. The fresh catalyst was a NEKTOR – 876G, manufactured by GRACE Davison.

The selection of the waste FCC catalyst was based on the fact that it is a zeolite based material with catalytic properties. To determine its suitability, it was necessary to characterize it. The parameters measured include chemical composition, physical characteristics such as specific surface area, pore volume, and particle size distribution and the zeta potential. In addition, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray spectroscopy (EDX) analyses were also performed, to determine other surface morphological properties.

3.1.1 Fresh and Spent FCC Catalyst

The catalyst used for the *Fluidized Catalytic Cracking* (FCC) process is basically a mixture of zeolite Y and a co-gelled mixture of silica and alumina, known simply as silica – alumina, (Gates, *et al.*, 1979; Gates, 1998; Sadeghbeigi, 2000). The proportion of the zeolite is, however, proprietary but has a minimum of 3% and a maximum of 25%. The main component of the catalyst is the zeolite Y but a catalyst made completely of it is far too active for the FCC process.

3.1.2 Activated Carbon

The Activated Carbon (AC) used was analytical grade granulated activated carbon manufactured by BDH chemicals. Before using it was ground in a mortar so that it could pass through a 1 mm mesh size sieve.

3.1.3 Phenol

There were two main sources of phenol used. These were analytical grade phenol manufactured by BDH Chemicals and phenol from the stripped sour water from the Tema Oil Refinery (TOR). It is worth noting that the phenol from the stripped sour water contains other forms of phenol in addition to the basic phenol, (Short, *et al.*, 1974) .

3.1.4 Other Materials

All other reagents used were all of analytical grade. Deionized water was used wherever water was required. The granite chipping used for the packing of the reactor were less than

1 cm in size and were thoroughly washed (*using pipe born water*) and dried before usage. The sea sand used for the control experiment was also washed (*using pipe born water*) thoroughly and dried before usage.

3.2 Methodology and Experimental Procedures

3.2.1 Determination of Phenol in Solution

The phenol concentration was determined according to EPA Method 9065 or ASTM D1783 - 01(2007) Standard Test Methods for Phenolic Compounds in Water.

A known volume of the phenol solution was diluted to 100 ml and transferred into a conical flask. Six ml of ammonium buffer ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) was added to the solution to adjust the pH to between 9.8 – 10.2. Two ml of a 20 g/L solution of 4-Aminoantipyrine was then added and stirred. Two ml of an 80 g/L solution of potassium ferric cyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) solution was added and stirred. The presence of phenol is indicated by a blood-red color. After 15 min of reaction time, the exact concentration of the phenol was determined using a SHIMADZU UV-1601 UV-Visible spectrophotometer using a wave length of 510 nm.

3.2.2 Gas Chromatographic (GC) Analyses

For the gas chromatographic analyses an *Agilent Technologies, 6890N Network GC system* model was used. The GC was fitted with an *HP – 5 Agilent* column and a Flame Ionization Detector (FID). In each case 4 μL of the sample was injected into the GC and allowed to run for about 26 min. The following were the details of the GC settings.

1. Set Point Temperature = 80°C
2. Programmed Temperature = 250°C
3. Set Point Pressure = 247 kPa

Under the conditions the retention time for phenol was between 6.7 – 7.3 min.

3 .2.3 Chemical Oxygen Demand (COD) Determination

Chemical oxygen demand (COD) was used to determine the level of oxidation of the phenols in the solution.

Two ml of the sample was pipetted into a 15000 ppm - HACH COD reagent and agitated until a uniform solution was obtained. The resulting solution was placed in a HACH COD reactor maintained at 120°C for 2 h after which the samples were cooled to room temperature. The COD of the samples were then determined using a *HACH Portable Data Logging Spectrometer*, model RS232 using the COD HR programme, (HACH, 2005).

3 . 3 Characterization of the Spent FCC Catalyst

3 .3.1 Physical Characterization

The physical parameters considered were the surface area, pore volume and particle size distribution.

The surface area and pore volume were determined based on the UOP (Universal Oil Product) method 425-86 which is based on the BET theory of multilayer adsorption of a gas by an adsorbent. The gas used was nitrogen. The surface area of the spent catalyst was

determined by measuring the volume of nitrogen gas adsorbed at liquid nitrogen temperature and relative pressures of $\frac{60 \text{ mmHg}}{760 \text{ mmHg}}$ and $\frac{160 \text{ mmHg}}{760 \text{ mmHg}}$ and applying the BET theory. The pore volume was determined by measuring the amount of gaseous nitrogen condensed in the pores at liquid nitrogen temperature and at a relative pressure of $\frac{735 \text{ mmHg}}{760 \text{ mmHg}}$.

The particle size distribution of the spent catalyst was determined by sieving. The mesh sizes of the sieves used were 20 μm , 40 μm , 80 μm , 105 μm and 149 μm . The stack of sieves was agitated by an electronic agitator.

3.3.2 Zeta Potential

To determine the zeta potential 0.5 g of the catalyst was added to 20 ml of ultra pure water and the resulting suspension placed in an ultrasonic bath for 5 min, after which the zeta potential was determined with a ZetaPlus, Brookhaven machine. Ten runs were made per minute.

Owing to the larger particle size of the spent catalyst its zeta potential could not be determined as the particles settled too quickly. Consequently only the zeta potential of the fresh catalyst was determined.

3.3.3 Chemical Characterization

The chemical characterization involved the determination of the metal and carbon composition of the spent catalyst.

The carbon content determination was based on the UOP method 703 – 98. Thus, a known amount of the spent catalyst was weighed into a ceramic crucible and placed in a high frequency induction furnace maintained at a temperature above 1000°C. The amount of CO₂ is determined using a solid state infrared detector and the carbon content is thus inferred.

The procedure for determining the metal composition of the spent catalyst was based on the UOP method 546-90. Thus, a known amount of the spent catalyst was placed in a furnace maintained at a temperature above 1000°C to burn off the carbon deposited on it. It was then dissolved in a solution of sulphuric acid (or perchloric acid) and hydrofluoric acid. The resulting solution was then aspirated into an Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP - AES) instrument which then determines the metal concentration using the appropriate standards.

3.3.4 Leaching Test

These tests were conducted to determine the mobility of the metals components on the spent catalyst in basic, acidic and neutral solutions. The experimental setup consisted of a 500 ml beaker placed on magnetic stirrer into which 200 ml of various concentrations of acidic and basic solutions were added. Ten grams of spent catalyst (*De-coked Spent Catalyst*) was added to the solution. The suspension was then stirred for 5 min and allowed to stand still for 1 minute. 7.5 ml of the resulting solution was pipetted after which the process was repeated. The process was repeated 9 times, thus the entire experiment lasted 50 min. The pH of each of the pipetted solution was determined using a pH meter whiles the concentrations of the dissolved metals was determined using an Inductively Coupled

Plasma (ICP) spectrometer. In these experiments 0.01 M, 0.0032 M and 0.001 M NaOH solutions were used as the basic media while 0.01 M, 0.0032 M, 0.001 M HCl solutions were used as the acidic media. In addition deionized water (pH = 6.18) was used as the neutral solution.

3.4 Adsorption Tests

3.4.1 Phenol Break through Curves for the Spent Catalyst

The experimental setup consisted of a 30 cm long column with internal diameter of 4.9 cm which was plugged with 0.86 g cotton wool at the bottom. The bottom was plugged in such a way as to make it act as a solution filter, that is, admit only the treated solution. The phenol solution was dispensed with a separating funnel. The column was packed to a height of 20 cm with the spent catalyst (*300 g of De-coked*). Before the phenol solutions were administered into the column, 300 ml of deionized water was passed through the bed to remove all water soluble compounds adsorbed on the spent catalyst and to wet the surface of the particles, fill the pores between the catalyst particles and remove all trapped air in the column.

After preliminary trials were made on the adsorption column solutions containing 1500 ppm, 2500 ppm and 3500 ppm of phenol similar to concentrations in process wastewater were prepared from analytical grade phenol and used as influent concentration.

The solutions were allowed to percolate through the column by gravity. Filtrate samples were taken every 2 min and their phenol concentrations determined.

3 .4.2 Comparison of Phenol Adsorption Capacities of the Spent FCC Catalyst and Activated Carbon

The experimental setup was as in section 3 .4.1. The spent catalyst required 300 g to attain a height of 20 cm while the Activated Carbon required 100 g to attain the same height. Before the phenol solutions were administered into the column 300 ml of deionized water was passed through the bed to remove all trapped air in the column. Filtrate samples were taken every 2 min and their phenol concentrations determined.

3 .4.3 Effect of Thermal Pre-treatment of the Spent Catalyst on Phenol Adsorption

In order to determine the effect of thermal pre-treatment on the adsorptive properties of the spent catalyst, samples of the spent catalyst were heat-treated at different temperatures and cooled before used for the adsorption tests. This test was necessary to determine whether the spent catalyst would retain its adsorptive capacity when the phenol adsorbed onto it is burnt away during regeneration. The mass of the heat-treated spent catalyst used for each of the adsorption test was 200 g. The thermal pre-treatment involved placing 500 g of the spent catalyst in a furnace maintained at a constant temperature for an hour. The pre-treatment temperatures considered were 300°C, 500°C and 700°C. In addition, a similar experiment was conducted using fresh FCC catalyst (*without thermal treatment*). 300 ml of deionized water was passed through the bed to condition it as in section 3.4.1. Two samples of the wastewater were taken at different times from the *Dissolved Air Floatation (DAF)* unit of the Tema Oil Refinery and used as the phenol solution. The phenol

concentration of the wastewater samples were 544.4 ppm and 620.5 ppm. Filtrate samples were taken every 20 min and their phenol concentrations determined.

3.4.4 Effect of Acid and Base Washings on the Phenol Adsorption Capacity of the Spent Catalyst

These tests were conducted to determine whether the adsorption capacity of the spent catalyst would be altered by washing off the metals adsorbed on its surface. The washing process involved soaking 500 g of the spent catalyst in 1000 ml of a mild acidic solution, neutral solution or basic solution for an hour, after which the solution was drained off and the paste-like spent catalyst air dried under normal laboratory conditions for 24 h on a flat tray. In this experiment a 0.001M HCl solution was used as the mild acidic solution while a 0.001M NaOH solution was used as the mild basic solution. Deionized water (pH =6.18) was used as an approximately neutral solution. For each of the experiments 200g of the washed spent catalyst was used. Two samples of wastewater were taken at different times from the *Dissolved Air Flootation (DAF)* unit of the Tema Oil Refinery and used as the phenol solution. The phenol concentration of the wastewater samples were 648.65 ppm and 653 ppm. Filtrate samples were taken every 20 min and their phenol concentrations determined.

3.4.5 Determination of Equilibrium Adsorption Capacity

The experimental setup consisted of a 500 ml beaker placed on a magnetic stirrer. Ten grams of the spent catalyst was put in the beaker and 250 ml of a solution of known phenol

concentration was added and stirred gently for a period of 9 min. After the 9 min, the suspension was made to stand for 1 minute and 2 ml of the solution was pipetted and its phenol concentration determined with a UV spectrometer. The process was repeated continuously for 2 h. The phenol concentration used for these experiments were 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm, 2500 ppm and 3000 ppm.

3.4.6 Effect of Thermal Pre-treatment on Phenol Adsorption Capacity at Equilibrium

The effect of thermal pre-treatment on the equilibrium adsorption capacity was determined by heating 250 g of the spent catalyst in a furnace maintained at constant temperatures of 400°C, 500°C, 600°C and 800°C for an hour after which it was cooled. Ten grams of the spent catalyst was then used as before. The phenol concentration of the solution used was 1500 ppm.

3.5 Phenol Oxidation Tests

3.5.1 Catalyst Preparations

The spent FCC catalyst was modified by impregnating them with three main metal oxides, namely:

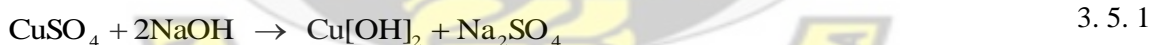
1. Cupper(II) Oxide (CuO)
2. Iron(II) Oxide (Fe_2O_3)
3. Manganese(IV) Oxide (MnO_2)

The general procedure for the impregnation involved producing the metal hydroxide on the spent FCC catalyst and calcining the result, (Nielsen, 1998).

3.5.2 Preparation of CuO impregnated Catalyst

12.82 g of anhydrous CuSO_4 was dissolved in 200 ml of deionized water. 6.63 g NaOH was dissolved in 100 ml of deionized water. The resulting NaOH solution was then added to the CuSO_4 solution thereby precipitating $\text{Cu}[\text{OH}]_2$ out. The suspension produced was then added to 245 g of the spent FCC catalyst and the mixture stirred thoroughly until a uniform slurry was formed. The spent-catalyst- $\text{Cu}[\text{OH}]_2$ slurry was then placed on a hot plate maintained at 300°C and continuously stirred until partially dried. The partially dried catalyst was then placed in a furnace maintained at 350°C for 2 h. The expected Cu^{2+} / spent catalyst ratio was 2.08% (not counting the amount of Cu already on the spent catalyst) and that of the CuO / spent catalyst was 2.61%.

The relevant reactions are, (Richardson, 1998; Patnaik, 2003):



3.5.3 Preparation of Fe_2O_3 impregnated Catalyst

16.104 g $\text{FeNH}_4[\text{SO}_4]_2$ was dissolved in 500 ml of deionized water. 9.687 g of NaOH was dissolved in 200 ml of deionized water. The NaOH solution was then added to the $\text{FeNH}_4[\text{SO}_4]_2$ solution thereby precipitating out $\text{Fe}(\text{OH})_3$. The suspension was then added to

500 g of the spent catalyst and the mixture stirred continuously until a uniform slurry was obtained. The spent – catalyst – FeHO_2 slurry was then placed on a hot plate maintained at 300°C and stirred until it was partially dried. The partially dried catalyst was then placed in a furnace maintained at 350°C for 2 h.

The relevant reactions are, (Stolzenberg, 1998; Patnaik, 2003):

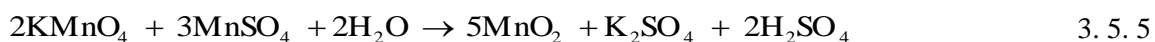


There were three other Fe_2O_3 concentrations considered using the same procedure, giving amounts of 1.43%, 3.57% and 7.14% of the Fe_2O_3 on the spent catalyst.

3.5.4 Preparation of MnO_2 impregnated Catalyst

In the case of MnO_2 , 3.45 g of KMnO_4 was dissolved in 100 ml of deionized water. Five grams of MnSO_4 was dissolved in 200 ml of deionized water. The MnSO_4 solution was added to 300 g of the spent catalyst and the mixture stirred continuously until a uniform slurry was obtained. The KMnO_4 solution was then added to the spent catalyst slurry and stirred until a uniform slurry was obtained. The slurry was placed on a hot plate maintained at 300°C and stirred continuously until it was partially dried. The partially dried catalyst was placed in a furnace maintained at 350°C for 2 h.

The relevant reactions are, (Patnaik, 2003)



3.5.5 Reactor Design and Setup

In the design of the reactor for the phenol oxidation for the purpose of these experiments, the following were considered:

1. The reactor must hold the adsorbent – catalyst in a way so as to promote the efficiency of the process.
2. It should make it possible for the introduction of air into the column
3. It should be possible to introduce heat into the column.

Accordingly, a tube reactor 250 mm long with internal diameter of 25 mm which was placed in a heating mantle was used. The details of the setup are shown in Figure 3. 5. 1

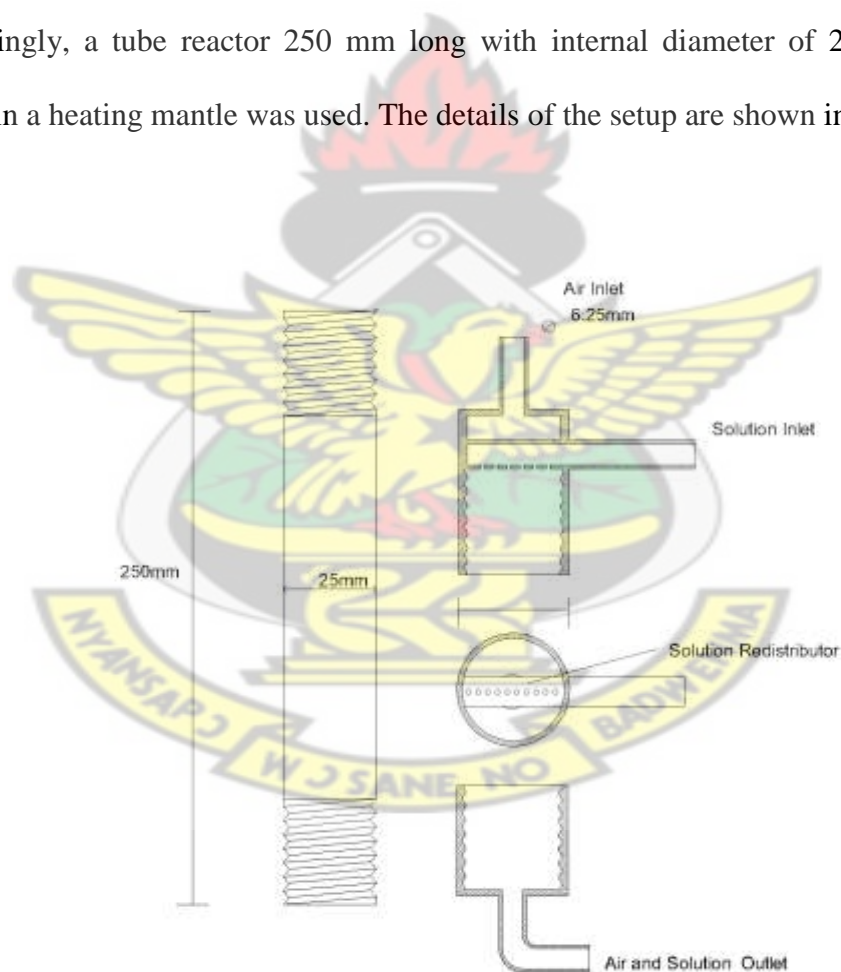


Figure 3. 5. 1 Schematic View of the Tube Reactor

3.5.6 Heating Mantle Design

The heating mantle casing was from steel plates and was lined with 10 mm thick leather dried clay, after which it was carefully lined with a total of 800 mm long heating element with a maximum capacity of 800 watt using plastic wet clay as adhesive so that the heating element formed one complete loop. The clay lining was then allowed to dry to a bone dried state under an electric fan. The entire casing was fired gently until the clay become brick red. The ends of the heating elements were then connected to an external circuit box fitted with a thermostat. The heating mantle after testing had a maximum internal temperature of 100°C and an effluent temperature of 50°C.

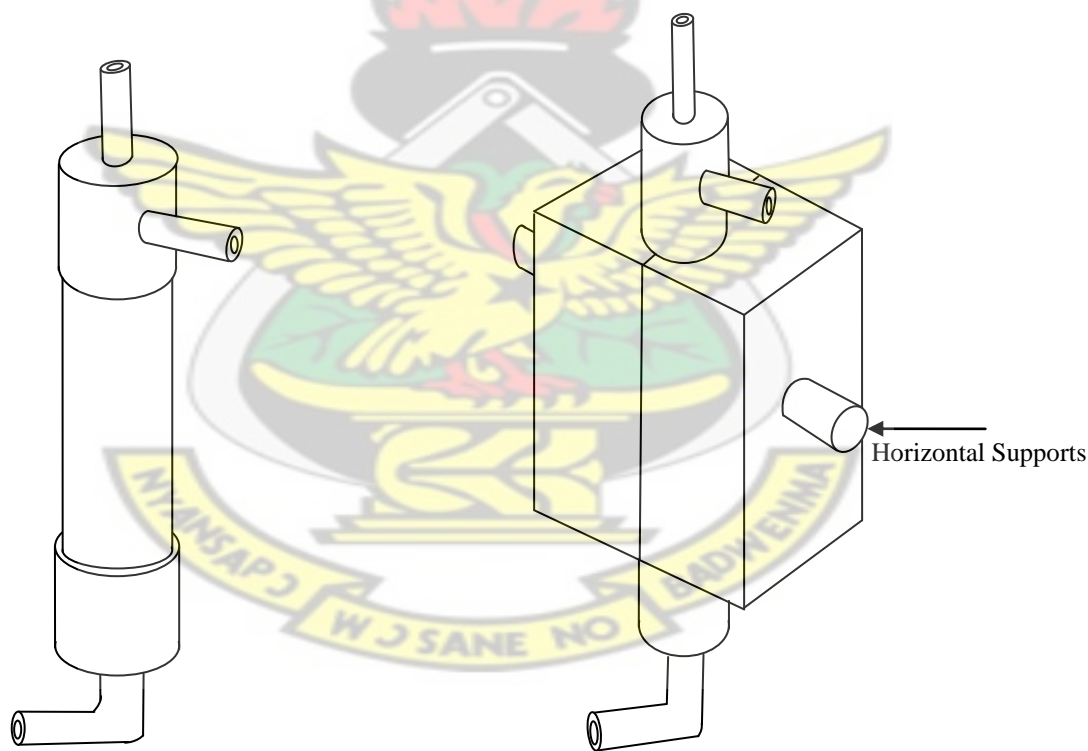


Figure 3. 5. 2 Sketch of assembled Tube Reactor (a) and with heating mantle (b)



Figure 3. 5. 3 Color Plate of Experimental Setup

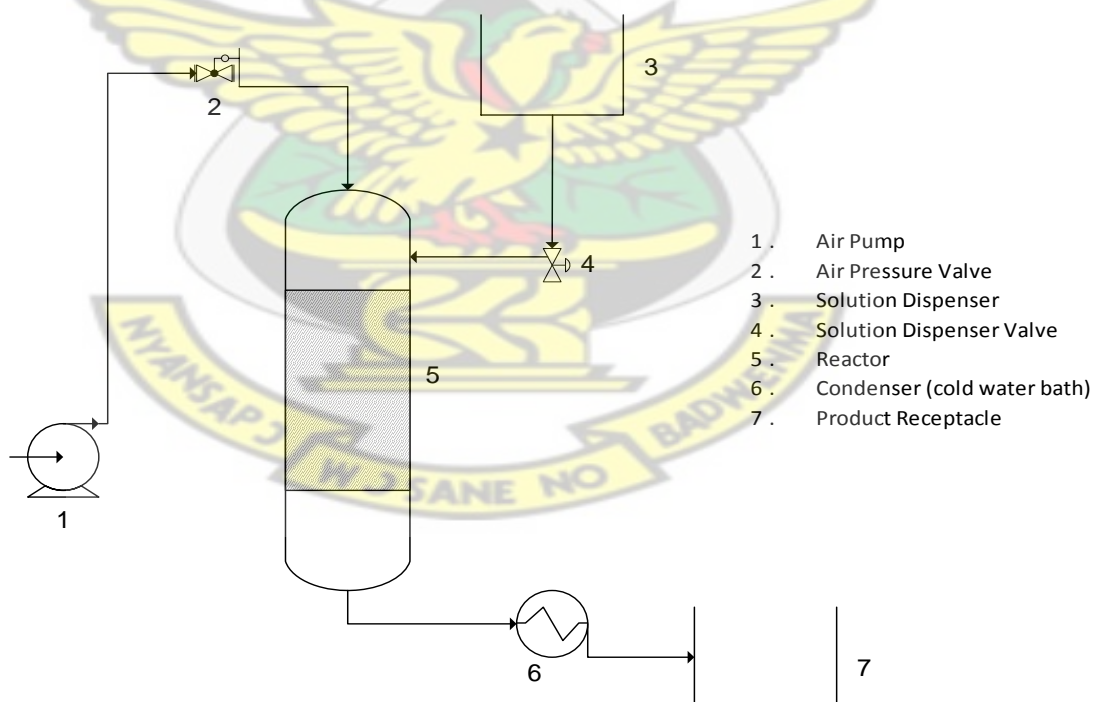


Figure 3. 5. 4 Schematic View of Experimental Setup in Use

3.5.7 Initial Tests to Determine Conditions of Oxidation

According to Cullis (1967), there is considerable similarity between the homogeneous catalysis and heterogeneous catalysis. Thus the performance of the insoluble metal oxides catalysts is somehow dependent on how well they would perform if they were soluble ions. Thus before the spent catalyst was impregnated with the metal oxides, soluble salts of the metals were introduced in minute quantities into the phenol solution and their catalytic performance evaluated. Preliminary trials revealed that without a radical initiator there was no noticeable amount of oxidation that can be achieved with the spent catalyst even in its modified form. This observation was consistent with the work of Santos *et al.* (2007). Consequently, small amounts of hydrogen peroxide were introduced into the phenol solution. In addition, preliminary experiments were also conducted in which the phenol solution was made basic (*pH 10*) by the addition of NaOH solution to ensure that the phenolate ion, which is easily oxidized compared with the phenol itself, is released, (Steenken and Neta, 2003). The results did not show any significant improvement in performance. Consequently, the pH of the phenol solutions used were not altered.

3.5.8 Effect of Cu^{2+} and Fe^{3+} Ions on the Liquid Phase Oxidation of Phenol Using Unmodified Spent Catalyst

The base of the reactor was plugged with 2.6 g of glass wool, after which it was packed with alternating layers of unmodified spent catalyst and granite chippings (*particle size between 5 – 10 mm*). Each layer of the unmodified spent catalyst was 5 g and that of the granite chippings was 17 g. Thus in total 25 g and 68 g of the unmodified spent catalyst and granite chippings respectively were used. *The use of the granite chippings was primarily to*

reduce channeling and the effect of compaction of the spent catalyst by the air. The reactor was then placed in the heating mantle maintained at 100°C for 30 min to ensure that the reactor was brought to an even temperature as the heating mantle.

150 mg of Cu^{2+} and Fe^{2+} were added in separate runs to 1L of a 1000 ppm phenol solution and swirled to obtain a uniform solution. Ten ml of a 50% H_2O_2 solution was added to the resulting solution and allowed a reaction time of 30 min. Samples were then taken for GC and COD analysis after which the solution was fed into the reactor as shown in Figure 3. 5.

4. Effluent samples from the reactor were taken every 30 minutes for analysis. The air pressure was maintained at 0.4 cmHg (533 Pa). After 2 h the solution flow was turned off and only air admitted into the reactor for an hour after which the solution was readmitted. This on and off procedure was done three times to complete an experiment. Thus in total each experiment lasted 9 h.

3.5.9 Effect of Cu^{2+} Ions Concentration on the Liquid Phase Oxidation of Phenol Using CuO Impregnated Spent Catalyst

In order to determine the effect of Cu^{2+} concentration on the liquid phase oxidation of phenols 25g of CuO impregnated spent catalyst was used as in the previous section. In addition, 100, 150 and 200 mg of Cu^{2+} were added in separate runs to 1L of a 1000 ppm phenol solution and the procedure repeated as in the previous section.

3 .5.10 Control Experiment with sand instead of spent catalyst

In order to find out the effect of the spent catalyst on the liquid phase oxidation of the phenol catalyzed by soluble transition metal ions, a control experiment was conducted in which instead of the spent catalyst, thoroughly washed and dried sea sand was used as the packing material. Below are the details of the experiment procedure.

The reactor was packed with 120 g of thoroughly washed and dried sea sand. 150 mg of Cu^{2+} was added to 1L of a 1000 ppm phenol solution and swirled to obtain a uniform solution. Ten ml of a 50% H_2O_2 solution was added to the resulting solution and allowed a reaction time of 30 min and procedure repeated as before.

3 .5.11 Effect of Fe_2O_3 Content on the Liquid Phase Oxidation of Phenol Using Spent Catalyst Impregnated With Fe_2O_3

In order to determine the effect of the amount of Fe_2O_3 on the phenol oxidation, 25 g of the spent catalyst impregnated with various amounts of Fe_2O_3 was used in separate runs in this section. Known amounts of a 50% H_2O_2 solution was added to 1L of a 1000 ppm phenol solution and the procedure repeated as before. The amounts of Fe_2O_3 considered were 0.97, 1.43, 3.57 and 7.4% while 10 ml and 20 ml of the H_2O_2 solutions were used.

3 .5.12 Effect of H_2O_2 Content on the Liquid Phase Oxidation of Phenol Using Spent Catalyst Impregnated With 2.58% CuO and 1.58% MnO_2

This experiment was conducted to determine the effect of hydrogen peroxide content on phenol oxidation using spent catalyst impregnated with 2.58% CuO and 1.58% MnO_2 . In each run, 25 g of the oxide impregnated spent catalyst was used. Known amounts of a 50% H_2O_2 solution were added to 1L of a 1000 ppm phenol solution and the procedure repeated as before. The amounts of H_2O_2 considered were 10 ml and 20 ml.

3 .5.13 Control Experiment Using Unmodified Spent Catalyst

In order to find out the effect of the metal oxide on the liquid phase oxidation of phenol, a control experiment was conducted in which only unmodified spent catalyst was used and procedure repeated as before.

3 .5.14 Wastewater (*stripped sour water*) treatment using the spent catalyst modified with 0.97% Fe_2O_3

After initial tests with solutions prepared with analytical grade phenol, tests were conducted with a refinery wastewater stream (*stripped sour water*). The experimental setup was as before. 20, 30 and 50 ml of 50% H_2O_2 solution were added to 800 ml of *stripped sour water* from a refinery. In each case 25 g of Fe_2O_3 -impregnated spent catalyst was used.

Chapter 4

Results

Table 4. 1.1 Abbreviation

ΔVol	Volume of solution collected within the sampling period of 30 min, ml
C_1/C_0	Ratio of the initial phenol concentration to the filtrate phenol concentration
EPC	Effluent Phenol Concentration , ppm
MPRS	Mass of Phenol Removed from Sample, g
ND	Not Detected
NMPA	Normalized Mass of Phenol Adsorbed, g/g
PAP	GC Peak Area of Phenol
ST	Sampling Time, min
TCV	Total Cumulative Volume of filtrate, ml
Temp.	Temperature of the solution, °C
TMPA	Total Mass of Phenol Adsorbed, g
TMPR	Total Mass of Phenol Removed, g
TMUP	Total Mass of Untreated Phenol, g
TVPS	Total Volume of Phenol Solution, ml
ΔPAC	Change in Phenol Adsorption Capacity

4.2 Characterization of the Fresh and Spent FCC catalyst

4.2.1 Physical Characterization

The results of the morphological analysis are presented in Table 4.2.1

Table 4. 2.1 Physical Properties of the Fresh and Spent FCC Catalyst

Property	Fresh Catalyst	Spent Catalyst
Total Surface Area, m ² /g	300	113
Pore Volume, cm ³ /g	0.4	0.9

Property	Fresh Catalyst	Spent Catalyst
	(by H ₂ O adsorption)	(by Nitrogen adsorption)
Apparent Bulk Density, g/ cm ³	0.76	0.4
Zeta Potential	43.87 ± 3 mV	-

Table 4. 2.2 Particle Size Distribution of the Fresh and Spent FCC Catalyst

Size Range, μm	Fresh Catalyst, %	Spent Catalyst, %
0 – 20	1	0.1
0 – 40	15	1.8
0 – 80	60	42.1
0 – 105	-	70.0
0 – 149	95	92.4
Average Particle Size (APS), μm	70	86.2

4.2.2 Chemical Characterization

Results of the chemical characterization of fresh and spent catalyst are presented in table 4.2.3

Table 4. 2.3 Chemical Composition of the Fresh and Spent FCC Catalyst

Component	Fresh Catalyst	Spent Catalyst
Al ₂ O ₃	54 %	47.60 %
Na ₂ O	0.30 %	0.50 %
RE ₂ O ₃ (Rare Earth Oxides)	3.6 %	3.50 %
SiO ₂	42.1 %	45.52 %
CaO	ND	0.20 %
Carbon	ND	0.04 %
Fe	ND	1.01 %

Component	Fresh Catalyst	Spent Catalyst
Cu	ND	95.9 ppm
Strontium	ND	3.5 ppm
Vanadium	ND	1719 ppm
Nickel	ND	14558 ppm

4.2.3 Scanning Electron Microscopic (SEM) Analyses

Results of scanning electron microscopic characterization are presented in Figure 4.2.1 – 4.2.4

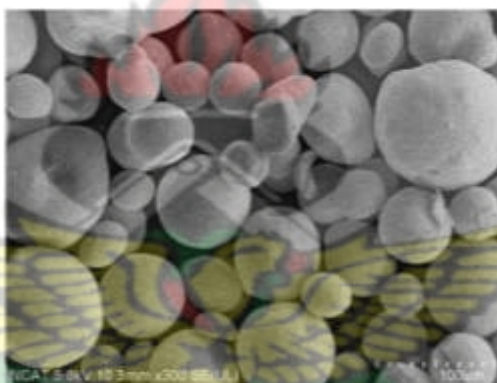


Figure 4. 2. 1 Spent Catalyst at magnification of 300x

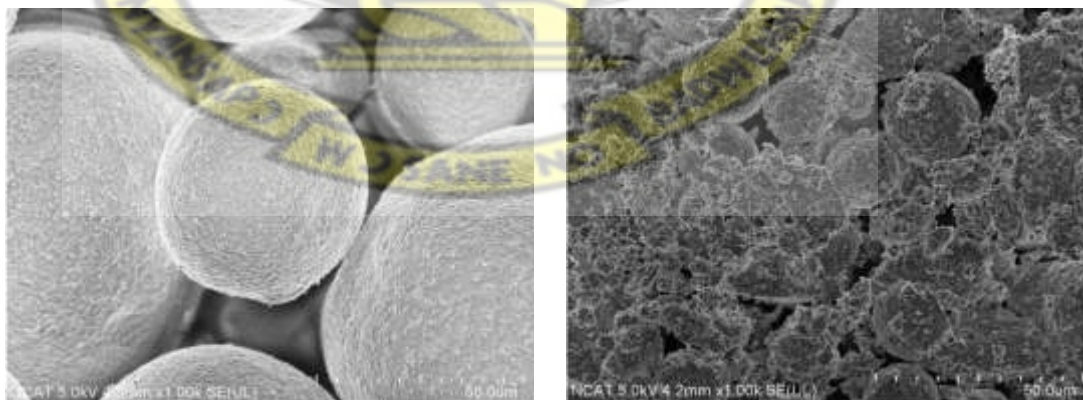


Figure 4. 2. 2 Spent and Fresh Catalyst at a magnification of 1,000x respectively

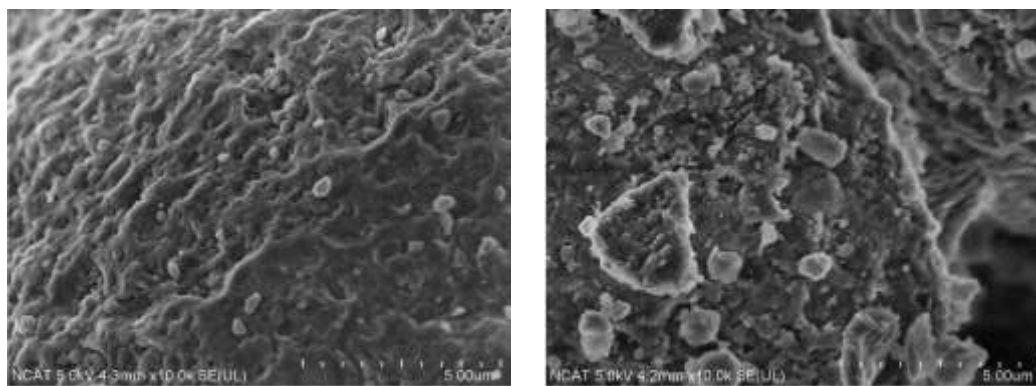


Figure 4. 2. 3 Spent and Fresh Catalyst at a magnification of 10,000x respectively

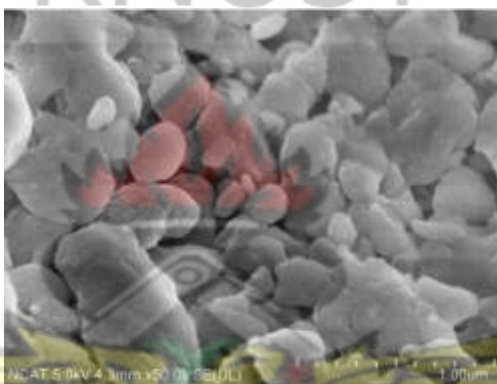


Figure 4. 2. 4 Spent Catalyst at a magnification of 50,000x

4 .2.4 Energy Dispersive X-Ray spectroscopic (EDX) Analyses

The EDX analyses of the fresh and spent catalysts showing the distribution of Na, Si, Al and O are presented in Figure 4.2.5 – 4.2.7 whiles the surface compositions are presented in Tables 4.2.4 – 4.2.5.

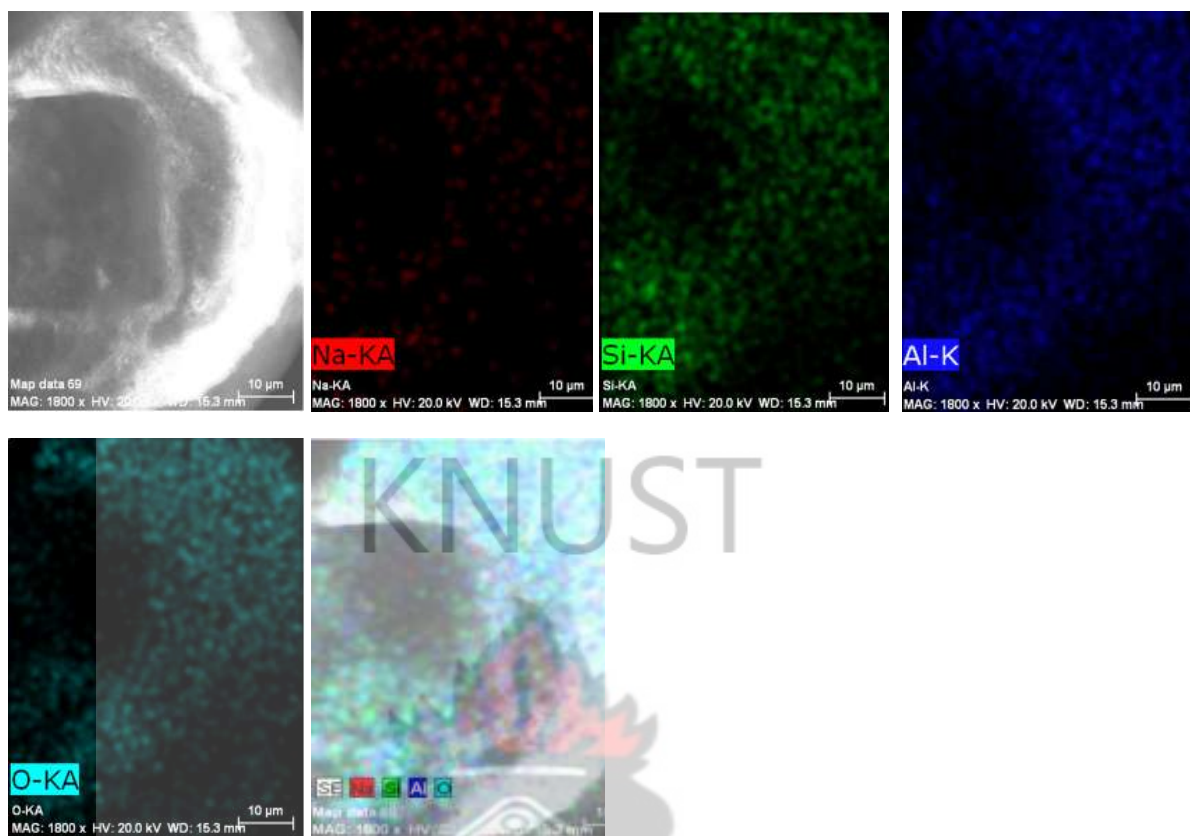
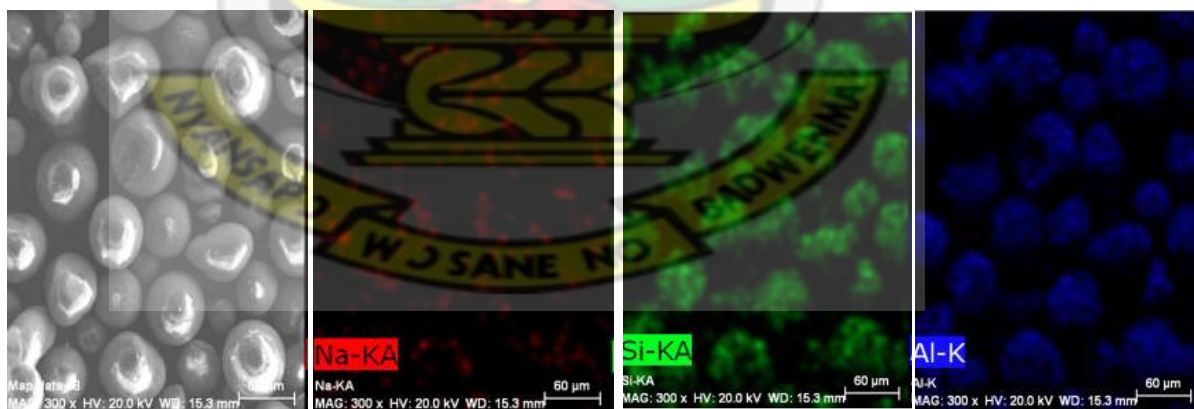


Figure 4. 2. 5 EDX Pictures of a Particle of the Spent Catalyst at a magnification of 1800x



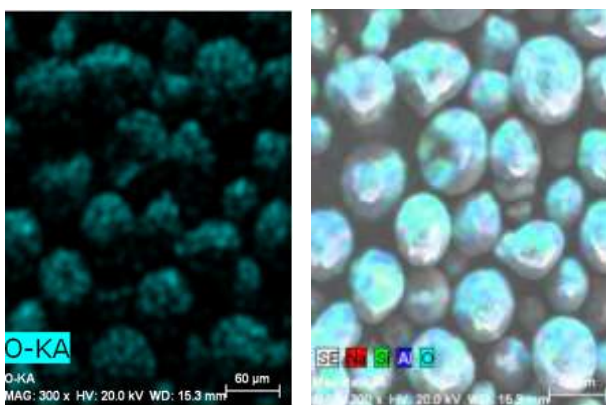


Figure 4. 2. 6 EDX Pictures of a Particle of the Spent Catalyst at a magnification of 300x

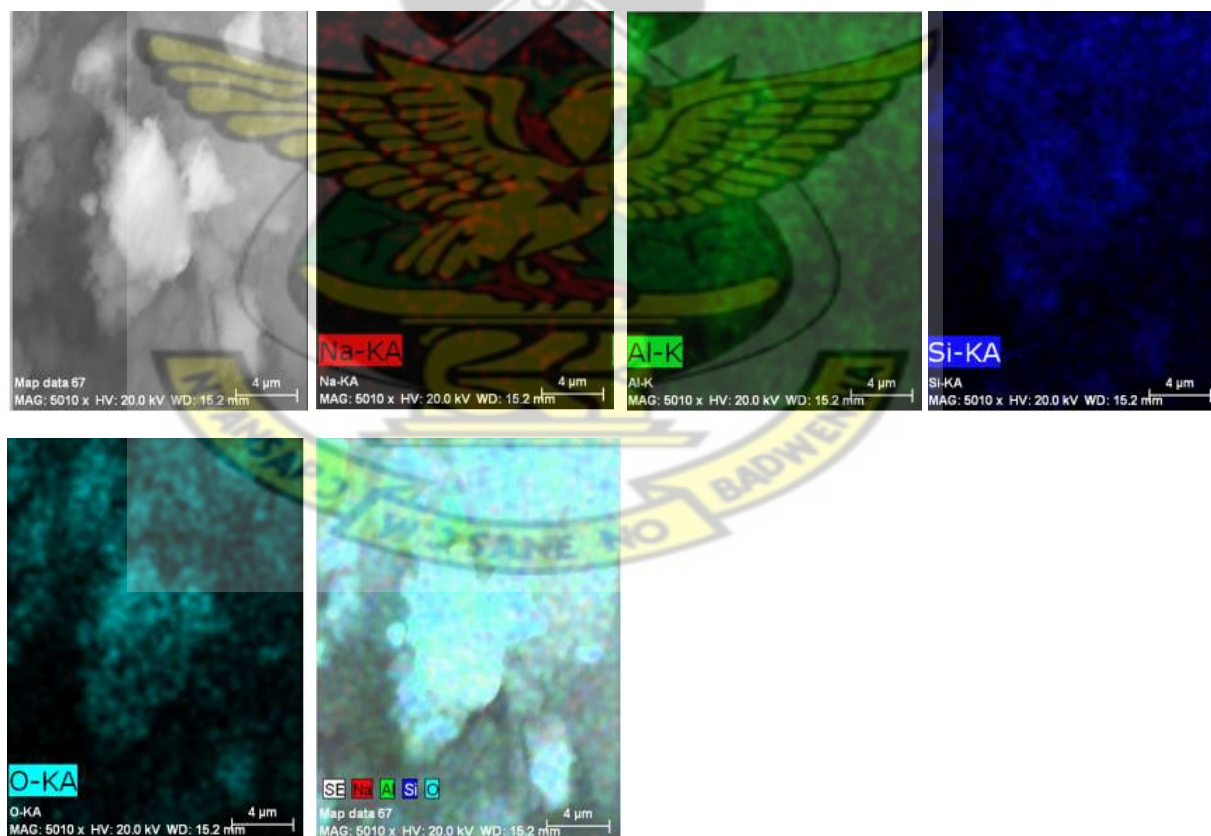


Figure 4. 2. 7 EDX Pictures of a Particle of the Fresh Catalyst at a magnification of 5010x

Table 4. 2.4 Elemental composition of the surface of the Spent FCC catalyst

Element	Unn. C (wt %)	Norm. C (wt %)	Atomic. C (at %)	Error (wt %)
Oxygen	54.30	55.58	68.07	7.0
Sodium	1.03	1.05	0.09	0.1
Aluminum	26.58	27.20	19.76	1.3
Silicon	15.79	16.16	11.28	0.7

Table 4. 2.5 Elemental composition of the surface of the Fresh FCC catalyst

Element	Unn. C (wt %)	Norm. C (wt %)	Atomic. C (at %)	Error (wt %)
Oxygen	38.84	53.73	66.51	5.1
Sodium	0.06	0.08	0.07	0.0
Aluminum	21.29	29.45	21.61	1.1
Silicon	12.11	16.75	11.81	0.6

4.3 Results of Leaching Experiments

Experimental data on the concentration of selected metals after the spent catalyst had been leached in different media are presented in Tables 4.3.1 – 4.3.7

Table 4. 3.1 Results of Leaching Test Conducted with 0.01M HCl (pH = 2.08)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0.3049	0.0101	0.0537	0.3056	0.0828	0
5	1.96	0.4106	0.8463	16.42	1.401	4.358
10	2.0678	0.4149	0.6539	16.4393	1.4443	3.89311
15	2.06318	0.4351	0.6405	16.874	1.4961	3.83114
20	2.30901	0.4152	0.6252	16.2261	1.6053	3.28888
25	0.48704	0.0859	0.1594	3.0241	1.4302	0.80076

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
30	2.41383	0.4038	0.6403	16.3968	1.5663	2.94356
35	2.4332	0.4059	0.7024	16.3115	1.6415	2.84436
40	2.5689	0.406	0.8701	16.6581	1.6474	2.73964
45	2.5199	0.4254	0.7913	17.1901	1.639	2.76764
50	2.51858	0.4192	0.8344	17.0576	1.6701	2.67754

Table 4.3.2 Results of Leaching Test Conducted with 0.0032M HCl
(pH = 2.5)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0.4671	0.0049	0.0448	0.3136	0.0484	0.0000
5	0.9164	0.0666	0.2174	20.1100	0.5029	1.4970
10	0.7884	0.0844	0.4186	20.4950	0.6217	1.4826
15	0.9145	0.7494	0.4713	20.9760	0.7163	1.4271
20	0.9347	0.1088	0.4931	21.1535	0.7252	1.4439
25	1.0890	0.1175	0.4340	21.4000	0.7411	1.3195
30	0.8609	0.0826	0.4032	21.0506	0.6569	1.2897
35	1.0355	0.0879	0.5749	21.4310	0.8035	1.3399
40	1.1380	0.0994	0.5291	21.6449	0.8210	1.2559
45	1.0533	0.0999	0.5604	21.1479	0.8305	1.2370
50	1.2739	0.1050	0.5673	22.0290	0.8521	1.0566

Table 4.3.3 Results of Leaching Test Conducted with 0.001M HCl
(pH = 3.02)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0.2128	0.0027	0.0576	0.3373	0.0598	0
5	1.5940	0.3079	0.5411	22.4100	1.1160	2.2890

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
10	1.7717	0.3287	0.6455	23.1126	1.1988	2.0234
15	1.7757	0.3280	0.7189	22.8351	1.2515	1.7412
20	1.8246	0.3300	0.8229	22.7464	1.3119	1.5034
25	1.9342	0.3299	0.8751	22.7464	1.3484	1.4150
30	2.3291	0.3211	1.0193	23.3233	1.3963	1.2151
35	2.1098	0.3149	1.1022	22.1608	1.4421	1.2120
40	2.1872	0.3201	1.2070	22.8319	1.4627	1.1396
45	2.3643	0.3298	1.2301	23.3149	1.5047	1.1551
50	2.2265	0.3298	1.2559	22.9638	1.4756	1.0591

Table 4. 3.4 Results of Leaching Test Conducted with De-ionized Water
(pH = 6.18)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0.0552	0	0.0219	0.1792	0.0487	0.0173
5	0.1338	0.0101	0.3048	2.9530	0.0925	4.0670
10	0.1337	0.0078	0.3049	3.6787	0.1350	4.7812
15	0.1915	0.0034	0.3332	4.1342	0.1505	4.9670
20	0.1159	0.0047	0.2863	4.3339	0.1612	5.1339
25	0.2256	0.0047	0.3286	4.6722	0.1552	5.1806
30	0.1168	0.0081	0.3202	4.1433	0.1258	5.3423
35	0.1351	0.0066	0.4086	4.4851	0.1808	5.2261
40	0.1655	0.0034	0.3085	4.9047	0.1475	5.3832
45	0.1860	0.0063	0.3786	4.8984	0.1956	5.4385
50	0.2150	0.0072	0.4163	5.0057	0.2193	5.4206

Table 4. 3.5 Results of Leaching Test Conducted with 0.001M NaOH
(pH = 10.45)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0	0	0.0517	20.25	0.0582	0
5	0.3202	0.0193	0.3565	4.5710	0.1265	4.7270
10	0.4792	0.0065	0.3468	5.6865	0.2658	5.4267
15	0.1076	0.0106	0.3559	3.9679	0.1161	5.5105
20	0.0878	0.0123	0.3371	4.0824	0.1314	5.6977
25	0.1365	0.0089	0.3471	4.1818	0.1283	5.7190
30	0.1070	0.0096	0.3599	4.2208	0.1657	5.7954
35	0.1090	0.0103	0.3922	4.1782	0.1856	6.0364
40	0.1404	0.0052	0.3620	4.4356	0.1518	5.9708
45	0.1709	0.0114	0.4757	4.5686	0.1808	6.0569
50	0.0810	0.0087	0.4013	4.3301	0.1850	6.0608

Table 4. 3.6 Results of Leaching Test Conducted with 0.0032M NaOH
(pH = 10.95)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0	0.0045	0.0837	66.9	0.0416	0
5	0.0657	0.0037	0.3877	15.4000	0.1353	4.5860
10	0.0225	0.0118	0.3551	13.8793	0.1107	5.1298
15	0.0751	0.0062	0.3562	12.5935	0.1293	5.2917
20	0.0713	0.0053	0.3138	12.0078	0.0987	5.3964
25	0.0710	0.0119	0.3062	11.7103	0.0974	5.3624
30	0.0867	0.0037	0.3265	11.5884	0.1319	5.4957
35	0.0956	0.0071	0.3329	11.6116	0.1415	5.6584
40	0.2790	0.0078	0.2821	12.5704	0.0995	5.7757
45	0.1945	0.0058	0.2934	11.6816	0.1331	5.5646

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
50	0.1397	0.0092	0.3486	11.5028	0.1404	5.6223

Table 4. 3.7 Results of Leaching Test Conducted with 0.01M NaOH
(pH = 11.50)

Time, min	Calcium, ppm	Copper, ppm	Iron, ppm	Sodium, ppm	Nickel, ppm	Vanadium, ppm
0	0.0236	0.0031	0.1235	163	0.0402	0
5	0.1659	0.0042	0.6685	59.6700	0.2581	4.7550
10	0.1547	0.0003	0.3046	58.0626	0.0859	5.3652
15	0.3097	0.0079	0.3265	55.3061	0.1055	4.9601
20	0.1090	0.0043	0.6903	54.3299	0.3212	5.0586
25	0.0686	0.0047	0.3630	56.8629	0.1253	5.5652
30	0.0952	0.0102	0.3988	57.0173	0.1771	5.9194
35	0.0689	0.0026	0.4400	55.2735	0.1661	5.2483
40	0.1229	0.0036	0.3736	56.5273	0.1131	5.4275
45	0.1337	0.0058	0.4732	56.1983	0.2069	5.6235
50	0.1210	0.0068	0.4215	57.0198	0.1584	5.7924

4.4 Adsorption Tests (Adsorption Characteristics of the Spent FCC catalyst)

4.4.1 Determination of Phenol Break-Through Curves

The results of adsorption test under various conditions are presented in Tables 4.4.1 – 4.4.3.

Table 4.4.1 Experimental Data on Phenol adsorption using the spent FCC catalysts and an initial phenol concentration of 1500 ppm

Time, min	C_1/C_0^c	NMPA, g/g	Time, min	C_1/C_0^c	NMPA, g/g
0	5.40×10^{-4}	0.00	334	4.67×10^{-2}	7.55×10^{-3}
10	6.37×10^{-4}	2.27×10^{-4}	344	5.00×10^{-2}	7.77×10^{-3}
20	0	4.53×10^{-4}	354	6.02×10^{-2}	7.98×10^{-3}
30	0	6.80×10^{-4}	359	6.43×10^{-2}	8.09×10^{-3}
40	0	9.07×10^{-4}	370	6.92×10^{-2}	8.32×10^{-3}
50	0	1.13×10^{-4}	380	8.53×10^{-2}	8.53×10^{-3}
251	0	5.69×10^{-3}	397	9.52×10^{-2}	8.88×10^{-3}
261	0	5.92×10^{-3}	407	0.104	9.09×10^{-3}
272	0	6.17×10^{-3}	417	0.112	9.29×10^{-3}
282	1.84×10^{-3}	6.39×10^{-3}	428	0.115	9.51×10^{-3}
293	8.01×10^{-3}	6.64×10^{-3}	438	0.121	9.72×10^{-3}
303	1.69×10^{-2}	6.87×10^{-3}	449	0.128	9.93×10^{-3}
313	3.61×10^{-2}	7.09×10^{-3}	463	0.170	1.02×10^{-2}
323	4.14×10^{-2}	7.31×10^{-3}			

Table 4.4.2 Experimental Data on Phenol adsorption using the spent FCC catalysts and an initial phenol concentration of 2500 ppm

Time, min	C_1/C_0^c	NMPA, g/g	Time, min	C_1/C_0^c	NMPA, g/g
0	0.00	0.00	36	0.00	1.55×10^{-3}
10	0.00	4.31×10^{-4}	44	0.00	1.89×10^{-3}
19	0.00	8.18×10^{-4}	52	0.00	2.24×10^{-3}
27	0.00	1.16×10^{-3}	195	0.00	8.40×10^{-3}

Time, min	C_1/C_0^c	NMPA, g/g
205	0.00	8.83×10^{-3}
213	0.01	9.17×10^{-3}
221	0.01	9.51×10^{-3}
231	0.02	9.94×10^{-3}
239	0.03	1.03×10^{-2}
248	0.03	1.07×10^{-2}

Time, min	C_1/C_0^c	NMPA, g/g
258	0.11	1.11×10^{-2}
266	0.14	1.14×10^{-2}
274	0.23	1.17×10^{-2}
283	0.33	1.21×10^{-2}
292	0.52	1.24×10^{-2}
300	0.49	1.27×10^{-2}

Table 4.4.3 Experimental Data on Phenol adsorption using the spent FCC catalysts and an initial phenol concentration of 3500 ppm

Time, min	C_1/C_0^c	NMPA, g/g	Time, min	C_1/C_0^c	NMPA, g/g
0	0	0.0	209	2.07×10^{-3}	1.27×10^{-2}
9	0	5.49×10^{-4}	217	4.33×10^{-3}	1.32×10^{-2}
17	0	1.04×10^{-3}	226	6.33×10^{-3}	1.38×10^{-2}
26	0	1.59×10^{-3}	234	8.95×10^{-3}	1.43×10^{-2}
36	0	2.20×10^{-3}	241	1.93×10^{-2}	1.47×10^{-2}
45	0	2.74×10^{-3}	252	3.09×10^{-2}	1.53×10^{-2}
53	0	3.23×10^{-3}	261	5.69×10^{-2}	1.58×10^{-2}
184	0	1.12×10^{-2}	270	5.27×10^{-2}	1.64×10^{-2}
192	0	1.17×10^{-2}	278	0.249	1.67×10^{-2}
200	6.40×10^{-4}	1.22×10^{-2}	287	0.446	1.70×10^{-2}

4.4.2 Comparison of Phenol Adsorption Capacities of the Spent FCC Catalyst and Activated Carbon

Experimental data on the comparison of phenol adsorption on the spent FCC catalyst and activated carbon are presented in Tables 4.4.1 – 4.4.2

Table 4.4.1 Results of adsorption test conducted with 300 g spent FCC catalyst using an initial phenol concentration of 2500 ppm.

Time, min	EPC, ppm	TMPA, mg	NMPA, g/g
0	0	0.00	0.00
10	0	0.13	4.31×10^{-4}
19	0	0.25	8.18×10^{-4}
27	0	0.35	1.16×10^{-3}
36	0	0.47	1.55×10^{-3}
44	0	0.57	1.89×10^{-3}
52	0	0.67	2.24×10^{-3}
195	0	2.52	8.40×10^{-3}
205	0	2.65	8.83×10^{-3}
213	4.30	2.75	9.17×10^{-3}
221	6.30	2.85	9.51×10^{-3}
231	11.68	2.98	9.94×10^{-3}
239	17.88	3.09	1.03×10^{-3}
248	18.07	3.20	1.07×10^{-3}
258	71.70	3.33	1.11×10^{-3}
266	87.58	3.43	1.14×10^{-2}
274	145.79	3.52	1.17×10^{-2}
283	211.67	3.63	1.21×10^{-2}
292	337.53	3.73	1.24×10^{-2}
300	313.46	3.82	1.27×10^{-2}

Table 4.4.2 Results of adsorption test conducted with 100 g Activated Carbon using an initial phenol concentration of 2500 ppm.

Time, min	EPC, ppm	TMPA, mg	NMPA, g/g
0	0	0.00	0.00
10	0	0.11	1.07×10^{-3}
21	0	0.22	2.24×10^{-3}
31	0	0.33	3.31×10^{-3}
42	0	0.45	4.48×10^{-3}
52	0	0.55	5.55×10^{-3}
189	0	2.02	2.02×10^{-2}
199	0	2.12	2.12×10^{-2}
210	7.15	2.24	2.24×10^{-2}
220	22.41	2.35	2.35×10^{-2}
230	50.20	2.45	2.45×10^{-2}
241	64.93	2.57	2.57×10^{-2}

4.4.3 Effect of Thermal Pre-treatment of the spent FCC on Phenol Adsorption

Experimental data obtained on the effect of heat treatment at different temperatures on phenol adsorption are presented in Tables 4.4.3 – 4.4.7

Table 4.4.3 Results of adsorption tests using 200 g of untreated fresh FCC catalyst and using 544.4 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
60	74.90	21.56	0.14	1.08×10^{-4}
120	248.10	35.16	0.46	1.76×10^{-4}
166	360.22	41.65	0.66	2.08×10^{-4}
207	418.72	45.59	0.77	2.28×10^{-4}
250	424.25	49.55	0.78	2.48×10^{-4}
291	471.30	51.84	0.87	2.59×10^{-4}

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
332	470.64	54.15	0.86	2.71×10^{-4}
392	457.67	58.14	0.84	2.91×10^{-4}

Table 4.4.4 Results of adsorption tests using 200 g of *De-coked* spent FCC catalyst and using 544.4 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
20	0.00	61.34	0	3.07×10^{-4}
43	0.00	131.88	0	6.59×10^{-4}
65	0.00	199.36	0	9.97×10^{-4}
87	0.00	266.83	0	1.33×10^{-3}
108	0.00	331.24	0	1.66×10^{-3}
129	14.45	393.94	2.65×10^{-2}	1.97×10^{-3}
149	47.39	449.94	8.70×10^{-2}	2.25×10^{-3}
169	59.69	504.56	0.110	2.52×10^{-3}
191	73.85	562.88	0.136	2.81×10^{-3}

Table 4.4.5 Results of adsorption tests using 200 g of spent FCC catalyst thermally pre-treated a temperature of 300°C and using 544.4 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
20	0	64.36	0	3.22×10^{-4}
40	0	128.73	0	6.44×10^{-4}
60	0	193.09	0	9.65×10^{-4}
80	0	257.45	0	1.29×10^{-3}
102	6.58	327.39	1.21×10^{-2}	1.64×10^{-3}
121	29.75	385.20	5.46×10^{-2}	1.93×10^{-3}
141	65.98	441.76	0.12	2.21×10^{-3}
163	92.39	500.54	0.17	2.50×10^{-3}
183	75.135	556.02	0.14	2.78×10^{-3}
203	71.08	611.98	0.13	3.06×10^{-3}

Table 4. 4.6 Results of adsorption tests using 200 g of spent FCC catalyst thermally pre-treated a temperature of 500°C and using 544.4 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C ₁ /C ₀ ^c	NMPA, g/g
20	0	63.43	0	3.17 x 10 ⁻⁴
40	0	126.85	0	6.34 x 10 ⁻⁴
61	0	193.45	0	9.67 x 10 ⁻⁴
82	11.40	258.65	2.09 x 10 ⁻²	1.29 x 10 ⁻³
102	27.56	318.86	5.06 x 10 ⁻²	1.59 x 10 ⁻³
123	75.76	376.19	0.139	1.88 x 10 ⁻³
144	97.73	430.84	0.180	2.15 x 10 ⁻³
164	105.03	482.02	0.193	2.41 x 10 ⁻³
186	137.35	534.19	0.252	2.67 x 10 ⁻³
206	157.47	579.27	0.289	2.90 x 10 ⁻³

Table 4. 4.7 Results of adsorption tests using 200 g of spent FCC catalyst thermally pre-treated a temperature of 700°C and using 620.45 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C ₁ /C ₀ ^c	NMPA, g/g
20	0	73.35	0	3.67 x 10 ⁻⁴
42	0	154.04	0	7.70 x 10 ⁻⁴
63	0	231.06	0	1.16 x 10 ⁻³
83	2.77	304.09	4.46 x 10 ⁻³	1.52 x 10 ⁻³
104	22.89	378.27	3.69 x 10 ⁻³	1.89 x 10 ⁻³
125	64.55	447.28	0.104	2.24 x 10 ⁻³
146	94.21	512.61	0.152	2.56 x 10 ⁻³
168	109.46	579.06	0.176	2.90 x 10 ⁻³
188	127.34	637.36	0.205	3.19 x 10 ⁻³
203	143.79	679.63	2.32E-01	3.40 x 10 ⁻³

4.4.4 Effect of Acid and Base Washings on the Phenol Adsorption Capacity of the Spent Catalyst

Results of adsorption tests conducted on the spent FCC catalyst pre-washed in different media are shown in Tables 4.4.8 – 4.4.10.

Table 4.4.8 Results of adsorption tests using 200 g of spent FCC catalyst pre-washed with 0.001M HCl solution and using 648.65 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
20	0	90.51	0	4.53×10^{-4}
40	0	181.02	0	9.05×10^{-4}
61	21.79	272.86	3.36×10^{-2}	1.36×10^{-3}
82	83.05	355.73	0.13	1.78×10^{-3}
103	142.93	429.82	0.22	2.15×10^{-3}
123	188.55	494.02	0.29	2.47×10^{-3}
144	217.30	557.22	0.33	2.79×10^{-3}
164	258.63	611.64	0.40	3.06×10^{-3}
172	272.84	632.62	0.42	3.16×10^{-3}

Table 4.4.9 Results of adsorption tests using 200 g of spent FCC catalyst pre-washed with *De-ionized* water and using 648.65 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
20	0	73.16	0	3.66×10^{-4}
41	0	149.97	0	7.50×10^{-4}
61	0	223.13	0	1.12×10^{-3}
82	0	299.94	0	1.50×10^{-3}
102	0	373.10	0	1.87×10^{-3}
123	3.48	449.50	5.33×10^{-3}	2.25×10^{-3}

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
143	22.22	520.15	3.40×10^{-2}	2.60×10^{-3}
164	61.17	589.72	9.37×10^{-2}	2.95×10^{-3}
184	104.88	651.05	0.16	3.26×10^{-3}
204	139.64	708.45	0.21	3.54×10^{-3}
225	157.99	766.56	0.24	3.83×10^{-3}
245	188.12	818.50	0.29	4.09×10^{-3}
266	205.67	870.96	0.31	4.35×10^{-3}

Table 4. 4.10 Results of adsorption tests using 200 g of spent FCC catalyst pre-washed with 0.001M NaOH solution and using 648.65 ppm phenol solution.

Time, min	EPC, ppm	TMPA, mg	C_1/C_0^c	NMPA, g/g
20	0	84.61	0	4.23×10^{-4}
41	0	173.44	0	8.67×10^{-4}
61	0	258.05	0	1.29×10^{-3}
82	29.80	342.81	4.59×10^{-2}	1.71×10^{-3}
102	71.94	418.03	0.11	2.09×10^{-3}
123	121.05	490.29	0.19	2.45×10^{-3}
143	128.67	558.11	0.20	2.79×10^{-3}
164	138.73	627.95	0.21	3.14×10^{-3}
184	168.34	690.60	0.26	3.45×10^{-3}

4 .4.5 Equilibrium Adsorption Capacity Determination

Results of test conducted to determine the equilibrium adsorption capacity of the spent FCC catalyst at different phenol concentrations are presented in Tables 4.4.11 – 4.4.16. In each case 10 g of the spent FCC catalyst was contacted with 250ml of the phenol solution.

Table 4.4.11 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 500 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	287.40
21	298.63
32	297.96
43	262.01
53	290.62
64	283.85
74	275.27
85	282.7
96	259.06
107	284.13
117	268.02
127	291.67
Average	281.78

Table 4.4.12 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 1000 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	559.80
22	561.59
32	583.24
42	631.96
52	590.96
63	533.09
74	598.21
84	633.77
94	603.36
104	520.98

Time, min	Phenol Conc. in Solution, ppm
114	558.92
124	558.92
Average	577.9

Table 4. 4.13 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 1500 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	829.92
21	915.32
31	1053.76
40	898.92
51	835.64
62	835.64
74	842.48
85	782.24
96	769.28
107	843.24
118	689.16
129	776.12
Average	839.31

Table 4. 4.14 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 2000 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	1152.36
20	1233.42
30	1446.42

Time, min	Phenol Conc. in Solution, ppm
39	1205.18
51	1392.06
62	846.88
73	1123.18
84	1141.3
94	980.74
104	1003.62
114	1185.54
124	1190.88
Average	1158.47

Table 4. 4.15 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 2500 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	1547.68
20	1432.88
30	1501.46
39	2051.4
51	1684.78
61	1639.58
72	1657.52
83	1424.3
93	1972.54
104	1881
114	1868.04
124	1954.2
Average	1717.95

Table 4.4.16 Results of tests on the equilibrium adsorption capacity determination at an initial phenol concentration of 3000 ppm.

Time, min	Phenol Conc. in Solution, ppm
10	2192.00
20	1986.28
30	1879.80
39	1746.56
51	1995.80
61	2183.80
72	2491.80
83	2034.60
93	1926.02
104	1916.10
114	2016.40
124	2050.00
Average	2034.93

4.4.6 Effect of Thermal Pre-treatment of the Spent FCC Catalyst on Equilibrium Adsorption Capacity

Data on the test to determine the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst is presented in Tables 4.4.17 – 4.4.21. For these tests, 10 g of the pre-treated spent FCC catalyst was contacted with 250ml of a 1500 ppm phenol solution.

Table 4.4.17 Results of tests on the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst using a pre-treatment temperature of 400°C.

Time, min	Phenol Conc. in Solution, ppm
10	1258.2
21	1258.2

Time, min	Phenol Conc. in Solution, ppm
31	958.8
40	850.88
51	1102.2
62	1109.08
74	1215.48
85	1386.36
96	1052.64
107	993.52
118	858.52
129	1130.8
Average	1097.89

Table 4. 4.18 Results of tests on the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst using a pre-treatment temperature of 500°C.

Time, min	Phenol Conc. in Solution, ppm
10	903.52
21	1335.64
31	828.76
40	1225.8
51	1217
62	1180.4
74	1238.24
85	1090.76
96	1147.96
107	1080.84
118	1033.56
129	1199.84
Average	1123.53

Table 4.4.19 Results of tests on the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst using a pre-treatment temperature of 600°C.

Time, min	Phenol Conc. in Solution, ppm
10	1112.12
21	1065.6
31	916.08
40	946.24
51	829.12
62	838.68
74	808.56
85	756.68
96	1083.92
107	1016.4
118	1099.56
129	905.04
Average	948.17

Table 4.4.20 Results of tests on the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst using a pre-treatment temperature of 700°C.

Time, min	Phenol Conc. in Solution, ppm
10	873.36
21	926
31	964.16
40	816.16
51	770.04
62	1032.04
74	980.16
85	755.16

Time, min	Phenol Conc. in Solution, ppm
96	833.32
107	779.56
118	825.32
129	923.72
Average	873.25

Table 4. 4.21 Results of tests on the effect of thermal pre-treatment on the equilibrium adsorption capacity of the spent FCC catalyst using a pre-treatment temperature of 800°C.

Time, min	Phenol Conc. in Solution, ppm
10	968.72
21	1032.4
31	1033.56
40	1026.32
51	944.32
62	1231.12
74	1000.76
85	1120.12
96	941.64
107	1117.84
118	915.32
129	1035.84
Average	1030.66

4.5 Phenol Oxidation on Spent FCC catalyst

4.5.1 Effect of Cu^{2+} And Fe^{2+} Ions on the Liquid Phase Oxidation of Phenol Using Unmodified Spent Catalyst

Experimental data on the effect of Cu^{2+} and Fe^{2+} ion on the liquid phase oxidation of phenols using unmodified spent FCC catalyst have been presented in Tables 4.5.1 – 4.5.2. For these experiments the mass of unmodified spent FCC catalyst used was 25 g while the mass of the granite chippings used was 68g. The phenol concentration of the solution used was 1000 ppm. In total 1000 ml of the phenol solution was treated per experiment. 10 ml of a 50% H_2O_2 solution was used for each experiment.

Table 4. 5.1 Results of tests on the effect Cu^{2+} ions on the liquid phase oxidation of phenols using unmodified spent FCC catalyst and 30 ml of a 5000 ppm solution of Cu^{2+} . The COD of the initial solution was 985 ppm while its pH was 4.21 at 29.1°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.33	25.2	ND	106	0	0.078	0.078
60	6.63	25.5	ND		0	0.060	0.138
90	5.89	25	ND		0	0.084	0.222
120	5.68	25.7	ND	151	0	0.079	0.302
150	5.62	26.4	ND	140	0	0.086	0.388
180	5.51	26.5	ND		0	0.078	0.466
210	5.49	26.9	ND		0	0.088	0.554
240	5.48	29	ND	160	0	0.092	0.646
270	5.69	27.2	ND	154	0	0.081	0.727
300	5.65	26.8	ND		0	0.071	0.797
330	5.53	26	ND		0	0.083	0.881
360	5.67	26.7	ND	114	0	0.052	0.932

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.1 – 4.5.4.

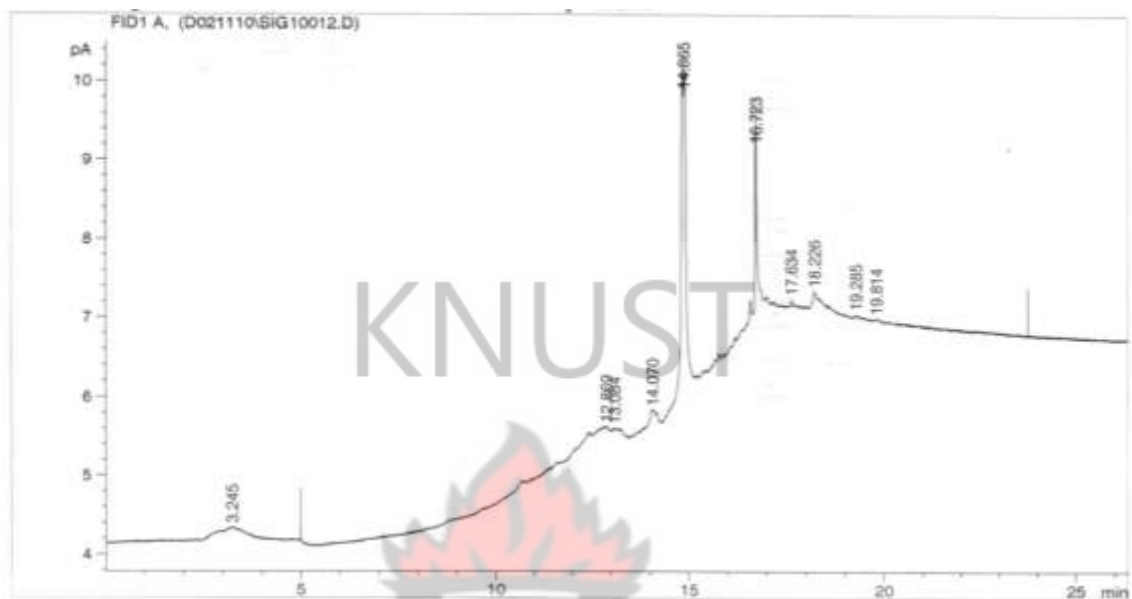


Figure 4. 5. 1 Time = 30 min

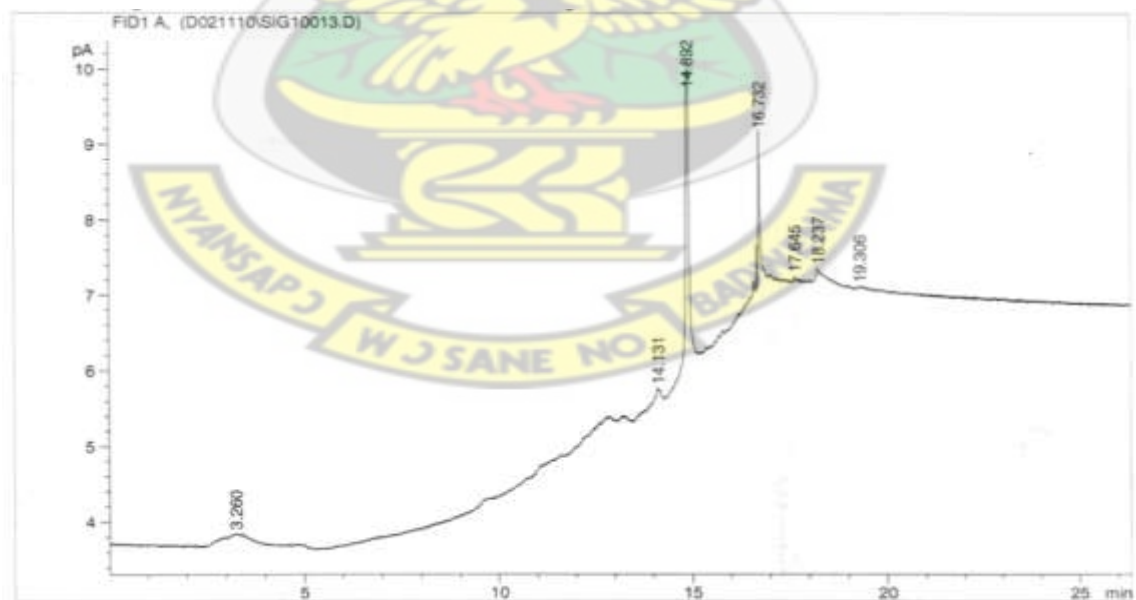


Figure 4. 5. 2 Time = 60 min

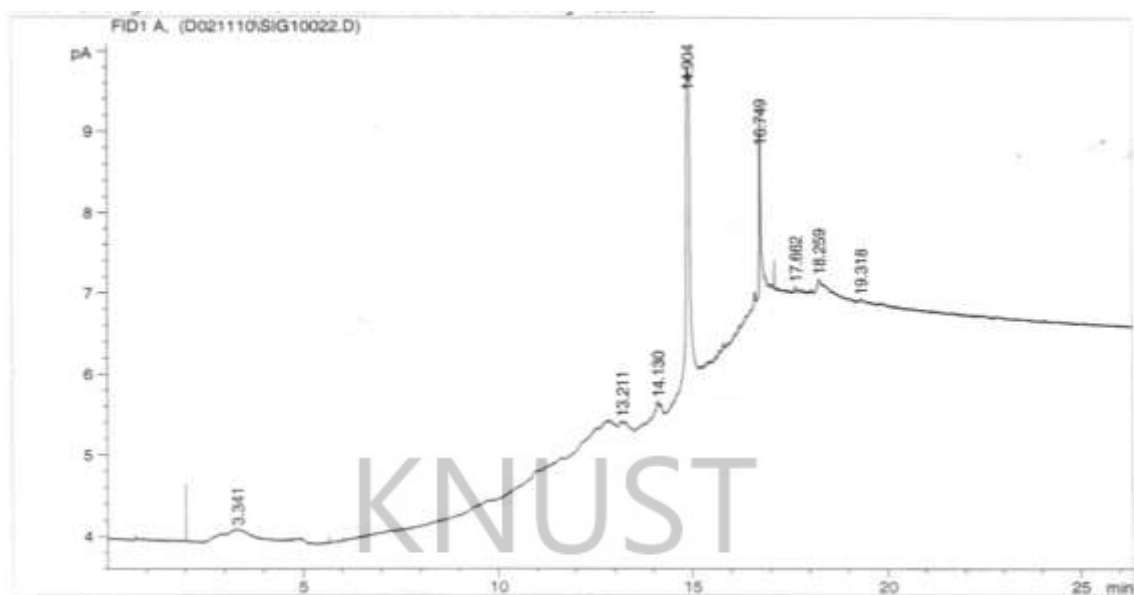


Figure 4. 5. 3 Time = 330 min

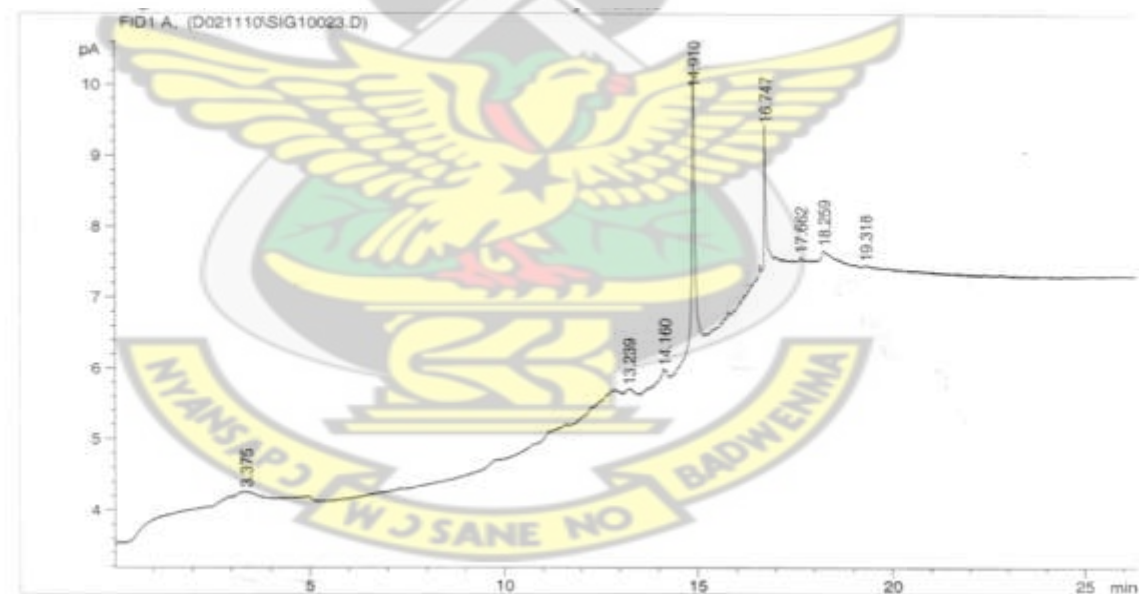


Figure 4. 5. 4 Time = 360 min

Table 4.5.2 Results of tests on the effect Fe^{2+} ions on the liquid phase oxidation of phenols using unmodified spent FCC catalyst and 150 ml of a 1000 ppm solution of Fe^{2+} . The COD of the initial solution was 369 ppm while its pH was 3.58 at 30.7°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.62	26	ND	106	0	0.087	0.087
60	6.07	27.4	ND		0	0.104	0.191
90	5.88	27.8	ND		0	0.094	0.285
120	5.87	28.8	ND	124	0	0.103	0.388
150	5.66	28	ND	191	0	0.070	0.458
180	5.69	28.7	ND		0	0.094	0.552
210	5.68	30	ND		0	0.080	0.633
240	5.69	28.1	ND	175	0	0.095	0.728
270	5.67	30.3	ND	184	0	0.086	0.813
300	5.82	27.6	ND		0	0.048	0.861
330	5.87	27.5	ND	147	0	0.050	0.912

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.5 – 4.5.8.

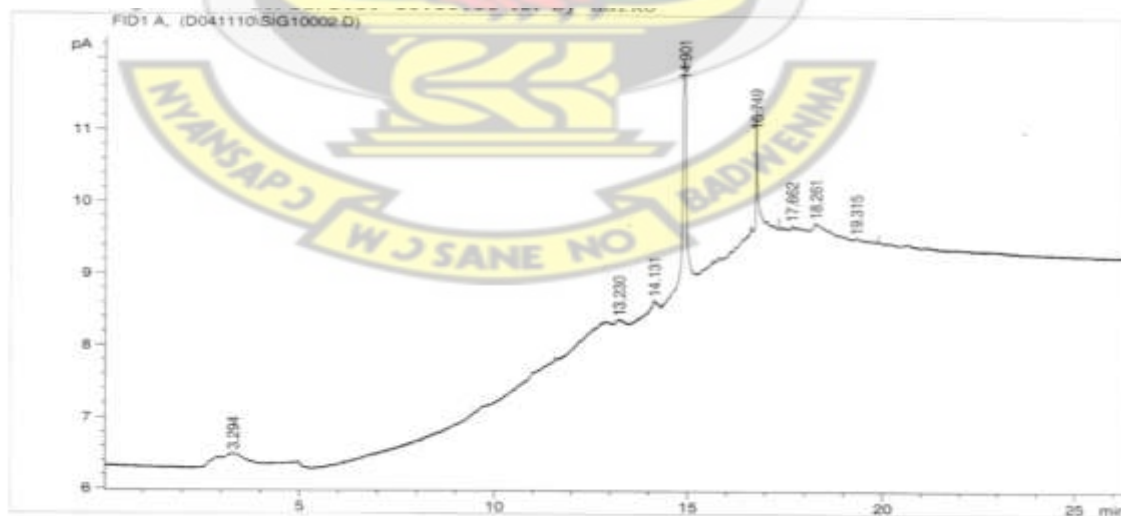


Figure 4.5.5 Time = 30 min

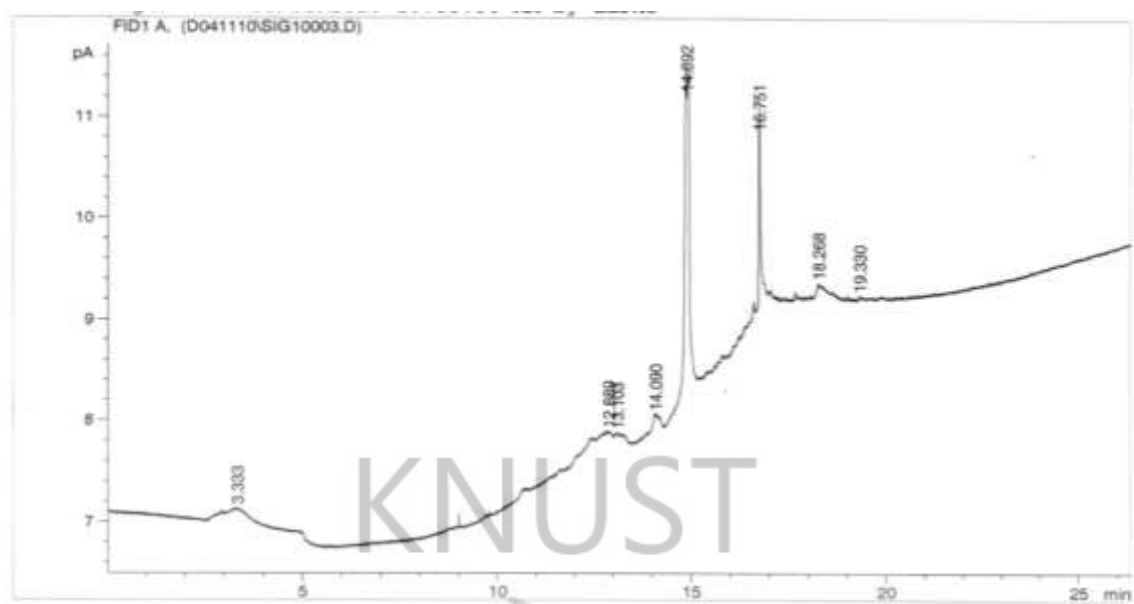


Figure 4. 5. 6 Time = 60 min

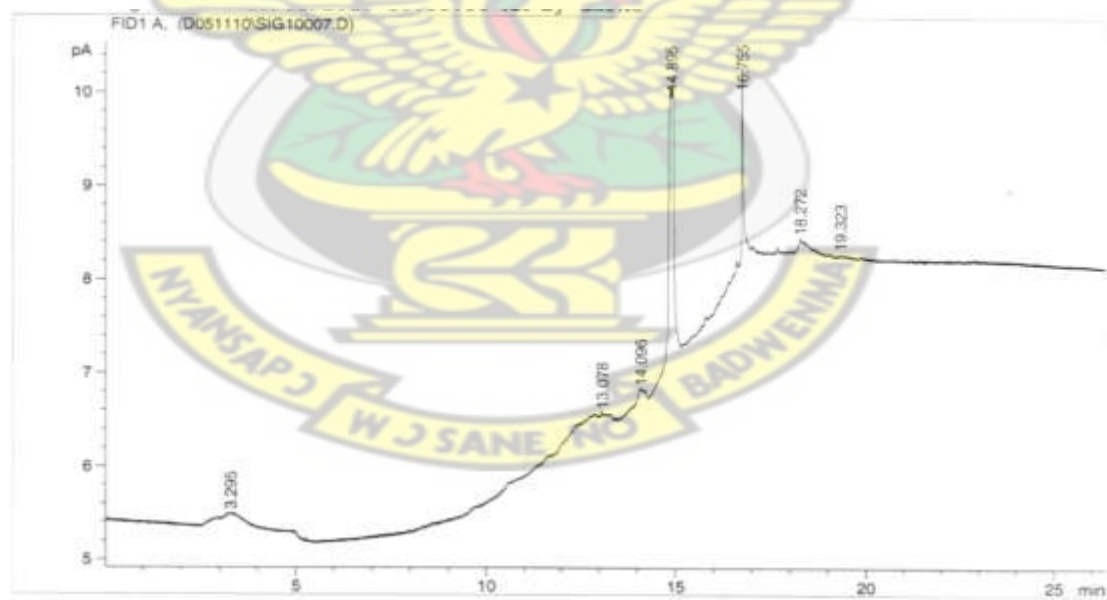


Figure 4. 5. 7 Time = 300 min



Figure 4. 5. 8 Time = 330 min

4.5.2 Effect of Cu^{2+} Ions Concentration on the Liquid Phase Oxidation of Phenol Using CuO Impregnated Spent Catalyst

Experimental data on the effect of Cu^{2+} ion on the liquid phase oxidation of phenols using CuO impregnated spent FCC catalyst (2.6% CuO) have been presented in Tables 4.5.3 – 4.5.5. For these experiments the mass of modified spent FCC catalyst used was 25 g while the mass of the granite chippings used was 68g. The phenol concentration of the solution used was 1000 ppm. In total 1000 ml of the phenol solution was treated per experiment. 10 ml of a 50% H_2O_2 solution was used for each experiment.

Table 4. 5.3 Results of tests on the effect Cu^{2+} ions on the liquid phase oxidation of phenols using CuO impregnated spent FCC catalyst and 20 ml of a 5000 ppm solution of Cu^{2+} . The COD of the initial solution was 1257 ppm while its pH was 4.16 at 27.9°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.78	24.7	4.57	99	64.60	0.059	0.059
60	6.98	24.6	5.09		71.99	0.055	0.114
90	6.5	26	7.19		101.71	0.063	0.178
120	6.16	25.2	ND	235	0	0.066	0.243
150	6.17	27	ND	168	0	0.063	0.306
180	6.14	27.5	ND		0	0.056	0.362
210	6.09	27.6	ND		0	0.069	0.431
240	5.92	27.7	ND	184	0	0.073	0.504
270	6.11	28.2	ND	192	0	0.056	0.560
300	6.07	28.8	ND		0	0.065	0.625
330	5.88	29.2	ND		0	0.071	0.695
360	5.9	28.9	ND	147	0	0.070	0.765
390	5.92	27.6	ND		0	0.078	0.843

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.9 – 4.5.12.

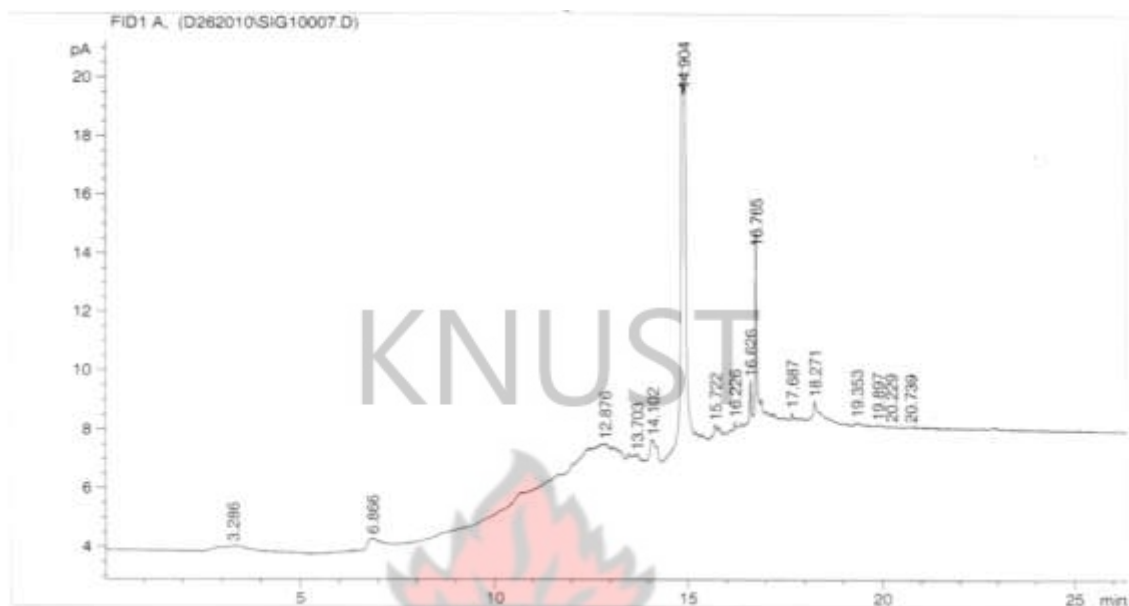


Figure 4. 5. 9 Time = 30 min

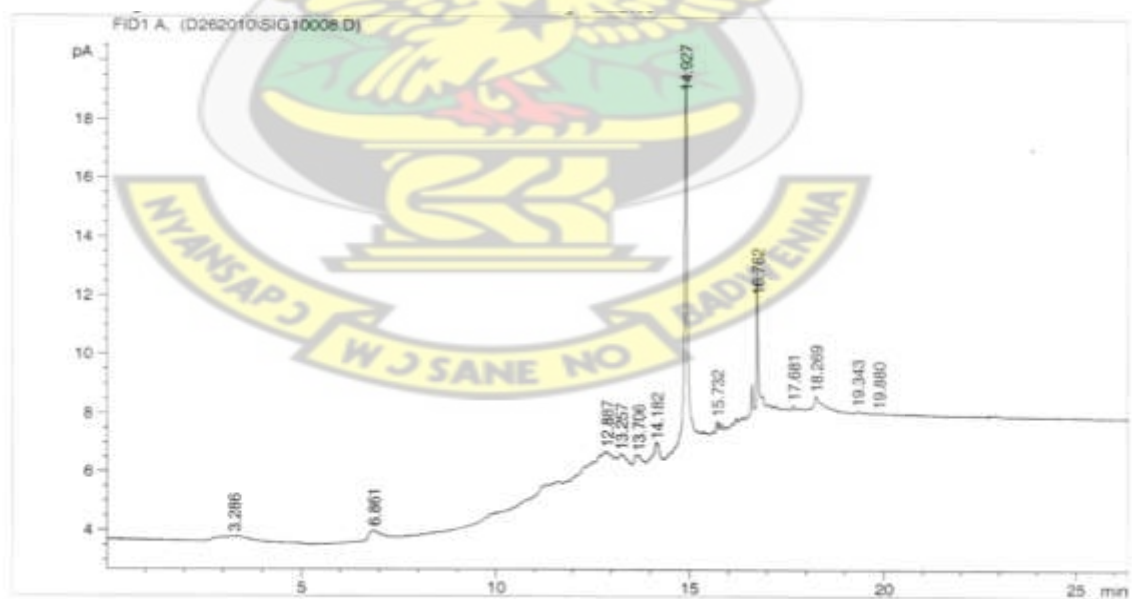


Figure 4. 5. 10 Time = 60 min

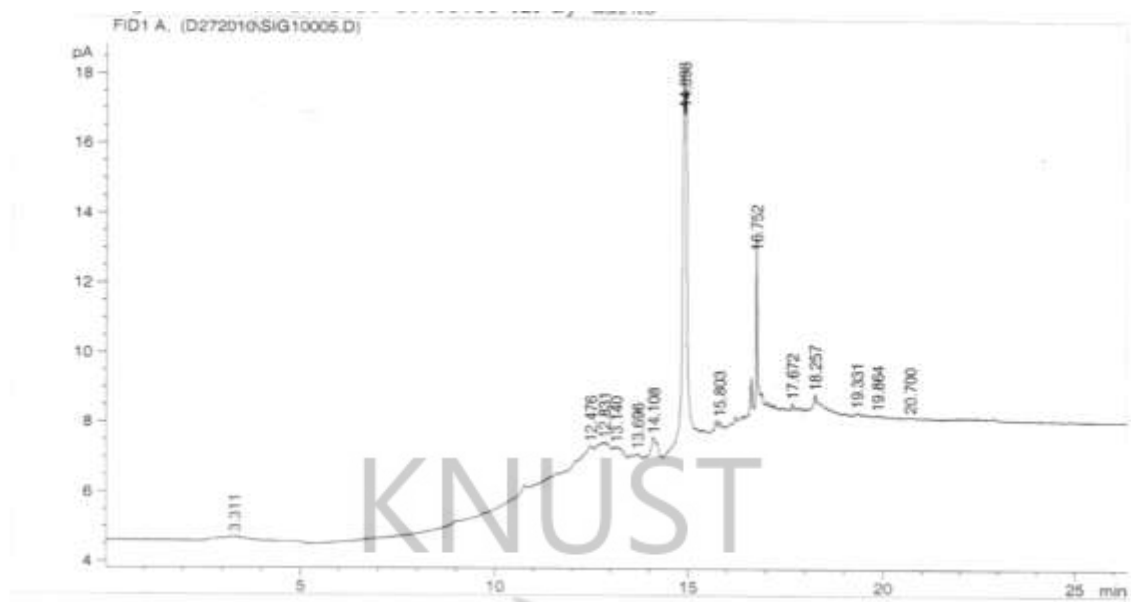


Figure 4. 5. 11 Time = 330 min

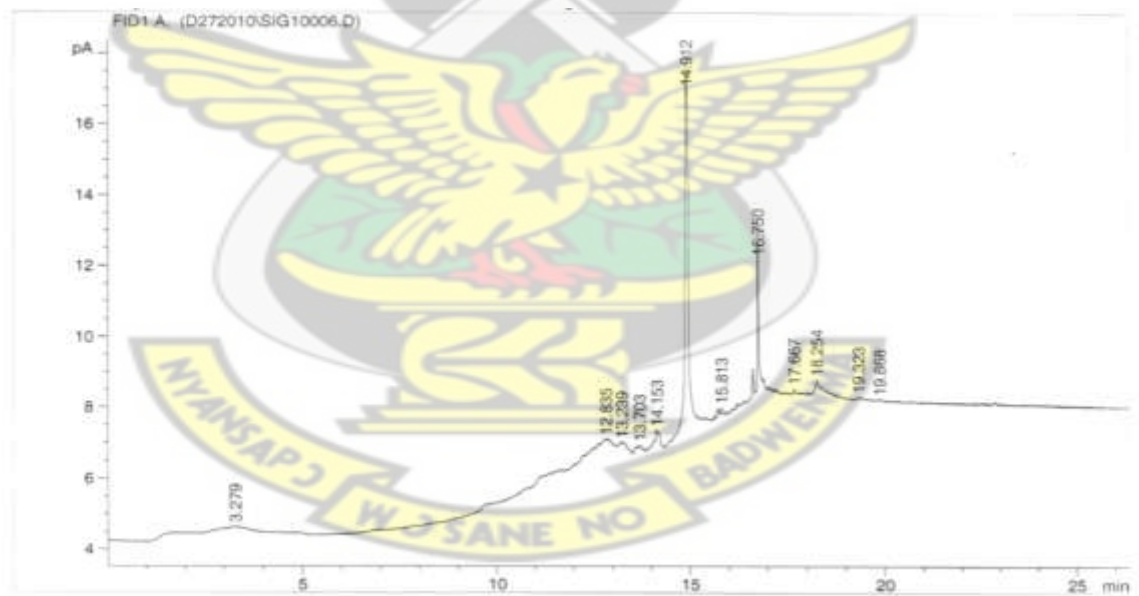


Figure 4. 5. 12 Time = 360 min

Table 4. 5.4 Results of tests on the effect Cu^{2+} ions on the liquid phase oxidation of phenols using CuO impregnated spent FCC catalyst and 30 ml of a 5000 ppm solution of Cu^{2+} . The COD of the initial solution was 1008 ppm while its pH was 4.14 at 28.1°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.41	25.1	ND	82	0	0.075	0.075
60	6.91	24.6	ND		0	0.080	0.155
90	6.15	23.7	ND		0	0.080	0.235
120	6.1	24.3	ND	148	0	0.081	0.316
150	6.16	26.3	ND	122	0	0.076	0.392
180	5.99	24.9	ND		0	0.087	0.479
210	5.98	26	ND		0	0.079	0.558
240	5.95	26.2	ND	133	0	0.070	0.628
270	5.96	24.2	ND	134	0	0.074	0.702
300	5.91	24.3	ND		0	0.075	0.778
330	5.88	25.1	ND		0	0.063	0.841
360	5.82	26.2	ND	128	0	0.088	0.929

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.13 – 4.5.16.

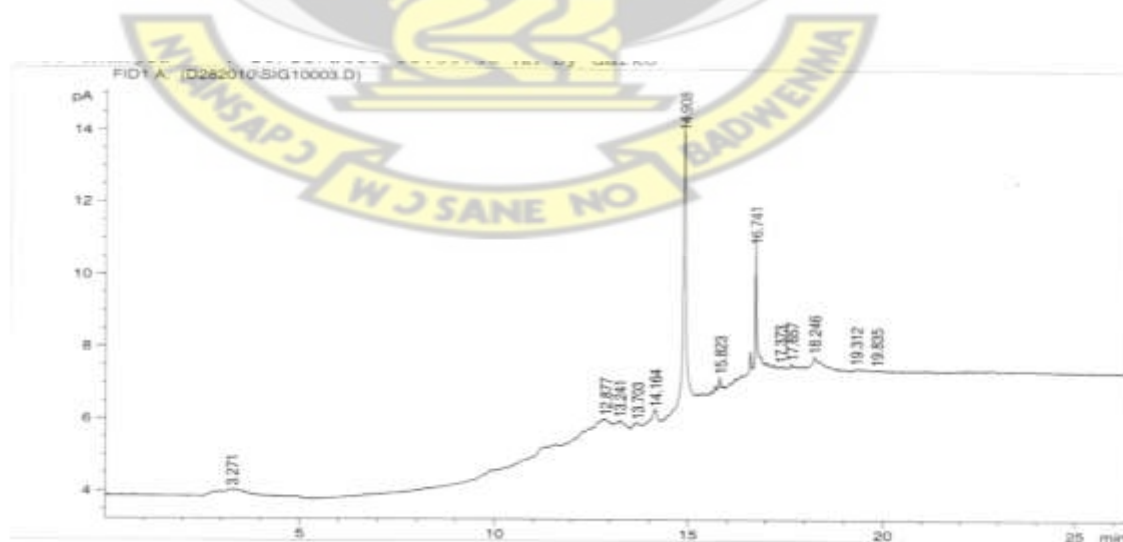


Figure 4. 5. 13 Time = 30 min

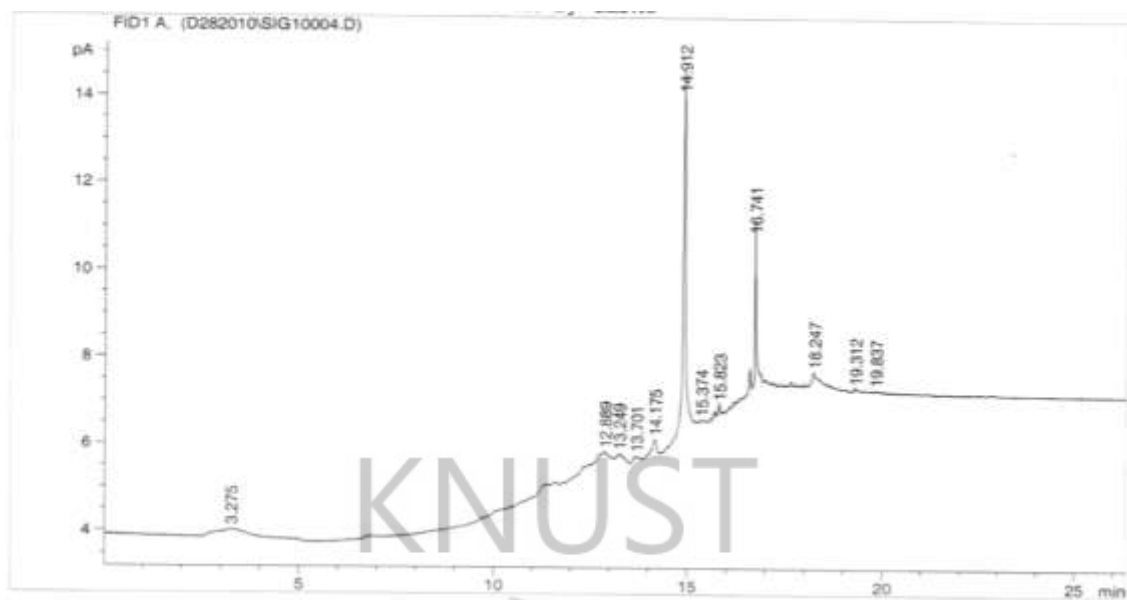


Figure 4. 5. 14 Time = 60 min

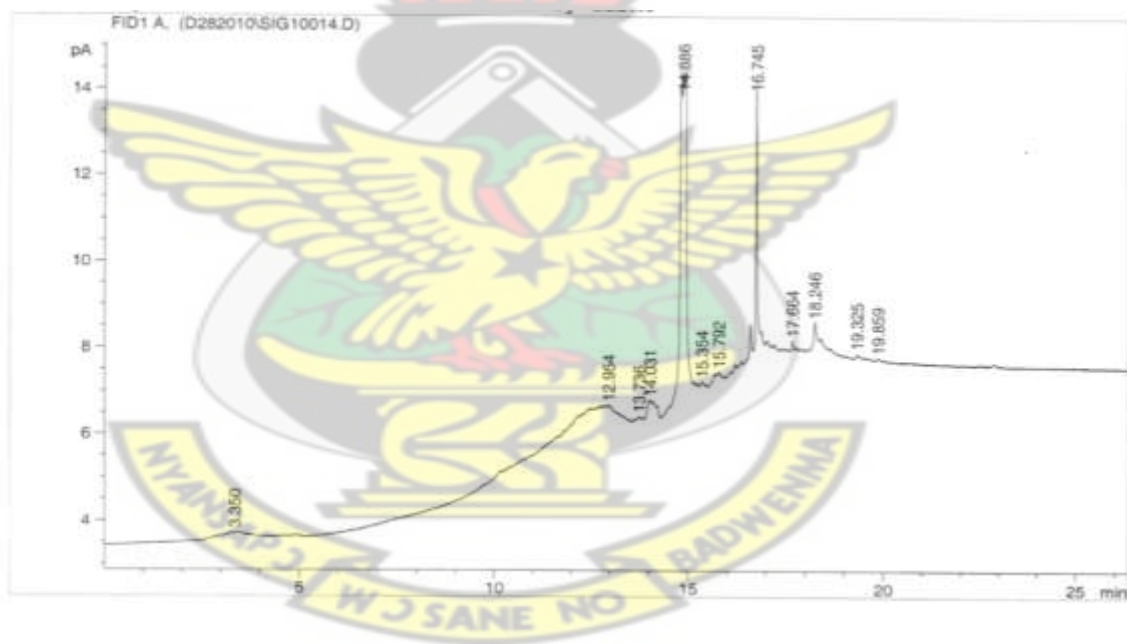


Figure 4. 5. 15 Time = 330 min

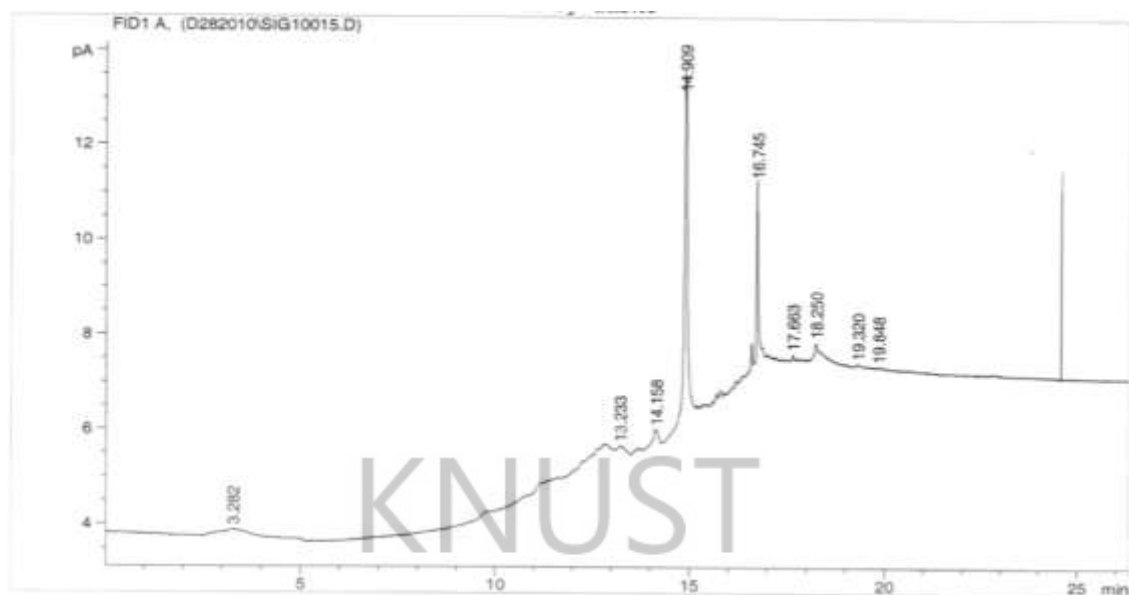


Figure 4. 5. 16 Time = 360 min

Table 4. 5.5 Results of tests on the effect Cu^{2+} ions on the liquid phase oxidation of phenols using CuO impregnated spent FCC catalyst and 40 ml of a 5000 ppm solution of Cu^{2+} . The COD of the initial solution was 874 ppm while its pH was 4.27 at 27.7°C .

ST, min	pH	Temp, $^\circ\text{C}$	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.25	23	ND	80	0	0.076	0.076
60	6.42	23.5	ND		0	0.096	0.173
90	6.21	24.4	ND		0	0.090	0.262
120	6.15	24.7	ND	139	0	0.083	0.345
150	6.13	26.4	ND	130	0	0.081	0.426
180	6.09	27	ND		0	0.085	0.511
210	6.04	25.1	ND		0	0.082	0.593
240	5.94	25.9	ND	157	0	0.090	0.683
270	5.85	26.2	ND	160	0	0.078	0.760
300	5.85	25.1	ND		0	0.065	0.826
330	5.85	25.9	ND		0	0.049	0.875
360	5.92	26.3	ND	113	0	0.052	0.927

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.17 – 4.5.20.

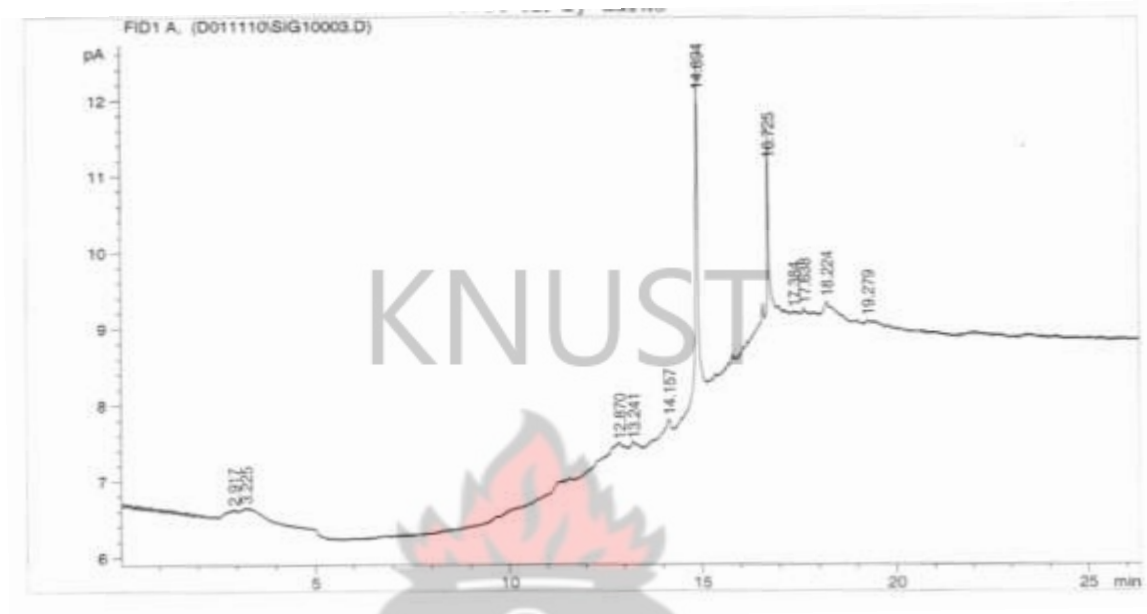


Figure 4. 5. 17 Time = 30 min

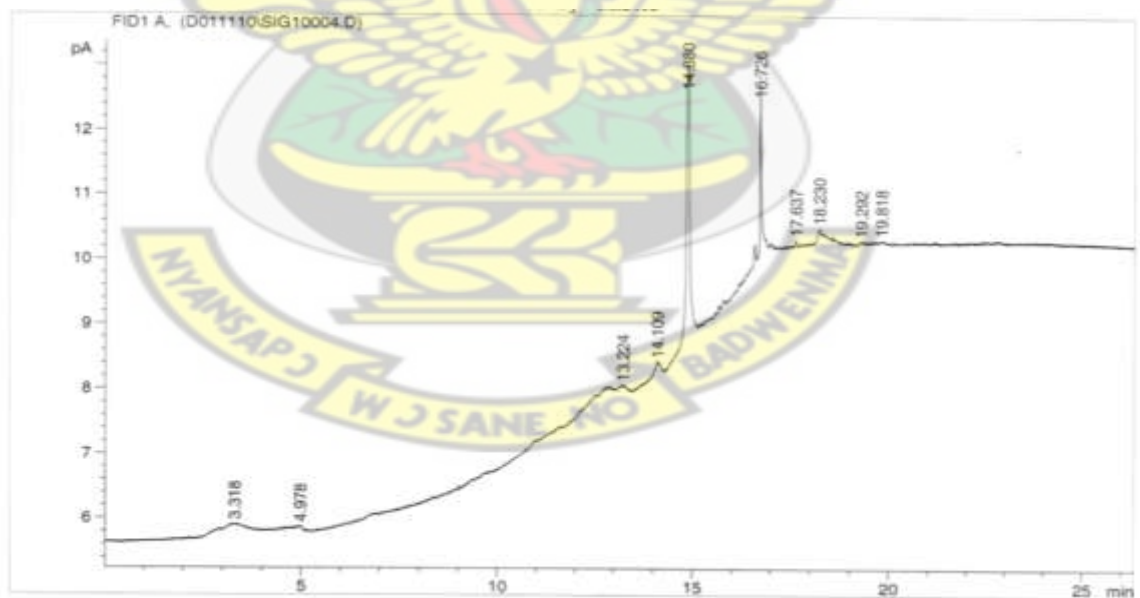


Figure 4. 5. 18 Time = 60 min

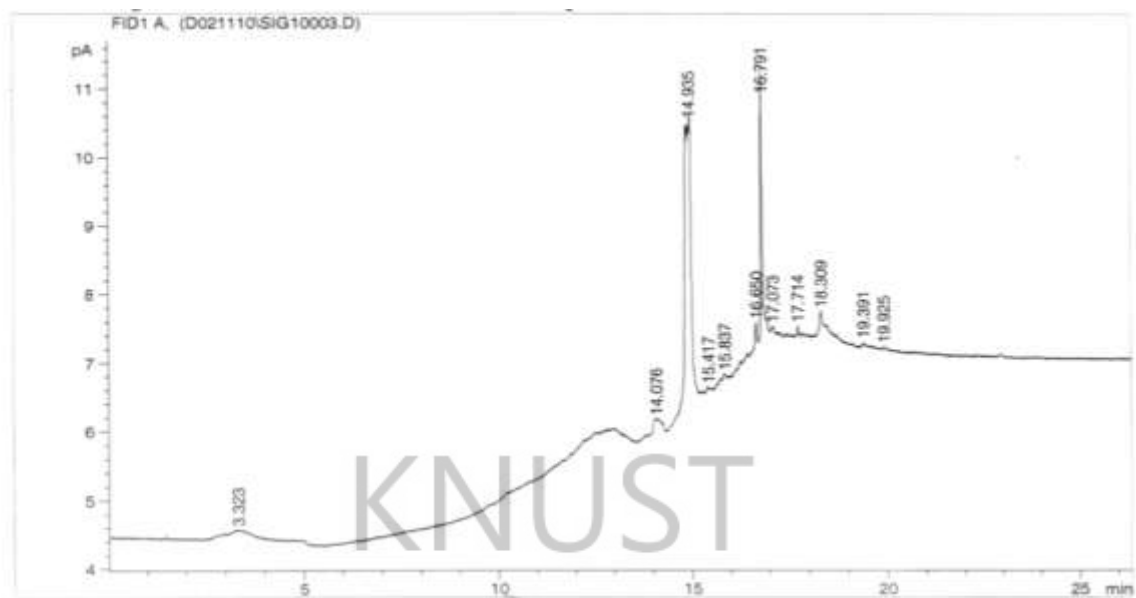


Figure 4. 5. 19 Time = 330 min

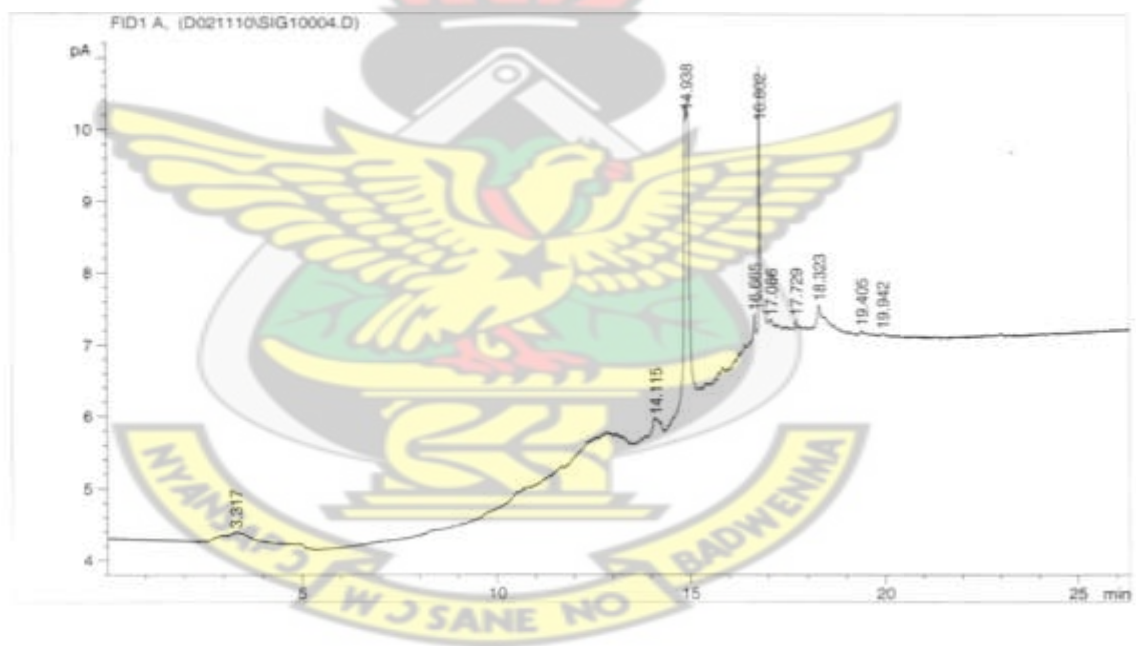


Figure 4. 5. 20 Time = 360 min

4.5.3 Effect of Fe₂O₃ Content on the Liquid Phase Oxidation of Phenol Using Spent Catalyst Impregnated With Fe₂O₃

Experimental data on the effect of Fe₂O₃ content on the liquid phase oxidation of phenols using Fe₂O₃ impregnated spent FCC catalyst have been presented in Tables 4.5.6 – 4.5.13. For these experiments the mass of modified spent FCC catalyst used was 25 g while the mass of the granite chippings used was 68g. The phenol concentration of the solution used was 1000 ppm. In total 1000 ml of the phenol solution was treated per experiment. The amount H₂O₂ was also varied from 10 ml to 20 ml. The various Fe₂O₃ amounts considered were 0.97, 1.43, 3.57 and 7.14%.

Table 4.5.6 Results of tests on the effect Fe₂O₃ on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 0.97% Fe₂O₃ and 10 ml of H₂O₂ (50%). The COD of the initial solution was 1276 ppm while its pH was 7.54 at 28°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.67	25	3.92	202	54.51	0.063	0.063
60	7.31	26.7	4.06		56.43	0.064	0.127
90	7.23	26.4	2.64		36.65	0.080	0.207
120	7.12	26.5	ND	252	0	0.071	0.278
150	6.77	27.7	ND	239	0	0.081	0.359
180	6.4	24.9	ND		0	0.093	0.453
210	6.14	25.7	4.70		65.24	0.083	0.536
240	6.03	28	ND	303	0.00	0.079	0.615
270	5.95	27	3.02	280	41.93	0.083	0.698
300	5.98	27	3.50		48.55	0.058	0.756
330	5.99	28	4.58	263	63.59	0.063	0.818

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.21 – 4.5.24.

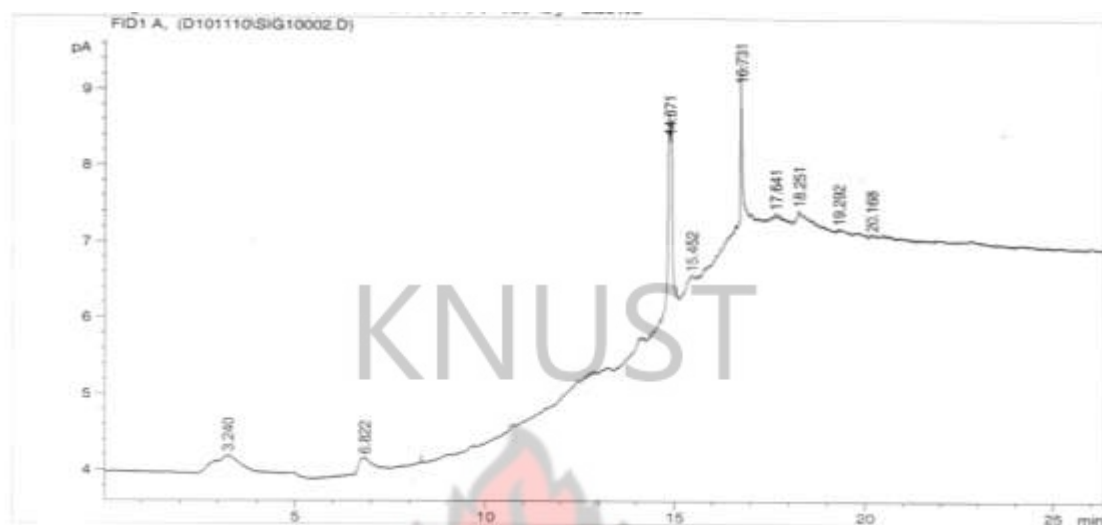


Figure 4. 5. 21 Time = 30 min

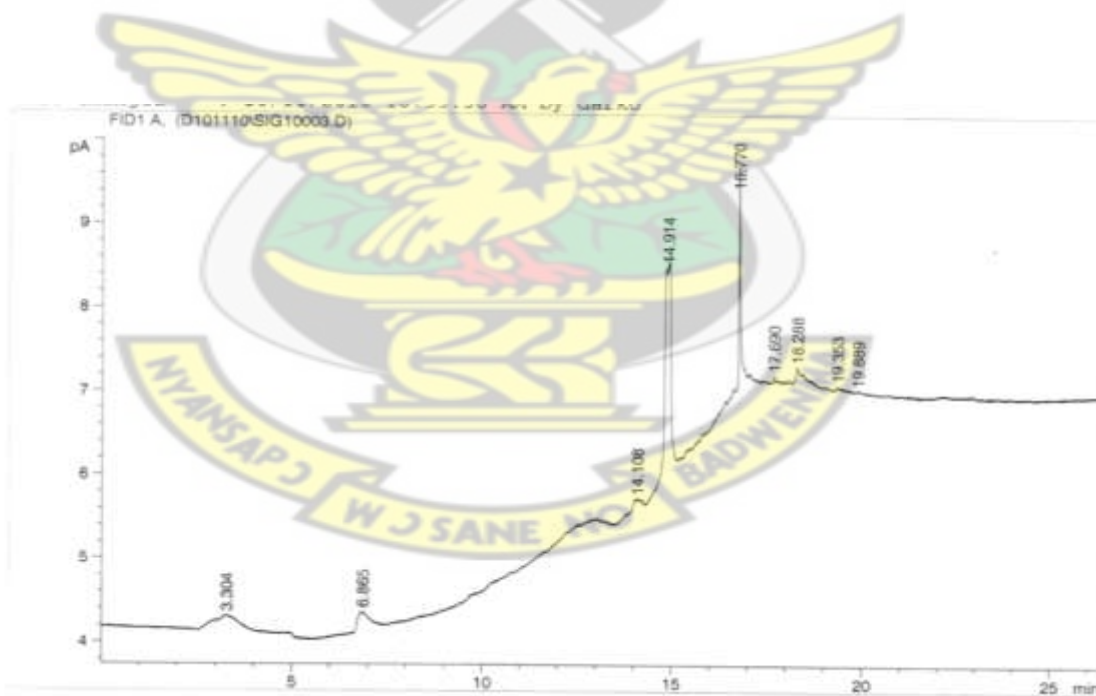


Figure 4. 5. 22 Time = 60 min

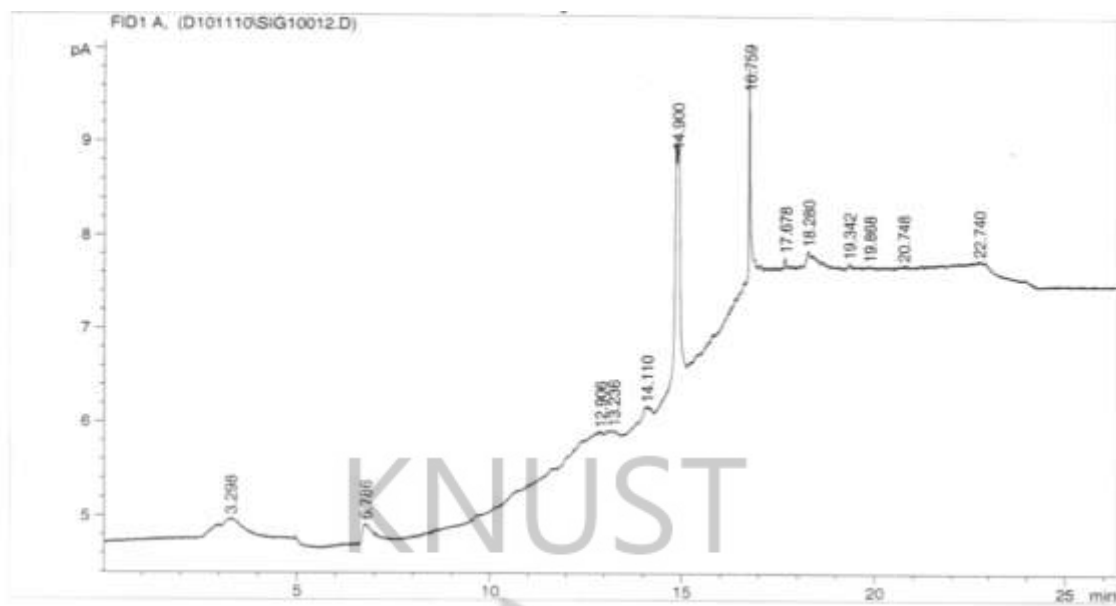


Figure 4. 5. 23 Time = 300 min

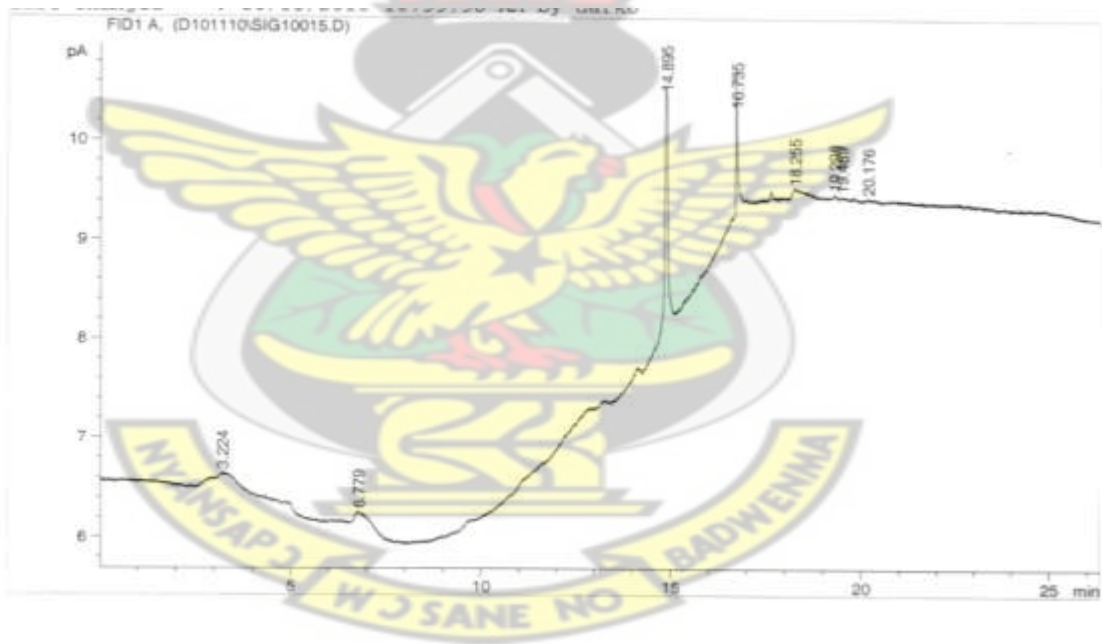


Figure 4. 5. 24 Time = 330 min

Table 4.5.7 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 1.43% Fe_2O_3 and 10 ml of H_2O_2 (50%). The COD of the initial solution was 1316 ppm while its pH was 4.51 at 27.1°C .

ST, min	pH	Temp, $^\circ\text{C}$	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.94	24.3	25.16	849	349.50	0.059	0.059
60	8.28	20.5	30.69		426.27	0.042	0.101
90	8	21.4	32.20		447.22	0.040	0.141
120	7.75	22	37.27	1144	517.64	0.039	0.180
150	7.22	24.3	23.15	937	321.53	0.058	0.238
180	7.14	24.6	23.02		319.74	0.050	0.288
210	7.01	25.5	22.27		309.31	0.051	0.339
240	6.77	26.5	28.21	940	391.84	0.049	0.388
270	6.5	25.1	22.24	673	308.84	0.055	0.394
300	6.43	25.2	13.91		193.21	0.067	0.461
330	6.18	25.9	12.15		168.72	0.067	0.528
360	6.14	26.2	12.88	672	178.85	0.035	0.564

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.25 – 4.5.28.

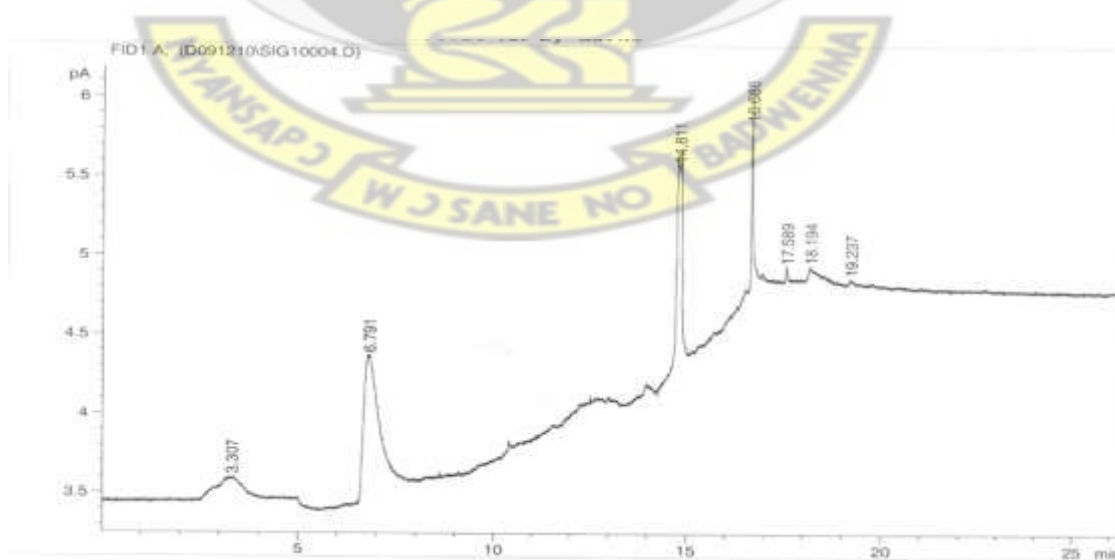


Figure 4. 5. 25 Time = 30 min

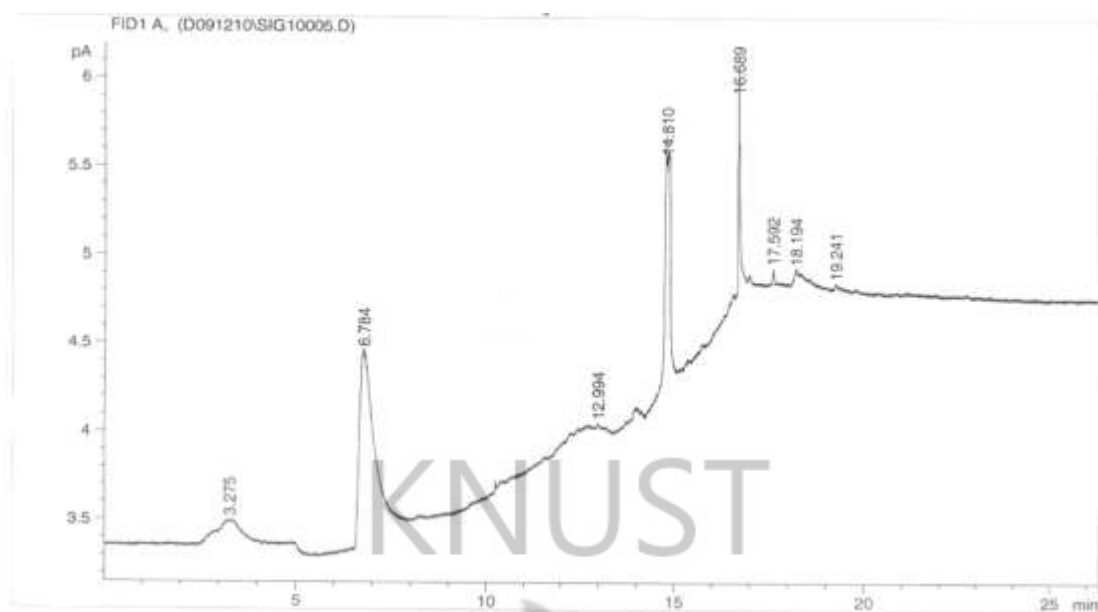


Figure 4. 5. 26 Time = 60 min

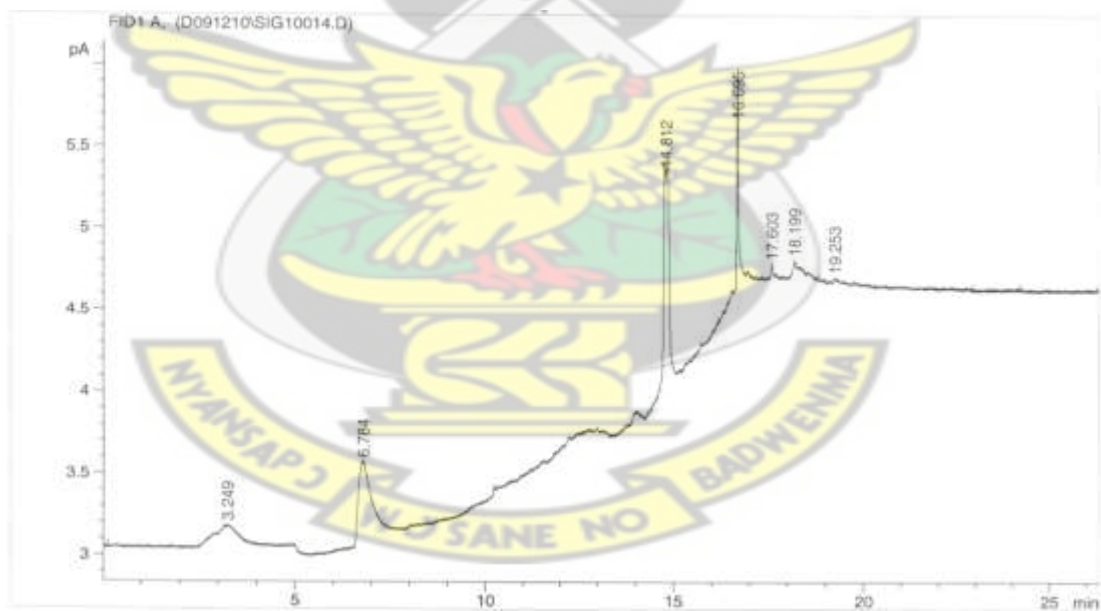


Figure 4. 5. 27 Time = 330 min

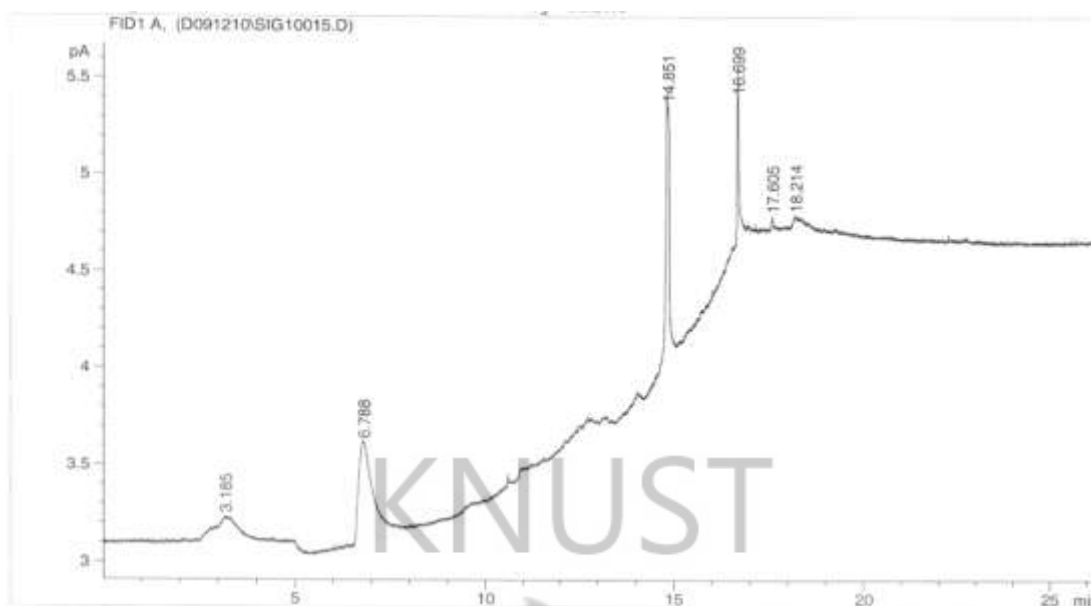


Figure 4. 5. 28 Time = 360 min

Table 4. 5.8 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 3.57% Fe_2O_3 and 10 ml of H_2O_2 (50%). The COD of the initial solution was 1325 ppm while its pH was 4.42 at 25.6°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	8.25	23.3	48.96	1230	680.06	0.023	0.023
60	8.76	23.7	47.52		660.04	0.024	0.048
90	8.69	23.2	42.54		590.90	0.031	0.079
120	8.54	22.8	44.62	1266	619.75	0.028	0.107
150	8.9	25.6	41.89	1203	581.84	0.034	0.141
180	7.95	25.9	35.94		499.20	0.043	0.184
210	7.83	26	42.62		591.99	0.028	0.212
240	7.45	27.3	36.31	1162	504.26	0.038	0.250
270	7.09	26.1	30.57	1011	424.56	0.036	0.248
300	7.1	26.1	18.11		251.60	0.057	0.305
330	6.71	26.4	22.98		319.23	0.057	0.362
360	6.45	26.6	21.06	885	292.47	0.069	0.431

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.29 – 4.5.32.

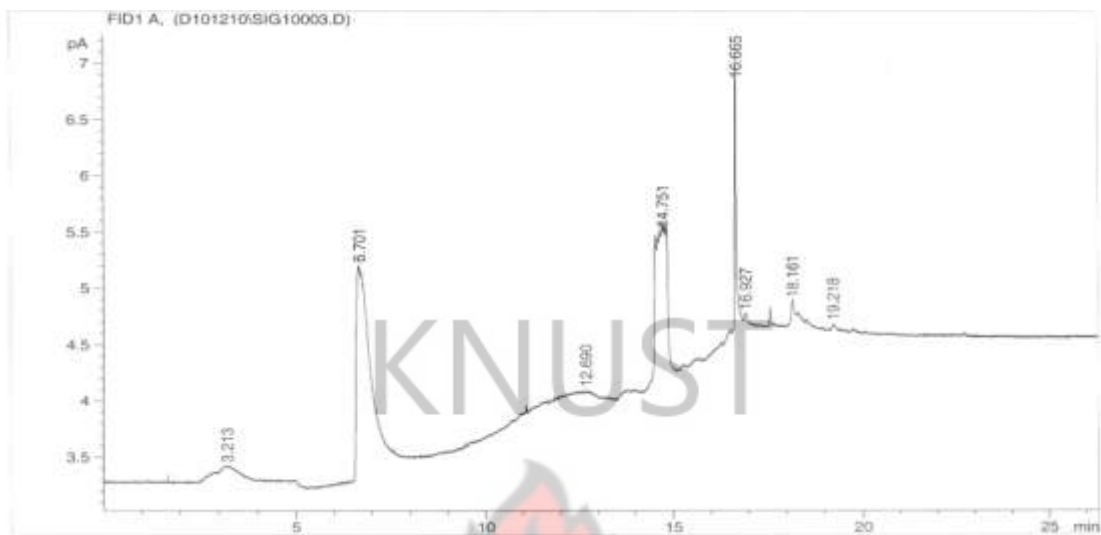


Figure 4. 5. 29 Time = 30 min

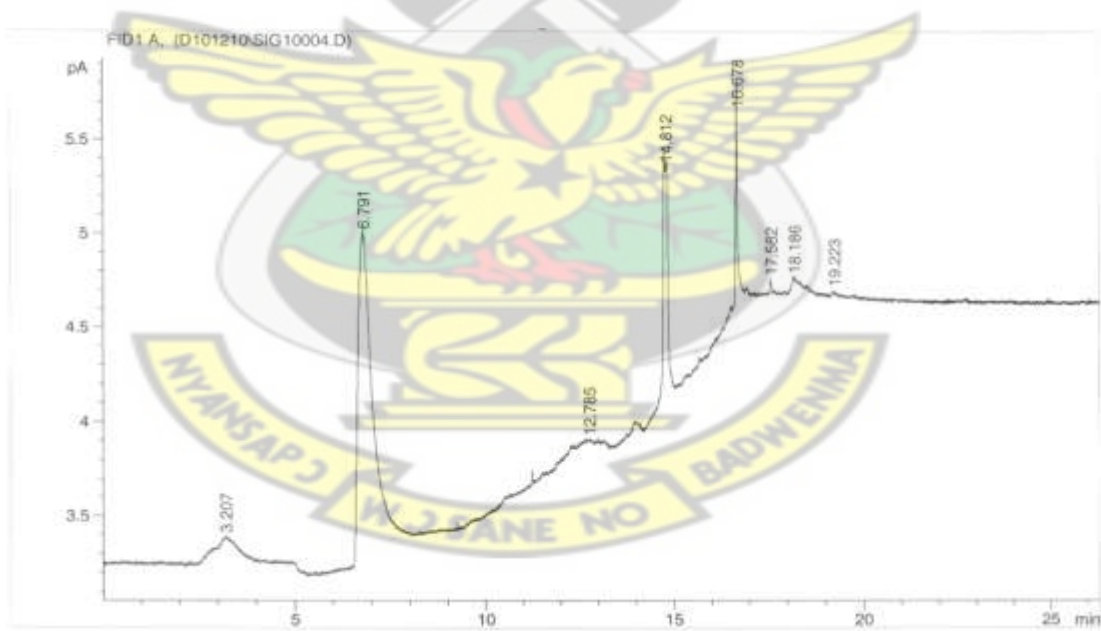


Figure 4. 5. 30 Time = 60 min



Figure 4. 5. 31 Time = 330 min

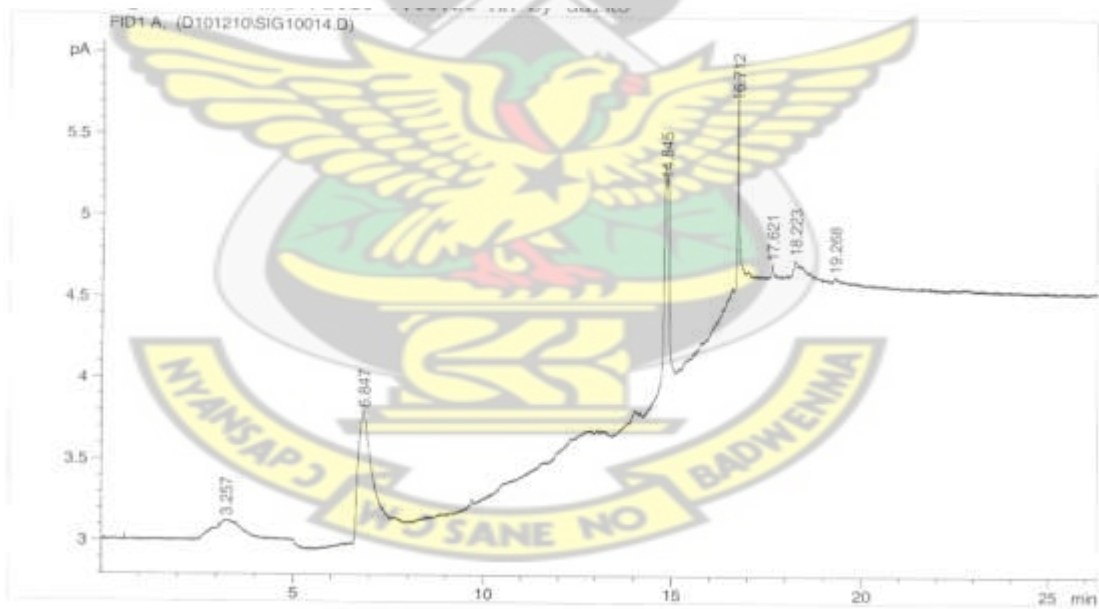


Figure 4. 5. 32 Time = 360 min

Table 4. 5.9 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 7.14% Fe_2O_3 and 10 ml of H_2O_2 (50%). The COD of the initial solution was 1325 ppm whiles its pH was 4.56 at 25.6°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	9.13	22.2	41.91	1190	582.05	0.034	0.034
60	9.66	21.4	69.20		961.09	0.004	0.038
90	9.6	21.2	38.95		541.01	0.037	0.074
120	9.42	21.7	51.61	1238	716.82	0.022	0.096
150	9.15	25	44.78	1236	621.92	0.035	0.132
180	9.16	25.5	38.29		531.85	0.040	0.171
210	8.98	26.1	35.14		488.04	0.035	0.207
240	8.85	26.6	45.98	1227	638.55	0.029	0.236
270	8.62	26.3	36.74	1182	510.26	0.034	0.241
300	8.62	25.8	36.69		509.56	0.040	0.280
330	8.54	26	35.55	1244	493.81	0.049	0.329

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.33 – 4.5.36.

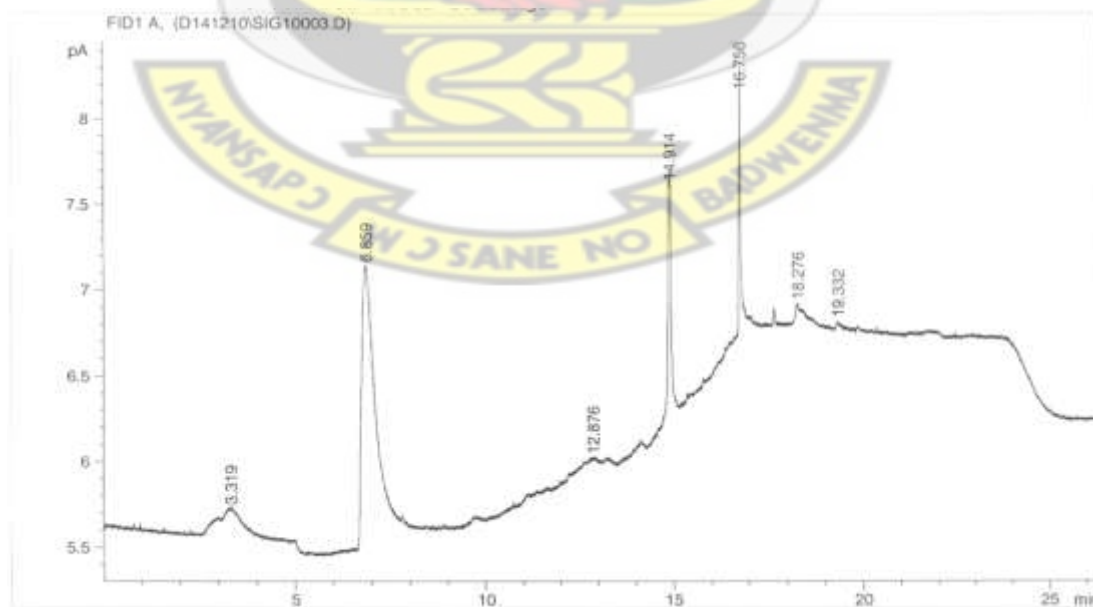


Figure 4. 5. 33 Time = 30 min

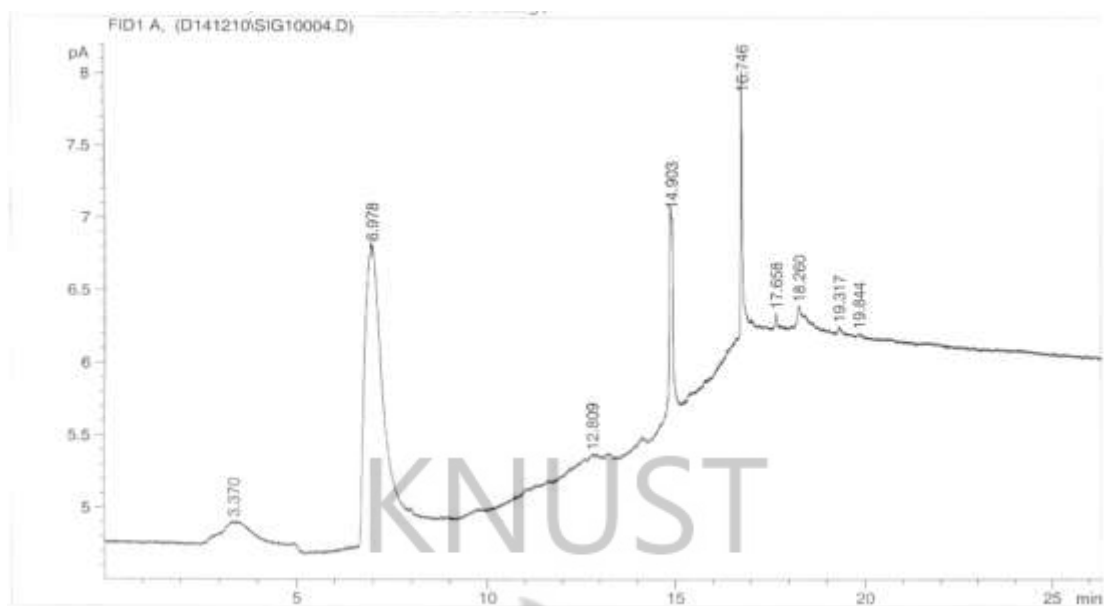


Figure 4. 5. 34 Time = 60 min

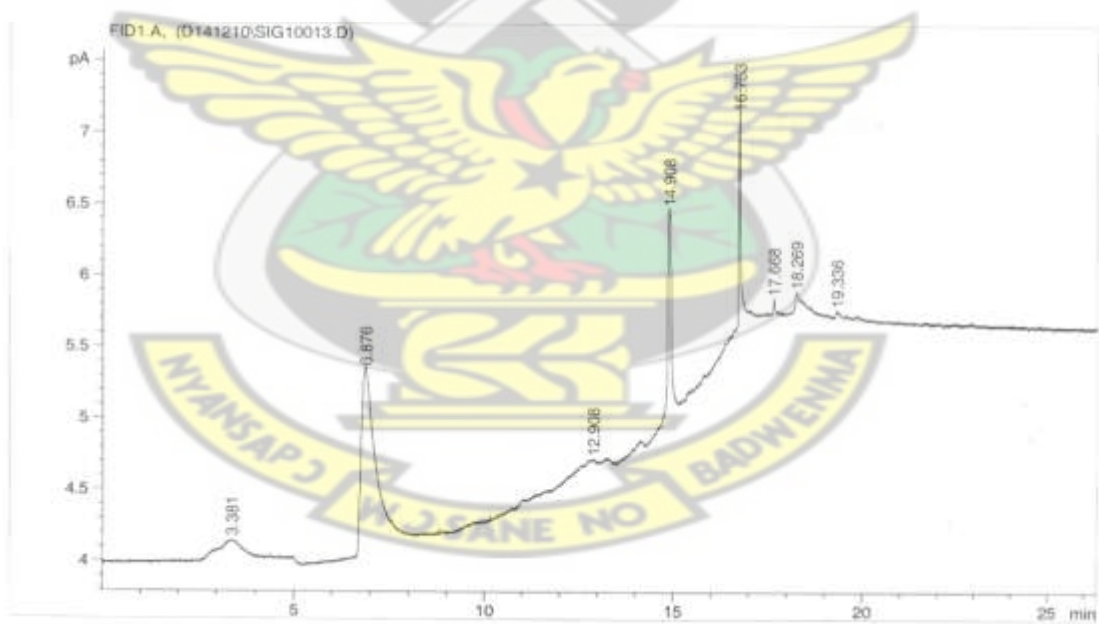


Figure 4. 5. 35 Time = 330 min

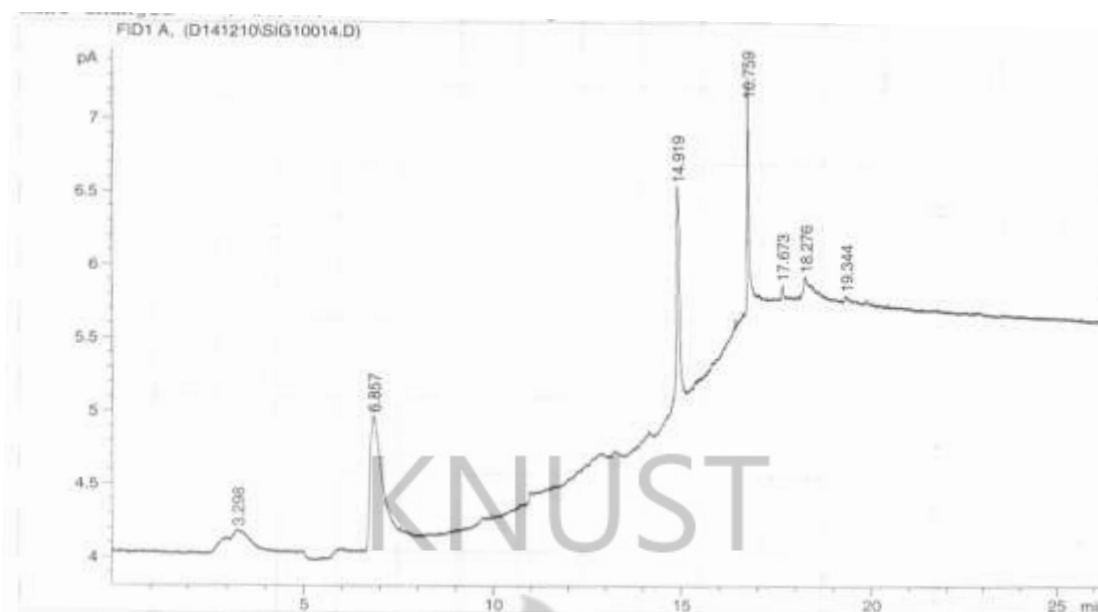


Figure 4. 5. 36 Time = 360 min

Table 4. 5.10 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 0.97% Fe_2O_3 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2025 ppm while its pH was 6.53 at 31.5°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.69	25.3	ND	145	0	0.082	0.082
60	7.23	29.1	ND		0	0.091	0.173
90	7.06	28.1	ND		0	0.080	0.253
120	6.82	27.3	ND	119	0	0.078	0.331
150	6.47	28.5	ND	116	0	0.084	0.415
180	6.5	30.5	ND		0	0.085	0.500
210	6.34	28.3	ND		0	0.069	0.569
240	6.28	30.2	ND	99	0	0.077	0.646
270	6.03	29	ND	114	0	0.093	0.739
300	6.18	30.5	ND		0	0.073	0.812
330	6.1	31.3	ND	88	0	0.086	0.898

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.37 – 4.5.40.

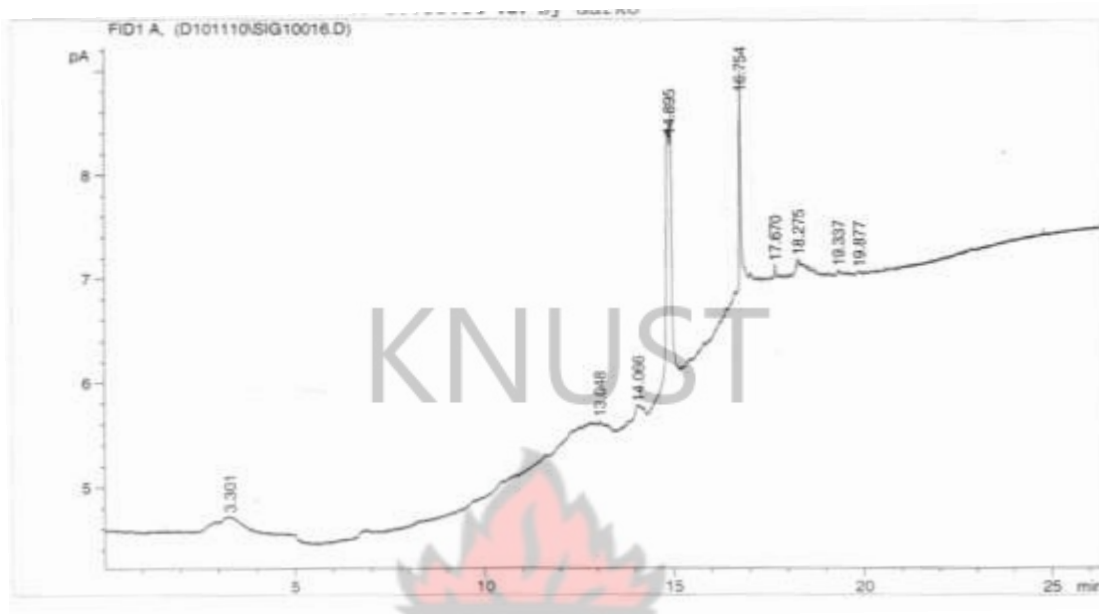


Figure 4. 5. 37 Time = 30 min

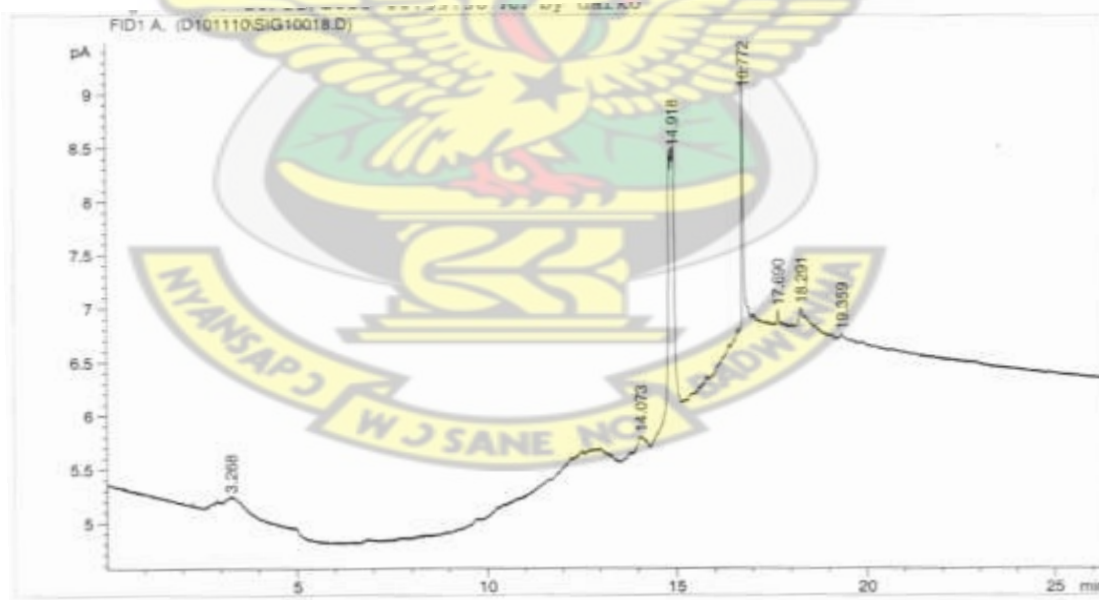


Figure 4. 5. 38 Time = 60 min

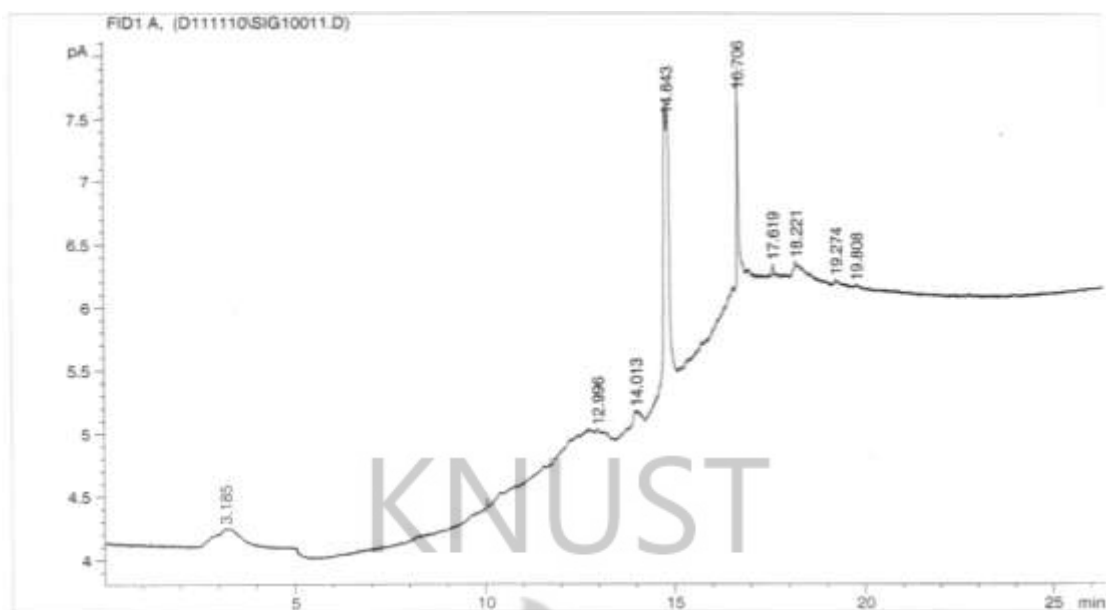


Figure 4. 5. 39 Time = 300 min

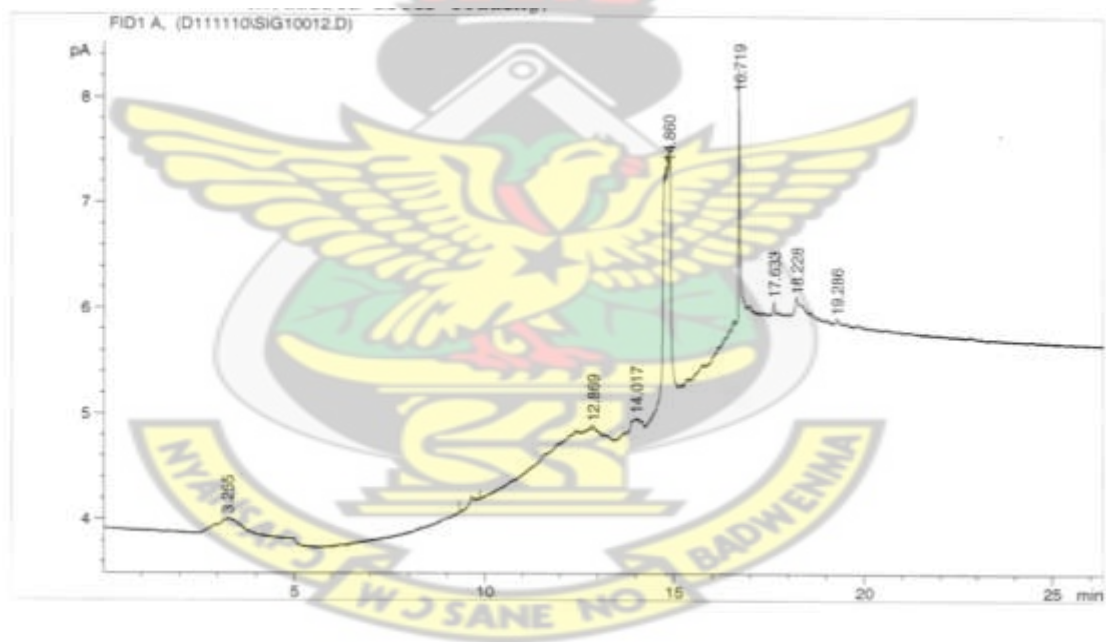


Figure 4. 5. 40 Time = 330 min

Table 4.5.11 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 1.43% Fe_2O_3 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2590 ppm while its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.05	24.2	15.67	552	217.59	0.068	0.068
60	6.34	24	7.66		106.42	0.070	0.137
90	5.73	24.4	3.55		49.31	0.087	0.224
120	5.48	27	3.05	352	42.31	0.082	0.306
150	5.34	26.5	0	276	0	0.097	0.404
180	5.24	26.8	0		0	0.097	0.501
210	4.78	27.4	0		0	0.097	0.598
240	4.61	28	0	198	0	0.097	0.696
270	4.6	29	0	193	0	0.085	0.683
300	4.99	29	0	160	0	0.044	0.726
330	4.86	29.2	0	161	0	0.057	0.784

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.41 – 4.5.44.

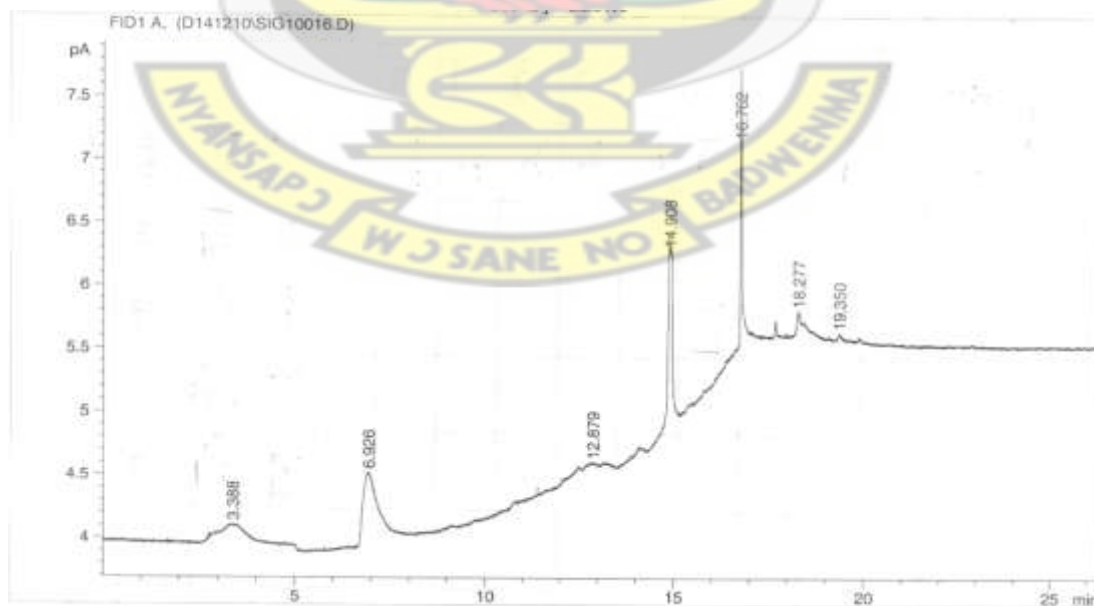


Figure 4. 5. 41 Time = 30 min

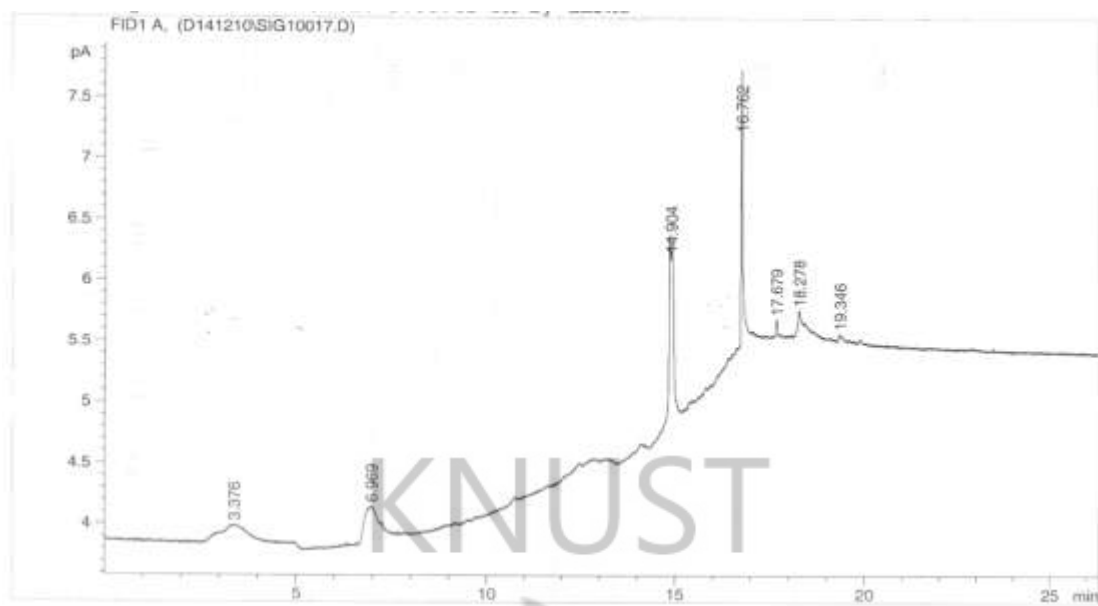


Figure 4. 5. 42 Time = 60 min

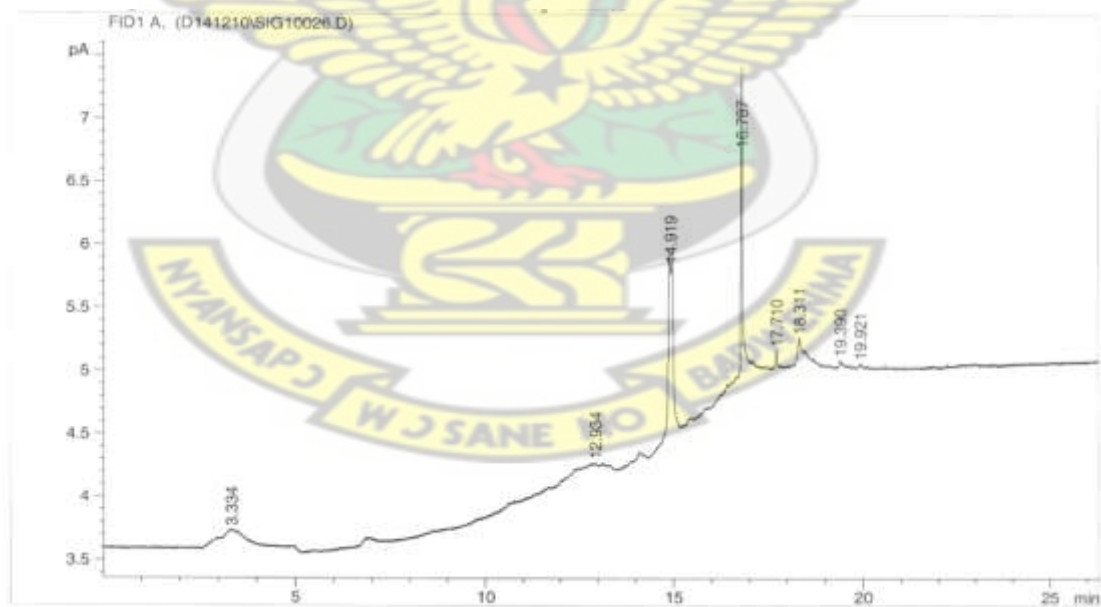


Figure 4. 5. 43 Time = 300 min

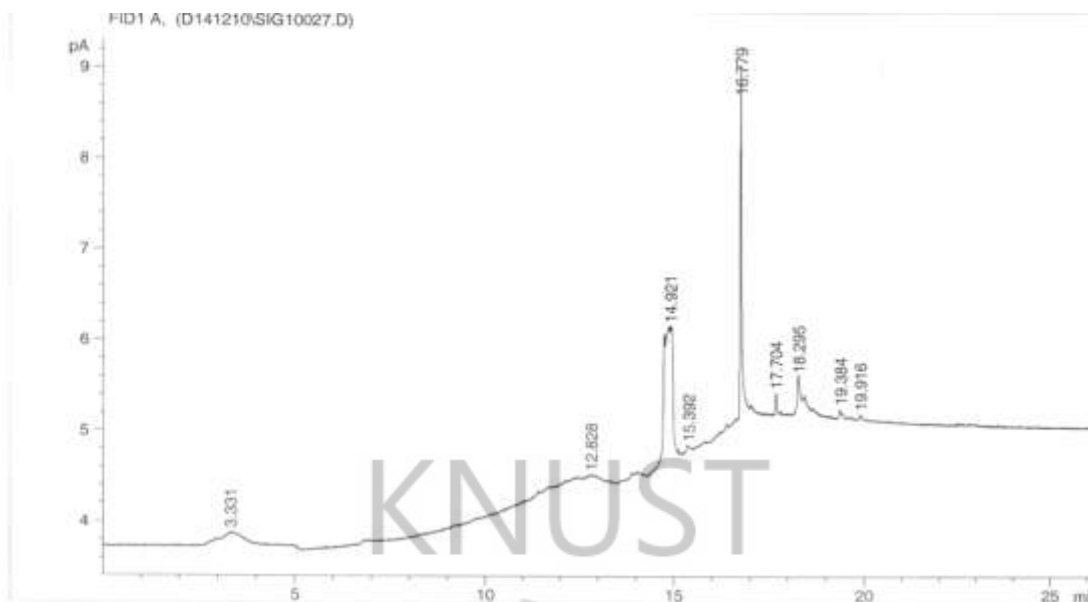


Figure 4. 5. 44 Time = 330 min

Table 4. 5.12 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 3.57% Fe_2O_3 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2590 ppm whiles its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.43	23.9	16.45	1035	205.60	0.070	0.070
60	8.01	23.3	25.61		320.07	0.065	0.135
90	7.72	25.2	44.69		558.57	0.037	0.172
120	7.3	25.9	29.02	1154	362.74	0.061	0.233
150	6.97	27.3	33.81	1009	422.62	0.049	0.282
180	6.9	27.5	36.08		451.03	0.051	0.333
210	6.62	27.9	24.05		300.62	0.061	0.394
240	6.35	28.4	11.66	844	145.71	0.070	0.464
270	6.13	27.1	7.70	615	96.20	0.083	0.477
300	5.98	28.5	8.89		111.12	0.067	0.544
330	6.07	28	0	387	0	0.061	0.605

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.45 – 4.5.48.

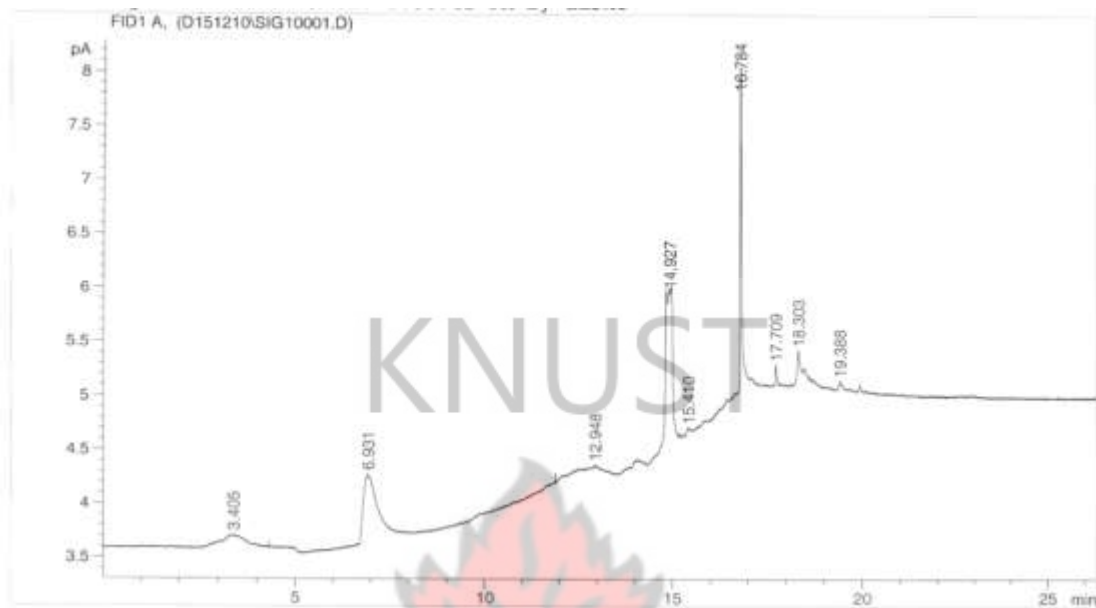


Figure 4. 5. 45 Time = 30 min

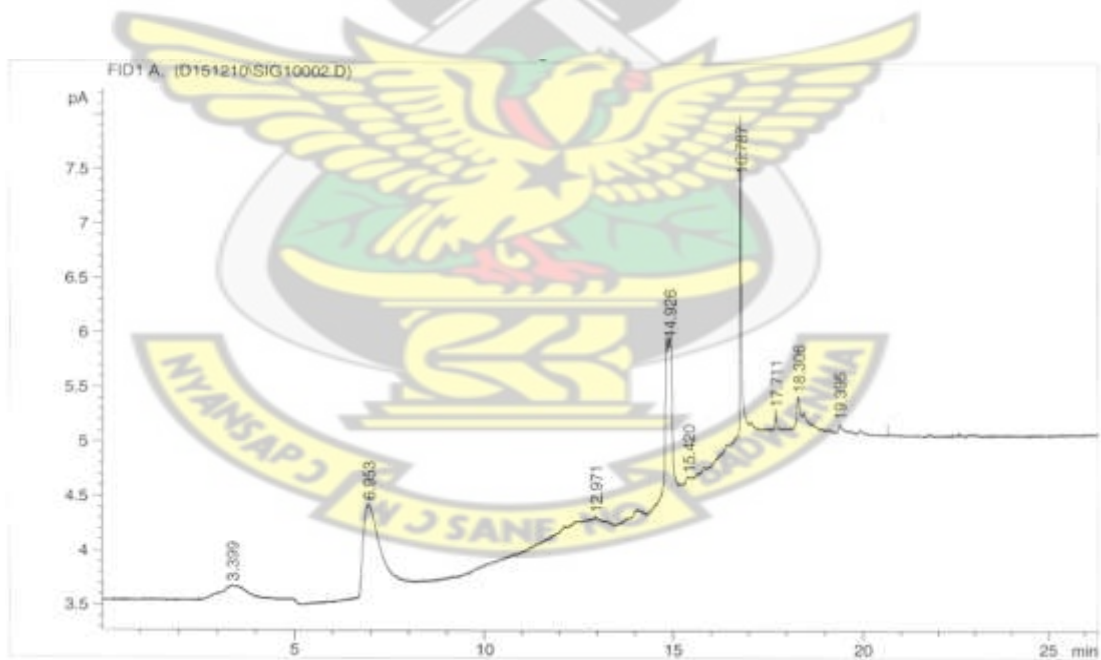


Figure 4. 5. 46 Time = 60 min

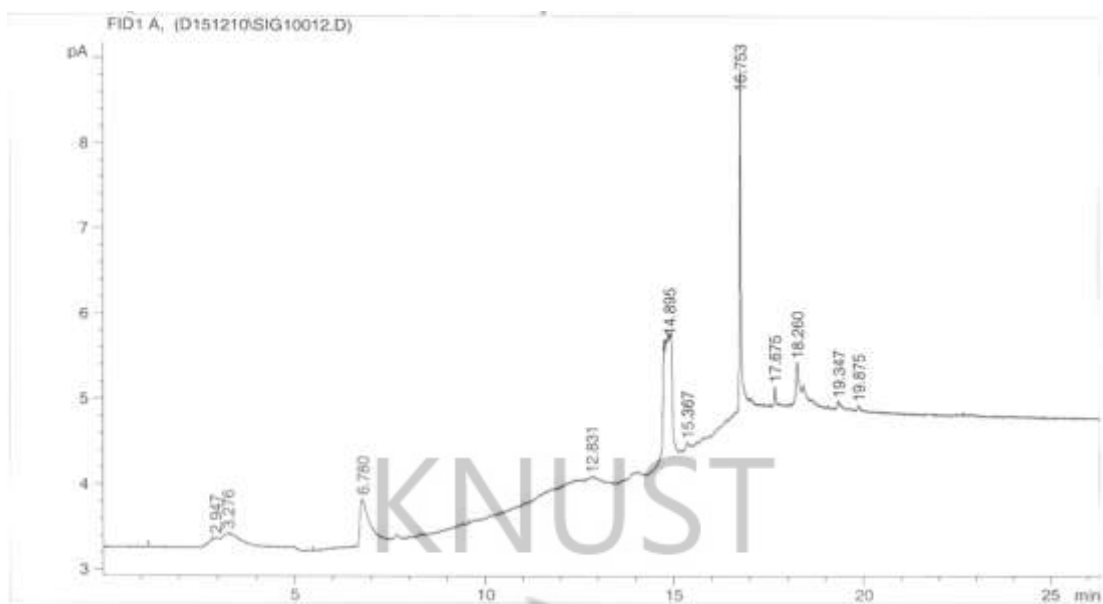


Figure 4. 5. 47 Time = 300 min

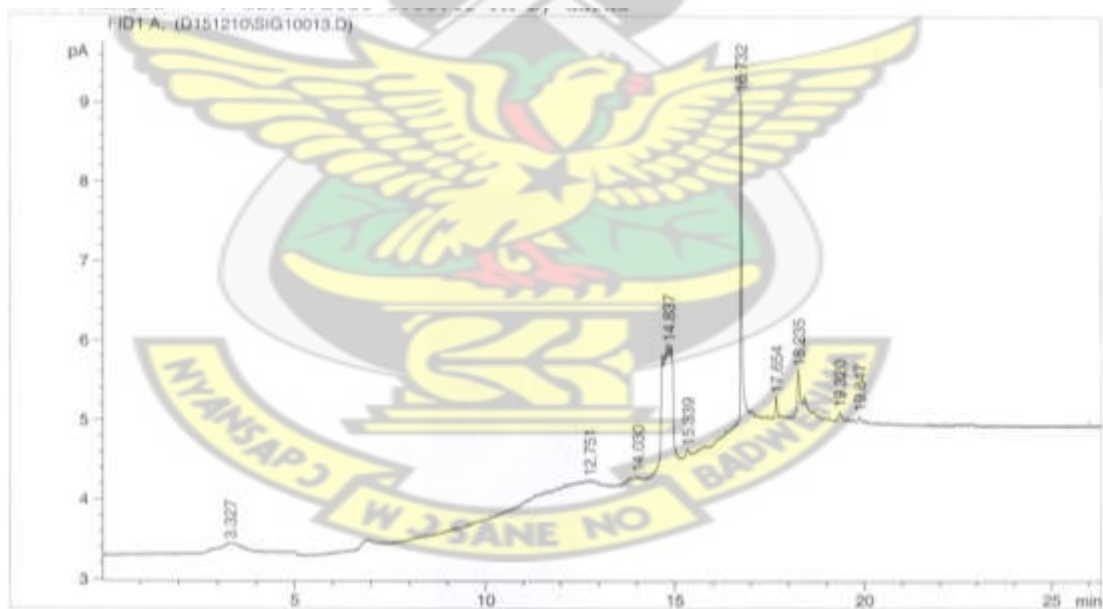


Figure 4. 5. 48 Time = 330 min

Table 4.5.13 Results of tests on the effect Fe_2O_3 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 7.14% Fe_2O_3 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2590 ppm while its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	9.1	23.7	32.13	1185	79.72	0.087	0.087
60	9.39	22.8	67.22		166.80	0.075	0.162
90	9.11	24.2	81.06		201.14	0.059	0.221
120	8.9	25	150.22	1243	372.76	0.053	0.275
150	8.29	27.3	98.89	1117	245.38	0.066	0.340
180	8.57	27.6	107.83		267.58	0.061	0.401
210	8.39	28.6	122.45		303.84	0.063	0.465
240	8.27	28.8	148.64	1225	368.83	0.050	0.515
270	7.74	29.3	150.67	1039	373.87	0.038	0.503
300	7.83	29.9	180.36	0	447.55	0.041	0.545
330	7.58	30.5	133.59	1147	331.48	0.062	0.607

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.49 – 4.5.52.



Figure 4.5.49 Time = 30 min

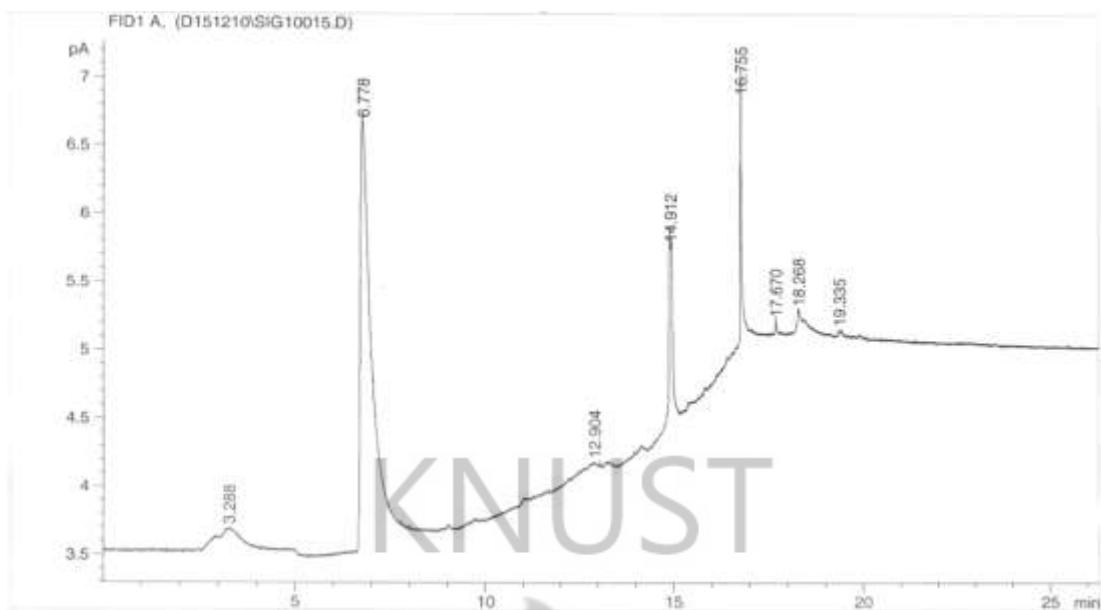


Figure 4. 5. 50 Time = 60 min

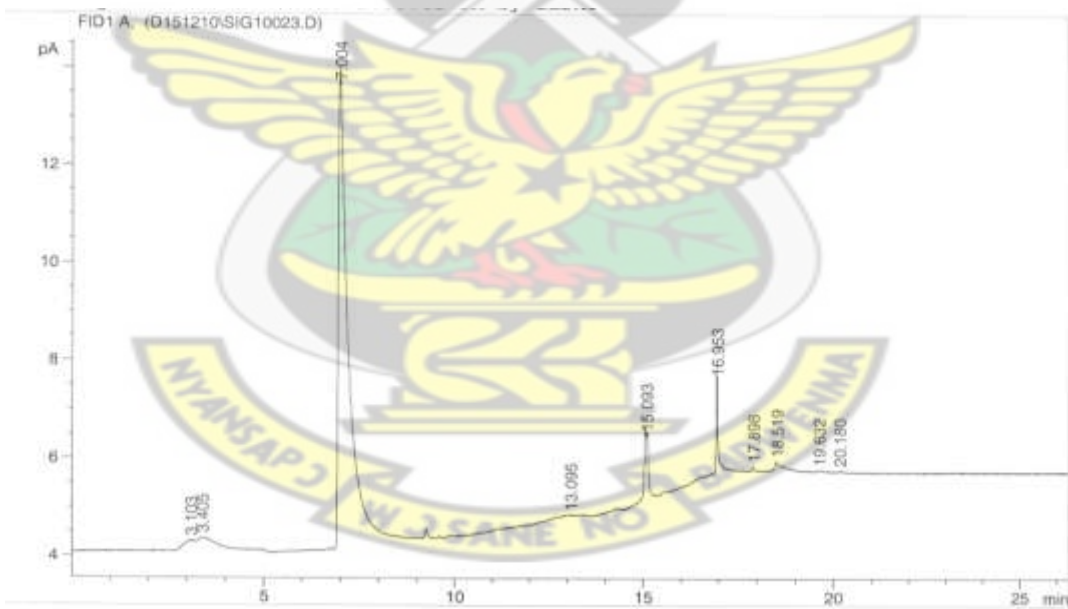


Figure 4. 5. 51 Time = 300 min

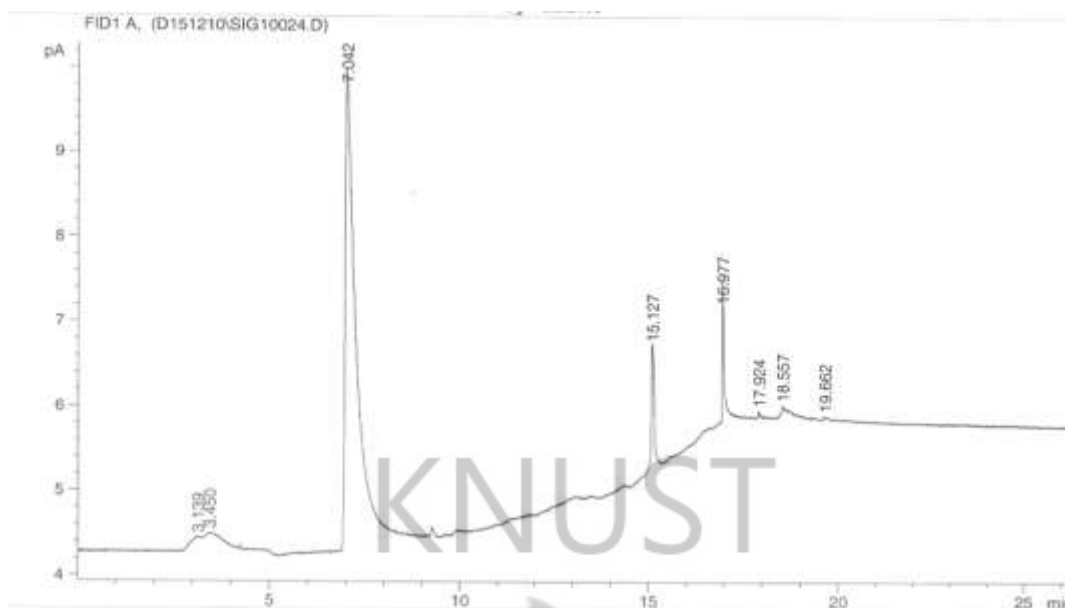


Figure 4. 5. 52 Time = 330 min

4 .5.4 Effect of H_2O_2 Content on the Liquid Phase Oxidation of Phenol Using Spent Catalyst Impregnated With 2.58% CuO

Experimental data on the effect of H_2O_2 content on the liquid phase oxidation of phenols using CuO impregnated spent FCC catalyst(2.58%) have been presented in Tables Table 4. 5.14 - Table 4. 5.15. For these experiments the mass of modified spent FCC catalyst used was 25 g whiles the mass of the granite chippings used was 68g. The phenol concentration of the solution used was 1000 ppm. In total 1000 ml of the phenol solution was treated per experiment. The amount H_2O_2 was also varied from 10 ml to 20 ml.

Table 4.5.14 Results of tests on the effect H₂O₂ on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 2.58% CuO and 10 ml of H₂O₂ (50%). The COD of the initial solution was 1316 ppm whiles its pH was 4.51 at 27.1°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.33	21.4	11.63	362	164.55	0.085	0.085
60	6.32	22.7	23.72		335.69	0.059	0.144
90	6.17	23.3	23.18		327.99	0.062	0.206
120	6.03	24.8	19.89	711	281.41	0.066	0.272
150	5.56	25.8	8.61	559	121.82	0.082	0.354
180	5.45	26.3	16.18		229.03	0.067	0.420
210	5.3	26.9	17.64		249.67	0.061	0.482
240	5.29	26.3	9.51	706	134.63	0.070	0.552
270	5.17	27.6	8.43	579	119.35	0.081	0.563
300	5.13	27.6	18.89		267.28	0.056	0.619
330	5.3	27.7	21.18	683	299.65	0.032	0.651

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.52 – 4.5.56.



Figure 4. 5. 53 Time = 30 min

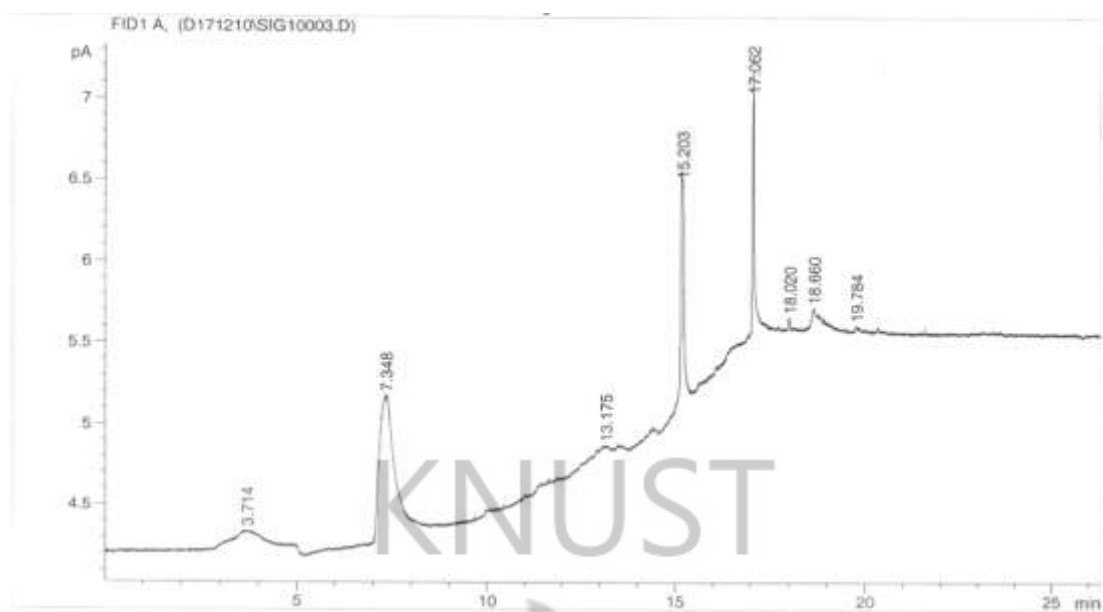


Figure 4. 5. 54 Time = 60 min

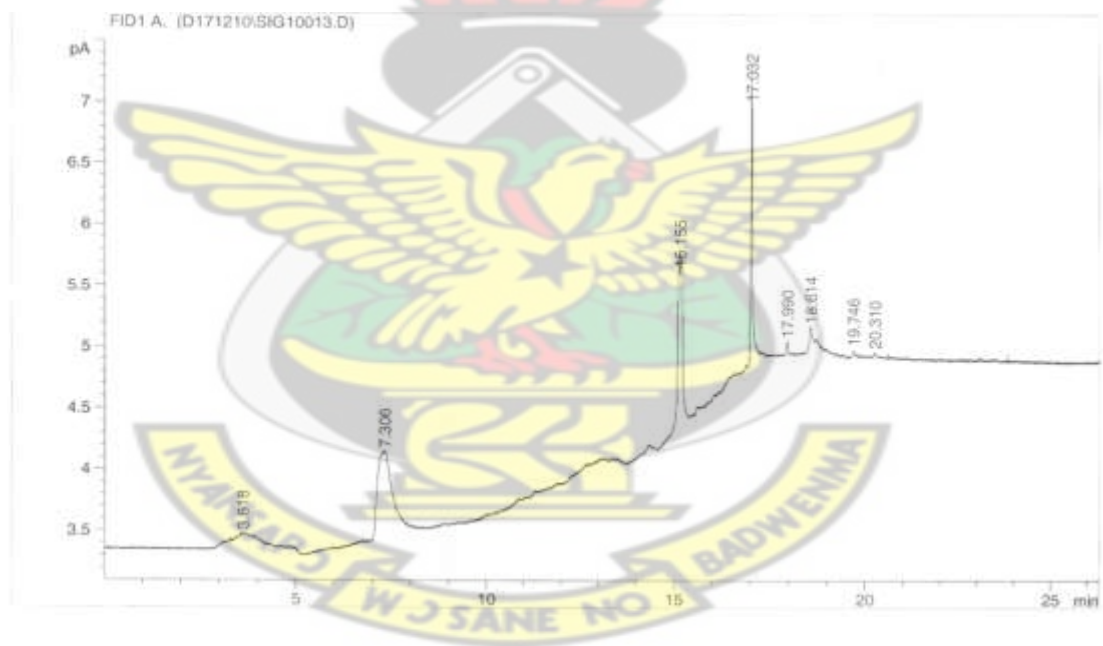


Figure 4. 5. 55 Time = 300 min



Figure 4. 5. 56 Time = 330 min

Table 4. 5.15 Results of tests on the effect H_2O_2 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 2.58% CuO and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2590 ppm while its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.41	21.6	2.42	134	34.28	0.070	0.070
60	6.25	21.5	10.57		149.56	0.075	0.145
90	6.18	22.4	12.41		175.55	0.068	0.214
120	5.86	23.6	9.59	453	135.65	0.079	0.292
150	5.55	25.3	6.51	395	92.12	0.073	0.365
180	5.31	25.5	3.71		52.52	0.083	0.448
210	5.22	26.5	3.61		51.15	0.077	0.525
240	5.02	27.1	4.71	383	66.67	0.085	0.610
270	4.88	28.5	0.00	347	0	0.102	0.627
300	4.77	28.1	3.99	0	56.49	0.082	0.709
330	4.63	27.3	3.39	325	47.90	0.061	0.769

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.57 – 4.5.60.

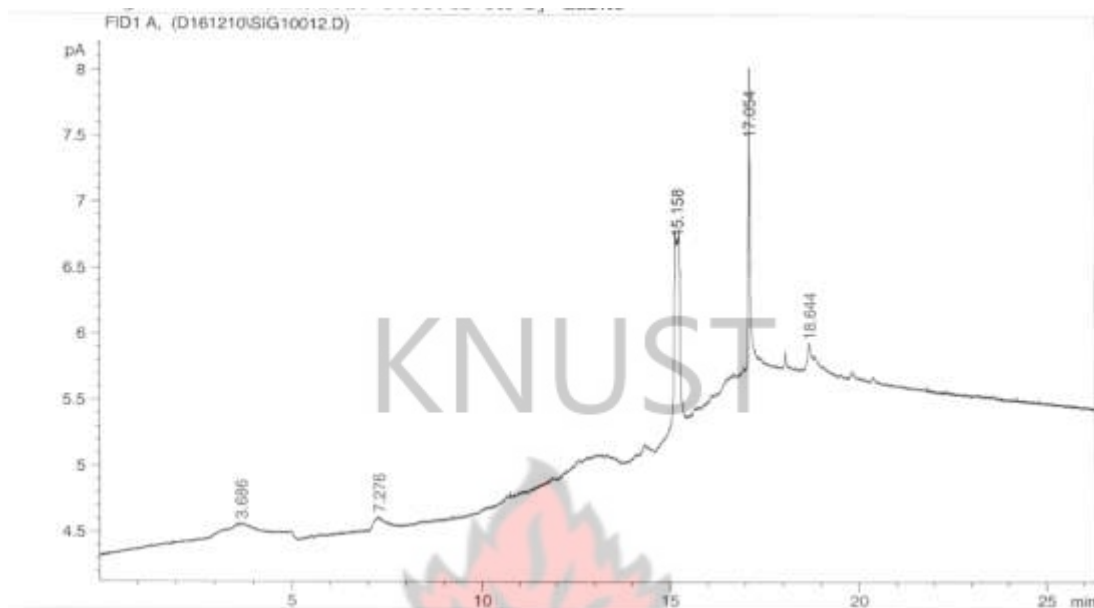


Figure 4. 5. 57 Time = 30 min

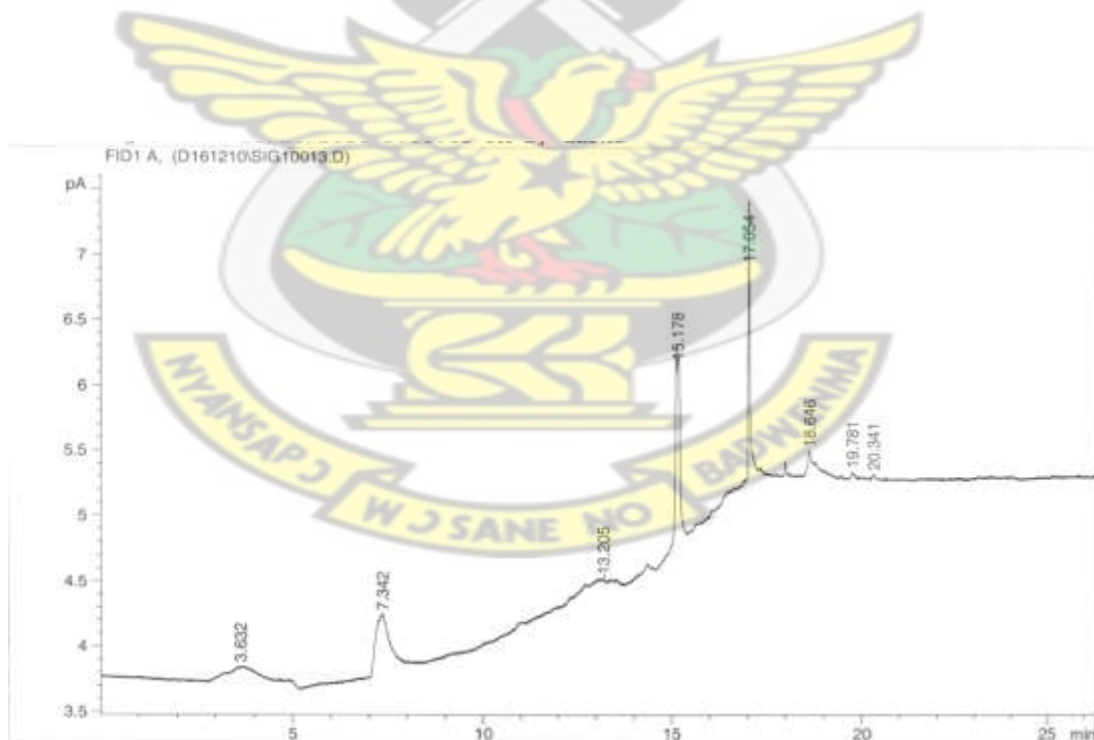


Figure 4. 5. 58 Time = 60 min

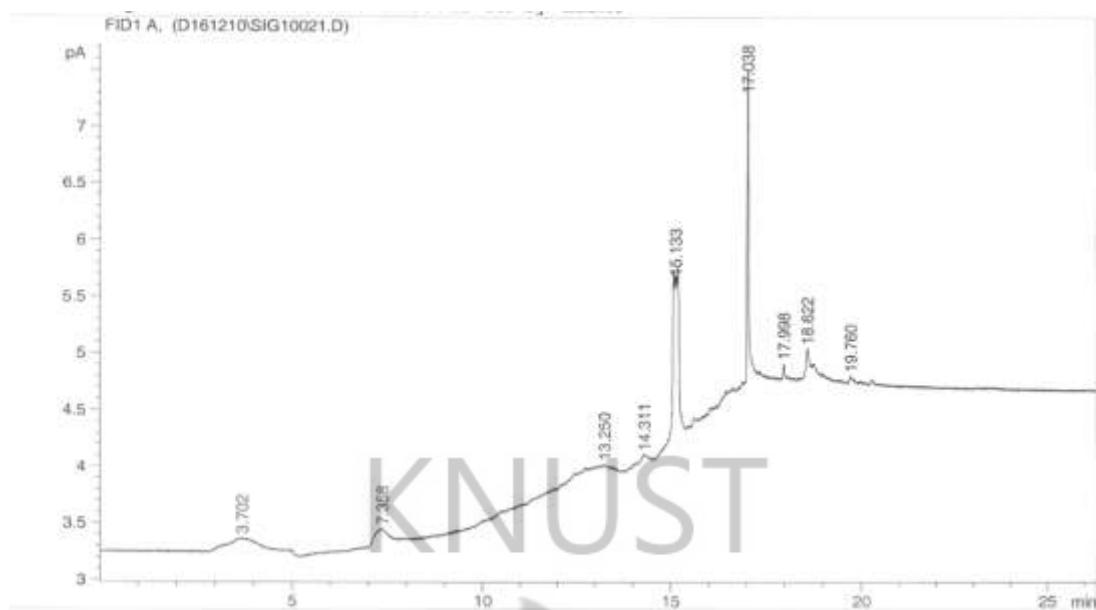


Figure 4. 5. 59 Time = 300 min

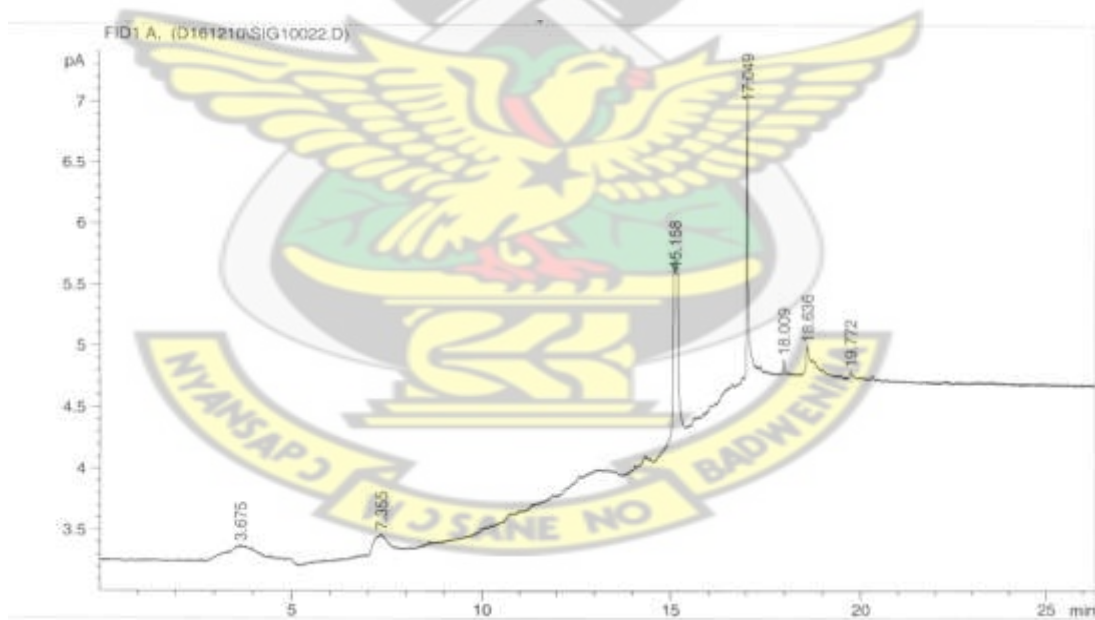


Figure 4. 5. 60 Time = 330 min

4.5.5 Effect of H₂O₂ Content on the Liquid Phase Oxidation of Phenol Using Spent Catalyst Impregnated With 1.58% MnO₂

Experimental data on the effect of H₂O₂ content on the liquid phase oxidation of phenols using MnO₂ impregnated spent FCC catalyst (1.58%) have been presented in Tables Table 4. 5.16 - Table 4. 5.17. For these experiments the mass of modified spent FCC catalyst used was 25 g while the mass of the granite chippings used was 68g. The phenol concentration of the solution used was 1000 ppm. In total 1000 ml of the phenol solution was treated per experiment. The amount H₂O₂ was also varied from 10 ml to 20 ml.

Table 4. 5.16 Results of tests on the effect H₂O₂ on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 1.58% MnO₂ and 10 ml of H₂O₂ (50%). The COD of the initial solution was 1276 ppm while its pH was 4.59 at 27.0°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.56	24.2	8.50	214	118.10	0.083	0.083
60	6.7	22.6	35.25		489.61	0.032	0.115
90	6.93	23	62.69		870.73	0.009	0.125
120	7.05	25	57.65	1218	800.65	0.016	0.140
150	6.91	25.3	48.29	974	670.64	0.020	0.160
180	7.01	26.2	46.40		644.43	0.023	0.183
210	7.14	26.4	47.17		655.20	0.019	0.202
240	7.15	26.7	49.12		682.19	0.024	0.226
270	7.18	27.4	59.62	1167	827.99	0.013	0.240
300	7.28	23.7	36.23	1019	503.19	0.032	0.272
330	7.31	24	63.37		880.20	0.008	0.280
360	7.27	25.4	60.98	1191	846.94	0.010	0.290

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.61 – 4.5.64.



Figure 4. 5. 61 Time = 30 min

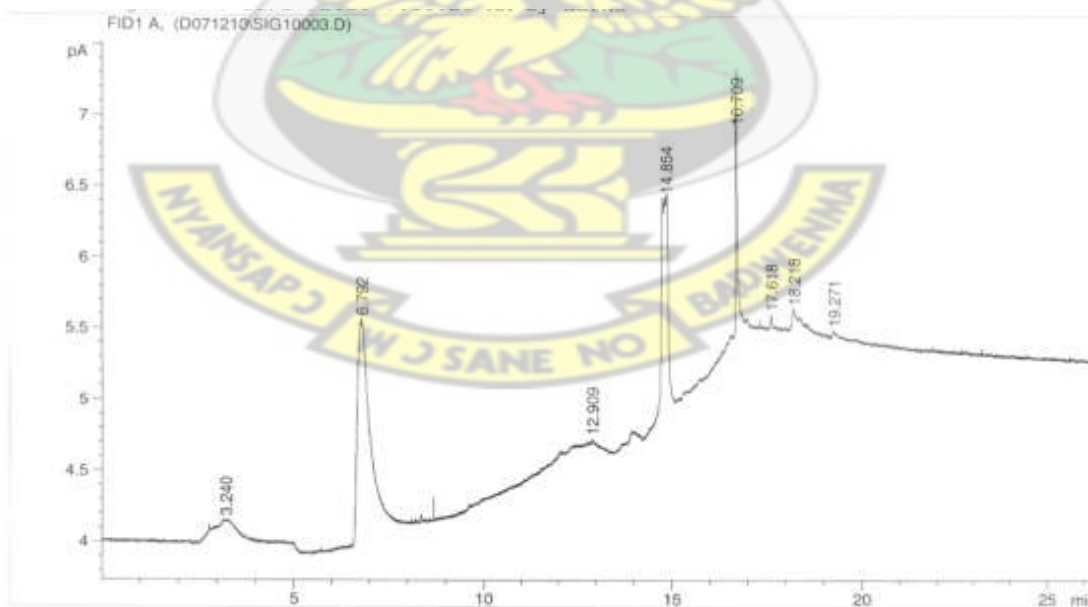


Figure 4. 5. 62 Time = 60 min

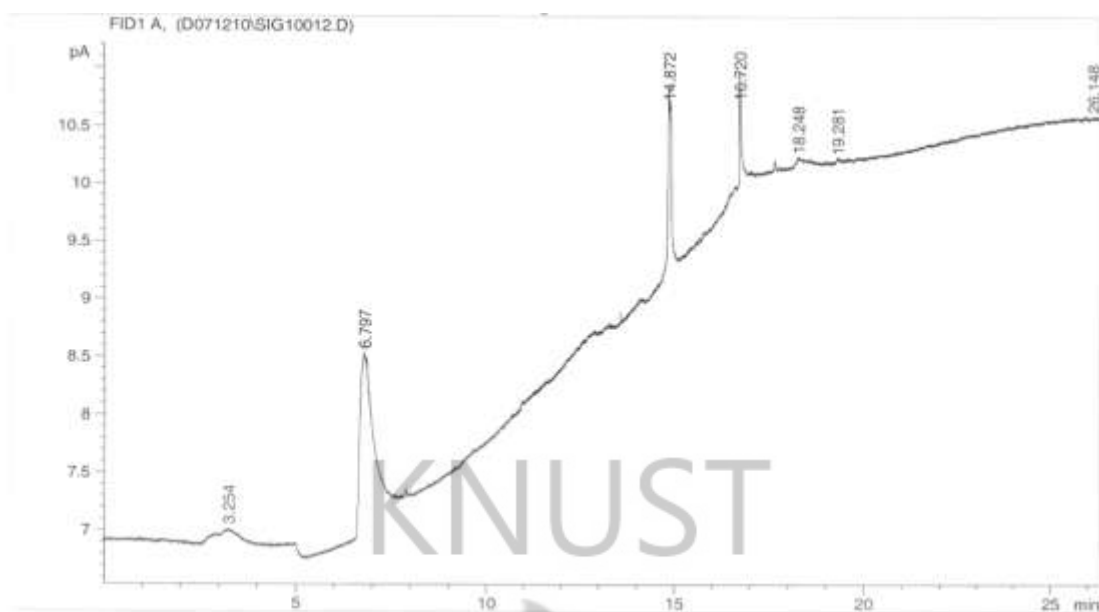


Figure 4. 5. 63 Time = 330 min

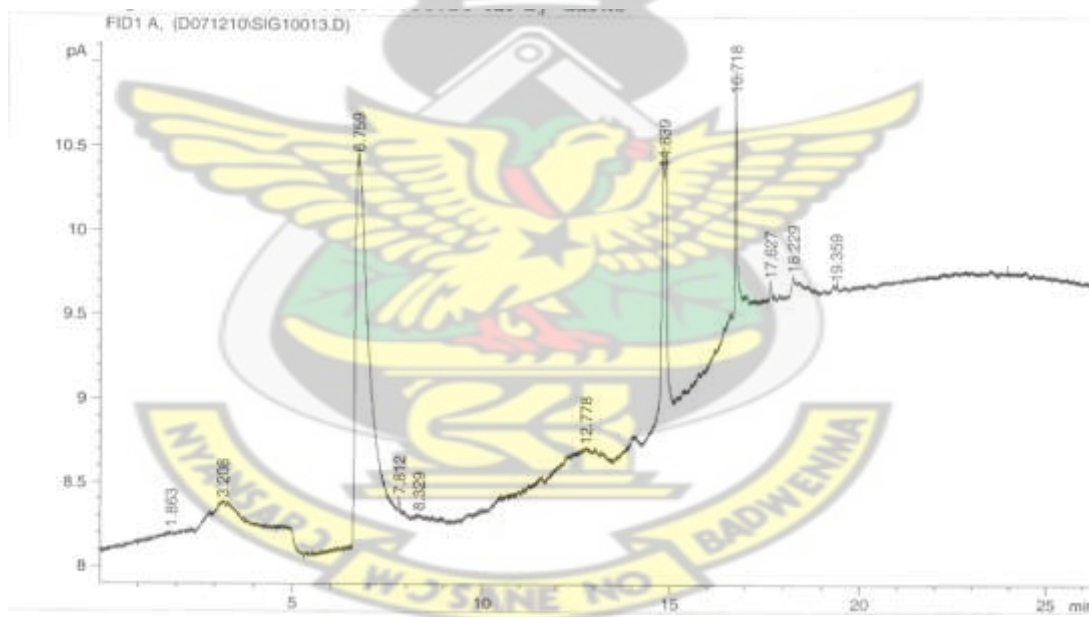


Figure 4. 5. 64 Time = 360 min

Table 4.5.17 Results of tests on the effect H_2O_2 on the liquid phase oxidation of phenols using spent FCC catalyst impregnated with 1.58% MnO_2 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2590 ppm whiles its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.48	26.4	49.39	355	122.56	0.072	0.072
60	6.23	25.3	202.21		501.75	0.046	0.118
90	6.41	26.4	243.31		603.74	0.036	0.153
120	6.41	28.1	233.80	1151	580.15	0.038	0.192
150	6.13	28	38.17	792	530.21	0.038	0.230
180	6.22	27.9	38.56		535.50	0.037	0.267
210	6.34	28	155.28		384.59	0.039	0.306
240	6.21	27.8	34.04		472.73	0.040	0.346
270	5.7	28.6	15.31	613	212.58	0.068	0.374
300	5.72	28.1	8.44		117.23	0.070	0.443
330	5.61	27.7	5.45	374	75.71	0.065	0.508

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.65 – 4.5.68.

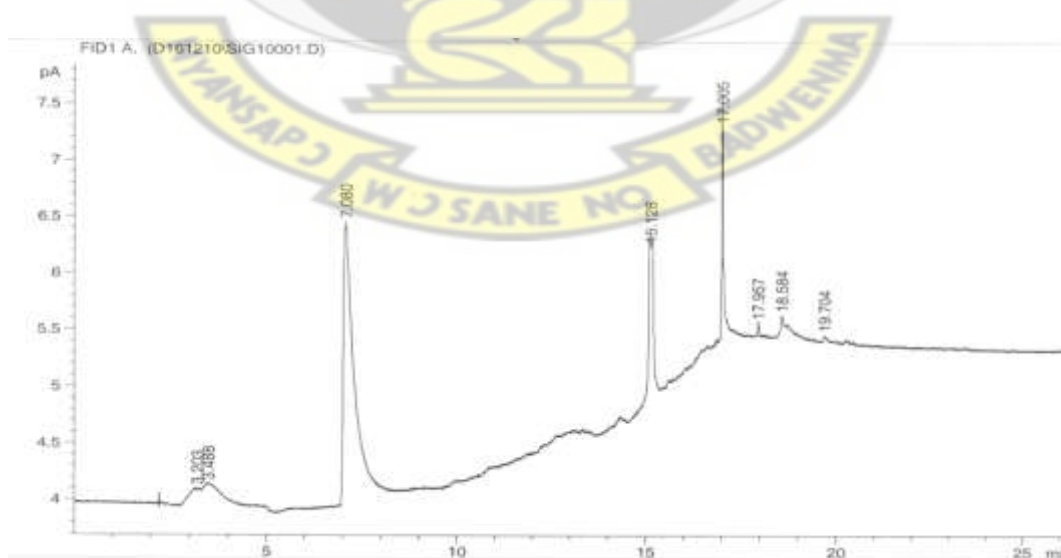


Figure 4. 5. 65 Time = 30 min

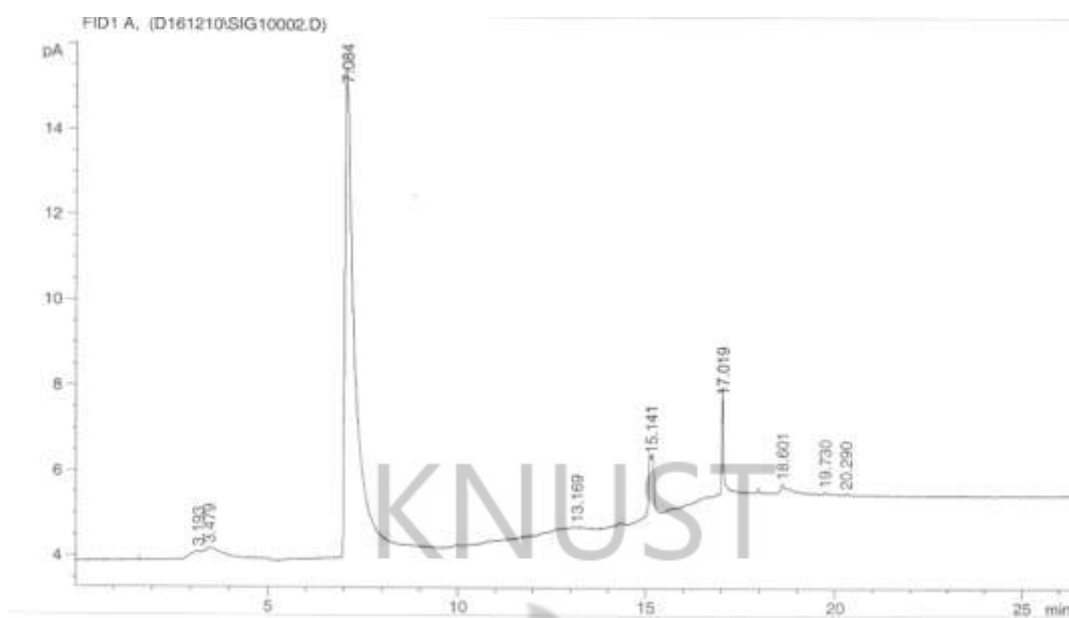


Figure 4. 5. 66 Time = 60 min

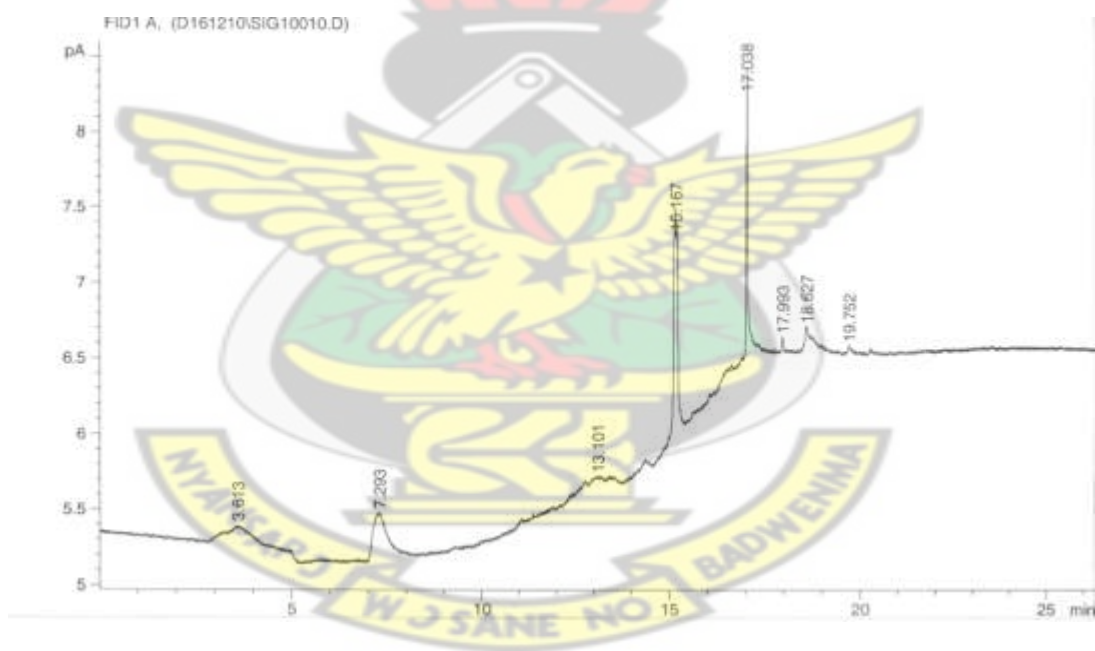


Figure 4. 5. 67 Time = 330 min

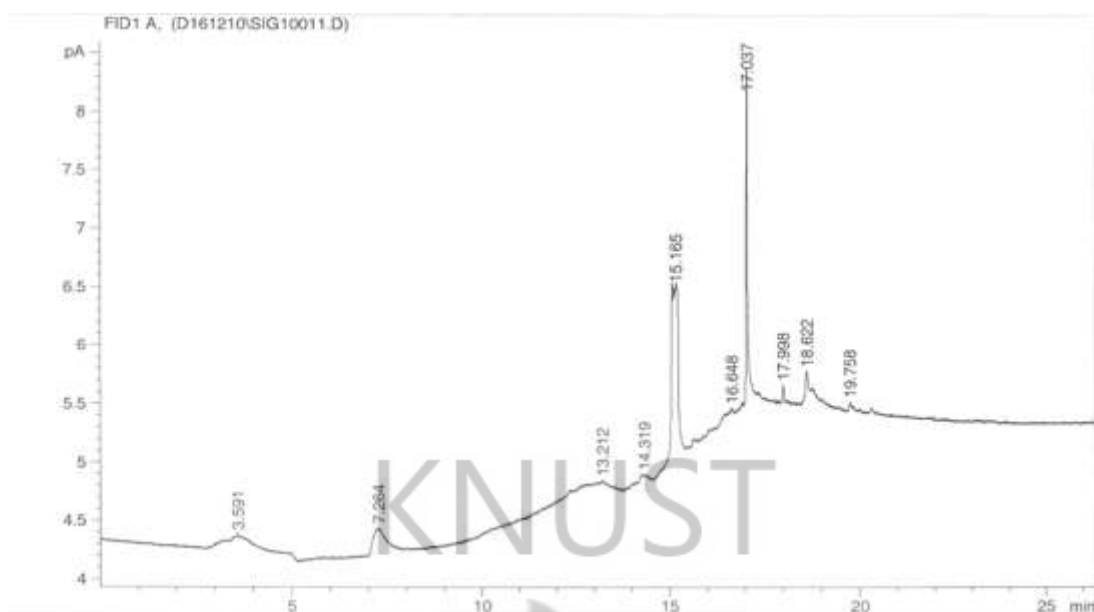


Figure 4. 5. 68 Time = 360 min

4 .5.6 Control Experiments

Experimental data on the effect of spent FCC catalyst on the liquid phase oxidation of phenols using homogeneous catalyst (Cu^{2+}) has been presented in Table 4. 5.18 . For this experiment the 120g of sea sand was used as the parking material instead of the spent FCC catalyst. The phenol concentration of the solution used was 1000 ppm. 10 ml of H_2O_2 (50%) was used. In addition 30 ml of a 5000 ppm Cu^{2+} solution was used.

Experimental data on the effect of the metal oxides on the liquid phase oxidation of phenols have also been presented in Tables 4.5.19 – 4.5.20. In these experiments 25 g of unmodified spent FCC catalyst was used as well as 68 g of granite chippings. The H_2O_2 as varied from 10 ml to 20 ml.

Table 4. 5.18 Results of tests on the effect of the spent FCC catalyst on the liquid phase oxidation of phenols using Cu^{2+} as homogeneous. The COD of the initial solution was 1055 ppm while its pH was 4.27 at 30°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	9.67	25.2	9.74	450	135.23	0.067	0.067
60	8.36	28	ND		0	0.061	0.128
90	8.3	29	ND		0	0.063	0.191
120	7.98	30.7	ND	320	0	0.068	0.259

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.69 – 4.5.72.

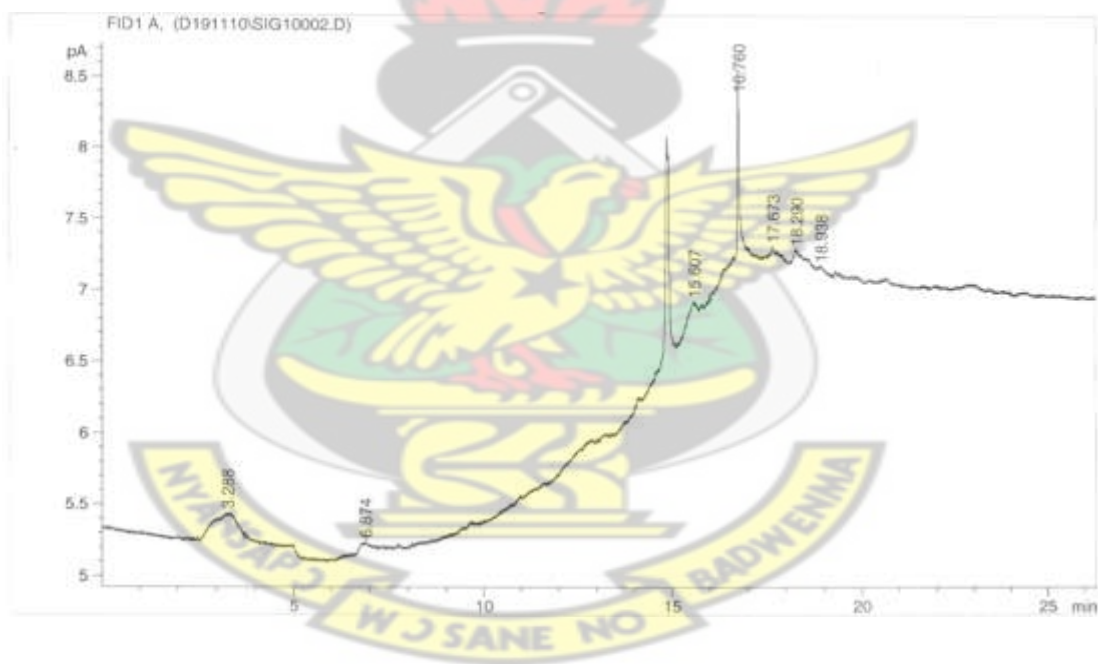


Figure 4. 5. 69 Time = 30 min

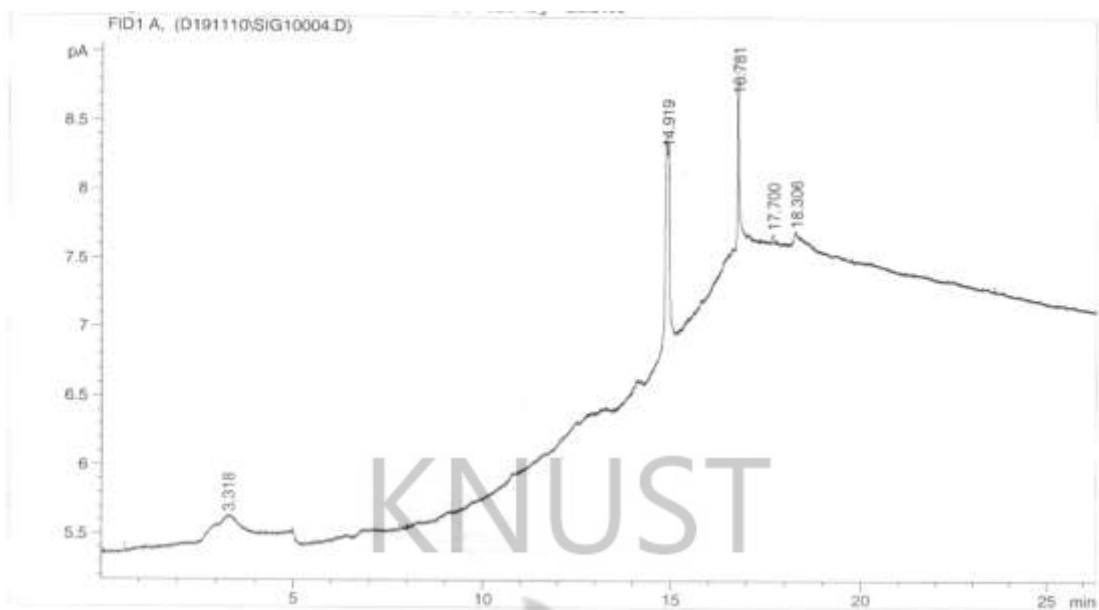


Figure 4. 5. 70 Time = 60 min

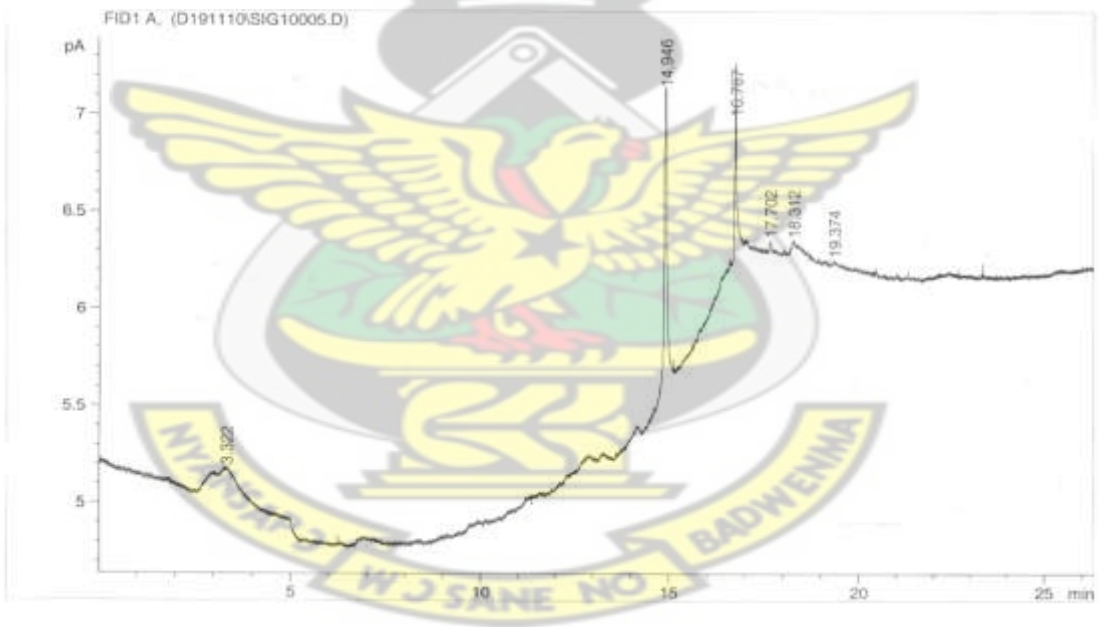


Figure 4. 5. 71 Time = 90 min

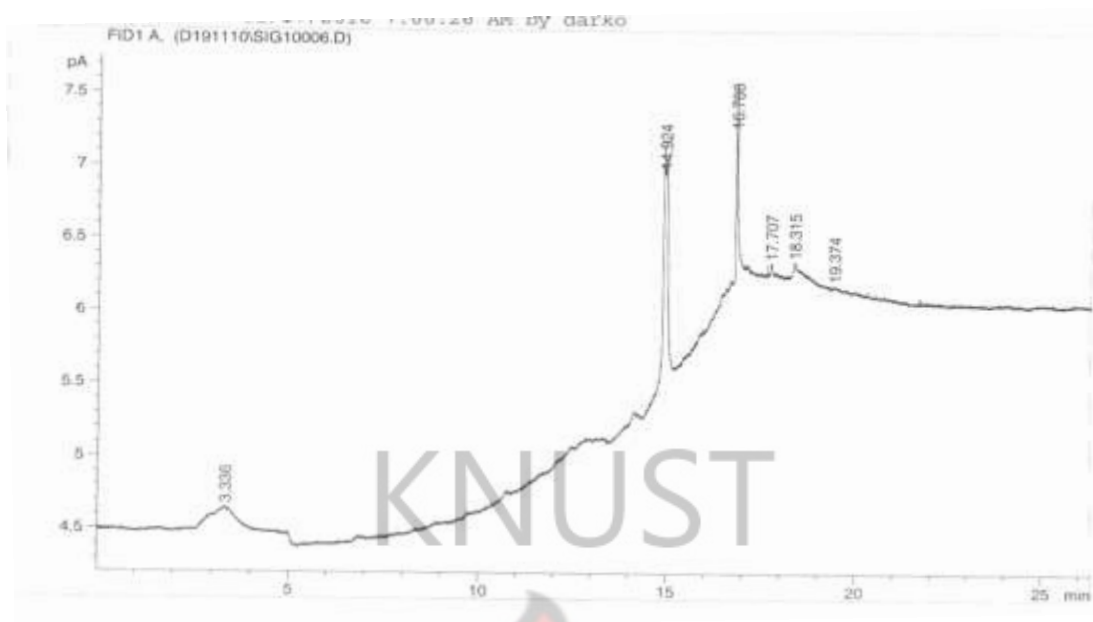


Figure 4. 5. 72 Time = 120 min

Table 4. 5.19 Results of tests on the effect of metal oxides on the liquid phase oxidation of phenols using spent FCC catalyst and 10 ml of H₂O₂ (50%). The COD of the initial solution was 1660 ppm whiles its pH was 4.51 at 27.1°C.

ST, min	pH	Temp, °C	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.43	19.1	144	20.78	0.081	0.081
60	6.25	18.5		205	0.069	0.151
90	5.95	20.4		231.5	0.051	0.202
120	5.96	21.1	744	170.86	0.054	0.256
150	5.69	23.7	776	174.86	0.044	0.300
180	5.56	24.2		101.64	0.086	0.387
210	5.31	25.4		155.98	0.058	0.445
240	5.03	22.9	1160	168.58	0.058	0.503
270	4.85	22.6	500	147.22	0.069	0.514
300	4.89	22.9		137.68	0.071	0.585
330	4.74	23.3	412	136.92	0.064	0.649
360	4.66	23.3		123.96	0.090	0.739

Table 4. 5.20 Results of tests on the effect of metal oxides on the liquid phase oxidation of phenols using spent FCC catalyst and 20 ml of H₂O₂ (50%). The COD of the initial solution was 2590 ppm while its pH was 4.28 at 27.2°C.

ST, min	pH	Temp, °C	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	6.97	19.8	97	23.26	0.078	0.078
60	6.68	21.3		204.52	0.051	0.129
90	6.46	21.8		132.72	0.063	0.192
120	6.12	22.3	379	107.93	0.084	0.276
150	5.86	21.8	305	48.34	0.082	0.358
180	5.52	22.5		102.21	0.069	0.427
210	5.33	23		88.48	0.046	0.473
240	5.1	23.3	253	61.02	0.077	0.550
270	5.07	24	285	58.45	0.055	0.528
300	4.79	24.5		45.39	0.080	0.608
330	4.66	24.8		43.1	0.085	0.693
360	4.49	25.4	279	34.61	0.082	0.775

4.5.7 Wastewater (*stripped sour water*) treatment using the spent catalyst impregnated with 0.97% Fe₂O₃

Experimental data on the waste water (*stripped sour water*) treatment using Fe₂O₃ impregnated spent FCC catalyst (0.97%) has been presented in tables 4.5.16 – 4.5.17. For these experiments the mass of modified spent FCC catalyst used was 25 g while the mass of the granite chippings used was 68g. The phenol concentration of the waste water used was 778 ppm. In total 800 ml of the phenol solution was treated per experiment. The amount H₂O₂ was also varied from 20 ml to 50 ml.

Table 4. 5.21 Results of waste water treatment using spent FCC catalyst impregnated with 0.97% Fe_2O_3 and 20 ml of H_2O_2 (50%). The COD of the initial solution was 2950 ppm whiles its pH was 7.63 at 31.3°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.81	29.9	ND	163	0	0.055	0.055
60	7.23	26.7	ND		0	0.059	0.114
90	7.23	27.3	ND		0	0.066	0.180
120	7.04	27.5	ND	228	0	0.066	0.246
150	6.8	28.5	ND	271	0	0.066	0.313
180	6.66	26.8	ND		0	0.074	0.387
210	6.54	28.8	ND		0	0.065	0.451
240	6.48	29.8	ND	301	0	0.074	0.525

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.73 – 4.5.76.

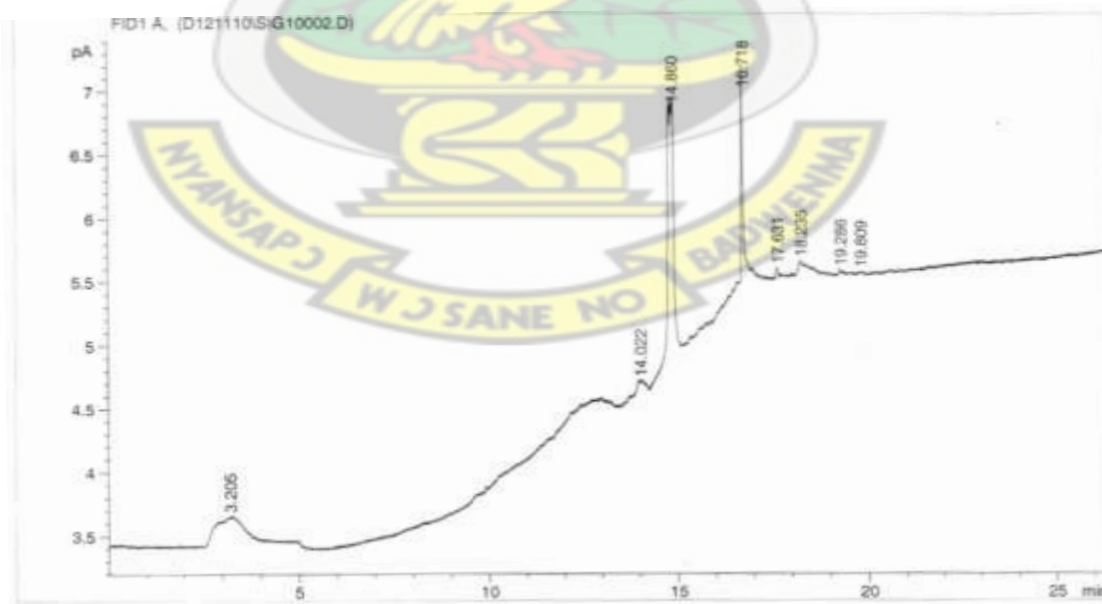


Figure 4. 5. 73 Time = 30 min

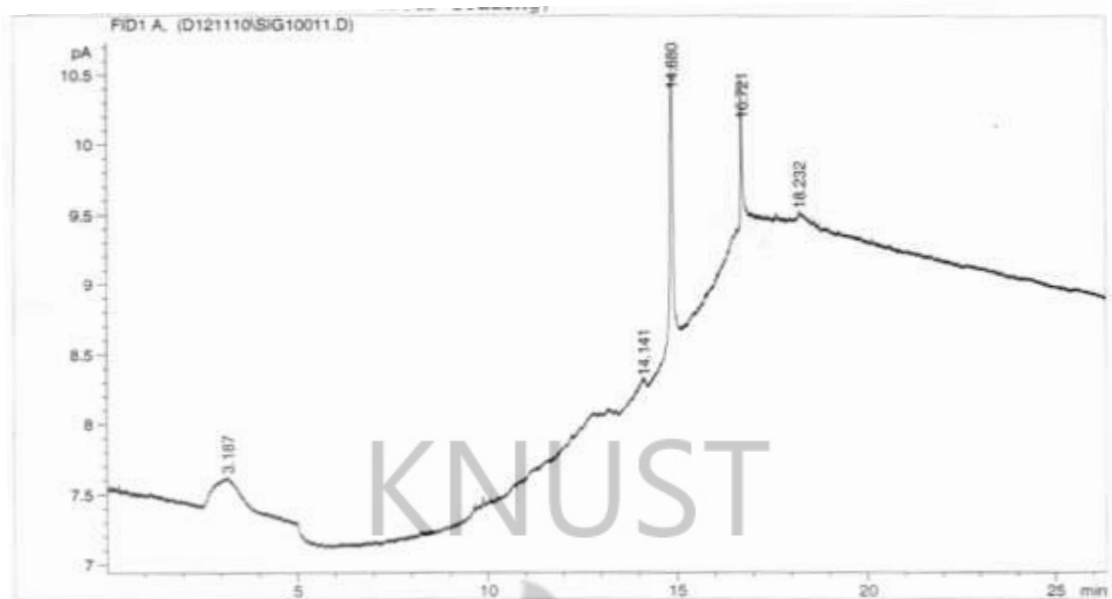


Figure 4. 5. 74 Time = 60 min

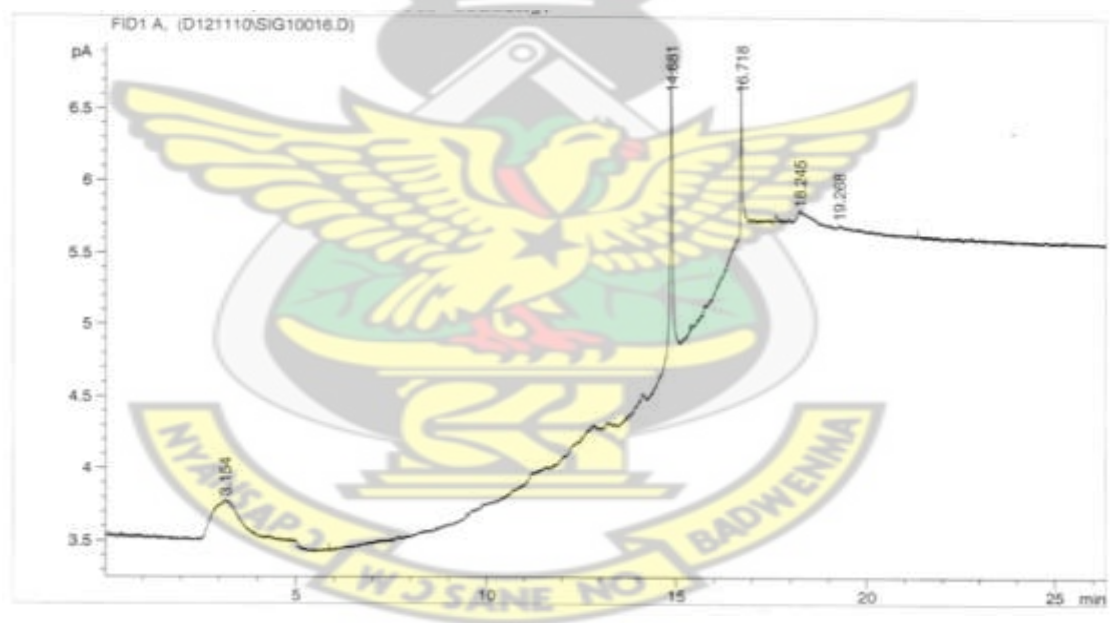


Figure 4. 5. 75 Time = 210 min



Figure 4. 5. 76 Time = 240 min

Table 4. 5.22 Results of waste water treatment using spent FCC catalyst impregnated with 0.97% Fe_2O_3 and 30 ml of H_2O_2 (50%). The COD of the initial solution was 3860 ppm while its pH was 6.71 at 31.1°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.43	26.7	ND	158	0	0.065	0.065
60	6.61	27.1	ND		0	0.065	0.130
90	6.2	28.4	ND		0	0.079	0.210
120	6.04	30.8	ND	393	0		0.210
150	5.94	27.3	ND	428	0	0.074	0.283
180	5.87	28	ND		0	0.066	0.350
210	5.75	29.7	ND		0	0.073	0.423
240	5.67	30.7	ND	444	0	0.078	0.501

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.77 – 4.5.80.

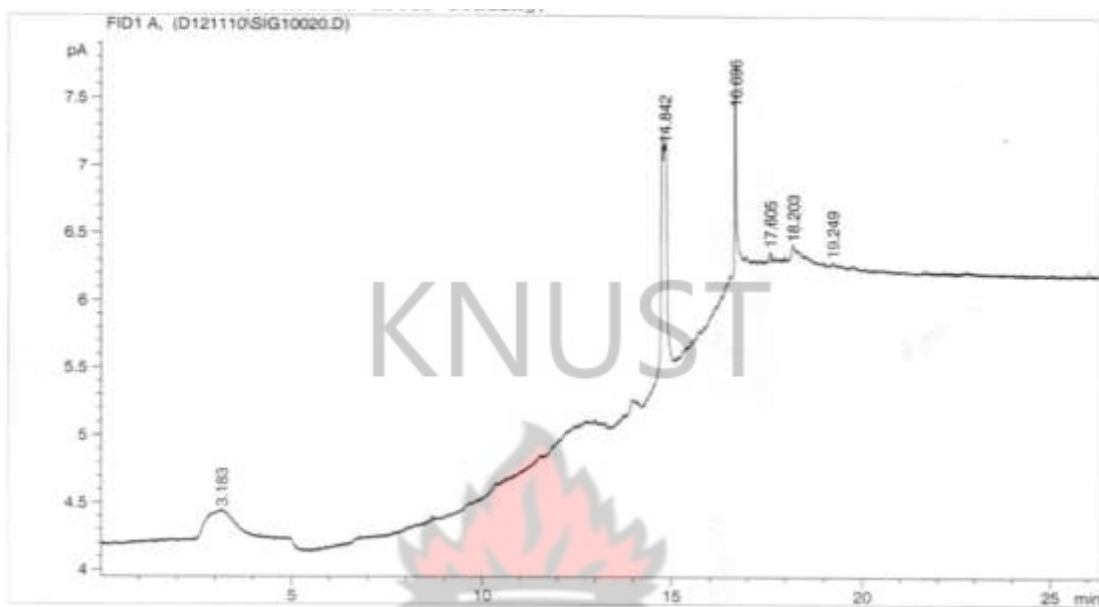


Figure 4. 5. 77 Time = 30 min

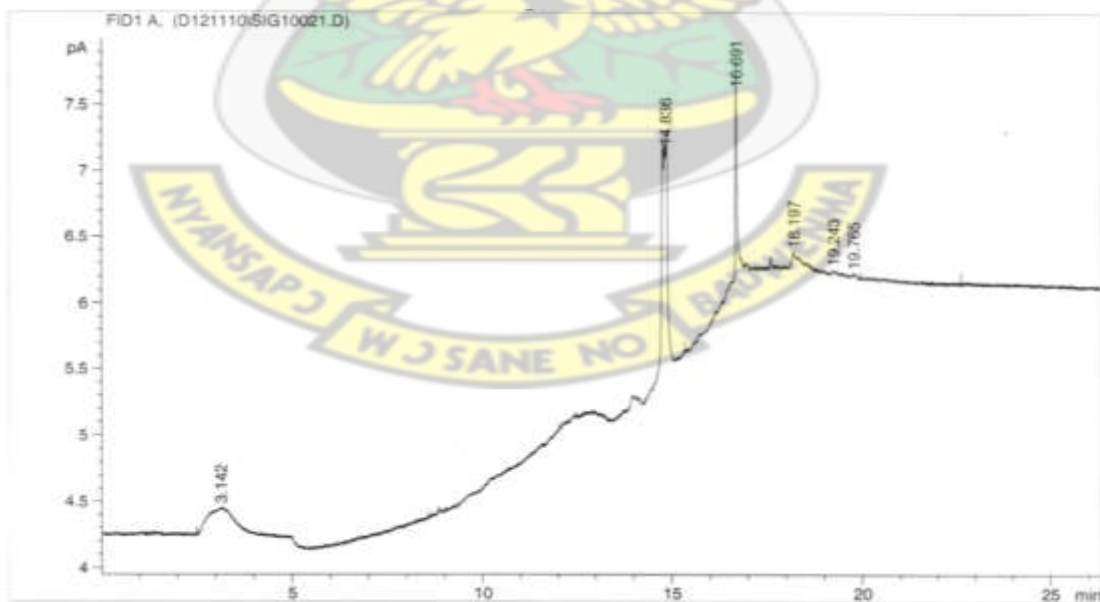


Figure 4. 5. 78 Time = 60 min

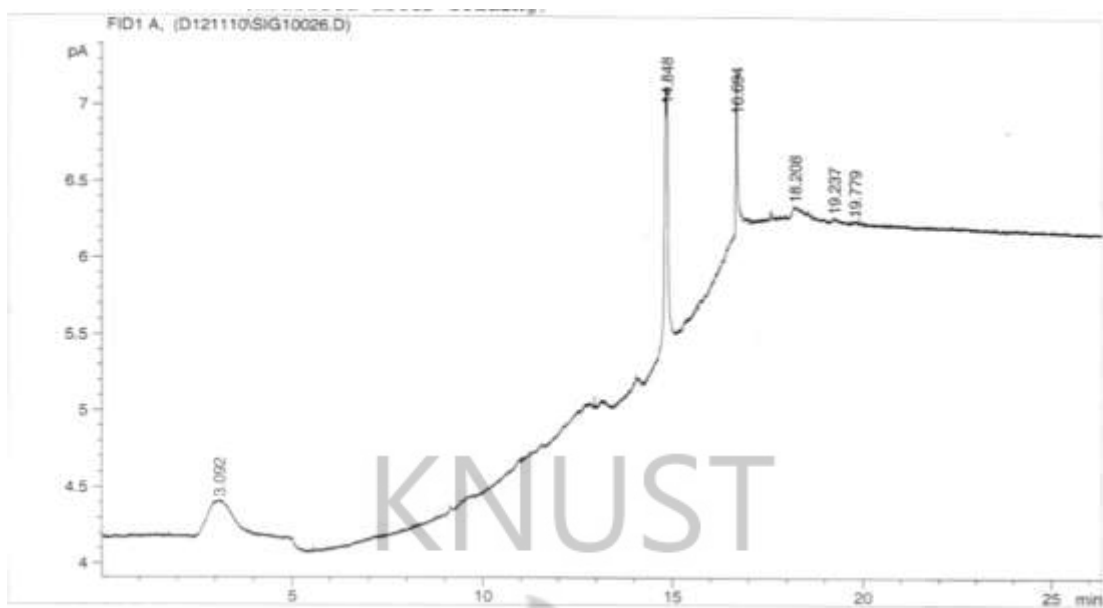


Figure 4. 5. 79 Time = 210 min

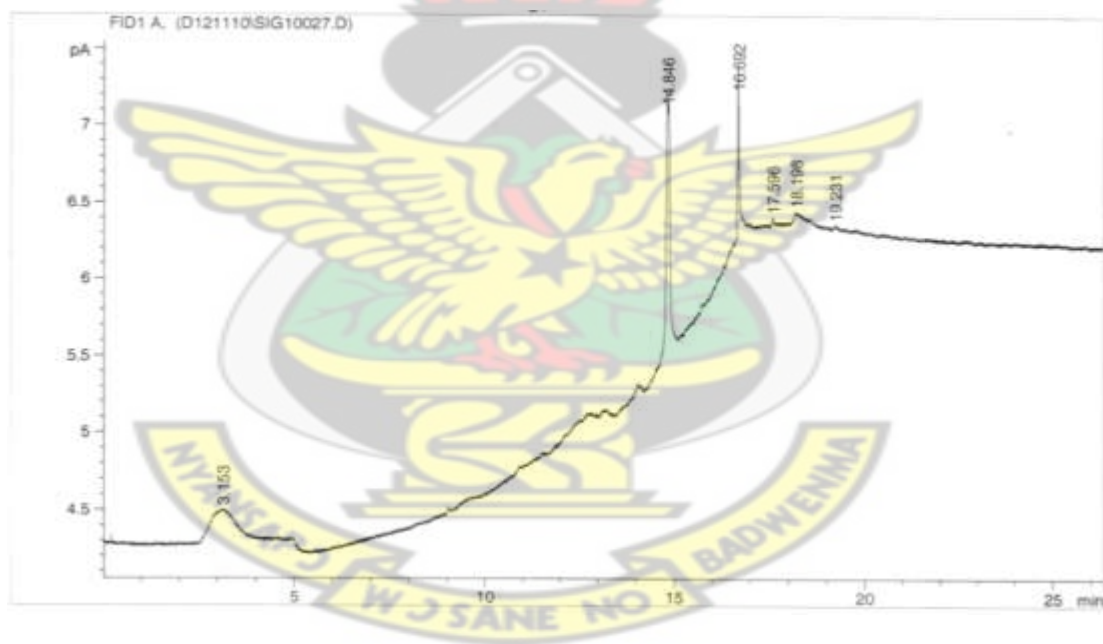


Figure 4. 5. 80 Time = 240 min

Table 4. 5.23 Results of waste water treatment using spent FCC catalyst impregnated with 0.97% Fe_2O_3 and 50 ml of H_2O_2 (50%). The COD of the initial solution was 5065 ppm whiles its pH was 6.98 at 31.9°C.

ST, min	pH	Temp, °C	PAP	COD, ppm	EPC, ppm	MPRS, g	TMPR, g
30	7.13	28.9	1.95	367	21.07	0.067	0.067
60	6.53	27.7	ND		0	0.074	0.142
90	6.35	29.9	ND		0	0.060	0.201
120	6.12	31.5	ND	894	0	0.078	0.279
150	6.14	30.5	ND	601	0	0.068	0.347
180	6.09	27.4	ND	0	0	0.068	0.414
210	5.97	28.5	ND	0	0	0.076	0.490
240	5.94	30.5	ND	864	0	0.087	0.577

Gas chromatography plots of effluents taken at various times are presented in Figure 4.5.81 – 4.5.84.

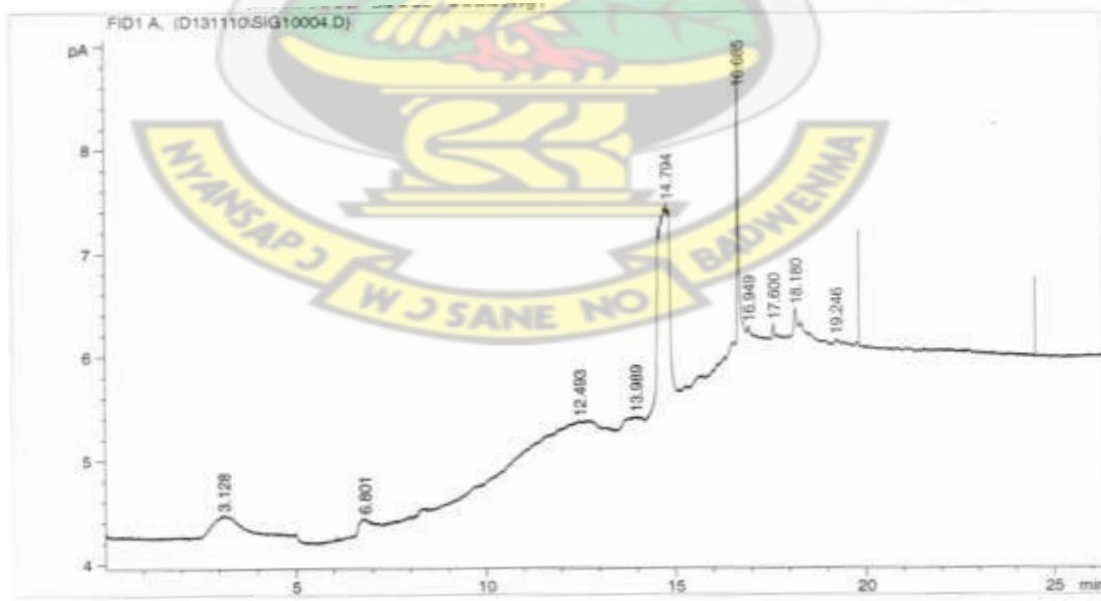


Figure 4. 5. 81 Time = 30 min

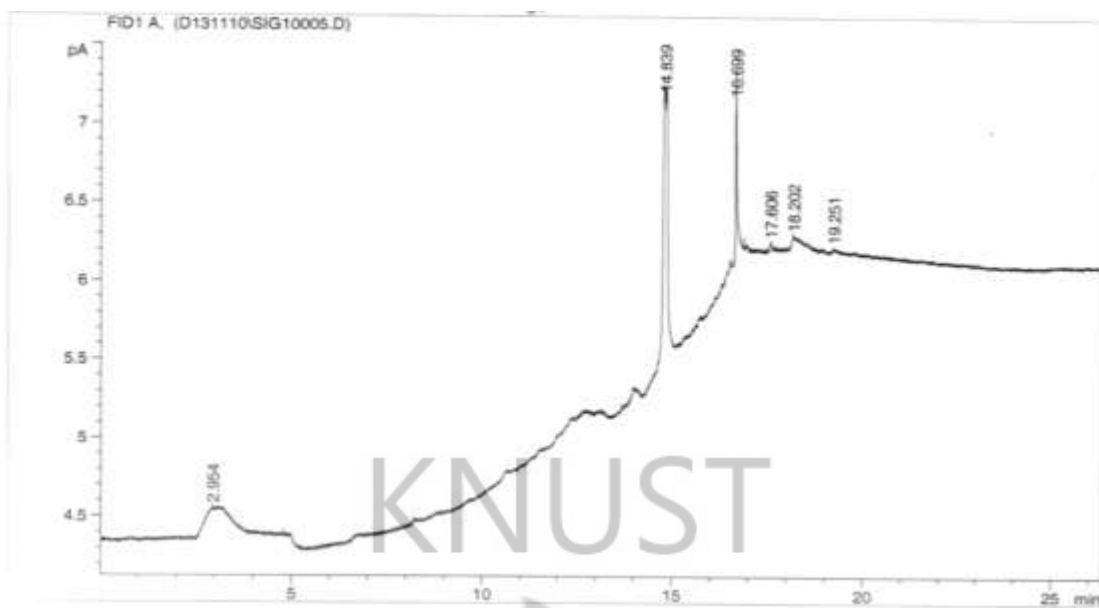


Figure 4. 5. 82 Time = 60 min

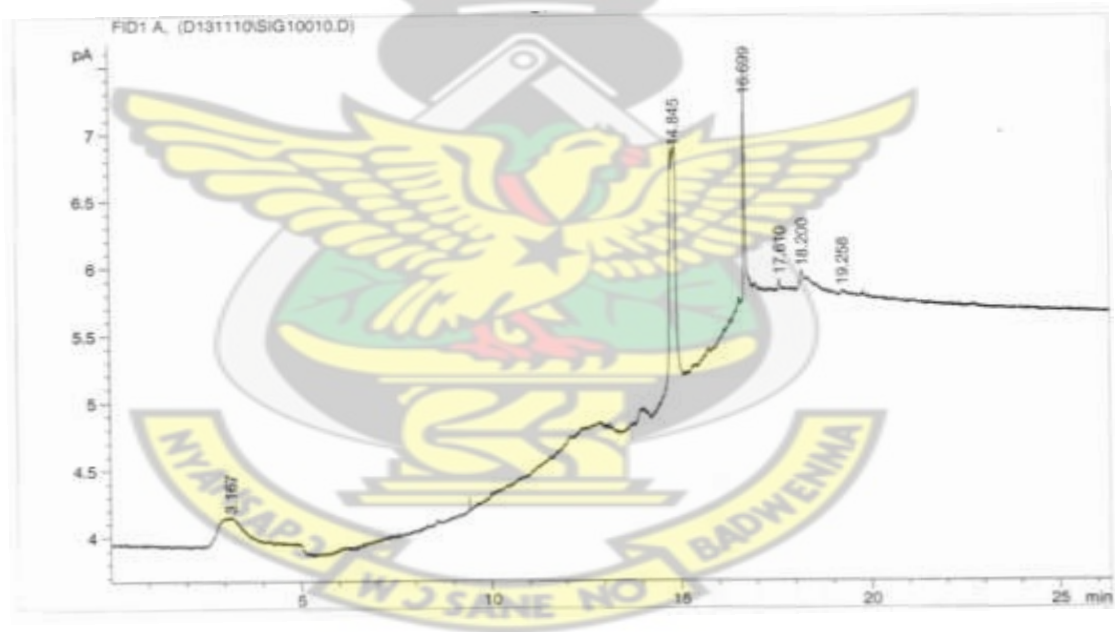


Figure 4. 5. 83 Time = 210 min

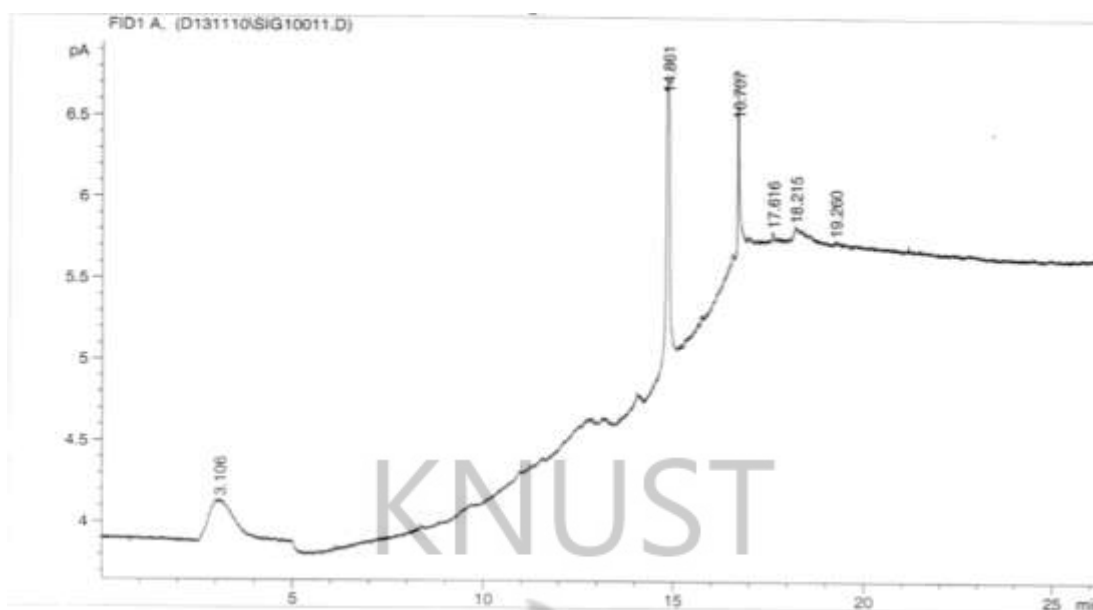
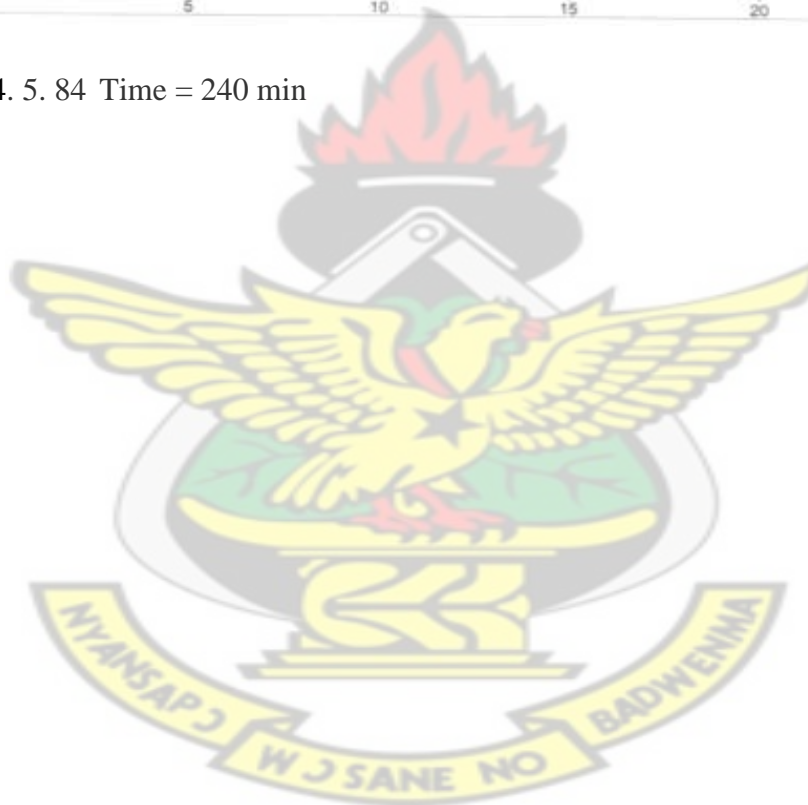


Figure 4. 5. 84 Time = 240 min



Chapter 5

Discussion

5.1 Introduction

Owing to the nature of the experimental results obtained the discussion will be divided into four distinct sections, namely;

- Characterization of the FCC catalyst
- Adsorption characteristics of the spent FCC catalyst
- Liquid phase oxidation of phenol using the spent FCC catalyst
- Refinery waste water treatment using the spent FCC catalyst

5.2 Characterization of the FCC Catalyst

5.2.1 Physical Characterization of the Fresh and Spent FCC Catalyst

A comparison of the morphological data of the spent and fresh FCC catalyst as presented in Tables 4.2.1 shows that the fresh catalyst undergoes significant changes during the FCC process. Whereas the surface area and apparent bulk density decreased, the pore volume increased. Although the exact mechanism of the phenol adsorption by the spent catalyst is not exactly known, since it is zeolite based this increase in pore volume implies smaller molecules like water will easily pass through it while larger molecules like phenol would be trapped in these pores (Kohl & Kresge, 1998). A graph (Figure 5.2.1) of the percentage cumulative undersize (using data from Table 4.2.2) showed that there has been some

agglomeration of the particles. This observation has been confirmed by the SEM analysis of both the spent and fresh catalyst (Figure 4.2.3-a and Figure 4.2.4-b). The SEM micrograph at 50,000 magnification also revealed that the spent catalyst particles are made up of an agglomeration of smaller 1 - 10 μm particles. The average particle size of the fresh catalyst was 70.0 μm while that of the spent catalyst increased to 86.2 μm .

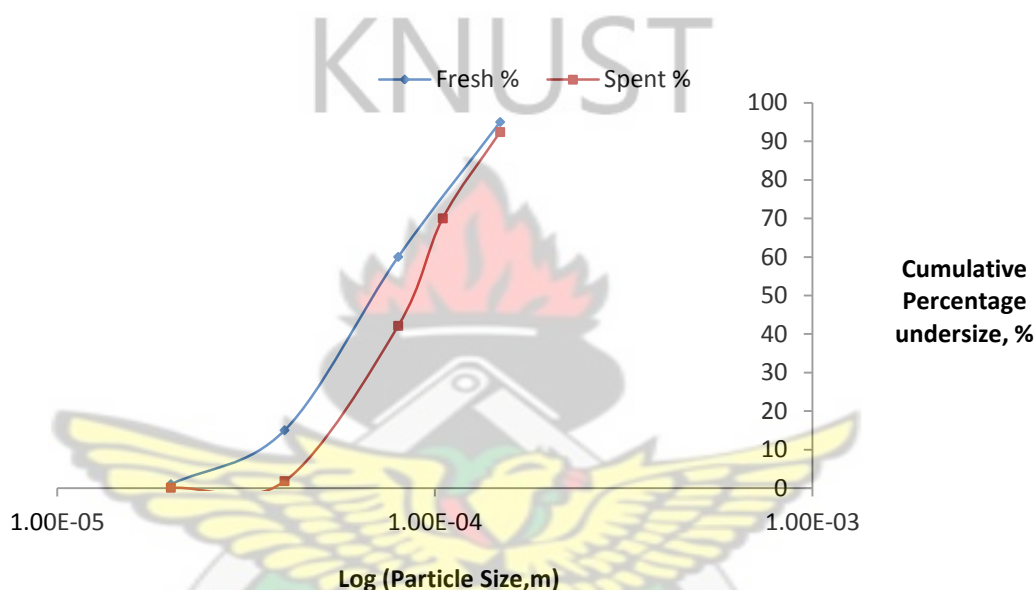


Figure 5. 2. 1 Particle size distribution of the Spent and Fresh FCC catalyst

5 . 3 Chemical Characterization of the FCC catalyst

5 .3.1 Chemical Composition of the Spent and Fresh FCC catalyst

Table 4.2.3 shows that the chemical composition of the FCC catalyst is altered during the FCC process, that is, 6.4% decrease in the Al_2O_3 and 3.4% increase in the SiO_2 contents. It can be observed from the table that aside the main components of the fresh catalyst other components such as Ca, Fe, Cu, Ni, V and Sb are present on the spent catalyst. In addition

the Na content of the spent catalyst is more than that of the fresh. These erstwhile non-existing components trace their origin to the residual fuel being cracked. The residual oil being cracked on average contains about 12.1 ppm Ni, 1.4 ppm V, 12 ppm Fe, 3.1 ppm Na and 3 ppm Ca. It is important to note that the oxides of some of these metals such as Fe, Cu, Ni and V possess significant catalytic properties which they impart to the spent catalyst.

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5.4 Leaching tests on the Spent Catalyst

Data from Tables 4.2.6 – 4.2.12 were used to plot the concentration versus time graphs for the leaching of Ca, Cu, Fe, Na, Ni and V from the spent FCC catalyst using dilute HCl and NaOH solutions. With the exception of vanadium, the low values obtained for leaching with NaOH is not surprising. This is because unless hydroxide complexes of the metals are formed the products from the reaction would be simple hydroxides such as $\text{Cu}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ would be formed. Since these hydroxides are not soluble they would not be leached into solution. Vanadium on the other hand is very soluble in basic solutions when in its vanadate form.

In acid solutions however, the dissociation of these elements increased with acid concentration and with time.

These results are relevant for any possible regeneration of the spent catalyst for re-use in the FCC units. In addition they speak to the stability of the spent catalyst when used in aqueous solutions. Further tests would have to be conducted to validate and also to optimize conditions, which is not part of the objectives of this study.

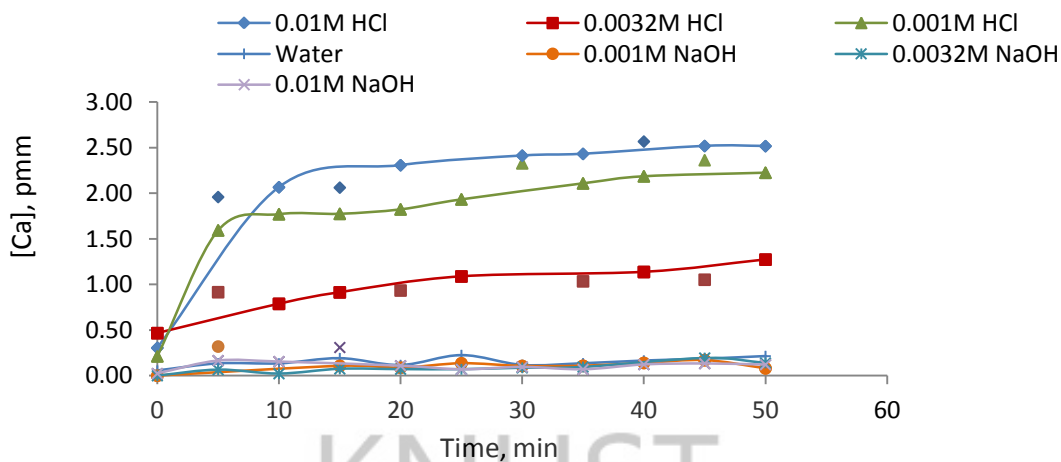


Figure 5. 4. 1 Concentration of Calcium in leached solution versus time

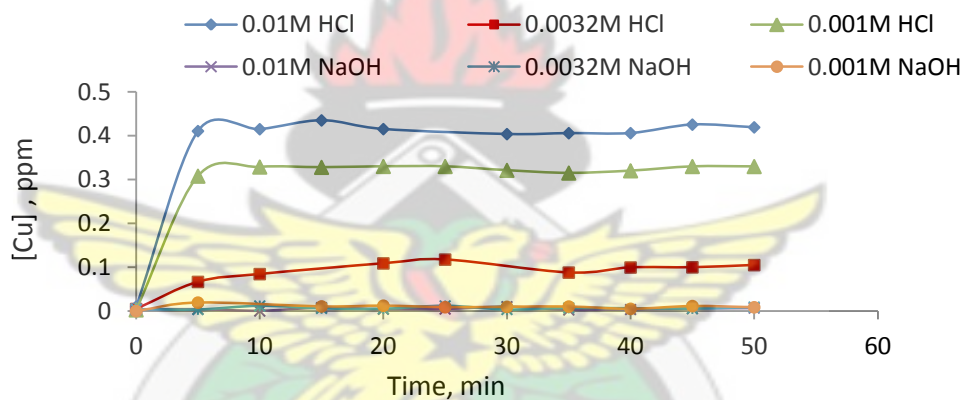


Figure 5. 4. 2 Concentration of Copper in leached solution versus time

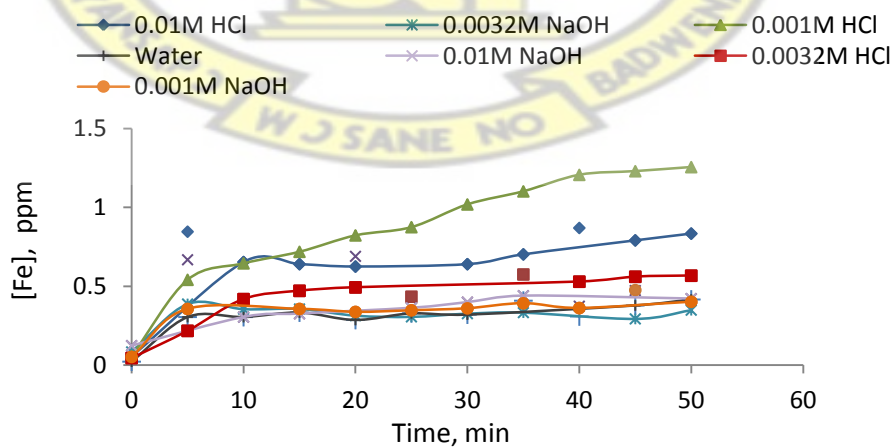


Figure 5. 4. 3 Concentration of Iron in leached solution versus time

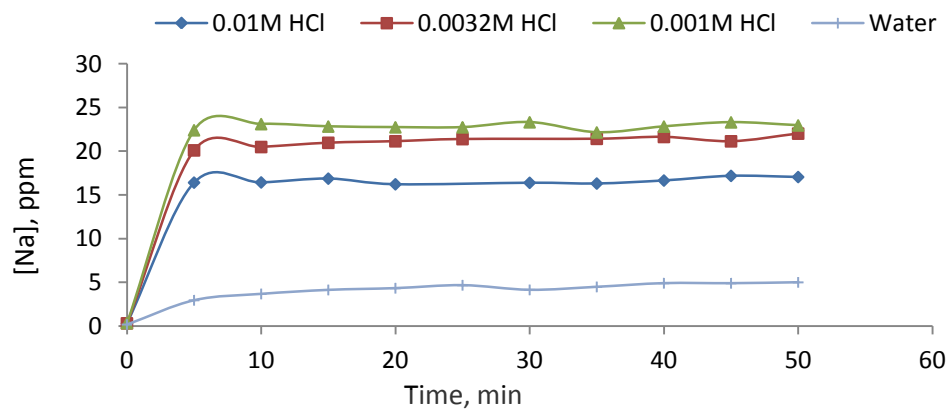


Figure 5. 4. 4 Concentration of Sodium in leached solution versus time

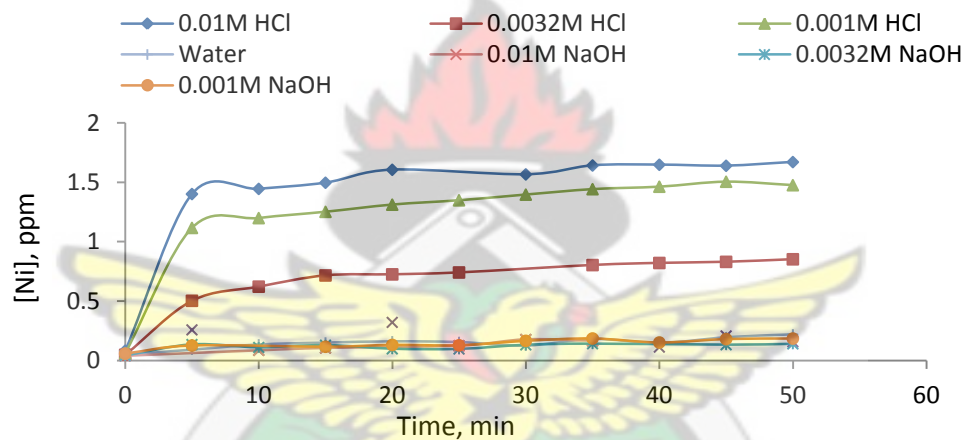


Figure 5. 4. 5 Concentration of Nickel in leached solution versus time

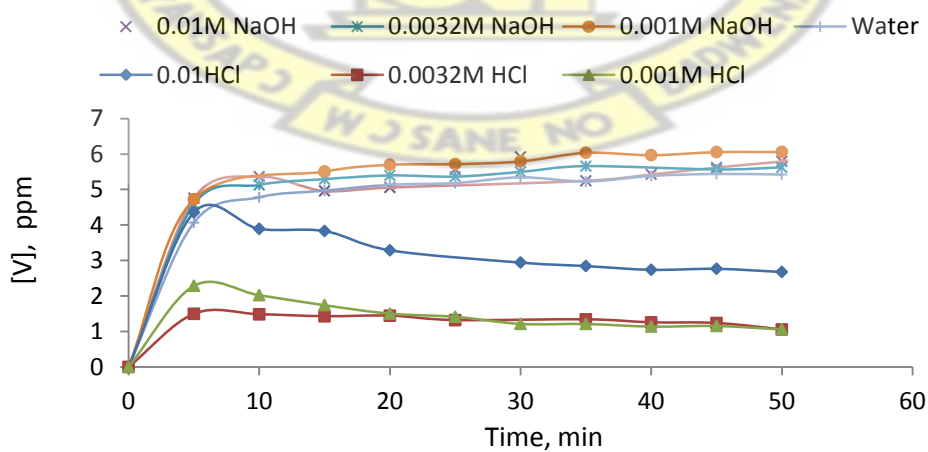


Figure 5. 4. 6 Concentration of Vanadium in leached solution versus time

5.5 Adsorption Characteristics of the FCC catalyst

Initial tests on the spent FCC catalyst indicated that its phenol adsorption property has significantly changed as compared with the fresh FCC catalyst (Figure 5.5.1). Consequently, the spent catalyst was tested for its phenol adsorption characteristics. The tests conducted include:

1. Effects of initial phenol concentration on adsorption
2. Effect of thermal pre-treatment on adsorption
3. Comparison of its adsorptive strength with activated carbon
4. Test to fit its adsorptive capacity to the Freundlich adsorption isotherm

In addition some reasons were also put forward to explain why the spent FCC catalyst adsorbs phenol while the fresh FCC catalyst doesn't.

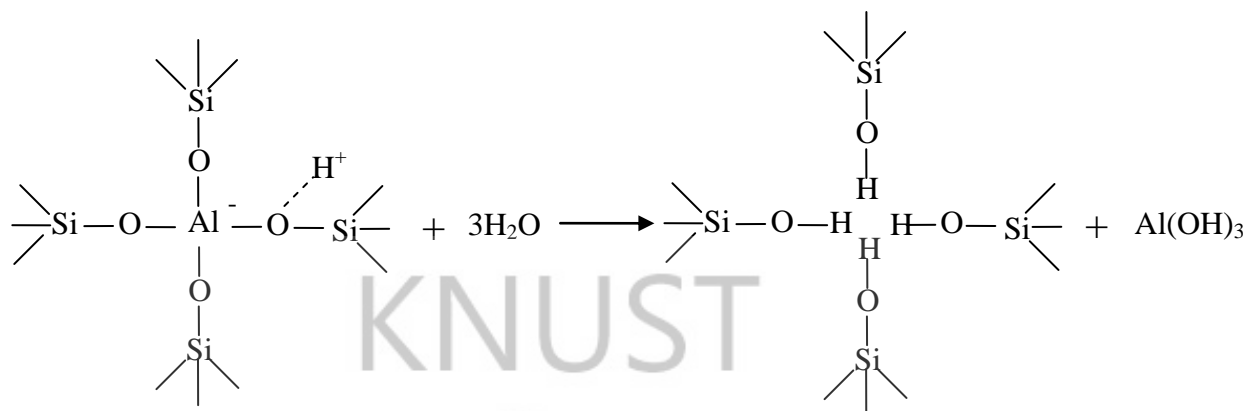
5.5.1 Development of Adsorptive Properties by the FCC catalyst.

The spent catalyst though considerably ineffective as an FCC catalyst, possesses significant hydrophobic characteristics which make it useful as an adsorbent of organic compounds in aqueous solutions: effectively, approaching that of silicalites, (Ruthven, 1998).

The cause of this increased adsorption capacity by the spent catalyst may be seen by considering the various stages the catalyst goes through when being used.

The activation of the fresh catalyst, which takes place in the reactor results in the removal of some framework aluminum. According to Gates, *et al.*, (1979), 2 atoms are removed

from each of the 8 sodalite cages. The following surface reaction below explains the phenomenon.



Hydrolysis of zeolite with a corresponding dealumination

5. 5. 1

The removal of the framework aluminum is referred to as *dealumination*. Dealumination results in a zeolite which is very stable, (Gates, *et al.*, 1979; K hl & Kresge, 1998; Mehrotra, *et al.*, 1995). However uncontrolled dealumination eventually results in the collapse of the zeolite structure. Additionally dealumination reduces the acidity of the zeolite, which is very important in the catalysis of the FCC process, (Gates, *et al.*, 1979). Thus to control this dealumination, Rare Earth oxides (RE₂O₃) are incorporated into the catalyst, (K hl & Kresge, 1998). According to Gates, *et al.* (1979), it is believed that the RE₂O₃ control the dealumination by filling some of the sodalite cages with RE – O – RE units. When dealumination occurs, the Si/Al ratio of the zeolite increases; thereby making the resulting zeolite increasingly hydrophobic (Crittenden and Thomas, 1998).

From Table 4.2.3 the $\frac{\text{Si}}{\text{Al}}$ for the fresh and spent FCC catalyst are 0.7796 and 0.9685

respectively. These values confirm the occurrence of dealumination. Figure 5.5.1 shows the

break – through curves of the fresh and spent catalysts. From it, it can be seen that whereas the phenol break – through point occurs at 108 min for the spent catalyst that of the fresh occurs at 0 min.

5.5.2 Phenol Break through Curves

The spent catalyst as mentioned earlier shows good phenol adsorption. This property which is not found in the fresh catalyst is evident in the Figure 5.5.1. Fluid transport of a phenol solution through the fresh catalyst is considerably slower than in the spent catalyst, that is 0.765 ml/min and 5.634 ml/min for the fresh and spent catalyst respectively. This behavior of the fresh catalyst is expected as the various components of the fresh catalyst are polar in nature and is expected that they would adsorb polar molecules like water thus impeding the flow of the water through it, (Ruthven, 1998) . In addition the increased flow rate for the spent catalyst can also be attributed to its relatively big pore volume ($0.9 \text{ cm}^3/\text{g}$) as compared with that of the fresh catalyst ($0.4 \text{ cm}^3/\text{g}$). Despite the more than seven times faster rate of fluid transport down the spent catalyst, its phenol adsorption characteristics were much better than that of the fresh catalyst.

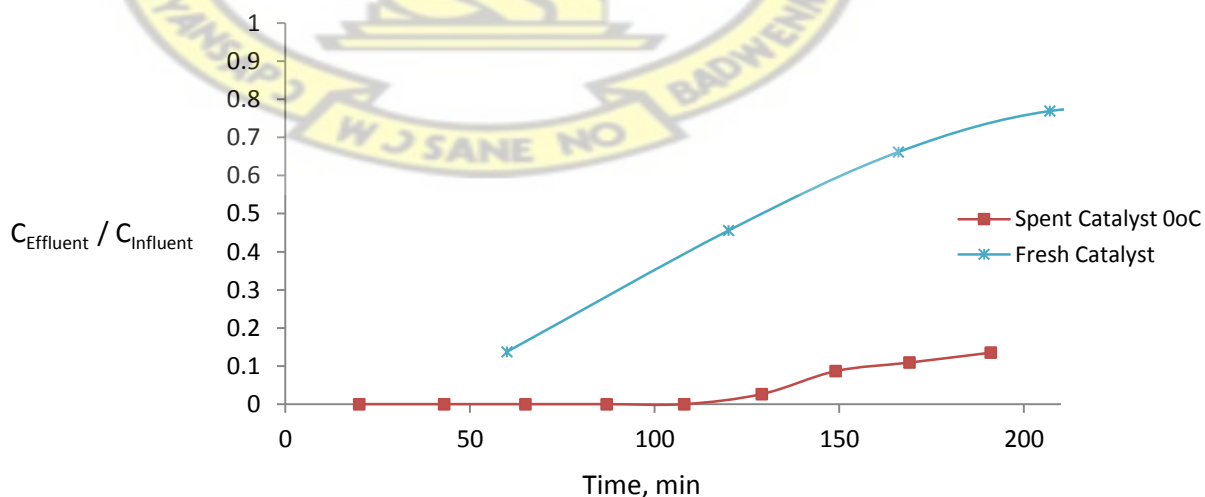


Figure 5. 5. 1 Comparison of the Phenol-Fresh Catalyst and Phenol-Spent Catalyst Break-Through Curves

5.5.3 Effect of Initial Phenol Concentration on Adsorption

The spent catalyst's ability to adsorb from aqueous solutions of phenols is quite remarkable as can be seen from Figure 5.5.2. The spent catalyst can adsorb phenol equivalent to 1.2 % its mass at the break-through point for an initial phenol concentration of 3500 ppm. Additionally, for the same initial phenol concentration at 5% saturation (that is, $C_i / C_o = 5\%$) the amount of phenol can rise up to 1.6 % the weight of the spent catalyst. The amount of phenol adsorbed at the break-through point for the 1500 ppm phenol solution was 0.6% the mass of the adsorbent whiles that of the 2500 ppm phenol solution was 0.9% the mass of the adsorbent. From these differing break-through point adsorption capacities, it can be seen that the mass of phenol adsorbed is concentration dependent. This then suggests that phenol adsorption by the spent catalyst is equilibrium dependent.

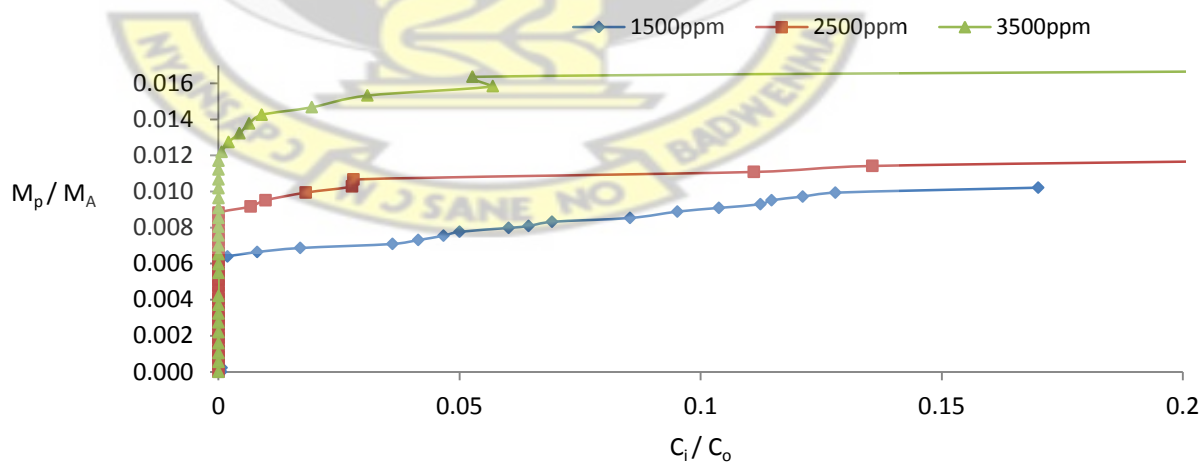


Figure 5. 5. 2 Effect of initial phenol concentration on adsorption

5.5.4 Effect of thermal pre-treatment on phenol adsorption

Generally, thermal pre-treatment of the spent catalyst reduces its phenol adsorption capacity. However depending on the furnace temperature the reduction in capacity may be negligible. This decrease in adsorption capacity can be attributed partly to the fact that during the heating process the deposited coke on the spent catalyst, which accounts partly for the phenol adsorption capacity of the spent catalyst, gets burnt away. Table 5.5.1 shows the equilibrium amounts of phenol adsorbed for the various pre-treated spent catalyst as well as the untreated spent catalyst which is denoted by 25°C along-side their coke contents. Figure 5.5.3 shows the phenol break-through curves for the thermally pre-treated spent catalyst for an initial phenol concentration of 1500 pm. The anomaly at 700°C could not be explained and could be a matter of further investigations.

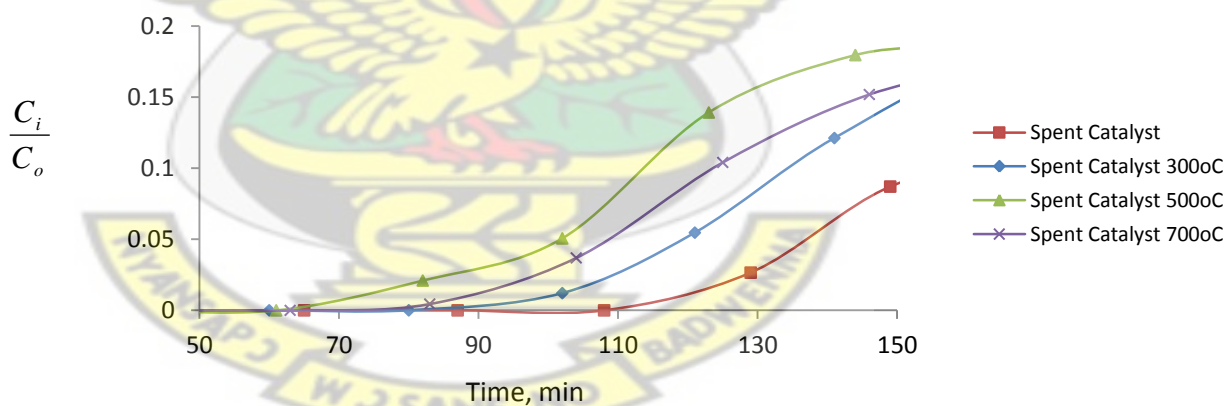


Figure 5. 5. 3 Effect of Thermal Treatment on Phenol Adsorption at the Break through Point

Table 5.5.1 Effect of Coke Content and thermal pre-treatment on phenol adsorption

Temp, °C	Coke, %	C_i / C_o	M_P / M_A
25	0.011	8.4×10^{-4}	0.01656
300	0.008	1.1×10^{-3}	0.01011
500	0.002	1.12×10^{-3}	0.00947
600	0.002	9.5×10^{-3}	0.01384
700	0.002	8.7×10^{-4}	0.01571

5.5.5 Comparison of the phenol Adsorption Capacities of the Spent FCC catalyst to Activated Carbon

Phenol adsorption capacity of the spent catalyst, it is only 16.62% the adsorption capacity of the activated carbon at the break through point. This can be seen from the break through curves in Figure 5.5.4.

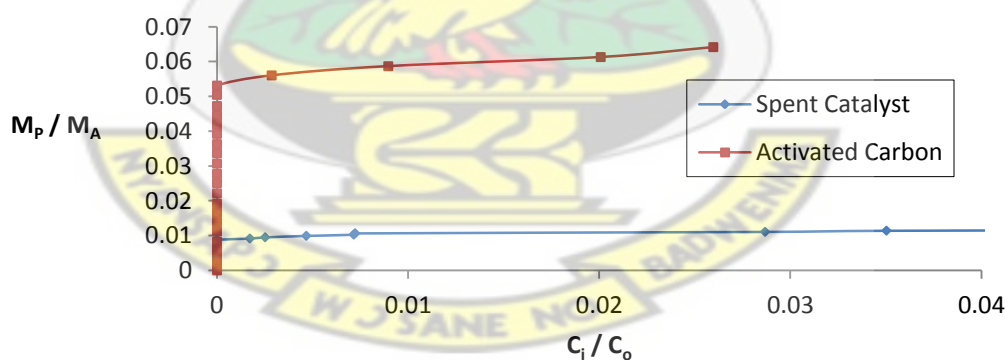


Figure 5.5.4 Phenol break - through curves for the spent catalyst and activated carbon

5.5.6 Equilibrium Adsorption Characteristics of the Spent Catalyst

As would be expected the adsorption of the phenol by the spent catalyst fits quite well to the Freundlich adsorption model. After fitting the obtained data to the Freundlich adsorption model, the following graph was obtained.

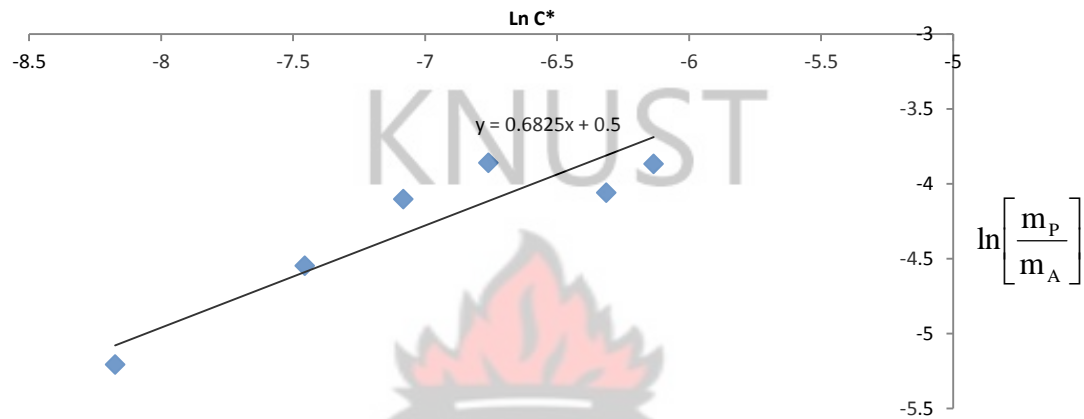


Figure 5. 5. 5 Freundlich Adsorption Isotherm for a Spent catalyst – Phenol system

From the plot (graph) $\ln[k] = 1.649$ and $n = 0.682$ which is less than 1 and hence data fits the Freundlich adsorption model.

Thus the adsorption model may be stated as:

$$\rho = 1.649 C^{*0.682} \quad 5.5.2$$

where $\rho = \frac{\text{Mass of Phenol Adsorbed}}{\text{Mass of Spent Catalyst}}$ and C^* is the mass fraction of the phenol in the

solution at equilibrium.

5.6 Liquid Phase Oxidation of Phenols Using Soluble Transition Metal Ions and the Spent Catalyst

Oxidation of hydrocarbons as mentioned earlier goes through three distinct phases namely:

- Initiation Phase
- Propagation Phase
- Termination Phase

The initiation reaction as has been mentioned requires a radical to start. This initial radical can be produced by several means, notable among them being as a result of a redox reaction between a transition metal ion and a peroxide:



In this work the transition metal ions considered were Cu^{2+} and Fe^{2+} while hydrogen peroxide was used as the peroxide. Thus the expected reactions were as follows:

For the Cu^{2+} system, the reactions were:



For the Fe^{2+} system the reactions were:



5.6.2 Effect of Cu^{2+} and Fe^{2+} on the Liquid Phase Oxidation of Phenols

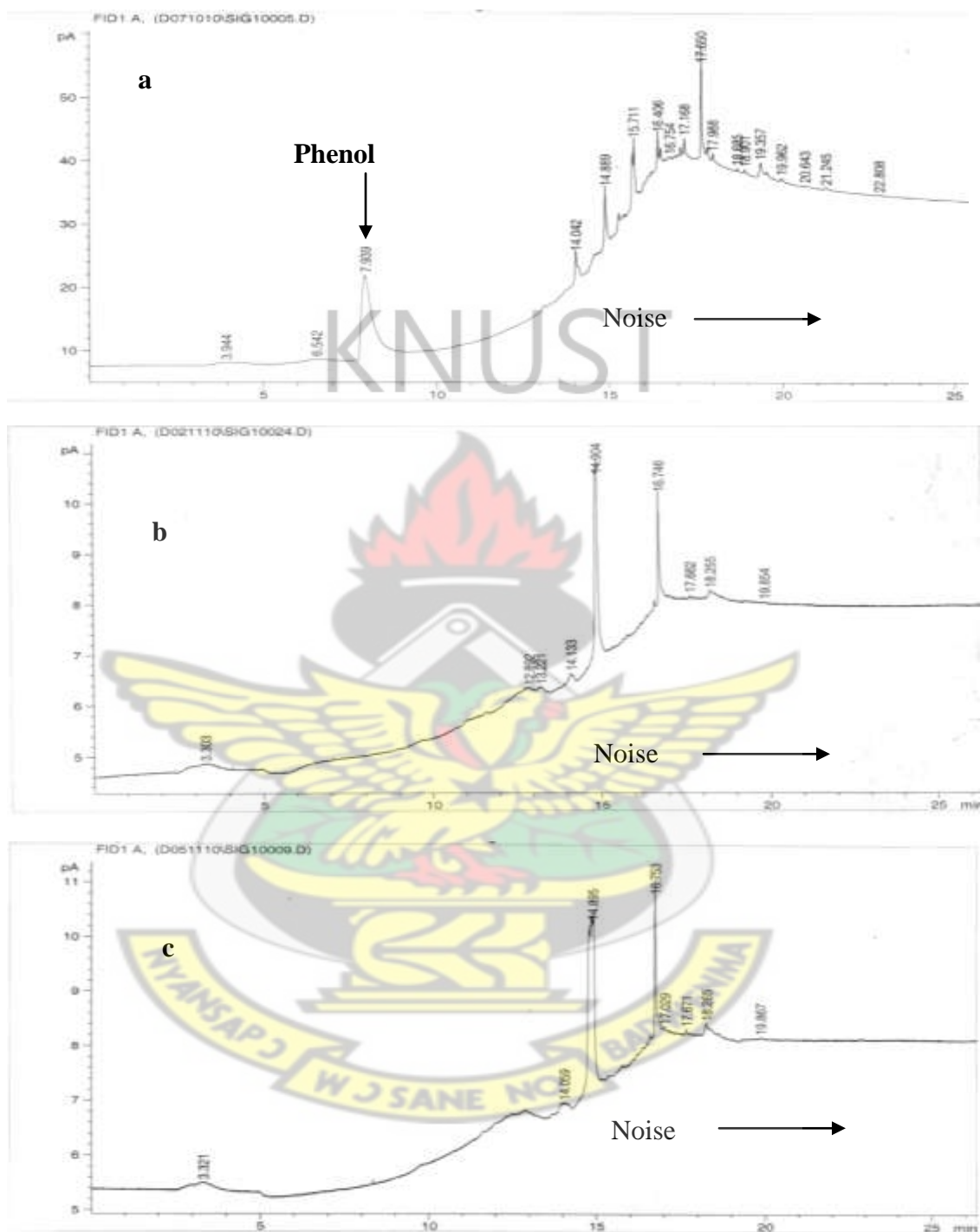


Figure 5. 6. 2 GC plots of (a) 1000 ppm phenol solution, (b) 1000 ppm phenol solution + 10 ml 50% H_2O_2 + 150 mg Cu^{2+} (c) 1000 ppm phenol solution + 10 ml 50% H_2O_2 + 150 mg Fe^{2+}

After allowing 30 minutes of reaction time for both the Fe^{2+} and Cu^{2+} systems, 100% phenol conversion was achieved as can be seen figure 5.6.1. It was also observed that the Fe^{2+} system was considerably fast while the Cu^{2+} system was slow. For instance when 10ml of a 50% H_2O_2 was added to separate phenol solutions that contained equal amounts of the Fe^{2+} and Cu^{2+} respectively, the browning of the solutions, which suggested the production of catechol, hydroquinone and benzoquinone, (Inchaurredo *et al.*, 2012) was very rapid (*less than 10 minutes*) with the Fe^{2+} - Phenol solution, while that of the Cu^{2+} - Phenol solution was very slow, taking about 30 minutes for the browning to show.

From Figure 5.6.3 it can be seen that the initial COD (time = 0 min) of the solution before entering the reactor was considerably high. The initial COD for the Cu^{2+} system was 985ppm while that of the Fe^{2+} system was 369ppm. These figures suggest that Fe^{2+} is better at catalyzing the liquid phase phenol oxidation than Cu^{2+} since by just reacting the phenol with Fe^{2+} in the presence of H_2O_2 it was able to reduce the initial COD of the solution from 1276 ppm to 369 ppm. From Figure 5.6.2 it can also be seen that for the Cu^{2+} system increasing the Cu^{2+} above 150 mg/L does not necessarily improve upon the COD of the effluent from the reactor. It is worth noting that the COD value is not limited to the measurement of organic compounds but inorganic compounds present in the solution as well and hence increasing even the ion concentration also affects its measured value.

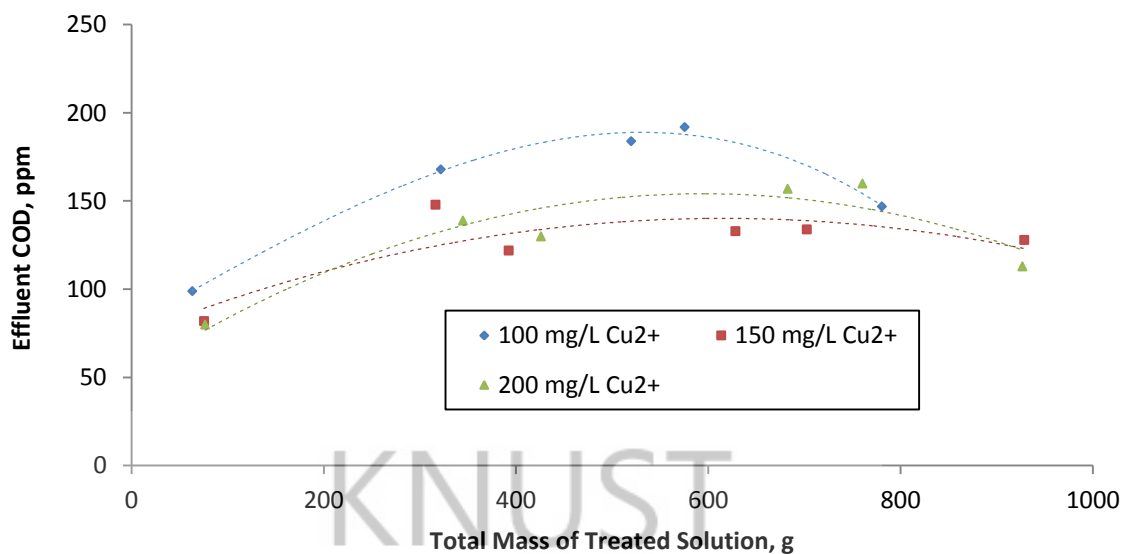


Figure 5. 6. 3 Change in COD during phenol oxidation at various Cu²⁺ concentrations using 1.0% CuO supported on spent catalyst + 10ml H₂O₂ (50%) -Time

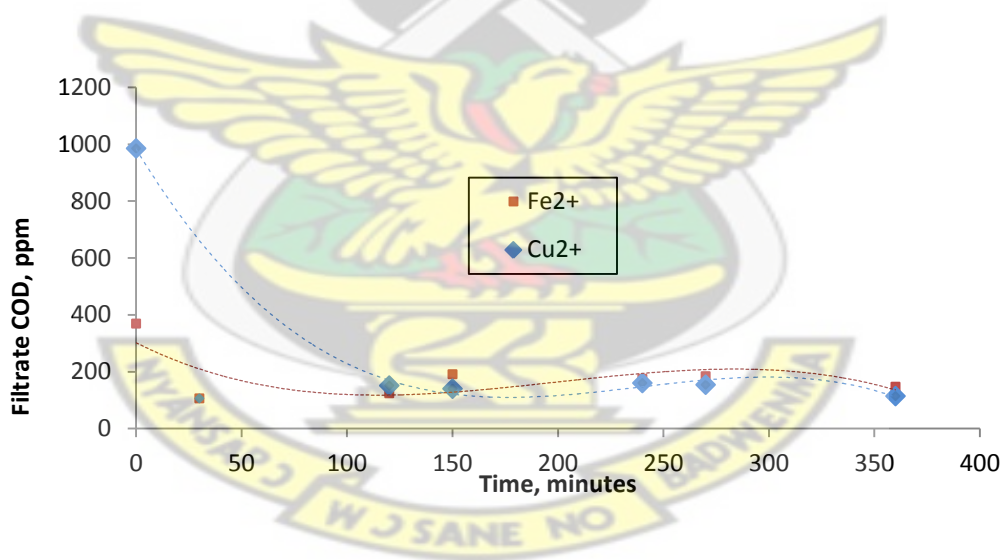


Figure 5. 6. 4 Effect of metal ion type on the liquid phase oxidation of Phenol

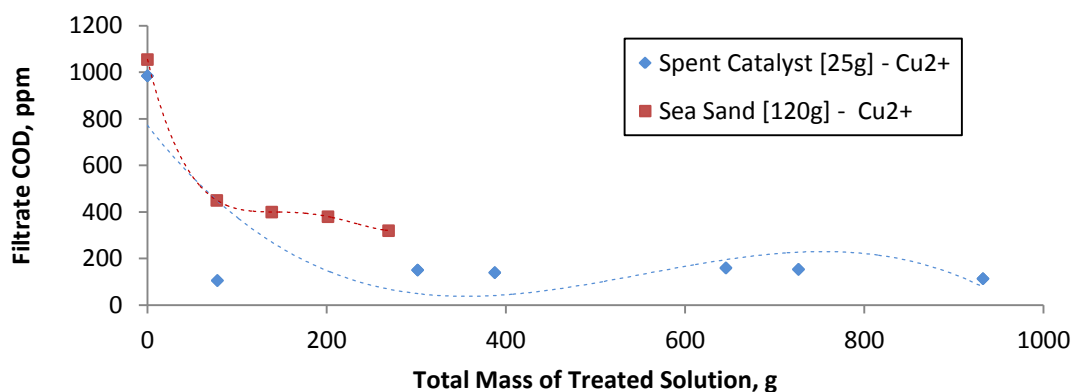


Figure 5. 6. 5 Effect of adsorbent (Packing) type on the liquid phase oxidation of phenol

5 .6.3 Control Experiment Using Sea Sand

Irrespective of the metal ion type used the COD of the effluent was not significantly different. This observation can be seen from Figure 5.6.3 where the COD profiles of the Fe²⁺ and Cu²⁺ systems were approximately the same after 100 min. This observation implies that aside the metal ion used the packing in the reactor (column) also play an important role. To investigate the relevance of the presence of the spent catalyst a control experiment was conducted in which the packing was thoroughly washed sea – sand. Sea sand was chosen as the packing material because it was considered inert under the reaction conditions. During the liquid phase oxidation of the phenols, the spent catalyst provides an increased surface area that allows for intimate contact between the reactants, that is, the oxygen in the air and the phenol or organic compounds in the solution. A graphical comparison of the results is presented in Figure 5.6.4. From the graph, it could be seen that the spent catalyst was better than the sea sand. However in both cases the there was reduction in the COD of the influent solution but that of the spent catalyst was much better even though the mass of the spent catalyst used was only 25 g whiles that of the sea sand

was 120 g. This observation indicates that the spent catalyst itself contributes to the liquid phase oxidation of the phenol.

5.7 Liquid Phase Oxidation of Phenols Using Transition Metal Oxide - Impregnated Spent Catalysts

From the experiment conducted using the soluble metal ions it was observed that the phenol oxidation catalyzed by the Fe^{2+} ions was relatively fast whiles that catalyzed by the Cu^{2+} ions was generally very slow, but once commenced proceeds very fast.

5.7.1 Comparison of the Effectiveness of the Various Metal Oxide Impregnated Spent Catalyst

The spent catalyst was impregnated with metal oxides and used as the catalyst in separate runs. Figures 5.7.1 and 5.7.2 show a graphical representation of the experimental data presented in Tables 4.5.7, 4.5.11 and 4.5.14 - 4.5.17. In these graphs it can be seen that the Fe_2O_3 impregnated spent catalyst exhibited good properties in catalyzing the liquid phase oxidation of phenol when the H_2O_2 was 20 ml whiles its effect was slightly lower than that of CuO when the H_2O_2 was 10 ml. This drop in performance may be attributed to the long induction period which characterized its oxidation when the H_2O_2 concentration was low. In addition, from the graphs it can be seen that the least effective oxide was the MnO_2 .

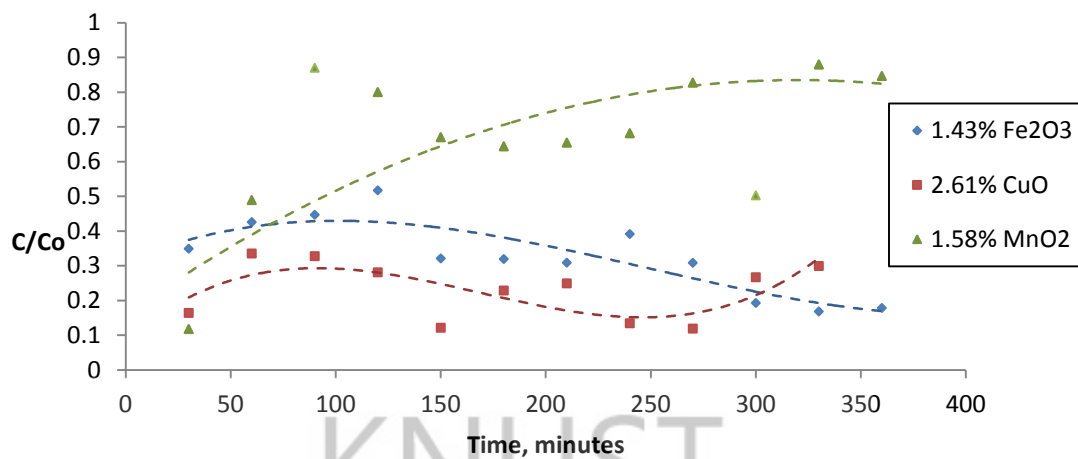


Figure 5.7.1 Concentration profiles of the different metal oxide – impregnated spent catalyst at 10 ml H₂O₂ (50%)

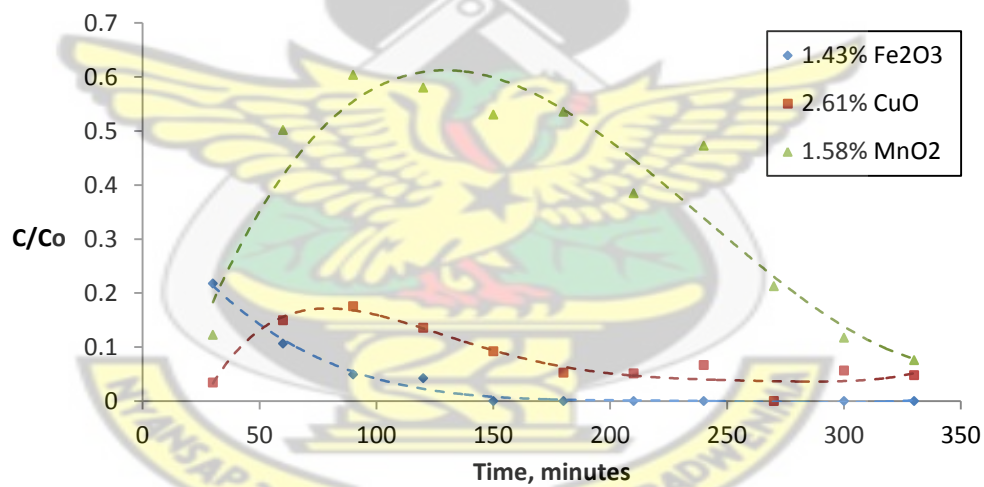


Figure 5.7.2 Concentration profiles of the different metal oxide – impregnated spent catalyst at 20 ml H₂O₂ (50%)

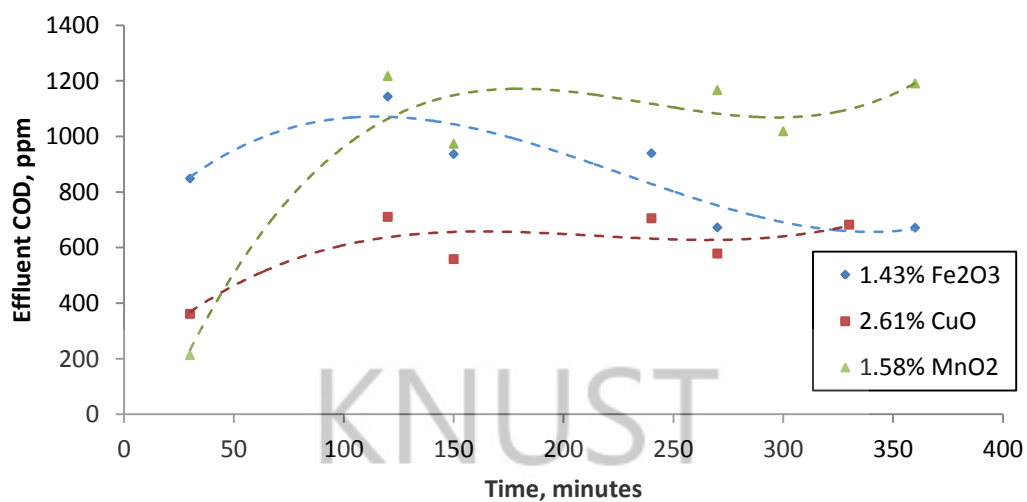


Figure 5. 7. 3 COD profiles of the different metal oxide – impregnated spent catalyst at 10 ml H₂O₂ (50%)

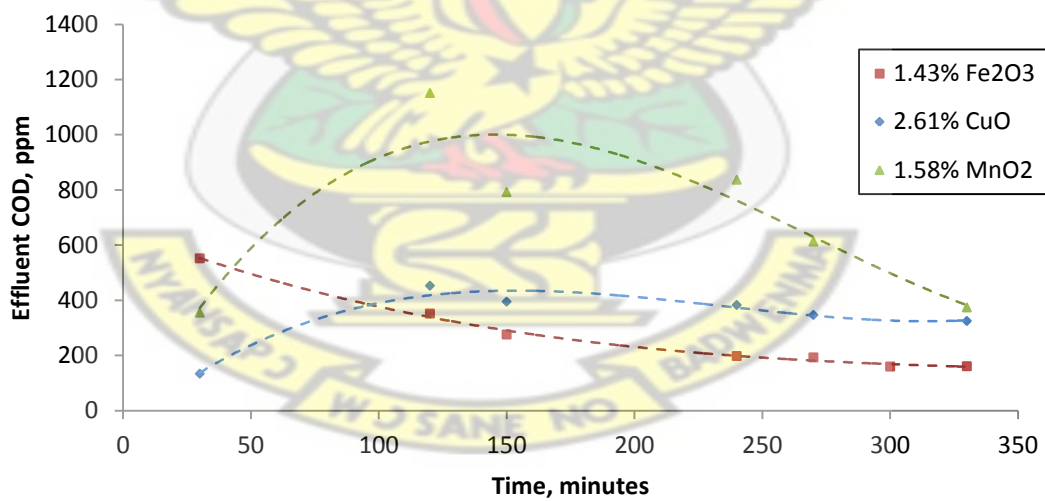


Figure 5. 7. 4 COD profiles of the different metal oxide – impregnated spent catalyst at 20 ml H₂O₂ (50%)

Figures 5.7.3 and 5.7.4 show the effects of the various type of oxide used on the COD of the effluent (treated solution) from the reactor (column). The trend of the result is generally like that obtained when following the phenol concentration. However the 100% phenol conversion in the Figures 5.7.2 corresponds to a COD below 200 ppm in Figures 5.7.4, which is below the maximum allowable COD level of 250 ppm by Ghana EPA for waste water. The GC plots of the effluent solutions which also confirm this observation are shown in Figure 4.5.41 – 4.5.44, 4.5.57 – 4.5.60, 4.5.65 – 4.5.68.

In the experiments in which 10ml of H_2O_2 (50%) was used as radical initiator it can be seen that in the case of the MnO_2 impregnated spent catalyst, the extent of phenol oxidation was very low since the measured COD values of the treated solutions were generally approximately the same as the initial solution (see Table 4.5.16), although there were some phenol concentration changes. This low performance of the MnO_2 -impregnated spent FCC may be due to the fact that under the conditions MnO_2 would not get into solution and hence be able to effect meaning oxidation.

5.7.2 Effect of the Content of the Fe_2O_3 in the Impregnated Spent Catalyst on the Phenol Oxidation

The effect of the amount of Fe_2O_3 on the liquid phase oxidation was also studied. A graphical representation of the results of these experiments can be found in Figure 5.7.5 – 5.7.8 (using data from tables 4.5.6 – 4.5.13). It was observed that increasing the Fe_2O_3 content of the spent catalyst did not result in improved performance of the modified spent catalyst. The loss in performance may be due to the loss in surface area of the spent catalyst as more oxide would have been deposited in the pores of the zeolite.

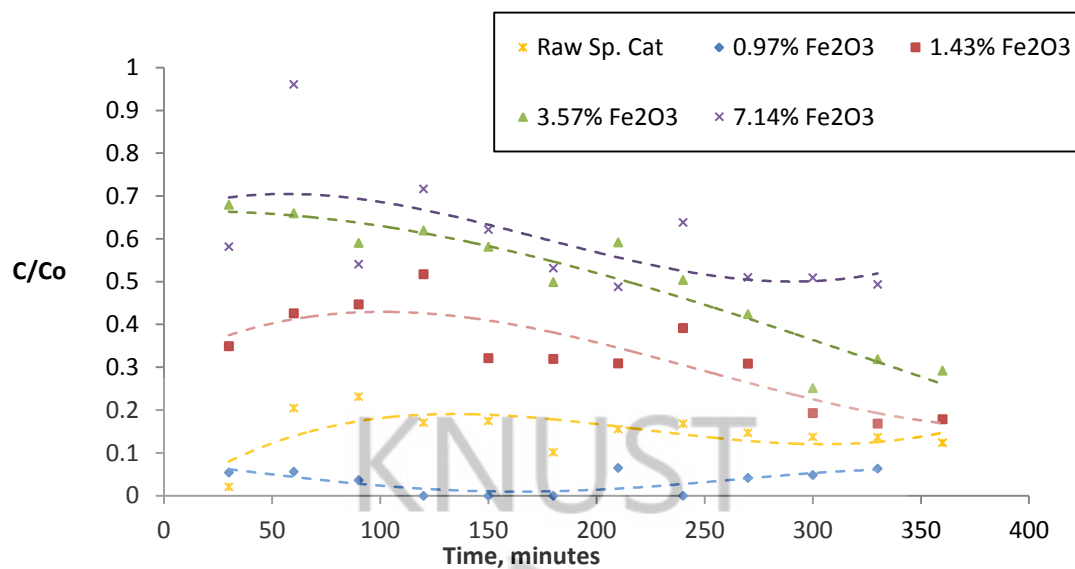


Figure 5.7.5 Concentration profile of the various Fe₂O₃ – impregnated spent catalyst at 10 ml H₂O₂ (50%)

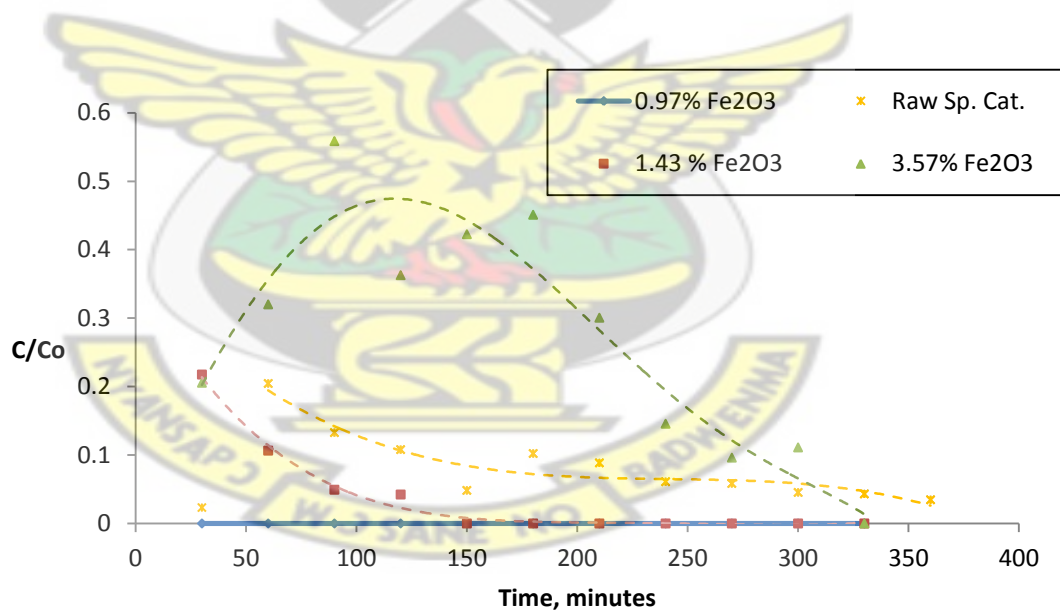


Figure 5.7.6 Concentration profile of the various Fe₂O₃ – impregnated spent catalyst at 20 ml H₂O₂ (50%)

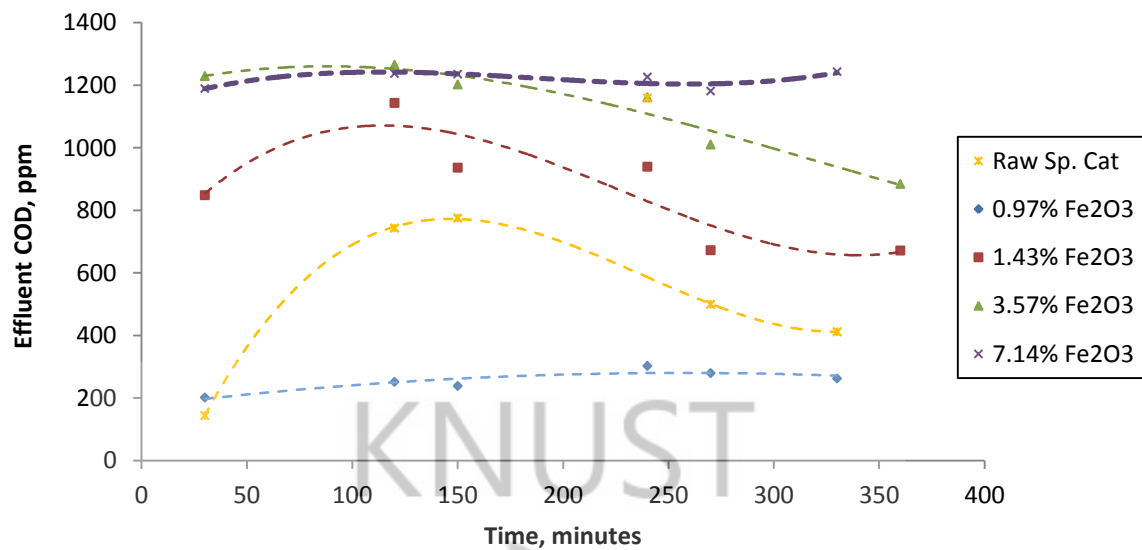


Figure 5.7.7 COD profile of the various Fe₂O₃ – impregnated spent catalyst at 10 ml H₂O₂ (50%)

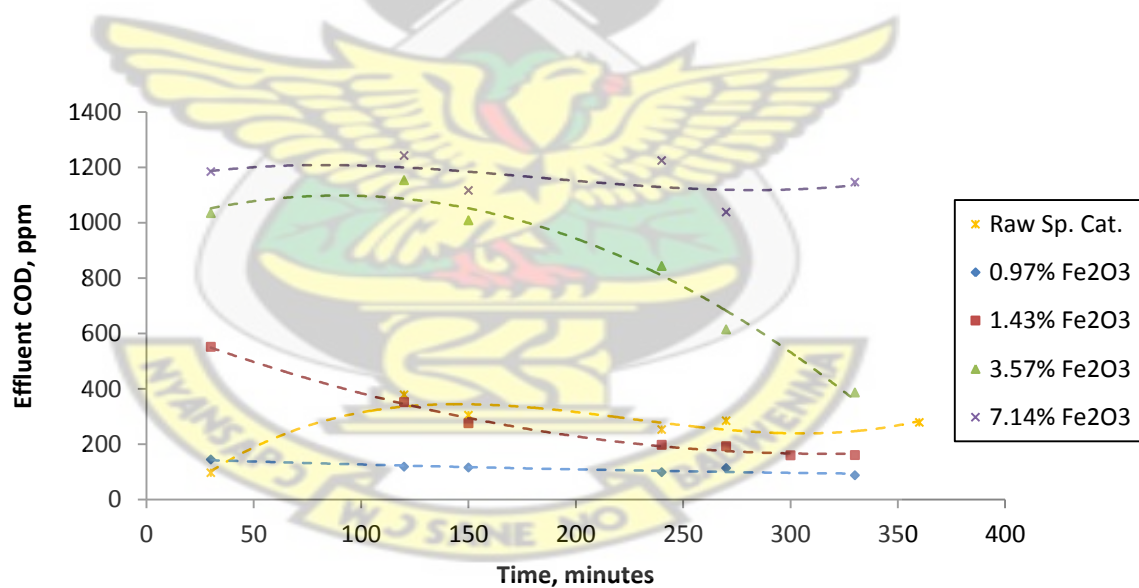


Figure 5.7.8 COD profile of the various Fe₂O₃ – impregnated spent catalyst at 20 ml H₂O₂ (50%)

From the results, it can be seen that using 10ml of H_2O_2 (0.5 vol %) about 97% conversion was achieved with the spent catalyst that contained 0.97% Fe_2O_3 where as for the same modified spent catalyst 100% conversion of phenol was achieved when the H_2O_2 amount was increased to 20ml (1.0 vol %). The least effluent COD values were also obtained using the spent catalyst impregnated with 0.97% Fe_2O_3 . The GC plots of the effluent can be found in Figures 4.5.21 – 4.5.52.

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5.7.3 Effect of H_2O_2 Amount on the Liquid Phase Oxidation of Phenols

The H_2O_2 amount, as can be seen from the results presented in Figure 5.7.9 and 5.7.10 has a profound impact on the extent of the oxidation. This observation is very consistent with the works of Rivas, *et al.*, (1998). That said, it is also worth noting that the H_2O_2 itself contributes to the increase in the COD of the solution. The COD of a 1000 ppm phenol solution + 0.5 vol. % H_2O_2 was 1300 ppm while the COD of the same amount of phenol but this time, with 1.0 vol. % H_2O_2 was 2600 ppm. This observation suggests that any residual H_2O_2 could also contribute to the measured COD values of the effluents obtained from the column.

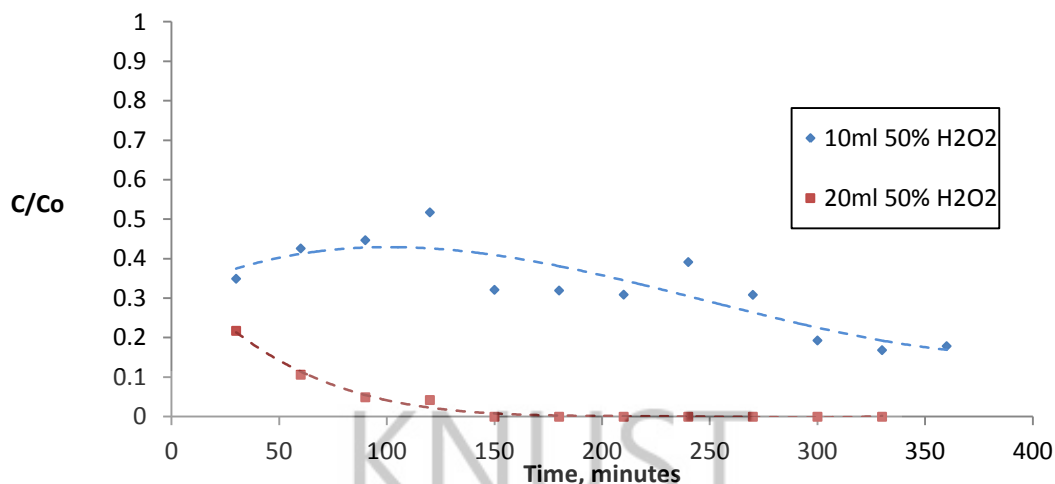


Figure 5. 7. 9 Effect of H_2O_2 amount on phenol concentration profile using spent catalyst impregnated with 1.43% Fe_2O_3

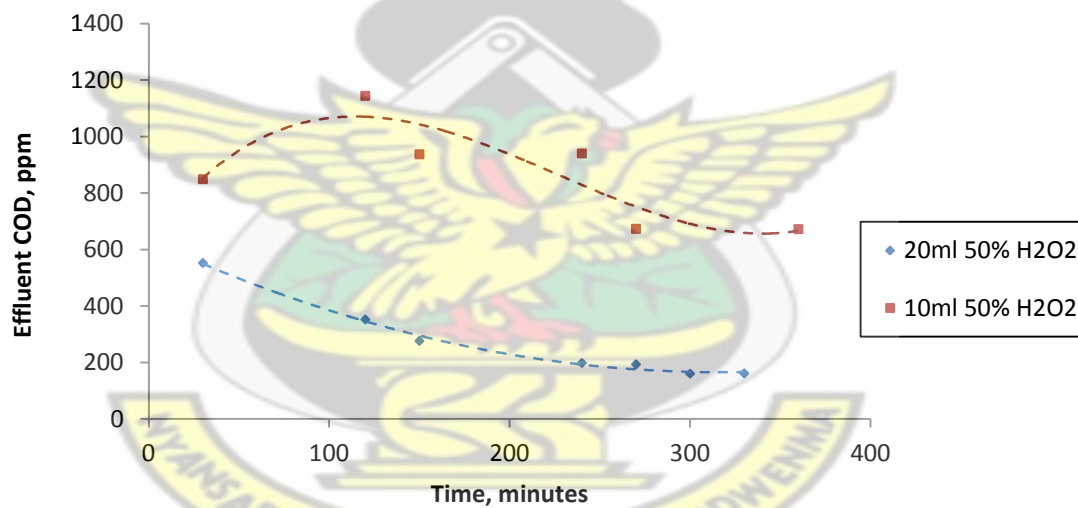


Figure 5. 7. 10 Effect of H_2O_2 amount on the COD profile using spent catalyst impregnated with 1.43% Fe_2O_3

5.7.4 pH and Liquid Phase Oxidation of Phenols

As has been mentioned earlier in the literature review (Debellefontaine, *et al.*, 1996; Hobbs, 1998), during the hydroperoxide cycle alcohols get converted to carbonyl compounds, which upon further reaction get converted to carboxylic acids. These carboxylic acids cause the pH of the reaction medium to drop as they increase in concentration. In addition if the reaction goes to completion and the partial pressure of the formed CO_2 is sufficiently high it can form carbonic acid which also leads to a drop in the pH of the solution. Thus as would be expected, the pH of the treated solutions progressively reduced. From Figures 5.7.11 – 5.7.12 it can be seen that for each of the experiments there was an initial increase in the pH of the solution (*that is, from its original value of 4.3*) after which the pH starts dropping. This initial increase in pH may be due to the residual NaOH that might be in the metal oxide – impregnated spent catalyst since it was not washed before usage.

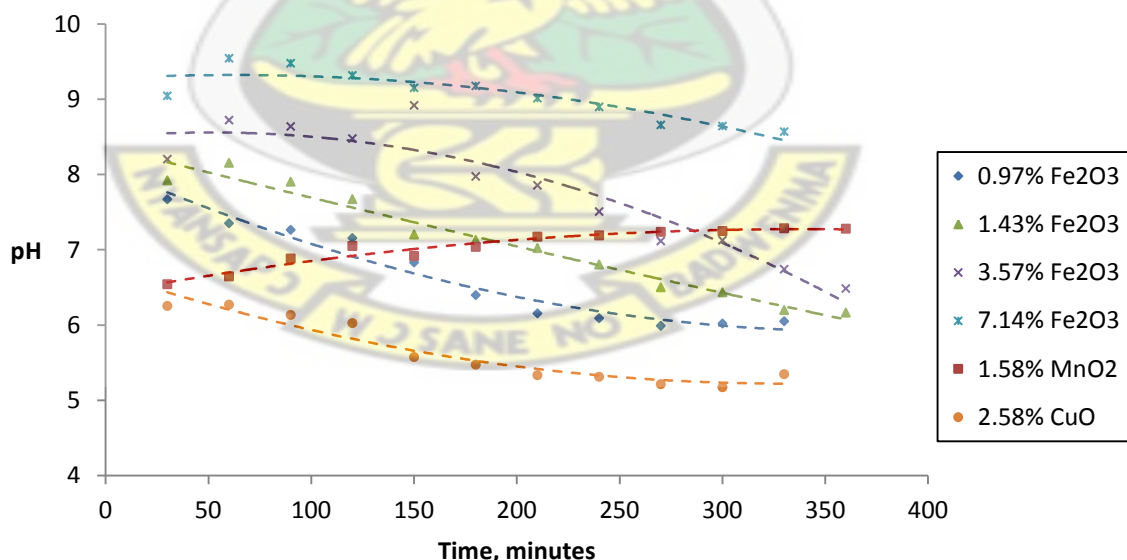


Figure 5. 7. 11 pH profile of effluent solutions for the various metal oxide impregnated – spent catalyst using 10ml H_2O_2

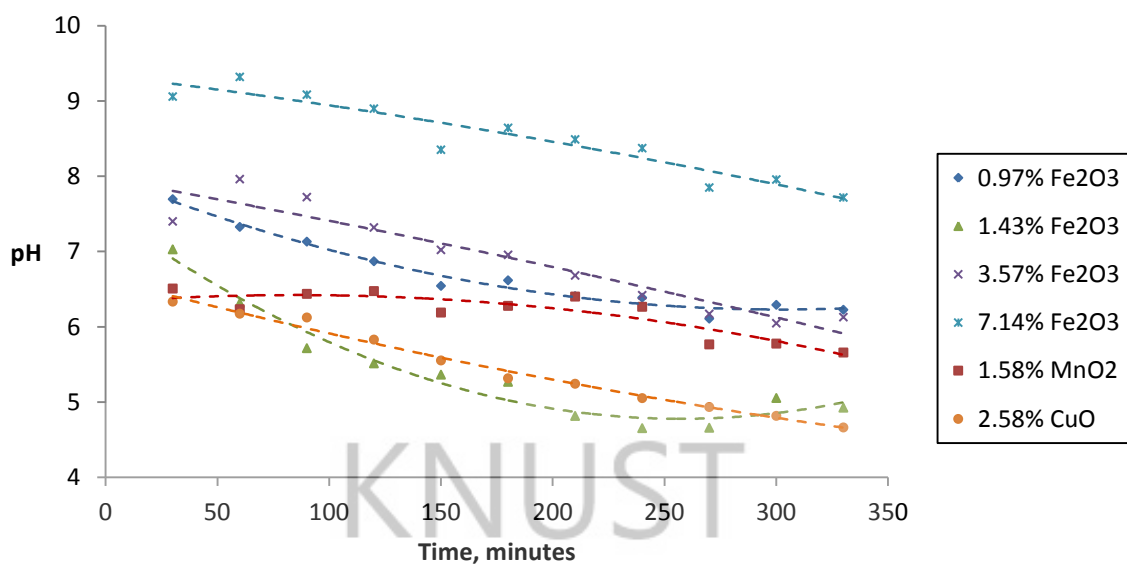


Figure 5. 7. 12 pH profile of effluent solutions for the various metal oxide impregnated – spent catalyst using 20ml H₂O₂

Considering that fact the overall air pressure maintained throughout the reactor was 0.4 cmHg (533 Pa) gauge and also the fact that excess air was used the contribution of carbonic acid to the pH drops can be said to be less significant. This implies that for complete mineralization to have occurred the pH of the treated solutions must approach neutral, since that would mean the formed carboxylic acids were ultimately broken down to CO₂ and H₂O. This observation can somewhat be made on the experiments conducted with the spent catalyst impregnated with 0.97% Fe₂O₃ since its pH ranged between 7.67 to 6.05 and 7.70 to 6.23 when 10ml H₂O₂ and 20ml H₂O₂ were used respectively. This observation is further corroborated by the fact that these experiments also recorded the least COD values.

5.7.5 Mechanism of Oxidation of Phenols Using Spent FCC Catalyst

It is not exactly clear as to the mechanism of oxidation. The process requires the presence of phenol, H₂O₂, O₂, the spent catalyst and metal oxides. It would therefore appear that the oxidation process is complex. The spent catalyst has Ni, Cu, Fe, and V on its surface which may contribute to the oxidation reaction. It has also been observed that there is a period of induction prior to the oxidation (mineralization). Consequently the following 3 – stage process, similar to the proposal by Suarez-Ojeda, *et al.*, (2004) is being suggested. They are:

1. Adsorption stage
2. Induction stage
3. Mineralization stage

During the adsorption stage it is expected that phenol is adsorbed. The adsorption as has been noted earlier is according to the Freundlich isotherm. Additionally, during this stage oxygen and H₂O₂ may also be adsorbed.

With the reacting species adsorbed on the surface the induction stage now sets in. Rivas, *et al.*, (1998) have published an extensive investigation on the reaction mechanism and the kinetics of the wet air oxidation of phenols. Their study unlike the current one does not employ the use of an adsorbent nor a catalyst. In their work however the following are some of the expected reactions during this stage:





The mineralization stage is the stage during which the adsorbed phenol actually gets broken down into carbon dioxide and water through the formation of intermediate products. Some of the intermediate products according to Suarez-Ojeda, *et al.*, (2004) include oxalic acid, acetic acid, formic acids, malonic acid, maleic acid, fumaric acids, hydroquinone, catechol and benzoquinones.

5.7.6 Infrared Analyses

Beyond GC and COD analysis of the treated phenol solution, infrared (IR) analyses were also conducted on the treated solution to determine whether there were other products of the oxidation of the phenol. Figure 5.7.19 presents the IR spectrum of a treated phenol solution using spent catalyst impregnated with 0.97% Fe₂O₃.

From the IR spectrum in Figure 5.8.19 it can be seen that absorbances above the mid section are located at 2955.57 cm⁻¹, 2923.75 cm⁻¹ and 2852.15 cm⁻¹. These wave numbers correspond to C-H stretchings from an aliphatic hydrocarbon (3000 – 2800 cm⁻¹), (Stuart, 2004). However the wave number 2852.15 cm⁻¹ also could corresponds to a C-H stretching from an aldehyde (2900 – 2700 cm⁻¹). Since there is no absorbance that correspond to a C=O bending or stretching this wave number could not be an aldehyde but rather C-H stretchings from the CHCl₃ which was used as the solvent. This conclusion is further corroborated by the fact that there are absorbances at 1262.61 cm⁻¹, 1094.57 cm⁻¹ and

1012.60 cm^{-1} which correspond to C-H bendings (1275 cm^{-1} – 1000 cm^{-1}) from an aliphatic hydrocarbon.

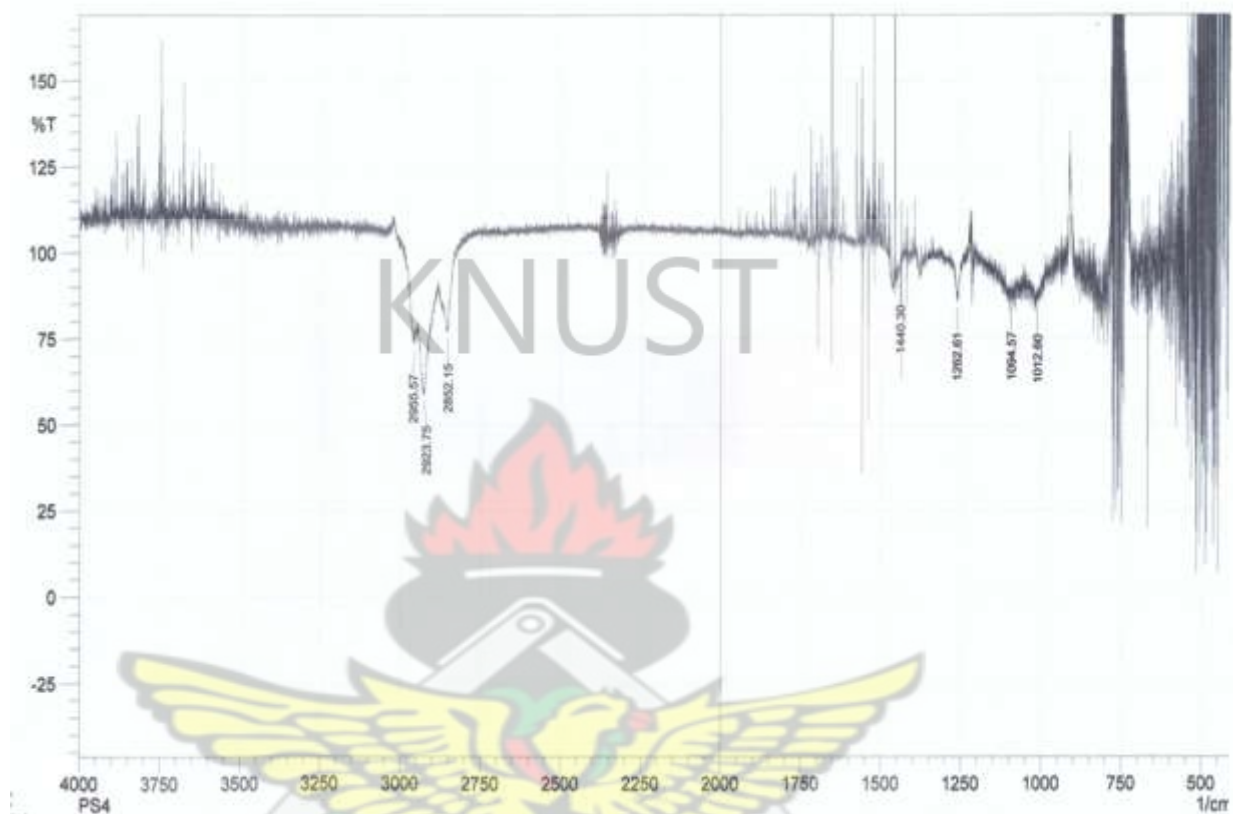


Figure 5. 7. 13 IR Spectrum of a treated phenol solution

In the finger print region the sample also absorbs at 1440.30 cm^{-1} which suggests the presence of C-O-H in-plane bending from a carboxylic acid. However the characteristic peaks for carboxylic acid at 1700 cm^{-1} , 1430 cm^{-1} , 1240 cm^{-1} and 930 cm^{-1} are visibly absent and so cannot be concluded as being present. Thus the IR spectrum confirms the absence of phenol, aldehydes, ketones, carboxylic acids and aromatic compounds.

5.8 Wastewater Treatment

5.8.1 Summary of Previous Research on Wastewater Treatment using the CWAOP Process

The liquid phase oxidation of phenols in wastewater has been done by number of researchers, (Mishra, *et al.*, 1995) . In most of the proposed methods the operation conditions are so harsh that the method altogether seems to lack industrial practicability. Some of these conditions have been presented in Table 5.9.1. To recap for emphasis, pressures usually ranged from 2 – 14 bars and temperature from 100 – 320°C.

Table 5.8.1 Operating conditions of several phenol oxidation methods

Author(s)	Phenol Conc. g/l	Temperature °C	Pressure, MPa*	Source of Oxidant
Shibaeva <i>et al.</i> , 1969	1.4 – 8.9	180 - 210	0.8 – 3.5	Oxygen
Proden and Le, 1976	1.4 – 3	200- 250	5.5 – 15 total pressure	Air
Hellin <i>et al.</i> , 1981	2.5 – 10	185 - 230	10.4 – 15.6	Oxygen
Balilod and Faith, 1983	5	204 – 260	2 – 2.5	Oxygen
Harris <i>et al.</i> , 1983	0.01 – 0.1	175 - 220	9.3	Oxygen
Willms <i>et al.</i> , 1987	0.14 – 0.154	130 – 200	13.8 air pressure	Air
Jaulin and Chornet, 1987	1	140 – 180	2.6 to 5.0 total pressure	Oxygen
Mundale <i>et al.</i> , 1991	0.2	150 – 195	0.2 – 1.0	Oxygen
Joglekar <i>et al.</i> , 1991	0.2	150 – 180	0.3 – 1.1	Oxygen
Chang <i>et al.</i> , 1995	1	170 – 230	2.9 – 3.9 total pressure	Oxygen

*Oxygen partial pressures.

The importance of the high pressures in these methods appears to be quite obvious, which is to ensure that the solution remains in the liquid phase during the process. However, as

has been observed earlier in the literature, for liquid phase reactions high pressures increase the impact of the caging which usually makes complete phenol conversions unattainable in the absence of a suitable radical source. Additionally, the oxygen employed in these methods is very much in excess of the phenolic compound. The obvious missing link in these methods is the surface area for reaction. Some of these methods either do not employ adsorbent, (Debellefontaine, *et al.*, 1996) or use adsorbents with low surface area. The most popular adsorbent used activated carbon has a disadvantage of being susceptible to oxidation under the reaction conditions and thus contributes to the already prohibitory cost of these processes. The current research has utilized a waste material as adsorbent, a much lower temperature of about 50°C and a relatively low pressure of 0.4 cmHg (533 Pa) gauge. The waste water stream considered was the stripped sour water from a petroleum refinery plant. The stripped sour water basically was a solution containing H₂S, RSH, Phenol, NH₃ and some small quantities of insoluble hydrocarbons. The phenol concentration of the feed solution was 778 ppm.

5.8.2 Stripped Sour Water Treatment

As with typical CWAQ processes, the proposed waste water treatment method is an unselective one and as such breaks down any soluble or insoluble organic compound found in the solution to be treated. Figures 5.8.1 and 5.8.2 show the GC plots of the stripped sour water before and after the treatment.

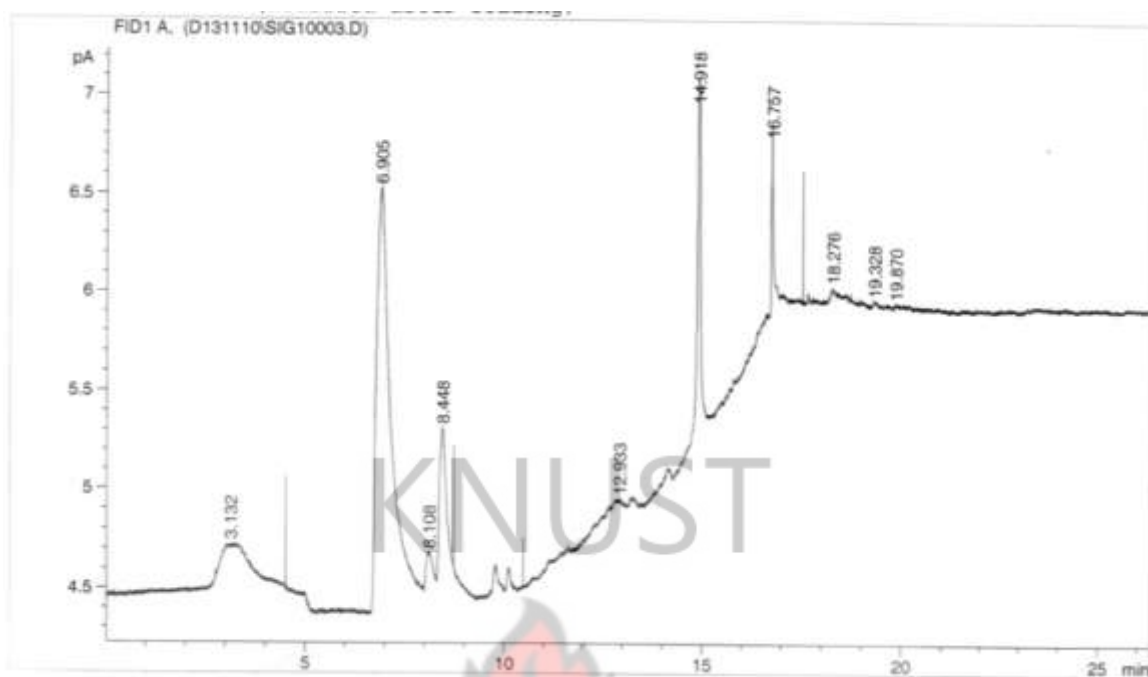


Figure 5. 8. 1 GC Plot of the stripped sour water before treatment

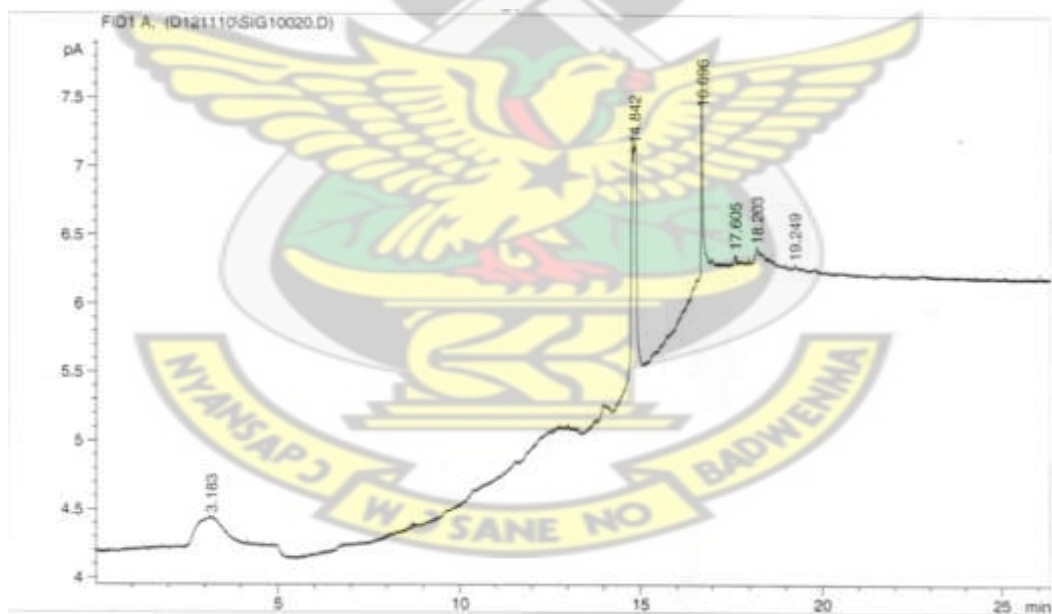


Figure 5. 8. 2 GC Plot of treated stripped sour water after treatment

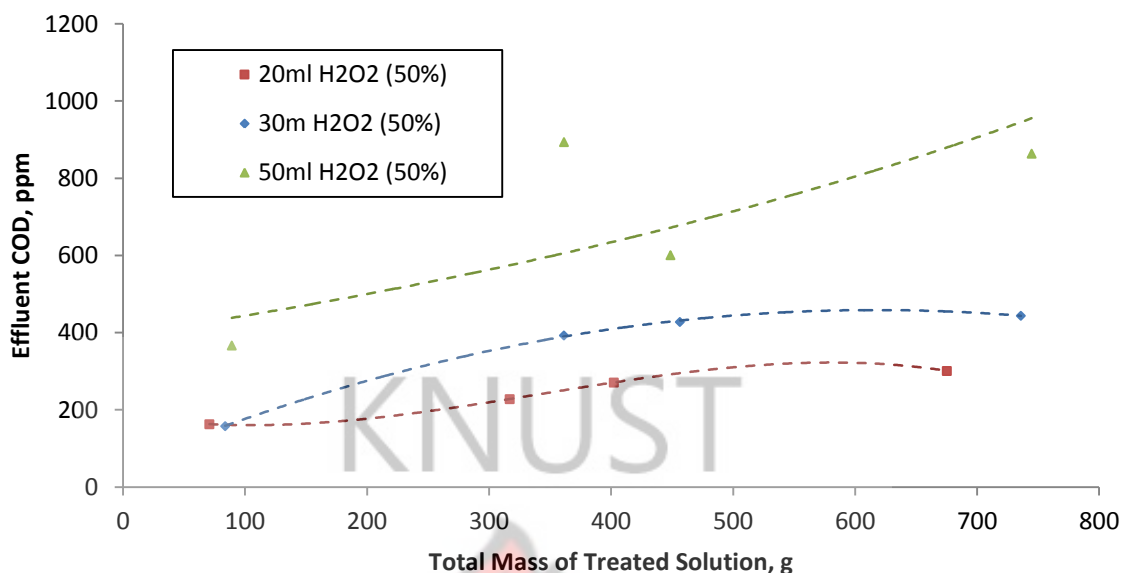


Figure 5. 8. 3 COD profile at various H₂O₂ amount for the treatment of stripped sour water using spent catalyst impregnated with 0.97% Fe₂O₃

The GC plots show the efficacy of the proposed treatment method. The characteristic smell of the stripped sour water was absent in the treated waste water. Because there was complete phenol conversion during the process the phenol concentration could not be used to monitor the progress of the reaction, thus the COD of the treated solution was used and is presented in Figure 5.8.3. An increase in the amount of the H₂O₂ beyond 20 ml did not result in the expected efficiency as it contributed to the measured COD of the treated solution. Table 5.8.2 shows the effect the H₂O₂ alone had on the measured COD of the initial solution.

Table 5. 8.2 Effect of amount H_2O_2 alone on the COD of the stripped sour water

H_2O_2 , ml	COD, ppm
0	2030
20	2950
30	3860
50	5065



Chapter 6

Conclusion and Recommendations

6.1 Summary of Findings

The spent FCC catalyst has been proven to be a good adsorbent of phenols, a property not found in the fresh catalyst. Its performance as phenol adsorbent has also been compared with activated carbon and has been found to be about 16.62% that of activated carbon. Its phenol adsorption has been fitted satisfactorily to the Freundlich adsorption isotherm and may be stated as follows:

$$\rho = 1.649C^{*0.682}$$

where $\rho = \frac{\text{Mass of Phenol Adsorbed}}{\text{Mass of Spent Catalyst}}$ and C^* is the mass fraction of the phenol in the solution at equilibrium.

The spent catalyst has been characterized and has been found to be different in many ways from the fresh catalyst. The surface area of the spent catalyst is only about 38% that of the fresh catalyst. Its pore volume is more than twice that of the fresh catalyst. It has a d_{50} of 88 μm while the fresh catalyst has a d_{50} of 68 μm . In addition, unlike the fresh it contains several transition metals which have potential catalytic properties.

The spent catalyst has been impregnated with varying amounts of CuO , Fe_2O_3 and MnO_2 and its performance tested for the liquid phase oxidation of phenols. The spent catalyst upon impregnation with 0.97% Fe_2O_3 oxide has been proven to be a very effective catalyst

for the in-situ liquid phase oxidation of phenol using 1 vol. % H_2O_2 as a radical initiator and a relatively low air pressure of 0.4 cmHg (533 Pa) gauge and temperature of 50°C .

The resulting modified catalyst has been tested on refinery stripped sour water with about 100% mineralization.

The current research has thus proposed a cost effective Catalytic Wet Air Oxidation (CWAO) process that uses slightly modified spent FCC catalyst which erstwhile was discarded as a waste material and relatively mild operation conditions.

6.2 Recommendations For Further Studies

Based on the findings of the research the following areas of research are recommended.

1. The spent catalyst contains several metal oxides which possess catalytic properties. However the contribution of these metal oxides to the catalytic properties of the spent catalyst could not be investigated. Thus it is recommended that an investigation be conducted in this area as from such a study a much optimized catalyst could be developed.
2. Since the exact reaction mechanism has not been studied in this work the actual kinetic data governing the reactions could not be made available. It is therefore recommended that an investigation be conducted in the reaction mechanism and kinetics of the liquid phase oxidation of phenols using the modified spent catalyst as from such a study a suitable cost effect reactor could be designed.

3. The maximum life span of the modified spent catalyst was not reached in this study.

Further work on this area would make available useful information which would inform waste management of the exhausted catalyst.

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