



Removal of Phenol from Contaminated Water by Newly Prepared Nickel Catalyst

By

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**FACULTY OF EARTH SCIENCE
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DECLARATION

I declare that this thesis entitled “Removal of Phenol from Contaminated Water by Newly Prepared Nickel Catalyst” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Removal of Phenol from Contaminated Water by Newly Prepared Nickel Catalyst

ABSTRACT

Organic pollutant like phenol is preliminary considered as pollutant which is toxic and harmful and non-biodegradable. Although many methods have been employed to remove the phenol from the contaminated water, but the cost of designed catalyst are quite expensive. Thus, a low cost catalyst with selective capability removal of phenol as a water pollutant is generate. This study is focused on explores the preparation and characterization of Nickel-Tannin/Chitosan catalyst and evaluate the catalytic activity of the newly prepared catalyst in the oxidation of phenol in aqueous medium. The catalyst was prepared by reaction of Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and the Tannin-Chitosan support and undergoes several process such as hydrogenation to form Nickel-Tannin/Chitosan catalyst. The prepared catalyst was characterized using FTIR, XRD and SEM. The prepared Nickel-Tannin/Chitosan was used as catalyst for oxidative degradation of 0.5M phenol in aqueous medium. The catalytic performance of Nickel-Tannin/Chitosan was carried out by varying time, temperature(38°C, 48°C, 58°C) and concentration of phenol. It was found that 98% of phenol was degrade at 58°C which is the optimal temperature for the phenol to degrade in the presence of catalyst and Hydrogen peroxide(H_2O_2). This result shows that Nickel-Tannin/chitosan very useful as an effective catalyst for oxidative degradation of phenol.

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**Pemecatan Fenol dari air tercemar oleh Pemangkin Nikel yang Baru
Disediakan**

ABSTRAK

Bahan cemar organik seperti fenol adalah awal dianggap sebagai pencemar yang beracun dan berbahaya dan tidak mesra alam. Walaupun banyak kaedah telah digunakan untuk membuang fenol dari air tercemar, tetapi kos pemangkin direka agak mahal. Oleh itu, pemangkin dengan kos yang rendah dan mempunyai keupayaan menyingkirkan fenol sebagai pencemar air telah dijana. Kajian ini memberi tumpuan kepada meneroka penyediaan dan pencirian Nikel Tanin / Kitosan pemangkin dan menilai aktiviti pemangkin yang baru disediakan untuk pengoksidaan fenol dalam medium akueus. Pemangkin ini telah disediakan oleh reaksi Nikel Nitrat hexahidrat ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) dan sokongan Tanin-Kitosan dan menjalani beberapa proses seperti hidrogenasi untuk mendapatkan pemangkin Nikel Tanin / Kitosan. Pemangkin yang disediakan dicirikan melalui menggunakan FTIR, XRD dan SEM. Nikel Tanin / Kitosan yang disediakan telah digunakan sebagai pemangkin kepada degradasi oksidatif 0.5M fenol dalam medium akueus. Prestasi pemangkin Nikel-Tanin / Kitosan telah dijalankan pada masa yang berbeza-beza, suhu (38°C , 48°C , 58°C) dan kepekatan fenol. Ia telah mendapati bahawa 98% daripada fenol telah tergradasi di 58°C yang merupakan suhu optimum untuk fenol degradasi dengan kehadiran pemangkin dan hidrogen peroksida (H_2O_2). Keputusan ini menunjukkan bahawa Nikel Tanin / Kitosan akan berguna sebagai pemangkin yang berkesan untuk degradasi oksidatif fenol.

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Formula	Page
$\text{Degradation (\%)} = \frac{(R)_0 - (R)_t}{(R)_0} \times 100$	16



LIST OF ABBREVIATION

T/C Support	Tannin-Chitosan Support
FTIR	Fourier transforms infrared spectroscopy
XRD	X-ray Diffractometer
SEM	Scanning Electron Microscopy
(Ni (NO ₃) ₂ ·6H ₂ O)	Nickel nitrate hexahydrate
UV-Visible Spectrophotometer	Ultraviolet-Visible Spectrophotometer
H ₂	Hydrogen
H ₂ O ₂	Hydrogen peroxide (A. Alenjandre, 1998)

CHAPTER 1

INTRODUCTION

1.1 Background study

The organic compound like phenol is preliminary considered as pollutant which is toxic and harmful and non-biodegradable (Alenjandre *et al.*, 1998). The pollutant generated from industrial discharge such as phenol is formed in high concentration and a large amount in water bodies (Jhansi *et al.*, 2013). Thus, the control by direct removal or in the formed of very low concentration is inappropriate. This is because the recovery will leads to limited economic recovery. There are several different methods that can be used to remove or to treat the pollutant. The level of phenol concentration, economics and easy control are the indicator that can be used in order to choose the treatment can be used (Randall & Knopp, 1980). One of the treatments that can be used is impregnation. Impregnation is contact between solid and liquid that can make the components to be deposited on the surface. Impregnation can be made by eight other different methods which one of it is by soaking with an overabundance of solution that will be used in this study (Haber *et al.*, 1995).

A useful and inexpensive alternative process can be used in removing the organic compounds. The process is the oxidation of dilute aqueous solution for organic pollutants using the air or oxygen over solid catalyst. The organic compound can be oxidised to carbon dioxide and water (Bahadori, 2014). Strong oxidation condition of the process may lead the catalyst to undergo serious losses and deactivation activity (Alejandre *et al.*, 1998). Hence, the choose of appropriate

catalysts needs to consider in order to prevent the losses and deactivation activity in oxidation process.

The formation of primary amines in the preparation of nickel-based catalysts is lead from the use of basic support. This formation can lead to hydrogenation process which is the chemical reaction between molecular hydrogen (H_2) with another compound or element that usually occur in the presence of catalyst such as nickel, palladium or platinum. Bifunctional mechanism can be used in the gas-phase hydrogenation of acetonitrile. Metal will be located at the active site of the hydrogen while the acid function will be catalyzes the transamination reaction that lead to secondary and tertiary amines which is situated on the support. However, this mechanistic approach is not fully success due to this cannot be applied to other systems. This is because its needs of reaction steps that converting nitriles into different amines that should take place on the surface of metals. Therefore, there are much work still needs to be done in order to understand the mechanism that can be used in the hydrogenation process. (Infantes-Molina *et al.*, 2004)

Metal based such nickel have been investigated for several years as a catalyst because this material is widely used such as in the food preparation equipment, mobile phones, medical equipment, transport, buildings and also power generation. Nickel are chosen in this study due to nickel is highly abundance, economically feasible and suitable for the application in their number compared to other metals. Other than that, nickel also exists in the different forms of oxides (Jankovic *et al.*, 2008)

This study aims to explore the possible development of an efficient catalytic method for the purification of contaminated water containing organic compound using low- cost nickel oxide catalyst.

1.2 Problem statement

Phenol is currently abundance used as disinfectant and also for cleaning. Phenol also used in the chemical industry, agriculture industry as substance in pesticides and also, in textile manufacture (Galbickova *et al.*, 2014). Although many methods have been employed to remove the phenol from the contaminated water, but the cost of designed catalyst are quite expensive. Thus this research will generate a low cost catalyst (Zhuang *et al.*, 2015) with selective capability removal of phenol as a water pollutant.

1.3 Objectives

1. To characterize prepared tannin-chitosan nickel doped catalyst.
2. To evaluate the catalytic activity of the newly prepared catalyst in the oxidation of phenol.

CHAPTER 2

LITERATURE REVIEW

2.1 Phenol

Phenol is an aromatic organic compound with the molecular formula C_6H_5OH . It is white crystalline volatile solid. The compound consists of a phenyl group bonded to a hydroxyl group. Phenol additionally contains an alcohol group so it is not able to form a very strong hydrogen bond with different molecules but this bond contributes to phenol's affinity toward polar substances. As a polar molecule, phenol is solvent in water. (Wade, 2016) The physical properties of phenol incorporate its physical condition of colorless liquid and its high boiling point. Phenol's higher boiling point contributes to the strong hydrogen bonds. At the room temperature, the solid form of phenol is white in color and having a sweet odor.

Phenol has an aromatic compound structure which is compound that form a cyclic ring containing double and single bonds. Aromatic compounds are referred to as benzene in phenol. Diagram below shows the structure of benzene ring or phenol structure.

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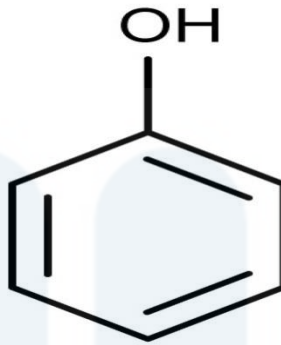


Figure 2.1 Structure of phenol.

Phenol is usually found in the manufacturing industries that release their effluent in the water bodies. Surface waters, rainwaters, sediment, drinking water are also the sources of water that might contain phenol as their chemical substances. Lakes and rivers that are serve as water sources and also discharge receivers from industrial activity that using phenol substance are foundly appear with the higher level of phenol.

2.2 Tannin-Chitosan support

Tannin is any group of astringent polyphenolic vegetable principles or compounds, chiefly complex glucosides of catechol and pyrogallol. It also can call as tannic acid (Reed *et al.*, 2014).

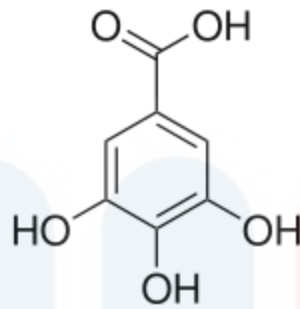


Figure 2.2.1 Structure of Tannin

Chitosan is the sugar that can obtain or extracted from the hard outer skeleton of shellfish such as lobster, crab, shrimps and others. Mostly, chitosan is used for medicine. Chitosan which is derived from the outer skeleton of shellfish is also soluble biopolymer (Younes&Rinaudo,2015)

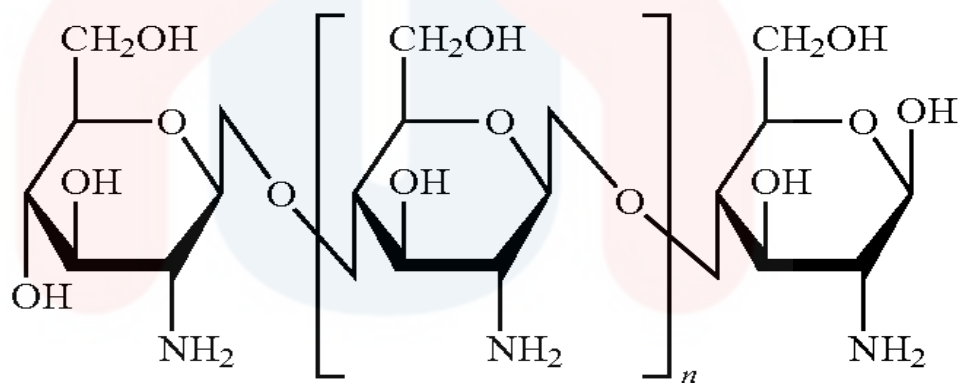


Figure 2.2.2 General structure of Chitosan

Tannin and Chitosan can form a strong polymer. The polymer of Tannin-Chitosan can be used as solid support. It is because Tannin-Chitosan composite has stronger properties that make it become solid support. The solid support is used as a based to stabilize the catalytic particles by deposition onto supports. Usually the catalytic particles such as metal, oxide or sulphide will hold the active sites. The particles will attach only onto the surface of the support without absorbing into it. The uses of glutaraldehyde in the preparation of

Tannin/Chitosan support as a crosslinked agent that will make the support become stronger than other support. (Reed *et al.*, 2014)

2.3 Contaminated Water

Contaminated water is the contact of water body with the discharge of sewage water that will represent the major global source of pollution. The present of pollutants in the sewage water can determine the quality of sewage water or determine how much the water has been contaminated. It is necessary to monitor pollutant in the aquatic surroundings to satisfy the requirements of legislative frameworks and directives, as many of these chemical compounds can affected and threat to both human health and ecosystem . The water pollutant is all partitioned up into the different evaluation . Each class of pollutants has its own specific method of entering the environment and its own specific dangers. All classes have significant pollutants in it that are known to many people, because of the various health effects. (Lenntech, 1998).

Types of contaminants in the water is the most important thing that most people do not know and need to understand. Water contaminant is not that simple . It has several types of contaminants. One of the types is inorganic minerals. Inorganic minerals are the contaminants of water that includes the minerals and toxic metals. There are several way that inorganic metals get contact in water for example calcium and magnesium that is naturally occurring while copper and lead usually getting into the water through pipes. Some of these contaminants like lead and arsenic are quite dangerous when get into contact with it (Hutchinson & Meema, 1987)

Radioactive minerals also types of contaminants in water (Drive, 2004). This group of contaminants is obviously dangerous such as uranium, plutonium, and radium. The organic contaminants can also be found in the water. The organic contaminant mostly in the form of carbon-based contaminants that derived from the petroleum. (Water, 2010). The carbon-based though can easily bind with human tissue and extremely toxic in the small quantities. The examples of organic contaminants are dioxin and PCBs that are dangerous. (Water, 2010). The other type of contaminants is biological contaminant. Biological contaminant is the most common contaminant that had been found in the water which is bacteria and parasitic microorganisms. Even though the bacteria and microorganism are the tiny and small organism, the treatment of that contaminants need to consider and treat to the right place because it can be very dangerous outbreaks if isn't in place.

2.4 Catalyst

A catalyst is used to accelerates a chemical reaction by forming bonds with the responding molecules and allowing these to react to a product which isolates from the catalyst and leaves it unaltered such that it is available for the reaction . In other words, the catalyst is a substance that accelerates the rate of response by lowering the activation energy of the reaction. Collision with a certain minimum energy(Activation Energy) is the result of chemical reaction. The catalytic reaction starts spontaneously by bonding the reactants A and B to the catalyst. (Chorkendorff, 2007).

The formation of the complex will undergo an exothermic reaction which is the free energy is lowered. The reaction associated with an activation energy

while the reaction between A and B are bound to the catalyst and the final product will be separated from the catalyst in an endothermic reaction (Ross, 2012). The uncatalyzed reaction is mostly bigger than the activation of the catalytic reaction hence, the rate of the catalytic reaction is much larger (Chorkendorff, 2007).

There are many types of catalyst which one of the types is heterogeneous catalysis. Heterogeneous catalysis is a surface process. Heterogeneous catalysis consists of two stage process which is solid phase(catalyst) and gas or liquid phase(reactants). Other than the two phase, the adsorption of reactants onto the surface of the catalyst(active site), reaction and desorption of products also can be the mechanism of the heterogeneous catalysis (Argyle & Bartholomew, 2015).

The catalyst can be prepared with many ways. One of the ways to prepare the catalysts is impregnation. Impregnation can be identified as ion exchange or adsorption processes and the interaction with the support is dominant (Ross, 2012). Impregnation also can be determined by contacting a solid with a liquid containing the component to be placed on the surface. The impregnation process will consist of different process that will take place with different rates. The process are selective adsorption of species (charged or not) by van der Waals forces or H-bonds, ion exchange between the charge surface and the electrolyte, polymerisation or depolymerisation of the molecules or ion that attached to the surface and partial dissolution of the surface of the solids. This process will produce their own products. The product that produced during this process depends on the nature of both reactant(the solid and liquid phase) and also the reaction condition of the process. In this process, the parameters also need to be considered as it will affect the process (Haber *et al.*, 1995). The pH, nature of

solvent, the nature and concentrations of dissolve substances will be the main parameters to be measure.

Impregnation can be made by mostly eight various methods and one of the methods is impregnation by soaking or with an excess of solution(Haber *et al.*, 1995). Excess liquid is eliminated by evaporation or by draining. The quantity deposited depends on the solid or liquid ratio. In this method, deposition is slow and requiring several hours or days. These methods have the weakness which is the extensive restructuring of the surface(loss of surface area) may occur. Despite the weakness, these methods allows the distribution of the species to very well controlled and high dispersions may be obtained. This method can work best if ions or solid interactions are involved. The most intensive method used to prepare them is by using nickel nitrate (Infantes-Molina, 2004).

2.5 Nickel Based Catalysts

Nickel is a chemical element with the chemical symbol Ni and atomic number 28. It is silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals and is hard and ductile (Sankar, 2012). Nickel is reactive with oxygen to the extent that native nickel is rare on Earth's surface. Native nickel is always found on Earth alloyed with iron. As a compound, nickel has a number of process in chemical manufacturing uses, such as a catalyst for hydrogenation. Enzymes of some microorganisms and plants contain nickel as an active center, which makes the metal an essential nutrient for them.

Nickel-based catalyst meets the criteria in the entire scope of chemical reactions and therefore often the preferred choice. Its ability to adsorb huge

amounts of hydrogen can be the key characteristic of nickel in these catalysts and thereby greatly increase the efficiency of the reaction. (Duchesne, 2007) Additionally, nickel is less costly in respect to competing materials of the platinum group (Zhuang, et al., 2015). Nickel-based catalysts utilize as a part of hydrogenation and methane reforming (to produce hydrogen) reactions. For the hydrogenation of benzene, the nickel catalyst is derived from nickel acetate precursors. Nickel-based catalyst can be the more active and dynamic compared to other catalyst.

Nickel-based catalyst used nickel acetate as the precursor as catalyst for catalysing methane reforming process that is highly important for the production of hydrogen. Nickel-based catalyst used in the process that involves the decomposition of methane will produce very pure hydrogen (H_2) and will not produce carbon dioxide (Randhava & Rehmat, 2014). This process does not need the separation of gaseous mixtures. Furthermore, the use of this nickel acetate derived catalyst will save time and energy by the elimination of the pre-treatment step. In addition, the deactivated catalysts on regeneration with steam produce an extra H_2 and preserve nickel in its metallic form. The result of hydrogen produced in the reforming methane process can be applied in various areas such as in petroleum refineries and the production of ammonia (Duchesne, 2007).

Hydrogenation is a chemical reaction between molecular hydrogen (H_2) with another compound or element that usually occur in the presence of a catalyst such as nickel, palladium or platinum. The reaction of hydrogen depends on the choice of catalyst. Mostly, all the organic compound contain multiple bonds and can react with hydrogen in the presence of the catalyst. The catalysts that most commonly used for the hydrogenation reactions are the metal-based catalyst such as nickel, platinum, palladium and their oxides.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich, Malaysia, tannin that purchased from Merck KGaA, Germany and chitosan from Sigma-Aldrich, USA, hydrogen peroxide and phenol was purchased from Bendosen Laboratory Chemicals, Malaysia

3.1.1. Instrumentation

UV-Visible spectrophotometer (from Merck KGaA) model Spectroquant Pharo 300, Fourier Transform Infrared Spectroscopy (FTIR) from Thermo Scientific, model iZ10, X-Ray Diffraction (XRD) from Bruker with serial no. Of 208493, Scanning Electron Microscope (SEM) with JEOL JSM 6360LA.

3.2. Methodology

3.2.1. Preparation of Tannin/Chitosan support

The support was prepared by adding 3.0 g of Tannin in deionized water and dissolves it. After that, followed by addition 5.0 g of chitosan and continue to dissolve. The mixture was stirred on the hot plate for three hours without stop. Subsequently, the product (T/C support) then was filtered and fully washed with deionized water. The filtered product was then dried in the oven with temperature 40°C .

3.2.2. Preparation of Catalyst

The catalyst was prepared according to the method published early by (Lee *et al.*, 2015) and it was described as below. Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was measured with the same volume of pores in the T/C support. The volume of T/C support needs to be measured first. After the Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) had been measured, it was dropped on the T/C support. Then, the mixture of that was dried to remove the entire volatile component that attached to it. After the process of dried the mixture, it was undergoing the process hydrogenation which is to reduce Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) into nickel compound. The final product that had been produced was nickel-Tannin/Chitosan which was undergoing the activation process to attach each other.

3.2.3. Characterization of catalyst

Phenol and nickel has their own functional groups. Various type peaks of nickel catalysts was observed using FTIR spectrum. The certain range was assigned to Ni-O bond and the water molecule. In other range peaks, was contributing to OH group coordinated to nickel (Al-Sultani Kadhim & Al-Seroury, 2012) . The catalyst that had been prepared early was characterized using the FTIR spectrum to identify their functional groups.

XRD spectrum nickel catalyst was observed the diffraction that corresponding to the hexagonal crystalline structure. The crystalline structure of the catalyst was observed and analyzed using this XRD spectrum.. A key component of all diffraction is the angle between the incident and diffracted rays. Generally, XRD is based in diffracted ray of monochromatic X-ray and a

crystalline sample where crystalline structure will act as three-dimensional diffracting grating for the x-ray wavelengths. This is similar to the spacing of planes in a crystal lattice (Bish, 1989)

SEM or scanning electron microscopy is widely used to study the morphological features and surface characteristics of absorbent materials. In this study, the adsorbent material was analyzed to determine whether it shows greater extent of adsorption the catalyst as the nickel and Tannin-chitosan support was used (Shirsath & Shrivasta, 2015).

3.2.4 Catalytic experiment

This method had been adopted from (Saeed *et al.*,2016). Oxidative degradation experiment of phenol (pH 2.5) was catalyzed by Nickel-Tannin/Chitosan and it were carried out with three different temperature(38,48,58°C). The reaction flask then was charged with 40 mL solutions of phenol. By used the hot plate, the temperature of the reaction mixture was kept constant while stirred the solution continuously for 30 minutes. After 30 minutes stirred, 0.5 mL sample was taken out to observed if had any variation in concentration of phenol during heating and stirring process. 1 mL hydrogen peroxide was added as an oxidant to reaction flask while the mixture was stirred continuously for another 30 minutes. After that, again another 0.5 mL sample was taken out to observed the variation in concentration of phenol solution. Then, the reaction mixture was added with the 0.1g of nickel catalyst and stirred continuously in appropriate time intervals. 0.5 mL samples was taken out from the reactor.

To analyse the reaction mixture, the UV-Visible Spectrophotometer was used and the percent degradation of phenol were calculated using following equation.

$$\text{Degradation (\%)} = \frac{(R)_0 - (R)_t}{(R)_0} \times 100 \quad (1)$$

where $(R)_0$ and $(R)_t$ represent initial concentration and concentration of phenol at various time intervals respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Catalyst

4.1.1 FTIR Analysis

A series of Tannin/Chitosan (TC) support and Nickel Tannin Chitosan were synthesized using a procedure similar to the previously reported by (Samadi *et al.*, 2014). This research are initial attempt at preparing the Nickel catalyst on the Tannin Chitosan support despite of copper.

The FTIR spectrum of Tannin/chitosan(TC) support and Nickel Tannin/chitosan catalyst was given in the figure 4.1.1.1 and 4.1.1.2. In FTIR spectrum of TC support, a broad peak was observed at 3211 cm^{-1} , which can be assigned to (OH) stretching vibration. A weak peak at 2114 cm^{-1} can be attributed as (CH₂) stretching vibration (Brugnerotto *et al.*, 2001). A medium naturally peak at 1606 cm^{-1} can be assigned to the (N-H) stretching vibration. However, the peak at 1539 cm^{-1} , 1445 cm^{-1} and 1329 cm^{-1} can be attributed to (C=C) and (N-O) stretching vibration respectively. A strong peak at 1199 cm^{-1} and 1026 cm^{-1} can be attributed to the (C-O) stretching vibration (Sionkowska *et al.*, 2014).

Similarly, the peaks observed on the Tannin Chitosan support can be observed on the FTIR spectrum of the Nickel Tannin/Chitosan shown in figure 4.1.1.2. The range of peaks and the functional groups that observed on the FTIR spectrum of Nickel Tannin/Chitosan was attributed to mostly same as the FTIR spectrum of Tannin Chitosan support because it shows that Nickel are actually attached to the Tannin/Chitosan support.

The shift Ni (OH) peak in Nickel Tannin/Chitosan catalyst indicate the involvement of OH and nickel in bonding. The shift Ni (NH) peaks at 1667cm^{-1} indicated the involvement of NH group bonding with Nickel (Stringer *et al.*, 2009)

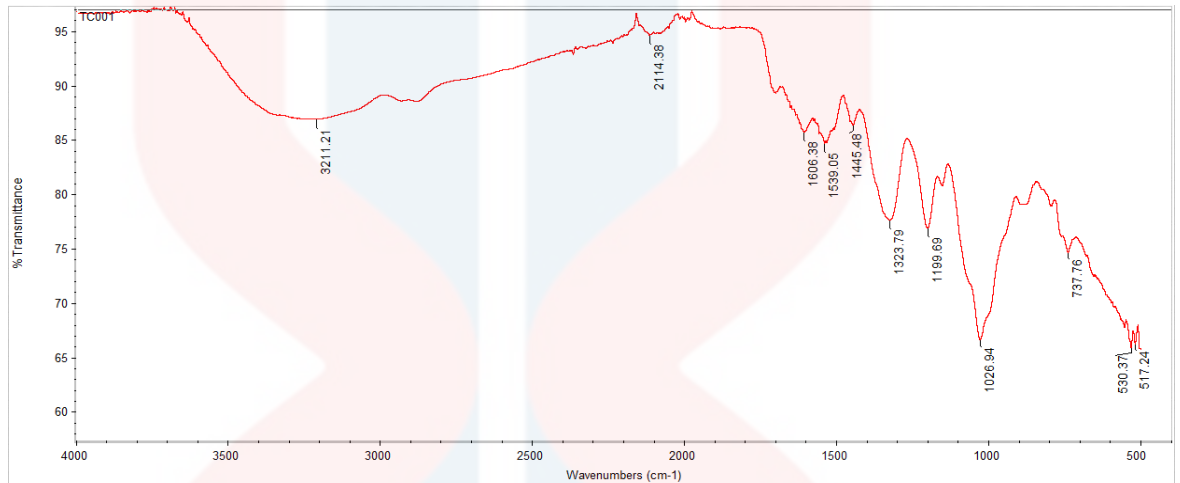


Figure 4.1.1.1 FTIR spectrum of Tannin Chitosan support

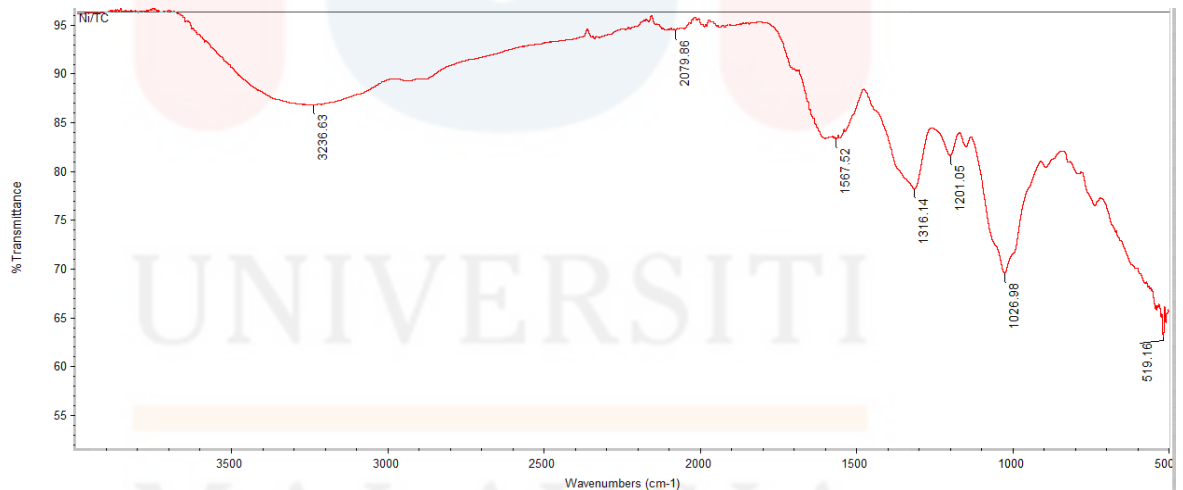


Figure 4.1.1.2 FTIR spectrum of Nickel-Tannin/Chitosan

4.1.2 XRD Analysis

X-ray diffraction is now common technique for study of crystal structures an atomic spacing. Its application are to characterisation of crystalline materials, identification of fine-grained minerals that are difficult to determine optically, determination of unit cell dimensions and measurement of sample purity. The analyzed materials were usually finely ground and homogenized before being tested (Cullity, 1978)

Figure 4.1.2.1 shows the XRD spectrum of Nickel-Tannin/Chitosan. The spectrum was dominated by sharp and intensive diffraction peaks corresponding to hexagonal crystalline structure. The cristanallinity of Nickel-Tannin/Chitosan from 10.002 to 89.977 (Saeed *et al.*, 2015). The a value which as the parameter was 9.8155. An intense peak shown by Tannin Chitosan support near 20° with 777 counts intensity.

The XRD spectrum of Tannin chitosan support was shown in the figure 4.1.2.2. The spectrum shows slightly similar to the spectrum of Nickel Tannin/Chitosan shown in figure 4.1.2.1 as Nickel actually attached to the Tannin/Chitosan support. The cristanallinity of Tannin Chitosan support from 10.002 to 89.977 and it was also dominated by sharp and intensive diffraction peaks corresponding to hexagonal crystalline structure. The a value that known as parameter was 18.61. An intense peak shown by Tannin Chitosan support near 20° with 1539 counts displays the possible content of contaminant. As the stongest peaks in diffractogram with intensity counts, it is shown as other crystalline substance as the peaks is not consistent to diffractograms of other studies (Al Sagheer *et al.*, 2009).

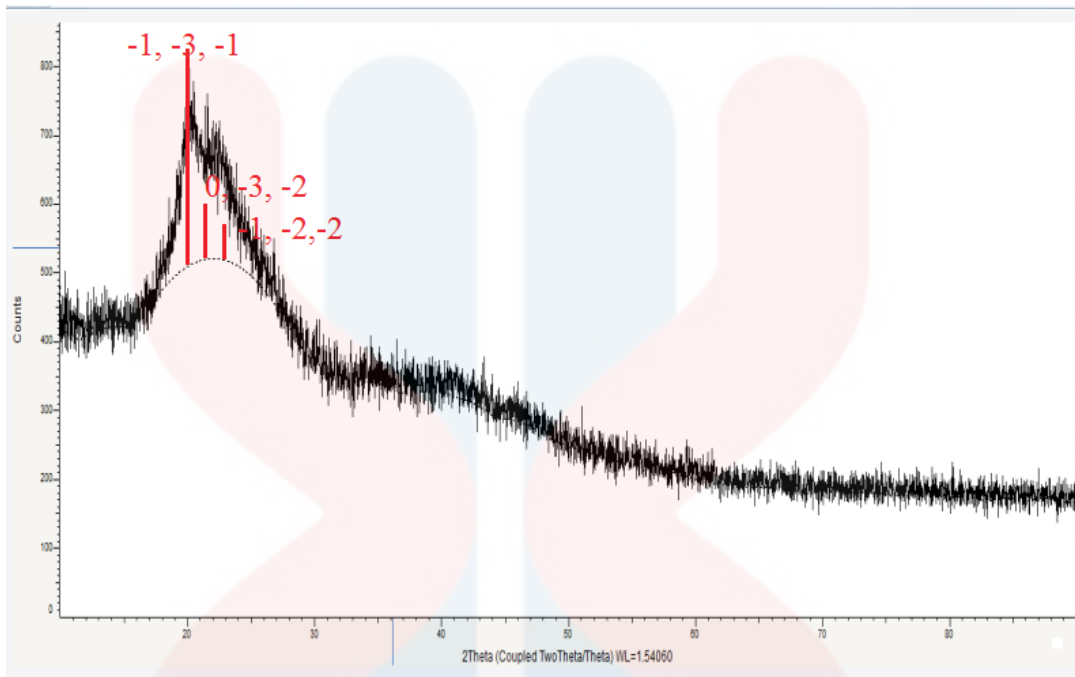


Figure 4.1.2.1 XRD spectrum of Nickel-Tannin Chitosan

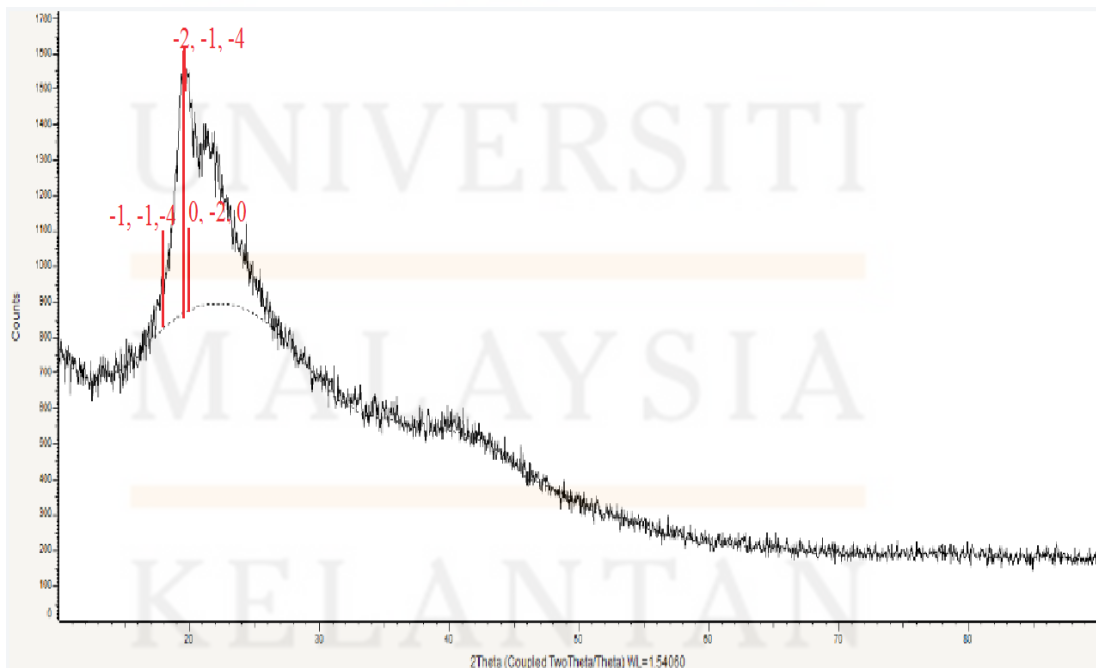


Figure 4.1.2.2 XRD spectrum of Tannin Chitosan support

4.1.3 SEM Analysis

Scanning Electron Microscopy (SEM) analysis was a non-destructive testing where x-ray generated by electron interactions do not lead to volume of the sample, so it was possible to analyze the same sample repeatedly. The SEM projects visualisation at the surface of solid specimens from the signal derived from the focused beam of high-energy electron emitted, which was called as surface morphology(Goldstein, 2003)

Figure 4.1.3.1 and 4.1.3.2 shows the homogeneity of the particle's shape of Tannin Chitosan support and Nickel Tannin/Chitosan respectively. SEM was shows that the particles sizes of the Nickel-Tannin/Chitosan and Tannin Chitosan support were in range of micron size (Saeed & Ilyas, 2013).

Figure 4.1.3.1 shows that the surface of Tannin Chitosan supports in 20 000 x magnification. The morphology has globules of crystalline structure with smooth surface. As it was prepared as fine ground powder, the morphology shows that the specimen was in particles structures. SEM had been used as it offers simple method to investigate the surface morphology of samples at high magnification and optimal condition. (Shirsath & Shrivasta, 2015).

As shown in figure 4.1.3.2 the SEM micrograph of Nickel Tannin Chitosan it can be observed that the structure of nickel was deposited on the Tannin Chitosan support under the 20 000 x magnification too. The morphology has globules of crystalline structure with smooth surface as same as the morphology of Tannin Chitosan support (Zhang *et al.*, 2012). Even the figure shows the globules of nickel on the surface of Tannin/Chitosan support, it still shows the smoothness of Tannin/Chitosan as the nickel was deposited or attached on the Tannin/Chitosan

support. It was shows that the smoothness of Tannin/Chitosan support does not affected on the absence of nickel on to it.

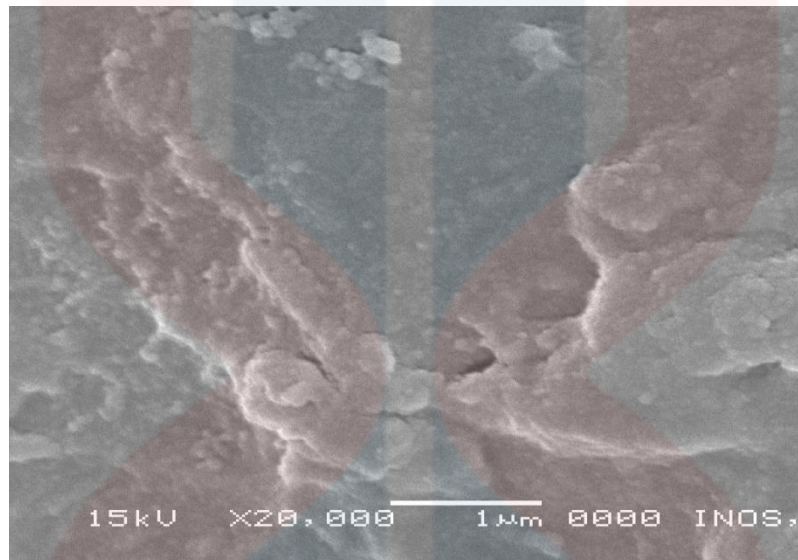


Figure 4.1.3.1 SEM of Tannin Chitosan support

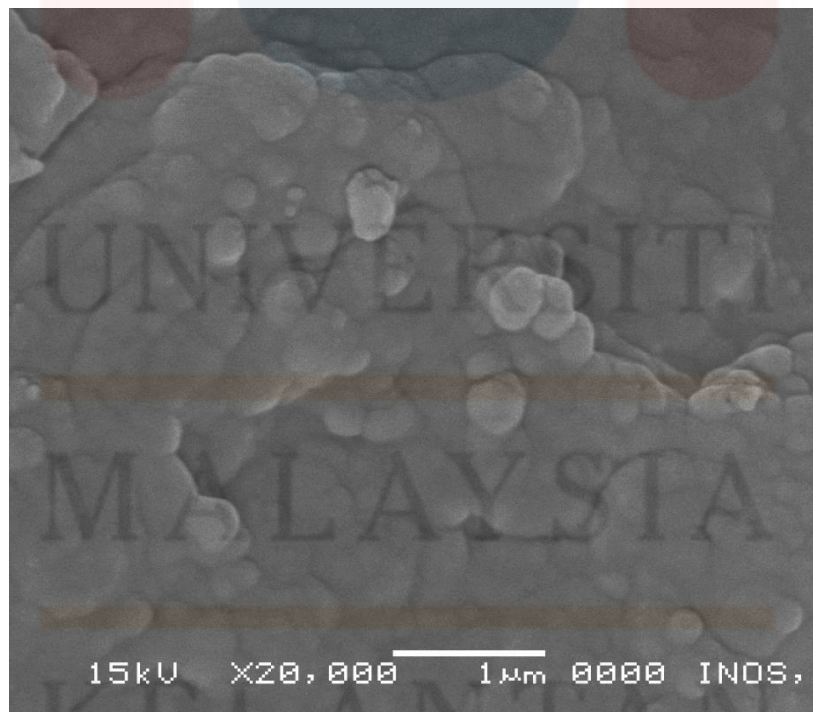


Figure 4.1.3.2 SEM of Nickel-Tannin Chitosan

From the characterization of Nickel catalyst using FTIR, XRD and SEM, the result that was obtained from the three machines used shows that it was related each other. The related of the result of this three machines in this research was to determined and examined the presence or existence of nickel on the Tannin/Chitosan support. FTIR, XRD and SEM machines were used to examined whether the nickel attached or not on the Tannin/Chitosan support before it can be used as catalyst to remove the phenol in contaminated water. Based on the observation it shows that there was nickel deposited on the surface of Tannin/Chitosan support which was then can be used in the catalytic experiment to remove phenol.

4.2 Catalytic degradation

The oxidative degradation of the phenol over the Nickel- Tannin/Chitosan is given in the figure 4.2.1, 4.2.2, 4.2.3 and 4.2.4. It was done with 40 mL of 0.5M of phenol solution with the presence of 1 mL of hydrogen peroxide and also 0.1g of Nickel- Tannin/Chitosan catalyst. The mixture was then stirring at 500 rpm and carried out at 38°C, 48°C and 58°C (Saeed *et al.*, 2015) . Based on the result, it can be revealed that temperature will greatly affects the degradation of the phenol (Rajani & Reshma, 2016). This investigation was accomplished with four phase. The first phase which is only the degradation of phenol. The phenol was degraded 58% at 38°C and decrease to 54% and 14% at 48°C and 58°C respectively.

The second phase was phenol with the presence of H₂O₂. The percentage degradation was shown in the figure 4.2.2. The percentage of degradation was calculated after the concentration of phenol were determined based on the calibration

curve that had been done before using the absorbance reading with the wavelength of 269 nm as the reference graph to determined the concentration of phenol.

The next phase was phenol with the presence of catalyst which is Nickel-Tannin/Chitosan catalyst. It was noted that 16% of phenol was degraded at 38°C and gradually increase about 24% and 44% at 48°C and 58°C respectively. In the present of catalyst, the percentage of degradation increase and it shows that the catalyst had the role to degrade the phenol. The UV- visible spectrophotometer were used in this study to determined the absorbance of the phenol. The absorbance of phenol can determined the concentration of phenol. The higher the absorbance value, the higher the concentration of phenol.

Lastly, the degradation of the phenol are determined with the presence of both H_2O_2 and also Nickel-Tannin/Chitosan catalysts (Akpan & Hameed, 2009). The degradation of the phenol increase gradually with the presence of this both H_2O_2 and also Nickel-Tannin/Chitosan catalysts which are 92%, 97% and 98% at 38°C, 48°C and 58°C respectively. The data for this catalytic experiment for phenol to degrade was tabulated and shown in the graph below.

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Table 4.2.1 Table data of phenol degradation

Time(min)	Degradation (%)
9.17	58
19	54
23.36	14

Table 4.2.2 Table data of phenol degradation in presence of H₂O₂

Time(min)	Degradation (%)
4.08	74.4
24.3	58.8
39.15	36

Table 4.2.3 Table data of phenol degradation in presence of Nickel Tannin/Chitosan catalyst

Time(min)	Degradation (%)
3.52	16
12.25	24
31.31	44

Table 4.2.4 Table data of phenol degradation in presence of H₂O₂ and Nickel Tannin/Chitosan catalyst

Time(min)	Degradation (%)
3.48	92
12.07	97
31.14	98

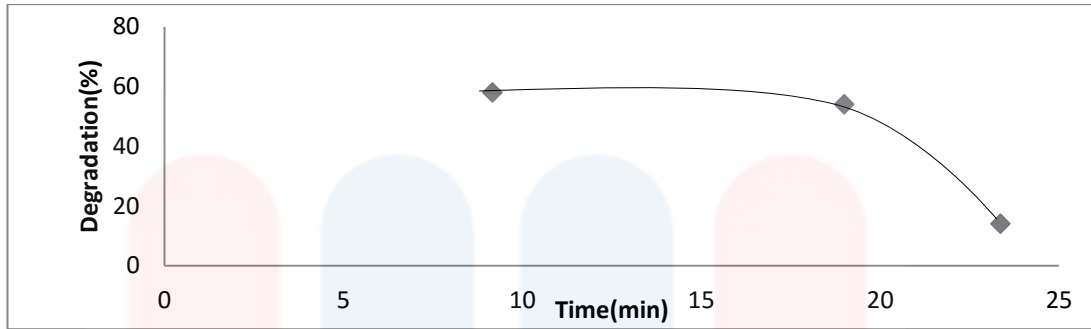


Figure 4.2.1 Time profile data of phenol degradation

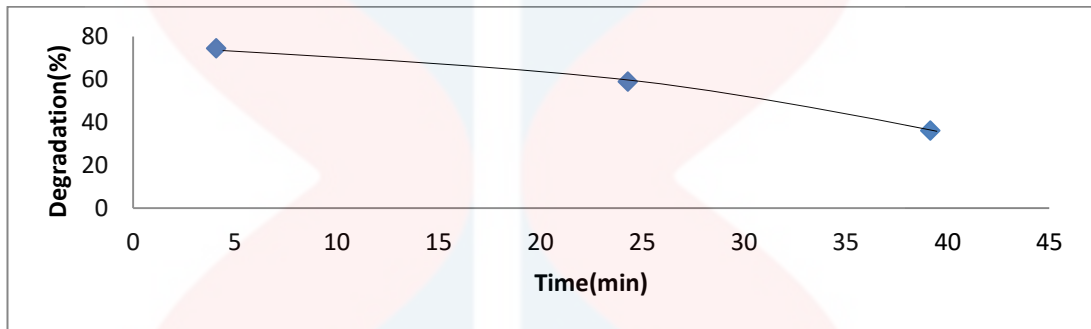


Figure 4.2.2 Time profile data of phenol degradation in presence of H₂O₂

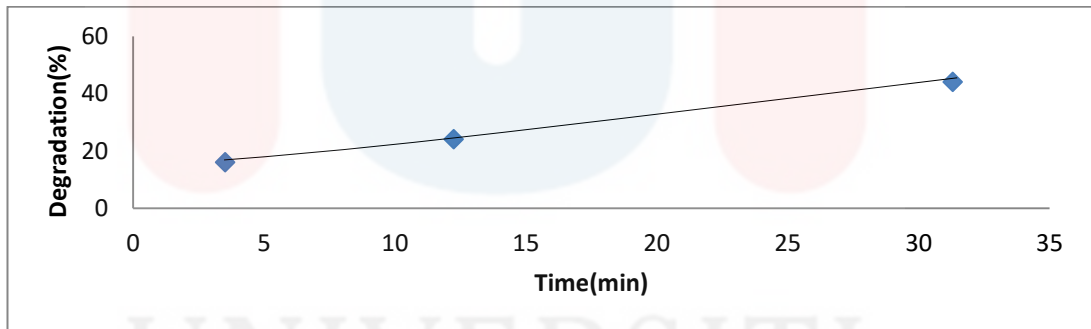


Figure 4.2.3 Time profile data of phenol degradation in the presence of Nickel Tannin/Chitosan catalyst

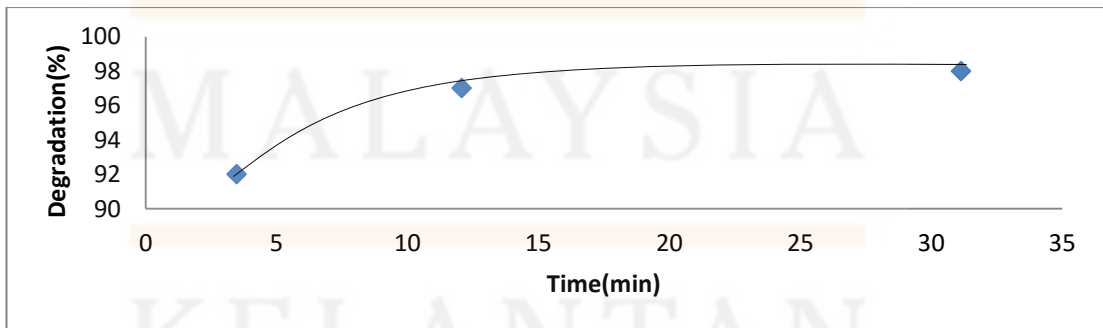


Figure 4.2.4 Time profile data of phenol degradation in presence of H₂O₂ and Nickel-Tannin/Chitosan catalyst

Based on the percentage degradation of phenol, it can say that the temperature plays important role in determine the degradation. In this research, the optimal temperature is 58°C because only at this temperature, the degradation of only phenol increase with the presence of catalyst which from 14% to 44% and follow by 98% when phenol were mix with H₂O₂ and catalyst.

Despite of the temperature, the concentration of phenol also give greatly affect in determine the percentage degradation of the phenol. The result also shows that there is no appreciable change in concentration of phenol while doing this experiment. This is shows that Nickel-Tannin/Chitosan was acts as an effective catalyst for phenol in aqueous solution (Saeed & Ilyas, 2013)

4.2.1 Kinetic Analysis

In this present study, kinetics were used in determined the degradation of phenol in the presence of catalyst. It was determined using zero,first and second order reaction by Fenton oxidation process. The regression analysis of the phenol in the presence of catalyst degradation based on zero, first and second order reaction in Fenton oxidation process was conducted and the data shown in table and figure 4.2.1.1 below.

Table 4.2.1.1 Zero,First,Second order reaction kinetic of Phenol in presence of catalyst by Fenton reaction

Time(min)	Concentration(M)		
	Zero order	First order	Second order
5	0.08	1.83	12.5
10	0.1	1.61	10.0
15	0.12	1.43	8.33
20	0.14	1.27	7.14
25	0.16	1.14	6.25
30	0.168	1.09	5.95
35	0.188	0.98	5.32
40	0.224	0.8	4.46
45	0.244	0.72	4.1
50	0.264	0.64	3.79
55	0.284	0.57	3.52
60	0.324	0.43	3.09

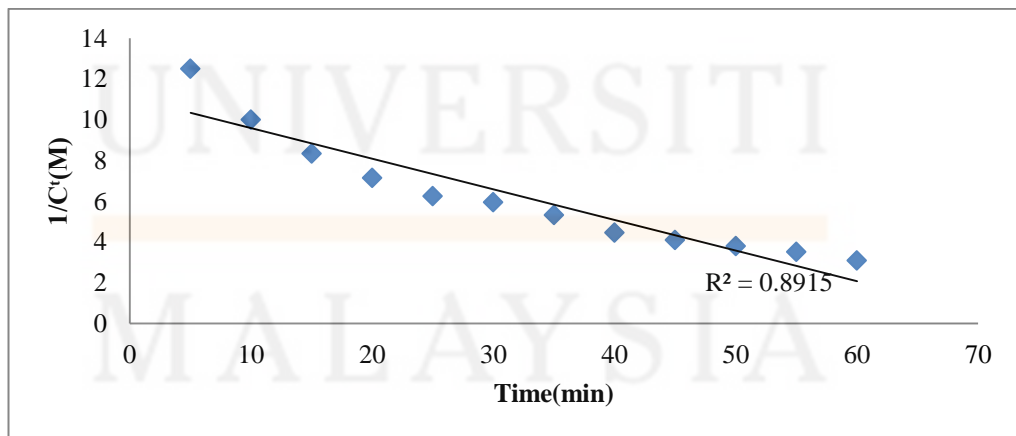
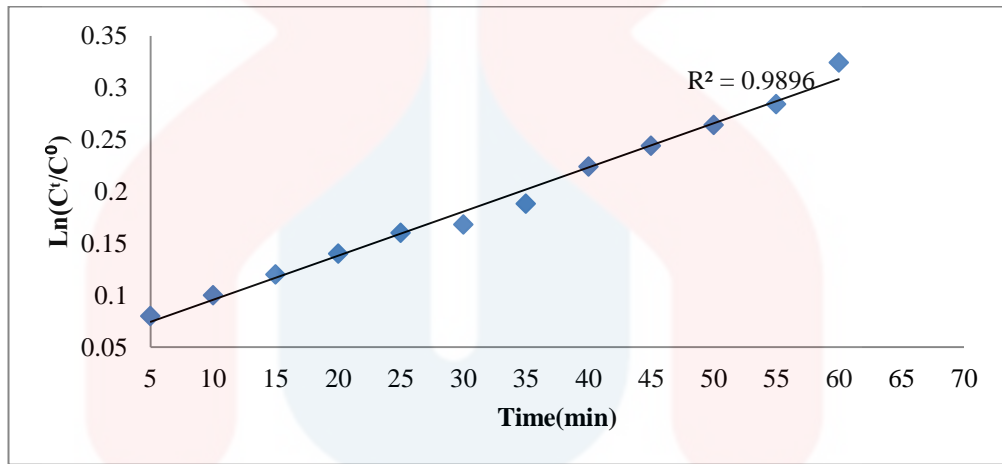
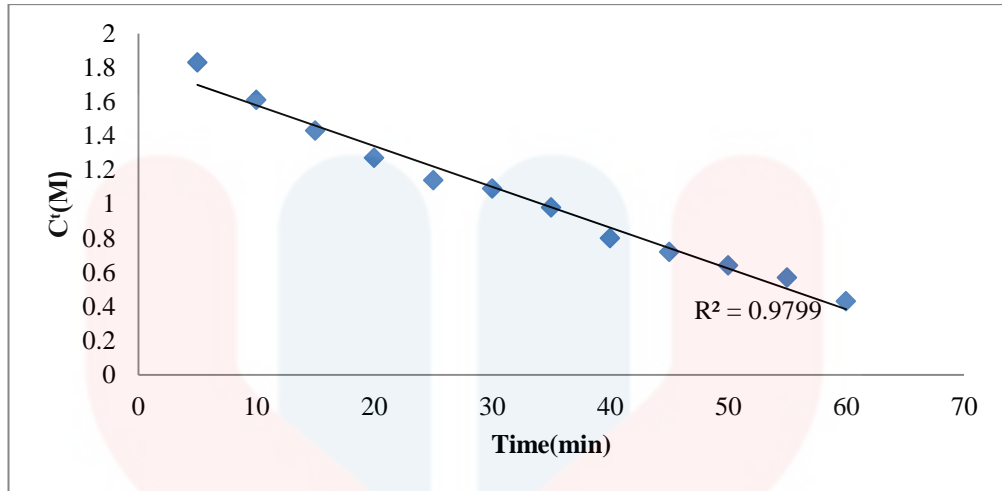


Figure 4.2.1.1 Zero, First and second order reaction kinetic of Phenol in presence of catalyst by Fenton reaction

By comparing the regression coefficient(R^2) that shown in the figure 4.2.1 (a)-(c), it can be conclude that R^2 for first order reaction which is $R^2=0.9896$ is the much better compared to the R^2 for zero and second order which are $R^2=0.9799$ and $R^2= 0.8915$ respectively (Dixit *et al.*, 2010). Based on the regression coefficient (R^2) that was obtained, it can be indicated that the kinetic degradation of phenol in the presence of catalyst followed the first order rection kinetics.

Figure 4.2.1.2 represent the kinetic regression analysis phenol degradation in the presence of catalyst and H_2O_2 . Presence of catalyst and H_2O_2 will increase the rate of reaction of degradation of phenol. As kinetic reaction of phenol in the presence of catalyst, the kinetic reaction for phenol in presence of catalyst and H_2O_2 was also determined using zero,first and second order reaction by Fenton oxidation process.

Based on the coefficent regression(R^2) that shown in figure, it state that the kinetic degradation of phenol in the presence of catalyst and H_2O_2 followed the first order rection kinetics as the $R^2=0.6576$ due to comparing of it coefficent regression(R^2) with other. By comparing the figure 4.2.2 (a)-(c), it can determined that (R^2) for first order is much better which $R^2=0.6576$ than others which $R^2=0.6386$ and $R^2= 0.6059$ for zero and second order kinetic respectively(Youssef *et al.*, 2015)

Table 4.2.1.2 Zero,First,Second order reaction kinetic of Phenol in presence of catalyst and H₂O₂ by Fenton reaction

Time(min)	Concentration(M)		
	Zero order	First order	Second order
5	0.1	1.61	10
10	0.12	1.43	8.3
15	0.122	1.41	8.2
20	0.122	1.41	8.2
25	0.123	1.4	8.13
30	0.124	1.39	8.06
35	0.124	1.39	8.06
40	0.125	1.38	8.00
45	0.126	1.37	7.94
50	0.13	1.35	7.69
55	0.132	1.33	7.58
60	0.134	1.32	7.46

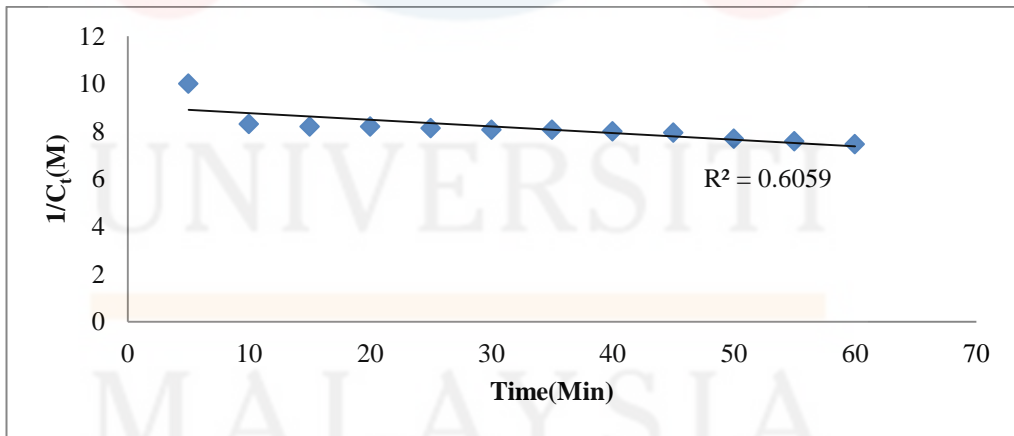
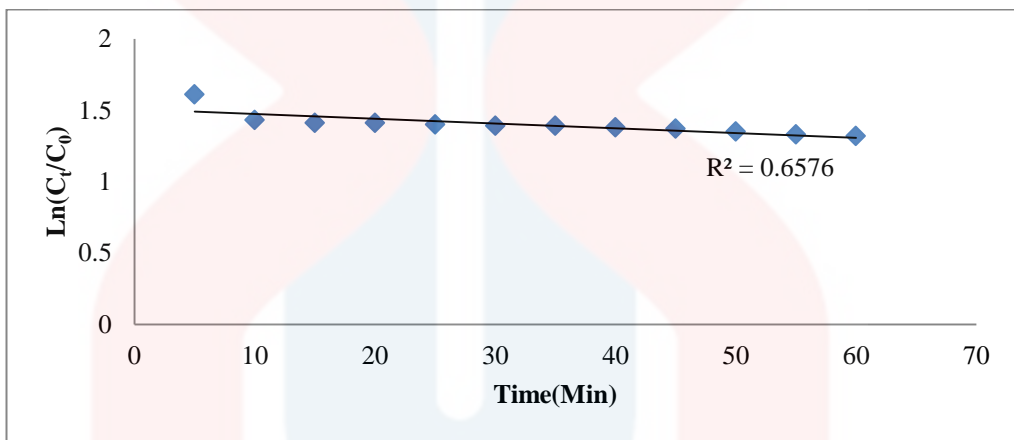
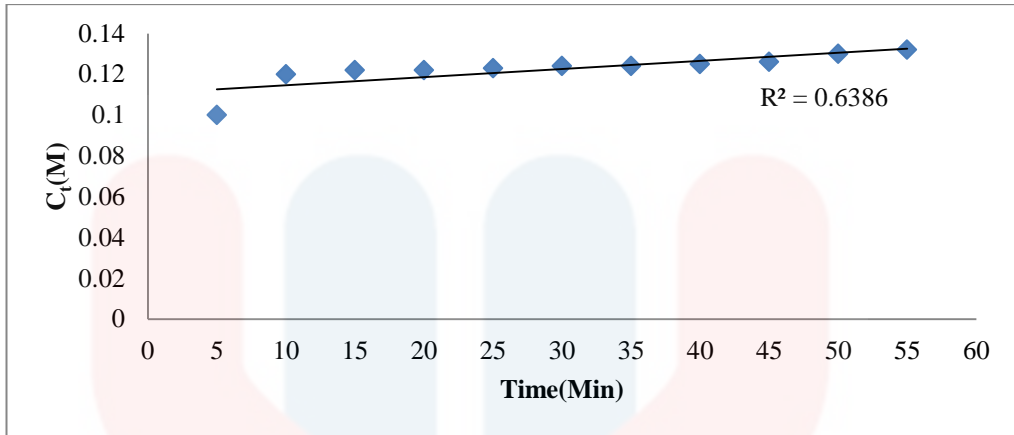


Figure 4.2.1.2 Zero, First and Second order reaction kinetic of Phenol in presence of catalyst and H_2O_2 by Fenton reaction

Table 4.2.1.3 Summary of the result in the characterization of catalyst and catalytic activity.

Instrument	Function	Result	Conclusion
FTIR analysis	The catalyst that had been prepared early was characterized using the FTIR spectrum to identify their functional groups	OH,CH ₂ ,N-H, C=C, N-O and C-O stretching vibration can be observe in Tannin/Chitosan support while in Nickel Tannin/Chitosan had shift of Ni(OH) and Ni(NH).	
XRD analysis	XRD spectrum nickel catalyst was observed the diffraction that corresponding to the hexagonal crystalline structure	Sharp and intensive diffraction peaks corresponding to hexagonal crystalline structure in both Tannin/Chitosan support and Nickel Tannin/Chitosan.	Based on the observation, it shows that nickel was deposited on the Tannin/Chitosan support and can be used as catalyst in the catalytic experiment to remove phenol.
SEM analysis	In this study, the adsorbent material was analyzed to determine whether it shows greater extent of adsorption the catalyst	In Tannin/Chitosan support, the morphology shows it has globules of crystalline structure with smooth surface while in Nickel Tannin/Chitosan it shows that globules of nickel deposited on the Tannin/chitosan support.	
Catalytic experiment	Oxidative degradation experiment of phenol (pH 2.5) was catalyzed by Nickel Tannin/Chitosan with three different temperature (38,48,58°C).	The optimal temperature is 58°C because only at this temperature, the degradation of only phenol increase with the presence of catalyst which from 14% to 44% and follow by 98% when phenol were mix with H ₂ O ₂ and catalyst.	Nickel Tannin/Chitosan can be considered as an effective catalyst abatement of phenol because it can speed up the reaction and increase the degradation of phenol.
Kinetic analysis	Kinetics were used in determined the degradation of phenol in the presence of catalyst and to determined which order of kinetic it used.	R ² for first order reaction which is R ² =0.9896 is the much better compared to the R ² for zero and second order which are R ² =0.9799 and R ² = 0.8915 respectively.	

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study shows that the lab prepared Nickel-Tannin/Chitosan can be used as an effective catalyst for oxidative degradation of phenol. The prepared nickel catalyst was characterizes by different technique. The technique that had been used are using the Fourier Transform Infrared Spectroscopy (FTIR) Fourier, X-ray Diffraction and Scanning Electron Microscopy (SEM) . Although, this three machine show different function but used of this three machine in this study to show that nickel was fully deposited on the Tannin/Chitosan support. The Nickel-Tannin/Chitosan can be considered as an effective catalyst abatement of phenol in aqueous medium. Nickel-Tannin Chitosan shows that it can speed up the reaction and also increase the degradation of the phenol. The preparation of catalyst was well supported by the obtained result.

On the basis of the catalytic activity, nickel catalyst exhibit moderate catalytic activity in degrading phenol. On the basis of percent degradation, the optimum temperature for the phenol to degrade was 58°C where the catalytic activity of nickel catalyst was maximum. Thus, this was an attempt to generate a new catalyst with enhance of catalytic activity in present of H_2O_2 . For the degradation of phenol, concentration and temperature greatly affect the the catalytic degradation or removal of phenol. Temperature and the concentration gives more effectiveness for catalyst to speed up the reaction and degradation of phenol. High concentration of phenol increase the degradation of phenol as well as temperature. High temperature increase

the degradation of phenol. Concentration and temperature help the catalyst react more effectively in degrading the phenol.

5.2 Recommendations

For further research of this study, it is recommended that optimum of temperature will be run in this experiment with more different temperatures and find the optimal temperature that the catalyst will effectively degrade the phenol. Despite of that, it is recommended to investigate the effect of stirring speed of the mixture whether it will affect the catalyst in order to complete the degradation process. The amount of catalyst used and the reusability of the catalyst also need to be a concern in further study. Furthermore, the catalytic degradation should be tested in waste water with the presence of phenol.

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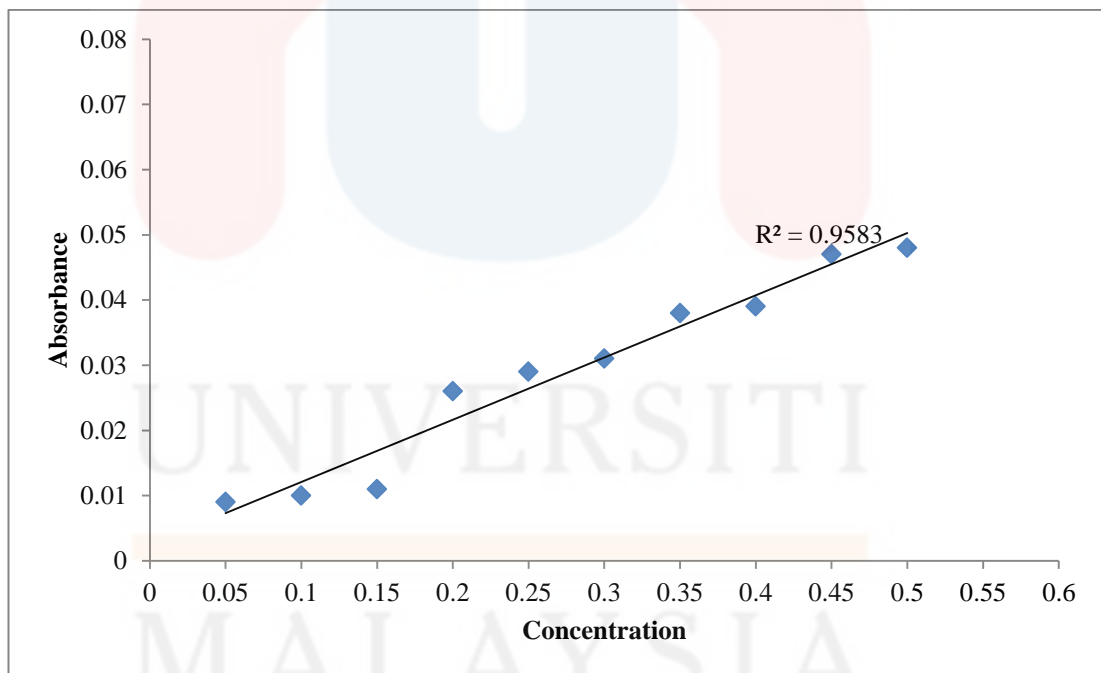
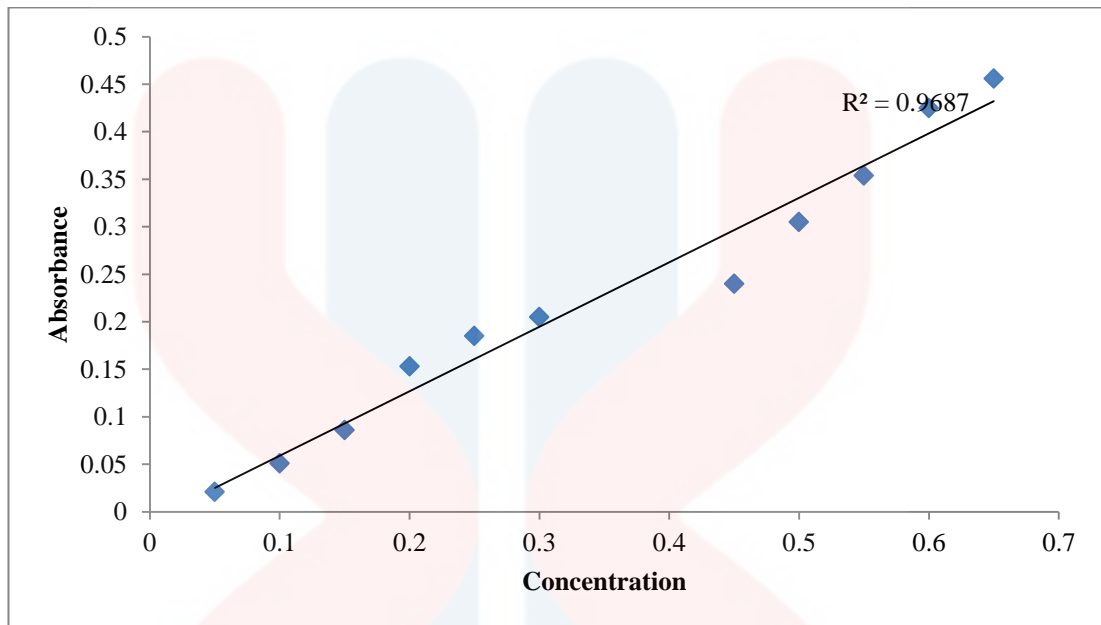
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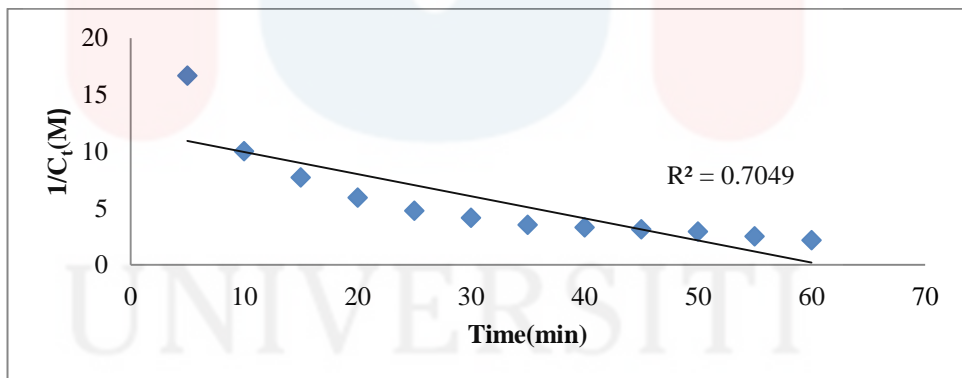
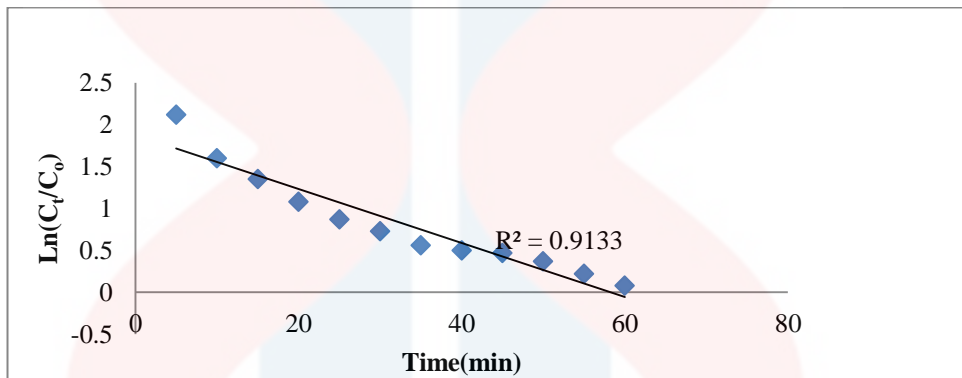
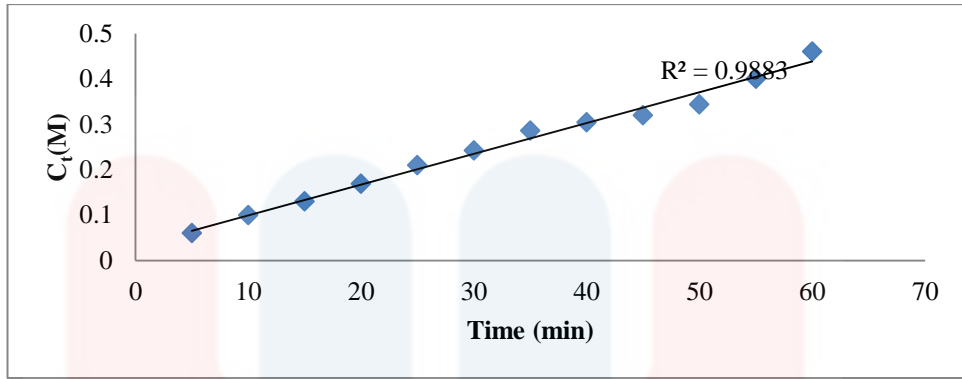
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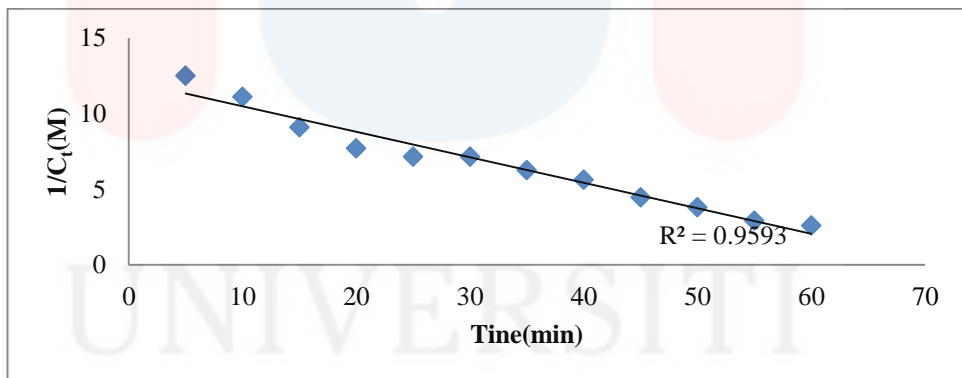
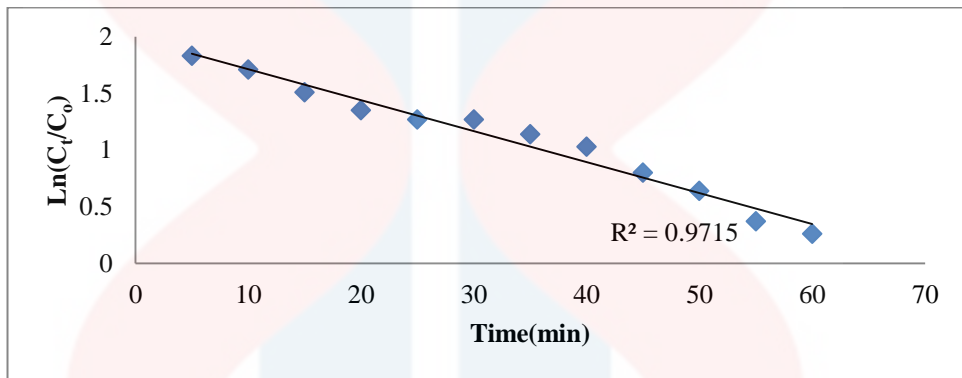
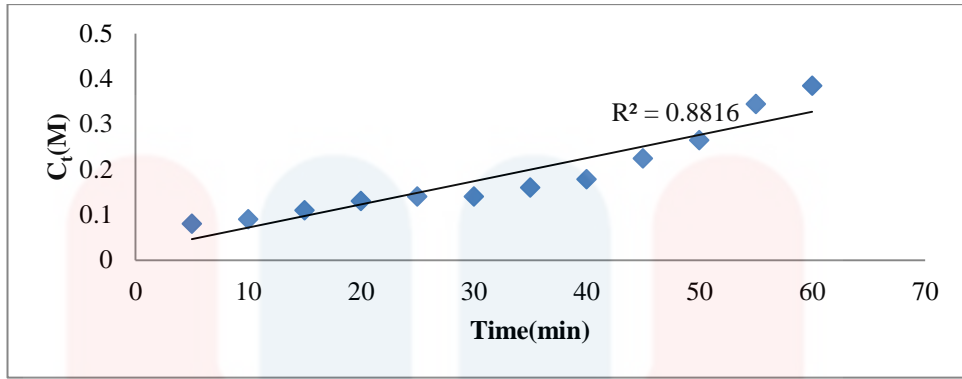
APPENDICES



APPENDIX A : Calibration curve of Phenol in the presence of H_2O_2 and calibration curve of phenol in the presence of H_2O_2



APPENDIX B : Zero, First and Second order reaction kinetic of Phenol in presence of H_2O_2 by Fenton reaction



APPENDIX C : Zero, First and Second order reaction kinetic of Phenol by Fenton reaction