Removal of Methylene Blue from Contaminated Water by Newly Prepared Nickel Catalyst

by

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DECLARATION

I declare that this thesis entitled " Removal of Methylene Blue 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.

Signature : ______________________________

Name : ______________________________

Date : ______________________________

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ABSTRACT

Water bodies had been polluted with contaminants discharged from industrial activities like dyes, pesticides and pharmaceutical in recent years. So, many alternatives had been used to treat the water contamination in water stream like activated carbon and adsorption methods. This research aim is to study the preparation and characterization of Nickel-Tannin/Chitosan by evaluating the catalytic activity effects on newly prepared catalyst. The catalyst was prepared by added Nickel Nitrate Hexahydrate, $Ni(NO_3)6H_2O$ with Tannin-Chitosan support which form Nickel-Tannin/Chitosan when undergoes several steps of reaction like hydrogenation process. The prepared Nickel-Tannin/Chitosan was characterized using FTIR, XRD and SEM then used as catalyst in aqueous medium for oxidative degradation of 0.5M methylene blue. In this study, methylene blue acted as the pollutants to test the ability of Nickel Tannin/Chitosan as catalyst. Three different temperatures of 38°C,48°C and 58°C were conducted to test the percentage of dye degraded where time and concentration of methylene blue was observed in catalytic activity. From the results, about 74% of methylene blue degraded at 58°C with the presence of catalyst and hydrogen peroxide. This research showed Nickel Tannin/Chitosan has great ability as new catalyst which exhibit catalytic performance which can be used in the future especially for water treatment technology.

Pemecatan Metilena Biru Dari Air Tercemar Menggunakan Penyediaan Baru Nikel Pemangkin

ABSTRAK

Badan-badan air telah tercemar dengan bahan pencemar dilepaskan daripada aktiviti perindustrian seperti pewarna, racun perosak dan farmaseutikal pada tahun-tahun kebelakangan ini. Jadi, banyak alternatif telah digunakan untuk merawat pencemaran air di aliran air seperti karbon dan penjerapan kaedah diaktifkan. Objektif kajian adalah untuk mengkaji penyediaan dan pencirian Nikel Tanin/Kitosan dengan menilai kesan aktiviti pemangkin kepada pemangkin baru yang disediakan. Pemangkin ini telah disediakan dengan menambah Nikel Nitrate Hexahydrate, $Ni(NO_3)6H_2O$ dengan sokongan Tanin-Kitosan yang membentuk Nikel Tanin/Kitosan apabila menjalani beberapa langkah tindak balas seperti proses penghidrogenan.Nikel-Tanin/Kitosan yang tersedia dicirikan menggunakan FTIR, XRD dan SEM kemudian digunakan sebagai pemangkin dalam medium akueus untuk degradasi oksidatif 0.5M metilena biru. Dalam kajian ini, metilena biru bertindak sebagai pencemar untuk menguji keupayaan Nikel Tanin/Kitosan sebagai pemangkin. Tiga suhu yang berbeza daripada 38°C, 48°C dan 58°C telah dijalankan untuk menguji peratusan pewarna degradasi di mana masa dan kepekatan metilena biru diperhatikan dalam aktiviti pemangkin. Daripada keputusan, kira-kira 74% daripada metilena biru degradasi pada suhu 58°C dengan kehadiran pemangkin dan hidrogen peroksida. Kajian ini menunjukkan Nikel Tanin/Kitosan mempunyai keupayaan yang besar sebagai pemangkin baru yang mempamerkan prestasi pemangkin yang boleh digunakan pada masa akan datang terutama untuk teknologi rawatan air.

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LIST OF ABBREVIATIONS

°C	Celsius
M	Molar
H_2O_2	Hydrogen peroxide
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Powder Diffraction
SEM	Scanning Electron Microscopy
ppm	Parts per million
COD	Chemical oxygen demand
pH	Potential of hydrogen
TPR	Temperature-programmed reduction
Ni	Nickel
g	Grams
ml	Millilitre
K	Kelvin
TC	Tannin/chitosan
kV	Kilovolts
cm	Centimetre
µm	Micrometre
nm	Nanometre

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The contamination of natural resources primarily water can cause undesired impact on human health. The contaminants discharged into water into water bodies from industrial effluent like textile are usually dyes, substantial metals, pharmaceutical, pesticides, flouride, phenols, bug sprays, pesticides and detergent (Reddy & Lee, 2012).

The dyes, radioactive, physical or pathogenic microbial substances can also contaminate the water sources. The water pollutants can be generated either from direct or indirect point sources. The point sources are discharged from a factory or sewage outfall while non-point sources produced from urban stormwater runoff, agricultural runoff and other area-wide sources (Hogan, 2014).

The dye ‘methylene blue’ with molecular formula $C_{16}H_{18}CIN_3S$ is listed as the basic of aniline dye (Shahryari et al., 2010). It exists as an odorless, solid dark green powder that produces a blue solution when dissolved in water at room temperature. It had been used as a dye for coloring hair, cotton wool, paper, and leather. Methylene blue also can detect oxidizing agents and biologists need it to stain samples of tissue and nucleic acids (Samiey & Ashoori, 2012).

The deposition of component in liquid on solid surface are known as impregnation. The impregnation can occur via selective adsorption, selective exchange and polymerization or depolymerization and partial dessortation on the solid surface as stated by (Haber et al., 1995). Thus, in this research, the impregnation method was utilized to deposit nickel on Chitosan-Tannin organic support. The catalytic activity of prepared catalyst will be evaluated by monitoring the degradation of methylene blue.

1.1 PROBLEM STATEMENT

The abundance of methylene blue in water can cause huge damage to environment, particularly water resources. Textile industry brought harm to environment when dyes was discharged as wastewater which is toxic and caused hazardous effect to water bodies along with aquatic life (Ahmad et al., 2016).Thus, effective method are forced constantly to remove the methylene blue from water.

1.2 OBJECTIVES

1) To characterize prepared Tannin-Chitosan nickel doped catalyst.
2) To evaluate the catalytic activity of newly prepared catalyst in oxidation of methylene blue.

CHAPTER 2

LITERATURE REVIEW

2.1 Water Pollution

Water pollution means the contamination of water caused by human activities that give effect to water sources such as rivers, lakes and oceans (Agrawal et al., 2010). Water quality is vital for living things to enhance physiological action for a biological cell. Contaminants released by human into water bodies that affect its original state cannot be used as drinking reason and biotic community support for aquatic life like fish.

Basic forms of water contamination can be divided into two which are the modifying of types and materials quantity brought along with water and physical changes of criteria in water bodies (Gupta et al., 2009). Water that polluted by contaminants become a serious problem worldwide. Instead of pesticides from agricultural activities, natural phenomena like algae blooms, earthquakes, algal blooms also the cause depletion of water quality. Contaminated water released from industry activities contain rainwater pollution and sewage water that comes from residential area (Ashraf et al., 2010).

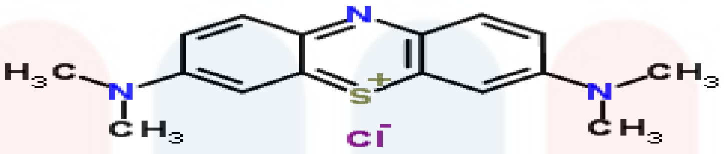
Critical water pollution issues result from dyes released to environment especially water bodies which affect aquatic life when light is blocked by into the water. Even small quantity of dyes contaminates the water streams less than 1ppm it can be easily seen (Mishra & Kumar, 2014). Water pollution is one of serious environmental pollution since water is crucial for all living organism in the 21st century. It continues to discharge from industrial wastage and domestic sewage although many awareness campaigns already been conducted (Singh & Tshering, 2014).

The over discharge of pollutants and chemicals from industries are the main sources of water pollution. So, waste water released need an effective treatment technology to ensure clean water for safe use. There are an abundant number of methods such as coagulation, reverse osmosis, and adsorption by activated carbon has been used in the past to treat decolourisation and dyes degradation in water streams (Gajbhiye, 2012).

2.2 Dyes

Dyes are fluorescent organic substances that colored the substrate through light absorption selectively. The solubility properties of dyes allow them to go through an application temporarily or permanently by destroying the structure of a crystal by solution and mechanical retention, absorption or by chemical bonds (ionic and covalent bond). It plays an important role in fabric production. Dyes are divided into two group which are natural and synthetic but natural dyes used decrease rapidly in textile industry purpose after synthetic dyes were found in 1856 (Mitra & Das, 2015).

A significant source of water pollution contains dye bearing effluent. Dyes produced for printing, paper, textile, carpet, food, plastic and cosmetic industries. Dyes are mainly grouped into anionic, cationic, and non-ionic dyes. The evacuation of anionic dyes is considered as the most difficult task. The reason dyes produce very bright colors in water because of its acidic properties and solubility in water. It has been estimated in the textile industry that the total dye consumption is more than 10,000 tons per year and about 10–15% of these dyes are discharged as effluents during the dyeing processes (Dawood & Sen, 2013).



(Sources: Mishra & Kumar, 2014)

Figure 2.2.1: Structure of Methylene Blue

Methylene Blue is also known as methylthioninium chloride and is commonly needed in biology and chemistry as a stain. The chemical formula $C_{16}H_{18}N_3SCl$ form a heterocyclic aromatic chemical compound. Methylene blue is odorless, solid and dark green powder at room temperature which produces a blue solution in water. If methylene blue not handle properly it may lead to serious health issues like hard breathing, mental disorder and sweating (Tabbara & El Jamal, 2012).

The effluents released from industries actually has dyes residual. Improper treatment of colored wastewater or dyes can cause severe effects such as toxicity rising and chemical oxygen demand (COD) to the water body. Moreover, light penetration into the water is lowering because of colored effluent from water surface (Mohammed et al., 2014). Methylene blue is an example of dyes which commonly discharged from industries like pharmaceutical, textile, and plastics that caused water pollution afterward.

2.3 Impregnation Methods

Impregnation involves the exchange of ion between the electrolyte and charge surfaced (Haber et al., 1995). In impregnation, the pH, solvent characteristic and concentration of dissolved solid are the major parameters used for the liquid form. Dry impregnation method is suitable for species deposition that reacts poorly on the surface and passes the number of adsorption sites. Wet impregnation needs a precise volume of solution to respond when a reaction takes place which turns catalyst wet.

Impregnation is useful to remove the contaminants in effluents because of efficient progress, cheap cost and simple way to handle the unresponsive towards toxic chemicals. Various types of effective materials are used to enhance the impregnation ability and preparation cost in impregnation process (Boutalaha et al., 2012). Impregnation which uses low-cost adsorbents is an impressive technique for handling water decontamination. It has a huge capability to lower adsorbent dose and control disposal issues. In the recent study, chitosan has been examined as biosorbent to trap dyes dissolved in aqueous solutions. Chitosan is a low cost material that can bind tightly to pollutants and which have the ability to remove color make it an efficient biosorbent (Crini & Badot, 2008).

2.4 Nickel Catalyst

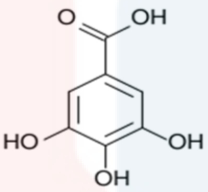
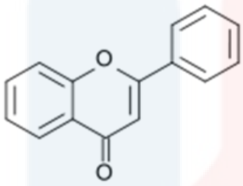
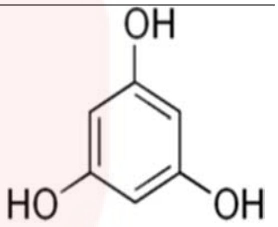
Nickel is higher in abundance, financially possible and suitable for various applications when contrasted with other metals. It also exists in the various type of oxides. Oxides of nickel have increased much consideration since these materials are vital for some electrochemical frameworks particularly alkaline systems like fuel cells, electrolyzers, and batteries. These materials are likewise critical because of low cost, great qualities, and appreciable catalytic activities (Saeed et al., 2003).

Catalyst is a substance that speeds up a chemical reaction, but is not affect the result of reaction; Hence catalyst can be regained chemically without changing at the end of the reaction it has been used to catalyze. The rate of a reaction can speed up by increasing the number of successful collisions. Application of catalyst on the reaction is as an alternative to lower down the activation energy of the reaction. Activation energy means the minimum energy a reactant needed to react. If the activation energy is high, only small proportion of molecular can make the reaction occurs using normal temperature (Triyona, 2004).

In utilization of nickel-based catalysts, wetness impregnation will initiate with various salt solutions.To prepare them mainly nickel nitrate is the most widely utilized strategy used. However, current works proved that nickel citrate can give ascent to catalysts which contain high level of nickel dispersion. A nickel catalyst are form by exchanging the ion which display the greatest nickel dispersion rate as proposed from XRD, H_2-TPR and H_2 chemisorption systems which are the best catalytic performance (Infantes-Molina et al., 2004).

2.5 Tannin-chitosan support

Table 2.5.1 Types of Tannin

Base unit:	 **Gallic Acid**	 **Flavone**	 **Phloroglucinol**
Class/ Polymer:	Hydrolyzable Tannins	Condensed Tannins	Phlorotannins
Sources:	Plants	Plants	Brown Algae

Tannin can be divided into three groups which are hydrolyzable tannins, condensed tannins, and phlorotannins as shown in Figure 2.5.1.They originate from plants and brown algae. Tannin can be produced from vegetation decomposition.Tannin commonly appears at the shallow wells or water supplies. Tannin can result in the conversion of a brown cast in water from yellow which disturbs the odour and taste (Ashok & Upadhyaya, 2012).

Inexpensive cost and easy availability make tannin one of important adsorbent. In developing countries, tannin is widely used because of efficient adsorbing properties in water treatment. Tannin is soluble in water and has magnificent adsorption capability when reacting with metal ions like uranium, copper, and arsenic (Mulani et al., 2014). Tannin also has an ability in the filtration process. A recent study shows that tannin capable of filtering sludged formed when acted as coagulant aid make filtration process more simple (Ozacar & Sengil, 2002). So, it will be useful in helping of dye removal from contaminated water.

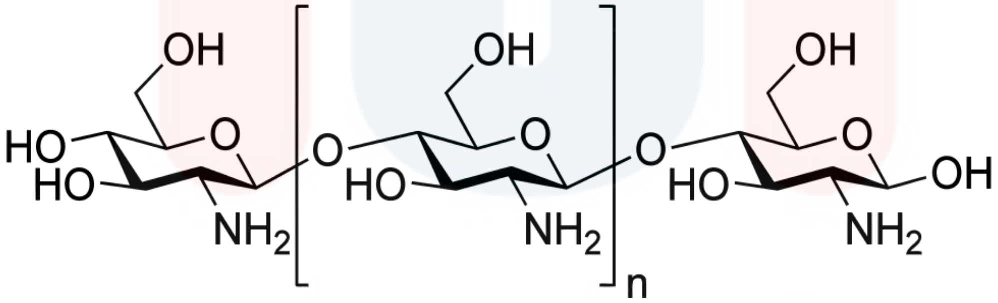


Figure 2.5.2: Chitosan structure

Chitosan giving more benefits as helpful bioactive polymer after being extracted in chitin. Abundant of reactive amino side groups present in chitosan allow chemical adjustment despite its biodegradability. Chitin and chitosan also are non-toxicity, biocompatibility and adsorption which make it a magnificent renewable polymer with superb properties (Dutta et al., 2004). Besides, chitosan consists linear polysaccharide which composed by distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It already contributed in biomedical uses, seed treatment and agriculture like provide resistance for plants to avoid fungal infections.

Chitosan also used variously in the field of waste water treatments, biomedicine, and flocculation due to biodegradable properties. But, its applications limited as it dissolves in selected dilute acid solutions only (Alves & Mano, 2008). In a recent study, chitosan properties like immune-activating effects, anti-allergic and anti-fungal enable it to become a choice, especially in industrial usage. Although, the stability and flexibility of materials may be dropped if chitosan is using inside substrate polymer as it becomes heterogeneous (Sakai et al., 2002).

CHAPTER 3

MATERIAL AND METHODS

3.1 MATERIAL

Nickel nitrate ($Ni(NO_3)_2$) was purchased from Sigma-Aldrich, Malaysia while tannin from Merck, Germany and chitosan was procured from Sigma-Aldrich, Iceland. Hydrogen peroxide (H_2O_2) was purchased from Bendosen Laboratory Chemicals, Malaysia and methylene blue ($C_{16}H_{18}CIN_3S$) was obtained from R&M Marketing, Essex, U.K.

3.2 METHODS

3.2.1 Instrumentation

UV-Vis absorption spectra was measured using Ultraviolet-Visible Spectrophotometer from Thermo Fisher Scientific, model 4001/4. Fourier Transform Infrared Spectroscopy (FTIR) from Thermo Scientific, model iZ10 was used to measure the spectrum. X-ray Diffraction (XRD) measurements were conducted using XRD machine from Bruker with serial number of 208493. The scanning electron microscope (SEM) results were obtained with JEOL JSM-6360LA model operating at 15kV voltage.

3.2.2 Preparation of Tannin-chitosan support

About 3.0 g of tannin was added to 100.0 ml of deionized water, followed by 5.0 g of chitosan. The resultant mixture was stirred at room temperature for 3 hours. Then, the reaction was stirred again at 318 K for 6 hours. The T-C support was filtered, cleaned with deionised water and dried in vacuum for 12 hours.

3.2.3 Preparation of catalyst

1g of $Ni(NO_3)6H_2O$ was measured using the same volume of pores in T-C support and dropped on the support. The support containing Nickel Nitrate Hexahydrate, $Ni(NO_3)6H_2O$ was dried to remove the volatile component. After the mixture was dried, Nickel Nitrate Hexahydrate, $Ni(NO_3)6H_2O$ was reduced to into nickel compound through hydgogenation process. The Nickel-Tannin Chitosan produced was undergoing activation process to attach each other.

3.2.5 Characterization of catalyst

The catalyst was characterized by using Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and scanning electron microscope (SEM) to study the characteristic of catalyst using different analysis produced by these machines.

Fourier Transform Infrared Spectra of Nickel Tannin/Chitosan was obtained using Fourier transform infrared spectroscopy (FTIR) from Thermo Scientific, model iZ10 which operated at 450-3500cm^{-1}. FTIR spectrum enables the nickel catalysts in which various peaks can be determined. Peaks in the range were attributed to Ni-O bond and physiosorbed of water molecules. The peaks actually were assigned to OH group that composed to nickel.

The patterns of XRD were identified using X-ray powder diffraction machine with serial no. of 208493. The function of XRD is to identify the sample crystalline phased in inorganic compounds or minerals where XRD scans was performed on Nickel Tannin/Chitosan. It is powerful technique to identify the unknown materials.

SEM with JEOL JSM-6360LA model operating at 15kV voltage was used to identify the surface morphology and size of the catalyst. This tool is easy to handle and can deal with any thickness of a sample to characterize the solid materials where about 3000-6000 times of magnification was performed.

3.2.4 Catalytic activity

The catalytic experiment was carried out according to method proposed by Saeed et al (2016). The nickel tannin chitosan batch oxidative degradation of methylene blue was conducted using three different temperatures of 38°C, 48°C. And 58°C. The flask was filled with 40ml of dye and the reaction mixture was stirred constantly using a hotplate. The water samples containing different quantity of methylene blue was took to observe any variation in dye concentration during heating and stirring time after stirring the solution for a few minutes. Hydrogen peroxide as an oxidant was added into the flask continuously during stirring of the mixture. After stirring the mixture for a few minutes, the samples of water was took and observed whether any variations in dye concentration. The pre-determined quantity of nickel catalyst was added to the mixture reaction and stirred continuously. At approximate time intervals about 30 minutes, samples was took from the flask and UV-Visible spectrophotometer was used for reaction mixture analysis. The percentage of degradation of a dye was calculated using the following the equation.

$$\text{Degradation (\%)} = [(R)_0 - (R)_t] / (R)_0 \ (x)\ 100\%$$

$(R)_0$ show the initial concentration and $(R)_t$ show the concentration of dye at different time interval.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 FTIR Analysis

The FTIR spectrum of Tannin/chitosan(TC) support and Nickel Tannin/chitosan catalyst was showed in the Figure 4.1.1 and Figure 4.1.2. In FTIR spectrum of T/C support, a broad peak was observed at 3211 cm^{-1}, which can be assigned to (OH) stretching vibration (El-Kemary et al., 2013). A weak peak at 2114 cm-^{1} can be attributed as (CH_2) stretching vibration. A medium naturally peak at 1606 cm^{-1} can be assigned to the (N-H) stretching vibration. However, the peaks 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 (Silva et al., 2012).

Similarly, the peaks shown on the Tannin Chitosan support was observed on the FTIR spectrum of Nickel Tannin/Chitosan. 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.

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

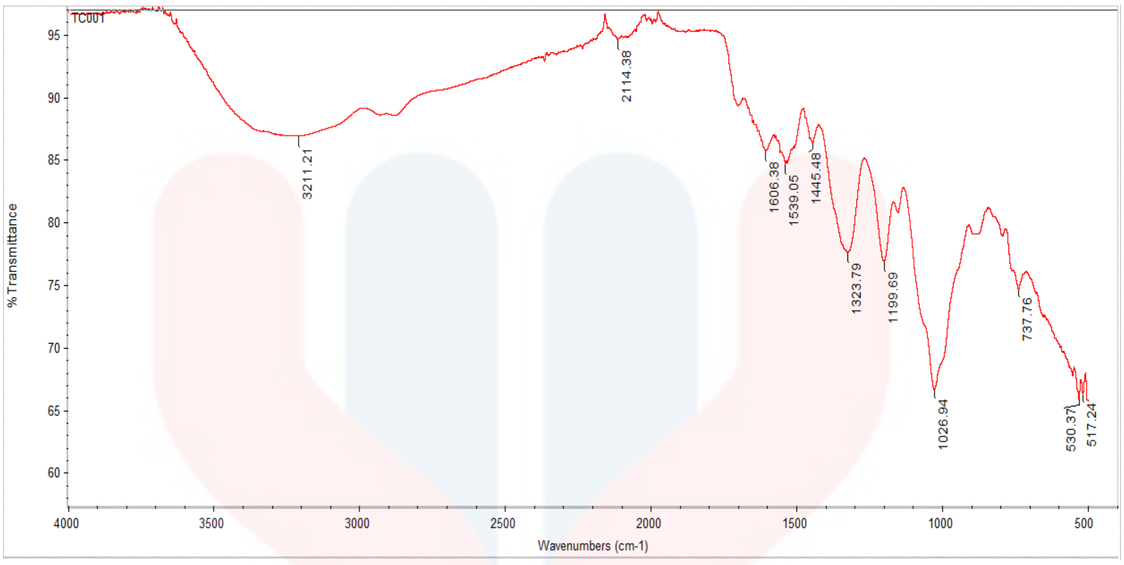


Figure 4.1.1 Tannin/chitosan (TC) support

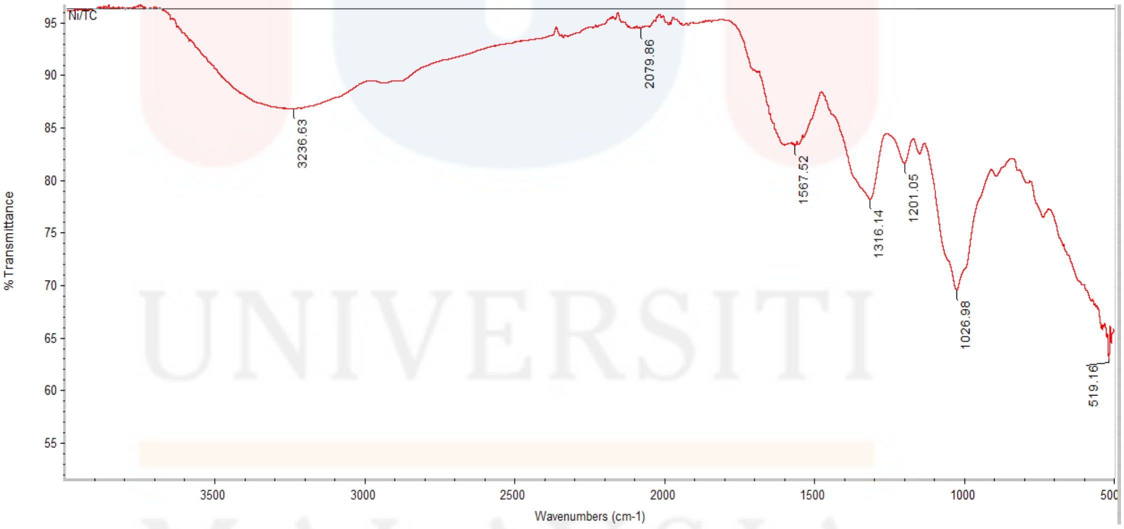


Figure 4.1.2 Nickel Tannin/Chitosan

4.2 XRD Analysis

The crystalline nature of Tannin-chitosan support was identified through XRD analysis graph as in Figure 4.2.1 and Figure 4.2.2. From the XRD spectrum it showed three discrete peak at 19.366º, 18.809º and 18.657º that referred to 2θ value and corresponding lattice plane was (-2,-1,-4), (-1,-1,-4) and (0,-2,0) for Tannin/Chitosan (TC) support. The crystallinity of this spectrum was observed from 10º to 90º for both graph. It shows sharp and intensive diffraction peaks corresponding to hexagonal crystalline structure. An intense peak observed near 20º with 1539 counts intensity. The main broad scattered from 20º to 35º as shown by the pattern without exceed the maximum height of 19.366º (Beyki et al., 2016).

In Nickel Tannin/Chitosan it shows three discrete peak from XRD spectrum at 20.166º, 21.583º and 24.134º that referred to 2θ value and corresponding lattice plane was (-1,-3,-1), (-1,-2,-2) and (0,-3,-2). The peaks showed sharp reflection from XRD pattern which proved the growth of Ni crystalline sizes (El-Kemary et al., 2013). Nickel Tannin/Chitosan shows an intense peak which near 20º with 777 counts intensity. From the pattern, the broad showed by nickel tannin/chitosan also scattered from 20º to 30º and with maximum height 24.134º. The crystallinity nature was identified by using DiffractEva software from Bruker.

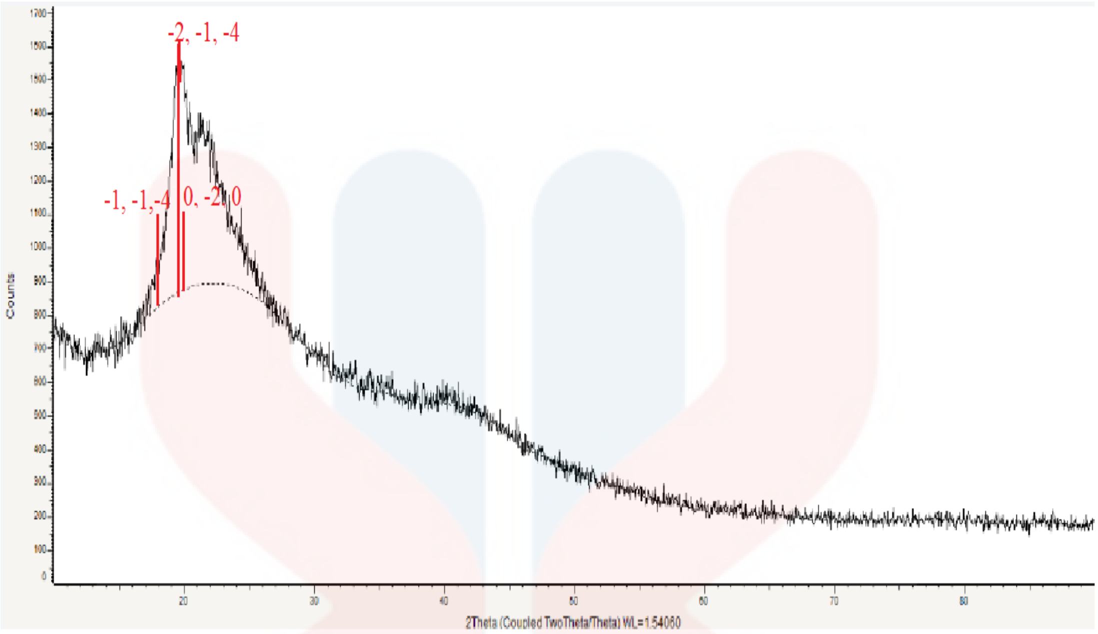


Figure 4.2.1 Tannin/Chitosan (TC) support

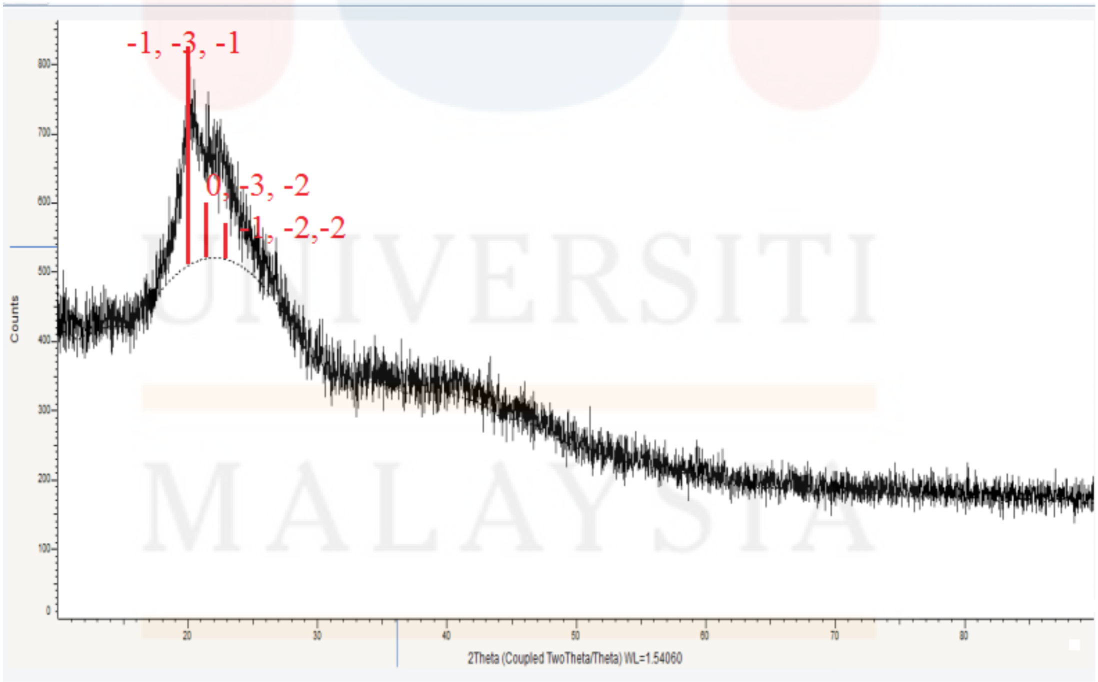


Figure 4.2.2 Nickel Tannin/Chitosan

4.3 SEM Analysis

As shown in Figure 4.3.1, SEM analysis of Tannin/Chitosan support used 3000 times magnification to analyse the particles. About 15kV of voltage was used and about 5μm scale was applied by Scanning Electron Microscopy (SEM). Figure below showed the image produced by Tannin/Chitosan support. The morphology shows globules of crystalline structure with smooth surface. Smaller the probe current result in the sharper image, but reducing the surface smoothness. The adsorption ability of an adsorbent also increased for surface area or morphology of particles due to binding sites present more (Taty-Costodes et al., 2003).

For SEM analysis of Nickel Tannin/Chitosan the scale used was about 2μm where 15kV of voltage operated by scanning electron microscopy. The magnification used is 6000 times as showed in Figure 4.3.2. The image produced showed the surface morphology of Nickel Tannin/Chitosan is smooth same as surface morphology shows by Tannin/Chitosan support. Besides, nickel observed also deposited on Tannin/Chitosan support and attached to it. The image resolution and sharpness more precise at the higher voltage.

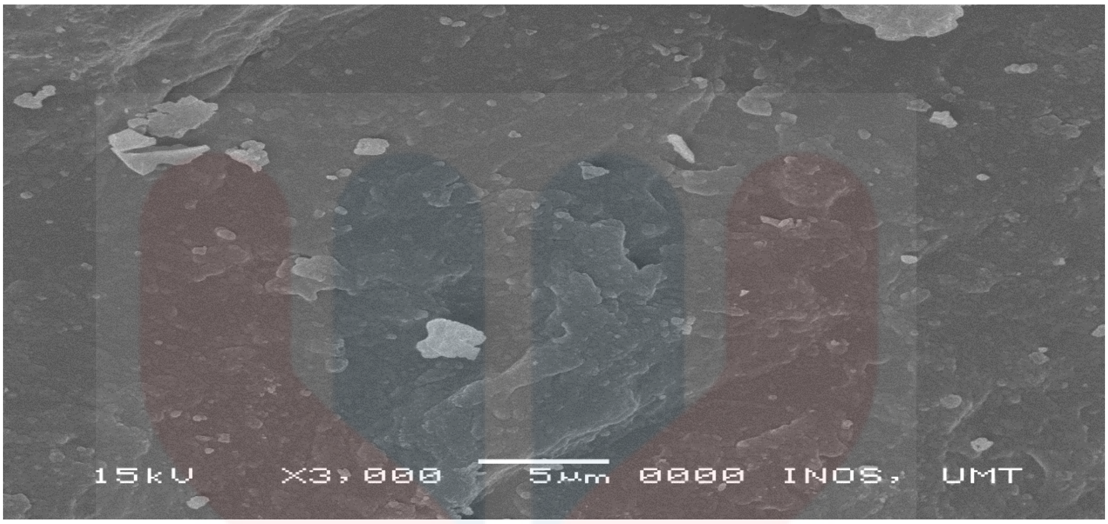


Figure 4.3.1 Tannin/Chitosan (TC) support

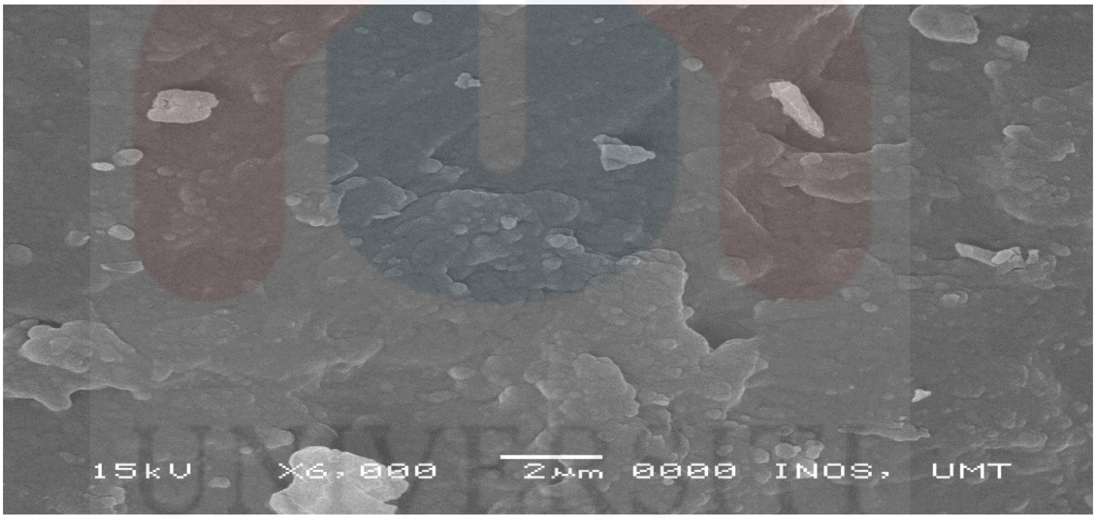


Figure 4.3.2 Nickel Tannin/Chitosan

From the study, Nickel catalyst was characterized using FTIR, XRD and SEM machine which related to each other. The machines have their own function which was to identified and examined the existence of nickel on the Tannin/Chitosan support. The deposited nickel attached to Tannin/Chitosan support was observed to prove whether it can be used as catalyst to remove the methylene blue in contaminated water. Based on the study, it shows that nickel was deposited on the surface of Tannin/Chitosan support. It was used in catalytic activity to remove methylene blue by determined the degradation of dye and kinetic experiment.

4.4 Catalytic activity

From the study, the calibration curve of methylene blue using H_2O and H_20_2 was being carried out in order to determine the percentage degradation of methylene blue. Different concentration of methylene blue was used from 0.05M until 0.5M with 3 different trials to determine the absorbance using UV-Visible Spectrophotometer. Then, the graph was plotted based on catalytic degradation experiment where three different temperatures was used at 38°C, 48°C and 58°C.

Methylene blue was used alone, added with H_20_2, catalyst and in the presence of catalyst and H_20_2 where H_2O was used as blank. When using methylene blue alone and H_20_2 the absorbance rise while using catalyst and catalyst in the presence of H_2O_2 the absorbance slightly decreased. This shows that degradation of dyes has great effect when temperature increased as the time increased to achieve certain temperature (Ahmad et al., 2016).

The rate of diffusion rise when temperature became higher which result from decreasing the viscosity of dye (El-Wakil et al., 2015). The absorbance result was noted to determine the concentration of dye so percentage of degrade dye can be calculated as shown in Table 4.4.1 by referring to the calibration curve of methylene blue whether it used H_2O or H_2O_2. The following equation is used.

$$\text{Degradation (\%)} = [(R)_0 - (R)_t] / (R)_0 \ (x)\ 100\%$$

$(R)_0$ show the initial concentration and $(R)_t$ show the concentration of dye at different time interval (Saeed et al., 2003).

About 0.5M concentration of dye was used as initial concentration while the concentration at time interval is determined at calibration curve of methylene blue depend on the presence of H_2O or H_20_2. The degradation of dye showed a decreasing results for dye alone and dye with H_20_2 while using catalyst and catalyst in the presence of H_20_2 the degradation of dye increased slightly as the time increased. For dye alone, the degradation decreased from 48% in 10.21 minutes to 40% in 16.05 minutes and at 58°C degrade to 28% in 25.12 minutes only same with using H_20_2 where degradation depleted from 70%, 67% and 54% as the temperature and time increased.

When nickel catalyst was used with dye to each temperature of 38°C, 48°C and 58°C, the degradation of methylene blue rise from 26% to 44% in 12.30 minutes and reached 54% in 22.30 minutes only. Lastly, when nickel catalyst in the presence of H_20_2 was tested the degradation shows an increasing. At 38°C degradation is 46% as the time and temperature increased it degraded to 60% in 9.46 minutes and reached 74% at 58°C in 20.05 minutes. So, catalytic activity and degradation of methylene blue at different temperature rise rapidly when catalyst was applied compared when using alone or added with H_20_2. As the catalyst was added the time taken to degrade also decreased at certain temperature same in the presence of both catalyst and H_2O_2 compared when using alone or added with H_2O_2. This shows catalyst can speed up the degradation of methylene blue where 58°C was the optimal temperature for dye to degraded.

Table 4.4.1 Methylene blue percentage degradation

Temperature (°C)	Methylene blue alone (%)	Methylene blue + H_2O_2 (%)	Methylene blue +catalyst (%)	Methylene blue + H_2O_2 + catalyst (%)
38	48	70	26	46
48	40	67	44	60
58	28	54	54	74

Table 4.4.2 Degradation of methylene blue against time for methylene blue alone, methylene blue in the presence of H_2O_2, methylene blue in the presence of catalyst and methylene blue in the presence of catalyst and H_2O_2

Methylene blue alone	
Time (min)	Degradation (%)
5.01	70
14.32	67
25.03	54
Methylene blue in the presence of H_2O_2	
Time (min)	Degradation (%)
10.21	48
16.05	40
25.12	28
Methylene blue in the presence of catalyst	
Time (min)	Degradation (%)
8	26
12.3	44
22.3	54
Methylene blue in the presence of catalyst and H_2O_2	
Time (min)	Degradation (%)
4.15	46
9.46	60
20.05	74

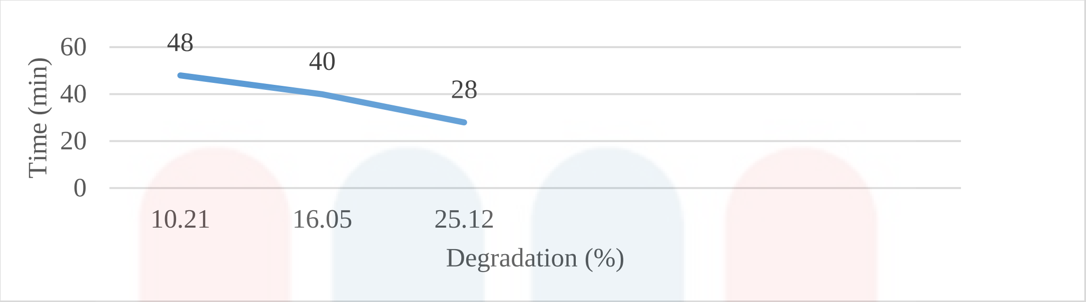


Figure 4.4.3 Methylene blue alone

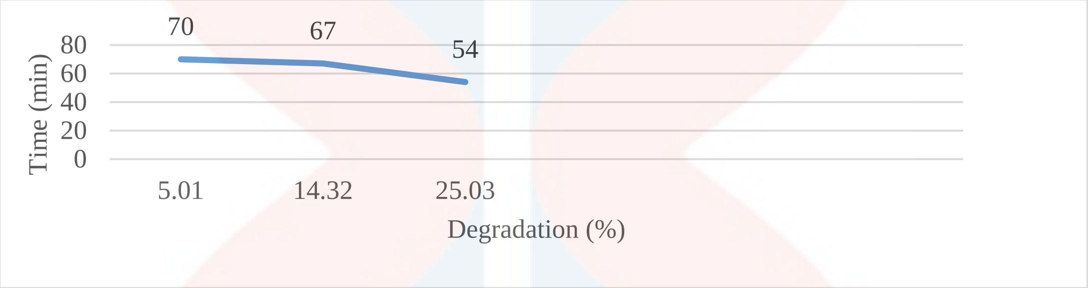


Figure 4.4.4 Methylene blue in the presence of H_2O_2

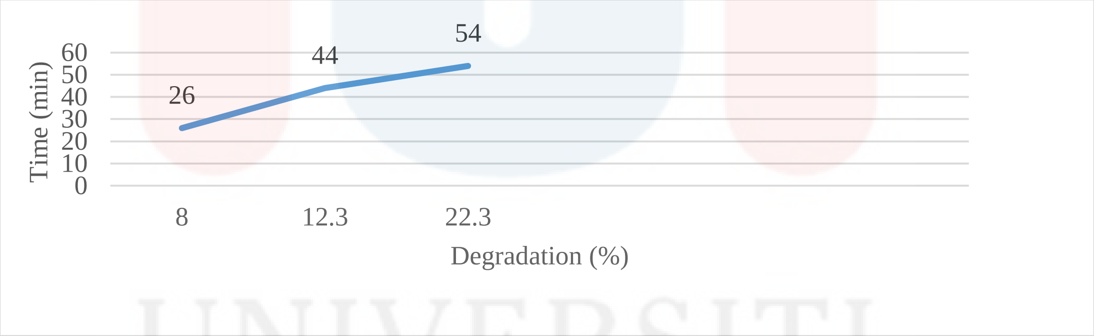


Figure 4.4.5 Methylene blue in the presence of catalyst

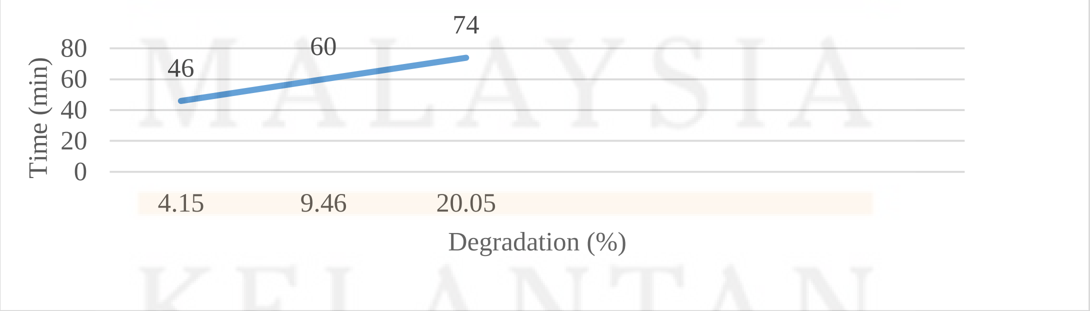


Figure 4.4.6 Methylene blue in the presence of catalyst and H_2O_2

4.5 Kinetic experiment

In kinetic experiment, different time was used from 5 minutes until 60 minutes means every 5 minutes the absorbance reading from UV-Visible Spectrophotometer was taken. Methylene blue was tested alone, with H_20_2, catalyst and catalyst in the presence of H_20_2 same as catalytic degradation experiment before. The concentration of each time was determined by referring to the calibration curve from absorbance results. From the graph plotted, it shows increasing trend of concentration against time for zero-order reaction kinetics in the presence of catalyst same when tested in the presence of catalyst and H_2O_2 as shown in Figure 4.5.1 and 4.5.2.

When dye was used to plot graph of first-order reaction kinetics, it shows decreasing results of methylene blue degradation as concentration actually affects by time by referred to Figure 4.5.3 and 4.5.4. The second-order reaction kinetics also prove that concentration of methylene blue gradually decreased whether using with catalyst only or in the presence of catalyst and H_2O_2 in the Figure 4.5.5 and 4.5.6. This is because the scavenging effect by excess amount of H_20_2 to HO which deflect the degradation efficiency of methylene blue (Youssef et al., 2016).

The kinetic reaction of zero-order, first-order and second-order was determined using Fenton oxidation process. The regression coefficient (R^2) shown in Figure 4.2.1 which $R^2 = 0.986$ of zero-order reaction kinetics for methylene blue in the presence of catalyst was better compared to R^2 value of first-order and second order reaction kinetics. The regression coefficient (R^2) were $R^2 = 0.831$ and $R^2 = 0.685$ respectively. The results indicate that kinetic degradation of methylene blue followed the zero-order kinetics.

The kinetic experiment of methylene blue in the presence of catalyst and H_2O_2 also showed that regression coefficient (R^2) which is R^2= 0.984 was much better from reaction kinetics of first-order and second order. So, it can be concluded that kinetic degradation using H_2O_2 followed the zero-order reactions.

1) Zero-order reaction kinetics

Table 4.5.1 Methylene blue in the presence of catalyst

Time (min)	Concentration (M)
5	0.07
10	0.14
15	0.18
20	0.23
25	0.3
30	0.33
35	0.38
40	0.4
45	0.45
50	0.47
55	0.5
60	0.57

Table 4.5.2 Methylene in the presence of catalyst and H_2O_2

Time (min)	Concentration (M)
5	0.12
10	0.16
15	0.18
20	0.2
25	0.22
30	0.25
35	0.28
40	0.32
45	0.35
50	0.4
55	0.43
60	0.48

2) First-order reaction kinetics

Table 4.5.3 Methylene blue in the presence of catalyst

Time (min)	Concentration (M)
5	1.96
10	1.27
15	1.02
20	0.78
25	0.51
30	0.42
35	0.27
40	0.22
45	0.15
50	0.1
55	0.06
60	0.01

Table 4.5.4 Methylene blue in the presence of catalyst and H_20_2

Time (min)	Concentration (M)
5	1.42
10	1.13
15	1.02
20	0.91
25	0.8
30	0.69
35	0.58
40	0.44
45	0.35
50	0.22
55	0.15
60	0.04

3) Second-order reaction kinetics

Table 4.2.5 Methylene in the presence of catalyst

Time (min)	Concentration (M)
5	14.2
10	7.14
15	5.5
20	5.0
25	4.5
30	4.0
35	3.5
40	3.1
45	2.2
50	2.1
55	2.0
60	1.7

Table 4.2.6 Methylene in the presence of catalyst and H_20_2

Time (min)	Concentration (M)
5	8.3
10	6.25
15	5.5
20	5
25	4.5
30	4
35	3.57
40	3.12
45	2.85
50	2.5
55	2.32
60	2

1) Zero-order reaction kinetics

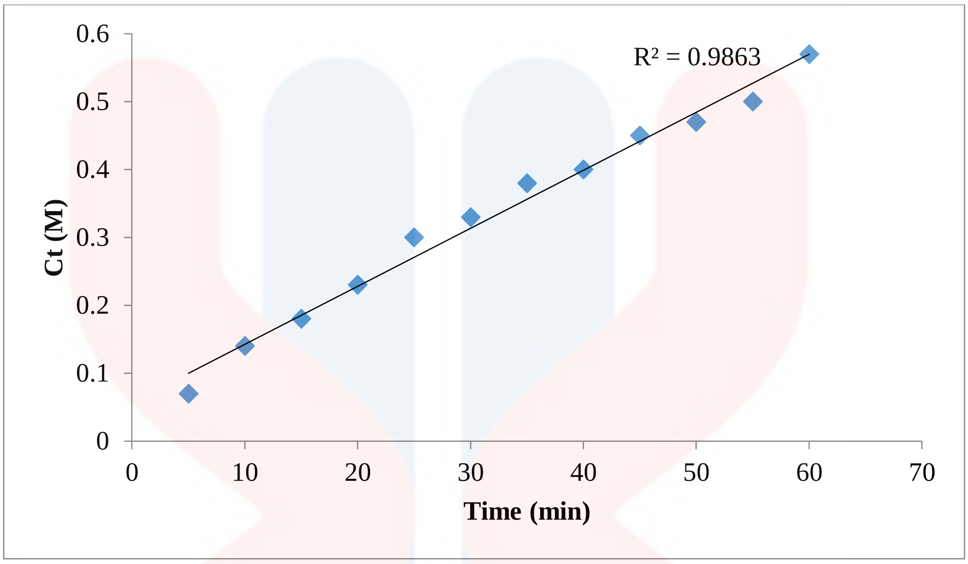


Figure 4.5.7 Methylene blue in the presence of catalyst

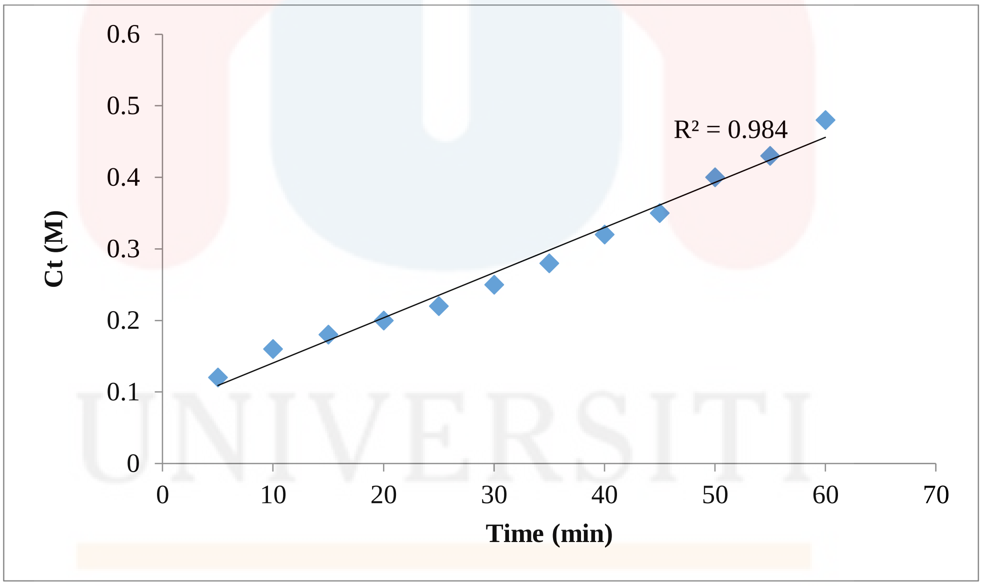


Figure 4.5.8 Methylene blue in the presence of catalyst and H_2O_2

2) First-order reaction kinetics

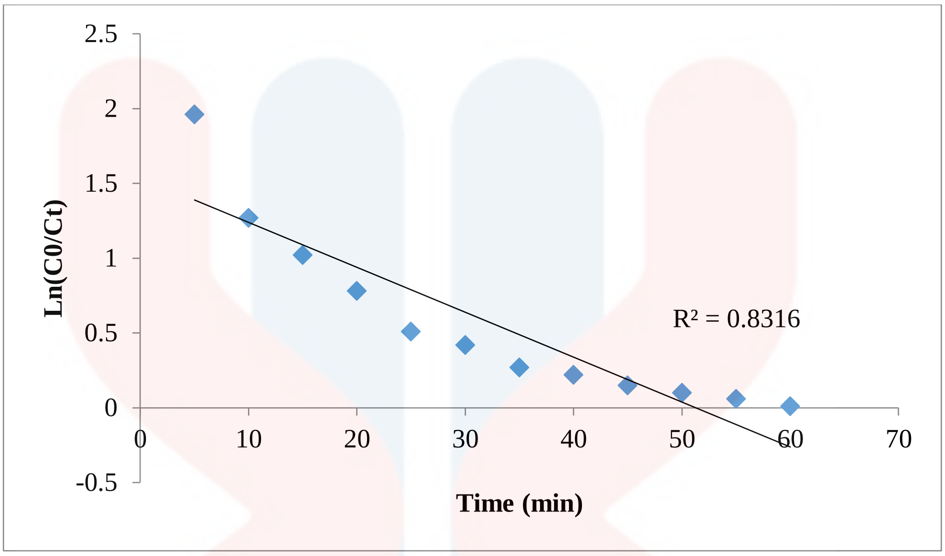


Figure 4.5.9 Methylene blue in the presence of catalyst

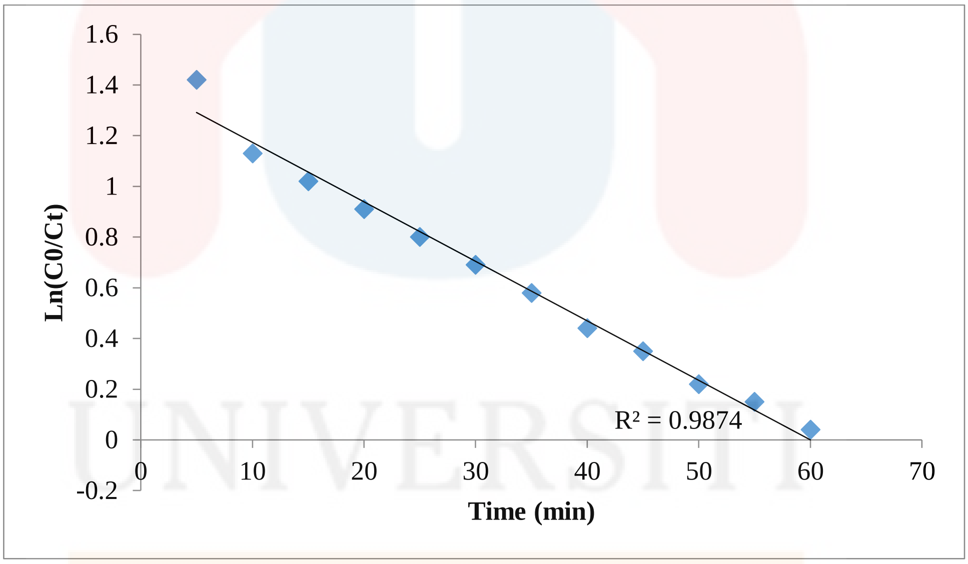


Figure 4.5.10 Methylene blue in the presence of catalyst and H_2O_2

3) Second-order reaction kinetics

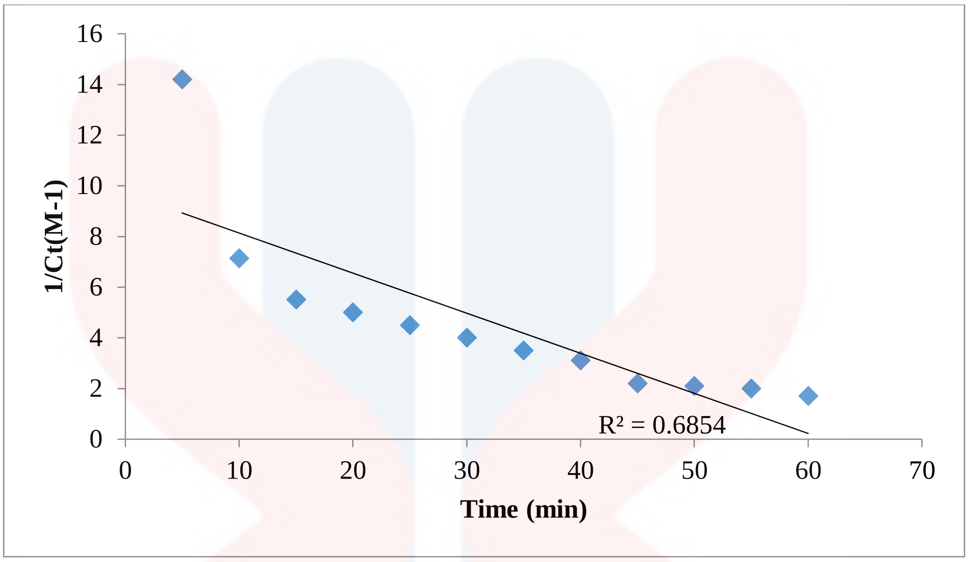


Figure 4.5.11 Methylene blue in the presence of catalyst

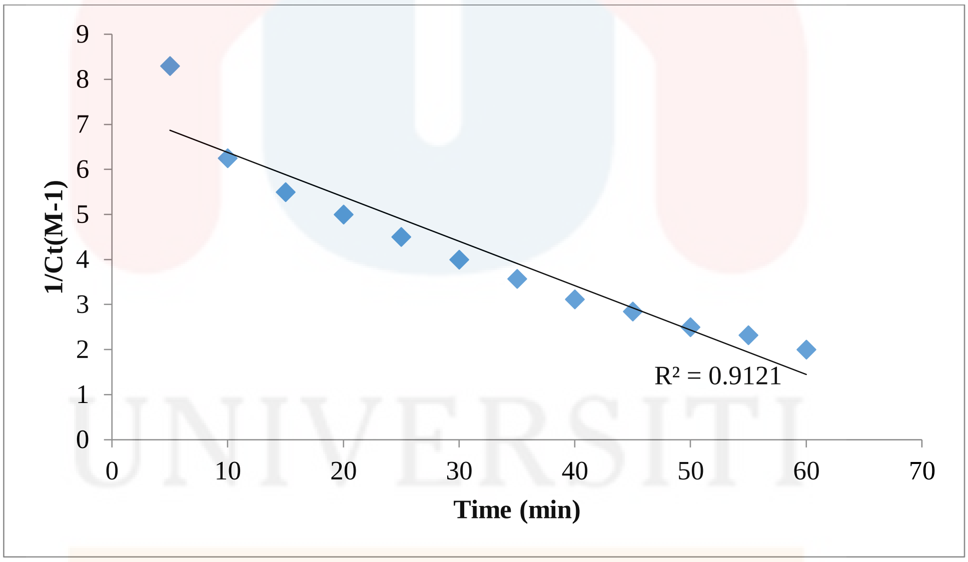


Figure 4.5.12 Methylene blue in the presence of catalyst and H_2O_2

Table 4.5.13 Summary of result in the characterization of catalyst and catalytic activity

Instrument	Function	Result	Conclusion
FTIR analysis	The catalyst prepared was characterized using FTIR spectrum to identify their functional groups presence.	OH, CH_2,N-H,C=C, N-O and C-O stretching vibration was observed in Tannin/Chitosan support while Ni(OH) and Ni(NH) shift in Nickel Tannin/Chitosan.	The study shows nickel deposited at Tannin/ Chitosan support when characterized using FTIR, XRD and SEM.
XRD analysis	XRD spectrum of nickel catalyst was observed to identify the diffraction that corresponding to hexagonal crystalline structure.	The peaks shows sharp diffraction corresponding to hexagonal crystalline structure in both Tannin/Chitosan support and Nickel Tannin/Chitosan.	
SEM analysis	The adsorbent material was analysed to identify the adsorption capability of catalyst.	The morphology of Tannin/Chitosan support shows a smooth surface and nickel deposited on Tannin/Chitosan support in Nickel Tannin/Chitosan.	
Catalytic activity	Nickel Tannin/Chitosan was used with three different temperature of 38,48 and 58°C to test the oxidative degradation of methylene blue.	The degradation of methylene blue increased from 54% in the presence of catalyst and improved to 74% after added with H_2O_2 at optimal temperature of 58°C.	Nickel Tannin/Chitosan have the ability to speed up the reaction and increase the degradation of methylene blue as catalyst.
Kinetic analysis	Kinetics experiment were tested the degradation of methylene blue and determine the order for reaction kinetics.	The value of R^2=0.986 of zero-order reaction kinetics was much better compared to first order and second-order which R^2=0.831 and $R^{2=}$0.685 respectively.	

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study focus on removal of pollutants like methylene blue which was can effects human health either biologically or physically such as hard to breath, mental disorder and over-sweating. Nickel catalyst was prepared by adding Nickel Nitrate Hexahydrate, $Ni(NO_3)6H_2O$ to T-C support and dried. Three different machines were used to characterize the nickel catalyst which is FTIR, XRD and SEM. Methylene blue was chosen as the pollutants that need to be removed using nickel catalyst. Different temperature of 38°C, 48°C and 58°C was tested to increase the catalytic activity and UV-Visible Spectrophotometer was used to measure the absorbance so that the effectiveness of nickel catalyst in removing methylene blue can be identified. The methylene blue degradation increased from 54% in the presence of catalyst and enhanced to 74% when added with H_2O_2 at optimal temperature of 58°C. From this study, it was proved that nickel has the ability to become alternative catalyst in removing pollutants in contaminated water.

5.2 RECOMMENDATIONS

In this study, freshly prepared nickel was used as catalyst to remove methylene blue from polluted water. It is recommended that more research to be conducted in future in different ways such as production of nickel and other metal that can be used in removal of methylene blue. Besides, nickel catalyst also can be tested in removal other pollutants in water bodies such as detergent, insecticides, herbicides, organohalides which might be more efficient, low cost and environmental friendly.

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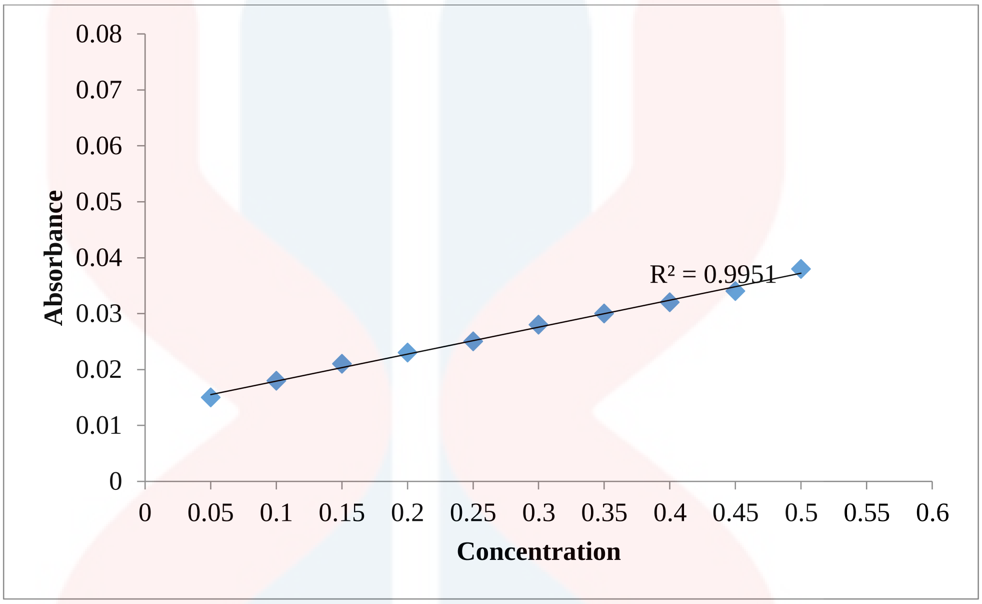
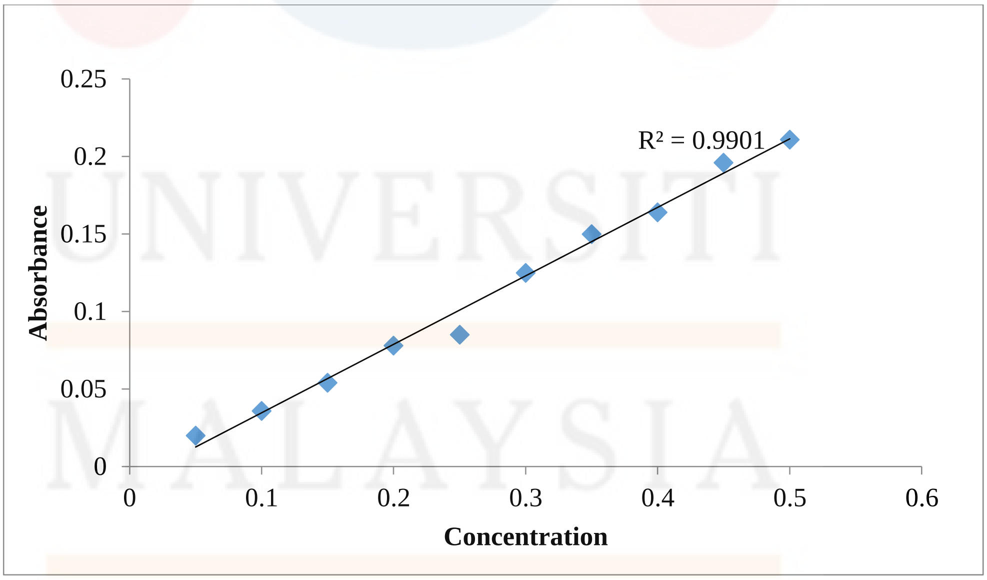
APPENDIX A

Calibration curve of methylene blue in the presence of H_2O

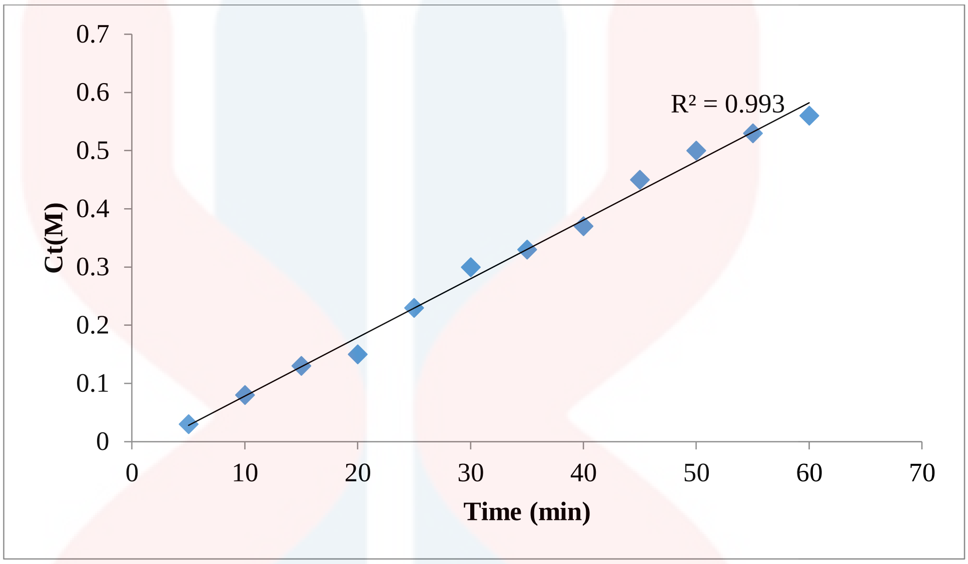


Calibration curve of methylene blue in the presence of H_2O_2

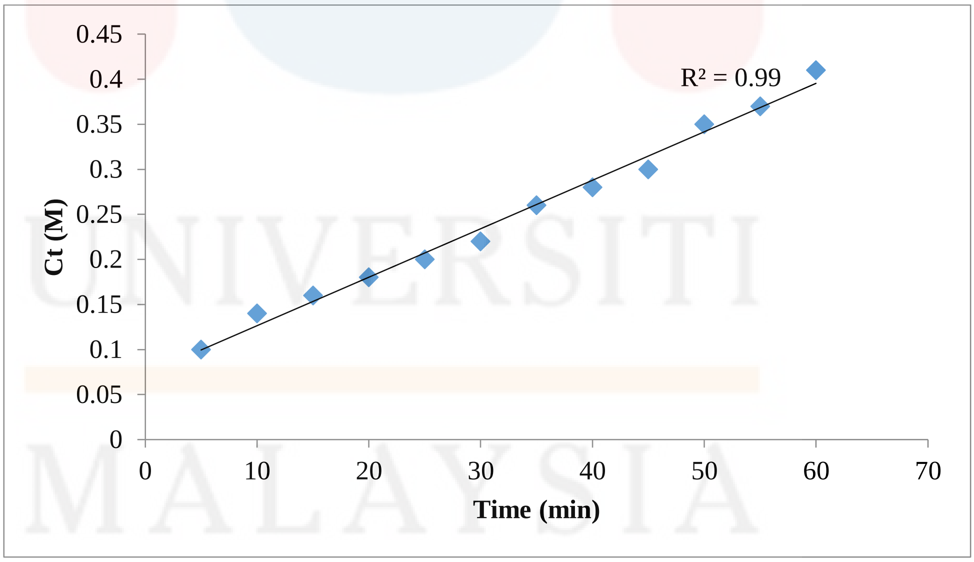


APPENDIX B

Zero-order reaction kinetics of methylene blue alone

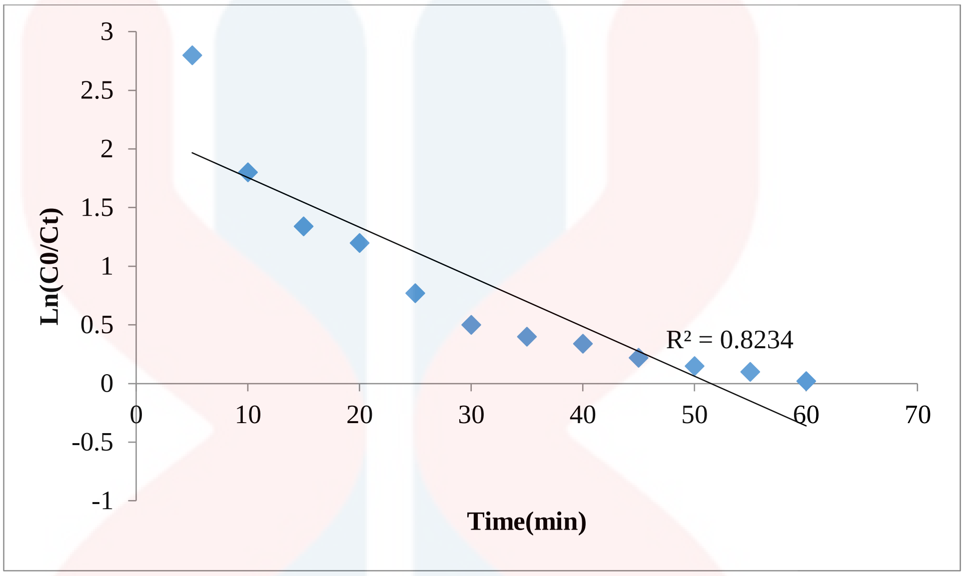


Zero-order reaction kinetics of methylene blue in the presence of H_2O_2

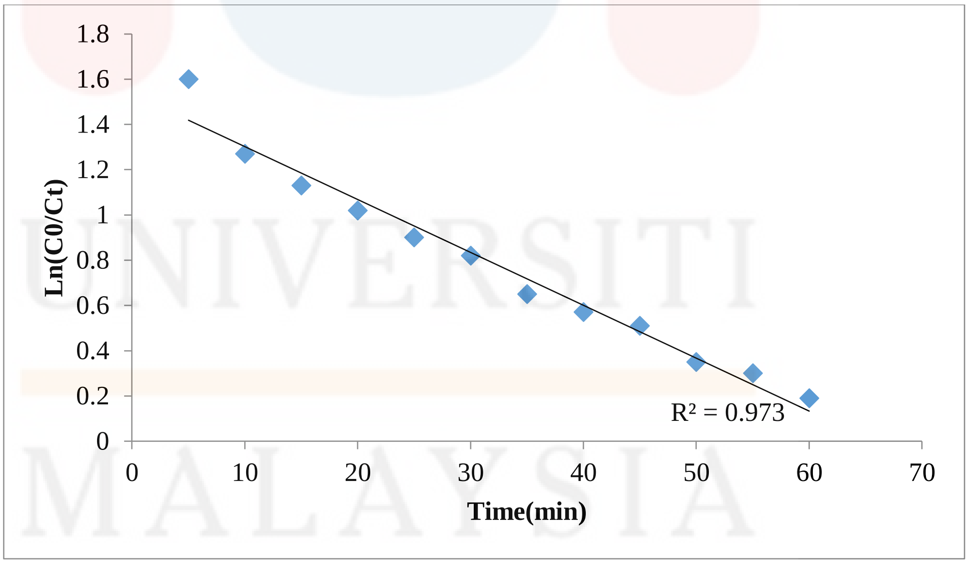


APPENDIX C

First-order reaction kinetics of methylene blue alone

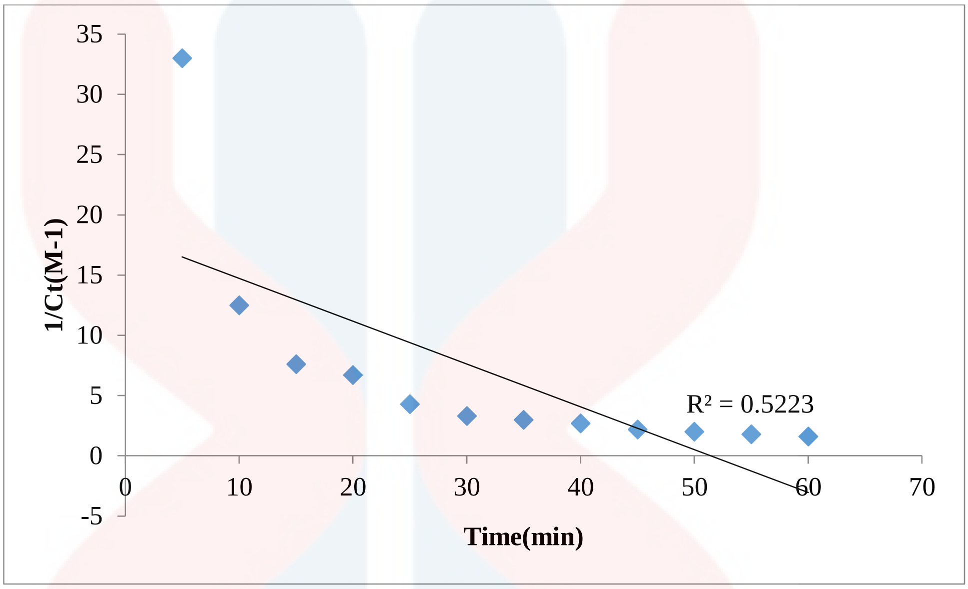


First-order reaction kinetics of methylene blue in the presence of H_2O_2

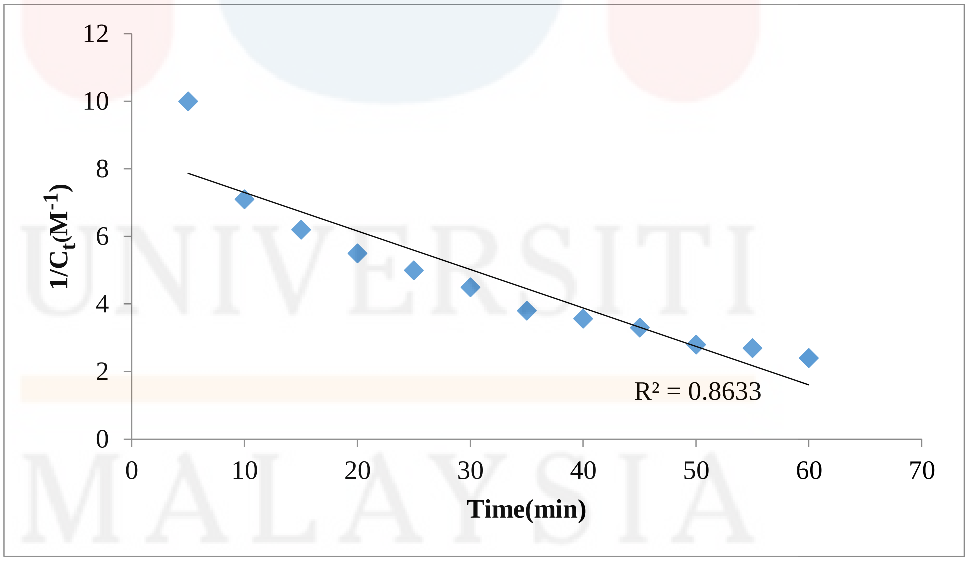


APPENDIX D

Second-order reaction kinetics of methylene blue alone

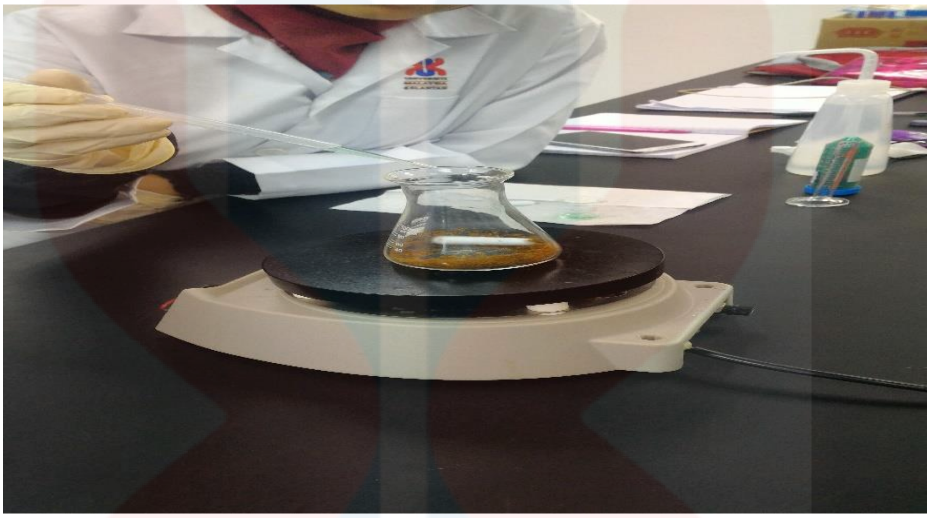


Second-order reaction kinetics of methylene blue in the presence of H_2O_2

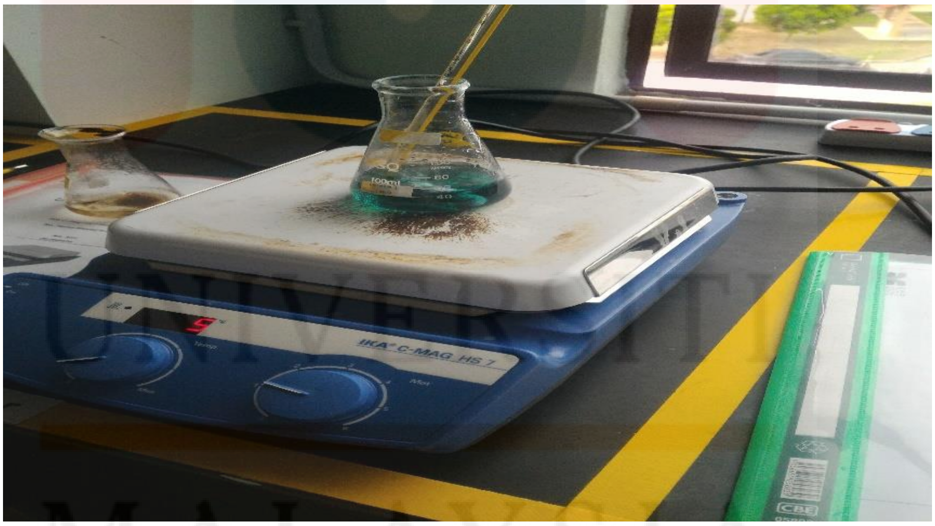


APPENDIX E

Preparation of Nickel Tannin/Chitosan



Catalytic degradation of methylene blue



Apparatus needed for lab work

Prepared Nickel Tannin/Chitosan