Removal of Methyl Orange from Contaminated Water by Newly Prepared Nickel Catalyst

by

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DECLARATION

I declare that this thesis entitled **“**removal of methyl orange 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 : Fatin Mardhiah Binti Nordin

Date :

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ABSTRACT

Contaminated water can cause by industries and anthrpogenic activities. Nowadays, the communities faced water problems due to the usage of dyes in industries and it was an urgent need to overcome this problem using cheaper catalyst such as nickel. The research was done to characterize the prepared tannin chitosan nickel doped catalyst and to evaluate the catalytic activity of the newly prepared catalyst in the oxidation of methyl orange. The nickel catalyst was prepared by dry impregnation method and characterized by different techniques such as using Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). From the FTIR spectrums, the shift in OH and NH peaks in nickel catalyst indicated the involvement of OH and NH groups binding with the nickel. From the SEM, the tannin chitosan support has a smooth surface and the nickel was supported on the tannin chitosan support when the nickel was dropped on the support. The XRD spectrums showed both tannin chitosan support and nickel catalyst were an amorphous phase with a monoclinic crystal system. The catalytic activity was carried out in three different temperatures (313, 323 and 333 K) and observed by degradation percentage of methyl orange. The highest degradation percentage of catalytic activity was at 313 K as the degradation efficiency was at maximum.

Pembuangan Metil Jingga Dari Air yang Tercemar Oleh Pemangkin Nikel yang Baru Disediakan

ABSTRAK

Air tercemar berlaku disebabkan industri dan aktiviti manusia. Masyarakat mengalami masalah air disebabkan penggunaan pewarna oleh industri dan sangat penting untuk mengatasi masalah ini dengan menggunakan pemangkin yang murah seperti nikel. Kajian ini dilakukan untuk mencirikan pemangkin nikel yang didopkan dengan tanin chitosan dan untuk menilai aktiviti pemangkin bagi pemangkin yang baru disediakan dalam pengoksidaan metil jingga. Pemangkin nikel disediakan dengan kaedah pengisitepuan and dicirikan dengan menggunakan teknik seperti Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) dan X-Ray Diffraction (XRD). Daripada spektrum FTIR, anjakan puncak OH dan NH dalam pemangkin nikel menunjukkan penglibatan kumpulan OH dan NH dalam proses pengikatan dengan nikel. SEM menunjukkan bahawa sokongan tanin chitosan mempunyai permukaan yang rata dan nikel disokong oleh sokongan tanin chitosan apabila nikel digugurkan di atas sokongan. Spektrum XRD menunjukkan kedua-dua sokongan tanin chitosan dan pemangkin nikel merupakan fasa amorfus dengan monoklin. Aktiviti pemangkin dijalankan dalam tiga suhu yang berbeza (313, 323 and 333 K) dan diperhatikan dengan peratusan penurunan metil jingga. Peratusan penurunan bagi aktiviti pemangkin pada suhu 313 K adalah yang paling tinggi disebabkan kecekapan penurunan adalah maksimum.

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List of Abbreviation

FTIR	Fouirer Transform infra-red
g	Gram
K	Kelvin
mg	milligram
ml	mililitre
methyl orange	methyl orange
nm	nanometer
pH	Power of Hydrogen
SEM	Scanning Electron Microscopy
UV-Visible Spectrophotometer	Ultra Violet -Visible spectrophotometer
XRD	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Organic pollutants, heavy metals, and pathogenic microorganisms are the main sources of the contamination of water (UN-Water, 2015). These pollutants can enter water bodies from anthropogenic activities as well as the industries for example textile industry. Most of the waste products of textile industry will flow to the water stream. Dyes from various industries such as textile, paper, plastics and cosmetic are considered as main sources of pollutants which causing water pollution (Umpuch & Sakaew, 2013). Annodurai et al., (2008) stated that collection of dyes in waste water from industries has been regarded as an important source of water pollution. Kyzas et al., (2014) reported that minor amount of dye can give color changes in water whereas reduce the light penetration into the aquatic environment and this effects the various biological processes. The dyes are synthetic in origin and their aromaticity is non-biodegradable in nature (Ma et al., 2012).

There are many biological, physical and chemical methods which have been used to remove the dye from waste water (Yao et al., 2011; Zhang et al., 2011; Fang et al., 2010 and Ruan et al., (2010). Impregnation is one of the methods which has been used by many researchers as it is an efficient process, low cost, simple, easy to perform and insensitive to the toxic substance as reported by Gucek et al., (2005) . Impregnation is an important method to ensure separation of pollutants from effluents (Boudiaf et al., 2012).

Crini & Badot (2008) stated that impregnation techniques provide a potential for removal of dyes from aqueous solutions. Crini (2006) also observed that impregnation technologies as one of the capable methods because of its low operation temperature and several coloring materials can be discharged simultaneously.

The catalyst is used to speed up the rate of reactions (Clark, 2002). Nickel catalyst will be used in this research because nickel is abundance in quantity, suitable for many applications, economically feasible compared to other metal, cheaper in price, have good stabilities and appreciable catalytic activities (Saeed et al., 2016).

1.2 Problem Statement

Currently, the passing of dyes is one of the major water problems faced by both urban and rural communities due to increased usage of dye in the various industrial such as textile, food processing and also anthropogenic activities to produce a interesting and colourful products. Ogugbue and Sawidis (2011) studied that up to 200,000 tons of dyes are released to effluents every year during the process of dyeing and finishing operations, caused by the inefficiency of the dyeing process. There is an urgent need to address this problem by designing a catalyst which is cheap in order to replace the catalysts based on a metal such as palladium, platinum, and rhodium.

1.3 Objectives

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

CHAPTER 2

LITERATURE REVIEW

2.1 Water Pollutant

The substance that introduced to water bodies (lake, ocean, stream and river) and contaminated the water sources and cause water pollution is defined as a water pollutant. Based on Corcoran et al., (2010), water is an element of one or more of domestic effluent which consist of blackwater (excreta, urine and faecal sludge) and grey water (kitchen and bathing wastewater), water from commercial establishments and institutions such as hospitals, industrial effluent, storm water and urban run-off and agricultural, horticultural and aquaculture either dissolved or un-dissolved matter. Increase population, urbanization, and industrialization which mainly constitute by organic matter and heavy metals are the main causes of discharging a huge amount of polluted water into the environment (Lalevic et al., 2012). Akolekar et al., (2002) reported that waste stream produced by most industrial processes may contain a high concentration of pollutants such as phenols, carboxylate, carbonyls, amines and ammonia which does not follow the environment standards and need requires treatment to discharge.

2.1.1 Sources of Water pollutant

According to Environment Protection Authority Victoria (2012) pollution can come from point sources and non-point sources. Point sources are the pollutant that comes from single and identifiable sources and one of the examples of point sources pollutant is the industry. Most of the industry used hazardous materials including chemicals and then the wastes were discharged to the water sources. The waste then polluted the water sources.

Environmental Protection Agency (2016) stated that non- point sources are the pollutant that comes from many sources and it can cause by rainfall or flow through the ground and then deposit to the water streams. Environment Protection Authority Victoria (2012) recorded that non-point sources if water pollution occur over a large area and not easily attributed to a single sources. Non-point sources often caused by land uses as opposed to individual point sources discharges which include urban land uses, agricultural land uses and forestry land uses.

2.1.2 Different Classes of Water Pollutant

There are many classes of water pollutants which have negative impact on water bodies which are organic pollutants, pathogens, inorganic pollutants and others (Ghangrekar, n.d.).

1. Organic pollutants

Ghangrekar (n.d.) reported that organic pollutants can be divided into oxygen demanding waste, synthetic organic compounds and oil. The waste water have significant concentration of biodegradable organic compounds either in suspended, colloidal or dissolved form which undergo degradation and decomposition by bacterial activity. The organic matter that present in the waste water will consume the dissolved oxygen available in the water body by aerobic oxidation. Thus, this will affect the aquatic life if the dissolved oxygen falls below 4.0 mg/L. The examples of waste water from oxygen demanding waste are food processing industries, paper and pulps mills and tanneries.

Synthetics organic compounds enter the ecosystems through many human activities for instance production of synthetic compounds like synthetic pesticide, synthetics detergents, food additives and paints and also spillage during transportation. The synthetic compound are very toxic and biorefractory organics which means resistant to microbial degradation. These compounds are extremely persistent and high in stability to chemical reagents (Ghangrekar , n.d.).

Oil is a product naturally resulting from the fossilized plant that remained over a millions of years under marine conditions. Oil is a complex mixture of hydrocarbons and degradable under bacterial actions. Oil can enter the water bodies through oil spills, leaks from oil pipes and also from production and refineries. Since oil is lighter than water, the separating of the water and oil will cause reduction of dissolved oxygen. Oil is responsible in the reduction of light transmission through surface water hence reducing the photosynthesis activity of the aquatic plants (Ghangrekar, n.d.).

2. Inorganic pollutants

Natural and anthropogenic activities can cause the abundance of heavy metals in the environment (Wilson & Pyatt, 2007; Khan et al., 2008). Based on Ghangrekar (n.d.), inorganic pollutants can contaminate the water bodies via sewage and industrial waste and high concentration of heavy metals. These compounds are non-biodegradable and persist in the environment. The inorganic pollutant can include mineral acids, inorganic salts metals, metals compound and sulphates. The collection of heavy metals may have unfavourable effect on aquatic flora and fauna and thus affect the public health problems which consume the contaminated organisms for food. The examples of metal which in high concentration can be toxic to biota are cadmium, copper and lead.

2.2 Dyes

Accumulation of dyes has been regarded as a significant source of water pollution Umpuch & Sakaew (2013). Dye is a natural or synthetic substance that gives colour or change the colour of anything. It has been used in many industries such as cosmetics, paper, rubber and textiles produced colour wastewater (Ma et al., 2012). Even in a minimum amount of dyes discharged to the stream can cause many problems such as chemical oxygen demand and also decreasing the light penetration into the water bodies thus affect the photosynthesis process of the plants (Hameed & Ahmad, 2009). However, the dyes harmed the aquatic life as dyes contain toxic, structurally complex, synthetic origins, high water solubility (Salleh et al., 2011) and its aromatic structure are biologically non-biodegradable (Ma et al., 2012).

Abrahart, (1977) stated that dyes contain at least one chromophore (colour bearing group) and auxochrome (colour helpers) that give colour to wastewater. Biradar et al., (2016) stated that organic dyes usually in solid form as they have auxochromes such as amino, alkylamino, hydroxy, alkoxy and nitro groups in a molecule. Stated by Kolorjet Chemical, (n.d.), the aryl rings in the chromophore make it has a delocalized electron which is responsible for electromagnetic radiation absorption and auxochrome is a group of atoms which is attached to chromophore which responsible in providing solubility, cohesiveness and modify the ability of the chromophore to absorb lights.

Methyl orange is one of the examples of dye used in many industries such as textiles and printing. Mittal et al., (2007), stated that it is one of the acidic/anionic dyes which is commonly used in textile, printing, paper, food and pharmaceutical industries and research laboratories. The molecular formula of methyl orange is $C_{14}H_{14}N_3NaO_3S$.

Methyl orange is a useful for pH indicator and titrations due to its clear colour change. It exists almost entirely as the yellow negative ion in the solution of more basic than pH 4.4 and protonated to form a red dipolar ion in solution which is more acidic that pH 3.2. Senese (2005) reported that methyl orange is synthesized by diazotization which includes sulfanilic acid, sodium nitrite, and dimethylaniline. The sulfanilic dissolved in dilute aqueous solution and diazonium salt is produced when sodium nitrite is added to the solution. The diazonium salt then coupled with dimethylaniline.

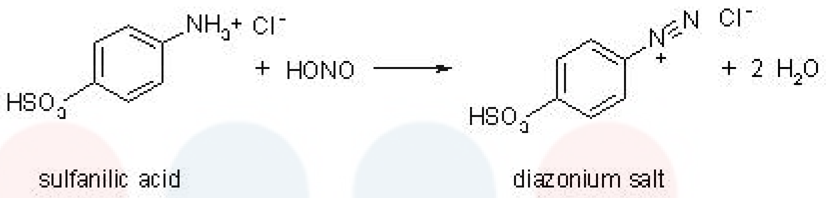


Figure 2.2.1 : Production of diazonium salt

(Source: Senese, 2005)

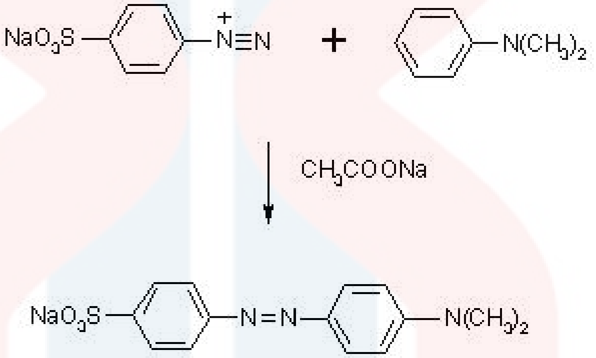


Figure 2.2.2: Coupling of diazonium salt with dimethylaniline

(Source: Senese, 2005)

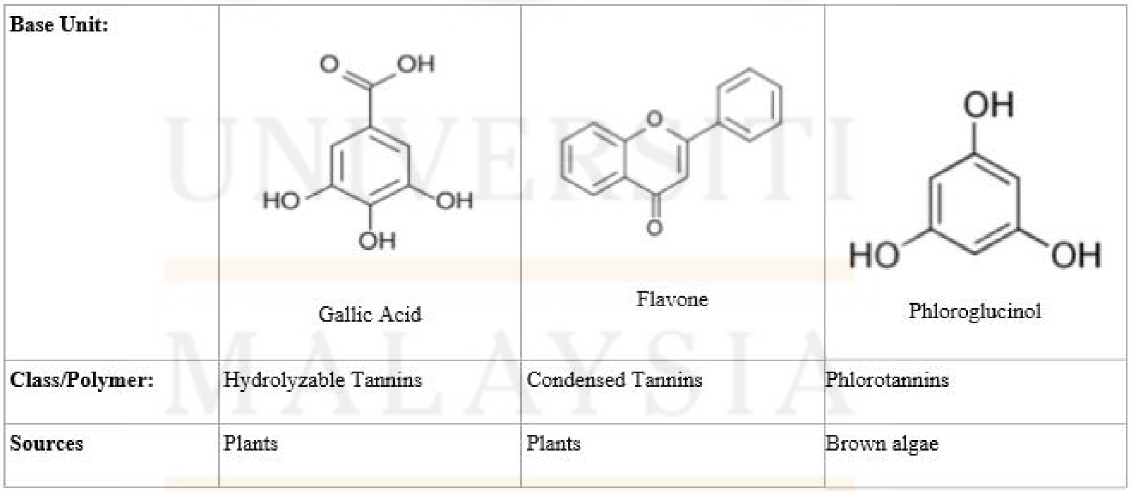
2.3 Catalyst

The catalyst is used to speed up the rate of reaction (Clark, 2002). The catalyst helps in an acceleration of chemical reaction and forming a bond with reacting molecules and by allowing these to react to a product, which detaches from the catalyst, and leaves it unaltered for further reactions (Chorkendorff & Niemantsverdriet, 2007). The catalyst will be used in this proposal is nickel catalyst. Nickel is used as it is abundance in amount, suitable for many applications, economically feasible compared to other metal, low in price, good stabilities and appreciable catalytic activities (Saeed et al., 2016). Saeed et al., (2016) also reported that nickel oxides get much attention since it is useful for many electrochemical systems such as fuel cells, batteries, and electrolyzers. Nickel has many forms of oxides (Jancovic et al., 2008) and these oxides are rich in oxygen and make nickel can exist in many oxidation state (Saeed et al., 2016).

2.4 Tannin and Chitosan

MacAdam et al., (2003) reported that tannin is a group of chemical compounds which are produced by a number of broad leaf forage plants which can bind protein. Tannins are bitter plant polyphenols which bind proteins (Ashok & Upadhyaya, 2012). The segregation of tannins in plant would not disrupt the metabolism activities which carried out by the proteins (MacAdam et al., 2003). Tannins are found in shapeless yellowish or light brown colour powder, flakes or sponge (Ashok & Upadhyaya, 2012). It is used in preserving (tanning) the leather because the tannin bind to the collagen protein in animal skins which preventing the microbial breakdown (MacAdam et al., 2003). Ashok & Upadhyaya, (2012) declared that dyeing, photography, refining wine and beer and astringent of medicine also used tannins in the process. Khanbabaee & Ree (2001) expressed that tannins are used in dyestuff industry as a caustics for cationic dyes (tannin dyes) and the production of inks (iron gallate ink).

Chitosan is a linear-chain copolymer composed of D-glucosamine and N-acetyl-D-glucosamine that obtained by the partial deacetylation of chitin (Alvarenga, 2011). Alvarenga, (2011) also reported that it is the methyl orange plentiful basic polymer and its structure is similar to cellulose. Mentioned by Dutta et al.,(2004), in textiles industries, chitosans able to remove methyl orange dyes from dye processing effluents. Bhavani & Dutta (1999) also studied that chitosans have been used as an adsorbent for in methyl orange of colour from dye house effluents. Chitosans have been used in photography, biotechnology, cosmetics, food processing, biomedical products (artificial skin, wound dressing, contact lens), system of controlled liberation of medicines (capsules and microcapsules), treatment of industrial effluents for removal of metallic and coloring ions (Alvarenga, 2011). Kumar (2000) stated that chitosans have been used in many researches due to its biocompability, non-toxicity and biodegradability.



Base Unit:	Gallic Acid	Flavone	Phloroglucinol
Class/Polymer:	Hydrolyzable Tannins	Condensed Tannins	Phlorotannins
Sources	Plants	Plants	Brown algae

Figure 2.4 : Groups of tannin

(Source: Ashok & Upadhyaya, 2012)

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Nickel nitrate hexahydrate ($Ni(NO_3)6H_2O$), tannin and chitosan were purchased from Sigma Aldrich from Iceland. Glutaraldehyde ($C_5H_8O_2$) was purchased from R&M Chemicals from Malaysia. Hydrogen peroxide (H_2O_2) was purchased from Bendosen from Malaysia. Methyl orange ($C_{14}H_{14}N_3NaO_3S$) was purchased from Merck, Germany.

3.2 Instrumentation

Fourier Transform Infrared (FTIR) from Thermo Fisher Scientific with model iZ10 from Malaysia was used to observe the different functional groups. The images from Scanning Electron Microscopy (SEM) were obtained from model JOEL JSM-6360LA. X- Ray Diffraction (XRD) from Bruker AXS model D2 with serial number 208439 from Germany was used to identify the crystallinity and phase components of samples. UV-Visible spectrophotometer from Thermo Fisher Scientific model Genesys 20 from Malaysia was used to observe the absorbance of the reaction mixture.

3.3 Methodology

3.3.1 Preparation of tannin chitosan support

3.0 g of tannin was added to 100 ml of deionized water, followed by 5.0 g of chitosan. The mixture was stirred for 3 hours at room temperature. 50.0 ml of glutaraldehyde solution was added to the mixture. The mixture was stirred for 6 hours on magnetic stirred at 318 K. The tannin chitosan support was filtered, washed with deionized water and was dried in vacuum for 12 hours.

3.3.2 Preparation of nickel catalyst

The catalyst was prepared by impregnation method. Nickel nitrate hexahydrate, $Ni(NO_3)6H_2O$ was dropped one at a time on the tannin chitosan support. The tannin chitosan support containing $Ni(NO_3)6H_2O$ was dried in the oven for 3 hours at 315 K to remove all the volatile component.

3.3.3 Characterization of catalyst

The catalyst was characterized by Fouirer Transform infra-red (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD was used to identify the sample crystalline phased. SEM was used to identify the surface methyl orange morphology and size of the catalyst. FTIR was used to observe the various peaks of nickel catalysts.

3.3.4 Catalytic experiment

The catalytic experiment was according to the method proposed by Saeed et al., (2016). The nickel tannin chitosan oxidative degradation of methyl orange was carried out at three different temperatures (313 K, 323 K and 333 K). 40ml of dye solution was poured in the flask. The flask was heated using the hotplate with the stirrer at desired temperature. 0.5 ml sample was taken after stirring at desired temperature for 30 minutes to observe any variation in concentration of dye during heating and stirring period. 1 ml of H_2O_2 was added to the flask while stirring mixture continuously. 0.5 ml sample was taken after stirring at desired temperature for 30 minutes to observe any variation in concentration of dye. Then, 100 mg of nickel catalyst was added into the flask and stirred continuously. Then, 0.5 ml sample was taken after stirring at desired temperature for 30 minutes. UV-Visible spectrophotometer was used to analyse the reaction mixture. The wavelength of 464 nm was used for methyl orange dyes. The percentage of degradation of dye was calculated by using:

$$\text{Degradation (\%)} = [(R)_0 - (R)_t] / (R)_0 \text{ X } 100\% \qquad (1)$$

where $(R)_0$ representing initial concentration and $(R)_t$ representing the concentration of dye at a various time interval.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization Of Nickel Doped Tannin Chitosan

4.1.1 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) was used to observe the various peaks that showed different functional groups in the tannin chitosan support and nickel catalyst.

Figure 4.1.1.1 and 4.1.1.2 showed that the FTIR spectrum of tannin chitosan support and nickel catalyst respectively. From FTIR spectrum of tannin chitosan support, a broad peak was observed at 3211.21 cm^{-1} which can be assigned to (OH) stretching vibration. A weak peak at 2900 cm^{-1} can be attributed (CH_2) stretching vibration. A medium intensity peak at 1606.38 cm^{-1} can be assigned to (NH) stretching vibration. However, the peaks at 1539.05 cm^{-1}, 1445.48 cm^{-1} and 1323.79 cm^{-1} can be attributed as (C=C) and (NO) stretching vibration respectively. A strong peak at 1199.69 cm^{-1} and 1026.94 cm^{-1} can be attributed to (CO) stretching vibration.

Similarly, shift in (OH) peak in nickel catalyst indicated the involvement of OH functional group in bonding with nickel. The shift in (NH) peaks at 1567.52 cm^{-1} indicated the involvement of NH group binding with nickel.

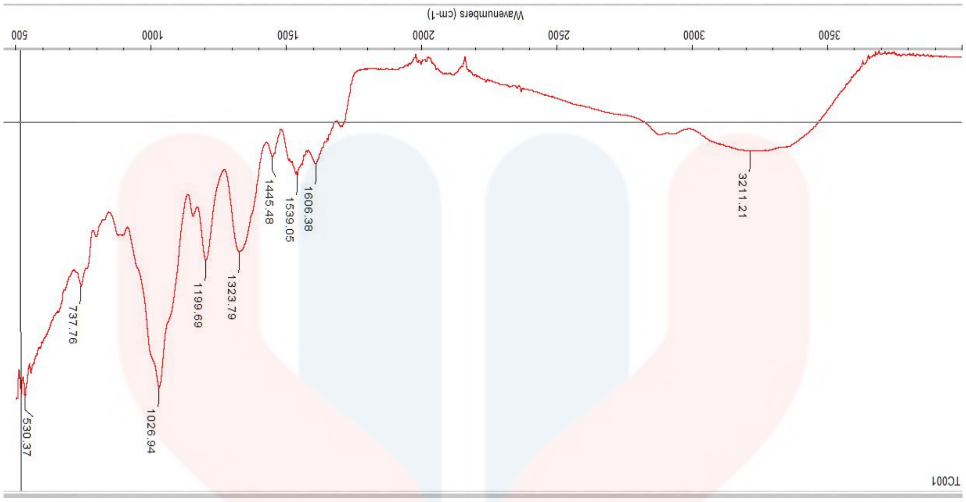


Figure 4.1.1.1 : Fourier Transform Infrared spectrum for tannin chitosan support

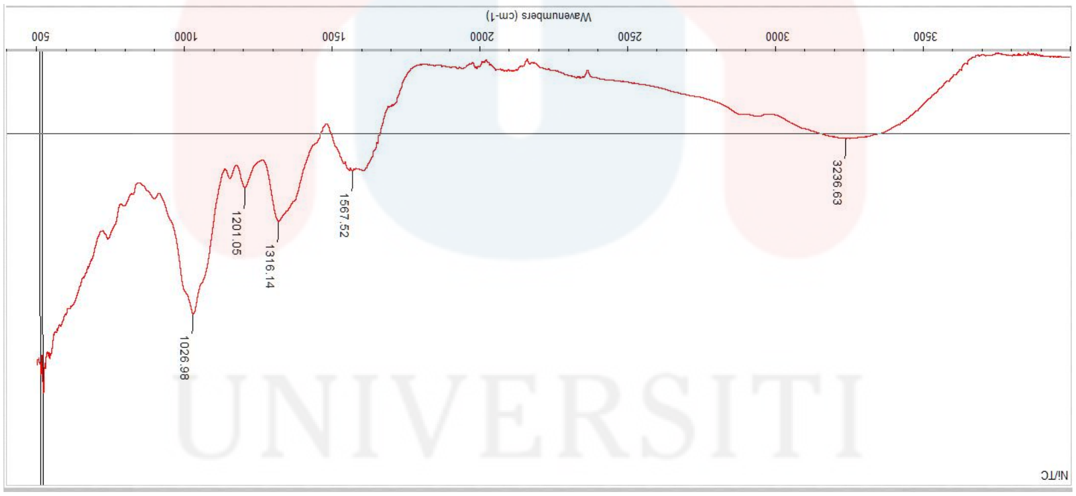


Figure 4.1.1.2 : Fourier Transform Infrared spectrum for nickel catalyst

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4.1.2 Scanning Electron Microscopy (SEM)

The scanning of tannin chitosan support and nickel catalyst was investigated by using SEM analysis. SEM offers a relatively simple method of studying the surface morphology of samples at high magnification under optimal conditions (Gomes et al., 2010).

From figure 4.1.2.1 and 4.1.2.2, tannin chitosan support have a smooth surface morphology at 1µm with 20000 times magnification. This result was supported by Shih et al., (2009) which stated that when chitosan content in blend films increases, their surface tends to become smoother. However, when the nickel was dropped on the tannin chitosan support surface, the nickel was stuck on the tannin chitosan support at 2 µm with 6000 magnification. This showed that the tannin chitosan supported the nickel which has crystalline structure.

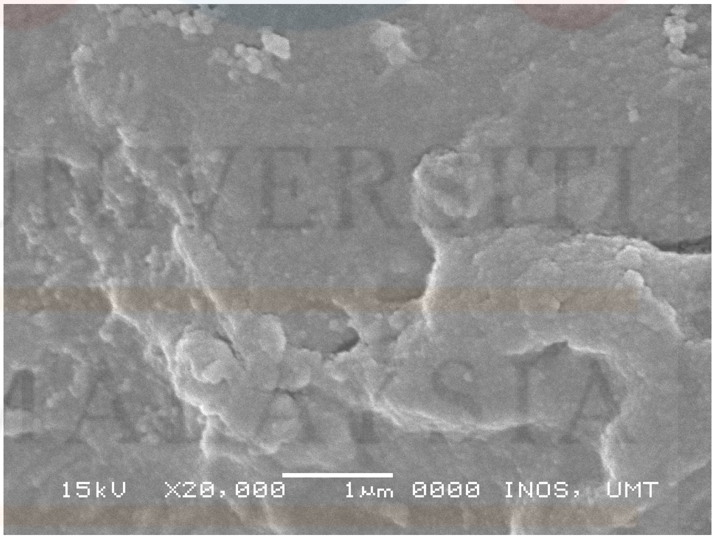

Figure 4.1.2.1 : Scanning Electron Microscopy for tannin chitosan support

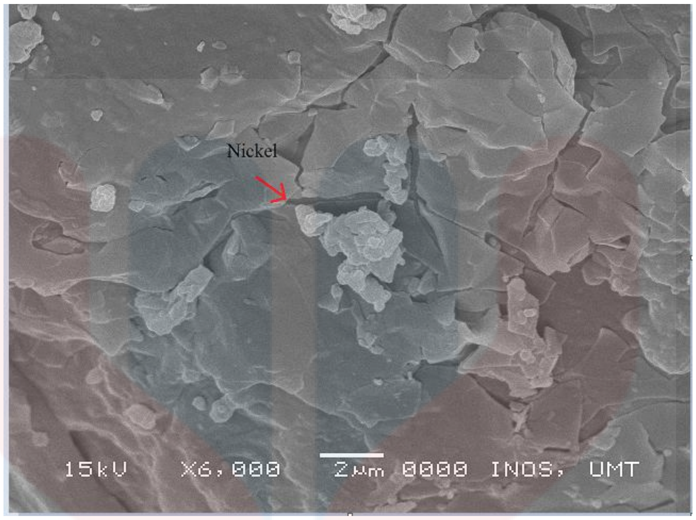

Figure 4.1.2.2 : Scanning Electron Microscopy for nickel support

4.1.3 X-ray Diffraction (XRD)

The crystallinity and phase components of samples were examined by powder X-ray diffraction.

The corresponding lattice plane value of tannin chitosan support were at (-1 -1 -4), (-2 -1 -4) and (0 -2 0) with lattice parameter of a=5.02 Å . The d spacing values were 1.18, 1.095 and 1.255. The crystallite sizes were 32.24, 34.74 and 30.31 nm respectively. The percentage of amorphous of tannin chitosan support was 64.4 % higher than the percentage of crystallinity which was only 35.6 %. The corresponding lattice plane value of tannin chitosan support were at (-1 -3 -1), (0 -3 -2) and (-1 -2 -2) with lattice parameter of a=12.14 Å. The d spacing value were 3.660, 3.367 and 4.047 and the crystallite size were 18.8, 20.44 and 17 nm respectively. The percentage of amorphous of nickel catalyst was 56.7 % higher than the percentage of crystallinity which was only 42.3 %. Both tannin chitosan support and nickel catalyst had monoclinic crystal system and crystallinity of both spectrum was noticed from 10.002 to 89.977.

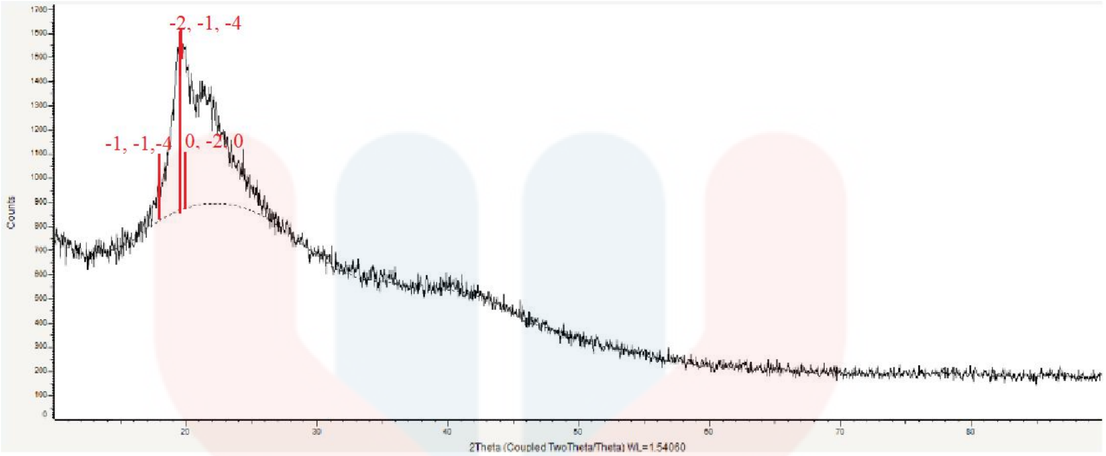

Figure 4.1.3.1 : X-ray Diffraction spectrum of tannin chitosan support

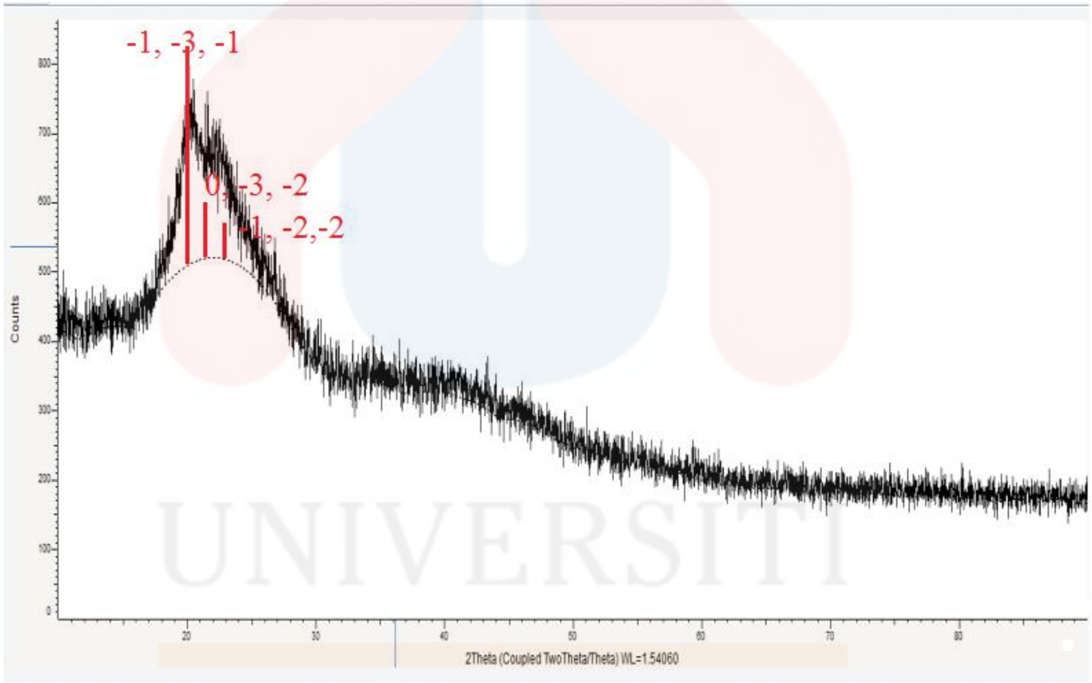

Figure 4.1.3.2 : X-ray Diffraction spectrum of nickel catalyst

4.2 Catalytic Degradation

Before the catalytic degradation experiment was done, a calibration curve of methyl orange with distilled water and methyl orange with H_2O_2 were obtained to identify the concentration of solutions for each absorbance.

The catalytic experiment were tested by using four solutions which are 40 ml of methyl orange alone, 40 ml of methyl orange with 1 ml of H_2O_2, 40 ml of methyl orange with 100 mg of nickel catalyst and 40 ml of methyl orange, 1 ml of H_2O_2 and 0.1g of nickel catalyst. The catalytic experiments were carried out in three different temperatures (313 K, 323 K and 333 K) to observe the percentage degradation of the dye.

From figure 4.2.1, the degradation of methyl orange was highest at 313 K and the lowest is at 333 K. The degradation of methyl orange decreased from 69.2 % in the first 30 minutes to 30.8% after 90 minutes. However, the degradation of methyl orange was highest at 333 K and lowest at 313 K from the degradation of methyl orange with nickel catalyst. The percentage increased from 25 % at the first 30 minutes to 62.5 % after 90 minutes. This was because the catalyst will enhanced the degradation process in methyl orange solution. This result can be proved by the previous research made by Bhakya et al., (2015). Bhakya et al., (2015) reported that the increasing dose of catalyst increased the degradation of dyes.

For the catalytic degradation of methyl orange with H_2O_2 and methyl orange with H_2O_2 and nickel catalyst, both solutions have highest percentage degradation at 313 K and lowest at 333 K. From figure 4.2.3, the methyl orange degraded from 69.2 % at the first 30 minutes and decrease to 30.8 % at 90 minutes. Similarly at 333 K in figure 4.2.4, the degradation of methyl orange decreased from 85.6 % to 70 % after 30 and 90 minutes respectively. This result can be related to the previous research done by Youssef et al., (2016). Youssef et al., (2016) reported that the degradation efficiency of methyl orange decreased when high dosage of H_2O_2 was used mainly because of the scavenging effect of excessive H_2O_2 to HO.

Table 4.2.1 : Table of degradation of MO

Temperature (K)	Absorbance	Degradation (%)
313	2.963	69.2
323	2.961	42.2
333	2.958	30.8

Table 4.2.2 : Table of degradation of MO with nickel catalyst

Temperature (K)	Absorbance	Degradation (%)
313	3.18	25.0
323	3.2	37.5
333	3.24	62.5

Table 4.2.3 : Table of degradation of MO with H_2O_2

Temperature (K)	Absorbance	Degradation (%)
313	2.843	69.2
323	2.865	42.2
333	2.880	30.8

Table 4.2.4 : Table of degradation of MO with H_2O_2 and nickel catalyst

Temperature (K)	Absorbance	Degradation (%)
313	2.909	85.6
323	2.995	73.0
333	3.017	70.0

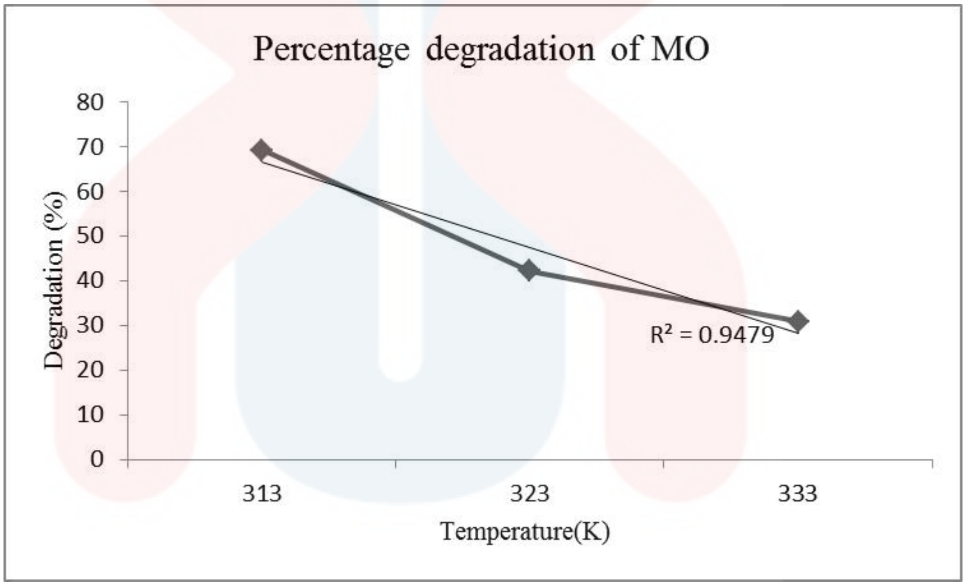

Figure 4.2.1 : Percentage degradation of methyl orange

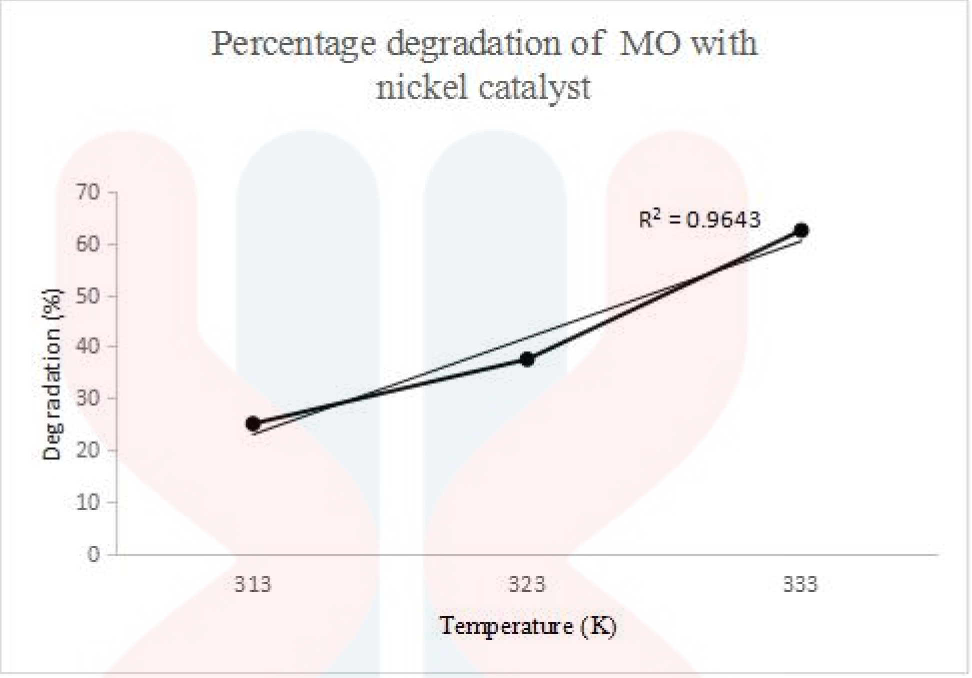

Figure 4.2.2 : Percentage degradation of methyl orange with nickel catalyst

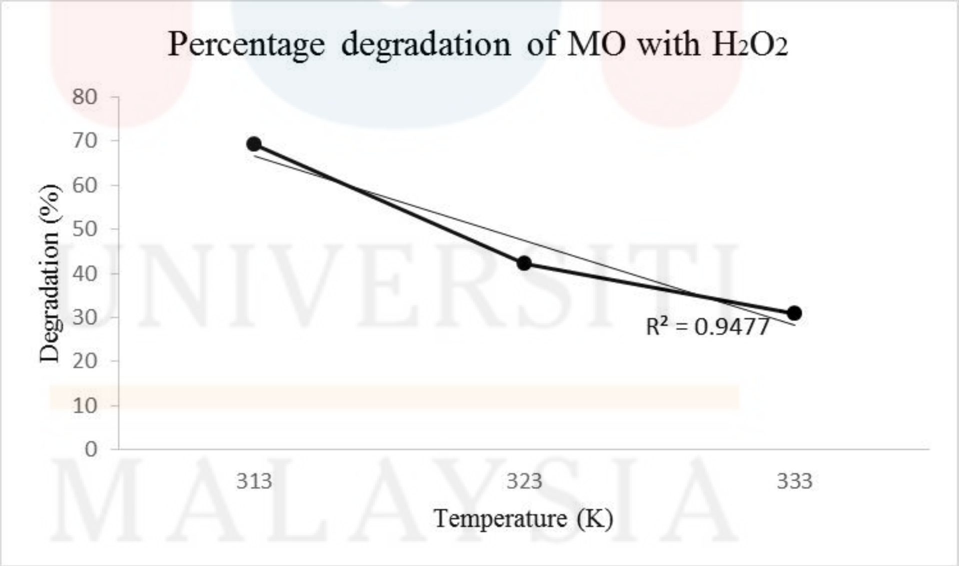

Figure 4.2.3 : Percentage degradation of methyl orange with H_2O_2

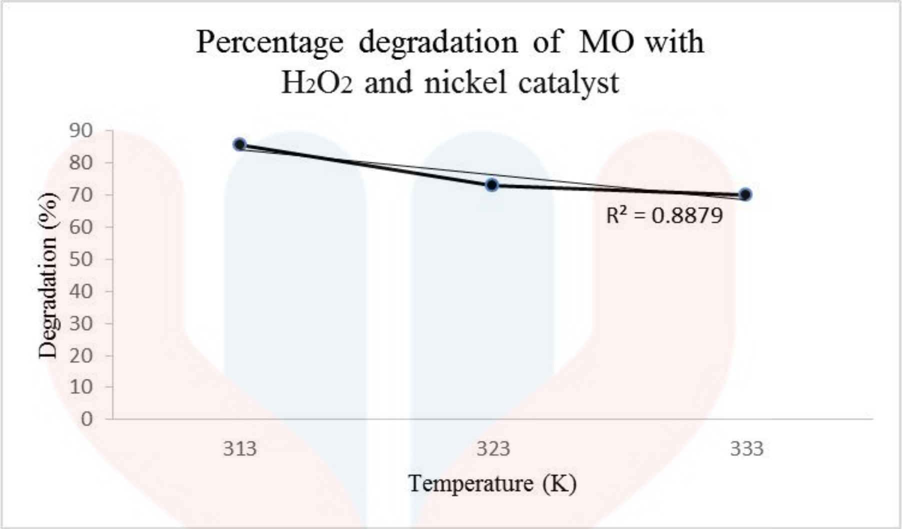

Figure 4.2.4 : Percentage degradation of methyl orange with H_2O_2 and nickel catalyst

4.3 Kinetic Activity

The kinetics activity were tested by using 40 ml of methyl orange, 40 ml of methyl orange with catalyst, 40 ml of methyl orange with 1 ml of H_2O_2 and 40 ml methyl orange, 1 ml H_2O_2 and 100 mg of catalyst. Each solution were left at room temperature for 1 hour and the absorbance were taken every 5 minutes.

According to Youssef et al., (2016), zero, first- and second-order reaction kinetics were used to study the degradation kinetics of methyl orange. The equation expression was presented as below:

- Zero-order reaction kinetics:

$$(dc/dt) = -k_0 \tag{2}$$

- First-order reaction kinetics:

$$(dc/dt) = -k_1C \tag{3}$$

- Second-order reaction kinetics:

$$(dc/dt) = -k_2C^2 \tag{4}$$

where C is the concentration of methyl orange, k_0, k_1 and k_2 are the apparent kinetic rate constants of zero, first- and second-order reaction kinetics respectively and t is the reaction time.

By integrating the equation (2) to (4), equation (5) to (7) can be obtained.

- $C_t = C_0 - K_0t$ (5)

- $Ct = C_0e^{-k1t}$ (6)

- $1/C_t = 1/C_0 + k_2t$ (7)

where Ct is the concentration of methyl orange at reaction time, t .

4.3.1 Methyl orange

Figure 4.3.1.1, 4.3.1.2 and 4.3.1.3 showed the kinetic activity of the concentration of methyl orange. The kinetic activity of methyl orange was obeyed zero-order reaction kinetics. The degradation efficiency of methyl orange was decreased within 15 minutes. From figure 4.3.1.2, the graph of 1/ Concentration of methyl orange was first-order reaction kinetics. The degradation efficiency of methyl orange was increased within 15 minutes. From figure 4.3.1.3, the graph of $Ln(R_0/R_t)$ was a first-order reaction kinetics. The degradation efficiency increased gradually within 15 minutes and increased slowly until 1 hour.

Regression analysis based on the zero, first-order and second-order reaction kinetics were conducted and the results are shown in figure 4.3.1.1, 4.3.1.2 and 4.3.1.3. The results showed that the regression coefficient (R^2) obtained in first-order reaction kinetics in figure 4.3.1.2 is 0.6633 and better than the zero order reaction kinetics (R^2=0.5932) and first-order reaction kinetics in figure 4.3.1.3 with the R^2 was 0.6506.

Since the concentration of methyl orange obeyed zero-order reaction kinetics, equation (4) was used to calculate the kinetic rate constants, $k_{o.}$ The concentration of methyl orange at reaction time, C_t was taken at the concentration at 30 minutes which was 0.0057 and initial concentration was 0.008. The apparent kinetic rate constants, k_o of degradation of methyl orange was found to be 7.66x10^{-5} M^{-1} min^{-1} at concentration of methyl orange was 0.01M at room temperature.

Table 4.3.1 : Kinetic activity of methyl orange

Time (minute)	Absorbance (A)	Concentration	1/ Concentration	Ln (Ro/Rt)
5	2.968	0.008	125	1
10	2.964	0.007	142.88	1.14
15	2.961	0.006	166.67	1.33
20	2.96	0.0059	169.49	1.36
25	2.959	0.0058	172.41	1.38
30	2.958	0.0057	175.44	1.4
35	2.958	0.0057	175.44	1.4
40	2.957	0.0056	178.57	1.42
45	2.957	0.0056	178.57	1.42
50	2.956	0.0056	178.57	1.42
55	2.955	0.0055	181.82	1.45
60	2.955	0.0055	181.82	1.45

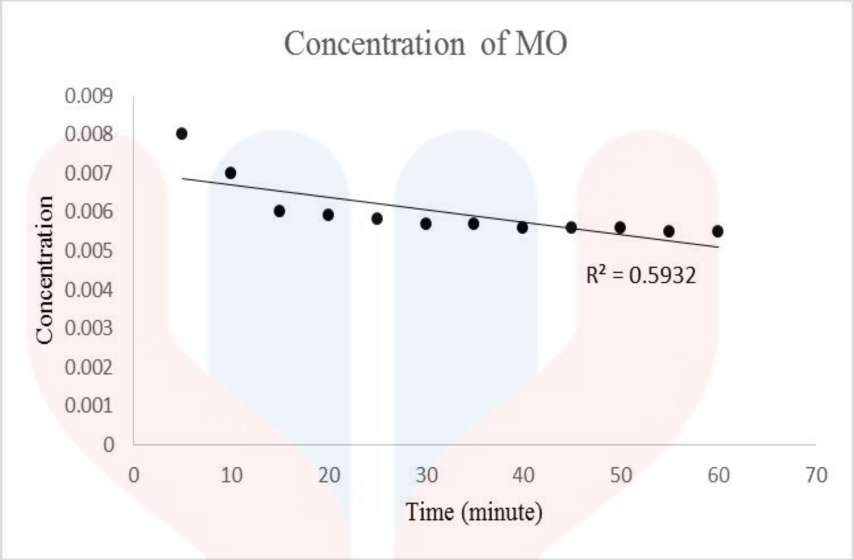

Figure 4.3.1.1 : Concentration of methyl orange

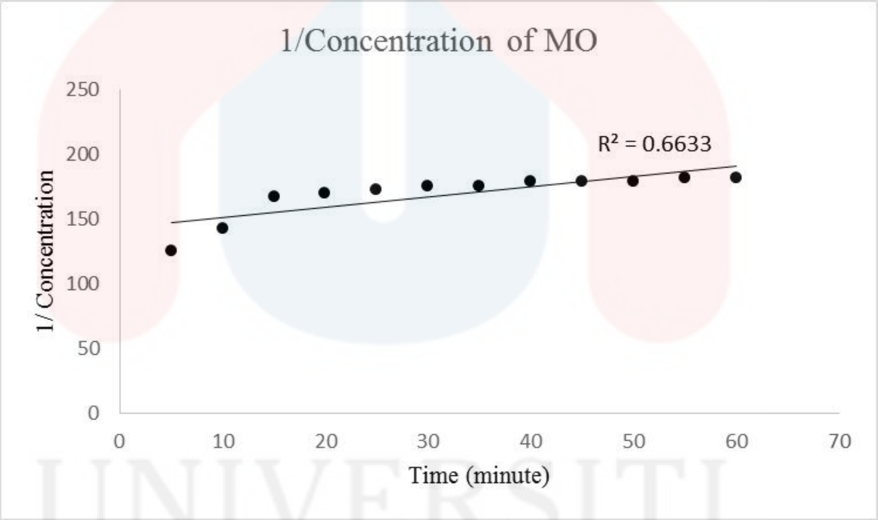

Figure 4.3.1.2 : 1/ Concentration of methyl orange

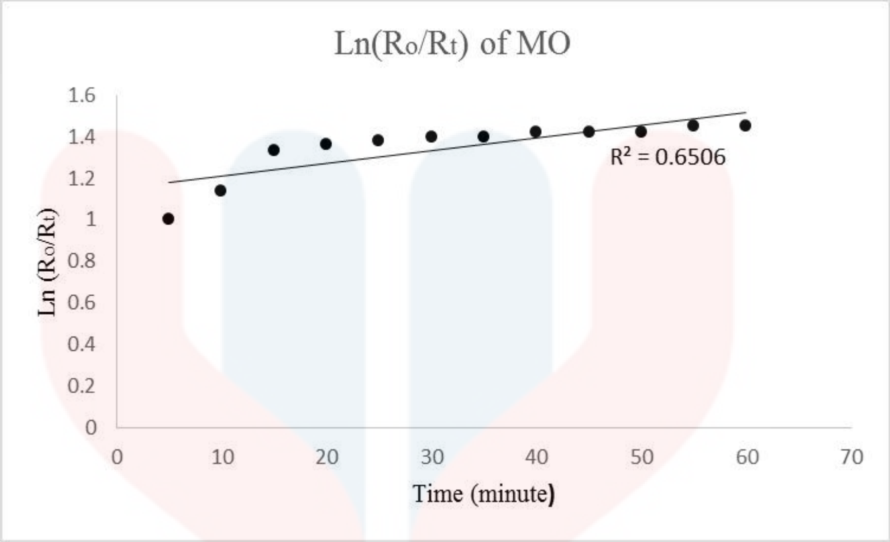

Figure 4.3.1.3: Ln(R_o/R_t) of methyl orange

4.3.2 Methyl orange with nickel catalyst

Figure 4.3.2.1, 4.3.2.2 and 4.3.2.1 showed the kinetic activity of methyl orange with nickel catalyst.

From figure 4.3.2.1, the concentration of methyl orange with catalyst was zero-order reaction kinetics. The degradation efficiency of methyl orange was increased gradually for an hour. From figure 4.3.2.2, the graph of 1/ Concentration of methyl orange with catalyst was first-order reaction kinetics. The degradation efficiency of methyl orange was decreased. From figure 4.3.2.3, the graph of Ln(R_0/R_t) was a first-order reaction kinetics. The degradation efficiency decreased gradually slowly.

The results showed that the regression coefficient (R^2) obtained in zero-order reaction kinetics in figure 4.3.2.1 is 0.9851 and better than the first order reaction kinetics (R^2=0.9311) and first-order reaction kinetics in figure 4.3.2.3 with the R^2 was 0.9322.

Since the concentration of methyl orange with nickel catalyst obeyed zero-order reaction kinetics, equation (4) was used to calculate the kinetic rate constants, k_o. The concentration of methyl orange at reaction time, C_t was taken at the concentration at 30 minutes which was 0.011 and initial concentration was 0.007. The apparent kinetic rate constants, k_o of degradation of methyl orange was found to be -1.33x10^{-4} M^{-1} min^{-1} at concentration of methyl orange with nickel catalyst was 0.01M at room temperature

Table 4.3.2 : Kinetic activity of methyl orange with nickel catalyst

Time (minute)	Absorbance (A)	Concentration	1/ Concentration	Ln (Ro/Rt)
5	2.971	0.007	142.86	11.86
10	2.991	0.008	125	10.37
15	2.992	0.0085	117.65	9.76
20	2.996	0.009	111.11	9.22
25	3.011	0.01	100	8.3
30	3.019	0.011	90.91	7.55
35	3.028	0.012	83.33	6.92
40	3.041	0.0125	80	6.64
45	3.044	0.013	76.93	6.38
50	3.045	0.013	76.92	6.38
55	3.048	0.014	71.83	5.93
60	3.06	0.015	66.67	5.53

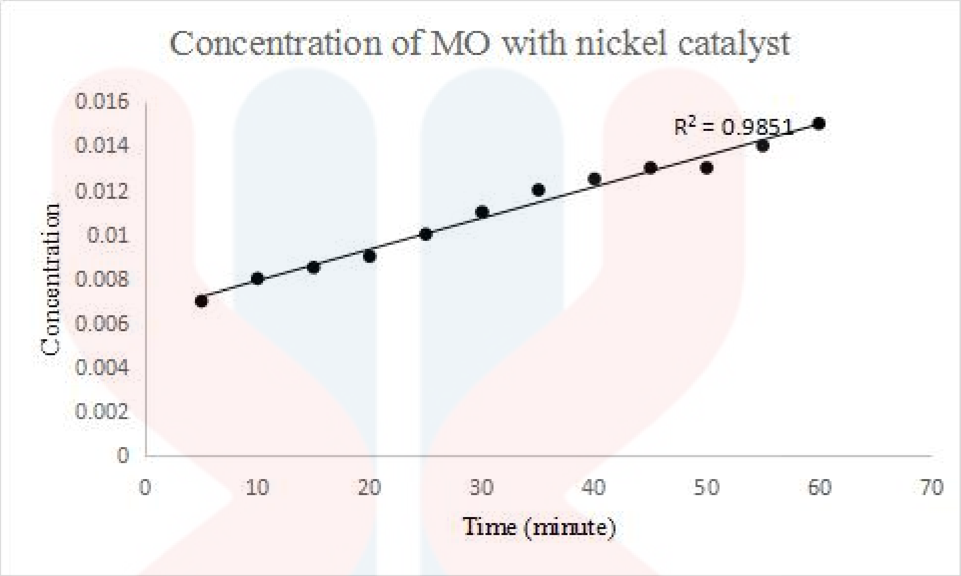

Figure 4.3.2.1 : Concentration of methyl orange with nickel catalyst

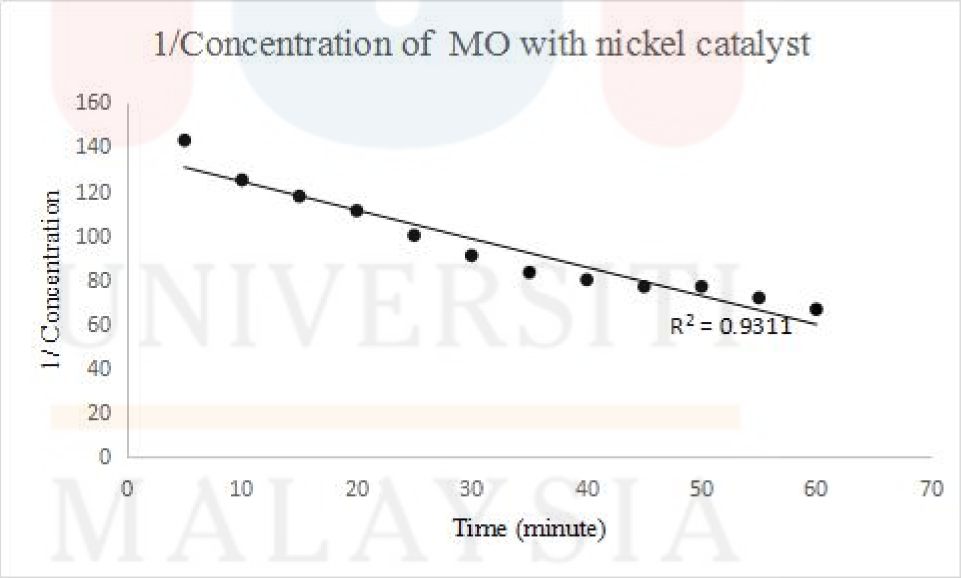

Figure 4.3.2.2 : 1/ Concentration of methyl orange with nickel catalyst

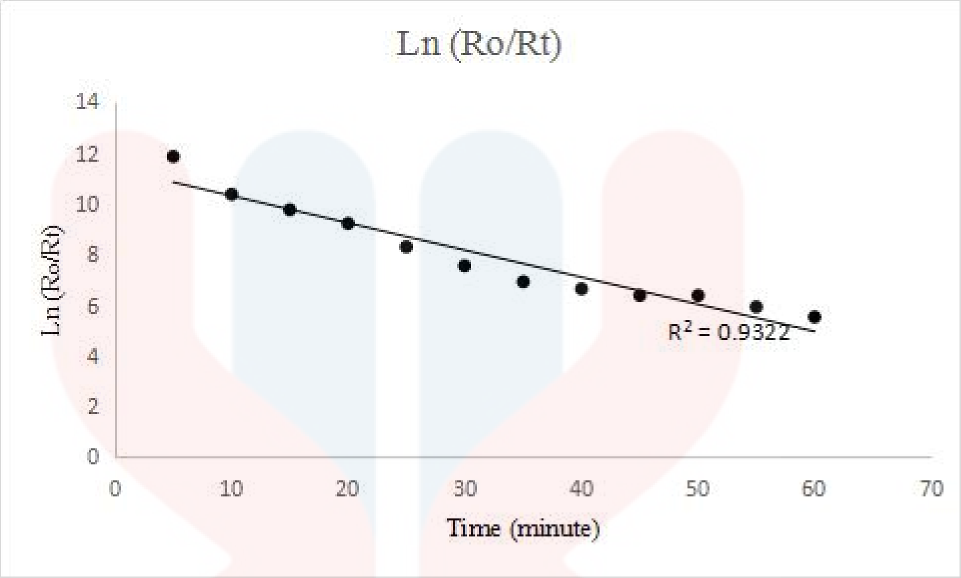

Figure 4.3.2.3 : Ln (R_o/R_t) of methyl orange with nickel catalyst

4.3.3 Methyl orange with H_2O_2

Figure 4.3.3.1, 4.3.3.2 and 4.3.3.3 showed the kinetic activity of methyl orange with H_2O_2. From figure 4.3.3.1, the concentration of methyl orange with H_2O_2 was zero-order reaction kinetics. The degradation efficiency of methyl orange was increased gradually within 25 minutes. From figure 4.3.3.2, the graph of 1/ Concentration of methyl orange with H_2O_2 were first-order reaction kinetics. The degradation efficiency of methyl orange was decreased within 30 minutes. From figure 4.3.3.3, the graph of Ln(R_0/R_t) was a first-order reaction kinetics. The degradation efficiency decreased gradually within 40 minutes.

The results showed that the regression coefficient (R^2) obtained in zero-order reaction kinetics in figure 4.3.3.1 is 0.8905 and better than the first order reaction kinetics (R^2=0.7351) and first-order reaction kinetics in figure 4.3.3.3 with the R^2 was 0.7343.

Since the concentration of methyl orange with H_2O_2 obeyed zero-order reaction kinetics, equation (4) was used to calculate the kinetic rate constants, $k_{o.}$ The concentration of methyl orange at reaction time, C_t was taken at the concentration at 30 minutes which was 0.004 and initial concentration was 0.002. The apparent kinetic rate constants, k_o of degradation of methyl orange was found to be -6.67×10^{-5} M^{-1} min^{-1} at concentration of methyl orange was 0.01M at room temperature.

Table 4.3.3 : Kinetic activity of methyl orange with H_2O_2

Time (minute)	Absorbance (A)	Concentration	1/ Concentration	Ln (Ro/Rt)
5	2.836	0.002	500	6.5
10	2.837	0.0025	400	5.2
15	2.838	0.003	333.33	4.33
20	2.84	0.0035	285.71	3.71
25	2.841	0.0038	263.16	3.42
30	2.843	0.004	250	3.25
35	2.844	0.0041	243.9	3.17
40	2.845	0.0042	238.1	3.095
45	2.845	0.0042	238.1	3.095
50	2.847	0.0043	232.56	3.023
55	2.849	0.0045	222.22	2.89
60	2.85	0.005	200	2.6

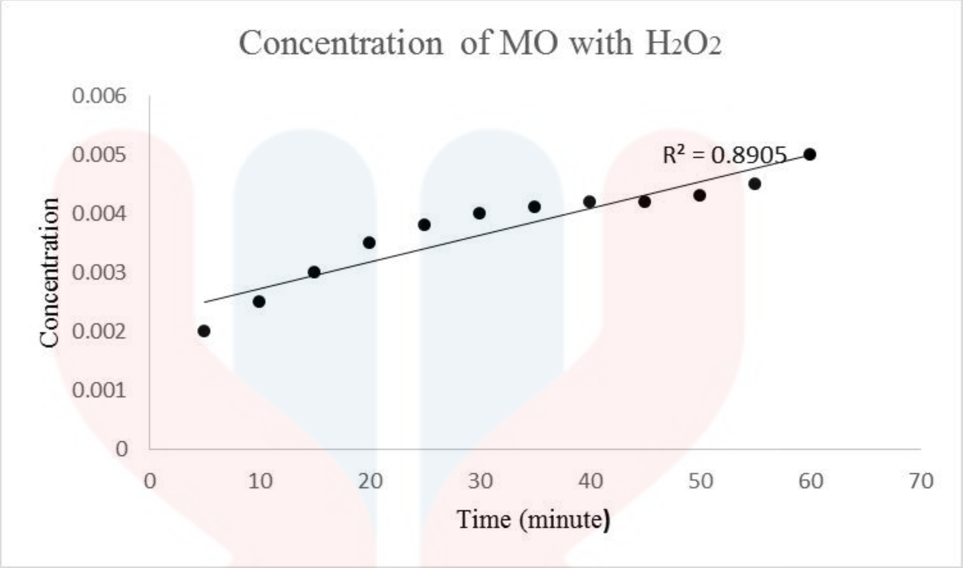

Figure 4.3.3.1 : Concentration of methyl orange with H_2O_2

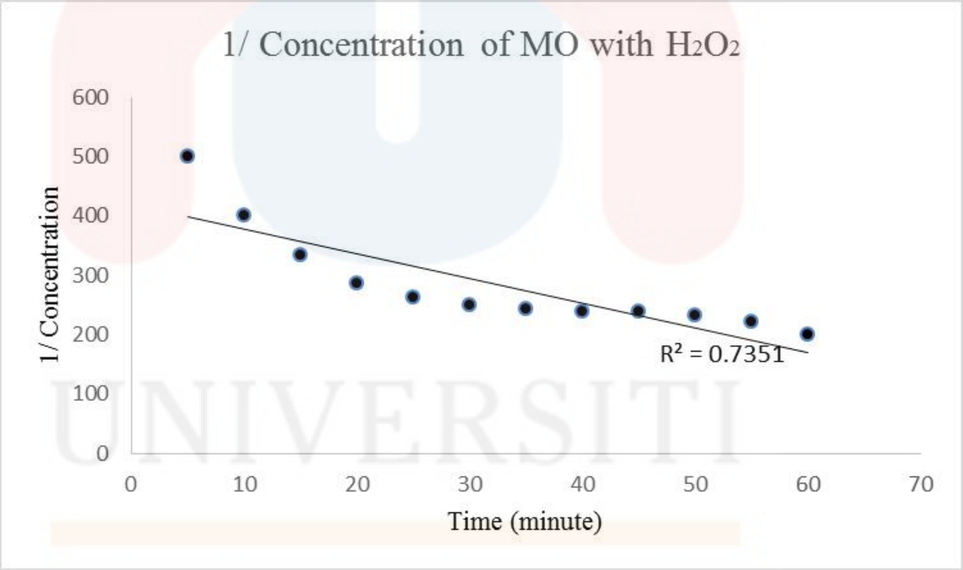

Figure 4.3.3.2: 1/ Concentration of methyl orange with H_2O_2

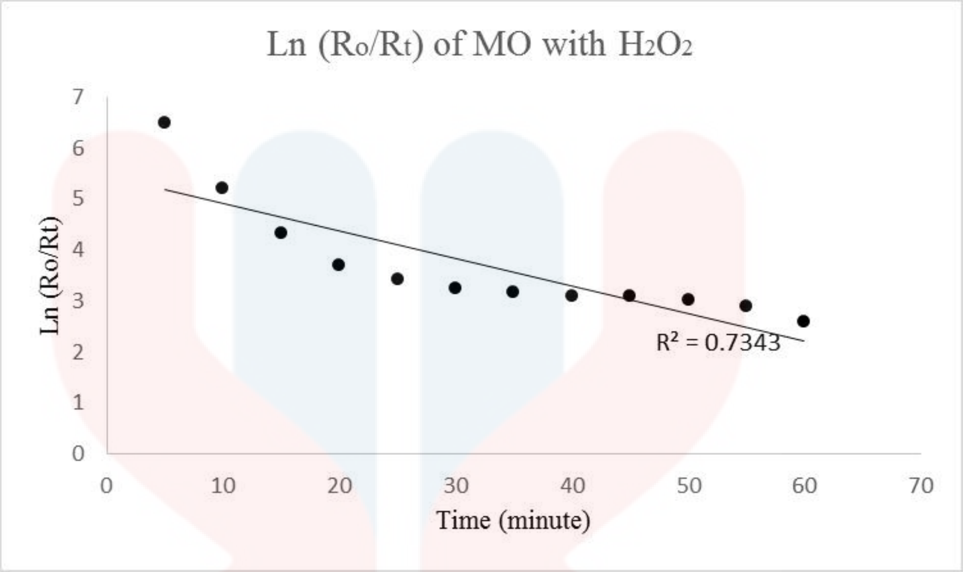

Figure 4.3.3.3 : Ln (R_o/R_t) of methyl orange with H_2O_2

4.3.4 Methyl orange with H_2O_2 and nickel catalyst

The kinetic activity of methyl orange, H_2O_2 and nickel catalyst were shown in figure 4.3.4.1, 4.3.4.2 and 4.3.4.3. From figure 4.3.4.1, the concentration of methyl orange with H_2O_2 and catalyst was zero-order reaction kinetics. The degradation efficiency of methyl orange was increased within one hour. From Figure 4.3.4.2, the graph of 1/ Concentration of methyl orange with H_2O_2 and catalyst was first-order reaction kinetics. The degradation efficiency of methyl orange was decreased within 45 minutes. From figure 4.3.4.3, the graph of Ln (R_0/R_t) was first-order reaction kinetics. The degradation efficiency decreased gradually within 35 minutes.

The results showed that the regression coefficient (R^2) obtained in zero-order reaction kinetics in figure 4.3.4.1 is 0.7262 and better than the first order reaction kinetics (R^2=0.7351) and first-order reaction kinetics in figure 4.3.4.3 with the R^2 was 0.726.

Since the concentration of methyl orange withH_2O_2 obeyed zero-order reaction kinetics, equation (4) was used to calculate the kinetic rate constants, $k_{o.}$ The concentration of methyl orange at reaction time, C_t was taken at the concentration at 30 minutes which was 0.0035 and initial concentration was 0.001. The apparent kinetic rate constants, k_o of degradation of methyl orange was found to be -8.33 x10^{-5} M^{-1} min^{-1} at concentration of methyl orange was 0.01M at room temperature.

Table 4.3.4.1 : Kinetic activity of methyl orange with H_2O_2 and nickel catalyst

Time (minute)	Absorbance (A)	Concentration	1/ Concentration	Ln (Ro/Rt)
5	2.828	0.001	1000	90
10	2.833	0.0015	666.67	60
15	2.836	0.002	500	45
20	2.837	0.0025	400	36
25	2.838	0.003	333.33	30
30	2.84	0.0035	285.71	25.71
35	2.842	0.0039	256.41	23.08
40	2.844	0.0041	253.9	21.85
45	2.848	0.0044	227.27	20.45
50	2.848	0.0044	227.27	20.45
55	2.851	0.005	200	18
60	2.857	0.006	166.67	15

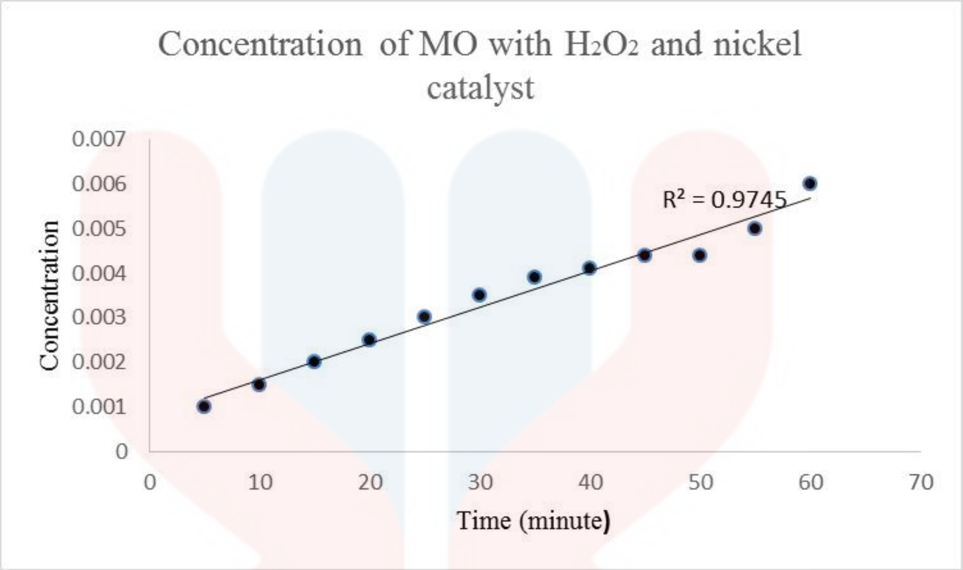

Figure 4.3.4.1 : Concentration of methyl orange with H_2O_2 and nickel catalyst

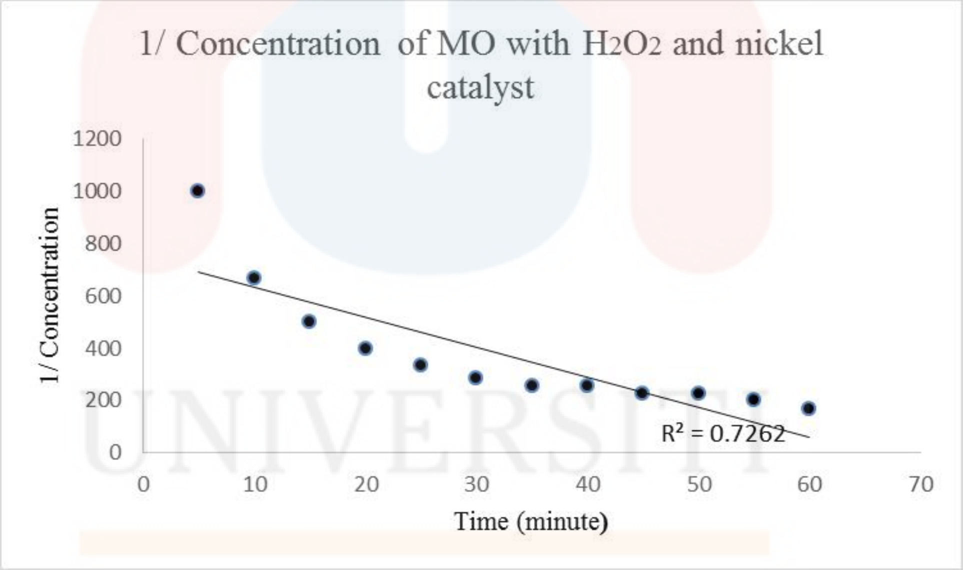

Figure 4.3.4.2 : 1/ Concentration of methyl orange with H_2O_2 and nickel catalyst

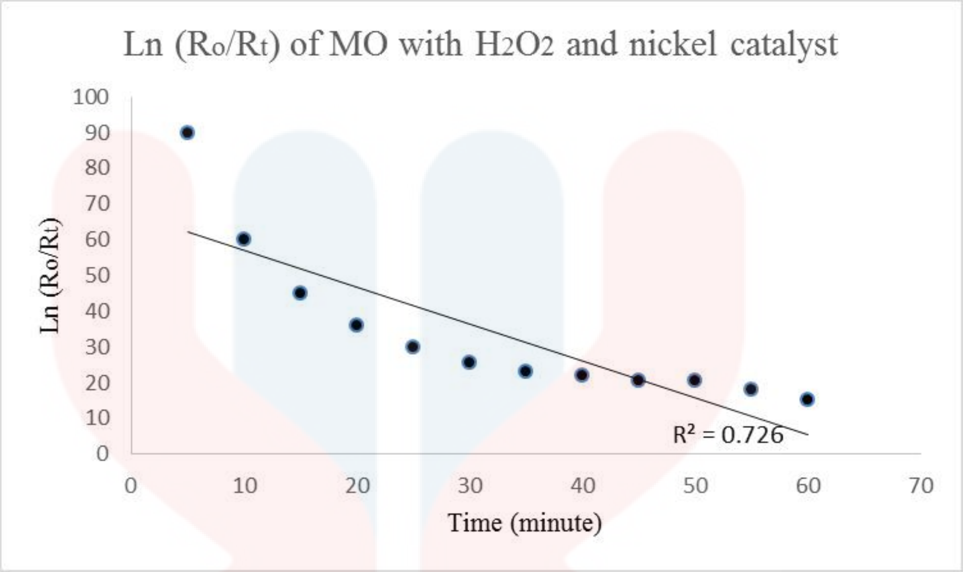

Figure 4.3.4.3 : Ln(R_o/R_t) of methyl orange with H_2O_2 and nickel catalyst

Table 4.3.4.2 : Summary of the results

Instruments	Function	Results obtained	Relationship
Fourier Transform Infrared (FTIR)	To observe the various peaks that indicate different functional groups in tannin chitosan support and nickel catalyst	Functional groups of OH, CH2, NH, C=C, NO and CO were observed at the peak of tannin chitosan support spectrum. The shift in OH and NH groups indicated the involvement of OH and NH groups with the nickel in nickel catalyst spectrum.	With the helped from the instruments, the results were obtained. This proved that the instruments can helped in identify the tannin chitosan support and nickel catalyst.
Scanning Electron Microscopy (SEM)	To identify the surface methyl orange morphology and size of the catalyst	Tannin chitosn support had a smooth surface morphology. When nickel was dropped on the support, nickel was stuck on the support.	
X-ray diffraction (XRD)	To identify the crystallinity and phase components of samples.	The percentage of amorphous of tannin chitosan support and nickel catalyst were 64.4% and 56.7% respectively higher than the percentage of crystallinity which were only 35.6% and 42.3%. Both tannin chitosan support and nickel catalyst had monoclinic crystal system.	
UV-Visible spectrophotometer	To observe the absorbance of the reaction mixture.	The degradation of methyl orange was highest at 313 K and the lowest is at 333 K. However, the degradation of methyl orange with nickel catalyst was highest at 333K and lowest at 313K. For catalytic degradation of methyl orange with H_2O_2 and methyl orange with H_2O_2 and nickel catalyst, both solutions have highest percentage degradation at 313 K and lowest at 333 K.	

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the prepared nickel catalyst has been characterized by impregnation method. The preparation of catalyst was used by obtained results. The tannin chitosan support and nickel catalyst were characterized by using FTIR, SEM and XRD.

FTIR was used to observe the functional groups for both tannin chitosan support and nickel catalyst. From the results obtained, the shift in OH and NH peaks at the nickel catalyst FTIR spectrum showed the involvement of OH and NH groups binding with nickel.

SEM was used to identify the surface morphology of the tannin chitosan support and the nickel catalyst. The tannin chitosan support has a smooth surface and the nickel was supported by the tannin chitosan support when it was dropped on the support.

XRD was used to examine the crystallinity and phase components of both tannin chitosan support and the nickel catalyst. From the spectrum of both tannin chitosan support and the nickel catalyst, both were amorphous phase and were a monoclinic crystal.

On the basis of catalytic activity, nickel catalyst exhibited moderate catalytic activity in degrading methyl orange. On the basis of percentage degradation, optimum temperature was 38 % where catalytic activity of methyl orange at maximum. These for an attempt to generate new catalyst with enhance catalytic activity in presence of H_2O_2.

5.2 Recommendations

As for recommendations, the future research should be tested using the real polluted water from industries such as from waste water textiles, food processing and cosmetics that used various dyes to make the products more colourful and interesting. Other than that, this research should be tested using different dyes such as natural dyes and synthetic dye that can pollute the environment such as methylene blue, crystal violet and others so that the colour waste water can be degraded by impregnation method. Besides that, different methods should be tested by researchers so that they can examine which method can degrade more dyes.

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