NICKEL AND PALLADIUM CATALYSTS FOR DEGRADATION OF DYE POLLUTANTS

by

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A report submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Natural Resources Science) with Honours

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DECLARATION

I declare that this thesis entitled “Nickel and palladium catalysts for degradation of dye pollutants” 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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Date : 10 December 2018

APPROVAL

"I hereby declare that I have read this thesis and in our opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Natural Resources Science) with Honours"

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Date : 23 / 12 / 2018

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Nickel and palladium catalysts for degradation of dye pollutants

ABSTRACT

Azo dyes are complicated organic molecules which are often tough to degrade. They additionally might also produce greater unsafe intermediates for the duration of treatment processes. A novel catalytic approach to deal with these dyes is the need of time. However, there is a need to optimize the effective amount of catalyst and suitable pH to degrade pollutants and establish the rate of reactions or rate of degradation. It is crucial for the conversion of dye pollutants to non-harmful ones. This study has been carried out to study the kinetics of nickel and palladium catalysts using UV-visible spectrophotometer. This study is focused on the preparation of nickel and palladium catalysts to degrade Congo Red and Methyl Orange dyes. The catalysts were prepared by reaction of nickel nitrate hexahydrate (Ni $(NO_3)_2 6H_2O$) and palladium chloride ($PdCl_2$) with the support of tannin-chitosan. The results revealed that the optimized pH for nickel and palladium to degrade the dyes used was at pH 6. The catalytic activity showed that 80 mg of palladium and 60 mg of nickel have the highest degradation efficiency. From this study, it is revealed that the most efficient degradation occurred when palladium degraded methyl orange with the kinetic analysis of R^2 equals to 0.9881 under optimized conditions.

Pemangkin nikel dan paladium untuk pemecatan bahan pencemar pewarna

ABSTRAK

Pewarna Azo adalah molekul organik rumit yang sukar untuk diuraikan. Mereka juga boleh menghasilkan perantaraan yang tidak selamat bagi tempoh proses rawatan. Pendekatan pemangkin novel untuk menangani pewarna ini adalah keperluan masa. Walau bagaimanapun, terdapat keperluan untuk mengoptimumkan jumlah pemangkin yang berkesan dan pH yang sesuai untuk merendahkan pencemaran dan menentukan kadar tindak balas atau kadar pemecatan. Penukaran bahan cemar pewarna kepada yang tidak berbahaya adalah penting. Kajian ini telah dijalankan untuk mengkaji analisis kinetik pemangkin nikel dan paladium menggunakan spektrofotometer yang boleh dilihat UV. Kajian ini memberi tumpuan kepada penyediaan nikel dan pemangkin paladium untuk menurunkan pewarna kongo merah dan metil oren. Pemangkin disediakan oleh tindak balas nikel nitrat hexahydrate ($Ni(NO_3)_2 6H_2O$) dan paladium klorida ($PdCl_2$) dengan sokongan tannin-chitosan. Hasilnya menunjukkan bahawa pH yang dioptimumkan untuk nikel dan palladium untuk merendahkan pewarna yang digunakan adalah pada pH 6. Aktiviti pemangkin menunjukkan bahawa 80 mg paladium dan 60 mg nikel mempunyai kecekapan pemecatan yang tertinggi. Melalui kajian ini, terbukti bahawa degradasi paling berkesan berlaku apabila palladium terdegradasi metil oren dengan analisis kinetik R^2 bersamaan dengan 0.9881 di bawah keadaan yang dioptimumkan.

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LIST OF ABBREVIATIONS

mg	milligram
mins	minutes
ml	mililitre
m/L	milligrams per litre
nm	Nanometer
pH	Potential of Hydrogen
ppm	Parts per million
R^2	Regression
UV-visible spectrophotometer	Ultra Violet -Visible spectrophotometer

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Thousands of synthetic dyes have been manufactured all over the world. Actually, there are approximately 10,000 different synthetic dyes available in the market with a global annual production of almost 800,000 tons (Ayadi & Souissi, 2015). Such dyes are defined as coloured matters and when applied they are to substrates may provide them with a permanent colour that by any means will not be affected by sun rays, soap and water. Each year, nearly 140 000 tons of synthetic dyes are lost into the environment because of the dyeing process. The discharge of dye-containing effluents has obvious negative effects. Those effluents are characterized by strong colours, high pH variations, high chemical oxygen demand (COD) and increased biotoxicity against bacteria (Umpuch & Sakaew, 2013).

A catalyst offers an alternative and energetically favourable mechanism to the non-catalytic reaction (Chorkendorff, 2005). Catalysts are the good approach to deal with dye pollutants. The conversion of dye pollutants to non-harmful dyes are optimized by the chemical reactions based on the effects of pH, catalyst loading and rate of degradation. Nickel and palladium are used as the catalyst for the degradation process of pollutants. These catalysts are chosen for the degradation of dye pollutants due to their abundances and feasibilities in the market.

1.2 Problem Statement

The use of dyes and their release into the environment by different industries have a huge impact on the ecosystem. A novel catalytic approach to deal with these dyes is the need of time. A suitable method for determining the reaction rate is required to study the degradation of pollutants. Furthermore, the study on kinetics, pH and catalyst loading of palladium and nickel catalyst based on tannin-chitosan support is limited. Therefore, there is a need to optimize the effective amount of catalyst to degrade pollutants and establish the rate of reactions or rate of degradation.

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1.3 Objectives

The objectives of this study are:

i) To study the kinetics of nickel and palladium catalysts using UV-visible spectrophotometer
ii) To optimize the effects of pH and catalyst loading for degradation of azo dyes

1.4 Scope of study

The study focused on the kinetics of nickel and palladium catalysts with tannin-chitosan support using UV-visible spectrophotometer. UV-visible spectroscopy is the measurement of the attenuation of a beam of light after through a sample or after reflection from sample surface. The measurements can be at a single wavelength or over an extended spectral range. The conditions for maximum Congo Red and Methyl Orange degradation were optimized in terms of catalyst loading and initial pH of the solution.

1.5 Significance of study

The effluents from clothes and Batik industries consist of large quantities of dye ingredients which have a strong detrimental impact on human health as well as on the environment due to their toxic, non-biodegradable and mutagenic properties. Thus, the adversity of these dyes even at trace level attracts the scientists to develop efficient processes for their degradation. It is important for the conversion of dye pollutants to non-harmful ones. From this study, the effective amount of catalyst to degrade the dye pollutants was determined.

CHAPTER 2

LITERATURE REVIEW

2.1 Dyes

Dyes have colour, ionizing and aromatic organic compounds which demonstrate an affinity towards the substrate to which it is being connected. It is generally applied in aqueous solution. Dyes may also require a mordant to better the fastness of the dye on the material on which it is applied. Both dyes and pigments appear to be coloured because they absorb some particular wavelengths of light more than others. In contrast with a dye, a pigment generally is insoluble and has no affinity for the substrate.

Increasing environmental pollution caused by toxic dyes due to their hazardous nature is a matter of great concern. Even small traces of the non-biodegradable and highly toxic dyes can prove harmful to the mankind. Effluents from dye production and dying mills are highly objectionable if discharged into open water without any proper treatment. The presence of colouring material in water system also reduces penetration of light and thereby affecting photosynthesis in aquatic planktons (Mittal, 2007). Dyes are also major component of the laboratory wastes, which are then led into the soil and water bodies and also need to be removed.

Dyes are classified in several ways according to their chemical constitution, application, origin and use. Dyes are divided into two groups which are natural and synthetic but natural dyes used decrease rapidly in textile industry purpose after synthetic dyes were found in 1856 (Kakhia, 2007). Moreover, dyes are characterized into acidic, basic, mordant, direct, reactive, vat, disperse, sulphur and azo based on their applications. However, a minimum amount of dyes discharged to the stream causes many problems such as chemical oxygen demand and also decrease of the light infiltration into the water bodies thus influences the photosynthesis process of the plants.

According to (Biradar et al., 2016), organic dyes are usually in solid form as they have auxochromes such as amino, alkylamino, hydroxy, alkoxy and nitro groups in a molecule. 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.

Two types of dyes are used in this study. Dyes that are used in this research are methyl orange and congo red. Methyl Orange is an acid base indicator changing colour at different pH. The molecular formula for methyl orange is $C_{14}H_{14}N_3NaO_3S$ with an IUPAC name of sodium:4-[4-(dimethylamino)phenyl]diazenyl]benzenesulfonate. The structure of Methyl Orange is shown in Figure 2.1. Methyl Orange is a water-soluble azo dye which is widely used in the textile, printing, paper manufacturing, pharmaceutical, food industries and also in research laboratories. It is mainly used as an acid base indicator due to its ability to function as weak acid as the aqueous solution of the dye has a pH value of approximately 6.5 (Mittal, 2007). At a pH greater than 4.4, it turns orange in colour. At a pH of less than 3.2, it turns a dark red colour. Thus it is possible to determine if certain substances are acids or bases when mixed with methyl orange. Synthesis of Methyl Orange involves the coupling of an azo group between a diazonium ion and an aromatic substrate.

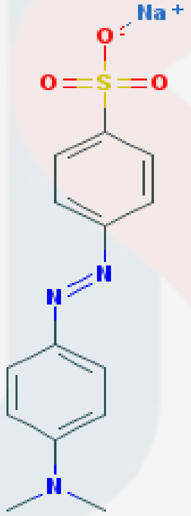

Figure 2.1: Structure of Methyl Orange

Congo Red is the sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid; a diazo dye that is red in alkaline solution and blue in acid solution and used especially as an indicator and as a biological stain (Zhu et al., 2009). The molecular formula for Congo Red is $C_{32}H_{22}N_6Na_2O_6S_2$. The structure of Congo Red is shown in Figure 2.2. It is a benzide-based anionic diazo dye and one of the most frequently used secondary diazo dye. Its structural stability makes it highly resistant to biodegradation and obviously its bright colour and toxicity are entirely undesirable in the environment. Congo Red is an anionic dye surrogate indicator due to its chemical composition and environmental concern (Vimonses et al., 2009). Congo Red is soluble in ethanol, very slightly soluble in acetone and practically insoluble in ether. Hence, Congo Red effluents are highly coloured, have low biological oxygen demand (BOD) and high chemical oxygen demand (COD) while they contain high amounts of dissolved solids (Sakkas, 2010).

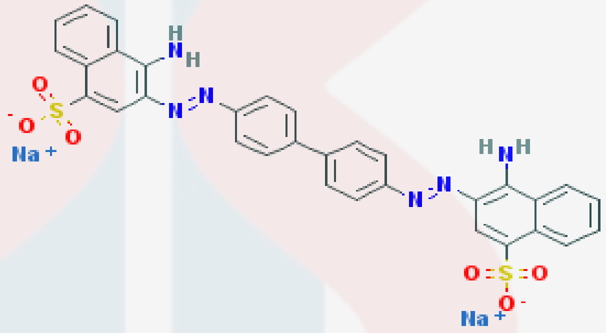

Figure 2.2: Structure of Congo Red

2.2 Tannin-Chitosan Support

Tannin commonly referred as tannic acid which are water-soluble polyphenols that are present in many plant food (Chung et al., 2010). Tannin has high molecular weight polycyclic aromatic compounds widely distributed through the plant kingdom (Mahmut et al., 2002). The structure of tannin is shown in Figure 2.3. Tannin is the polyphenol reached substrate that has high affinity to bound metal ions (Mulani et al., 2014). Tannin has been found in a variety of plants utilized as food and feed. Tannin is a group of chemical compounds which are produced by a number of broad leaf forage plants which binds with protein. Tannin is astringent, bitter plant polyphenols that either bind and precipitate or shrink proteins (Shamsi, 2017). Tannin is defined as water-soluble phenolic compounds with molecular weights ranging from 500 to 3000 that have the property of combining with proteins, cellulose, gelatin, and pectin to form an insoluble complex (Garg, 2017). These polyphenols contain a large number of hydroxyl or other functional groups and therefore are capable of forming cross-linkages with proteins and other macromolecules. Tannin is an important group of secondary plant metabolites that were originally used in the leather production industry in the tanning of animal hides. Tannin is soluble in water and has magnificent adsorption capability when reacting with metal ions like uranium, copper and arsenic.

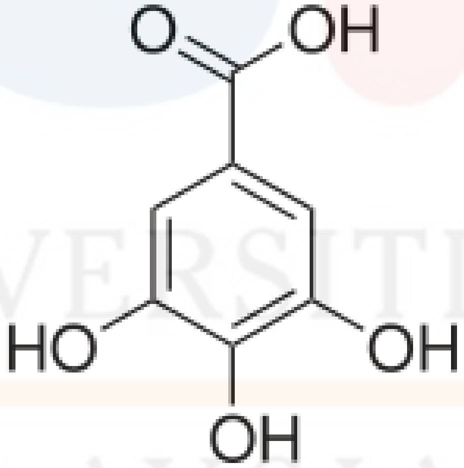

Figure 2.3: Structure of Tannin

Chitosan is a type of fiber derived from chitin, a substance that develops in the hard outer shells of crustaceans such as crab, crayfish, shrimp and squid. Chitosan is a straight-chain copolymer composed of D-glucosamine and N-acetyl-

D-glucosamine being obtained by the partial deacetylation of chitin. The structure of chitosan is shown in Figure 2.4. Chitosan is the most abundant basic biopolymer and is structurally similar to cellulose, which is composed of only one monomer of glucose. Chitosan's solubility, biodegradability, reactivity, and adsorption of many substrates depend on the amount of protonated amino groups in the polymeric chain, therefore on the proportion of acetylated and non-acetylated D-glucosamine units (Alvarenga, 2011). Chitosan is insoluble in water, organic solvents and aqueous bases and it is soluble after stirring in acids such as acetic, nitric, hydrochloric, perchloric and phosphoric (Kumar, 2000). Chitosan is a bio-based polymer which has similar characteristics to those of cellulose, exhibits cationic behaviour in acidic solutions and strong affinity for metals ions (Lee et al., 2015). Thus, it has received increased attention for the preparation of heterogeneous catalysts. In the solid state, chitosan is a semi-crystalline polymer (Rinaudo, 2006). Chitosan is used variously in the field of wastewater treatments, biomedicine, and flocculation due to biodegradable properties. Chitosan is considered one of the most valuable polymer for biomedical and pharmaceutical applications due to its biodegradability, biocompatibility, antimicrobial, non-toxicity, and anti-tumor properties (Alvarenga, 2011). Chitosan-based catalysts have high sorption capacities, chelating activities, stability and versatility which could be potentially applied as green reactants in various scientific and engineering applications. According to Dutta et al., (2004), chitosan is being used in a vast array of widely different products and applications, ranging from pharmaceutical and cosmetics products to water treatment and plant protection. Besides, chitosan is able to remove dyes from dye processing effluents where chitosan have remarkable contribution to medical related textile sutures, threads and fibres (Dutta, 2004).

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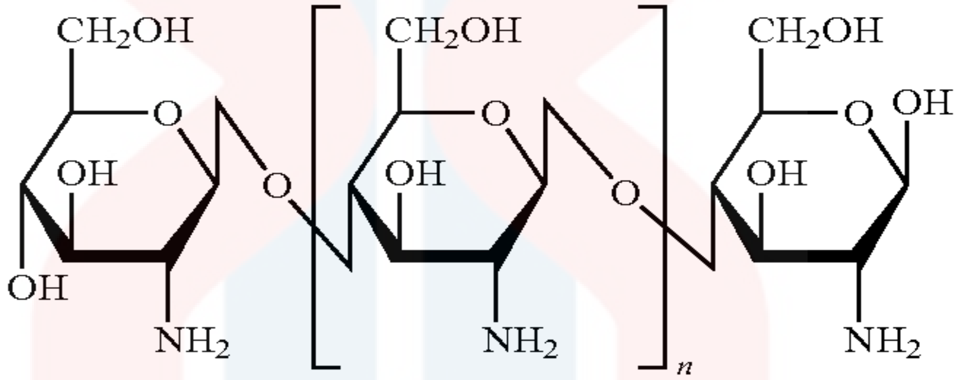

Figure 2.4: Structure of Chitosan

2.3 Catalyst

Catalysts typically speed up a reaction by reducing the activation energy or changing the reaction mechanism (Schmidt, 2004). Catalysts come in a multitude of forms, varying from atoms and molecules to large structures such as zeolites or enzymes. In addition they may be employed in various surroundings such as in liquids, gases or at the surface of solids. Common types of catalysts include enzymes**,** acid-base catalyst, and heterogeneous catalysts**.**

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 processes which is solid phase (catalyst) and gas or liquid phase (reactants). Other than the two phases, 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).

Catalysts work by providing an alternative mechanism involving a different transition state and lower activation energy. Hence, catalysts can assist reactions that would not run without the presence of a catalyst, or perform them much faster, more specifically, or at lower temperatures. This means that catalysts reduce the amount of energy required to initiate a chemical reaction (Chorkendorff, 2005). 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. A catalyst changes the kinetics but not the thermodynamics. A catalyst does not initiate a thermodynamically either possible or impossible reaction, but only accelerates a possible reaction (Triyono, 2004).

Catalysts are suitable in industrial processes if they are selective, stable and have high activity under the conditions of the process. Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favourable thermodynamic regime, and at much lower temperatures and pressures. In this way efficient catalysts, in combination with optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of a chemical processes (Chorkendorff, 2005).

2.4 Nickel and Palladium based catalysts

Nickel is a naturally occurring, lustrous and silvery-white metallic element. It is the fifth most common element on earth and occurs extensively in the earth's crust. Nickel belongs to the transition metals and is hard and ductile. Nickel is highly reactive, capable of rapidly reducing alkenes, alkynes, and carbonyls. Nickel has slow rate of oxidation at room temperature and it is considered corrosion-resistant. The key characteristic of nickel is its ability to adsorb huge quantities of hydrogen thereby greatly increasing the efficiency of the reactions. Additionally, nickel is less costly relative to competing materials of the platinum group (Duchesse, 2007). 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 produces very pure hydrogen (H_2) and will not producing carbon dioxide (Randhava & Rehmat, 2014). This process does not need the separation of gaseous mixtures. Furthermore, the used 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 produces an extra H_2 and preserves nickel in its metallic form. The result of hydrogen produced in the reforming methane process can be applied in various are such as in petroleum refineries and the production of ammonia (Duchesse, 2007).

Palladium is a rare, lustrous and silvery-white metal. Palladium (Pd) is a well known transition metal catalyst for carbon-carbon bond formation, hydrogenation and acetalization in the area of organic chemistry. Palladium is most popularly used as the main ingredient of the noble catalyst and where in a co-catalyst comprising a metal, which exhibits by itself no catalytic activity for the specified reaction hence used in combination with the noble catalyst (Daniel et al, 2010). Palladium is remarkable in its capacity to absorb up to 900 times its own volume of hydrogen. As it absorbs the hydrogen, it expands visibly, like a sponge swelling up when absorbing water. Palladium catalysts offer an abundance of possibilities of carbon-carbon formation (Tsuji, 2004). It has tolerance to functional groups such as carbonyl and hydroxyl group.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2 6H_2O$) and palladium chloride ($PdCl_2$) were purchased from Sigma-Aldrich, Malaysia, tannin from Merck KGaA, Germany and chitosan from Sigma-Aldrich, USA. In addition, glutaraldehyde ($C_5H_8O_2$) was purchased from R&M Chemicals from Malaysia. Methyl orange ($C_{14}H_{14}N_3NaO_3S$) and congo red ($C_{32}H_{22}N_6Na_2O_6S_2$) were purchased from Merck, Germany.

3.1.1 Instrumentation

Ultraviolet-Visible Spectrophotometer from Merck KGaA model Spectroquant Pharo 300.

3.2 Methodology

3.2.1 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 45 ^{0}C. The tannin-chitosan support was filtered, washed with deionized water and it was dried in vacuum for 12 hours.

3.2.2 Preparation of Catalyst

Nickel nitrate hexahydrate (Ni $(NO_3)_2 6H_2O$) and palladium chloride ($PdCl_2$) were weighed and added to the above support. Then, the mixture of that was dried to remove the entire volatile components that are attached to it. After the process of drying the mixture, nickel nitrate hexahydrate (Ni $(NO_3)_2 6H_2O$) was reduced into nickel compound palladium chloride ($PdCl_2$) into palladium compound. The final products undergo activation process to attach each other.

3.2.3 Catalytic Activity

The catalytic experiment was carried out according to the method proposed by Saeed et al., (2015). The nickel tannin-chitosan oxidative degradation of Methyl Orange and Congo Red were carried out. The concentration of Methyl Orange and Congo Red dye solutions were diluted to i.e. 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm, 12 ppm, 14 ppm, 16 ppm, 18 ppm and 20 ppm respectively Wavelength of 462 nm and 497 nm were used for Methyl Orange and Congo Red dyes respectively. The percentage of degradation of dyes was calculated by using:

$$\textit{Degradation}\ (\%) = \frac{(R)_0 - (R)_t}{(R)_0} (x)\ 100$$

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

In order to investigate the effect of nickel and palladium on tannin-chitosan support loading on dye degradation, different catalyst loadings (20, 40, 60, 80 and 100 mg) were tested. Not only that, in this study the effect of pH was examined as well by adjusting the initial pH of dye solution in the range of 4–10 for a period of 60 minutes. This is to identify the degradation efficiency of dye solutions.

The apparent kinetics of disappearance of the substrate Methyl Orange and Congo Red were determined according to the optimized conditions of nickel and palladium at various time intervals using UV–visible spectrophotometer.

For studying the reaction kinetics of dye degradation, the absorbance values of the dyes were measured with time. The decrease in concentration value of dye solution can be related in terms of the degradation efficiency. The change in concentration value of the dye solutions during its degradation were used to find out the reaction kinetics. The Methyl Orange and Congo Red degradation fitted best to the following pseudo first-order kinetic equation which is given by:

$$\ln (C_0/C_t) = k_{obs}{}^{t}$$

where C_0 is the initial concentration of dye solution, C_t is the concentration of dye solution at time t, and k_{obs} is the observed reaction rate constant obtained from the slope of the line in the plot of $\ln(C_0/C_t)$ versus time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Calibration curves

In this experiment calibration curves of Methyl orange and Congo Red were prepared from concentration of 1000 ppm. The concentration of Methyl Orange and Congo Red dye solutions were diluted to i.e. 2 ppm, 4 ppm, 6 ppm, 8 ppm, 10 ppm 12 ppm, 14 ppm, 16 ppm, 18 ppm and 20 ppm respectively. The plotted calibration graphs were shown as in the Figure 4.1 and Figure 4.2 below:

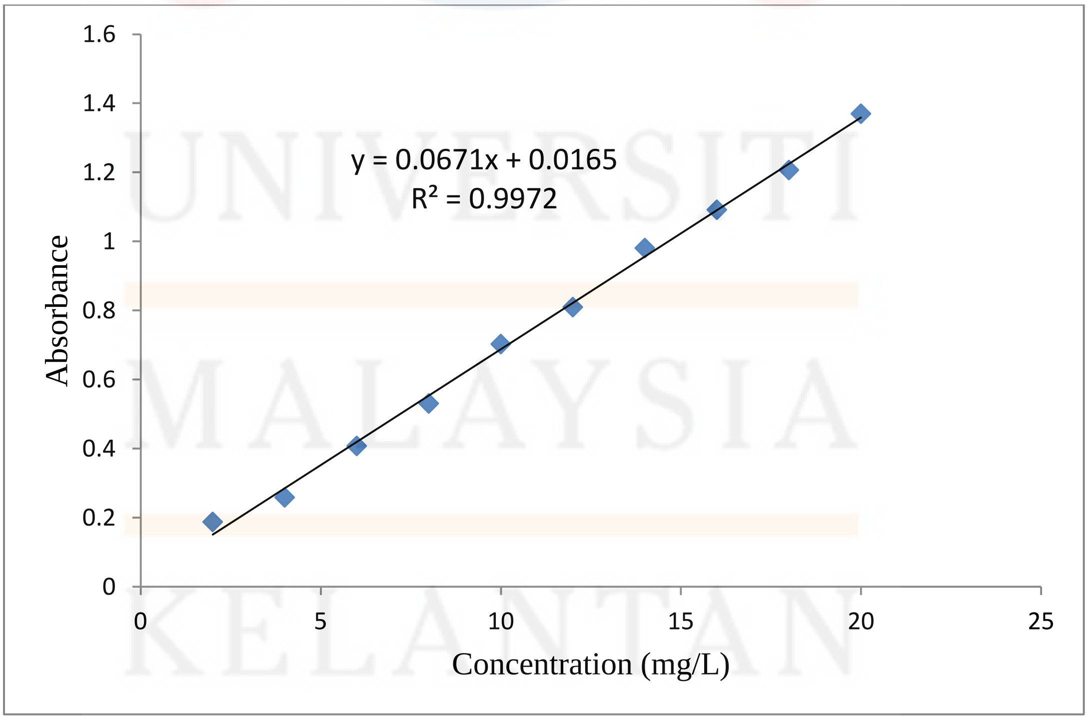

Figure 4.1: Calibration curve of Methyl Orange

Calibration graphs were plotted in this experiment with the concentration range from 2 ppm until 20 ppm. These calibration graphs are very important in calculation the degradation efficiency of a dye solution. Based on the Figure 4.1 and 4.2, it was found that calibration graphs plotted are almost accurate enough because the R² values are equal to 0.9972 and 0.9553 for Methyl Orange and Congo Red respectively. The good fit model for R² value is when it is closer to 1. A serial dilution was required to obtain a good calibration curve of linearity.

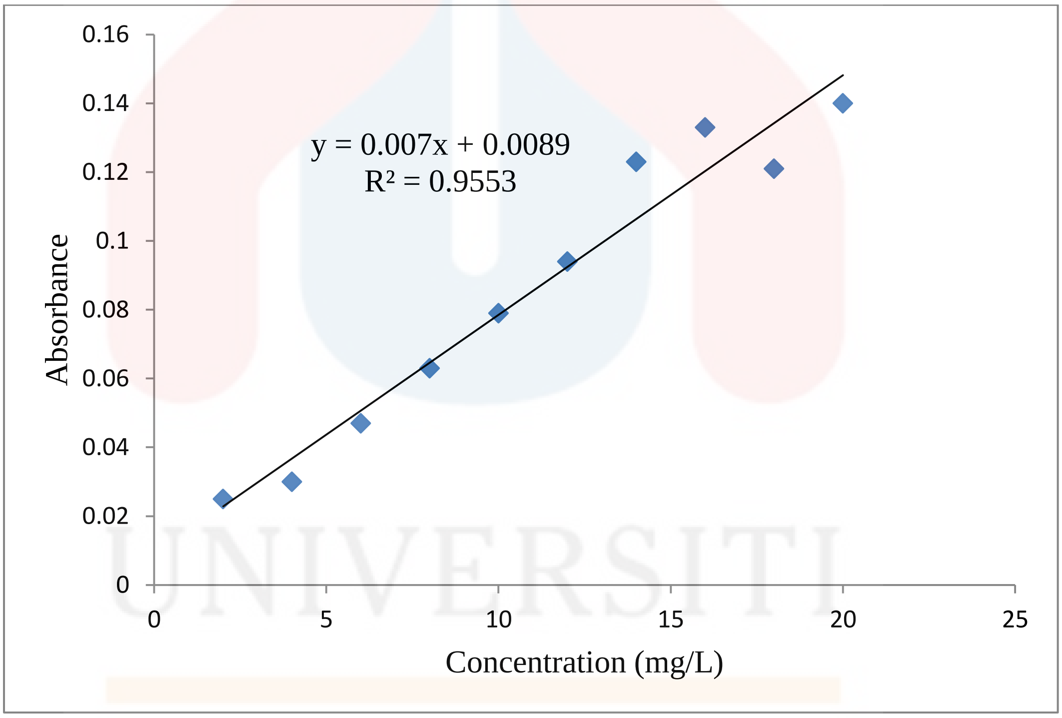

Figure 4.2: Calibration curve of Congo Red

4.2 Optimization of the reaction conditions

4.2.1 Effect of pH on degradation efficiency of Congo Red with catalysts

The results revealed that the degradation efficiency percentage was different at various pH values. Based on Figure 4.3 and 4.4, it was found that the degradation efficiency was efficient for Congo Red with palladium and nickel catalyst was at pH 6 with 61.03% and 83.91% respectively.

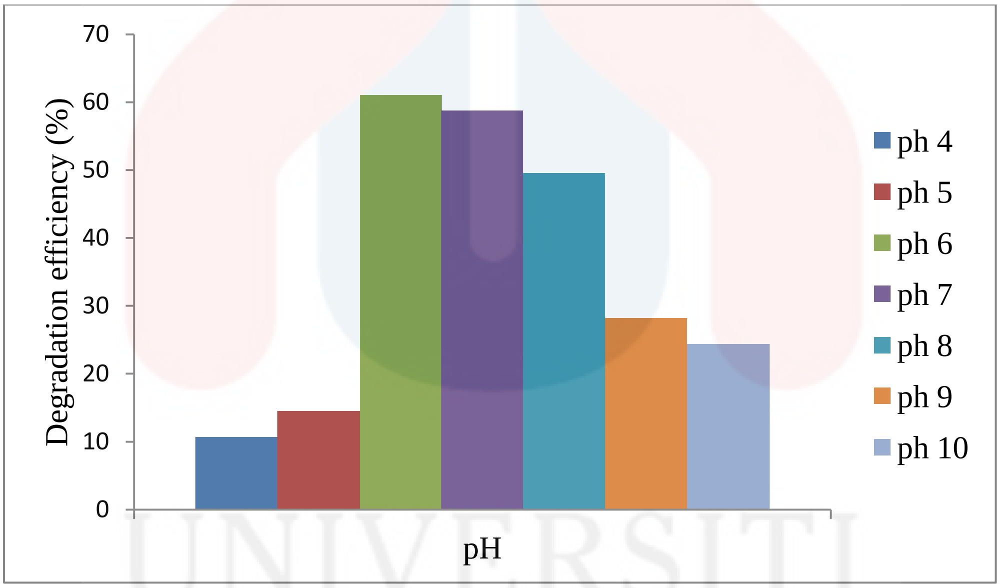

Figure 4.3: Degradation efficiency of Congo Red with palladium

The solution pH significantly influences the degradation of organic dyes. There are several factors which influence the effect of pH on dye degradation (Sharma et al., 2012). These include the surface area of the catalyst, nature of the dye and extent of the substrate adsorption on the catalyst surface.

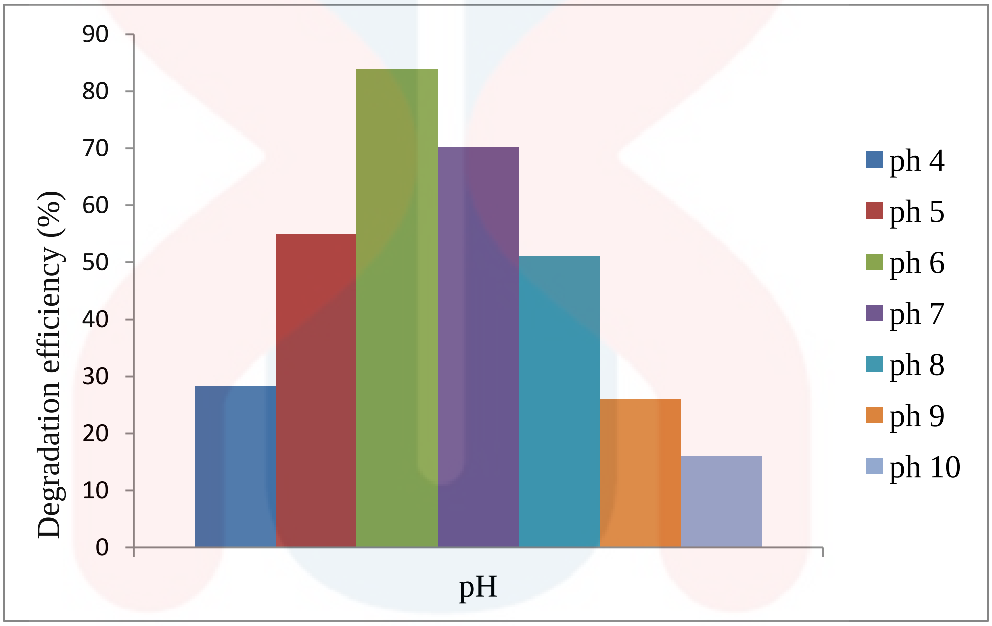

Figure 4.4: Degradation efficiency of Congo Red with nickel

4.2.2 Effect of pH on degradation efficiency of Methyl Orange with catalysts

Meanwhile, based on Figure 4.5 and 4.6, it was observed that the degradation efficiency of Methyl Orange with palladium and nickel catalyst was also at pH 6 with 99.08% and 51.57% respectively. In this study the effect of pH were examined by adjusting the initial pH of dye solution in the range 4–10 for a period of 60 minutes. The degradation decreased by further increasing the pH value. This is because of the reason that at higher pH values, less H+ is available for adsorption to mask the surface of the catalyst. On the other hand, degradation percentage was also less in basic media as compared to the neutral pH.

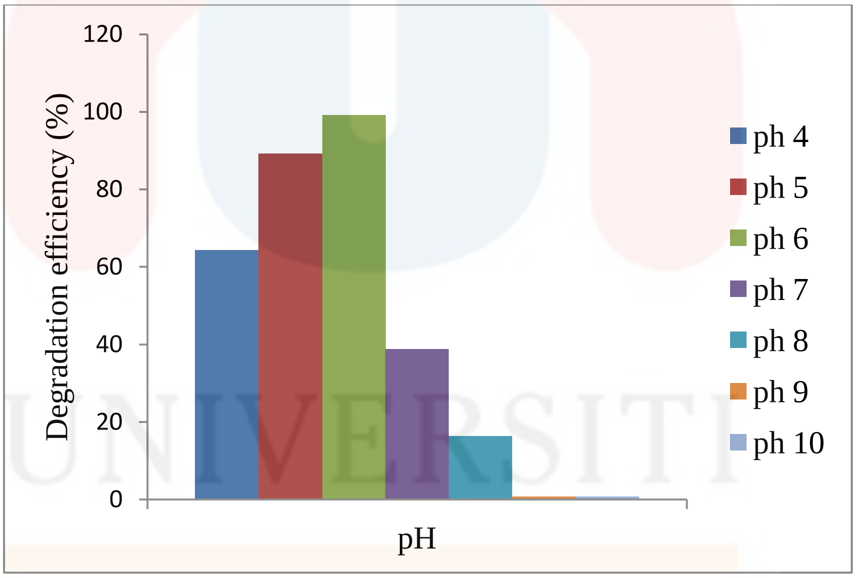

Figure 4.5: Degradation efficiency of Methyl Orange with palladium

This can be explained on the basis that at high pH values, OH ions will be preferably adsorbed on the catalyst surface thus reducing the overall efficiency of the catalyst. The pH of the solution is a key factor affecting solution chemistry, chemical speciation of metal ions and the degree of ionization of functional groups on an adsorbent surface. It does not only affect metal species in solution but also influences the surface charges (Xiaojuan et al,. 2017).

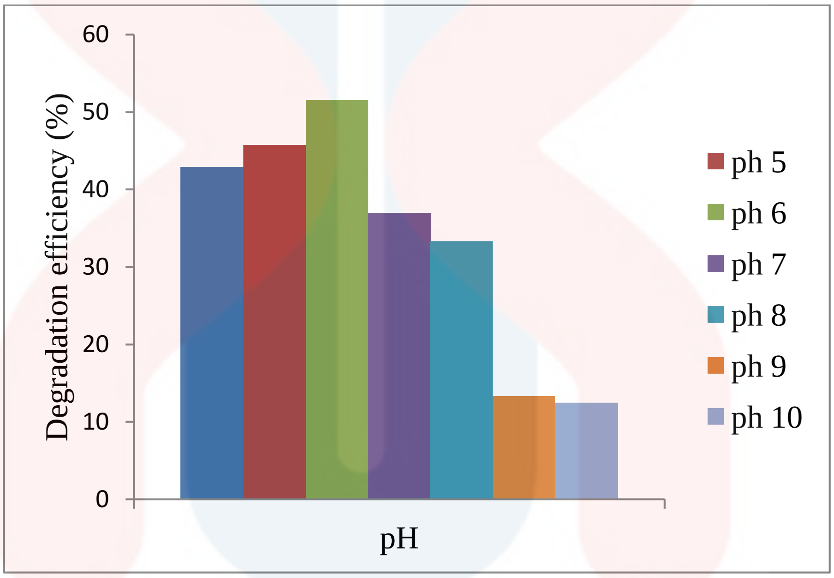

Figure 4.6: Degradation efficiency of Methyl Orange with nickel

Congo Red and Methyl Orange are fused poly-nuclear aromatic compound with an extensive π electron conjugation which can easily form a stable complex by donating electrons to the vacant d-orbital of the nickel and palladium. In other words, the Methyl Orange and Congo Red dyes act as strong Lewis base and can easily adsorb on the catalyst surface.

4.2.3 Effect of catalyst loading on degradation efficiency of Congo Red with catalysts

The results revealed that the degradation efficiency was efficient for Congo Red and Methyl Orange with palladium and nickel catalyst was at the loading of 80mg and 60mg respectively at pH 6. Based on Figure 4.7 and 4.8, the degradation percentage of Congo Red with 80mg palladium catalyst loading was 48.06% and 60mg nickel catalyst loading was 87.72%.

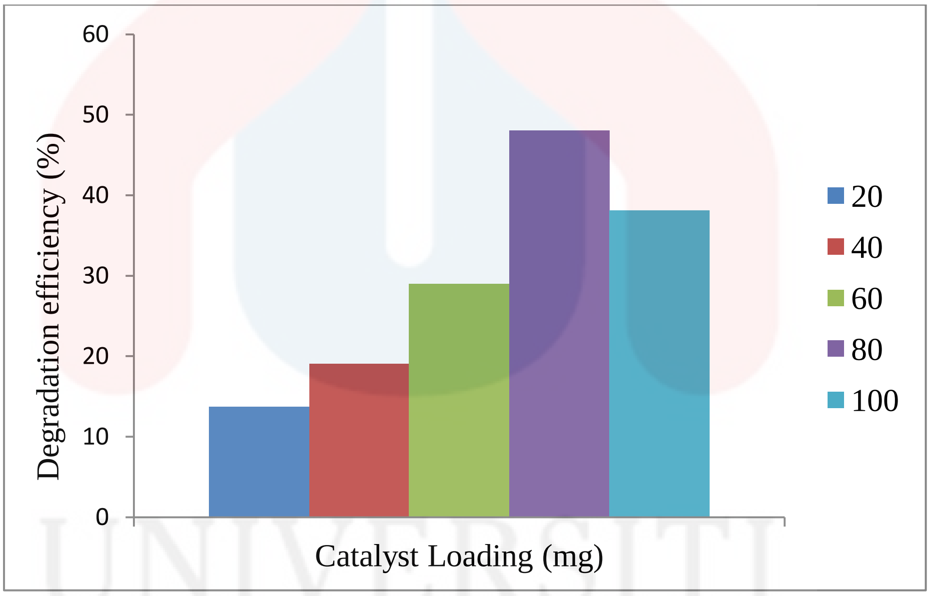

Figure 4.7: Degradation efficiency of Congo Red at various palladium catalyst loading

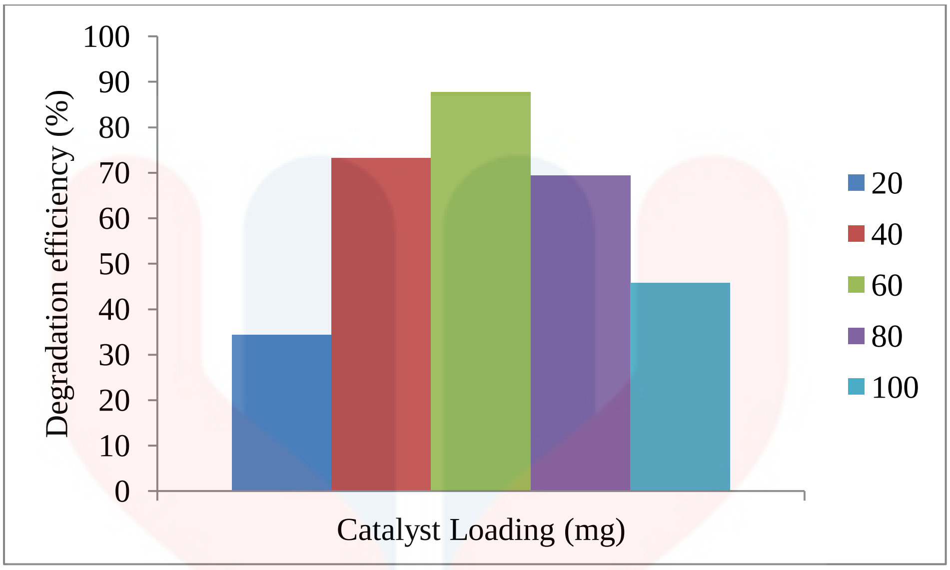

Figure 4.8: Degradation efficiency of Congo Red at various nickel catalyst loading

As the concentration of the catalyst was increased, the number of dye molecules adsorbed is increased owing to an increase in the number of palladium and nickel particles. Above certain level, the dye molecules available were not sufficient for adsorption by the increased number of palladium and nickel particles. Hence, the additional catalyst was not involved in the catalysis activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit.

4.2.4 Effect of catalyst loading on degradation efficiency of Methyl Orange with catalysts

Meanwhile, based on Figure 4.9 and 4.10, the degradation percentage of Methyl Orange with 80mg palladium catalyst loading was 69.23% and 60mg nickel catalyst loading was 49.2% at pH 6. It can be seen that with increasing concentration of the catalyst, there was decrease in the residual concentration of dye in the solution indicating increase in the degradation of dye.

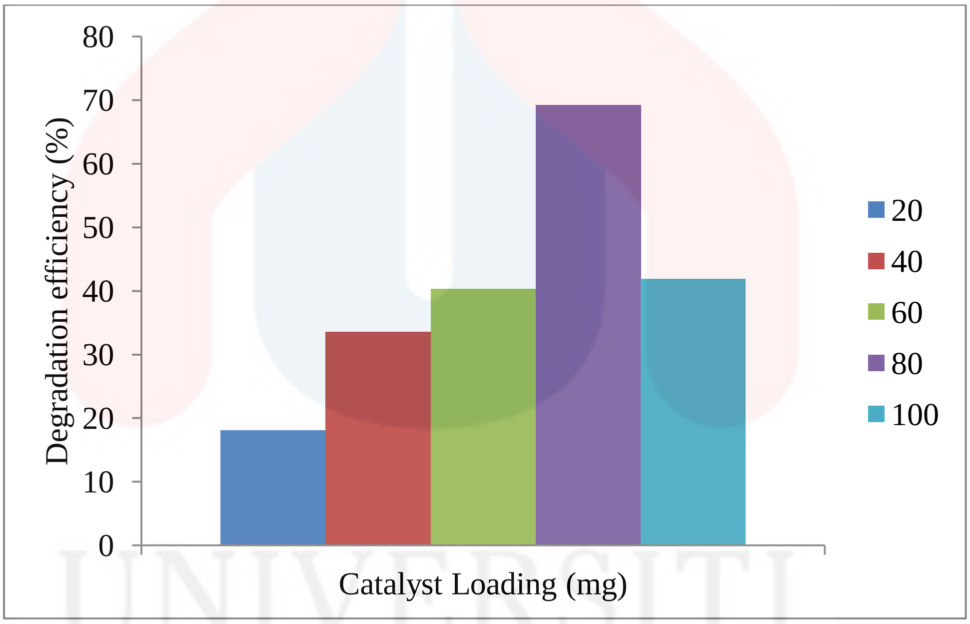

Figure 4.9: Degradation efficiency of Methyl Orange at various palladium catalyst loading

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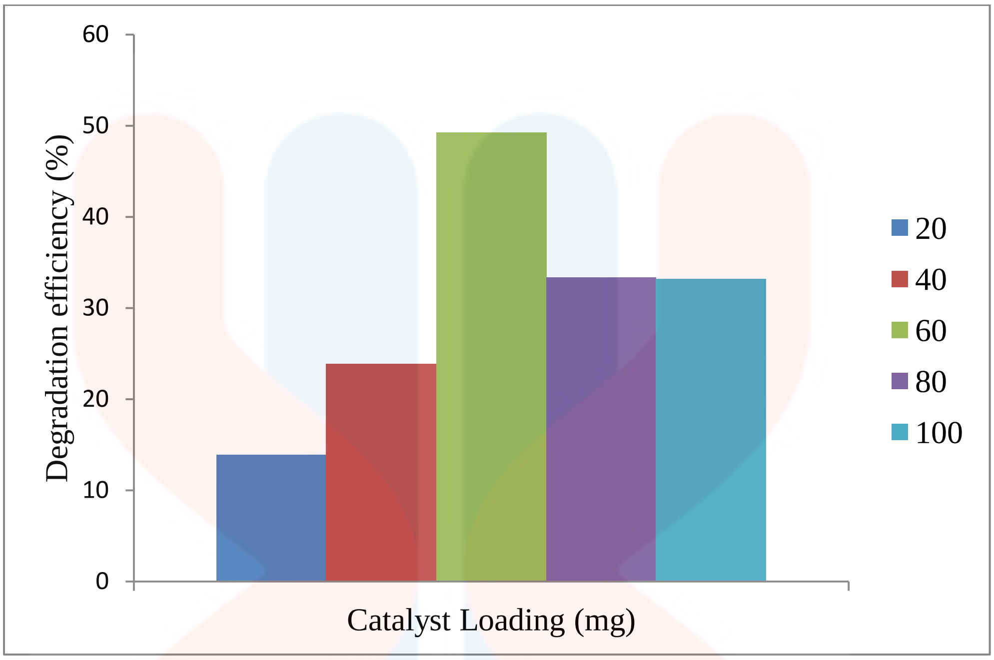

Figure 4.10: Degradation efficiency of Methyl Orange at various nickel catalyst loading

During degradation, the catalysis occurred on the surface region of catalyst, therefore increasing the surface area availability where it significantly improved the efficiency of the catalyst. This result can be proven by the previous research made by (Bhakya et al., 2015) where it was reported that the increasing dose of catalyst increased the degradation of dyes.

4.3 Kinetic studies

4.3.1 Kinetic analysis of degradation of Congo Red under optimized conditions

The results revealed that the pH and catalyst loading of this study were optimized for both dyes used. The optimized pH was at pH 6 and 80 mg for palladium and 60 mg for nickel. The apparent kinetics of disappearance of the substrate Congo Red was determined by following the concentration of the substances at various time intervals using UV–visible spectrophotometer. It was examined that the regression coefficient (R^2) obtained for degradation efficiency of Congo Red in Figure 4.11 was 0.9079 was better than reaction kinetics in Figure 4.12 with the R^2 was 0.9108.

(i) Congo Red with palladium

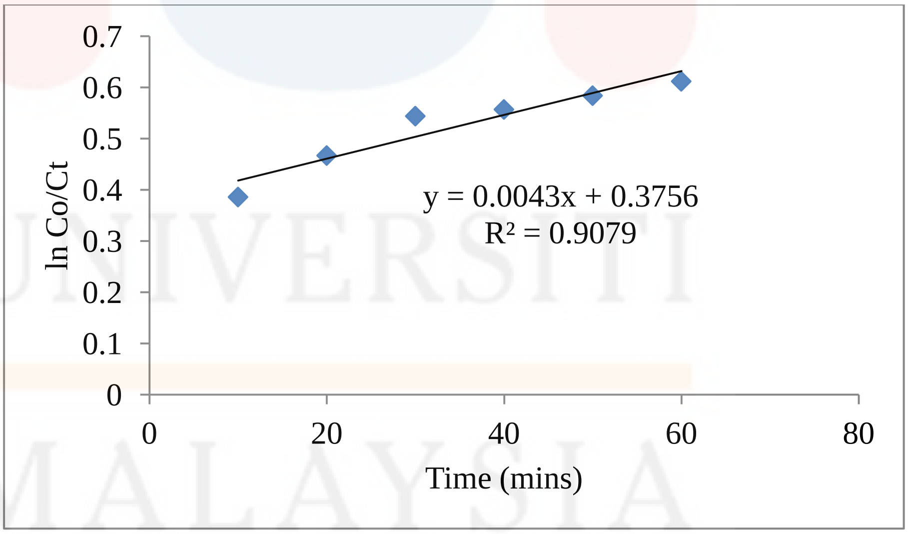

Figure 4.11: Kinetic analysis of degradation of Congo Red with palladium

It was observed that concentration of Congo Red decreased drastically due to saturation of adsorption of the dye over the catalyst surface. The decrease in concentration value of dye solution can be related in terms of the degradation efficiency (Sharma, 2012). The change in concentration value of the dye solution during its degradation was used to find out the reaction kinetics.

(ii) Congo Red with nickel

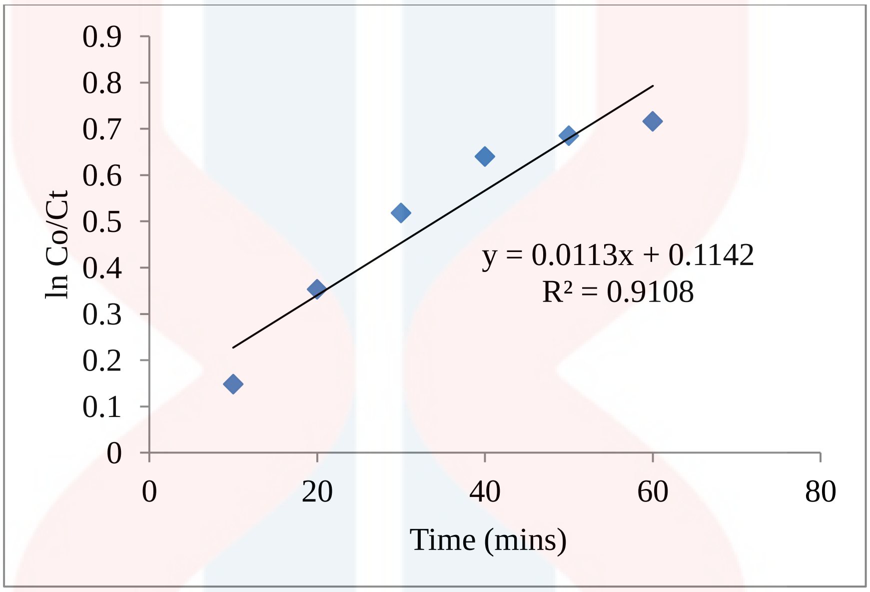

Figure 4.12: Kinetic analysis of degradation of Congo Red with nickel

The degradation efficiency of Congo Red with palladium and nickel were decreased within 60 minutes. The results showed that the regression coefficient (R^2) obtained was pseudo first-order reaction kinetics. The reaction rate constant value obtained for Congo Red with palladium was 0.0043 and 0.0113 with nickel. The reaction of kinetics of Congo Red was more efficient with palladium compared to nickel. This can be proven with the value of reaction rate constant obtained from the slope of the line in the plot of ln(Co/Ct) versus time.

4.3.2 Kinetic analysis of degradation of Methyl Orange under optimized conditions

Meanwhile, the regression coefficient (R^2) obtained for degradation efficiency of Methyl Orange in Figure 4.13 is 0.9881 was better than reaction kinetics in Figure 4.14 with the R^2 was 0.8302.

(i) Methyl Orange with palladium

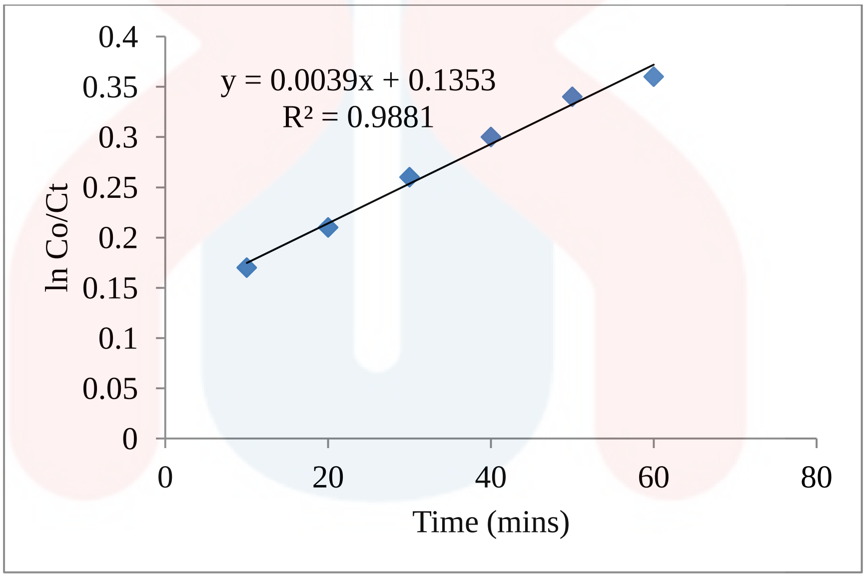

Figure 4.13: Kinetic analysis of degradation of Methyl Orange with palladium

The reaction of kinetics of Methyl Orange was also more efficient with palladium compared to nickel. The reaction rate constant value obtained for Methyl Orange with palladium was 0.0039 where it was smaller than nickel with 0.0053. The smaller value of the slope indicated the high kinetic analysis of degradation of the catalyst used.

(ii) Methyl Orange with Nickel

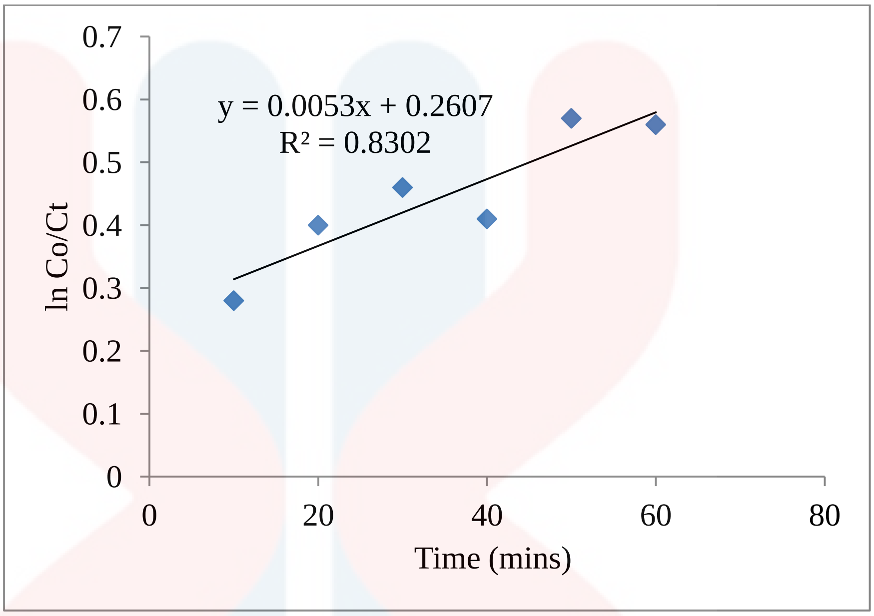

Figure 4.14: Kinetic analysis of degradation of Methyl Orange with nickel

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study it was highlighted the use of the palladium and nickel catalyst to degrade the Congo Red and Methyl Orange dyes pollution. The catalysts produced from this experiment can be considered as successful because it has high percentage removal of Congo Red and Methyl Orange dye solution. The highest degradation percentage was 87.72 % that was tested by Congo Red with nickel at pH 6 with 60 mg catalyst loading.

Besides, the degradation efficiency reached its optimum level with 80 mg of palladium and 60 mg of nickel for both the dyes used. The catalysis process was carried in the period of 60 minutes. Each reading of the absorbance was taken in the interval of 10 minutes.

Moreover, the kinetic analysis of degradation of efficiency of Methyl Orange with palladium is the most efficient under optimized conditions where palladium was 80 mg and pH was at 6. The R^2 obtained is 0.9881 with 0.0039 slope value. The smallest slope value indicates that the R^2 is closer to 1.

In a nut shell, it can be concluded that nickel exhibited better catalytic behaviour than palladium in degradation process of Congo Red and Methyl Orange. Furthermore, pH and the catalyst loading gives more effectiveness for a catalyst to speed up the reaction and degrade the dyes used.

5.2 Recommendations

Dyes are very dangerous because it can affect the chemical and physical properties of water and the aquatic flora and fauna. Besides that, dyes are also resistant to the light exposure and difficult to fade away because of their stable chemical structure which can give problems to the aquatic life and the food chain (J., Sharma and B., 2008). In conjunction to that it is recommended that further study need be carried out using different dyes such as natural dyes and synthetic dyes that can pollute the environment, for example dyes like Methylene Blue, crystal violet and etc.

It is also recommended to degrade dyes by using different types of catalyst. This can vary the results of degradation efficiency of catalysts used. It will be more efficient and effective if catalysts are prepared in small amount. Not only that, it is better to reduce the storage time for catalysts as it works more vigorously with if it is newly prepared.

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APPENDICES

Table 4.1: Degradation efficiency of Congo Red with palladium

pH	Degradation efficiency (%)
4	10.69
5	14.5
6	61.03
7	58.74
8	49.58
9	28.23
10	24.41

Table 4.2: Degradation efficiency of Congo Red with nickel

pH	Degradation efficiency (%)
4	28.23
5	54.92
6	83.91
7	70.18
8	51.11
9	25.94
10	16.02

Table 4.3: Degradation efficiency of Methyl Orange with palladium

pH	Degradation efficiency (%)
4	64.28
5	89.25
6	99.08
7	38.86
8	16.4
9	0.81
10	0.66

Table 4.4: Degradation efficiency of Methyl Orange with nickel

pH	Degradation efficiency (%)
4	42.92
5	45.73
6	51.57
7	36.94
8	33.32
9	13.29
10	12.48

Table 4.5: Degradation efficiency of Congo Red at various palladium catalyst loading

Catalyst Loading (mg)	Degradation efficiency (%)
20	13.73
40	19.08
60	28.99
80	48.06
100	38.14

Table 4.6: Degradation efficiency of Congo Red at various nickel catalyst loading

Catalyst Loading (mg)	Degradation efficiency (%)
20	34.33
40	73.23
60	87.72
80	69.41
100	45.77

Table 4.7: Degradation efficiency of Methyl Orange at various palladium catalyst loading

Catalyst Loading (mg)	Degradation efficiency (%)
20	18.1
40	33.61
60	40.34
80	69.23
100	41.96

Table 4.8: Degradation efficiency of Methyl Orange at various nickel catalyst loading

Catalyst Loading (mg)	Degradation efficiency (%)
20	13.88
40	23.86
60	49.2
80	33.32
100	33.17

Table 4.9: Kinetic activity of Congo Red with palladium

Time (mins)	Absorbance	Co	Ct	ln (Co/Ct)
10	0.098	18.729	12.729	0.386
20	0.091	18.729	11.738	0.467
30	0.085	18.729	10.871	0.544
40	0.084	18.729	10.738	0.557
50	0.082	18.729	10.443	0.584
60	0.08	18.729	10.157	0.612

Table 4.10: Kinetic activity of Congo Red with nickel

Time(mins)	Absorbance	Co	Ct	ln (Co/Ct)
10	0.122	18.729	16.157	0.148
20	0.101	18.729	13.157	0.353
30	0.087	18.729	11.157	0.518
40	0.078	18.729	9.871	0.64
50	0.075	18.729	9.442	0.685
60	0.073	18.729	9.157	0.716

Table 4.11 : Kinetic activity of Methyl Orange with palladium

Time (mins)	Absorbance	Co	Ct	ln (Co/Ct)
10	1.153	20.17	16.94	0.17
20	1.109	20.17	16.28	0.21
30	1.055	20.17	15.48	0.26
40	1.02	20.17	14.96	0.3
50	0.978	20.17	14.33	0.34
60	0.959	20.17	14.05	0.36

Table 4.12 : Kinetic activity of Methyl Orange with nickel

Time (mins)	Absorbance	Co	Ct	ln (Co/Ct)
10	1.04	20.17	15.25	0.28
20	0.922	20.17	13.49	0.4
30	0.873	20.17	12.76	0.46
40	0.913	20.17	13.36	0.41
50	0.785	20.17	11.45	0.57
60	0.787	20.17	11.48	0.56