ELECTROCHEMICAL REDUCTION OF NITRATES AND NITRITES USING COPPER MODIFIED PLATINUM ELECTRODE

SREE AMERTHARAJ RATNAM

UNIVERSITI SAINS MALAYSIA

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by

SREE AMERTHARAJ RATNAM

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LIST OF SYMBOLS

A	electrode surface area, cm^2
Ǻ	Angstrom, unit length equal to 10^{-10} m
α_c	charge transfer coefficient
C	analyte concentration, mol dm^{-3}
C_d	double-layer capacitance
D	diffusion coefficient, cm^2 s^{-1}
E	potential, V
E_p	peak potential, V
i_p	peak current, A
k	rate of nitrate reduction, min^{-1}
n	number of electrons per mole of reactant
Ω	resistant
Q_H	charge under the curve for hydrogen adsorption/ desorption
r	radius of the electrode
ν	potential scan rate, V s^{-1}

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
DNA	Deoxyribonucleic acid
GCE	Glassy Carbon Electrode
EDX	Energy Dispertive X-ray
HER	Hydrogen Evolution Reaction
IHP	Inner Helmholtz Plane
IP_6	Inositol Hexaphosphate
LOD	Limit of Detection
MCL	Maximum Contaminant Level
NRR	Nitrate Reduction Reaction
OFN	Oxygen free nitrogen
OHP	Outer Helmholtz Plane
OPD	Over potential Deposition
PG	Pencil Graphite
ppm	parts per million
RDS	Rate Determining Step
RHE	Reversible Hydrogen Electrode
RNA	Ribonucleic acid
SAM	Self Assembled Monolayer
SEM	Scanning Electron Microscopy
UPD	Under potential deposition
WE	Working Electrode
WHO	World Health Organization
XRD	X-ray Diffraction

PENURUNAN ELEKTROKIMIA NITRAT DAN NITRIT MENGGUNAKAN ELEKTROD PLATINUM TERUBAHSUAI DENGAN KUPRUM

ABSTRAK

Elektropenurunan nitrat dan nitrit dalam kajian ini dijalankan dengan menggunakan elektrod platinum terubahsuai dengan kuprum di dalam larutan 0.05 M KCl melalui teknik voltammetri kitaran. Satu perbandingan telah dilakukan dengan menggunakan pelbagai elektrod kerja seperti kuprum, elektrod kuprum terubahsuai dengan kuprum (Cu-Cu) dan elektrod pensil grafit terubahsuai kuprum (PG-Cu). Proses permendapan zarah kuprum ditetapkan sebanyak 30 kitaran/ 18 saat untuk semua elektrod yang diubahsuai dengan kuprum bagi mendapatkan nisbah yang terbaik. Luas permukaan sebenar bagi elektrod Pt, Cu, Cu-Cu, PG-Cu dan Pt-Cu dianggarkan sebanyak 1.747 cm^2, 0.814 cm^2, 0.988 cm^2, 1.146 cm^2 and 2.259 cm^2. Aktiviti dan pemilihan elektropenurunan nitrat dan nitrit adalah lebih memuaskan jika menggunakan elektrod Pt-Cu. Plot i_p vs. $\nu^{1/2}$ menunjukkan bahawa elektron yang dipindahkan dalam langkah penentu kadar tindakbalas adalah 1.51, 1.66, 1.88 dan 2.05 melalui elektrod Cu, Cu-Cu, PG-Cu dan Pt-Cu yang menunjukkan penurunan kepada nitrit. Pada keupayaan yang lebih negatif, bilangan elektron yang dipindahkan ialah 5.15, 5.26, 5.35 dan 6 masingmasing pada elektrod Cu, Cu-Cu, PG-Cu dan Pt-Cu, yang menunjukkan pengeluaran ammonia. Tertib tindakbalas di elektrod Pt-Cu ialah 0.97 dan 0.90 untuk kedua-dua tindakbalas penurunan elektro nitrat dan nitrit. Pemalar kadar elektropenurunan nitrat (2.228 × 10^2 min^{-1}) dan nitrit (4.690 × 10^2 min^{-1}) apabila menggunakan elektrod Pt-Cu adalah lebih tinggi daripada elektrod yang lain di dalam kajian ini. Keputusan membuktikan bahawa prestasi elektrod Pt-Cu adalah lebih baik

daripada elektrod Cu-Cu dan PG-Cu. Perlakuan elektrokimia elektrod Pt-Cu dalam elektropenurunan ion nitrat dan nitrit juga dikaji di dalam medium alkali (0.05 M NaOH) dengan kehadiran 5 mM natrium inositol heksafosfat ($NaIP_6$). Komposisi elektrod yang berbeza (Cu, Pt, and Pt-Cu) telah digunakan untuk mengkaji aktiviti dan pemilihan elektrod terhadap elektropenurunan nitrat dan nitrit dengan menggunakan voltammetri kitaran. Elektrod Pt-Cu menunjukkan prestasi yang terbaik. Penambahan $NaIP_6$ adalah untuk mengelakkan pengoksidaan atom kuprum kepada ion kuprum. Kesan $NaIP_6$ pada aktiviti dan kestabilan elektrod juga disiasat di dalam kajian ini. Kehadiran $NaIP_6$ meningkatkan prestasi elektrod Pt-Cu terutama sekali kestabilan elektrod. Akhir sekali, prestasi elektrod Pt-Cu dianalisis selanjutnya untuk kajian ion penganggu. Gangguan daripada ion nitrat dan nitrit pratambah terhadap proses elektropenurunan keseluruhannya ditentukan di dalam 0.05 M KCl. Di sini, pemalar kadar elektropenurunan nitrat yang lebih tinggi diperhatikan di dalam sistem tanpa nitrit (2.215×10^2 min^{-1}) berbanding sistem nitrit ditambah terlebih dahulu (55.97 min^{-1}). Pemalar kadar elektropenurunan nitrit pula adalah lebih tinggi di dalam sistem tanpa ion nitrat (3.954×10^2 min^{-1}) berbanding dengan sistem dimana nitrat di tambah terlebih dahulu (3.349×10^2 min^{-1}). Pada kepekatan nitrit yang tinggi, kadar elektro penurunan merosot. Elektropenurunan nitrat dan nitrit berlaku lebih dengan kehadiran ion Cl^-, ClO_4^- berbanding dengan ion yang lebih besar seperti ion SO_4^- dan Br^-. Tertib tindak balas dianggarkan kepada 1 iaitu tertib pertama. Kadar tindak balas untuk elektropenurunan nitrat dan nitrit adalah tertinggi di dalam larutan KCl. Pemindahan elektron untuk langkah elektropenurunan nitrat adalah hampir kepada dua elektron manakala bilangan elektron yang dipindahkan untuk langkah elektropenurunan nitrit

ialah daripada empat hingga enam elektron. Untuk analisis kation penganggu, aktiviti elektropenurunan diperhatikan bagi kation bercas 1. Tertib tindakbalas yang diperoleh ialah kira-kira 1 untuk kedua-dua elektropenurunan nitrat dan nitrit. Untuk penurunan elektro nitrat, kadar tindak balas adalah lebih tinggi ion K^+ (2.213×10^2 min^{-1}) daripada ion Na^+ (2.143×10^2 min^{-1}) sementara kadar meningkat dalam urutan Cu < Mg < Al < Ca. Kadar tindak balas yang tinggi juga diperhatikan untuk elekropenurunan nitrit dalam kehadiran ion Na^+ (5.571×10^2 min^{-1}) berbanding K^+ ion (4.699×10^2 min^{-1}) manakala ion Ca^{2+}menghasilkan kadar tertinggi (6.397×10^2 min^{-1}). Had penentuan terendah untuk mengesan kepekatan diperoleh sebanyak 1.61×10^{-7} M.

ELECTROCHEMICAL REDUCTION OF NITRATES AND NITRITES USING COPPER MODIFIED PLATINUM ELECTRODE

ABSTRACT

The electroreduction of nitrates and nitrites were carried out in this study using a copper modified platinum (Pt-Cu) electrode in the presence of 0.05 M KCl solution using cyclic voltammetry. Comparison was carried out using various working electrodes such as Cu, copper modified copper electrode (Cu-Cu) and copper modified pencil graphite electrode (PG-Cu). For the copper modified electrodes, the deposition of the copper particles was maintained at 30 cycles/ 18 seconds as the best ratio. The real surface area Pt, Cu, Cu-Cu, PG-Cu and Pt-Cu electrodes were estimated to be 1.747 cm^2, 0.814 cm^2, 0.988 cm^2, 1.146 cm^2 and 2.259 cm^2 respectively. The activity and selectivity for electroreduction of both nitrates and nitrites were better at the Pt-Cu electrode. The plot $i_p$vs$v^{1/2}$ shows that the electrons transferred in the rate determining step was 1.51, 1.66, 1.88 and 2.05 on the Cu, Cu-Cu, PG-Cu and Pt-Cu respectively indicating the electroreduction of nitrate to nitrite. At more negative overpotentials, the number of electrons transferred was approximately 5.15, 5.26, 5.35 and 6 on the Cu, Cu-Cu, PG-Cu and Pt-Cu electrodes respectively, corresponding to the production of ammonia. The order of the reaction in the presence of Pt-Cu electrode was 0.97 and 0.90 for the electroreduction reaction of nitrate and nitrite respectively. The rate constant of electroreduction of nitrate (2.228×10^2 min^{-1}) and nitrite (4.690×10^2 min^{-1}) when using Pt-Cu electrode was relatively higher compared to other electrodes studied which proved that Pt-Cu electrode performance is the best compared Cu, Cu-Cu and PG-Cu electrodes. The electrochemical behavior of a Pt-Cu electrode on the electroreduction of nitrate and nitrite ions has been investigated in an alkaline medium (0.05 M NaOH) in the presence of 5 mM sodium inositol hexaphosphate ($NaIP_6$). Different electrode compositions (Cu, Pt, and Pt-Cu) were used to study their activity and selectivity towards the electroreduction of nitrates and nitrites using cyclic voltammetry. The Pt-Cu electrode shows the best performance. The addition of $NaIP_6$ is to prevent the oxidation of copper atoms to copper ions. The effect of $NaIP_6$ on the optimization of the electrode activity and stability was investigated in this study. The presence of $NaIP_6$ further improves the performance of the Pt-Cu electrode especially the stability of the electrode. The effect of the interfering ions on the performance of the Pt-Cu electrode was also carried out. The effect of the pre-added nitrate and nitrite to the overall electroreduction process was determined in the 0.05 M KCl. Here, a higher rate constantfor nitrate reduction was observed in the system without pre-added nitrite (2.215×10^2 min^{-1}) compared to the system with added nitrite (55.97 min^{-1}). The rate constant of reduction of nitrite was higher without the presence of nitrate ions (3.954×10^2 min^{-1}) compared to those in the presence of nitrate (3.349×10^2 min^{-1}). At higher concentration of nitrite the rate constant of reduction deteriorates. The electroreduction of nitrate and nitrite was observed to be more feasible in the presence of Cl^- and ClO_4^- ions compared to the larger SO_4^- and Br^- ions. The order of the reaction was approximated to 1. The rate constant of the nitrate and nitrite electroreduction was the highest in the KCl solution. Electron transfer for nitrate reduction step is nearly two electrons while the number of electrons transferred for the nitrite reduction steps varied according to the adsorption ability of the preceding nitrate ions which ranged from four to six electrons. For the interfering cations analysis, the electroreduction activity was feasiblefor the singly charged cations. The order of reaction attained was approximately 1 for both nitrate and nitrite reduction. For the nitrate reduction, the rate of the reaction was higher in the presence of K^+ ions (2.213×10^2 min^{-1}) than the Na^+ ions (2.143×10^2 min^{-1}) while the rate constant increased in the sequence Cu <Al<Mg<Ca for the rest of the cations per mol of NO_3^- and NO_2^-.. A higher reaction rate constant for nitrite reduction was observed in the presence of the Na^+ ions ($5.571\times10^2 min^{-1}$)than the K^+ ions (4.699×10^2 min^{-1}) while Ca^{2+} ion produced the highest rate (6.397×10^2 min^{-1}) for the rest of the cations. The limit of detection of nitrate concentration was determined as 1.61×10^{-7} M.

CHAPTER 1

INTRODUCTION

1.1 Nitrogen Cycle

Denitrification of nitrogen compounds to molecular nitrogen from terrestrial and marine ecosystems plays an important role in the nitrogen cycle. Nitrogen predominantly can be found in several oxidation states such as in nitrate (+5) and ammonia (-3). The biogeothermal nitrogen cycle (Fig. 1.1) allows the interconversion of free atmospheric nitrogen to nitrogenous compounds to maintain the equilibrium between them in a huge reservoir. Many oxidative and reductive processes happen in the nitrogen cycle (Cabello et al., 2004). All living things need nitrogen to build protein and other important biological and chemical molecules such DNA and RNA. One of the important nitrogen compounds in the cycle is nitrate which is fixed from the environment by nitrogen fixing microorganism, plants and industrial process (Galloway et al., 2004). Soils, water and plants such as legumes are the main source of nitrates. Nitrate is required as the building block for plant growth and development. When animals and humans die, nitrates will be returned to nature by microbial degradation or decomposition which will be further reduced to nitrogen. Nitrates have the tendency to be converted into nitrites and vice versa in nature (Imsande and Touraine, 1994).

1.2 Nitrate and its derivatives uses

Nitrate is generally used as a precursor to produce useful products such as ammonia, hydroxylamine, hydrazine, nitrous oxide and many more in laboratories industries. The

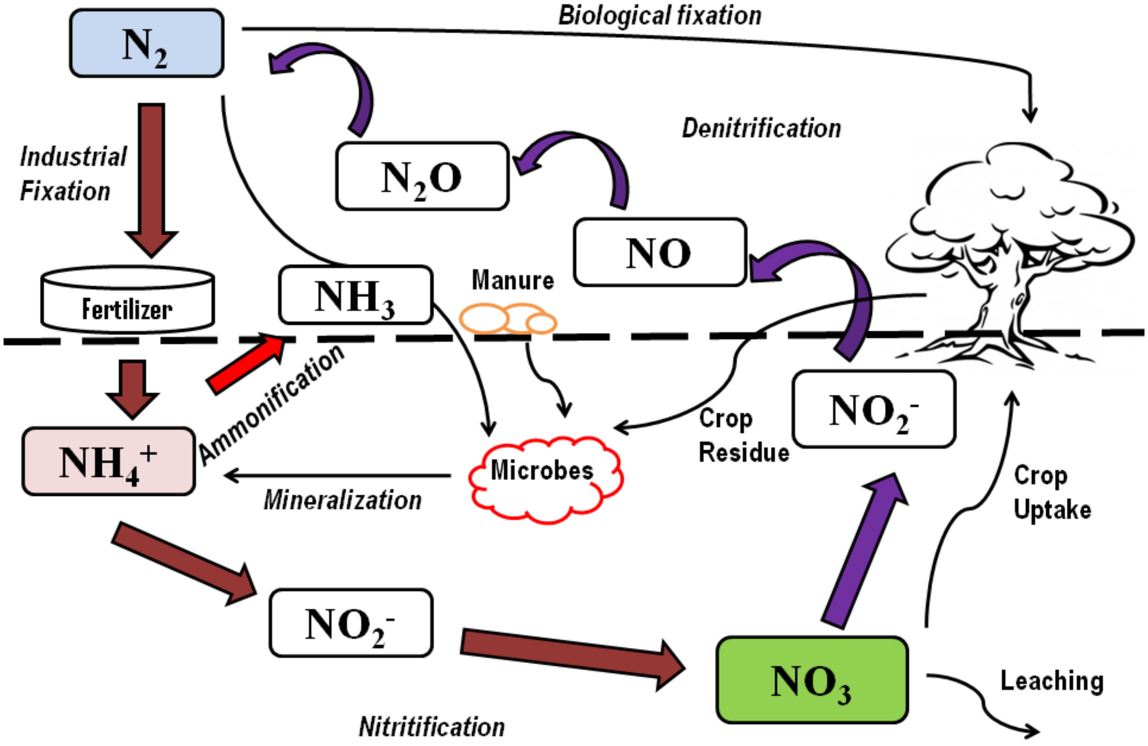

Figure 1.1 The nitrogen cycle and various processes of nitrification and denitrification (adapted from Cabello et al., 2004).

versatility of this chemical agent ensured the wide range exploration not only in the industrial sector ranging from manufacturing of fireworks, explosive materials and production of dyes but as an anti microbial agent (Moorcroft et al., 2001; Saiful Alam et al., 2012).

The nitrogen gas produced from nitrate reduction used in the Haber process (Modak, 2002) in the presence of hydrogen gas to produce ammonia. The reaction that takes place is as follows:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad (1.1)$$

This process in indirectly important for the agricultural sector where ammonia based fertilizer can be produced. The nitrogen source in the ammonia based fertilizer is useful for the uptake by the plant. In the nuclear industry, strong alkaline solution is used to neutralize the nitric acid in the waste cleanup solution. The recycling of the alkaline solution after neutralization applies the theory of the conversion of nitrate into ammonia (Xing et al., 1990).

Manufacturing of caprolactam has gained increasing interest as it is an intermediate required for the production of nylon-6 fiber and resins. Hydroxylamine is added in the earlier part of the synthesis together with cyclohexanone to produce caprolactam (Ichihashi and Sato, 2001). Nitrate is also used as a starting material for the production of hydrazine and azides (Bae et al., 2007) which are precursors for polymer synthesis and manufacture of pesticides. In the food industry, nitrites are constantly added into meat products as a preservative agent. This is to extend the shelf life of the processed food and to prevent food poisoning by microorganisms such as *Clostridium* *botulinum* (Swann, 1977). Reduction of nitrate also plays a vital part in the medical field where nitrous oxide (N_2O) also known as laughing gas is used as an anesthetic. Patients are given a low concentration of N_2O as a pre-surgical procedure (Jevtovic-Todorovic et al., 1998). In biological processes, nitrate is assimilated by microorganisms through fixation of inorganic nitrogen in the atmosphere which is taken up by plants as nutrients for the photosynthesis process. The nitrogen component in nitrate is equally important at the molecular level. The nitrogen atom is vital for production of amino acids production which in turn act building blocks for nucleic acids and other cellular components (Patey et al., 2008).

1.3 Environmental and Health Risks

The nitrogen cycle is further divided into three reservoirs of nitrogen such as the atmosphere, soils and marine. Increasing human activities annexing a new reservoir for nitrogen thus changes the established equilibrium of the nitrogen cycle (Smil, 2011). The contamination of nitrate and its derivatives slow down efforts on achieving a global clean environment. Most of the contamination happens on surface and in groundwater due to various factors. Urbanization and industrialization increases human activities and industrial discharge that contain nitrate without proper treatment into the rivers or lakes (Hasnat et al., 2011). The perturbation of the nitrogen cycle generates severe consequences such as acid rain and greenhouse effect to the current environment due to extensive urbanization and human activities (Estudillo-Wong et al., 2013). In the agriculture sector, overuses of fertilizers in the plantations have been known as one of the major causes of nitrate contamination in water (Cuibus et al., 2012). Higher dosage of nitrogen based fertilizers was used to intensify the agricultural activity (Massai et al., 2009). Another source of nitrate contamination is the animal faeces or manure. Improper removal of animal faeces from farms causes the leaching of nitrate into ground water. Furthermore, certain farmers store manure as a cheaper alternative to fertilizers. However, the efficiency of this organic fertilizer compared to more expensive commercial fertilizers is way lower and this encourages those farmers to apply an excess of manure, which indirectly increases nitrate concentration in groundwater (Hallberg and Keeney, 1993). In addition, the activity of microbial and usage of pesticides also elevate the nitrate concentration in agricultural land (Mahvi et al., 2005). Irrigation impact and storm runoffs also increase nitrate leaching into the ground water (Kim et al., 2007). Excessive accumulation of nitrates and its derivatives can cause eutrophication due to algae and phytoplankton bloom of rivers, lakes and seas. This thus lowers the level of oxygen in water and further deteriorates the habitat of aquatic organisms (Platt et al., 2003; Saiful Alam et al., 2012). Besides atmospheric deposition of nitrates and ammonia affecting the natural ecosystem, the emission of nitrous oxides from industrial area and vehicle contributes to the greenhouse gas accumulation behind CO_2 and $CH_{4.}$

Nitrates are generally less hazardous but readily converted or reduced to nitrite and other nitrogenous compounds such as ammonia (NH_3), nitrous oxide (N_2O), nitrogen dioxide (NO_2) and many more that cause serious threat to human health. The high solubility of nitrates in water and the reduction from certain bacteria in food products and human intestines enhance the conversion into nitrite (Badea et al., 2001). Nitrites on the other hand, upon reaching the blood circulation system will react with hemoglobin to form methemoglobin by oxidizing the Fe^{2+}. Methemoglobin reduces the efficiency to transport oxygen to vital organs in the human body thus contributing to a condition known as methemoglobinemia (Huang et al., 1998). Methemoglobinemia also occurs in infants which is known as blue baby syndrome (Lecloux, 1999 and Pintar, 2003). Besides, Epron et al. (2001) also reported that elevated blood pressure which leads to hypertension occurs when the level of the nitrate is high in the human body.

Nitrosamine which is a carcinogenic compound is formed by the reaction between nitrite and amines, amides or other nitrogenous compounds. Nitrate ingestion also linked to mutagenic, teratogenic effects and induces cancer to certain vital organs such as the liver and stomach (Moorcroft et al., 2001).

The intake of excessive red and processed meat which is cured with nitrite can cause food poisoning by increasing the formation of N-nitroso compounds (NOC) in humans. Again this compound induces several types of human cancer which includes tumor of the thyroid gland, ovary and kidney (Habermeyer et al., 2015).

1.4 Regulations and Recommendations

Although the nitrate has its own demands and drawbacks, certain regulations needed to be undertaken in order to minimize the health risk factor to humans. The major source of exposure to humans is through drinking water. The World Health Organization has imposed the maximum permissible level of nitrate, nitrite and ammonia at 50 mg L^{-1}, 3 mg L^{-1}, and 0.5 mg L^{-1} respectively (Manea et al., 2010; World Health Organization, 2011). The European Union states that 50 mg L^{-1} of nitrate is the legally permissible level in potable water (Badea, 2009). The United States Environmental Protection Agency (EPA), 2012 regulates the level of nitrate and nitrite in drinking water at 10 mg L^{-1} and 1 mg L^{-1} respectively. The Malaysian government through the Ministry of Health regulates the maximum contaminant level (MCL) of nitrate and nitrite at 10 mg L^{-1} and at 1.5 mg L^{-1} for ammonia (Ministry of Health Malaysia, 2010).

1.5 Denitrification- Past and Current technologies

There are many techniques including biological, chemical and physiochemical methods such as reverse osmosis, ion exchange chromatography and catalytic reduction by hydrogen which have been reported for the reduction of nitrates. The development of denitrification method is used to fulfill the demand of uncontaminated drinking water.

1.5.1 Biological Denitrification

Biological removal of nitrates from water depends on heterotrophic microorganisms which require an organic carbon source. Since drinking water does not have enough carbon sources, it was added externally by means of methanol, ethanol, shredded newspapers and wheat straw. Post treatment of water effluent is needed to remove color from the wheat in the water (Aslan and Turkman, 2005). Furthermore biological denitrification (reduction) requires continuous monitoring with addition of carbon sources, temperature and pH control (Reyter et al., 2006). In addition, the rate of biological denitrification is very slow which is a major setback for the current fast paced world. It is difficult to control the parameters for optimum removal of nitrate. The cost of maintenance is extremely high and the organic substrate needed for the process has to be supplied constantly (Polatides and Kyriacou, 2005). Generation of biological waste and large residence time restrict the employment of biological denitrification (Barrabes et al., 2006).

1.5.2 Chemical Denitritfication

Nitrates can be also removed chemically in the presence of Fe^0. However, this reaction depends on the initial solution pH. At higher acidity, nitrates were rapidly removed by Fe^0. Iron oxidation consume H^+ thus a constant supply of acid or organic buffer solution is required to maintain the reduction at a high rate (Xu et al., 2012). On top of that, Fe^0 efficiency deteriorates once an oxide layer is formed therefore anoxic conditions need to be maintained throughout the reduction process. Fe^0 is added to the contaminated water as a sample pre-treatment step which needs to be cleaned to produce iron free water at the end of the analysis (Huang et al., 2003). Another parameter of concern is the ratio between the catalyst and substrate. A precise ration between Fe^0/NO_3 is needed to efficiently remove nitrate from the system in a stipulated time. Furthermore, control of pH is vital for the reduction of nitrate by iron (Huang et al., 1998). Polatides and Kyriacou (2005) reported that chemical methods require large quantities of metal, therefore the cost of operation might escalate if noble metals such as platinum or palladium are used as reducing agent. In addition, the production of toxic by product if is not treated properly could further cause negative impact to the environment.

1.5.3 Physio-chemical Denitrification

As for the physio-chemical method, reverse osmosis technique was used to remove nitrates from salt water, to purify industrial effluents and reduce water hardness. This technology is widely employed due to its low specific energy consumption and to excellent performance. However, the desalination process cost more as it needs to utilize extensive energy and produces high amount of CO_2 due to consumption of fossil fuels

(Qiblawey et al., 2011). Spectrophotometry technique normally applied to determine nitrite. This can be done by reacting sulphanilamide and N-1-naphthylenediamine which require utmost control of the level of acidity for each step in the process. The carcinogenic effect and interference presence in the sample matrix could tamper the result and make it unreliable. Furthermore, many steps of sample pre-treatment was needed before a proper sample analysis can take place. Ion Chromatography and High Performance Liquid Chromatography method are much faster, reliable and have higher sensitivity than spectrophotometric method although they too are often time consuming for sample analyzing and need for the sample to be treated earlier (Badea et al., 2001). Ion exchange resins are also widely being used. Even though the process is selective i.e. removes only the required nitrate from potable water, the production of a large excess of regeneration agent, NaCl, is inevitable. The used regeneration solution is contaminated by nitrates and post treatment of effluents is thus needed to remove nitrates so that the NaCl solution can be reused again (Katsounaros and Kyriacou, 2007).

1.5.4 Catalytic Hydrogenation

Catalytic hydrogenation using various bimetallic systems has been another alternative way to remove nitrate to atoxic nitrogen from contaminated water in a versatile conditions (Krawczyk et al., 2011). In spite of that, costly H_2 consumption and optimum catalysis fabrication present some drawbacks to this method (Reyter et al., 2008a).

1.5.5 Electrochemical Denitrification

Electrochemical methods have advantages such as no requirement of chemicals before and after the treatment, producing no sludge, requirement of a small area and low investment cost. Furthermore, one can selectively reduce nitrate ions to the desirable products such as nitrogen and ammonia (Koparal and Ogutveren, 2002). Manea et al. (2010) reported that electrochemical treatment is user friendly as it produces rapid response towards the reduction activity and simple operation. This method also can be applied for large scale nitrate reduction where higher concentrations of nitrate can be used without any requirement of a reduction agent. The final products of the nitrate electroreduction depends on electrolyte pH, cathode material and applied potential (Badea, 2009). Electrochemical methods also register higher current efficiencies where most of the charge produced is converted to useful current which drives the electrochemical system or reaction. Currently, the need for more green, clean and much safer waste water treatment ensures that the electrochemical method is the better option (Ohmori et al., 1999). The long term performance over 24 hours of continued usage is another added advantage of these electrochemical methods. Electrode cleaning and activation is made by applying a low intensity. In spite of this, direct nitrate reduction has shown poor sensitivity on unmodified electrodes, marked irreproducibility and happens at negative overpotentials which need to be attended to produce optimum results (Luo et al., 2013; Moorcroft et al., 2001).

1.6 Problem Statement

The electrochemical reduction of nitrate faced continuous problem on the reliability of unmodified electrodes, surface passivation and interference by other ions in the working solutions. The combinations of different electrode materials are needed to tackle these problems. The addition of $NaIP_6$ in the working system especially in the sodium hydroxide solution seems to improve the electrode surface corrosion but work need to be carried out to investigate the effect on the nitrate reduction reaction.

1.7 Research Aims and Objectives

The aim of the current study is to compare the electrochemically modified working electrode performance in various factors that influences the electroreduction of nitrates and nitrites by the means of cyclic voltammetry. The first part of this study is focused on electrode preparations, characterization, polarization and kinetic studies. The overall performance of copper modified platinum electrode (Pt-Cu) is compared with copper modified pencil graphite, copper modified copper electrode, and bare copper and platinum electrodes. The activity of the electrode is mainly concentrated in the neutral media (potassium chloride) to reduce the interferences from other factors. The investigation in this study will concentrate on Pt-Cu as the electrode of interest. The final part of the study is concerned on the optimization of the Pt-Cu electrode on the electroreduction of nitrates and nitrites in the alkaline medium, initial nitrate and nitrite concentration, influence of different cations, influence of supporting electrolyte and limit of detection of nitrates and nitrites. The addition of inhibitor $NaIP_6$ reduced the surface passivation of copper based electrodes thus extend the usage of the copper modified electrodes in alkaline medium. The electrodeposition of copper for the electrode modification will be carried out electrochemically and was characterized by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The summary of the overall objectives of this study are as follows:

i. To prepare the copper, platinum, copper modified copper, copper modified pencil graphite and copper modified platinum electrodes electrochemically.

ii. To characterize, compare and evaluate electrochemically the performance of the Pt-Cu electrode with PG-Cu, Cu-Cu, Pt and Cu electrodes in potassium chloride medium.

iii. To evaluate the effect of the corrosion inhibitor, $NaIP_6$ on the Pt-Cu electrode in alkaline medium, NaOH

iv. To evaluate performance of the Pt-Cu electrode under various parameters that influences the electroreduction of nitrate and nitrite.

CHAPTER 2

LITERATURE REVIEW

In this study, the electrochemical method was employed to evaluate the electroreduction activity of nitrates and nitrites. Cyclic voltammetry technique is known for its vast applications and advantages (Bard and Faulkner, 2001; Luo et al., 2013). The dependence of nitrate reduction on the nature or type of electrode surface makes this process interesting. Several factors influence the electroreduction of nitrate and nitrite which was pointed out by Dima et al., (2003) such as nature of electrode materials, electrode potential, and presence of any additives on the solution and electrolyte pH.

2.1 Electrode Materials

The fabrication of an electrode or catalyst is important to ensure the electroreduction process that was undertaken will give a desirable result. Some of the electroreduction work has been carried out on unmodified electrodes while certain researchers have opted for modified electrodes which take different electroreduction pathways or mechanisms. Although the bare or unmodified electrodes are a good option to reduce nitrate, the extensive surface passivation affects the ability of the electrode to reproduce the results. Furthermore, lower sensitivity for nitrate reduction is also observed (Davis et al., 2000). One of the metals that are vastly used as an electrode material is platinum. Platinum based electrode material displays an excellent stability and good reduction properties especially in aqueous solutions which is further enhanced by the fabrication of the bimetallic electrode or catalyst (Kerkeni et al., 2002). Silver based bimetallic electrodes are been good promoters for nitrate reduction, nearly same level as those of copper. The more noble a metal is (Au > Pt > Pd), the less active for it to reduce nitrate (Gauthard et al., 2003).

Yang et al. (2013) reported that promoter metal is important to enhance the adsorption of nitrate to the Pt surface. Although the rate determining step is the reduction of NO_3^- to NO_2^- , the concentration of nitrite near the interfacial surface of the electrode determines the intermediate and the end product of the reaction. One of the intermediate product is nitrous acid where it decomposes to NO which is reduced to N_2O (important intermediates for N_2 production) on the Pt surface. However, this happens only in acidic media. Another setback occurs here is the hydrogen evolution potential where the formation of the N_2O is retarded. Here, nonvolatile hydrogenated products are formed such as hydroxylamine and ammonia.

Copper on the other hand have been reported to be an efficient electrocatalyst for the nitrate reduction. The activity and the rate concerning the nitrate reduction are greatly improved in different medium. A better activity is also observed in copper among all coinage metals i.e. Cu, Ag and Au (Dima et al., 2003, Majidi et al., 2011, Polatides & Kyriacou, 2005; Tada & Shimazu, 2005). Copper shows that chemisorptions do not solely influences the surface of the electrode (Shiddiky et al., 2011).

The dependence of nitrates reduction on the nature or type of electrode surface makes the nitrate reduction interesting. The surface composition of bimetallic electrode influences the final product of the electroreduction of nitrate. Simpson et al. (2004) reported that changing the ratio of element in Cu-Ni alloys produces ammonia for

$Cu_{75}Ni_{25}$ and hydroxylamine for $Cu_{50}Ni_{50}$ and $Cu_{25}Ni_{75}$ respectively. The synergistic effect of bimetals can be explained where different adsorption sites for H-atoms (on the Ni) and NO_3^- (on Cu) co-exists. Macova and Bouzek (2005) showed that increasing the weight percentage of Zn on copper electrode (from 30 wt % to 41 wt %) increases the activity of the modified catalyst. However the end product detected in their system was ammonia. In a work by Pronkin et al. (2007), the modification of metal particles (Pd nanoparticles) by foreign adatoms (Cu atoms) increases the rate of electroreduction process. Pt atom shows similar characteristics as Pd in such way that it is highly selective for nitrite reduction (Barrabes et al., 2006).

The porosity of the surface of electrodes increases the catalytic capacity of the bimetallic and tri-metallic electrodes (Hasnat et al., 2011). The amount of coverage of N-species on the surface determines the reduction products. High coverage leads to nitrogen formation while low coverage leads to ammonia formation (de Vooys et al., 2000). The structural defects on the surface of an electrode act as preferential site for nitrate adsorption thus improving the reduction activity of nitrates. The rate of reduction of analyte (NO_3^-) increases as the surface of the electrode in contact with the electrolyte increases bearing other variables are kept constant. Deposition of nano-size materials on monometallic electrodes changes the surface area thus modifying the chemical, physical and mechanical properties (Reyter et al., 2006).

On the deposition of particles on electrode surfaces, Dai et al. (2004) stated that the deposition time is directly proportional to the size of deposited material. It means that the longer the deposition time, the more visible the material that was being deposited. Increase in concentration of solution will also increase the tendency for nanoparticles formation. Wang et al. (2006) reported that smaller particles were achieved when electrodeposition of copper was carried out at more negative potentials. Although the nitrate reduction capacity was increased when increasing the deposition amount, the electrode shows a negative trend on the nitrite reduction capacity when too much of the secondary particles were deposited on the electrode.

Electrodeposition of copper in acidic solutions is a slow and a kinetically controlled process. However, in the presence of bisulfate and chloride, the deposition of copper is enhanced kinetically. The large anions disturbed the salvation shell of strongly hydrated Cu^{2+} ions hence partially reducing to Cu^+ via complexation with Cl^- at the overpotential deposition potential region and further to Cu atoms (Markovic et al., 1995). Specific anion in the electrodeposition bath affect the morphology of the deposited Cu. Chloride ion improves electrodeposition of Cu atoms by increasing the surface roughness and waviness which increases the number of active sites. However it also oxidized 40-60% of deposited copper when an anodic potential sweep was applied. Nitrate interacts with copper thus induces dissolution. The presence of chloride in nitrate containing bath prevent the aforementioned reaction. Sulphate ions modify the morphology and brighten the copper electrodeposits (Chrzanowska et al., 2012, de Almeida et al., 2002; Ramos et al., 2001).

2.2 Kinetic and Mechanism studies of NRR in different Medium and pH

According to de Groot et al. (2004), the type of electrolyte used plays an important role in the reduction of nitrate. In perchloric acid solution the co-adsorption of ClO_4^- ion is very weak and considered negligible when compared to sulphate. This has a profound effect on the reaction rate. At a higher concentration of nitrate, negative reaction order was obtained. Santos et al., (2008), elaborated that at a low concentration of H^+, different mechanism for reduction of nitrate was observed. The surface passivation on the surface of platinum electrode hindered the appearance of extra peak which was only observed in the concentration of < 10 mM. The peaks were produced at different potentials (-0.13 V and 0.1 V *vs* RHE) and showed different reaction orders indicating that different products were produced.

The pH influences the thermodynamic of the electroreduction of the nitrate and nitrite. In acidic pH, neutralization process take place thus increasing the rate of reaction in the surface of the electrode. However, at basic pH, with the environment already rich with OH^- species, the addition OH^- species generated will passivate the diffusion of NO_3^- to the electrode surface thus reducing the rate of reduction.

In an alkaline medium, most of the electrochemical reduction mechanisms lead to the formation of nitrite and ammonia especially on the nickel, lead, zinc and iron electrode (Li and Chambers 1988). Similarly, when using copper electrode, there are several important electrochemical reactions involving the nitrate reduction that can be portrayed as follows (Reyter et al., 2006):

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^- \qquad (2.1)$$

$$NO_3^- + 3H_2O + 5e^- \longrightarrow 1/2N_2 + 6OH^- \qquad (2.2)$$

$$NO_2^- + 5H_2O + 6e^- \longrightarrow NH_3 + 7OH^- \qquad (2.3)$$

$$NO_2^- + 4H_2O + 4e^- \longrightarrow NH_2OH + 5OH^- \qquad (2.4)$$

$2NO_2^- + 4H_2O + 6e^- \longrightarrow N_2 + 8OH^-$ (2.5)

$2NO_2^- + 3H_2O + 4e^- \longrightarrow N_2O + 6OH^-$ (2.6)

$NO_2^- + H_2O + e^- \longrightarrow NO + 2OH^-$ (2.7)

$N_2O + 5H_2O + 4e^- \longrightarrow 2NH_2OH + 4OH^-$ (2.8)

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (side reaction) (2.9)

Reyter et al, (2008a) outlined that at negative overpotential (-1200 mV), hydroxylamine is produced via Eq. 2.4 using copper electrode. The charge transfer here was quasi-reversible. This is followed by a irreversible six electrons transfer to ammonia as in Eq. 2.3. The unstable hydroxylamine is immediately reduced to ammonia as it is not detected in the prolonged electrolysis samples.

In contrast, Badea (2009) found that the electrochemical reduction of nitrate in the alkaline medium follows a three charge transfer steps at specific potentials corresponds to the formation of nitrite, nitrogen and ammonia. At the more positive potential, nitrogen evolution is more predominant at low cathodic overpotential while ammonia at the high cathodic overpotential following the scheme below:

$NO_3^- \longrightarrow NO_2^- \longrightarrow (1/2)\ N_2$ E° = (-1230 mV) (2.10)

$NO_3^- \longrightarrow NO_2^- \longrightarrow NH_3$ E° = (-1400 mV) (2.11)

The first step for the electroreduction process consists of the reversible chemical reaction which is followed by the irreversible charge transfer from NO_3^- to NO_2^- in accordance to Nicholson-Shain scheme (case IV). The reversible chemical reaction is the adsorption of nitrate onto the copper electrode. The second charge transfer followed case VIII of Nicholson-Shain scheme where catalytic chemical reaction and irreversible charge transfer were involved (Nicholson and Shain, 1964). The dimerisation of NO^- intermediate leads to formation of $N_2O_2^{2-}$ which then generates the N_2O species via chemical reaction. Finally N_2 is produced via irreversible charge transfer mechanism at -1230 mV. All the reactions were shown in Eq 2.12 to 2.16 below:

$$2(NO_2^-)_{ads} + 2H_2O + 4e^- \longrightarrow 2(NO^-)_{ads} + 4OH^- \qquad (2.12)$$

$$2(NO^-)_{ads} \longleftrightarrow (N_2O_2^{2-})_{ads} \qquad (2.13)$$

$$(N_2O_2^{2-})_{ads} + H_2O \xrightarrow{rds} (N_2O)_{ads} + OH^- \qquad (2.14)$$

$$(N_2O)_{ads} + H_2O + 2e^- \longrightarrow N_2 + 2OH^- \qquad (2.15)$$

$$2NO_2^- + 5H_2O + 6e^- \longrightarrow N_2 + 10OH^- \qquad (2.16)$$

At the more negative overpotentials, the evolution of H_2 influences the generation of final product into ammonium where again chemical reaction precedes the irreversible charge transfer (Eq. 2.17 and 2.18).

$$(N_2O_2^{2-})_{ads} + 2H_2O \xrightarrow{rds} (H_2N_2O_2)_{ads} + 2OH^- \qquad (2.17)$$

$$(H_2N_2O_2)_{ads} + 8H_2O + 8e^- \longrightarrow 2NH_4OH + 8OH^- \qquad (2.18)$$

Hasnat et al. (2011) discussed that in a neutral medium (0.5 M KCl), the mechanism of nitrite reduction follows a two-step charge transfer. The formation of NO adlayer on the surface of electrode in the first step (Eq. 2.7) precedes the production of either hydroxylamine or ammonia. Around four electrons transfer was involved in the second charge transfer that either reaction 2.2 or 2.3 might take place:

$$NO + 4H_2O + 5e^- \longrightarrow NH_3 + 5OH^- \qquad (2.19)$$

$$NO + 3H_2O + 3e^- \longrightarrow NH_2OH + 3OH^- \qquad (2.20)$$

The rate constant and order of reaction in other working environments were tabulated in Table 2.1.

2.3 Electrode Reliability in the Alkaline Medium

Copper exhibits a better electrocatalytic capacity on reducing nitrate to nitrite as an intermediate product and ammonia as the final product in a weakly alkaline solution. Comparatively, lower reduction activity was observed for the Ni, graphite and Pt electrodes. Although similar behavior with Cu was observed on Ni, a different mechanism and electrocatalytic activity was noticed on the graphite and Pt electrode (Bouzek et al., 2001). Afshari and Deghaniann (2009) summarized that the smaller crystal size influenced the corrosion of electrode material (Fe) in alkaline medium. This is due to the high density of nucleation sites of the passive film which decreases the corrosion rates. Luo et al. (2010) reported that the three major copper corrosion reactions taking place were as follows:

$$2Cu + 2OH^- \longrightarrow Cu_2O + H_2O + 2e^- \qquad (2.20)$$

Table 2.1 Kinetic data from various studies involving nitrate and nitrite reduction reaction

Electrode composition	Medium	Mechanism	Rate constant	Order of Reaction	References
$Sn_{85}Cu_{15}$	0.1 M K_2SO_4	$NO_3^- \rightarrow NO_2^-$ $NO_2^- \rightarrow NH_3$ $NO_2^- \rightarrow N_2$	$4.9\times10^{-4}\ s^{-1}$ $1.76\times10^{-5}\ s^{-1}$ $7.66\times10^{-3}\ s^{-1}$	-	Polatides and Kyriacou, (2005)
Ag	KCl	$NO_3^- \rightarrow NO_2^-$ $NO_2^- \rightarrow NH_3$	$35.1\times10^{-3}\ min^{-1}$ $6.5\times10^{-3}\ min^{-1}$	1st 1st	Saiful Alam et al., (2012)
Pt(110)	$HClO_4$	$NO_3^- \rightarrow$ Product	-	1st	Taguchi and Feliu, (2008)
$Cu_{45}Tl_{55}$	10 mM NaOH	$NO_3^- \rightarrow NO_2^-$ $NO_2^- \rightarrow$ Product	-	0.72 0.69	Casella and Gatta, (2004)
Pd-Rh	$NaNO_3$	$NO_3^- \rightarrow NO_2^-$	$39.1\times10^{-3}\ min^{-1}$	-	Hasnat et al. (2010a)
Ag-Pd **Ag-Pt-Pd**	KNO_3	$NO_3^- \rightarrow NO_2^-$	$25.1\times10^{-3}\ min^{-1}$ $84.3\times10^{-3}\ min^{-1}$	-	Hasnat et al. (2011)
Pd **Pt-Pd, Ni-Pd,** **Ag-Pd, Cu-Pd** **Rh-Pd**	$NaNO_2$	$NO_3^-/ NO_2^- \rightarrow NH_3$	$2.3\times10^{-3}\ min^{-1}$ $8.1\times10^{-3}\ min^{-1}$ $21.1\times10^{-3}\ min^{-1}$		Hasnat et al. (2009)
Sn	0.1 M K_2SO_4	$NO_3^- \rightarrow NO_2^-/ NH_3/ N_2$	$104\times10^{-3}\ min^{-1}$	1st	Katsounaros et al. (2006)

$$Cu_2O + 2OH^- \longrightarrow 2CuO + H_2O + 2e^- \quad (2.21)$$

$$Cu_2O + 2OH^- \longrightarrow 2Cu(OH)_2 + 2e^- \quad (2.22)$$

The corrosion of copper based electrodes in alkaline medium involves complex chemistry. Kang et al. (2002) reported that the Cu(OH) species was observed over the entire potential region before the formation of Cu_2O on the anodic scan therefore confirming the species plays an important role in the dissolution of copper electrode. At the higher pH, formation of $Cu(OH)_2$ is prevalent than CuO which is thermodynamically preferred. It is also noted that light influences the overall reduction of oxidized copper. In fact, both $Cu(OH)_2$ and Cu_2O species directly reduced to Cu as follows (Mayer and Muller 1992):

$$2CuO + H_2O + 2e^- \longrightarrow 2Cu_2O + 2OH^- \quad (2.23)$$

$$Cu_2O + H_2O^- + 2e^- \longrightarrow 2Cu + 2OH^- \quad (2.24)$$

$$Cu(OH)_2 + 2e^- \longrightarrow Cu + 2OH^- \quad (2.25)$$

The addition of corrosion inhibitor is vital to impede the rate of dissolution of electrode material in the course of experiment. Phytic acid is a naturally occurring plant antioxidant which is known for suppressing the oxidation process in iron based biological processes. The availability of OH^- radical species causes the damaging effect on the iron catalyzed reactions which is prevented by phytic acid (Graf and Eaton 1990). This made Notoya et al. (1995), investigate the effect of phytic acid and its salt as inhibitor of copper corrosion in potable water. Phytic salts which are also known as inositol hexaphosphate (IP_6) inhibit the pitting corrosion on copper tubing that carries water. Cu_2O is mainly formed when phytic salts were used as inhibitor thus retarding the formation of the main corrosion product, CuO. Wang and He (2012) showed that the copper inhibition efficiency by IP_6 depends on the NaOH concentration. Although the inhibitor IP_6 promotes the formation of Cu_2O passive layer, further oxidation into CuO species was inhibited.

The mechanism of corrosion inhibition by IP_6 on the metal surface was by self-assembled monolayer (SAMs) method. The interaction between the IP_6 and oxide of copper produces Cu_x-IP_6 which will be detached and exposes the inner Cu_2O layer. Therefore double protection is viable in the presence of IP_6. Furthermore the detachment of Cu_x-IP_6 layer produces the self cleaning process by removing some oxide species on the surface of the copper (Yang et al., 2005).

2.4 Influence of Electrode Potentials on the NRR

Reyter et al. (2008a, b) stated that reduction of nitrate leads to formation of many intermediate products such as nitrite, hydrazine, hydroxylamine, ammonia, nitrogen and other oxygen based nitrogen species. However, the main reduction product was ammonia especially at very negative over potentials and nitrites at more positive over potentials. Hasnat et al. (2010a & 2011) stated that the nitrate reduction on cathode sometimes hindered at the negative potentials that contribute to hydrogen gas evolutions which hindered the adsorption of the nitrate ion on the electrode surface. The reduction rate of nitrate ($\boldsymbol{k_1}$) was decreased at more negative potentials where the rate of removal of nitrite ($\boldsymbol{k_2}$) increases (Fig. 2.1) with selectivity towards ammonia is prevalent.

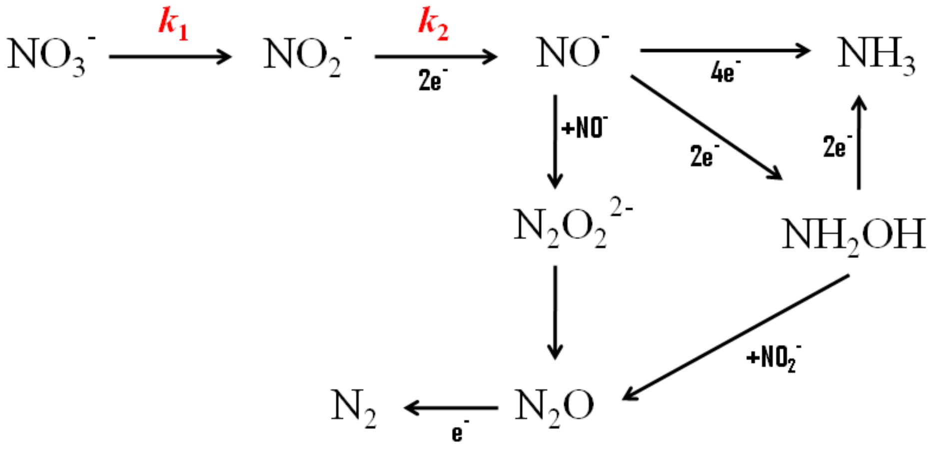

Figure 2.1 Schematic diagram of the nitrate and nitrite reduction pathways in various electrochemical systems (adapted from Pronkin et al., 2007).