SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

CRYSTALLIZATION OF IRON OXIDE NANOTUBES BY ANODIZATION AND THEIR RELATION TO PHOTOCATALYTIC PROPERTIES

By

NORAHASYIMA RAMLI

Supervisor: Associate Professor Dr. Zainovia Lockman

Dissertation submitted in partial fulfillment

of the requirement for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Crystallization of Iron Oxide Nanotubes by Anodization and Their Relation to Photocatalytic Properties**". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

Name of Student : Norahasyima Ramli Signature:

Date : 25th June 2018

Witnessed by

Supervisor : Assoc. Prof.Dr. Zainovia Lockman Signature:

Date : 25th June 2018

ACKNOWLEDGEMENTS

Alhamdulillah, in the Name of God the Most Gracious, Most Merciful and Almighty that I have successfully completed my Final Year Project entitled "Crystallization of Iron Oxide Nanotubes by Anodization and Their Relation to Photocatalytic Properties". Firstly, I would like to sincerely thank my supervisor, Associate Professor Dr. Zainovia Lockman for her guidance, advice and support to bring this research project to completion. I always admire her passion in working and teaching diligently.

I gratefully appreciate School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM) for providing required environment and equipment to perform my research. Also, completing this work would have been all more difficult were it not for the support provided by the technical staffs of the School of Materials and Mineral Resources Engineering.

Besides, I would like to convey my appreciation to Dr. Zainovia's research team for providing the necessary help as well as the valuable advice on the experimental work, whenever I needed.

I also would like to thank all of my fellow classmates, friends and roommates who were always willing to share knowledges and always there to give emotional supports.

Lastly, my deepest gratitude were for my beloved parents and my sisters for their kindness and mental support during my study especially. Thanks for their endless love, support and encouragement.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

0 – D	Zero Dimensional
1 – D	One Dimensional
2 – D	Two Dimensional
3 – D	Three Dimensional
FESEM	Field Emission Scanning Electron Microscope
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction

LIST OF SYMBOLS

at %	Atomic percent
wt %	Weight percent
°C	Degree Celsius
°C/min	Degree Celsius per Minute
ppm	Part per million
Cr (VI)	Hexavalent Chromium
Cr (III)	Trivalent Chromium

Penghabluran Tiub Nano Ferum Oksida oleh Anodisasi dan Hubungannya dengan Sifat Fotokatalik

ABSTRAK

Cr (VI) adalah logam berat bertoksikan tinggi dan telah diklasifikasikan sebagai karsinogen kepada manusia. Cr (VI) memasuki alam sekitar daripada sumber seperti industri pembuatan kulit dan penyamakan, aloi dan keluli dan getah dan terutamanya industri tekstil yang menggunakan Cr(VI) sebagai pigmen dan pewarna. Kajian ini adalah untuk.menilai kebolehgunaan ferum oksida poros berstruktur nano, untuk penyingkiran Cr (VI) daripada larutan akueus. Struktur nano disintesis dengan teknik pengoksidaan anodik keluli karbon dan kemudian sepulindap untuk penghabluran ferum oksida. Selepas disepuhlindap, α-Fe_2O_3 terhasil disintesis kemudiannya telah dicirikan oleh Mikroskop Elektron Pengimbas Pencaran Medan (FESEM) dan Pembelauan X-Ray (XRD) untuk kajian morfologi dan fasa, masing-masing. Parameter yang dikaji adalah kesan masa penganodan, kesan voltan dan kesan isipadu peratusan H_2O dalam etilena glikol yang digunakan dalam elektrolit. Campuran nanoporous nanokeping dan nanodawai diperhatikan dalam eksperimen ini. Struktur nano filem anodik dihasilkan melalui proses penganodan, dengan 3 ml H_2O dan 50 V. Nanokepingan dengan campuran nanodawai terbentuk. Nanokepingan terhasil membentuk jajaran sel nanokepingan yang saling-hubung dengan luas sel 26.5 nm to 66.2 nm. Mekanisma penghasilan nanoporous dan sel nanokepingan saling-berhubung dicadangkan. Ferum oksida berstruktur nanoporos dan sel nanokepingan saling-berhubung digunakan untuk proses penurunan Cr(VI) di bawah pancaran matahari. Peratusan penurunan Cr (VI) pada pH 2 adalah yang tertinggi untuk sampel penurunan selepas satu jam.berbanding pada pH 4 and 6.

Crystallization of Iron Oxide Nanotubes by Anodization and Its Relation to Photocatalytic Properties

ABSTRACT

Cr(VI) is heavy metal of high toxicity and has been classified as human carcinogen. Cr(VI) enters into environment from sources such as manufacturing industries of leather and tanning alloys and steel, rubber and more importantly textile industries which utilizes Cr(VI) as pigments and dyes. This study is on the applicability of nanostructured porous iron oxide for the removal of Cr(VI) from aqueous solution. The nanostructured iron oxide anodic films were synthesized by direct anodic oxidation technique of carbon steel and then annealed for crystallization of iron oxide. After annealing, α-Fe_2O_3 formed was characterized by Field Emission Scanning Electron Microscope (FESEM) and X-Ray Diffraction (XRD) for morphologies and phases studies respectively. The parameters experimented were anodization time, effect of voltage and effect of percentage volume of H_2O in ethylene glycol used in electrolyte. A mixture of nanoporous, nanosheet and nanowires was observed from these experiments. The nanosheets formed as interconnected nanosheets arrays cell with cell width varies from 26.5 nm to 66.2 nm. Nanoporous structure were formed at 10 minutes anodization time, with 3 ml H_2O and 50 V. Nanosheets with mixtures of nanowire were formed. Nanoporous and interconnected nanosheets arrays of iron oxide were used as photocatalysts to reduce Cr(VI) under sunlight. The reduction percentage of Cr(VI) at pH 2 was the fastest after one hour of exposure to sunlight.

CHAPTER 1

INTRODUCTION

In this project, anodization of carbon steel was done to form iron oxide as the surface anodic oxide with nanostructures. The nanostructures were found to be in form of nanopores, nanosheets and nanowires but with majority of samples comprising of interconnected nanosheet arrays. The nanostructured iron oxide produced was then used as photocatalyst to reduce hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) under sunlight radiation. This chapter is on the background, problem statements, objectives, scopes of work and outline of the report.

1.1 Background

Water is the most essential compound on earth. Sustaining clean water is the prime requirement to ensure human will not face health problem by consuming dirty and polluted water. Nevertheless, water pollution is increasing worldwide due to rapid growth of industry, increase human population, and domestic and agricultural activities which leads to the life time threatening diseases (Schwarzenbach et al., 2010). In ensuring cleaner water for human consumption, wastewater from industries must be treated before it can be safely discharged to the environment. It is known that degradation of water quality due to industrial pollution causes negative effects to aquatic life forms, disturbs the balance of life and reduces the bioavailability of clean water (Afroz et al., 2014).

However, in most of developing country water resources management is a problem due to lack of awareness and supervisory body apart from government bodies. In Malaysia, Department of Environment (DOE) under Ministry of Natural Resources &

Environment is responsible in controlling the regulation in ensuring clean water discharge from industries. DOE take roles to prevent, eliminate, control pollution and improve the environment hence consistent with the purposes of the Environmental Quality Act 1974. The regulations there under DOE are also adhered well to conventions of the international environment meetings such as ‘Vienna Convention for the protection of the ozone layer’ in 1985, ‘Montreal Protocol on substances that deplete the ozone layer’ in 1987, and ‘Basel Convention on the transboundary movement of hazardous waste and their disposal act’ in 1989.

Nevertheless, even though large cooperation really obeys the regulation, there are small to medium industries that have neglected on ensuring the cleanliness of wastewater discharged treatment or not paying too much attention to it. There are various types of pollutants activity that can significantly affect human and environment. Afroz et al. in 2014 reported that there are three main sources of river pollution in Malaysia that is residential, agricultural and industrial wastes. One of the major impacts of water pollutions is that it will block the water clarity as pollution that built up on the water surface decreased the amount of sunlight available for photosynthesis of aquatic life. A suspended particle interferes with filter feeding and respiration through gills of aquatic microorganism for instance fish. In recent years, the treatment of clean raw water from surface water sources for human consumption and for industrial use has become more complex and becomes costlier and complex because of the sources of water pollution can be varied as shown in Figure 1.1

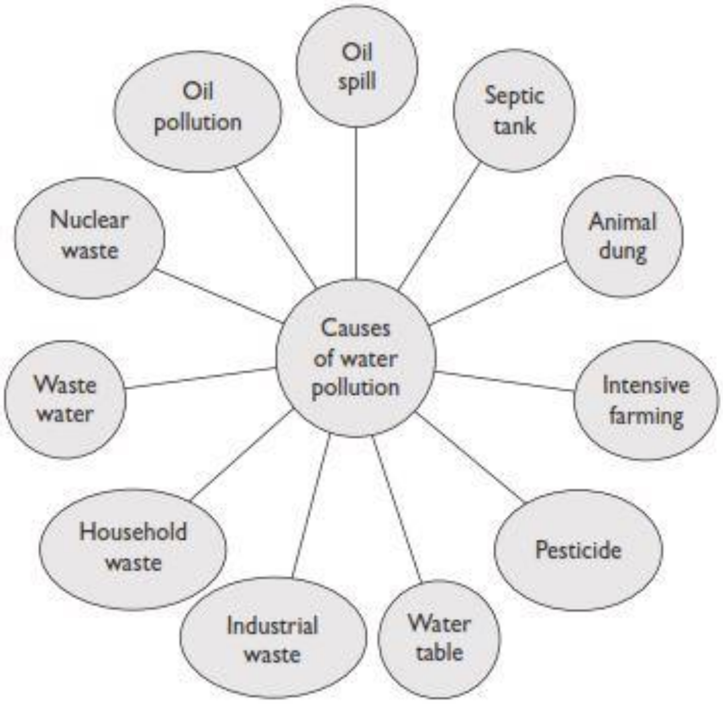

Figure 1.1: Major cause of water pollution in Malaysia (Afroz et al., 2014).

Among various major pollutants listed, industrial waste is perhaps the most severe as normally the waste is high in volume and may contains various types of complex toxic compounds. Among them, heavy metal ions are known to be one of the major pollutants. Heavy metal ions are however required for some industries despite they have adverse effect to human and ecology. Heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals such as, chromium (Cr), mercury (Hg), cadmium (Cd), arsenic (As), nickel (Ni) and lead (Pd) are naturally occurring elements that have a high atomic weight and a density at least 5 times greater than that of water (Järup, 2003). A recent study was conducted in Penang on the distribution of heavy metals (Cr, Cu, Cd, Co, Fe, Pb, Ni, V, and Zn) in the river sediments at Bayan Lepas Free Industrial Zone. Ten sampling stations were selected and sediment samples were collected during low tide. With guidelines from Interim Sediment Quality Guidelines (ISQGs), the pollution from heavy metal was found in these stations causes from discharges from factories drained into canals and the Keluang River, and subsequently into the coastal area near Jerjak Island and the Penang Second Bridge (Khodami et al., 2017). The pollution level despite moderate is not desired as accumulation of heavy metals can occur in aquatic animals exposed to the contaminated costal water. Moreover, bioaccumulation that is accumulation of heavy metal ions in an aquatic organism is possible and through food chain, local people may be exposed to contaminated seafood.

Heavy metals can enter the food web through direct consumption of water or organisms or through uptake processes and be potentially accumulated in edible fish or other types of seafood such as shrimp, oysters and mussels (Canli and Atli, 2003). Heavy metal when consumes can lead to various health effect including liver, kidney and gastrointestinal damage as well as bone defect. However the most severe would be mental retardation in children and changes in children behavior has found as a result of highly exposure of heavy metal to the human health (Singh et al., 2011).

Among various heavy metal ions, Cr(VI) is known to be carcinogenic; a cancer causing compounds. Cr(VI) compounds are however very important for producing various consumer products and used highly in metal industries. They can be usually found at work environment and industrial wastewater of metal processing sites, plating industries, textile, leather tanneries, agricultural fertilizer, paint, steel, iron mill, fireproof products, chromate, and chromate pigment and welding. There have been reports on the danger posed by workers exposed in industries that release chromium, for instance those working as metal cleaners, painters, pottery glazers, steel workers and wood preservative workers (Khadem et al., 2017). The route of exposure here may be from inhalation. Occupational Safety and Health Administration (OSHA) stated that the exposure limit of chromium to workers expressed as a time-weighted average without adverse effect averaged over a normal 8 hours workday or 40 hours workweek (OSHA, 1998). Cr(VI) can induce headache, diarrhea, nausea, vomiting, and even worse can cause lung cancer and kidney failure (Babel and Kurniawan, 2003).

One industry that produces high volume of contaminated wastewater is textile industry. Textile products are basically made from yarn and colour, the colourants for the yarn come from dyes or pigments. Some of the dyes and pigments contain heavy metal particles such as chromium, lead and mercury, for instance chrome orange contains lead carbonate, chrome yellow contains lead chromate and vermilion contains mercuric sulphide. In textile industry, only 90% of dyes or pigments will be used up for colouring yarns and another 10% will flow out as waste in water. Therefore, if untreated, wastewater from textile industry may contain all of these heavy metal ions.

Wastewater from batik industry also contains grease, wax and heavy metal suspended solids (McClatchy, 2011). In Malaysia, suspended solid is thought to be one of the main pollution of river water. The wastewater if not treated will flow to nearby river contaminating the river water with all of these pollutants. When this happen, heavy metal particles for instance will accumulate either in the water or as sediment and heavy metals particles can enter the food web through direct consumption of water or aquatic organism like fish, shrimp and crab. If the water is used for irrigation, there is also a possibility of plant uptakes of the heavy metal ions which then induce contamination of the plants. In recent years, there have been reports on the existence of heavy metal in rice. For instance in 2015, Zeng et al reported on the accumulation of Cd, Cu, Cr, Ni, Pb and Zn in rice grain near electroplating industry (Zeng et al., 2015).

In correlation to this alarming issue, industries are urged to relook into their wastewater treatment system. Perhaps a simple and cost effective water treatment system can be fixed in order to reduce water contamination. In this project, photocatalytic technology was assessed for the removal of Cr(VI) ions from water. As mentioned Cr(VI) ions are typically discharged from leather industries, alloys and metal forming industries, plating and, coating industries, paint and tanning factory. Thus, in this research first a photocatalyst material based on α-Fe_2O_3 with nanostructures was first fabricated by anodization of carbon steel. The carbon steel was collected from steel waste. Then, the nanostructured α-Fe_2O_3 was characterized and used to remove Cr(VI) to Cr(III) under sunlight illumination. The main aim is to completely reduce the existence of Cr(VI) in test solution in the presence of the α-Fe_2O_3 under sunlight.

Iron oxide in the phase of hematite (α), α-Fe_2O_3 was selected as the semiconductor photocatalyst that can reduce hexavalent chromium (Cr(IV)) to Cr(III). In the reaction process, electron-hole pairs must be generated when α-Fe_2O_3 is irradiated with photon energy larger than its bandgap energy, which is 2.5 eV. Upon illumination electron–hole pairs formed with electrons in the conduction and holes in valence band of the semiconductor. These charge carriers, can migrate to the semiconductor surface and they are, capable in reducing or oxidizing species adsorbed to the surface of the oxide with suitable redox potential (Barakat, 2011). The mechanism for visible-light photocatalytic reduction of Cr(VI) using iron oxide on in Figure 1.2.

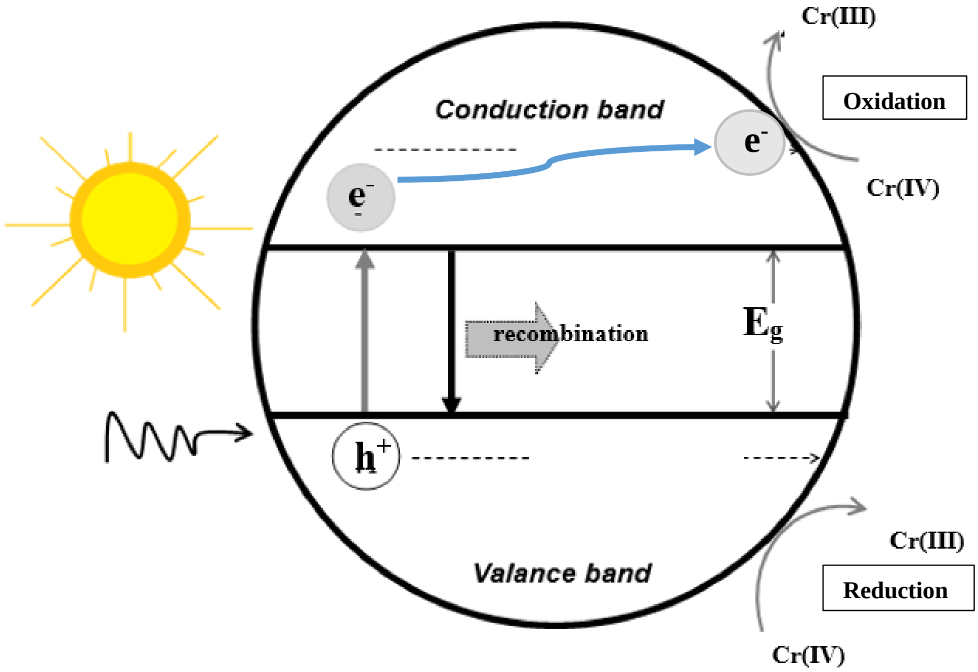

Figure 1.2: Schematic diagram on mechanism for photocatalytic reduction of Cr(VI) under irradiation of visible light (Shi et al., 2015).

From Figure 1.2, the photogenerated electron is expected to diffuse to the surface of α-Fe_2O_3 photocatalyst then it can reduce heavy metal ion, in this case Cr(VI), adsorbed on the surface of the oxide to Cr(III). Photocatalytic reaction for Cr(VI) reduction has been considered as a simple, inexpensive and effective ways in ensuring total removal of heavy metal ions from wastewater (Wang, 2012).

In this work, α-Fe_2O_3 was formed by anodization of waste steel plates. Anodization is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal. The process is called anodizing because the part to be treated forms the anode electrode of an electrical circuit (Stępień et al., 2014). Anodization was done because it can give anodic oxide with nanostructures. As reported by Rozana 2015, nanoporous α-Fe_2O_3 can be formed by anodisation of iron. In this work, anodisation of waste steel was carried out with oxidation parameters studied to produce various surface anodic oxide nanostructures.

1.2 Nanomaterials

Recently, nanomaterials have been used as the main material for purification wastewater. Nanomaterial is commonly referred as a material with structure of size ranging from 1 to 100 nm at least in one dimension (Xu et al., 2012). Generally, nanoadsorbents can come from organic or inorganic materials that have high reactivity and hence have high affinity to adsorb substances.

Nanomaterials can be classified into three categories; zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D). Among these nanostructure, thin film comprised of ordered aligned nanopores has been seen as a potential material in adsorption materials to treat effluent from industrial wastewater. It have a larger surface area, which in return more large area for adsorption of effluents (Haripriya et al., 2006). Thus, in this research, anodic film with nanoporous or interconnected nanosheet arrays on carbon steel plates were produced and on these nanostrutured α-Fe_2O_3 photoreduction of Cr(VI) was done.

1.3 Fe_2O_3 as Photocatalytic Material

In recent years, photocatalytic process using suspension of semiconductor particles has been receiving considerable attention as a method to treat polluted water. Semiconductor materials have shown good photocatalytic activity in removing various types of pollutants. However, commercial photocatalysts like TiO_2 show some disadvantages; it is a wide gap semiconductor and hence can only be activated under ultra violet radiation which accounts for only 4 % in sun light radiation. Recently, narrower band gap oxide semiconductors like α-Fe_2O_3 have been recognized as compatible candidates for photocatalysts under sun light (Santhosh et al., 2016). Activation under sunlight is desired as UV light activation would require an artificial source of light for catalysts activation.

There are three most stable phases of iron oxide materials: α-Fe_2O_3, γ-Fe_2O_3 and Fe_3O_4. Among these phases, α-Fe_2O_3 can be considered as good photocatalyst due to the appropriate valence band position for oxygen evolution and conduction band electrons with energy suitable for reduction of Cr(VI) to Cr(III).

1.4 Problem statement

Textile industry accounts for 91.4% investment based on Malaysian Investment Development Authority (MIDA) report in 2016. With more exporting activity of textile products, there will be more production of textile and hence more factories are to be built as to fulfil the demand. Concurrently there will be more effluent from these industries and waste will be released. A proper treatment is required as not to pollute ground and surface water from textile waste.

Batik is a very popular traditional handmade craft in Malaysia that its production started since 1960s. Batik industry is a substantial industry where largely run by small Malay entrepreneurs mostly in Kelantan and Terengganu. Some of batik factories were built alongside the river or even at the back of an owner's house (Syuhadah et al., 2015). It is known that batik industry consume a large amount of water in dyeing process and mostly still using traditional method, in said that will release untreated toxic effluent that have high chemical oxygen demand (COD) and total suspended solid (TSS) contents as being reported by Syuhadah et al. (2015). Chemical Oxygen Demand (COD) is a measure of oxygen requirement of a sample that is disposed to oxidation by strong chemical oxidant. COD is the most popular alternative test to BOD for establishing the concentration of organic matter in wastewater samples. Chemical Oxygen Demand test is used to indirectly measure the amount of organic compound in water, while Total Suspended Solid (TSS) is a measured of small solid particles which remain in suspension in water as a colloid and it is used as one of indicator of water quality.

The dyes discharged may also contain heavy metal ions including Cr(IV), lead and mercury. Consequently, a treatment that is easy and simple to be implemented is necessary in order to encourage small and medium enterprise (SMEs) like batik industry to treat the wastewater before it can be safely discharged to the environment (Yaacob and Zain, 2016).

In this research, a simple method for heavy metal treatment was proposed to be done by photocatalytic reduction on semiconducting Fe_2O_3. The oxide was made by anodization of carbon steel waste. Anodization was done as to produce anodic oxide with desired nanostructures. Nanostructured Fe_2O_3 is preferred due to:

1. Nanostructured materials exhibit high surface area to volume ratio hence more sites for Cr(IV) to be adsorbed increasing chances for Cr(VI) removal. It is expected that only small amount of material is needed for removal of heavy metal ions.
2. Nanostructured materials have more surface atoms with high surface energy because of the surface atoms have unsatisfied bonds at the surface forming daggling bonds that increase the reactivity of the material. High reactivity material can be expected to reduce Cr(VI) at a faster rate.

3. Nanostructured α-Fe_2O_3 is also expected to have much better light absorption properties hence generation of electron-hole pairs is more efficient.
4. Reduction process on α-Fe_2O_3 requires electron-hole pairs generation and transfer to adsorbed Cr(VI). When α-Fe_2O_3 is made with nanostructure, the diffusion path of the electrons to the surface of the oxide will be shorter hence, recombination is expected to be much lesser. This can further improve the catalytic properties of the oxide.

Nevertheless, the process for making nanostructured iron oxide on steel by anodisation is not as well documented as that on pure iron. Here, anodization conditions that produce surface oxide on waste steel with specific nanostructure were identified and characterizations were done to study the nanostructured α-Fe_2O_3.

Photocatalytic activity refers to the catalytic properties of materials in the presence of light, and photocatalysis is the acceleration of the rate of a chemical reaction by activating a catalyst by light. Nevertheless, the most used catalysts now is TiO_2 but this oxide is wide gap semiconductor that can only be activated under UV light. UV light only account for less than 4 % in the solar spectrum. TiO_2 cannot be activated under sunlight. Whereas α-Fe_2O_3 can be activated under sunlight for photocatalytic applications due to its narrow band gap of about 2.0–2.2 eV (Mishra and Chun, 2015). It can absorbs light up to 600 nm in visible light range as being highlighted in Figure 1.3 (Liu et al., 2015), hence will make photocatalytic testing more convenient and cheaper since using natural light was enough to reduce Cr(IV). α-Fe_2O_3 can collects up to 40% of the solar spectrum energy as shown in Figure 1.3, which is the highest among metal oxides group. α-Fe_2O_3 is stable in most aqueous solutions and thus is one of the cheapest semiconductor materials available (Mor et al., 2007). However, not a lot has been reported on the ability of α-Fe_2O_3 to reduce Cr(VI). Here, assessment was made to study the capability of this oxide made by anodic process for Cr(VI) reduction under sunlight.

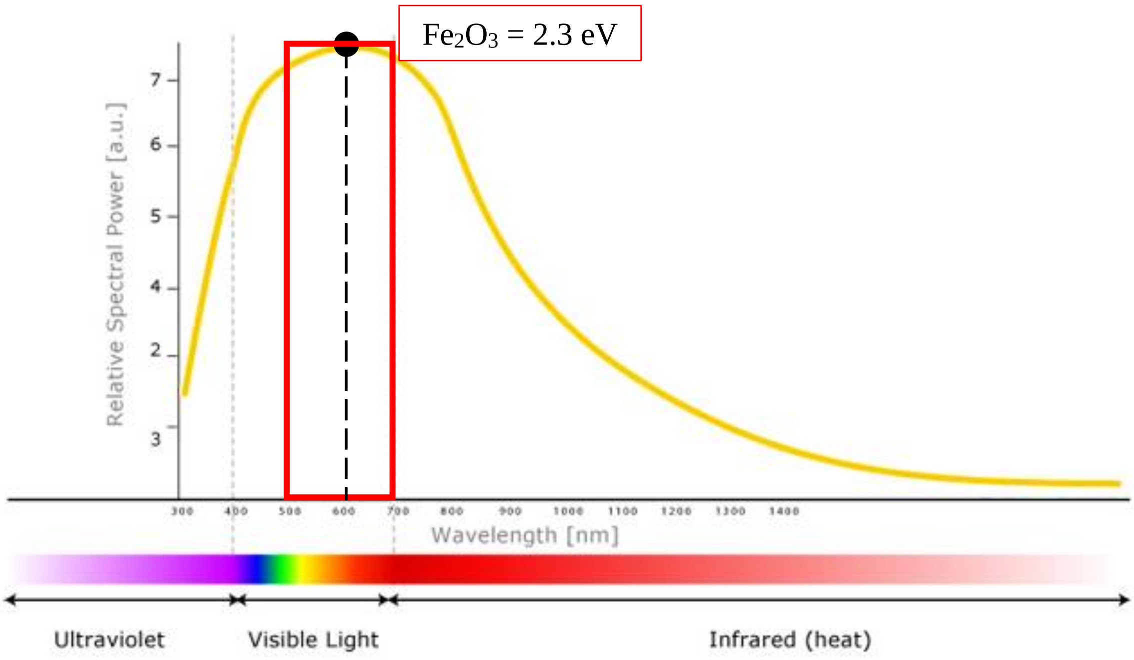

Figure 1.3: Diagram of the solar spectrum where the highest absorption of iron oxide are at the range of 600nm (Liu et al., 2015).

It is known that an efficient catalyst for photoreduction of Cr(IV) must possess such characteristics:

1. Enough electrons, e^- are generated under light illuminations to efficiently reduce adsorbed Cr(IV) ions.
2. The generated e^- must have sufficient kinetic energy to enable it to be transferred out to reduce adsorbed Cr(VI).

3. The generated e^- must not be allowed to recombine with holes in the valance band and hence electrons transfer must be made faster than recombination.
4. The generated e^- must have reduction potential more negative than the reduction potential of Cr(VI) to Cr(III) that is +1.33 V as to allow for reduction to happen.

α-Fe_2O_3 is capable in reducing Cr(VI) as the standard reduction potential of Cr(IV) to Cr(III) is +1.33V which is within the energy bandgap of Fe_2O_3 as shown in Figure 1.4. Iron oxide can generate enough electrons by excitation process when the oxide is illuminated with sunlight. However, Fe_2O_3 has short carrier lifetime, and short hole diffusion length (Ahn et al., 2014) hence electron-hole pairs are easily recombine. Thus, various ways have been propose to improve α-Fe_2O_3 performance. By utilizing nanostructured α-Fe_2O_3, it is hypothesized that the path for electrons to diffuse out will be shorter hence less recombination is expected. This will lead to more efficient reduction process.

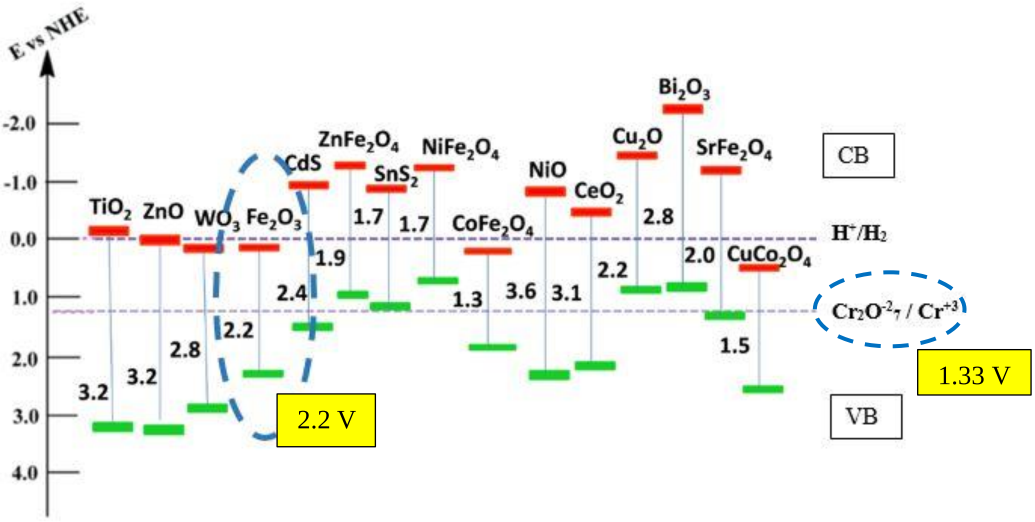

Figure 1.4: The band edge potentials and band gaps of different semiconductors that for photocatalytic reduction of Cr(VI) (Acharya et al., 2018).

As mentioned, there are a lot of works on anodization of iron not steel. In this work, instead of using a pure Fe foil, carbon steel or mild steel that typically has low carbon content and approximately contain 98% of iron, 0.05%-0.25% carbon and up to 0.4% manganese were used. Carbon steel or mild steel used was from waste steel collected from Material and Mineral Resouces Engineering School’s workshop. The reasons for using waste steel were to assess on the:

(i) Anodic film on waste steel can be fabricated to produce nanostructured oxide similar to on pure iron as Rozana et al. in 2015 in fabricating nanoporous iron oxide on pure Fe foil by anodization process.

(ii) Possibility of the oxide formed on reduction performance of Cr(VI) to Cr(III).

Moreover, it also to recycle waste steel into useful semiconductor photocatalyst for heavy metal removal from wastewater and thus can reduce amount of waste in the future. Furthermore, as being reported by Deng et al. in 2016, compared with high purity iron foil, carbon steel has many advantages such as higher strength and lower cost. Since there are not many of report on the formation of nanostructured anodic film on carbon steel by anodization process, this project was conducted in order to assess on the possibility of producing nanostructured anodic film on steel similar to on pure iron.

1.5 Objectives

The main objectives of this research work are:

1. To synthesize and characterize nanostructured α-Fe_2O_3 by electrochemical anodization of waste steel.

2. To assess the performance of the nanostructured anodic α-Fe_2O_3 in reducing Cr(VI) to Cr(III) under sunlight irridation.

1.6 Scope of Work

This project covered the investigation on the formation of iron oxide nanotubes and their ability on Cr(VI) photocatalytic reduction to reduce Cr(VI) to Cr(III). Anodization method was selected for the synthesis of iron oxide nanotubes, where the effect of time, voltage and water content in electrolyte were studied followed by annealing of the sample for the crystallization of iron oxide formed. Mild steel was used in this research as substrate for anodization process. Phase and morphology characterization of the nanostructure iron oxide was determined by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR) Spectroscopy, and Field Emission Scanning Electron Microscopy (FESEM). The photocatalytic performance were assess using UV-Visible Spectrophotometer.

1.7 Outline of Chapters

This thesis consists of five chapters. Chapter one discusses on the introduction, objectives, research motivation, problem statement and study scopes of the project. Meanwhile, the concept, theory and literature review related to the fabrication of iron oxide nanostructures by using thermal oxidation method are explained in Chapter two. In Chapter three, experimental details and characterization approaches are explained respectively. While Chapter four focuses on presenting the results and discussion of this project. Finally, conclusion of this project and recommendations of future work are stated in Chapter five.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This project was on the formation of porous iron oxide nanostructure as photocatalyst by anodic oxidation of carbon steel for the removal of hexavalent chromium. This chapter focuses on the low carbon steel properties and the problems of chromium as heavy metal ions pollutant in the environment. Then approaches to remove hexavalent chromium are reviewed. The later part of this chapter describes iron oxide as the material chosen and its general properties as well as the synthetization process.

2.2 Low carbon steel and its properties

Carbon steels are alloys made from a combination of iron (Fe) and carbon (C) which maximum carbon content of 1.5% along with small percentages of silica, sulphur, phosphorus and manganese as residual elements (Puneeth and Srikantappa, 2017). By varying the percentage of carbon, it is possible to produce steel with a variety of different qualities. In general, the higher the carbon level, the stronger and more brittle the steel. With more carbon content, the metal gains hardness and strength but becomes less ductile and more difficult to weld. Moreover, higher carbon content will lowers steel melting point and its temperature resistant in general. Other element such as alloying element also added in steel to improve its properties.

Basically, carbon steels categorized into 3 main groups (Chaturvedi, 2015):

(1) Low carbon steel - contain 0.15% to 0.45% carbon

(2) Medium carbon steel - contain 0.45% to 0.8% carbon

(3) High carbon steel - contain 0.8% to 1.5% carbon

Low carbon steel also known as mild steel, is easy to work and suitable for decorative products such as fencing or lamp posts, car body panels, nuts and bolts, food cans, metal chains, wire ropes, engine parts, bicycle rims, nails and screws and various outdoor uses. Low carbon steel used to be the most common steel in industries as it have low carbon percentage which give it low strength properties thus it is cheap, weldable and easy to deform (Sekban et al., 2017).

Alloying elements are added to achieve certain properties in the material. Commonly, alloying elements are added in lower percentages less than 5% to increase strength or hardenability and in larger percentages over 5% to achieve special properties, such as corrosion resistance or extreme temperature stability. Some of the common alloying elements in steels are:

Manganese (Mn)	➢ Usually contain at least 0.30% because it assists in the deoxidation of the steel, prevents the formation of iron sulphide and inclusions, and promotes greater strength by increasing the hardenability of the steel. (Kah et al., 2015).
Silicon (Si)	➢ Increases strength and hardness but to a lesser extent than manganese. It is one of the primary deoxidizers used in the making of steels to improve soundness, for instance, shrinkages, cavity or defect that may cause failure.

Carbon (C)	➢	Carbon is the most important element in steel, it is essential in steels which have to be hardened by quenching and the amount of carbon controls the hardness and strength of the material, as well as response to heat treatment.
Phosphorus (P)	➢	Phosphorus contain up to 0.10% of in low-alloy high-strength steels will increase the strength as well as improve the corrosion resistance (Chaturvedi, 2015).
Chromium (Cr)	➢	Primarily used to increase hardenability of steel and increase the corrosion resistance as well as the yield strength of the steel material. (Chaturvedi, 2015).
Aluminum (Al)	➢	Aluminum is one of the most important deoxidizers at 0.02% amounts in the material, and helps form a more fine-grained crystalline microstructure and increase steel toughness (Kah et al., 2015).

2.3 Chromium

Chromium (Cr) with atomic number 24, molecular weight 51.1 and density 7.19 g/cm^3 is a silver colour hard metal was discovered in 1797 as part of the mineral crocoite, use as pigment due to its intense coloration. Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm, ranging in soil, in seawater and in rivers and lakes. The main sources of Cr pollution of the environment are from chrome plating and leather tanning, metal manufacturing (Khadem et al., 2017).

Chromium is listed as one of the 18 core hazardous air pollutants (HAPs), 33 urban air toxicants, 188 HAPs by Environmental Protection Agency (EPA), and been ranked the 7th among the top 20 hazardous substances by the Agency for Toxic Substances and Disease Registry (Oh et al., 2007).

Chromium is highly soluble under oxidizing conditions and forms, exhibiting a wide range of possible oxidation states that from -2 to +6, but hexavalent chromate Cr (VI) and trivalent chromite Cr(III) forms are the most common and stable in the natural environment (Ashraf et al., 2017).

Chromium is usually found in the trivalent form (Cr(III)), and this form is reported as an essential element in mammals as it takes effective role in glucose, lipid, and protein metabolism. Cr(III) have poor membrane permeability, non-corrosiveness and very less tendency to accumulate in the food chain, thus it can be said that toxicity of trivalent chromium is very low (Bakshi and Panigrahi, 2018). Hexavalent chromium, Cr(VI) was considered to be more noxious than trivalent form, Cr(III) because of its easy permeability through the cell membrane which undergoes metabolic reduction within the cell and altering the cell which causing fatal effects in the affected individual.

Chromium is a common contaminant of surface waters and ground waters because of its natural occurrence in nature, as well as anthropic sources (Babula et al., 2008). Cr(III) and Cr(VI), being the most stable are also the important in terms of environmental contamination. The most important sources of Cr(III) are fugitive emissions from road dust and industrial cooling towers; also, Cr(VI) compounds are still used in the manufacture of pigments, in metal-finishing and chromium-plating, in stainless steel production, in hide tanning, as corrosion inhibitors, and in wood preservation (Shtiza et al., 2008).

2.4 Chromium Effect to Human and Environment

Cr(VI) can induce headache, diarrhoea, nausea, vomiting, and even worse can cause lung cancer and kidney failure to human (Babel and Kurniawan, 2003). Moreover, a study from Gibb et al. in 2000 state that genotoxic effects like chromosomal aberrations or sister chromatid exchanges in workers that exposed to hexavalent chromium have been reported in studies on occupational exposure. Excess risk of lung cancer is also related to occupational exposure to hexavalent chromium.

A study on acute toxic effects of chromium in fresh water fish was being studied by Bakshi and Panigrahi in 2018. The findings were that fish that were exposed to chromium-contaminated environment prone to be hyperactivity and erratic in swimming. Moreover, the fish have been found to lose their body balance with restlessness, lowered breathing rate and higher rate of mucus secretion. Haematological alteration such as decreased haemoglobin percentage, decreased red blood cell count, breakage of DNA have been reported as genotoxic impact of chronic chromium exposure in fish. Significant deterioration has been found in gill, liver, kidney and intestine of experimental organisms even when exposed at low concentration. This should be an eye opener on the toxic effect of chromium to both human and edible fish since we may consume the fish that already exposed to heavy metals in contaminated river due to releases of waste from factory such as batik industry or even metal plating industries.

In addition, a study on chromium contain on soil and plant also investigated by Shahid et al. in 2017. This study reported that chromium mainly accumulates in vacuoles of root cells. Inside plants, Chromium mainly accumulates in root tissues with limited translocation to plant shoots. Chromium mainly accumulates in vacuoles of root cells. However, hyperaccumulators of Cr can transfer high levels to shoot tissues. Hence, chromium uptake by vegetables and accumulation in edible plant parts can induce numerous health risks to consumers.

2.5 Remediation of Chromium

Here, techniques that can use to treat Cr(VI) and other toxic heavy metal pollutants from wastewater is reviewed. Various methods such as membrane filtration, electrochemical treatment, chemical precipitation, ion exchange and adsorption being can be used on reduction of Cr(VI).

2.5.1 Membrane Filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent. It is capable of removing suspended solid, organic compounds and inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater.

It utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000– 100,000 Da). Depending on the membrane characteristics, membrane filtration can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure. It also presents some advantages such as lower driving force and a smaller space requirement due to its high packing density.

2.5.2 Ion Exchange

Ion exchange is the process which the ions on the surface of the solid has been exchanged for ions of the similar in the solution with which the solid is in contact. The dissolved Cr(VI) will bind to the resin and displace the previously bound ions (Cl^- or OH^-) when water flows through it (Gunatilake, 2015).

2.5.3 Electrodialysis

Electrodialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membranes as shown in Figure 2.1 (Gunatilake, 2015)

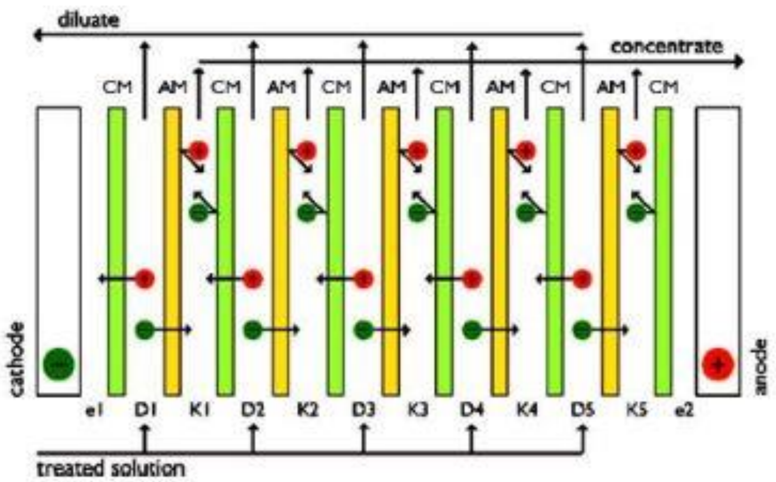

Figure 2.1: Electrodialysis principles (Gunatilake, 2015).

A noticeable disadvantage is membranes replacement and the corrosion process. Using membranes with higher ion exchange capacity resulted in better cell performance. Effects of flow rate, temperature and voltage at different concentrations using two types of commercial membranes, using a laboratory electrodialysis cell, on lead removal were studied.

2.5.4 Coagulation

The coagulation-flocculation mechanism was based on zeta potential (ζ) measurement as the criteria to define the electrostatic interaction between pollutants and coagulant-flocculants agents. Coagulation Metal Precipitation process is reducing the net surface charge of the colloidal particles to stabilize by electrostatic repulsion process as shown in Figure 2.2.

Figure 2.2: Coagulation Metal Precipitation process (Gunatilake, 2015).

Flocculation process continually increases the particle size to discrete particles through additional collisions and interaction with inorganic polymers formed by the organic polymers added. Once discrete particles were flocculated into larger particles, they can be removed or separated by filtration, straining or floatation. Production of sludge, application of chemicals and transfer of toxic compounds into solid phase are main drawbacks of this process.

2.5.5 Absorption

Adsorption has emerged out as effective, economical and eco-friendly treatment technique. It is a process potent enough to fulfil water reuse obligation and high effluent standards in the industries. Adsorption is basically a mass transfer process by which the metal ion is transferred from the solution to the surface of sorbent, and becomes bound by physical or chemical interactions (Gupta and Nayak, 2012). Nanoparticles formed by metal or metal oxides are other inorganic nanomaterials, which are used broadly to remove heavy metal ions in wastewater treatment. Nanosized metals or metal oxides include nanosized silver nanoparticles, ferric oxides, manganese oxides, titanium oxides, magnesium oxides, copper oxides, cerium oxides, and so on, all these provide high surface area and specific affinity. Besides, metal oxides possess minimal environmental impact and low solubility and no secondary pollution, have been adopted as sorbents to remove heavy metals (Wang, 2012). However, nanosized metal oxides show great removal efficiency of heavy metal in wastewater, owing to their higher surface areas and much more surface active sites than bulk materials. Nevertheless, it is very difficult to separate them from the wastewater due to their high surface energy and nanosized scale.

2.5.6 Photocatalysis

Photocatalytic process of heavy metal ions removal can be done by utilizing electrons from the catalysts generated when the catalysts is illuminated. The electrons can be used to reduce Cr(VI) to less toxic Cr(III) in aqueous solution. Photocatalytic process is rapid and efficient for the destruction of many environmental pollutants in water (Barakat, 2011). Photocatalysis can be used to perform redox reaction with reduction of Cr(VI) to Cr(III) and oxidation of water on oxide photocatalyst as illustrated in Figure