THE FORMATION OF IRON OXIDE NANOWIRES AND NANOSHEETS BY THERMAL OXIDATION OF IRON FOR Cr(VI) REMOVAL BY ADSORPTION

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS ii

TABLE OF CONTENTS iv

LIST OF TABLE viii

LIST OF FIGURE x

LIST OF ABREVIATIONS xv

LIST OF SYMBOLS xvi

ABSTRAK xvii

ABSTRACT xix

CHAPTER 1 - INTRODUCTION 1
- 1.1 Introduction 1
- 1.2 Problem statements 6
- 1.3 Objectives study 8
- 1.4 Research scope 8
- 1.5 Outline of thesis 9

CHAPTER 2 - LITERATURE REVIEW 11
- 2.1 Introduction 11
- 2.2 Chromium 11
- 2.3 Chromium effect to human 13
- 2.4 Chromium (VI) treatment technologies 14
  - 2.4.1 Chemical precipitation 14
  - 2.4.2 Ion exchange 14
  - 2.4.3 Electrokinetic 15
  - 2.4.4 Reverse osmosis 16
  - 2.4.5 Ultra violet treatment 17
  - 2.4.6 Adsorption 18

2.4.6.1. Physical adsorption 18
2.4.6.2. Chemical adsorption 19
2.4.7 Comparison of Cr(VI) treatment technologies 19
2.5 Evaluation of adsorptive properties 21
2.5.1. Kinetic adsorption 21
2.5.2. Adsorption isotherm 23
2.5.2.1. Langmuir model 23
2.5.2.2. Freundlich model 24
2.6 Cr(VI) adsorbent material 25
2.6.1 Activated carbon 25
2.6.2 Agricultural by product and seed 26
2.6.3 Biosorbent 27
2.6.4 Metal oxide 28
2.6.5 Industrial waste by product 29
2.7 Adsorbent material selection 30
2.8 Cr(VI) adsorption mechanism by iron oxide 31
2.9 Surface chemistry of iron oxide 34
2.10 Iron oxide protonation 35
2.11 One dimensional and two dimensional oxide material 37
2.12 Iron oxide 40
2.13 Thermal oxidation of iron 43
2.13.1 Introduction 43
2.13.2 Thermodynamic of iron oxide formation 44
2.13.3 Mechanism of iron oxidation 46
2.13.4 Iron oxidation at temperature above 570 ^{o}C 48
2.13.5 Iron oxidation at temperature below 570 ^{o}C 50
2.13.6 Diffusion 51
2.13.7 Internal stress in iron oxide formation 54
2.13.8 Morphology of oxidised iron 58
2.13.9 Iron oxide nanowires growth mechanism 63
2.13.10 Some applications of iron oxide nanowires and nanosheets 66
2.13.11 Influence of iron surface condition on iron oxidation 67
2.13.12 Oxidation of iron in water vapour 68

CHAPTER 3 - METHODOLOGY 74

3.1 Introduction 74
3.2 Raw materials and chemicals 75
3.3 The effect of surface pre-treatment 75
3.4 Synthesis 76
    3.4.1 The effect of oxidation temperature 77
    3.4.2 The effect of water vapour 78
    3.4.3 The effect of oxidation time 80
    3.4.4 Temperature range for nanowires formed 80
3.5 Characterisation technique 81
    3.5.1 Scanning electron microscopy (SEM) 81
    3.5.2 X-ray diffraction spectrometry (XRD) 83
    3.5.3 Transmission electron microscopy (TEM) 84
    3.5.4 Raman spectroscopy 84
    3.5.5 X-Ray photoelectron spectroscopy (XPS) 84
    3.5.6 UV-visible spectrophotometry (UV-VIS) 85
    3.5.7 Atomic force microscopy (AFM) 85
3.6 Cr(VI) adsorption experiments 86
    3.6.1 Adsorbate 86
    3.6.2 Hexavalent chromium detection and measurement 87
    3.6.3 Adsorption studies 88

CHAPTER 4 - RESULTS AND DISCUSSION 91
4.1 Introduction 91
4.2 Structural observation 91
    4.2.1 The effect of sample preparation 92
    4.2.2 The effect of oxidation temperature and water vapour 96
    4.2.3 Phase identification 103
    4.2.4 Range temperature for NWs formed 112
    4.2.5 The effect of oxidation time at 800 ^{o}C in water vapour 114
    4.2.6 The effect of oxidation time at 500 ^{o}C in water vapour 118
4.3 Growth mechanism of α-Fe_2O_3 NWs 121
    4.3.1 Initial oxidation 121
    4.3.2 Oxide scale formation 123

4.3.3 Growth stress 126
4.4 Growth mechanism of α-Fe_2O_3 NSs.. 134
4.5 Adsorption of Cr(VI) on α-Fe_2O_3 NWs and NSs 138
4.6 Cr(VI) adsorption mechanism 142
4.7 Evaluation of adsorptive studies... 146
4.7.1 Kinetic study of Cr(VI) adsorption.. 147
4.7.2 Isothermal study of Cr(VI) adsorption 150

CHAPTER 5 - CONCLUSION AND SUGGESTIONS 154

REFERENCES 157

LIST OF PUBLICATIONS 168

APPENDICES

LIST OF TABLE

Table 1.1	Examples of Cr(VI) pollution in the world	2
Table 2.1	General properties of chromium	12
Table 2.2	Comparison between physisorption and chemisorptions	19
Table 2.3	Comparison of Cr(VI) treatment technologies	20
Table 2.4	Cr(VI) adsorption studies by activated carbon material	26
Table 2.5	Cr(VI) adsorption studies on agricultural products	27
Table 2.6	Cr(VI) adsorption studies on biosorbent material	28
Table 2.7	Point zero charge of various metal oxides	29
Table 2.8	Cr(V) adsorption studies on metal oxide	29
Table 2.9	Cr(VI) adsorption studies on industrial waste	30
Table 2.10	Cr(VI) adsorption studies on iron oxide material	34
Table 2.11	Nanomaterial synthesis process	40
Table 2.12	General properties of iron oxide	41
Table 2.13	Standard free energies of Fe-O reaction	45
Table 2.14	Unit cell data for iron and its oxides	56
Table 2.15	Summary of iron oxide nanowires work	60
Table 2.16	Steel corrosion	68
Table 2.17	Literature review for oxidation of iron in water vapour	70
Table 2.18	Summary of morphology formed of oxidised iron foil in dry oxygen and water vapour	73
Table 3.1	Summary of chemicals and materials used for this research work	75

Table 3.2 Parameters used in studying the effect of sample preparation 75

Table 3.3 Summary of parameters used in studying the oxidation temperature in dry air atmosphere 78

Table 3.4 Summary of parameters used in studying the effect of oxidation temperature and atmosphere 79

Table 3.5 Summary of parameters used in studying the effect of oxidation time 80

Table 3.6 Summary of parameters used in studying the temperature range for nanowires structure formed 81

Table 3.7 XRD reference data 83

Table 3.8 Summary of adsorption studies 89

Table 3.9 Summary of isothermal and kinetic studies 89

Table 4.1 Roughness of iron foil after pre-treatment 94

Table 4.2 Raman band positions of α-Fe_2O_3 and Fe_3O_4 107

Table 4.3 Ionic radius of hydrogen, iron and oxygen 123

Table 4.4 Chemical reaction of iron oxidation at 800 ^{o}C 126

Table 4.5 Pilling-Bedworth Ratio of iron oxide 127

Table 4.6 Distribution of α-Fe_2O_3 surface charge in the solution 143

Table 4.7 Comparison of kinetic studies 150

Table 4.8 Initial (C_o) and equilibrium concentration (C_e) of Cr(VI) in this experiment 151

Table 4.9 Summary of isothermal studies 152

Table 4.10 Comparison of Cr(VI) adsorption studies on iron oxide material 153

LIST OF FIGURE

Figure 1.1 Schematic illustration of the formation of α-Fe_2O_3 nanowires as Cr(VI) adsorbent material 5

Figure 2.1 Speciation of Cr(VI) in aqueous solution 12

Figure 2.2 Schematic illustration of chemical precipitation 14

Figure 2.3 Schematic illustration on exchange process 15

Figure 2.4 Schematic illustration of electrokinetic process 16

Figure 2.5 Osmosis working principle: (a) direct osmosis, (b) osmotic equilibrium and (c) reverse osmosis 17

Figure 2.6 Reduction of Cr(VI) to Cr(III) by UV light 17

Figure 2.7 The adsorption interaction: (a) physisorption and (b) chemisorption 18

Figure 2.8 Schematic illustration of Fe dissolution by protonation of iron oxide 36

Figure 2.9 One dimensional and two dimensional nanomaterial 38

Figure 2.10 Ellingham/Richardson diagram showing free energies of formation for various oxides as a function of temperature 45

Figure 2.11 Transport process in thermal oxidation (a) cation mobile and (b) anion mobile 47

Figure 2.12 Oxidation of iron above 570 ^{o}C 48

Figure 2.13 Formation of iron oxide layers at temperature above 570 ^{o}C 50

Figure 2.14 Oxidation of iron at (a) 400 and (b) 600 ^{o}C in dry air for 60 minutes 51

Figure 2.15 Formation of iron oxide layers at temperature below 570 ^{o}C 51

Figure 2.16 Types of diffusion 54

Figure 2.17 Schematic illustration of stress due to volume difference 56

Figure 2.18 Schematic illustration of crystal slip 57

Figure 2.19 Screw dislocation: (a) slipping crystal and (b) the end of screw dislocation 57

Figure 2.20 SEM image of oxidised iron at 600 ^oC in CO_2 + SO_2 + NO_2 + H_2O atmosphere for 10 hours 59

Figure 2.21 Schematic illustration of NWs growth mechanism: (a) evaporation and condensation, (b) internal diffusion along the core of a screw dislocation and (c) surface diffusion along the sidewall of a nanowire 64

Figure 2.22 Schematic illustration of nanowires growth mechanism showing the central tunnel and nucleation 65

Figure 2.23 Schematic illustration of nanowires growth mechanism 66

Figure 2.24 SEM image of oxidised iron foils at 700 ^oC in 240 sccm flow of oxygen for 16 hours: (a) mid region and (b) edge region 67

Figure 2.25 Oxidation kinetic of iron in: (a) O_2 and (b) O_2 + 40% H_2O atmosphere 70

Figure 2.26 Mechanism of iron oxide scales formation at 650-750 ^oC in water vapour atmosphere 72

Figure 3.1 Flowchart of overall research work 74

Figure 3.2 Heating profile for iron oxide synthesis by thermal oxidation 76

Figure 3.3 Summary of synthesis process of iron oxide nanowires and nanosheets by thermal oxidation 77

Figure 3.4 Experimental set up for thermal oxidation in dry air condition 78

Figure 3.5 Experimental set up for thermal oxidation in water vapour condition 79

Figure 3.6 Experimental set up for adsorption process 86

Figure 3.7 Diphenyl-carbazide colourimetry method 87

Figure 3.8 Calibration curve for Cr(VI) measurement 88

Figure 4.1 Illustration to show the position of FESEM images captured of the oxidised iron foils at 800 ^{o}C in water vapour for 2 hours at (a) surface top part and (b) side of sample. The sample was tilted 45^{o} 93

Figure 4.2 FESEM images of iron oxide wires after annealing at 800 ^{o}C in water vapour for 2 hours after pre-treatment: (a) polishing, (b) etching and (c) grinding. The sample was tilted 45^{o} 94

Figure 4.3 The effect of roughness for the formation of iron oxide NWs 95

Figure 4.4 FESEM image shows the distribution of iron oxide wires on the top of sample with ground pre-treatment at 800 ^{o}C in water vapour for 2 hours. The sample was tilted 45^{o} 96

Figure 4.5 Physical appearance of oxidised iron foils at 400-800 ^{o}C for 2 hours 97

Figure 4.6 FESEM image of iron foils oxidised at 400-800 ^{o}C for 2 hours in dry air and water vapour atmosphere. The samples were tilted 45^{o}. 99

Figure 4.7 Quantitative analysis of oxidised iron foils at 400 to 800 ^{o}C in air and water vapour for 2 hours 99

Figure 4.8 Cross sectional SEM image of iron foils oxidised at 800 ^{o}C in: (a) dry air and (b) water vapour 100

Figure 4.9 TEM image of single iron oxide nanowire 102

Figure 4.10 (a) TEM image of single wires at 800 ^{o}C in water vapour and (b) FESEM image of sheets at 500 ^{o}C in water vapour 103

Figure 4.11 XRD patterns of oxidised iron at 400 to 800 ^{o}C in: (a) dry air and (b) water vapour 105

Figure 4.12 XRD patterns of oxidised iron foils at 500 and 800 ^{o}C in air and water vapour conditions 106

Figure 4.13 Raman spectra of oxidised iron foils at 500 and 800 ^{o}C 107

Figure 4.14 (a) HR-TEM image of single α-Fe_2O_3 NW and its EDX mapping for: (b) carbon, (c) iron and (d) oxygen element 108

Figure 4.15 (a) HR-TEM image of single α-Fe_2O_3 NS and its EDX mapping for: (b) iron and (c) oxygen element 109

Figure 4.16 XPS spectra of α-Fe_2O_3 NWs (a) wide scan, (b) Fe 2p spectrum and (c) O 1s spectrum 111

Figure 4.17 FESEM image of oxidised iron foils for 2 hours in water vapour at temperature: (a) 775, (b) 800, (c) 825, (d) 850, (e) 875 and (f) 900 ^{o}C. The samples were tilted 45^{o} 113

Figure 4.18 Quantitative analysis of iron oxide NWs at 775 to 850 ^{o}C in water vapour for 2 hours: (a) length and width and (b) aspect ratio and areal density 114

Figure 4.19 FESEM images of oxidised iron foils at 800 ^{o}C in water vapour condition for (a) 5 ,(b) 15, (c) 30, (d) 60 and (e) 120 minutes. The samples were tilted 45^{o} 116

Figure 4.20 Quantitative analysis of oxidised iron foils at 800 ^{o}C in water vapour: (a) length and diameter and (b) aspect ratio and areal density 117

Figure 4.21 FESEM image of oxidised iron foils at 500 ^{o}C in water vapour for (a) 5, (b) 15, (c) 30, (d) 60 and (e) 120 minutes. The samples were tilted 45^{o} 119

Figure 4.22 Quantitative analysis of oxidised iron foils at 500 ^{o}C in water vapour: (a) length and diameter and (b) aspect ratio and areal density 120

Figure 4.23 Chemisorption of oxygen gas 121

Figure 4.24 Cross sectional FESEM images of oxidised iron foils at 800 ^{o}C for 2 hours in water vapour: (a) etched and (b) not etched 124

Figure 4.25 Growth stress at $Fe_2O_3|Fe_3O_4$ interface 128

Figure 4.26 FESEM images of α-Fe_2O_3 NWs oxidised at 800 ^{o}C in water vapour showing the initial growth of NWs on the grain of Fe_2O_3. The sample was tilted: (a) 45^{o} and (b) 0^{o} 128

Figure 4.27 Schematic illustration of NWs growth: (a) screw dislocation and (b) surface diffusion at screw dislocation spot 130

Figure 4.28 FESEM image shows the growth of NWs via surface diffusion 131

Figure 4.29 Low magnification of HR-TEM image of single α-Fe_2O_3 NW 132

Figure 4.30 HR-TEM image shows a central tunnel in the NWs and twinning boundaries 133

Figure 4.31 High magnification of HR-TEM image of single α-Fe_2O_3 NW 134

Figure 4.32 Cross sectional FESEM image of oxidised iron foils at 500 ^oC for 2 hours in water vapour condition: (a) tilted 45^o and (b) polished and tilted 90^o 135

Figure 4.33 Schematic illustration of NSs growth mechanism (a) growth stress at oxide interface and (b) screw dislocation growth 137

Figure 4.34 FESEM image of α-Fe_2O_3 NSs oxidised at 500 ^oC in water vapour for 2 hours showing the nucleation of diffusing species on the NSs tip 137

Figure 4.35 Low magnification of HR-TEM image of single α-Fe_2O_3 NS 138

Figure 4.36 Physical observation of Cr(VI) solution adsorption by iron oxide sample 139

Figure 4.37 Aliquot of samples after DPC treatment from 0 to 90 minutes 140

Figure 4.38 Cr(VI) adsorption behaviour on α-Fe_2O_3 NSs and NWs with Cr(VI) initial concentration 200 mg/L. 141

Figure 4.39 Cr(VI) adsorption behaviour by α-Fe_2O_3 NSs and NWs with Cr(VI) initial concentration 200 mg/L. 142

Figure 4.40 Physical appearance of iron oxide sample: (a) before and (b) after adsorption 145

Figure 4.41 XPS spectra of Cr 2p on the α-Fe_2O_3 NWs (before and after adsorption) 146

Figure 4.42 Cr(VI) adsorption behaviour on α-Fe_2O_3 NWs with several Cr(VI) initial concentration 147

Figure 4.43 Linear fit of kinetic study into: (a) pseudo-first order, (b) pseudo-second order and (c) intra-particle diffusion 149

Figure 4.44 Linear fit of equilibrium study into: (a) Langmuir and (b) Freundlich model 152

LIST OF ABREVIATIONS

DPC	Dyphenil-carbazide
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
α-Fe_2O_3	Hematite
HRTEM	High Resolution Transmission Electron Microscopy
HCl	Hydrochrolic acid
Fe	Iron
γ-Fe_2O_3	Maghemite
Fe_3O_4	Magnetite
NWs	Nanowires
NSs	Nanosheets
$K_2Cr_2O_7$	Potassium Dichromate
FeO	Wustite
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

LIST OF SYMBOLS

at %	Atomic percent
cm	Centimetre
°	Degree
°C	Degree Celsius
°C/min	Degree Celsius per Minute
g	Gram
h	Hour
%	Percentage
<	Less than
L	Litre
m	Meter
min	Minute
mL	Millilitre
mm	Millimetre
mg/L	Miligram per litre
>	More than
nm	Nanometer
s	Second
d	Thickness
λ	Wave length

PENGHASILAN WAYAR NANO DAN KEPINGAN NANO FERUM OKSIDA DENGAN PENGOKSIDAAN TERMA UNTUK PENYINGKIRAN Cr(VI) MELALUI PENJERAPAN

ABSTRAK

Pengoksidaan termal Fe telah dihasilkan dalam keadaan udara kering dan wap air pada suhu 400-800 ^{o}C untuk pembentukan wayar nano dan kepingan nano α-Fe_2O_3 bagi penyingkiran Cr(VI) di dalam larutan akueus. Di dalam kajian ini, beberapa parameter telah dikaji, iaitu kesan pra-rawatan permukaan, kesan suhu oksidasi, masa dan wap air untuk pembentukan. Ternyata peningkatan kekasaran menerusi pengisaran menghasilkan wayar nano secara seragam meliputi permukaan logam Fe dengan ketumpatan permukaan yang tinggi. Suhu pengoksidaan bagi penghasilan wayar nano adalah pada 400 dan 800 ^{o}C manakala bagi kepingan nano pada 500 and 600 ^{o}C. Pada suhu 700 ^{o}C, permukaan oksida membentuk struktur koral. Suhu 800 ^{o}C adalah suhu pengoksidaan yang paling optimum untuk pembentukan wayar nano dengan nisbah aspek yang tinggi iaitu 27. Wayar nano dengan areal densiti yang tinggi terbentuk ketika oksidasi dilakukan di wap air kerana pengaruh proton dari air yang terdisosiasi. Jangka masa untuk pengoksidaan pada suhu 800 ^{o}C di dalam kehadiran wap air telah dijalankan untuk menyiasat pembentukan wayar nano. Wayar nano mengambil masa 5 minit untuk terhasil, namun untuk mendapatkan nisbah aspek yang tinggi, masa yang diambil adalah 120 minit. Mekanisma pembentukan wayar nano dan kepingan nano telah dicadang untuk mengikuti mekanisma dorongan tekanan melalui dislokasi skru sebagai pusat wayar nano untuk terbentuk. Hasil daripada HR-TEM, XRD dan Raman, fasa wayar nano dan kepingan nano adalah α-Fe_2O_3. Kajian penjerapan menunjukkan Cr(VI) dengan kepekatan 200 mg/L di dalam larutan berjaya disingkirkan oleh wayar nano α-Fe_2O_3 dalam masa 90 minit sedangkan kepingan nano hanya dapat menjerap 112 mg/L. Kinetik dan pembelajaran isotermal menerangkan tingkah laku penjerapan mengikut model pseudo order kedua dan model Langmuir. Kapasiti penjerapan nanowayar α-Fe_2O_3 ialah 61.57 mg/g. Mekanisma utama penyingkiran Cr(VI) oleh α-Fe_2O_3 adalah kerana reaksi elektrostatik di antara ion kromat negatif dan cas positif penjerap.

THE FORMATION OF IRON OXIDE NANOWIRES AND NANOSHEETS BY THERMAL OXIDATION FOR Cr(VI) REMOVAL BY ADSORPTION

ABSTRACT

Thermal oxidation of iron foil was done in dry air and water vapour at 400-800 ^{o}C to form α-Fe_2O_3 nanowires (NWs) and nanosheets (NSs) as adsorbent to remove Cr(VI) from aqueous solution. Oxidation parameters studied were the effect of surface pre-treatment, the effect of oxidation temperature, time and water vapour on the NWs or NSs formation. It appears that the increase of Fe roughness (by grinding) produced NWs and NSs uniformly covering the surface of the Fe metal with high areal density. Oxidation at different temperatures resulted in the formation of NWs at 400 and 800 ^{o}C while at 500 and 600 ^{o}C, NSs formed. At 700 ^{o}C, the surface oxide has coral-structure. Temperature 800 ^{o}C was acknowledged as the best oxidation temperature for high aspect ratio (27) NWs formation. Higher areal density NWs were formed when oxidation was done in water vapour due to the influence of proton from water dissociation. Different oxidation time at 800 ^{o}C in water vapour was conducted to investigate the growth of NWs. NWs started to form at 5 min but for high areal density 23 NWs/100 μm^2 and aspect ratio of 27, oxidation must be done for 120 minutes. Mechanism of NWs formation was proposed to follow the stress-driven mechanism being the screw dislocations as the nucleation centres for the NWs formation. From HR-TEM, XRD and Raman spectroscopy, the NWs were found to be α-Fe_2O_3. Cr(VI) with concentration 200 mg/L was successfully adsorbed on the α-Fe_2O_3 NWs within 90 minutes, whereas on NSs, 112 mg/L was adsorbed. The kinetic and isothermal studies described the adsorption behavior of Cr(VI) on α-Fe_2O_3 to follow pseudo-second order and Langmuir's model respectively. The adsorption capacity of α-Fe_2O_3 NWs is 61.57 mg/g. The main mechanism of Cr(VI) removal by the α-Fe_2O_3 NWs due to electrostatic reaction between negative chromate ions and positively charge of adsorbent.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Chromium is classified as one of heavy metal elements and has been used in various industrial processes especially steel and plating industries for more than a century (Guertin et al., 2004). To date, the uses of chromium are essential in human activities and unavoidable. Moreover, it also has been long acknowledged that the industrial uses of chromium have introduced substantial amount of this heavy metal into the atmosphere and into the aquatic environments.

Chromium exists in the form of either trivalent (Cr(III)) or hexavalent ions (Cr(VI)). While Cr(III) is rather benign, Cr(VI) has been classified as carcinogenic and toxic matter (Guertin et al., 2004). Excessive inhalation of Cr(VI) could lead to the risk of lung cancer (Grevatt, 1998). Dermal exposure may risk in dermatitis and sensitive skin (EPA, 1998) and when indigested, it causes diarrhoea, internal haemorrhage or kidney damage (Mohan and Pittman, 2006). Therefore, Cr(VI) ions from industrial effluent need to be removed before the waste water is safe to be discharged. According to the World Health Organization (WHO) drinking water regulation, the parameter limit of effluent of Cr(VI) is 0.05 mg/L (WHO, 2011). Recently, Environmental Protection Agency (EPA) of California has stricter regulation: the maximum concentration level of allowed Cr(VI) is 0.01 mg/L, effective 1st July 2014 (EPA California, 2014). However, Cr(VI) release to the environment from industrial processes sometimes exceed such permissible levels polluting groundwater and soil around the area. Table 1.1 examples of water pollution caused by Cr(VI) for the last 6 years.

Table 1.1. Examples of Cr(VI) pollution in the world

Year	Place	References
2014	Hinkley Valley, California	(Izbicki, 2014)
2011	Yunnan Province, China	(Green Peace, 2011)
2010	Citarum River, Indonesia	(Roosmini et al., 2010)
2010	Peninsular, Malaysia	(Zulkifli et al., 2010)
2009	Karachi, Pakistan	(Nadeem-ul-Haq et al., 2009)
2009	Bangalore, India	(Shankar, 2009)

There have been several methods employed for Cr(VI) removal from polluted water or wastewater such as membrane filtration (Muthukrishnan and Guha, 2008), electrochemical treatment (Olmez, 2009), chemical precipitation (Ku and Jung, 2001), ion exchange (Galan et al., 2005) and adsorption (Hu et al., 2005, Burks et al., 2014). To select on the best method, one needs to consider several factors: (i) energy requirements, (ii) efficiency, (iii) economic and (iv) easy operation (Xu et al., 2012). Among various methods mentioned, adsorption is believed to be a rather efficient and cost effective to remove Cr(VI) thus is seen as a promising technique (Ahn et al., 2009, Burks et al., 2014). Moreover the process has other significant advantages such as potential for regeneration (reusable adsorbent), availability of various types of adsorbents and efficiency especially when dealing with low concentration of Cr(VI) (Rafatullah et al., 2010, Lens et al., 2013).

Adsorption is a surface property of a certain material which has an ability to attract molecules (Butt et al., 2006). Adsorption process requires a solid surface (i.e. the adsorbent) which the species to be adsorbed (adsorbate) will be attached by either physical or chemical process. Various adsorbent materials have been reported to remove Cr(VI) such as activated carbon (Khezami and Capart, 2005), biosorbent (Loukidou et al., 2004), clay mineral (Tahir and Rauf, 2006), metal oxides (Tel et al., 2004, Rodrigues et al., 2010), zeolites (Leyva-Ramos et al., 2008), industrial waste (Gupta et al., 2010) and agricultural products (Wartelle and Marshall, 2005). Adsorbent material such as biosorbent and agricultural product can be selected due to their low cost process. However, each country in the world has different ecosystem and climate thus the availability of those adsorbent is limited for some country and maybe season dependence. Activated carbon material offers high adsorption capacity and there are many sources of carbon that can be used (Mohan and Pittman, 2006). But its complex fabricability may lead to high cost. Use of metal oxide on the other hand offers many benefit such as its availability, easy fabrication and simple external separation especially when magnetic oxide is used, it can be simple removed from the treated water by a magnet (Hu et al., 2005).

In this present work, iron oxide film in a form of nanowires (NWs) was produced as an adsorbent material and Cr(VI) adsorption was investigated on these nanostructures. The use of adsorbent material in nanoscale has been suggested due to its efficiency and cost-effective process (Xu et al., 2012). Nanomaterial is defined as a class of material with dimension ranging from 1-100 nm at least in one dimension (Schobek et al., 2009). In here, the iron oxide is now consisted of structure in nanoscale, then it is expected that more surface area generated would improve the adsorption performance.

Iron is the second most abundant metal on earth (Jambor and Dutrizac, 1998). Its oxide mostly exists in the form of magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) or hematite (α-Fe_2O_3) (Cornell and Schwertmann, 2006). Recently, iron oxide has attracted attention due to its capabilities on removing heavy metal such as Pb(II) (White et al., 2009), As(V) (Li et al., 2006), Hg (II) (White et al., 2009), Cu(II) (Kim et al., 2003), Cr(VI) (Burks et al., 2014), Ni(II) (White et al., 2009) and Cd(II) (White et al., 2009) from water or wastewater. Its unique amphoteric properties offers the flexibility on shifting the surface charge of iron oxide, hence allowing either anion or cations adsorption from aqueous environment (Guertin et al., 2004). Additionally, the worth mentioned advantages using iron oxide are: (i) economical, (ii) availability, (iii) environmentally friendly, (iv) high corrosion resistant and (v) easy separation (Hu et al., 2005, Carabante et al, 2009, Fan et al., 2012). There have been reports on the use of iron oxide as Cr(VI) adsorbent such as γ-Fe_2O_3 nanoparticles (Hu et al., 2005), core-shell of α-Fe_2O_3 nanoflower (Zhong et al., 2006), mesoporous γ-Fe_2O_3 (Wang and Lo, 2009), Fe^{3+} oxide/hydroxide NP (Zelmanov and Semiat, 2011) and 3-Mercaptopropionic acid coated supermaramagnetic iron oxide nanoparticles (Burks et al., 2014), but the adsorbent properties of α-Fe_2O_3 nanowires synthesized by thermal oxidation have not been reported.

There are various different ways in the formation of metal oxide nanowires such as sol-gel (Wu et al., 2005), hydrothermal (Liu and Zeng, 2003), chemical vapour deposition (Chang et al., 2004) and thermal oxidation (Vincent et al., 2012). In this present work, iron oxide nanowires were grown from Fe substrate by thermal oxidation and were utilised as an adsorbent material for Cr(VI), as illustrated in