

**REMOVAL OF CADMIUM AND CHROMIUM  
USING TITANIUM DIOXIDE NANOWIRES  
UNDER ULTRAVIOLET RADIATION**

**NURRAFIQ ARINA BINTI RAFINDI**

**UNIVERSITI SAINS MALAYSIA**

**2022**

**REMOVAL OF CADMIUM AND CHROMIUM  
USING TITANIUM DIOXIDE NANOWIRES  
UNDER ULTRAVIOLET RADIATION**

**NURRAFIQ ARINA BINTI RAFINDI**

**UNIVERSITI SAINS MALAYSIA  
2022**

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING**  
**UNIVERSITI SAINS MALAYSIA**

**REMOVAL OF CADMIUM AND CHROMIUM USING TITANIUM DIOXIDE  
NANOWIRES UNDER ULTRAVIOLET RADIATION**

By

**NURRAFIQ ARINA BINTI RAFINDI**

**Supervisor: PROF. DR. ZAINOVIA LOCKMAN**

Dissertation submitted in partial fulfillment of the requirements for the degree of  
Bachelor of Engineering with Honours  
(Materials Engineering)

Universiti Sains Malaysia

**August 2022**

## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled '**Removal of Cadmium and Chromium using titanium dioxide nanowires under ultraviolet radiation**'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student: Nurrafiq Arina binti Rafindi

Signature:

Date: 18/8/2022



Witness by

Supervisor: Prof. Dr. Zainovia Lockman

Signature:



Date: 18/8/2022

## ACKNOWLEDGEMENT

Hereby I would like to express my highest gratitude to all who had provided me support throughout this project.

Firstly, I would like to thank my supervisor, Prof. Dr. Zainovia binti Lockman for her guidance and advice to enable me to complete this work. She provided a lot of useful advice on my work, supportive and she is generous in sharing her experiences with me.

Next, I would like to thank the Materials and Mineral Resources Engineering, Universiti Sains Malaysia (USM) for giving this opportunity to conduct this work. School provided good environment and adequate equipment for my study. The special acknowledgment is also extended to the Dean of the School, Professor Ir. Dr. Mariatti Jaafar and Deputy Dean, Assoc Prof. Dr. Nurulakmal Mohd Sharif for their thoughtfulness. Besides, the technical staffs of the School of Materials and Mineral Resources Engineering had helped me in giving me countless assistance concerning experimental equipment during lab work.

Also, I am very thankful to Prof Zainovia's team who are Nurhaswani Alias and Dr Fasihah for their guidance, support, help and experience throughout my project. Also, my FYP teammate Hui Sin, Min Li and Gang Yang for supporting each other to bring this work to completion.

Lastly, I am grateful to have my beloved parents, siblings and my friends who had given me their support both mentally and physically during completion of work.

## TABLE OF CONTENTS

<b>ACKNOWLEDGEMENT.....</b>	<b>iii</b>
<b>TABLE OF CONTENTS .....</b>	<b>iv</b>
<b>LIST OF TABLES .....</b>	<b>vii</b>
<b>LIST OF FIGURES.....</b>	<b>ix</b>
<b>LIST OF SYMBOLS.....</b>	<b>xii</b>
<b>LIST OF ABBREVIATIONS .....</b>	<b>xiii</b>
<b>ABSTRAK .....</b>	<b>xiv</b>
<b>ABSTRACT.....</b>	<b>xvi</b>
<b>CHAPTER 1 INTRODUCTION .....</b>	<b>1</b>
1.1 Background.....	1
1.1.1 Heavy metal pollution .....	1
1.1.2 Cadmium and Chromium.....	3
1.1.3 Source of cadmium and chromium pollution.....	4
1.1.4 Cadmium and chromium in paddy .....	5
1.1.5 Cadmium and chromium removal by TiO <sub>2</sub> photocatalyst .....	5
1.1.6 Nanomaterials .....	7
1.2 Problem statement.....	8
1.3 Objectives .....	10
1.4 Scopes of work .....	10
1.5 Outline of chapters.....	11
<b>CHAPTER 2 LITERATURE REVIEW .....</b>	<b>12</b>
2.1 Introduction .....	12
2.2 Cadmium and chromium.....	12
2.3 Cadmium and chromium pollution .....	14
2.4 Cadmium and chromium toxicity .....	16

2.5	Methods to remove Cd(II) and Cr(VI).....	17
2.5.1	Adsorption.....	17
2.5.2	Photocatalysis.....	18
2.6	Photocatalysis removal of Cd(II) and Cr(VI) reduction by TiO <sub>2</sub> .....	19
2.7	Nanowires.....	24
2.8	Titanium dioxide (TiO <sub>2</sub> ) as nanowires.....	25
2.9	Synthesis of TiO <sub>2</sub> nanowires.....	27
2.10	Synthesis and formation of TiO <sub>2</sub> nanowires by thermal oxidation.....	28
2.11	Growth mechanism of TiO <sub>2</sub> nanowires via thermal oxidation .....	31
<b>CHAPTER 3 METHODOLOGY .....</b>		<b>32</b>
3.1	Introduction .....	32
3.2	Materials and reagents .....	32
3.3	Experimental procedure .....	33
3.4	Sample preparation .....	34
3.5	Synthesis of TiO <sub>2</sub> Nanowires by thermal oxidation.....	35
3.5.1	Photocatalytic reduction of Cd(II).....	37
3.5.1(a)	Preparation of Cadmium stock solution.....	37
3.5.1(b)	Preparation of Alizarin Red S (ARS) indicator.....	37
3.5.1(c)	Removal experiment.....	38
3.5.2	Photocatalytic reduction of Cr(VI).....	38
3.6	Experimental design.....	39
3.6.1	Effect of oxidation time .....	39
3.6.2	Effect of oxidation environment .....	40
3.7	Photocatalytic process.....	40
3.8	Characterization techniques .....	41
3.8.1	Field Emission Scanning Electron Microscopy (FESEM) .....	42
3.8.2	X-ray Diffraction (XRD) .....	43

3.8.3	Raman spectroscopy .....	44
3.8.4	UV-Visible Spectroscopy (UV-Vis).....	45
<b>CHAPTER 4</b>	<b>DISCUSSIONS .....</b>	<b>47</b>
4.1	Introduction .....	47
4.2	Thermal oxidation of TiO <sub>2</sub> nanowires.....	47
4.2.1	Effect of oxidation time .....	48
4.2.2	Effect of different concentration of KOH.....	52
4.2.3	Effect of oxidation time for 3M KOH.....	57
4.3	Growth mechanism of TiO <sub>2</sub> nanowires .....	59
4.4	Crystallinity studied of nanowires .....	60
4.5	Photocatalyst reduction experiment.....	64
4.5.1	Photocatalyst reduction of Cd(II) by TiO <sub>2</sub> nanowires .....	64
4.6	Photocatalyst reduction of Cr(VI) by TiO <sub>2</sub> nanowires .....	72
4.6.1	Photoreduction mechanism of Cr(VI) by TiO <sub>2</sub> nanowires.....	75
<b>CHAPTER 5</b>	<b>CONCLUSION AND FUTURE RECOMMENDATIONS.....</b>	<b>78</b>
5.1	Conclusion.....	78
5.2	Recommendations for Future Research .....	79
<b>REFERENCES</b>	<b>.....</b>	<b>80</b>



## LIST OF TABLES

	<b>Page</b>
Table 1.1	Classification of heavy metals .....2
Table 2.1	Element properties of cadmium ..... 13
Table 2.2	Element properties of chromium (Lunk, 2015) ..... 14
Table 2.3	Summary of studies of photocatalyst reduction of Cd(II) on TiO <sub>2</sub> ....21
Table 2.4	Summary of studies of photocatalyst reduction of Cr(VI) on TiO <sub>2</sub> ...23
Table 2.5	Summary of studies of synthesis of TiO <sub>2</sub> nanowires by thermal oxidation .....30
Table 3.1	List of materials and reagents used .....32
Table 3.2	Parameters values on the synthesis of TiO <sub>2</sub> nanowires in various oxidation time and oxidation environment .....40
Table 3.3	Parameters values on the synthesis of TiO <sub>2</sub> nanowires in various oxidation environment.....40
Table 3.4	Parameters involved in photocatalytic reduction of Cd(II) .....41
Table 3.5	Parameters involved in photocatalytic reduction of Cr(VI) .....41
Table 4.1	Summarizes average length and diameter of TiO <sub>2</sub> nanowires with 2M KOH .....52
Table 4.2	Summarizes the average length and diameter of TiO <sub>2</sub> NWs with different oxidative environment for 60 minutes .....57
Table 4.3	Summarizes the average length and diameter of TiO <sub>2</sub> NWs with 3M KOH .....58
Table 4.4	List of position and plane for rutile phase .....62
Table 4.5	Crystallite size of oxidized Ti sample with KOH vapour .....63
Table 4.6	Removal efficiency of Cr(VI) with TiO <sub>2</sub> nanowires grown under different concentration of KOH .....74



## LIST OF FIGURES

	<b>Page</b>
Figure 1.1	Types of sources of heavy metals (Vanisree et al., 2022) .....4
Figure 1.2	Cadmium and chromium uptake and transportation to food chain (Vanisree et al., 2022) .....5
Figure 1.3	Schematic diagram of photocatalysis mechanism for Cd <sup>2+</sup> /TiO <sub>2</sub> system (Anthapaththu, 2013).....6
Figure 1.4	Photo-activation of a semiconductor and primary reactions occurring on its surface (Colmenares and Luque, 2014) .....7
Figure 1.5	Flow chart of stages for the whole research ..... 11
Figure 2.1	Schematic diagram of photocatalysis mechanism for Cd <sup>2+</sup> / TiO <sub>2</sub> system.....20
Figure 2.2	Energy band diagram of n-type TiO <sub>2</sub> semiconductor (Aguirre et al., 2017).....26
Figure 2.3	Crystallographic structures of TiO <sub>2</sub> in different phases anatase, brookite and rutile (Stephen, 2020).....26
Figure 2.4	SEM images of TiO <sub>2</sub> nanowires formation via thermal oxidation for 4 hours (a-b) 700°C, c) 800°C, d) 900°C (Arcadipane et al., 2016)....29
Figure 3.1	General flowchart of experimental stages in the whole study .....34
Figure 3.2	Set up of equipment for synthesis of TiO <sub>2</sub> nanowires by thermal oxidation .....36
Figure 3.3	Heating profile for thermal oxidation of Ti foil.....36
Figure 3.4	General process flow of thermal oxidation of Ti foil.....37
Figure 3.5	Schematic diagram of experimental set up for photocatalyst of Cd(II) and Cr(VI) under UV light .....38
Figure 3.6	a) Schematic Diagram of a FESEM and its components, b) Interaction of the electron beam (Walock & Michael, 2012).....43

Figure 3.7	Schematic diagram for Bragg's law .....	44
Figure 4.1	Physical appearance of Ti foil a) as-received b) after cleaning process and after thermal oxidation at 750°C for c) 30 min, d) 60 min and e) 90 min under 2M KOH mist .....	50
Figure 4.2	FESEM images of oxidized Ti foil at 750°C with 2M KOH for (a-b) 30 minutes, (c-d) 60 minutes and (e-f) 90 minutes (FESEM images were done at Quanta FEG 650) at Centre for Global Archaeological Research, (CGAR) and High Resolution FESEM (XHR-FESEM) (FEI Verious 460L at SERC, USM)) .....	51
Figure 4.3	Physical appearances of Ti foil after thermal oxidation at 750°C with a) 0.5M KOH, b) 2M KOH and c) 3M KOH for 60 minutes .....	53
Figure 4.4	FESEM images of TiO <sub>2</sub> nanowires after thermal oxidation for 60 minutes at 750°C with; (a-b) 0.5 M KOH, (c-d) 1 M KOH, (e-f) 2 M KOH and (g-h) 3M KOH deposition (FESEM images were taken by Ultra High Resolution-SEM (Hitachi-Regulus) and SEM (Quanta FEG 650) at Centre for Global Archaeological Research).....	55
Figure 4.5	FESEM images of TiO <sub>2</sub> nanowires after thermal oxidation for 30 minutes at 750°C with 3M KOH at magnification a)5k and b)100k .	58
Figure 4.6	Mechanism of formation of TiO <sub>2</sub> nanowires .....	60
Figure 4.7	XRD pattern of sample oxidized at 750°C for 60 minutes under various concentration of KOH .....	62
Figure 4.8	Raman shift for oxidized Ti foil in the presence of KOH at different concentrations for 60 minutes .....	64
Figure 4.9	Digital photograph of colour changes when Cd(II) samples mixed with ARS for each collection a) 0.5M, b) 1M, c) 2M, d) 3M under UV light.....	66
Figure 4.10	Graph of C/Co vs time under 60 minutes in dark environment and 120 minutes under UV light irradiation .....	69
Figure 4.11	Removal efficiency of Cadmium vs time under 60 minutes dark environment and 120 minutes under UV light irradiation.....	70

Figure 4.12	Removal efficiency of Cadmium with and without the presence of methanol vs time under 60 minutes dark environment and 120 minutes under UV light irradiation .....	71
Figure 4.13	Position of conduction band and valence band edges for TiO <sub>2</sub> , reduction potentials for Cd <sup>2+</sup> and radicals •CH <sub>2</sub> OH (Chenthamarakshan & Rajeshwar, 2000).....	72
Figure 4.14	Graph of C/Co vs time under 30 minutes in dark environment and 120 minutes under UV light irradiation .....	74
Figure 4.15	Removal efficiency of Chromium vs time under 30 minutes dark environment and 120 minutes under UV light irradiation.....	74
Figure 4.16	Photoreduction of Cr(VI) to Cr(III) mechanism by TiO <sub>2</sub> nanowires .	77

## LIST OF SYMBOLS

%	Percentage
°	Degree
°C	Degree Celcius
°C/min	Degree Celcius/min
Nm	Nanometer
$2\theta$	Diffraction angle
$\text{Cd}^{2+}$	Cadmium (II) ions
$e^-$	Electron
g	Gram
$h^+$	Holes
$h\nu$	Photons energy
M	Molarity
Ppm	Parts per million
$\text{OH}^-$	Hydroxyl ions

## LIST OF ABBREVIATIONS

1D	One-dimensional
a.u	Arbitrary Unit
Cd(0)	Cadmium metallic
Cd(II)	Cadmium divalent
d	Lattice spacing
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
XRD	X-ray Diffraction
pH	Hydrogen potential
NWs	Nanowires
UV	Ultraviolet Radiation

## ABSTRAK

Kadmium divalent dan kromium hexavalent adalah bahan kimia yang mempunyai tahap toksik yang tinggi di mana ia akan menyebabkan keracunan kepada manusia jika pengambilannya terlalu tinggi dan memberikan ancaman yang berbahaya kepada manusia dan alam sekitar. Di dalam kajian ini, fokus utama adalah untuk mengkaji kebolehan wayar nano  $\text{TiO}_2$  dalam penurunan  $\text{Cd(II)}$  dan  $\text{Cr(VI)}$  dari larutan akueus. Wayar nano  $\text{TiO}_2$  telah disintesis melalui pengoksidaan termal dengan kepekatan  $\text{KOH}$  pemangkin yang berbeza. Sintesis ini melibatkan satu langkah pengoksidaan. Kesan waktu pengoksidaan dan pengoksidaan persekitaran dikaji untuk membentuk wayar nano. Keadaan yang paling optimum dalam sintesis wayar nano yang padat dan tumbuh hanya pada paksi-c melalui pengoksidaan termal didapati adalah pada suhu  $750^\circ\text{C}$  selama 60 minit waktu pengoksidaan di bawah persekitaran 2M  $\text{KOH}$ . Wayar nano yang terhasil adalah panjang, nipis dan menutupi seluruh permukaan kerajang Titanium.  $\text{KOH}$  sangat penting untuk pertumbuhan wayar nano kerana ia bertindak sebagai pemangkin untuk menolak wayar nano untuk tumbuh secara menegak dan menghalang pertumbuhan secara melintang. Teknik penyaringan yang digunakan untuk meneliti dawainano  $\text{TiO}_2$  termasuk FESEM, HRTEM dan XRD. Keberkesanan sintesis wayar nano dikaji di atas penurunan  $\text{Cd(II)}$  dan  $\text{Cr(VI)}$  kepada keadaan yang tidak bertoksik melalui tindak balas fotopemangkin dibawah cahaya UV. Kepekatan diukur dengan mengambil nilai penyerapan dari specktrometer UV-Vis kerana kepekatan berkadar langsung dengan penyerapan berdasarkan undang-undang Beer-Lambert. Ia didapati, wayar nano tumbuh dibawah keadaan 2M  $\text{KOH}$  selama 60 minit menunjukkan penurunan  $\text{Cd(II)}$  paling tinggi iaitu 34.52% dan  $\text{Cr(VI)}$  iaitu 34.57%. Penurunan  $\text{Cd(II)}$  paling rendah didapati oleh wayar nano tumbuh dibawah keadaan 1M iaitu 1.5% manakala wayar nano terbentuk di



bawah keadaan 3M KOH mempunyai kebolehan untuk menurunkan Cr(VI) sehingga 17.11%.

# REMOVAL OF CADMIUM AND CHROMIUM IN RICE USING TITANIUM DIOXIDE NANOWIRES UNDER ULTRAVIOLET RADIATION

## ABSTRACT

Divalent cadmium, Cd(II) and hexavalent chromium, Cr(VI) are high toxicity chemical substance which may harmful for human being if the amount uptake is too high through consumption and give great threat to our environment. In this study, it focuses on the ability of TiO<sub>2</sub> nanowires to remove Cd(II) and Cr(VI) from aqueous solution. The TiO<sub>2</sub> nanowires were synthesized by thermal oxidation with different concentration of KOH catalyst. It involves one step oxidation in this synthesis. The effect of oxidation time and oxidation environment were investigated in the formation of nanowires. The optimum condition in synthesizing vertically array and dense TiO<sub>2</sub> nanowires via thermal oxidation was found to be at 750°C for 60 minutes under 2M KOH mist environment. The nanowires formed were long, thin and have full coverage on Ti foil. KOH is very vital for the growth of nanowires as it acts as catalyst for push nanowires to grow longer vertically and inhibit lateral growth. Characterization technique used to investigate and support the formation of TiO<sub>2</sub> nanowires include FESEM, HRTEM and XRD. The effectiveness of the synthesized TiO<sub>2</sub> nanowires were investigated upon removal of Cd(II) and Cr(VI) to a non-toxic state via photocatalyst reaction under UV light. The concentration measured by taking absorbance value from UV-Vis spectrophotometer as concentration is directly proportional to the absorbance based on Beer-Lambert's Law. It was found that, nanowires grown under 2M KOH for 60 minutes shows the highest reduction of Cd(II) and Cr(VI) which is 34.52% and 34.57% respectively. The lowest reduction of Cd(II) shown by TiO<sub>2</sub> nanowires grown under 1M KOH (1.5%) and TiO<sub>2</sub> nanowires formed under 3M KOH have ability to reduce to 17.11% of Cr(VI).



# CHAPTER 1

## INTRODUCTION

This study is focused on the formation of TiO<sub>2</sub> nanowires by thermal oxidation of foil at several parameters to produce TiO<sub>2</sub> nanowires at as short oxidation time as possible. The TiO<sub>2</sub> nanowires were then used as photocatalyst to remove cadmium Cd(II) and chromium Cr(VI) ions under UV light. In this chapter, background of this study includes problem statements, objectives, scopes of study and outline of the report are shown.

### 1.1 Background

#### 1.1.1 Heavy metal pollution

Heavy metal pollution is becoming an increasingly significant issue that is impacting the environment and biodiversity. Heavy metal ions have accumulated in aquatic life due to their constant release into water bodies. They can accumulate in aquatic animals and get biomagnified (Hashmi & Varma, 2018). Heavy metals are defined as elements and metalloids which occur in nature, having atomic number greater than 20 and atomic density above 5 g cm<sup>-3</sup> also show the metal properties. They are also can be defined as metals with high densities located in group 3 to 16 in periodic tables (Aryama et al., 2022). From the table 1.1, heavy metals are classified into two categories which are of essential and non-essential of heavy metals. Essential heavy metals has important role in biochemical and fundamental process growth of living organisms and needed in trace amounts approximately 10-15 ppm. Plants especially need them since they produce cofactors that are pertinent for enzymes and other proteins. Whistle, non-essential heavy metal are not required by plants in metabolic process though in trace amounts (Sarmistha et al., 2021).

Table 1.1 Classification of heavy metals

Essential Heavy Metals	Non-Essential Heavy Metals
Cobalt	Arsenic
Copper	Cadmium
Manganese	Mercury
Molybdenum	Lead
Zinc	Chromium(V)

Heavy metals are released into the environment from both anthropogenic and natural sources. Anthropogenic sources are direct discharges from industrial sources (industrial establishments that use heavy metals in their processes or mining and mineral processing), in other words, a product of human activity. Heavy metals also can contaminate chains (Parihar et al., 2019). Agriculture is one of the most significant human activities that releases heavy metals into the environment. For instance, by using wastewater as fertilizer for agricultural soils resulted in significantly higher levels of heavy metals in the edible parts of the crops on these soils, according to the study by (Parihar et al., 2019). In fact, wastewater from the industry contains lots of heavy metal, which can accumulate over time in soil deposits along wastewater channels. Wastewater is defined as a complex matrix including high levels of solids with total solids 350–1200 mg/l), dissolved and particulate matter like chemical oxygen demand 250–1000 mg/l), microorganisms (up to 10<sup>9</sup> number/ml), micropollutants, nutrients and heavy metals (Vanisree et al., 2022).

Contamination in water bodies like river, ground water and lake with heavy metals must be avoided even at low concentrations since accumulation is unavoidable, especially in aquatic life also accumulation of heavy metals in agriculture soils will be absorbed by plants (Chen et al., 2018) When crops are consumed by humans, ions can be transported and accumulated, resulting in detrimental health effects as well as contamination of heavy metals in aquatic life. Therefore, bioaccumulation would occur in humans if they were consumed (Rajeshkumar et al., 2018).

### 1.1.2 Cadmium and Chromium

According to International Agency for Research on Cancer (IARC), cadmium are classified in group 1 which means carcinogenic to humans (IARC, 2018). There are several research have been studied regarding carcinogenicity of cadmium to living organisms. Hence, from the studies, can be concluded that there is sufficient evidence to prove that cadmium is carcinogen which can cause cancer in humans. Cadmium (Cd) is also one of the most hazardous heavy metals with a biological half-life of 10-30 years. Zhen et al., 2008 reported that 10% of 91 rice samples contained  $>200 \mu\text{g}/\text{kg}$  of Cd at chinese market and after 10 years, Zhen et al., 2018 found that there is no decreasing in the exceedance rate with 10% of samples still detected containing  $>200 \mu\text{g}/\text{kg}$ . Since then, many countries have issued standards for maximum allowable limit in soil and rice including Malaysia with range between 0.4 or 0.2 mg Cd per kg rice (Shin et al., 2020). According to WHO standards, the permissible limit of total Cd level in an agriculture soil is not more than 5 Mg/kg (WHO, 2011). Cadmium widely used to manufacture rechargeable batteries used for electric vehicles. Cadmium has become an important part of modern technology, having several uses in the electronics, communications, power generation, and aerospace industries (Kinuthia et al., 2020).

Chromium is categorized as Group 1 materials which is human carcinogen by International Agency for Research on Cancer (IARC). Sharma, 2014 stated that by consuming excessive amount of Cr(VI) can cause severe health problems such as damage of liver and kidney as well as the central nerve system. Maximum allowable concentration for Cr(VI) in rice grain is 1 mg/kg in China as agreed by World Health Organization (WHO) and other regulatory bodies. Cr(VI) intake via ingestion can lead to ulcers in the stomach and intestine. Chromium(III) is essential in human body with daily intake range from 50 to 200  $\mu\text{g}/\text{d}$  for adults. It is important to avoid contamination

of Cr(VI) in rice because it would caused detrimental effect to human. Cadmium and chromium was studied in this work because of the uncontrollable cadmium and chromium content in paddy soils and rice grains can contribute to various health disease to human being due to Cd and Cr contamination and come out with the method on how to overcome the issue.

### 1.1.3 Source of cadmium and chromium pollution

There are two main reason to cause high soil Cd and Cr concentration. One is the natural sources that comes from volcanic erruption and during the mineral rock weathering process. Cd and Cr is a naturally occurring and non-essential trace element with an average content of 0.01-2.00 mg/kg in world soils and a range of 0.10 to 1.80 mg/kg in China (Zou et al., 2021). In addition, sources of Cd and Cr contamination also due to anthropogenic activities include mining, metallurgical industry and sewage irrigation.

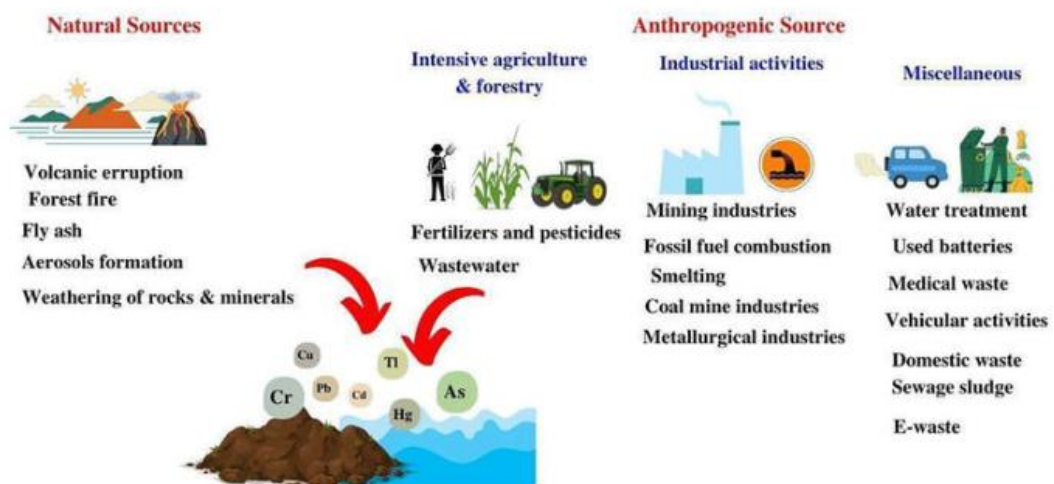


Figure 1.1 Types of sources of heavy metals (Vanisree et al., 2022)

#### 1.1.4 Cadmium and chromium in paddy

Cadmium and chromium are absorbed by crops/paddy from contaminated land and barometrically measured particle matter from various sources. It is absorbed by roots and transported to various cell and parts of paddy plants by multiple channels. In addition, cadmium accumulated more in the shoots than in roots (Hashimi & Varma, 2018). Resulting in the degradation of crop developmental traits due to changes in metabolic, physiological, and biochemical activities (Singh et al., 2016). The presence of these hazardous components in crops might cause poisoning indications with serious implications for instance cell death, enzyme exhibition, growth inhibition and genotoxicity. Also cause disease as cancers, renal disease, osteoporosis and kidney problems (Zou et al., 2021).

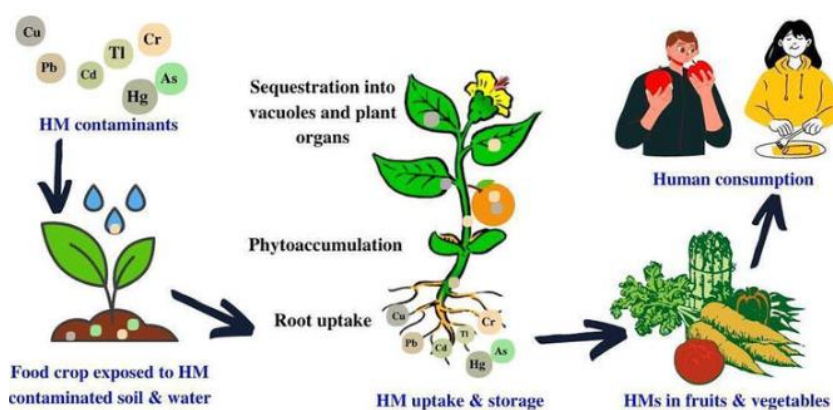


Figure 1.2 Cadmium and chromium uptake and transportation to food chain (Vanisree et al., 2022)

#### 1.1.5 Cadmium and chromium removal by TiO<sub>2</sub> photocatalyst

In order to remove cadmium and chromium contamination in wastewater from transferring into the soil and paddy plants, there are several methods used such as chemical precipitation, adsorption, filtration, electro dialysis and semiconductor photocatalyst (Yang et al., 2019). All of these treatments have their own advantages and drawbacks. However semiconductor photocatalysis can be considered as the most



promising technique since can treat even a small concentration of Cd(II) and Cr(VI). Photocatalysis technology relies on the electron from semiconductor to reduce Cd(II) to Cd(0) and Cr(VI) to Cr(III) a low toxic state. Reduction process from photocatalyst is much easier and simple than other methods. In this technique, semiconductor as substance (photocatalyst) absorb light energy to generate electron-hole pair. The photogenerated electrons are used to reduce Cd(II) and Cr(VI). Among all those semiconductor, TiO<sub>2</sub> was chosen in this study as it is chemically stable, non-toxic, photostable and inexpensive (Rahmat et al., 2019).

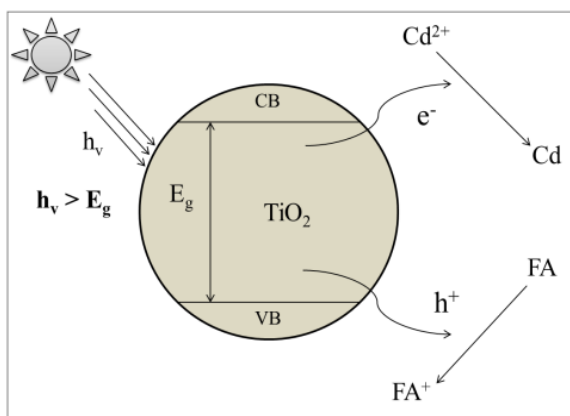
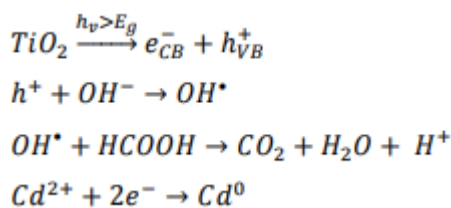


Figure 1.3 Schematic diagram of photocatalysis mechanism for Cd<sup>2+</sup>/TiO<sub>2</sub> system (Anthapaththu, 2013)



The first reaction illustrates the generation of electron-hole pairs when TiO<sub>2</sub> is exposed to sunlight radiation. Upon the separation of electron-hole pairs, the combination of holes with water to create hydroxyl radicals as shown in second reaction above. Hydroxyl radicals oxidize dissolved organic compounds and convert them to carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and other inorganic products. Metal ions

( $\text{Cd}^{2+}$ ) use photo-generated electrons in the conduction band to get reduced to  $\text{Cd}(0)$  (a less toxic form of cadmium) based on forth reaction (Yang et al., 2019).

In addition, electron will be excited from valence band to conduction band when  $\text{TiO}_2$  is illuminated with light having energy greater than its energy bandgap and leave hole behind. Electron in conduction band can react with  $\text{Cr(VI)}$  ions absorbed on the surface. The holes in conduction band produced radical  $\cdot\text{OH}$  and there is possibility that oxidizing species can induce backward reactions and make it to turn to the original state  $\text{Cr(III)}$  to  $\text{Cr(VI)}$ . In order to avoid this which gives disadvantage to the photocatalyst, hole scavenger like methanol, ethanol and EDTA is used to scavenge the holes and enhance photocatalytic reduction (Athapaththu, 2013).

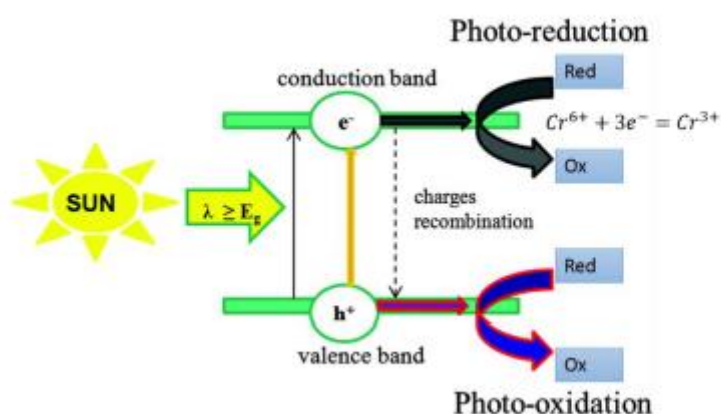


Figure 1.4 Photo-activation of a semiconductor and primary reactions occurring on its surface (Colmenares and Luque, 2014)

### 1.1.6 Nanomaterials

Nanomaterials are defined as material with external dimension in nanoscale with size range approximately 1nm to 100nm. Fabricated nanomaterials in this study is focussed on formation of nanowires. Nanowires commonly known as 1-D nanomaterial from a sub-category of nanofibre with two similar external dimension in nanoscale. Nanowires is an electrically conducting or semi-conducting nanofibre

(Jayaprakash, 2014). Nanowire have been used in this study due to high surface area, surface ratio and surface energy. Surface atoms have different properties than atoms in bulk which makes them more reactive and increase photocatalytic performance (Wang & Ni, 2018). TiO<sub>2</sub> nanowires were fabricated by thermal oxidation of titanium foil. The nanowires were formed at the surface of the foil. The growth of oxide increases quickly when conducted at high temperature due to fasten growth of oxide film. Thus, fabrication of nanowires can be done at elevated temperatures with KOH is selected to assist nanowires growth. Oxidized titanium were then characterized using Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction (XRD), Raman spectroscopy and High-Resolution Transmission Electron Microscopy (HRTEM). While reduction performance of TiO<sub>2</sub> nanowires can be analysed by UV-Visible spectrophotometry (UV-Vis).

## **1.2 Problem statement**

Heavy metal for example cadmium, chromium, lead and arsenic have contribute a lot to wastewater pollution. They have threaten living organism including human being after consuming rice grains that have been polluted by cadmium and chromium. Asia is the major producer for rice in the world. Hence, it is important to secure and maintain rice production as rice is their staple food (Zhou 2021). Suda and Makino reported that japanese obtain half of their Cd in rice. Many researchers agree cadmium and chromium pollution mainly comes from industrial wastewater and travel to the crops which causes accumulation in rice grains. Therefore, efficient technology for reducing Cd and Cr in rice become increasingly important to improve health of consumers. Semiconductor photocatalysis is chosen as it is the most method as its

ability to reduce small amount of Cd(II) and Cr(VI) concentration. Therefore, TiO<sub>2</sub> is chosen as photocatalyst in reduction of heavy metal, cadmium and chromium.

TiO<sub>2</sub> nanowires were synthesized via thermal oxidation on the surface of Ti foil. It is a 1-D nanostructure material. Other than thermal oxidation, there are several routes to synthesize nanowires for instance hydrothermal, sol-gel, liquid phase deposition (Guoquan, 2017) and thermal oxidation with Au catalyst. Thermal oxidation is very simple and easy method however, proper planning and strategies needed to produce c-axis growth nanowires hence various methods and parameters have been studied. In order to produce longer and dense nanowires, longer oxidation time is needed which often up to days. Therefore, in this study, oxidation environment has been studied and applied to induce fast growing process by introducing catalyst. With the presence of KOH, can assist oxidation process and undergo thermal oxidation at short oxidation time for large scale production. KOH is non-toxic material and quite cheap.

Nanowires formed will be used as a catalyst during photocatalysis of Cd (II) and Cr(VI). It is important to remove cadmium and chromium from waste water as of its toxicity. However, limited number of publications published by researcher on the removal of cadmium by TiO<sub>2</sub> nanowire as photocatalyst. Thus, in this work, removal of Cd (II) and Cr(VI) on TiO<sub>2</sub> nanowire are performed and the performance of the nanowires to completely 100% adsorb and remove within short period. The photocatalyst reduction process are implemented under UV light instead of under sunlight as TiO<sub>2</sub> has wide band gap and can be only activated under UV light. Also, photoreduction under sunlight expected to be slow as it has only 5% of UV light. As a result, under UV light, photocatalyst can be performed to the maximum.

### **1.3 Objectives**

The objectives of this study are:

1. To determine the optimum conditions in synthesizing vertically aligned and dense TiO<sub>2</sub> NWs by thermal oxidation on titanium foil.
2. To investigate the performance of TiO<sub>2</sub> NWs as photocatalyst for removal of Cd(II) and Cr(VI) in wastewater under light irradiation.

### **1.4 Scopes of work**

The scope of this work mainly covers the fabrication of TiO<sub>2</sub> nanowires by thermal oxidation with KOH and its capability as photocatalyst in photocatalytic reduction to reduce toxic cadmium, Cd(II) and chromium Cr(VI). The parameters involved in this study such as, oxidation time, and concentration of KOH were studied for the growth of nanowires. Thermal oxidation was carried out in horizontal tube furnace. Only high purity titanium were used as substrate to avoid contamination and disruption on nanowires growth. The sample were then characterized using Field Emission Scanning Electron Microscopy (FESEM) and X-ray diffraction (XRD) respectively to determine morphology and phase. In addition, the removal efficiency percentage could be determined using UV-Visible spectrometer after exposing the solution with TiO<sub>2</sub> nanowires as photocatalyst to light irradiation for a period of time.

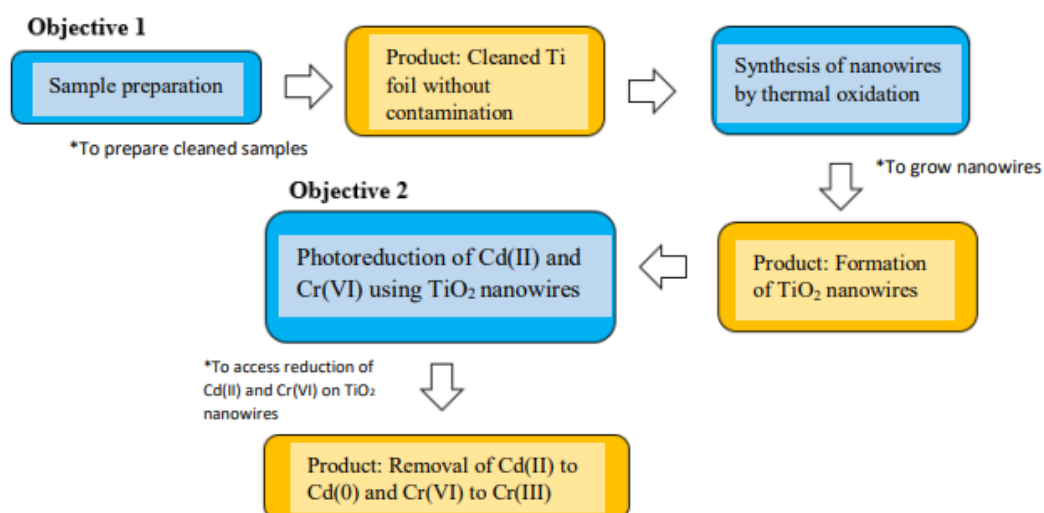


Figure 1.5 Flow chart of stages for the whole research

## 1.5 Outline of chapters

This thesis consist of five chapters where chapter one focuses on introduction, background of study, problem statement, objective and scope of the work. In chapter two, contains literature review and theory as well as basic concept regarding cadmium and chromium pollution, titanium, TiO<sub>2</sub>, synthesis of TiO<sub>2</sub> via thermal oxidation with potassium hydroxide, KOH, growth mechanism and photocatalysis reduction of Cd(II) and Cr(VI). Moreover, chapter three discusses on methodology used in this work includes materials, experimental design as well as characterization techniques. In addition, in chapter four, all results and observation regarding the research will be discussed including the effect of oxidation parameters. Last but not least, in chapter five will conclude all the findings throughout this study as well as recommendations for next research.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Introduction**

This chapter highlights on cadmium and chromium as of heavy metals that pollutes water. This chapter also focuses on several methods used to remove Cd (II) that have been studied by most researchers. On later part will discuss on the fabrication of TiO<sub>2</sub> nanowires by thermal oxidation, growth mechanism of TiO<sub>2</sub> nanowires and photocatalysis application in removal of Cd(II) ions in paddy field.

#### **2.2 Cadmium and chromium**

Cadmium is a chemical element and a metal from Group 12 from the periodic table also has atomic number 48 and atomic mass 112. Cadmium is a silver-white in colour, soft as tin as it produce crackling sounds when bent and can be rolled into sheets. Cadmium has low melting (321°C) and boiling temperature (765°C). The metal is permanent in dry air, but becomes coated with the oxide in moist air, burns to a red colour when heated, and is easily soluble in mineral acids. Cadmium usually does not have any odor and taste also has eight stable isotopes: 106 Cd, 108 Cd, 110 Cd, 111 Cd, 112 Cd, 113 Cd, 114 Cd, and 116 Cd. However, the most common isotopes are 112 Cd and 114 Cd (Adriano, 2001). Based on the history, during the early 1800, the apothecaries of Hanover, Germany, produced zinc oxide by heating a naturally occurring zinc carbonate called cadmia. When Friedrich Stromeyer of Göttingen University investigated the problem (product was discoloured rather than being pure white), he traced the discoloration to a component he could not identify, which he assumed, it must be an undiscovered element. He separated this as brown oxide and heated it with lampblack (carbon) to generate a sample of a blue-grey metal, which he

named cadmium after the mineral's name. That was in the year 1817. Meanwhile, two other Germans working on the same topic, Karl Meissner in Halle and Karl Karsten in Berlin, announced the finding of cadmium. It can be manufactured in a variety of commercial forms to go along with zinc manufacturing. It is utilised in electroplating (auto industries) and pigment manufacture (cadmium sulphate, cadmium selenide), as well as polyvinyl plastic stabilisers and batteries (rechargeable Ni-Cd batteries) (Adriano, 2001).

Table 2.1 Element properties of cadmium

<b>Properties</b>	<b>Cadmium</b>
Atomic number	48
Atomic weight	112.414
Density (g/cm <sup>3</sup> )	8.69
Melting point	321°C (610°F)
Boiling point	765°C (1409°F)
Specific gravity	8.65 at 20°C (68°F)
Oxidation state	+2
Electron configuration	(Kr)4d <sup>10</sup> 5s <sup>2</sup>

Chromium is a transition element that located in group 6 period 4 in Periodic Table also known as refractory metals (Lunk, 2015). It also have atomic number of 24 and atomic weight of 51.996. Since it is a transition, hence it can be appeared in various colour. For example, Lead chromate (PbCrO<sub>4</sub>) appear as yellow compound while chromic oxide (Cr<sub>2</sub>O<sub>3</sub>) appear as green compound. Previous name of chromium is “*chroma*” which is come from the Greek which means colour that suggests a compound's ability to produce a wide range of colour. Louis-Nicholas Vauquelin, a French chemist was first discovered chromium in the form of oxide (CrO<sub>3</sub>) in 1797 while conducting an experiment with mineral crocoite (PbCrO<sub>4</sub>). The next year, he was able to obtain metallic chromium (Cr) by heating chromium in charcoal oven and recently chromium is obtained from chromite ore (FeCr<sub>2</sub>O<sub>4</sub>) by heating it in the presence of either silicon or aluminium



Table 2.2 Element properties of chromium (Lunk, 2015)

<b>Properties</b>	<b>Chromium</b>
Atomic number	24
Atomic weight	51.996
Melting point	1907°C
Boiling point	2671°C
Density	7.19 g/cm <sup>3</sup>

Chromium can produce 20 different isotopes but naturally occurs in three stable isotopes, <sup>52</sup>Cr, <sup>53</sup>Cr and <sup>54</sup>Cr. Also, has wide range of oxidation states from -2 to +6, with +3 being the most stable energetically (GracePavithra et al., 2019). The most common oxidation states of chromium compounds are +3 and +6.

### **2.3 Cadmium and chromium pollution**

Heavy metal pollution have gradually become a major issue to the world, in which they contribute towards pollution in environment explicitly water pollution. Heavy metals are usually nondegradable and can accumulate in living organism which posing a risk to entire food chain. Despite the fact that heavy metals are naturally occurring compounds, anthropogenic activities could contribute excessive quantity of contaminations and impose threats on human and environmental (Abhishek et al., 2018).

Major contribution of heavy metal pollution to the environment primarily due to anthropogenic activities which comes from mining the metal, smelting, and other industries from metal-based. Contamination can also come from landfills, incineration, excretion, road works and ect. Second highest source of contribution to the pollution is the use of heavy metal in agricultural fields such as pesticides, insecticides and fertilizers. The increase of heavy metal can also comes from natural occurrence like soil erosion, volcanic activity and metal corrosion.

Cd is most commonly found in Ni/Cd batteries, which are rechargeable or secondary power sources with high output, long life, little maintenance, and strong resistance to physical and electrical stress. Cadmium coatings give excellent corrosion protection to vessels and other vehicles, especially in high-stress environments like the maritime and aerospace industries. Cadmium can also be found in phosphate fertilisers, detergents, and refined petroleum products as an impurity. Furthermore, acid rain and the resulting acidification of soils and surface waters has increased the geochemical mobility of Cd, causing its surface-water concentrations to rise when the pH of lake water falls (Campbell, 2006). Cadmium is a naturally occurring by product of the zinc and lead refining processes. The use of agricultural inputs such as fertilisers, pesticides, and biosolids (sewage sludge), as well as the disposal of industrial wastes and the deposition of atmospheric contaminants, raises the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake is significant (Wegler et.al., 2004).

Cr pollution mainly comes from anthropogenic activities like electroplating, tanning, metal processing and printing of circuit board (Trejo-Valdez et al., 2019). Electroplating of chromium on other metal for wear resistance and decorative purpose. Chromium are well-known for their variety in coloration which leads to their widely used in pigmentation and dyes (Verger et al., 2018). Also, as reported by Lunk, 2015, Cr(III) mostly used in tanning of leather especially chromium alum,  $KCr(SO_4)_2 \cdot 12H_2O$  which then ended up in soil or water. This indicates that there is a highly alarming level of chromium pollution in our marine environment. It has gradually grown to be a serious problem that endangers the biodiversity of our natural world. Our marine organisms, particularly birds and mammals, could go extinct if the levels of chromium in our marine environment consistently and considerably exceed allowed values. This

eventually has an impact on the food chain in nature, which affects all organisms, including humans, who eat these marine animals every day.

#### **2.4 Cadmium and chromium toxicity**

Cadmium is highly biopersistent, yet it has little toxicological effects, and once absorbed, it stays in the body for many years. The kidneys, lungs, and bones are the main targets of cadmium toxicity. This metal is also recognized as carcinogen that can harm kidney, lungs, pancreas and prostate (Azeh et al., 2019). Humans exposure to cadmium can be due to consumption of certain shellfish and vegetables. Concern regarding the use sewage sludge (Cd-rich biosolids) to soils to increase the production number of food crops which eventually cause cadmium to travel into human body and affect several enzymes. The kidney damage that leads to proteinuria is thought to be caused by Cd interfering with enzymes involved in protein reabsorption in kidney tubules (Manahan, 2003). The intake of cadmium by people in Jintsu River valley, near Fuchu Japan were experiencing itai-itai disease, which means ouch-ouch in Japanese. It is sort of bone disease affiliated with kidney malfunction. Cadmium poisoning in the Jintsu River Valley was blamed on irrigated rice polluted by a Pb, Zn, and Cd mine upstream. Chronic accumulation in the kidneys, which leads to renal impairment, is the most serious threat to human health. Cd enters the body mostly from food consumption and tobacco smoking (Manahan, 2003).

Chromium is a class-one carcinogen element. Although chromium has few oxidation states, the toxicity level of different oxidation states is far way difference between them where Cr(III) is a non-toxic state while Cr(VI) is a strong oxidizing agent with high toxicity and carcinogenic potential to living organisms even in small intake quantity (Ma et al., 2018). The intake of Cr(VI) in drinking water that exceed

the limitation of 0.05ppm will cause severe effects on human health such as organ damage especially lung and liver. According to Mahiya et al., 2014, intake of Cr(VI) through inhalation increase the potential of getting lung cancer. Electroplating worker are easily exposed to Cr(VI) which can caused DNA damage associated with the level of chromium in erythrocytes (biomarker) for Cr(VI) (Lunk, 2015). The level of chromium in erythrocytes, a biomarker for Cr(VI), was linked to this damage (Lunk, 2015). Therefore, those who work in the electroplating sector and even the wood preservative industry are exposed to extremely high levels of industrial pollution.

## **2.5 Methods to remove Cd(II) and Cr(VI)**

### **2.5.1 Adsorption**

In order to remove heavy metal such as cadmium by adsorption technique, there are lots of different type of adsorbents need to be produced. Adsorbents include materials that produce activated carbon which are from industrial waste, biomass, organic mass and ect. Based on Lewinsky (2007), have been studied that low cost material for instance clay, chitin, lignin and seaweed can be used as adsorbents for heavy metal removal and showed good adsorption capacities as well as plant waste include rice husks, fruit waste, spent grain and weed (Wan Ngah & Hanafiah, 2008). Naiya et al., states that the adsorption of  $Cd^{2+}$  and  $Pb^{2+}$  on activated alumina and found that it was a suitable adsorbent in the wastewater treatment process.

Moreover,  $TiO_2$  serves as both an adsorbent and a catalyst in photocatalytic processes for heavy metal removal. A negatively charged  $TiO_2$  surface with pH above 6.9 gives a better  $Cd^{2+}$  adsorption onto  $TiO_2$  surface while pH less than 3 gives better adsorption for Cr(VI). The removal process involves suspending the adsorbent into an aqueous solution that contains chromium, where the adsorbent will absorb the Cr(VI)

and subsequently reduce it to Cr(III) . One of the most often utilised adsorbents for the elimination of Cr(VI) is activated carbon. The higher concentration of activated carbon, the higher removal rate of Cr(VI) but decrease in absorption capacity (Yang et al., 2018).

For a greater adsorption efficiency, higher concentration of adsorbent is significant as surface area available for adsorption is also higher (Athapaththu, 2013). Contact time also play the role in order to achieve “adsorption equilibrium” phase. The longer the contact time between adsorbate and adsorbent, the more adsorbate will be adsorbed onto the surface. However, when the adsorbent surface continues to saturate with the adsorbate, the rate slows until the adsorbent and adsorbate achieve equilibrium. Usually, adsorption rate at the beginning of the process is faster. Also, it is imperative to increase the surface area of adsorbent to evade un-adsorbed particles which results in low adsorption efficiency (Athapaththu, 2013).

### **2.5.2 Photocatalysis**

Based on Bhattacharrya, 2002 described that photocatalysis is a combination of catalysis and photochemistry, suggesting that both light and catalysis are necessary to carry out a chemical reaction. In photocatalyst, a reaction can be accelerated with the aid of catalyst. Some opinion on the use of photocatalysis stated by Nguyen, 2006 are the low cost process, ability to use solar light, ability to conduct process in different environment and medium. Nevertheless, photocatalysis has its own limitation where the solution need to partly transparent to allow absorption of light intensity.

Compared to conventional removal techniques such as ion exchange and membrane separation have some drawbacks where metal ions will be merely removed from the solution but remain in their toxic form. Cd(II) and Cr(VI) able to be removed

by adsorption onto  $\text{TiO}_2$  surface. While in photocatalysis process,  $\text{Cd(II)}$  and  $\text{Cr(VI)}$  are reduced to its less toxic form which is  $\text{Cd(0)}$  and  $\text{Cr(III)}$ . Hence, As a result, heavy metal removal via adsorption and photocatalysis allows for the removal and recovery of dissolved metal ions from wastewater, as well as the reduction of their valence to pure or zero.

## **2.6 Photocatalysis removal of $\text{Cd(II)}$ and $\text{Cr(VI)}$ reduction by $\text{TiO}_2$**

Semiconductor has a valence and a conduction band where they are separated by a region free of energy levels which is called band gap energy. When solar light struck the semiconductor, it will absorb the energy greater than its band gap resulting in transfer of electron from valence band onto the conduction band. Hence, generate a hole in valence band. These electrons and holes separate and move to the  $\text{TiO}_2$  surface, where they participate in oxidation and reduction reactions. The holes in the valence band will be utilised in an oxidation reaction, while the electrons in the conduction band will be used in a redox reaction with the metal ions adsorbed on the surface of the semiconductor. In addition, if there is no electron acceptor or electron donor in the solution, the electron-hole pair can recombine (Prairie et al., 1993).

In order to stop recombination of electron-hole pair, trapping either photogenerated electrons or photogenerated holes should be done. Recombining will evade oxidation and reduction reactions which are needed for degradation of pollutants (Fox & Dullay, 1993). Holes at the valence band react with water to produce hydroxyl radicals, then hydroxyl radicals oxidized dissolved organic compound and convert them to carbon dioxide, water and inorganic product. While, the electron react with dissolved oxygen to form hydroxyl radicals too (Nguyen, 2006). Moreover, the formation of superoxide, dissolved metal ions able to be reduced by electrons. Since

the reduction of metal ions which is  $\text{Cd}^{2+}$  to its valence band is the main point to be focused on, hence it is important to prevent electron-hole recombination so that redox reaction between  $\text{Cd}^{2+}$  and electrons occurred (Chowdhury, 2012). Figure 2.1 shows photocatalysis mechanism for  $\text{Cd}^{2+}/\text{TiO}_2$  system.

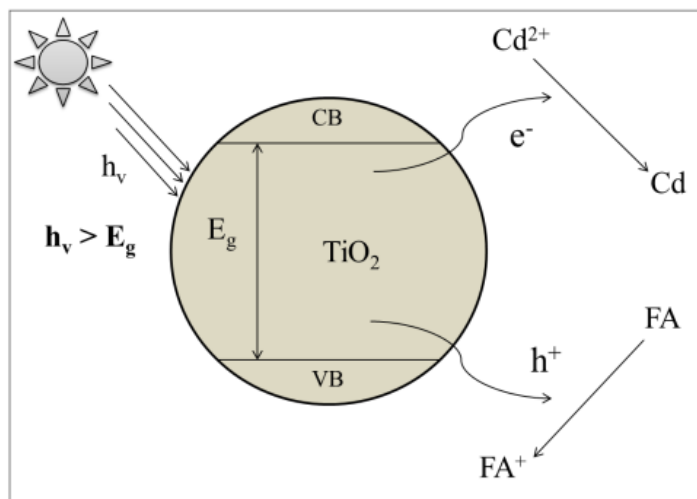
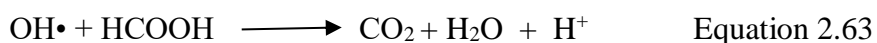


Figure 2.1 Schematic diagram of photocatalysis mechanism for  $\text{Cd}^{2+}/\text{TiO}_2$  system

Based on Athapaththu, 2013, the removals of metals involves 2 steps which are physical adsorption of metal ions onto the surface of the semiconductor photocatalyst and photo reduction of these metal ions from a higher oxidation state to lower oxidation state due to the activation of the semiconductor catalyst. The reaction in semiconductor photocatalysis are as follows:-



The first reaction illustrates the generation of electron-hole pairs when  $\text{TiO}_2$  is exposed to UV radiation. Upon the separation of electron-hole pairs, the combination of holes with water to create hydroxyl radicals as shown in second reaction above.

(Chowdhury, 2012; Nguyen, 2006; Bhattacharyya, 2002) explained that hydroxyl radicals oxidize dissolved organic compounds and convert them to carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O) and other inorganic products. Metal ions (Cd<sup>2+</sup>) use photo-generated electrons in the conduction band to get reduced to Cd<sup>0</sup> (a non-toxic form of cadmium) based on forth reaction.

At pH 7, the Cd(II)/Cd(0) standard redox potential is -0.403V barely below the TiO<sub>2</sub> conduction band of -0.240V, result in modest driving force for photocatalytic reduction (Ruvarac et al., 2005). Hence, hole scavenger such as methanol and formic acid needed to initiate photoreduction process also in suppressing charge carrier recombination and producing secondary reducing hydroxyl and carboxyl radicals (Nguyen at al., 2003).

Table 2.3 Summary of studies of photocatalyst reduction of Cd(II) on TiO<sub>2</sub>

References	Photocatalyst	Pollutants	pH	Light source	Percent removal(%)
Zha et al., 2014	TiO <sub>2</sub> particles	Cd(II)	5-6	Visible light	-
Allen et.al, 1999	TiO <sub>2</sub> suspensions	Cd(II)-EDTA	2.5	UV light	-
Fatehizadeh et al., 2014	TiO <sub>2</sub> (Degussa P25)	Cd	11	UV light	99.8
Nguyen et al., 2003	TiO <sub>2</sub> (Degussa P25)	Cd	7	UV light	60



Athapaththu, 2013	TiO <sub>2</sub> suspensions	Cd(II)	7	UV light	86.86
----------------------	---------------------------------	--------	---	----------	-------

There are a lot of studies done on Cr(VI) removal by photocatalytic reaction with TiO<sub>2</sub> but there are not many work reported the use of TiO<sub>2</sub> nanowires and nanotubes. Cheng et al., 2017 reported, the removal efficiency synthesized by TiO<sub>2</sub> nanocrystal under UV lamp for 120 min is better than P25 TiO<sub>2</sub>. Removal of Cr(VI) by irradiating the tungsten-doped TiO<sub>2</sub> sample with white light shows better removal percentage than undoped- TiO<sub>2</sub> (Trejo-Valdez et al., 2019). Another work done by Yin et al., 2018, the reduction of Cr(VI) by Cu- TiO<sub>2</sub> reached maximum at pH 5, under UV-A irradiation without any hole scavenger.

Cr(VI) can be in wastewater in form of HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>CrO<sub>4</sub> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and mainly depends on pH of the solution (Ku and Jung, 2001). Adsorption of Cr(VI) can be influenced by pH of the solution. H<sub>2</sub>CrO<sub>4</sub> exist at pH less than 2.0. Positive charge on the surface of the TiO<sub>2</sub> results to a weaker Cr(VI) adsorption. Hence, the degradation rate of Cr(VI) decreases. HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> exist at pH of 2.0 to 4.0. This makes concentration of the anion increases, leading to better adsorption on the catalyst surface and increases the degradation rate. At pH above 4.0, the surface charge of TiO<sub>2</sub> decreases, thereby reducing the adsorption of Cr(VI) and slowing down the photocatalytic reaction. Therefore, acidic solution of Cr(VI) which is pH 2 is suitable for photocatalysis process to occur.

Table 2.4 Summary of studies of photocatalyst reduction of Cr(VI) on TiO<sub>2</sub>

References	Photocatalyst	Pollutants	pH	Light source	Percentage removal(%)
Wu et.al, 2017	TiO <sub>2</sub> thin film	Cr(VI)	2	300W Xe-lamp	99.5
Li et al., 2014	TiO <sub>2</sub> doped with tungsten	Cr(VI)	4	White lamp	100
Chen et al., 2017	TiO <sub>2</sub> nanocrystals P25 Degussa	Cr(VI)	2.7	UV light	100 12
Liu et al., 2014	TNTs	Cr(VI)	3	UV light	97.9
Tsai et al., 2011	TiO <sub>2</sub> P25 Degussa	Cr(VI)	3	UV light	100
Cheng et al., 2015	TiO <sub>2</sub> P90	Cr(VI)	3	UV light	100
Mu et al., 2010	TiO <sub>2</sub> NW	Cr(VI)	2.5	UV light	75
Yang et al., 2015	TiO <sub>2</sub> NW	Cr(VI)	13	UV light	100
Yin at al., 2003	TiO <sub>2</sub> doped with copper	Cr(VI)	5	UV light	90

## 2.7 Nanowires

Nanomaterials are materials with any of the external dimension or internal structure or surface structure in nanoscale which is less than 100nm. Fabricated nanomaterials in this study is focussed on formation of nanowires. Nanowires falls under category one-dimensional (1-D) nanomaterial along with nanorods and nanotubes where one of the dimension is in nanoscale while two other dimensions are in microscale, more than 100nm. The reason of using nanowire is because in photocatalytic reduction of Cd(II) and Cr(VI), the electron excited by the photon and jumping to conduction band will recombine quickly as electron hole pair. Hole scavenging with organic compounds is one of the method to prohibit this recombination. Another alternative is to decrease the path of electron travels within the materials. This can be achieved by creating the material with nanostructure which can decrease the length for the electrons need to cover before they can be transferred out. In order to decrease electron travel path, one dimensional nanostructured metal oxide semiconductor is proposed in this work. The nanowires will provide direct travel path for electrons in the excited state to move towards their active site, preventing the recombination. This is due to a dense network of nanowires can offer direct connectivity of electron movements and also high surface area (Othman et al., 2014). Nanowires exists for numerous applications such as in electronic devices like logic gates, junction diodes and transistors. Also, metallic nanowires can be used to create a thermoelectric cooling system. The physical characteristic of nanowires are dependent on the structure of nanowires, diameter dependent band gap and carrier density of states. Nanowires can be manufactured by suspension and deposition.