



Ain Shams University



Faculty of Science

# **Removal of Metal ions from Industrial Wastewater by photocatalysis**

## **A DISSERTATION**

Presented to  
Chemistry Department  
Faculty of Science  
Ain Shams University

**By**

**Shimaa Mohamed Abdel Moniem Mohamed**

Water Pollution Department  
National Research Centre  
*B.Sc.(2004); M. Sc.(2010) (Cairo University)*

**For**

The Degree of  
Doctor of Philosophy in *Science, PhD*  
(*Chemistry*)

**2017**





Ain Shams University



Faculty of Science

# **Removal of Metal ions from Industrial Wastewater by photocatalysis**

## **A Thesis**

Submitted By

**Shimaa Mohamed Abdel Moniem Mohamed**

Water Pollution Department

National Research Centre

*B.Sc.(2004); M. Sc.(2010) (Cairo University)*

## **PhD Thesis**

Under the Supervision of

**Prof. Dr. Mohamed F. El-Shahat**

Prof. of Inorganic and Analytical Chemistry. Chemistry Department

Faculty of Science Ain Shams University

**Prof. Dr. Azza M. Ashmawy**

Professor of wastewater treatment technology Water Pollution Department

National Research Centre

**Prof. Dr. Hanan S. Abdel Rahman**

Professor of wastewater treatment technology Water Pollution Department

National Research Centre

**Prof. Dr. Tarek A. Gad-Allah**

Professor of wastewater treatment technology Water Pollution Department

National Research Centre

Chemistry Department

Faculty of Science

Ain Shams University

2017





Ain Shams University



Faculty of Science

# **Removal of Metal ions from Industrial Wastewater by photocatalysis**

**A Thesis**

Submitted By

**Shimaa Mohamed Abdel Moniem Mohamed**

For the degree of  
Doctor of Philosophy in *Science, PhD*  
(Inorganic Chemistry)

Thesis supervisors

Signature

**Prof. Dr. Mohamed Fathy El-Shahat**

Prof. of Analytical and Inorganic Chemistry.

Faculty of Science, Ain Shams University

**Prof. Dr. Azza M. Ashmawy**

Professor of wastewater treatment technology

Water Pollution Department- National Research Centre

**Prof. Dr. Hanan S. Abdel Rahman**

Professor of wastewater treatment technology

Water Pollution Department- National Research Centre

**Prof. Dr. Tarek A. Gad-Allah**

Professor of wastewater treatment technology

Water Pollution Department National Research Centre

**Prof. Dr. Ibrahim H.A. Badr**

**Head of Chemistry Department  
Faculty of Science, Ain Shams University**



## *ACKNOWLEDGEMENTS*

My great thanks to **ALLAH** for all HIS gifts.

Acknowledgement is due to **Ain-Shams University** and **National research centre** for their support in carrying out this research.

Firstly I wish to express my deep feeling of gratitude to **Professor Dr. Mohamed Fathi El-Shahat**, Professor of Inorganic and Analytical Chemistry, Faculty of Science, Ain-Shams University, for his sponsorship, encouragement, and continuous support.

It is my pleasant duty to assure my sincere appreciation, my deepest thanks and gratitude to **Professor Dr. Azza Mohamed Abdel Moniem Ashmawy**, Professor of wastewater treatment technology, Water Pollution Research Department, National Research Centre, for suggesting the topic of this study, her kind supervision, valuable assistance, valuable advice, guidance and suggestions through these studies.

My sincere appreciation, deepest thanks and gratitude to **Professor Dr. Hanan Sayed Abdel-Rahman**, Professor of Wastewater Treatment technology, Water Pollution Research Department, National Research Centre, from whom I received the most important support during this study.

My sincere thanks also go to **Assoc. Professor Dr. Tarek Abdel shafi Gad-Allah**, who also gives me valuable advises on my study and research. Studying and working with him is a pleasure experience.

I would like to express my great thanks to the staff members of the Water Pollution Research Department of the National Research Centre (NRC), Egypt.

Last but not least, I would like to thank with all my heart my dear parents, my lovable sisters, their families, my truehearted husband **Dr. Mohamed Eid Ali**, my son "**Ali**", and my daughter "**Roaa**" for their spiritual support and continuous encouragement. I owe deep gratitude to my parents for educating me and for their endless love and understanding.

*SHIMAA MOHAMED*

*ABDEL MONTEM*





## Abbreviations

<b>A</b>	Acceptor
<b>APHA</b>	American Public Health Association
<b>ASTM</b>	American Society for Testing and Materials
<b>BET</b>	Brunauer-Emmett- Teller
<b>cb</b>	Conduction Band
<b>COD</b>	Chemical Oxygen Demand
<b>D</b>	Donor
<b>e<sup>-</sup></b>	electron
<b>E<sub>g</sub></b>	Band gap Energy
<b>EPA</b>	Environmental Protection Agency
<b>FTIR</b>	Fourier Transform Infrared spectroscopy
<b>h<sup>+</sup></b>	hole
<b>HM</b>	Heavy Metals
<b>ICSD</b>	Inorganic Crystal Structure Database
<b>JCPDS</b>	Joint Committee on Powder Diffraction Standards
<b>NIST</b>	National Institute of Standards and Technology
<b>pH<sub>pzc</sub></b>	Point of Zero Charge
<b>SC</b>	Semiconductor
<b>TEM</b>	Transmission Electron Microscopy
<b>TP</b>	Total Phosphorous
<b>UV</b>	Ultraviolet
<b>UV-vis</b>	UV - visible light
<b>vb</b>	Valance Band
<b>V<sub>fb</sub></b>	The flat band potential
<b>XRD</b>	X-ray Diffraction (XRD)



## ABSTRACT

**Name:** Shimaa Mohamed Abdel Moniem Mohamed

**Title:** Removal of Metal ions from Industrial Wastewater by photocatalysis

**Degree:** Doctor of Philosophy (Ph.D.)

Removal of metal ions from industrial wastewater by photocatalysis using simulated sun light as a source of green energy are the main aim of research study. It involves detoxification of metal ions in order to reduce their contamination into the environment and recovery of precious metal from industrial wastewater. Commercially available  $\text{TiO}_2$  was used in comparing with new prepared nano-structured photocatalysts such as simonkolleite- $\text{TiO}_2$  photocatalyst with different Zn contents and metal-free graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) photocatalyst. The used photocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), FT-IR, Raman and UV–Visible diffuse reflectance spectroscopy (DRS). The DRS confirmed that both the new prepared photocatalysts have narrower bandgap energy comparing with that of  $\text{TiO}_2$ . Formic acid was used as a holes scavenger in order to improve the photocatalytic reduction mechanism. Under simulated sunlight, the best efficiency of  $\text{Cr(VI)}$  photoreduction has been achieved using 1000 ppm simonkolleite- $\text{TiO}_2$  photocatalyst of 5%  $\text{Zn/TiO}_2$  weight ratio, 100 ppm  $\text{g-C}_3\text{N}_4$  photocatalyst, when pH of the medium was set at 2-2.5 comparing with only 47.3% reduction efficiency at 1500 ppm  $\text{TiO}_2$ . Furthermore, the best efficiency of  $\text{Ag}^+$  photoreduction has been achieved using 200 ppm simonkolleite- $\text{TiO}_2$  photocatalyst of 5%  $\text{Zn/TiO}_2$  weight ratio, 100 ppm  $\text{g-C}_3\text{N}_4$  photocatalyst, at pH 4, comparing with only 38.3% reduction of silver ions using  $\text{TiO}_2$  photocatalyst. Integrated management of wastewater generated from a hard chrome metal plating workshop were applied through waste minimization, maintenance of the industrial facilities led to reducing the consumption of hazardous chemicals during two shift (16h) by 83.3%, and achieving a rinse-water reduction of 99.8%. (about  $41.56 \text{ m}^3$  of water was reduced). Furthermore, implementation of solar photocatalytic reduction process for the discharged wastewater at the optimum operating reaction conditions was very effective in complete detoxification of  $\text{Cr(VI)}$  ions into  $\text{Cr(III)}$ .



# CONTENTS

	<b>Page</b>
Acknowledgment.....	i
Abbreviations.....	ii
Abstract.....	iii
List of Tables.....	viii
List of Figures.....	ix
 <b>Chapter I</b>	
<b>1. Introduction</b>	
1.1 General Introduction.....	1
1.2. The Objectives .....	6
1.3. Study Activities.....	6
1.4. Literature Review.....	8
1.4.1. The Environmental Impact of Heavy Metal ions.....	8
1.4.2. Conventional Method of Treatment for Heavy Metal ions.....	11
1.4.2.1. Chemical Precipitation.....	12
1.4.2.2. Adsorption.....	12
1.4.2.3. Ion Exchange.....	13
1.4.2.4. Electrochemical Treatments.....	13
1.4.2.5. Membrane Filtration.....	14
1.4.2.6. Photocatalytic Reduction of Heavy Metal ions.....	15
1.4.2.6.1. Photocatalytic reduction of Cr(VI) using titania based material.....	17
1.4.2.6.2. Photocatalytic reduction of Cr(VI) using non-titania based material.....	23
1.4.2.6.3. Photocatalytic reduction of Ag(I) using titania based material.....	26
1.4.2.6.4. Photocatalytic reduction of Ag(I) using non-titania based material.....	29
1.4.2.6.5. Factors affecting the rate of photocatalytic reduction process.....	30
1.4.2.6.5.1. Effect of pH.....	30
1.4.2.6.5.2. Effect of Photocatalyst dosage.....	31
1.4.2.6.5.3. Effect of the presence of hole scavenger.....	31
 <b>Chapter II</b>	
<b>2. Experimental</b>	
2.1 Materials and Reagent .....	33
2.2. Experimental Methods.....	33
2.2.1. Photocatalysts preparations.....	33
2.2.1.1. Simonkolleite-TiO <sub>2</sub> composite photocatalyst.....	33
2.2.1.2. Graphitic Carbon Nitride (g-C <sub>3</sub> N <sub>4</sub> ) photocatalyst .....	34
2.3. Characterization of Photocatalyst.....	35

	<b>Page</b>
2.4. Evaluation of photocatalytic activity.....	37
2.5. Reusability of different photocatalyst and Recovery of silver	40
2.6. Analytical Methods.....	40
2.7. Kinetic Studies.....	41
<b>Chapter III</b>	
<b>3. Results and Discussion</b>	
3.1. Titania based material for photocatalytic reduction of metals....	42
3.1. 1. Characterization of TiO <sub>2</sub> photocatalyst.....	42
3.1. 2. Photocatalytic reduction of hexavalent chromium using commercial TiO <sub>2</sub> photocatalyst.....	47
3.1. 2.1. Adsorption behavior of Cr(VI) ions on TiO <sub>2</sub> photocatalyst.....	47
3.1. 2.2. Effect of pH on photocatalytic reduction of Cr(VI) using TiO <sub>2</sub> .photocatalyst.....	48
3.1. 2.3. Effect of TiO <sub>2</sub> dose on photocatalytic reduction of Cr(VI).....	51
3.1. 2.4. Effect of hole scavenger dose on photocatalytic reduction of Cr(VI) using TiO <sub>2</sub> .photocatalyst.....	53
3.1. 2.5. Effect of hexavalent chromium concentration on photocatalytic reduction process.....	55
3.1. 2.6. Reusability of TiO <sub>2</sub> photocatalyst for photocatalytic reduction of hexavalent chromium.....	56
3.1.3. Photocatalytic reduction of silver ions using commercial TiO <sub>2</sub> photocatalyst.....	58
3.1.3.1. Adsorption behavior of Ag <sup>+</sup> ions TiO <sub>2</sub> Photocatalyst.....	58
3.1.3. 2. Effect of pH on photocatalytic reduction of silver ions using TiO <sub>2</sub> photocatalyst.....	59
3.1.3. 3. Effect of TiO <sub>2</sub> dose on photocatalytic reduction of silver ions.....	61
3.1.3. 4. Effect of hole scavenger doses on photocatalytic reduction of silver ions using TiO <sub>2</sub> .photocatalyst.....	62
3.1.3. 5. Effect of silver ion concentrations on photocatalytic reduction process.....	64
3.1.3. 6. Reusability of TiO <sub>2</sub> photocatalyst and recovery of silver ions.....	65
3.2. Titania doped material for photocatalytic reduction of metals.....	67
3.2.1. Characterization of simonkolleite-TiO <sub>2</sub> photocatalyst .....	67
3.2.2. Photocatalytic reduction of hexavalent chromium using simonkolleite-TiO <sub>2</sub> photocatalyst.....	75

	<b>Page</b>
3.2.2.1. Adsorption behavior of Cr(VI) ions on simonkolleite-TiO <sub>2</sub> photocatalyst.....	75
3.2.2.2. Effect of doping ratio on photocatalytic reduction of Cr(VI).....	76
3.2.2.3. Effect of pH on photocatalytic reduction of Cr(VI).....	77
3.2.2.4. Effect of simonkolleite-TiO <sub>2</sub> concentration on photocatalytic reduction of Cr(VI).....	80
3.2.2.5. Effect of Cr(VI):MeOH ratio on photocatalytic reduction of Cr(VI).....	82
3.2.2.6. Effect of hole scavenger type on photocatalytic reduction of Cr(VI).....	83
3.2.2.7. Reusing of simonkolleite-TiO <sub>2</sub> photocatalyst in photocatalytic reduction of hexavalent chromium.....	85
3.2.3. Photocatalytic reduction of silver ions using simonkolleite-TiO <sub>2</sub> photocatalyst.....	87
3.2.3.1. Adsorption behavior of Ag <sup>+</sup> ions on simonkolleite-TiO <sub>2</sub> Photocatalyst.....	87
3.2.3. 2. Effect of pH on photocatalytic reduction of silver ions using simonkolleite-TiO <sub>2</sub> photocatalyst.....	88
3.2.3. 3. Effect of doping ratio on photocatalytic reduction of silver ions.....	90
3.2.3.4. Effect of hole scavenger concentration on photocatalytic reduction of silver ions using simonkolleite-TiO <sub>2</sub> photocatalyst.....	93
3.2.3.5. Effect of silver ion concentrations on photocatalytic reduction process using simonkolleite-TiO <sub>2</sub> photocatalyst.....	94
3.2.3.6. Reusing of simonkolleite-TiO <sub>2</sub> photocatalyst and Recovery of silver.....	95
3.3. Non-titania based material for photocatalytic reduction of metals .....	98
3.3.1. Characterization of g-C <sub>3</sub> N <sub>4</sub> photocatalyst.....	99
3.3.2. Photocatalytic reduction of hexavalent chromium using g-C <sub>3</sub> N <sub>4</sub> photocatalyst.....	103
3.3.2. 1. Adsorption behavior of Cr(VI) ions on g-C <sub>3</sub> N <sub>4</sub> photocatalyst.....	103
3.3.2.2. Effect of pH on photocatalytic reduction of Cr(VI) using g-C <sub>3</sub> N <sub>4</sub> photocatalyst.....	104
3.3.2.3. Effect of g-C <sub>3</sub> N <sub>4</sub> photocatalyst concentration on photocatalytic reduction of Cr(VI).....	106