



REMOVAL AND RECOVERY OF SOME HEAVY METALS FROM DILUTED SOLUTIONS WHICH HAVE THE SAME RECIPES OF SIMULATED INDUSTRIALWASTEWATERS BY CEMENTATION

BY

Heba Ali Mohamed Abd El Gawad

A Thesis Submitted to the

Faculty of Engineering at Cairo University in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2017

REMOVAL AND RECOVERY OF SOME HEAVY METALS FROM DILUTED SOLUTIONS WHICH HAVE THE SAME RECIPES OF SIMULATED INDUSTRIALWASTEWATERS BY CEMENTATION

BY

Heba Ali Mohamed Abd El Gawad

A Thesis Submitted to the

Faculty of Engineering at Cairo University in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

Under the supervision of

Prof. Dr. Ahmed Nasr El Dien Mahdy Prof. Dr. Ibrahim Abd El Hamid Khattab

Prof. of Chemical Eng. Department Faculty of Engineering, Cairo University Prof. of Chemical Eng. & Pilot Plant Department National Research Centre

Prof. Dr. Osama Abd El Bary Ibrahim

Prof. Dr. Hossam El Dosoky Moselhy

Prof. of Chemical Eng. Department Faculty of Engineering, Cairo University

Prof. of Chemical Eng. Department Higher Institute of Engineering in El- Shorok City

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2017

REMOVAL AND RECOVERY OF SOME HEAVY METALS FROM DILUTED SOLUTIONS WHICH HAVE THE SAME RECIPES OF SIMULATED INDUSTRIALWASTEWATERS BY CEMENTATION

BY

Heba Ali Mohamed Abd El Gawad

A Thesis Submitted to the

Faculty of Engineering at Cairo University in Partial Fulfillment of the

Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

Approved by the Examining Committee

1. Prof. Dr. Ahmed Nasr El Dien Mahdy (Thesis main advisor)

2. Prof. Dr. Ibrahim Abd El Hamid Khattab (Advisor)

Prof. of Chemical Eng. & Pilot Plant Department National Research Centre

3. Prof. Dr. Omar El-Farouk Abd El-Salam (Internal examiner)

4. Prof. Dr. Ahmed Farid Shaban (External examiner)

Prof. of Chemical Eng. & Pilot Plant Department National Research Centre

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
2017

Engineer: Heba Ali Mohamed Abd El-Gawad

Date of Birth: 14 / 5 / 1984 **Nationality:** Egyptian

E-mail: eng_houuuba @yahoo.com

Phone: 01000506684

Address: 8 Ghoniem st. – Salah Salem - Cairo

Registration Date: 1 / 10 / 2012 **Awarding Date:** / / 2017

Degree: Doctor of Philosophy **Department:** Chemical Engineering

Supervisors:

Prof. Dr. Ahmed Nasr El Dien Mahdy

Prof. Dr. Ibrahim Abd El Hamid Khattab

Prof. of Chemical Eng. & Pilot Plant Department National Research Centre

Prof. Dr. Osama Abd El Bary Ibrahim

Prof. Dr. Hossam El Dosoky Moselhy

Prof. of Chemical Eng. Department Higher Institute of Engineering in El- Shorok City

Examiners:

Prof. Dr. Ahmed Nasr El Dien Mahdy (Thesis main advisor)

Prof. Dr. Ibrahim Abd El Hamid Khattab (Advisor)

Prof. Dr.Omar El-Farouk Abd El-Salam(Internal examiner)Prof. Dr.Ahmed Farid Shaban(External examiner)

Prof. of Chemical Eng. & Pilot Plant Department

National Research Centre

Title of Thesis:

REMOVAL AND RECOVERY OF SOME HEAVY METALS FROM DILUTED SOLUTIONS WHICH HAVE THE SAME RECIPES OF SIMULATED INDUTRIAL WASTEWATERS BY CEMENTATION

Key Words: Heavy metals; Cementation kinetics; Silver removal/recovery; Copper and Lead removal/recovery; Simultaneous removal.

Summary:

The process of copper, lead and silver ions cementation from mono-metallic, bi-metallic and tri-metallic solutions utilizing simple-agitated reactor is reported in this thesis. The results of investigating the diverse parameters affecting the cementation process, such as initial ions concentration, initial pH, rotational speed, reaction temperature and mass of sacrificial metal are demonstrated and discussed. In this dissertation, as well, a special concern was directed to the kinetics of cementation reaction with a view to demonstrate the effect of each parameter on the apparent rate constant of the cementation reaction. Ultimately, a correlation for predicting the rate constant was obtained by utilizing statistical regression technique.



Acknowledgments

I am grateful to numerous local and global "peers" who have contributed towards shaping this thesis.

At the outset, I would like to express my sincere gratitude to my advisor Professor Dr. **Ibrahim khattab** for the continuous support of my Ph.D study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D study.

Besides my advisor, I would also like to thank my thesis committee members: Professor Dr. Ahmed Nasser El Dien, Professor Dr. Osama Abd El Bary and Professor Dr. Hossam El Dosoky for their brilliant comments, suggestions and encouragement, but also for the hard question which incented me to widen my research from various perspectives, thanks to all of them.

A special thanks to my family. Words cannot express how grateful I am to my mother and father for all of the sacrifices that have made on my behalf. Their prayer for me was what sustained me thus far. I would also like to thank all of my friends who supported me in writing, and incented me to strive towards my goal. At the end I would like express appreciation to my beloved Husband Dr. **Mostafa Hassanein.** Thank you for supporting me for everything, and especially I can't thank you enough for encouraging me throughout this experience. To my beloved daughter **Retal Mostafa Hassanein**, I would like to express my thanks for being such a good girl always cheering me up.

Table of Contents

| ACK | NOWLI | EDGMENTS | I |
|-------------|---------|--|------------|
| TABI | LE OF (| CONTENTS | . II |
| LIST | OF TA | BLES | . V |
| LIST | OF FIG | GURES | VI |
| NOM | ENCLA | ATURE | IX |
| ABST | RACT | | . X |
| CHAI | PTER 1 | : INTRODUCTION | 1 |
| 1.1 | | Y METALS | |
| 1.2 | MAJO | UR SOURCES AND TOXICITIES OF HEAVY METALS | 2 |
| 1.3 | TREA' | TMENT METHODS FOR REMOVAL OF HEAVY METALS | 3 |
| 1.4 | THE A | AIM AND OBJECTIVES | 5 |
| 1.5 | | IS OUTLINE | |
| CHAI | | : LITERATURE REVIEW | |
| 2.1 | | NTATION FUNDAMENTAL CONCEPT | |
| 2.2 | | NTATION REACTIONS | 7 |
| 2.3 | | NTAGES AND DISADVANTAGES OF CEMENTATION | |
| | | ESS | |
| 2. | | ADVANTAGES | |
| 2. | | DISADVANTAGES | |
| 2.4 | | MODYNAMIC OFCEMENTATION | |
| 2.5 | | S EVOLVED IN A CEMENTATION REACTION | |
| 2.6 | | PETITION REACTIONS | |
| 2. | 6.1 | REACTIONS AT CATHOD | |
| | 6.2 | REACTIONS AT ANOD | |
| | | ORS AFFECTING CEMENTATION RATE | |
| 2.8 | CEME | NTATION OF COPPER | |
| | 8.1 | EFFECT OF pH _o | |
| | | EFFECT OF C _o | |
| | .8.3 | EFFECT OF FLOW RATE | |
| 2. | .8.4 | EFFECT OF TEMPERATURE | |
| 2. | .8.5 | EFFECT OF SACRIFICIAL METAL | |
| | 8.6 | EFFECT OFTHE MASS/AREA OF SACRIFICIAL METAL | |
| 2.9 | CEME | INTATION OF LEAD | |
| | .9.1 | EFFECT OF pH _o | |
| | .9.2 | EFFECT OF C _o | |
| | .9.3 | EFFECT OF FLOW RATE | |
| | 9.4 | EFFECT OF TEMPERATURE | |
| | .9.5 | EFFECT OF SACRIFICIAL METAL | |
| | | INTATION OF SILVER | |
| | | VLEDGE GAP AND CURRENT RESEARCH CONTRIBUTION | |
| CHAI | PTER 3 | : METHODOLOGY | 35 |

| 3.1 | EXPER | RIMENTAL SET-UP | 35 |
|-----|--------|---|-----------|
| 3.2 | MATE | RIALS | 35 |
| 3.3 | EXPER | RIMENTAL PROCEDURE | 36 |
| 3. | 3.1 | REMOVAL FROM MONO-METALLIC SOLUTIONS | 36 |
| | 3.3.1. | 1 REMOVAL OF COPPER IONS | 36 |
| | 3.3.1. | | |
| | 3.3.1. | REMOVAL OF SILVER IONS | 37 |
| 3. | 3.2 | REMOVAL FROM BI-METALLIC SOLUTIONS | 37 |
| | 3.3.2. | 6 | |
| | 3.3.2. | \mathcal{C} | |
| | 3.3.2. | | |
| 3. | | REMOVAL FROM TRI-METALLIC SOLUTIONS | |
| 3.4 | | URING EQUIPMENTS | |
| | | pH METER | |
| | | MEASUREMENT OF CONCENTRATIONS | |
| | | EDX | |
| | | RESULTS AND DISCUSSION | |
| 4.1 | | VAL/RECOVERY OF Cu, Pb AND Ag FROM MONO-METALLIC | |
| _ | | TIO | |
| 4. | | REMOVAL OF Cu ²⁺ FROM MONO-METALLIC SOLUTION | |
| | 4.1.1. | 1 | |
| | 4.1.1. | | |
| | 4.1.1. | | |
| | 4.1.1. | | |
| | 4.1.1. | | |
| | 4.1.1. | | |
| | 4.1.1. | | |
| 4. | | REMOVAL OF Pb ²⁺ FROM MONO-METALLIC SOLUTION | |
| | 4.1.2. | 1 | |
| | 4.1.2. | | |
| | 4.1.2. | | |
| | 4.1.2. | | |
| | 4.1.2. | | |
| | 4.1.2. | | |
| 4 | 4.1.2. | | |
| 4. | | REMOVAL OF Ag ⁺ FROM MONO-METALLIC SOLUTION | |
| | 4.1.3. | 1 | |
| | 4.1.3. | ϵ | |
| | 4.1.3. | | |
| | 4.1.3. | | |
| | 4.1.3. | | |
| | 4.1.3. | | |
| | 4.1.3. | 7 EDX ANALYSIS OF DEPOSITED SILVER | 54 |

| 4.1.3. | 8 EFFECT OF MASS OF IRON SHEET 5 | 54 |
|--------|---|---|
| REMO | VAL/RECOVERY Ag, Cu AND Pb FROM BI-METALLIC | |
| SOLU | ΓΙΟΝS5 | 55 |
| .2.1 | REMOVAL OF Ag & Cu FROM BI-METALLIC SOLUTION 5 | 5 |
| .2.2 | REMOVAL OF Ag & Pb FROM BI-METALLIC SOLUTION 5 | 58 |
| .2.3 | REMOVAL OF Cu & Pb FROM BI-METALLIC SOLUTION 6 | 60 |
| REMO | VAL/RECOVERY Ag, Cu AND Pb FROM TRI-METALLIC | |
| | | |
| PTER 5 | : CEMENTATION KINETICS | 53 |
| | | |
| META | | |
| .1.1 | | |
| .1.2 | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| .2.2 | | |
| | | |
| .2.3 | | |
| | | |
| | _ | |
| | | |
| | | |
| | ** | |
| | | |
| | ** | |
| | | |
| | | |
| | | |
| | | |
| RECO' | VEKY OF SILVEK FROM FILMS | 57 27 |
| | | |
| | | |
| | | 92 |
| | REMO SOLUTION 2.1 2.2 2.3 REMO SOLUTION PTER 5 CEME META 1.1 1.2 1.3 CEME SOLUTION 2.1 2.2 2.3 CEME SOLUTION PTER 6 CORR ONTO | REMOVAL/RECOVERY Ag, Cu AND Pb FROM BI-METALLIC SOLUTIONS |

List of Tables

| Table 1.1: Major sources and toxic effects of some heavy metals | 2 |
|---|----|
| Table 1.2: The Maximum Contamination Limit standards | 3 |
| Table 1.3: Advantages and disadvantages of different treatment methods | 4 |
| Table 2.1: Cementation of copper | 12 |
| Table 2.2: Cementation of lead | 19 |
| Table 2.3: Cementation of silver | 25 |
| Table 2.4: Knowledge gap and contribution of thesis | 29 |
| Table 3.1: Chemicals used in the experimental work | 36 |
| Table 3.2: Studied parameters and their ranges for copper removal | |
| Table 3.3: Studied parameters and their ranges for lead removal | |
| Table 3.4: Studied parameters and their ranges for the removal of silver | |
| Table 4.1: Standard Reduction Potentials in Aqueous Solution at 25°C | 40 |
| Table 4.2: Remained Zn and concentration of Cu^{2+} in solution at $pH_0 = 1$ | 41 |
| Table 4.3: Remained Zn and concentration of Cu^{2+} in solution at $pH_0 = 5.22$ | 41 |
| Table 4.4: Composition of deposited copper | 45 |
| Table 4.5: Composition of deposited lead | |
| Table 4.6: Composition of deposited silver | 54 |
| Table 6.1: The apparent rate constants and their correlation coefficients | 83 |
| Table 6.2: Value and p-value of each term coefficient | 83 |
| Table 6.3: Value and p-value of each term coefficient | 84 |
| Table 6.4: Value and p-value of each term coefficient | |
| Table 7.1: Composition of deposited silver | 89 |
| | |