شبكة المعلومات الجامعية

بسم اللّه الرحمن الرحيم

شبكة المعلومات الجامعية

التوثيق الالكتروني والميكروفيلم

شبكة المعلومات الجامعية

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

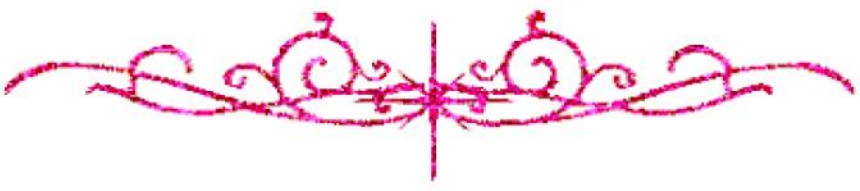
نقسم باللّه العظيم أن المادة التي تم توثيقها وتسجيلها علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات

يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار

شبكة المعلومات الجامعية

بعض الوثائق الأصلية تالفة



بالرسالة صفحات
لم ترد بالأصل

OPTIMAL REMOVAL OF NITRATE AND PHOSPHATE IONS FROM AQUEOUS SOLUTIONS USING SYNTHESIZED ACID ACTIVATED RICE STRAW NANO-ADSORBENT AND INDUSTRIAL WASTE FROM ELECTRIC ARC FURNACE

By

Dalia Amer Ahmed Ali

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
Year 2020

OPTIMAL REMOVAL OF NITRATE AND PHOSPHATE IONS FROM AQUEOUS SOLUTIONS USING SYNTHESIZED ACID ACTIVATED RICE STRAW NANO-ADSORBENT AND INDUSTRIAL WASTE FROM ELECTRIC ARC FURNACE

By
Dalia Amer Ahmed Ali

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. Nagwa Mahmoud Mohamed Al-Mansi

Professor of Chemical Engineering
Chemical Engineering
Faculty of Engineering, Cairo University

Prof. Dr. Mohamed Amin El-Shahir Sadek

Professor of Chemical Engineering
Chemical Engineering
Faculty of Engineering, The British University in Egypt (BUE)

Dr. Ahmad Wafiq Aboelnasr

Doctor
Chemical Engineering
Faculty of Engineering, Cairo University

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
Year 2020

OPTIMAL REMOVAL OF NITRATE AND PHOSPHATE IONS FROM AQUEOUS SOLUTIONS USING SYNTHESIZED ACID ACTIVATED RICE STRAW NANO-ADSORBENT AND INDUSTRIAL WASTE FROM ELECTRIC ARC FURNACE

By

Dalia Amer Ahmed Ali

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

_____

Prof. Dr. Nagwa Mahmoud Al-Mansi Thesis Main Advisor

_____

Prof. Dr. Mohamed Hanafy Mahmoud Internal Examiner

_____

Prof. Dr. Mostafa Abdel Salam Radwan External Examiner

- Professor in Chemical Engineering at The British University in Egypt (BUE)

FACULTY OF ENGINEERING, CAIRO UNIVERSITY
GIZA, EGYPT
Year 2020

Engineer's Name: Dalia Amer Ahmed Ali
Date of Birth: 02/07/1989
Nationality: Egyptian
E-mail: Dalia.Amer@bue.edu.eg
Phone: 01000415745
Address: 2A- Bani Amer street - Giza

Registration Date: 01/10/2016
Awarding Date: …./…./2020
Degree: Doctor of Philosophy
Department: Chemical Engineering

Supervisors:

Prof. Nagwa Mahmoud Mohamed Al-Mansi
Prof. Mohamed Amin El-Shahir Sadek
Head of Chemical Engineering Department at (BUE)
Dr. Ahamd Wafiq Aboelnasr

Examiners:

Prof. Nagwa Mahmoud Al-Mansi (Thesis main advisor)
Prof. Mohamed Hanafy Mahmoud (Internal examiner)
Prof. Mostafa Abdel Salam Radwan (External examiner)
Professor in Chemical Engineering at The British University in Egypt

Title of Thesis:

Optimal Removal of Nitrate and Phosphate Ions from Aqueous Solutions Using Synthesized Acid Activated Rice Straw Nano-Adsorbent and Industrial Waste From Electric ARC Furnace

Key Words: (must be 5 words only)
Nitrate ; Phosphate; Adsorption; Optimization; Rice straw

Summary: (not more than 150 word and the summary must be in the same page)

The removal of nitrate and phosphate from wastewater has a major concern nowadays. Excessive intake of nitrates and phosphate by humans in drinking water and food can induce methemoglobinemia and stomach cancer. Adsorption process using nano adsorbents can be used for removal of nutrients from aqueous solutions. Acid activated rice straw supported nano zero valent iron is used for nitrate ion removal from an aqueous solution. Also, an industrial waste from electric arc furnace is used for simultaneous removal of nitrate and phosphate from an aqueous solution.

Disclaimer

I hereby declare that this thesis is my own original work and that no part of it has been submitted for a degree qualification at any other university or institute.

I further declare that I have appropriately acknowledged all sources used and have cited them in the references section.

Name: Dalia Amer Ahmed Ali Date: ../../…

Signature:

Dedication

I would like to dedicate this work to my parents and my husband for their continuous guidance, encouragement, prayers, love and support throughout my life.

Acknowledgments

I would like, first to express my deepest appreciation for the technical guidance and support given by my research advisors, Prof. Nagwa Mahmoud Al-Mansi, Prof. Mohamed Amin El-Shahir and Dr. Ahmad Wafiq. Also, I would like to thank Prof. Mostafa Radwan and Prof. Mohamed Hanafy for being my examiners. Finally, I would like to thank the Nano Technology Research Center (NTRC) in the British University in Egypt (BUE) for their funding support for the BUE staff to complete the required analysis in my PhD thesis.

Table of Contents

DISCLAIMER ..... **I**

DEDICATION ..... **II**

ACKNOWLEDGMENTS ..... **III**

TABLE OF CONTENTS ..... **IV**

LIST OF TABLES ..... **VIII**

LIST OF FIGURES ..... **VIII**

NOMENCLATURE ..... **XI**

ABSTRACT ..... **XIII**

CHAPTER 1 : INTRODUCTION **1**

1.1. NITRATE AND PHOSPHATE IMPACT ON HEALTH AND ENVIRONMENT 1

1.2. AVERAGE REPORTED NITRATE AND PHOSPHATE CONCENTRATIONS IN THE INDUSTRIAL WASTEWATER AND DOMESTIC WASTEWATER IN EGYPT 2

1.2.1. Industrial Wastewater 2

1.2.2. Domestic Wastewater and Drinking Water in Giza Governorate, Egypt 3

1.2.2.1. Nitrate Constituent 3

1.2.2.2. Phosphate constituent 4

1.3. ADSORPTION USING NANO-ADSORBENTS 6

1.4. AIM OF WORK 6

CHAPTER 2 : LITERATURE REVIEW **8**

2.1. THE PHOSPHOROUS CYCLE 8

2.2. THE NITROGEN CYCLE 9

2.3. WASTEWATER TREATMENT 10

2.4. TECHNOLOGIES OF NUTRIENTS REMOVAL FROM WASTEWATER 10

2.4.1. Chemical Method 10

2.4.1.1. Phosphate Removal By Chemical Precipitation 11

2.4.1.2. Nitrate Removal By Chemical Reduction 11

2.4.2. Ion Exchange 12

2.4.2.1. Removal Of Nitrate By Ion Exchange Method 12

2.4.2.2. Phosphate removal by ion exchange method 12

2.4.3. Membrane Filtration 12

2.4.4. Biological Method 13

2.4.4.1. Types Of Biological Processes 13

2.4.4.2. Biological Removal of Nitrate 15

2.4.4.3. Biological Removal of Phosphate 15

2.4.5. Adsorption 16

2.4.5.1. Adsorption Applications 16

2.4.5.2. Factors Affecting Adsorption of Nitrate and Phosphate 17

2.4.5.3. Types Of Materials Used For Adsorption Of Different Pollutants From Wastewater 18

2.4.5.3.1. Conventional Adsorbents 19

2.4.5.3.2. Non-conventional Adsorbents 20

2.4.5.4. Adsorption of Nitrate and Phosphate Using Rice straw……..23
2.4.5.4.1. Energy Valorization Process.....*23*
2.4.5.4.2. Activated Carbon Prepared from Rice Straw and $ZnCl_2$.....*23*
2.4.5.4.3. Modified carbon residue from rice straw gasification……..*24*
2.4.5.4.4. Activated Carbon from Rice Straw-Nano Zero Valent Iron (AC-nZVI) Composite…… ..*25*
2.5. NANOTECHNOLOGY.....26
2.5.1. Different Methods For Synthesis of Nano Adsorbents.....27
2.5.2. Nano Adsorption For Nitrate and Phosphate From Wastewater.....28
2.5.3. Nano-adsorbents.....29
2.5.3.1. Carbon Based Nano-adsorbents.....29
2.5.3.1.1. Carbon Nano Tubes (CNTs).....*29*
2.5.3.2. Graphene Based Nano-adsorbents…..30
2.5.3.3. Metal Based Nano-adsorbents……31
2.5.3.4. Polymeric Based Nano-adsorbents…….32
2.6. CONTACTING SYSTEMS.....32
2.7. DESORPTION OF POLLUTANTS.....33
2.8. ADSORPTION KINETICS.....34
2.9. SINGLE COMPONENT ADSORPTION ISOTHERM MODELS.....35
2.9.1. One-Parameter Isotherm.....35
2.9.1.1. Henry's Isotherm.....35
2.9.2. Two-Parameter Isotherm Models.....35
2.9.2.1. Langmuir.....35
2.9.2.2. Freundlich.....36
2.9.2.3. Halsey.....36
2.9.2.4. Dubinin-Radushkevich.....36
2.9.2.5. Brunauer-Emmett-Teller (BET).....36
2.9.3. Three-Parameter Isotherm Models.....37
2.9.3.1. Koble-Carrigan.....37
2.9.3.2. Langmuir-Freundlich.....37
2.9.4. Four-Parameter Isotherm Models.....37
2.9.4.1. Fritz-Schlunder Isotherm.....37
2.9.5. Five-Parameter Isotherm Model.....38
2.10. MULTI-COMPONENT ADSORPTION ISOTHERM MODELS.....38
2.10.1. Extended Freundlich.....38
2.10.2. Extended Langmuir.....39
2.10.3. Modified Langmuir.....39
CHAPTER 3 : EXPERIMENTAL MATERIALS AND METHODOLOGY.....40
3.1. MATERIALS.....40
3.2. EQUIPMENT USED IN BATCH ADSORPTION EXPERIMENTS AND IN THE CHARACTERIZATION OF AARS-NZVI SYNTHESIZED ADSORBENT AND FD-EAF INDUSTRIAL WASTE……..40
3.2.1. UV (Ultraviolet) Spectrophotometer.....40
3.2.2. Water Conditioning Photometer.....42
3.2.3. Vacuum Filtration unit.....44
3.2.4. Vacuum Dryer.....45
3.2.5. Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX)…… 47
3.2.6. X-Ray Diffraction (XRD).....49
3.2.7. Fourier Transformation Infrared (FTIR).....50

3.2.8. Brunauer-Emmett-Teller (BET) 52
3.2.8.1. History of BET 52
3.2.8.2. BET Assumptions 52
3.2.8.2.1. Homogeneous surface *52*
3.2.8.2.2. Limited molecular interactions *52*
3.2.8.2.3. Local equilibrium *52*
3.2.8.2.4. Kinetically limited process *52*
3.2.8.2.5. BET theory *53*
3.2.9. Zeta potential 54
3.3. SYNTHESIS OF AARS-NZVI ADSORBENT 56
3.4. FUME DUST FROM ELECTRIC ARC FURNACE (FD-EAF) INDUSTRIAL WASTE 57
3.5. BATCH EXPERIMENTS 59
3.6. PARAMETERS OF BATCH EXPERIMENTS FOR AARS-NZVI SYNTHESIZED ADSORBENT AND FD-EAF INDUSTRIAL WASTE 59
3.6.1. Initial pH of Solution 59
3.6.2. Initial Nitrate and Phosphate Ions Concentrations 59
3.6.3. Adsorbent Dose For AARS-nZVI Synthesized Adsorbent 59
3.6.4. Contact Time For AARS-nZVI Synthesized Adsorbent 60
3.6.5. Adsorbent Dose For FD-EAF Waste 60
3.6.6. Contact Time of FD-EAF Waste 61

CHAPTER 4 : RESULTS AND DISCUSSION 62

4.1. RESULTS AND DISCUSSION OF NITRATE REMOVAL FROM AN AQUEOUS SOLUTION USING AARS-NZVI SYNTHESIZED ADSORBENT 62
4.1.1. Surface Characterization of AARS-nZVI Adsorbent 62
4.1.1.1. Scanning Electron Microscopy (SEM) 62
4.1.1.2. Brunauer-Emmett-Teller (BET) 63
4.1.1.3. X-Ray Diffraction (XRD) 63
4.1.1.4. Fourier Transformation Infrared (FTIR) 66
4.1.1.5. Zeta Potential Analysis 67
4.1.2. Adsorption Kinetics Study 68
4.1.3. Adsorption Isotherm Study 70
4.1.4. Adsorption Mechanism of Nitrate ion Using AARS-nZVI Synthesized Adsorbent 71
4.1.5. Removal of Nitrate Ion from Aqueous Solutions using AARS-nZVI Synthesized Adsorbent and Other Adsorbents at Different Adsorption Conditions 72
4.1.6. Regression Model Equation Development 73
4.1.7. Model Adequacy and Checking 76
4.1.8. Effect of the Solution's pH on Nitrate Ion Reduction Using AARS-nZVI Synthesized Adsorbent 77
4.1.9. Effect of Initial Nitrate Ion Concentration on Nitrate Ion Reduction Using AARS-nZVI Synthesized Adsorbent 77
4.1.10. Effect of Adsorbent Dose on Nitrate Ion Removal Using AARS-nZVI Synthesized Adsorbent 78
4.2. RESULTS AND DISCUSSION FOR SIMULTANEOUS REMOVAL OF NITRATE AND PHOSPHATE IONS FROM AN AQUEOUS SOLUTION USING FD-EAF INDUSTRIAL WASTE 79
4.2.1. Surface Characterization 79