Ain shams university

Institute of Environmental Studies and Research

DEPOLUTION OF INDUSTERIAL WASTE WATER BY OXIDATION IN AQUEOUS SOLUTION USING SUPPORTED METAL COMPLEXES

Submitted By

RADWA MOHAMED WAGDY ABD ALLAH

B.Sc., (Chemistry), Faculty of science, Ain Shams University, 1999 Diploma in Environmental Sciences, Institute of Environmental Studies & Research, Ain Shams University, 2005

A Thesis Submitted in Partial Fulfillment
Of
The Requirement for Master Degree
In
Environmental Sciences

Department of Environmental Basic Science
Institute of Environmental Studies and Research
Ain Shams University

2017

DEPOLUTION OF INDUSTERIAL WASTE WATER BY OXIDATION IN AQUEOUS SOLUTION USING SUPPORTED METAL COMPLEXES

Submitted By

RADWA MOHAMED WAGDY ABD ALLAH

B.Sc., (Chemistry), Faculty of science, Ain Shams University, 1999 Diploma in Environmental Sciences, Institute of Environmental Studies & Research, Ain Shams University, 2005

A Thesis Submitted in Partial Fulfillment
Of
The Requirement for Master Degree
In
Environmental Sciences

APROVED BY SUPERVISORS

Prof. Dr. Salah A. Hassan

Professor of Physical Chemistry
Faculty of Science
Ain Shams University

Dr. Hamdy A.H. Sokkar

Ass. Professor of Physical
Chemistry- Faculty of Science
Ain Shams University

2017

APPROVAL SHEET

DEPOLUTION OF INDUSTRIAL WASTE WATER BY OXIDATION IN AQUEOUS SOLUTION USING SUPPORTED METAL COMPLEXES

Submitted By

RADWA MOHAMED WAGDY ABD ALLAH

B.Sc., (Chemistry), Faculty of science, Ain Shams University, 1999 Diploma in Environmental Sciences, Institute of Environmental Studis & Research, Ain Shams University, 2005

A Thesis Submitted in Partial Fulfillment
Of
The Requirement for Master Degree
In
Environmental Sciences

APROVED BY THE COMMITTEE:

Prof. Dr. Salah A. Hassan
Professor of Physical Chemistry
Faculty of Science, Ain Shams University

Prof. Dr. Mohamed M. Selim
Professor of Physical Chemistry
Department of Physical, Chemistry Laboratory of Surface Chemistry and Catalysis, National Research Center

Prof. Dr. Nadia A. Yousef
Professor of physical Chemistry
College of Girl
Ain Shams University

ACKNOWLEDGEMNT

Foremost, I would like to express my deep and sincere gratitude to ***Prof. SALAH A. HASSAN***. Professor of Physical chemistry, Faculty of Science, Ain Shams University, for suggesting the subject of this study, useful guidance, continuous supervision and his great help in the interpretation of the results.

Also, deep sense of gratitude is to Dr. Hamdy A. H. Sokkar for his careful supervision, valuable suggestions and continuous support.

Moreover, deep thanks and gratitude are also due to Dr. Radwa Abbas EL-Salamony Egyptian Petroleum Research Institute (EPRI) for the appreciated help in performing numerous measurements and valuable discussion of some application results.

I highly acknowledge the friendly atmosphere offered by my Basic Science Department at Institute of Environmental Studies and Research.

RADWA M. WAJDY

Dedication

I would like to dedicate my thesis

To

My beloved late Father and

My beloved admirable Mother

Also deep gratitude to my sister and my brother for their real support that pushed me up to achieve this work

RADWA M. WAJDY

ABSTRACT

In the present study, new composites based on local rice straw ash (RSA) were synthesized. The RSA was supplied by controlled burning of rice straw at 600^{o} C for 4 h. The synthesized composites, by incorporating titania (TiO_2, 10 – 50 wt %), copper phthalocyanine complex (CuPc, 1.0 wt %) or TiO_2 – CuPc combination, beside the pristine RSA, were pressed at (2000 psi) into disc-shaped forms. In this process, recycled polymer foam (Ps F-2000/ chloroform) was used as binder. For comparative purposes, composites of RSA-TiO_2 were also studied in powder form. Physicochemical characterization of various composites was performed adopting the XRD, N_2-physisorption, FTIR, EDX, TEM, and SEM techniques. The as-synthesized composites were successfully applied for removal of hazardous textile dyes (represented in this study by methylene blue, MB) as well as some heavy metal ions (represented by Cd, Pb and Cu), causing environmental pollution and toxic problems in industrial waste water. Different kinetic variables of the dye or the heavy metal ions removal in aqueous solutions were investigated, e.g., order, model and mechanism of reaction, effect of initial concentrations, pH, temperature, stability and reusability of the used composite.

- LIST OF TABLE I
- LIST OF FIGURE....................II

....

- AIM OF WORK VI
- PLAN OF WORK.................... VII

CHAPTER I: INTRODUCTION

1.1. General concept 1
1.2. Nature of Municipal waste -Water 2
1.3. Wastewater treatment 6
1.4. Chemical unit processes 8
(A) Chemical precipitation 8
(B) Disinfection 10
(B) Dechlorination 11
1.5. Wastewater treatment from organic substances 11
1.6. Dye pollution.................... 12
1.7. Heavy metals Pollution 17
1.7.1. Heavy metal removal.................... 20
1.7.2. Adsorption.................... 24
1.7.2.1. Low cost adsorbents Definition.................... 25
1.7.2.2. Adsorption process 25
1.7.3. Literature survey of some examples for heavy metal removal.......... 25
1.7.3.1. Removal of Chromium 25
1.7.3.2. Removal of Copper.................... 27
1.7.3.3. Removal of lead 30
1.8. Remarks on Some materials used 34
(a) Rice straw ash.................... 34
(b) Titanium dioxide and photocatalysis 36

CHAPTER II: EXPREMENTAL

2.1. Materials 39

2.2. Preparation of rice straw ash (RSA) 40
2.3. Preparation of titania (TiO_2) nano particles 40
2.4. Preparation of RSA-based photocatalytic composite discs 40
2.5. Photocatalytic activity measurements in removal of dyes 41
2.6. Preparation of methylene blue solution 43
2.7.Determination of metal ion concentration in solution by (Atomic Absorption Spectroscopy AAS)... 43
2.8. Catalysts Characterization 44
2.8.1.X- ray diffraction (XRD)... 44
2.8.2.N_2 –physisorption.. 44
2.8.3.High resolution transmission electron microscopy (HRTEM)........... 45
2.8.4.Scanning electron microscope (SEM) 45
2.8.5.Fourier transform infrared (FTIR)... 45
2.9.Kinetic analysis of removal data of dyes or heavy metal ions in aqueous solution.. 45

CHAPTER III: RESULTS & DISCUSSIONS

3.1. Catalytic material.. 47
3.2. Physicochemical Characterization... 47
3.2.1. XRD analyses... 47
3.2.2. Surface characteristics 52
3.2.3. FTIR spectroscopy.. 63
3.2.4. Morphology from TEM and EDX 69
3.3.Application of different composites under study in removal of methylene blue (MB) dye in aqueous solution 73
3.3.1. RSA-TiO_2 nanocomposites in powder form. 73
3.3.2.RSA-based nanocomposites containing TiO_2 and CuPc in disc form 75
(A) General considerations... 75
(B) Investigation of the reaction kinetics in dark (adsorption)................. 78
(C) Photocatalytic degradation kinetics in the visible light...................... 80
(D) Effect of initial concentrations of MB 83

(E) Langmuir- Hinshelwood kinetic study 85

(F) Dye degradation from absorption spectra 87

(G) Recycling studies 90

3.4. Application of RSA-based composites discs in removal of some heavy metals 91

3.4.1. General remarks 91

3.4.2. Removal of Cd^{+2} ions by adsorption using RSA composites discs 95

(A) Adsorption efficiency of the used RSA-based composites 95

(B) Kinetic treatment of adsorption process 95

(C) Intra-particle diffusion model 98

(D) Elovitch model 99

3.4.3. Removal of Pb^{+2} ions by adsorption using RSA composite discs 100

(A) Effect of initial concentration Pb^{+2} ions 100

(B) Kinetic analysis of adsorption data 101

(C) Intra-particle diffusion model 104

(D) Elovitch model 105

(E) Effect of temperature on Pb^{2+} ions adsorption using different initial concentrations 105

3.4.4. Adsorption of Cu^{+2} ions using RSA –polymer binder composite disc 106

(A) Effect of initial concentration Cu^{+2} ions and temperature of adsorption 106

(B) Effect of pH. 107

CHAPTER IV: Summary and Conclusions 109

REFERENCES 10913

TABLE 1: Typical composition of untreated domestic waste-water 4

TABLE 2: Imortant contaminants in waste-water 5

TABLE 3: Waste-water treatment unit operation and processes................. 7

TABLE 4: Maximum acceptable metal concentration in drinking water according to the USEPA 20

TABLE 5: Mineral content (wt %) in RSA 47

TABLE 6: Textural and structural properties of original RSA, RSA-binder, TiO2, RSA-TiO2 (50%), RSA-CuPc and RSA-TiO2-CuPc composites 51

TABLE 7: Analysis data derived from EDX analysis of RSA 69

TABLE 8: Analysis data derived from EDX analysis of RSA-TiO_2 70

TABLE 9: Adsorption kinetic parameters of MB dye over the studied composites discs 79

TABLE 10: Derived kinetic data of Cd^{2+} ions removal according to pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models 96

TABLE 11: Derived kinetic data of Pb^{2+} ions removal according to pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models 103

Fig.1: Crystal structures of tatiania (a) anatase, (b) rutile, (c) brookite .. 36

Fig.2: Structure of Methylene Blue [www.wikipedia.org] 39

Fig.3:Photographs of Rice Straw (RS), Rice Straw Ash (RSA), Rice Straw Ash/recycled polymer foam (P.F.-2000) (RSA-P.F.), RSA-TiO2, RSA-CuPc and RSA -TiO2-CuPc composite disc 41

Fig.4: Schematic diagram of photo-reactor and composite disc 42

Fig.5: XRD patterns of (a) RSA, RSA-binder and RSA-CuPc (b) TiO2, RSA-TiO2 and RSA-TiO2-CuPc composite, (c)TiO2, RSA-TiO2(10), RSA-TiO2(10), RSA-TiO2(10), RSA-TiO2(10).......... 49

Fig.6: N_2 adsorption-desorption isotherm for (a) RSA 53

Fig.7: PSD curves for (a) RSA and (b) TiO_2 58

Fig.8: FTIR Spectra of (a) Pristine RSA and (b) pure TiO_2 66

Fig.9: EDX data for RSA... 69

Fig.10:EDX data for RSA-TiO_2 ……………………………………..70

Fig.11:Joined TEM (from EDX) images of (a) RSA, (b) Nano TiO_2 and (c) RSA- TiO_2 Composite... 71

Fig.12: TEM image of RSA-TiO_2 (50) composite 72

Fig.13:Photocatalytic degradation of MB dye using the pristine RSA, pure TiO_2 and different RSA-TiO_2 (10-50wt%) powder catalysts……………………………………………..………..73

Fig.14:Apparent first-order kinetic data for the RSA-TiO_2 photocatalysts 75

Fig.15:Photocatalytic degradation of MB dye using the RSA, TiO_2, RSA-TiO_2 (50), RSA-CuPc and RSA-TiO_2-CuPc in disc form……………………..……………………………..……..76

Fig.16:kinetic results of MB adsorption over RSA, RSA-TiO_2, RSA-CuPc and RSA-TiO_2- CuPc composites according to: (a) Pseudo first-order kinetic model and (b) Pseudo second-order kinetic model 78

Fig.17: Pseudo first order kinetic plots and rate constants (k) of photo-degradation of 25 ppm of MB on RSA-TiO_2, RSA-CuPc and RSA-TiO_2-CuPc discs under visible light, pH= 5.85…………..…81

Fig.18:Photo-degradation mechanism of MB by visible light in presenc of pure TiO_2 (a), CuPc sensitization (b) and sensitized TiO_2 by CuPc…………………………………………………….…. .. 83

Fig.19:Effect of initial dye concentration on MB removal on (a) RSA and (b) RSA-TiO_2 (50) composite discs under visible light, pH= 5.85. 84

Fig.20:linear correlation of $1/r_0$ versus $1/C_0$ using RSA and RSA-TiO_2 86

Fig.21:Spectral profiles obtained for MB dye on (a) RSA, (b) RSA-CuPc, (c) RSA-TiO_2 and (d) RSA-TiO_2-CuPc composite discs as a function of time of irradiation with visible light. The irradiation times were (top to bottom): 1, 5, 14, and 21h respectively. 89

Fig.22:Reproducibility of the RSA, RSA-TiO_2, RSA-CuPc and RSA-TiO_2-CuPc composite discs for 25 ppm of MB under visible light, pH= 5.85 and irradiation time of 120 min (a) Disc and (b) Powder…………………………………………..……………91

Fig.23:Removal % of Cd^{+2} ions using the RSA, RSA-CuPc, RSA-TiO_2 and RSA-TiO_2-CuPc catalysts at the reaction conditions (C_o= 500 ppm, T = 25 ˚C, pH= neutral)……………………………….95

Fig.24:Pseudo-first order kinetic of removal of Cd^{+2} ions using the RSA, RSA-CuPc, RSA-TiO_2 and RSA-TiO_2-CuPc catalysts at the reaction conditions:(C_o = 500 ppm, T = 25 ˚C, pH= neutral) 97

Fig.25:Pseudo-second order kinetic of removal of Cd^{+2} ions using the RSA, RSA-CuPc, RSA-TiO_2 and RSA-TiO_2-CuPc catalysts at the reaction conditions:(C_o = 500 ppm, T = 25˚C, pH= neutral) 97

Fig.26:Intra-particle diffusion model of removal % of Cd^{+2} ions using the RSA, RSA-CuPc, RSA-TiO_2 and RSA-TiO_2-CuPc catalysts at the reaction conditions: (C_o = 500 ppm, T = 25˚C, pH= neutral) 99

Fig.27:Elovich model of removal of Cd^{+2} ions using the RSA, RSA-CuPc, RSA-TiO_2 and RSA-TiO_2-CuPc catalysts at the reaction conditions (C_o = 500 ppm, T = 25˚C, pH= neutral)................................. 100

Fig.28:Removal % of Pb^{+2} ions using the RSA disc, at the reaction conditions: (C_o = 100, 200, 250 ppm, T = 25˚C, pH= neutral) .. 101

Fig.29:Pseudo-first order kinetic of removal of Pb^{+2} ions using the RSA .. disc, at the reaction conditions: (C_o = 100, 200, 250 ppm, T = 25 ˚C, pH= neutral)... 102

Fig.30:Pseudo-second order kinetic of removal of Pb^{+2} ions using the RSA disc, at the reaction conditions: (C_o = 100, 200, 250 ppm, T = 25 ˚C, pH= neutral)... 102

Fig.31: Intra-particle diffusion model of removal of Pb^{+2} ions using the RSA disc, at the reaction conditions: (C_o = 100, 200, 250 ppm, T = 25 ˚C, pH= neutral)... 104

Fig.32:Elovich equation of removal of Pb^{+2} ions using the RSA disc, at the reaction conditions:(C_o = 100, 200, 250 ppm, T = 25 ˚C, pH=neutral) 105

Fig.33:Effect of temperature on removal of Pb^{+2} ions using the RSA disc, at the reaction conditions: (C_o = 100, 150,200, 250 ppm, T = 20 - 50 ˚C, pH= neutral)... 106

Fig.34:Removal % of Cu^{+2} ions using the RSA powder, at the reaction conditions: (C_o = 100, 200, 300, 400 ppm, T = 20 - 60 ˚C, pH= neutral) 107

Fig.35:Effect of PH on removal of Cu^{+2} ions using the RSA powder, at the reaction conditions: (C_o = 200, 400 ppm, T = 25 ˚C, pH= 1.8-7)... 107