



***SYNTHESIS, CHARACTERIZATION AND  
APPLICATION OF NOVEL  
METALLONANOCOMPOSITE SYSTEMS IN  
VARIOUS PROCESSES OF ENVIRONMENTAL AND  
INDUSTRIAL IMPACT***

A Thesis Submitted By

***Safaa Rushdy Atia Fodua***

B.Sc. and M.Sc.

For the Award of

***Ph.D. degree in Chemistry***

Under supervision of

***Prof. Salah A. Hassan***

***Professor of Physical Chemistry,***

***Faculty of Science, Ain-Shams University.***

***Dr. Nour El-Din Ahmed  
Abd-El Star***

***Lecture of Organic Chemistry  
Faculty of Science, Ain-Shams  
University.***

***Dr. Atef Samir Darwish***

***Lecturer of Physical Chemistry  
Faculty of Science, Ain-Shams  
University.***

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

**2016**

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(قالوا سبحانك لا علم لنا  
الا ما علمتنا انك انت  
العظيم الحكيم)



(البقرة: الآية ٣٢)



*SYNTHESIS, CHARACTERIZATION AND APPLICATION OF  
NOVEL METALLONANOCOMPOSITE SYSTEMS IN  
VARIOUS PROCESSES OF ENVIRONMENTAL AND  
INDUSTRIAL IMPACT*

**Thesis submitted to:** Faculty of Science, Ain-Shams University

**For the award of:** Ph.D. degree in Chemistry

**By Safaa Rushdy Atia Fouda**

**Thesis Supervisors:**

**Approved**

***Prof. Salah A. Hassan***

*Professor of Physical Chemistry,  
Faculty of Science, Ain-Shams University.*

***Dr. Atef Samir Darwish***

*Lecturer of Physical Chemistry  
Faculty of Science, Ain-Shams University.*

***Dr. Nour El-Din Ahmed Abd-El Star***

*Lecture of Organic Chemistry  
Faculty of Science, Ain-Shams University.*

**Head of Chemistry Department**

***Prof. Dr.***



*Ain-Shams University*  
*Faculty of Science*  
*Chemistry Department*

# ***Qualifications***

**Student name :** Safaa Rushdy Atia Fouda

**Bachelor degree:** 2003

**Master degree :** 2011

**Name of Faculty:** Faculty of Science

**University:** Tanta University

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

***Prof. Dr.***

*To my Father,mother,  
the dearest children of  
mysister*

*(Mohammed, Basant  
and Malk),  
sister(Marwa) and my  
brother  
(Moustafa)*

# Acknowledgement

## *In the name of Allah, Most Gracious, Most Merciful*

It is my duty, as a start to praise Almighty Allah, lord of the world, whose guidance, blessings and help enabled me to take my first step on the path of improving my knowledge through this humble effort.

I would like to express my deepest respect and most sincere gratitude to my supervisor, **Prof. Salah A. Hassan**, Professor of Physical Chemistry, Faculty of Science, Ain-Shams University, who initiated and assigned this study. His valuable advice, help, guidance, encouragement at all stages of my work, stimulating discussion and also reviewing critically the manuscript. His constructive criticism and comments from the initial conception to the end of this work are highly appreciated. I am greatly indebted to his assistance and understanding in matters of non-academic concern, which have helped me endure some difficult times during my study period.

I also wish to express my heartfelt thanks and appreciation to **Dr. Atef Samir Darwish**, lecturer of Physical Chemistry, Faculty of Science, Ain-Shams University, for his support, tolerance, fruitful and valuable advice, help, guidance, encouragement at all stages of my work, stimulating discussion and also reviewing critically the manuscript.

Also all thanks to **Dr. Nour El-Din Ahmed Abd-El Star** Lecture of Organic Chemistry, Faculty of Science, Ain-Shams University, who helped me more in this work, her advices were very useful in

solving all the problems that I faced specially through nanocomposites synthesis and discussion.

A very special appreciation is due to **my parents, my sister and my brother** not only for their constant encouragement but also for their patience and understanding throughout. May God bless them in all their endeavors because without their unreserved support, completion of this study would not have been possible.

Also, I would like to thank my lab friends, for their cooperation and assistance during the achievement of this work.

Finally, I thank **each person** who had helped me in accomplishing this work especially my colleagues.

***Candidate***

***Safaa Rushdy***

***2016***

# ***Abstract***

***Name: Safaa Rushdy Fouda***

***Thesis title: Synthesis, Characterization, and Application of Novel metallonanocomposite systems in various processes of Envirnomental and Industrial impact.***

In the present work, magnetite nanoparticles (M NPs) were incorporated into poly (amido amine) (PAMAM, G=2) dendrimer matrix to form the mother composite M NPs ( $1 \times 10^{-3}$  M)@PAMAM. Dendrimer-modified composites were synthesized through conjugation with rice straw ash (RSA) or montomorillonite (MMT). Hybrid composites were obtained by applying ( $1 \times 10^{-3}$  M,  $3 \times 10^{-3}$  M and  $6 \times 10^{-3}$  M) M NPs, namely M NPs @PAMAM@RSA and M NPs @PAMAM@MMT. In addition polyaniline based-RSA composite was prepared, followed by application of M NPs to form M NPs @PANI@RSA hybrid nanocomposite with the same molar ratios.

Structural characteristics of the various samples were investigated through XRD, FTIR techniques. Morphological textural characteristics were estimated from TEM, SEM and low-temperature adsorption-desorption isotherms of N<sub>2</sub> and pore size distribution analysis. The stability of colloidal system and conductivity were investigated by DLS and zeta potential.

Different linkages and interactions during the synthesis processes were investigated.

All the synthesized hybrid composites were applied in removal of hazardous dyes (e.g., XO, MG and ROS.HCl), ions (e.g., Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup>) and heavy metals (e.g., Hg).

## **Keywords:**

Magnetite nanoparticles; PAMAM dendrimer; Polyaniline; Hybrid nanocomposites; Montomorillonite; Rice Straw Ash



# *Aim of the Work*

## *Aim of the Work*



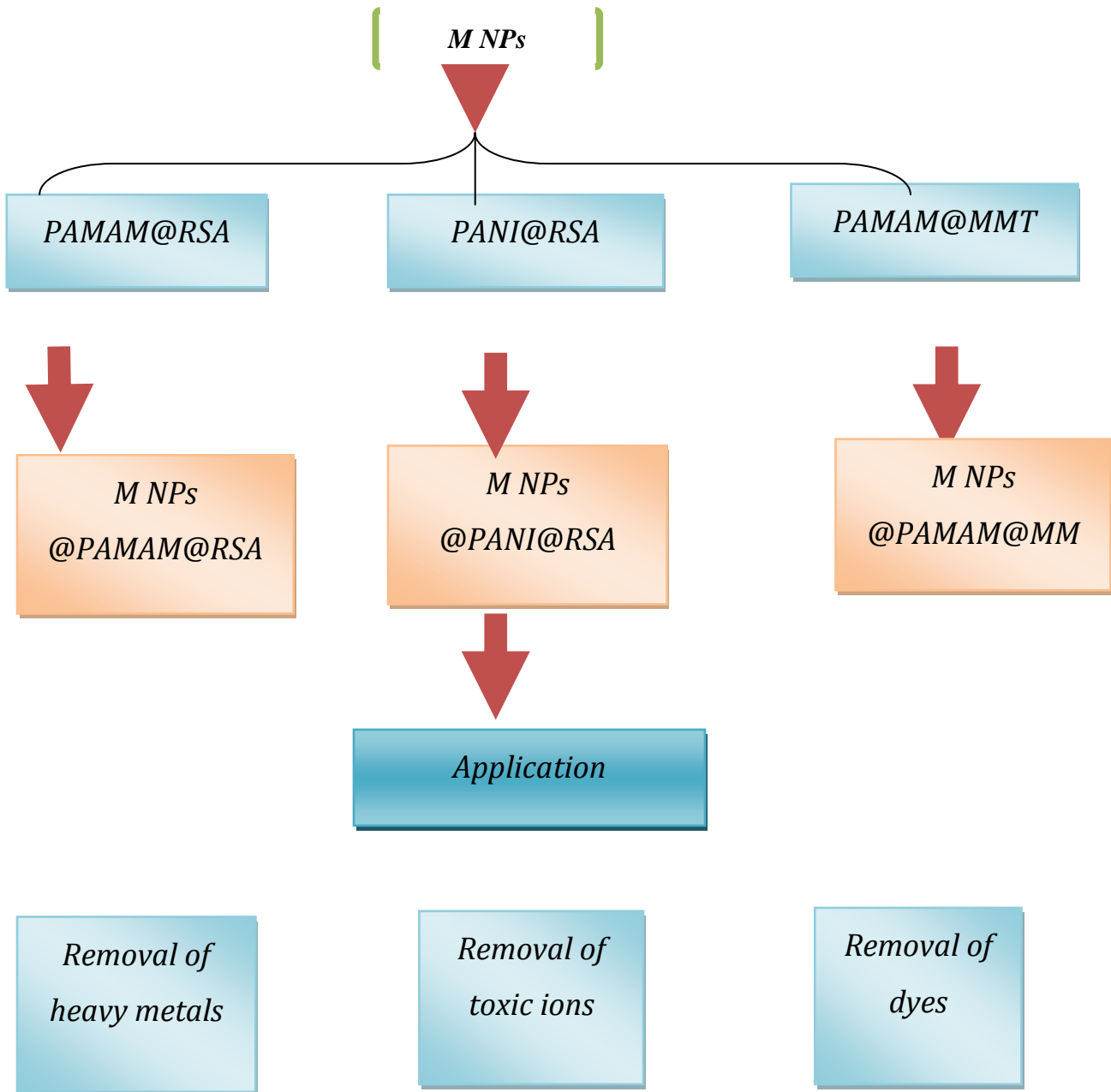
## ***THE AIM OF WORK***

This work is aimed at manipulation of novel nanocomposites based on M NPs@PAMAM dendrimer and using them as efficient nancatalysts and adsorbents for removal of dyes and toxic ions from wastewater.

This study included the following items:-

- Synthesis of magnetite nanoparticles in the absence and in the presence of PAMAM dendrimer as mother nanocomposite for further modification.
- Synthesis of modified MMT by intercalation of PAMAM dendrimer into Na-MMT matrix with applying the magnetite nanoparticles in different ratios ( $1 \times 10^{-3}$  M,  $3 \times 10^{-3}$  M and  $6 \times 10^{-3}$  M) M NPs @PAMAM@MMT.
- Synthesis of RSA-conjugated PAMAM dendrimer with applying magnetite nanoparticles of different concentrations M NPs @PAMAM@RSA.
- Synthesis of RSA-conjugated polyaniline with applying magnetite nanoparticles of different concentrations M NPs @PANI@RSA.
- Performing physicochemical characterization of different composites, by adopting XRD, FTIR, N<sub>2</sub>-physisorption, TEM, SEM and DLS techniques.
- Study of the catalytic removal (adsorption) efficiencies of the as-synthesized composites towards the dyes ,e.g., XO, MG, ROS-HCl dyes) and ions, e.g., Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> as well as heavy metals, e.g., Hg.
- Examination of adsorption kinetic models in all cases.

# PLAN OF WORK



## *Abbreviations*

Poly(amidoamine) dendrimer	PAMAM
Sodium montmorillonite	Na <sup>+</sup> -MMT
Cation exchange capacity	CEC
Magnetite nanoparticles	M NPs (Fe <sub>3</sub> O <sub>4</sub> )
Rice straw ash	RSA
X-ray diffraction	XRD
Fourier Transform infrared	FTIR
Transmission electron microscope	TEM
Scanning electron microscope	SEM
Specific Surface area	S <sub>BET</sub>
BET-C energetic constant	C <sub>BET</sub>
Monolayer coverage	V <sub>m</sub>
Pore size distribution	P <sub>a</sub> SD
Dynamic light scattering	DLS
Zeta potential	Z
Xylenol orange	XO
Malachite green	MG
Rosaniline-hydrochloride	ROS-HCl
The initial concentration of dye in liquid phase	C <sub>0</sub>
Dye concentration in liquid phase at equilibrium	C <sub>e</sub>
The volume of the dye used	V
The mass of adsorbent used	M
Maximum wavelength of absorbance	λ <sub>Max</sub>

# Contents

Subject	Page
<b>I. Introduction</b>	
1.1 General statements.....	1
1.2 Metal-polymer nanocomposites.....	2
1.2.1 Examples of metal-polymer nanocomposites.....	6
1.3 Metal-polymer-clay nanocomposites.....	8
1.3.1 Structure of montmorillonite clay (MMT).....	10
1.3.2 Interaction with organic compounds.....	11
1.3.2.1 Sorption of organic molecules.....	11
1.3.2.2 Ion exchange.....	12
1.3.3 Clay modification. ....	13
1.3.3.1 Organoclay synthesis.....	14
1.3.4 Types of polymer-clay nanocomposites structure	15
(a) Intercalated nanocomposites.....	16
(b) Flocculated nanocomposites.....	16
(c) Exfoliated nanocomposites. ....	16
1.4 Methods of preparation of polymer-clay nanocomposites.....	17
1.4.1 In situ polymerization.....	17
1.4.2 Solvent Method.....	18
1.4.3 Melt intercalation.....	18
1.4.4 Examples of polymer-clay nanocomposites.....	19
1.5 Dendrimers nanocomposites.....	22

1.5.1	Dendrimers synthesis.....	26
1.5.1.1	Divergent synthesis. ....	26
1.5.1.2	Convergent synthesis. ....	26
1.5.2	Unique dendrimer properties. ....	27
1.5.2.1	Monodispersity.....	27
1.5.2.2.	Nanoscale container and scaffolding properties.....	27
1.5.2.3.	Amplification and functionalization of dendrimer surface groups.....	27
1.5.2.4.	Nanoscale dimensions and shapes that mimic proteins.....	27
1.5.2.5.	Physical characteristics of PAMAM dendrimers...	27
1.6.	Metal-clay-PAMAM dendrimers nanocomposites.	31
1.6.1.	Dendrimers containing metal ions in structure.....	32
1.6.2.	Metal ions bound to ligands on the surface of dendrimers.....	32
1.6.3.	Dendrimers containing nonstructural metal ions through their interior.....	33
1.7.	Introduction to dendrimers containing zerovalent metal clusters.....	34
1.7.1.	Dendrimers encapsulated metal nanoparticles.....	34
1.7.2	Catalysis using transition-metal nanoparticles.....	35
1.8	Intradendrimer complexes between PAMAM dendrimers and metal ions.....	36
1.9	Synthesis and characterization of dendrimer- encapsulated metal nanoparticles. ....	37
1.9.1	Direct reduction of dendrimer/metal ion	37

	composites.....	
1.9.2	Displacement reaction method. ....	38
1.10	Application of dendrimers as catalysts.....	39
1.11	Metal- rice straw ash and metal-silica nanocomposites.....	39
1.12	Metal-rice straw ash-polyaniline nanocomposite and its applications.....	41
1.12.1	Conducting polymers .....	41
1.12.2	Polyaniline (PANI).....	42
	(a) Oxidation state forms of PANI .....	42
	(b) PANI synthesis. ....	43
	(c)Application of polyaniline nanocomposite.....	47
1.13	Application of various nanocomposites.....	49
1.13.1	Removal of dyes. ....	49
1.13.2	Removal of heavy metals.....	50
1.13.3	Removal of anions and cations.....	51
1.13.3.1	Removal of cations.....	51
1.13.3.2	Removal of anions.....	55
1.13.3.2.1	Removal of nitrate.....	55
1.13.3.2.2	Removal of Bromide.....	56
1.14	Aim of the work.....	58

## **II: Experimental**

2.1	Materials and measurements.....	58
2.1.1	Materials .....	58
2.1.2	Measurements.....	58
2.1.2.1	UV-VIS absorption spectra .....	58