



كلية العلوم – قسم الكيمياء



# **Radiation Modification of Some Polymers and their Possible Biomedical and Industrial Applications**

Thesis Submitted by

**Mai Fouad Ahmed Elshahawy**

B.Sc.(Chemistry) 2011

M.Sc. (Chemistry) 2016

**For the requirement of Ph.D. Degree of Science in Chemistry**

***Prof. Dr. Al-Sayed Ahmed Soliman***

*Professor Dr. of Organic Chemistry,  
Faculty of Science, Ain Shams University.*

***Prof. Dr. Amr El-Hag Ali Sayed***

*Professor. Dr. of Radiation Chemistry,  
National Center for Radiation Research and Technology,  
Egyptian Atomic Energy Authority*

***Prof. Dr. Ghada A. Mahmoud***

*Professor. Dr. of Radiation Chemistry, head of polymers chemistry department,  
National center for Radiation Research and Technology,  
Egyptian Atomic Energy Authority.*

***Prof. Dr. Amany Ismail Mahmoud Rafaat***

*Professor. Dr. of Radiation Chemistry,  
National Center for Radiation Research and Technology,  
Egyptian Atomic Energy Authority*

**To**

**Department of Chemistry**

**Faculty of Science, Ain Shams University**

**2020**



كلية العلوم – قسم الكيمياء



# **Radiation Modification of Some Polymers and their Possible Biomedical and Industrial Applications**

By

**Mai Fouad Ahmed Elshahawy**

Thesis Advisors

Approved

***Prof. Dr. Al-Sayed Ahmed Soliman***

*Professor Dr. of Organic Chemistry,  
Faculty of Science, Ain Shams University.*

***Prof. Dr. Amr El-Hag Ali Sayed***

*Professor Dr. of Radiation Chemistry,  
National Center for Radiation Research and Technology,  
Egyptian Atomic Energy Authority*

***Prof. Dr. Ghada A. Mahmoud***

*Professor Dr. of Radiation Chemistry head of polymers chemistry  
department, National center for Radiation Research  
and Technology, Egyptian Atomic Energy Authority.*

***Prof. Dr. Amany Ismail Mahmoud Rafaat***

*Professor Dr. of Radiation Chemistry,  
National Center for Radiation Research and Technology,  
Egyptian Atomic Energy Authority*

**Head of Chemistry Department**

***Prof. Dr. Ayman Ayoub Abdel-Shafi***



كلية العلوم – قسم الكيمياء





## **Acknowledgment**

*First of all, thanks to GOD for the infinite help and persistent supply of patience and efforts to accomplish this work.*

*I would like to express my deep gratitude and thanks to **Prof. Dr. Al-Sayed A. Soliman**, Faculty of Science, Ain Shams University, for his interest, and deep concern in this work.*

*I offer my sincerest gratitude to my supervisor, **Prof. Dr. Amr El-Hag Ali Sayed**, National Center for Radiation Research and Technology, who for his continues guidance, honest assistance interest, wise guidance, kind supervision, and continuous encouragement throughout this work.*

*Deepest thanks and sincere gratitude to **Prof. Dr. Ghada A. Mohmoud**, Prof. of Radiation Chemistry, National Center for Radiation Research and Technology (NCRRT), for suggesting, planning the point of research, her eminent supervision and valuable discussions. Also, for her encouragement and support throughout this work.*

*I would like to offer my deep thanks to **Prof. Dr. Amany Ismail Raafat** Prof. of Radiation Chemistry, National Center for Radiation Research and Technology for suggesting, planning the point of research, for her supervision encouragement and support throughout this work. Also for her honest assistance to have this work done. I think without her help this work wouldn't come out.*

*I would like to give thanks for deep gratitude to **Dr. Asmaa Abu-Bakr Hassan**, Associate Professor, Radiation Biology Department, National Center for Radiation Research and Technology, for performing cytotoxicity evaluation and her fruitful discussion. Also, deep gratitude to **Dr. Eman Araby**, Associate Professor, Radiation Microbiology Department, National Center for Radiation Research and Technology, for antibacterial assessment and her good interpretation and discussion.*

*Special thanks to my all colleagues and staff members of Polymer Chemistry Department, National Center for Radiation Research and Technology (NCRRT) for their help and facilities provided throughout this work.  
There are no enough words to express my gratitude to all of you"*

*This Work Is Dedicated  
To My parents, my family, Without  
Their Support, Endless Help and  
Continues Encouragement All the Time  
I cloud Never Finish This Work  
So Giver of all my best for them and  
give thanks  
Thank you.....*



# *Contents*

## Table of content

List of Abbreviations	
List of Figures	I
List of Tables	VII
Aim of work	IX
Abstract	XI

### Chapter I

#### Introduction

1.1. Hydrogels: definition and classification	1
1.2. Hydrogel synthesis	4
1.2.1 Hydrogel Synthesis by Physical Crosslinking	4
I-H-bonded hydrogel	5
II-Ionic interaction	6
III-Heat induced aggregation (Maturation)	6
IV-Heating/cooling a polymer solution	7
V- Complex coacervation.	8
VI-Freeze-thawing	9
1.2.2. Chemical cross-linking	9
I- Chemical cross-linkers	9
1.2.3. Grafting	10
I-Chemical grafting	11
II- Radiation grafting	11
1.2.4. Radiation crosslinking.	12
I-Irradiation in aqueous state	12
II- Irradiation in paste-like state	14
1.3. Hydrogel characterization	15
1.3.1. Gelation	15
1.3.2. Swelling measurement	15
1.3.3. Surface topography	16
1.3.4. Chemical and Physical analysis	16
1.3.5. Biocompatibility evaluation	16
1.4. Improvement of hydrogel capabilities	17
I- hydrogel nanocomposites	17
II- Nanoparticles for photocatalysis	18
III-Hydrogel loaded with medicinal plant extract	21
1.5. Haemostatic medicinal plant extracts	23
<i>I. Capsella bursa-pastoris (l.) Medik (shepherd's purse)</i>	24
<i>II. Salvadorapersica(miswak)</i>	25
<i>III. Achillea millefolium(yarrow)</i>	25



<i>Iv. Equisetum arvense</i> I. (horsetail)	27
1.6. Applications of hydrogels	28
1.6.1. Photo catalytic wastewater treatment	29
1.6.2. Haemostatic dressing hydrogels	32

## **Chapter II**

### **Literature Review**

2.1. Radiation synthesis of hydrogels:-	35
2.2. Applications of the hydrogels:-	44
2.2.1. Industrial applications (photocatalysis for dyes degradation)	46
2.2.2. Biomedical applications (haemostatic dressing hydrogels)	72

## **Chapter III**

### **Materials and Experimental Techniques**

3.1. Materials	91
3.2. Experimental techniques	93
3.2.1. Gamma radiation source	
3.2.2. Preparation of Graphene oxide	93
3.2.3. Preparation of reduced graphene oxide	93
3.2.4. Preparation of (AAc/PVA) hydrogels	94
3.2.5. Preparation of (AAc/PVA)-GO and (AAc/PVA)-RGO nano-composites	94
3.2.6. Preparation of (AAc/PVA)-GO- TiO <sub>2</sub> and (aac/PVA)-RGO- TiO <sub>2</sub> nanocomposites	94
3.2.7. Preparation of medicinal plant extract	95
3.2.8. Preparation of (HEC/CP) based haemostatic dressing hydrogels.	95
3.3. Characterization methods	96
Gel content	
3.3.1. Swelling degree	96
3.3.2. Freeze drying process	97
3.3.3. Fourier transform infrared spectroscopy (FTIR)	97
3.3.4. The X-ray Diffraction (XRD)	97
3.3.5. Raman spectroscopy	97
3.3.6. Scanning electron microscopy (SEM)	97
3.3.7. Transition electron microscopy measurements (TEM)	97
3.3.8. Ultraviolet (UV) measurements	98
3.4. Evaluation of prepared hydrogels and nanocomposites	
3.4.1. Evaluation of (AAc/PVA) hydrogel as photocatalysis Photocatalytic Decolorization Experiments	98
3.4.2. Evaluation of the (HEC/CP) –MPE haemostatic sponges Blood collection and platelet isolation	99

3.4.2.1. Preparation of Simulated Body Fluid (SBF)	99
3.4.2.2. Porosity measurement	100
3.4.2.3. Measurement of density of freeze-dried sponges	100
3.4.2.4. In vitro Hydrolytic biodegradation	100
3.4.2.5. Fluid absorption Degree	101
3.4.2.6. Milk-clotting activities	101
3.4.2.7. Whole blood clotting test	101
3.4.2.8. In vitro blood plasma coagulation assay	102
3.4.2.9. Platelet adhesion and aggregation	103
3.4.2.10. Protein adsorption	103
3.4.2.11. In-vitro Antimicrobial activity	104
3.4.2.12. In vitro cytotoxicity evaluation (MTT) assay	104
3.4.2.13. In- vivo haemostatic performance evaluation	106
I- haemostasis of lacerated liver	
II- histological evaluation	106

## **Chapter IV**

### **Results and Discussion**

#### **Part A**

4A.1. Characterization of GO and RGO	107
4A.1.1. X-ray diffraction (XRD)	
4A.1.2. Raman spectrum analysis	109
4A.1.3. Fourier Transforms Infrared Spectroscopy (FTIR)	110
4A.1.4. Scanning Electron Microscope (SEM)	112
4A.1.5. Transmission Electron Microscope (TEM)	113
4A.2. Radiation synthesis of (AAc/ PVA) hydrogel	113
4A.2.1. Optimizing the radiation synthesis conditions of AAc/PVA hydrogel	116
4A.3. Radiation synthesis of (AAc/ PVA) based GO/TiO <sub>2</sub> , RGO/TiO <sub>2</sub> nanocomposite hydrogels	117
4A.3.1. Effect of GO and RGO content on the gelation percentage of the nanocomposites	118
4A.4. Characterization of the (AAc/ PVA) hydrogel and its corresponding GO/TiO <sub>2</sub> , RGO/TiO <sub>2</sub> nanocomposite hydrogels	119
4A.4.1. Swelling Behavior	
4A.4.1.1. Effect of total feed concentration	119
4A.4.1.2. Effect of the irradiation dose	120
4A.4.1.3. Effect of the feed solution composition	121

4A.4.1.4. Effect of nano filler content	122
4A.4.1.5. Effect of pH of medium	124
4A.4.2. X-Ray diffraction (XRD)	125
4A.4.3. Fourier transforms infrared spectroscopy (FTIR)	128
4A.4.4. Scanning electron microscope (SEM)	131
4A.4.5. Transmission electron microscope (TEM)	132
4A.5. Photocatalytic Activity	133
4A.5.1. Photocatalytic decolorization of DB71 dye	137
4A.5.2. Effect of Initial DB71 dye concentration	138
4A.5.3. Effect of pH	140
4A.5.4. Effect of hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	142
4A.5.5 The reaction kinetics	144
4A.5.6. Reusability of (AAc/ PVA)-RGO-TiO <sub>2</sub> nanocomposite	148

## Part B

4B.1. Radiation synthesis of haemostatic dressing hydrogels	150
4B.2. Radiation synthesis and characterization of (HEC/Cp) hydrogels	152
4B.3. Gelation degree	154
4B.3.1. Effect of (HEC) feed solution concentration	154
4B.3.2. Effect of carbopol content	155
4B.4. Swelling characteristics	156
I- Effect of carbopol content	
4B.5. Preparation and characterization of the (HEC/Cp) haemostatic dressing hydrogels reinforced with different haemostatic medicinal plant extract (MPE).	157
4B.5.1. Effect of medicinal plant extract on the gelation degree	158
4B.6. Preparation of porous the different spongy (HEC/Cp) -MPE haemostatic dressings	159
4B.6.1. Porosity on the developed spongy (HEC/Cp)-MPE haemostatic dressings	160
4B.6.2. Density on the developed spongy (HEC/Cp) -MPE haemostatic dressings	162
4B.6.3. Surface morphology	162
4B.6.4. Swelling characteristics	165
4B.6.5. Fluid absorption capacity	166
4B.6.6. In vitro biodegradation on the developed spongy (HEC/Cp)-MPE haemostatic dressings	170
4B.7. In-vitro assessment of (HEC/Cp)-MPE haemostatic activity	172
4B.7.1. Astringent characteristics	173

4B.7.2. Blood absorption efficiency	175
4B.7.3. Swelling in plasma	177
4B.7.4. Whole blood clotting assay and SEM analysis	179
4B.7.5. Protein adsorption	184
4B.7.6. Antimicrobial performance	186
4B.7.7 In vitro cytocompatibility	187
4B.8. Biological activities of (HEC/Cp)-MPE haemostatic dressing	189
4B.8.1. In-vitro Blood coagulation activity assay	
4B.8.2. Platelet adhesion and SEM analysis	190
4B.8.3. Haemostasis time and weight of blood of lacerated liver	195
4B.8.4. Total serum Calcium concentration	198
4B.8.5. Total serum transferrin	201
4B.8.6. Histological examination	204
References.	205
Summary and conclusions.	239
Arabic summary and conclusions.	247
Arabic abstract	

## List of Abbreviations

<b>AAc</b>	Acrylic acid
<b>PVA</b>	Polyvinyl Alcohol
<b>HEC</b>	Hydroxyethyl Cellulose
<b>Cp</b>	Carbopol 940
<b>GG</b>	Graphite
<b>GO</b>	Graphene Oxide
<b>RGO</b>	Reduced graphene oxide
<b>TiO<sub>2</sub></b>	Titanium dioxide nanoparticles
<b>DB71</b>	Direct blue dye 71
<b>NPs</b>	Nanoparticles
<b>MPE</b>	Medinical Plant Extract
<b>SBF</b>	Simulated body fluide
<b>PBS</b>	Phosphate buffer saline
<b>BSA</b>	Bovine serum albumin
<b><i>S aureus</i></b>	<i>Staphylococcus aureus</i>
<b><i>E. coli</i></b>	<i>Escherichia coli.</i>
<b>TF</b>	Transferrin



## List of Figures

<b>Figure (1):</b>	Schematic illustration of (a) chemical (covalent crosslinking) and (b) physical (non covalent crosslinking). Examples of physical crosslinking are (c) helix formation by hydrogen bonds e.g. crosslinking of carragenan and agar-agar and (d) cation chelation e.g crosslinking of alginate	4
<b>Figure (2):</b>	Hydrogel network formation due to intermolecular H-bonding in CMC at low pH.	5
<b>Figure (3):</b>	Ionotropic gelation by interaction between anionic groups on alginate (COO <sup>-</sup> ) with divalent metal ions (Ca <sup>2+</sup> ).	6
<b>Figure (4):</b>	Maturation of gum arabic causing the aggregation of proteinaceous part of molecules leading to cross-linked hydrogel network.	7
<b>Figure (5):</b>	Complex coacervation between a polyanion and a polycation	8
<b>Figure (6):</b>	Schematic illustration of using chemical crosslinker to obtain crosslinked hydrogel network.	10
<b>Figure (7):</b>	Grafting of a monomer on performed polymeric backbone leading to infinite branching and crosslinking.	11
<b>Figure (8):</b>	Structure of (A) Graphene Oxide (GO) and (B) Reduced graphene oxide (RGO)	21
<b>Figure (9):</b>	Picture of <i>Capsella bursa-pastoris</i> (L.) Medik plant	24
<b>Figure (10):</b>	Picture of <i>Salvadora Persica</i> (Miswak) plant	25
<b>Figure (11):</b>	Picture of <i>Achillea millefolium</i> , known as yarrow plant	26
<b>Figure (12):</b>	Picture of <i>Equisetum arvense</i> , known as Horsetail plant	27
<b>Figure (13):</b>	Images of wastewater	30
<b>Figure (14):</b>	photocatalysis process	31
<b>Figure (15):</b>	Image of haemostasis process	33
<b>Figure (16):</b>	Images of forms for hemostatic hydrogels (A) dressings, (B) sponges, (C) powders, and (D) injection gel.	33
<b>Figure (17):</b>	photographic picture of plant extracts	93
<b>Figure (18):</b>	XRD patterns of (a) Graphite, (b) GO and (c) RGO.	108
<b>Figure (19):</b>	Raman spectra of (a) GO and (c) RGO.	110
<b>Figure (20):</b>	FTIR spectra of (a) GG, (b) GO and (c) RGO	111
<b>Figure (21):</b>	SEM of (a) GO and (b) RGO	112
<b>Figure (22):</b>	TEM of (a) GO and (b) RGO	113