



شبكة المعلومات الجامعية

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ





شبكة المعلومات الجامعية



شبكة المعلومات الجامعية

التوثيق الالكتروني والميكرو فيلم

جامعة عين شمس

التوثيق الالكتروني والميكرو فيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأفلام قد اعدت دون أية تغيرات



يجب أن

تحفظ هذه الأفلام بعيداً عن الغبار

في درجة حرارة من 15 – 20 مئوية ورطوبة نسبية من 20-40 %

To be kept away from dust in dry cool place of
15 – 25c and relative humidity 20-40 %



شبكة المعلومات الجامعية



بعض الوثائق الأصلية تالفة



شبكة المعلومات الجامعية



بالرسالة صفحات
لم ترد بالأصل

**PREPARATION AND THERMAL BEHAVIOUR STUDIES OF
SOME NEW POLYMERS AND THEIR USES IN METAL
COMPLEXES AND HEAVY METAL IONS REMOVAL FROM
AQUEOUS SOLUTION**

By
MOHAMMED KASSEM OTHMAN
B.Sc., M. Sc.

A Thesis
Submitted to The Faculty Of Science
Zagazig University Benha Branch
For The Degree of Ph. D.
In
Chemistry

Supervised by
PROF. DR. Abd El-Fattah Fadel SHAABAN
Professor of Organic Chemistry
Faculty of science
Zagazig University Benha Branch

PROF. DR. Ahmed Mahmoud DONIA
Professor of Inorganic Chemistry
Faculty of Science Menoufia University

DR. Mohammed Morsy AZAB
Assistant Prof. Of Organic Chemistry
Faculty of Science
Zagazig University Benha Branch

2003



B
1-211

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿وَعَلَّمَكَ مَا لَمْ تَكُن تَعْلَمُ وَكَانَ فَضْلُ

اللَّهِ عَلَيْكَ عَظِيمًا﴾

صدق الله العظيم

النساء آية رقم ١١٣



ACKNOWLEDGEMENT

Firstly I would like to express my deepest thank to God "Allah" for bestowal, continues giving and help to finish this work.

The author wishes to express his sincere gratitude and deep appreciation to **Prof. Dr. ABDEL-FATTAH FEDEL SHAABAN**, Professor of organic chemistry, faculty of science, Zagazig University, Benha Branch, **Prof. Dr. AHMED MAHMOUD DONIA**, Professor of inorganic chemistry, faculty of science, Menoufia University and **Dr. MOHAMMED MORSY AZAB**, Assistant Prof. of organic chemistry, faculty of science, Zagazig University, Benha Branch, for suggestion the plane of work, supervision, careful guidance and valuable discussion.

I would like to express my deepest thank to the staff members of department of chemistry, faculty of science Zagzig University, Benha Branch.

Last but not last my deep heartly thanks to may family for their continuous encouragement, mortal support and patience throughout my study period.

CONTENTS

	Page
Acknowledgement	III
List of Tables	V
List of Figures	VII
List of symbols and abbreviations	VIII
Aim of the work.....	X
Abstract	1
Chapter (I) Introduction.....	24
Chapter (II) Experimental.....	24
Preparation of poly-Glycidylmethacrylate and its. solid complexes	
Preparation of poly- Glycidyl methacrylate (XIII)	24
Preparation of poly-Glycidyl methacrylate bearing ethylenediamine (XIV)... ..	24
Preparation of poly- Glycidyl methacrylate bearing 4-aminoantipyrine (XV).. ..	24
Preparation of poly- Glycidyl methacrylate bearing 2-aminothiazole (XVI)... ..	25
Preparation of metal complexes of poly-Glycidyl methacrylate bearing ethylenediamine (XVII).....	25
Preparation of metal complexes of poly- Glycidyl methacrylate bearing 4-aminoantipyrine (XVIII).....	25
Preparation of metal complexes of poly- Glycidyl methacrylate bearing 2-aminothiazole (XIX).....	25
Preparation of chelating resins	
Preparation of AN-MBA copolymers (XX) and (XXI).	26
Preparation of oxime chelating resins (XXII) and (XXIII).	26
Preparation of GMA-DVB copolymers (XXIV) and (XXV)	26
Preparation of aminated chelating resins (XXVI) and (XXVII)	27
Preparation of dithiocarbamate chelating resin (XXVIII)	27
Uptake of metal ions	
Batch method	27
Column method.....	28
Techniques	
Elemental analysis.....	28
Infrared (IR)	28
Electronic spectra.....	29
Thermal analysis.....	29

LIST OF TABLES

	Page
Table (1) Elemental analysis and TG results of complexes (XVIII) and (XIX) ...	48
Table (2) DTA and TG results of chelating resins (XXII) and (XXIII)	55
Table (3) Effect of pH on uptake of (Cu^{2+}) by resins (XXII) and (XXIII) after 30 min.	62
Table (4) Uptake of (Cu^{2+}) by chelating resins (XXII) and (XXIII) at different time periods and pH = 10	62
Table (5) Effect of pH on uptake of (Ni^{2+}) by chelating resins (XXII) and (XXIII) after 30 min.	67
Table (6) Uptake of (Ni^{2+}) by chelating resins (XXII) and (XXIII) at different time periods at pH = 10	67
Table (7) Uptake of (Zn^{2+}) by chelating resins (XXII) and (XXIII) at different time periods at pH = 8.....	73
Table (8) Effect of ionic radii of metal ion on their uptake values by chelating resins (XXII) and (XXIII) after 60 min and pH = 10	73
Table (9) Uptake of non-transition metals (Zn^{2+} , Cd^{2+} and Hg^{2+}) by chelating resins (XXII) at different time periods.	79
Table (10) Effect of ionic radii on uptake of metal ions (Zn^{2+} , Cd^{2+} and Hg^{2+}) by chelating resins (XXII) after 20 min.	79
Table (11) Uptake values of metal ions by chelating resins (XXII) at pH = 10 after 40 min	80
Table (12) Efficiency of separation between metal ions.	80
Table (13) Effect of pH on uptake of (Cu^{2+}) by chelating resin (XXVI) after 60 min	93
Table (14) Effect of pH on uptake of (Cu^{2+}) by chelating resins (XXVII) after 60 min.	93

Table (15)	Uptake of (Cu^{2+}) by chelating resins (XXVI) and (XXVII) at different time periods and pH = 10	94
Table (16)	Uptake of (Ni^{2+}) by chelating resins (XXVI) and (XXVI) at different time periods and pH = 10.....	94
Table (17)	Uptake of (Zn^{2+} , Cd^{2+} and pb^{2+}) ions by chelating resin (XXVI) at different time periods.....	100
Table (18)	Efficiency of seperation between metal ions after 30 min for chelating resin (XXVI)	100
Table (19)	Uptake of metal ions by chelating resin (XXVI) at 30 min	101
Table (20)	Uptake of metal ions by (pb^{2+} and Hg^{2+}) by chelating resin (XXII) and (XXVI) at different time periods	104
Table (21)	Uptake of (Co^{3+}) by chelating resins (XXII) and (XXVI) at different time periods.....	109
Table (22)	Effect of ionic radii of metal ions on their uptake values	109
Table (23)	Uptake of (Cu^{2+}) by chelating resin (XXVI) as column at pH = 10	117
Table (24)	Uptake of (Cu^{2+} , Hg^{2+} and pb^{2+}) by dithiocarbamate chelating resin (XXVIII') at different time periods.	120

LIST OF FIGURES

Figure	Page
Fig. (1-a) IR- Spectra of poly (GMA) (XIII) and poly (GMA bearing en) (XIV).....	32
Fig. (1-b) IR-Spectra of poly(GMA bearing en) metal complexes (XVII).	33
Fig. (2-a) Electronic spectra of poly(GMA bearing en) Copper complex ..	34
Fig. (2-b) Electronic spectra of poly (GMA bearing en) Cobalt complex...	35
Fig. (2-c) Electronic spectra of poly (GMA bearing en) Nickel-complex...	36
Fig. (3-a) DTA and TGA of poly (GMA bearing en) (XIV)	37
Fig. (3-b) DTA and TGA of poly (GMA bearing en) Copper complex.....	38
Fig. (3-c) DTA and TGA of poly (GMA bearing en) Cabalt complex.....	39
Fig. (3-d) DTA and TGA of poly (GMA bearing en) Nickel complex	40
Fig. (4-a) IR spectra of poly GMA (XIII) and poly GMA bearing 4aapy (XV)	43
Fig. (4-b) IR spectra of poly (GMA bearing 4aapy) Copper complex (XVIII)	45
Fig. (5-a) TGA of poly (GMA bearing 4aapy) Copper complex (XVIII).....	45
Fig. (6-a) IR-Spectra of poly (GMA) and poly (GMA bearing 2ath) (XVI).	49
Fig. (6-b) IR-spectra of poly(GMA bearing 2ath) Copper complex (XIX).	50
Fig. (7) TGA of poly(GMA bearing 2ath) Copper complex (XIX).... ..	51
Fig.(8-a) IR-spectra of copolymer (XX) and chelating resin (XXII) (9 :1 mole ratio).	56
Fig.(8-b) IR-spectra of copolymer (XX) and chelating resin (XXII) (7 : 3 mole ratio).	57

Fig.(9-a)	DTA and TGA of chelating resin (XXII) (9 : 1 mole ratio)	58
Fig.(9-b)	DTA and TGA of chelating resin (XXIII) (7 : 3 mole ratio)....	59
Fig.(10)	Effect of pH on uptake of Cu^{2+} by chelating resins (XXII) and (XXIII) after 30 min	63
Fig.(11)	Uptake of (Cu^{2+}) by chelating resins (XXII) and (XXIII) at different time periods and pH = 10	64
Fig.(12)	Effect of pH on uptake of Ni^{2+} by chelating resins (XXII) and (XXIII) after 60 min.	68
Fig.(13)	Uptake of Ni^{2+} by chelating resins (XXII) and (XXIII) at different time periods and pH = 10.....	69
Fig.(14)	Uptake of Zn^{2+} by chelating resins (XXII) and (XXIII)at different time periods and pH = 10	74
Fig.(15)	Rate of uptake of metal ions (Cu^{2+} , Ni^{2+} and Zn^{2+}) by chelating resins (XXII) and (XXIII)	75
Fig.(16)	Effect of pH on uptake of metal ions (Zn^{2+} and Cd^{2+}) by chelating resins (XXII) after 60 min.....	81
Fig.(17)	Uptake of non-transition metals (Zn^{2+} , Cd^{2+} and Hg^{2+}) by chelating resins (XXII) at different time periods.....	82
Fig.(18)	Effect of ionic radii on the uptake of metal ions by chelating resins (XXII) after 20 min.....	83
Fig.(19-a)	IR-spectra of copolymer (XXIV) and chelating resin (XXVI) (9 :1 mole ratio).	86
Fig.(19-b)	IR-spectra of copolymer (XXIV) and chelating resin (XXVI) (7 :3 mole ratio).	87
Fig. (20-a)	DTA and TGA of chelating resin (XXVI) (9 : 1 mole ratio)...	88
Fig. (20-b)	DTA and TGA of chelating resin (XXVII) (7 : 3 mole ratio).	89

Fig. (21)	Effect of pH on uptake of Cu^{2+} by chelating resin (XXVI) after 60 min	95
Fig. (22)	Uptake of (Cu^{2+}) by chelating resin (XXVI) and (XXVII) at different time periods and pH = 10	96
Fig. (23)	Uptake of Nickel by chelating resin (XXVI) and (XXVII) at different time periods and pH=10 min.....	97
Fig. (24)	Uptake of (Zn^{2+} , Cd^{2+} and pb^{2+}) ions by chelating resin (XXVI) at different time periods.....	102
Fig. (25)	Uptake of (Hg^{2+}) by chelating resin (XXII) and (XXVI) at different time periods.....	105
Fig. (26)	Uptake of (pb^{2+}) by chelating resin (XXII) and (XXVI)at different time periods.....	106
Fig. (27)	Effect of pH on uptake of Co^{2+} by chelating resin (XXII) after 60 min.....	110
Fig. (28)	Uptake of (Co^{2+}) by chelating resin (XXII) at different time periods & pH = (6.5 and 10)	111
Fig. (29)	Effect of ionic radii on uptake of metal ions (Zn^{2+} , Ni^{2+} , Cu^{2+} and Co^{2+}) by chelating resin (XXII) and pH = 10.....	112
Fig. (30)	Effect of ionic radii on uptake of metal ions (Zn^{2+} , Ni^{2+} , Cu^{2+} and Co^{3+}) by chelating resin (XXII) and pH = 10.....	113
Fig. (31)	Effect of ionic radii on uptake of metal ion (Zn^{2+} , Ni^{2+} , Cu^{2+} and Co^{2+}) by chelating resin (XXII) and pH = 10.....	114
Fig. (32)	Uptake of Co^{2+} by chelating resin (XXVI) at different time periods and pH = (6.5 and 10)	115
Fig. (33)	Column technique apparatus	118
Fig. (34)	Uptake of metal ions (Cu^{2+} , Hg^{2+} and pb^{2+}) by chelating resin (XXVIII)at different time periods.....	121

SYMBOLS AND ABBREVIATION

GMA	Glycidyl methacrylate
4aapy	4-Amino-antipyrine
2ath	2 Amino-thiazole
DVB	Divinylbenzene
(AIBN)	2.2, Azobisisobutyronitrile
(BzO ₂)	Benzoylperoxid
MBA	Methylene 2, 2 -N,N - bis-acrylamide
AN	Acrylonitrile
en	Ethylenediamine
CS ₂	Carbon disulphide
PVA	Polyvinylalcohol