PURIFICATION OF WASTEWATER FROM HEAVY METAL IONS USING MODIFIED POLYMERS

By

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ABSTRACT

The present work is aiming to synthesis new monomers by reacting acryloyl chloride with different organic compounds capable to react with it such as aniline, 2-hydroxybenzoic acid, 1- aminonaphthalene, quinoline and others. Polymerization reaction of these monomers was carried out and the structures of the polymers were confirmed. As the polymers obtained differ from each other in their chemical structure they could be applied in different fields of application after its complete characterization. The polymers were characterized by using elemental analysis, solubility, molecular weight determination, spectroscopic and thermal analysis. The evaluation of the efficiency of these polymers in recovery of heavy metals showed that poly (2- acryloyloxy benzoic acid) is the most proper one. Blend of this polymer with chitosan was obtained and evaluated for the recovery of different ions of heavy metal.

Key words: Heavy metals, waste water purification.

1. INTRODUCTION

Discharging of heavy metal ions into water resources even in a small amount can affect the aquatic life and food web. Most of these heavy metal ions are harmful when brought in contact with living tissues for a long time. When present at high concentrations in the human body, copper can cause liver and kidney damage. The legislation limits for discharge of copper are recommended to be less than $2mg\ L^{-1}$ by WHO. Therefore, the removal of heavy metal ions from various water resources is of great scientific and practical interest. The sorption technique is

proved to be an effective and attractive process for the treatment of wastewaters [**Han et al., (2006)**]. Organo-clays and surface-modified mesoporous materials, [**Sayari, et al., (2005)**], activated carbons [**Clifford (1986)**] and a number of low-cost adsorbents such as agricultural residues and peat [**Al-Asheh (1997); Wafwoyo (1999); Suh(2000) and Reddad (2002)**] have been used for the removal of heavy metal cations

Functionalization of polymer is very interesting field of research and finds wide applications. These applications include engineering, physical and biological behaviors. The polymers can be functionalized either by introducing function groups in the chemical structure of the polymer using normal chemical reaction or by physical methods such as gamma irradiation grafting [**El Nesr et al., (1997) and Abdel-Bary et al., (1998 & 1997 & 1999 & 1998)**] for polymers not including function groups in their chemical structure such as polyethylene or polypropylene. The other method of modification is to synthesis new monomers containing the desired function groups followed by polymerization reaction of the monomers obtained. The first route of modification of existing polymers is faced by some problems such as the medium of the reaction and the extent of modification

Functionalized and reactive polymers have been of great scientific and commercial interest since the beginning of macromolecular chemistry. Many naturally occurring macromolecules, such as cellulose or rubber, have been chemically modified to control, mechanical properties or solubility. In recent decades, many synthetic polymers containing reactive groups have enabled the rapid development of markets for high molecular weight organic materials. Increased polymer recycling has also led to polymers containing enzymatically or chemically degradable functional groups. A polymer with amino groups bound directly to the backbone was obtained by copolymerization of the vinyl amine precursor such as *N*-vinyl-*tert.*-butylcarbamate with styrene, methyl methacrylate, or meth acrylic acid and a cross linking agent. The styrenic resin was selective for Cu(II) over Pb(II) and Cd(II) ,[**Tbal *et al.*, (1992)**]. Also, a polymer containing the amino group within the main chain of the polymer has been synthesized and roughly tested for the metal complexation behavior. Such polymers are polyalkylene polyamines [**Abdelaal (1997)**].

A chelating resin containing benzoylacetanilide or isothiouronium groups are capable of selective separation of different metal ions from the

mixture of the ions depending on the pH of the media, **[Majee (1988); (1989) and Schilde (1992); (1993)]**

ymeric materials carrying different ligands such as pyridine, imidazole, oxime, hydroxylamine, Schiff base, crown ethers, sulfur- and phosphorous-based ligands, pyridylazo-β-naphthol (PAN), etc. have been used similarly, **[Alexandratos (1996); Hwang (1997); Abdelaal (2000) and Kenawy (2000)]**

2 .Instruments and Techniques:
2.1- Instruments:
2.1.1- Infrared spectrophotometer:

IR spectroscopic analysis were carried out using a Perkin-Elmer model 1430 spectrophotometer in the range of 4000- 200 cm^{-1}, the samples were pressed as tablets with KBr.

2.1.2- The pH measurements:

pH of each sample solution was adjusted to be within the range of 2- 11 using a Beckman (Fullerton, CA) digital pH meter with glass and saturated calomel electrodes, calibrated on the operational state using standard buffer solutions at 25 ± 0.1 °C.

2.1.3- Ultraviolet / visible spectrophotometer

UV spectra were recorded on a Kontron Uvikon 810 double beam spectrphotometer. It was used for measuring the extent of discoloration of the degraded samples as a function of the degradation time.

2.1.4- Atomic absorption spectrophotometer. (AAS)

Metal analysis by using the AAS technique followed the direct aspiration into an air-acetylene flame using the atomic absorption spectrophotometer (Perkin- Elmer 2380,USA). The optimum experimental conditions for the Instrumental metal analysis are as follows: air flow rate 21dm^3/min. fuel flow rate 6dm^3/min, burner height 2.1 cm and working range 0-10 µg /ml. The wave length for Cd, Hg, Co, Cu, Pb, Fe are 228.8 nm, 253.7 nm, 232.0 nm, 324.8 nm, 217 nm, 248.3 nm respectively.

2.1.5- Thermal properties (TGA and DSC)

Differential Scanning Calorimeter (DSC) and Thermal gravimetric analysis (TGA) were carried out using thermo-analyzer (D-50),

Shimadzu, Japan. Samples were heated at heating rate 15° C/ min in presence dry nitrogen. The thermally inert reference material was sintered alumina (α- Al_2O_3).

2.1.6- Melting point apparatus
Melting points were uncorrected and taken on a Yanako micro melting apparatus.

2.2Materials
2.2.1. Available commercial polymers:
Chitosan was purchased from Sigma. It is of medium molecular weight having a degree of acetylation 69%.

2.2.2. Monomer
Acryloyl chloride was purchased from Aldrich and used as received without further purification.

2.2.3. Other chemicals
Aniline, 2- hydroxybenzoic acid, 1- aminonaphthalene were obtained from Adwic Company while 8- amino quinoline was obtained from (ICI) Tokyo Kasel. p-hydroxybenzaldehyde, thiourea and diethyl malonate were supplied by BDH.London,UK.

2.2.4. Solvents
Methanol, ethanol, toluene, methylene chloride, tetrahydrofuran (THF) and dimethyl formamide (DMF) were obtained from ADWIC Company. Anhydrous diethyl ether was obtained from SRL (SISCO Research laboratories), PVT.LTD, India.
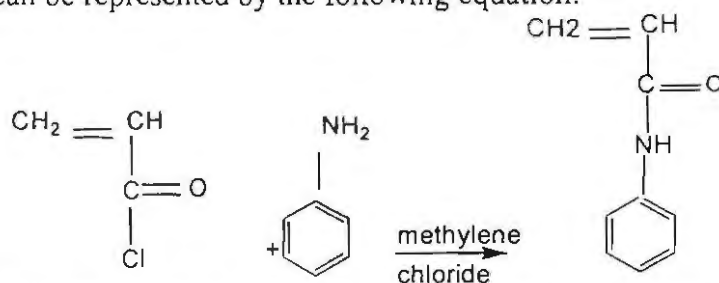
2.2.5. Initiators
Dibenzoyl peroxide (DBP) and Azo-bis-isobutyro-nitrile (AIBN) was supplied by Merck Germany.

2.3 Techniques
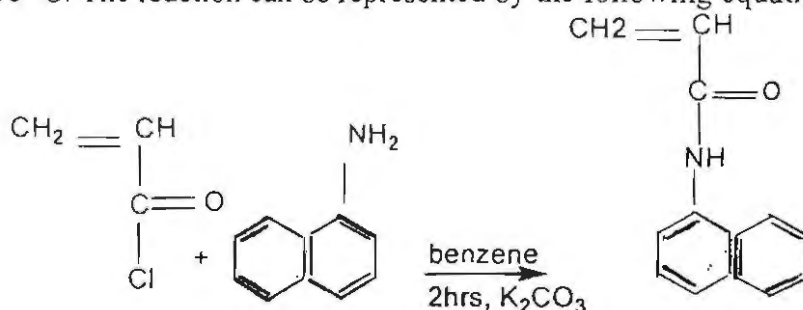### 2.3.1 Synthesis of N-acryloylanilide

The reaction can be represented by the following equation:

Acryloyl chloride was added dropwise to cooling stirred solution of (0.03 mole) aniline in 50 ml methylene chloride. The stirring was continued for 30 min .The product was extracted from methylene chloride by washing with 5 ml of hydrochloric acid solution, 5 ml of sodium hydroxide solution and finally 5ml water. The organic layer was separated in each case and the solvent was removed by rotary evaporation .The product was re-crystallized from ethanol. The melting point of the product =103 - 104°C.

2.3.2 Synthesis of N –acryloyl naphtylamide

Acryloyl chloride was added dropwise to cooling stirred solution of (0.03 mole) naphtyl amine in 50 ml methylene chloride. The reaction mixture was stirred for 2 hrs at room temperature. The reaction mixture was filtered off and the product was washed several times with water and then re-crystallized form ethanolic solution. The melting point for the product is 145-146° C. The reaction can be represented by the following equation:

2.3.3 Synthesis of N-8- aminoquinolione

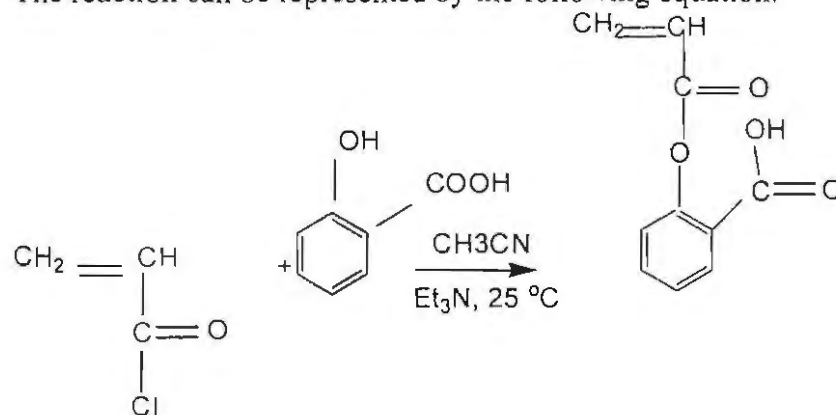This compound was prepared according to the method which described the reaction presented by this equation:
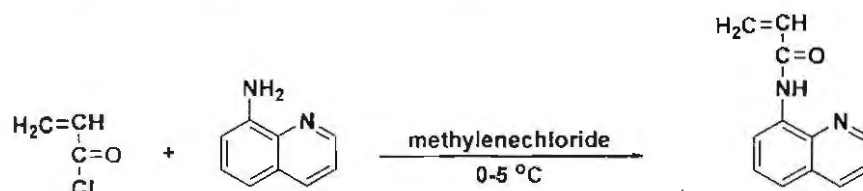
Eq. 3.5

The melting point is 78- 79 °C

2.3.4 Synthesis of 2- acryloyloxy benzoic acid

This compound was prepared according to the method previously described by Boudreaux (1997)].

The reaction can be represented by the following equation:

A 0.28 mole of acryloyl chloride in 50 ml acetonitrile was added dropwise to stirred solution of 2- hydroxy benzoic acid 0.26 mole and triethylamine 0.78 mole in 350 ml acetonitrile. After complete addition of acryloyl chloride, the solution was still stirred for 6hr at 25 °C. The solution mixture was filtered off and the precipitated triethylamine hydrochloride salt was removed. The filtrate was extracted with methylene chloride, wash with 1M hydrochloric acid solution and saturated sodium chloride solution. The methylene chloride was removed by rotary evaporation and the product was purified by coloum

chromatography silica gel (stationary phase) and (75: 22: 21) acetonitrile: methanol: ether solvent mixture.

2.3.5 Synthesis of polymers

The monomers obtained were characterized and subjected to polymerization using the following general method:

'In 50 ml of THF, monomer was dissolved and placed in a 100 ml, three necked, round bottom flask equipped with a nitrogen inlet tube, a rubber septum and a condenser connected to a water trap. The solution was purged with nitrogen for 30 min, using 1 mole % dibenzoyl peroxide as initiator dissolved in THF was injected through the rubber septum. The polymer was precipitated into 400 ml of anhydrous diethyl ether; the polymer was dried under vacuum at room temperature. The polymer of 4-acroyloxy benzoic acid was precipitated using methanol.
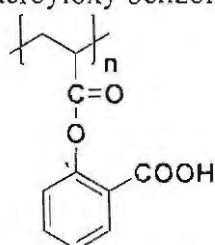
2.4. Analytical part:
2.4.1. Investigation for the efficiency of the modified polymer
2.4.1.1 Batch method

A sample solution (50 ml) containing a mixture of the studied heavy metal ions (100 µg ml^{-1}), were transferred to a glass stoppard bottle (250ml); after adjusting its pH to the optimum value, 0.1 g polymer was added to each solution. These solutions were stirred for 30 min with a mechanical stirrer. After filtration. the polymer was washed with bidistilled water, and the sorbed metal ions were eluted with 5 ml of 2 mol l^{-1} HCl and the resulting solution was adjusted to a final volume of 100 ml and determined by prestandardized flame AAS.

2.4.1.2 Effect of pH

The optimum pH for metal sorption was determined using the batch equilibrium technique. Excess metal ion (50 ml of 100 µg ml^{-1}) was stirred with 100 mg of polymer for 30 minutes in the presence of different buffer solutions in the 1.0 –8.0 pH range. The ionic strength of these solutions was kept constant at 0.1 mol l^{-1} using potassium nitrate

solution. After equilibrium, the polymer was filtered off through a sintered glass Goosh (G_4), and the concentration of the metal ion remained in the filtrate was determined spectrophotometrically or by AAS as usual.

2.4.1.3. Determination of the resin capacity

The capacity of the resin was determined by stirring excess (100 ml of 100 µg ml^{-1}) of the studied metal ion solution, with 100 mg of the polymer for 2 h at the optimum sorption pH. The resin was filtered off and the capacity of the resin was determined as usual.

2.4.1.4. Kinetics of metal ion sorption

To determine the exchange kinetics for the metal ion under investigation, 100ml of 100 µg ml^{-1} of metal ions at optimum pH were stirred with 100 mg of the polymer at room temperature for different time intervals up to 60 min. Then the concentration of sorbed metal ion was determined after elution step; as usual.

3- RESULTS AND DISCUSSION

3.1 Recovery of heavy metal:

Functionalized polymer can be used for recovery of heavy metals acting as ion exchanger. This occurs when the function group in the polymer is able to form salt like compound or to chelate the metal ions in the polymer. Thus if one examines the chemical structure of poly(N-acroylanilide) and poly(N-acrloylnaphthylamide) cannot find function groups able to form salts or chelate the metal ions. For this reason our trials to examine these polymer to recovery heavy metal showed that only poly (2-acroxylyl benzoic acid) is capable to chelate the metal ions. Accordingly, its efficiency has been carefully investigated as follows.

3.2 IR Absorption bands poly (2-acryloyloxybenzoic acid) PAOB:

The characteristic absorption IR bands for 2-acryloyloxybenzoic acid are listed in Table (2):

Table (1): IR spectral data of 2-acryloyloxybenzoic acid.

Group	Absorption, v cm^{-1}
O-H (stretch)	3020
C-H (olefinic)	2714, 2659, 2596
C=O (ester)	1747
C=O (acid)	1679
CH$_2$=CH- (stretch)	1616
C=C (aromatic)	1620, 1460, 1416

After polymerization of 2-acryloyloxybenzoic acid by the method mentioned in experimental part. the corresponding poly (2-acryloyloxybenzoic acid) was obtained. The IR spectra showed that the absorption band of the vinyl group disappeared indicating the complete polymerization of the monomer.

The polymer has the chemical structure:
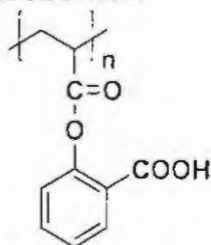
The polymer was found to be soluble in tetrahydrofuran (THF), dimethylformamide (DMF), dioxin and DMSO while it was found to be insoluble in water, alcohols and diethyl ether and benzene.

3.3 Thermal characterization analysis:

From **DSC diagram** of **poly** (2-acryloyloxybenzoic acid), it can be seen that (Tg) is about 190^{0}c and the oxidation exothermic peak appears at 457^{0}c. The high (Tg) value of this polymer compared to poly (N-acryloylanilide) may be due to the intramolecular hydrogen bonding in polymer structure which may restrict the rotation around the sigma bond in the backbone chain of the polymer. It is interesting to note that the exthothermic peak in case of poly (2-acryloyloxybenzoic acid) is slightly less than in case of poly (N-acryloylanilide) and poly (N-acryloylnaphthylamide). This may be attributed to the ease of oxidation of the functional group of this polymer.

TGA of poly (2-acryloyloxybenzoic acid) was measured. From the results obtained it can be seen that the polymer starts to lose about 62% of its original weight at 140^0C and about 14% at 300^0C this indicates that polymer is less thermally stable than poly (N-acryloylanilide) and poly (N-acryloylnaphthyamide). The loss in weight in this case of this polymer occurs as a result of decarboxylation of the carboxylic group. The energy band of this group is low at 92^0C followed by the capture of COO group at 250^0C and the backbone chain C-C started to break at 415^0C.

3.4 Recovery of metal ions by poly (2-acryloyloxybenzoic acid) PAOB:

The main factors affecting the recovery of heavy metals are pH of the medium and stirring time [Maloon C." (1999) ,Kenawy I (2000). Hafez M.(2000); Akl (2005)]

These two factors were investigated and the results obtained are given below:

3.4.1- Effect of pH:

The pH value of the medium is known as a controlling factor and it has a direct effect on most of the investigated processes. In the current investigation, Figure (1) shows the effect of pH on the sorption efficiency of the different investigated metal ions by the polymer-supported salicylic acid as an extracting matrix. It can be noticed from figure (1) that the sorption process is pH- controlled and there is a proper pH for each type of metal ions. This proper pH value lies around pH = 4.5 for all investigated metal ions.
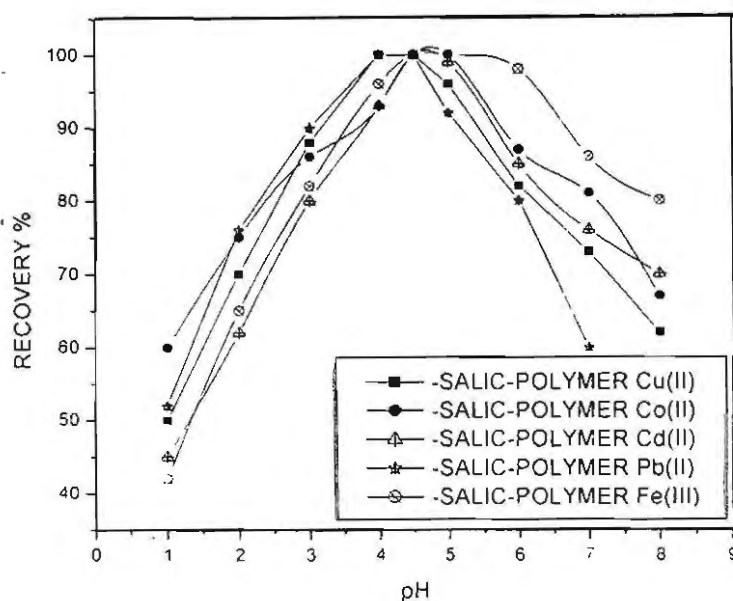
Fig (1): Effect of pH on the sorption efficiency of Co (II), Cu (II), Cd (II). Pb (II) and Fe (III) by using polymer-supported salicylic acid. (Conditions: mass of polymer =100mg, stirring time =30 min at.25°C).

3.4.2 Stirring time:

To determine the rate of sorption of metal ions on the polymer. batch experiments were elaborated by stirring 100 mg of the polymer with 50 ml of feed solution containing metal ion at room temperature (25°C). Aliquots of 1ml solution were taken out for analysis at pre-determined intervals. The concentration of metal ion in the supernatant solution was determined and the amount of metal ion sorbed on the modified resin was consequently calculated by mass balance.

From fig.(2), it can be observed that the maximum sorption of Co (II), Fe (III) Cu (II), Cd (II) and Pb (II) on the polymer reaches its equilibrium time after 12, 15, 20, 20, and 25 min, respectively. This indicates that stirring time is a factor playing an important role in the sorption process. It helps the metal ions to reach the chelating centers in the polymer matrix through a possible diffusion controlled process.
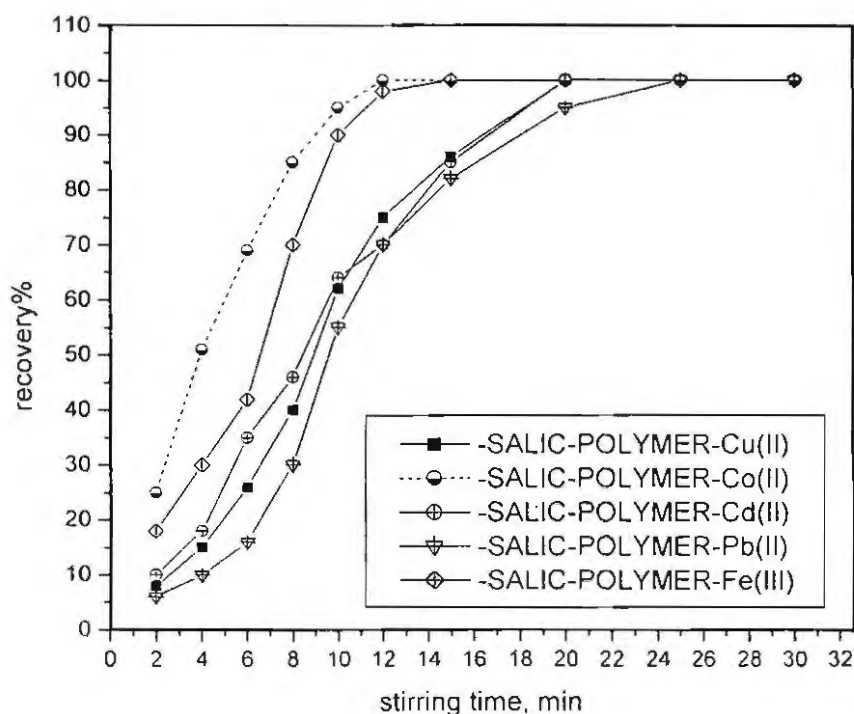
Fig (2): Effect of stirring time on the sorption efficiency f polymer-supported salicylic acid. Co (II), Cu (II), Cd (II), Pb (II) and Fe (III). (Conditions: mass of polymer =100mg, pH =4.5 at 25°C).

3.4. 3- Choice of eluent:

It was found that, 5ml of 2mol/l of all acids could afford quantitative elution of metal ions from the polymer. Subsequent elution of the metal ion was carried out with hydrochloric acid solution taken the advantage that, chloride ion is an acceptable matrix for most of the techniques which are practically applied for the determination of metal ions. Figure (3) represents the behavior of the investigated polymer-supported salicylic acid as an extracting matrix towards the different metal ions under consideration.

It was also noticed that, the lower the concentration of hydrochloric acid, the larger the volume of acid solution needed for the quantitative stripping of metal ions. This has, of course, its impact on the heavy metal ion recovery from an economical point of view.
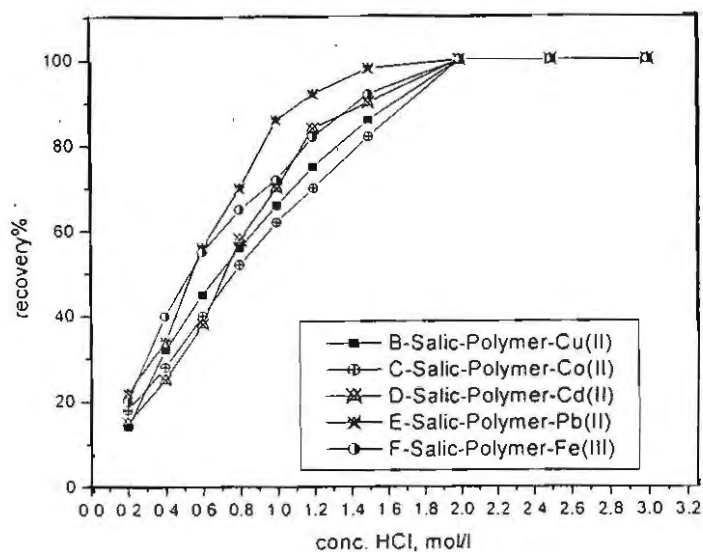
Fig (3): Effect of the concentration of HCl on the recovery of Co (II), Cu (II), Cd (II), Pb (II) and Fe (III) by polymer-supported salicylic acid. (Conditions: volume of eluent = 5 ml, mass of polymer =100mg, stirring time =30 min at 25°C).

3.5 - Determination of sorption capacity:

The sorption capacity of the polymer for the metal ions under investigation was determined by stirring excess metal ion with 100 mg of the resin under optimum conditions. The maximum sorption capacity (mg g^{-1}) for Co (II), Fe (III) Cu (II), Cd (II), and Pb (II) is 41.5, 30, 40.0, 36, 21.0 and 21.0 mg/g polymer (PAOB), respectively.

3.6 Characterization of the chelated poly (2-acryloyloxybenzoic acid) with some metal ions:

3.6.1 Infrared spectroscopy:

The modified polymeric products and their complex with different metal ions were characterized by IR spectroscopic analyses. The results are summarized in Table (3). Comparison of the IR spectra of the polymer before and after chelation with the investigated metals ions after drying in a vacuum dissector for 24 hs shows that the absorption bands corresponding to the carbonyl groups for both ester and carboxylic groups are shifted as a result of the interaction between the polymer and the metal ion under investigation. Such interaction can be explained by a

bond formation between the carbonyl group and the metal ions. In addition, a new band appears at the range from $531 cm^{-1}$ to $518 cm^{-1}$ due to the bond formed between oxygen and metal ions for all complexes. The polymeric legand and its complexes under investigation are characterized by the presence of water molecules to fulfill the co-ordination of the metal ions. After chelation, the absorption band corresponding to C=O of the ester group has been shifted from $1748 cm^{-1}$ to $1740 cm^{-1}$ in case of Cu (II) and to about $1715 cm^{-1}$ in case of chelation with Pb(II) and Co(II) while shifted into $1700 cm^{-1}$ in case of chelation with Fe(III). Also, the absorption band at $1662 cm^{-1}$ corresponding to C=O of the free carboxylic acid group has been shifted in to $1657 \pm 2 cm^{-1}$ after chelation with the investigated metal ions.

Besides, the absorption band at $3249 cm^{-1}$ corresponding to OH group of the free carboxylic acid functionality has been shifted to about $3238 cm^{-1}$ In addition, an absorption band at $525 \pm 5 cm^{-1}$ corresponding to the band formed between the metal ion and the oxygen atom of the carboxylic acid grouping the form of metal carboxylate (M-O) was observed after chelation. This observed shift in the absorption band OH group and the appearance of M-O absorption band after chelation indicates that the carboxylic group has been involved in the chelate formation and, thus, chelation can be performed through coordination with the carboxylic group and /or by replacing the acidic hydrogen of the carboxylic group in the polymer. The probable modes of chelation of poly (2-acryloyloxybenzoic acid) with metal ions schematically represented in scheme 1 [Bellamy (1964)],
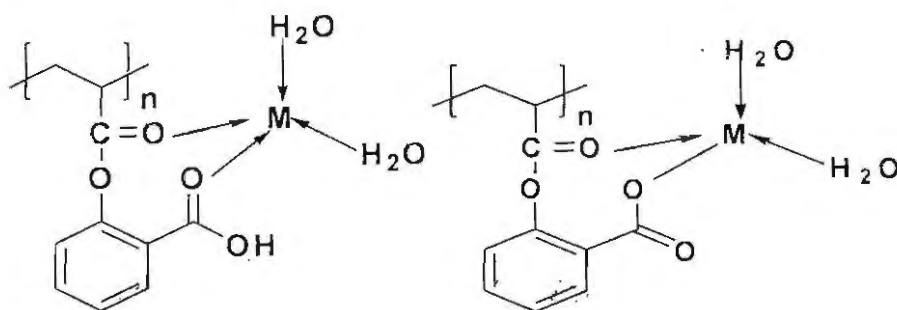
Scheme (1): Probable modes of chelation of poly (2-acryloyloxybenzoic acid) with metal ion.

Table (2): Infrared spectrum data of poly(2-acryloxy benzoic acid and its complexes with some metal ions and their colour.

Compound	Colour	Band Assignment	IR band v, cm^{1-}
Poly(2-Acryloxyl benzoic acid)PABA	Pale white	v (O-H)	3249
		v (C=O)ester	1748.5
		v (C=O) acid	1662.4
		v (C-H) aliphatic	3053,2938
		v (C-H) aromatic	2087,1983,1953
		v (C=C) ring	1610.11
PABA-Cu(II)	Green	v (O-H)	3228
		v (C=O)ester	1740
		v (C=O) acid	1659
		v (M-O)	531
PABA-Fe (III)	Brown	v (O-H)	3238.7
		v (C=O)ester	1700
		v (C=O) acid	1657
		v (M-O)	518
PABA-Pb (II)	Pale white	v (O-H)	3238.7
		v (C=O)ester	1714
		v (C=O) acid	1659
		v (M-O)	520
PABA-Co (II)	Pale yellow	v (O-H)	3237.7
		v (C=O)ester	1716
		v (C=O) acid	1655
		v (M-O)	520

3.6. 2. - Thermogravimetric analysis:

Thermogravimetric analysis has been conducted for Cu (II); Fe (III) and Hg (II) chelated with chitosan as representatives for metal ions in addition to the chitosan alone for comparison. From comparison of the thermographs in all cases, one can easily notice similarity of chitosan to poly(2-acryloyloxybenzoic acid). The only difference between chitosan and poly (2-acryloyloxybenzoic acid) is in the extent of thermal degradation of the investigated polymer under the effect of these chelated metal ions. This is not due to the thermal stability of the polymer it self, but may be due to the less amount of the free metal ions exiting in the polymer matrix.

3.7 Utilization of chitosan in metal ion recovery:
3.7.1. Factors affecting metal recovery by chitosan:

Two factors have been investigated as they are expected to be the highly effective on the metal recovery by chitosan, namely, pH, and stirring time. A range of pH has been tested from pH =3 up to pH=8. Figure (4) shows the dependence of metal recovery on pH for Cu (II) and Hg (II) sorbet by chitosan and PAS. It can be noticed that chitosan reaches its maximum efficiency to sorbs Hg (II) at pH = 4.5-5. While it was attained at pH=5 and extends up to pH=7 for Cu (II).
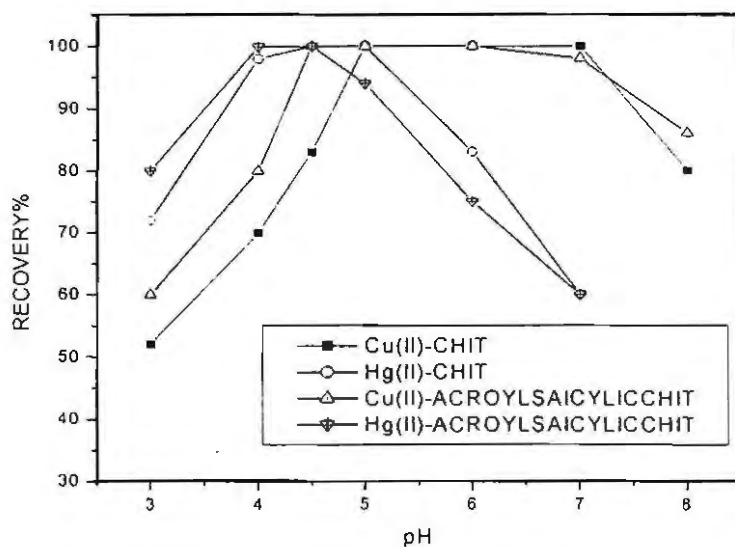

Fig (4): Effect of pH on the sorption efficiency of Cu (II) and Hg (II). For chitosan and its blends with PAS (Condition: mass of polymer =100mg, stirring time =30

Investigation of the dependence of metal recovery on the stirring time is shown in Fig (5). It is clear that the extent of metal ions recovery increases with increasing the time of stirring until equilibrium which can be attained firstly for Cu (II) after about 10 min: while it needs at least 20 min for Hg (II)
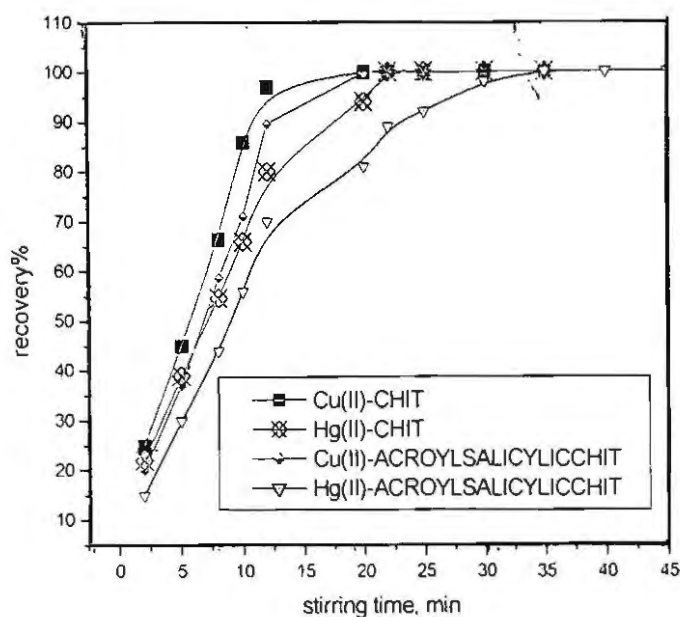
Fig (5): Effect of stirring time on the sorption efficiency of Cu (II) and Hg(II) for chitosan and its blends with PAS.

3.7.2 Determination of sorption capacity:

The sorption capacity of chitosan and blended chitosan with poly (2-acryloyloxybenzoic acid) for the metal ions under investigation was determined by shaking excess metal ion with 100 mg of chitosan and blended chitosan with poly (2-acryloyloxybenzoic acid) under optimum conditions. The maximum sorption capacity (mg g^{-1}) for Cu (II) and Hg (II) is 140, 180 and 105, 120 mg / g polymer blend (PAOB/Chitosan), respectively.

3.7.3. Characterization of chelated chitosan:
3.7.3.1- Infrared spectroscopy

The absorption band at 1725 cm^{-1} corresponding to amide I functionality and characteristic for chitosan with the N-acetylated units is present in all the IR spectra obtained. In case of chelated chitosan with metal ion, a new absorption band at 1632 cm^{-1} appears which is corresponding to the bending in plane (scissoring) of N-H band. This absorption band is also present in the un-chelated chitosan but as a shoulder at 1605 cm^{-1} which is shifted to a higher wave number due to the

interaction with the investigated metal ions. In the region of 3000 cm^{-1} to 3700 cm^{-1} of the spectrum, chitosan exhibits absorption band corresponding to the stretching vibrations of OH the groups. Such absorption band overlaps the stretching vibrations band of NH causes broadening of the OH absorption band at the concerned region. On interaction of chitosan with metal ions, the absorption bands will be separated and the stretching of O-H band was observed at 3443 cm^{-1} and 3111 cm^{-1}, while the stretching vibration band of N-H band was observed at 3264 cm^{-1}.

Another significant change was observed in the region from 1000 cm^{-1} to 1200 cm^{-1}. In this region chitosan presents a broad band centered at 1076 cm-1 associated with the stretching vibration of C-O bond. This band is unfolded in presence of metal ions and appears as a band at 1116 cm^{-1} corresponding to the stretching vibration of C-O bond of C3 of chitosan (secondary OH). The absorption band at 1023 cm^{-1} is produced by the C-O stretching vibration at C6 of chitosan (primary OH) while the absorption band at 1076 cm^{-1} corresponds to the symmetric stretching vibration of C-O-C bond. The asymmetric stretching of C-O-C bond appears also at 1155 cm^{-1}.

The above-mentioned interpretation of the observed absorption bands in the IR spectra verifies the interaction of, not only the amino groups of chitosan, but also the OH groups with of Cu (II) and Hg (II) (Figs. 6 and 7). This is most probable due to formation of complexes with the investigated metal ions.
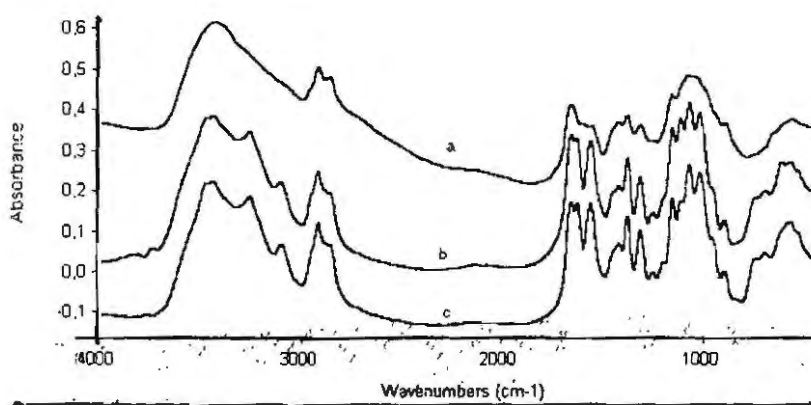

Figure (6): FT-IR Spectra of a) Chitosan, b) Chitosan -Cu and c) Chitosan–Hg.
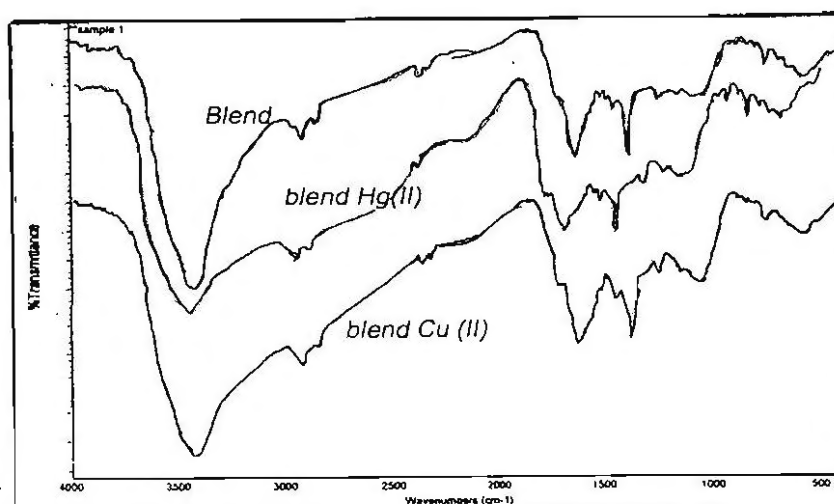
Figure (7): IR Spectra of blend Chitosan with poly(2-acryloyloxybenzoic acid); blend Hg(II); blend Cu(II)

3.7.4. Chitosan blended with poly (2-acryloyloxybenzoic acid) for metal recovery.

A trial has been made to investigate the possibility to use a combination of chitosan and poly (2-acryloyloxybenzoic acid) as both possess higher recovery of metal ions from their aqueous solution as mentioned before. Thus, the two polymers were dissolved in the proper solvent for each.

Evaporation of the solvent after mixing resulted in formation of a blend from chitosan and poly (2-acryloyloxybenzoic acid). The obtained blended has been characterized by IR spectroscopic analysis and by thermogravimtric analysis.

Recalling the dependence of metal recovery on pH for the chitosan blend, Fig. 4 shows that the maximum metal recovery could be attended in case of chitosan blends at pH slightly lower than that required for chitosan itself. pH = 4:4.5 was required for Hg (II) while pH = 4-5 was required for Cu (II) using chitosan blend.

On other hand, dependence of sorption of efficiency of metal ions on the stirring time for chitosan blend has been investigated. Figure (5) shows clearly that there is almost no difference between blended and unblended chitosan in case of Cu (II). In both cases, about 10 min were readied for maximum sorption of Cu (II) to be attended. In case of Hg

(II), 35 min were required for unblended chitosan.

TGA showed a loss of weight of 48% starts at about 120 °C. A second stage of weight loss starts at about 500 °C reaches 29% with peak temperature at 593 °C. Apart from the small extent of the weight loss at about 80 °C, the obtained blend can be considered thermally stable. Thus blend has been tested for utilization in metal ion recovery using Cu (II) and Hg (II) as representatives for metal ions to be recovered. The chelated blend showed similar behavior to that for chitosan in the light of their ability to recover metal ions from aqueous solution.

TGA of the blended chitosan after metal recovery was carried out for three different metal ions.. It is very important to observe that the weight loss depends again on the type of metal ions present in the polymer matrix after recovery of metal ions for example; Hg (II) as mentioned before, slightly affects the degradation of the polymer. It seems that Fe (III) markedly affects the extent of weight loss compared with Cu (II). Thus, the efficiency of blended chitosan to absorb these metal ions can be arranged in the following order: Fe (III)> Cu (II) >Hg (II). On comparison of the thermal stability of the blended chitosan with that of poly (2-acryloyloxybenzoic acid), it can be noticed that the thermal stability is higher for the blended chitosan while still lower than that for the unblended chitosan. This indicates that the concentration ratio of the blend components is not 1:1 as it has been prepared during the metal recovery from their corresponding solutions. Poly (2-acryloyloxybenzoic acid) may enable chitosan to be dissolved in water due to protonation by its carboxylic group. This means that one has to consider this behavior when chitosan will be mixed with other polymers containing carboxylic groups hence, concentration of chitosan in its blended may be decreased and this explains the lower efficiency of the blended chitosan in metal ion recovery compared with the unblended chitosan as mentioned before.

3.7.5 Thermogravimetric analysis:

Thermogravimetric analysis has been conducted for Cu (II); Fe (III) and Hg (II) chelated with chitosan with as representatives for metal ions in addition. to the chitosan alone as a· blank for comparison. Comparison of the thermographs in all cases, one can easily notice that similar observation to those for poly(2-acryloyloxybenzoic acid) were found in case of chitosan. The only difference between chitosan and poly (2-acryloyloxybenzoic acid) is in the extent of thermal degradation of the investigated polymer under the effect of these metal ions. This is not due

to the thermal stability of the polymer itself, but may be due to less amount of the free metal ions exiting in the polymer matrix as the efficiency of chitosan in chelating seems to be higher than that poly (2-acryloyloxybenzoic acid). It is interesting to notice that in the case of Hg (II) recovered by chitosan, it has practically no effect on the degradation of chitosan as Hg (II) is not able to induce the thermal degradation of the investigated polymer.

4- CONCLUSIONS

Some of the synthesized polymers are able to recover some heavy metals from their aqueous solution, the efficiency of the recovery dependence on the chemical structure of the polymer and the type of heavy metal.

The most effective polymer for recovery of heavy metal is poly (2-acryloyloxybenzoic acid). The maximum sorption capacity (mg g-1) for Co (II), Fe (III) Cu (II), Cd (II), and Pb (II) is 41.5, 30, 40.0, 36, 21.0 and 21.0 mg/g polymer, respectively.

Blends the poly (2-acryloyloxybenzoic acid) with chitosan lower the efficiency chitosan itself in recovery of heavy metal.. The maximum sorption capacity (mg g^{-1}) for Cu (II) and Hg (II) is 140, 180 and 105, 120 mg / g polymer, respectively.

5- ACKNOWLEDGEMENT

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تنقية مياه الصرف من أيونات العناصر المعدنية الثقيلة باستخدام بلمرات معدلة كيميائيا

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يتناول هذا البحث تخليق مونمرات جديدة عن طريق تفاعل اكريلويل كلوريـــد مـــع مركبـــات عضوية مختلفة مثل الانيلين و ٢- هيدروكسى حمض البنزويك و ١- امينونافثالين وكينـــولين وغيرها . وتم بلمرة هذه المونمرات ، واثبات تراكيبها الكيميائية. وحيث ان البلمرات الناتجـــه مختلفة فى تراكيبها الكيميائية فلابد ان يكون لها تطبيقات مختلفة فى مجالات متعـــددة. وتـم توصيف هذه البلمرات باستخدام طرق التحليل الدقيق للعناصر واختبار النوبانيه وتعيين الكتلة الجزيئية بدلالة اللزوجة وكذلك طرق التحليل الطيفى والحرارى. كما تم تقـــويم كفـــاءة هـــذ البلمرات فى استخلاص ايونات المعادن الثقيلة حيث وجد ان بولى(٢-اكريل اوكسى حمـــض البنزويك) هو افضل البلمرات موضع الدراسة. كما درس تاثير توئيفة من هـــذا البلمـــر مـــع الكيتوزان كبلمر طبيعى المنشأ على كفاءة استخلاص ايونات العناصر الثقيلة.