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Novel Complexes of Copper with modified grafted cellulose copolymer and its application

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Abstract

Complex of grafted cellulose copolymer was prepared from the reaction of cellulose with monomer (N-methacryloxyphthalimide). This monomer was prepared from the reaction of metha acrylic acid with N-hydroxyphthalimid in presence of N,N-Dicyclohexylcarbodiimide(DCC). The prepared compounds were characterized by IR,^{1}HNMR, X-ray, scanning electron microscopy (SEM), transmission electron microscopy(TEM), electronic spin resonance(ESR) and the Biological activity for these compounds were also studied and give positive antibacterial and antifungal

Keywords: Monomer(n-methahydroxyphthalimid), cellulose- salt of copper chlorid.

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1. Introduction

The last years have seen the rise in popularity of attaching chemically reactive species to insoluble supports. A wide variety of vinyl-derivatized molecules can be obtained and polymerized or copolymerized to produce functionalized supports. Among the active groups that have been introduced into polymer chains are groups which are known to act as stabilizers, complexing agents, pharmaceuticals and catalysts. Several activated esters and amides of acrylic and methacrylic acid and their polymers have been described.

The work is now extended to the synthesis and polymerization of N-methacryloyloxyphthalimide as well as the reaction of the resulting polymer with hydroxy and amine compounds [1].

Metal coordination polymers have been widely studied as they represent an important interface between synthetic chemistry and material sciences. The synthesis of coordination polymers with different metal ions and ligands has led to a wide range of potential applications as, e.g,. molecular wires, electrical conductors, molecular magnets, in host–guest chemistry and in catalysis. Briefly, these materials consist of inorganic metal centers assembled by means of multifunctional polydentate organic ligands.

The structure and properties of coordination polymers depend on the coordination habits and geometries of both metal ions and connecting ligands, as well as on the influence of secondary interactions such as hydrogen bonding, π–π stacking interactions and so on. Several factors, including the coordination bonds and secondary interactions, the metal-to-ligand molar ratio, the coordinative function of the ligands, the type of metal ions, the presence of solvent molecules, counter ions and organic guest molecules should be taken into account in the process of the design and synthesis of metal coordination polymers [2].

Graft copolymers separate or enrich metal ions by simple chelation, adsorption, ion exchange or simple sorption processes. These can be tailored to combine most of these attributes to increase their efficiency for use in water technologies. Grafting is a simple technique to incorporate desired active functional groups on the backbone of polymers for the sorption of metal ions. Use of different types of graft copolymers and networks based on cellulosics and other natural polymers is an area of recent research interest in the field of active polymer supports for metal ion sorption [3].

2. Experimental

2.1. Materials

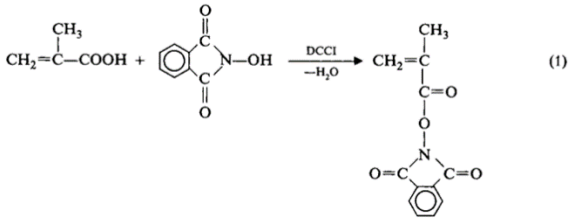
N,N-Dicyclohexylcarbodiimide(DCC),methacrylic acid and the free radical initiator(azoisobutyronitrile (AIBN),ceric ion) ,Cellulose and N-hydroxyphthalimide were from Aldrich. salts of copper chloride were from E. Merck. All solvents used were of reagent grade and were purified by distillation before use

2.2. Method

2.2.1. Synthesis of monomer (N-methacryloyloxyphthalimide)

N-mthacryloxyphthalimid was prepared according to a known general procedure [1] To a well stirred cold solution (0"C to 5 "C) of N-hydroxyphthalimide (2 mol) and methacrylic acid (2 mol) in 50 ml of dry dichloromethane, (2 mol) N,N-dicyclohexyl-carbodiimide(DCC) were added in one portion. The

reaction mixture was stirred for 8 h. The precipitated dicyclohexylurea was then removed by filtration and the filtrate was dried in vacuo. The residue was then recrystallized from benzene/petroleum ether (40-60ºC), 20/80, v/v). the yield of recrystallized product usually ranged from 92- 96%, m. p. 114- 115 "C

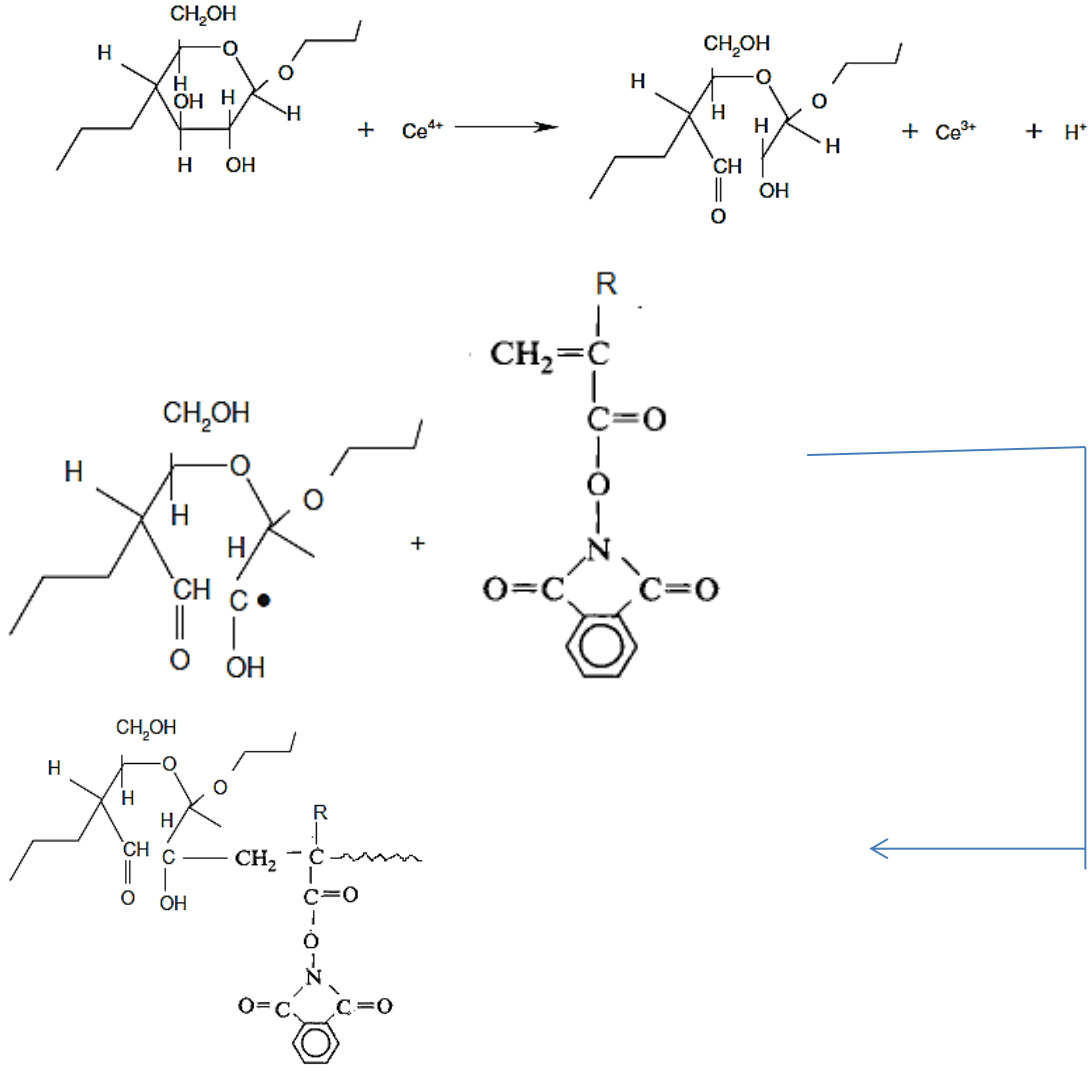


N-methacryloyloxyphthalimide (mon. 2)

The monomers were a crystalline solid, yellowish white, easily soluble in most organic solvents, but sparingly soluble in aliphatic hydrocarbons, such as n-hexane and petroleum ether

2.2.2. CoPolymerization of cellulose with prepared monomer (modified cellulose)

Solution(1gm) of the prepared monomer and(1gm) cellulose in(4ml) DMF was treated with CAN(ammonium ceric nitrate) (0.1gm)were mixed in a polymerization tube and kept in a thermostated water bath, the reaction mixture was allowed to stand at 70°C for 12 h. The polymer was obtained by reprecipitation in methanol, forming a viscous sticky white precipitate, which was isolated, washed with methanol and purified by repeated precipitation by methanol from a solution of DMF. The yield



Copolymer (cellulose with monomer) Scheme 1

2.2.3. Synthesis of cellulose polymer complexes with copper metal

Polymer Complex of copper metal with every one of (monomer, cellulose and copolymer) is prepared by molecular Wight of salt of copper chloride, monomer (N-mthacryloxyphthalimid), cellulose and copolymer where there are four cases. In every case dissolve the salt and the ligand two beaker with aliphatic alcohol(methanol) and heat the two beakers in weak temperature, reflux more than 100 ºC for 8 hours after that we heat the mixture for 15 minutes from 60c to70 ºC don't increase 80c and dry the mixture in dish for two days or more even form crystalline. The colored crystals were obtained (green for copper – purple for cobalt – reddish brown for iron).

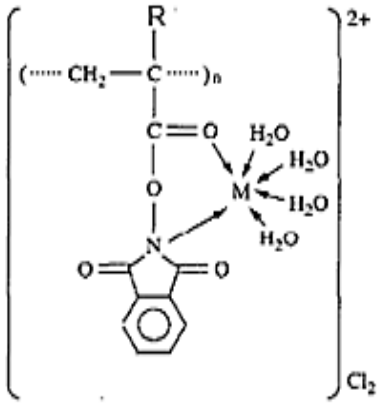


Fig (1): complex of monomer {N-methacryloyloxyphthalimid} with copper metal [5]

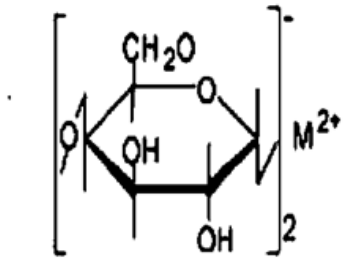


Fig (2): Polymer complex (cellulose with copper)[6]

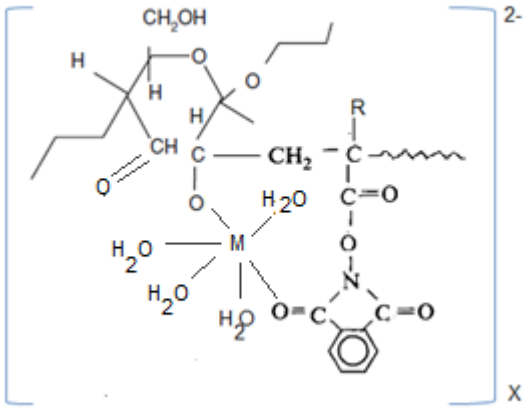


Fig (3): Polymer complex (copolymer with metal)
Where M= cu(II) R= CH_3 X=Cl_2

2.3. Characterization

Characterization of the core polymer supports, and their functional derivatives were done by chemical and spectral analysis.

1) The structures of monomer were confirmed by analysis, IR and ^{1}HNMR spectroscopy.
2) Cellulose and copolymerization was confirmed by IR.
3) We investigated the polymer complexes by IR, esr, x-ray (sem & tem) and anti-biological effect.

3. Results and discussion

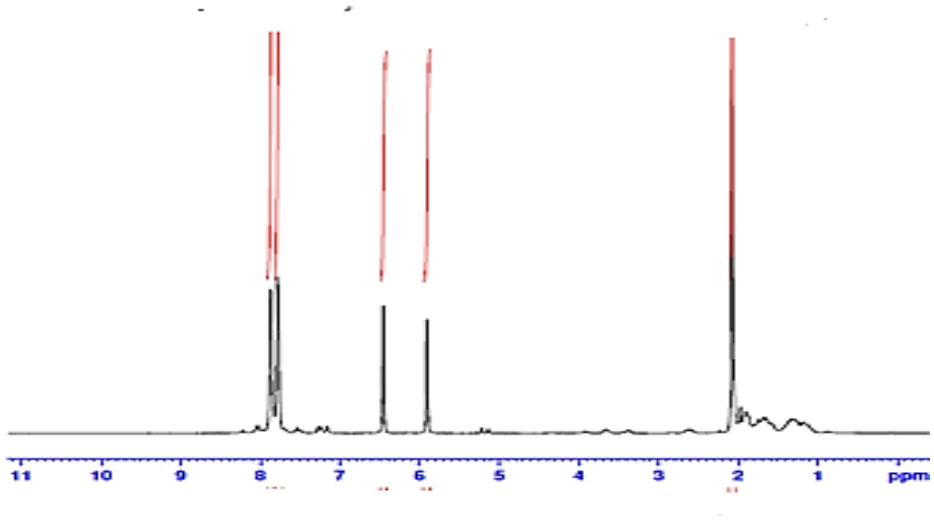


Fig (4): [1]HNMR spectrum of monomer (2) N- methaacryloyloxyphthalimid

It shows resonance absorption at 7.80 and7.76 ppm (aromatic protons), 6.4 and 5.85 ppm (2H) [olefinic protons]. The methoxy protons give a peak at 2.2 ppm [8].

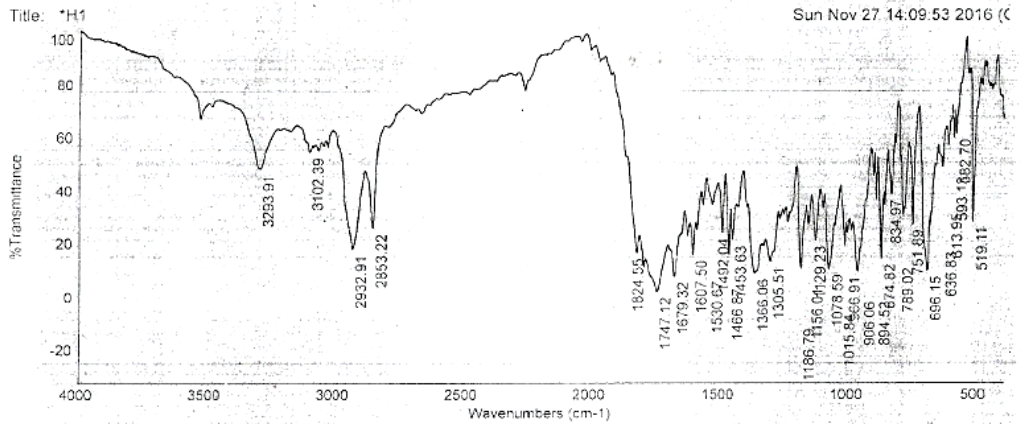


Fig (5): IR spectra of monomer N- methacryloyloxyphthalimid

IR (cm−1): 3102 (aromatic C-H stretching), 2932 (olefinic C-H stretching) correspond to the C-H stretching of methyl and methylene groups., 1824 (-CO-OR) ester group, 1747 (C=0 stretching due to phthalimido group), 1679 (olefinic C=C stretching) [8].

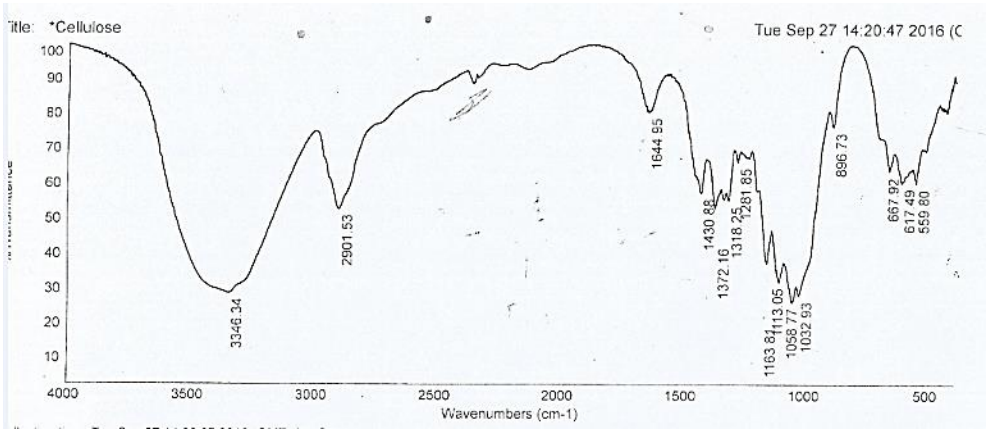


Fig (6): IR of cellulose

The IR spectrum of cellulose exhibited the main characteristic cellulose peaks. Absorbance at 3348 cm^{-1} (-OH stretching), 2903 cm−1 (C-H stretching), 1664 cm^{-1} (C-C ring stretching and –OH in plane bending), 1430 cm^{-1} (-CH2 bending), 1371 cm^{-1}

(-CH bending) and 1058 cm−1 (C-O-C stretching) [7].

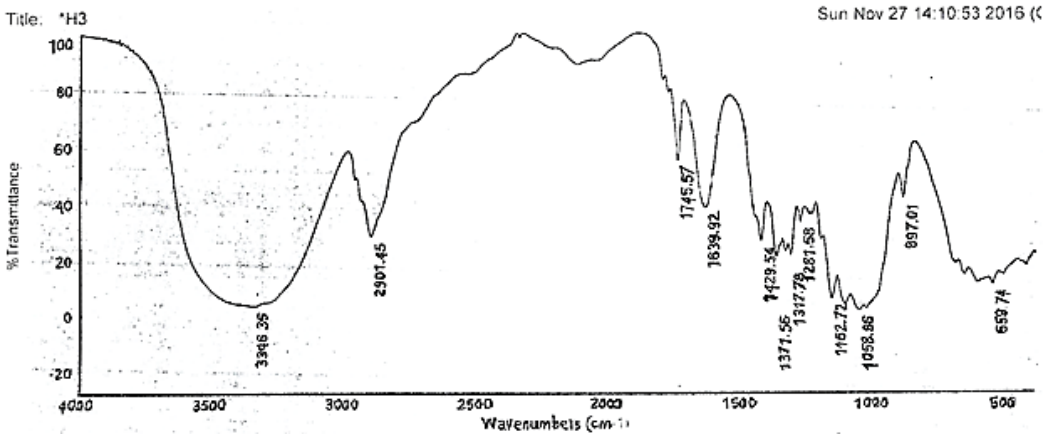


Fig (7): IR spectra of copolymer compound

The spectrum of the grafted cellulose shows the -OH stretching frequency appeared at 3345 cm^{-1} while that of the imine -CH stretching frequency appeared at 2903 cm^{-1}. in addition to the characteristic peaks of the cellulose, on oxidation the pyranose ring is cleaved at C2-C3 and hence the C-C ring stretching frequency is not observed in the modified cellulose. A new peak at 1639 cm^{-1} is supports the formation of methyl benzalaniline pendent groups in the chemically modified cellulose and strong sharp band at 1745 cm which corresponds to the stretching of the carbonyl group of the grafted [7].

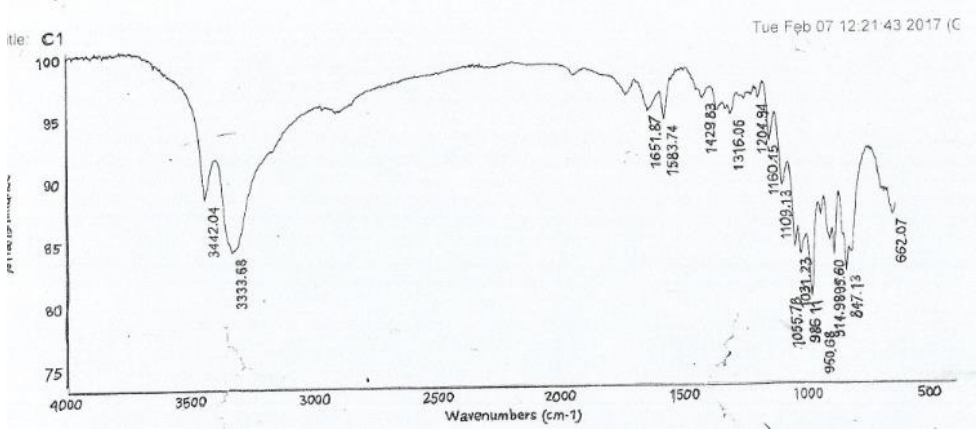
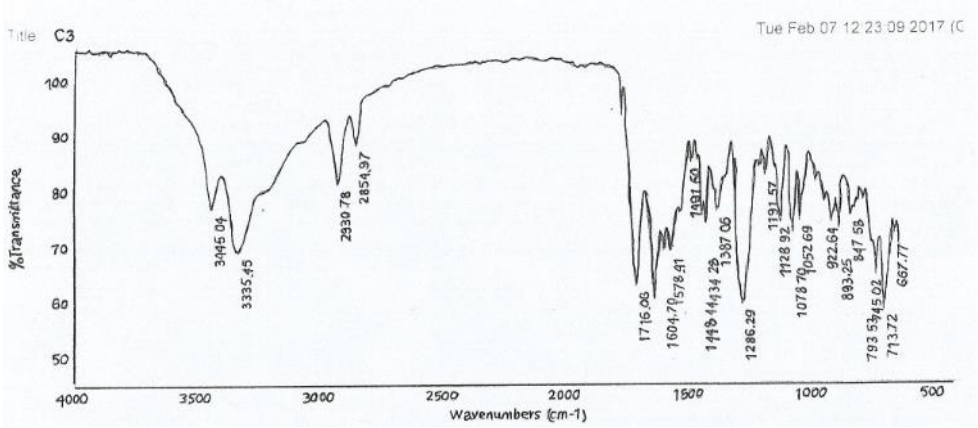
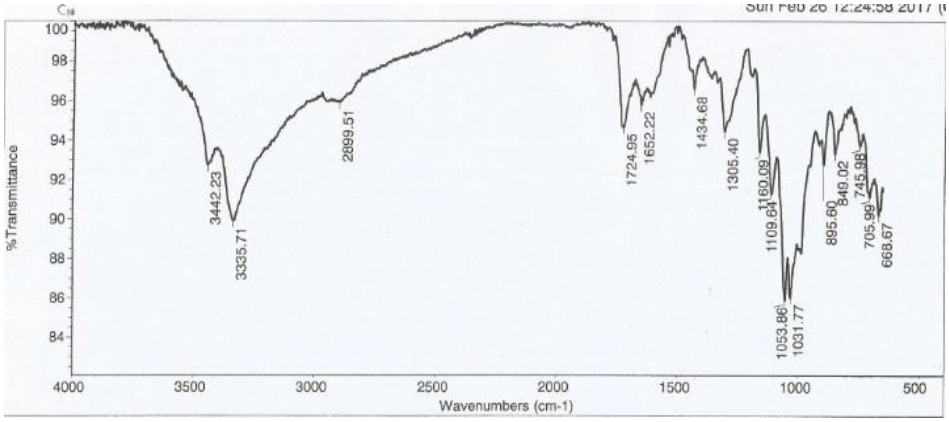


Fig (8): IR of CU metal with cellulose(I)



Fig(9): IR of Cu metal with monomer(II)



Fig(10): IR of Cu metal with copolymer(III)

Table (1): IR of complexes of cu metal

complex	color	-CN stertching	OH stertching	C=O stertching	-C-O- stertching	$-CH_3$ bending	$-CH_2$ bending	O-M bending
(I)	Light Green	------ (cell)	3442 (3348)	1651 ---------	1160 (1058)	1583 ----------	1429 -------	662
(II)	Dark Green	2854 (mon-3518)	3445 (3102)	1716 (1743)	1191 (1808)	1604 (1607)	1443 (1453)	667
(III)	Pale Green	2899 (cop- 3348)	3442 (2901)	1724 (1664)	1160 (1058)	1652 (1639)	1434 (1429)	668

Electronic spin resonance of Cu – complexes

The e.s.r spectrum of cupric complex shows a strong signal characteristic to that of bivalent copper which is attributed to In the center. The g –values of the chelating polymer were determined indicating generally a positive contribution from the values of the free electron which is due to high covalent bonding Between ligand and metal ion [5].

Table (2): Copper complex have Hight peaks due to hi free radicals.

Sample name	Peak height	Weight gm	ΔH	
C1(Cu+cell)	1585	0.0243		
C3(Cu+M2)	552	0.0206		
C8(Cu+M1)	814	0.0216		
C10(Cu+Copo)	2148	0.0214	118.84	7.8805E+21

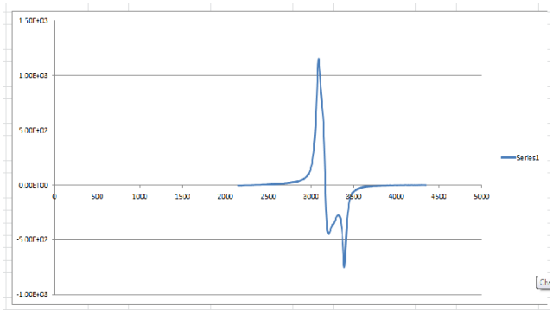


Fig (11): The curve for complex Cu-cell

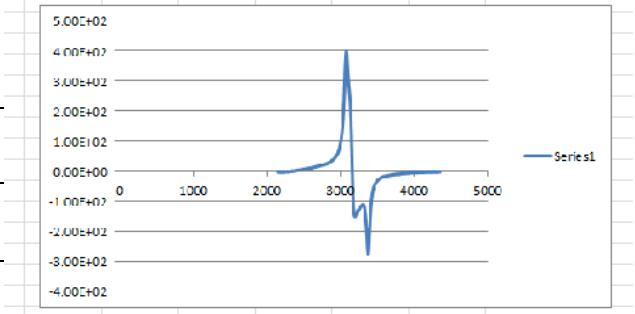


Fig (12): The curve for complex Cu-monomer

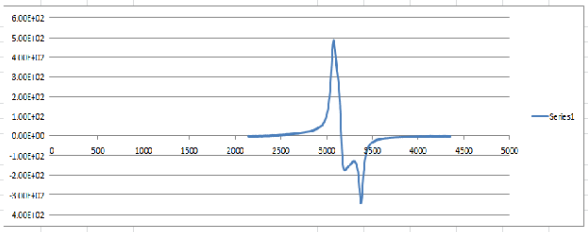


Fig (13): The curve For complex Cu-copolymer

X-ray diffraction

X-ray diffraction is a method used generally to evaluate the degree of crystallinity of several materials [9].

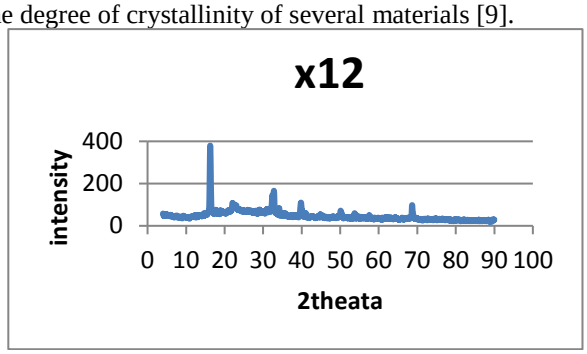


Fig (14): The shape of x-ray diffraction Cu- cell complex

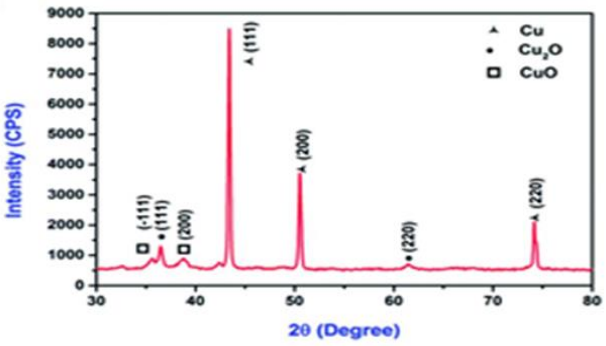


Fig (15): Stander curve of copper metal in x-ray diffraction

Table (3): x-ray diffraction of complex (Cu with cellulose)

Name of complex	Theta (2θ)	Stander Theta (2θ) For copper metal
(x12)Cu-cell	16 34 40 50 58 68	--- 34 43 50 62 74

the X-ray diffractograms of the cellulose samples studied.

Crystallographic planes

In the peaks for metal copper appeared at (2theta) in 16,34,40,50,58,68

A scanning electron microscope (SEM)

is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image [10].

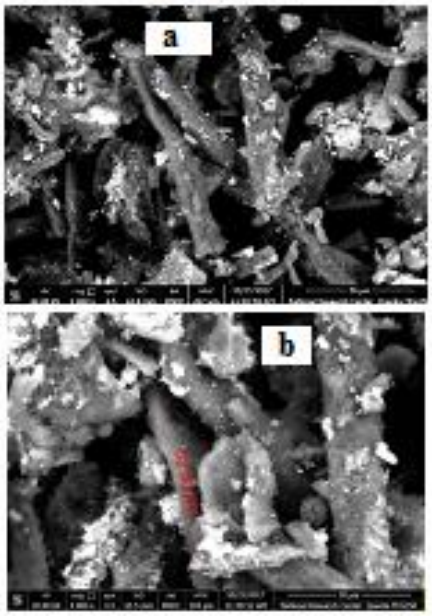


Fig (16): Images for CU-copolymer complex by scanning electron microscope (SEM) (a) at magnification 2000x & (b) at magnification 4000x.

surface is more irregular, rough and has needles shape. The value of the average particle size of the adsorbent provides more surface area for the removal of Cu2 from the aqueous media.

Transmission Electron Microscopy (TEM)

The electron microscopy is the use of specialized microscopes that interact a high energy electron beam with samples as a means to probe a material's structure.

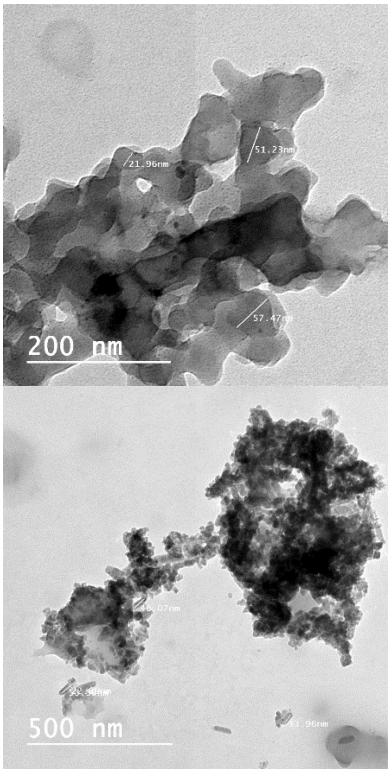


Fig (17): Images for Cu-copolymer complex by Transmission electron microscope (TEM) at magnification 500nm and200nm

Transmission electron micrographs of melt complexes Modified cellulose surface is more irregular, rough and has open porous structure. The presence of pores suggests the possibility of the metal ions to be trapped and adsorbed onto the surface. These cavities are large enough to allow the metal ions to penetrate into the surface and interact therein with the surface chelating groups. Surface morphology of the metal ion adsorbed shows layers of metal ions on to porous surface

The particle size was measured by particle size analyzer and was found to be as in previous figures.

The value of the average particle size of the adsorbent provides more surface area for the removal of Cu from the aqueous media.

Biological activity

Many polymers with reactive functional groups are synthesized, tested and used not only for their macromolecular properties, but also for the properties of their functional groups. These functional groups provide an approach to a subsequent modification of the polymer for specific end applications

Cu- complexes were screened for their antimicrobial activity using the diffusion agar techniques were tested against bacterial species as well as against fungal species. these species are:

1. Gram positive bacteria.

Staphylococcus aureus(St)+ Bacillus subtilis

2. Gram negative bacteria.

Escherichia coli(Es)+ Salmonella

3. fungai

Aspergillus flavus. (AS)+*Candida albicans.* (CA)

The results of antimicrobial activity showed that modified cellulose was found to have exhibited effect against Gram negative bacteria and Gram-positive bacteria.

Conclusion

On the evidence presented in this study, there exists significant potential for future research on the use of modified cellulose materials as heavy metal adsorbents. specific focus should be placed on modification of the cellulose backbone, cross-linking as a means of enhancing stability.

modified Cellulose copolymers can be prepared by synthesis of some monomers and after polymerization it we can received copolymer with cellulose to form polymer cellulose as modified Cellulose.

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