Synthesis and Characterization of Some New Ion-polymer Complexes as Topical Agents الجديدة الأيونية البوليمرات معقدات بعض وتوصيف تحضير خارجي للإستعمال عبد لقاء...

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Synthesis and Characterization of Some New Ion-polymer Complexes as Topical Agents

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Abstract:

Complexes with some metal ions (Al^{3+}, Cu^{2+}, Ag^{+}) with some polymers were prepared. The new complexes were studied by Ultraviolet Visible and (FTIR) spectrophotometer. The distinguish bands of synthetic complexes were characterized. The complexes use topically. They be divided into broad categories based on their usual action or use .The result shows they are protective, antimicrobial and a stringent compounds of silver complex is more than others. Some of the agents have uses extending beyond the limits of specific category. It also be noted that they are overlap between categories. The uses depend on the area of application, the concentration of the complex and the solubility.

***Key words**: polymer-metal complexes, antimicrobial, topical agent.*

تحضير وتوصيف بعض معقدات البوليمرات الأيونية الجديدة للإستعمال خارجي

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الخلاصة:

حضرت معقدات الصمغ العربي والبولي اثيلين كلايكول لايونات الالمنيوم والنحاس والفضة. درست المعقدات الجديدة بمطياف الأشعة فوق البنفسجية ومطياف الأشعة تحت الحمراء، كما شخصت الامتصاصات الطيفية المميزة للمعقدات المحضرة. المعقدات التي تستعمل موضعيا مقسمة الى مجاميع إعتمادا على عملها او استخداماتها. اوضحت الدراسة ان الفعالية الحامية والمضادة والمكمشة لمعقد الفضة اكثر من بقية المعقدات, كذلك لوحظ الاستعمال يعتمد على مساحة التطبيق، تركيز وذوبانية المعقد.

Introduction:

The pharmacological effects of topical compounds are evidenced primary at the surface to which they are applied. The inorganic compounds used topically will be divided into broad categories based on their usual action or use. The categories are protective, antimicrobial and astringent compounds.

It may also be noted that there is a tremendous amount of overlap between categories where the particular use will depend on the area of application, preparation and the solubility such as zinc oxide and Aluminum oxide [1] Natural polymeric materials have been used in medicine with the major purpose to assist damaged tissues for their healing[2]. Collagen has the longest history as biodegradable material, but it is clinical applications are limited to narrow fields such as homeostasis, mobilization, and wound covering. A marked of collagen over synthetic biodegradable polymers, its high affinity to fibroblast, leading to accelerated regeneration of tissues [3,4]. Sodium alginate is water soluble polymer has been studied as dressing for dermal wound [5]. Sodium alginate can be converted to insoluble calcium salt, which is then formed into film.

The dressing is useful in the management of burns and donor sites, leg ulcers and infected traumatic wounds [6]. Inorganic polymeric comprise a very unique area of polymer science. High polymers with inorganic elements in structure offer a new area with broad opportunities for material scientists and technologists for biomedical application [7].

Polyphosphazenes are comprised of an inorganic backbone of repeating phosphorus and nitrogen atoms with alternating single and double bonds (figure- 1)[8]. Extending from each of the phosphorus atoms are two organic side chains, which can range from alkoxy and aryloxy substituents to amino acids, giving a large variety of potential polymers [9]. Also an approach to hydrogels have been synthesized [10].

Gum Arabic (GA), is an edible biopolymer, used in pharmaceutical preparations and as a carrier of drugs since it is considered a physiologically harmless substance. Additionally, recent studies have highlighted GA antioxidant properties [11] and antimicrobial activity. As for the antimicrobial activity of GA, few studies have been performed, mainly reporting [12]. Kamyar Shameli et.al [13] was show PEG was appropriate as a stabilizer and polymeric media for reducing the $AgNO_3$ using β-D-glucose as a green reducing agent. The schematic illustration of the synthesis of Ag NPs capped with PEG is depicted schematically in Figure-2.

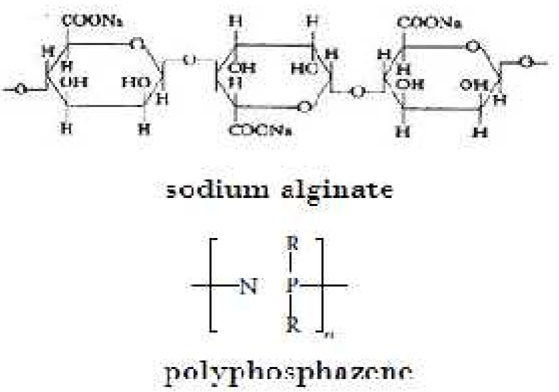

Figure-1: chemical structure of sodium alginate and polyphosphazene.

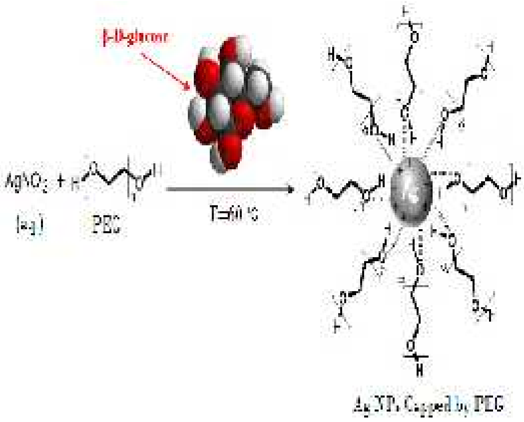

Figure-2: Interaction hydroxyl group of PEG with Ag.

Polyethylene glycol (PEG) present with the surface of positive charge of silver nanoparticles [Ag (PEG)].As shown hydroxyl group of PEG as a capping agent can cover in the surface of Ag NPs. This is due to the surface of Ag NPs which is positively charged. Certainly, we suppose that colloidal stabilization for [Ag(PEG)] occur due to the presence of van der waals forces between the oxygen negatively charged groups present in the molecular structure of the PEG, and the positively charged groups that surround the surface of inert Ag NPs. Figure 2 illustrates the nature of the interaction between the charged Ag NPs and PEG [14,15].

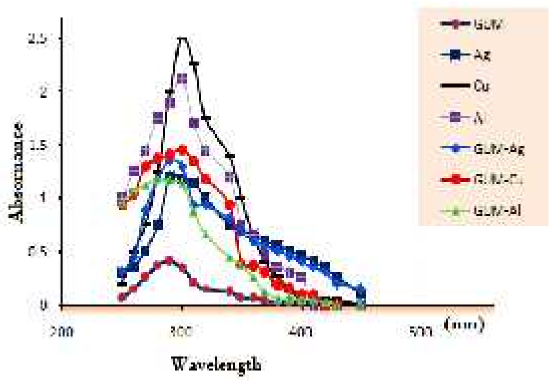

Figure-3:UV-Vis. Spectra of Gum and its complexes with Al (III), Cu (II) and Ag(I) ($0.1x10^{-2}$ M).

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Materials and Methods:

Materials:

All materials supplied from Fluka and Merck chemical companies (Aluminum nitrate, Cupper nitrate, Silver nitrate, Gum Arabic, Polyethylene glycol (PEG) and doubly distilled water.

FTIR spectra were recorded on a Shimadzu Bruker model Equinor 55. U.V–Visible spectra were recorded on analytic Jena model spectra 40.

Methods:

Preparation of solutions:

The solutions of (0.01M) were prepared by dissolving the accurate weight of Al $(NO_3)_2.9H_2O$, Cu $(NO_3)_2$, $AgNO_3$ and complete the volume with (100 ml) distilled water to each ions solutions. The 0.1M solutions of Gum and PEG were prepared by dissolving the accurate weight of polymer and complete the volume with 100 ml distilled water.

Preparation of Gum complexes:

The Gum complexes were prepared by mixed (10 ml) of ($0.1x10^{2-}$M) of Gum solution with (10 ml) of Al^{3+}, Cu^{2+} and Ag^{+} ($0.1x10^{2-}$ M) metal ions solutions with concentration ($0.1x10^{2-}$ M) . The stirring placed 10 min. then the solvent was evaporated. The ($1x10^{3-}$ M) of the complexes were prepared.

The UV.Vis spectra was recorded at the rang (250-500 nm) for each complexes and Gum with used distilled water as blank as shown in figure 3 . The formation complexes was dried and collected as solid complexes. FTIR spectra was recorded for the solid complexes and Gum as pure materials as shown in figures (5-8).

Preparation of PEG complexes:

The PEG complexes were prepared by mixed (10 ml) of ($0.1x10^{2-}$ M) PEG solutions with (10 ml) of Al^{3+}, Cu^{2+} and Ag^{+} metal ions solutions with concentration ($0.1x10^{2-}$M). The stirring placed 10 min then the solvent was evaporated. The ($1x10^{3-}$M) of the complexes were prepared. The UV.Vis. Spectra was recorded at the rang (250-500 nm) for each complexes and PEG solution with use distilled water as blank as shown in figure 4. The formation complexes were dried and collocated as solid complexes. FTIR spectra was recorded for the solid complexes and PEG as pure materials as shown in figures (9-12).

Result and discussion:

In this research, GUM and PEG were appropriate as a stabilizer and polymeric media for reducing the Ag, Cu and Al.

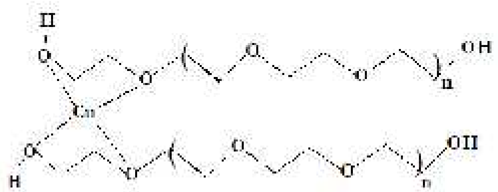
Expected, after dispersion of silver ions in the PEG aqueous solution equation 1, PEG reacted with Ag to form a PEG complex $[Ag(PEG)]^{+}$ [13].

$$\underset{aq.}{Ag^{+}} + \underset{aq.}{PEG} \longrightarrow \underset{aq.}{[Ag(PEG)]^{+}} \text{ ---------- } 1$$

Also, complexation of polyethylene glycol with Cu^{2+} can represent by equation 2, which involve the coordination of the hydroxyl (OH) and ether groups of PEG with Cu ions.

$$\underset{aq.}{Cu^{2+}} + \underset{aq.}{2PEG} \longrightarrow \underset{aq.}{[Cu(PEG)_2]^{2+}} \text{ -------- } 2$$

The proposal structure may be as the following[17]:



Where, PEG-Al complex can represent as equation 3:

The formation of polymer-metal complexes can be followed from their characteristic absorption bands in visible, infra-red and by comparing them with the corresponding low molecular weight complexes.

$$\underset{aq.}{Al^{3+}} - \underset{aq.}{3\,PEG} \longrightarrow \underset{aq.}{[Al(PEG)_3]^{3+}} \text{ ------------ } 3$$

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IR absorption by polymer as ligand is usually shifted by complex formation with metal ions.

FTIR spectra were shown several distinguish band. Table-1, shown the compares' between polymers and its complex. Generally stretching vibration of hydroxyl group was shifted to low frequency and broad in the complexes due to formation of Coordination bonds.

The very little shifted in silver complex estimate to formation of monovaliant salt with negative charge of resin. The FTIR spectra for PEG and its complex with Al^{3+}, Cu^{2+} and Ag^{+} as shown in figures (5-12).

The spectrophotometer study shows the characters of the products .The UV. Vis. Spectra of Gum shows one types of transition (π - π*) at λ=300 nm.

The Gum–complexes with Al^{3+} Cu^{2+} and Ag^{+}, were shown the same transition (π - π*).

The high intensity of transition of complex due to charge transfer as shown in figure 3. The UV. Vis spectra of PEG was shown one type of transition at 285 nm due to (π-π*) transition. PEG complexes with Al^{3+} , Cu^{2+} and Ag^{+}, were show the same type of transition with red shift due to charge transfer complexes as shown in figure 4 [16].

The antibacterial activity against both G^{+} and G^{-} staphylococcus aureus microorganism were studied by diffusion agar method [18].

Table-2, shown the antibacterial activity of silver complex against both types' staphylococcus aureus, but G^{+} bacteria are more than G^{-} bacteria. Silver ion precipitation of protein involves interactions between the cation and various polar groups on the protein molecules. However the action is somewhat localized is due to precipitation with tissues proteins and chloride ions in the tissue fluids [19]. Silver preparation is bacteriostatic at concentrations of silver ion below that required for protein precipitation. It will precipitate both bacterial and human protein. However silver ion was prepared as complex with polymer to decrease systemic absorption of ions and long duration of antibacterial activity [20]. Aluminum (III) and Cu (II) are also an effective protein precipitant[21,22] . Both Al(III) and Cu(II) have ability to formation strong coordination bonds with Gum and PEG, Therefore the antibacterial activity were lower than of Ag(I) complexes as shown in table(2)[1]. Gum is a mixture of polysaccharides containing D- galacturonic acid, other sugars and traces of starch and cellulose. It is use as preserving ointments in perfumery cosmetics and topical protecting; Gum was prepared as tincture used topically as antiseptic and to promote healing. Also used as an inhalant for bronchitis, and orally as an expectorant[23]. Complex polymer solutions are subject to the same slow ionization of silver as mentioned earlier with tissue proteins (sustained action).

The mechanisms of action of inorganic antimicrobial agents divided into three general categories, oxidation, halogenations' and protein precipitation. The antimicrobial agents were estimated by interactions between complexes and microbial protein and result in the death of microbe or inhibition of its growth. The some metal ions have ability to oxidation of protein containing sulfhy dryl group[24].

Conclusion:

Both Gum and PEG complexes with Al(III), Cu(II) and Ag(I) were prepared. The UV.Vis spectra of the complex was shown one π - π* transition with different intensities.

The products were characterized by FTIR spectra. The FTIR spectra shown the important absorption bands. The antimicrobial activity against both G^{+} and G^{-} bacterial of staphylococcus areas was studied.

The result shown the silver complex was effect on both type of

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Staphylococcus areas and also higher antibacterial activity than others.

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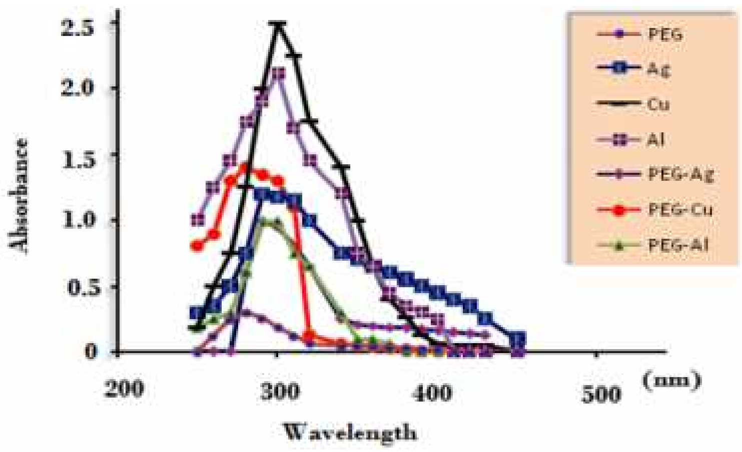

Figure-4: UV-Vis. Spectra of PEG and its complexes with Al(III), Cu(II)and Ag(I) at (0.1 x10^{-2} M).

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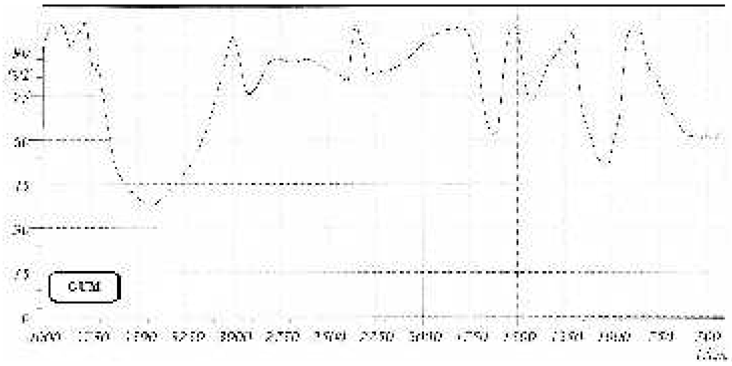

Figure-5: FTIR spectra of GUM.

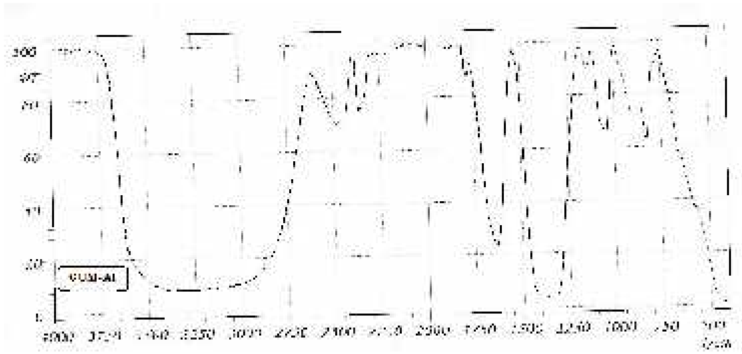

Figure-6: FTIR Spectra of GUM-Al complex

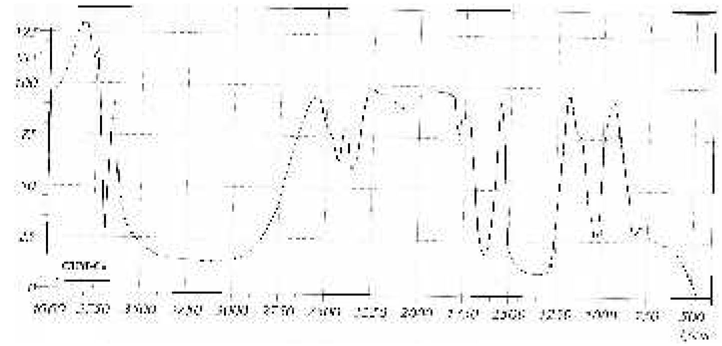

Figure- 7: FTIR Spectra of GUM-Cu complex.

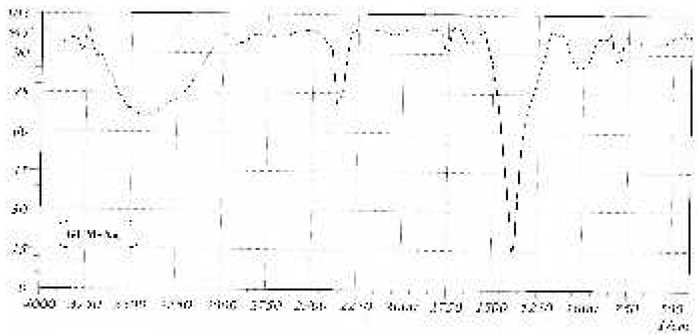

Figure -8: FTIR Spectra of GUM-Ag complex.

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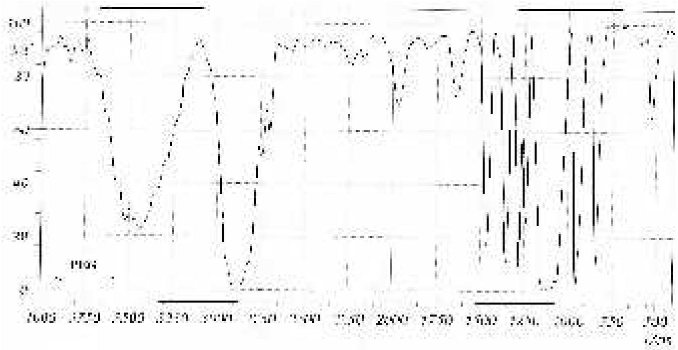

Figure-9: FTIR spectra of polyethylene glycol PEG.

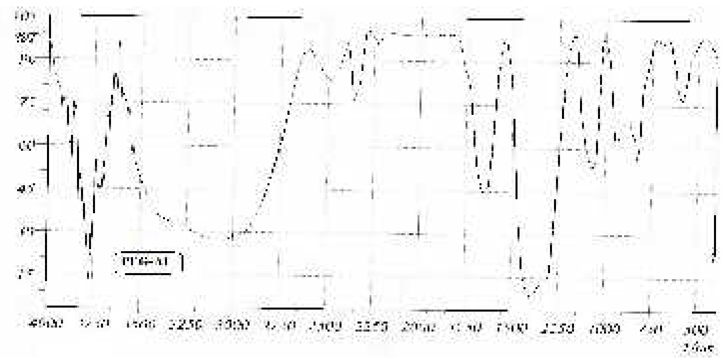

Figure 10-: FTIR spectra of PEG-Al complex.

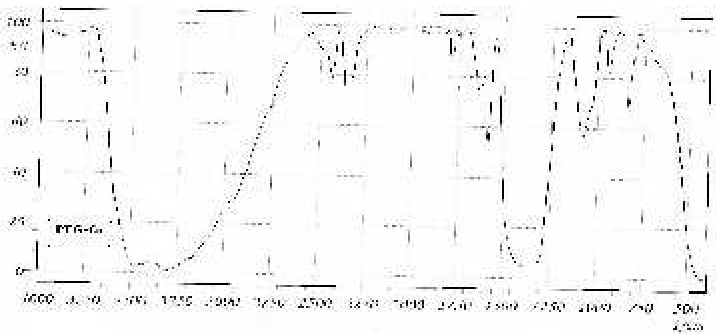

Figure 11-: FTIR spectra of PEG-Cu complex.

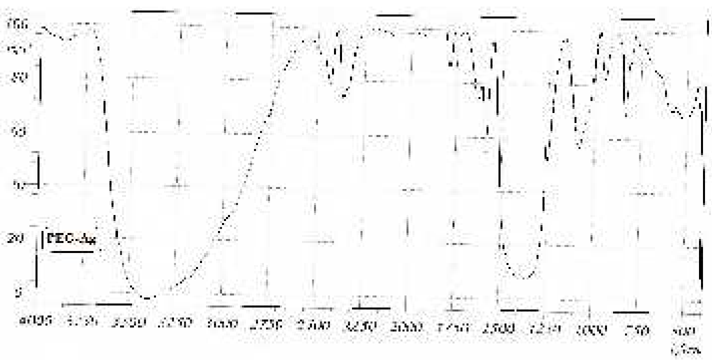

Figure12- : FTIR spectra of PEG-Ag complex.

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Table-1: FTIR spectra of Gum and PEG with their complexes

Compound	υO-H streach cm^{-1}	υ C-H Aliphatic streach cm^{-1}	C-H Bending cm^{-1}	C=O Streach cm^{-1}	υ C-OH streach cm^{-1}	υc-o cm^{-1}
GUM	3625-3125	2280	1425 broad	1638	1135	1073
GUM-Al complex	3600-2875 broad	3086	1420 broad	1625	1130	1047
GUM-Cu complex	3625-2750 broad	2927	1500-1400 broad	1620	1125	1018
GUM-Ag complex	3640-3100	3016	1375	1600	1005	1033
PEG	3500-3250	2280	1490 & 1375	-	1125	1070
PEG-Al complex	3750-3500 Broad	** broad	** 1450 & 1350	-	1100	1074
PEG-Cu complex	34950-2800	** broad	** broad	-	1200	1097
PEG-Ag complex	3500-2750	** broad	** broad	-	1100	1081

**** = incorporated with other bands as broad**

Table -2: Antibacterial activity of polymers and metal-complexes synthesized against both G^- and G^+ *Staphylococcus Aureus*

Compounds	Zone of inhibition G^+ (mm)	Compounds	Zone of inhibition G^-(mm)
Gum	-	Gum	-
Gum-Al complex	6	Gum-Al complex	-
Gum-Cu complex	-	Gum-Cu complex	9
Gum-Ag complex	19	Gum-Ag complex	8
PEG	-	PEG	-
PEG-Al complex	-	PEG-Al complex	5
PEG-Cu complex	-	PEG-Cu complex	5
PEG-Ag complex	17	PEG-Ag complex	8