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NanoSilver/CS Solutions Optical Characterizations and Some Applications

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1. INTRODUCTION

The chemical and physical and features of Nobel metals such as gold, silver and platinum can drastically improve or changed when applied to nanotechnology methods to reduce particle size to nanoscale [1-3]. CS is a chitin derivative of which is the second predominant naturally occurring polymer after celluslose.it has aroused a lot of interest since it may degrade in the body to form the building block of the body's tissues [4]. The polymer are excellent hosts for metal nanoparticles since they may act as reducing agent participating in NP synthesis. The rise in the interest in polymer/ Ag metal nanocomposites is due to bring biological, optical, electronic, and magnetic useful.

The noble metal nanoparticles, including silver and gold may show size-dependent electrical, optical and biological features [5, 6].

There are many developed approaches such as chemical [7], electrochemical [8] and decreasing photochemical [9], ultrasound [10], microwave [11], and irradiations of both gamma [12] and electron to [13-19] synthesize Ag-NPs by various stabilizers [20-23]. Ag-NPs depending on sizes and forms utilized in biosensors materials, cosmetics, antimicrobial uses, conducting materials and electrical constituents.

In recent years, silver nanoparticles have increasing interest due to exhibiting antibacterial activity [24], so silver nanocomposites showed extra efficiency against microbial infections than silver alone does [25].

In 1889, Lee was the first to develop colloidal silver for medical applications such as disinfectant in first world war for wound dressing, but today, nano silver is wide spread worldwide in various sciences especially in electronics devices due optical, electrical and thermal compared with other metals. In health and medicine field, studies attempt for additional data on the destruction effects of nano silver particles on tissues and cell of flesh. Various toxins and could have effects on the immune system and blood cells as a disadvantage for health body. Most toxin is in the body and enters the liver for detoxificating and this work investigates the Ag NPs-CS optical properties and its effect on human blood serum. The bactericidal nano material examination significance is due to the new resistance bacteria strains against antibiotics. It seems that silver ions particles are useful and effective in bactericidal uses including water treatment [26, 27]. The silver ion action of bactericidal and nano colloidal silver particles (20-140) nm spread in various medium is common [28, 29]. There has been a use of a solution with Ag as antimicrobial agent in different applications due to their growth and inhibition against microorganisms. Yet, silver nanoparticle helped touching Ag surface with microorganisms to grow and release Ag ions slowly. Despite the fact that the Ag nanoparticles kill many microorganisms such as virus, fungus and bacterium due to its non-toxicity with no skin irritations [30, 31] and Ag-NPs-CS can work as anticontamination for water samples from selected location from the sides of Gherait of Dyala and Tigris River.

In this research novel, clean, easy, nearly to be fast, low cost,

green process and no waste final products Photo reduction method used for synthesis nano structures silver particles presented and establishes in Iraqi labs within radiation safety standards. Silver nobel metal is known to kill 650 microorganisms due to nano size which offer large surface area per unit mass, which improves the activities in low concentration compared with other photo reduction method such as UV and optical light related to higher energy of gamma radiation source. The prepared Nano Silver/CS Solutions based chitosan hybrid nanocomposite is safely used for human or environment subjects in some biomedical or anticontamination applications due to effectiveness and easy to be mixed with liquid material or used alone for coating, sputtering, surface penetration or blended with other solutions.

2. THE EXPERIMENT

2.1 Materials and chemicals

Analytical grades are to all reagents with no additional purification when received. The silver nitrate (AgNO₃; 99.98 percent) is selected as silver ion precursor which Merck, Germany provides. Nanoparticles stabilizers used the Carboxymethyl CS which is low molecular weights from Sigma Aldrich in America which has an isopropanol solvent, glacial acetic acid (HAC, 99 percent which the next figure shows. It is a double-distilled water (DD-water) for making every aqueous solution.



Figure 1. (a) Carboxymethyl CS materials and (b)The molecular structure of Carboxymethyl CS

2.2 Methods

To create a stock solution of CS, we dissolved 3 grams of CS in 150 ml of acetic acid using 14:1 distilled water, and left it for 8 hours. Next, we added 0.6 grams of silver nitrate to 20 ml of deionized water and mixed it with the CS solution in a glass ampoule. To prevent the formation of free radicals, we added 23 grams of isopropanol, as shown in Figure 1, and deaerated the solution by bubbling pure nitrogen for 20 minutes. The ampoule was then sealed and exposed to Co-60 1/5 -ray sources. Then 23 g of isopropanol was added as a free radical scavenger as shown in Figure 1 and deaerated with bubbling pure N₂ for 20 minutes. It then sealed to irradiate with Co-60 $1/5 \gamma$ -ray sources. The RD is 8 Gy/hr regulating its total doses when conducting the experiment through adjusting the irradiation time as in Table 1.

The outcome viscous solution, manufactured by AgNPs showed color shift from yellow to brown (Figure 2) because silver salt through reduces by dropping of the compounds in the CM CS extract.

So, Ag ions concentration is $(1.76 \times 10^{-5} \text{ mol/ml})$, the –NH2 and the concentration of the groups is $(9.35 \times 10^{-5} \text{ mol/ml})$ and that of the isopropanol reaches $(1.9 \times 10^{-3} \text{ mol/ml})$. The

solution pH reaches (3.0). We used diluted irradiation-degrade AgNPs/CS solutions for fixing the made silver particles from radiation–reduction. The RD rates and Times (hr.) to Ag-NPs /CM-CS - isopropanol is seen in the table below with additional physical features.

Table 1. Gamma dose and time of irradiation and properties

	1	2	3
Sample Code	A1	A2	A3
RD (Gv)	768	1151	1920
Irradiation Time (hr.)	96	144	240
PH.	5	4.8	5
Con.%	0.182	0.19	0.264
T°C	27	26	26



Figure 2. a) Preparation of AgNO₃, b) AgNO₃ sample before, c) after gamma irradiation Treatment

There were many sprays of silver solutions on glass substrates to the distribution of the size which AFM (Angstrom dvancedtypeAA3000) determines. X-rav diffraction were used for the silver thin films samples for crystalline structures [32-38]. For the influence of AgNPs on human blood; the experiment was conducted on six donner mal health adult. We labeled the samples and the controls (B1-B6) and examined pre and post nano silver particles injecting to blood, urea, blood creatinine, and phosphates of alkaline test by Uv-Vis spectrophotometer (SP-3000 Optima-plus- Chapan) [36, 39-55]. The former was red upper level and yellow color serum lower level. We established the tests for both with injecting 0.1 ml (volume ratio) of sample A3 of AgNPs solution besides the controls.

To evaluate the antimicrobial efficiency of AgNPs solutions for river water treatment, we considered the following;

i) We collected five water samples from different locations along the Dyala River, which flows primarily through Iraq. In addition, we collected one water sample from the Al-Gherait riverbank, and each sample was labeled and placed into standard containers that had been treated with AgNPs solutions (sample A3). These samples were selected due to their contamination status.

ii) The samples above evaluate as antimicrobial efficiency for achieving through the standard approach to inspect water inspections in the aerobic nutrient agar for whole bacteria inspections and macconky broth counts tocoliform and to the testing of the fecal coliform bacterias [56].

3. RESULTS AND DISCUSSION

3.1 Structure properties

Ag-NPs / (CM CS – isopropanol) is from reducing AgNO₃ into ions (Ag+) of positive silver helped by fragmenting large Ag-NPs in γ -irradiation [12]. The figure below shows the manufactured Ag-NPs. The Ag-NPs / (CM CS-isopropanol

color intensity rose step by step. The A0 sample with not ray shows a clear yellow solution (as Figure 3 shows). The colloidal solution turned dark brown which is the -rays strengthened (samples A1-A3), yet the AgNO₃ solution had no color as in Figure 3). The Ag-NPs/CM CS-isopropanol change the pure yellow colloidal solution from light to dark brown after gamma irradiations (samples (A0-A3). This confirms Hanan et al. [57], Shriram et al. [58], and M.S.N. Salleh et al. [23] to form AgNPs by the reduction of AgNO₃.



Figure 3. Feature shifts in the color of colloidal solutions which can be Ag-NPs /(CM CS - isopropanol)) after being exposed to (0, 768, 1151, 1920 Gy) doses (A0–A3, respectively)

Peng Chen Briefly reported photo-induced fragmenting Ag-NPs [19, 59]:

 $(Ag)_n + 2hv \rightarrow (Ag)_n^+ + e_{aq}^-$ (1)

$$(Ag)_n^+ + e_{aq}^- \to (Ag)_n \tag{2}$$

$$(Ag)_{n}^{+} \rightarrow (Ag)_{n-1} + Ag^{+}(Ag)_{n}^{+} \rightarrow (Ag)_{n-1} + Ag^{+}$$
 (3)

Here: (Ag)n = The silver nanocluster with (n) silver atoms e -= The aqueous electrons

On gamma -irradiation on aqueous suspending CS/ silver nitrate (Cts/AgNO₃). In addition to the, the aqueous electrons decrease the positive silver ions into silver.



Figure 4. (a)TEM and (b) XRD results of Ag /CM-CSs sample A3

Figure 4 is the x-ray diffraction of the silver samples for studying their structure showing the crystalline which as patterned with 2Θ (33.0337) of highest positions along the high intensities (100%) to plane (111) and second peak positions 2Θ (43.9817) with relative intensities (52%) to plane (200), (220) band for face-centered cubics (fcc) structure of Ag-NPs [24, 58].

The XRD shows the most suitable gamma dose for gaining silver nano particle because the Co-60 is 1920 Gy over 240 hr [25]. The produced AgNPs morphology and particle size distributions were examined by Transmission Electron Microscopy (TEM) imaging. Also the figure below is a typical sample A3olution TEM image with dispersed well Ag-NPs in the (CM-CS-isopropanol) matrix.



Figure 5. The size distribution (a) and (b) AFM image of AgNPs (A3) sample

The AgNP TEM images and size distributions shows the average diameter of the nanoparticles in sample A3 ranging 40 and 50 nm along with the cubic phases. Yet, that of the A1 and A2 is larger than 100 nm.

Figure 5 is the spherical AgNPs (A3) particle AFM made by gamma irradiation with (40-100) nm distribution.

3.2 UV-visible spectroscopy analysis

This research included studying the optical properties of the samples prepared by irradiation method using cobalt (Co 60) source as finding the optical energy gaps for the permissible direct electronic transitions, by recording the absorption and transmittance spectra of the prepared solutions within the wavelength range (400-1100) nm.

UV-seen absorbing spectra are sensitive to form Ag-NPs as Ag-NPs show intense absorption peak because of the SPR. Figures 6 is UV-vis silver nanoparticle spectra at constant CM-CS and it is also at silver nitrate concentrations yet at other gamma irradiation doses (768, 1151, 1920 Gy) to (96, 144, and 240 hr), in the same order.

All spectra show an absorption band (370–470 nm). It is a Ag-NPs SPR band. Weak peaks around 330 and 560 nm indicate the nanoparticle aggregations. One strong peak with a

highest of d 430 nm was seen in the UV–vis spectra corresponding to the specific SPR of electrons from the of Ag-NPs surface. The nanoparticle synthesis efficiency rises gamma irradiation doses rise (768, 1151, 1920 Gy) because oxidating hydroxyl set of CM-CS by silver ions rises. Also, in producing nanoparticle rise by monitoring silver nitrate when gamma irradiation doses increase, and Figure 6 displays their respective spectra. The absorption of the solution intensity rose when the gamma irradiation doses increased, in particular by A3 subjected a 1920Gy gamma dose of irradiations sample A3:



Figure 6. UV– silver nanoparticle visible absorption spectra of CM -CS- isopropanol by various gamma irradiation doses: (AI) at 768Gy dose for 96hr, (A2) at 1151Gy dose for 144 and (A3) at 1920Gy dose for 240 hr





Figure 6 is specific UV-visible absorption spectra to the silver solutions. It reveals the highest absorbance in a set of spectra band. There is a dominate SP absorption peak (420-430 nm).

This research founds the optical energy gap value for the permissible direct electronic transitions, by recording the absorption and transmittance spectra of the prepared solutions within the wavelength range (400-1100) nm by plotting the graph between (hU) on the X-axis and (α hU)² on the Y-axis and drawing the tangent, we can extract the value of the energy gap. The optical energy gaps are fulfilled by scheming (α hv) against (hv) as shown in Figure 7. It increases from the values of the energy gap of the films grown at (96, 144 and 240) hr were (1.9, 2.32 and 2.33) eV. Respectively.

The variation of the optical energy with correlated to the change of the radiation rate, as shown in the Table 2 [60].

 Table 2. Cs/Ag nanocomposite solution energy gaps with Irradiation Gamma dose rate

Sample Code	A1	A2	A3
RD (Gy)	768	1151	1920
Irradiation Time (hr.)	96	144	240
PH.	5	4.8	5
Con.%	0.182	0.19	0.264
Т°С	27	26	26
Eg (ev)	1.9	2.33	2.34

Figure 8 shows the optical transmission ratio behavior for the three Samples (A1-A3). Sample A3 show the highest ratio of transmission light in a range of 489-789 nm due to its particle nano size than the others.



Figure 8. The Transmitions optical features (T%) versus wave length (180-1100) nm for Ag-NPs stabilized (CM -CSisopropanol) using various gamma irradiation doses

It is obvious that the optical energy gap and light transmission percent widely depended on gamma irradiation energy dose rate.

3.3 Applying Ag-NPs / CM CS – isopropanol.

I) Effect of AgNPS on human blood

Nanosilver solution prepared by gamma RDrate (sample A3- 1920 Gy) using gamma source Co-60 within CS agent. Sample (A3) with particle size about 40 nm with 0.63 ppm of concentration inserted into second group (B1-B6). We measured the concentration of the Serum concentration through biochemical spectrophotometer and biochemical devices and calculated the Urean, Alkaline phosphate and blood crentinine. Tables 3, 4, 5 are the examinations of to six blood sample outcomes.

Table 3. Blood urea results

Sample	No.		B1	B2	B3	B4	B5	B6
B.Urea	Befor AgNPs	Ingection	50.8	37.7	28	46	31	31
B.Urea	after AgNPs Ingection	upper level	27	26	14	31	21	23
B.Urea	after AgNPs Ingection	lower level	49	36.3	27	44	31	29

Table 4. Blood crentinine result

Sample No.	B1	B2	B3	B4	B5
B.Crentinine befor AgNPs ingection	1.27	0.94	0.7	1.1	0.7
B.Crentinine after AgNPs ingection upper level	0.67	0.65	0.3	0.7	0.5
B.Crentinine after AgNPs ingection lower level	1.22	0.9	0.7	1.1	0.7

 Table 5. Alkaline phosphates examinations

Sample	No.			B1	B2	B3	B4
A.Phos.	before AgNPs	injection		8.2	15.1	9	10
A.Phos.	after AgNPs	Injection	upper level	10.7	11.4	8	7
A.Phos.	after AgNPs	Injection	lower level	8.4	14.6	9	10

The group (B1-B6) contained the control identical to the treated samples to the compared methods. Tables 3, 4, 5 are the mean Urea, phosphate and crentinine of the six samples for two blood levels, the upper of which is red cells group and the lower is yellow. The results make it clear that the nanosilver particle impact (sample A3) contradictorily on upper (red one) with no effect on the yellow. Reducing urean, alkaline, phosphate and blood crentinine could is possibly treated by the aggregating influence of nanosilver particles on blood cells. The influence on nanosilver particles (Figure 9) in the blood cells cause reduces parameters injected in the liver kidney factors [60, 61].

II) Effect of AgNPS with river water treatment

The Purification of water by silver seems to be wide spread to a long time and traditionally applied in in different fields [62, 63]. Evaluations of antimicrobial effect of AgNPs against contaminated river water was achieved to six samples from Dyala and Al Gherait river and tested by the standard methods for water inspection. Tables 6 and 7 is one good activity obtained by using AgNPs concentration (5.3 - 33.03) ppm as antimicrobial water bacteria.

Table 6 and Table 7 show good activity by AgNPs techniques as antimicrobial water bacteria in which the typical images (Figure 10) are the for total water sample count inspecting. In addition, the good agreement between the

AgNPS efficiency in each sample of Al_Gherai't and Dyala is reported regardless of the highly contaminated water in Dyala River water in comparison to Al_Gherai't, and the various concentration uses where we have Table 6 of silver shows no inhabitation in the bacteriological purification.

Table 6 is the outcomes of the silver (5.3-33.03) ppm concentration to all samples and the inspiring activities. In addition, sample (5) exhibits some aerobic bacteria. The quantity is suitable based on the Iraqi standard for bacteriology water inspections. The Dyala contamination is bigger than that of Al_Gherai't which encouraged greater silver concentration (33.03) ppm in purifying the sample of the later. Table 7 showed that the in Bridge – Dyala and Join Dyala aerobic bacteria and the Tigris are somehow larger than the rest of the areas because of their high contamination.



Figure 9. Effect of AgNPs: Aggregate morphology of red blood cells (in vitro application)

Sample No.	C1	C2	C3	C4	C5	C6
AgNPs concentration (ppm)	5.3	7.05	12.82	14.87	28.09	33.03
Total count	0	0	0	0	9	0
coliform	0	0	0	0	0	0
Fecal coliform	-140	-1/0	-1/0	-140	-140	-140

 Table 6. Bacteriology effective treating AgNPS on AL-Gherait side river water

Table 7. Bacterio	ology effective	treating Agl	NPs on Dya	ala side r	iver water

Site of the sample	Location 1- Alsdur	location 2- Baquba	location 3- Dyala Bridge	Location 4 new Dyala Bridge	Location 5- join Dyala river with Tigris river
Water to AgNPs ratio	03:01	03:01	03:01	03:01	03:01
Total count	1	1	2	1	2
coliform	0	0	0	0	0
Fecal coliform	-ve	-ve	-ve	-ve	-ve



Figure 10. Typical picture for total count inspecting water samples

4. CONCLUSIONS

Ag-NPs stabilized in (CM -CS- isopropanol) were prepared by -irradiation method with (40-500) nm particle size distribution form the use of RDrates. The wavelength at the highest absorptions changed to longer with the initial concentration rise of AgNPs ions. A silver nanoparticle smaller size was obtained by the use of CS as stabilizer. The unique shows that the -irradiation is suitable in particular. In producing colloidal and nano Ag-NPs on large scales. The process of producing is through the economic and available methods, tools and materials. This work examined the physiological influence that nanosilver particles (sample A3) at (0.63) ppm concentrations with (0.1) ml volume ratio injected to human blood samples. The study showed reduced urea, blood crentinine and alkaline phosphate values. There is also extreme stability of these nanoparticles at physiological conditions and the blood was compatible for use to more potent antiplatelet agent than aspirin.

There is a successful silver solution development for bacteriological water purification proving their effectiveness at various concentration to various contaminated water samples of. Using various concentration of Ag-NPs in CM - CS- isopropanol for Al_Gherai't samples (5.3- 33.03) ppm were positive.

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