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# Green Synthesis of Gold Nanoparticles Reduced and Stabilized By Carboxyethyl Chitosan for Viscose Fabric Finishing

**Maysa M. Reda [1]* and Ibrahim Moussa [2]**

[1] High institute of applied arts, the 5thP District, Cairo, Egypt

[2]Solid State Physics department, Institute of Physics Research, National Research Centre, 33 El Bohouth st., Dokki, Cairo, Egypt, P.O.12622

**Abstract**

A green chemistry methodological approach was used in the preparation of nanostructures, which is a result of incredible and innovative medical applications. Polysaccharides were utilized as a reducing and stabilizing agent in the synthesis of gold nanoparticles (AuNPs). We used carboxyethyl chitosan (CECS) as a reducing agent and a gold nanoparticle as a capping agent in this study. CECS is made by reacting chitosan with acrylic acid in an alkaline media, as described previously. At 100 oC for 1 hour, AuNPs were made with varied concentrations of carboxyethyl chitosan (0.2 percent w/v, 0.5 percent w/v, and 1 percent w/v). The nitrogen content, carboxyl content, and FTIR spectra were used to characterize CMCS. UV spectrophotometry and TEM images were used to identify AuNPs. Finally, the cytotoxicity of the produced AuNPs was assessed using an MMT assay for cell viability and IC50 values in comparison to AuNPs synthesized via chemical techniques. The results reveal that AuNPs have a normal distribution with 15-25 nm particle size and that their cytotoxicity is reduced when made using this green approach, indicating that GNPs can be used safely in skin contact medical therapy

Keywords: Carboxyethyl chitosan, gold nanoparticles, green synthesis, cytotoxicity, and Utilization, viscose fabrics.

## 1. Introduction

There is a lot of work being done in nanoscale science and engineering to prepare metal nanoparticles, which can be used in bionanotechnology for their catalytic activity, new electrical properties, and peculiar magnetic properties. [1-3]. New materials and devices in the nanometer range have been created by using nanotechnology. For the smart devices, gold nanoparticles were the most compatible nanomaterials (AuNPs). Bioimaging, biotherapeutic, and bio diagnostic tool suitable for nanomaterial [4].

Chemical reduction of metal salts using reducing agents such as citric acids, borohydrides, or other organic molecules typically yields metal nanoparticles. [5].They have cytotoxic effects on biological threats. The use of environmentally friendly chemistry to reduce or eliminate waste and to establish a long-term strategy [6]. In this way, AuNPs can be synthesized biologically. Researchers use colloidal gold nanoparticles because of their remarkable properties. [7].

When Raveendran et al. started making silver nanoparticles, they were the first to adopt the green notion of employing glucose as a reducing agent and starch as a capping agent. [8, 9]. The solvent, reducing agent, and capping agent used in the green approach of generating nanoparticles were all examined. .

Gold nanoparticles can be prepared in a variety of ways. The most frequently used method generates AuNPs with a size range of 15-20 nm. by reducing In the presence of trisodium citrate, auric chloride ($HAuCl_4$). A wide range of applications depends on metal nanoparticles, from photonics and photography to catalysis and biological labeling to textiles. [10-14]. the shape, size, composition, and structure of metal nanoparticles dictate their properties. AuNPs can be prepared in some cases using silver nano boxes as follows:

*Corresponding author e-mail: maysareda@aol.com (Maysa Reda)

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$$3Ag\ (S) + HAuCl4\ (aq.) \longrightarrow Au\ (S) + 3AgCl\ (aq.) + HCl\ (aq.)$$

Biotechnological applications of chitosan include cosmetics and pharmaceuticals, food, and biotechnological applications of chitosan. [15-22]. The amino groups in chitosan biopolymer are employed to stabilize gold nanoparticles during the production process. [23, 24]. To prevent nanoparticle aggregations, however, rigorous management is required [23, 25].Chitosan has a low solubility. Nanocomposites containing chitosan, as well as gold nanoparticles, have been investigated. infrequently in the literature [26-29].

AuNPs have been utilized in several research fields, including memory enhancement. [30] and inks for electronic printing [31]. AuNPs are used to permanently colour cotton and wool fabrics. [32]. Many fields, including textiles and biomaterials, are seeing rapid growth in the preparation of nanoparticles for their eventual use. AuNPs also serves as an anti-aging factor for the skin. [33].

Biocompatibility, biodegradability, and nontoxicity are just a few of the innovative biological properties of chitosan. Then there's the fact that it's a potent immunological, antibacterial, antioxidant, and haemostatic agent. [34, 35]. Resulting from these characteristics, chitosan has been employed in a variety of biomedical and pharmaceutical applications. Due to its rigid crystalline structure and the presence of strong intermolecular hydrogen bonds, chitosan's use in water at pH levels higher than 6 is restricted. [36-38].

Numerous attempts have been made to develop water-soluble chitosan products, such as succinyl- and carboxymethyl-chitosan, to broaden their applications in a wide range of industries, including but not limited to plant protection and human health. The increased water solubility of these chitosan derivatives at a wide range of pH values improved their antioxidant and antitumor activities. [14, 39, 40].

Carboxyethyl chitosan is important water-soluble chitosan. Carboxyethyl chitosan can be made from the hydrolysis and dehydrogenation reactions of chitosan and halo propionic acids when there is an excess of sodium hydroxide, according to numerous studies. [41].

In addition, carboxyethyl chitosan (CECS), a water-soluble chitosan derivative, is also biodegradable and biocompatible. Carboxyethyl chitosan has both carboxylic and amino groups utilized to stabilize AuNPs, hence it can be employed as both a capping agent and a reducing agent. [42-45].

In this study gold nanoparticles with low cytotoxicity on skin cells were the goal of our research. Carboxyethyl chitosan was referred to as both a reducing agent and a capping agent to achieve the synthesis of gold nanoparticles. The reduction procedure requires no additional chemical ingredients. To protect the environment, this procedure was carried out with an aqueous solution. The produced AuNPs were characterized using UV spectrophotometry and TEM imaging. Final testing was performed to determine the cytotoxicity of these nanoparticles in comparison to those generated by a standard chemical reduction process.

## 2. Experimental

### Materials

Hydrochloroauric acid ($HAuCl_4$) was purchased from Sigma-Aldrich, USA. Chitosan (CS) (Aldrich, viscosity1860cps, degree of deacetylation85.0 %). Sodium hydroxide (Modern Lab chemicals), Acrylic acid LR 99% (AA) was reagent grade and purchased from Molychem, Mumbai, India. are used without further purification. All other chemicals and reagents were of analytical grade and were used without further purification.

### Methods

### Preparation of Carboxyethyl chitosan

Carboxyethyl chitosan was made by Michael condensation of chitosan with acrylic acid as follows: 5 g of chitosan was first dissolved in 250 ml of distilled water containing 10.97 ml acrylic acid. A three-necked flask with a mechanical stirrer, condenser, and thermometer was used to store this solution. The reaction mixture was kept at 60 $^oC$ for two days. After cooling to room temperature, the reaction mixture was precipitated to remove excess acetone before being filtered to remove the solvent. The filtrate was washed with 70%, 80%, and 100% acetone aqueous solutions, respectively. For 24 hours, the final product was dried at 40$^oC$ under a vacuum. [46].

### Preparation of Gold Nanoparticles (AuNPs)

Before use, glassware was thoroughly cleaned in a bath of freshly prepared aquaregia solution (HCl: HNO3 3:1). 1 percent CECS in Millipore water was used to prepare the stock solution for the preparation of AuNPs. Overnight stirring produced a

homogeneous solution. Mixing $HAuCl_4$ with carboxyethyl chitosan solution and heating it to 100 ºC on a water bath with magnetic stirring resulted in a reddish-brown liquid. [47].

**Finishing of Fabrics with Gold nanoparticles**

On washed and dried viscose fabrics, we applied our newly fabricated gold nanoparticles (AuNPs), which had been prepared by the pad-dry-cure method. Each treatment was carried out on 30x30 cm of fabric that had been immersed in the gold nanoparticles (AuNPs) solution (0.005-0.5 g/ml) with an acrylate binder (1 percent) for 30 minutes. Drying at 80°C for 5 minutes was followed by thermo-fixation at 140°C for 3 minutes. Finally, samples were cleaned and dried so that they could be used for characterization and antibacterial evaluation.

**Characterizations of Gold Nanoparticles (AuNPs)**

- Fourier transform infrared (FT-IR) spectra of the samples were recorded by using an FT-IR spectrophotometer (Nexus 670, Nicolet, USA) in the region of4000-400cm$^{-1}$ with spectra resolution of 4 cm$^{-1}$.
- UV–vis spectroscopy of AuNPs was recorded on Shimadzu (UV-2450) to confirm the presence of AuNPs in the reaction medium at range 510–560 nm.
- The shape and size of gold nanoparticles (AuNPs) were investigated using JEOL, JXA-840 electron probe microanalyzer, Japan.
- The UV-protection factor (UPF) indicates the ratio of sunburn-causing UV measured without and with the fabric's protection. The ultraviolet protection factor (UPF) of untreated and finished fabric samples (size 3 x 3 cm) was determined according to the Australian/New Zealand standard (AS/NZS 4399-1996: Sun protective clothing-Evaluation and classification) using a UV-Shimadzu3101 PC spectrophotometer at wavelengths 280–390nm, which includes the UVB (280–320nm) and the UVA (320–400nm) according to the following equation:

$$UPF_i = \frac{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{\lambda=280}^{400} E_\lambda \times S_\lambda \times T_\lambda \times \Delta\lambda}$$

in which: E is the relative erythemal spectral effectiveness, S is the total solar spectrum irradiance, T is the average spectral transmission of the specimen, and is the length of time between measurements (nm) If the UPF values of the fabric range from 15 to 24, 25 to 39, and more than 40 (40+), they are classified as good, very good, or excellent UV protection, according to the manufacturer.

Using a scanning electron probe microanalyzer (type JXA 840A)–Japan–we investigated the SEM and EDX results of the treated fabrics.

Surface morphologies were imaged at various magnifications with a 30kV accelerating voltage to determine their characteristics.

They were conducted at the National Research Center's Central unit for analysis and scientific services, which is part of the National Research Center.

**Evaluation of cytotoxicity of AuNPs (In-vitro)**

**Cell culture**

The culture was maintained in Dulbecco's Modified Eagle's medium (DMEM) medium (in case of A549), and supplemented with 10% fetal bovine serum at 37°C in 5 % $CO_2$ and 95% humidity, cells were sub-cultured using trypsin versene 0.15 %. Notable, skin normal human cell line (BJ-1) " Immortalized normal foreskin fibroblast cell line "was obtained from Karolinska Center, Department of Oncology and Pathology, Karolinska Institute and Hospital, Stockholm, Sweden. Other cell lines "were obtained from Vacsera (Giza, Egypt).

**Cell viability assay**

After about 24 h of seeding 20000 cells per well in the case of A-549 cells (in 96 well plates), the medium was changed to serum-free medium containing a final concentration of the extracts of 100 µg/ml in triplicates. The cells were treated for 24 h. 100 µg/ml doxorubicin was used as positive control and 0.5 % distilled water was used as a negative control. Cell viability was determined using the MTT (3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide) assay as described by Mosmann 1983 with minor modifications as shown in equation (3) [48, 49].

$$\boldsymbol{Percent\ cytotoxicity} = \left[\mathbf{1} - \frac{\boldsymbol{Av(x)}}{\boldsymbol{Av(NC)}}\right] \times \mathbf{100} \quad (3)$$

Where Av: average, X: absorbance of the sample well measured at 595 nm with reference 690 nm, NC: absorbance of negative control measured at 595 nm with reference 690.

**3. Results and Discussion**

***Preparation and characterization of CECS***

Carboxyethyl chitosan was produced as a result of the reaction of chitosan with acrylic acid via the Michael reaction in water as the solvent under the

following reaction conditions: chitosan (5 g), acrylic acid (10.97 ml), reaction time (2 days), and temperature (60°C) (Fig. 1).

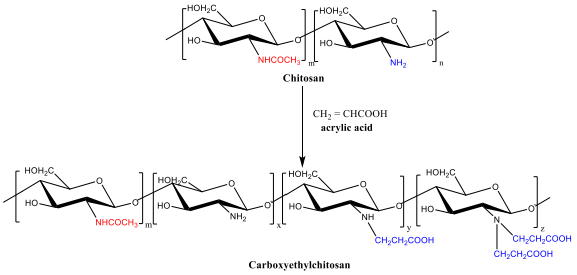


Fig. 1. Carboxymethylation of chitosan with acrylic acid via Michael reaction

The formation of carboxyethyl chitosan by the Michael reaction is regarded as a typical 1,4 nucleophilic addition, in which the nucleophile is added to the -carbon and the hydrogen is added to the -carbon to form the carbonyl group.

The nitrogen content of chitosan has been used to verify the conversion of chitosan into carboxyethyl chitosan by changing the percent of nitrogen from 6.9 percent for native chitosan to 3.4 percent for carboxyethyl chitosan. Nitrogen content changes because of the transformation of both NH2 and $CH_2OH$ into $NHCH_2COOH$ and $CH_2OCH_2COOH$, respectively.

The structure of both chitosan and carboxyethyl chitosan can be determined with the assistance of infrared spectroscopy using the Fourier transform (FT-IR). In Figure 2, you can see the FT-IR spectra of native chitosan and carboxymethyl chitosan, which were both prepared. Bands at 3423 cm-1 were observed in the Chitosan spectrum to correspond to NH and OH stretching vibrations; 1647 and 1572 cm-1 were observed for NH bending (amide I and II), and bands at 1401 and 1375 cm-1 were observed for amide III. [50, 51]. In addition, there are two absorption bands at 1151 cm-1 for CO bridging and two peaks at 1074 and 1025 cm-1 for CO stretching, which are both visible in the spectrum. The stretching COOH groups (asymmetric and symmetric) of carboxyethyl chitosan exhibit strong absorption bands at 1553 and 1404 cm-1 for both asymmetric and symmetric stretching [41, 52]. Aside from that, The amino groups that are characteristic of the amino acids are shifted as a result of the interference of amino groups with carboxylic groups that have been prepared, which confirms the conversion of chitosan into carboxyethyl chitosan [53-56].

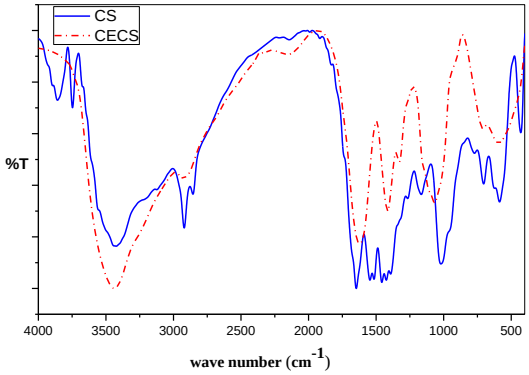


Fig. 2. FTIR spectrum of chitosan (CS) and carboxyethyl chitosan (CECS) prepared by reaction of 5gm chitosan with 10.97 mL acrylic acid at 60°C for 2 days

### 3.2. Preparation and characterization of gold nanoparticles (AuNPs)

Carboxyethyl chitosan (CECS) is used to reduce and stabilize gold nanoparticles (AuNPs) via its amino groups [42, 57]. As mentioned in the experimental part AuNPs can be prepared vis to consecutive steps heating of HAuCl4 at 100 0C followed by ultra-sonication with high power frequency at 53 Hz for 45 min [23, 42, 57].

The presence of AuNPs was confirmed by the change in colour of the HAuCl4 solution from yellow to reddish-brown to red.

The UV-Vis spectra of AuNPs capped in CECS are shown in Fig. 3a. A peaks signal is detected at 520-530 nm with no there has been a shift in the peak position, indicating that there is no agglomeration of nanoparticles. [58]. In addition, Fig. 3a depicts different concentrations of a substance have different effects. HAuCl4 (0.025-0.075 wt. %) and CECS (0.1-0.3 wt. %) on the efficiency of nanoparticle formation. As the concentration of HAuCl4 increased, the efficiency of AuNPs formation increased because the gold ions increased the oxidation power of the hydroxyl groups of CEMCS. As the concentration of CECS increased, the concentration of AuNPs increased until it reached 0.15 wt.% concentration, when this occurred, the efficiency decreased as a result of the steric effect of CECS.

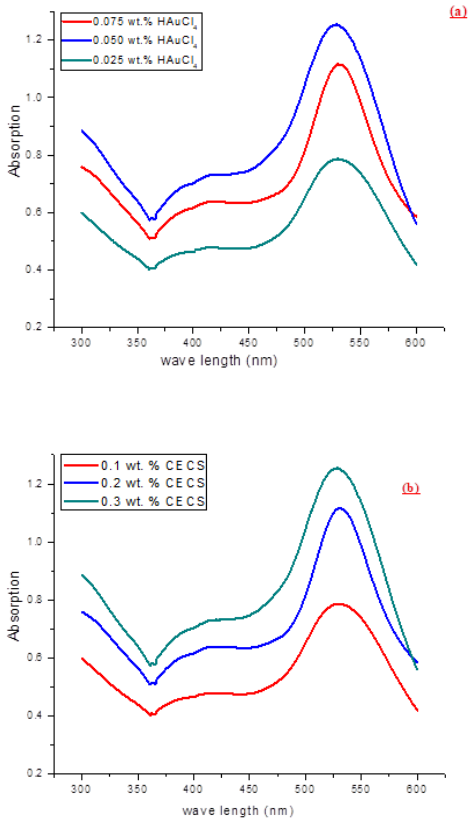


Fig. 3. UV-visible spectra of gold nanoparticles (AuNPs) stabilized in CECS as hydro chloroauric acid concentration changes (a) and CECS concentration changes (b)

Figure 2 shows transmission electron microscopy gold nanoparticle images stabilized by carboxyethyl chitosan. It was discovered that the AuNPs were encapsulated by CECS and that their sizes ranged from 5 to 15 nm. In contrast to the majority of gold colloid samples, only a small number of non-spherical particles were observed in addition to the majority of spherical particles. During the nucleation process, these non-spherical particles appeared to be created by the accumulated interference of two or three spherical particles [42, 59].

**Finishing of Viscose Fabrics with Gold Nanoparticles (AuNPs)**

Pad dry cure was used to apply gold nanoparticles (AuNPs) to viscose fabrics before they were dyed. The addition of AuNPs to viscose fabrics gives them new properties, particularly ultraviolet protection (UPF). The results of the anti-UV efficacy tests conducted on the untreated and AUNPs-loaded substrates are shown in Figure 3. It demonstrates that treating fabrics with AuNPs results in a noticeable increase in their UV-protection function. Based on their UV-protection properties, the untreated viscose fabrics provided poor protection against UV radiation, with a UPF of only 20. When comparing the protection values of the viscose fabrics before and after post-treatment with AuNPs, it is found that their differences in fabric construction are to blame for the variation in UPF values [60].

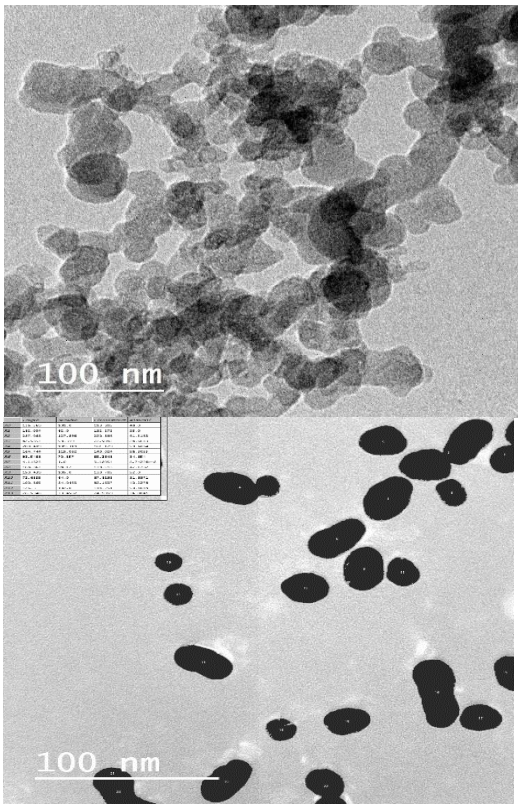


Fig. 4. Transmission electron microscopy (TEM) image of gold nanoparticles stabilized by CECS

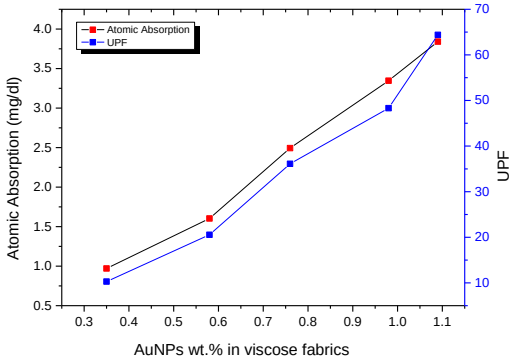


**Fig. 5. Atomic absorption and UPF values of the fabrics treated with AuNPs**

Figures 4 illustrate the results of a scanning electron microscope (SEM/EDX) analysis demonstrating the presence of Au nanoparticles in the investigated fabrics. The surface morphology of the fabric treated with Au nanoparticles appears to be a smooth surface with a nanoparticle deposit on top. While it is clear that the prepared Au nanoparticles have a more homogeneous and regular surface distribution and have higher intensity peaks, it is also clear that the Au nanoparticles EDX analysis indicates that the Au nanoparticles have content of 0.57 and a weight of 7.29; and have lower intensity peaks [61].

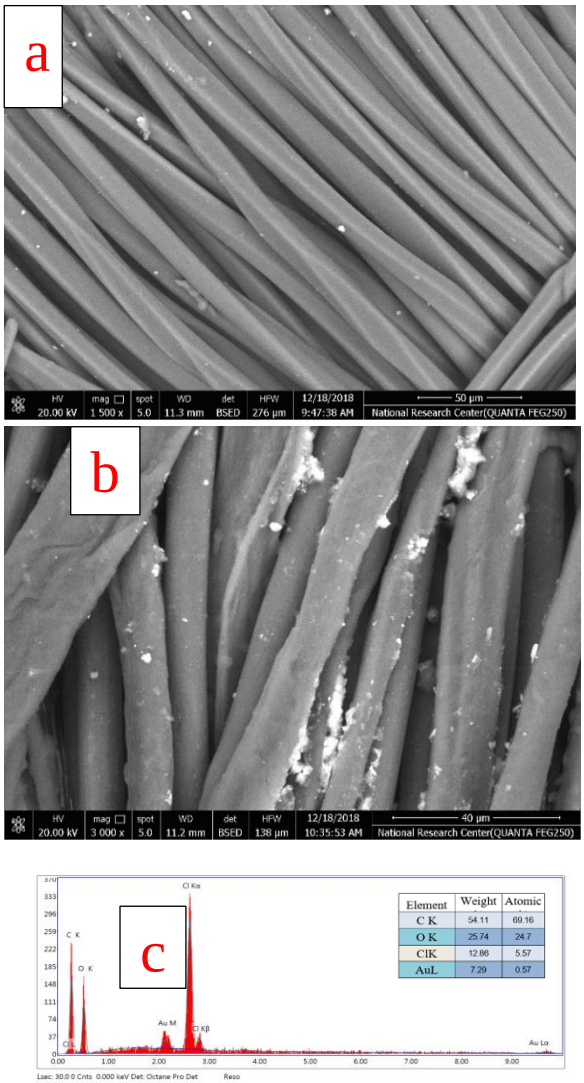


Fig. 6. SEM of untreated viscose fabric (a), gold nanoparticles treated viscose fabrics (b) and EDX spectra of viscose fabrics treated with AuNPs (c)

The surface texture of the Au nanoparticles coating appears to be dense and low porosity based on the observations made of it, and the nanoparticles appear to have coated the fibers and appear to be of a consistent size as shown in SEM images (Figure 4). The surface of the sample was coated with an Au nanoparticles film, which was formed and firmed over time. The use of Au nanoparticles did not affect the morphology of the surface under the conditions of experimentation and reaction. Due to the extremely strong electrostatic or chemical interactions between the gold nanoparticles and the fabric, , the Au nanoparticles were affixed tenaciously to the fibers [61].

**Cytotoxicity of AuNPs suspensions evaluated using MTT protocol**

MTT assay is used to determine the viability of cells as expressed by a decrease in mitochondrial activity. (Table3). A549 cells exposed to the three agents exhibit a decrease in mitochondrial function. GNPs types; CECS, CEMCS reduced AuNPs and chemical reduced AuNPs at different concentrations, from 0.025 wt.% to 0.075 wt.% concentration of $HAuCl_4$, for 24 h to evaluate the viable cells according to MTT protocol. The viable cells of chemical reduced AuNPs were decreased from 52.1±0.3% to 14.01±0.3% as the concentration of Au increased from 0.025 wt. % to 0.075 wt.% whereas these viable cells were changed from 97.1±0.4 % to 93.2±0.5 % for CECS reduced AuNPs at the same concentrations as shown in Fig. 9. Therefore, there is illustrated an increase in cytotoxicity of chemically reduced AuNPs whereas, there is no sign in cytotoxicity of CMCS reduced AuNPs. So that CMCS loaded AuNPs are non-toxic, safe and cell compatible and can be used as a biomaterial for drug delivery.

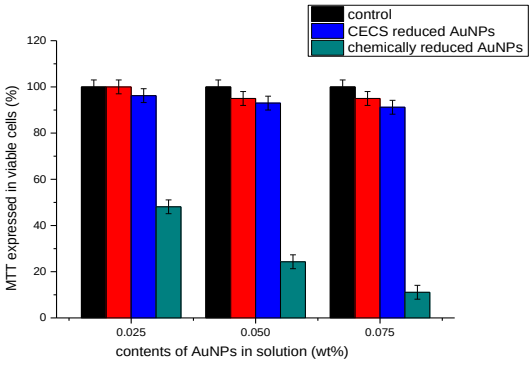


Fig. 7. Cytotoxicity of gold nanoparticles (AuNPs) reduced by carboxyethyl chitosan (CECS) and AuNPs reduced chemical reduction method in Epiderm cell ($5 \times 10^3$ cells)
Data are expressed as mean ± S.D. where n = 3.

## 4. Conclusion

Gold nanoparticles (AuNPs) were prepared in a simple and environmentally friendly manner by employing CMCS as agents capable of both reducing and stabilizing. AuNPs were prepared at 100 oC for 1 hour with various concentrations of carboxyethyl chitosan (0.2 percent w/v, 0.5 percent w/v, and 1% w/v). Nitrogen content, carboxyl content, and FTIR spectra were used to characterize CMCS. UV spectrophotometry and TEM images were used to characterize AuNPs. The cytotoxicity of the chemically synthesized AuNPs was determined using a cell viability assay based on MMT, and the IC50 values were compared to those synthesized chemically. . The results indicate that AuNPs have a normal distribution with a particle size of 5-15 nm and that their cytotoxicity was decreased when prepared using this green method, indicating that AuNPs can be used safely in skin-to-skin medical treatment.

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