Copper and Copper Oxides Nanoparticles Synthesized by Electrochemical Technique in Chitosan Solution

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Abstract

A synthesis of chitosan copper and copper oxides nanoparticles (Cs-Cu, CuO) NPs via electrochemical technique has been reported. Chitosan copper complexes were prepared by electrochemical oxidation technique at duration time followed by reduction using different reducing agents for producing chitosan copper nanoparticles, Cs used as stabilizer and capping agent. The nanocomposites were characterized by using ultraviolet-visible spectroscopy (UV-vis). Transmission electron microscope (TEM) images were investigated emphasized formation the formation of NPs with different shapes. The average size of formed NPs is 28 nm. X-ray diffraction (XRD) is used to investigate the formation of the crystalline structure of prepared samples exhibited presence of copper and copper oxides in the formed complexes and nanocomposites. Analysis of FTIR showed chelation of Cu^{+2} with chitosan in complex form and electrostatic interaction between chitosan and copper nanoparticles.

Keywords: Chitosan, Chitosan Copper complex, copper and copper oxide nanoparticles

1. INTRODUCTION

In recent years, many researches were carried out on preparation of nanomaterials. Nanoparticles (NPs) show different physical, chemical and biological properties rather than bulk materials due to a high specific surface area to volume ratio [1]. The nanophase is intermediate between microstate and macrostate showed different properties than them. In last decades metallic NPs are widely used in many fields of science, industry and in medical applications due to their properties. They are utilized in many biomedical applications such as in the cosmetics industry, drug delivery and hyperthermia [2].

Nowadays, chitosan metal complexes and chitosan metal nanocomposites were studied extensively due to their applications in biological fields. Copper is considering as one of the most important nanometal in such composites. Chitosan copper $[Cs-Cu]^{+2}$ complexes and nanocomposites of chitosan (copper and copper oxides) have excellent antimicrobial activity against various bacterial strains [3], also exhibited antitumor applications [4, 5].

Copper is essential for metabolic processes and organs function, also provides a role in development and maintenance of cardiovascular system, the skeletal system, human immune system and function of the nervous system. It has good antimicrobial and antibiotic properties [6].

For the last years, many efforts have been made on the synthesis of metallic copper nanoparticles in condensed phase with shape, size and growth control [7]. Copper NPs syntheses by many methods such as metal-vapor synthesis[8], radiation methods[9], vacuum vapor deposition[10], thermal reduction [11], chemical reduction[12], laser ablation[13] and microemulsion techniques[14]. The major limitation in these syntheses are their highly costing and toxically for environment. Electrochemical technique first developed by Reetz and Helbig in 1994 is a very promising technique for the production of metal nanoparticles because of their simplicity, environment-friendly process (eco-friendly) and their versatile application in the preparation of particles with different shapes and sizes. In their setup, a sacrificial anode is used as the metal source, which released ions and the resulting metal ions were reduced at cathode, forming metallic particles stabilized by tetraalkylammonium salts [15]. Usually, the electrolytic solution used for the production of metal nanoparticles contains (metal salt in acidic medium, surfactant stabilizer to form complexation or chelation with metal ions and reducing agent). Chitosan has been used as electrolytic solution for preparing green nanocomposites. Nowadays, most important copper nanocomposites are copper chitosan complexes and nanocomposites [16]. Chitosan is a partially deacetylated derivative of chitin. Chitosan is the second most used natural polysaccharides after cellulose [17]. Chitosan extracted from the shells of crustaceans like crabs, lobsters and prawns. Owing to its unique properties such as biodegradability, biocompatibility, and biological activity, chitosan has been widely applied in the food and cosmetics industry as well as the biomedical applications in relation to tissue engineering, antimicrobial, non-toxicity, anti-tumor properties, and the pharmaceutical industry relating to drug delivered [18]. It is recommended that chitosan of lower molecular weight exhibited strong bacterial and superior biological activities than high molecular weight [19]. It have been pointed out that the –OH and –NH2 groups on the chitosan back bone are very active chelating groups to coordinate with transition metal ions to form two types of chitosan metal complexes named "bridge model" and "pendant model [20]. Also it is shown that coordinating bond may lead to weak point on the chitosan chain which in turn leads to degradation of chitosan [21]. Degradation of chitosan and chitosan metal complexes can be occurred by electrochemical oxidation technique [22, 23]. Degradation rate found to be dependent on the time of process, which lead to controlling the molecular weight [24].

The aim of our study in the present manuscript describes a strategy which depends on preparation of chitosan copper complex having different copper/chitosan ratio by electrochemical oxidation technique and followed by reduction (using ascorbic acid, NaBH4 and N2H4 reducing agents) to produce chitosan copper nanocomposites.

2. EXPERIMENTAL TECHNIQUES

2.1. Chemical and methods

Chitosan Mw = 600,000 g/mol and Deacetylation degree (DD) is 75% (Aldrich chemical co.), De-ionized water (resistivity >2x10^{8}Ωcm) was used for all samples preparation, Acetic acid of analytical grade, Platinum sheets Sigma-Aldrich, used as

counter electrode (cathode). Copper plates from Sigma-Aldrich of purity 99.999%, was used as source electrode (anode).

2.2. Synthesis of chitosan Copper Complex and copper nanoparticles

[Cs-Cu] $^{+2}$ complexes were produced by using the electrochemical technique of copper metal in an aqueous acidic medium. The electrochemical process was carried out at constant potential of 1.5V to avoid the hydrolysis of water. Electrolytic solution was prepared by dissolving 1 wt% chitosan into 100 ml deionized water containing 1% acetic acid, then solution placed on magnetic stirrer for 24 hrs. The pH of solution is adjusted at 4.6 before running the experiment. This pH value was fixed for the preparation of used complexes. The cell used to prepare chitosan copper complex [Cs-Cu]$^{+2}$ consists of Platinum sheet (cathode) and Copper sheet (anode) were dipped in the electrolytic solution separated by a fixed distance 5 cm from each other. The electrodes were connected to a suitable variable resistor and constant-voltage power supply (Model 1030A, U.S.A). The temperature was held constant at 25˚C by using a rotating water bath (VEB MLW, Type U4; GDR).Preliminary experiments were carried out for different running times ranged at (8hrs, 12 hrs, 16 hrs., and 20 hrs.). The solution was centrifuged by IEC Micromax microcentrifuge at speed (10,000 rpm for 30 min.), and filtered to remove any debris. Then the pH value is readjusted at 5 for the chitosan-copper complexes. These complexes were reduced by different types of reducing agent such as ascorbic acid, hydrazine hydrate and sodium borohydride. The samples were casted onto petri dishes (diameter 11cm) and left to dry at room temperature. After complete drying, samples are removed from the dishes and divided into pieces for measurement of some physical properties with different techniques.

2.3. Characterization

Chitosan, chitosan copper [Cs-Cu] $^{+2}$ complexes and Cs-Cu nanocomposites were characterized by following measurements. ATI Unicom UV–Vis spectrophotometer which working in the range of 200–900 nm. (NICOLET-IS10 FTIR located at chemistry department, faculty of science, Mansoura University) show spectra of [Cs- Cu] $^{+2}$ complexes and NPs. Transmission Electron Microscope (JEOL JEM - 2100 located in Mansoura University) with acceleration voltage of 160 kV was utilized to determine the size and distribution of nanoparticles in prepared samples. X-ray powder diffraction (XRD) patterns of Cs-Cu NPs were obtained by using Siemens D5000 diffractometer. The source of X-ray was Cu Kα radiation (40kV, 30mA). Differential thermal analyzer (DTA) (sltimad24 Japan located in Cairo University) under nitrogen gas.

3. RESULTS AND DISCUSSION

3.1. Chitosan copper complexes

The atomic absorption spectrometry is used to record the amount of copper molar ratios in prepared samples (chitosan copper complexes) at different duration time (8h, 12h, 16h, and 20h). It was found that the amount of copper content increase by increasing the complexation time. This behavior is shown in Figure (1) and represented by the polynomial empirical formula:

$$C = A + B_1 t + B_2 t^2 + B_3 t^3$$

Where C is the concentration at any time (t) and, where A is constant= 47.26 and B_1 is constant = 58.58, B_2 = -3.38 and B_3 = 0.067
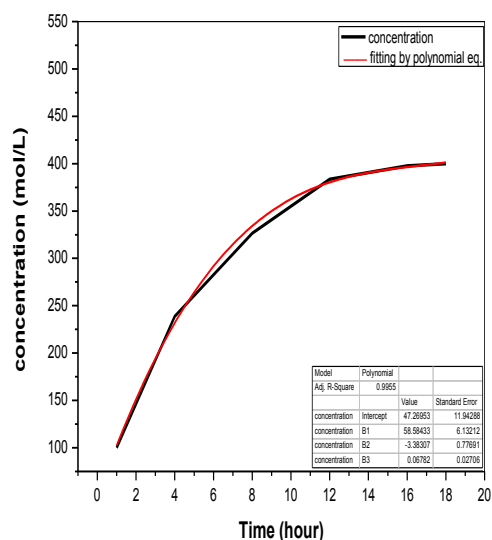

Figure (1) copper concentration in chitosan solution.

3.2. Optical characterization

A- UV/Vis absorption spectra of chitosan copper complexes

Figure (2) represents the UV/Vis absorption spectra of copper ions with chitosan at different experimental duration time of electrochemical oxidation. It shows the appearance of absorption peaks at 258 nm, 294 nm and broad one at 750 nm for all prepared samples. Band at 258 nm may be due to Cu(I) ions, and at 258 nm due to Cu (II) ions chelated with chitosan [25]. The peak around 750 nm is a common peak at all complexation of copper with any ligands, appeared due to complexation of copper with chitosan, this broad peak is existed in all formed complexes. This hump peak is attributed to the d–d transition of Cu^{+2} ions [26]. The intensity of this peak was increased by increasing the duration time. This peak vanished when using reducing agent due to conversion of [Cs-Cu]$^{+2}$ complex to chitosan copper and copper oxides nanocomposites as shown in figure (3).

B- UV/Vis absorption spectra of chitosan copper nanocomposites

UV-Vis spectra of chitosan copper nanocomposites with different reducing agents. From this spectrum the broad band of complex is completely disappeared while new characteristic bands appeared as represented in figure (3). Figure (4) exhibits peaks at about 360 nm and 314 nm that may be attributed to oxides nanocomposites phase (CuO, Cu_2O) [22, 27]. The sample which reduced by ascorbic acid (a), has peaks of Cu NPs appeared at 314 nm, 360 nm and 400 nm, which refer to Cu NPs in different shape and size [28]. The sample which reduced by $NaBH_4$ (c), showed the peaks of copper and copper oxides at 314 nm, 360 nm and 427 nm. The sample which reduced by N_2H_4 (d) contains a set of peaks for copper and copper oxides at 314 nm, 360 nm and 484 nm. The peak at 484 nm is a very broad peak is due to existence of different sizes of Cu NPs. The chemical reduction method using copper salt usually characteristic peak of copper around at (556-600 nm), but in our experimental it has not appeared at this wavelength. This is due to the lack of homogeneity in the shape and size of nanoparticles NPs, where the dipolar plasma resonance is found dependent on the shape of NPs ((spheres- pentagonal – triangular prisms)) [29].
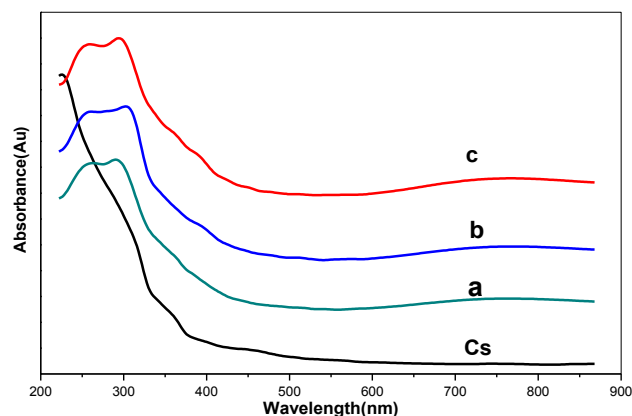

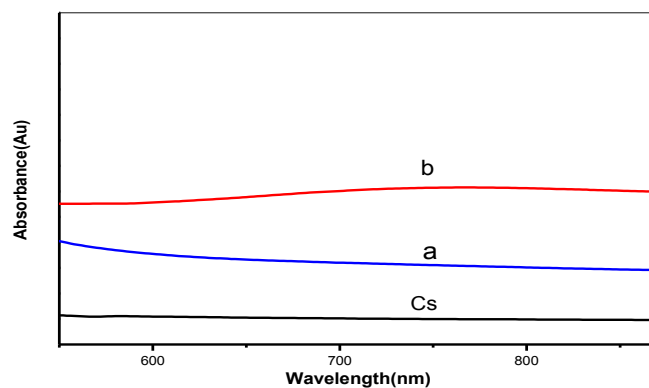Figure (2): UV spectra of CS and its complexes at different complexation time (a) 8h, (b) 12h and(c) 16h.

Figure (3): UV spectra of the disappeared of hump peak: CS and it's (a) after reduction and (b) complex at time16h.
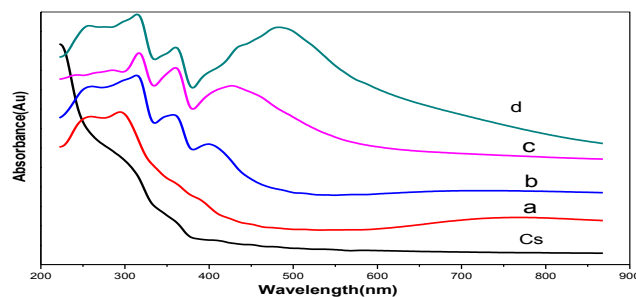

Figure (4): optical absorption spectra of: (a) complex at duration time (16h), (b) reduced chitosan copper complex at

complexation time (16h) with ascorbic acid, (c) reduced with NaBH$_4$, (d) reduced with hydrazine.

3.3. Fourier transformation Infra-Red (FTIR) analysis

FTIR characteristic bands of chitosan there are shown in figure (5). Chitosan exhibit abroad band at 3482 cm^{-1} attributed to –NH$_2$ symmetrical stretching and hydrogen bonded –OH [30]. The peaks at 2918 cm^{-1} and 2827 cm^{-1} corresponded to CH$_2$ asymmetrical and symmetrical stretching [31]. Furthermore, the peak at 1423 cm^{-1} assigned to CH$_2$ bending vibration[32]. The band at 1648 cm^{-1} assigned to C=O stretching vibration of amide bond resulted from traces of chitin [20]. The band at 1598 cm^{-1} corresponds to NH$_2$ bending vibration [33]. The peak at 1384 cm^{-1} attributed to C-H asymmetrical bending vibration. The band at 1253 cm^{-1} assigned to C-N stretching vibration, the peak at 1067 cm^{-1} related to O-H groups of chitosan.

FTIR spectra of chitosan copper complexes exhibited some vibrational modes that differ from chitosan as shown in figure (5). The broad band at 3482 cm^{-1} shifted to 3434 cm^{-1} assigned to stretching vibration of –NH$_2$ and –OH groups, with increasing the Cu^{+2} content in complexes through increasing the duration time of oxidation, the band become less broadening, which also indicated decrease the intermolecular force (hydrogen bond) within the molecules and become more ordered. The bands at 1598 cm^{-1} corresponds to NH$_2$ bending vibration shifted toward 1561 cm^{-1} this referred to the chelation of NH$_2$ and OH functional groups of chitosan with Cu^{+2}.

Figure (6) shows FTIR spectra for [Cs-Cu]$^{+2}$ complex at duration time (16h) that reduced by different types of reducing agents (N$_2$H$_4$ (a), NaBH$_4$ (b) and ascorbic acid (d)). With ascorbic acid (d) the peak at 2927 cm^{-1} attributed to C-H asymmetric stretching vibration has become more sharp after reduction by ascorbic acid, a two peaks at 1634 and 1770 cm^{-1} attributed to NH$_2$ bending and C=O stretching respectively. The peak at 774 cm^{-1} assigned to Cu-N stretching vibration, which an evidence for electrostatic attraction between Cu and chitosan. There is no peak for oxidation of Cu due to ascorbic acid act as antioxidant[34]. In samples which reduced by N$_2$H$_4$ (a) and NaBH$_4$(b) the peak at 525 cm^{-1} and 646 cm^{-1} were assigned to the stretching vibration N with cupric oxide (Cu$_2$O) and cuprous oxide (CuO) respectively [35, 36].
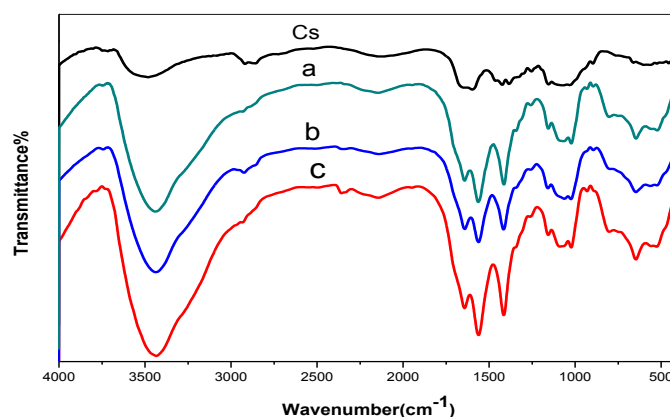

Figure (5) FTIR spectra of Cs, Chitosan copper complexes prepared at different duration time: (a) 8h, (b) 12h, and (c) 16h
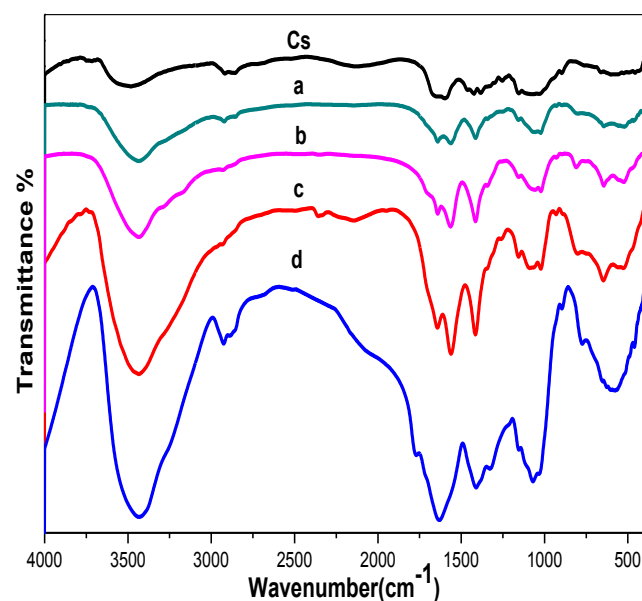

Figure (6): FTIR spectra of Cs, (c) chitosan – Cu complex 16h, (a) reduced the [Cs-Cu]$^{+2}$ complex with hydrazine, (b) reduced [Cs-Cu]$^{+2}$ complex with NaBH$_4$, (d) reduced [Cs-Cu]$^{+2}$ complex with ascorbic acid.

3.4. X-Ray diffraction (XRD)

X-Ray powder diffraction patterns of pure chitosan, chitosan copper complex and Cu NPs are shown in Figure (7).The diffraction pattern of chitosan is characteristic of amorphous structure, diffractogram of Cs has the characteristic peaks at diffraction angle 2θ equal to 10° and 20° were found in

literatures [37, 38] and it contains a crystalline seed at angle 2θ equal to 29.7 °. When the process was running to form the [Cs-Cu] $^{+2}$complex lead to formation of different crystalline forms of chitosan their characteristic peaks appeared at angle 2θ equal to (11°, 12.6°, 17°, 19°, 22°, 25°) and a small peaks at angle 2θ equal to 32.6°, 34°, 36.7° and 40.8° referred to formation small amount of copper and copper oxides nanoparticles [39]. The existence of copper and copper oxides nanoparticles confirmed that the chitosan act as reducing and capping agent [40]. The intensity of [Cs-Cu] $^{+2}$complex become sharper after adding different types of reducing agents. A number of peaks at angle 2θ equal to 32.6°, 34°, 36.7°, 40.8° and 44° in samples which reduced by N_2H_4 and $NaBH_4$ (c and d) characterized for formation CuO and Cu_2O. In sample which reduced by ascorbic acid (b) which contain peaks characteristic for copper NPs at diffraction angle 2θ equal to 43.19°, 50.36° and 74.12° corresponding to (111), (200) and (220) planes of FCC crystalline structures of Cu respectively [41] . Ascorbic acid act as antioxidant and strong reducing agent, lead to disassembles of CuO and Cu_2O NPs[42].
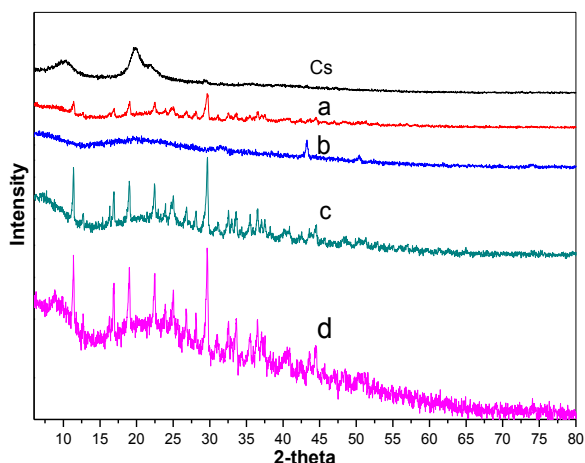

Figure (7): (XRD) for Cs, (a) [Cs-Cu] $^{+2}$ complex (16h), (b) reduction by ascorbic acid, (c) reduction by hydrazine, (d) reduction with $NaBH_4$.

3.5. Differential thermal analysis (DTA)

DTA Thermograms for pure chitosan (Cs) is shown in figure (8). For pure chitosan, we can notice that the endothermic peak at 15.7 C° is due to lose of free water or moisture evaporation. The broad peak indicates that Cs has amorphous structure. Chitosan is a non-thermoplastic material, the melting endothermic temperatures peak was completely absent in the curve because Cs does not have the melting or glass transition temperatures [43,

44]. In the samples (c and d) the [Cs-Cu] $^{+2}$complex show endothermic peaks at 42.19C°, 47.9 C° and 52.6 C° respectively due to moisture evaporation. Sample (b) doesn't contain any peaks due to the presence of copper NPs and have no copper oxide. The samples (a), (c) and (d) contain two crystalline phases at exothermic peaks at 306 C°, 309 C° and 324 C° which may be characteristics for crystalline behavior of both CuO and Cu_2O, existing due to building up of atoms, self-arrangements, in an ordered shape.
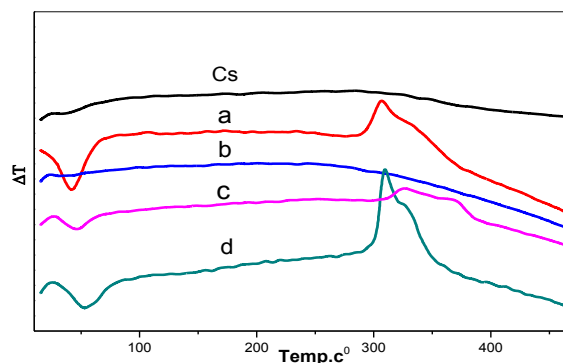

Figure (8) DTA for Cs, (a) [Cs-Cu] $^{+2}$ complex (16h), (b) reduction by ascorbic acid, (c) reduction with $NaBH_4$, (d) reduction by hydrazine.

3.6. Particle size and structure

The Cu NPs were synthesized and confirmed with particles size as shown in TEM micrograph (9). These particles, essentially, were very fine and roughly monodispersed, revealing that the presence of chitosan, indeed, restricted the growth of Cu nanoparticles efficiently. The average size of formed NPs is 28 nm. Figure (9) illustrate high resolution transmission electron microscopy images (HRTEM) of formed NPs. Most of formed crystals have FCC structure in samples that reduced by ascorbic acid which also confirmed by electron diffraction and lattice space images as shown in figure 9 (b and c). Figure 9 (e and f), shows the formation of fivefold crystals of reduced copper nanoparticles by $NaBH_4$ formed Cu this attribution was frequent in the literature [45].
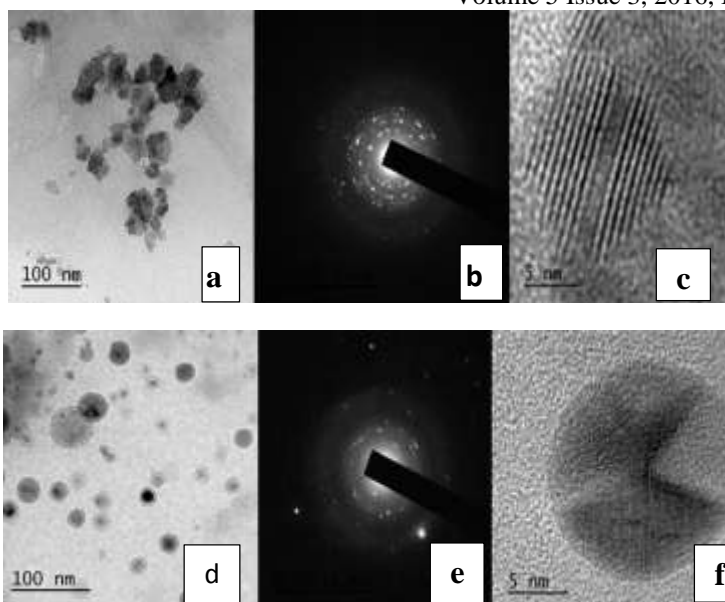
Figure (9): (a, d) TEM images of the CS-Cu NPs for samples reduced with ascorbic acid and NaBH$_4$. (b, e) electron diffraction for sample reduced with ascorbic acid and NaBH$_4$. (C and f) HRTEM image of lattice fringes were corresponding to CS-Cu and CuO or Cu$_2$O NPs planes for the samples (a) and (d).

4. CONCLUSION

In this paper, chitosan copper and copper oxides nanoparticles were successfully synthesized at room temperature by using electrochemical technique. Chitosan copper complex were reduced by different types of reducing agents such as (ascorbic acid, N$_2$H$_4$, NaBH$_4$). The presence of copper metal and copper oxides nanoparticles were confirmed by the appearance of the surface Plasmon resonance on these colloids, which their bands appeared in the FT-IR to investigate the interaction between copper nanoparticles and –NH$_2$, -OH function groups of chitosan. The TEM studies showed that the mean size of the NPs is 28 nm. The electrochemical technique is simple, cost-effective and the product which could use in many pharmaceutical and biomedical applications, all the materials used in the study were non-toxically for environment.

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