CHAPTER 2
SYNTHESIS AND CHARACTERIZATION OF METALLIC NANOPARTICLES

2.1 INTRODUCTION

In recent decades, nanotechnology has attracted scientists from many different fields. The fundamentals of nanotechnology lie in the fact that properties of substances dramatically change when their size is reduced to the nanometer range, as reported by Chattopadhyay, 2006 and Patel & Chattopadhyay, 2007 [1-2]. When a bulk material is divided into small size particles with one or more dimensions (length, width, or thickness) in the nanometer range or even smaller, the individual particles exhibit unexpected properties which are different from those of the bulk material. Metal nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, catalysis, etc. The optical properties of small metal nano-particles are dominated by the collective oscillation of conduction electrons resulting from the interaction with electromagnetic radiation. These properties are mainly observed in Au, Ag, and Cu, because of the presence of free conduction electrons. Such particles are under active research because they possess interesting physical properties differing considerably from that of the bulk phase as reported by Chattopadhyay and Patel, 2009 [3]. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nano-particles is the reduction of metal ions in solution as reported by Chattopadhyay and Patel, 2009, 2010 and Jana, Wang and Sau, 2000 [4, 5, 6]. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

Attempts have been made to develop a simple method for synthesizing metal nano-particles of Copper, Silver and Zinc in colloidal solution form. Metallic nano-particles were prepared in aqueous solution by chemical reduction method using sodium borohydride as reducing agent. The metallic nano particles produced was either immediately capped with sodium lauryl sulphate (SLS) or trisodium citrate (TSC). The stability of nano-particles in the dispersion was monitored through the analysis of absorbance spectra at different stages during the process of synthesis. The stability of the nano-particles dispersed in aqueous medium was also examined at different time
intervals. Their stability was examined in presence of various capping agents used. The size and size distribution of the particles were investigated by particle size analyzer. The morphology of the particles synthesized was examined by particle size analyzer and atomic force microscope (AFM) studies. A novel in-situ stabilization (i.e. the particles were formed and stabilized in-situ in fiber matrix itself) technique has also been developed and analyzed.

2.2 MATERIALS

Various chemicals and material used for the study are listed in Table 2.1 and 2.2. The polyester fabric supplied by Kiran Threads, Vapi (Gujarat) was mild scoured (5% soap Lissapol L, and 2% soda ash at boil for 15 min.) and thoroughly washed with distilled water before use.

Table: 2.1 Chemical specifications

<table>
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<tr>
<th>Sr no</th>
<th>Name</th>
<th>Formula</th>
<th>Grade</th>
<th>Mol.wt. gm/mol</th>
<th>Supplier</th>
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<td>1</td>
<td>Copper sulphate</td>
<td>CuSO₄·5H₂O</td>
<td>AR</td>
<td>249.68</td>
<td>Sd Fine chemicals.</td>
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<tr>
<td>2</td>
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<td>AgSO₄·5H₂O</td>
<td>AR</td>
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<tr>
<td>3</td>
<td>Zinc nitrate</td>
<td>Zn(NO₃)₂·6H₂O</td>
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<td>4</td>
<td>Sodium borohydride</td>
<td>NaBH₄</td>
<td>AR</td>
<td>37.83</td>
<td>Sd Fine chemicals.</td>
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<tr>
<td>5</td>
<td>Tri-sodium citrate</td>
<td>C₆H₅Na₃O₇·2H₂O</td>
<td>AR</td>
<td>294.10</td>
<td>Sd Fine chemicals.</td>
</tr>
<tr>
<td>6</td>
<td>Sodium lauryl sulphate</td>
<td>CH₃(CH₂)₁₁OSO₃Na</td>
<td>AR</td>
<td>288.38</td>
<td>Qualigens Fine Chemicals</td>
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<tr>
<td>7</td>
<td>Lissapol L</td>
<td>-</td>
<td>LR</td>
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Table: 2.2 Polyester material specifications

<table>
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<th>Sample</th>
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<td>Weft</td>
</tr>
<tr>
<td>128d</td>
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2.2.1 Equipments

Three metallic nanoparticles namely, Cu, Ag and Zn in colloidal form were synthesized by chemical reduction technique. For the synthesis and characterization of these nano particles various equipments were used. Name and make of the equipments are listed below.

- Reaction Chamber (In-house designed) with N\textsubscript{2} gas supply unit and high speed magnetic stirrer as shown in figure 2.1. Experiment was carried out at Department of Textile Chemistry, The M.S. University of Baroda.

- Laboratory two bowl padding mangle: (EEC Pvt. Ltd., Mumbai). Experiment was carried out at Department of Textile Chemistry, of The M.S. University of Baroda.

- Spectrophotometer (interphased with computer colour matching system): Spectra scan 5100 (RT) (Premier color scan instrument), India test was performed at Department of Textile Chemistry, The M.S. University of Baroda.

- SEM/EDX Model JSM-5610 LV Japan, with oxford Inca Software for characterizing surface morphology and elemental analysis of nano particles, The test was performed at Department of Metallurgical and materials Engineering, The M.S. University of Baroda.

- UV-VIS Spectrophotometer (Shimadzu UV-2450, Japan): for determining absorbance of nano colloidal solution, at the Department of Applied Chemistry, The M.S. University of Baroda.

- Particle Size analyzer: MAL 501131, DTS version UK, Malvern Instrument was used for analysis the particle size. Test was performed at Department of Pharmacy, The M.S. University of Baroda.

- AFM; Easy Scan 2, Nanosurf AG, Switzerland, was used to examine morphology of nanoparticles deposited on glass plate.

- X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan); For quantitative and qualitative elemental analysis of the polymer nano composite materials. Test was performed at Department of Metallurgical and materials engineering, The M.S. University of Baroda.
2.2.2 Reaction chamber designed and used

The reaction chamber designed and used for the synthesis of nano particles is shown in figure 2.1. As seen in the figure, the experiment setup consists of the actual reaction chamber, nitrogen gas supply unit with pressure gauge, magnetic stirrer and stainless steel clamp.

![Figure 2.1 Experimental setup; reaction chamber with N₂ gas supply](image1)

The reaction chamber was made of toughened glass with a capacity of 500 ml. The glass chamber was equipped with three inlets. One for the introduction of nitrogen gas in the reaction mixture, the constant pressure of the nitrogen gas was ensured and monitored through the pressure gauge. Other inlet contains burette along with knob for the insertion of reducing agent inside the chamber. The third inlet was for the insertion of capping agent but initially it was kept closed. The reaction chamber was placed on magnetic stirrer, which ensures constant stirring throughout the experiment. The chamber was kept erect on the magnetic stirrer with the help of clamp. The schematic animated model of the chamber is shown in figure 2.2.

![Figure 2.2 Schematic presentation of Reaction proceeding in reaction chamber](image2)
2.3 EXPERIMENTAL METHODS

2.3.1 Preparation of copper nano colloids by chemical reduction technique

Metal nanoparticles, due to their special properties and also small dimensions, find important applications in optical, magnetic, thermal, sensoric devices, SERS (surface enhanced Raman scattering), catalysis, etc. The optical properties of small metal nanoparticles are dominated by the collective oscillation of conduction electrons resulting from the interaction with electromagnetic radiation. These properties are mainly observed in Au, Ag, and Cu, because of the presence of free conduction electrons. These particles are under active research because they posses interesting physical properties differing considerably from that of the bulk phase. It comes from the small sizes and high surface/volume ratio. The most common method employed for the synthesis of metal nanoparticles is the reduction of metal ions in solution. However, the control of size and shape at the nanometer level is a real problem, as the mechanism of size/shape control is still left largely unresolved.

In this work, an attempt has been made to analyze formation of Cu nanoparticles from copper salt at different stages of synthesis as well as after storing for variable time in atmospheric condition. The effect of time after synthesis on the shape and size of these particles was investigated using Particle size analyzer, SEM and AFM systems. Further, the effect of trisodium citrate as stabilizer for the nano particles was also investigated.

2.3.1.1 Preparation technique

Copper nanoparticles were prepared in aqueous solution by chemical reduction technique using sodium borohydride as reducing agent to reduce copper sulphate to metallic nano copper. In a typical set, 100 ml of 1x10^{-3} M CuSO_4 (CuSO_4.5H_2O, 0.3 gm, 4.17 mmol in 100ml water) solution was purged with N_2 gas for 10 min to remove the dissolved oxygen. 10 ml of 2x10^{-3} M aqueous solution of sodium borohydride (NaBH_4, 0.1gm, 3.83 mmol in 50ml water) was then added drop wise to it under constant stirring in nitrogen atmosphere. The colour of the solution was changed to dark yellow on gradual addition of reducing agent indicating the formation of copper nanoparticles. 10 ml of (1x10^{-3} M) sodium lauryl sulphate or tri-sodium citrate (C_6H_5Na_3O_7.2H_2O, 0.1gm, 29.41mmol in 100ml water) was added and allowed to stir for another 10 min for capping of the nanoparticles. Distilled water was used for preparing the solutions of all the chemicals. Scheme 1 gives schematic presentation of Cu nano particle formation and their stabilization by capping agent. The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer at different stages of synthesis.
Addition of Electron donor in solution

Scheme 1 Schematic process diagram of synthesis

2.3.1.2 Stabilization study of copper nano particles

The stability of copper nano colloid in absence of capping agent at different time intervals viz, after 12 hrs, 24 hrs 72 hrs and 4 weeks was examined by monitoring its absorbance in UV-VIS spectrophotometer. The effect of time after synthesis on the shape and size of these particles were investigated using particle size analyzer, SEM and AFM systems. Further, the effect of capping agents on the stability of nano particles were studied using two types of stabilizers viz. sodium lauryl sulphate and tri-sodium citrate.

Finally, a novel in-situ synthesis and stabilization technique was adopted i.e. the particles were formed and stabilized in-situ within the fiber matrix itself.

2.3.1.3 In situ synthesis and stabilization technique

The cleaned (100%) polyester fabric was used for this experiment. The fabric was first padded with chilled 2x10⁻³ M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was then further padded with 1x10⁻³ M copper salt (CuSO₄) solution using again 2-dip-2-nip padding technique. Finally, the fabric is cured in the curing chamber at 180 °C for 60 seconds.

Figure 2.3 Schematic process design for in situ synthesis of metallic nano on textile
2.3.1.4 **Characterization of copper nano particles**

*UV-visible spectrophotometry*

The absorbance of nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range: 300 nm to 700 nm.

*Particle size analyzer*

The particle size and size distribution of Cu nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

*Scanning Electron Microscopy (SEM)*

Scanning Electron Microscopy was used to characterize the nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100Å. Stabilized solution of copper nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

*Elemental analysis by Oxford-Inca software on SEM*

The elemental analysis of the synthesized copper nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The copper nano particles were deposited on carbon coated aluminum sheet and further coated with gold. EDX analysis of these samples was carried out using Oxford-Inca software on scanning electron microscope. The instrument reports the presence of elements in pure and oxide state qualitatively.

*Atomic Force Microscopy (AFM)*

Morphology of Cu nanoparticles deposited on glass plate was examined with the help of AFM operated in a contact mode (cantilever force constant 3 N/m).

*Determination of colour of the colloidal solution*

The changes in colour of the colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

*X-Ray fluorescence spectroscopy (EDX)*

For the elemental analysis of polyester fabric before and after in-situ generation of copper nano technique were performed by X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.
2.3.2 Preparation of silver nano colloids by chemical reduction technique

Metallic silver colloids were first prepared more than a century ago. Ag nanoparticles can be synthesized using various methods, such as chemical, electrochemical, \( \gamma \)-radiation, photochemical, laser ablation, etc. [10,11]. The most popular preparation of Ag colloids is chemical reduction of silver salts by sodium borohydride or sodium citrate. This preparation is simple, but the great care must be exercised to make stable and reproducible colloid. The purity of water and reagents and cleanliness of the glassware are critical parameters. Solution temperature, concentrations of the metal salt and reducing agent and reaction time influence particle size. Controlling size and shape of metal nanoparticles remains a challenge. The size-induced properties of nanoparticles enable the development of new applications or the addition of flexibility to existing systems in many areas, such as catalysis, optics, microelectronics and textiles.

Silver nano is a trademark name of an antibacterial technology which uses silver nanoparticles in washing machines, refrigerators, air conditioners, air purifiers and vacuum cleaners. Antimicrobial effect of silver nanoparticles on textiles has already been shown by various researchers [12-15]. In this section of the present chapter experimental results of the synthesis of silver nano particles by reduction of silver salt (AgSO\(_4\)) with sodium borohydride in the presence of tri-sodium citrate are discussed. The stability of the nano Ag particles dispersed in aqueous medium was investigated at different time intervals.

2.3.2.1 Preparation technique

The 100 ml solution of 1x10\(^{-3}\) M AgSO\(_4\), kept in the earlier discussed reaction chamber (Figure 2.1), was slowly reduced by drop-wise addition of very dilute chilled solution of sodium borohydride in a nitrogen atmosphere. During the process of reaction the solution mixture was stirred vigorously with the help of magnetic stirrer. When the colour of the solution turned to light yellow, 5 ml of 1x10\(^{-3}\) M trisodium citrate were added drop by drop with constant stirring. Distilled water was used for preparing the solutions of all the chemicals.

2.3.2.2 Stabilization study of silver nano colloidal particles

The formation of Ag nanoparticles from silver salt at different stages of synthesis as well as their stability after storing for variable time in atmospheric condition has been monitored using UV-VIS spectrophotometer. Stability of synthesized Ag nano colloid in air (in absence of capping agents) was recorded at different time intervals i.e. after 12
hrs, 24 hrs 72 hrs and 4 weeks. The effect of capping agents on the stability of Ag nano colloidal particles was studied using TSC (Electrostatic stabilization).

2.3.2.3 In-situ synthesis and stabilization technique

The cleaned polyester fabric was used for this experiment. The fabric was first padded with chilled $2 \times 10^{-3}$ M reducing agent (sodium borohydride solution) using 2-dip-2-nip padding technique at 70% padding expression at room temperature on laboratory two bowl padding mangle. The wet fabric was then further padded with $1 \times 10^{-3}$ M silver salt ($\text{AgSO}_4$) solution using again 2-dip-2-nip padding technique.

Finally, the fabric is cured in the curing chamber at 180 °C for 60 seconds. The fabric samples were thoroughly washed.

2.3.2.4 Characterization of silver nano colloidal particles

UV-visible spectrophotometry

The absorbance of silver nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range: 300 nm to 700 nm.

Particle size analyzer

The particle size and size distribution of Ag nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to characterize the Ag nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100Å. Stabilized solution of silver nano coated aluminum sheet was dried and illuminated under scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized silver nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The silver nano particles were deposited on carbon coated aluminum sheet and further coated with gold. Elemental analysis of samples using Oxford-Inca software on scanning electron microscope reports the presence of elements in pure and oxide state qualitatively.

Determination of colour of the colloidal solution

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The changes in colour of the silver colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

X-Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of silver nano technique were performed by X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

2.3.3 Preparation of zinc nano colloids by chemical reduction technique

Quality of human life is highly influenced by the progress of technology and progress of technology depends on developments in novel material and their processing techniques. At present most of material processing technology are based on top-down technique. Recently, numbers of work have been reported on the developments of nano sized materials and their effect. Havaneak, (2003) [17]; Efras and Rosen (2003) [18] has reported that most of the novel devices of the future will be based on properties of nanomaterials [19]. Furthermore, Dutta and Sugunan (2004) [20]; Gates et.al (2004) [21] has also mentioned that the traditional approaches is not sufficient to achieve size selective nano particles. Various techniques of nano synthesis has been reported in chapter 2, in case of preparation of zinc nano particles , controlled precipitation from precursor dissolved in a solution is most popular.

In this work, zinc nano particles were prepared by wet chemical method. After synthesis the particles were stabilized with tri-sodium citrate. Stability of particles was observed in atmospheric condition and also under different light sources. Finally the synthesized nano particles were examined by particle size analyzer, their morphology and micro structure were observed and elementally detected through scanning electron microphotography.

2.3.3.1 Preparation technique

Zinc nano-particles were prepared by wet chemical method using zinc nitrate and sodium borohydride as reducing agent and tri-sodium citrate as stabilizing agent. 100 ml solution of Zinc nitrate (1 x 10⁻³ M), kept in reaction chamber (Figure 2.1), was slowly reduced by drop wise addition of 5 ml solution of sodium borohydride (2 x 10⁻³ M). During the process of reaction the solution mixture was stirred vigorously. As the drop wise addition of sodium borohydride solution completed, 5 ml of 1 x 10⁻³ M tri-sodium citrate were added drop by drop with vigorous stirring. The reaction was allowed to
proceed for 2 hours after complete addition of tri-sodium citrate. Distilled water was used for preparing the solutions of all the chemicals.

2.3.3.2 Stabilization study of zinc nano colloidal particles

The synthesized Zn nano colloidal particles (in absence of capping agent) has been monitored with computer colour matching system after storing for variable time in atmospheric condition. Stability of synthesized Zn nano colloid in air was recorded after different time intervals i.e. freshly prepared, after storing for 48 hrs and after storing for 72 hrs, without capping.

2.3.3.3 In-situ synthesis and stabilization technique

100% polyester fabric samples were impregnated and padded with very dilute chilled solution of $2 \times 10^{-3}$ M sodium borohydride (NaBH₄, M.W. 37.83, 0.1gm, in 50 ml water) using automatic padding mangle using 2-dip-2-nip padding technique at 70% padding expression on laboratory two bowl padding mangle. The wet sample was further padded with the solution of $1 \times 10^{-3}$ M Zinc nitrate (Zn(NO₃)₂·6H₂O, M.W. 297.47) using 2-dip-2-nip padding technique (Figure 2.3). The padded substrates were air dried and finally cured at 180 °C for 60 seconds in curing oven. The fabric samples were thoroughly washed.

2.3.3.4 Characterization of zinc nano colloidal particles

UV-visible spectrophotometry
The absorbance of zinc nano colloidal solution was recorded using UV-visible spectrophotometer in the wavelength range 300 nm to 700 nm.

Particle size analyzer
The particle size and size distribution of Zn nano particle were measured using particle size analyzer. The instrument was based on the diffraction/scattering of laser beam by particle in stable suspension. The statistical graph was formed using laser granulometries statistical method.

Scanning Electron Microscopy (SEM)
Scanning electron microscopy was used to characterize the Zn nano particles shape and size. SEM image was formed using transmitted electrons (instead of the visible light) which can produce magnification up to 1, 00,000 X with resolution up to 100Å°. Stabilized solution of zinc nano coated aluminum sheet was dried and illuminated under
scanning electron microscope. Scanned images with different magnification and resolution were recorded on computer.

Elemental analysis by Oxford-Inca software on SEM

The elemental analysis of the synthesized zinc nano particles was performed on scanning electron microscope (SEM) using Oxford Inca Software. The zinc nano particles were deposited on carbon coated aluminum sheet and further coated with gold. Elemental analysis of samples using Oxford-Inca software on scanning electron microscope reports the presence of elements in pure and oxide state qualitatively.

Determination of colour of the colloidal solution

The changes in colour of the zinc colloidal solution were examined and recorded using spectrophotometer interphased with computer colour matching system.

X-Ray fluorescence spectroscopy (EDX)

For the elemental analysis of polyester fabric before and after in-situ generation of zinc nano technique were performed by X-ray fluorescence spectrometer (EDX 800). The instrument reports the presence of elements in pure and oxide state both qualitatively and quantitatively.

2.4 RESULTS AND DISCUSSION

This section interprets the findings on synthesis, characterization and stabilization of copper nano particle.

2.4.1. Synthesis of colloidal copper nano particles

Copper nano particles were prepared by chemical reduction of copper salt as discussed earlier. The change in colour of the copper sulphate solution was captured at different stages during synthesis of copper nano colloid. Figure 2.4 shows how the blue-green colour of the copper sulphate solution gradually changed at different stages during synthesis. The optical properties of metal nanoparticles depend strongly upon the particle size and shape as reported by Mulvaney, 1996 [9]. The formation of nano sized Cu was noticed by the change in the optical properties of the reaction solution. The blue-green colours of CuSO\(_4\) solution gradually change to intense yellow when the particle size of copper was reduced to nano level. The Cu nano particles in the solution were analyzed by particle size analyzer. The particles were also observed using SEM and AFM. The presence of Cu was detected by Energy dispersive X-ray spectroscopy (EDX).
2.4.1.1 Studies on stability of synthesized copper nano colloidal solution in atmospheric condition

The stability of the copper nano colloid in absence of any capping agent stored for 24 hours in atmospheric condition was examined using particle size analyzer, SEM and AFM. The results are compared with the results of the freshly prepared copper nano colloid kept in similar environment. Particle size analysis gives an idea of the changes in size and size distribution of the particle with time. Nano particles are prone to cluster with time. The specialities of the nano particles are associated to its size. With increases in size its specialities also get reduced and after a certain point it starts behaving like normal (bulk) metal atoms. It is seen from the figure 2.5(a) and 2.5(b) that the size of the majority of the nanoparticles when prepared fresh was about 70 nm but after storage for 24 hours the same was increased to about 400 nm. This is due to the aggregation of nanoparticles which resulted a broadening of peak as seen in Figure 2.5 b. The inset photographs show the change in colour.

Figure 2.4 Progressive colour change of copper sulphate solution during the preparation of copper nano particles.
Stability of the nano Cu particles colloid (in absence of capping agents) in atmosphere was not satisfactory as observed from the change in colour. Scanning electron micrographs of freshly prepared Cu nano particles and after storing for 24 hours in air are represented in figure 2.6. From the SEM photograph we can see that the size of nanoparticles is increased, after 24 hours, which is also supported by the atomic force microscopic images presented in figure 2.7.
Figure 2.6 Scanning Electron Microscope (SEM) images of synthesized copper nanoparticles [(a) Freshly prepared; (b) After 4 week of Synthesis]

Figure 2.7(a) Atomic force microscopic image of freshly prepared Cu nano colloids and (b) After storing over 24 hrs.

Cu nanoparticles because of their high reactivity tend to form aggregates. The tendency of getting aggregated was therefore controlled by the stabilizer or capping agents reported in the following section.
2.4.1.2 Stability with different capping agents

We have seen in the previous section that the stability of copper nano colloid gets affected with time. It was found that even after 24 hours the size of the particles, ranged between 200-1000 nm due to aggregation (Figure 2.5). To enhance the stability of the copper nano colloid two methods of stabilizations were investigated i.e. Steric Stabilization (SLS) and Electrostatic stabilization (TSC).

(A) Effect of Steric Stabilization (SLS)

During the synthesis of copper nano particles as the colour of solution change to yellow the Cu nano colloidal particles were stabilized with the addition of Sodium Lauryl Sulphate (SLS) (1×10^{-3} M). In the present experiment the steric stabilization of colloidal particles was achieved by attaching SLS macromolecules to the surfaces of the copper nano particles.

To check the efficiency of SLS as stabilizing agent for Cu nano colloid, we have examined and recorded the variation of colour of the SLS stabilized Cu nano colloids at different time intervals using computer colour matching system (CCM). The results recorded at different time intervals are shown in figure 2.8. There was no significance change in colour up to 48 hrs, but after that the colour changed to light green and further storing for 72 hrs the colour was changed to greener blue. The steric stabilization was thus not found to be very effective in arresting particle aggregation for a longer time as evaluated from the change in colour of the copper nano colloid with time.
Figure 2.8 Change in colour of the SLS stabilized Cu nano colloidal solution on storage in atmospheric condition for different time intervals.

(B) Effect of Electrostatic stabilization (TSC)

Figure 2.9 shows the colour difference and actual photographs of the TSC stabilized freshly prepared copper nano colloid and stored for 72 hours and 4 weeks. From the
Colour Difference Image at time interval

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<td>Yellower +Db 4.49</td>
<td>TSC Stabilized Cu nano (Fresh)</td>
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<tr>
<td>-Da -4.49 Greener</td>
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<tr>
<td>-DL -3.28 Darker 0</td>
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<td>+Da 4.49 Redder</td>
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<td>TSC Stabilized Cu nano (After 72 hrs)</td>
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<td>-DL -13.82 Darker 0</td>
<td>68.19</td>
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<tr>
<td>+Da 66.80 Redder</td>
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Figure 2.9 Colour difference in TSC stabilized Cu nano colloidal solution on storage in atmospheric condition

It is seen that in contrast to SLS stabilized solution the colour of the TSC stabilized copper stored for 72 hours is more yellowish which indicates a better stabilization in the latter case. After 4 weeks, the colour is changed to redder side. Cu
nano particles get surrounded by the citrate ions released from tri-sodium citrate and each sphere of Cu the nano particles surrounded by the citrate anions repelled each other and prevented further aggregation of the nano particle.

Figure 2.10 UV-VIS spectra of TSC capped Cu nano colloids of various time intervals [Time after synthesis: (a) 12 hours, (b) 18 hours and (c) 24 hours]

The stability of the TSC capped copper nano colloid was then assessed by examining the absorbance spectras of the solution for finer time intervals viz. 12 hours, 18 hours and 24 hours. From figure 2.10 (a & b) it is found that there was no change in $\lambda_{\text{max}}$ value for storing the solution for 12 hours and 18 hours but the colour intensity was increased after 18 hours as seen from the increase in absorbance value. As the particles gain size, the absorption peak usually shifts towards redder side as we find in Figure 2.10 c. Increase in absorption indicates that the quantity of Cu nanoparticles increased. The stable position of absorbance peak in Figure 2.10 a and 2.6 b indicate that new particles do not aggregate. During the initial trial experiments when Cu nanoparticles were synthesized without the addition of stabilizing agent, the yellow colour of the solution was persisted for few hours only in atmospheric condition. Further work, therefore, confined to TSC stabilized nano colloids.

2.4.1.3 Characterizations of synthesized and TSC stabilized copper nanoparticles

Figure 2.11 (a, b and c) represent the absorption spectra of different stages during the formation of Cu nanoparticle colloid from copper sulphate solution. It is seen from
the inset photographs of the absorbance curves that show a blue green solution of copper sulphate gradually turned to yellow indicating the formation of Cu nanoparticles.

![Absorbance Curves](image)

**Figure 2.11** The UV-VIS spectrums of Cu nano colloids at different stages of synthesis [(a) Stage 1: Cu salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Cu nano colloids and (d) Stage4: TSC stabilized Cu nano colloids.]

The shifting of blues-green color of CuSO₄ solution to intense yellow is due to the surface plasmon resonance, with a significant contribution from the interband transition which produces yellow colour hydrosol having maximum absorption at 580 nm (Figure 2.11 c & d) indicating nano Cu particles generation. The plasmon resonance of Cu nano particles was also observed at near 580 nm by Kazakevich et al [7]. Metals with free electrons possess plasmon resonances in the visible spectrum, which give rise to such intense colours. These properties are mainly observed in Au, Ag, and Cu because of the presence of free conduction electrons. The electric field of the incoming radiation induces the formation of a dipole in the nanoparticle. A restoring force in the nanoparticle tries to compensate for this, resulting in a unique resonance wavelength as reported by Henglein [8]. The wavelength of oscillation depends on a number of factors, among which particle size and shape, as well as the nature of the surrounding medium, are the most important factors.[9]

The particle size and size distribution of the prepared and stabilized Cu colloid were analyzed on Malvern instrument. Figure 2.12 (a) shows the intensity size distribution of Cu nano particles dispersed in water.
Figure 2.12 Particles Size and its distribution for synthesized and TSC stabilized Cu nano colloids; (a) by Intensity

The first peak at around 10 nm was arised from dispersion; the peak position at around 70 nm arises from stabilized Cu nano particles. Elemental analysis of gold coated Cu nano particles were performed on oxford Inca software using Scanning Electron Microscope (SEM). Figure 2.13 (a) shows the image analysis results of Cu nano particles. The elemental analysis results presented in Figure 2.13 (b) confirms the presence of copper particles. Peaks for carbon, gold, sodium also observed which got contaminated during the preparation of sample for elemental analysis.

Figure 2.13 (a) SEM image of selected area of gold coated Cu nano particles (b) Elemental analysis of the synthesized particles using Inca software.

Figure 2.14 shows the scanning electron micrographs of stabilized Cu nano particles deposited on carbon coated aluminum sheet. From the images observed at 2700X, 10000X and 27000X it seems that the synthesized Cu nano particles were roughly spherical in shape.
Figure 2.14 Scanning Electron Microscope (SEM) images of copper nano particles

The average size as seen from the scale of the photograph is about 60-100 nm which is also in agreement with the size distribution found using particle size analyzer.

Figure 2.15 Atomic Force Microscopic image and topography of synthesized and TSC stabilized Cu nano colloids
The copper nano particles were deposited on glass plate for observation under atomic force microscopy (AFM). The size of nano Cu particles as seen from the scale on the AFM image (Figure 2.15) and topography lies below 100 nm, which also supports the results, obtained using particle size analyzer and SEM.

2.4.1.4 In situ formation and stabilization of copper nanoparticles on polyester fabric

As discussed in section 2.1.2, the in-situ synthesis and stabilization of the copper nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with copper sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 2.16 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized copper nano particles. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 2.17. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.

Figure 2.16 Colour difference values of copper nano loaded polyester fabric
The amount of copper as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm².

Both the treated and untreated polyester were analyzed on X-ray fluorescence spectroscopy for the detection and measurement of elemental copper respectively. The amount of copper found in the treated polyester was about 0.36 µg against nil for untreated one.

Table 2.3 Amount of copper detected on 78.5 mm² polyester with XRF

<table>
<thead>
<tr>
<th>Structure</th>
<th>Amount of copper, µg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Nil</td>
</tr>
<tr>
<td>Cu/PET fabric</td>
<td>0.36</td>
</tr>
</tbody>
</table>

2.4.2 Synthesis of colloidal silver nanoparticles

Silver nano colloidal particles were synthesized from silver salt by chemical reduction technique. The reduction of silver salt to silver nano particles was observed at different stages by computer colour matching system. The change in the colour of silver salt solution with the addition of reducing agent is shown in Figure 2.18. The progressive changes in the colour of the solution during the synthesis of silver nano particles were captured using computer colour matching system.
2.4.2.1 Change in colour of the synthesized silver nano colloid stored in atmospheric condition without stabilizing agent

After synthesis, silver nano colloidal particles (in absence of capping agent) were analyzed for its change in colour using CCM system at different time intervals i.e. (i) just after synthesis, (ii) after storing for 48 hrs, and (iii) after storing for 72 hrs in atmospheric condition. From the results presented in Figure 2.19, it can be seen that even after storing for 72 hrs in atmospheric condition the colour of solution shifted towards red. But after 4 week of storing time the colour of the colloidal solution, changed to black.
2.4.2.2 Stability of the TSC capped silver nano colloids in atmospheric condition

For examining the stability of the TSC capped nano silver colloid stored in atmospheric condition, the absorption spectra of the colloid were recorded measured at different time intervals viz. after 1 h, 2 weeks and 4 weeks which are shown in Figure
2.20. The UV-VIS spectrums recorded after different time intervals are shown in Figure 2.20 (a, b and c).

It is found that the stabilized silver nano colloidal solution gives an absorbance peak at 445 nm due to plasmon resonance of the nanoparticles. Similar observation was also reported by Šileikaitė et al [15]. The plasmon peak and the full-width of half-maximum (fwhm) depend on the extent of colloid aggregation.

![UV-VIS spectra of Ag colloids](image)

**Figure 2.20** UV-VIS spectra of Ag colloids [time after synthesis: (a) 1 h, (b) 2 weeks and (c) 4 weeks]

There was no change in the peak position found even after storing for 4 weeks. The inset photograph (Figure 2.20) shows that there is no reasonable change in the colour of the colloidal solutions except little darkening of colour when stored for 4 weeks. The stable position of the absorbance peak (\(\lambda_{\text{max}}\)) indicates that the particles do not aggregate. The increase in absorbance value after storing for 4 weeks is indicative of increase in concentration of the nanoparticles through the generation of new particles.

2.4.2.3 Characterizations of synthesized and TSC stabilized colloidal silver nanoparticles

Nano sized Ag particles in colloidal form prepared by chemical reduction technique were characterized for their size, shape and elemental analysis. The particle size and size distribution of stabilized nano Ag colloid were analyzed on Malvern instrument. Figure 2.21 shows the intensity size distribution of Ag nanoparticles dispersed in water. The first peak at around 110 nm arises from the dispersion.
The peak positioned at 4 microns was arised from the stabilized Ag nanoparticles. The presence of the second peak has resulted in the Z-average diameter for this sample increasing to 62.06 nm. It is also evident from the particle size analysis that most of the nano particles are in the range of 60 nm to 120 nm.

Figure 2.22a shows the scanning electron microphotographs of stabilized Ag nanoparticles deposited on carbon coated aluminum sheet. The average size as seen from the scale of the photograph is approximately below 90-100 nm which also supports the size obtained using particle size analyzer. Figure 2.22b represents the microphotographs of the gold coated Ag nanoparticles. It can be seen from the figure that the shape of the gold coated particles is spherical and the size of nanoparticles is increased by 500 – 800 nm due to the gold coating.
Elemental analysis of gold coated nanoparticles was performed on the scanning electron microscope using special software. The result observed in this test is shown in Figure 2.23. Presence of silver is confirmed by the elemental analysis curve. The peaks for carbon, gold and sodium have also been observed.

2.4.2.4 In situ formation and stabilization of silver nanoparticles on polyester fabric

The in-situ synthesis and stabilization of the silver nano particles were done by impregnating polyester fabric first with chilled sodium borohydride followed by padding with silver sulphate solution and finally in-situ synthesis of nano particles and their locking in the fibre structure were done by curing at high temperature 180 °C for 60 seconds. Figure 2.24 shows the image and CCM colour coordinate of the fabric loaded with in-situ synthesized silver nano particles. It can be seen from the figure that the colour of polyester fabric after synthesis of silver nano by in-situ technique was turned to yellow. Scanning electron microphotographs of the untreated and treated polyester are shown in figure 2.25. The surface deposited nano particles are seen in the SEM image of the treated polyester fabric.
Colour Difference

<table>
<thead>
<tr>
<th>Colour Difference</th>
<th>Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow +Db 3.00</td>
<td></td>
</tr>
<tr>
<td>Da -3.00</td>
<td></td>
</tr>
<tr>
<td>Greener +Da 3.00</td>
<td></td>
</tr>
<tr>
<td>Redder -3.00</td>
<td></td>
</tr>
<tr>
<td>Blue -Dl 3.00</td>
<td></td>
</tr>
<tr>
<td>Darker 0</td>
<td></td>
</tr>
</tbody>
</table>

Photograph of fabric loaded with In-situ synthesized Ag nano particles

Figure 2.24 Colour difference values of Ag nano loaded polyester fabric

Figure 2.25 Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized silver nano particles on polyester fabric

The amount of silver as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm². From Table 2.4 it can be seen that the amount of silver found in the treated polyester was about 0.273 µg against nil for untreated one.
Table 2.4 Amount of silver detected on 78.5 mm² polyester with XRF

<table>
<thead>
<tr>
<th>Structure</th>
<th>Amount of copper, µg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Nil</td>
</tr>
<tr>
<td>Ag/PET fabric</td>
<td>0.273</td>
</tr>
</tbody>
</table>

2.4.3 Synthesis of colloidal zinc nanoparticles

Zinc nano colloidal particles were synthesized from zinc salt by chemical reduction technique. The absorption spectrum of the prepared colloidal solution dispersed in water is shown in Figure 2.26. It is found that the solution after synthesis gives an absorbance peak at 370 nm. Similar observation at ~375 nm was also reported by Zhang, et al (2002) [22]. Figure 2.26 (a, b and c) represent the absorption spectra of different stages during the formation of zinc nanoparticle colloid from zinc salt solution. It is seen from the absorbance curves that how a clear solution of zinc salt gradually turned to milky white indicating the formation of zinc nanoparticles.

Figure 2.26 The UV-VIS spectrums of Zn nano colloids at different stages of synthesis [(a) Stage 1: Zn salt solution, (b) Stage 2: After the addition of reducing agent, (c) Stage 3: formation of Zn nano colloids and (d) Stage4: TSC stabilized Zn nano colloids.]

2.4.3.1 Stability of the synthesized zinc nano colloid stored in atmospheric condition without stabilizing agent

After synthesis, zinc nano colloidal particles were stored in atmospheric condition for different time intervals, i.e. (i) for 48 hrs and (ii) storing for 72 hrs in atmospheric condition. The colour difference evaluated by CCM and corresponding photographs of the solution given in Figure 2.27, it can be seen that after storing for 72 hrs in atmospheric condition the intensity of the solution was slightly changed. But after
that the bigger particles settled down at bottom of the flask and the solution become clear.

<table>
<thead>
<tr>
<th>Colour Difference</th>
<th>Image at time interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn nano (Freshly prepared)</td>
</tr>
<tr>
<td></td>
<td>Zn nano (after storing for 48 hrs)</td>
</tr>
<tr>
<td></td>
<td>Zn nano (after storing for 72 hrs)</td>
</tr>
</tbody>
</table>

**Figure 2.27** Colour difference in Zn nano colloidal solution on storage in atmospheric condition without capping

### 2.4.3.2 Characterizations of synthesized and TSC stabilized colloidal zinc nanoparticles

Zinc particles were prepared by reduction of zinc salt and stabilized with citrate anions. The nano Zn particles in the solution were characterized for their size, shape and elemental analyses
The particle size and size distribution of the prepared and stabilized Zn colloid were analyzed on Malvern instrument. Figure 2.28 shows the intensity size distribution of Zn nano-particles dispersed in water. The first peaks at around 15 nm arise from dispersion; this peak represents nano particles of size 13.14 nm diameter. The presence of second peak has resulted in the average diameter of 81.62 nm. Figure 2.29 shows the scanning electron micrographs of Zn nano-particles. The average size as seen from the scale of the photograph is below 100 nm which is in agreement with the size distribution found using particle size analyzer.

Figure 2.28 Particle size distribution of stabilized Zn nanoparticles by intensity

Figure 2.29 Scanning electron microphotographs of silver nanoparticles (a) deposited on carbon coated aluminum sheet and (b) coated with gold and deposited on carbon coated aluminum sheet
Figure 2.30 SEM micrograph and EDX spectrum of selected area of nano-particles deposited carbon coated aluminium sheet and further coated with gold.

Figure 2.30 represents the elemental analysis result which confirms the presence of zinc. Peaks for carbon, gold, sodium also were observed which are used for the preparation of sample for elemental analysis.

2.4.3.3 In situ formation and stabilization of zinc nanoparticles on polyester fabric

As shown in the Figure 2.3 an experimental set up was designed for the continuous synthesis and simultaneous application of Zn nano particles to polyester fabric. The SEM microphotograph of treated polyester fabric (Figure 2.31) confirms the uniform deposition of nano particles on the surface of the fabric. The SEM image also confirms that the average size of the synthesized Zn nanoparticles is remaining below 100 nm and the shape of the particle is spherical.

Figure 2.31 Scanning Electron Microscope (SEM) images of (a) normal polyester fabric and (b) in-situ synthesized and stabilized zinc nanoparticles on polyester fabric
The amount of zinc as element in the polymer structure was detected and measured using an X-ray fluorescence spectrometer (EDX 800 Simadzu, Japan). The operating X-ray source voltage and current were 35 kV and 26 mA respectively. Registration time was 30 s and the investigated area was 78.5 mm².

<table>
<thead>
<tr>
<th>Structure</th>
<th>Amount of zinc, µg</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Nil</td>
</tr>
<tr>
<td>Zn/PET fabric</td>
<td>0.228</td>
</tr>
</tbody>
</table>

The results given in Table 2.5 show that the amount of zinc found on treated polyester was about 0.228 µg against nil for untreated one.

2.5 REFERENCES


