Some Uptake Studies of Metal Ions and the Formation of Cu₂O Particles in Wool

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Abstract

This research programme is concerned with the uptake studies of Cu^{2+} , Zn^{2+} and Mn^{2+} at different conditions, by merino wool fibres and also uptake studies of Cu^{2+} ions by chemically modified wool fibres. Cu_2O particles and Cu complexes are formed within merino wool by an *in situ* reaction with sodium borohydride and thioglycolic acid respectively.

The d-block elements have the ability to bind chemically to certain functional groups present within the keratin protein of wool. The absorption of the Cu^{2+} , Mn^{2+} and Zn^{2+} from solution by wool fibres under different conditions notably, time, temperature and initial concentration have been studied. The optimum temperature and reaction time to give highest absorption of the Cu^{2+} by the wool fibre was found to be 90°C and one hour without modifying the nature of the wool, from a solution of Cu^{2+} concentration of 450 mg L^{-1} . Cu^{2+} was found to give the greatest absorption by the wool fibres, whereas Zn^{2+} and Mn^{2+} were found to be absorbed the least. The absorption of Cu^{2+} ions increases with increasing temperature. At the higher temperature of 90°C , the -S-S- bonds in the cystine amino acids break more readily, generating thiol and cysteic acid groups to bind with copper ions. The uptake of Cu^{2+} by ethylenediaminetetraacetic dianhydride (14 mg g^{-1} of wool) or thioglycolic acid (42.5 mg g^{-1} of wool) or sodium borohydride (41.8 mg g^{-1} of wool) treated merino wool fibres increases with respect to unmodified wool (8 mg g^{-1} of wool). NaBH_4 treated merino wool reduces Cu^{2+} ions to Cu_2O particles which form within the wool fibres by an *in situ* reaction. TGA treated merino wool provides additional functional groups to bind with copper ions and Cu_2O particles also likely to be formed within TGA treated wool composites. The metal ions were absorbed into the fibres under various conditions and the extent of absorption was quantified. The form and binding of the Cu_2O particles or Cu^{2+} ions onto the wool fibres are studied using UV-Visible, FTIR, XRD, SEM, EDS and TEM methods.

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Glossary

XRD	X-ray diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
EDS	Energy dispersive x-ray spectroscopy
UV-Vis	Ultraviolet Visible
FAAS	Flame atomic absorption spectroscopy
FTIR	Fourier transform infrared
TA	Tannic acid
CMC	Cell membrane complex
NaBH ₄	Sodium borohydride
EDTA dianhydride	Ethylenediaminetetraacetic dianhydride
TGA	Thioglycolic acid

CHAPTER 1

1 INTRODUCTION

1.1 General overview

Previous studies have shown that various metal ions can be absorbed by wool fibres.¹⁻⁴ The rate and extent of uptake depends on various factors, such as the kind of metal ion and its valence state, the solution concentration, pH, reaction time and temperature.³ Also, the uptake of metal ions can be enhanced by the wool which has been modified chemically with external reagents.⁵⁻¹⁰ Since wool is a protein fibre, it has polar and ionisable groups on the side chains of constituent amino acid residues, which are able to bind with other charged organic molecules tannic acid (TA) or ethylenediaminetetraacetic dianhydride (EDTA dianhydride) or solutions of inorganic ions (Ag^+ , Au^{3+} , Hg^{2+} , Pd^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} or Mn^{2+}). Studies on the treatment of protein fibres with these metal ions have provided insight into various chemical, physical and structural features of the fibres. In addition, the possibility of inducing useful changes in fibre properties and developing functional protein metal complexes has attracted the interest of scientists. In their review, McLaren and Milligan¹¹ showed that several reactions of metal ions with keratin fibres effectively improved dyeability, wrinkle recovery, shrinkage, abrasion and flame resistance of wool. Also some of these wool-metal complexes (Ag^+ and Cu^{2+} treated wool fibres) were responsible for antimicrobial activity against *Cornebacterium* and *Escherichia coli*.^{10,11}

These EDTA dianhydride and tannic acid treated wool fibres can be developed to new types of polymer-based sorbents, applicable to the removal of heavy metal pollutants (Cu, Zn, Ni, Cd, Pd and Hg) from industrial effluents and in the purification of contaminated water supplies.^{6,10,12,13}

Previous studies have shown the various methods of preparing metal nanoparticles externally.¹⁴⁻¹⁷ Also, these metal ions can be formed into metal nanoparticles within the wool fibres by *in situ* reactions.¹⁸⁻²¹ The metal nanoparticles that have been incorporated into wool fibres are stable for washing. It is unlikely for those particles to be desorbed from the wool fibres once they are bound to wool fibres. Therefore these metal nanoparticles present in the wool fibres can be applied in the fibre authentication and traceability industry based upon the chemical and optical signatures from the metal nanoparticles formed in the wool.²²⁻²⁵

Traceability industry refers to the ability to track or to trace every step of manufacturing woollen garments. These steps are yarn, spinning, knitting, cutting and stitching.

1.2 Merino and crossbred wool

Merino wool is utilized widely by the textile industry for high quality clothing and interior furnishings. Merino is obtained from the wool of merino sheep. The diameter of merino wool fibre is typically less than 25 microns.²⁶ The soft texture of merino wool is due to its fine structure.

When a fine-wool sheep is mated to one of the British long-wool sheep, the resulting offspring is referred to as a crossbred sheep. The diameter of crossbred wool is around 25-40 microns.²⁶ The crossbred wool is used mainly for interior furnishings, bedding items and in the carpet industry.

1.2.1 Chemical structure of wool

Wool is chemically a protein²⁷ and it is a member of a group of proteins known as keratins. Wool fibres are not chemically homogeneous. These fibres consist of a complex mixture of widely different polypeptides. Proteins are formed by condensation of α -amino acids via their carboxyl and amino groups. Amino acid residues that are reported in wool are outlined in Table 2.1.

Table 1.1: Amino acid composition of fine merino wool.²⁸

Amino acid	Concentration ($\mu\text{mol g}^{-1}$ of wool)
Hydrocarbons	
Glycine	760
Alanine	470
Valine	490
Leucine	680
Isoleucine	270
Phenylalanine	260
Hydroxyl	
Serine	900
Threonine	570
Tyrosine	350
Acidic	
Aspartic acid	200
Glutamic acid	600
Basic	
Histidine	80
Arginine	600
Lysine	250
Heterocyclic	
Tryptophan	40
Sulfur containing	
Cystine	460
Cysteine	10
Methionine	50

As described earlier wool fibres are mainly composed by keratine polypeptides. Some of these keratine fibres consist of α -helical configurations which are the most energetically favourable configuration and therefore the most stable.²⁷ The rest of the keratin proteins form the amorphous proteinaceous of the wool fibres. The flexibility and elasticity of wool is due to the α -helix, which essentially behaves like a spring. The α -helical structure results in close packing, but the large number of bulky groups hinders perfect crystallization, hence the crystallinity of wool peptides is low. In addition to the presence of intermolecular bonds between the different polypeptide chains, intramolecular bonds exist within the same polypeptide chain. The individual peptide chains in wool are held together by various types of crosslinks and non-covalent interactions (Figure 1.1).^{26,29}

Figure 1.1: Protein structure of wool.²⁶

The main components in wool are keratinous protein, non-keratinous protein and non-protein matter such as lipids, which constitute approximately 82%, 17% and 0.8-1.0% of the total fibre mass respectively.²⁶ Keratinous proteins contain a high sulfur content, mainly present in the form of the disulfide containing cystine residues. The disulfide bonds of cystine form crosslinks, either between different protein chains or within the same protein chain. Non-keratinous proteins contain a lower concentration of disulfide crosslinks which makes the protein more pliable, less resistant to chemical attack and more soluble than the keratinous components of the fibre.

1.2.2 Chemical properties of wool

1.2.2.1 Effect of acid

Influence of acids on the mechanical and dyeing behaviour of wool fibre is of great practical importance.²⁷ The isoelectric region of wool fibre is between pH 3.5-5.0.²⁶

Figure 1.2: Amphoteric nature of wool fibre.²⁶

$$\text{H}_3\text{N}^+ - \text{Wool} - \text{COO}^- + \text{H}^+ \longrightarrow \text{H}_3\text{N}^+ - \text{Wool} - \text{COOH}$$

For the mechanical properties of wool, the following aspects apply.²⁷

- #### 1.2.2.2 Effect of alkali

$$\begin{array}{c} \text{H}_2\text{N} \quad \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{CH}-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH} \\ \diagup \quad \diagdown \\ \text{HOOC} \quad \text{COOH} \end{array} \xrightarrow{\text{OH}^-} \begin{array}{c} \text{NH}_2 \\ | \\ \text{C}=\text{CH}_2 \\ | \\ \text{COOH} \end{array} + \begin{array}{c} \text{NH}_2 \\ \diagup \\ \text{S}-\text{S}-\text{CH}_2-\text{CH} \\ \diagdown \\ \text{COOH} \end{array}$$

1.2.2.3 Effect of reducing agent

5

Figure 1.5: Reduction of disulfide bonds.²⁷

1.2.2.4 Effect of oxidizing agents

Bleaching agents and other oxidizing agents damage the wool fibre. These are very reactive with the disulfide bonds and form thiol and sulfonic acid groups (Figure 1.6).²⁷

Figure 1.6: Oxidation of disulfide bonds.

1.2.3 Physical structure of wool

The complex morphological structure of fine wool fibres is shown schematically in Figure 1.7.

Figure 1.7: Schematic diagram of the morphological components of a fine wool fibre.²⁶

The wool consists of two types of cells: the internal cells of the cortex and external cuticle cells that form a sheath around the fibre. Cuticle cells or scales overlap like tiles on a roof, making wool unique amongst textile fibres. An important function of cuticle cells is to anchor wool

fibres in the skin of sheep. The exposed edge of each cuticle cell points from the fibre root towards the tip. This gives rise to a larger surface frictional value when a fibre is drawn in the tip to root direction than in the opposite direction. The frictional difference helps to expel dirt and other contaminants from the fleece, and it is also responsible for wool's important properties such as tactile and felting behaviour.^{26,33}

1.2.3.1 Cuticle cells

The cuticle consists of the epicuticle, exocuticle and endocuticle. It is resistant to alkalis, acids, oxidizing agents, and enzymatic attack. The epicuticle is a thin membrane and is associated with lipids (fatty acids) of cell membrane complex to form outermost hydrophobic layer of wool. This hydrophobic character hinders the entry of dye into the fibre. Treatment of wool with potassium t-butoxide in anhydrous t-butanol removes lipids from the cell membrane complex (CMC) at the point where this component extend to the fibre surface, markedly improving the dyeing rate and the uniformity of uptake of anion dyes.²⁶

1.2.3.2 Exocuticle cells

The exocuticle is the layer of keratinous protein immediately below the epicuticle. The exocuticle has a relatively high crosslink density due to the high concentration of cystine.²⁶

1.2.3.3 Endocuticle cells

The endocuticle is a layer of non-keratinous proteins which is well defined and lying below the exocuticle. The low cystine content makes the endocuticle more susceptible to chemical attack than the exocuticle.²⁶

1.2.3.4 Cortex

The cortex constitutes almost 90% of the wool fibres. The cortex of fine wool consists of closely packed, overlapping cortical cells, arranged parallel to the fibre axis. The cells of the cortex are composed of rod like elements of low sulfur crystalline proteins (microfibrils) surrounded by an amorphous matrix of high sulfur content. The microfibrils are grouped together in aggregates, known as macrofibrils. Fine wool fibres contain two main types of cortical cells, orthocortical and paracortical. The cells of orthocortex contain a higher proportion of microfibrils and therefore are richer in proteins with low sulfur content. On the other hand, paracortical cells contain a higher proportion of matrix and hence a greater proportion of high sulfur content. The bilateral segmentation of ortho and para cortical cells predominates in fine wool, (up to 25 μm) which is associated with the highly desirable natural crimp of the fibres. The crimp enhances the fibres elasticity and resilience, allowing it to bend and be twisted over several

times without becoming damaged. Also it promotes the entrapment of air between the wool fibres, acting as an insulator against both hot and cold temperatures.²¹ The orthocortex is more chemically reactive than the paracortex. Basic dyes (positively charged dyes), cation surfactants and many high relative molecular mass ions containing heavy metals preferentially stain the more accessible orthocortex. Some dyes are transferred from the non-keratinous region of the CMC, into the sulfur rich proteins of the matrix in the cortical cells. Dye also transfers from the endocuticle to the exocuticle. It appears that the high level of cystine present in the matrix of the cortical cells and the exocuticle has a greater affinity for wool dyes.²⁶

1.2.3.5 Cell membrane complex

The cuticle cells are separated from the cortex, and individual cortical cells are separated from each other by the cell membrane complex. The cell membrane complex is the only continuous phase in wool. The CMC consists of lightly crosslinked non-keratinous protein, lipid component and a chemically resistant proteinaceous membrane. Although the CMC comprises only around 5% of the total fibre mass, it plays an important role in the overall properties of the wool. It is a region of relatively low mechanical strength in the fibre composite. Since the CMC is only slightly crosslinked, it is more susceptible to chemical attack than any other region of the fibre.²⁶

1.3 Diffusion of metal ions into wool fibres

Figure 1.8: Diagram of diffusion of metal ions into wool fibres.³⁴

Figure 1.8 shows the pathway of diffusion of metal ions or metal complexes into the wool fibres. When wool fibres are treated with metal ions they are unable to penetrate through the surface of the cuticle cells due to the presence of highly crosslinked regions.^{26,34} Therefore the

exocuticle acts as a barrier to the diffusion of metal ions through the surface of the cuticle cells. Metal ions diffuse first through the intercuticular regions and then into the nonkeratinous regions of the endocuticle, the intercellular cement and the intermacrofibrillar cement. As the absorption of metal ions continues, the metal ions penetrate throughout the whole nonkeratinous network of the fibre and simultaneously can be transferred from the endocuticle to the sulfur rich exocuticle.^{26,34}

The sorption of metal ions (M) on to a wool fibre (W) can be described by the following equation.

Four steps are involved in the process of metal ion uptake by wool fibres.^{35,36}

- a) Diffusion of metal ions from the bulk, through the static liquid film to the surface of the wool fibre.
- b) Diffusion of metal ions within the fibre to appropriate sites (functional groups of wool fibres)
- c) Binding of metal ions to those sites by physical or chemical interactions.

1.3.1 Diffusion of metal ions through a solution film.

The metal ions diffuse from the bulk, through the static liquid film to the surface of the wool fibres. Wool fibres may be surrounded by an immobile solution film. When the sorption process is limited by diffusion of the Cu^{2+} species through the solution at the wool fibre interface, the rate law takes the following form:^{37,38}

$$\frac{dQ}{dt} = R(Q_{Eq} - Q) \quad (1.2)$$

Which, when integrated with respect to time, becomes:

$$Q = Q_{Eq}(1 - e^{(-Rt)}) \quad (1.3)$$

Where Q and Q_{Eq} are the amounts of Cu^{2+} sorbed by the wool fibres at time t , and at equilibrium, $t = \infty$ and R is defined as follows:

$$R = \frac{3D}{r \cdot \Delta r \kappa} \quad (1.4)$$

Where D is the diffusion coefficient of metal ions, r is the radius of the wool fibre, Δr is the thickness of the diffusion layer and κ is the distribution coefficient (defined as the ratio of the equilibrium metal ion concentration in the wool fibre to the concentration in the solution). The relationship assumes that D , Δr and κ is constant throughout the approach towards equilibrium. This is true in cases where the metal ion solution is at infinite dilution. However this model can also be applied in cases where the metal ions present at very low concentrations. This form of the rate law is identical to the rate law for first order kinetics.

1.3.2 Diffusion of metal ions through the wool fibres

When the diffusion of metal ions from the surface to the centre of the wool fibre is the rate determining step, the form of equation is different. The integrated form of the rate law is:^{37,38}

$$\frac{Q}{Q_{Eq}} = \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \frac{-Dn^2\pi^2 t}{r^2} \quad (1.5)$$

In cases where the system is significantly distant from equilibrium $\left(\frac{Q}{Q_{Eq}} < 0.05\right)$, the above equation simplifies to:

$$\frac{Q}{Q_{Eq}} = \frac{6}{\sqrt[3]{\pi^3}} \sqrt[3]{(Bt)} \quad (1.6)$$

$$\frac{Q}{Q_{Eq}} \approx 1.08 \sqrt{(Bt)} \quad (1.7)$$

Where

$$B = \frac{D\pi^2}{r^2} \quad (1.8)$$

As indicated above, the relationship in equation (1.6) is true only in systems for which the attainment of equilibrium is slow, small values of time (t), for small diffusion coefficients of metal ions (D) and/or for large diameter of wool fibre (r). Only in those cases can this method be employed.

The rate limiting step of the diffusion of metal ions by wool fibre is step “c” (diffusion control). The diffusion limited steps may not be apparent in the overall rate law in cases of very low metal ion concentrations and initial absorption of metal ions by wool fibre. This system is controlled by the step “a”³⁵.

1.4 Absorption of transition metal ions onto wool

Wool contains many functional groups including amines, hydroxyls and carboxyl groups. The lone pairs of the N and O atoms in amines, hydroxyl groups and carboxyl groups on wool can ligate to transition metals and form complexes easily. Transition metals form complexes having high coordination numbers due to the availability of empty d orbitals of the transition metal. The availability of bonding of the functional groups of wool fibres depends on the pH of the medium (Fig 1.2). When the solution is acidic, more protonated amine groups attach to negative charged groups with attractive forces. When the solution is less acid more carboxylate groups attached to cations. Also when pH is greater amine groups are more easily coordinated to cations. The carboxyl groups of aspartic and glutamic amino acids are available for bonding with transition metal ions.^{39,40,41,42} On the other hand the amine groups of arginine and lysine and hydroxyl groups of serine, tyrosine and threonine are available for bonding with metal ions.^{28,40,41} Also metal ions may bind not only to carboxyl, hydroxyl and amine groups but thiol and cysteic acid groups as well.

1.4.1 Coordination of Cu^{2+} ions to carboxyl and cysteic acid groups in merino wool

Figure 1.9: Binding and formation between Cu^{2+} ions and carboxylic and cysteic acid groups in wool fibres.⁴³

Figure 1.9 shows the ligation of Cu^{2+} to carboxylic and cysteic acid groups in keratin proteins in wool fibres. Since Cu is a transition metal, it has empty d orbitals that are available for binding and form complexes having high coordination numbers.

1.4.2 Identification of Cu^{2+} coordinated carboxyl and amine groups of amino acids by FTIR spectroscopy

In the IR spectrum, the band that is assigned to carboxyl groups of amino acids ($\nu_s(\text{COO}^-)$) is in the region of $1400\text{--}1425\text{ cm}^{-1}$. The peak of these vibrations is usually of strong intensity and broad. Once Cu^{2+} ions coordinate to carboxyl groups of amino acids, the peak which is assigned to the $\nu_s(\text{COO}^-)$ vibrations shifts to lower frequencies in agreement with the participation of C-O bond in Cu^{2+} binding.⁴⁴ The symmetric stretching vibrations of Cu-O lie in the region $250\text{--}350\text{ cm}^{-1}$. When Cu^{2+} coordinates to amine groups of amino acids through N, the vibrations of Cu-N occur in the region $450\text{--}500\text{ cm}^{-1}$.⁴⁴ In IR spectra, the $\nu(\text{N-H})$ stretching vibrations appear at $3000\text{--}3300\text{ cm}^{-1}$. When the NH_2 groups interact with Cu^{2+} ions, the band at $3000\text{--}3300\text{ cm}^{-1}$ shifts to a higher frequency.^{45,46}

1.5 Uptake of metal ions by wool fibres

The uptake of metal ions by wool is mainly affected by^{6,10,13,47}

- Type of metal ion
- Metal ion concentration or the applied amount of metal ions
- Time
- Temperature
- pH
- Chemical modification of wool

1.5.1 Type of metal ion

The absorption behaviour of Cu^{2+} , Zn^{2+} and Ni^{2+} ions on wool was investigated. Assuming that the wool keratin fibre is a cylinder, the apparent diffusion coefficient of Cu^{2+} and Zn^{2+} ions is calculated by Hill's equation³ of diffusion explained in equation 1.6.

The apparent diffusion coefficient (D_a) of Cu^{2+} and Zn^{2+} is shown in Table 1.2

Table 1.2: Apparent diffusion coefficient (D_a) of metal cations on wool fibre ($T = 50^\circ\text{C}$, $\text{pH} = 5$ and metal ion concentrations: $5 \times 10^{-4} \text{ M}$).³

Metal Ion	$D_a \times 10^{-8} (\text{cm}^2 \text{ min}^{-1})$
Cu^{2+}	2.53
Zn^{2+}	1.17

The apparent diffusion coefficient of Cu^{2+} in water is greater than other metal ions present.³ Therefore uptake of Cu^{2+} by wool is significantly increased compared to other metal ions. This is shown in Figure 1.10.

Figure 1.10: Uptake of metal ions by wool fibre at 50°C , $\text{pH} = 5$ and metal ion concentration: $5 \times 10^{-4} \text{ M}$.³

The amount of applied metals per gram of wool and the uptake percentage of the metals are given by the table below.

Table 1.3: Uptake % of different metals with a treatment time of 25 min³

Metal	Applied metals (mg g^{-1} wool)	Uptake of Cu (mg g^{-1} wool)	Uptake of metal (%)
Cu^{2+}	6.3	5.7	90
Ni^{2+}	5.9	2.5	42
Zn^{2+}	6.5	2.6	40

1.5.2 Initial metal ion concentration/Amount of applied metal ions

The following two equations are assumed to represent the metal cations binding to carboxyl groups of the proteins in the wool.

The apparent diffusion coefficient of metal ions becomes progressively greater as the concentration of metal ions is raised (Figure 1.10). At high concentrations of Cu^{2+} , it is likely equation (1.9) is the rate determining step, and the equilibrium is shifted more towards the right. Therefore in slightly acidic conditions ($4 < \text{pH} < 6$), more Cu^{2+} ions bind to carboxyl groups than other functional groups present in the wool. At high concentrations of Zn^{2+} and Ni^{2+} , equation (1.10) is most likely the rate determining step. Equation (1.10) is not as greatly influenced by the concentration of metal ions as equation (1.9). When the metal ion concentration is very low, the apparent diffusion coefficients of both Cu^{2+} and Zn^{2+} are reduced and become very close to each other³ (Figure 1.11).

Figure 1.11: Relationship between apparent diffusion coefficient (D_a) and initial metal ion concentration at $\text{pH} = 5$ and $T = 50^\circ \text{C}$.³

Figure 1.12: Effect of applied Cu amount on total copper taken up by wool ($T \geq 85^\circ\text{C}$).³⁹

Figure 1.13: Effect of applied Cu amount on fraction of copper taken up by wool ($T \geq 85^\circ\text{C}$).³⁹

When the amount of applied copper increases, the total uptake increases, but the fraction of applied copper taken up by wool decreases (Figures 1.12 and 1.13). More copper leads to higher level of Cu^{2+} in the residual solution (exhaust bath) and % of uptake is reduced (Figure 1.13).

When wool fibre is saturated with more Cu^{2+} ions, there will be greater electrostatic interactions experienced by these ions and their diffusion into wool will be somewhat less than expected. However the total uptake still increases with the applied amount of Cu (Figure 1.12).

There are a finite number of sorption sites available per gram of wool at a given pH. Therefore the plateauing off of Cu^{2+} uptake is observed when the applied amount is more than 25 mg per gram of wool (Figures 1.12 and 1.13).

1.5.3 Reaction time and temperature

The uptake of metal cations by wool increases with increased temperature and time. (Figures 1.14, 1.15 and 1.16).³

Figure 1.14: Cu(II) uptake³

Figure 1.15: Zn(II) uptake³

Figure 1.16: Ni(II) uptake³

When sorption time increases, more metal ions are attached to the available sites of amino acids in the wool. The amount of Cu^{2+} ions in the wool fibre is greater when compared to Zn^{2+} and Ni^{2+} ions at the same time, pH and initial concentration. The plateauing of Zn^{2+} and Ni^{2+} is found to be reached within a short time compared to Cu^{2+} . This may be due to the low apparent diffusion coefficient of Zn^{2+} and Ni^{2+} .

Table 1.4: Effect of bath temperature on copper uptake (treatment time = 60 min and amount of Cu applied = 23.7 mg g⁻¹ of wool)³⁹

Temperature (°C)	Uptake of Cu ²⁺ (mg g ⁻¹ wool)	Uptake of Cu ²⁺ (%)
30	1.9	7.9
50	3.4	14
70	6.7	28
90	8.8	37

Copper uptake increases rapidly when temperature increases (Figure 1.14 and Table 1.4).

As temperature increases, more metal ions have energy to overcome their activation energy of the reaction and become available for bonding with the sorption sites of wool. At very high temperatures (≥ 85 °C), the -S-S- bonds in the cystine amino acids break more readily, generating more sulfur sites and thiol groups which may bind with copper.⁴⁸ Therefore, when heating above 85 °C, usually for more than 8 hours, the high copper uptake may be attributed to the formation of copper sulfide and to the ligation of carboxylate to copper ions.^{40,49}

1.5.4 pH

Uptake increases strongly and linearly with increasing pH up to a value of ≈ 6 and above pH 6, Cu(OH)₂ starts to precipitate.⁴² When pH increases, not only are there more carboxylate ions present in the amino acids but the amine groups may also participate for bonding with copper ions.¹⁰ At high pH, (pH ≥ 6) the precipitation of Cu(OH)₂(s) occurs and amount of Cu²⁺ taken up by wool may be less. At lower pH, the reaction medium will be more acidic and the affinity to bind Cu(II) with the sorption sites of wool will be much less.⁵⁰ The absorbed metal can be desorbed at acidic pH, apart from that bound to thiol groups. The reversibility of the wool-metal interaction shows competition between metal and hydrogen ions for the same binding sites (equation 1.9).¹⁰

As shown in the study of Kokot *et al*,⁴⁰ two types of Cu(II)-wool complexes are formed. One is stable at pH < 6 (green Cu(II) complex) and the other stable at pH > 6 (brown Cu(II) complex).⁴² The green coloured wool complexes are formed by binding of Cu²⁺ ions to carboxyl (glutamyl and aspartyl) groups of amino acids in the wool. The brown coloured wool complexes are formed due to the formation of copper sulfide within the wool fibres. The binding of Cu²⁺ ions to wool fibres was confirmed by the electron spin resonance study by Kokot *et al*.⁴⁰ When

the isoelectric point of for wool is at a pH of around 6, not only the carboxyl groups in the wool, but also the NH₂ groups take part in binding to form the green Cu(II)-wool complexes.^{40,42}

1.5.5 Formation of Cu_xS (1<x<2) and copper coordinated mercaptide groups in the wool.

When wool treated with copper solutions at higher temperatures (~ 90 °C), for a longer period (≥ 8 hours), disulfide bonds in wool were hydrolysed according to the reaction proposed by Schoberl.^{40,41} This is shown in Figure 1.17(a), in which an unstable sulfenic acid species is formed (WCH₂SOH). The other reaction usually takes place in an alkali medium. However it may be applicable to the higher temperatures applied to the treatment bath as well. This reaction proceeds via the unstable thiocarbonyl species (WCH=S). This is shown in Figure 1.17(b).

Reaction a

Reaction b

W = wool

Figure 1.17: Hydrolysis of disulfide bonds in the wool (a) in the presence of acidic conditions and (b) basic conditions.

Water or hydroxyl groups acting as nucleophiles, attack the –S–S– bonds in the wool and yield mainly H₂S and thiol groups. Both of these substances may readily react with Cu²⁺ to yield either a copper(I) complex with thiols (WCH₂S[–]Cu⁺) or sulfides of copper. These CuS compounds are brown-red in colour.⁴⁰ The reaction of the formation of copper sulfides during the Cu²⁺/wool interaction is represented by the following equations (1.11 and 1.12).

Cu^{2+} is reduced by the thiol groups to Cu^+ and the thiol groups will be reoxidized to disulfide linkages in the wool. These Cu^+ may react with other thiol groups in the wool to form the copper coordinated mercaptide groups. The formation of copper coordinated mercaptide groups is represented by the following equation (1.13).^{51,52}

However the $\text{WCH}_2\text{S}^-\text{Cu}^+$ complex is highly unlikely to exist at high temperatures ($\geq 90^\circ\text{C}$), because C-S bonds of the complex break more readily and form CuS, when such temperatures are used.^{40,53}

1.5.5.1 Identification of Cu-S bond by UV-Vis and FTIR spectroscopy

In the IR spectrum, the two major peaks at 1114 and 619 cm^{-1} can be attributed to Cu-S stretching and bending respectively.⁵⁴

In the UV spectrum, the absorbance at 475 nm is due to the chalcocite, Cu_2S .^{55,56}

1.5.6 Chemical modification of wool with EDTA-dianhydride

The uptake of metal ions can be enhanced by chemically modified wool, due to the availability of more sorption sites. Wool can be modified by acylation with EDTA-dianhydride, at $70\text{--}75^\circ\text{C}$, for a period of $1\text{--}7\text{ hr}$, prior to the addition of copper ions.^{10,6}

The structure of EDTA-dianhydride is given in Figure 1.18.

Figure 1.188: Structure of EDTA-dianhydride.⁵⁷

The amine groups of amino acid residues (lysine, histidine and arginine) and hydroxyl groups of serine, threonine and tyrosine are the most important reactive sites for EDTA-dianhydride. These reactive sites in the wool bind to EDTA-dianhydride with strong covalent bonds. Therefore uptake of EDTA-dianhydride is significantly greater than TA.¹⁰

Figure 1.19: Adsorption of Cu^{2+} by wool untreated, modified with tannic acid and acylated with EDTA-dianhydride as a function of pH (33.3 mM CuNO_3 , 25 °C for 30 hr).¹⁰

In acidic and neutral pH, the opening of the EDTA-dianhydride rings provide, additional negatively charged carboxyl groups to bind with copper ions.⁸ The stability of EDTA-dianhydride treated metal complexes is believed to be greater than untreated wool fibres. Since significant amount of copper ions were effectively absorbed over a wide pH range, the EDTA-dianhydride treated technique appears to be an attractive method (Figure 1.19). Since the use of tannic acid does not appear elsewhere in this research project the absorption of Cu^{2+} by tannic acid was not explained.

1.5.6.1 The UV-Vis spectrum of Cu^{2+} /EDTA complex

Figure 1.190: UV-Vis absorption spectrum of Cu^{2+} /EDTA complex.⁵⁸

Figure 1.20 shows the UV-Vis spectrum of Cu^{2+} coordinated to EDTA through N and O. The band in the visible region is quite broad and strong. The spectral maximum is identified at around 680 nm. For the Cu^{2+} /EDTA complex, the absorption at 680 nm has been assigned to the d-d transition and the MLCT (metal to ligand charge transfer) absorption typically which begins at about 500 nm.^{58,59}

1.5.7 Chemical modification of wool with thioglycolic acid (TGA)

Wool can be modified by treatment with thioglycolic acid (0.5 M), at 50 °C and pH ~ 6 for a period of 60-120 min.⁶⁰

The chemical structure of thioglycolic acid is given in Figure 1.21.

Figure 1.201: Structure of thioglycolic acid.⁶¹

Thioglycolic acid is known as a powerful reducing agent for wool⁶⁰ and the reaction takes place as given in Figure 1.22.

Figure 1.212: Reduction of disulfide linkage in wool.⁶⁰

The dye uptake and the resistance of wool to moths were improved by thioglycolic acid modified wool, without the deterioration of physical properties (shrinkage and tensile strength) of the wool.⁶⁰

When TGA is added to Cu^{2+} solution the following reactions will occur.^{51,52}

So, the net result is:

The complex $\text{RS}^- \text{---} \text{Cu}^+$ is responsible for the pale yellow colour, where mono-valent copper is present.⁵¹ The colour develops when the metal: TGA ratio is more than 0.5 and a violet colour appears when the ratio is near 0.5. The reaction for the violet coloured complex is shown in equation 1.17.⁵¹

The mixed-valence copper complex with thiol compounds may give various colours when bound to wool fibres. The mono valent complexes ($\text{RS}^- \text{---} \text{Cu}^+$) show no absorption peaks in the

visible region of the electromagnetic spectrum and only a slight yellow colour is due to the tail of the UV absorption. The violet coloured complexes absorb at the wavelength 520 nm in the visible spectrum.⁵¹

1.6 Nanostructured materials

Nanostructured materials can exist either as individual particles, or clusters of nanoparticles of various shapes and sizes. Examples for nanoclusters are Cu_2O ,¹⁶ ZnS ,⁶² ZnO ⁶³ and CdSe ^{64,65} etc. The size and shape of the particles are controlled by the reductant type, reductant concentration, metal ion concentration, pH, reaction time and temperature.⁶⁶⁻⁶⁸ By definition the size of nanomaterials falls between 1 – 100 nm.⁶⁵ Nanomaterials are of interest because they can bridge the gap between bulk and molecular levels and lead to an entirely new avenue for applications in industrial, biomedical and electronic fields⁶⁹ due to the presence of novel properties (magnetic, optical and catalytic), which are absent in the bulk material. These properties are caused by surface and quantum confinement effects of nanoparticles. As the size of an object material decreases, the surface to volume ratio increases. Hence, the number of surface atoms on the surface of the nanoparticle increases. This in turn causes the reactivity of the particle increases, i.e. greater reactivity of platinum or palladium catalysts.⁶⁴ The bulk semiconductors have fixed band gaps while nanosize quantum dots show size dependent band gaps. When a semiconductor is brought to the nanoscale, containing lesser number of molecules, the quantised energy levels become distinct. Thus the removal of atoms significantly increases the band gap energy of the conduction and valence bands and making the band gap size dependent, i.e. the band gap of CdSe quantum dots is size-dependent.⁷⁰ Figure 1.23 shows the size of the nanoparticles between atomic level and bulk level. This size dependent variation of optical properties is also present in materials such as gold and silver nanoparticles that display surface plasmon resonance (SPR).^{70,71}

Figure 1.223: diagram of the changes of the diameter of the species with the changes in the number of atoms in the material.⁶⁹

1.6.1 Formation of Cu₂O nanoparticles by an *ex situ* reaction

Cu₂O nanoparticles have been prepared externally by many methods, such as electrochemical,⁷² sonochemical,⁷³ thermal decomposition,⁷⁴ microwave irradiation,⁷⁵ solution phase^{16,76} and sol-gel.⁷⁷ Since NaBH₄ was used as an external reducing agent to prepare Cu₂O particles within wool fibres, the preparation of Cu₂O nanoparticles by solution method using NaBH₄ is explained briefly below.

1.6.1.1 Preparation of Cu₂O nano-colloid¹⁶

The starting materials for the synthesis of Cu₂O nano-colloids were copper sulfate (CuSO₄·5H₂O), sodium borohydride (NaBH₄) and sodium alginate. Alginate is a polysaccharide which is a linear co-polymer of β-D-mannuronic acid and α-L-gluconic acid units.¹⁶

The alginate groups of sodium alginate direct the nanoparticle formation, control the size of the particles formed and stabilize the Cu₂O nano-colloids.¹⁶ The NaBH₄ reduces the Cu²⁺ to Cu⁺ ions and these Cu⁺ ions react with the OH⁻ ions to form cuprous hydroxide. The cuprous hydroxide eventually degrades to Cu₂O.

The overall reaction steps for the formation of Cu₂O nanoparticles are given below.¹⁶

This author was unable to find any literature* in producing copper or copper oxide nanoparticles within wool fibre by an *in situ* reaction, other than Au and Ag nanoparticles.^{18,20,21,66,78}

5 mL of 0.01% NaBH₄ sodium alginate solution was added to 2 X 10⁻⁵ M CuSO₄·5H₂O solution and heated to 50 °C. To the warm solution 5 mL of NaBH₄ solution was added in drops. A stable yellow coloured solution (Cu₂O nano-colloid) was prepared.¹⁶

* Sci Finder scholar 2007, American Chemical Society in Washington, DC USA. Author did the search on 10-8-2011.

Cu₂O-nanocolloid was characterized by UV-Vis spectroscopy, FTIR spectroscopy, Powder X-ray diffraction and TEM.¹⁶

1.6.1.2 UV-Vis spectroscopy

Figure 1.234: UV-Vis spectrum of sodium alginate capped Cu₂O nanoparticles.¹⁶

A broad absorbance ($\lambda_{\text{max}} = 448 \text{ nm}$) is observed in the UV-Vis spectrum of the Cu₂O colloid (Figure 1.24).

1.6.1.3 FTIR spectroscopy

Figure 1.245: FTIR spectra of sodium alginate capped Cu₂O nanoparticles.¹⁶

A peak at 620 nm is caused by Cu⁺-O vibrational mode (Figure 1.25).

1.6.1.4 X-ray diffraction (XRD)

Figure 1.256: X-ray diffraction pattern of sodium alginate capped Cu_2O nanoparticles.¹⁶

All the peaks appearing in the X-ray diffraction pattern are indexed based on Cu_2O (JCPDS file # 78-2076). The crystal structure is cubic.

1.6.1.5 TEM

The TEM analysis indicates the formation of cubic particles⁷⁶ with an average particle size of around 100 nm.¹⁶

1.7 Wool digestion methods

The metal-wool composites can be digested and the metal content determined by atomic absorption spectrometry. Wool can be digested by several methods and few are given as follows:

1.7.1 Dry digestion method (In an electric furnace)

Previous work has shown that a wool sample placed in a porcelain crucible can be ashed in an electric furnace at a temperature of 370 °C for 2 hours. The ash residue may then be dissolved in HNO_3 .⁷⁹

1.7.2 Wet digestion method (Conventional digestion method)^{79,80}

Previous work has shown that a wool sample can be heated on a hot plate at 110 °C for 55 min with a HNO₃/H₂O₂ (2/1) mixture. Increase of H₂O₂ amount from 2:1 to 1:1 did not influence the decomposition of wool sample for wet digestion.

1.7.3 Microwave digestion method

Approximately 0.2-0.4 g of the wool sample was digested with 3 ml of HNO₃ and 2 ml of H₂O₂ in a microwave reactor. The temperature programme was as follows: 8 min at 130 °C, 5 min at 155 °C and 12 min at the maximum temperature of 170 °C. In all cases the power setting was 80 W. The sample digestion was performed in pressurised PTFE sealed vessels using microwave heating.⁸¹

The main advantages of microwave digestion methods are given below.

- Faster reaction
- Excellent recovery and higher purity: Minimize the formation of side products and avoid losses of the material.
- Minimize the contamination
- Reproducibility: The homogeneous microwave irradiation inside the reactor, in addition to precise control of reaction parameters, notably, temperature, pressure and power, ensure the same analytical results of the digested sample.

The advantages mentioned above prove that the microwave digestion procedure is the better digestion method to digest the wool samples, compared to dry and wet procedures.^{79,82}

1.8 Scope of the Thesis

- Investigate the metal ions uptake (Cu²⁺, Zn²⁺ and Mn²⁺) by merino wool fibres at different conditions and metal ion concentrations.
- Investigate and characterize the uptake of Cu²⁺ ions by pre treating merino wool with EDTA dianhydride and thioglycolic acid, followed by doping with Cu²⁺ solution.
- Characterize the Cu₂O particles formed within the wool fibres by an *in situ* reaction, in the presence of thioglycolic or NaBH₄ as reducing agents.

CHAPTER 2

2 EXPERIMENTAL METHODS

2.1 Materials

The merino wool used in this study was supplied by Ashford Handicrafts Ltd. All chemical employed were of analytical grade and used as received unless otherwise stated. The chemicals used in this study were as follows.

- Copper(II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was supplied from Carlo Erba Reactifs.
- Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and manganous sulfate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) were supplied by BDH Chemicals Ltd.
- Thioglycolic acid (Minimum 98%), edtylenediaminetetraacetic dianhydride (98%) and sodium borohydride (2.0 M solution in triethylene glycol dimethyl ether) were provided by Sigma Aldrich.
- Sodium hypochlorite (12.5-15%) supplied from Pure Science NZ.
- Dimethylformamide (DMF) supplied from BDH chemicals.
- Zinc, copper and manganese standards for AAS were provided by Fluka analytical.

2.2 Preparation

2.2.1 Preparation of merino wool-copper composites

0.16 mol L^{-1} ($10,000 \text{ mg L}^{-1}$) Cu^{2+} solution was prepared from $\text{CuSO}_4(\text{s})$ and diluted to $7.8 \times 10^{-5} \text{ mol L}^{-1}$ ($\sim 5 \text{ mg L}^{-1}$), $1.6 \times 10^{-4} \text{ mol L}^{-1}$ ($\sim 10 \text{ mg L}^{-1}$), $3.1 \times 10^{-4} \text{ mol L}^{-1}$ ($\sim 20 \text{ mg L}^{-1}$), $7.8 \times 10^{-4} \text{ mol L}^{-1}$ ($\sim 50 \text{ mg L}^{-1}$) and $1.6 \times 10^{-3} \text{ mol L}^{-1}$ ($\sim 100 \text{ mg L}^{-1}$) solutions. The concentrations of the solutions were determined by atomic absorption spectrometry, i.e. $6.3 \times 10^{-5} \text{ mol L}^{-1}$ (4 mg L^{-1}), $1.6 \times 10^{-4} \text{ mol L}^{-1}$ (10 mg L^{-1}), $2.8 \times 10^{-4} \text{ mol L}^{-1}$ (18 mg L^{-1}), $7.2 \times 10^{-4} \text{ mol L}^{-1}$ (46 mg L^{-1}) and $1.3 \times 10^{-3} \text{ mol L}^{-1}$ (85 mg L^{-1}) respectively. 1 g of merino wool was soaked with 100 mL of each of those solutions at 20°C and 50°C with a treatment time of 1 h, 5 h, 12 h and 24 h and 90°C with a treatment time of 1 h and 24 h respectively. These wool composites were prepared in a temperature controlled shaking water bath.

2.2.2 Preparation of merino wool-zinc composites

0.15 mol L⁻¹ (10,000 mg L⁻¹) Zn²⁺ solution was prepared from ZnSO₄(s) and diluted to 7.6 X 10⁻⁵ mol L⁻¹ (~5 mg L⁻¹), 1.5 X 10⁻⁴ mol L⁻¹ (~ 10 mg L⁻¹), 3.0 X 10⁻⁴ mol L⁻¹ (~ 20 mg L⁻¹), 7.6 X 10⁻⁴ mol L⁻¹ (~ 50 mg L⁻¹) and 1.5 X 10⁻³ mol L⁻¹ (~ 100 mg L⁻¹) solutions. The concentrations of the solutions were determined by atomic absorption spectrometry, i.e. 4.6 X 10⁻⁵ mol L⁻¹ (3 mg L⁻¹), 1.1 X 10⁻⁴ mol L⁻¹ (7 mg L⁻¹), 2.3 X 10⁻⁴ mol L⁻¹ (15 mg L⁻¹), 6.1 X 10⁻⁴ mol L⁻¹ (40 mg L⁻¹) and 1.2 X 10⁻³ mol L⁻¹ (80 mg L⁻¹) respectively. 1 g of merino wool was soaked with 100 mL of each of those solutions at 20 °C and 50 °C with a treatment time of 1 h, 5 h, 12 h and 24 h and 90 °C with a treatment time of 1 h and 24 h respectively. These wool composites were prepared in a temperature controlled shaking water bath.

2.2.3 Preparation of merino wool-manganese composites

0.18 mol L⁻¹ (10,000 mg L⁻¹) Mn²⁺ solution was prepared from MnSO₄(s) and diluted to 9.1 X 10⁻⁵ mol L⁻¹ (~ 5 mg L⁻¹), 1.8 X 10⁻⁴ mol L⁻¹ (~ 10 mg L⁻¹), 3.6 X 10⁻⁴ mol L⁻¹ (~ 20 mg L⁻¹), 9.1 X 10⁻⁴ mol L⁻¹ (~ 50 mg L⁻¹) and 1.8 X 10⁻³ mol L⁻¹ (~ 100 mg L⁻¹) solutions. The concentrations of the solutions were determined by atomic absorption spectrometry, i.e. 1.1 X 10⁻⁴ mol L⁻¹ (6 mg L⁻¹), 2 X 10⁻⁴ mol L⁻¹ (11 mg L⁻¹), 4.5 X 10⁻⁴ mol L⁻¹ (25 mg L⁻¹), 1.1 X 10⁻³ mol L⁻¹ (60 mg L⁻¹) and 2 X 10⁻³ mol L⁻¹ (110 mg L⁻¹) respectively. 1 g of merino wool was soaked with 100 mL of each of those solutions at 20 °C and 50 °C with a treatment time of 1 h, 5 h, 12 h and 24 h and 90 °C with a treatment time of 1 h and 24 h respectively. These wool composites were prepared in a temperature controlled shaking water bath.

2.2.4 Preparation of chemically unmodified merino wool-copper composites

1 g of merino wool was soaked with 100 mL of 450 mg L⁻¹ Cu²⁺ solution at 90 °C for 60 min in a shaking water bath. The pH of the uptake mixture (Cu²⁺ solution + merino wool) was measured before heating. The pHs of these solutions are ~ 4.5. The merino wool treated with Cu²⁺ only was considered as a control sample for chemically modified merino wool-copper composites described below. These wool samples were removed from the residual solution and washed with distilled water and air dried at ~ 40 °C for 12 hours.

2.2.5 Preparation of ethylene diaminetetraacetic (EDTA) dianhydride modified (treated) merino wool-copper composites

0.3 g of EDTA dianhydride was dissolved in 20 mL of dimethylformamide, followed by addition of 1 g of merino wool. The reaction mixture was heated at 80 °C for 60 min. Treated wool fibres were wiped with paper towels gently and doped with 100 mL of 450 mg L⁻¹ Cu²⁺ solution at 90 °C for 60 min. The pH of the uptake mixture (Cu²⁺ solution + merino wool + DMF + EDTA dianhydride) was measured before heating to 90 °C. The pHs of these solutions are ~ 4.5. These wool samples were removed from the residual solution and washed with distilled water and air dried at ~ 40 °C for 12 hours.

2.2.6 Preparation of copper-containing particles on the surface of the merino wool fibres, using thioglycolic acid (TGA), with in situ binding.

2 M TGA solutions were prepared from the original TGA having concentration 14 mol L⁻¹. The 1 mL (2 mmol) and 0.5 mL (1 mmol) of 2 M TGA solutions and 25 µL (0.35 mmol) and 600 µL (8.4 mmol) of 14 M TGA solutions were dissolved in 20 mL of distilled water separately. Each of these TGA dispersed solutions were mixed with 1 g of merino wool at room temperature (20 °C) for 60 min. The 1 mL and 0.5 mL of 2 M TGA treated wool fibres were wiped with paper towels gently and soaked with 100 mL of 450 mg L⁻¹ Cu²⁺ solutions at 90 °C for 30 min and 60 min respectively whereas 25 µL and 600 µL of 14 M TGA treated wool fibres were soaked with 100 mL of 450 mg L⁻¹ Cu²⁺ solution at 90 °C for 60 min and 20 °C for 60 min respectively. All these wool samples were vigorously shaken at room temperature for 12 hours before removing from the residual solution. These wool samples were washed with distilled water and air dried at ~ 40 °C for 12 hours.

2.2.7 Preparation of Cu₂O particles on the surface of the merino wool fibres, using sodium borohydride (NaBH₄), with in situ binding.

1 mL (2 mmol) of 2 M NaBH₄ solution was dissolved in 20 mL distilled water, followed by addition of 1 g of merino wool. These NaBH₄ treated wool samples were soaked with 100 mL of 450 mg L⁻¹ Cu²⁺ solutions at 90 °C for 5 min and 30 min separately. All these reaction mixtures were gently shaken at room temperature for few hours (1-2 hours). The wool samples which were prepared at 90 °C for 5 min were removed from the residual solutions and washed with distilled water and dried in the air for 12 hours. The samples which were prepared at 90 °C for

30 min were removed from the residual solutions and washed with distilled water and air dried at $\sim 40\text{ }^{\circ}\text{C}$ for 12 hours.

2.2.8 Preparation of Cu^{2+} treated merino wool composites aged with TGA

1 g of merino wool was soaked with 100 mL of $450\text{ mg L}^{-1}\text{ Cu}^{2+}$ solution at $90\text{ }^{\circ}\text{C}$ for 60 min in a shaking water bath. Approximately 0.5 g of this wool sample was aged with 100 μL of 2 M TGA in 50 mL of distilled water at $50\text{ }^{\circ}\text{C}$ for 7 days. These wool samples were removed from the residual solution and washed with distilled water and dried at $\sim 40\text{ }^{\circ}\text{C}$ for 12 hours.

2.2.9 Preparation of Cu^{2+} treated merino wool composites aged with NaBH_4

1 g of merino wool was soaked with 100 mL of $450\text{ mg L}^{-1}\text{ Cu}^{2+}$ solution at $90\text{ }^{\circ}\text{C}$ for 60 min in a shaking water bath. Approximately 0.5 g of this wool sample was aged with 500 μL of 2 M NaBH_4 in 50 mL of distilled water at $50\text{ }^{\circ}\text{C}$ for 7 days. These wool samples were removed from the residual solution and washed with distilled water and dried at $\sim 40\text{ }^{\circ}\text{C}$ for 12 hours.

2.2.10 Quantitative determination of metal content of the wool

Once each treated and untreated wool-metal composites was removed from the residual solution, the solution was filtered on a folded filter paper to remove any fibres. The filtered solution was analysed by atomic absorption spectrometry to thereby determine the actual metal content present in the wool. Also, the amount of metal present in the wool was determined quantitatively by the method of microwave digestion of wool composites followed by atomic absorption analysis. The determination of metal content of the wool was described as follows.

2.2.10.1 Method of analysing metal content in the residual solution

The uptake of metal ions by wool fibre was quantified using flame atomic absorption spectrometry. The residual solution (filtrate) was analysed for metal content and if the original concentration of metal solution was known, the relative amount absorbed onto wool was calculated. The calculation of metal content in the wool is given as follows.

Concentration of initial metal ion solution: **a mg L^{-1}**

Concentration of residual metal ion solution: **b mg L^{-1}**

Concentration of metal ions uptake per gram of wool: $[(a-b) \text{ mg L}^{-1}] / [\text{Mass of wool (g)}]$

The amount of metal ions present per gram of wool, when volume of 100 ml of metal ion solution was used: $[(a-b) \text{ mg L}^{-1} \times 100 \text{ mL}/1000 \text{ mL L}^{-1}] / [\text{Mass of wool (g)}]$

2.2.10.2 Method of microwave digestion of wool samples followed by analysing the metal content

Approximately 0.2 g of dried merino wool-copper sample was placed into a PTFE (polytetrafluoroethylene) vessel (height = ~ 13 cm) and 25 mL of 12.5-15% NaOCl solution was added. This sample vessel was placed into a microSYNTH microwave oven and heated at 220 °C for 30 min at a pressure of 15 bar. Once the digestion of the sample was completed, the vessel was cooled to room temperature and the solution in the vessel was diluted to meet the volume required for atomic absorption (AA) analysis. The copper content in the diluted solution was determined quantitatively by flame atomic absorption spectrometry. The amount of copper present in the wool is calculated as in Section 3.2.1.2. Figure 2.1 shows the microwave oven and the PTFE vessel used to digest the wool samples.

Figure 2.1: The microwave oven and the PTFE digesting vessel.

2.3 Characterization

2.3.1 Flame atomic absorption spectroscopy (FAAS)

The quantification of the uptake of metal ions (Cu^{2+} , Mn^{2+} and Zn^{2+}) within the wool fibres for all preparation methods (with and without external reducing agents - TGA and NaBH_4) were undertaken by measuring the amount of residual metals in solution following composite preparation, by flame atomic absorption. An acetylene/air flame and the relevant hollow cathode lamp for each metal were used with a GBC 906AA spectrometer. All metal solutions were filtered to remove any remaining fibres prior to analysis. The analysis methods employed for using the given AA spectrometer were as recommended by the manufacturer.⁸³ The calibration of the instrument was accomplished using copper standards, manganese standards and zinc standards with the following concentrations: 1, 2, 3, 4, 5 mg L^{-1} for Cu, 10, 15, 20, 25 mg L^{-1} for Mn and 0.2, 0.4, 0.6, 0.8 and 1.0 mg L^{-1} for Zn respectively.⁸³

2.3.2 UV-Visible transformed reflectance spectroscopy

Figure 2.2: TGA treated wool-copper composite (brown coloured sample) placed in a sample holder.

UV-Vis reflectance spectroscopy was used as a tool to determine the absorption characteristics in the visible region, resulting from the Cu^{2+} , Mn^{2+} and Zn^{2+} ions within the respective merino wool composites. The shift of the absorption maxima or a broadening of the absorption peaks suggested the change of the approximate size of the particles containing copper or the dielectric constant of the reaction medium of reducing agents (TGA and NaBH_4) treated merino wool-copper composites. TGA treated wool-copper composite fibres (brown coloured fibres) were stretched across a sample holder (Figure 2.2) and their UV-Vis spectra measured in reflectance, due to their opaque nature. Measurements were taken on a Varian Cary 100 scan UV-Vis spectrometer. The obtained reflectance spectra were converted to the colour depth (K/S) by applying to the Kubelka-Munk equation (Equation 2.1):⁷⁸

$$f(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \quad (2.1)$$

Merino wool fibres are a diffusively scattering medium, and reflectance is affected by both absorption and scattering properties, as described by Kubelka-Munk equation. R is the absolute reflectance of the sampled layer, K is the light absorption coefficient and S for the light scattering coefficient.

2.3.3 FTIR spectroscopy

Figure 2.3: TGA treated merino wool-copper composite (violet coloured sample) in KBr was pressed into a 13 mm diameter disk.

Each wool sample was finely ground and dried. Approximately 3 mg of it ground with ~ 300 mg of dried KBr. The sample mixture was pressed into a KBr disk and IR spectra were collected (8 scans, resolution 4 cm^{-1} , range 4000-400 cm^{-1}) using a Perkin Elmer Spectrum One FTIR Spectrometer. Comparing slight changes in the IR spectra of the merino wool to those of the wool composites, suggested the nature of the interaction between the metal ions (Cu^{2+} , Zn^{2+} and Mn^{2+}) and the merino wool. Also, comparing the significant changes in the IR spectra of TGA treated merino wool-copper composites (violet coloured sample) to those of the control samples suggested the nature of the interaction between the Cu^{2+} and the TGA treated merino wool.

2.3.4 Scanning electron microscopy (SEM)

Figure 2.4: Individual wool fibres and their cross sections were mounted on aluminium specimen stubs with double sided carbon adhesive tapes and coated with carbon.

SEM is an important characterization technique for studying the morphology of the wool fibres and the metal-wool composites. The particles containing copper on the surface of TGA and NaBH_4 treated merino wool copper composites were compared with chemically unmodified merino wool-copper composites. Individual fibres were mounted on aluminium specimen stubs with double sided carbon adhesive tape and sputter coated with a 3-4 nm thickness of carbon by a Quorum carbon coater (Figure 2.4). The samples were coated by carbon in order to reduce the build up of charges on the surface of the sample. Imaging of the wool samples was carried out on a JEOL 6500 F field emission gun scanning electron microscope at a series of different magnifications. Images were taken at various positions throughout the samples in order to obtain an accurate representation of the surface of the wool composites. The particles containing copper were more apparent due to their high molecular weight in the backscattered mode of SEM.

Energy dispersive spectroscopy (EDS) shows the elemental distribution of certain elements on the surface of the fibres of merino wool and the metal wool composites. The aggregation and the accumulation of the particles containing copper were studied by SEM-EDS analysis. Composite fibres were sandwiched between carbon tapes and frozen with liquid nitrogen. The frozen carbon tape sliced with a sharp scalpel, giving surfaces of fibre cross sections. For TGA

and NaBH_4 treated merino wool-copper composites C, N, O, S and Cu were mapped. In the case of NaBH_4 treated wool-copper composite Na was additionally mapped.

2.3.5 Transmission electron microscopy (TEM)

Figure 2.5: (a) Chemically unmodified merino wool-copper fibres in a resin; (b) Thin film section of a sample embedded in the resin.

TEM is a complementary characterisation method to SEM as it allows for greater spatial resolution. The nanoparticles and nano-structured materials that are too small to be viewed on the SEM may be studied. TEM analysis of chemically unmodified merino wool-copper composites were undertaken on a JEOL 2010 high resolution instrument with a LaB_6 filament operated at 200 kV. Other chemically modified merino wool-copper composites were not analysed by TEM due to the unavailability of the instrument during my period of research. Wool samples were embedded into a resin (Figure 2.5(a)), from which thin film sections of the resin were prepared (Figure 2.5 (b)) for TEM analysis. It is necessary to prepare the thin film sections of the resin in order to pass the electron beam through the sample. The resin used had a 54:32:12:1 Procure 812(epoxy resin):NMA(epoxy hardner):DDSA(epoxy hardner):BDMA(epoxy resin accelerator) composition.

Sample preparation of chemically unmodified merino wool-copper composites was undertaken using the following methodology. Merino wool-copper composites were dehydrated in a series of ethanol solutions, 10 min in each (50%, 70%, 90% and 100% consecutively). This was followed by two consecutive 10 min soak periods in 100% propylene oxide. Composites were then infused with a 1:1 propylene oxide:resin mixture for one hour, followed by infusion with 100% resin overnight. These were then transferred into plastic embedding moulds and cured at 60 °C for 48 hours. Semi thin (1-2 μm) sections of the embedded composites were undertaken using a glass knife on a Reichert-Jung Ultracut E microtome, so as to identify the area of interest. Ultra thin (70-90 nm) sections were then cut using a Diatome diamond knife and

picked up on gold grids (200 thin bar hexagonal grids). The grids were coated with 3-4 nm carbon by a Quorum carbon coater to minimise charging.

2.3.6 X-ray diffraction (XRD)

Figure 2.6: (a) Flat stage sample holder; (b) TGA treated merino wool-copper sample (violet coloured sample) was stretched and wrapped around a glass slide.

XRD provides information about the crystal structure of particles containing copper on the surface of the merino wool. Also, it enables the identification of crystalline materials as used here. To determine the crystallinity of the TGA treated merino wool-copper composite (violet coloured sample), the wool fibres were stretched as much as possible and wrapped around a glass slide (Figure 2.6 (b)). Following this, the glass slide with the sample was placed on the flat stage sample holder (Figure 2.6 (a)) of a Philips X'Pert Pro MPD X-ray diffractometer (X-ray source was $\text{CuK}\alpha$ having a wavelength of $1.54 \text{ \AA}$). The applied voltage was 45 kV and the current was 40 mA. The sample was then scanned from $2\theta = 10$ to 80° , step size = 0.0065° , time per step = 76.50 s.

CHAPTER 3

3 RESULTS AND DISCUSSIONS OF UPTAKE STUDIES OF CHEMICALLY UNMODIFIED AND MODIFIED MERINO WOOL-METAL COMPOSITES

3.1 Characterization of merino wool

The merino wool is characterized initially by scanning electron spectroscopy and Infrared spectroscopy. The morphology of the surface and the cross section of the pure merino wool are given below (Fig 3.1 and Fig 3.2).

3.1.1 Scanning electron microscopy (SEM)

Figure 3.1: Morphology of the surface of merino wool fibre.

The structure and chemical components of wool have previously been explained in the Chapter 1.2. Figure 3.1 shows the shape of the wool fibre is a cylinder and main features of the surface of the wool are cuticular scales which overlap like tiles on a roof.²⁶ The edges of these cuticle scales appear to be somewhat smooth. The diameter of the wool fibre is around $\sim 25 \mu\text{m}$ (Figure 3.1).

Figure 3.2: Morphology of the cross section of merino wool fibre.

Figure 3.2 shows the morphology of the cross section of merino wool fibre. It consists a bundle of corticle cells (cortex) surrounded by a thin sheath of cuticle cells.

3.1.2 Infrared spectroscopy (FTIR)

The band frequencies of the functional groups of merino wool fibre are given in Figure 3.3. This spectrum is obtained as part of the research work.

Figure 3.3: FTIR spectra of merino wool fibre.

The band frequencies of wool fibre (Figure 3.3) are generally in good agreement with the assignments from previous work.^{7,49,84,85} This is illustrated in Table 3.1.

Table 3.1: Band frequencies of wool fibre.^{49,84-87}

Experimental (cm ⁻¹)	Literature (cm ⁻¹)	Assignment
3350-3250	3400-3200	N–H stretching of amide bands and O–H stretching
3072	3070	N–H stretching
2960-2927	2928-2859	Asymmetric and symmetric CH ₂ and CH ₃ stretching
1654	1716-1630	C=O stretching from –COOH dimer or amide group
1541	1541-1505	N–H bending or symmetric stretching of –COOH
1449	1453-1443	CH ₂ and CH ₃ bending modes or symmetric stretching of COOH
1389	1400-1380	Symmetric stretching of –COOH dimer.
1336	1339-1280	N–H bending of amide III vibrations
1234	1240-1225	O=C–N bending of amide III vibrations
1294	1260-1255	C–H stretching of amide III vibrations or symmetric stretch of COOH dimer.
1172	1175	Uncertain
1120	1120	Symmetric stretching of C–C, and C–N or C–O bond of –COOH dimer
1076	1075	Symmetric stretching of C–C, and C–N, C–O bond of –COOH dimer and S–O bonds.
1046	1040	Symmetric stretching of C–C, and C–N, C–O bond of –COOH dimer or S–O bonds.
499 (vw)	499 (vw)	Stretching vibrations of –S–S–
932	900-960	Stretching vibrations of –COO ⁻

vw – very weak

As outlined in introduction, wool has a protein structure which consists of amino acids.

Therefore the main functional groups existing in the wool fibre are COOH, NH₂, CONH, S–S and

OH.^{26,29} Since some wool protein has an alpha helix configuration, there is high possibility that some of these COOH groups exist as a dimer. The structure of carboxylic acid dimer is given in Figure 3.4.

Figure 3.4: Carboxylic acid dimer present in wool.

The broad peak assigned to the band frequency of O-H stretch is around $3350\text{--}3250\text{ cm}^{-1}$. The strong peak assigned to the frequency of carbonyl group has been shifted to lower number (1654 cm^{-1}).⁴⁹ A medium peak and weak shoulder peak of COOH dimer may be present at 1389 cm^{-1} and 1294 cm^{-1} respectively.⁴⁹ The COOH groups suggested a slightly broader band at 1389 cm^{-1} . A strong peak at 1541 cm^{-1} and a medium peak at 1449 cm^{-1} are assigned to symmetric stretching of COOH groups.⁴⁹ Weak peaks at 1120 cm^{-1} , 1076 cm^{-1} and 1046 cm^{-1} are attributed to the symmetric stretch of C-C, C-N and C-O vibrations.⁸⁶ Also 1046 cm^{-1} may be assigned to vibrations of cysteic acid groups.^{84,85} A very weak band at 499 cm^{-1} is assigned to the symmetric stretch of -S-S- vibrations.⁸⁷

3.2 Uptake of metal ions by untreated (chemically unmodified) merino wool

All wool samples were soaked in metal sulfate solutions (CuSO_4 , ZnSO_4 and MnSO_4) at different original metal ion concentrations, have pHs between 4.5-5.5. Wool doping with metal ions was processed at different time intervals (1, 5 12 and 24 hours) and different temperatures ($20\text{ }^\circ\text{C}$, $50\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$). Room temperature was taken as $\sim 20\text{ }^\circ\text{C}$. The experimental programme was carried out to investigate the effect of the absorption of metal ions by wool at different concentrations and processing conditions. These metal wool composites were characterized initially by considering spectroscopic methods such as flame atomic absorption spectroscopy, UV-Visible or FTIR spectroscopy and the results thus obtained are further investigated by use of

microscopy such as SEM and TEM. Crystallographic studies, in particular XRD were attempted on some metal wool samples.

3.2.1 Atomic absorption spectroscopic analysis

The metal ion content of merino wool was determined quantitatively by flame atomic absorption spectrometry.

3.2.1.1 Quantitative determination of metal ion content of the wool by the method of measuring residual metal ion concentration

As outlined in section 2.2.10, the metal ion content of original metal ion solution and the residual solution after doping wool with metal ions were analysed by flame atomic absorption spectrometry. The method of calculating the actual metal content in 1 g of wool was given in Section 2.2.10.1.

3.2.1.1.1 Uptake studies at room temperature (~ 20 °C)

Uptake of various metal ions by wool fibre having different initial concentrations at room temperature is shown below. The initial metal ion concentrations are shown in the legend.

(a)

(b)

Figure 3.5: (a) Uptake of metal ions at room temperature, having initial concentrations (Zn²⁺: 3 mg L⁻¹, Mn²⁺: 6 mg L⁻¹, Cu²⁺: 4 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.5 shows the uptake of various metal ions by wool from metal solutions at initial concentrations of Zn²⁺, Mn²⁺ and Cu²⁺ were 3 mg L⁻¹, 6 mg L⁻¹ and 4 mg L⁻¹ respectively. At very low initial concentrations of metal ions (≤ 6 mg L⁻¹), most of the metal ions applied are absorbed within an hour or less. The sorption of metal ions by wool fibre is constant for each metal ion, when processing time increases (Fig 3.5a). Figure 3.5(b) shows the percentage of uptake of Zn²⁺, Mn²⁺ and Cu²⁺ by wool fibre with processing time of 24 hours. These percentages were calculated based on initial metal ions applied. The uptake of Zn²⁺ and Mn²⁺ is around ~ 85% where the uptake of Cu²⁺ is 95%.

(a)

(b)

Figure 3.6: (a) Uptake of metal ions at room temperature, having initial concentrations (Zn²⁺: 7 mg L⁻¹, Mn²⁺: 11 mg L⁻¹, Cu²⁺: 10 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.6 shows the uptake of various metal ions by wool from metal solutions where the initial concentration of Zn²⁺, Mn²⁺ and Cu²⁺ was 7 mg L⁻¹, 11 mg L⁻¹ and 10 mg L⁻¹ respectively. Figure 3.6(a) shows that when the metal ion has a low initial concentration (≤ 11 mg L⁻¹), the binding of metal ions onto wool fibre occurs quickly. Also there is no significant change of sorption for each metal ion when processing time increases. The percentage of uptake of Zn²⁺, Mn²⁺ and Cu²⁺ by wool fibre with processing time of 24 hours was given in Figure 3.6(b). The uptake of Mn²⁺ is 62%, Zn²⁺ is 86% and Cu²⁺ is 92%. The uptake % of Mn²⁺ is much less than that of the other two metal ions at initial concentrations ≥ 6 mg L⁻¹.

(a)

(b)

Figure 3.7: (a) Uptake of metal ions at room temperature, having initial concentrations (Zn^{2+} : 15 mg L^{-1} , Mn^{2+} : 25 mg L^{-1} , Cu^{2+} : 18 mg L^{-1}). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.7 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 15 mg L^{-1} , 25 mg L^{-1} and 18 mg L^{-1} respectively. The uptake of Mn^{2+} is 38%, Zn^{2+} is 64% and Cu^{2+} is 83%.

The uptake of Cu^{2+} and Zn^{2+} ions shows an initial rise with a turning point at 5 hours, corresponding to 1.2 mg of Cu^{2+} and 0.8 mg of Zn^{2+} per gram of wool. Afterward, it proceeds at a lower rate, reaching a maximum sorption of metal content of Cu^{2+} and Zn^{2+} are 1.4 and 0.9 mg per gram of wool respectively after 12 hours sorption time. The uptake of Mn^{2+} is constant when processing time increases (0.9 mg g^{-1} of wool). The metal solutions at initial concentrations 15 -25 mg L^{-1} , the saturation of solution film (The metal solution intact with wool fibre) occurs after about 12 hours and there after the uptake of metal ions reaches the

equilibrium. Also the absorption of Zn^{2+} and Mn^{2+} is less compared to Cu^{2+} . This will be explained in detail in later sections.

(a)

(b)

Figure 3.8: (a) Uptake of metal ions at room temperature, having initial concentrations (Zn^{2+} : 40 mg L⁻¹, Mn^{2+} : 60 mg L⁻¹, Cu^{2+} : 46 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.8 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 40 mg L⁻¹, 60 mg L⁻¹ and 46 mg L⁻¹ respectively. The uptake of Mn^{2+} is 15%, Zn^{2+} is 33% and Cu^{2+} is 48%. The uptake of metal ions shows an initial rise with a turning point at 5 hours, corresponding to a metal ion content of Cu^{2+} and Zn^{2+} are 1.8 and 1.1 mg per gram of wool respectively. Afterward, it proceeds at a lower rate, reaching a maximum uptake of Cu^{2+} and Zn^{2+} are 2.3 and 1.2 mg per gram of wool

respectively after 24 hours sorption time. The uptake % of metal ions by wool fibre is less compared to the metal ion solutions having initial concentrations 15-25 mg L⁻¹. Also the Cu²⁺ absorption is greater than the Mn²⁺ and Zn²⁺. The uptake of Mn²⁺ is less at 12 hours with comparison to 24 hours. This may be due to the reason of instrumental uncertainty.

(a)

(b)

Figure 3.9: (a) Uptake of metal ions at room temperature, having initial concentrations (Zn²⁺: 80 mg L⁻¹, Mn²⁺: 110 mg L⁻¹, Cu²⁺: 85 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.9 shows the uptake of various metal ions by wool from metal solutions at initial concentrations of Zn²⁺, Mn²⁺ and Cu²⁺ were 80 mg L⁻¹, 110 mg L⁻¹ and 85 mg L⁻¹ respectively. The uptake of Mn²⁺ is 8%, Zn²⁺ is 20% and Cu²⁺ is 28%. The uptake of Cu²⁺ and Zn²⁺ takes more than 24 hours to reach the saturation whereas the solution at low initial concentrations

($\leq 100 \text{ mg L}^{-1}$) takes less than 24 hours to reach the saturation. The uptake of Mn^{2+} is less at 12 hours with comparison to 24 hours. This may be due to the reason of instrumental uncertainty. The uptake % of metal ions by wool fibre is less compared to the metal ion solutions having initial concentrations 40-60 mg L^{-1} . Also the Cu^{2+} absorption is greater than the Mn^{2+} and Zn^{2+} .

3.2.1.1.2 Uptake studies at 50 °C

Uptake of various metal ions by wool fibre having different initial concentrations at 50 °C is given below. The initial metal ion concentrations are shown in the legend.

(a)

(b)

Figure 3.10: (a) Uptake of metal ions at 50 °C, having initial concentrations (Zn^{2+} : 3 mg L^{-1} , Mn^{2+} : 6 mg L^{-1} , Cu^{2+} : 4.5 mg L^{-1}). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.10 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 3 mg L^{-1} , 6 mg L^{-1} and 4.5 mg L^{-1} respectively. Figure 3.10(b) shows the percentage of uptake of Zn^{2+} , Mn^{2+} and Cu^{2+} by wool fibre at 24 hours. The uptake of Mn^{2+} is 88%, Zn^{2+} is 100% and Cu^{2+} is 100%. At very low initial concentrations of metal ions ($\leq 6 \text{ mg L}^{-1}$), most of the metal ions applied are absorbed within an hour or less except Mn^{2+} (Figure 3.10(a)).

(a)

(b)

Figure 3.11: (a) Uptake of metal ions at 50 °C, having initial concentrations (Zn^{2+} : 7 mg L^{-1} , Mn^{2+} : 13 mg L^{-1} , Cu^{2+} : 8 mg L^{-1}). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.11 shows the uptake of various metal ions by wool from metal solutions at initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 7 mg L^{-1} , 13 mg L^{-1} and 8 mg L^{-1} respectively. The percentages of uptake of Zn^{2+} , Mn^{2+} and Cu^{2+} by wool fibre at 24 hours was given in Figure 3.11(b). The uptake of Mn^{2+} is 71%, Zn^{2+} is 97% and Cu^{2+} is 96%. Figure 3.11(a) shows the metal

solutions at low initial concentrations ($\leq 13 \text{ mg L}^{-1}$), the binding of metal ions onto wool fibre becomes fast and within an hour or less the sorption of Cu^{2+} and Zn^{2+} ions is significantly greater than Mn^{2+} ions. The negative slope of Mn^{2+} may be due to the desorption of Mn^{2+} from the wool fibre.

(a)

(b)

Figure 3.12: (a) Uptake of metal ions at 50 °C, having initial concentrations (Zn^{2+} : 15 mg L⁻¹, Mn^{2+} : 25 mg L⁻¹, Cu^{2+} : 15 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.12 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 15 mg L⁻¹, 25 mg L⁻¹ and 15 mg L⁻¹ respectively. The uptake of Mn^{2+} is 43%, Zn^{2+} is 71% and Cu^{2+} is 93%. The uptake of copper ions shows an initial rise with a turning point at 1 hour, corresponding to 1.2 mg per gram of wool.

Afterward, it proceeds at a lower rate, reaching a maximum copper uptake of 1.4 mg g^{-1} of wool after 12 hours sorption time. The irregular patterns of the uptake curves of zinc and manganese ions are due to the desorption of the metal ions from the wool fibre. The uptake % of metal ions by wool fibre is less compared to the metal ion solutions having initial concentrations $\leq 13 \text{ mg L}^{-1}$. Also the absorption of Cu^{2+} is greater than the Mn^{2+} and Zn^{2+} .

(a)

(b)

Figure 3.13: (a) Uptake of metal ions at 50 °C, having initial concentrations (Zn^{2+} : 35 mg L^{-1} , Mn^{2+} : 60 mg L^{-1} , Cu^{2+} : 40 mg L^{-1}). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.13 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn^{2+} , Mn^{2+} and Cu^{2+} were 35 mg L^{-1} , 60 mg L^{-1} and 40 mg L^{-1} respectively. The uptake of Mn^{2+} is 16%, Zn^{2+} is 40% and Cu^{2+} is 66%. The uptake of copper ions

shows a similar trend as given in previous graphs. The uptake % of metal ions by wool fibre is less compared to the metal ion solutions having initial concentrations 15-25 mg L⁻¹. Also the absorption of Cu²⁺ is significantly greater than the Mn²⁺ and Zn²⁺. The irregular patterns of the uptake curves of zinc and manganese ions are due to the desorption of the metal ions from the wool fibre.

(a)

(b)

Figure 3.14: (a) Uptake of metal ions at 50 °C, having initial concentrations (Zn²⁺: 70 mg L⁻¹, Mn²⁺: 120 mg L⁻¹, Cu²⁺: 90 mg L⁻¹). Wool applied at a loading of 1 g per 100 mL of metal solution. (b) Uptake % of different metal ions at 24 h.

Figure 3.14 shows the uptake of various metal ions by wool from metal solutions where the initial concentrations of Zn²⁺, Mn²⁺ and Cu²⁺ were 70 mg L⁻¹, 120 mg L⁻¹ and 90 mg L⁻¹ respectively. The uptake of Mn²⁺ is 15%, Zn²⁺ is 23% and Cu²⁺ is 45%. The uptake of copper ions shows an initial rise with a turning point at 12 hours, corresponding to a 2.9 mg of Cu²⁺ content.

Afterward, it proceeds at a lower rate, reaching a maximum uptake of Cu^{2+} is 4.0 mg g^{-1} of wool after 24 hours sorption time. The uptake of Zn^{2+} shows similar trend as previous graphs where as the uptake of Mn^{2+} is constant when processing time increases. The uptake % of metal ions by wool fibre is less compared to the metal ion solutions having initial concentrations $35\text{-}60 \text{ mg L}^{-1}$. Also the absorption of Cu^{2+} is significantly greater than the Mn^{2+} and Zn^{2+} .

3.2.1.1.3 Comparison of uptake studies at 50°C and 90°C

Table 3.2 shows the uptake studies, when the wool fibres soaked with metal ions having original concentration $\sim 450\text{-}500 \text{ mg L}^{-1}$ ($\sim 45\text{-}50 \text{ mg g}^{-1}$ of wool applied) at two different temperatures (50°C and 90°C). Wool applied at a loading of 1 g per 100 ml of solution.

Table 3.2: Effect of bath temperature on metal uptake (processing time: 1 h and 24 h, applied metals: 45-50 mg, loading 1 g of wool).

Metal	Temperature	Processing time (h)	Metal content in 100 ml uptake solution (mg g^{-1} of wool)	Metal uptake (mg g^{-1} of wool)	Metal uptake %
Cu	50	24	45	8.0	18
	90	1	45	8.5	19
	90	24	45	14	31
Zn	50	24	46	5.0	11
	90	1	46	5.1	11
	90	24	46	8.0	17
Mn	50	24	50	1.0	2
	90	1	50	1.0	2
	90	24	50	2.0	4

The absorption of metal ions on wool at 90°C and the processing time of 24 hours, is greater compared to 50°C with the same processing time (Table 3.2). At very high temperatures ($\sim 90^\circ\text{C}$), the $-\text{S}-\text{S}-$ bonds in the cystine residues break more readily and oxidize into cysteic acid residues.^{27,84}

These cysteic acid ($\text{-RSO}_3\text{H}$) groups may bind with metal ions ($\text{M}^{2+}_{(\text{aq})}$). When heated above 85°C , usually for more than 8 hours, the high metal uptake may be attributed to the formation of metal sulfide and to the ligation of cysteic acid groups to metal ions.^{40,43} There is no dramatic change of the uptake of metal ions between 90°C , 1 hour and 50°C , 24 hours (Table 3.2). Therefore it can be confirmed that similar results can be observed when wool samples treated with low temperature, longer period of time and high temperature, for shorter time periods. Similar uptake results on both samples proved that number of sorption sites of wool available for bonding is constant.

When wool fibres were soaked with copper ions at 90°C for a longer period of time, the colour of the wool samples gradually become brown (Fig 3.15). This may be due to the formation of CuS or Cu_2S .

Figure 3.15: Merino wool doped with Cu^{2+} , at 90°C , 24 hours.

The mechanism of formation of copper sulfide (CuS or Cu_2S) is given below (Fig 3.16).

Figure 3.16: Mechanism of formation of copper sulfide.

When wool samples are treated at high temperatures (90°C) for long periods (24 h), a significant amount of disulfide bonds are fully oxidized to cysteic acid groups.⁸⁴ Therefore wool

samples degraded easily when stretched, having poor tensile properties.²⁶ Due to this reason all future samples having initial metal ion concentration $\sim 450\text{-}500 \text{ mg L}^{-1}$ were treated at 90°C with a sorption time of 1 hour.

3.2.1.2 Quantitative determination of metal ion content of the wool by the method of microwave digestion

As outlined in Section 2.2.9.2, the 0.2 g of copper wool composite was digested with 12.5-15% NaOCl solution using the method of microwave digestion and the copper ion uptakes was analysed directly by flame atomic absorption spectrometry. The copper ion content in the wool having different original concentrations is calculated as follows;

Concentration of original solution before doping wool with Cu^{2+} = 10.9 mg L^{-1}

Mass of wool sample digested = 0.2 g

Total volume of digested wool sample diluted = 100 mL

Concentration of metal ion uptakes through the method of microwave digestion

$$= 2.02 \text{ mg L}^{-1}$$

$$\text{Mass of copper per gram of wool} = \frac{2.02}{1000} \times \frac{100}{0.2} \text{ mg}$$

$$= 1.01 \text{ mg g}^{-1} \text{ of wool}$$

Concentration of original solution before doping wool with Cu^{2+} = 105 mg L^{-1}

Mass of wool sample digested = 0.2 g

Total volume of digested wool sample diluted = 250 mL

Concentration of metal ion uptakes through the method of microwave digestion

$$= 3.42 \text{ mg L}^{-1}$$

$$\text{Mass of copper per gram of wool} = \frac{3.42}{1000} \times \frac{250}{0.2} \text{ mg}$$

$$= 4.27 \text{ mg g}^{-1} \text{ of wool}$$

Table 3.3 and 3.4 show the copper ion uptakes by per gram of wool analysed by two different methods calculated in sections 3.2.1.1 and 3.2.1.2. The wool sample that was produced in section 3.2.1.1 was analysed by the microwave digestion method to compare the mass of copper present in both methods.

Table 3.3: Metal ion uptakes by the method given in Section 3.2.1.1.

Concentration of original solution before doping wool with Cu^{2+} (mg L^{-1})	Concentration of residual solution after doping wool with Cu^{2+} (mg L^{-1})	Concentration of copper ion uptakes calculated by the method given in section 3.2.1 (mg L^{-1})	Mass of copper when wool applied at a loading of 1 g per 100 mL of Cu^{2+} solution (mg g^{-1})
10.9	0.83	10.09	1.01
105	62.37	43.19	4.32

Table 3.4: Metal ion uptakes by the method given in Section 3.2.1.2.

Concentration of original solution before doping wool with Cu^{2+} (mg L^{-1})	Concentration of copper ion uptakes through the method of microwave digestion (mg L^{-1})	Mass of copper when wool applied at a loading of 1 g per 100 mL of Cu^{2+} solution (mg g^{-1})
10.9	2.02	1.01
105	3.42	4.27

The mass of copper per gram of wool at same initial concentrations, calculated by the two methods mentioned above are in good agreement (Table 3.3 and 3.4).

The reaction in a wool fibre in contact with a metal solution (M^{2+}) can be given by the following process (equation 3.1).^{35,36,88}

a: Diffusion of metal ions from the bulk, through the solution film to the surface of the wool fibre.

b: Diffusion of metal ions through the wool fibre.

c: Metals (M_{solid}) or metal ions ($M^{2+}_{\text{aq}}/M^{+}_{\text{aq}}$) bind to available sites of the wool by physical or chemical interactions.

At very low metal ion concentrations (Figures 3.5, 3.6, 3.10 and 3.11) most of the metal ions that are being applied bind to the surface of the wool fibre within an hour or less. When temperature increases more sorption sites (carboxyl and thiol groups) of the wool are available for interaction with metal ions and thereby uptake of metal ions at 50 °C is greater than at room temperature. This is clearly shown in the graphs, Figures 3.5(b), 3.6(b), 3.10(b) and 3.11(b). The percentage of Cu^{2+} uptake is somewhat greater than Mn^{2+} and Zn^{2+} . At 50 °C, the initial rise of metal ions had taken place within a short time frame and reached the equilibrium much faster than at room temperature.

The diffusion of the ions in the liquid film to the surface of the wool fibre increases at high concentrations of the solutions (Figures 3.7, 3.8, 3.9, 3.12, 3.13 and 3.14). Also diffusion of metal ions is much faster than low concentrations. At the beginning of the reaction the curves of the graphs are increase steeply. This is proved that the binding of metal ions to the surface of the wool fibre becomes more favourable at the initial stage of the reaction. When the solution film (static liquid film) that surrounds the wool fibre is saturated (step “a” is at equilibrium), the diffusion of metal ions through the wool fibre is the rate determining step (step “b”). Therefore, transport of metal ions through the wool fibre becomes very much slower than the migration of metal ions to the surface of the fibre. Therefore, after the solution film becomes saturated the rise of uptake curve decreases (Figures 3.7(a) – 3.9(a) and 3.12(a) – 3.14(a)). At higher initial concentrations ($\geq \sim 20 \text{ mg L}^{-1}$) saturation of the solution film (static liquid film) becomes somewhat fast and the total amount of metal ions absorbed increases and occurs much quicker. The percentage uptake of metal ions by wool fibre becomes less compared to the metal ions having low initial concentrations ($\leq \sim 20 \text{ mg L}^{-1}$). This is shown in Figures, 3.7(b) – 3.9(b) and 3.12(b) – 3.14(b). Equation 3.2 shows the diffusion through the wool fibre in situations where the step “b” is the rate limiting step.

$$\frac{Q_t}{Q_e} \approx \frac{A \sqrt{Dt}}{r} \quad (3.2)$$

Where;^{36,37,88}

Q_t = Amount of metal ions sorbed by the wool at time t

Q_e = Amount of metal ions sorbed by the wool at equilibrium, $t = \infty$

D = Diffusion coefficient

r = Radius of the wool fibre

t = Sorption time

A = Constant

The equation (3.2) holds true in systems for which the attainment of equilibrium is slow, small values of time (t), for small diffusion coefficients of metal ions (D) and/or for large diameter of wool fibre (r).^{37,88}

The diffusion coefficient of Cu^{2+} in the initial absorption is much greater when compared to Zn^{2+} and Mn^{2+} , as the original concentration of metal ions increases. Therefore according to equation 3.2, when the diffusion coefficient increases, the rate of uptake of copper ions increases.³ Since copper has higher diffusion coefficient, it is more likely that Cu^{2+} is coordinated to the functional groups of amino acids in the fibre such as carboxyl, NH_2 groups and may be to thiol residues at high temperatures.⁴⁰⁻⁴² These Cu^{2+} complexes maybe more stable than Zn^{2+} and Mn^{2+} complexes.⁸⁹ The formation of Mn^{2+} complexes in the wool fibre becomes increasingly difficult, when Mn^{2+} is coordinated with carboxyl groups of the wool fibre, due to conformational and steric reasons.⁸⁹

3.2.2 UV-Visible spectroscopic analysis

The UV-Vis reflectance spectra detect the electronic transition of metal wool composites and the type of ligand associated with metal ions determined.

Figure 3.17: UV-Vis K/S spectrum of merino wool, inset, photograph of merino wool.

Figure 3.17 shows, only broad peaks and shoulders in the visible region (wavelength 400-800 nm) of the absorption spectrum of merino wool, revealing that merino wool itself is off white to the naked eye. A small well define shoulder peak exists at the 400 nm wavelength reveals some absorption is taking place at the end of the blue region (violet) of the visible spectrum which reflects as impure white (faded white). Therefore merino wool itself is not pure white. The broad peak observed in the UV region (wavelength < 400 nm) may be due to the aromatic amino acid residues or their oxidation products.⁹⁰

Figure 3.18: UV-Vis absorption spectra of metal ions doped merino wool.

Figure 3.19: Merino wool doped with (a) Cu^{2+} ions, (b) Mn^{2+} ions and (c) Zn^{2+} ions.

The wool samples (a)-(c) in Figure 3.19 are related to the UV-Vis K/S spectra of Figure 3.18. The broad peak of the spectrum “a” in Figure 3.18, lies within the red region (630-850 nm) of the visible spectrum. This means the wool composite appears green (Figures 3.18 and 3.19(a)). Also a well defined broad shoulder peak occurs at a wavelength of 400 nm. This may be attributed to some charge transfer bands of copper complexes (Figure 3.18).^{71,89} The broad band presents in the red region of the visible spectrum is due to the d-d transitions in copper complexes.^{71,89} The spectrum of zinc wool composite is similar to merino wool, having small shoulder peak at the end of the blue region (violet) of the spectrum. This provides a slight yellow colour on zinc-merino wool composite which is similar to merino wool itself. The spectrum of manganese merino wool composite shows no well defined peaks, but a slight shoulder peak in the blue region of the spectrum results in the composite material having a slight pink colour. This shoulder peak has a high absorption with respect to Zn-wool composite.

3.2.3 FTIR spectroscopic analysis

Some peaks of the spectra suggest conformational rearrangements of functional groups of wool induced by metal interactions or new peaks caused by metal binding.⁵

Figure 3.20: IR spectra of merino wool and copper ions doped merino wool in the region of 2000-400 cm⁻¹.

Figure 3.21: IR spectrum of Cu ions doped merino wool in the region of 1000-400 cm⁻¹.

The metal-doped wool spectra are generally similar to those of merino wool itself. The most significant changes with respect to the control sample (merino wool) concern the bands at 1386, 1076 and 614 cm^{-1} (Figures 3.20 and 3.21). The intense narrow peak at 1386 cm^{-1} may be assigned to the symmetric stretching of the carboxylic acid dimer induced by copper ions.^{5,44} The H bonds present between COOH groups of COOH dimer in wool readily break after doping wool with copper ions. These carboxyl groups coordinate with copper ions and exist as an intense narrow peak at 1386 cm^{-1} with comparison to merino wool having broad peak at similar position.⁹¹ A slight shoulder peak at 1386 cm^{-1} attributed to the uncoordinated carboxyl groups.⁹¹ Refer to Table 3.1 for further clarification. The coordination of Cu^{2+} ions to carboxyl residues in wool is represented in Figure 3.22.

Figure 3.22: Ligation of carboxylate to Cu^{2+} in merino wool.

The broad intense peak at 1076 cm^{-1} , may be assigned to combination of vibrations of C-O bonds of carboxylic acid dimer, C-C, C-N or S-O stretching modes of vibrations induced by copper ions.⁸⁶ Figure 3.21 shows a new peak at about 614 cm^{-1} . This may be attributed to the vibrations of Cu-S bonds or the SO_4^{2-} ions (CuSO_4), which absorbs at 675-565 cm^{-1} .^{54,56} The absence of weak peak at 499 cm^{-1} (Figure 3.21) assigned to -S-S- group⁸⁷ may be due to the ligation of Cu^{2+} to sulfide groups. The peak at 1449 cm^{-1} may be assigned to uncoordinated COOH groups with copper ions.⁹¹

Figure 3.23: IR spectra of merino wool and metal ions doped merino wool in the region of 2000-400 cm^{-1} .

The IR spectra of Mn and Zn wool composites are given in Figure 3.23. There is no significant change in the spectra of Mn and Zn wool composites with respect to merino wool, suggesting less interaction (coordination) of Mn^{2+} and Zn^{2+} ions towards carboxyl and thiol groups in the wool.

3.2.4 SEM and EDS analysis

Previous work by Kelly^{20,78} and Burrige²¹ has shown the formation of gold and silver nanoparticles on wool occurs by an *in situ* reaction. The distribution of these nanoparticles on wool was investigated by SEM and EDS analysis. Copper nanoparticles were expected to form in similar manner by soaking merino wool with Cu^{2+} solution. Since the standard reduction potentials of $\text{Au}^{3+}/\text{Au}^0$ and Ag^+/Ag^0 have large positive values, the Au^{3+} and Ag^+ ions are easily reduced to their respective low oxidation states by oxidizing wool fibres. Therefore the copper ions are expected to reduce to their zero oxidation state by oxidizing the wool fibres as the standard reduction potential of $\text{Cu}^{2+}/\text{Cu}^0$ is +0.34.

The distribution of Cu^{2+} on the surface and the cross section of merino wool is shown in Figures 3.24(a – c) and 3.25.

Figure 3.24: (a) Secondary electron image of Cu-wool composite, inset, sample of Cu^{2+} treated merino wool (diameter of ~ 2 cm); (b) Backscattered electron image of Cu-wool composite; (c) EDS map of the distribution of copper on the surface of the wool; (d) EDS map of the location of calcium on the surface of the wool. Magnification X 1000.

The morphology of the surface of copper-wool composites given in Figures 3.24(a) and (b). There are no significant changes of the morphology of the surface of the copper wool composite with respect to merino wool fibre, given in Figure 3.1. The green coloured wool sample is evidence for absorption of copper ions by the wool. Initially, the penetration of copper ions occurs on the underside of the cuticle cells and subsequently, reaches the cortex by diffusion between the cuticle cells. The EDS elemental analysis map of Cu is shown in Figure 3.24(c). The small white and green dots throughout the fibre are evident of the uniform distribution of Cu (Figure 3.24(c)). The Cu is expected to distribute uniformly when the solution film that surrounds the wool fibre is saturated. The homogeneous distribution of copper could be evidence of the absence of identifiable metallic copper nanoparticles formed by the method explained in Section 2.24 and suggests that wool itself does not behave as a reducing agent in

the presence of copper ions. However the previous studies have shown that Au and Ag nanoparticles are produced by the oxidation of wool and are concentrated more on the cuticle edges of the wool.^{18,21,66,78} The lower concentration of white spots is evidence of lower degree of Cu uptake by wool (Figure 3.24(c)). The white spots shown in Figure 3.24(d) are calcium. Calcium is present on wool samples as calcium silicate. The experimental work undertaken for this thesis was performed in a lab where calcium silicate materials are also produced. As a result, calcium silicate particles are frequently seen as an adventitious impurity.

Figure 3.25: (a) SEI image of the cross section of Cu-wool composite; (b) Backscattered electron image of the cross section of Cu-wool composite; (c) EDS map of the cross section of Cu-wool composite. Magnification X 2300.

There are no significant changes of the morphology of the cross section of copper wool composites with respect to merino wool fibre, given in Figure 3.2. The presence of Cu throughout the cross section of wool fibre is similar to the surface. This is evident from the spectra given in Figure 3.26.

Figure 3.26: (a) EDS elemental analysis of the surface of Cu-wool composite and (b) the cross section of Cu-wool composite.

The presence of copper within the composite is confirmed by a peak at 8 keV corresponding to Cu-K line. Samples were prepared on aluminium stubs; therefore this element is additionally present. The number of counts of Cu on the surface of the wool fibre is similar to the cross section (Figure 3.26).

3.2.5 TEM analysis

Figure 3.27: TEM image of the cross section of a merino wool doped with Cu.

TEM analysis was unable to detect any copper nanoparticles on wool (Figure 3.27). Previous studies have shown that wool is easily oxidized, in the presence of some metal ions where the magnitude of standard reduction potential is large and positive (Au and Ag).^{18,66,78} The Au^{3+} and Ag^+ ions reduce to Au^0 and Ag^0 respectively.^{18,21,66} This behaviour is evidence for the formation of Au and Ag nanoparticles on wool. The absence of Cu nanoparticles on wool confirmed that

Cu^{2+} ions are not reduced by wool fibre by the method given in Section 2.2.4. This revealed the importance of using external reducing agents, such as thioglycolic acid and sodium borohydride, to wool fibres doped with copper ions. This will be explained in Chapter 4.

3.2.6 X-ray diffraction analysis

Figure 3.28: XRD pattern for merino wool and copper-wool composite.

Figure 3.28 shows the X-ray diffraction analysis pattern of merino wool and Cu^{2+} treated merino wool. Since both merino wool and wool-copper composite show the same diffraction pattern, this suggests the absence of crystalline forms of copper or its compounds formed within merino wool. The XRD pattern for a copper-wool composite could not detect the peaks assigned to crystalline copper or copper compounds. The broad peak presented at 20° 2θ may be attributed to amorphous structure of keratin fibres (Figure 3.28).⁹²

3.3 Uptake of copper ions by pre treating merino wool with EDTA dianhydride

The previous results of untreated metal wool composites presented herein has shown that uptake of copper ions by wool was greater than the uptake of zinc and manganese ions. Therefore, chemical modification of wool by treatment with EDTA dianhydride prior to the addition of copper solution was undertaken in order to increase the copper uptake. The chemically unmodified copper-wool composite was used as a reference to investigate the effect of sorption of copper ions onto wool which had been treated with EDTA dianhydride. All chemically modified wool fibres were soaked with copper solution having initial concentration of 450 mg L^{-1} , at 90°C for one hour. The absorption and binding of copper ions to chemically modified wool was then characterized by the previously mentioned spectroscopic and microscopic methods.

3.3.1 Atomic absorption spectroscopic analysis

The copper ion content of merino wool pre treated with EDTA dianhydride was determined quantitatively by flame atomic absorption spectrophotometry by the method given in Section 3.2.1.1.

Figure 3.29: Uptake of copper ions by (a) unmodified wool and (b) modified wool, having initial concentration of Cu^{2+} solution 450 mg L^{-1} , sorption temperature at 90°C and time for 60 min. Wool applied at a loading of 1 g per 100 mL of Cu^{2+} solution.

The uptake of copper ions by EDTA dianhydride treated wool is 14 mg g^{-1} of wool (% uptake of copper is 31%), while unmodified wool is 8 mg per gram of wool (% uptake of copper is 17%). The copper uptake of modified wool is nearly double the uptake of unmodified wool (Figure 3.29).

3.3.2 UV-Visible reflectance spectroscopic analysis

Figure 3.30 shows the UV-Vis K/S spectra of chemically unmodified and modified merino wool by treatment with EDTA dianhydride, doping with copper solution.

Figure 3.30: UV-Vis K/S spectra of (a) unmodified wool and (b) modified wool doped with copper ions.

Figure 3.30 shows well defined broad absorption bands at 630 to 850 nm ($\lambda_{\text{max}} = 725 \text{ nm}$) of both spectra “a” and “b”. The copper–wool composite (spectrum “b”) absorbs in the red-orange region of the visible spectrum, therefore the composite appears blue,⁵⁸ whereas in spectrum “a” the peak (630-850 nm) shifts to more towards the red end of the visible spectrum, therefore the colour of the complex is green. The energy associated with the d-d transitions of EDTA dianhydride modified wool-copper composites is slightly greater than the transitions in the wool-copper composite. The absence of defined broad shoulder peaks at the

violet region (~ 400 nm) of the spectrum “b” may be attributed to the absence of charge transfer bands in the chemically modified wool-copper composites.⁵⁸

3.3.3 FTIR spectroscopic analysis

Figure 3.31 shows the FTIR spectra of merino wool and chemically modified merino wool by treatment with EDTA dianhydride at pH ~ 7.0

Figure 3.31: IR spectra of merino wool and merino wool treated with ethylenediaminetetraacetic dianhydride in the region of $2000\text{--}400\text{ cm}^{-1}$.

In acidic and neutral pH, the opening of EDTA dianhydride rings provide additional negatively charged carboxyl groups to bind with functional groups of amino acids in the wool. The merino wool acylated with EDTA dianhydride shows significant spectral changes at 1386, 1313, 1172, 1092 and 907 cm^{-1} with respect to merino wool. A narrow peak at 1386 cm^{-1} may be assigned to conformational rearrangement of carboxyl groups of amino acid residues in wool due to the interaction with COOH groups of EDTA dianhydride.⁹¹ A weak sharp peak at 1313 cm^{-1} may be assigned to carboxylate groups of EDTA dianhydride.^{7,91} The small sharp peak at 1092 cm^{-1} can be attributed to C-N vibration modes of EDTA dianhydride.⁹¹ Peaks at 1172 and 907 cm^{-1} may be attributed to C-O-C vibrational modes of EDTA dianhydride.^{7,91}

Figure 3.32: 2000-400 cm^{-1} IR spectra of (a) unmodified wool and (b) modified wool doped with copper ions in the region of 2000-400 cm^{-1} .

Figure 3.32 displays the IR spectra of (a) wool soaked with copper ions and (b) chemically modified wool by treatment with EDTA dianhydride soaked with copper ions. In the “b” spectrum, peak at 3289 cm^{-1} may be attributed to the N-H and free O-H groups, whereas peak at 3397 cm^{-1} may be attributed to the interaction of copper ions with groups containing nitrogen.^{45,46,86} The band between $3500\text{--}3150 \text{ cm}^{-1}$ gets broadened in the EDTA dianhydride treated wool-copper composite with respect to the control sample, suggesting the presence of hydrogen bonds between O-H and N-H and O-H groups.^{93,94} A weak broad shoulder at $1780\text{--}1700 \text{ cm}^{-1}$ arises from the free carbonyl groups formed by opening of the anhydride ring of the EDTA dianhydride. A sharp narrow intense peak at 1384 cm^{-1} is attributed to tertiary amine absorption bands arises from the coordination of Cu^{2+} to lone pairs of O and N in EDTA dianhydride.⁹⁴ A band at 1309 cm^{-1} appears to be less wide and shifts to high frequency with respect to control sample (1294 cm^{-1}) and arises from coordinating copper ions to carboxylate groups of EDTA dianhydride. A peak at 1084 cm^{-1} assigned to C-N vibration modes shift to a high frequency with respect to the control sample (1079 cm^{-1}).^{7,91} This peak can be attributed to vibrations of SO_4^{2-} , which is present in CuSO_4 . In the spectrum “b”, an intense peak at 923 cm^{-1} may be attributed to combination of C-O-C vibration modes of EDTA dianhydride^{7,93} and conjugated carboxyl groups of the merino wool whereas in the “a” spectrum a less intense peak at 928 cm^{-1} arises from COOH groups only.

3.3.4 SEM and EDS analysis

The SEM images of the surface and the cross section of EDTA dianhydride treated wool-copper composite and the distribution of copper within the chemically modified wool together with the spectrum of copper are given in Figure 3.33.

Figure 3.33: (a) SEM (secondary electron image) of treated wool doped with copper ions, inset, sample of EDTA dianhydride modified merino wool-copper composite (diameter of ~ 2 cm); (b) SEM (backscattered electron image) micrograph of treated wool doped with copper ions; (c) EDS map of the distribution of copper within the treated wool and (d) X-ray spectrum of copper in the backscattered mode of SEM. Magnification X 2700.

There are no significant changes of the morphological features of surface and the cross section of EDTA dianhydride treated wool-copper composite with respect to the control samples (Figures 3.24 and 3.25). The EDS elemental analysis map of Cu is shown in Figure 3.33(c). The image shows copper distributed homogeneously throughout the fibre, but less densely on the cross section areas. This is evidence of deposition of copper ions more on the surface rather

than their diffusion through the treated wool fibre. The concentration of copper is higher on treated samples than the control, when both control and chemically modified wool samples were subjected to EDS mapping under the same conditions. This result is confirmed further by the spectra of copper given in Figures 3.26 (a) and 3.33 (d). The peak is attributed to the presence of copper is higher in chemically modified wool than the unmodified wool. These results are evidence of high absorption of copper ions onto chemically modified wool.

Wool fibres are modified by treatment with an acylating agent, EDTA dianhydride, which exhibits chelating activity toward metal ions. When wool is treated with EDTA dianhydride, amine and hydroxyl groups of amino acid residues of wool bind to EDTA dianhydride with strong covalent bonds (amide or ester bonds) thereby resulting in the opening of the EDTA anhydride ring.^{6,10} This reaction provides additional negatively charged carboxyl groups to coordinate with copper ions. These carboxyl groups form complexes with Cu^{2+} ions having a higher coordination number. The unique structure of this complex reflects in the blue region of the UV-Visible spectrum. The different nature of this complex, when compared to unmodified wool, results in a blue shift in the absorption peak in the visible spectrum.

The opening of the EDTA dianhydride ring in the presence of hydroxyl groups of amino acid residues of wool and its chelating activity towards copper ions are given in Figure 3.34.

W = Wool

Figure 3.34: The mechanism of opening of the EDTA dianhydride ring and its chelating activity towards Cu^{2+} .

The chemical modification of wool fibres with chelating agents, obtained by acylation with EDTA dianhydride, effectively promoted the absorption and binding of copper ions at the pH range 4.0-5.0. Thereby the uptake of copper ions by chemically modified wool fibre is nearly double the amount of unmodified wool fibre (Figure 3.29).

3.4 Uptake of metal ions by pre treating merino wool with thioglycolic acid (TGA)

The chemical modification of wool by treatment with TGA prior to the addition of Cu^{2+} solution was undertaken in order to increase the copper uptake. The present study investigates the effect of uptake of copper ions on chemically modified wool by treatment with thioglycolic acid. The absorption of copper ions to chemically modified wool is initially characterized by atomic absorption spectroscopic methods.

3.4.1 Atomic absorption spectroscopic analysis

The copper content of merino wool, pre treated with thioglycolic acid was determined quantitatively by the method explained in Section 3.2.1.1.

Figure 3.35: Uptake of copper ions by (a) unmodified wool (b) modified wool with 0.002 mol of TGA followed by treating with copper ion solution at 90 °C for 30 min, (c) 0.001 mol of TGA followed by treating with copper ion solution at 90 °C for 30 min and (d) 0.001 mol of TGA followed by treating with copper ion solution at 90 °C for 60 min. The initial concentration of Cu^{2+} solution is 450 mg L⁻¹. Wool applied at a loading of 1 g per 100 mL of Cu^{2+} solution.

Figure 3.35 shows uptake of copper ions by thioglycolic acid treated wool is significantly greater than the untreated wool. Sample “b’ was produced by pre treating 1 g of wool with 0.002 mol of TGA followed by soaking with copper ion solution at 90 °C for 30 min. Samples “c” and “d” were produced pre treating wool with 0.001 mol of TGA followed by soaking with copper ion solution at 90 °C for 30 min and 60 min respectively. The copper uptake on samples “b”, “c” and “d” are 42.5, 30 and 35 mg g⁻¹ of wool respectively. Sample “b” has the highest uptake with respect to the control sample. The copper uptake of sample “b” (Uptake % of copper is 94%) is about 5 times higher than control sample (Uptake % of copper is 18%).

3.5 Uptake of metal ions by pre treating merino wool with sodium borohydride (NaBH₄)

The chemical modification of wool by treatment with NaBH₄ prior to the addition of Cu²⁺ solution was undertaken in order to increase the copper uptake. The present study investigates the effect of uptake of copper ions on chemically modified wool by treatment with sodium borohydride. The absorption of copper ions to chemically modified wool is initially characterized by atomic absorption spectroscopic methods.

3.5.1 Atomic absorption spectroscopic analysis

The copper uptake by merino wool, pre treated with NaBH₄ was determined quantitatively by the method described in section 3.2.1.1.

Figure 3.36: Uptake of copper ions by (a) unmodified wool and (b) modified wool with 0.002 mol of NaBH₄ followed by treating with copper ion solution at 90 °C for 5 min and (c) 0.002 mol of NaBH₄ followed by treating with copper ion solution at 90 °C for 30 min. The initial concentration of Cu²⁺ solution is 450 mg L⁻¹. Wool applied at a loading of 1 g per 100 mL of Cu²⁺ solution.

Figure 3.36 shows uptake of copper ions by NaBH₄ treated wool is significantly greater than the untreated wool. Samples “b’ and “c” were produced pre treating wool with 0.002 mol of NaBH₄ followed by soaking with Cu²⁺ solution at 90 °C for 5 min and 30 min respectively. The copper uptake on samples “b” and “c” are 34.6 and 41.8 mg g⁻¹ of wool respectively. Sample “c” has the highest uptake with respect to the control sample. The copper uptake of sample “c” (Uptake % of copper is 92%) is about 5 times higher than the control sample (Uptake % of copper is 18%).

Modification of wool fibres by treatment with thioglycolic acid provides additional ligands to bind with metal ions. TGA has two functional groups (-COOH and -SH) that could bind to reactive groups (-OH, -NH₂ and -SH) of amino acids in wool. The carboxyl groups of TGA may covalently bond to hydroxyl or amine groups in wool and thereby, additional -SH groups present to bind with Cu²⁺ ions. When the thiol groups of TGA crosslink with the sulfhydryl groups (-SH) present in wool, the carboxyl groups of TGA become available as additional sorption sites to coordinate with copper ions. This is illustrated by the following diagram (Figure 3.37).

Figure 3.37: Ligation of Cu^{2+} to carboxyl and thiol groups of TGA treated merino wool.

Since thioglycolic acid is known as a reducing agent, the following reactions may take place within the wool as given in Figure 3.38.^{52,60}

Figure 3.38: Reduction of disulfide linkages in wool and coordination of Cu^+ to thiol groups of reduced wool.

Cystine linkages in wool may be reduced by thioglycolic acid and additional thiol groups produced by this reduction are then available to bind with copper ions (Figure 3.38).

The thiol groups of reduced wool, thiol groups and carboxyl groups of thioglycolic acid present as additional reactive sites which may bind to copper ions. Therefore sorption of copper ions by TGA treated wool (42.5 mg g^{-1} of wool) is about 3 times higher than EDTA dianhydride treated wool (14 mg g^{-1} of wool) under identical conditions. In wool-TGA-Cu complexes, copper ions form stable mercaptides with cysteine amino acid residues⁵¹ of wool at 90°C . Therefore the stability of these wool complexes is greater than the stability of wool-EDTA-Cu complexes.

NaBH_4 is a strong reducing agent. When wool is treated with NaBH_4 , cystine linkages in wool may be reduced by the NaBH_4 and produce more thiol groups to bind with copper ions, resulting in higher copper uptake with respect to EDTA dianhydride treated wool. The sorption of copper ions by NaBH_4 treated wool (41.8 mg g^{-1} of wool) is about 3 times higher than EDTA dianhydride treated wool (14 mg g^{-1} of wool).

CHAPTER 4

4 RESULTS AND DISCUSSIONS OF FORMATION OF Cu_2O OR COPPER-CONTAINING PARTICLES WITHIN WOOL FIBRES USING THIOGLYCOLIC ACID AND SODIUM BOROHYDRIDE

4.1 Formation of *in situ* copper-containing particles on pre treated woollen samples

TGA and NaBH_4 treated merino wool-copper composites were synthesised as described in Sections 2.2.6 and 2.2.7. These merino wool-copper composites were analysed by scanning electron microscopy together with EDS, UV-Vis and FTIR spectra and XRD.

4.1.1 Use of Thioglycolic acid

Thioglycolic acid is a reducing agent which has a standard reduction potential of -0.33 V .⁹⁵ The standard reduction potential of $\text{Cu}^{2+}/\text{Cu}^+$ is $+0.15\text{ V}$ and $\text{Cu}^{2+}/\text{Cu}^0$ is $+0.34\text{ V}$.⁹⁶ Therefore TGA can reduce copper ions (Cu^{2+}) to their respective low oxidation states (Cu^+ or Cu^0). As outlined in section 2.2.6, 1 g of wool fibres were treated with 2 mmol of TGA at $20\text{ }^\circ\text{C}$ for 60 min, followed by soaking with Cu^{2+} solution (450 mg L^{-1}) at $90\text{ }^\circ\text{C}$ for 30 min and 60 min, producing violet and brown coloured samples respectively. Cu^{2+} can be reduced by TGA treated merino wool, either to Cu^+ ions or to particles containing copper. The deposition of these particles containing copper on the surface of the wool fibre and the formation of copper ion complexes within TGA treated merino wool fibres will be shown later in this section.

4.1.1.1 SEM and EDS analysis

The morphology of the TGA treated wool- copper composites and the distribution of copper within the chemically modified wool is investigated using SEM micrographs and EDS maps respectively (Figure 4.1).

Figure 4.1: (a) Secondary electron image, inset, violet coloured sample (diameter of ~ 2 cm); (b) backscattered electron images of treated wool doped with copper ions; (c) EDS map of copper on the surface of treated wool. Magnification X 1000.

1 g of wool fibres were treated with 1 mL of 2 M TGA at 20 °C for 60 min and thereafter soaked with Cu^{2+} solution (450 mg L^{-1}) at 90 °C for 30 min, producing a violet coloured sample. The morphological features of the surface of these wool composite and the distribution of copper on the surface of the wool fibres are significantly changed with respect to control and EDTA dianhydride modified wool-copper composites (Figures 3.24 and 3.33). The main changes are:

1. Some clumps of particles containing copper are observed at the end of the cuticle scales and these edges appear to be somewhat rougher than the control sample, thereby the surface of the wool fibre is rather inhomogeneous (Figure 4.1(a)).

2. In the backscattered image, bright white particles containing copper are accumulated along the edges of the cuticles (Figure 4.1(b)).
3. The distribution of copper is visible along the edges of the cuticles (Figure 4.1(c)).

The deposition of particles along the cuticle edges of the wool fibre is due to the higher surface free energy and electrostatic interactions associated with an edge rather than a planar surface. The above mentioned changes are more clearly observed at higher magnification (X 3500) of SEM (backscatter) and further proved by the analysis of the EDS pattern of copper (Figure 4.2).

Figure 4.2: (a) SEM (backscatter) at X 3500 magnification of TGA treated wool-copper composite together with EDS maps of (b) copper (c) oxygen and (d) sulfur.

Figure 4.2 shows the backscattered electron SEM of the surface of TGA treated wool-copper sample, together with the EDS elemental analysis maps of copper, oxygen and sulfur. In the backscattered image of SEM, the elements which have higher atomic masses are visible as brighter white spots. The carbon, nitrogen, oxygen, sulfur and copper are the main elements in the wool-copper composite that were detected by the EDS. The relative atomic mass of Cu (63.5) is greater than the other elements mentioned (C-12, N-14, O-16 and S-32). Therefore, the clumps of particles containing copper exhibit in agglomerated form at the scale edges and are visible as a bright white region (Figure 4.2(a)). Also some copper ions may form complexes with

thiol groups of TGA and are concentrated more along the cuticle edges. These are confirmed to contain copper through EDS analysis of the same region under the microscope (Figure 4.2(b)-Cu). Black spots appearing on the surface of the wool fibre are due to the damage of electron beam. Figure 4.2 (b) and(c) show a definite correlation of Cu and O with comparison to Cu and S. The direct correlation of Cu and O gives some kind of evidence that it is likely to form copper oxides within the wool fibres, but the formation of copper oxides need to be further characterized by XRD and TEM analysis. A slight correlation between Cu and S (Figures (b) and (d)) suggests that copper ions (Cu^{2+} and Cu^+) may bind to thiol groups of TGA and are concentrated more along the cuticle edges. The mechanism of binding of Cu^+ to thiol groups of TGA will be illustrated later in this chapter.

The area “A” in Figure 4.2(a) is enlarged and represent in Figure 4.3

Figure 4.3: (a) Secondary electron and (b) backscattered electron images at X 15,000 magnification of TGA treated wool-copper composite; (c) X-ray spectrum of spot analysis indicated by “B” (clumps of particles containing copper).

Figure 4.3 shows the SEM image of TGA treated wool-copper composite at 15,000 times magnification together with the spectrum of spot analysis of copper. Clumps of particles containing copper are visible at 15,000 times magnification at the cuticle edges (Figure 4.3(a)). These are observed as white bright particles under the backscattered mode. Most of the particles are agglomerated, but very few take a definite shape of triangles and rectangles (Figure 4.3(b)). The size of the rectangular shape particle is about 300 nm. These clumps of particles (likely to be copper oxides) are confirmed to contain copper through the spectrum shown in Figure 4.3(c). The peak caused by the presence of copper at “B” reach 325 counts, suggesting a high concentration of copper in that area.

Figure 4.4: (a) SEM (backscatter) at X 37,000 magnification of TGA treated wool-copper composite; (b) SEM (backscatter) at X 80,000 magnification of the image “D”; (cI) X-ray spectra of particles I and (dII) II containing copper.

Figure 4.4 shows the morphology of the particles containing copper on the surface of the wool fibre at 37,000 and 80,000 times magnification, together with the spectra of spot analysis of particles I and II containing copper. Figure 4.4(b) is the image of “D” that was zoomed into

80,000 times magnification. Most of the particles are agglomerated and only a few appearing as individual particles. Particles I and II have definite rectangular shapes while particle II is smaller than particle I. The size of particle I is about 375 nm while particle II is about 250 nm. These particles are confirmed to contain copper through the spectra given in Figure 4.4 (c) and (d). The Cu-K peaks caused by particles I and II have constant counts under same scanning conditions, i.e. about 100 each. These particles are likely to be copper oxides due to the evidence given by the EDS map in Figure 4.2.

Figure 4.5: (a) SEM (backscatter) at X 2300 magnification of the cross section of TGA treated wool-copper composite; (b) X-ray spectrum of copper of image (a); (c) EDS map of Cu.

There are significant changes to the morphological features and the distribution of copper at the cross section area of TGA treated wool-copper composite with respect to control and EDTA dianhydride modified wool-copper composite (Figures 3.25 and 3.33). The main changes are:

1. Clumps of particles containing copper are observed at the outer edge of the cross section and they exhibit as bright white particles in the backscattered mode of SEM.
2. Also some copper may form complexes with TGA and exhibit at the outer edge of the cross section.

3. Intensity of the peak Cu-K (> 50 counts) is greater than the control (< 50 counts) under the same magnification.
4. The distribution of copper is rather heterogeneous and mainly confined to the outer edge of the cross section (Figure 4.5 (c)).

The EDS analysis map of copper shows that particles containing copper and copper complexes are concentrated more on the outer region of the cross section of the wool fibres. This is evidence of depositing particles containing copper only on the surface but not throughout the centre of the fibre. The concentration of copper ions is much less at the inner region of the cross section with comparison to control and EDTA dianhydride treated wool-copper composite. This is evidence that Cu^{2+} ions get reduced by TGA and deposited as clumps of particles and copper complexes at the outer edge of the cross section of the wool fibres.

Figure 4.6: (a) SEM (Backscatter) at X 2300 magnification of the surface of TGA treated wool-copper composite, inset, brown coloured sample (diameter of ~ 2 cm); (b) EDS map of image (a); (c) backscattered image at X 4300 magnification of the cross section of TGA treated wool-copper composite; (d) EDS map of image (c).

1 g of wool fibres were treated with 0.5 mL of 2 M TGA and thereafter soaked in a copper ion solution (450 mg L^{-1}) at 90°C for 60 min. The colour of these wool samples is brown. The morphological features of the surface and the cross section of these wool composites and the distribution of copper on the TGA treated wool fibres are not significantly changed with respect to the violet coloured samples (Figure 4.1 and 4.5).

The formation of particles containing copper within wool fibres is presumed to be the same as for violet coloured samples.

4.1.1.2 UV-Visible reflectance spectroscopic analysis

Figure 4.7 shows the UV-Vis reflectance spectra of chemically unmodified and modified wool by treatment with variable amounts of TGA at 20°C for 60 min followed by doping with 100 mL of Cu^{2+} solution (450 mg L^{-1}) at different conditions.

Figure 4.7: UV-Vis K/S spectra of (a) unmodified wool; (b) 2 mmol of TGA treated wool doped with Cu^{2+} solution at 90°C for 30 min; (c) 1 mmol of TGA treated wool doped with Cu^{2+} solution at 90°C for 60 min; (d) 1 mmol of TGA treated wool doped with Cu^{2+} solution at 90°C for 30 min; (e) 0.35 mmol of TGA treated wool doped with Cu^{2+} solution at 90°C for 60 min; (f) 8.4 mmol of TGA treated wool doped with Cu^{2+} solution at 20°C for 60 min .

A range of colours of wool composites were produced when wool fibres were modified by treatment with different compositions of TGA, followed by doping with Cu^{2+} solutions (450 mg L^{-1}) at variable conditions. This is clearly shown in Figure 4.8.

Figure 4.8: (a) Untreated merino wool-copper composite and (b-f) range of colours of TGA treated merino wool-copper composites.

The wool sample (a)-(f) in Figure 4.8 are related to the UV-Vis spectra of Figure 4.7. Figure 4.8 shows the variation of colours of untreated and TGA treated wool samples. Untreated sample (a) is green while all the TGA treated wool composites (b-f) have range of colours (brown, violet, brown-grey, brown-green and off white). The range of colours of TGA treated wool samples are due to different compositions of TGA and different soaking conditions of wool by copper ion solution.

Figure 4.7 shows characteristic bands at 425 nm in the spectra of “c”, “d” and “e”. The spectrum “e” has a band in the blue-violet region 350-520 nm (maxima at 425 nm) as well as end of red region (850 nm) of the visible spectrum, therefore the composite appears brown-green. The band in the red region shifts more towards the lower energy of the spectrum with comparison to spectrum of unmodified wool composite, where the band is at 630-850 nm (maxima at 700 nm). The spectrum “a” has a slight shoulder peak whereas spectra “c” and “d” have define broad peaks (maxima at 425 nm) in the blue violet region. The intensity of the band at 425 nm of the spectrum “d” is slightly higher than the spectrum “c”, reflecting the brown-grey and brown colour of the samples respectively. The violet coloured sample shows a well defined broad band at 500-700 nm (maxima at $\sim 600 \text{ nm}$) and a slight hump at 425 nm, in the visible spectrum “b”. The absence of defined bands in the visible region of the spectrum “f” is consistent with the off white colour of the wool. The absence of bands in the red region (700-850 nm) of the spectra “b”, “c”, “d” and “f” may be due to the negligible amount of Cu^{2+} in the wool samples.^{71,89} The presence of bands in the blue-violet region (350-520) of the spectra “b”, “c”, “d” and “e” may be attributed to the electronic transitions or charge transfer bands of Cu-O-Cu ^{71,89} exhibited by the wool composite. Also the absence of defined band at blue-violet

region of the spectrum “f” may be due to the negligible formation of Cu_2O . The brown-grey wool samples are obtained with 1 mmol of TGA, while violet samples are obtained with 2 mmol of TGA under the same soaking conditions. The off white wool samples are obtained when the compositions of TGA are much greater than 2 mmol, irrespective of the soaking conditions. Brown-green wool samples are obtained with 0.35 mmol of TGA while the brown samples are obtained with 1 mmol of TGA under same soaking conditions. When the colour changes from brown-green to brown or to violet, the intensity of the peak at $\lambda_{\text{max}} = 425 \text{ nm}$ reduces and some absorption bands appear in the region 500-700 nm. The violet coloured sample shows a broader absorption band in the region 500-700 nm with respect to the other samples, suggesting the presence of a range of particle sizes in the violet coloured sample.⁷⁸ The bands in the UV region ($\lambda_{\text{max}} \sim 250 \text{ nm}$) may be due to the aromatic amino acid residues or their oxidation products.⁹⁰

4.1.1.3 FTIR spectroscopic analysis

Figure 4.9 shows the FTIR spectra of merino wool and chemically modified merino wool by treatment with 2 mmol of TGA at 20 °C for 60 min.

Figure 4.9: IR spectrum of merino wool and TGA treated merino wool in the spectral region of 2500-400 cm^{-1} .

The merino wool treated with thioglycolic acid shows significant spectral changes at 1384, 1532, 2352 and 626 cm^{-1} with respect to merino wool. A narrow peak at 1384 cm^{-1} may be assigned to conformational rearrangements of carboxyl groups of amino acid residues in wool due to the interaction with COOH groups of TGA. A very weak peak at 2352 cm^{-1} may be assigned to symmetric stretching of unassociated SH groups of TGA.⁴⁶ The broad intense band at 1532 cm^{-1} shifts to low frequency with respect to merino wool (1543 cm^{-1}). The band is shifted due to the presence of conjugated COOH groups in the wool fibre, which is caused by interaction with COOH groups of TGA. The peak which is attributed to symmetric stretching of S-O vibrations (1046 cm^{-1}) is absent in the IR spectrum of TGA treated merino wool. When merino wool is treated with TGA, it reduces the disulfide bonds of cystine amino acids to thiol groups and prevents the oxidation.⁹⁷ A weak peak at 626 cm^{-1} may be assigned to the symmetric stretching of C-S vibrations of TGA.⁹⁸

Figure 4.10: IR spectra of (a) chemically unmodified wool and (b) modified wool with TGA followed by doping with Cu^{2+} solution at 90 °C for 30 min in the spectral region of 4000-400 cm^{-1} .

Figure 4.11: IR spectrum (b) of TGA treated wool-copper composite in the region of 1000-400 cm^{-1} .

Figure 4.10 displays the IR spectra of chemically unmodified and modified merino wool by treatment with 2 mmol of TGA at 20 °C for 60 min followed by doping with copper ion solution (450 mg L^{-1}) at 90 °C for 30 min. Figure 4.11 shows the spectrum “b” in the region of 1000-400 cm^{-1} . In the spectrum “b” peak at 3289 cm^{-1} may be attributed to the N-H and free O-H groups,⁸⁶ whereas broad shoulder peak at 3425 cm^{-1} may be attributed to the bonded OH groups with TGA.⁸⁶ The band between 3500-3150 cm^{-1} gets broadened in the TGA treated wool-copper composite with respect to the control sample, suggesting the presence of H bonds between O-H and N-H and O-H groups. The absence of the peak at 2352 cm^{-1} in the spectrum “b”, may be due to the oxidation of TGA in the presence of wool. The -SH groups of TGA oxidized and formed -S-S- linkages.^{51,60,98} The broad intense peak at 1544 cm^{-1} shifts to high frequency with respect to the control sample (1534 cm^{-1}), suggesting coordination of copper ions to carboxylate groups in the wool. In the spectrum “b” the medium sharp carboxyl acid dimer peak at 1383 cm^{-1} is less intense with comparison to the control sample and a new peak⁹⁸ occurs at 1409 cm^{-1} , suggesting some of the carboxyl groups in the wool are bonded to carboxyl groups of TGA by hydrogen bonds. The new peak at 1409 cm^{-1} does not appear in the TGA modified wool, but it appears in the TGA modified wool-copper composite. This assignment suggests conformational rearrangement of carboxyl acid dimer which is induced by binding of copper ions through sulfur in TGA. Since TGA is a reducing agent, it may reduce Cu^{2+} to Cu^{+}

which coordinates to thiol groups in TGA.^{51,52,97} This conformational rearrangement can be illustrated as in Figure 4.12. The mechanism of binding of Cu^+ to sulfur from TGA will be illustrated later in this chapter.

Figure 4.12: The conformational rearrangement of carboxylic acid dimer induced by binding of Cu^+ ions.

The conformational rearrangement shown in Figure 4.12, may not exist on TGA treated merino wool, as the peak at 1409 cm^{-1} is absent in the spectrum given in Figure 4.9. Also some carboxylic groups of TGA may covalently bond to hydroxyl groups in wool and form $-\text{SH}$ groups as additional binding sites to bind with copper ions (Figure 3.36). Therefore C-O-C bonds may be formed when carboxylic groups of TGA bond to hydroxyl groups in wool. A definite weak peak at 1172 cm^{-1} may be attributed to C-O-C vibration modes in the spectrum “b” whereas in the spectrum “a” it appears as a shoulder peak. A broad intense peak at 1080 cm^{-1} may be assigned to C-O vibration modes induced by copper ions.⁸⁶ These copper ions coordinated to carboxylic groups in the TGA treated merino wool. This peak shifts to a slightly higher frequency with respect to the control sample (1078 cm^{-1}). A well defined intense, slightly broader peak at 611 cm^{-1} in the spectrum “b” may be attributed to vibration modes of Cu-S or Cu_2O .^{16,54} The copper may form copper ion complexes with sulfur from TGA or Cu_2O within wool fibres. This peak is clearly shown in Figure 4.11.

Figure 4.13: IR spectra of (a) chemically unmodified wool and (b-d) modified wool with increasing TGA, followed by doping with Cu^{2+} ions at different soaking conditions.

When the amount of TGA increases, a large number of carboxyl groups in the wool bond to carboxyl groups in TGA and form new carboxyl acid dimers in wool fibres. When the TGA content increases, the intensity of the peaks at 1409 cm^{-1} increases. Also when TGA content increases, Cu-S bond or Cu_2O formation increases, thereby the intensity of the peak (611 cm^{-1}) that may be attributed to the vibration modes of Cu-S or Cu_2O increase (Figure 4.13).

4.1.1.4 XRD analysis

Figure 4.14: XRD pattern for TGA treated wool-copper composite.

Figure 4.14 shows the X-ray diffraction analysis of chemically modified merino wool by treatment with 2 mmol of TGA at 20 °C for 60 min, followed by doping with copper ion solution at 90 °C for 30 min. The X-ray diffraction analysis was conducted to investigate the crystalline form of any copper containing particles formed on the surface of merino wool. The XRD pattern for TGA treated wool-copper composite is similar to control sample shown in Figure 3.27. Any peaks assigned to crystalline materials could not be detected by the Philips X'pert Pro MPD XRD instrument, suggesting the absence of formation of crystalline forms of copper-containing particles or Cu_2O particles on the surface of wool fibres. The broad peak presented at 20 ° 2θ may be attributed to amorphous structure of keratin fibres (Figure 4.14).⁹² Since some copper-containing particles were observed under SEM, this suggests either limited resolution of the detectors of the XRD instrument or a poorly crystalline nature of these particles. Also the abundance of these particles in the wool samples may not be enough to be detected by the XRD instrument. Synchrotron-based instruments having a higher resolution may be required to determine the crystalline forms of copper-containing particles within these wool fibres.

SEM micrographs proved that the size of particles containing copper is around 200-300 nm. Also some smaller particles were present which agglomerated and exhibited on the cuticle edges of wool fibres. The formation and the size of copper-containing nanoparticles need to be

confirmed further by TEM analysis. The formation of copper-containing particles and their respective sizes could not be confirmed due to the unavailability of TEM during the period of my research.

The reaction medium of TGA treated wool-copper composite is acidic (pH ~ 3.0). Therefore the wool fibres exist as the protonated form.

At this pH, it is unlikely that Cu^{2+} will bind to NH_2 groups in the wool. There is a high probability that carboxyl groups in the wool exist as carboxylic acid dimers.⁹⁸ Since TGA is a reducing agent, it reduces merino wool (degradation of disulfide bonds to thiol groups)⁶⁰ as well as Cu^{2+} to Cu^+ .⁵¹ Thereby TGA itself oxidizes and form oxidized TGA which has disulfide bonds.^{51,60} The Cu^+ ions may coordinate to sulfur from thiol groups in TGA. This redox system in TGA treated merino wool can be represented by the model given below (Fig 4.15).⁹⁹

Cu^{2+} : Oxidized copper ions
 Cu^+ : Reduced copper ions.
 W-SH : Thiol groups of wool (Reduced wool)
 W-SS-W : Disulfide crosslinks of wool
W: Wool
 R-SH : Thioglycolic acid
 R-SS-R : Oxidized TGA
R: $-\text{CH}_2-\text{COOH}$

Figure 4.15: The model of redox system exists in wool.

The proposed mechanism of reduction of disulfide linkages in wool by TGA can be illustrated as in Figure 4.16.

Figure 4.16: Mechanism of reduction of disulfide linkages in wool by TGA.

The proposed mechanism of binding of Cu^+ ions to thiol groups of TGA treated merino wool can be illustrated as in Figure 4.17.

Figure 4.17: Mechanism of binding of Cu^+ ions to thiol groups of TGA treated merino wool.

Figure 4.16 shows the reduction of disulfide linkages in wool by the reducing agent, TGA and Figure 4.17 shows one of the possible ways of binding of reduced copper species (Cu^+) to sulfhydryl groups of TGA treated merino wool. When wool is treated with TGA, the disulfide bonds in cystine amino acid residues readily break and present as cysteine amino acid residues. TGA may present as oxidized TGA as shown in Figure 4.16. In the presence of TGA, Cu^{2+} reduces to Cu^+ ions and coordinated to sulfhydryl groups of TGA treated merino wool.^{51,52} Figure 4.17 shows that some of the carboxyl groups in TGA bonded to carboxyl groups of wool by hydrogen bonds and form new carboxyl acid dimers (Figure 4.17). This conformational rearrangement of carboxyl acid dimer gives a new peak at 1409 cm^{-1} in the IR spectrum shown by Figure 4.10(b).

Figure 4.18: (a) Backscattered electron image of 2 mmol of TGA treated merino wool-copper composites, inset, violet coloured sample (diameter of $\sim 2\text{ cm}$); (b) backscattered electron images of 1 mmol of TGA treated merino wool-copper composites, inset, brown coloured sample (diameter of $\sim 2\text{ cm}$).

The range of colours observed in Figure 4.8 may be due to the formation of different copper complexes with TGA within the wool fibres. As seen in Figure 4.3, the copper-containing particles form aggregates on the surface of the wool fibre. The agglomeration or the size of the particles increases when the volume of reducing agent increases. Therefore similar results expected when the amount of TGA increases. The particles containing copper seem to be highly agglomerated or larger in size when 2 mmol of TGA is used with comparison to 1 mmol. Thereby the copper-wool composites become more inhomogeneous when the amount of TGA increases. This is clearly shown in Figure 4.18.

The violet coloured samples may contain large copper-containing particles or highly agglomerated particles with comparison to brown coloured samples. The increase in average size of the particles or the presence of highly agglomerated particles on the surface of merino

wool fibres correspond to a colour change from brown to violet (Figure 4.18). The change in the reflected colours (brown to violet) suggested the change of the absorption bands in the visible spectra (Figure 4.7). The violet coloured of the wool sample may be due to the formation of $[\text{Cu}(\text{RS}^-\text{Cu}^+)_4]^{2+}$ complex⁵¹ ($\text{R} = \text{CH}_2\text{COOH}$) within the wool fibre. The broadening of all the peaks in the visible spectra may likely to be due to the large distribution of particle size (Figure 4.7(b-e)).⁷⁸ When 8.4 mmol of TGA is used as the reducing agent, the resulting merino wool-copper composite is off white/pale yellow, suggesting the absence of defined absorption bands in the visible region of the spectrum “f”. The off white/pale yellow coloured of the wool sample is may be due to the formation of $\text{R}-\text{CH}_2-\text{S}^--\text{Cu}^+$ complex ($\text{R} = \text{wool or COOH of TGA}$) within the wool fibre. The colour of $\text{R}-\text{CH}_2-\text{S}^--\text{Cu}^+$ complex is pale yellow.⁵¹ In Figure 4.7, no surface plasmon resonance bands ($\lambda_{\text{max}} = 575 \text{ nm}$) occur due to $\text{Cu}_{(\text{s})}$. Therefore it is unlikely that copper particles formed within wool fibres.

4.1.2 Use of sodium borohydride

Sodium borohydride is a strong reducing agent which has a standard reduction potential of $-1.23 \text{ V}^{100,101}$ with comparison to thioglycolic acid, i.e. -0.33 V^{95} . The standard reduction potential for the $\text{Cu}^{2+}/\text{Cu}^+$ couple ($\text{Cu}^{2+}_{(\text{aq})} + \text{e}^{-}_{(\text{aq})} \rightarrow \text{Cu}^{+}_{(\text{aq})}$) is $+0.15 \text{ V}$, i.e. less than half of the $+0.34 \text{ V}$ needed to fully reduce Cu^{2+} to Cu^0 . As outlined in Section 2.2.7, 1 g of wool fibres were treated with 2 mmol of NaBH_4 at 20°C for 60 min, followed by soaking with Cu^{2+} solutions (450 mg L^{-1}) at 90°C for 5 min and 30 min, producing brown and dirty-green coloured samples respectively. Cu^{2+} can be reduced by NaBH_4 treated merino wool, either to metallic copper ($\text{Cu}_{(\text{s})}$) or to Cu_2O depending on the pH of the medium.¹⁰⁰ The deposition of the Cu_2O particles on the surface of the wool fibres will be shown in this section.

4.1.2.1 SEM and EDS analysis

The morphology of the NaBH_4 treated merino wool-copper composites and the distribution of copper within the chemically modified wool are investigated using scanning electron micrographs and EDS maps respectively (Figure 4.19).

Figure 4.19: (a) Secondary and (b) backscattered electron images at X 1000 magnification of NaBH_4 treated wool-copper composites together with (c) EDS map of copper on the surface of treated wool; (d) SEM (backscatter) at X 22,000 magnification of the image “D”. Inset, brown coloured sample (diameter of ~ 2 cm).

1 g of wool fibres were treated with 1 mL of 2 M NaBH_4 at 20 °C for 60 min and thereafter soaked with Cu^{2+} solution (450 mg L^{-1}) at 90 °C for 5 min, producing brown coloured samples. Figure 4.19(d) shows the backscattered electron image at 22,000 times magnification of “D” given in Figure 4.19(b). The morphological features of the surface of these wool composites and the distribution of copper on the surface of the wool fibres are significantly changed with respect to control and EDTA dianhydride modified wool-copper composites (Figures 3.24 and 3.33), while features are more similar to TGA modified wool-copper composites with minor changes. The changes are:

1. Some clumps of particles containing copper are observed at the end of the cuticle scales and these edges appear to be somewhat rougher than the control and EDTA dianhydride modified samples. Therefore the surface of the wool fibres is rather inhomogeneous (Figure 4.19(a)).

2. Bright white particles containing copper appear to be crystalline and deposit along the edges of the cuticles in the backscattered electron images of SEM (Figures 4.19(b and d)). These aggregates are more rectangular shaped with respect to TGA treated wool-copper composites.
3. A large number of particles which contain copper are visible on the carbon tape, suggesting less adherence of the particles to the surface of the wool fibres with respect to the TGA treated wool-copper composites (Figures 4.19(b and c)).
4. The deposition of copper-containing particles is accumulated along the edges of the scales of the wool fibres and the distribution of copper is similar to TGA treated wool-copper composites (Figure 4.1(c)).

The above mentioned changes are more clearly observed at higher magnifications (X 2000 and X 10,000) of SEM (backscatter) images and further proved by the analysis of the EDS pattern of copper (Figure 4.20).

Figure 4.20: (a-b) Backscattered electron images at X 2000 and X 10,000 magnifications of NaBH₄ treated wool-copper composites; (c) EDS map of Cu of image (b).

Figure 4.20(b) shows the backscattered electron image at 10,000 times magnification of “D” given in Figure 4.20(a). The deposition and adherence of particles containing copper along the cuticle edges are somewhat less than the TGA treated wool-copper composites (Figure 4.1(b)). The deposition of copper along the cuticle edges further confirmed by the EDS map of copper (Figure 4.20(c)). The particle “E” was enlarged and shown in Figure 4.21.

Figure 4.21: (a) SEM (backscatter) at X 80,000 magnification of NaBH_4 treated wool-copper composite together with EDS maps of (b) copper (c) sulfur and (d) oxygen.

Figure 4.21 shows the morphology of particle “E” at 80,000 times magnification, together with the EDS elemental analysis maps of copper, sulfur and oxygen. The size of particle “E” is around 250 nm and is same as particle II in Figure 4.4(b). The particle “E” contains Cu and O which is confirmed by analysis of the EDS maps of Cu and O. Since there is a direct correlation of Cu and O, this suggests the formation of copper oxide particles (Cu_2O or CuO) within the wool fibres. The sulfur in the wool is masked by these copper oxide particles and this is clearly shown by the EDS map of sulfur.

Figure 4.22: (a-b) Secondary and backscattered electron images at X 4000 magnification of the cross section of NaBH_4 treated wool-copper composites; (c) EDS map of copper and (d) X-ray spectrum of copper of image (b).

Figure 4.22 shows the scanning electron micrograph at 4000 times magnification of the cross section of NaBH_4 treated wool-copper composite, together with EDS elemental analysis map and X-ray spectrum of copper. There are significant changes to the morphological features and the distribution of copper at the cross section area of NaBH_4 treated wool-copper composites with respect to control and EDTA dianhydride modified wool-copper composites (Figure 3.25 and 3.33), while features are somewhat similar to TGA modified wool-copper composites with minor changes. The main changes are:

1. Clumps of copper oxide particles are observed at the outer edge of the cross section and the surface of the wool fibres. They exhibit as bright white particles in the backscattered mode of SEM. Also these particles are highly agglomerated or larger in size with respect to TGA treated wool-copper composites (Figures 4.5(a) and 4.6(c)).
2. The intensity of peak Cu-K is ~ 250 counts while the control, EDTA dianhydride and TGA treated wool-copper composites have less than 100 counts under same scanning conditions.

3. The distributions of copper oxide particles are rather inhomogeneous and mainly confined to outer edge of the cross section and the surface of the wool fibres. The discontinuous deposition of the particles at the outer edge of the cross sections is observed with comparison to TGA treated wool-copper composite.

The EDS analysis map of copper shows the outer region of the cross section and the surface of the wool fibres has more white areas while inner region has a few of them. This is evidence of depositing more copper oxide particles on the surface of the wool fibres, with very few of them present throughout the centre of the fibres. These particles present in the inner region of the cross section of the wool fibres are quite large and very few. Therefore it is unlikely that these particles diffused through the fibres from the surface. There is a high chance that these particles may have fallen from the surface of the wool fibres to the inner region of the cross sections during the preparation of the cross section of the wool samples for SEM analysis. The concentration of copper is much less at the inner region of the cross section with comparison to control and EDTA dianhydride treated wool-copper composites, suggesting the copper oxide particles are formed at and near the surface of the wool fibres as a result of the Cu^{2+} reacting with the NaBH_4 in the fibres.

Figure 4.23: (a-b) SEM (Secondary and backscatter) at X 2300 magnification of NaBH₄ treated wool-copper composite; (c) Secondary electron image at X 18,000 magnification of the area “D”; (d) Backscattered mode of SEM at 18,000 magnification of the image (c). Inset, dirty green coloured sample (diameter of ~ 2 cm).

1 g of wool fibres were treated with 1 mL of 2 M NaBH₄ at 20 °C for 60 min and thereafter soaked with Cu²⁺ solution (450 mg L⁻¹) at 90 °C for 30 min, producing dirty green coloured samples. Figure 4.22 shows the scanning electron micrographs (SEI and backscatter) of NaBH₄ treated wool-copper composites at 2300 and 18,000 times magnification. The area “D” is zoomed into 18,000 times magnification and represented in Figures (c) and (d). The morphology and the deposition of particles are quite similar to brown coloured samples shown in Figure 4.20. Discontinuous deposition of the particles is observed along the cuticle edges with respect to TGA treated wool-copper composites shown in Figures 4.2 and 4.3.

Figure 4.24: EDS elemental analysis maps of Cu, S, Na and O together with the spectrum of copper of image in Figure 4.23(d). Magnification X 18,000.

Figure 4.24 shows the EDS maps of Cu, S, O and Na and their respective spectrum in the backscattered mode of SEM at 18,000 times magnification shown in Figure 4.23(d). The copper oxide particles covered the region of sulfur on the surface of the wool fibres. Thereby the EDS could not detect the S in the region where copper oxide is present within the wool fibres. The similar EDS pattern is observed in the brown coloured samples shown in Figure 4.21. Since there are not many copper oxide particles present in this image, there is not much contribution of the oxygen from copper oxide compared to the wool fibres. Therefore the contrast between

the oxygen from copper oxide and wool is much less. The Na may exist as Na^+ ions, the source of which is NaBH_4 is used to reduce Cu^{2+} ions. The Na-K peak partially coincides with the Cu-L peak suggesting that Na is present where Cu is located. The EDS map of Na shows the higher concentration of Na^+ ions with respect to Cu under the same scanning conditions. The high concentration of Na^+ ions may be due to the both signals Cu-K and Na-K. This is in contrast with the results of actual percentages of Na and Cu atoms present in the region “D” of the wool fibre, i.e. Na-K is 0.07% and Cu-K is 1.1%. The presence of a high concentration of Na^+ within the wool fibres is unlikely, since the wool samples are washed with distilled water before preparing the samples for SEM analysis. However, if the wool samples are not properly washed some percentage of Na may still be present within the wool fibres. The amount of Na remaining in the wool fibres should be less than Cu.

Figure 4.25: (a) SEM (backscatter) at X 18,000 magnification of NaBH_4 treated wool-copper composite; (b) X-ray spectrum of spot analysis indicated by “A”.

Figure 4.25 shows the backscattered electron image at X 18,000 magnification together with the X-ray spectrum of the spot analysis indicated by “A”. The intensity of the Cu-K peak is much greater than the TGA treated wool composites under similar conditions, suggesting an extremely high content of copper is present in the particle “A”. This indicates the copper oxide particles aggregate and accumulate on the surface of the wool fibres.

Figure 4.26: (a-b) SEM (SEI and backscatter) images at X 3700 magnification of the cross section of NaBH₄ treated wool-copper composite; (c) EDS map of image (b).

Figure 4.26 shows the scanning electron micrographs (SEI and backscatter) of the cross section of NaBH₄ treated wool-copper composite at 3700 times magnification, together with the EDS analysis map of Cu. The morphological features and the distribution of Cu on the cross section of these wool fibres (green coloured samples) are similar to brown coloured samples (Figure 4.22).

4.1.2.2 XRD analysis

Figure 4.27: X-ray diffraction (XRD) pattern of (a) dirty green (b) brown coloured samples and (c) Reference pattern of Cu₂O (JCPDS # 77-0199).

Figure 4.27 (a) and (b) show the X-ray diffraction patterns of the dirty green and brown coloured samples respectively. The diffraction pattern is more or less the same for both samples. The peaks at 36.5, 42.4 and 61.5 ° 2θ represent the (111), (200) and (220) planes of the cubic structure of Cu₂O with the space group of Pn-3m (JCPDS No 77-0199).¹⁶¹⁶¹⁶¹⁶¹⁶¹⁶¹⁶¹⁶ Therefore the copper oxide particles observed by SEM-EDS were Cu₂O.

4.1.2.3 UV-Visible reflectance spectroscopic analysis

Figure 4.28 shows the UV-Vis K/S spectra of chemically unmodified and modified wool by treatment with 2 mmol of NaBH₄ at 20 °C for 60 min followed by doping with Cu²⁺ solution (450 mg L⁻¹) at 90 °C for different period of time.

Figure 4.28: UV-Vis K/S spectra of (a) unmodified wool; (b) 2 mmol of NaBH₄ treated wool doped with Cu²⁺ solutions at 90 °C for 5 min and (c) 30 min.

The wool fibres are modified by treatment with 2 mmol of NaBH₄, followed by soaking with Cu²⁺ solution (450 mg L⁻¹) at 90 °C for 5 min and 30 min producing brown and dirty green coloured samples respectively. The brown and dirty green coloured samples are shown in Figure 4.29.

Figure 4.29: (a) Untreated merino wool-copper composite; (b-c) NaBH₄ treated merino wool-copper composites.

The colour of untreated (control) sample (a) is green while the NaBH₄ treated wool samples (b) and (c) have brown and dirty green colours respectively. Figure 4.28 shows that both spectra "b" and "c" have characteristic bands in the region 320-520 nm as well as in the red region 630-850 nm (maxima ~ 700 nm) of the visible spectrum. The broad band at ~ 700 nm appears in the red region of all spectra ("a", "b" and "c"), suggesting the presence of Cu²⁺ in the wool

composites.^{71,89} The spectrum “b” shows a band at $\lambda_{\text{max}} \sim 450$ nm whereas in spectrum “c” it appears at ~ 400 nm in the blue violet region of the spectrum. The presence of bands in the blue-violet region of the spectra “b” and “c” may be attributed to the electronic transitions or charge transfer bands of Cu-O-Cu exhibited by the wool composites.^{71,89} Cu₂O nanoparticles are known to show a broad absorption band at 448 nm in the UV-Vis spectrum of the Cu₂O nano-colloid.^{16,76} The broad absorption bands noticed in Figure 4.28 may be due to the presence of a range of Cu₂O particle sizes within wool fibres.¹⁷ The presence of shoulders in the UV region (~ 250 nm) may be due to the aromatic amino acid residues or their oxidation products.⁹⁰

4.1.2.4 FTIR spectroscopic analysis

Figure 4.30 shows the FTIR spectra of merino wool and chemically modified merino wool by treatment with 2 mmol of NaBH₄ at 20 °C for 60 min.

Figure 4.30: IR spectra of merino wool and NaBH₄ treated merino wool in the spectral region of 2500-400 cm⁻¹.

The IR spectrum of merino wool treated with NaBH₄ is generally similar to merino wool itself. The peak which is attributed to symmetric stretching of S-O vibrations (1046 cm⁻¹)⁸⁵ is absent in the IR spectrum of NaBH₄ treated merino wool. When merino wool is treated with NaBH₄, it reduces the disulfide bonds in the wool to thiol groups (-S-H) without oxidizing to cysteic acid

residues ($-\text{SO}_3\text{H}$). A small very weak peak at 499 cm^{-1} , which may be attributed to $-\text{S}-\text{S}-$ vibrations⁸⁷ is absent in the IR spectrum due to the reduction of disulfide linkages by the influence of NaBH_4 .

Figure 4.31: IR spectra of (a) unmodified wool; (b-c) modified wool with NaBH_4 followed by doping with Cu^{2+} ions at $90\text{ }^\circ\text{C}$ with different treatment time in the spectral region of $2500\text{--}400\text{ cm}^{-1}$.

The control sample is represented in spectrum “a” whereas NaBH_4 treated merino wool, doped with Cu^{2+} solution with a treatment time of 5 min and 30 min given in spectra “b” and “c” respectively (Figure 4.31). In the spectra “b” and “c”, the shapes of the peak at 1385 cm^{-1} are more or less the same while different to the spectrum “a”. In the control sample a slightly intense peak is observed at 1385 cm^{-1} , whereas the NaBH_4 treated wool-copper composites, the intensity of the respective peak is low. Also, in the control sample a slight shoulder peak is observed closer to the peak at 1385 cm^{-1} while a well defined shoulder peaks are observed in the NaBH_4 treated wool-copper composites. The peak at 1385 cm^{-1} may be assigned to carboxyl acid dimers in the wool.⁸⁶ When wool is treated with NaBH_4 followed by doping with Cu^{2+} solution the arrangement of carboxyl groups may differ. A slight reduction of the height of the peak at 1385 cm^{-1} (spectra “b” and “c”) is observed with respect to the unmodified merino wool. The intensity of these peaks is measured with comparison to the peak at 1448 cm^{-1} . The broad intense peak at 1079 cm^{-1} , may be assigned to combination of vibrations of C-O bonds of

carboxylic acid dimer, C-C and C-N stretching modes of vibrations induced by copper ions. The shoulder peaks are observed at 1048 cm^{-1} in the spectra “b” and “c”, whereas it is absent in the spectrum “a”. The peak at 1048 cm^{-1} may be assigned to vibrations of S-O bonds.⁸⁵ The absence of this peak in the control sample may be due to the interaction of S-O bonds with Cu^{2+} ions. A peak due to the $\text{Cu}^+\text{-O}$ vibrational mode appears at around 620 cm^{-1} .^{14,16,17} A similar peak is observed at around 618 cm^{-1} , which may be assigned to $\text{Cu}^+\text{-O}$ stretching vibrations of Cu_2O (spectra “b” and “c”). These Cu_2O compounds exist within the wool fibres.

Cu^{2+} can be reduced by NaBH_4 either to metallic copper or to Cu_2O depending on the pH value of the reaction medium.¹⁶ The pH of the reaction medium is ~ 5.0 , when merino wool is treated with NaBH_4 , followed by doping with Cu^{2+} solution at 90°C . At this pH, it is unlikely that metallic copper is formed within the wool fibres. In the reaction medium water is always present and will undergo reduction with NaBH_4 . This is shown by the following reaction (equation 4.1).^{100,102,103}

At pH 5.0-6.5, Cu^{2+} can be reduced by NaBH_4 to Cu_2O . This is given by equation 4.2.¹⁰⁰

The Cu_2O particles formed in brown and dirty green coloured wool samples (Figure 4.27). These particles can be seen in SEM images and EDS maps given in Figures 4.20-4.22, 4.23-4.24.

In the presence of oxygen some other reactions may occur. They are re-oxidation of reduced species to Cu^{2+} ions and oxidation of borohydride. These reactions are given by equations 4.3 and 4.4.¹⁰⁰

The dirty green coloured samples may contain the re-oxidized reduced species, i.e. oxidation of Cu_2O to Cu^{2+} . The re-oxidation of these Cu_2O takes place rapidly when brown coloured samples are heated at 50°C for 6 hours. The presence of excess Cu^{2+} may cause the colour change from brown to dirty green. The reduction of water by NaBH_4 restricts the reduction of Cu^{2+} to Cu_2O .¹⁰⁰ The equation 4.1 is more favourable at low pH ($\text{pH} < 3.0$) while less favourable at high

pH ($\text{pH} > 5.0$). Therefore at pH 5.0 the equation 4.2 may overcome the equation 4.1. Also there is a possibility that oxidation of borohydride inhibits the reduction of Cu^{2+} to Cu_2O .

4.2 Formation of *in situ* copper nanoparticles on aged woollen samples

Previous work by Burridge²¹ has shown that Au nanoparticles can be readily synthesized on wool by treating wool fibres with Au^{3+} solution at room temperature (0-48) hours, followed by treatment with tannic acid or trisodium citrate, which behave as reductants as well as stabilizers at 50 °C for 1-2 days under *in situ* conditions.^{18,21,66} As outlined in sections 2.2.7 and 2.2.8, particles containing copper or Cu_2O particles were expected to form in a similar manner, by treating the wool fibres with a Cu^{2+} solution initially, followed by ageing with TGA or NaBH_4 which behave as reductants at 50 °C for 7 days. These merino wool-copper composites were analysed by scanning electron microscopy together with EDS, UV-Vis and FTIR spectra.

4.2.1 Use of thioglycolic acid

As described in section 4.1.1, TGA was used as a reductant to reduce $\text{Cu}^{2+}_{(\text{aq})}$ either to copper oxides or copper-containing particles within the wool fibres. The deposition of these particles on the surface of the wool fibres will be shown in this section.

4.2.1.1 SEM and EDS analysis

The morphology of the merino wool doped with Cu^{2+} solution followed by ageing with TGA and the distribution of copper within the merino wool are investigated by scanning electron micrographs and EDS maps respectively (Figure 4.32).

Figure 4.32: (a-b) SEM (secondary and backscatter) of merino wool soaked with Cu^{2+} solution followed by ageing with TGA at 1000 times magnification; (c) EDS map of copper on the surface of merino wool. Inset, sample of Cu^{2+} treated wool aged with TGA (diameter of ~ 2 cm).

1 g of wool fibres were treated with 100 mL of $450 \text{ mg L}^{-1} \text{ Cu}^{2+}$ solution at 90°C for 60 min and thereafter 0.5 g of wool-copper composite was aged with $100 \mu\text{L}$ of 2 M TGA in 50 ml of distilled water at 50°C for 7 days. The colour of these wool composites is dark dirty green. The morphological features of these wool composites and the distribution of copper on the surface of the wool fibres are significantly changed with respect to TGA treated merino wool followed by soaking with Cu^{2+} solution (Figure 4.1). The main changes are:

1. The amount of particles containing copper lying on the cuticle edges is markedly less with respect to TGA treated merino wool-copper composite.
2. The distribution of copper on the surface of the wool fibres is rather homogeneous with respect to TGA treated wool-copper composite. Slight amount of copper are concentrated on the cuticle edges (Figure 4.32(b)).

The area “A” is zoomed into 7000 times magnification and represented in Figure 4.33.

Figure 4.33: The backscattered electron image at X 7000 magnification of the area “A” given in Figure 4.32(b) together with EDS map of copper.

The SEM image shows the particles containing copper aggregates and are deposited along the cuticle edges of the wool fibres and further confirmed by the EDS map of copper (Figure 4.33).

As outlined in section 2.2.7, 100 mL of $450 \text{ mg L}^{-1} \text{ Cu}^{2+}$ solution was applied to 1 g of wool at 90°C for 60 min. These merino wool-copper composites were aged with distilled water together with TGA. The uptake of Cu^{2+} solution per gram of merino wool fibres is 8 mg. The 0.5 g of this wool composite may contain $\sim 4 \text{ mg}$ of Cu^{2+} ions. Therefore the particles on the surface of the wool fibres contain copper in small amount, when $\sim 4 \text{ mg}$ of Cu^{2+} is reduced by the TGA (Figure 4.32).

42.5 mg of copper is present within the wool fibres when wool is pre treated with 2 mmol of TGA at 20°C for 60 min followed by soaking with 100 mL of $450 \text{ mg L}^{-1} \text{ Cu}^{2+}$ solution at 90°C for 30 min. The Cu^{2+} content in 100 mL of uptake solution (original solution) at a loading of 1 g of wool is 45 mg. Almost all the Cu^{2+} content in the uptake solution may be reduced by TGA and form particles containing copper. All these particles in the reaction mixture are absorbed into wool fibres under rapid shaking at room temperature.

4.2.1.2 UV-Visible reflectance spectroscopic analysis

Figure 4.34 shows the UV-Vis reflectance spectrum of merino wool doped with 100 mL Cu^{2+} solution (450 mg L^{-1}), followed by ageing with 100 μL of 2 M TGA in 50 mL of distilled water at 50°C for 7 days.

Figure 4.34: UV-Vis K/S spectra of the control sample and the merino wool doped with Cu^{2+} solution followed by ageing with TGA in distilled water.

The spectral pattern of this wool composite is similar to the TGA treated wool-copper composites given in Figure 4.7. Figure 4.34 shows the characteristic bands both the visible range (350-500 and 700-850 nm) and in the UV range (225-275 nm). The bands in the blue violet region 350-500 nm ($\lambda_{\text{max}} = 425 \text{ nm}$) may be attributed to electronic transitions or charge transfer bands of Cu-O-Cu exhibited by the wool composites.^{71,89} The band in the UV region ($\sim 250 \text{ nm}$) may be due to the transitions of electrons of amino acids (phenylalanine, tryptophan and tyrosine) in the wool.⁹⁰ Also the band in the red region (700-850 nm) may be due to the Cu^{2+} in the wool samples.^{71,89} The dirty green coloured sample absorbs in the red and blue-violet region of the visible spectrum (Figure 4.34).

4.2.1.3 FTIR spectroscopic analysis

Figure 4.35 shows the FTIR spectrum of merino wool doped with 100 mL of Cu^{2+} solution (450 mg L^{-1}), followed by ageing with 100 μL of 2 M TGA in 50 ml of distilled water at 50°C for 7 days.

Figure 4.35: IR spectrum of merino wool doped with Cu^{2+} solution followed by ageing with TGA in distilled water.

The spectral pattern of these wool composites are more or less similar to TGA treated wool-copper composites given in Figure 4.10. A slight hump at 1409 cm^{-1} is indicated the interaction of copper ions with carboxyl acid dimer. As described in section 4.1.1.3 (Figure 4.12), the carboxyl acid dimers may be produced by both carboxyl groups of TGA and wool.

The pH of the reaction medium of these copper-wool composites is ~ 3.3 . Therefore the mechanism of binding of copper to TGA treated merino wool will be similar to TGA treated merino wool-copper composites.

4.2.2 Use of sodium borohydride

As described in section 4.1.2, NaBH_4 was used as a reductant to reduce $\text{Cu}^{2+}_{(\text{aq})}$ either to metallic copper ($\text{Cu}_{(\text{s})}$) or Cu_2O depending on the pH of the medium.¹⁶

4.2.2.1 SEM analysis

The morphology of the merino wool doped with Cu^{2+} solution followed by ageing with NaBH_4 and the distribution of copper within the merino wool are investigated by scanning electron micrographs and EDS maps respectively (Figure 4.36).

Figure 4.36: (a-b) SEM (secondary and backscatter) images of merino wool soaked with Cu^{2+} solution followed by ageing with TGA at 1000 times magnification; (c-d) EDS map and the spectrum of copper on the surface of merino wool. Inset, sample of Cu^{2+} treated merino wool aged with NaBH_4 (diameter of ~ 2 cm).

1 g of wool fibres were treated with 100 mL of 450 mg L⁻¹ Cu²⁺ solution at 90 °C for 60 min and thereafter 0.5 g of wool-copper composite was aged with 500 µL of 2 M NaBH₄ in 50 mL of distilled water at 50 °C for 7 days. The colour of these wool composites is brown-yellow. The morphological features of these wool composites and the distribution of copper on the surface of the wool fibres are significantly changed with respect to NaBH₄ treated merino wool followed by soaking with Cu²⁺ solution (Figure 4.19). The main changes are:

1. The Cu₂O particles cannot be observed on the surface of the wool fibres when compared to NaBH₄ treated merino wool-copper composites.
2. The distribution of copper on the surface of the wool fibres is rather homogeneous and the amount of copper content within the wool fibres is negligible (Figures 4.36(c) and (d)).

As outlined in section 2.2.8, 100 mL of 450 mg L⁻¹ Cu²⁺ solution was applied to 1 g of wool at 90 °C for 60 min. These merino wool-copper composites were aged with distilled water together with NaBH₄. The uptake of Cu²⁺ solution per gram of merino wool fibres is 8 mg. The 0.5 g of this wool composite may contain ~ 4 mg of Cu²⁺ ions. SEM-EDS analysis could not detect the Cu₂O particles on the surface of the wool fibres (Figure 4.36). This may be due to two reasons:

1. Very low amount of Cu²⁺ (~ 4 mg) is reduced by NaBH₄.
2. There is a high possibility of reducing the water than the Cu²⁺ in the medium, when the NaBH₄ was added to 50 mL of distilled water directly. The reduction of water by NaBH₄ is given in equation 4.1 (refer to page 115).

41.8 mg of copper is present within the wool fibres when wool is pre treated with 2 mmol of NaBH₄ at 20 °C for 60 min followed by soaking with 100 mL of 450 mg L⁻¹ Cu²⁺ solution at 90 °C for 30 min. The Cu²⁺ content in 100 mL of uptake solution (original solution) at a loading of 1 g of wool is 45 mg. Almost all the Cu²⁺ content in the uptake solution may be reduced by NaBH₄ and form Cu₂O particles within the wool fibres. All these particles in the reaction mixture are absorbed into wool fibres under rapid shaking at room temperature.

4.2.2.2 UV-Visible reflectance spectroscopic analysis

Figure 4.37 shows the UV-Vis reflectance spectrum of merino wool doped with 100 mL Cu^{2+} solution (450 mg L^{-1}), followed by ageing with 500 μL of 2 M NaBH_4 in 50 mL of distilled water at 50°C for 7 days.

Figure 4.37: UV-Vis K/S spectra of the control sample and the merino wool doped with Cu^{2+} solution followed by ageing with NaBH_4 in distilled water.

The spectral pattern of these wool composites are similar to NaBH_4 treated wool-copper composites given in Figure 4.28 except a broad band in the red region of the visible spectrum. Figure 4.37 shows the characteristic band in the blue-violet region (maxima $\sim 400 \text{ nm}$) and a broad hump at $\sim 650 \text{ nm}$ of the visible spectrum together with a slight hump at $\sim 250 \text{ nm}$ in the UV range. The characteristic band in the blue-violet region either due to the trace amount of Cu_2O particles formed or some charge transfer bands of copper complexes formed within the wool fibres.^{71,89} A slight hump at around 250 nm may be caused by electron transitions of amino acids in the wool.⁹⁰ A slight hump at $\sim 650 \text{ nm}$ may be attributed to the presence of some Cu^{2+} in the wool sample.^{71,89}

4.2.2.3 FTIR spectroscopic analysis

Figure 4.38 shows the FTIR spectrum of merino wool doped with 100 mL of Cu^{2+} solution (450 mg L^{-1}), followed by ageing with 500 μL of 2 M NaBH_4 in 50 mL of distilled water at 50°C for 7 days.

Figure 4.38: IR spectrum of merino wool doped with Cu^{2+} solution followed by ageing with NaBH_4 in distilled water.

The spectral pattern of these wool composites is more or less similar to the merino wool itself in Figure 3.3, suggesting the negligible formation of Cu_2O within merino wool fibres. A broad shoulder at 3433 cm^{-1} may be due to the presence of OH groups bonded with hydrogen bonds in the wool fibre with respect to merino wool.

CHAPTER 5

5 CONCLUSIONS / SUMMARY

5.1 Uptake of metal ions by wool fibres

When the initial metal ion concentration (Cu^{2+} , Zn^{2+} and Mn^{2+}) is less than $\sim 10 \text{ mg L}^{-1}$, almost all the metal ions have been taken up by merino wool fibres at 20°C , 50°C and 90°C . When the concentration of metal ions is greater than $\sim 10 \text{ mg L}^{-1}$, the diffusion of copper ions to the surface of the wool fibre becomes favourable at the initial stage of the reaction and with time the transport of Cu^{2+} ions through the wool fibre becomes very much slower than the migration of Cu^{2+} to the surface of the fibre. Therefore at the beginning of the reaction the uptake curves of the graphs increase steeply and with the time the rise of uptake curve decreases and becomes constant. There is no definite pattern shown by other metal ions (Zn^{2+} and Mn^{2+}), with regard to metal ion concentrations greater than $\sim 10 \text{ mg L}^{-1}$. The irregular pattern of these uptake curves is may be due to the variation in the natural wool fibres or the desorption of the metal ions from the wool fibres. The Cu^{2+} ions was found to give the greatest absorption by wool fibres, whereas Zn^{2+} and Mn^{2+} were found to be absorbed the least.

5.2 Quantitative determination of metal ion content of the wool

Cu^{2+} ions present in wool composites were quantitatively determined by the two methods (methods of measuring residual metal ion content and microwave digestion followed by measuring metal ion content). The mass of copper per gram of wool at same initial concentrations, calculated by the two methods are in good agreement.

5.3 Binding of metal ions to wool fibres

The Cu^{2+} ions may bind to carboxyl and amine groups of amino acid residues when merino wool fibres treated with Cu^{2+} ions at 20°C and 50°C for 24 hours, $\text{pH} \sim 4.5\text{-}5.5$. When merino wool is treated with Cu^{2+} solution at $\sim 90^\circ\text{C}$ for more than 8 hours, $\text{pH} \sim 4.5\text{-}5.5$, the disulfide bonds in the cystine residues break more readily and produce thiol groups. Also the disulfide bonds may get oxidized and hydrolysed into cysteic acid residues. These copper ions that are coordinated to thiol groups are unstable at high temperatures and readily form brown coloured copper

sulfides. At high temperatures, the high metal uptake may be attributed to the formation of copper sulfides, coordination of Cu^{2+} to cysteic acid, carboxyl and amine groups in amino acid residues in the wool.

5.4 Uptake of copper ions by chemically modified wool fibres

The merino wool fibres can be chemically modified by treating with EDTA dianhydride, thioglycolic acid (TGA) or NaBH_4 , prior to the addition of Cu^{2+} ions. Overall, the uptake of metal ions by chemically modified merino wool fibres increases significantly with respect to unmodified wool. The % uptake of Cu^{2+} in control sample (chemically unmodified wool treated only with Cu^{2+} ions) was found to be 18%, (8 mg g^{-1} of wool) whereas the TGA and NaBH_4 modified wool was found to be 94% (42.5 mg g^{-1} of wool) and 92% (41.8 mg g^{-1} of wool) respectively. The % uptake of Cu^{2+} in EDTA dianhydride modified wool was found to be 31% (14 mg g^{-1} of wool) and it is almost double the uptake of unmodified wool (8 mg g^{-1} of wool). TGA and EDTA dianhydride contain additional binding sites to bind with Cu^{2+} ions other than the functional groups present in wool fibres.

5.5 Formation of Cu_2O particles within wool fibres by an *in situ* reaction, with the use of reducing agents

Thioglycolic acid (TGA) and NaBH_4 were used as reducing agents to reduce both Cu^{2+} ions and disulfide bonds on cystine residues. The NaBH_4 reduced Cu^{2+} ions to Cu_2O particles, some of which may be produced in nanoscale and present as Cu_2O nanoparticles within the wool fibres. From XRD, SEM and EDS analysis, it was proved that these particles are Cu_2O . There was no evidence to indicate that copper nanoparticles formed within the TGA treated wool-copper composites. Both EDS patterns and the shapes of the particles under SEM are similar for both TGA and NaBH_4 treated merino wool-copper composites. Therefore it is likely that Cu_2O forms in TGA treated wool-copper composite. However more characterization techniques need to be done for TGA treated merino wool for further clarification, such as TEM and synchrotron XRD.

5.6 Suggestions for further work

- Different samples of TGA and NaBH₄ treated merino wool-copper composites need to be further characterised by X-ray photoelectron spectroscopy (XPS) in order to understand to chemical bonding between the copper ions and the merino wool.
- The copper-containing particles produced on the surface of the TGA treated wool composites need to be further characterised by synchrotron-based (XRD) instrument and TEM.
- It would be interesting to study the formation of Cu₂O nanoparticles in trace levels (less than $\sim 10 \text{ mg L}^{-1}$) by an *in situ* reaction. Their applications in the fibre authentication and traceability industry based upon the chemical signature from the metal nanoparticles formed in the wool could then be explored.

Traceability industry refers to the ability to track or to trace every step of manufacturing woollen garments. These steps are yarn, spinning, knitting, cutting and stitching.

- It would be interesting to study the NaBH₄ modified wool composites to remove the copper ions from industrial effluents and contaminated water supplies.

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