Fabrication and Applications of Ultrafine Powder from Cashmere Guard Hair

by

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I am the author of the thesis entitled "Fabrication and applications of ultrafine powder from cashmere guard hair".

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Abstract

The present work has explored high value applications for animal hair fibre wastes, particularly cashmere guard hair, by milling it into ultrafine powder particles. Cashmere guard hair, an outer coat coarse hair of the Cashmere goat, comprising 55-70 % of its fleece, gets separated from the explicitly fine cashmere fibres during the “Dehairing” process. The separated cashmere guard hairs often find low value applications and are generally treated as a waste. To explore high value applications, cashmere guard hair has been partially acid hydrolysed and milled into fine particles using the process sequence: Chopping → Wet attritor milling → Spray drying → Air jet milling. The fabricated cashmere guard hair powder has been investigated for changes in structure and surface properties and its potential in environmental protection and surface functionalization applications has been examined.

The guard hairs were partially hydrolysed with hydrochloric acid, which increased the pulverization rate due to the deterioration in mechanical properties. The volume median particle size $d(0.5)$ was reduced from 2.328 $\mu$m to 0.461 $\mu$m after the treatment. FTIR and XPS studies revealed an oxidation of cashmere guard hair surface during the milling treatment. With an increase in the concentration of nucleophilic oxygen and nitrogen atoms, the oxidation became more evident.

The metal ion absorption properties of cashmere guard hair, both in the milled powder and its parent fibre forms, in comparison with wool and silk, were examined using heavy metal ions ($\text{Zn}^{2+}$, $\text{Co}^{2+}$ and $\text{Cr}^{6+}$) and their respective gamma emitting radioisotopes. The absorption of metal ions was found to be
governed by ionic interactions over different pH ranges. Cashmere guard hair powder absorbed cationic species of Zn\(^{2+}\) and Co\(^{2+}\) efficiently at alkaline pH (pH≥8) where its surface zeta potential was negative. In contrast, cashmere guard hair powder absorbed the anionic species of Cr\(^{6+}\) efficiently at an acidic pH of 2 where its surface zeta potential was positive. Furthermore, milled cashmere guard hair powder showed an enhanced initial absorption rate. Although the absorption yield at equilibrium was less than the parent cashmere guard hair for Zn\(^{2+}\) and Cr\(^{6+}\), the absorption yield for Co\(^{2+}\) was four times high. The absorption yield of Co\(^{2+}\) was mainly governed by specific surface area of cashmere guard hair sorbents. The absorbed heavy metal ions could also be desorbed from the cashmere guard hair sorbents when exposed to a buffer solution where the sorbent zeta potential turned into opposite charge. The study has also evaluated the effect of competing alkali and alkaline earth metal ions on the absorption of Co\(^{2+}\) from its aqueous solution. The Co\(^{2+}\) absorption was more affected by alkaline earth metal ions than the alkali earth metal ions.

The surface functionalization potential of cashmere guard hair powder has been explored by coating it electrostatically onto a polyester fabric. The electrostatic powder coating process was optimized for maximum powder loading by evaluating the effect of different process parameters on the powder coated fabric density. The powder coated fabric presented smooth surface texture with multilayered deposition of powder particles. Silver ions were subsequently loaded onto the powder coated fabric through a solution based absorption process. The effect of solution pH value and initial concentration of silver ions on the Ag\(^+\) absorption and antibacterial activity against *Escherichia coli* (*E.coli*) were examined. Silver ions were effectively loaded on cashmere guard
hair powder under alkaline conditions. Loading Ag⁺ to powder coated fabric was found to enhance the durability of antibacterial function against washing. In addition, the powder coating reduced the fabric permeability to air and water and improved its thermal resistance.

Overall, fibre wastes from animal hair fibre industry could be aptly used in high value technical applications by milling them into ultrafine powder particles. The newly opened-up trajectories of high value applications could potentially enhance sustainability of the industry.
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1.1 Background

Nature presents abundant structurally diverse materials in the form of protein fibres. Biosynthesis of protein fibres controls its composition, conformation and sequence of its building blocks with an unsurpassed capacity to make complex multicomponent composite structures through protein synthesis, mineralization and self-assembly. Besides functional proteins present in intracellular, extracellular matrices, cytoplasm and blood plasma of living organisms, certain protein fibres are synthesized on exoskeletal portion of most animals and certain insects for their protection. Keratin protein in the form of hairs and feathers protects animals from outside temperature and weather changes, whereas fibroin protein secretions of spiders and insects in the form of silk filaments do the similar job by forming nests, traps and cocoons. The unique physical and chemical properties of fine animal hairs and insect secreted silk filaments, such as durability, comfort, versatility, easy dyeability, static resistance, dirt resistance and noise resistance, have long been utilized in textiles made from these natural protein fibres.

Animal protein fibres contribute 8.4 % (2,634,000 tons), comprising hair fibres 7.1% and silk 1.3% to the total world production of natural fibres [1]. Although, animal hair fibres contribute significant proportion towards the animal protein fibres, they are facing increasing competition from the
Introduction

manufactured fibre sector and decreasing share in the global fibre market. Additionally, a considerable quantity of animal hair fibres is also segregated as a waste during processing, which is suitable only for low value applications. Consequently, animal hair fibre industry has been seeking alternative ways for their sustainability through innovative utilization of its waste, by-products and developing non-apparel uses for hair fibres themselves.

1.2 Animal hair fibres and challenges facing the industry

Animal hair fibres are differentiated based on the mammalian source. Wool, mohair, Angora, cashmere and alpaca are the major animal fibres of industrial importance due to their scale of production; wool being produced in large quantity and alpaca the least. Animal hair fibres excluding wool are normally referred as speciality animal fibres.

Wool fibres are derived from the furs of Caprinae family animals such as sheeps and goats; especially from sheeps. Although the very early breeds of sheeps had two coats of fibres – outer coat of coarse fibres and down coat of fine fibres, the outer coat has been bred out from most sheeps today. Sheeps from different geographic origin present varying wool productivity ranging from 0.4 kg to 5.6 kg per sheep [2]. The diverse breeds of sheeps bring a large variety of wool fibres with a range of fibre fineness deciding their value and end use. Almost half of the world wool output comes from Australia, PR China and New Zealand. Australia supplies 90% the world demand for the apparel quality wool whereas New Zealand mainly supplies wool for interior textiles.
Introduction

Apart from different body portions, sex and age of the same sheep breed, wool fineness varies significantly between breeds and ranges from 18-32 μm.

Mohair is the second largest animal hair fibre produced by Angora goats. South Africa is the largest mohair producing country contributing 60% of total world mohair production of 17000 tons per year [3]. Angora goats have single coat of fibres with few kems and produce 2-4 kg of mohair fibre per year over two harvests. The fibre fineness ranges from 23 μm in younger goats at the first shearing to 34 μm in older goats. The mohair fibres are suitable for different applications depending on their fibre fineness.

The smooth and silky angora fibres are produced by Angora rabbits and contribute 10,000 tons per annum to the animal hair fibre industry after wool and mohair. An angora rabbit typically produces 1 kg of down fibres per year over four harvests. Angora rabbits are mainly farmed in China which contributes 90% of the world angora fibre production. An Angora rabbit has two coats of fibres, outer coat of 10 cm long coarse guard hairs of 30-40 microns and shorter fine down hairs of ~15 microns. Fleece of Angora rabbits from certain geographic regions consists of 10-12% coarse guard hairs by weight [4, 5].

Cashmere fibres, as defined by Cashmere and Camel Hair Manufactureres Institute are the fine undercoat fibres produced by a cashmere goat (Capra hircus laniger) with a maximum mean diameter of 19 microns. Total world cashmere production is 8000-10000 tons per annum with China contributing 60% and most of the remainder from other Asian countries [6]. Cashmere fibres are obtained either by shearing before or combing during the spring moult of the under coat fibres. Individual Cashmere goat produces 50-300 g of
Introduction

down hair (undercoat) cashmere fibres per annum. The outer coat is made of 6-20 cm in length, 30-100 micron coarse hairs whereas the inner coat consists of 4-8 cm in length 12-18 micron down fibres. The coarse guard hairs are separated from the fine cashmere fibres by the “Dehairing” process in cashmere industry. As per a scientific study on different non-separated raw cashmere fleeces by Hermann et al [7], the major proportion of cashmere fleece consists of coarse guard hairs only with a mean cashmere yield of 45 %.

In a report to Rural Industries Research and Development Corporation (RIRDC), McGregor reported that the net cashmere yield on dehairing of Australian cashmere was only 33.8 % [8].

Alpaca fibre is produced by Alpaca, Llama, Guanaco and Vicuña camelids in the high altitudes of South American Andes with major contribution from the former two mammalians. Alpaca and llama are shorn annually with expected fleece length and weight between 90-160 mm and 3-5 kg respectively. Alpaca has a single coat of fibres while llama generally presents double coat of fibres and hence llama fleece is also dehaired like cashmere fleece. Llama fleece, especially from South American llamas, consists of around 20% guard hairs on weight basis [3]. The total world production of alpaca fibres is 6440 tons with more than 90% coming from Peru and Bolivia. The quantity of alpaca fibre on the world market is very small (about 0.1%) compared with wool [9].

Although the fine, single coat animal fibres, such as wool and mohair are normally used for making high quality apparels, the respective animal fleece also contains coarse fibres that are normally segregated during the shearing. Additionally, some of the fibres have weak spots along their length due to stressed animal living conditions. Such weak fibres get broken and removed as
waste during an industrial process called “Carding”. In the case of speciality animal fibres, even though they fetch good value due to their scarcity as well as quality attributes, a significant quantity of animal fleece is lost as a waste in the form of outer coat guard hairs. These segregated coarse and waste animal hair fibres normally get used for rugged and low value applications such as carpets, brushes and interlinings. Moreover, as per Oerlikon Textile GmbH & Co. KG's 
"The Fiber Year" report, world production of major animal hair fibre i.e. wool has decreased consistently in the first decade of the 21st century and reached 1.1 million tons clean weight in the year 2009; a fall of 7.4 % [10]. Thus animal hair fibre industry is facing challenges with its declining share in the global fibre market due to competition from the manufactured fibre sector in addition to losing significant proportions of animal fleece as a mere waste or a low value by-product.

Considering the tedious nature of proteinaceous waste handling due to the release of harmful gases such as CO, CO₂, H₂S and HCN on its incineration [11], considerably long decomposition time on land filling [12] and high energy requirements for other physical/chemical methods of proteinaceous waste processing [13], the animal hair fibre wastes have been mainly converted to protein hydrolysate feedstuffs with proteolytic micro-organisms i.e. enzymatic chemical hydrolysis [14, 15]. However feedstuffs from processed animal by-products have not been allowed in Europe since July 1994 [16]. The ban aims to create an efficient system of protecting human health within the European Union from infections caused by pathogenic micro-organisms of animal origin. Alternatively, the protein fibre waste could be aptly utilized by converting them into novel forms such as hydrogels, films, sponges and
Introduction

scaffolds or powders. These protein fibre materials in their new forms hold potential for high value applications in the field of medical science, environmental protection and composite structures, due to the diverse chemical nature of the parent animal protein fibres.

Therefore, the main purpose of this study is to explore new potential applications for animal hair fibre waste to gain better economic viability and sustainability to the animal hair fibre industry as a whole. A special case for outer coat guard hairs from cashmere goats (cashmere guard hairs) is presented in this study by converting them into ultra-fine powder particles, characterizing their toxic heavy metal ion sorption properties and utilizing their functional properties by coating them onto textile substrates.

1.3 Research problems and specific aims

Natural protein fibres can be converted into ultrafine powder form by either of the two methods: an indirect method with bottom-up approach of protein regeneration or a direct method with top-down approach of mechanical milling. Although each method has its own pros and cons, discussed in Chapter 2, research on protein fibre powders has remained mainly focused on either silk fibroin microspheres fabricated by an indirect technique of protein regeneration or keratin ultra-fine powder particles, mainly fabricated from wool by mechanical milling method. However, both of these fibres are costly raw materials for protein fibre powder fabrication due to their niche position in the field of traditional textiles. Therefore the first specific aim of this research is:

Specific Aim 1: Fabricate ultrafine cashmere guard hair powder particles by mechanical milling process sequence and characterize the same.
Introduction

Being an industrial waste fibre with proteinaceous nature, cashmere guard hair milled to ultrafine powder particles could be apt economical alternatives for wool and silk particles in many applications. Additionally the mechanical milling approach provides an easy option for scaled up production of powder particles and could come in handy for commercial applications requiring high quantities of protein fibre powders. It is therefore aimed to fabricate and characterize cashmere guard hair powder particles by exploring different mechanical milling apparatuses.

Specific Aim 2: Exploring the toxic heavy metal ion separation potential of cashmere guard hair powder in comparison with the parent hair fibre.

Presence of different nucleophilic groups such as amino (-NH₂), hydroxy (-OH) and thiol (-SH) has enabled animal protein fibres to bind to different organic and inorganic molecules of interest. It is anticipated that the improved specific surface area and reactivity of the milled cashmere guard hair could assist in improving performance of toxic heavy metal ion absorption from its aqueous solutions.

Specific Aim 3: Coating of cashmere guard hair powder on synthetic fabric for surface functionalization

Animal protein fibre powders have been applied on textile substrates to achieve improved dyeability, warmth retention, Ultra-violet protection, wrinkle recovery and moisture management properties. However, mechanical stability of the powder coating layer remained an issue. Therefore a further specific aim of this research work is to evenly coat cashmere guard hair powder on textile fabric with good mechanical stability against washing and abrasion and to explore its different functional properties.
1.4 Thesis outline

Chapter 2 – Is a literature review chapter that pinpoints some of the basic physico-chemical aspects of hair fibres, scrutinises state of the art natural protein fibre powder fabrication techniques and summarises different trajectories of applications.

Chapter 3 – Describes all materials, powder fabrication process, characterization methods, experimental procedures, test processes and instruments used during this project

Chapter 4 – Cashmere guard hair has been characterized for some of its physico-mechanical properties and its effect on the hair fibre’s milling behaviour has been reported. The milling behaviour of cashmere guard hair has also been compared with merino wool and eri silk wherever possible. Additionally, the hair fibre’s mechanical properties have been altered by partial acid hydrolysis, in order to assist in achieving fine powder particles. The morphology, particle size, specific surface area and chemical changes occurred at different stages of milling have been characterized.

Chapter 5 – Reports on toxic heavy metal ion absorption efficiency of cashmere guard hair powder by nuclear sensor technique. The effects of oppositely charged metal ions, metal ion solution pH and concentration on its absorption efficiency have been studied in comparison with the parent hair fibre. The role of zeta potential and free volume aspects of cashmere guard hair powder has been elucidated in metal ion absorption. The desorption potential of the absorbed heavy metal ions have also been explored.

Chapter 6 - Cashmere guard hair powder has been applied onto a fabric surface using an electrostatic powder coating technique. The powder coating
Introduction

process has been optimised for high powder utilization. The mechanical stability of the powder layer against weathering agents has been evaluated. The water pressure drop and thermal resistivity of the powder coated fabric have been characterized to show its applications.
Chapter 2

Literature review

This chapter summaries structure and sorption properties of animal hair fibres, various adopted milling methods for organic as well as inorganic materials, applications of milled animal hair powders and a potential powder coating technique for functionalization of textile fabrics.

2.1 Composition, structure and morphology of hair fibres

2.1.1 Chemical structure of hair fibres

The main chemical components of animal hair fibres are hard keratin proteins which primarily consist of carbon, hydrogen, oxygen, nitrogen, sulphur and ash. The elemental composition of merino wool as a representative animal hair fibre, as reported by Zahn et al is presented in Table 2.1. Except the large sulphur content in hair fibres, the elemental composition is typical of proteins. The keratin protein is comprised of “polypeptide chains”. The word polypeptide is formed from Greek words: “poly” meaning many and “peptos” meaning digested or broken down. The polypeptide chain is comprised of various amino acids which are joined together by a peptide bond (-NHCO-), extending from a terminal carbon atom of one amino acid to the terminal nitrogen atom of the next amino acid. The keratin protein in hair fibres is comprised of 18 different amino acids and their individual content differs with genetic related factors, sex, nutritional and weathering effects [17]. Table 2.2 illustrates the different amino acids in hair fibres along with their structures.
Literature review

Table 2.1 Merino wool elemental composition [18]

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>50-52</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.5-7.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>22-25</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>16-17</td>
</tr>
<tr>
<td>Sulphur</td>
<td>3-4</td>
</tr>
<tr>
<td>Ash</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The hair configuration is held in place by various bonds within and between polypeptide chains such as covalent bonds including disulphide bonds of cystine (-s-s-) and the isopeptide bonds as well as the noncovalant bonds including hydrogen bonds, ionic bonds and hydrophobic bonds. These bonds between the polypeptide chains are illustrated in Fig. 2.1.
### Table 2.2 Hair fibre constituting amino acids [19]

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Structure</th>
<th>Amino acid</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspratic acid</td>
<td>HOOC-(\text{CH}_2\text{CH(NH}_2\text{)COOH})</td>
<td>Cystine</td>
<td>HS-(\text{CH}_2\text{CH(NH}_2\text{)COOH})</td>
</tr>
<tr>
<td>Threonine</td>
<td>(\text{CH}_3\text{CH(OH)CH(NH}_2\text{)COOH})</td>
<td>Valine</td>
<td>(\text{CH}_3\text{CH(CH}_3\text{)CH(NH}_2\text{)}) COOH</td>
</tr>
<tr>
<td>Serine</td>
<td>(\text{HOCH}_2\text{CH(NH}_2\text{)COOH})</td>
<td>Methionine</td>
<td>(\text{CH}_3\text{-S-CH}_2\text{CH(NH}_2\text{)COOH})</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>HOOC-(\text{CH}_3\text{CH(NH}_2\text{)COOH})</td>
<td>Isoleucine</td>
<td>(\text{CH}_3\text{CH(CH}_3\text{)CH(NH}_2\text{)}) COOH</td>
</tr>
<tr>
<td>Glycine</td>
<td>(\text{H}_2\text{N-CH}_2\text{COOH})</td>
<td>Leucine</td>
<td>(\text{CH}_3\text{CH(CH}_3\text{)CH}_2\text{CH(NH}_2\text{)}) COOH</td>
</tr>
<tr>
<td>Proline</td>
<td><img src="image" alt="Proline structure" /></td>
<td>Tryptophan</td>
<td><img src="image" alt="Tryptophan structure" /></td>
</tr>
<tr>
<td>Histidine</td>
<td><img src="image" alt="Histidine structure" /></td>
<td>Phenylalanine</td>
<td><img src="image" alt="Phenylalanine structure" /></td>
</tr>
<tr>
<td>Lysine</td>
<td>(\text{H}_2\text{N-CH}_2\text{CH}_2\text{CH}_2\text{CH(NH}_2\text{)}) COOH</td>
<td>Alanine</td>
<td>(\text{CH}_3\text{CH(NH}_2\text{)COOH})</td>
</tr>
<tr>
<td>Tyrosine</td>
<td><img src="image" alt="Tyrosine structure" /></td>
<td>Arginine</td>
<td>(\text{H}_2\text{N-C(=NH)NHCH}_2\text{CH}_2\text{CH(NH}_2\text{)}) COOH</td>
</tr>
</tbody>
</table>
2.1.2 Morphological structure of hair fibres

Animal hair fibres are multicellular tissues comprising of several morphological components. Each morphological component has specific chemical composition. Hair fibres are roughly cylindrical in geometry with diameter ranging from 10 μm for fine fibres to more than 100 μm for coarse guard hairs.

In general, hair fibre is mainly composed of cortex and cuticle which are further subdivided into several other morphological structures. The cortex is made of cortical cells and the cell membrane complex. Each cortical cell is
Literature review

Further architecturally made from five to eight macrofibrils that are 200-300 nm in diameter at their widest point. The macrofibrils are cemented with an intermacrofibrillar material in a cortical cell. Each macrofibril further consists of hundreds of microfibrils (IFs), cemented together with an intermicrofibrillar matrix - composed of microfibril associated proteins (IFAP) from cytoplasmic and nuclear remnants. Each microfibril, in the further organisation of a single hair consists of 7 or 8 single or paired proto-filaments which are formed by twisting four alpha helices (Fig. 2.2). The “alpha helix” is a term usually opted for the polypeptide chain that forms the keratin protein in hair fibres. Thus, each microfibril contains 28-32 keratin chains [19]. All these different morphological components of cortex are wrapped up in the cuticle, an external sheath and thus ensemble the keratin polypeptide chains in a cylindrical form.

Figure 2.2 The structural components of a hair fibre (Produced by H. Roe from a drawing by Dr. R.D.B. Fraser) [21].
The cortex forms almost 90% of keratin fibres and is responsible for their primary mechanical properties. The cortical cells are approximately 100 μm long and 3-6 μm wide which are separated by a continuous cell membrane complex (CMC). The microfibrils of cortical cells are rich in low-sulphur proteins e.g., lysine, aspartic acid, glutamic acid and leucine; whereas the surrounding cell membrane complex is rich in high-sulphur, high – glycine/high-gyrosine proteins such as cystine, proline, serine and threonine. The cell membrane complex makes 3.3% of the weight of wool which consists of 1% of the readily extractable protein, 0.8 % of lipid and 1.5 % of a resistant membrane [20].

A cuticle layer surrounding the cortex is formed from packed dead flattened cells and constitutes approximately 10% of the hair fibre. Cuticle cells overlap both longitudinally and circumferentially with open scale edges pointing towards the fibre tip. Although in a mature fibre the cuticle cells primarily perform the protective function, they are responsible for most of the fibre surface properties and play an important role in the ingress of water and other chemicals. The cuticle cell dimensions are approximately 20 μm x 30 μm x 0.7 μm in merino wool hair fibre [21]. The cuticle of wool fibre is normally one cell thick except for the region where adjacent cells overlap and measures 0.3 – 0.5 μm. However the cuticle of human hair and most coarse keratin fibres is many layers thick. In wool, the cuticle cells have a higher proportion of cystine (15.6 mol %) than the whole fibre (10.3 mol %). The cuticle layer has a surface membrane called as “epicuticle” which contains lipids and proteinaceous components. The lipids from the epicuticle layer are long 21-carbon chain fatty acids and are linked covalently via thioester bonds to the
Literature review

proteins as shown in Fig. 2.3 [22]. Although the epicuticle comprises less than 0.1 % of fibre mass, it has a large influence on several important fibre properties.

![Figure 2.3 Epicuticle layer of hair fibre [24].](image)

At the centre of the hair structure, lies a central stream of cells interspersed with vacuoles and is termed as medulla. This central medullary canal is more prevalent in coarser hair fibres and is usually absent in fine wools [23]. The medulla is a part of the animal excretory system that houses any foreign debris, heavy metals and medications that are thrown off by the body.

2.2 Sorption properties of hair fibres and its derivatives

2.2.1 Physical structure and diffusion pathways in hair fibres

The reactive species from aqueous solutions get absorbed into hair fibres through the gaps between the cuticle cells and then diffuse into the nonkeratinous region of the cell membrane complex (CMC). CMC, the only
Literature review

continuous phase in hair fibres as depicted in Fig. 2.4, provides a pathway for aqueous solutions to reach the cortical cells located inside the fibre. The diffusion through the CMC is accompanied with simultaneous diffusion along the other nonkeratinous regions of the fibre (endocuticle, intermacrofibrillar matrix and nuclear remnants). The reactive species from the aqueous solution thus progressively transfer from the nonkeratinous regions into the sulphur rich protein matrix surrounding the microfibrils within each cortical cell at equilibrium [24].

![Figure 2.4 Cell Membrane Complex - a continuous phase in hair fibres [27.]](image)

**2.2.2 Sorption of metal ions from aqueous solution by hair fibres**

Hair fibres contain an intricate network of structural entities with functional groups such as carboxyl (COOH), amino (NH\(_2\)) and sulfhydryl (SH) that can bind to several organic and inorganic species. The intrinsic properties of hair fibres such as stability over a wide range of pH, structural toughness and high
Literature review

surface area are some other positive factors determining their application in the separation of toxic heavy metal ions from industrial effluents. The development of industries that transmit heavy metal ions to water has evolved into an extremely serious environmental problem of water pollution due to the hazardous effects of the metal ions on human health.

2.2.2.1 Metal ion sorption properties of hair fibres

Several researchers have examined the effectiveness of different types of hair fibres such as human hair, animal hair fibres especially wool and feathers, in the removal of heavy metal ions from aqueous solutions. The metal ion uptake capacity of human hair from single and mixed metal ion aqueous systems has been reported by Tan et al [25]. The human hair showed decreasing order of capacity to absorb Hg$^{2+}$ (Hg$^{+}$), Ag$^+$, Pb$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ (Cu$^+$), Cr$^{6+}$, Ni$^{2+}$ and Cr$^{3+}$. Negative effect on the metal ion uptake capacities was observed under multicomponent metal ion aqueous system. It was also reported that hair treatment with inorganic acids HCl and H$_2$SO$_4$ of concentrations up to 5 N and soaking times up to 48 h did not significantly change the Cu$^{2+}$ adsorption capacity of hair (0.1 mg/g). However, hair treatment under reducing alkaline conditions (0.1 N NaOH/0.1 N Na$_2$S for 20 min) demonstrated a significant increase in the adsorption capacity of Cu$^{2+}$ (35.5 mg/g of hair at 413 ppm initial Cu$^{2+}$ concentration).

Balkose et al [26] used wool fibre to absorb heavy metal cations Cu$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Ni$^{2+}$ from aqueous solutions at different initial metal ion concentrations and temperatures for 60 minutes. It was reported that the metal ion concentration below the hazardous waste limit could be achieved via a repeated absorption process by using fresh wool each time. Increasing
Literature review

temperature from 25 °C to 50 °C led to an increase in the uptake of Ni²⁺, Cd²⁺, Pd²⁺ and Hg²⁺, but this did not significantly affect the absorption of Cu²⁺ and Zn²⁺. The fast metal ion uptake by wool fibre within a few minutes indicated the possibility of using batch sorption process for waste water treatment.

Friedman et al [27] studied the mercury absorption properties of wool in the form of mercuric nitrate, mercuric chloride and methylmercuric chloride. They reported that mercury binding rate of nitrate was appreciably slower than chloride. Both the inorganic mercury compounds were reported to be efficiently taken up from acidic solutions.

Using wool to take up Co²⁺ from aqueous solutions containing copper (II) sulphate has been investigated by Sheffield et al [28]. They reported that Co²⁺ take up was increased with an increase in the temperature and time. The metal ion uptake increased with an increase in the amount of copper applied. However, the fraction of applied copper taken up by the fibres was decreased with the amount applied. The copper uptake was linearly increased with pH up to pH 6 whereas above pH 6, solid copper salt was precipitated.

Wool fibres have also demonstrated potential in actinide recovery especially Uranium from actinide containing wastewater [29].

Guthrie et al reported the uptake of Cu²⁺ using Mohair fibres [30]. They indicated that carboxyl groups were the primary but not the sole sites to bind Cu²⁺ in mohair keratin when the solution had a pH below 5.

Banat et al reported [31] the removal of Zn²⁺ and Cu²⁺ ions from single metal ion solutions under different experimental conditions using chicken feathers, human hairs and animal horns. The animal horn had the highest uptake towards Zn²⁺ and Cu²⁺ ions whereas chicken feathers showed higher Cu²⁺ ion and lower
Literature review

Zn$^{2+}$ ion uptakes compared to the human hair. Increasing the initial concentration of Zn$^{2+}$ or Cu$^{2+}$ ions (from 20 mg/l to 40 mg/l) or increasing the initial pH value (3.5 – 5) increased the metal ion uptake. For the majority of studied sorbent/metal ion combinations, the metal ion uptake decreased when the temperature was raised from 25 °C to 50 °C.

The recovery of precious metal ions such as gold and platinum by chicken feather has been reported by Sumaya et al [32]. It was found that the sequestering level of Au$^{3+}$, Pt$^{2+}$ and Pd$^{2+}$ approached about 17, 13 and 7 % of dry weight of chicken feather respectively. It was also reported that the presence of 100 fold (mol) coexisting cations did not discernibly affect the precious metal ion uptake rate and capacity of chicken feathers.

The metal ion sorption capacity of the waste hair fibres especially from the wool industry has also been reported. Waste wool samples, mainly dyed wool-synthetic blends discarded from wool manufacturing processes and wool from carpet waste has been examined for their ability to absorb mercury from aqueous solutions of mercury (II) chloride [33]. A high mercury removal efficiency of >90% from 100 ppm mercury solutions was reported. This study suggested the possible applications of hair fibre wastes, which are available at low cost and in large quantities, in the removal of mercury like heavy metal ions from industrial effluents.

2.2.2.2 Metal ion sorption properties of chemically modified hair fibres

The sorption ability of hair fibres for metal ions can be enhanced by chemical modifications. For example, recycled wool based non-woven material has been studied for their ability to remove metal cations from waste water after
Literature review
treatment with low temperature air plasma, chitosan and hydrogen peroxide [34, 35]. The low temperature plasma treated material exhibited a similar behaviour to that of the untreated material, whereas the chitosan and the hydrogen peroxide treatments increased the uptake of all investigated metal ions [34]. Under the conditions of pH 4.5, 20 °C, 100 mg/L initial metal ion concentration and contact time of 24 hours, the metal ion uptake was increased from 4.39 to 5.0 mg/g for Pd^{2+}, from 2.04 to 4.8 mg/g for Cu^{2+}, from 1.27 to 3.84 mg/g for Zn^{2+} and from 0.96 to 3.21 mg/g for Co^{2+} after the hydrogen peroxide treatment (20 ml/l) for 1 h at 70 °C and pH 9.4. In addition to its efficiency, the possibility of using recycled wool-based sorbent for wastewater purification was of great importance from the resource preservation and the cost-effectiveness point of view.

Taddei et al [36] reported the chemical modification of wool fibres with tannic acid (TA) and ethylenediaminetetraacetic (EDTA) dianhydride and its effect on Co^{2+} and Cu^{2+} binding under alkaline pH. The chemical modifications were found to substantially increase (~ 6-7 time increase) the Co^{2+} and Cu^{2+} binding capacities of wool fibre at 33.3 mM initial metal ion concentrations at 25 °C for 30 h under alkaline condition of pH 11.4. In the same report, the FTIR-ATR studies indicated that the interaction between fibre and metal depended on the chemical nature of the fibre, the metal cation and the modifying reagent. In an another study by the same research group [37], wool fibres modified with TA and EDTA–dianhydride were reported to be effective in enhancing their intrinsic ability to absorb and bind Ag^{+} and Cu^{2+}, where the extent of metal uptake was dependent on the fibre weight gain. The EDTA acylated wool fibres demonstrated effective metal cation uptake over a wide pH range,
Literature review

especially in the acidic and neutral regions where untreated or TA treated wool fibres absorbed only negligible amounts of metal ions.

2.2.2.3 *Metal ion sorption properties of hair fibre derivatives*

The keratinous materials have been derivatised into various forms by different researchers and their metal ion uptake properties have been investigated. The feasibility of porous polyurethane-keratin hybrid membranes prepared from different chicken feather keratin solutions for the removal of Cr$^{6+}$ through membrane separation technology has been investigated [38]. The mesoporous membranes presented better adsorption capacities at 5 nm pore size which was obtained by adding 15 wt. % keratin to the membranes. The maxium capacity of 38% chromium removal was reported with hybrid membranes prepared from chicken feather. Electrospun nanofibre membranes prepared from wool keratose and silk fibroin were also used for removal of metal ions [39]. Wool keratose was obtained by oxidising scoured merino wool fibres with formic acid and hydrogen peroxide. The electrospun wool keratose/silk fibroin membrane exhibited a high absorption capacity to Cu$^{2+}$ (2.88 µg/mg) when pH was 7 and contact time was 30 minutes. In comparison, wool sliver and filter paper had a absorption capacity of 0.71 and 0.23 µg/mg respectively. The high metal ion sorption ability of the blend nanofibre membrane was attributed to its large surface area and high porosity.

Crosslinked keratin gel in the form of solid particles was prepared and its chemical modification as well as Hg$^{2+}$ metal ion sorption properties were studied by Miyamoto *et al* [40-42]. The solid gel particles showed much higher Hg$^{2+}$ absorption capacity (72 mg/g at pH 7) compared to the native wool (12
Literature review

mg/g at pH 3.5) and commercial sorbents (e.g. 44 mg/g at pH 7). The Hg^{2+} ions were bonded with the keratin gel through its thiol and amino groups under acidic conditions; whereas electronegative atoms such as sulphur, nitrogen and oxygen were reported to be responsible for Hg^{2+} ion binding under alkaline conditions. It was also found that Hg^{2+} ion uptake rate was decreased with the decrease in the swelling volume of the gel. The S-substituted keratin gels outweighed untreated keratin gels in terms of the recovery of Hg^{2+}.

2.2.2.4 Recovery of metal ions

The recovery of metal ions is of interest mainly for two reasons: sorbent reusability and recovery of high value precious metal ions such as Au^{3+}, Pt^{2+}, Pd^{2+} etc.

Several chemical methods have been reported to recover metal ions from respective metal ion loaded hair fibres. The solution of 0.01M EDTA has been suggested for an economical recovery of metal ions [32]. EDTA was able to achieve a desorption ratio (i.e. percentage metal ion released from the absorbent after the metal absorption) of 88.6, 90.4 and 85.4 % for Cu^{2+}, Hg^{2+} and Ni^{2+} respectively from poly(isatin acrylic hydrazone) grafted wool fibres. The fibres were previously treated with respective 100 mg/l metal ion solution at 28 °C, pH 5 for 3 h. Friedman et al [27] tested the desorption efficiency of mercaptoacetic acid, mercaptoethanol, dithiothreitol, dithioglycerol (dimercaprol,BAL), 2-mercaptopropylglycine, ethylenediaminetetraacetic acid (EDTA), and citrate acid. In this study, the efficient conditions to recover mercury from wool were found to be 0.01M EDTA and 0.1 M citrate at pH 6. Mercury elution from wool fibres has also been achieved with 5% EDTA (pH
Literature review

6) and 0.1 N thioglycollic acid (pH 7) solutions [43]. Sulphuric acid (0.1 N) has also been used as eluting agents for silver loaded wool fibres [44]. With the initial Al content of 6.8 mg/g of wool, Edgar et al [45] studied the efficiency of 50% n-propanol and water at two different pHs (pH 3.4 and pH 6.2). They reported that water at pH 3.4 desorbed 22% of Al loaded and the % desorption decreased to 17.7 at higher pH of 6.2. However, in the case of 50% n-propanol, the trend was in reverse order.

2.2.2.5 Techniques used to measure metal ion sorption properties of hair fibres

Different techniques have been used to examine the metal ion sorption properties of hair fibres which include atomic absorption spectroscopy (AAS) [25], chelate titration [30], X-ray fluorescence spectroscopy [46], Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICPAES) [37], X-ray Photoelectron Spectroscopy (XPS) [47], ATR-IR spectroscopy [36] and Electron Spin Resonance (ESR) spectroscopy [48].

An alternative radioisotope tracer technique to measure metal ion concentration in its carrying medium offers various advantages such as easy and fast operation, broad concentration detection range and insensitivity to the media (i.e. solid or liquid). The technique uses gamma counter, an analytical instrument to quantify the activity of a gamma-emitting sample. The photons from the emitting γ radiations are detected by the gamma counter based on the scintillating detector principle. When the emitted γ radiations enter the scintillating crystal, the associated photons colloid with the crystal atoms and produce light, the energy of which is converted into an electric pulse. The gamma ray count rate (i.e. the number of electric pulses per unit time) on the
gamma counter is proportional to the radioisotope content in the carrying media. As the radioisotopes of an element have different number of neutrons but the same number of protons and therefore possess similar chemical behaviour, they can be used as a tracer to quantify the sorption of chemically identical nonradioactive atoms of the same element by an adsorbent, when used in a specific molar ratio.

2.2.3 Antibacterial finishing of textiles by treatment with metals ions

The growth of microorganisms such as bacteria and fungi onto textiles during their storage and usage is highly undesirable as it imposes various unwanted effects such as unpleasant odour, stains, discoloration, decrease in mechanical strength and contamination of the textile substrate. Although numerous antimicrobial agents such as quaternary ammonium compounds, polyhexamethylene biguanides (PHMB), triclosan, chitosan, N-halamine compounds, peroxyacids and dyes have been explored for textile finishing, heavy metal ions have maintained attention due to their biocidal activity at very low concentrations in its free state or in the form of compounds.

The metal particles that are incorporated into a textile substrate can diffuse onto the surface and transform into ion state in the presence of moisture. The biocidal activity of metal incorporated textile substrates is improved by binding the metal ions with intracellular proteins of microbial cells and thus deactivating them.

Two main approaches that can render textiles with antibacterial activity through treatment with heavy metals include adsorbing heavy metal ions from its solution medium or incorporating/precipitating metal/metal oxide nano
Literature review

particles using various methods. A few examples on applying metal ions onto textiles to provide antibacterial activity have been given below:

Cellulose fabrics have been treated with succinic anhydride for improved adsorption of metal ions \( i.e. \) \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) from its salt solutions such as copper sulphate and zinc sulphate. It was reported that the antibacterial activities of cellulose fabrics were effectively enhanced by the treatment with succinic anhydride and the metallic salt. The antibacterial activity was maintained even after ten cycles of launderings [49]. On similar lines, Freddi et al [37] modified wool fibres by treatment with tannic acid (TA) or ethylenediaminetetraacetic (EDTA) dianhydride for improvement of metal cation (\( \text{Ag}^+ \) and \( \text{Cu}^{2+} \)) adsorption and antibacterial properties. Copper containing wool fibres exhibited significantly lower activity against \textit{Cornebacterium} than the corresponding silver containing fibres. Although silver containing wool fibres showed a high activity against \textit{Cornebacterium}, the effect of chemical modification with TA or EDTA was not obvious.

Gulrajani et al [50] synthesized silver nanoparticles by reduction of silver nitrate with glucose using hydrazine as a reducing agent and poly(vinyl pyrrolidone) as a dispersing agent. The silk fabric after being treated with 60 ppm silver hydrosol at 40 °C showed 100% antibacterial activity against the gram positive bacterium \textit{S. aureus}. After 10 cycles of washing, the antibacterial activity was decreased to 80%.

The antibacterial activity of nano ZnO particles synthesised in water with starch stabilizer has been evaluated against bulk ZnO particles [51]. Nano-ZnO coating with 1.63% uptake on cotton textiles showed excellent antibacterial
Literature review

activity (reduction > 99.9%) against *Staphylococcus aureus* and *Klebsiella pneumoniae*, substantially better than bulk ZnO with 2.23% uptake.

Textile fibres treated with monovalent copper cations and borate/carbonate anions; either from a single solution bath or separate solution baths have been reported to render the fabric with antibacterial properties [52].

Textile fabrics with outstanding antimicrobial properties having good durability towards a number of laundering cycles have been prepared by interstitially precipitating cobalt (II, III) oxide. The process included treatment with divalent copper cations, followed by treatment with a strong alkali and a per-acid salt oxidiser to precipitate cobalt (II, III) oxide on the fabrics [53].

### 2.3 Derivatives of hair keratin

Animal hair fibres have been derivatised in different forms to explore their numerous molecular binding sites and consequent absorption properties in various applications.

#### 2.3.1 Hydrogel

Hydrogels form a specific class of biomaterials that are two or multicomponent systems, consisting of a three dimensional network of polymer chains and water that fills in the space.

In general, keratin hydrogels are prepared from clean, dry and degreased hair fibres which are reduced first with a reducing agent such as thioglycolic acid (1 M) to break the cystine bonds [54]. After the dialysis to cut off the low molecular weight substances and thus concentrating the viscous keratin
Literature review

solution (~15-20 wt %), a crosslinking treatment is conducted to turn the soluble protein into the water insoluble hydrogel. The hydrolytic stability of keratin hydrogel along with their ability to facilitate cell adhesion and proliferation has been studied. [55] The hydrogel has also shown excellent compatibility to biological systems. Furthermore, Sierpinski et al [56] demonstrated that keratin based hydrogels were neuroinductive and capable of facilitating peripheral nerve regeneration in a mice injury model. Human hair keratin has also been regenerated into a gel form to test its efficacy as a hemostatic agent to stop severe hemorrhage (i.e. excessive discharge of blood from blood vessels) [54].

2.3.2 Films

Protein films have been derivatised from wool and hair extracted keratins and mainly used for controlled drug release applications based on its structural and biological properties.

Fujii et al [57] have described a rapid casting method to prepare hair keratin films and subsequently revealed the feasibility of incorporating bioactive molecules such as alkaline phosphatase into the keratin films for controlled-release applications. However the films had poor strength and flexibility. Although pure keratin films are too fragile for practical use, Yamauchi et al [58] have demonstrated that the addition of glycerol into pure keratin results in a transparent, relatively strong, flexible, and biodegradable film. Blending natural or synthetic polymer with keratin has also improved structural properties of keratin films [59-61].
2.3.3 Keratin fibres

The abundance of potential biomedical applications of nanofibrous materials due to their enhanced physical configuration with small pore size, high porosity, three dimensional features and high surface area to volume ratio has motivated many researchers to use the electrospinning technique to prepare keratin nanofibres. Also, natural or synthetic polymer has been added to the pure keratin solutions to improve its processing ability during electrospinning [62, 63].

Traditional wet spinning technique has also been attempted to produce fibres from a blend of a synthetic polymer such as poly(-vinyl alcohol) and keratin [64]. The fibres showed good mechanical strength, water resistance and adsorption ability towards toxic substances. Furthermore, cellulose, a natural polymer blended keratin fibres have also been prepared by the wet spinning technique [65]. The cellulose blended keratin fibres have demonstrated better sorption properties and high hygroscopicity.

2.3.4 Keratin sponges and scaffolds

Tissue engineering involves using scaffolds to repair and regenerate organs and tissues. In the year 2001, Tachibana et al [66] reported the fabrication of first keratin sponge scaffold by lyophilisation of aqueous wool keratin solution after controlled freezing. The scaffold was rigid and heat stable having a homogeneously porous microarchitecture. Subsequently, the keratin sponge has also illustrated its potential in tissue engineering applications by demonstrating long term and high density cell cultivation.
Literature review

At several instances, the tissue engineering scaffolds are intended to carry bioactive molecules for controlled release to influence the cell growth behaviour. With the similar approach, chemically modified keratin sponges have been hybridised with calcium phosphate [67]. They have shown an ability to support osteoblast cultivation and enhance expression pattern of alkaline phosphatase.

Katoh et al [68] developed a compression molding/particulate leaching (CM/PL) method to fabricate keratin scaffolds with the ability to regulate pore size, porosity and pore interconnectivity to allow adequate cellular infiltration and nutrient delivery. The scaffolds fabricated by the CM/PL method were strong enough to handle. Additionally, the scaffolds were water insoluble and superior over collagen based scaffolds due to the water soluble feature of the uncrosslinked collagen [69].

2.3.5 Regenerated keratin powder

Katoh et al [64] reported the fabrication of keratin powder from wool keratin extract. The process involved spray drying keratin concentrate obtained from dialysing and vacuum evaporation of reduced wool filtrate solution. These keratin powders were further blended with poly(-vinyl alcohol) and then wet-spun into fibres. The fibres demonstrated good mechanical strength in comparison with wool fibres. Keratin-PVA fibres could also absorb Ag⁺ and formaldehyde gas with high efficiency than PVA fibre.
2.3.6 Milled hair keratin powder

The intrinsic ability of extracted keratin proteins to reorganise into porous and controllable morphological structures via bottom-up approach and the availability of cell binding sites such as leucine-aspartic acid-valine (LDV) and glutamic acid-aspartic acid-serine (EDS) residues have paved ways for the development of many regenerated keratin based biomaterials for use in biomedical applications. However, hair keratin based regenerated derivatives often get synthesised on laboratory scale, loose the native molecular architect in the parent hair fibres, make use of toxic chemicals and take a long time to synthesise (Fig. 2.5).

On the contrary, hair keratin can also be derivatised in the form of powder particles with the top-down approach of mechanical milling technology which is a straightforward and comparatively quick process. Hair keratin powder particles can be easily produced in bulk quantity by mechanical milling without
altering the native fibre molecular architecture and thus preserving the native physicochemical characteristics in the powder particles.

The remaining sections in this chapter address the mechanical milling technology in general. More specifically, they also report the fabrication of hair fibre powders and their applications.

2.4 Milling technology

Mechanical milling adopts a mechanical device to impart energy to a coarse grained material in order to reduce the particle size. The mechanical device is generally referred to as a “mill” and the process is known as a “milling process”.

Milling can be generally classified into two major classes, media milling and non-media milling depending on whether media (balls or beads) used.

2.4.1 Media milling

The media milling systems are particularly used for mechanical alloying – a technique that allows production of homogeneous materials from blended elemental powder mixtures. Some examples of media milling systems from a review by Claudia and Brianm [70] are given below:

**Shaker mills:** Shaker mills such as SPEX, mill about 10-20 g of powder at a time and are most commonly used for laboratory investigations. The mill has a clamp secured vial containing the sample to be milled and the milling media, which swings energetically back and forth several thousand times a minute. At each swing of the vial, the milling media, typically hard, spherical objects
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called “milling balls”, impact against each other and at the ends of the vial, both mixing and milling the sample at the same time.

**Planetary ball mills:** The planetary ball mill derives its name from the planet like movement of its vials and is sometimes also referred to as Pulverisette. The vials containing the sample to be milled and the milling media (i.e. the milling balls) are arranged on a rotating support disk and are driven around their own axes by a special drive mechanism. As the vials and the support disk rotate in opposite directions, the sample gets milled via the frictional and impact effects. The centrifugal force due to the vial rotations around its own axis makes the milling balls run down the inside of the vial wall, resulting in the sample grinding due to the friction effect. The centrifugal force in the opposite direction due to the rotating support disk lifts off the milling balls from the inner wall of the vial and makes them travel freely through its inner chamber and colloid with the opposing inner wall resulting in the impact effect on the sample.

**Attritor mills:** An attritor mill consists of a vertical drum with a series of impellers set progressively at right angles to each other. A motor rotates the impellers which in turn energises the milling media (i.e. milling balls) inside the drum causing powder size reduction due to impact between balls, between the balls and the inside wall of the drum and between the balls, the impeller shaft and the impellers. The milling can be carried out in either wet or dry state. The temperature inside the drum can be controlled by circulating chilled water through the jacket around the drum. Attritors are mostly used for ceramics and they are suitable for ultrafine and nano-scale particle production or its dispersion.
2.4.2 Non-media milling

In media milling, the vial, the media and the dispersant are the major sources of sample contamination. The major advantage of non-media milling over the
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media milling lies in the zero or limited sample contamination. Most commonly used non-media mills are rotary mills and air jet mills.

**Rotary mill:** The particle size reduction in rotary mill is achieved by the impact of the blades and the shear forces between the rotor blades and sieve rings.

![Figure 2.8 Rotary Mill](image)

**Air jet mill:** The air jet mill does not involve any mechanical action due to moving parts and usually employ compressed air or gas. Inside the mill, precisely aligned jets create an air vortex. Material is fed into this vortex along an engineered tangent circle and gets accelerated along the path. High-speed rotation subjects the material to particle-on-particle impact, creating increasingly smaller fines. The centrifugal force drives large particles towards the perimeter, whereas fine particles move towards the center where they exit through the vortex finder.
2.5 Milling of hair fibres

Although milling technology is often associated with inorganic material processing industries such as ceramic processing and powder metallurgy industries, a few literature reports, primarily patents, are also based on the milling of hair fibres. As the viscoelastic nature of hair fibre makes it difficult to mill into powder, different mechanical or chemical pre-treatments have been adopted, especially on wool fibres, followed by a milling process.

Li et al [71] invented an apparatus for preparing fine powders. They also reported a method for pulverizing natural organic substances (such as wool, silk, cotton etc.) into nano-scale fibrous materials [72]. In their method, the clean dry fibres were initially crushed into small pieces of 500 μm in length using a rotary crusher. A water suspension of these small fibre pieces was further processed on an ultrasonic crusher that resulted in a particle suspension with particle size smaller than 20 μm. Finally the suspension was fed into a nano colloid machine to prepare nano particles with a mean particle size of less...
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than 100 nm in diameter and 800 nm in length. The particle size was reported to be controllable through adjusting colloid pressure and colloid time. To achieve dry powder particles, the particle suspension was finally spray dried.

In a different attempt [73], small pieces of wool fibres, around 3 mm in length, cut by rotary blade were pretreated with 0.5% NaClO before grinding on a specially designed machine equipped with two milling pans. To get wool powder of different size, different time of grinding was applied. Wool powder, smaller than 2 μm in diameter and 5-10 μm in length was reported after 3 h of grinding. The ground wool powder exhibited no change in chemical composition with slightly decreased crystallinity and increased thermal stability.

Cheng et al [74] weakened wool fibres with hydrogen peroxide which were then subjected to a three step pulverisation process to finally achieve wool particles smaller than 100 nm in diameter. It was mentioned that the hydrogen peroxide treatment facilitated the powder making process. The pulverized wool powder showed no substantial chemical changes, but decreased the crystallinity.

Joko et al [75] reported dry and wet milling of native and chemically pretreated (sodium sulphite/sodium hydroxide) wool fibres using different mechanical techniques such as homogeniser, ball milling, jet milling and high speed rotor milling. Fractured wool products with different shapes and sizes (powders less than 10 μm in size and spindle shaped particles of around 80 μm in length) were reported, which was found to be dependent on the milling technique.
An explosive puffing treatment with saturated steam of 6 kg/cm² at 164.2 °C has been reported by Miyamoto et al to fracture unmodified and reduced wool fibres into fine powders [76].

Recently Wen et al [77] have explored wool powder fabrication through a process sequence of rotary chopper $\rightarrow$ rotary ceramic mill $\rightarrow$ air jet-mill. The mean wool particle size prepared was 6.2 μm.

### 2.6 Applications of milled hair keratin powder

The importance of fine powder particles lies in their inherent large surface-to-volume ratio. The high surface area of powder particles can potentially improve catalytic processes and inter-facially driven phenomena such as wetting and adhesion. Therefore, the increased specific surface area along with the native chemical reactivity of proteinaceous milled hair keratin powders have interested researchers to work out their applications in toxic chemical adsorption and composite structures.

#### 2.6.1 Toxic chemical adsorption

Due to the presence of nucleophilic groups such as amino (-NH₂), hydroxy (-OH) or thiol (-SH) and high specific surface area, protein fibre powders have huge potential to effectively remove water pollutants, both inorganic and organic in nature.

Wen et al [77] compared the reactivity of wool powder with the parent wool fibre via dye sorption properties and reported that the ability to absorb dyes increased with an increase in the effective surface area, on and inside the wool particles where the dyes can bind to the wool protein. In a different study [78],
they also reported that when the pH of the dye solution was increased from pH 2 to pH 10, the sorption capacity of wool powders to acid dyes decreased, but increased to basic dyes. With regard to hydrophobic and hydrophilic dyes, it was found that the effect of pH on the sorption of hydrophilic dyes to wool powders was more significant than that of the sorption of the hydrophobic dye. Comparison with activated charcoal and other sorbents indicated that the fine wool powders have excellent dye sorption capacity even at room temperature.

Naik et al [79] investigated the transition metal ions binding capacity of wool powders in comparison with the parent wool fibre and found that the rate of Cu$^{2+}$ uptake on the wool powder was dramatically faster (~ 42 fold) than that on the wool fibre. The wool powders also demonstrated a two to nine fold increase in metal ion binding capacity in comparison with commercial cation exchange resins. However, the total amount of Cu$^{2+}$ and Cd$^{2+}$ absorbed on the wool fibre did not change by the milling treatment. Time dependent desorption study revealed that the bound Co$^{2+}$ and Cd$^{2+}$ desorbed quickly whereas only 55% of Cu$^{2+}$ was released to pH 3 solution in 10 min.

The higher rate of sorption and reversible binding of transition metal ions, along with the higher loading capacity of wool powders to transition metal ions in comparison with commercial resins have illustrated the potential of hair keratin powders in the recovery and recycling of metal ions from industrial effluents and contaminated water.
2.6.2 Composite structures

Due to their high specific surface area, retained molecular architecture and inherent reactivity, hair keratin powders have also been processed into different composite structures to enhance their functionality.

2.6.2.1 Composite films

Synthetic polymer films such as polyurethane and polypropylene have been modified with milled keratin powders [80-82]. The milled keratin powders have been either blended with the polymer solution for film casting or with the polymer melt to form pallets which were further hot-pressed into films. The milled keratin powder blended synthetic polymer films have exhibited increased water permeability, moisture regain and dynamic storage modulus along with deteriorated mechanical properties. However, the change in thermal stability of synthetic films on keratin powder blending was not clear. The thermal stability of superfine wool powder blend films was decreased [81, 82] whereas that of superfine down powder blend films was increased in comparison to the respective pure synthetic films [80].

2.6.2.2 Composite fibres

Xushan et al [83] developed fibres from the wool powder and polypropylene blend (2-3% wool powder on weight basis). The fibre fineness in dtex/filament was 2.5-3.0. Although the mechanical properties of the blend fibre deteriorated, the elastic recovery, moisture absorption and dye uptake properties of the blend fibre were found to be improved, consequently conferring the comfort and linen like handle to the ultimate blend fibre shirts.
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2.6.2.3 Composite fabrics

The mechanically milled hair keratin powders have potential use in the apparel industry. They have been attempted to coat onto textile fabrics via different routes to regulate the functionality.

2.6.2.3.1 Solution (Pad-Dry-Cure) route

To explore the functional properties of the nano-wool fibrous materials, a pure cotton woven fabric has been padded, dried and cured with a wool powder emulsion to form a functional film on its surface [84]. During the treatment, the cotton fabric specimen was padded after dipping into the wool powder emulsion for 10 min which was further dried and cured in an oven at 130 °C for 5 min. The warmth retention property of the treated fabric was improved as the thermal conductivity and Qmax values (represents fabric cool sensation on touching) decreased from ~0.53 W/mk to ~0.48 W/mk and ~142 to ~129 respectively. Furthermore, the maximum moisture absorption rate, tested on the Moisture Management Tester, decreased from around 300 %/s for the untreated fabric to 20 %/s after the treatment.

Cheng et al [85] studied the ultraviolet protection and wrinkle recovery properties of the nano-wool powder coated cotton fabrics. Wool powder with a mean particle size of 76.8 nm was coated on cotton fabrics by a pad-dry-cure method. The wrinkle recovery angle of the treated cotton fabric increased from 70-90° to 120-130° in warp and weft directions, whereas the Ultraviolet protection factor (UPF) enhanced from ~7 to ~12.
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2.6.2.3.2 Dry powder coating

Xin et al [86] adopted a different approach to improve the dyeing ability of melt spun isotactic polypropylene (iPP) fibres. They coated the superfine down fibre powder (SDP) on the surface of the melting iPP fibres by passing it through an auxiliary apparatus, incorporated with a fan and heating element to control the speed and temperature of the airflow over the iPP fibres. The SDP coating on the iPP fibre surface led to a large improvement in its dyeing properties with increased K/S and a* values. However, the powder coated iPP fibres showed poor washing fastness due to dye migration from SDP and poor adhesion of SDP.

Although hair keratin powders can be used as a functional agent to regulate various functional properties of textile fabrics, the stability of powder coatings has remained a concern.

2.7 Electrostatic powder coating

The electrostatic powder coating technique relies on charge induction on the sprayed powder particles, seeking nearest grounded objects that are purposefully made to be the target substrates. The sprayed powder particles get repelled from each other due to the similar charge and transform in a cloud during their flight towards the substrate, which results in improved coating evenness and transfer efficiency. The deposited powder particles on the grounded substrate remains adhered to the product. Although electrostatic powder coating technique is widely adopted for coating of thermoplastic polymer powders which are later fused on the surface of the substrate by heat
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treatment, powder particles with natural origin could also be immobilized by adhesive which is pre-coated on the substrate.

In a typical electrostatic powder coating process, the powder to be coated is fluidised in a reservoir by blowing air through it from a perforated base. The fluidised powder is further blown along a feed pipe to a dispensing and charging nozzle. A cloud of the charged powder particles ejected from the nozzle flow towards the target substrate to be coated.

Although the electrostatic powder coating has been widely employed in painting and metal finishing industry, it remains almost unexplored in applying protein powders onto textiles. Only a few reports are available on electrostatic coating of thermoplastic polymer powders on textile substrates in literature. Woolard et al [87] described a method to fabricate glass fibre composites. They used an electrostatic powder spray gun to deposit thermoplastic polymer powder continuously on a moving glass fibre tow. The glass fibres were softened by using hot nitrogen and made conductive by applying fine water mist to assist in the powder coating process. The fibres in the tow were kept sufficiently separated from each other by passing over a nonconductive ceramic sphere to achieve even and all-over the fibre surface powder deposition. The fibre tow was thereafter guided over a grounded pulley where the powder gun nozzle was directed. The fibre tow was finally heat treated to fuse the electrostatically deposited polymer particles onto the fibre surface and form a composite structure.

2.7.1 Mechanisms of powder charging

There are three basic mechanisms by which powder particles could be charged in the dispensing and charging gun, namely corona, triboelectric and induction
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charging. The induction charging mechanism is typically ineffective for
 electrostatic powder coating process due to the inherent high volume resistivity
of many powders. Thus, there are two basic electrostatic powder coating
systems which are commonly used in commercial applications; the corona
charging system (corona gun) and the tribo charging system (triboelectric gun).

2.7.1.1 Triboelectric powder charging system

In a triboelectric gun, the powder particles are charged by the frictional contact
with the gun barrel and do not require an external voltage supply. The material
of the gun barrel should be able to maximise the triboelectric charging effect,
which is typically made from either teflon or nylon. The tribo charging system
produces better powder coating effects especially on substrates with complex
shapes and is therefore preferred in some applications.

2.7.1.2 Corona powder charging system

In the corona charging system, the powder particles are intensively charged by
ionic bombardment making the whole system more reliable and predictable. A
high voltage supply is needed for generating corona discharge which
consequently generates a strong electric field, driving the powder particles
towards the substrate. However all of the ions generated by the corona
discharge are not collected by the powder particles and move towards the
coating substrate where it may generates back corona discharge that is likely to
disturb the coating quality.
Figure 2.10 Schematic illustration of a. triboelectric (modified from [96]) and b. corona powder charging (modified from [97]) systems.
Chapter 3

Experimental methods

All materials, instruments, experimental procedures and characterization methods used during this study are presented in this chapter.

3.1 Materials

3.1.1 Natural fibres

Cashmere guard hair was supplied by Cashmere Connections Pty Ltd, Bacchus Marsh, Victoria, Australia. The guard hairs were mechanically dehaired from a scoured cashmere fleece at the supplier’s premises and were contaminated with vegetable matters and other foreign matters. Merino wool was procured from M/s Australian country spinners, Australia and eri silk cocoons from north east India.

3.1.2 Metal ions and buffer solutions

Metal ion absorption property of cashmere guard hair powder was analysed in comparison with similarly processed other natural protein fibre powders and its parent guard hair by radiotracer technique and involved cold (natural) metal ions, their respective hot (radioactive) metal ions and buffer solutions.

3.1.2.1 Cold (natural) metal ions

Cobalt chloride (1000 PPM, AAS standard) was used as cold $\text{Co}^{2+}$ source and was supplied by Australian Chemical Reagents (ACR). Zinc nitrate (0.1 M) and
Experimental methods

Ammonium dichromate (0.1 M) were respectively used as cold Zn\(^{2+}\) and Cr\(^{6+}\) sources and were purchased from Sigma Aldrich. NaCl and KCl were used as the source of alkali earth metal ions, whereas MgCl\(_2\).6H\(_2\)O and CaCl\(_2\).2H\(_2\)O were used as the source of alkaline earth metal ions during the competitive metal ion absorption studies.

3.1.2.2 Hot (radioactive) metal ions

High specific activity (SA) radioisotopes \(^{57}\)Co\(^{2+}\) (\(t_{1/2}=271.8\) days, SA=2.59 \(\times\) 10\(^5\) GBq/g), \(^{65}\)Zn\(^{2+}\) (\(t_{1/2}=243.66\) days, SA=151.63 GBq/g) and \(^{51}\)Cr\(^{6+}\) (\(t_{1/2}=27.7\) days, SA=20872.05 GBq/g) were used in the form of CoCl\(_2\), ZnCl\(_2\) and Na\(_2\)CrO\(_4\), respectively and they were purchased from Perkin Elmer.

3.1.2.3 Buffer solutions

The buffer solutions used during the metal ion sorption studies were: 0.1M KCl adjusted with 3.0M HCl for pHs 1 and 2; 0.1 M glycine/0.1M NaCl adjusted with 3.0 M HCl for pH 3; 0.1 M sodium acetate adjusted with 3.0 M HCl for pHs 4 and 5; 0.1M sodium phosphate dibasic adjusted with 3.0M HCl for pHs 6, 7 and 8, 0.1 M glycine/0.1M NaCl adjusted with 0.5M NaOH for pH 9. All reagents and solvents used were of analytical grade and were used as received. Milli-Q grade water was used in all metal ion related experiments.

3.1.3 Materials for powder coating

Polyester fabric (flat knitted from 100% polyester multifilament yarns with 90 denier linear density, 19 wales/cm, 26 courses/cm and 2.76 stitch length) was
Experimental methods

used as substrate for powder coating. Polymethyl-methacrylate (PMMA) based commercial resin (*Tubicoat S-1057 White*) from *M/s CHT Australia Pty Ltd* was used as an adhesive agent during the coating process.

### 3.1.4 Materials for antibacterial test

Antibacterial property of the silver ion treated cashmere guard hair powder coated fabric was evaluated against the gram negative bacteria *Escherichia coli* (*E. coli*) *ATCC*® *11229™*. The antibacterial study involved modified *Trypton* soya broth from *Oxoid Ltd., England* as the nutrient broth and *CMO131 Trypton soya agar* (from *Oxoid Ltd., England*) as the nutrient agar for the agar plates.

### 3.2 Powder production

The mechanical milling of cashmere guard hair was accomplished by a series of processes, in sequence as described herewith:

#### 3.2.1 Pre-cleaning

Cashmere guard hairs were decontaminated by passing them through a sample carding machine from *Mesdan, Italy* three times. The guard hairs were further manually cleaned to get rid of adhering traces of foreign matters. In case of merino wool, it was procured in the form of top and was free from contaminants and hence, was used as procured. Whereas, in case of eri silk, the cocoons were chemically cleaned by degumming with laboratory grade 2 g/L *Na₂CO₃* and 0.6 g/L sodium dodecyl sulphate at 100 °C, with a material-to-liquor ratio of 1:25 (kg/L) for 20 min in a *Thies* laboratory dyeing machine.
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The cocoons were subsequently washed thoroughly with warm distilled water followed by copious amount of cold distilled water and were finally dried overnight at 60 °C.

3.2.2 Chemical pre-treatment

Partial acid hydrolysis of the clean guard hairs was carried out, following the process developed by Előd et al. [88], in a Thies Eco-Block LFA package dyeing machine by using a loose stock carrier. Guard hairs were partially acid hydrolysed in two batches of 500 g each with a treatment time of 4 h for one batch and 10 h for the other. The partial acid hydrolysis was carried out by a treatment with 1 M HCl (35 % AR grade from Merck) and 1 % (wt/wt) Hydropol TN 450 (a non-ionic detergent from M/s Huntsman) at 80 °C with a material to liquor ratio of 1:68. The hydrolysed guard hairs were rinsed with water at room temperature followed by neutralising with 0.1 % ammonia solution (30%, AR grade from Chem Supply). Any remaining free ammonia was overcome by two final cold water rinses. The hydrolysed guard hairs were dried overnight in a laboratory convection oven (Heraeus Oven, Thermo Scientific) at 60 °C. The weight loss on hydrolysis was determined by weighing the guard hairs before and after the hydrolysis on conditioning at 65 ± 2 % RH and 20 ± 2 °C for 48 h.

3.2.3 Chopping

Pre-cleaned, dry control (i.e. as received) and partially acid hydrolysed cashmere guard hairs were initially chopped into approximately 2-3 mm hair snippets separately by using a laboratory scale commercial cutting mill,
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*Pulverisette 19* from *Fritsch GmbH, Germany* (Fig. 3.1). The cutting mill was equipped with a 316 stainless steel sieve cassette, having 1 mm trapezoidal perforations.

![Figure 3.1 Pulverisette 19 – Cutter Mill (Modified from the source: http://www.fritsch-milling.com).](image)

The grinding chamber of Pulverisette 19 houses a rotor at the centre, which in combination with three fixed blades, located at the inside wall of the chamber and set at different angles, gave the initial hair fibre size reduction. The guard hair fibres were repeatedly crushed and ground in the grinding chamber until they finally passed through the perforations in the sieve cassette and were carried by the air flow into the collection chamber.

### 3.2.4 Attritor milling

Cashmere guard hair fibre samples, in the form of snippets were separately wet milled in a batch size of 200 g by using an attritor mill (*IS, Union Process, USA*), equipped with a Teflon coated 9.5 l tank loaded with 20 kg yttrium doped zirconium oxide grinding media (5 mm) (Fig. 3.2). Deionised water was
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used to achieve a 1:10 material (kg) to liquor (L) ratio during milling. Stirrer speed and milling time were 280 rpm and 6 h, respectively. Cold water was circulated through the external jacket of the milling chamber to control the temperature of the milling slurry.

3.2.5 Spray drying

The attritor milled slurry of each cashmere guard hair fibre sample was separately spray dried by using B290 mini spray dryer from Buchi Labortechnik AG (Fig. 3.3). The slurry was fed to the spray dryer atomiser by a peristaltic pump at a rate of 10 ml/min. The atomiser was maintained at room temperature by circulating cold water through the external jacket. The incoming slurry at the atomiser was maintained under pressure and was intermittently subjected to the jet of compressed air (5 strokes/min). The sprayed slurry droplets were directed to a path governed by air flow with inlet air temperature maintained at 130 °C, while the outlet air temperature was
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around 70 °C. Dry cashmere guard hair powder particles were finally separated with the help of a cyclone and collected in a glass vessel.

![Figure 3.3 B290 – Mini Spray Dryer (Source: http://www.buchi.com).](image)

### 3.2.6 Air jet milling

Attritor milled – spray dried powder particles from each cashmere guard hair fibre sample were further subjected to the air jet mill, *Micronizer* from *Sturtevant Inc.*, *USA* (Fig. 3.4). The spray dried powder was fed to the mill in a continuous stream in conjunction with the compressed air (40 kg/cm²) which was further subjected to the grinding action in the grinding chamber through inter-particle collision under 110 kg/cm² grinding air pressure. The air jet milled powder particles were finally separated from the air stream by using a cyclone and collected in a stainless steel vessel.
3.3 Sample nomenclature

Control and chemically treated cashmere guard hairs as well as the corresponding attritor milled – spray dried and air jet milled powder particles are henceforth denoted by their nomenclatures as specified in Table 3.1.

Table 3.1 Sample Nomenclature

<table>
<thead>
<tr>
<th>Cashmere guard hair samples</th>
<th>Material Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control cashmere guard hair (no treatment)</td>
<td>CHF</td>
</tr>
<tr>
<td>Control merino wool fibre</td>
<td>MWF</td>
</tr>
<tr>
<td>Control eri silk fibre</td>
<td>ESF</td>
</tr>
<tr>
<td>4 hr partially hydrolysed cashmere guard hair</td>
<td>PH4CHF</td>
</tr>
<tr>
<td>10 hr partially hydrolysed cashmere guard hair</td>
<td>PH10CHF</td>
</tr>
<tr>
<td>Spray dried particles made from CHF</td>
<td>CHF-AM</td>
</tr>
<tr>
<td>Spray dried particles made from MWF</td>
<td>MWF-AM</td>
</tr>
</tbody>
</table>
Experimental methods

| Spray dried particles from ESF | ESF-AM |
| Spray dried particles made from PH4CHF | PH4CHF-AM |
| Spray dried particles made from PH10CHF | PH10CHF-AM |
| Air jet milled particles made from CHF-AM | CHF-AJ |
| Air jet milled particles made from PH4CHF-AM | PH4CHF-AJ |
| Air jet milled particles made from PH10CHF-AM | PH10CHF-AJ |

3.4 Sorption properties to heavy metal ions

3.4.1 Metal ion absorption of powder sorbents

Absorption property of the control cashmere guard hair powder particles (i.e. CHF-AM) towards the oppositely charged heavy metal ion species (cationic: Co$_{2+}$ and Zn$_{2+}$, anionic: Cr$_{6+}$ in the state of HCrO$_4^-$) was studied in comparison with the parent cashmere guard hair (CHF) and similarly processed merino wool fibre and eri silk fibre powders (MWF-AM & ESF-AM) by radiotracer technique. Due to their approximately similar particle sizes, only attritor milled-spray dried powder particles have been considered in the heavy metal absorption study.

The metal ion absorption property towards Co$_{2+}$, Zn$_{2+}$ and Cr$_{6+}$ was tested over the pH range of 3 to 9 for the former two and 1 to 8 for the later. A typical radiotracer technique based metal ion absorption study involved accurately weighing approximately 10 mg in quadruplicate of each sorbent (powders/fibres) followed by the addition of buffer solution (1.98 mL) at 21 °C. The sorbents were allowed to incubate in buffer solution for 30 min. Then a stock solution of Co$_{2+}$, Zn$_{2+}$ or Cr$_{6+}$ (as cobalt chloride, zinc nitrate or potassium dichromate) doped with their respective radioisotopes (i.e. $^{57}$Co$_{2+}$, $^{54}$Zn$_{2+}$, $^{51}$Cr$_{6+}$) was added to the buffer solution followed by further incubation for another 30 min. The amount of metal ions adsorbed was determined by measuring the radioactivity of the samples.
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$^{65}\text{Zn}^{2+}$ or $^{51}\text{Cr}^{6+}$) was prepared for each buffer condition. An aliquot of the stock solution was added to the suspension so that the final concentration of metal ions was $10^{-4}$ M in a total reaction mixture of 2 mL. Each reaction mixture contained approximately 100,000 counts per minute (CPM) of $^{57}\text{Co}^{2+}$, $^{65}\text{Zn}^{2+}$ or $^{51}\text{Cr}^{6+}$ as appropriate. The reaction mixtures were vortexed (SLRM-2M Intelli Mixer Rotomix) and then left to rotate at 30 rpm for up to 24 h. At set time intervals (Co$^{2+}$ & Zn$^{2+}$: $t$=5, 15, 30, 60 min and 24 h; Cr$^{6+}$: $t$=15 min, 2, 6 and 24 h), the mixtures were centrifuged at 5000 rpm for 5 min (Eppendorf 5804R) and supernatant sampled (3×20 µL). The radioactivity associated with each aliquot was determined using a gamma counter (Wallac Wizard 1480).

The gamma emissions used to monitor $^{57}\text{Co}^{2+}$, $^{65}\text{Zn}^{2+}$ and $^{51}\text{Cr}^{6+}$ radioisotopes were 122.1 keV, 1115.55 keV and 320.08 keV, respectively.

The concentration of the natural metal ion, $C$, has a linear relationship with the radioactivity count, $A$:

$$C = A \times a$$

----- Equation 3.1

where, $a$ is a coefficient related to the type of metal ions, the ratio between the natural metal ion and its radioisotope in the solution. Therefore the percentage of the metal ions removed by the sorbent, i.e. the absorption yield, at the given time point $t$ could be calculated as per the following equation:

$$\% \text{ Absorption Yield} = \frac{A_0 - A_t}{A_0} \times 100$$

----- Equation 3.2
Experimental methods

where, $A_0$ is the total amount of radioactivity added to the reaction mixture and $A_t$ is the radioactivity in the buffer solution at time $t$ after exposure to sorbent.

### 3.4.1.1 Effect of metal ion concentration

The effect of metal ion concentration on the absorption yield of the corresponding heavy metal ions by the controlled sorbent samples (i.e. CHF, CHF-AM, MWP and ESP) was examined at the optimum pH condition only by following the similar procedure to the metal ion absorption study with an initial metal ion concentration in the range from $1 \times 10^{-6}$ M to $1 \times 10^{-4}$ M. The absorption yield was monitored at two time points only (i.e. $t=15/30$ min and 1 day).

### 3.4.1.2 Effect of partial acid hydrolysis

The effect of partial acid hydrolysis of cashmere guard hair on the absorption yield of the heavy metal ions by the corresponding powder particles (i.e. PH4CHF-AM & PH10CHF-AM) was examined by following the similar procedure to the metal ion absorption study. The measurements were conducted at the optimum pH conditions only, i.e. pH 8 for Co$^{2+}$ & Zn$^{2+}$ and pH 2 for Cr$^{6+}$, which were determined in the absorption study.

### 3.4.1.3 Competitive metal ion absorption

Competitive metal ion absorption by the controlled sorbent samples was studied for Co$^{2+}$ only as the powdered sorbent samples were found to be more efficient in absorbing the metal ion during the absorption study. The absorption study was conducted from $10^{-4}$ M Co$^{2+}$ solution in Milli-Q water in competition with Na$^+$, K$^+$, Mg$^{2+}$ and Ca$^{2+}$. The alkali and alkaline earth metal
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Ions were selected for the competitive metal ion absorption study as they are often found in large quantities in industrial waste water streams. Co$^{2+}$ binding by the sorbent samples was monitored in competition with 200 PPM Na$^+$, 35 PPM K$^+$, 100 PPM Mg$^{2+}$ and 125 PPM Ca$^{2+}$ separately as well as in conjunction. The concentrations of the alkali and alkaline earth metal ions used during the study were close to their normally encountered concentrations in industrial effluents [89]. The absorption of Co$^{2+}$ was studied from the conjugate metal ion system in Milli-Q water only and did not involve buffer solutions so as to avoid competition from other ions present in the buffer solution. The rest of the procedure was similar to the binding study and involved centrifuging the reaction tubes containing the sorbent samples with absorbed $^{57}$Co$^{2+}$, taking aliquot samples at t=30 min & 1 day on centrifugation, and measuring radioactivity on the gamma counter.

### 3.4.2 Metal ion desorption of powder sorbents

To examine the desorption properties, each sorbent was preloaded with metal ion (doped with their respective radioisotope) by incubating for 24 h at the optimum pH condition. The samples after loading with metal ions were then separated from the buffer solution by centrifugation and then redispersed in a fresh buffer solution at a pH known to have poor respective metal absorption i.e. the desorbing buffer solution (pH 4 for Co$^{2+}$ & Zn$^{2+}$ and pH 8 for Cr$^{6+}$, respectively, as determined in the absorption study). The concentration of the metal ions was determined by measuring the radioactivity of the solution after desorption. The desorption yield was calculated by the following equation:
where, $A_0$ is the initial radioactivity of the solution for metal ion preloading onto sorbent at the optimum pH, $A_{t=24}$ is the radioactivity remaining in the solution after 24 hours of preloading and $A_{r,t}$ is the radioactivity released at time $t$ after exposure to the desorbing buffer solution.

3.4.3 Silver ion absorption of powder coated fabric

The powder coated fabric samples for silver ion loading were prepared by electrostatic powder coating (explained in the section 3.5). Powder coating was accomplished by feeding 1 g of control cashmere guard hair powder (CHF-AM) to the corona gun and employing optimized process parameters (i.e. $2 \times 10^5$ N/m$^2$ air pressure, 20 cm substrate distance, 60 kV applied voltage and 50 % relative humidity) with 20 % resin concentration.

The silver ion absorption potential of the cashmere guard hair powder and the powder coated fabric samples was studied with 50 ppm silver ion solution at different pH values (pH 1.4, 8.5, 10 and 11). The effect of silver ion solution concentration was also investigated at pH 10.

The pH of the 50 ppm silver ion solution, prepared in milli-Q water from the standard AAS grade stock solution (from BHD Chemical (Australia) Pty Ltd) was 1.4 and the same was adjusted with ammonium hydroxide (30% liquid ammonia solution) from Chem-Supply Pty Ltd., Australia. While adjusting the pH of the silver solution, the required volume of the standard stock solution was initially diluted with milli-Q water in a beaker; its pH was adjusted by
Experimental methods

drop wise addition of ammonium hydroxide under magnetic stirring and finally made up to the mark in the volumetric flask with further addition of milli-Q water. With the initial addition of ammonium hydroxide, silver solution appeared to be precipitating and transformed into a colloid. However the solution became clear with the further addition of ammonium hydroxide, at around pH 8.4. All the prepared silver ion solutions were filtered under vacuum with 542 Whatman filter paper before conducting the silver ion absorption studies.

The silver ion absorption studies were carried out in a batch process for experimental simplicity. A typical experimental batch consisted of four types of samples, each in duplicate: the base fabric, the resin coated fabric, the cashmere guard hair powder coated fabric and the powder itself. Each fabric sample was circularly cut (38 mm diameter) from the respective fabric type/swatch. In the case of the solo cashmere guard hair powder sample, the powder weight was equivalent to the average value of the actual powder weight onto each powder coated fabric sample. All samples were taken in separate reaction tubes and agitated with silver ion solution at 1:400 material (powder weight) to liquor ratio (MLR) under ambient conditions on a laboratory rotator. Measurements of silver concentration in the studied absorption system were carried out with a *Varian SpectrAA 140* atomic absorption spectrometer equipped with a flame furnace. A hollow cathode lamp (*Varian*) was used for the measurement of Ag at 338.3 nm wavelength and a 0.2 nm slit width was selected. Air/Acetylene mixture was used as the fuel gas with a flow rate of 3.5 l/min for air and 1.5 l/min for acetylene.

The silver ion absorption yield in the given absorption system was calculated as per the Equation 3.4. The standard deviation for each given sample type was
 Experimental methods
 illustrated as error bars in the corresponding graphical representation of the results.

\[ Ag \text{ Absorption Yield (\%)} = \frac{C_{t=0} - C_t}{C_{t=0}} \times 100 \]

-------Equation 3.4

where, \( C_{t=0} \) is the initial silver ion concentration and \( C_t \) is the silver ion concentration at time \( t \) minutes.

### 3.5 Powder coating on polyester fabric

Schematic of the electrostatic powder coating setup used in the control cashmere guard hair powder (CHF-AM) coating on the polyester fabric substrate has been illustrated in Fig. 3.5. A manual powder coating corona gun (\textit{MG 801} from \textit{Infratech, USA}) was horizontally arranged at a certain distance from the target fabric swatch clinging onto the grounded aluminium plate such that the HV electrode tip pointed perpendicularly towards its centre.

Prior to powder coating, 100 cm\(^2\) fabric swatches were cut from the base flat knit polyester fabric with a Zweigle GSM Cutter. Each fabric swatch was coated with a thin layer of resin (\textit{Tubicoat S-1057}) through a dip coating process. Briefly, the fabric swatch was first immersed in 20% resin solution for 1 minute under ambient conditions, and then passed through a single nip padding mangle (\textit{M/s Rapid Labortex Co. Ltd., Taiwan}) under 0.7 bar top roller pressure. Each resin treated wet fabric swatch was separately used as a target substrate for powder coating.
Experimental methods

After spraying the cashmere guard hair powder, the powder coated fabric swatches were immediately hot pressed for 10 minutes on a laboratory hot press (Industrial Hydraulics Services Pty Ltd., Australia). To achieve good coated powder stability and to avoid its delamination during hot pressing, the powder coated fabric was presented in an assembly of different components as shown in Fig. 3.6. Two stainless steel plates (1) were separately covered with synthetic foam (2) to provide cushioning to the fabric and were wrapped in aluminium foil (3) which held them together. Each of the metal plate assembly (1-2-3) was covered with a polytetrafluoroethylene (PTFE) film (4) to provide non sticky surface to the powder coated fabric (5) which was sandwiched in-between. The complete assembly with the powder coated fabric (powder coated surface facing up) was presented to the hot press at 90 °C under 0.7 bar pressure.

On hot pressing, the powder coated fabric was finally cured at 130 °C for 3 minutes in a laboratory stenter (Rapid Labortex Co. Ltd., Taiwan) to get the final cashmere guard hair powder coated fabric swatches.
Experimental methods

Figure 3.6 Hot pressing for the powder coated fabric.

On achieving considerably good powder coating, the electrostatic powder coating process was subsequently optimised to achieve maximum powder utilization. Process parameters considered during the process optimization were applied electrode (gun) voltage, substrate distance (distance between the electrode tip and the substrate), air pressure and relative humidity.

3.6 Antibacterial properties

Antibacterial activity of the base, resin coated and cashmere guard hair powder coated fabric samples was tested against gram negative bacteria, *Escherichia coli* (*E. coli*), before and after silver ion treatment at different concentrations (10, 50 and 100 ppm). The fabric samples were circularly cut (38 mm in diameter) from the respective fabric type/swatch, as in the silver ion absorption study. The silver ion treated fabric samples were prepared by treatment with the specific concentration silver ion solution at pH 10, 1:400 MLR for 72 h, followed by a final rinse with copious amounts of running deionised water.
Experimental methods

Silver ion treated fabric samples were also investigated for wash durability of their antibacterial activity. The silver ion treated fabric samples were washed with 1 g/l non-ionic detergent, *Hydropol TN 450* from *M/s Huntsman* at 1:50 MLR and 60 °C for 30 minutes. The fabric samples were rinsed and air dried after each wash.

The antibacterial activity test involved preparation of the bacterial inoculums in 5 ml of the nutrient having $10^8$ colony forming units (CFU) ml$^{-1}$. These bacterial inoculums were used to perform an antibacterial test onto the different fabric samples as per the *AATCC 100 - 2004* test standard. The solution from each sample containing bacterial inoculums was diluted $10^0$, $10^1$, $10^2$ and $10^3$ times with sterile Milli-Q water. Each diluted bacterial inoculums solution was plated in triplicate on agar plates and incubated at 37 °C for 18 h. Since the plates with $10^0$, $10^1$ and $10^2$ dilution had an uncountable number of bacterial colonies for the untreated base fabric sample; plates with $10^3$ dilutions were considered for evaluating the antibacterial activity which was expressed as the percentage reduction of the bacterial colonies by the treated fabric samples as shown in Equation 3.5 [90]:

\[
\text{% Antibacterial activity} = \frac{U - T}{U} \times 100
\]

-------- Equation 3.5

where, $U =$ average number of bacterial colonies in untreated fabric samples, $T =$ average number of bacterial colonies in fabric samples treated with silver ion solution.
Experimental methods

3.7 Materials characterizations

3.7.1 SEM

SEM (Supra 55 VP) from Carl Zeiss Microscopy GmbH, Germany was used to characterize the surface morphology of cashmere guard hair, its powder and the powder coated fabric samples. The morphology of cashmere guard hair was observed and compared with the fine cashmere fibres. Hair, fibre, powder and the powder coated fabric samples were coated with approx. 15 nm gold layer on a sputter coater (Bal-Tec sputter Coater SCD 050) before imaging. All the hair/fibre and powder surface morphologies were observed at 10 kV accelerated voltage, whereas 5 kV accelerated voltage was used for the powder coated fabric. The working distances used during imaging were: 24.5 mm for cashmere guard hair and cashmere fibre and 8.5 mm for all powder samples. Cashmere guard hair and the powder coated fabric samples were also characterized for their transverse morphology by taking respective 5 μm thin cross-sectional slices on microtome (CUT 5062 SLEE MAINZ, Germany). Cashmere guard hairs were embedded in a resin (TAAB, England) using a mould and cured overnight at 60 °C to assist its sectioning on the microtome. The sectioned slices were also gold coated (~15 nm layer) on the sputter coater before imaging. The transverse morphology of guard hair was observed at 10 kV accelerated voltage and 8.5 mm working distance, whereas that of powder coated fabric was observed at 5 kV accelerated voltage and 23.5 mm working distance.
Experimental methods

3.7.2 Single fibre analyser (SIFAN)

Guard hairs were conditioned for a minimum of 48 h at the standard atmospheric laboratory conditions (65 ± 2 % relative humidity and 20 ± 2 °C) before the measurements on the single fibre analyser (SIFAN) from BSC Electronics, Australia. Mean and standard deviation of hair diameter and hair tenacity examined on SIFAN were calculated and presented for the considered guard hair sample types.

3.7.2.1 Hair diameter

Control cashmere guard hairs (CHF) were characterised for their diameter by testing 50 single guard hairs on SIFAN. Middle portion from each guard hair was presented to SIFAN for its continuous optical measurement of hair diameter by scanning over the length of 30 mm. SIFAN reported average diameter of the examined guard hair over its scanned length.

3.7.2.2 Hair tenacity

Single hair tenacity of control (CHF) and partially acid hydrolysed (PH4CHF and PH10CHF) cashmere guard hairs were examined on SIFAN to determine the level of damage caused to the hair fibres by the chemical treatment. A gauge length of 40 mm and jaw separation speed of 500 mm/min were used during the breaking load measurements. 50 guard hairs were tested, from each cashmere guard hair sample. Guard hairs were conditioned for a minimum of 48 h at the standard atmospheric laboratory conditions before the measurement. The guard hair tenacity was calculated from the breaking load measurement on SIFAN and the linear density. The linear density in dtex or gram per 10,000 m
Experimental methods

was calculated by measuring the weight of 100 guard hairs cut into 40 mm length from middle hair portion.

3.7.3 Hair bending abrasion

For cyclic bending abrasion fatigue test, cashmere guard hairs were examined on FibreStress Tester from Textechno, Germany. The hairs were traversed over a 2 mm diameter stainless steel wire for 10 mm distance at 90 ° arc under 0.8 g tension. The number of cycles required to break the hair was automatically recorded by the instrument. Guard hairs were conditioned for a minimum of 48 h at the standard atmospheric laboratory conditions before the measurement. A total of 70 hairs were tested for each guard hair sample type and the mean and the standard deviation of number of cycles required to break the hair was reported.

3.7.4 Particle size analysis

Mastersizer 2000 from Malvern Instruments, UK was used to analyse the powder particle sizes via laser diffraction technique. The dispersion medium used during the measurement was deionised water for attritor mill slurry and propan-2-ol (from Sigma-Aldrich) for spray dried and air jet milled dry powder particles. Refractive index of 1.553 and imaginary refractive index of 0.01 for cashmere guard hair and its powders were used for necessary calculations by the operation software. The volume based size distribution of particles is used for reporting all particle size measurements.

The d(0.1), d(0.5) and d(0.9) values indicate that 10 %, 50 % and 90 % of the particles measured were less than or equal to the size stated. The span (η) is the
Experimental methods

width of the particle size distribution based on d(0.1), d(0.5) and d(0.9) which was calculated following the Equation 3.6 [91]:

\[ \eta = \frac{d(0.9) - d(0.1)}{d(0.5)} \]

----- Equation 3.6

There was no significant variation between the three d(0.5) measurements per given powder sample from Mastersizer 2000 and hence no error bars are plotted while reporting the results.

3.7.5 FTIR

The Fourier transform infrared (FTIR) spectra of cashmere guard hair and its powder samples were obtained under Attenuated Total Reflectance mode using Brucker VERTEX 70 spectrometer with a resolution of 4 cm\(^{-1}\) and 64 scans per sample.

3.7.6 XPS

The surface composition of the cashmere guard hair fibre and its powder samples was investigated using K-Alpha X-ray Photoelectron Spectrometer (XPS) from Thermo Fischer Scientific with monochromated X-rays focused on a 400 \(\mu\)m spot size. Excessive charging of the samples was minimised using a flood gun during XPS measurements. High resolution peak scans were performed at 20 eV pass energy. The peak scans were employed to obtain the elemental composition of C, O, N, and S.
Experimental methods

3.7.7 Zeta potential

The zeta potential of powder samples (CHF-AM, MWF-AM & ESF-AM) was determined by measuring electrophoretic mobility of the respective powder samples (0.1 g) in suspension with buffer solutions (1 ml) varying from pH 1-9 at 25 °C using Zetasizer Nano ZS (Malvern Instruments, UK) after incubating overnight. The measurement was repeated three times for each powder sample in suspension with fresh buffer solutions and the average value was reported along with the standard deviation.

3.7.8 TA DSC

Differential scanning calorimetry of the powder sorbents of interest was performed using a TA DSC Q 200. Approximately 5 mg of the powder sample was taken in the aluminium cells that were subsequently sealed to avoid moisture evaporation during the measurement. The materials under investigation were thermally scanned over the temperature range 30-350 °C under the heating rate of 10 °C/min. The spectra were later on analysed on the Thermal Advantage - Q Series instrument control application.

3.7.9 BET surface area

The BET surface areas were determined by the nitrogen adsorption technique using Tristar 3000 instrument from Micromeritics, USA. Approximately 0.5 g of specimen was placed in a glass sample holder. In the case of cashmere guard hairs, 2-3 mm snippets were used for the measurements. The samples were degassed under N₂ gas at 110 °C for 60 min prior to N₂ gas adsorption
Experimental methods

measurement under cryogenic conditions. The measurement was repeated three times to report average and standard deviation values for BET surface area.

3.7.10 Moisture regain

Glass beakers (50 ml capacity) were used as powder containers with small evaporating dishes as covering lids during the moisture regain measurement. All powder container assemblies were initially dried at 105 °C for 1 h in a laboratory convection oven (Heraeus Oven, Thermo Scientific) and weighted up to four decimal places (as W₀) by using XS204, Mettler Toledo weighing balance with an accuracy of 0.1 mg. Approximately 100 mg of each powder sample was taken in a separate container assembly with known W₀. The powder sample holding container assemblies were subsequently dried at 105 °C for 1 h, conditioned for a minimum of 48 h at the standard atmospheric laboratory conditions and weighed (as W₁). All powder sample holding assemblies were later-on dried at 105 °C for 30 min and weighed after each 20 min of further drying until the last three consecutive weights remained unchanged which was recorded as W₂. The percentage of moisture regain was finally calculated as below:

\[
\text{Moisture regain} \, (\%) = \left( \frac{W₁ - W₂}{W₂ - W₀} \right) \times 100
\]

----- Equation 3.7
Experimental methods

3.7.11 Powder densities and derived indices

The powder bulk density was examined by pouring each powder sample separately from a certain height in a measuring cylinder until it reaches the final 10 ml mark. Each powder sample weight with 10 ml volume was determined from the blank and filled measuring cylinder weights. The bulk density was subsequently determined in g/cm³ by dividing the powder weight (g) with its volume (cm³). For determining the powder tapped density, the 10 ml powder filled measuring cylinder with each powder sample was manually tapped consistently against a stable desk surface. Powder volume was measured after 100 taps and the new powder (tapped) density was calculated. The measurement was repeated four times for each powder sample and mean bulk density (ζ₀) and tapped density (ζ₁₀₀) were reported with respective standard deviations. All powder samples were conditioned under standard atmospheric laboratory conditions for a minimum of 48 h before the measurement.

The flow and cohesion properties of the powder samples were evaluated from the Carr’s flowability index (IC) [92] and the Hausner’s ratio (HR) [93] respectively as below:

\[
Carr \ Index = \frac{\zeta_{100} - \zeta_0}{\zeta_{100}} \times 100
\]

----- Equation 3.8

\[
Hausner \ ratio = \frac{\zeta_{100}}{\zeta_0} \times 100
\]

----- Equation 3.9
Experimental methods

3.7.12 Positron annihilation lifetime spectra (PALS)

For each of the studied protein fibres (CHF, MWF & ESF) and their respective powder samples (CHF-AM, MWF-AM & ESF-AM), PALS measurements were performed at room temperature. The lifetime spectra of positrons were measured using a conventional lifetime system with digital oscilloscope (LeCroy Wavepro). The positron annihilation signals were detected by two BaF₂ scintillators attached to H3378 (Hamamatsu Photonics) photomultiplier tubes (PMT). For each experiment, the same quantity of samples were sandwiched around a 10 micro curie positron source (²²Na), prepared by evaporating ²²NaCl solution on a Kapton foil of 7 mm thickness. Each spectrum contained about $6 \times 10^6$ counts. In order to determine a number of lifetime components, deconvolution was performed on the lifetime spectra. The observed spectra were analysed with a time resolution of about 170 ps by using the RESOLUTION computer program [94].

The free volume radius ($R$) in nanometres was calculated as per the simple relation (Equation 3.10), according to Nakanishi et al [95].

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}$$

-----Equation 3.10

where, $\tau_3$ (o-Ps lifetime) and $R$ (free volume radius) are expressed in ns and nm, respectively and $R_0 = R + \Delta R$, where $\Delta R$ is a constant for an electron layer thickness (0.166 nm).
Experimental methods

The average free volume size \( (V_f) \) was then simply evaluated as \( V_f = (4/3)\pi R^3 \), whereas the fractional free volume \( (F_v) \) was estimated as \( F_v = 0.0018 \times V_f \times I_3 \) [96].

3.7.13 Washing fastness

The stability of powder layer from the powder coated fabric towards the washing process has been evaluated as per the modified protocols of ISO 105 CO3 method. The 38 mm circular swatches of the powder coated fabric were loaded in the individual stainless steel pots (14 cm length and 5.5 cm internal diameter) of Ahiba Nuance Top Speed lab dyeing machine and treated with 2 g/l sodium carbonate and 5 g/l soap at 60 °C for 30 min with 1:50 material to liquor ratio (MLR) and 30 rpm pot rotation speed. To follow the powder loss on washing, % weight loss of the powder coated fabric after washing treatment was calculated as below:

\[
\% \text{ Weight loss} = \left( \frac{a - b}{a} \right) \times 100
\]

----- Equation 3.11

where, ‘a’ is the weight of the powder coated fabric before washing and ‘b’ is the weight of the powder coated fabric after washing. The weight of each powder coated fabric swatch was measured after drying and conditioning at 20 ± 2 °C and 65 ± 2 % relative humidity for a minimum of 48 h.

To verify whether the mass loss on washing was either due to the powder loss or resin loss, the resin treated fabric at different resin concentrations and its respective powder coated fabrics were simultaneously processed.
Experimental methods

3.7.14 Abrasion resistance
Abrasion resistance tests on the powder coated fabric samples were conducted on the Martindale abrasion tester in accordance with the standard ASTM D 4966 – 98 Option 3. Three samples from each powder coated fabric, being treated with different resin concentrations during the powder coating process were used to determine the mass loss up to 50000 cycles under 9 kPa pressure.

3.7.15 Air permeability
Air permeability of the powder coated fabric samples was measured in accordance with the British Standard BS 5636 onto Textest FX 3300 III instrument from Textest Instruments AG, Switzerland. The samples were conditioned under the standard atmospheric laboratory conditions (65±2 % relative humidity and 20±2 °C temperature) for a minimum of 48 h before the test. The test measurement was repeated five times for each sample and the corresponding standard deviation was illustrated as error bars in the graphical representation of the results.

3.7.16 Water pressure drop
Schematic of the experimental set-up used for measuring water pressure drop across the coated fabric sample is illustrated in Fig. 3.7. It involved a high precision pump delivering water at the predefined water flow rate (50 ml/h) through a tubing, a 2.25 cm² circular sample swatch (powder coated side facing the water flow) held with the help of clamps at one end and a pressure transmitter at the other end. The differential pressure during water penetration through the fabric was measured by the pressure transmitter and recorded on a
Experimental methods

computer. The test measurement was repeated five times for each sample and the corresponding standard deviation was illustrated as error bars in the graphical representation of the results.

Figure 3.7 Schematics of water pressure drop measurement set-up.

3.7.17 Thermal resistance

Thermal resistance of the fabric samples was measured by using the instrument *Thermo Labo II – KES F7* from *Kato Tech Co. Ltd., Japan*. The KES F7 instrument involved “T-Box” to detect the surface temperature (°C) in contact, “BT-Box” as a heat source (hot) plate and “Water Box” as a base plate with constant temperature (Fig. 3.8).

*BT-Box* of KES F7 consists of a 1 mm thick aluminium hot plate measuring 5 cm × 5 cm in size (Fig. 3.9). The temperature of the hot plate remains maintained within ± 0.1 °C accuracy with the help of a sheet like heater on the reverse side. The BT box comes insulated with a thin sheet-like heater and a temperature sensor on the reverse side of the hot plate. Whereas, the temperature of the *Water Box* surface plate remains maintained by the water circulation at room temperature.
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During the measurement, *BT-Box* surface plate temperature was maintained at approx. 37 °C, achieved by setting the heater temperature at 37.2 °C. The temperature of the heater in *BT-Box* is usually set 0.2 °C higher than the required hot plate temperature when the temperature gradient between the hot plate and the *Water Box* surface plate is 10 °C or more. The temperature of the *Water Box* surface plate was approx. 22 °C which was detected as $T_{\text{cold}}$ before each measurement by using the *T-Box*. The sample was subsequently presented on the *Water Box* surface plate (powder coated surface facing upside) and the hot plate of the *BT-Box* was brought in contact with the top surface of the sample. Heat flow in watts (W) and the *BT-Box* hot plate surface temperature ($T_{\text{hot}}$) was recorded at equilibrium. Thermal resistance of the sample was calculated as below:

$$\text{Thermal resistance } R \left( ^\circ C \cdot \frac{m^2}{W} \right) = \frac{(T_{\text{hot}} - T_{\text{cold}})A}{W}$$

----- Equation 3.12
3.7.18 UV-visible absorption spectrum (UV-VIS)

UV-visible absorption spectra of the powder coated fabric samples and the corresponding resin coated and the base fabric samples were recorded on USB4000 optical fibre UV-VIS spectrometer from Ocean Optics (Fig. 3.10). The spectrometer was equipped with a Mikropack DH2000-BAL UV light source with wavelength range of 230-2000 nm. All measurements were carried out in the standard atmospheric laboratory atmospheric conditions (65 ± 2 % relative humidity and 20±2 °C temperature).
Chapter 4

Cashmere guard hair powder

This chapter reports on the characterization and milling of cashmere guide hair. Effect of partial acid hydrolysis on the mechanical properties of the cashmere guard hair and consequently on its milling behaviour has been reported. The cashmere guard hair powders have also been characterized for their surface chemistry and physical properties in comparison with the parent cashmere guard hair fibre.

4.1 Cashmere guard hair morphology

The surface morphology of cashmere guard hair is similar to fine cashmere fibre with scales pointing towards the fibre tip. Both types of fibres are cylindrical in shape. However cashmere guard hair fibres are much coarser than their downy undercoat counterparts (Fig. 4.1a and 4.1b). Unlike the fine cashmere fibres, the guard hairs do not possess crimp or curvature (Fig. 4.1d). The cross-sectional view of the guard hairs shows that they have distinct medulla. The guard hairs have various cross-sectional shapes such as round, kidney shaped and flattened (Fig. 4.1c). However, the majority of the guard hairs were found to have noncircular cross-sectional shapes.
SIFAN tests showed that the average diameter of individual guard hairs varied from 43 μm to 120 μm. The mean hair diameter was 75.55 μm with a standard deviation of 16.9 μm. The SEM images agreed with the SIFAN results. Herrmann and Wortman reported a mean cashmere guard hair diameter of 95.1 μm with a large standard deviation of 25.69 μm [7]. On the other hand, McDonald et al [97] found, in a three year study, that the mean guard hair diameter in cashmere fleece varied with time, depending on the month of shearing. In their study, the mean guard hair diameter varied from 70 μm to 120 μm.
Cashmere guard hair powder

4.2 Mechanical properties of cashmere guard hair

The SIFAN measured mean tensile strength of the guard hair was 0.96 cN/dtex, which is close to the reported strength of wool (1.121 cN/dtex) and fine cashmere fibres (1.086-1.483 cN/dtex) [98]. The mechanical properties of cashmere guard hairs were also tested after partial acid hydrolysis prior to milling. The results are presented in Table 4.1. The tensile properties of the guard hairs deteriorated following the partial acid hydrolysis. The guard hairs retained 38% of their breaking elongation and 35% of their tenacity after 10 hr hydrolysis with 1M HCl at 80 °C. The reduction in their mechanical properties due to the partial acid hydrolysis was also reflected in the bending abrasion test results. With the increase in hydrolysis time, the number of cycles needed to break the fibres reduced. The PH10CHF fibres lasted only 5% of the number of cycles required to break untreated control fibres (CHF). Similar significant drop in the mechanical properties of silk after alkali hydrolysis during silk degumming has been reported [99].

Table 4.1 Change in mechanical properties of cashmere guard hairs on hydrolysis with 1M HCL at 80 °C for different time

<table>
<thead>
<tr>
<th></th>
<th>CHF</th>
<th>PH10CHF</th>
<th>PH10CHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Weight Loss</td>
<td>15.57</td>
<td>26.16</td>
<td></td>
</tr>
<tr>
<td>Tenacity (CN/dtex)</td>
<td>0.96 (0.49)</td>
<td>0.51 (0.36)</td>
<td>0.34 (0.22)</td>
</tr>
<tr>
<td>% Elongation</td>
<td>35.3 (13.14)</td>
<td>25.33 (15.41)</td>
<td>13.41 (15.86)</td>
</tr>
<tr>
<td>Bending Abrasion (No. of cycles)</td>
<td>51219</td>
<td>7923 (7041.26)</td>
<td>2561 (2483.68)</td>
</tr>
<tr>
<td></td>
<td>(63340.45)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Cashmere guard hair powder

*Figure in parenthesis indicates standard deviations. CHF – Control cashmere guard hair, PH4CHF- 4 hour partially acid hydrolysed cashmere guard hair, PH10CHF – 10 hour partially acid hydrolysed cashmere guard hair.

4.3 Wet attritor milling

Cashmere guard hairs with or without acid hydrolysis were wet milled using an attritor. The mean particle size (d(0.5)) as a function of milling time is presented in Fig. 4.2. As shown in Fig. 4.2a, the rate of pulverisation is enhanced after the acid hydrolysis treatment. The partially hydrolysed cashmere guard hairs took around 2 hrs to be pulverised into particles with a volume d(0.5) of 5 μm, while the untreated guard hairs took at least 4 hrs to reach the same size. However, continued milling for long hours did not further reduce the d(0.5) for all the samples. This finding is consistent with earlier findings on silk where reduction in the fibre tenacity improved milling time but could not reduce the particle size much [100]. The quicker pulverisation rate of partially hydrolysed hair samples can be attributed to the significant reduction in strength and elongation of fibres.

To compare the milling behaviour, wool milling was also performed under similar conditions. Silk milling results are reproduced from a published literature [100]. As shown in Fig. 4.2b, silk and wool follow a similar particle size reduction rate which appears to be different to that observed for cashmere guard hair during the initial milling period (< 100 min). The difference in the particle size at the early milling time is due to the larger diameter of cashmere guard hairs compared to wool and silk. However, all the materials were pulverised into particles with d(0.5) = ~5 μm after about 4 h of milling with no
Cashmere guard hair powder

further reduction in particle size when the milling was continued further. Similar milling characteristics have been earlier demonstrated by silk due to the dynamics of particle fragmentation and aggregation during long milling hours [99].

Figure 4.2 (a) Effect of acid hydrolysis on the particle size reduction rate during wet attritor milling of cashmere guard hair, and (b) particle size reduction rate of cashmere guard hair in comparison with eri silk (ESF) and merino wool (MWF) during wet attritor milling. * CHF – Control cashmere guard hair with no chemical treatment, PH4CHF – 4 hour partially acid hydrolysed cashmere guard hair, PH10CHF – 10 hour partially acid hydrolysed cashmere guard hair.
Cashmere guard hair powder

The spray dried particles of control cashmere guard hair (CHF) from its 6 hr attritor milled slurry appeared globular in shape with a mushroom like morphology (Fig. 4.3). The formation of mushroom like structure was also found during fracture of viscoelastic natural multifibrillar fibres [101, 102] and the same mechanism may apply to cashmere guard hairs. The shape and size of all the powder samples were similar with no significant effect of partial acid hydrolysis. The particle size from the observed SEM images was found to be in agreement with the particle size measurement data obtained from laser diffraction (Table 4.2).

![Figure 4.3 SEM image of CHF-AM.](image)

**4.4 Air jet milling**

Air jet milling was performed on spray dried particles. As shown in Table 4.2, all types of spray dried particles further decreased their size after air jet milling. Importantly, in the case of air jet milling, the reduction in size was proportional to the degree of hydrolysis of the material. The particle size, d(0.5), decreased
Cashmere guard hair powder

from 829 nm for PH4CHF-AJ to 461 nm for PH10CHF-AJ. Hence more brittle and weaker particles could be more effectively pulverised by air jet milling, whereas attritor milling gave no difference in the particle size after acid hydrolysis. The wet conditions during attritor milling may have hindered further reduction of particle size by softening the particles allowing more collision energy to be absorbed and by encouraging aggregation. On the other hand, air jet milling under dry conditions resulted in breaking down of these aggregates and/or further fracture of primary particles. The possibility of de-aggregation as well as further fracture of primarily particles is supported by the formation of more irregular particles (Fig. 4.4).

Table 4.2 Particle size measurement data from laser particle size analyser

<table>
<thead>
<tr>
<th></th>
<th>d(0.5)</th>
<th>d(0.9)</th>
<th>d(0.1)</th>
<th>(\eta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF-AM</td>
<td>4.805</td>
<td>8.777</td>
<td>2.622</td>
<td>1.28</td>
</tr>
<tr>
<td>CHF-AJ</td>
<td>2.328</td>
<td>3.843</td>
<td>1.472</td>
<td>1.02</td>
</tr>
<tr>
<td>PH4CHF-AM</td>
<td>5.389</td>
<td>9.389</td>
<td>1.472</td>
<td>1.47</td>
</tr>
<tr>
<td>PH4CHF-AJ</td>
<td>0.829</td>
<td>2.208</td>
<td>0.154</td>
<td>2.48</td>
</tr>
<tr>
<td>PH10CHF-AM</td>
<td>5.296</td>
<td>8.721</td>
<td>3.208</td>
<td>1.04</td>
</tr>
<tr>
<td>PH10CHF-AJ</td>
<td>0.461</td>
<td>1.989</td>
<td>0.103</td>
<td>4.09</td>
</tr>
</tbody>
</table>

* CHF-AM – Spray dried particles made from control cashmere guard hair (CHF), CHF-AJ – Air jet milled particles made from CHF-AM, PH4CHF-AM – Spray dried particles made from 4 hour partially acid hydrolysed cashmere guard hair (PH4CHF), PH4CHF-AJ – Air jet milled particles made from PH4CHF-AM, PH10CHF-AM - Spray dried particles made from 10 hour partially acid hydrolysed cashmere guard hair (PH10CHF), PH10CHF-AJ – Air jet milled particles made from PH10CHF-AM.
Furthermore, it was found that the span (η) values were also increased after air jet milling treatment with skewed particle size distribution, either having a longer left tail (finer particles) or a bimodal distribution for PH4CHF-AJ and PH10CHF-AJ powder particles (Fig. 4.5). This type of particle size distribution is due to the formation of a large amount of sub-micron particles which did not further aggregate, along with the presence of micron scale particles, resulting in wider span values (Table 4.2).
Cashmere guard hair powder

4.5 FTIR analysis

To investigate possible changes in the surface chemistry of cashmere guard hair with milling, FTIR analysis was performed. Apart from the classical amide absorption bands, the spectrum of cashmere guard hair (CHF) exhibited significantly strong absorption bands at 2920 cm\(^{-1}\) and 2850 cm\(^{-1}\) (Fig. 4.6) that were assigned to the C-H asymmetric and symmetric vibrations of alkyl [103, 104]. These peaks are attributed to the presence of long hydrocarbon lipid chains on the overlapping hair cuticle cells [105]. The disappearance of these absorption bands in the FTIR spectra after milling treatment (CHF-AM and CHF-AJ) thus indicates the disintegration of surface cuticle cells and exposure of inner cortical cells on the powder surface. Similar changes in FTIR spectra were observed for partially hydrolysed cashmere guard hairs and their powders.

![Figure 4.6 Infrared spectra of cashmere guard hair and powders.](image)

The epicuticle membrane of hydrocarbon lipid chains on the hair cuticle cells is known to render the hair surface hydrophobic and chemically resistant [106].
Cashmere guard hair powder

The disintegration of cashmere guard hair cuticle cells, including the hydrophobic epicuticle membrane, is therefore expected to affect the absorption of many chemical species.

4.6 XPS Analysis

The effect of milling on the surface chemistry of cashmere guard hair was studied by XPS. As evident in Table 4.3, the C and S contents of the guard hair (CHF) decreased while the N and O content increased after attritor milling (CHF-AM); whereas there was little change after the further air jet milling of the attritor milled powder (CHF-AJ). The chemical changes reflect the exposure of the N rich fibre cortex by removal of S rich cuticle [107] of cashmere guard hair, resulting in the decreased S and increased N contents of the powder surfaces (CHF-AM and CHF-AJ). These results confirmed the earlier FTIR findings of the disintegration of cashmere guard hair cuticle cells and exposure of the cortex. The XPS results for partially hydrolysed cashmere guard hairs and their respective powders as well were consistent with these findings (data not shown).

In Fig.4.7a, 4.7b and 4.7c, the peak at 284.6 eV, assigned to C-C, C-H and C-S species [108], can be attributed to the hydrocarbon backbone of covalently bound fatty acids and the side groups of amino acids in the case of cashmere guard hair (CHF). For the powders (CHF-AM and CHF-AJ), only the later contributes to the 284.6 eV peak. The peak at 288 eV (Fig. 4.7a) represents the amide group (-NH-CO-) of protein compounds [109]. Some oxidised species (C-O, O-C-O and C=O) were found in the powder samples (CHF-AM and CHF-AJ) which were evident as the peaks at ~286 eV and ~287.6 eV (Fig. 4.7b...
Cashmere guard hair powder & 4.7c) [110]. The peak corresponding to the amide bond (288 eV) appeared to overlap the strong C=O peak at 287.8 eV for sample CHF-AJ (Fig. 4.7c). Furthermore, the peak at ~168 eV along with the presence of disulfide bonds (peak at ~ 164 eV) [111] in the S2p spectra indicates the formation of sulfonate (RSO₃) species on the powder (CHF-AM and CHF-AJ) surface (Fig. 4.7e & 4.7f) [111, 112]. The appearance of photoelectron peaks associated with oxidised carbon and sulphur, along with the increase in the relative height of these peaks, indicates that the cashmere guard hair was oxidised during milling, possibly due to localized heat generation during the wet milling and exposure to hot air during the spray drying. The N1s and O1s spectra of the powder samples were similar to those of the unmilled hair with a single peak at 400 eV and 531 eV respectively (results not shown).

Table 4.3 Elemental composition of cashmere guard hair fibre and its powder samples in atom %

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF</td>
<td>76.33</td>
<td>6.68</td>
<td>14.79</td>
<td>2.2</td>
</tr>
<tr>
<td>CHF-AM</td>
<td>63.76</td>
<td>15.99</td>
<td>19.19</td>
<td>1.06</td>
</tr>
<tr>
<td>CHF-AJ</td>
<td>64.21</td>
<td>15.77</td>
<td>18.77</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Thus, the oxidised cashmere guard hair powder surface with its increased concentration of nucleophilic oxygen and nitrogen atoms, along with the disintegration of the hydrophobic surface cuticle cells, is likely to result in improved binding of reactive chemical species.
Cashmere guard hair powder

![Graph of XPS spectra](image)

Figure 4.7 Curve fitted C1s (a,b,c) and S2p (d,e,f) XPS spectra.

### 4.7 BET surface area

The specific surface area of cashmere guard hairs at different stages of milling is shown in Fig.4.8. The BET surface area of spray dried and air jet milled particles is compared with the respective cashmere guard hairs.

The larger specific surface areas of spray dried hydrolysed particles, in comparison with unhydrolysed particles, despite their similar size, suggests that hydrolysis led to the formation of a more porous structure. In addition, longer hydrolysis time resulted in higher specific surface area.

After air jet milling, the BET surface area increased only slightly despite significant differences in d(0.5), for all the hydrolysis conditions. This suggests that air jet milling resulted in deaggregation of primary particles from the porous aggregates which led to only a slight increase in surface area.
Cashmere guard hair powder

4.8 Powder moisture regain

The moisture regain of the control as well as the partially acid hydrolysed cashmere guard hair samples decreased with the milling treatment (Fig. 4.9). The decrease in moisture regain was consistent with the decrease in particle size for the given cashmere guard hair sample i.e. Cashmere guard hair (-CHF) > Spray dried powder particles (-AM) > Air jet milled powder particles (-AJ).

Figure 4.8 BET surface area of cashmere guard hair samples and their powders (n=3).

Figure 4.9 Effect of milling and partial acid hydrolysis on moisture regain.
Cashmere guard hair powder

The primary structure of hair fibre cuticle with gaps between the adjacent cells acts as the primary diffusion pathways and is responsible for the absorption of aqueous solutions [24]. As illustrated by FTIR results, the disintegration of cuticle cells on cashmere guard hair milling would have hindered the diffusion of moisture and this could be the reason for lowering the moisture regain of powder particles in comparison to the parent guard hairs.

Even though the disintegration of cuticle cells was valid for both the spray dried and the air jet milled powder particles, the moisture regain of the spray dried powder was higher than the corresponding air jet milled powder. The capillary action among the porous aggregates could be assisting spray dried powder particles for higher moisture retention in comparison to the primary disaggregated air jet milled powder particles.

It can also be inferred from the Fig. 4.9 that the partial acid hydrolysis of cashmere guard hair reduced its moisture regain (CHF>PH4CHF>PH10CHF). The irreversibly held hydrochloric acid by protonation of the molecular chains would have blocked the primary sites of moisture absorption i.e. the ionic side chains [113]. However, the magnitude of effect of milling on the moisture regains of the partially acid hydrolysed guard hair samples was different from the control guard hair sample. The combined effect of the deprotonation of molecular chains during wet milling as well as the unique tendency of particle aggregation could be governing the moisture regain of the resultant powder particles from the partially acid hydrolysed guard hairs.
Cashmere guard hair powder

4.9 Powder flowability and cohesivity

Powder flowability and cohesivity play distinct roles in powder storage, packing, transportation and use.

Flowability and cohesivity are contradictory to each other. If one is high, the other is usually low. Powder flowability and cohesivity can be judged respectively from Carr’s flowability index (IC) and Hausner’s ratio (HR) which are evaluated from the powder sample’s bulk and tapped densities. Flowability is considered as good when the IC value is below 15, poor when between 15 and 25 and bad when above 25. Whereas cohesivity is considered low for the HR value 1.0 - 1.2, medium for 1.2-1.4 and high above 1.4.

Table 4.4 Effect of milling and partial acid hydrolysis on cashmere guard hair powder flowability and cohesivity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Density (g/cm³)</th>
<th>Tapped Density (g/cm³)</th>
<th>IC</th>
<th>HR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF-AM</td>
<td>0.273 (0.010)</td>
<td>0.372 (0.011)</td>
<td>26.59</td>
<td>1.36</td>
</tr>
<tr>
<td>CHF-AJ</td>
<td>0.242 (0.001)</td>
<td>0.330 (0.004)</td>
<td>26.52</td>
<td>1.36</td>
</tr>
<tr>
<td>PH4CHF-AM</td>
<td>0.244 (0.006)</td>
<td>0.339 (0.013)</td>
<td>28.10</td>
<td>1.39</td>
</tr>
<tr>
<td>PH4CHF-AJ</td>
<td>0.189 (0.002)</td>
<td>0.236 (0.006)</td>
<td>19.92</td>
<td>1.25</td>
</tr>
<tr>
<td>PH10CHF-AM</td>
<td>0.218 (0.003)</td>
<td>0.316 (0.013)</td>
<td>31.18</td>
<td>1.45</td>
</tr>
<tr>
<td>PH10CHF-AJ</td>
<td>0.175 (0.003)</td>
<td>0.219 (0.003)</td>
<td>20.00</td>
<td>1.25</td>
</tr>
</tbody>
</table>

*Figure in parenthesis indicates standard deviations.

In general, flowability of cashmere guard hair powder samples is poor with either medium or high cohesivity (Table 4.4). Furthermore, the data also depicts that the IC values of air jet milled powder (-AJ) are lower than the
Cashmere guard hair powder corresponding spray dried powder (-AM). This suggests that further air jet milling of the spray dried powder particles improves its flowability. Low moisture regain of the air jet milled powder particles (Fig. 4.9) could be responsible for their improved flowability as the inter-particle bonding weakens with the decreased moisture regain [114].
Chapter 5

Absorption to heavy metal ions

This chapter reports on the heavy metal ion absorption potential of the cashmere guard hair powder (CHF-AM) in comparison with the parent cashmere guard hair (CHF) as well as the similarly processed merino wool (MWF-AM) and eri silk (ESF-AM) powders. The unique radio tracer technique was adopted for quantitative measurement of the metal ions in the studied absorption system to evaluate the effect of solution pH, absorption time, metal ion concentration in the aqueous system and partial acid hydrolysis of the parent cashmere guard hair on the absorption yield. Desorption yield of the bound metal ions was also examined in order to judge the potential of metal ion recovery or sorbent reuse.

5.1 Methodology

Heavy metal ion absorption studies specific to Zn$^{2+}$, Co$^{2+}$ and Cr$^{6+}$ were conducted. Zn$^{2+}$ as well as Co$^{2+}$ are stable in aqueous solution and remain at the same ionic state over a wide pH range (pH 1-8) [115]. In contrast, Chromium (VI) in aqueous solution can exist in different ionic forms, such as CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$ or HCrO$_4^-$ [115], and the proportion of the ionic species varies depending on the pH condition [116]. The anionic species of chromium (VI) and cationic species of other metal ions such as Zn$^{2+}$ & Co$^{2+}$ represent a valuable tool for screening the metal absorption properties of sorbents of interest and have been adopted in this study.
Absorption to heavy metal ions

As heavy metal ions in effluent streams are usually accompanied with huge quantities of alkali and alkaline earth metal ions [117], absorption yield to heavy metal ions by cashmere guard hair and other animal protein fibre sorbents in competition with the commonly encountered alkali (Na\(^+\) & K\(^+\)) and alkaline (Ca\(^{2+}\) & Mg\(^{2+}\)) earth metal ions would represent a scenario of real world significance and has been adopted in this study with a specific case to Co\(^{2+}\).

5.2 Metal ion absorption

5.2.1 Effect of pH

The pH of the metal ion aqueous solution matrix was found to affect the absorption yield of that metal ion by the studied animal protein fibre sorbents. Fig. 5.1 compares the absorption of Zn\(^{2+}\), Co\(^{2+}\) and Cr\(^{6+}\) to the cashmere guard hair powder (CHF-AM), the merino wool powder (MWF-AM) and the eri silk powder (ESF-AM) after 24 hours of incubation at various pH values. All the powder samples showed similar binding profiles for all the studied metal ions over the studied pH ranges. The Zn\(^{2+}\) and Co\(^{2+}\) had a sharp absorption peak at pH 8 for all the sorbents. Furthermore, a shoulder at pH 5-6 was also found, prominently in the case of Zn\(^{2+}\) absorption. In contrast, the Cr\(^{6+}\) absorption showed a peak at pH 2 for all the studied powder sorbents. A similar Cr\(^{6+}\) absorption behaviour on wool fibres was also reported by Dakiky et al [118]. The Cr\(^{6+}\) absorption curves also had an additional shoulder at pH 5 in case of keratin powders only i.e. CHF-AM and MWF-AM.
Figure 5.1 Absorption yield of control cashmere guard hair powder (CHF-AM, ), merino wool powder (MWF-AM, ) and eri silk powder (ESF-AM, ) to metal ions at different pH, a) Zn$^{2+}$ b) Co$^{2+}$ and c) Cr$^{6+}$ (initial concentration of metal ions=$10^{-4}$ M, temperature=21 °C, exposure time = 24h).
Absorption to heavy metal ions

The absorption yield of the powder sorbents for Zn\(^{2+}\) was the greatest for eri silk powder and decreased for wool powder followed by cashmere guard hair powder. In the case of Co\(^{2+}\) also, eri silk powder had the highest absorption yield; whereas the animal hair keratin powders (CHF-AM and MWF-AM) had almost similar absorption profiles. Interestingly, a reverse behaviour was observed in the absorption of Cr\(^{6+}\), where cashmere guard hair powder absorbed Cr\(^{6+}\) to the highest degree followed by wool powder and then silk powder. These results may reflect the amino acid composition of the respective fibres. Based on the calculations on reported amino acid composition data [119, 120], cashmere guard hair fibre and wool fibre have cumulative 15 mol % and 13.52 mol % of positively charged basic amino acids (i.e. Arginine, histidine and lysine), respectively, compared to only 5.1 mol % in eri silk [121]. The higher molar percentage of positively charged basic amino acids in cashmere guard hair fibre is likely to be responsible for higher absorption of Cr\(^{6+}\) which is mostly in its anionic form at pH 2 i.e. HCrO\(_4\)\(^-\). However the absorption behaviour for Zn\(^{2+}\) & Co\(^{2+}\) could not be readily explained by only the amino acid composition of respective fibre types. The types of donor and quaternary structure of protein are most likely to play a role in the absorption of cationic metal ions to the studied powder sorbents.

The zeta potential of the powders was measured at different pH values. The data reveals the ionic interactions of metal ions with the studied powder sorbents. As shown in Fig. 5.2, the zeta potential was positive when pH was below 5. This positive charge explains the high absorption of Cr\(^{5+}\) (in the form of HCrO\(_4\)\(^-\) anion) under low pH conditions. At a higher pH value, the dominant Cr\(^{6+}\) species were CrO\(_4\)\(^{2-}\) and therefore it was consistent that the cashmere powder would not absorb well at a high pH condition, because the surface was
Absorption to heavy metal ions

also negatively charged at this pH condition. With similar reasons, the weak absorptions of Zn$^{2+}$ and Co$^{2+}$ are not surprising at low pH conditions due to their cationic nature. With the increase in pH value, the absorption of the cationic metal ions was also increased. The poor absorption of the cationic metal ions at pH 9 may be explained by the possible stronger interaction of Zn$^{2+}$ and Co$^{2+}$ ions with buffer ligand (glycine/NaCl) than with the sorbents.

![Graph showing zeta potential vs pH](image)

Figure 5.2 Zeta potential of control cashmere guard hair powder (CHF-AM, ), merino wool powder (MWF-AM, ) and eri silk powder (ESF-AM, ) at different pH.

**5.2.2 Effect of time**

Fig. 5.3 shows the change of absorption yield over time for cashmere guard hair fibre (CHF) and its powder (CHF-AM) towards Zn$^{2+}$ and Co$^{2+}$ at pH 8 and towards Cr$^{6+}$ at pH 2, with the initial concentration of $10^{-4}$ M and under ambient conditions. For Zn$^{2+}$ and Co$^{2+}$, it was clear that the equilibrium was established quickly (< 10 minutes) for cashmere guard hair powder, while it
Absorption to heavy metal ions took a considerably longer time for the cashmere guard hair fibre (approximately 80 minutes). For Cr$^{6+}$, the absorption profile was different with equilibrium established only after 24 hours for both fibre and powder forms of the cashmere guard hair.

Cashmere guard hair powder absorbed all the studied metal ions abruptly on exposure to the metal ion solution at the set pH with no or very few further time dependent absorption. The initial rapid absorption of the metal ions to the cashmere guard hair powder is due to its high surface specificity with regard to its parent fibres.

Figure 5.3 Effect of time on the absorption yield of Zn$^{2+}$, Co$^{2+}$ and Cr$^{6+}$ under ambient conditions at optimum pH.

Cashmere guard hair powder absorption yield for Co$^{2+}$ was approximately four times higher than the parent guard hair fibre. The initial high absorption of Co$^{2+}$ by the cashmere guard hair powder was retained and could not be surpassed by the parent guard hair fibre which showed a little improvement in the absorption yield with time. However the equilibrium absorption of Zn$^{2+}$ and
Absorption to heavy metal ions

Cr\(^{6+}\) by the cashmere guard hair fibre was significantly higher than that of the powder with the same weight, indicating a definitive role of a time taking process - “diffusion”, besides its specific surface area and reactivity in the metal ion absorption.

Figure 5.4 PAL spectra of different animal proteins fibres and their powders.

The diffusion pathways in hair keratin based sorbents could be the gaps between the cuticle cells [24] and internal free volumes, also known as cavities, voids, holes and pores, present in the bulk of the sorbent [122]. They can act as a transport system for the molecular diffusion into the sorbent material and improve its absorption capacity for the given molecules. The breakdown of cashmere guard hair cuticle cells during milling has already been illustrated by the FTIR studies (Fig. 4.6), whereas the change in the internal free volumes could be inferred from the Positron Annihilation Lifetime Spectra (PALS).

The PAL spectra appeared very similar for all the studied fibre and powder samples (Fig. 5.4), however slight differences in \(\omega\)-Ps (\(\tau_3\)) and their corresponding intensities (\(I_3\)) were observed (Table 5.1). From the \(\omega\)-Ps results,
Absorption to heavy metal ions

mean free volume radius \( (R) \), mean free volume size \( (V_f) \) and fractional free volume \( (F_v) \) were calculated and presented in the Table 5.1. It can be readily realised from the table that the fractional free volume for CHF, MWF and ESF was decreased on milling by 3.46 %, 19.90% and 11.62 % respectively.

Table 5.1 Analysed PALS data

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_3 ) (ns)</th>
<th>( I_3 ) (%)</th>
<th>Avg. free volume radius (Å)</th>
<th>Avg. free volume size (Å³)</th>
<th>Fractional free Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF</td>
<td>1.788</td>
<td>19.45</td>
<td>2.650</td>
<td>77.77</td>
<td>2.72</td>
</tr>
<tr>
<td>CHF-AM</td>
<td>1.790</td>
<td>18.57</td>
<td>2.660</td>
<td>78.65</td>
<td>2.63</td>
</tr>
<tr>
<td>MWF</td>
<td>1.809</td>
<td>19.31</td>
<td>2.670</td>
<td>79.54</td>
<td>2.76</td>
</tr>
<tr>
<td>MWF-AM</td>
<td>2.000</td>
<td>12.58</td>
<td>2.860</td>
<td>97.76</td>
<td>2.21</td>
</tr>
<tr>
<td>ESF</td>
<td>1.851</td>
<td>21.27</td>
<td>2.720</td>
<td>84.09</td>
<td>3.22</td>
</tr>
<tr>
<td>ESF-AM</td>
<td>1.813</td>
<td>19.65</td>
<td>2.680</td>
<td>80.44</td>
<td>2.85</td>
</tr>
</tbody>
</table>

Thus, from the metal ion absorption point of view, although the ultrafine cashmere guard hair powder particles would provide improved surface area for immediate molecular adsorption, the breakdown of the cuticle cells and the decreased fractional free volume are likely to retard the time dependant molecular diffusion phenomenon as observed in the case of \( \text{Zn}^{2+} \) and \( \text{Cr}^{6+} \) absorption (Fig. 5.3). Therefore it could be inferred that the diffusion pathways are instrumental in the absorption yield of \( \text{Zn}^{2+} \) and \( \text{Cr}^{6+} \), whereas the absorption yield for \( \text{Co}^{2+} \) is mainly governed by the specific surface area of the cashmere guard hair based sorbents.
Absorption to heavy metal ions

### 5.2.3 Effect of metal ion concentration

Fig. 5.5 shows the influence of initial metal ion concentration ($10^{-6}$ M - $10^{-4}$M) on the absorption of Zn$^{2+}$, Co$^{2+}$ and Cr$^{6+}$ at the optimum absorption pH conditions by the studied animal protein fibre sorbents i.e. pH 8 for Zn$^{2+}$ & Co$^{2+}$ and pH 2 for Cr$^{6+}$.

As shown in Fig. 5.5, the absolute amount (milligrams) of absorbed metal ion per unit weight of the sorbent was increased with an increase in the initial metal ion concentration, in case of the each sorbent as well as the studied metal ion. The increase was dramatic, while going to high ($10^{-4}$ M) initial metal ion concentration. However, the percentage absorption yield figures (on top of each 1 day time point bar) were convenient in further distinguishing sorbent as well as the metal ion specific absorption trends.

Very little effect of the initial concentration on the percentage absorption yield of Zn$^{2+}$ was found in case of the studied powder sorbents (Fig. 5.5a). However, the Zn$^{2+}$ absorption yield by cashmere guard hair fibre (CHF) was substantially poor at low metal ion concentration. Therefore cashmere guard hair powder (CHF-AM) could be an effective adsorbent for Zn$^{2+}$ in comparison with its parent fibre at very low Zn$^{2+}$ concentrations. In case of Co$^{2+}$, the absorption yield by all the studied sorbents was decreased with an increase in the metal ion concentration (Fig. 5.5b) and interestingly an opposite phenomenon (increase in the absorption yield with increase in the metal ion concentration) was observed in the absorption of Cr$^{6+}$ (Fig. 5.5c).

The little metal ion concentration effect in the absorption yield of Zn$^{2+}$ could possibly be due to the quick absorption of most of the available metal ions by the abundantly available reactive sites in the studied animal protein fibre powders. This was also suffixed with the observed buoyancy in the Zn$^{2+}$
Absorption to heavy metal ions

absorption in few cases, where the metal ion absorption yield at 30 min time point was higher than the 24 h time point. Furthermore, it also appears that physical phenomenas like concentration gradient and metal ion diffusivity at the fibre-solution interface would be playing crucial roles in the absorption of Co\(^{2+}\) and Cr\(^{6+}\). With the initial high concentration gradient at an increased metal ion concentration, Cr\(^{6+}\) absorption yield may improve through diffusion. However the same was not found true in the case of Co\(^{2+}\). It is likely that Co\(^{2+}\) would not have been able to diffuse through the sorbent surface and the absorption would have been limited to the sorbent surface only as proposed earlier. This would result in decreased Co\(^{2+}\) absorption yield at increased initial metal ion concentration with the limited available sorbent surface area. However the metal ion diffusivities through the protein fibres and their powders need to be further examined to support the claims.

![Graph showing metal ion absorption yield](image)

Fig. 5.5 continued…..
Absorption to heavy metal ions

Figure 5.5 Effect of metal ion concentration on the absorption of a. Zn$^{2+}$ b. Co$^{2+}$ and c. Cr$^{6+}$ at optimum pH and ambient conditions.

5.2.4 Effect of partial acid hydrolysis

Absorption yield of similarly sized ‘attritor milled - spray dried’ powder particles from control cashmere guard hair (CHF-AM) and partially acid hydrolysed cashmere guard hairs (PH4CHF-AM and PH10CHF-AM) towards the studied heavy metal ions at optimum pH conditions from their respective
Absorption to heavy metal ions

$10^{-4}$ M buffered solutions in 24 hours at 1:200 MLR (material to liquor ratio) and under ambient conditions is showed in the Fig. 5.6.

Although there was no major influence of cashmere guard hair partial acid hydrolysis on the absorption of Cr$^{6+}$ by the respective powdered sorbents, opposing absorption trends were observed in case of Zn$^{2+}$ and Co$^{2+}$. The absorbed absolute quantity of Zn$^{2+}$ by partially acid hydrolysed cashmere guard hair powders, especially PH10CHF-AM was poor, whereas that of Co$^{2+}$ was nearly 2.5 times higher than the control cashmere guard hair powder (CHF-AM).

Crystalline content of the sorbent material controls the diffusivity of the molecules of interest. The higher the crystalline content of the sorbent material, molecular diffusivity through the sorbent would be poor. As shown in Fig. 5.7, the area covered by the DSC curve under the red line designates energy consumed by CHF-AM in its decomposition in J/g and the data could be
Absorption to heavy metal ions readily made available by using the instrument control application. This figure designates the extent of the crystalline content in the material under investigation. As the similar figures for PH4CHF-AM and PH10CHF-AM were 199.4 J/g and 215.9 J/g respectively against 103.6 J/g for CHF-AM, it clearly indicates that the powder sorbents from partially acid hydrolysed cashmere guard hairs had higher crystalline content than the powder sorbent from the controlled cashmere guard hair. Thus, PH4CHF-AM and PH10CHF-AM are likely to retard diffusivity of the studied heavy metal ions in comparison to CHF-AM, which has severely reflected in the absorption of Zn\(^{2+}\).

![Figure 5.7 DSC spectra of CHF-AM.](image)

However, in the case of Co\(^{2+}\), the absorption of which is expected to be limited to the sorbent surface only, its absorbed absolute quantity is likely to be good on the powder sorbents from the partially acid hydrolysed cashmere guard hairs due to their higher specific surface area in comparison to the powder sorbent from the controlled cashmere guard hair (Fig. 4.8).
Absorption to heavy metal ions

5.2.5 Competitive metal ion absorption

As real time industrial effluents contain large quantities of alkali and alkaline earth metal ions in addition to the toxic heavy metal ions [123], the effect of Na\(^+\) and K\(^+\), alkali earth metal ions and Mg\(^{2+}\) and Ca\(^{2+}\), alkaline earth metal ions on the absorption of Co\(^{2+}\) from Milli-Q water by control cashmere guard hair powder (CHF-AM) have been studied in comparison with its parent guard hair fibre (CHF) and other animal protein fibre powders such as merino wool powder (MWF-AM) and eri silk powder (ESF-AM).

![Figure 5.8 Effect of alkali and alkaline earth metal ions on the absorption of Co\(^{2+}\) from Milli-Q water in 24 h under ambient conditions.](image)

As shown in Fig. 5.8, the presence of alkali and alkaline earth metal ions has negatively affected Co\(^{2+}\) absorption yield for all the studied sorbents. Interestingly, the effect of alkaline earth metal ions (Mg\(^{2+}\) and Ca\(^{2+}\)) was more severe than the alkali earth metal ions (Na\(^+\) and k\(^+\)). It could be due to the
Absorption to heavy metal ions

difference in the oxidation numbers, an extra positive charge carried by the alkaline earth metal ions in comparison to the alkali earth metal ions.

It is worth to mention here that the Co$^{2+}$ absorption yield of cashmere guard hair powder (CHF-AM) was poor in comparison to its parent guard hair fibre (CHF). This is completely opposite to the findings of Co$^{2+}$ absorption from its buffered solution at pH 8 (Fig. 5.3). This indicates a distinct role of the phosphate buffer in the metal ion absorption by the sorbents under investigation.

5.3 Desorption properties

The release of bound metal ions was examined by re-dispersing the sorbents that were preloaded with metal ions in a fresh buffer solution at a pH condition known to have poor respective metal ion absorption, i.e. pH 4 for Zn$^{2+}$ and Co$^{2+}$ and pH 8 for Cr$^{6+}$. The Zn$^{2+}$ was released quickly (within 30 min) and completely (100%) for all the studied sorbents after exposing to pH 4 buffer solution. However, the behaviour of Co$^{2+}$ and Cr$^{6+}$ was not the same (Fig. 5.9), with both of the metal ions not getting completely released even after 24 h of dispersion by any of the studied sorbent.

Approximately 80% of Co$^{2+}$ was released quickly by CHF-AM on its exposure to the pH 4 buffer and there was very little improvement with time. Similar Co$^{2+}$ desorption trend was also exhibited by MWF-AM and ESF-AM. Although the desorption yield of Co$^{2+}$ by the parent cashmere guard hair fibre (CHF) was to the same extent as exhibited by its powder (CHF-AM), the metal ion release was slow and increased with time. The quick Co$^{2+}$ release by powder sorbents is likely due to its surface adsorption only.
Absorption to heavy metal ions

In the case of Cr\(^{6+}\), there was a 45% release at pH 8 by control cashmere guard hair powder (CHF-AM) but only 17% by its parent hair fibre (CHF) after 24 hours, suggesting strong binding of Cr\(^{6+}\) to the hair fibre. The desorption of Cr\(^{6+}\) from MWF-AM and ESF-AM was similar to that of CHF-AM, with only approximately 45% release after 24 hours. In contrast to Co\(^{2+}\) findings, there was delayed Cr\(^{6+}\) desorption by all powder sorbents whereas the parent cashmere guard hair fibre (CHF) exhibited quick Cr\(^{6+}\) release.

![Desorption Yield Graph](image)

Figure 5.9 Desorption yield of a. Co\(^{2+}\) and b. Cr\(^{6+}\).
Chapter 6

Electrostatic powder coating of textile fabric and its antibacterial properties

This chapter reports on applying cashmere guard hair powder (CHF-AM) on polyester fabric, its silver ion loading property and consequently imparted antibacterial activity. The chapter also investigates thermal resistance and UV-Vis absorbance properties of the powder coated fabric.

6.1 Methodology

The adopted electrostatic powder coating process, described in the experimental methods chapter, was optimised to achieve maximum powder loading. The effect of applied voltage, substrate distance, air pressure and atmospheric relative humidity on the coated fabric density was examined. The powder coated fabric was characterized for its morphology, stability of the powder coating and its permeability properties. The coated fabric was also evaluated for its silver ion loading properties, consequently imparted antibacterial activity and its wash durability. In addition, the fabric was examined for changes in its thermal resistance and UV-Vis absorbance properties.

6.2 Electrostatic powder coating - Process optimisation

For enhanced powder loading, the electrostatic powder coating was optimised for its different process parameters such as applied voltage, substrate distance,
Electrostatic powder coating of textile fabric and its antibacterial properties

air pressure and relative humidity. The optimum value of first process parameter, among the studied set of values was used while optimizing the next process parameter in sequence.

As shown in Fig. 6.1a, the powder coated fabric density was increased with an increase in the applied voltage. This was due to the powder particles carrying more charge at an increased applied voltage. As a result, less powder particles disperse to the surrounding atmosphere and thus more powder particles are deposited on the substrate. However at a high applied voltage (60 kV), the coated fabric density decreased with an increase in the substrate distance/deposition distance (distance between the substrate and the powder coating gun nozzle) and air pressure (Fig. 6.1b and 6.1c). As the deposition distance is inversely related to the electric field intensity, the decreased electric field and high air pressure should have given more room for the powder particles to disperse, leaving less powder particles to deposit onto the substrate.

In our experiment, 20 cm substrate distance and $2 \times 10^5$ N/m$^2$ air pressure were used for optimization of the next process parameter at 60 kV applied voltage i.e. relative humidity.

The powder coated fabric density decreased with an increase in the atmospheric relative humidity (Fig. 6.1d). The powder particles are likely to get discharged due to an increased conductivity of the surrounding air at an increased humidity and thus causing the powder particles to lose their traction.
Fig. 6.1 continued.....
Figure 6.1 Effect of a. applied voltage b. substrate distance c. air pressure and d. relative humidity on the powder coated fabric density in grams per square meter i.e. GSM (g/m²).

6.3 Fabric morphology

Upon electrostatically applying the cashmere guard hair powder under the optimised process parameters (60 kV applied voltage, 20 cm substrate distance, $2 \times 10^5$ N/m² air pressure and 50% relative humidity) on the base fabric, the fabric surface appeared glossy and uniform to the naked eyes in comparison to the uncoated base fabric surface (Fig. 6.2a). Under the SEM, cracks and hollow vacuoles were clearly identified on the coated fabric surface (Fig. 6.2b). The transverse view of the coated fabric confirmed that the powder coating was around 20-30 μm thick on one side of the fabric and the powder particles did not migrate across the fabric (Fig. 6.2c). Considering the mean particle size of the cashmere guard hair powder (4.805 μm) and the powder coating thickness, the powder coating would have been achieved with multilayer powder deposition.
6.4 Mechanical stability of the powder coating

The mechanical stability of the powder coating on fabric was evaluated through rigorous washing and abrasion treatment. As shown in Fig. 6.3, the percentage weight loss of the powder coated fabric after washing was very small, less than 3%. The concentration of pre-treatment resin influenced the weight loss, and with an increase in the resin concentration the weight loss increased. For comparison, the base fabric was treated with the resin only and its weight loss after washing was also measured. At the same resin concentration, the weight loss percentage of the resin coated fabric was slightly
Electrostatic powder coating of textile fabric and its antibacterial properties higher than that of the fabric coated with resin and powder. This suggests that the weight loss of the powder coated fabric is mainly caused by the resin loss during washing.

![Figure 6.3 Effect of resin concentration on wash fastness.](image)

When the powder coated fabric was subjected to a standard abrasion process, there was no powder mass loss detected after 50,000 cycles of abrasion. This indicated that the cashmere guard hair powder has been firmly immobilized by the resin on the fabric.

### 6.5 Permeability to air and water

The permeability of the powder coated fabric was evaluated for the passage of air as well as water. Without any coating treatment, the flat knit base polyester fabric had an air permeability of 142.67 cm³/cm²/s. The air permeability was decreased slightly when the resin was applied onto the fabric. Fig 6.4a shows the effect of the resin concentration on the air permeability. With an increase in the resin concentration, the permeability value reduced. In comparison to the
Electrostatic powder coating of textile fabric and its antibacterial properties

resin coating, the powder coating showed much larger effect on the permeability. When the cashmere guard hair powder was applied on the resin coated fabric, the air permeability of the fabric was decreased significantly. The resin concentration also influenced the air permeability of the powder coated fabric. The fabric coated with a resin of higher concentration showed lower air permeability after the powder coating. The reduced air permeability could be attributed to the blockage of the fabric pores on powder coating. Apparently larger powder areal density at higher resin concentration (Fig. 6.4c) would lead to larger air resistance, and hence lower air permeability.

The pressure drop for water to penetrate the fabric was used to measure the permeability of fabric to liquid water. A large pressure drop suggests low water permeability [124]. As with the air permeability, water pressure drop of the powder coated fabric was also adversely affected with an increase in the resin concentration and basically followed the powder areal density (Fig. 6.4b and 6.4c). The powder areal density and consequently the water pressure drop had a very little change when the resin concentration increased from 20% to 60%. However, a significant rise was noted in both when the resin concentration was 80%. This is likely due to the considerably increased solution viscosity at high resin concentration which would consequently increase the resin loading abruptly and not necessarily the actual powder areal density.

The water pressure drop for the cashmere guard hair powder coated fabric samples was in the range between 3.27 and 7.31 mm Hg. Such a low pressure level appears to be suitable even for a gravity fed water treatment device. However, further studies are warranted to explore the filtration membrane application trajectory for the cashmere guard hair powder coated fabric.
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Figure 6.4 Effect of resin concentration on a. air permeability, b. water pressure drop and c. powder areal density of the powder coated fabric.
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6.6 Silver ion absorption

Silver ion absorption ability of the cashmere guard hair powder and the powder coated fabric was evaluated. The cashmere guard hair powder and the fabric samples had poor silver ion absorption yield (< 40%) when the solution pH value was 1.4 (Fig. 6.5a). However, complete silver ion absorption (100%) onto the cashmere guard hair powder and the powder coated fabric was observed when the solution had a pH value greater than 8.5 (Fig. 6.5b, 6.5c and 6.5d). The poor silver ion absorption in acidic condition and very good absorption in alkaline condition suggested that the absorption of silver ion to cashmere guard hair powder followed an electrostatic interaction mechanism as the isoelectric point of cashmere guard hair powder is around pH 4 (Fig. 5.2). Similar metal ion absorption mechanism was also noted during Zn\(^{2+}\), Co\(^{2+}\) and Cr\(^{6+}\) absorption study on cashmere guard hair powder (Fig. 5.1).

For comparison, the silver ion absorption of uncoated base fabric and the fabric just coated with resin was also tested. The silver ion absorption onto the uncoated base fabric and the fabric just coated with resin was very low in yield (less than 10%) under all the studied experimental conditions. This indicated that the absorption of silver ion was mainly because of the cashmere guard hair powder on the powder coated fabric samples.

The silver ion absorption kinetics on the four samples, the base fabric, the resin coated fabric, the powder coated fabric and the solo cashmere guard hair powder was examined at all studied pH values (Fig. 6.5a – 6.5d). For the free, unbound solo cashmere guard hair powder, the ion absorption was maximum among the four samples. When the powder was coated onto fabric, the coated fabric showed a similar equilibrium silver ion absorption yield; however a delay in absorption time was observed, which is likely to come from the
Electrostatic powder coating of textile fabric and its antibacterial properties

coverage of the powder particles with the adhesive agent and the reduced surface area.

Fig. 6.5 continued.....
Electrostatic powder coating of textile fabric and its antibacterial properties

Figure 6.5 Ag⁺ absorption kinetics on  
- Base fabric,  - Resin coated fabric, 
- Powder coated fabric,  - Cashmere guard hair powder  
a. pH 1.4 / 50 ppm  
b. pH 8.5 / 50 ppm  
c. pH 10 / 50 ppm  
d. pH 11 / 50 ppm  
e. pH 10 / 10 ppm  
f. pH 10 / 100 ppm.
Electrostatic powder coating of textile fabric and its antibacterial properties

The pH value of the silver ion solution affected its absorption kinetics onto the studied sorbents. When the solution alkalinity was increased from pH 10 to pH 11, the equilibrium absorption time was decreased from 48 hours to 30 hours. However, the absorption kinetics was distinct at pH 8.5 (Fig. 6.5b), with comparatively high instantaneous silver absorption yield onto the cashmere guard hair powder and the powder coated fabric samples (~ 60%) and an equilibrium time of around 36 hours. At this pH condition, the silver ions were unstable and they tended to precipitate.

In addition to pH value, the initial silver ion concentration also influenced the absorption equilibrium time. At pH 10, with the increase in initial silver ion concentration from 10 ppm to 50 ppm and 100 ppm, the equilibrium time increased from 30 hours to 48 hours and more than 72 hours, respectively (Fig. 6.5e, 6.5c & 6.5f).

6.7 Antibacterial performance

Various products require different types of antibacterial properties. The antibacterial products have wide applications from preventing body odour and unhygienic conditions generated from next-to-skin clothings, skin medical applications to preventing the material biodegradation during storage and various usage environments. Anti-bacterial performance of the cashmere guard hair powder coated fabric was evaluated in comparison with the uncoated base fabric and the fabric, just coated with adhesive resin. All the studied fabric samples showed 100% antibacterial activity when they were treated with 50 ppm or 100 ppm silver ion solution under the same condition (i.e. pH 10, 1:400 MLR for 72 hours) and subsequently rinsed with copious amounts of running deionised water at room temperature (Fig. 6.6, Table 6.1). However, for the
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uncoated base fabric and the fabric just coated with adhesive resin, the antibacterial activity decreased when they were washed with non-ionic soap at 60 °C. In contrast, the powder coated fabric sample still retained a good antibacterial activity after washing.

Figure 6.6 Antibacterial activity of the base, resin coated and powder coated fabrics on treatment with 100 ppm silver ion solution and its washing durability.

The main reason for the poor washing durability of silver ion on uncoated base fabric and resin coated fabric is the lack of binding sites. The most likely prevailing van der Waal’s forces could be easily overcome by rigorous washing. However, in cashmere guard hair powder, silver ions could bind with
Electrostatic powder coating of textile fabric and its antibacterial properties

the active groups such as thiol groups and amino groups [125, 126] to form silver mercaptide and amino complex [44]. With low concentration of silver ion solution, all the available silver ions are likely to get bound at the abundantly available thiol sites in the powder. Although 10 ppm silver ion solution enabled to reach 100% silver ion absorption yield on the powder coated fabric (Fig. 6.5e), the bound ion cannot be released to perform antibacterial activity. This result is in good accordance with Fernandez et al’s [127] report on antibacterial activity of the loaded silver ions under protein rich environments. However, the rigorous washing could assist in releasing some of the silver ions from the powder.

Table 6.1 Effect of silver concentration and washing treatment on the antibacterial activity

<table>
<thead>
<tr>
<th>Treatment</th>
<th>% Antibacterial Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base</td>
</tr>
<tr>
<td>10 ppm - Rinsed</td>
<td>100.00</td>
</tr>
<tr>
<td>10 ppm - 1 Wash</td>
<td>99.84</td>
</tr>
<tr>
<td>10 ppm - 5 Washes</td>
<td>50.51</td>
</tr>
<tr>
<td>50 ppm - Rinsed</td>
<td>100.00</td>
</tr>
<tr>
<td>50 ppm - 1 Wash</td>
<td>100.00</td>
</tr>
<tr>
<td>50 ppm - 5 Washes</td>
<td>59.45</td>
</tr>
<tr>
<td>100 ppm - Rinsed</td>
<td>100.00</td>
</tr>
</tbody>
</table>
6.8 Thermal resistance

Fabrics with natural hand and good thermal resistance may be worthy inner lining materials for winter clothing and other applications. The cashmere guard hair powder (CHF-AM) coated fabric was consequently evaluated for its thermal resistance property. The effect of powder quantity used during the electrostatic powder coating process on the thermal resistance property was also examined.

![Figure 6.7 Thermal resistance of cashmere guard hair powder coated fabric.](image)

Thermal resistance of the resin coated fabric was improved on CHF-AM powder coating (Fig. 6.7). The thermal resistance increased with an increase in the powder quantity taken during the powder coating process. However, the thermal resistance of the resin coated fabric with no (zero gram) powder
coating decreased with the initial 1 g CHF-AM powder coating. The initial decrease in the thermal resistance could be attributed to the occlusion of the large apertures in the fabric surface on powder coating which was also reflected in the air permeability of the powder coated fabric (Fig. 6.4a). On occlusion of the apertures, the air entrapped in the fabric structure, having low thermal conductivity got replaced with the cashmere guard hair powder, having comparatively high thermal conductivity \(\text{[thermal conductivity for air = 0.0264 and for wool fibre = 0.2226 [128] and the same could be responsible for its decreased thermal resistance. With further powder coating, the increased bulk and the fabric thickness could be attributed to the improved fabric thermal resistance.}

6.9 UV-Vis absorption

The base flat knit polyester fabric was examined for any possible change in its Ultra Violet (UV) light or visible light absorption property on the resin as well as the cashmere guard hair powder coating. Absorbance in the UV light wavelength range (200-400 nm) would open up potential applications in the field of UV protection for the powder coated fabric, whereas the absorption in the visible light wavelength range (400-700 nm) would denote change in the aesthetic appeal of the fabric due to any colour change.

Fig. 6.8 shows the UV-Vis spectra of the cashmere guard hair coated fabric samples in comparison with the base and the resin coated fabric spectra. It could be noticed from the figure that there was no light absorption in the studied UV-Vis wavelength range for the base fabric since it was provided as the reference sample to the instrument and the corresponding absorption spectra have been used as the background for actual samples under
Electrostatic powder coating of textile fabric and its antibacterial properties investigation. Thus, with reference to the base fabric, the resin as well as the cashmere guard hair powder coated fabrics did not show any constructive absorption in the UV wavelength range, apart from a mere noise in the corresponding region of the spectra. However a prominent constructive change was observed in 400-500 nm visible light wavelength range representing fabric yellowness on resin as well as powder coating. Furthermore, the powder coated fabrics became stronger in hue with an associated increase in absorption in the corresponding region of the spectra when a large quantity of powder was used during coating.

Figure 6.8 UV-Vis spectra of cashmere guard hair powder coated fabric samples with different quantity of powder being used during the coating process.
Summary, conclusions and future prospects

Chapter 7
Summary, conclusions and future prospects

In short, during this PhD research work, cashmere guard hair, an industrial waste of animal hair fibre has been very first time converted into ultra-fine powder particles with an aim to explore high value technical applications. These newly developed powder particles have been utilized in the separation of toxic heavy metal ions. Furthermore, the powder particles have been successfully coated onto a textile fabric to impart functional properties such as antibacterial property. The electrostatic powder coating technique has been very first time applied in the coating of powder particles onto the textile fabric. The coated powder particles have showed good resistance to the commonly encountered weathering agents such as washing and abrasion.

Several conclusions from various studies undertaken hereto are listed herewith while highlighting the filled knowledge gaps. Prospective future works have also been discussed at the end.

7.1 Conclusions

7.1.1 Cashmere guard hair milling
Cashmere guard hair, an industrial protein fibre waste material has been very first time milled into powder particles. The milling performance of the control and partially acid hydrolysed cashmere guard hairs has been studied in comparison with wool and silk to generate new knowledge in the field. The
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Specific conclusions from this work in Chapter 4 could be summarised as below:

The milling of cashmere guard hair resulted in disintegration of surface cuticle cells and exposed the inner cortical cells on its powder surface along with oxidation of the powder surface.

The partial acid hydrolysis of cashmere guard hair led to a substantial deterioration in its mechanical properties and improved its pulverisation rate during wet attritor milling. The dynamics of particle fragmentation and aggregation during prolonged attritor milling resulted in the levelling-off of particle size to an approximately constant volume-based mean particle size \( d(0.5) \) of about 5 \( \mu m \), irrespective of the partial acid hydrolysis pre-treatment. The initial pulverisation rate of cashmere guard hair differed from wool and silk due to its large diameter. The partial acid hydrolysis of guard hairs assisted in achieving smaller particles during dry air jet milling and attained the smallest mean particle size of 0.461 \( \mu m \) for PH10CHF-AJ. However, similar partial acid hydrolysis assistance was not observed during the cashmere guard hair wet attritor milling. Air jet milling broke up the porous aggregates, created during the wet attritor milling into smaller particles and, as a result, although the mean particle sizes decreased substantially in each cashmere guard hair sample, the BET surface area showed only a slight increase.

In short, partial acid hydrolysis assists mechanical milling of cashmere guard hair into fine powder particles. Continued attritor milling for prolonged duration results into particle size levelling-off, generating porous particle aggregates that could be smashed into fine individual particles with further air jet milling. Furthermore, cashmere guard hair surface gets oxidised during milling along with an increase in the concentration of nucleophilic oxygen and
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nitrogen atoms and disintegration of the hydrophobic surface cuticle cells that is likely to improve binding of reactive chemical species.

7.1.2 Heavy metal ion removal from aqueous solutions

The newly developed ultra-fine cashmere guard hair powder particles have been explored for their toxic heavy metal ion removal potential from the industrial waste water streams. This work, discussed in Chapter 5, has very first time addressed the potential of protein fibre particles in the binding of oppositely charged heavy metal ions (cations: Zn$^{2+}$/Co$^{2+}$ and anion: CrO$_4^{3-}$). This work has also generated new knowledge on the fractional free volume (porosity) aspects of the animal protein fibres and their powder particles from the PALS work that has helped in interpreting the metal ion binding work. The specific conclusions from this work has been summarised herewith.

Cashmere guard hair powder (CHF-AM) has demonstrated good absorption kinetics towards the studied heavy metal ions \textit{viz.} Zn$^{2+}$, Co$^{2+}$ and Cr$^{6+}$, from their aqueous solutions. The heavy metal ion absorption was pH value dependent and mainly governed by ionic interactions. At basic solution pH, zeta potential values for CHF-AM, MWF-AM and ESF-AM were negative and the powder sorbents demonstrated highest absorption yields towards cationic metal ions only \textit{i.e.} Zn$^{2+}$ and Co$^{2+}$. Whereas, at an acidic solution pH of 2, the highest absorption yield was achieved for the anionic species of Cr$^{6+}$ as the zeta potential values for the powder sorbents were positive at this pH.

Cashmere guard hair powder can absorb heavy metal ions abruptly in comparison with its parent guard hair fibre which could be attributed to its high specific surface area. At equilibrium, although the absorption yield of the
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cashmere guard hair powder for Co$^{2+}$ was four times higher, the same for Zn$^{2+}$ and Cr$^{6+}$ lagged behind its parent guard hair fibre.

The absorption yield of Co$^{2+}$ was mainly governed by specific surface area of the cashmere guard hair sorbents; whereas diffusion pathways in the sorbent were instrumental in the absorption yield of Zn$^{2+}$ and Cr$^{6+}$.

The cashmere guard hair powder was more efficient in the absorption of Cr$^{6+}$ compared to wool and silk powders. However, absorption of Zn$^{2+}$ and Co$^{2+}$ appeared to be competent enough onto the cashmere guard hair powder, although it mainly lagged behind the silk powder.

Metal ion concentration gradient and metal ion specific diffusivity at the given fibre/powder – solution interface determines the respective metal ion absorption yield at a specific metal ion concentration. With increasing metal ion concentration, absorption yield of Co$^{2+}$ was decreased, whereas that of Cr$^{6+}$ was increased. Surface constrained absorption of Co$^{2+}$ and initial high Cr$^{6+}$ concentration gradient at powder-solution interface were responsible for the concentration dependent absorption yield trends.

The pH controlled metal ion desorption can make reuse of protein fibre powder sorbents and recovery of precious metal ions from their aqueous streams possible. The desorption yield of Zn$^{2+}$ and Co$^{2+}$ from cashmere guard hair powder was quick, 100% for Zn$^{2+}$ and well above 80% for Co$^{2+}$ within 30 minutes of exposure to pH 4 buffer solution. Although Cr$^{6+}$ binding was strong enough with approx. 45% desorption yield in 24 h on exposure to pH 8 buffer solution.

Alkali and alkaline earth metal ions hinder metal ion binding capacity of protein fibre powders from their aqueous solutions. The presence of alkaline earth metal ions (Mg$^{2+}$ and Ca$^{2+}$) affected heavy metal ion absorption more.
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severely than alkali earth metal ions (Na⁺ and K⁺) due to the difference in their oxidation numbers.

In short, cashmere guard hair powder may serve as an economical sorbent for removal of heavy toxic metal ions from water for environment protection purposes. Furthermore, cashmere guard hair powder could also serve as an economical alternative to wool and silk powders in metal ion binding applications.

7.1.3 Powder coated fabric and its multifunctional features

The cashmere guard hair powder particles have also been first time explored to impart functional properties to textile fabrics by successful surface coating that has showed good coated particle retentions against washing and abrasion. This work, discussed in Chapter 6, has used electrostatic coating technique in coating textile fabric that has never been used before to the best knowledge of available literature. Furthermore, the powder coated fabric has been loaded with silver ions to impart wash durable antibacterial properties. The specific conclusions from this work has been summarised as below:

The powder coating process, based on the electrostatic powder coating technique has proved to be an apt method to apply cashmere guard hair powder onto textile fabrics. Upon using a suitable resin to pre-treat the fabric substrate, the powder can be immobilized onto one side of the fabric with a good mechanical stability against washing and abrasion. The powder coated fabric was permeable to air and water that could be controlled with the resin concentration as well as the areal density of the coated powder.
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During the electrostatic powder coating process, the powder coated fabric density increased with an increase in the applied voltage; however the same was decreased with an increase in the substrate distance, air pressure and air humidity.

The cashmere guard hair powder coated fabric efficiently absorbed silver ions at alkaline pH; however the absorption kinetics delayed to the solo unbound cashmere guard hair powder due to the coverage of powder particles with resin and its limited specific surface area.

The powder coated fabric presented antibacterial features on silver ion loading to the coated cashmere guard hair powder. Although slightly high (at least 50 ppm) silver ion concentration was required to enable the loaded powder to demonstrate antibacterial properties, the powder coated fabric after loading with silver ions demonstrated improved antibacterial durability against washing.

Textile fabrics on cashmere guard hair powder coating can provide improved thermal insulation. The thermal insulation gets better with increased powder loading due to its poor heat conducting property.

To sum up, textile materials on coating with protein fibre powders acquire functional surfaces that could find novel applications in healthcare, filtration, decoration and functional textile areas.

7.2 Future work prospects

Taking hereto work as a reference, possible experimental works carrying future prospects towards improving know-how and exploring foreseen application
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trajectories as well as extending territories of already explored applications for protein fibre powders have been listed herewith.

(1) Experimental results from the wet attritor milling of cashmere guard hair have illustrated levelling-off of particle size after certain duration of milling. Dynamics of particle fragmentation and aggregation during long milling hours has been considered as a reason behind the phenomenon. However, further experiments to investigate the effect of different attritor milling parameters such as size of the milling media, material to liquor ratio (MLR) and quantity of media per unit volume of the milling chamber (g/cm$^3$) on the particle size levelling-off tendency could improve the know-how on the process.

(2) The standard design of a spray drier could be modified to incorporate a high voltage electric field after the atomiser. The similar charge generated on the individual particles in an aggregate would help to separate them and thus to achieve fine powder particles, with no possible need to air jet mill for disaggregation.

(3) Studies could be undertaken to mill protein fibre powders with improved porosity to assist molecular diffusion. The porosity could be indirectly interpreted from the change in moisture regain after milling. Protein fibre powders with improved porosity would be much more efficient in environmental protection applications such as absorbing toxic chemical species.

(4) Experimental results have shown surface absorption of Co$^{2+}$ on protein fibre powders from its aqueous buffered solution. Metal ion specific
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studies considering the respective ion radius and sorbent pore size would throw further light on the metal ion diffusion in the protein fibre sorbents.

(5) Animal hair fibres could be dissolved in ionic liquids and regenerated via self-assembly in the form of microspheres. Charactering mechanically milled as well as self-assembled animal hair powders simultaneously, would ascertain powder specific (milled or regenerated) application trajectories.

(6) The prospects of protein fibre powder coated fabrics as artificial leather could be investigated which may potentially open up an opportunity of mass powder consumption. This would also emphasize the need to develop continuous protein fibre powder coating process on fabrics.

(7) Wet attritor milled, protein fibre slurry could be co-spray dried with fragrant molecules to explore aesthetic applications.

(8) To explore and realise the full application potential of protein fibre powders in the field of medical science, fine powder particles with narrow particle size distribution are sought for drug and growth factor delivery. This could be potentially achieved in two ways, first by controlling or modifying the milling process and second by segregating the milled powder particles with wide particle size distribution into different size range batches.

(9) Mechanically milled protein fibre powder particles, even with a wide particle size distribution can potentially be used as drug/growth factor carriers in composite scaffolds, considering no major need of particle aqueous dispersability in the application. Attritor milled slurry could be co-sprayed with drug molecules on the spray dryer and the resultant powder particles may be incorporated in composite scaffolds. The powder
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particles would help in providing mechanical stability to the scaffold structure and could also assist in growth factor delivery. However, experimental efforts in this regard are missing.
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