REVIEW PAPER

Keratinous Materials as Novel Absorbent Systems for Toxic Pollutants

Arun Ghosh* and Stewart R. Collie

Food and Biobased Products Group, AgResearch, Canterbury 8140, New Zealand
*E-mail: arun.ghosh@agresearch.co.nz

ABSTRACT

A range of hazardous organic and inorganic compounds, and metal ions generated by human and industrial activities leads to serious concerns for environments. Adsorption technologies based on polymeric materials are being used to remove toxic substances from air and wastewater streams. Keratin protein, found abundantly in sheep's wool, human hair and bird feathers, is an interesting and potentially useful renewable biopolymer. It contains a variety of functional groups on the backbone and side chains of the proteins, and is an ideal component to fabricate a range of novel absorbent systems for separation of toxic pollutants via physisorption or chemisorption mechanisms. In this review article, the key activities on keratin research and development with respect to the novel properties of keratin proteins and their utilization as absorbents or filtration systems are summarized. It is apparent that keratins in the form of loose fibers, non-woven fabrics, short fibers or particles, membranes and colloids can be used as absorbents for air filtration and wastewater treatment. Keratin materials have potential to be applied in biological and chemical defence applications, and also in protection against radioactive elements.

Keywords: Keratin, absorbent, filtration, pollutant, environment

1. INTRODUCTION

Municipal, industrial and agricultural activities can generate pollutants, which are potentially hazardous to health and can cause serious pollution to air and water environments if not captured or neutralized before air or water discharges are released to the environment[1,2]. Commonly found inorganic pollutants are heavy metals including radioactive substances, which are highly toxic and carcinogenic in nature. Organic pollutants include pesticides, phenolic compounds, halogenated aromatic hydrocarbons, formaldehyde, normal hydrocarbons, alcohols and pharmaceutical reagents. Microbes also generate potentially toxic biochemical agents in the environment. These pollutants exist in environment either in solvated, colloidal or suspended forms[2,3].

Techniques based on distillation or evaporation, coagulation, precipitation, electrolysis, ion exchange and adsorption are used to remove pollutants[2,3]. Adsorption technology is being commonly used for the removal of organic and inorganic pollutants from the aqueous phase. Since its first introduction in the 1940s, activated carbon has become the standard adsorbent for the recovery of municipal and industrial wastewater to a potable water quality[1]. Adsorbents based on petro-derived synthetic polymers, agri-wastes, fly ashes, and mineral-based zeolites and geothites are also being used for removal of toxic pollutants from environment[2-4].

Among the natural materials, keratin proteins are potentially useful materials to use in absorbents or filtration systems for removal of toxic pollutants, because of the number of functional groups present on the backbone and side chains of the proteins. Keratins, predominantly found in wool, human hair and nails, horns and feathers, are cysteine-rich proteins with robust mechanical properties, thermal durability and resistance to physicochemical degradation from the exposed environment. Keratin wastes obtained from poor quality raw wool from the textile industry and feathers from poultry processing, amount to more than 5 million tons per year worldwide[5-8]. Therefore, keratin wastes represent an important renewable biopolymer source and opportunities exist in creating biodegradable filtration systems or absorbents for a range of applications related to air and water purification. This article discusses the key areas of emerging keratin research and development with respect to the novel properties of keratin proteins and their utilization for removal of hazardous pollutants.

2. GENERAL CHARACTERISTICS OF KERATINS

Keratin is an important structural protein in nature and is found in abundance in the integument in vertebrates. Keratinous materials can be considered as fiber-reinforced composites consisting of crystalline intermediate filaments embedded in an amorphous protein matrix[9,10]. They have different morphologies, protein profiles and functions. Keratins are broadly divided into two categories such as epithelial keratins and trichocyte keratins, which are also known as soft and hard keratins, respectively. The former are found in the stratum corneum of the skin, and the function of epithelial keratins is the stabilization of cells in epithelia. The general function of the trichocyte keratins is to act as structural scaffolding and they are found in a range of biological fibrous materials, including sheep's wool, human hair, feathers, and the nails and horns of mammals. Keratins are generally found in the form of, or associated with, filamentous structures, known as keratin

intermediate filaments[10-12]. In contrast to the epithelial keratins, which have low cysteine content (< 3 mol%), the hard keratins notably contain a high level of cysteine (4-17%)[6, 13], and are characterized by high levels of protein-protein crosslinking. In addition to cysteine, keratins are rich in glutamic acid, aspartic acid, threonine, leucine, proline, serine and glycine amino acids. The amino acids compositions of keratin proteins found in different biological materials are summarized in Table 1 with their side chain chemical structures.

There are four distinct keratin classes observed in mammalian fibers such as wool and hair. The major component is intermediate filament proteins with a cysteine content of 4 mol% - 6 mol% and a molecular weight range of 45 kDa - 60 kDa[14]. The remaining classes are described as keratin-associated amorphous proteins. This includes two classes of

high sulphur proteins, with molecular weights ranging from 10 kDa to 35 kDa, and also a class of proteins high in glycine and tyrosine, with a molecular weight range of 7 kDa - 9 kDa[15]. The intermediate filament proteins are highly structured; they have a high degree of α-helical structure and the central region is characterized by a heptad repeat moiety[15]. In biological materials, these proteins are assembled in coiled-coil structures with general dimension of 10 nm × 100 nm, and stabilized by salt bridges and hydrophobic interactions. Feather proteins are composed of β-keratin and the molecular mass of this keratin is in the range of 10 kDa - 30 kDa[10,16]. The folding pattern of β-keratin is β-sheet with a diameter of 4 nm. The intermediate filament of β-keratin of feather has a helical structure with a pitch of 9.5 nm and four turns per unit. Interestingly, it undergoes a phase transformation (α – β transition) under
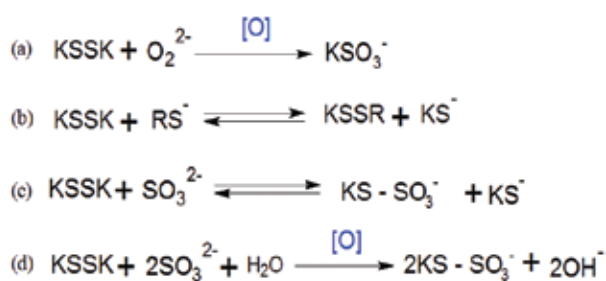
Table 1. Amino acid compositions (mol%) of keratinous materials

Amino acids			Sheep wool[7,21,96-100]	Human Hair[101-103]	Bird Feather[104,105]	Horn-Hoof[7]
Group	Name	Side chain				
'Acidic' amino acids with carboxyl group in side chain	Aspartic acid	—H$_2$C——COOH	7.0 – 11.0	5.2 - 7.6	5.4 – 7.3	8.7
	Glutamic acid	—(CH$_2$)$_2$—COOH	12.0 – 13.8	11.6	8.4 – 10.9	16.3
'Basic' amino acids with amino group in side chain	Lysine	—(CH$_2$)$_4$—NH$_2$	3.0 - 3.4	2.5 – 3.0	1.1 – 2.2	4.6
	Arginine	—(CH$_2$)$_3$—NHC—NH$_2$ ‖ NH	3.3 – 10.2	4.9 – 6.1	5.0 – 7.3	10.8
	Histidine	—H$_2$C—(imidazole)	0.8 – 1.3	0.8 - 1.1	0.5 – 1.6	1.3
Amino acids with hydroxyl group in side chain	Serine	—H$_2$C——OH	8.5 – 10.9	11.7 – 12.4	9.3 – 11.8	7.2
	Threonine	—HC —OH | CH$_3$	5.8 – 6.4	6.9 – 7.7	4.0 – 4.5	5.1
	Tyrosine	—H$_2$C—(ring)—OH	3.3 – 5.9	1.2 – 2.1	3.0 – 4.7	4.5
Sulfur containing amino acids	Cysteine	—H$_2$C—SH	5.8 - 11.3	10.0 – 16.8	5.1 – 7.7	7.1
	Methionine	—(CH$_2$)$_2$—S—CH$_3$	0.4 – 0.6	0.6 - 2.5	0.3 – 0.7	1.0
Amino acids without reactive groups in side chain	Isoleucine	—HC —CH$_2$—CH$_3$ | CH$_3$	3.1 – 3.5	2.9 - 3.1	3.5 – 5.0	4.1
	Leucine	—H$_2$C—CH(CH$_3$)CH$_3$	6.8 – 8.1	5.9 - 7.1	6.2 – 8.3	8.7
	Valine	—HC —CH$_3$ | CH$_3$	5.1 – 6.4	5.8 - 6.2	6.1 – 8.5	5.3
	Phenylalanine	—HC —CH$_3$ | CH$_3$	2.1 – 3.6	1.6 - 1.9	3.2 – 5.3	3.2
	Glycine	—H	4.6 – 9.4	5.6 - 6.6	7.6 – 8.1	4.0
	Alanine	—CH$_3$	3.3 – 8.1	4.3 - 5.2	3.3 – 4.7	3.7
	Proline	—C(pyrrolidine N—H)	5.7 – 7.1	7.7 - 9.6	9.0 – 10.2	4.4

tensile load[10]. As noted earlier, the high cysteine level within hard keratins leads to compact three-dimensional structures via extensive intra- and inter-molecular bonding that confers high stability[17].

3. EXTRACTION OF KERATINS AND FABRICATION OF MATERIALS

Keratins are structural proteins with high levels of intra- and intermolecular disulfide crosslinking, and as a consequence, extraction of keratins with retention of the desired properties is difficult. For the production of new materials from wool or feather, the necessary step is chemical deconstruction through targeted breaking of intermolecular disulfide bonds, while maintaining the covalent bonding of the primary protein chain. It can be achieved by reduction, oxidation, sulfitolysis or oxidative sulfitolysis processes[8]. When using strong oxidants such as hydrogen peroxide or performic acid, cysteine residues are converted to cysteic acid, generating soluble keratose (Scheme 1a), which is an irreversible process. Reduction of cysteine bonds with thiols such as mercaptoethanol or thioglycolic acid can produce soluble keratin via a reversible nucleophilic displacement reaction (Scheme 1b). Sulfitolysis cleaves the disulfide bond by sulfite ion and produces the S-sulfonate anion, which is a reversible reaction (Scheme 1c). Oxidative sulfitolysis converts the disulfide into two S-sulfonate anions in an irreversible reaction (Scheme 1d). In addition to cleavage of disulfide bonds, the extensive non-covalent attractive forces occurring within the wool or feather need to be overcome during solubilization. These include ionic interactions or salt bridges between charged acidic and basic amino acid residues, hydrogen bonding between polar amino acid side chains, and hydrophobic interactions or van der Waals forces, between non-polar regions of the protein. Therefore, aqueous solutions of chaotropic reagents such as urea or guanadinium hydrochloride are also needed to bring the bulk of the soluble proteins into solution[18-20]. There are reports of ionic liquids being used to solubilize keratin materials through breaking intermolecular disulfide and hydrogen bonds within keratin proteins[21-25].

(a) $KSSK + O_2^{2-} \xrightarrow{[O]} KSO_3^-$

(b) $KSSK + RS^- \rightleftharpoons KSSR + KS^-$

(c) $KSSK + SO_3^{2-} \rightleftharpoons KS\text{-}SO_3^- + KS^-$

(d) $KSSK + 2SO_3^{2-} + H_2O \xrightarrow{[O]} 2KS\text{-}SO_3^- + 2OH^-$

Scheme 1. Reaction mechanisms of keratin extraction: (a) oxidation, (b) reduction, (c) sulfitolysis, and (d) oxidative sulfitolysis

Extracted keratins have been used for fabrication of a range of products such as films, membranes, foams, scaffolds, hydrogels, particles and fibers or fabrics. Fabrication of fibrous membranes or mats based on functional polymers such as keratin with numerous polar and ion-exchangeable groups is advantageous for active filtration of toxic substances such as volatile organic compounds and heavy metals. Electrospinning is used commonly to create nano-fibrous membranes using an electric field. In general, nano-structured systems with high porosity, surface area and small inter-fiber pore size, exhibit good filtration efficiency, removing tiny particles (<0.3 micron)[5,26]. One potential disadvantage of extracted keratin-derived fibers is the poor physico-mechanical properties of the finished fiber, especially in the wet state. Pure keratin solutions also have a tendency to gel rapidly[27]. Therefore, particularly for applications requiring high mechanical performance, recent research has focused on blending of keratin with other polymeric materials using a common solvent system[11,27]. For instance, solubilized keratins can be blended with polymers such as polyamide 6, polyethylene-oxide and polyhydroxybutylate-co-hydroxyvalerate to produce materials with good mechanical properties and performance[5,6,26,28,29].

4. MECHANISMS OF POLLUTANT REMOVAL

The mechanisms by which keratin materials remove pollutants from a solution or atmosphere, are based on a combination of physiosorption and chemisorption[30]. Physisorption refers to trapping of pollutants in a porous network or on the surface of keratin materials. Chemisorption occurs at chemical functionalities present on keratin proteins. Particularly, the main functional groups including peptide bonds and side chains of amino acid residues offer active chemical sites for removal of metal ions and organic volatiles such as formaldehyde[5,6]. Natural hard keratin materials are highly organized at the protein molecular scale which can limit accessibility of reactive sites. In hairs, proteins are arranged into filaments surrounded by a matrix consisting of accessory proteins (so called keratin associated proteins). Keratin filaments are stabilized by a chemical bond network and by inter-protein interactions. They form hydrophobic stripes that infer a high level of stability on rod regions of keratin dimers[17]. Structural changes in the keratin materials due to chemical treatments, in particular those that disrupt the molecular organization, play a significant role in absorption of pollutants. Natural wool and feather have regular α-helix and β-sheet structures, which are converted into a random coil structure by disrupting the bond network and protein structure using chaotropes (Fig.1). A random coil is a looser structure of protein and hence more sites are available for pollutant absorption[31-33]. However, the pollutant absorption depends on a range of factors such as composition of absorbent and its amount, specific surface area and activity, physical form of absorbent, solution pH, initial concentration of pollutants, temperature, and also the presence of other pollutants and their concentrations.

Regeneration of sorbents is an important feature for their potential in commercial applications. In general, compared to loose fibrous or particulate sorbents, mesh-shaped fabrics with non-woven structures are ideal with respect to uniform and reproducible properties, which enable them to be cleaned and reused[31]. Keratin contains a large number of ionisable groups and its isoelectric point is 4.5[5]. This unique characteristic of keratin influences the structures and surface properties of keratinous materials and can affect the absorption and desorption characteristics of the absorbent systems via
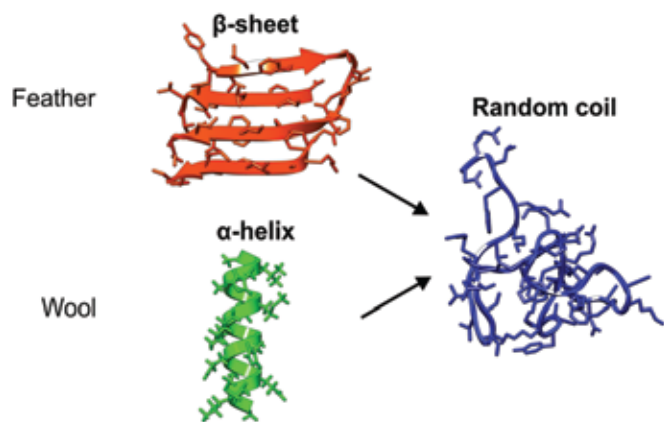
Figure 1. The random coiled structure of chemically extracted keratin has more loose structure with greater accessibility to reactive groups compared to α-helix and β-sheet structures of natural keratins (Courtesy of Duane Harland, AgResearch, New Zealand).

changing electrostatic or ionic interactions depending on solution pH (Scheme 2).

When the keratin material is being used as a filter, there are other mechanisms involved in removal of contaminants. For example, wool-based filters (and those made from other fiber types) remove contaminant particles (i.e. solid dust or liquid droplet) from airstreams via mechanical processes, specifically impaction, interception and diffusion[34]. Electrostatic wool-based filters (e.g. electrets) also remove contaminants via Coulombic attraction or dielectrophoretic effects[35].

5. ELECTROSTATIC CHARACTERISTICS OF KERATIN MATERIALS

Fibers generate static electricity during textile processing and in use, due to frictional contact and separation between dissimilar materials, which is referred to as tribo-electric charging. Accumulation of static charge can contribute to soiling in textiles, as dust particles are attracted to the material. However, the same phenomenon can be used for beneficial effect in electrostatic filters whereby electrostatic attraction works along side mechanical processes to remove contaminants from an airstream. Hersh and Montgomery appear to have been first to establish a triboelectric series for polymeric fibers[36], indicating the relative amount and sign of charge that would be generated when two materials are touched together and separated. For example, if wool and polyethylene were touched and separated, the wool would gain a high positive charge and the polyethylene a high negative charge. The triboelectric series is not as absolute as might be expected; factors such as moisture content of materials can influence it, and different

series have been derived. The wool fiber is usually at the positive extreme, with polytetrafluoroethylene at the negative extreme[37,38]. It has been claimed that wool could be made to occupy any position in the triboelectric series, by corona and/or chlorine treatment[39], creation of sulphonate groups[40] or acylation on the surface of the wool[41].

The electrostatic properties of wool, in combination with other materials, have been exploited in producing electrostatic filters, or 'electrets'. An electret is the electrostatic equivalent of magnet, being a material having balanced and durable positive and negative charges. The so-called Hansen Filter[42] is possibly the original wool based electret filter and consists of a wool fibrous assembly impregnated with pine resin particles, which loosely adhere to the wool fibers. In this filter, static electrical charges are generated during preparation and handling of the filter material. It has been observed that highly compressed filters have longer shelf-life than loose ones, up to 15 years[43]. Their filtration efficiency drops in use as charged aerosol particles are deposited, neutralizing the charge on the filter. Filters made using coarser wools would be expected to be less efficient, because of a lower specific surface area than fine fibers, which reduces the electrostatic forces involved. They are also less effective in their mechanical filtration role because of the smaller number of fibers and larger pore size. Kim[44] et al. reported the characteristics of wool-based filters ('Mighty-Micron Filter' and 'Uni-Micron Filter'), where a blend of wool and polyester was coated with p-t-butyl phenol formaldehyde resin, which was then mechanically fractured into particles, giving it a composition and structure reminiscent of a traditional Hansen filter. Resultant filters with 16 per cent resin by mass, showed 99.999 per cent efficiency with pollutant particles greater than 0.3 μm in an airstream of 0.05 m/s with a pressure drop of 30 Pa.

Electret filters based on binary mixtures of two discrete fibers (polypropylene and modacrylic) appear to have emerged in the 1980s[34, 45]. Wool-based filters have been prepared from binary mixtures of 21 μm carbonised wool and 3 denier polypropylene by carding and needling, and have been compared with a commercial conventional filter and a wool-resin filter[46]. The best filtration performance was achieved with a ratio that gives approximately equal total fiber surface area; for example, in a filter of 60 per cent wool and 40 per cent polypropylene, with the diameter of the polypropylene fiber approximately equal to that of the wool (the difference in mass ratio is necessary to compensate for the lower density of polypropylene fiber). In further work, respiratory filters for fire fighters were developed based on wool and heat resistant aramid fibers, which provided moderate filtration with high heat resistance[47].
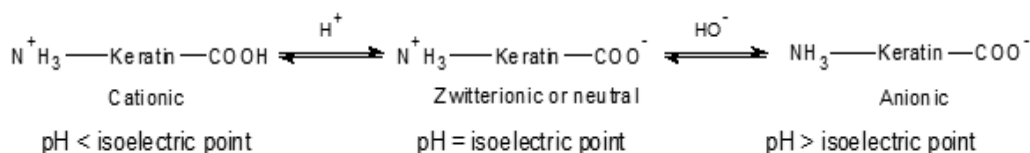
Scheme 2. Amphoteric behavior of keratin molecules, key mechanism of absorption and desorption of metal ions

6.   AIR FILTRATION BY KERATIN MATERIALS

Until the advent of synthetic polymers and fibers in the middle of the 20th century, natural fibers were utilized in filtration applications. Wool can be considered as a technical fiber with a variety of novel properties[48], and in recent years wool has tended to find commercial use in more specialized fields, such as electrostatic filters (electrets) and for removal of oil from water or airstreams[49].

6.1 Passive Uptake of Volatile

Wool keratin in the form of interior textiles such as carpets and upholstery has been demonstrated under passive uptake scenarios to improve indoor air quality by absorbing volatile compounds such as formaldehyde and oxides of sulfur and nitrogen. When simply placed in the same environment as the volatile, wool spontaneously absorbs the volatile from the atmosphere. When evaluating 150 g wool in a 0.158 m^3 chamber with initial formaldehyde concentration of 20 ppm, it absorbed the volatile completely in 4 h, indicating 0.026 mg formaldehyde absorption per gram wool[50]. Under the same conditions with 400 ppm formaldehyde, complete absorption was observed after 35 min, with the wool holding 0.42 mg formaldehyde per gram[50]. Formaldehyde can be released by paints or treated wood products. Oxides of sulphur and nitrogen are known air pollutants that can arise in the indoor environment from combustion processes, such as gas heating or cooking. When wool carpets were exposed to a stream of sulphur dioxide of 2.32 ppm, they absorbed the pollutant at a rate of 0.012 mg per gram of wool per minute initially, which had dropped to 0.003 mg per gram of wool per minute after 60 min[51].

When wool fabrics were exposed to a continuous flow of volatile organic solvents such as toluene and 2-butoxyethanol at 18 °C and 43% relative humidity, maximum uptakes on wool of 0.39% and 0.63% (by mass) were observed, respectively[52]. The absorption process was slow, being ~7.5 h and 28 h, respectively. Nonetheless, it appears that wool has a slight affinity for certain organic solvents, and binds them reasonably securely (approximately half of the toluene desorbed after 18.5 h, and about 12% of the 2-butoxyethanol after 20.5 h). Wool fabrics were used in a study of the uptake and release of cigarette smoke components. Untreated wool had a higher uptake of smoke and a lower desorption than a fluorocarbon-treated wool, and after desorption each gram of untreated wool contained 4 mg of smoke, indicating wool can securely bind smoke constituents[53].

6.2 Active Uptake of Volatile

Most research interest in wool's absorption of volatile has been in passive air filtering in the context of interior textiles and indoor air quality. However, some work is reported on the capacity for wool to provide active contaminant removal in filtration scenarios, i.e. with loose fiber or a non-woven pad having a contaminated airstream forced through it. In one study, the sulphur and nitrous oxides uptake of 35 μm wool before and after modification with various oxidizing agents (chlorine, permonosulphate and permanganate), in dry (7.7 to 10.4% moisture content) and moist (50% moisture content)

conditions were investigated[54]. The uptake of both gases was substantially increased in moist conditions (treated and untreated fiber), and after permanganate treatment. Untreated wool had an average sulphur and nitrous oxides absorption of 5% and 47% respectively, whereas permanganate treated wool absorbed 12% sulphur dioxide and 53% nitrous oxide. It indicated that wool has higher gas absorption capacity than that of activated carbon, for example, it can absorb 31% nitrous oxide[54].

In the 1970s, wool was investigated for use as a filter for cigarettes as an alternative to the standard cellulose acetate fiber material. It was postulated that its capacity to absorb compounds from the smoke-stream and potentially react with them, as well as the protruding scales on wool, would provide some benefit[55]. Particulate removal was found to be comparable to that of cellulose acetate, with a random fiber assembly performing best[55]. In a subsequent study, the filter performance of Indian 'canary-yellow' stained wool was compared with Merino wool and cellulose acetate[56]. Canary-staining is caused by warm humid conditions during wool growth; canary-stained wool is also thought to have no epicuticle. It was found that the canary-stained wool reduced the amount of nicotine in the downstream airflow to a greater degree than the Merino wool and the cellulose acetate.

Loose wool and woven wool fabric filters, each of 32 g, used in a 96 L closed chamber with formaldehyde concentration of 1 ppm, removed about 70% formaldehyde over a period of 3 h. The rate of formaldehyde uptake increased with higher air temperature and relative humidity, because the binding of formaldehyde to wool is via a chemical reaction that is accelerated by increased temperature and high humidity[57]. In another study, filters were fabricated with wool, carbon fiber and activated carbon particles; these showed almost twice the formaldehyde uptake compared to wool alone[58].

Formaldehyde uptakes of wool-based electrospun nano-fibrous membranes (a blend of wool keratin and polyamide) along with other polymeric filters were investigated using a 3.3 L chamber with initial formaldehyde concentration of 0.06 ppm. It was observed that a polypropylene filter and a multi-component filter based on polypropylene sheet and polyamide 6 nanofiber reduced the formaldehyde concentration by about 30% and 40%, respectively, which occurred via a physisorption mechanism. The formaldehyde reduction reached 70% in presence of the keratin based nanofiber due to both physisorption and chemisorption occurring simultaneously[6]. In general, keratin-rich nano-fibrous membranes showed better volatiles removal capacity than conventional wool fabrics and synthetic polymers, and the removal capacity increased with increasing keratin content in filtration systems. The amino groups present in the side chains of selected amino acid residues (lysine, arginine and histidine) of keratin proteins are likely to interact with formaldehyde (Scheme 3).

6.3 Removal of Oily Substances

The wool fiber surface has an intrinsic affinity for oily substances, so is likely to perform well in filtration scenarios requiring removal of oil. Commercial application of wool has been made in cleaning up oil spills, and for filtering oil from

$$Keratin{-}NH_2 + \underset{H\ \ \ H}{\overset{O}{\overset{\|}{C}}} \longrightarrow Keratin{-}\underset{}{\overset{H}{\overset{|}{N}}}{-}CH_2{-}OH$$

Scheme 3. Formaldehyde absorption by keratin: Available amino groups in keratins chemically interact with formaldehyde

aqueous waste streams. Wool-based filters for grease-laden airstreams have also been developed for use in extraction hoods over fryers and stoves in commercial kitchens[49]. When oil droplets land on the upstream surface of the fiber it is thought that they tend to spread over the fiber surface, instead of just accumulating on the upstream surface. In these circumstances, the pores in the filter remain open for longer, allowing the air stream to continue to penetrate into the fibrous assembly, increasing the filter's useful life. This attribute is not unique to wool; synthetic fibers can also have oleophilic surfaces, either intrinsically or via a surface treatment. It should be noted that wool's affinity for oil is associated with the cuticle of the fibers, and lipids bound to it. Removal of these layers by physical or chemical degradation will reduce the oleophilic nature of the fiber.

Table 2. Removal of metal ions by different forms of keratin materials

Keratin based absorbents	Metal ions (removal level, per gram absorbent)	Contact time	Initial ion concentration	Solution pH	References
Non-woven mesh based on duck feather (adhesive bonded)	Cu^{2+} (41%)	1 h	8 mM	11	Jin[31], et al.
Wool filter coated with Bauxal™	As^{3+} (34-53 %)	1 h	104 ppb	4-5	Hassan[67]
Wool filter produced by needle punching technology	Cu, Fe, Zn, Hg (~ 100 %); As (50 %); Cr (80 %)	24 h	5 ppm	--	McNeil[4]
Hybrid polyurethane membrane with 15 wt% chicken keratin (resin and fiber)	Cr^{6+} (38%)	-	100 ppm	6-7	Saucedo-Rivalcoba[60], et al.
Electrospun nano-fibrous membranes with 50 wt% keratin resin	Cr^{6+} (56 mg); Cr^{3+} (0.7 mg); Cu^{2+} (62-103 mg)	24 h – 48 h	Cr^{6+} (5-200 ppm); Cr^{3+} (0.05 ppm) Cu^{2+} (0.5-35 ppm)	2-5.8	Aluigi[5,6,26], et al.
Chicken feather (alkaline and ultrasonically treated)	Pb (3.83-12 mg); Cu (3.25 mg); Hg (4.36 mg); Cr (3.5 mg)	30 min	10-40 ppm	1.5-6	Kar & Misra[30]
Chicken feather treated with epichlorohydrin and ethylenediamine	Cr^{6+} (90%)	24 h	10-80 ppm	1 – 3	Sun[65], et al.
Poultry feather fiber	Pb^{2+} (0.8-8.3 mg)	5 h	10-200 mg/L	2-5	de la Rosa[62], et al.
Human hair fiber	Cu^{2+} (35 µg); Zn^{2+} (10 µg): Mn^{2+} (1.1 µg); As^{3+} (0.1 µg)	-	0.3 ppm	4.6-5	Fergusson[63], et al.
Human hair treated with $NaOH/Na_2S$	Hg^{2+} (104 mg); Cd^{2+} (53 mg); Cu^{2+} (29 mg)	20 min	900-1000 ppm	1-5	Tan[66], et al.
Chicken feather powder	Au^{2+} (60-160 mg); Pt^{2+} (40-85 mg); Pd^{2+} (20-60 mg)	1 h – 5 h	3 mM	1-3	Suyama[73], et al.
Chicken feather particle	Zn^{2+} (100%)	1 h	-	3-5	Aguayo-Villarreal[64], et al.
Chicken feather particle treated with NaOH and dodecyl sulphate	Cu (100%) Zn (100%)	20 min	10-100 ppm	-	Al-Asheh[69], et al.
Colloidal keratin solution	Pb^{2+} (43.3 mg)	10 min	1 mM	5	Sekimoto[72], et al.
Keratin amino acid immobilized silica particle	Ca, Fe, Mg and Mn (72-94%)	20 min – 30 min	50-1000 ppm	6-9	Sayed[59], et al.

7. REMOVAL OF METAL IONS

Metal ion contamination is a serious concern that makes water unsafe for drinking and other human activities. Metal ions also cause detrimental precipitation of scale or deposition of suspended matters, corrosion and increased energy consumption in industrial water systems[59]. Keratinous materials such as wool, human hair and bird feathers are being investigated in the form of particles, loose fibers, non-woven fabrics, membranes and colloidal dispersions for removal of toxic metals ions from wastewater streams (Table 2).

7.1 Keratin Membrane

Hybrid membranes based on chicken feather keratin for removal of toxic metals have been investigated[60, 61]. The membrane, consisting of synthetic polyurethane as support matrix and keratin biofiber or resin as active sites, was used to remove Cr^{6+} for wastewater treatment[60]. It showed good Cr^{6+} adsorption (38%) capacity when it had membrane pore size of 5 nm and keratin or biofiber content of 15 wt%. The elastomeric nature of polyurethane provided appropriate stiffness to the membrane. The structural changes of the membrane are significantly affected by the pH of keratin or biofiber solutions, which influenced metal ion removal[60].

Electro-spun membranes based on continuous randomly oriented nanofilaments of wool keratin and polyamide 6 (50/50 wt) blends have been created with a mean fiber diameter of 150-200 nm. They were used to remove Cr^{3+}, Cr^{6+} and Cu^{2+} ions[5, 6, 26]. While testing with Cr^{6+} ion with hydrolyzed keratin/polyamide nano-fibrous membrane, the adsorption capacity increased from 2.1 to 55.9 mg/g for the initial Cr^{6+} ion concentration of 5 to 200 ppm, which is attributed to the high driving force for mass transfer of the highly concentrated starting solutions[26]. In contrast, the removal Cr^{3+} is low, around 0.7 mg/g with the nanofibrous membrane with keratin content of 30 wt%. For Cu^{2+} ion removal, the maximum adsorption capacities for nanofiber mats containing 50, 70 and 90 % keratin were found to be 62, 90 and 103 mg/g, respectively[5]. The high Cu^{2+} ion removal capacity is due to the complex formation of Cu^{2+} with carboxyl groups of keratin proteins[5].

7.2 Keratin Fiber

Loose keratin fibers have been used to create absorbents for metal ion removal. Untreated keratin fibers exhibit low levels of metal ion absorptions. For example, when untreated feather fiber (0.5 cm in length) was used as an absorbent, Pb^{2+} removal was very low, the maximum removal was in the range of 0.8 to 8.3 mg/g with contact time of 5 h[62]. Untreated cleaned human hair (0.1–1.0 cm) absorbed low levels of Cu^{2+} (35μg/g), Zn^{2+} (10 μg/g), Mn^{2+} (1.1 μg/g) and As^{3+} (0.1 μg/g) from aqueous solutions with initial metal ion concentration of 0.3 ppm[63]. In general, with increasing initial metal ion concentration, the amount of absorbed metal ion increased. For example, when 100 ppm Zn^{2+} solution was used, the maximum sorption capacity of the ion was found to be 1.5 mg/g of cleaned chicken feather[64].

To improve metal ion removal capacity, keratin fibres were treated under different chemical conditions. Chicken feather fiber was chemically treated to create additional functionalities such as hydrophilic and chelation properties. In this case, feathers were first treated with aqueous NaOH that caused exfoliation of the keratin layer of the feather surface, and dissolved keratin fragments were then re-joined to the feather surface using epichlorohydrin as a cross-linker. Ethylenediamine was applied to provide additional amino groups on the feather surface to enhance metal ion absorption via chelation[65]. These changes of chemical structure and morphology of feather fiber due to treatment improved metal ion removal. For example, untreated and alkali treated fibers showed 30.5% and 43.5% Cr^{6+} removal, respectively. Cr^{6+} removal capacity of alkali-treated fiber increased to 81.4% on treatment with epichlorohydrin, which increased further to 90% on treatment with ethylenediamine[65]. In another study, human hair fiber was treated with $NaOH/Na_2S$ and it showed good adsorption capacity for various metal ions. One gram of treated hair fiber adsorbed 104 mg Hg^{2+}, 53 mg Cd^{2+} and 29 mg Cu^{2+} from solutions with initial metal ion concentrations in the range of 900–1000 ppm. In general, metal ion adsorption was found to decrease in the following order: Hg^{2+} (Hg^+), Ag^+, Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{6+}, Ni^{2+}, Cr^{3+}[66].

The pH of solution has a substantial effect on removal of metal ions by alkali-treated keratin fiber. Keratin fibres removed Cu^{2+} (3.25 mg/g) and Pb^{2+} (3.83-12 mg/g) from solutions at pH 5-6. They removed Cr^{6+} (3.5 mg/g) and Hg^{2+} (4.36 mg/g) from the solution of pH 1.5-6. Uranium removal was observed at relatively high pH values (pH 5-8). In all cases, the rate of metal ion removal was rapid and the adsorption process was completed in 30 min[30].

7.3 Non-woven Keratin Mesh

Non-woven filters or meshes based on Bauxsol™ immobilized wool fabrics were used to remove arsenite (As^{3+}), a common arsenic species in ground water. When tested at pH 4-5, wool filters coated with acid-neutralized Bauxsol™ removed only 53.3% As^{3+} from a water solution with initial 104 ppb arsenic, and also removed 96-100 % Pb^{2+} and Cu^{2+} from water with initial metal concentration of 5-510 ppb[67]. In another study, non-woven composite fabrics based on untreated and alkali-treated duck feathers and 20 − 30% bicomponent polyolefin adhesive were prepared using a thermal compression molding method. The untreated and alkali-treated feather fabrics showed average Cu^{2+} absorption capacity of 17 and 41%, respectively[31]. The fabrics also exhibited similar level of Cr^{6+} absorption from the aqueous Cr^{6+}/Cu^{2+} solution[31]. In a different study, feathers were fabricated into nonwoven-webs with good mechanical properties using air-laying followed by needle punching and thermal bonding processes. These webs were used as absorbents to remove metals including Cu, Zn, Ca and Mg from wastewater streams[68]. Non-woven wool filter, produced by needle punching technology, showed complete removal of various metal ions (Cu, Fe, Hg and Zn) and partial removal of As and Cr from a solution with initial ion concentration of 5 ppm[4].

7.4 Keratin Particles

Keratin particles obtained from feathers have been used to create absorbents to remove several metal ions. In one study, chicken feather particles were treated separately with NaOH and

anionic surfactant dodecyl sulfate solutions and used to remove Cu and Zn from aqueous solutions with ion concentration of 10-100 ppm. It showed that alkali-treated feathers adsorb more metal ions than those treated with the anionic surfactant, followed by the untreated feather. Generally, the kinetics of the metal removal for all sorbents was fast, removing most of the metals during first 20 minutes[69]. In another study, the amino acids extracted from chicken feathers using alkali treatment (NaOH/NaOCl) were immobilized on a silica surface to create regenerable particulate sorbents. They removed around 72 to 94% metals (Ca, Mg, Fe and Mn) from water at a pH of 6-9 within 20-30 minutes[59]. Milled wool or hair powder dramatically increased the rate of metal ion absorption[70, 71]; for example, milled wool powder showed ~42 fold higher uptake of Cu than that of the wool fiber[70].

7.5 Keratin Colloids

The removal of metal ions from aqueous solutions with a keratin colloid has been reported. Around 88% Pb^{2+} was removed from a solution via precipitation of a Pb-keratin aggregate after adding colloidal keratin into a Pb^{2+} contaminated solution at pH 5. The maximum Pb^{2+} uptake capacity of keratin in the colloidal solution was 43.3 mg/g[72]. The Pb–keratin aggregate was easily decomposed on addition of nitric acid, enabling the recovery of Pb^{2+} and keratin. The colloidal solution of keratin was also used successfully to remove other metal ions such as Cu^{2+}, Hg^{2+} and Cd^{2+} through the formation of metal-keratin aggregates and the rates of metal ion removal depended on the initial metal ion concentrations in solution[72].

7.6 Precious Metal Ion Removal

Chicken feather powder was successfully used to remove precious metals such as gold, platinum and palladium from dilute aqueous solutions. The sequestering level of precious ions, Au^{3+}, Pt^{2+} and Pd^{2+} approached about 17, 13 and 7% of dry weight of feather, respectively, with initial metal ion concentration of 3.0 mM and contact time of 5h. The presence of 100-fold higher concentration of coexisting metal ions such as Na^+, Fe^{2+}, Cu^{2+} and Ni^{2+} did not have any significant effect on the precious metal uptake rate by feather powder[73]. The selective recovery of these precious metals from the solutions is attributed to their large ionic radius. Around 55% of Au^{3+} loaded on feather particle was removed by 2% HCl solution at room temperature, leaving the feather stable for repeated usability[73].

7.7 Effects of Coexisting Ions

The presence of other ions in solution has a profound effect on the adsorption of a particular metal ion in a mixed ion systems. In one study the presence of nitrate and sulphate ions generally suppressed the adsorption of both Cu^{2+} and Ni^{2+}, however, the presence of nitrate in an acetate solution promoted the adsorption of Cu^{2+} while slightly suppressed that of Cd^{2+}[66]. In another study, the presence of Cu^{2+} severely inhibited the sorption of Zn^{2+} and Mn^{2+} onto human hair[63]. When testing metal ion removal using colloidal keratin solutions, the removal of Pb^{2+} from binary or ternary solutions with Zn^{2+}, Cd^{2+} and

Hg^{2+} ions clearly declined from 88% to 55%, depending on solutions. Pb^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} ions were also removed by adsorption onto the keratin[72].

When a three-metal solution system containing about 2ppm of Cu, Pb and Hg under acidic conditions (pH 1.9-5.9) was exposed to keratin fiber, the removal was done in the order of Pb (100%) >Hg (90-98%) >Cu (56-62%). In a five-metal solution system containing about 2 ppm of Cu, Pb, Zn, Cd and Ni at pH 4-6, exposed to keratin fiber, the metal removal was in the order of Pb (70-84%) >Cu (38-49%) >Cd (10-17 %) >Ni (7-11%) > Zn (0-4%). This metal ion removal order is ascribed to atomic size of the ion: the higher the atomic size, the greater the absorption[30]. In general, the outermost electron shell of metals with a large ionic radius is readily available for interaction with protein. Other factors, like a tendency to form complex or chelation of metal ions with keratin functional groups are critical in removing a preferred metal ion.

8. REMOVAL OF ORGANIC COMPOUNDS

Organic dyes such as brilliant blue FCF, malachite green, erythrosine and tartrazine are potentially hazardous chemicals, frequently used as food coloring agents and also in textile and leather industries. They can be removed from wastewater steams using keratin absorbents. The availability of sulfonic acid groups on the brilliant blue molecule makes it highly ionic and soluble in water and due to this reason this dye shows tremendous mobility in soils. Chicken feather acts as biosorbent for brilliant blue from wastewater, removing 100-70% of the dye with starting concentration range of 0.01 to 0.10μM[74]. Other water soluble organic dyes such as malachite green and erythrosine were also successfully removed using chicken feather. The uptake of these dyes depends on pH, temperature and concentration of the absorbent[75-77]. For example, feathers increased colour removal of malachite green from 38% to 86% following an increase in pH of the solution from 3 to 4[77]. The low absorption of the dye in highly acidic pH is attributed to the development of positive charge on the adsorbent, preventing the adsorption of dye on it[77]. Tartrazine was efficiently removed with chicken feather: it exhibited almost 100% removal at lower concentrations of $(1–3)\times10^{-2}$μM, whereas removal of 47-55% of the dye occurred at a concentration of 0.10 μM. Ostrich feather removed around 70-80% phenol from aqueous solutions at pH of 2 or 3, which dropped significantly at alkaline pH[78]. Human hair also absorbed phenol from aqueous solution, showing 74-92% removal of phenol at an initial concentration of 60 ppm[79]. The Freundlich and Langmuir adsorption isotherm models indicated a spontaneous and endothermic adsorption of the organic dyes via internal transport or a diffusion mechanism facilitated by the keratinous structure of feather[74,80].

Membrane-based chiral separation is regarded as an ecologically and economically promising method to obtain enantiomerically pure and precious compounds, and has potential applications in chemical industries involving pharmaceuticals, agrochemicals, fragrances and food additives[61,81,82]. In one study, chicken feather degraded by Meiothermus ruber H328 thermophilic bacteria was converted into chiral separation membranes using 1-octane thiol as a reducing agent. The degraded feather consisted of various

types of amino acid residues with L-configuration, expected to show optical resolution ability[61]. These keratin membranes were tested as a chiral separation system for three model racemic amino acids, such as racemic glutamic acids (Glu) with polar anionic side chains, racemic phenylalanines (Phe) with aromatic side chains and racemic lysines (Lys) containing polar cationic side chains. The keratin membrane exhibited chiral separation ability, with respect to transporting the D-isomer of Glu and Phe from the corresponding racemic mixtures, while the L-isomer of Lys was preferentially transported from the racemic mixture of lysines[61].

9. INTERACTION OF KERATIN WITH CHEMICAL WARFARE AGENTS

Owing to concerns about use of chemical and biological weapons in some regions, it is important to develop effective protective systems against chemical (nerve, blister, asphyxiants and pulmonary agents) and biological (anthrax, botulinum neurotoxin and cytotoxic proteins) warfare agents[83-86]. To improve the absorption and detoxification of warfare agents, the systems should possess a high surface area with highly interacting chemical functionalities that can detoxify the agents via converting them into non-toxic products. Systems containing charcoal impregnated with metal or metal oxides are currently being used for protection against chemical and biological aerosols and vapours[87-89]. Lightweight and portable products such as textile face masks or protective clothing would be ideal for such applications.

Many warfare agents are electrophilic and reactive to nucleophilic amino acid residues of keratin-like proteins. Keratins contain peptide and reactive pendant groups ($-NH_2$, $-COOH$, $-SH$ or $-SO_3H$) and can readily interact with warfare agents. For example, skin keratins are prone to modification by alkylating agents such as sulphur mustard. The interactions of the analogs of sulphur mustards such as chloroethyl ethyl sulfide and mechlorethamine (also known as nitrogen mustard) with the keratin intermediate filament, showed keratin filament destruction, leading to lysis of epidermal basal cells and skin blistering[90]. A study is reported on using model peptides containing cysteine, lysine and histidine residues to predict the interaction mechanisms of the nitrogen mustards (mechloroethamine and tris-2-chlorethylamine) to amino acid residues of proteins by means of liquid chromatography-tandem mass spectrometry. It is hypothesized that mustard agents react with all model peptides via initial formation of a reactive aziridinium intermediate, followed by covalent adduction to amino acid residues, and form stable adducts[91]. Keratins in human skin can interact with some model organophosphates such as paraoxon, parathion, diazinon and diisopropylfluorophosphate, and form covalent adducts with some amino acids such as tyrosine and serine via nucleophilic addition[92]. Wool keratin contains around 10 mole% and 5 mole% of serine and tyrosine, respectively[21,93]. Therefore, it is anticipated that keratin-based textiles such as wool and related materials would be valuable products for military operational or civil emergency conditions after large chemical incidents. During the World War I and World War II wool products were used as protective clothing[94,95]. Such protecting systems would

be useful for workers in the petrochemical, agricultural and mining sectors.

10. REGENERATION OF ABSORBENTS

Regeneration of absorbents is an important feature for their potential in commercial application. The structures and surface properties of keratinous materials are largely dependent on solution pH and can affect the absorption/desorption characteristics of the systems via changing electrostatic or ionic interactions (Scheme 2). When analysing the desorption of adsorbed Cr^{6+} on ethylenediamine grafted feather using 10 mmol NaOH, it was found that more than 90% of the adsorbed Cr^{6+} is desorbed from the sorbent, and in three consecutive adsorption-desorption cycles, the adsorption efficiency of feather sorbent for Cr^{6+} did not change noticeably[65]. In a separate study[31], non-woven mesh of duck feathers showed repeated capability to remove metal ions. After filtering Cu^{2+} from alkaline solution, the mesh was washed thoroughly with water followed by treating with acid solution and used for next sorption and desorption cycles. Interestingly, the fabrics showed 14% and 21% more Cu^{2+} sorption capacity at second and third cycle, respectively. This is attributed to more α-helix structures being present in feathers after it was desorbed in acid solution[31]. Around 55% of gold loaded on feather particle was removed by 2% HCl solution at room temperature, leaving the material stable for repeated usability[73]. Silica particles functionalized with feather amino acids, showed around 90% desorption of metal ions (Ca, Fe, Mg and Mn) on treatment with NaCl solution, indicating their potential application as regenerable sorbents[59].

Although acids are used as desorbing species, the metal ions such as Cu^{2+} and Mn^{2+} have potential to desorb other metal ions from keratinous sorbents, based on the ion exchange principle[63]. For example, an aqueous solution containing 0.17 $\mu g\ ml^{-1}$ to 10.0 $\mu g\ ml^{-1}$ Cu^{2+} removed 62-74 % Mn^{2+} and Zn^{2+} from human hair[63]. Therefore, keratin materials have potential to be used repeatedly in separation of metal ions. In general, compared to loose fibrous or particulate sorbents, fabrics with non-woven structures are ideal with respect to uniform and reproducible properties, which enable them to be cleaned and reused[31].

11. CONCLUSIONS

Keratinous materials sourced from biological streams such as sheep's wool, human hair and poultry feathers have significant potential to create effective absorbent or filtration systems for air purification and wastewater treatment. They can be applied in various forms including loose-fibers, non-wovens, hybrid membranes, short fibers or particles, and colloidal solutions. They can remove different substances from organic volatiles such as formaldehyde to metal ions such as radioactive minerals via the mechanisms of physisorption, chemisorption and electrostatic interactions. However, the efficiency of pollutant removal depends on factors such as specific surface area and activity of absorbents, solution pH, contact time, temperature, presence of other pollutants and their concentrations, and the chemical nature of the pollutants.

Studies have revealed that the structures and surface

properties of keratin materials depend on solution pH and the absorption/desorption of pollutants can be modulated via changing electrostatic or ionic interactions using appropriate eluting solutions. Therefore, keratin materials are anticipated to have potential for commercial applications as water and air purification systems because of the regenerative characteristics of keratin proteins. However, further research is needed to find potential applications of keratin materials as textile facemasks or clothing for military personnel to protect against chemical and biological warfare agents and also for mining and industrial workers to protect against radioactive or carcinogenic organic chemicals.

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CONTRIBUTORS

Dr Arun Ghosh has obtained a PhD in Polymer Science from Indian Institute of Technology Kharagpur in 2003. His past experience includes as post-doctoral fellow at the Case Western Reserve University, USA and University of Toronto, Canada. Presently working as a scientist in the Food and Biobased Products Group of AgResearch (a Crown Research Institute in New Zealand). He has published extensively in the areas of biopolymers and biomaterials, natural fiber and composites, polymer adhesion and elastomer technology. His current research interests include functional wool and keratin biomaterials, polymer coating and adhesion, and biomaterials from biological streams.

Dr Stewart Collie obtained his BSc(Hons) in Textile Technology from the University of New South Wales (Sydney) in 1994 and PhD (Chemistry) from Massey University in 2007. He is a textile technologist and science team leader in the Food and Biobased Products Group of AgResearch (a Crown Research Institute in New Zealand, which undertakes research to support New Zealand's pastoral agriculture sector). He has worked in wool textile research for 20 years, focusing initially on apparel technology and thermophysiological comfort, and more recently on technical textile applications, including filtration.