

Metal Ion Binding Properties of Novel Wool Powders

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ABSTRACT: Wool fibres have shown potential for the removal and recovery of toxic chemical and metal ions; however, their slow kinetics of binding has limited their widespread application. In this study three wool powders have been prepared from chopped wool fibre using various milling operations. Brunauer, Emmett, Teller analysis (BET) showed negligible change in surface area and Positron annihilation lifetime spectroscopy indicated no change in nanoporosity of the powders on processing. Binding of the transition metal ions, Co^{2+} , Cu^{2+} , and Cd^{2+} was investigated over the pH range 3–9 at ambient temperature (23°C) using their respective radioisotopes (i.e. ^{57}Co , ^{64}Cu , or ^{109}Cd). The optimum pH for binding of Cu^{2+} and Cd^{2+} was in the range 6–8, while Co^{2+} absorption peak was sharp at pH 8. The rate of uptake of Cu^{2+} for each of the wool powder was dramatically faster (~ 42 fold) than that of the wool fibre. In comparison with com-

mercial cation exchange resins, the wool powders showed significantly higher (two to nine fold) metal ion loading capacity. Selective binding of the metal ions could be enhanced by varying pH and/or incubation times. The use of radioisotopes to monitor the metal ion binding allowed the development of a highly sensitive and rapid high-throughput analysis method for assessing wool powder binding properties. The ability to produce large quantities of wool powders and their ease of handling indicate that they have potential for application in separation and recovery of metal ions from industrial effluents and environmental waterways. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1642–1650, 2010

Key words: wool powders; metal absorption; separation; radioisotopes; positron annihilation

INTRODUCTION

Natural protein fibres, such as wool and silk, have been used as raw materials for making fabrics for many millennia. However, fibres too short for weaving go to waste.¹ In recent times scientists have been exploring new methods to process and regenerate these short wool fibres and to develop new applications in areas, such as wound dressing, constituents of cosmetics, and pharmaceuticals. Unfortunately, most of the crystalline structure of the fibres is lost on regeneration and there are no viable industrial spinning processes available for regenerated protein fibres. As each species of pro-

tein fibre consists of unique amino acids and therefore has the potential to display unique chemical properties, it is important to maintain the crystalline structure of these fibres. The presence of a distinct set of ionisable functional groups, such as carboxylate, amino, and sulfide groups, makes these materials ideal for the selective binding of metal ions and various organic compounds. Such properties have attracted interest in the nontraditional application of wool in biological, environmental, and industrial processes.^{2–4}

The wool is estimated to consist of 170 different proteins, heterogeneously distributed throughout the fibre. The T. F. T. CSIRO information sheet explores the highly complex physical and chemical composition of wool fibres that has evolved to protect sheep from extremes of heat and cold.⁵ Eighteen out of 22 naturally occurring amino acids are the building blocks for the wool fibres, essentially providing its unique chemical properties. Disulphide bonds between the polypeptide structures generate a quaternary structure that yields a protein that is insoluble in water and displays extraordinary stability against chemical and physical attack.

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In this study, we explore the metal binding properties of three transition metal ions Cu^{2+} , Co^{2+} , and Cd^{2+} , which possess distinctly different coordination chemistry and kinetics for complexation. The three metals are borderline Lewis acids with relative acidity strength of the order of $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$. They all bind Lewis bases such as $-\text{OH}$, $-\text{NH}_3$, and $-\text{CO}$, which are widely available on proteins. In general, their binding preference for this donor groups is of the order $\text{OH} < \text{NH}_3 < \text{CO}$.⁶

Production of wool powders using milling processes has a number of inherent advantages over chemical regeneration methods, including a reduction in the use of harsh chemicals, time, and cost for their production. More importantly, milling processes are now sufficiently advanced to be able to take advantage of the inherent multi-level structures and nanoscale fibrils of natural fibres to produce the micro and nanoparticles⁷⁻⁹ while maintaining inherent high microstructure, crystallinity, and porosity of the protein.

In traditional processing of wool fibres, metal salts are used in their processing operations, to generate colour or increase their resistance to burning, shrinkage, abrasion, and wrinkling.¹⁰ Potential industrial applications for wool fibres have been proposed. They include absorption of various metal ions from industrial effluents, purifying contaminated water supplies and the recovery of precious metal ions from liquid wastes.¹¹⁻¹³ These studies have mainly focused on the use of native wool,^{11,13,14} chemically-modified wool fibres,^{15,16} and derivatives of wool (e.g. regenerated protein^{17,18}) as the sorbents for metal ions, such as, Hg^{2+} , Ag^{2+} , Ni^{2+} , Cr^{3+} , Cu^{2+} , Al^{3+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , and Co^{2+} . The effects of the concentration of the metal ion,^{13,14} temperature,¹⁹ and pH (2–11)²⁰ on absorption behaviour have also been reported. Once absorbed the metal ions can be removed using various methods. Mercury has been reported to be desorbed from wool after treatment with ethylenediaminetetracetic acid, citric acid (pH 6), or hydrochloric acid (6M). Copper can be released from wool using dilute hydrochloric acid (0.05–0.1M), while use of sulphuric acid is preferred for removing silver from wool fibre. Interestingly, chemical modification of wool, employing reduction or oxidation methods before alkylation for the introduction of additional functional groups, has been reported to enhance the binding and specificity of various metal ions to wool fibres.^{15,20-22}

Despite the selective binding of metal ions demonstrated by the wool fibres, there is little evidence of wool fibres being used routinely in commercial or biological applications. This is most likely due to slow absorption kinetics and comparatively lower loading capacities of the natural fibres compared to commercial resins. However, the generation of wool powders has shown in our laboratory to increase the absorption

of dyes, absorbing 100 times more dye at room temperature after 10 min compared to the wool fibre.²³

Current studies used to investigate the absorption of metal ions on to solid sorbents include techniques, such as X-ray fluorescence spectroscopy,¹³ atomic absorption spectroscopy,¹¹ and chelate titration.²⁴ These systems require large test samples and processing of solution to determine available (or unbound) metal ion. An alternative approach to determine metal ions present in solution, which does not require extensive processing of solution before analysis, is the use of radioisotopes of the metal ions (i.e. radio-metal ions). To measure the metal ion bound to a wool powder or present in solution, a radio-metal ion can be used to track the movement of the natural metal ion. For example, tracking Cu^{2+} movement in solution and binding to wool can be easily achieved using $^{64}\text{Cu}^{2+}$, which has 12.7 h half-life and a gamma emission that can be readily detected well below nanomolar concentrations or at 10^{-3} ppb and in various media, even strong electrolyte. High-throughput assays can be developed that are fast and highly accurate, requiring small sample batches. Once the radio-metal ion has decayed, the wool sample may be analyzed by other complementary techniques.

This study compares the transition metal ion binding properties of a range of novel wool powders (of different particle size) with their parent wool fibre.

MATERIALS AND METHODS

Equipment and chemicals

The equipment used for the binding and loading capacity studies was Eppendorf 5804R centrifuge, Wallac Wizard 1480 gamma counter and MyLab SLRM-2M Intelli Mixer rotomix. SEM was performed using a Leica S440 microscope at 5 kV acceleration.

The equipment used for wool powder production is detailed below. The particle size of wool powders was measured by means of a laser diffraction scattering type Malvern Mastersizer 2000 with a hydro 2000s particle analyzer. Micromeritics ASAP 2400 equipment was used to measure the surface area.

All reagents and solvents used (without further purification) were of analytical grade and obtained from commercial sources. All water used was Milli-Q grade. High specific activity (SA) radioisotopes ^{57}Co ($t_{1/2} = 271.8$ days; SA = 185 GBq/mg), ^{64}Cu ($t_{1/2} = 12.7$ h; SA = 500 GBq/mg), and ^{109}Cd ($t_{1/2} = 461$ days; SA = 0.12 GBq/mg) were purchased from MDS Nordion, ANSTO Radiopharmaceuticals and Industrials (Sydney, Australia) and Perkin Elmer (Sydney, Australia), respectively. The gamma emissions used to monitor each radioisotope

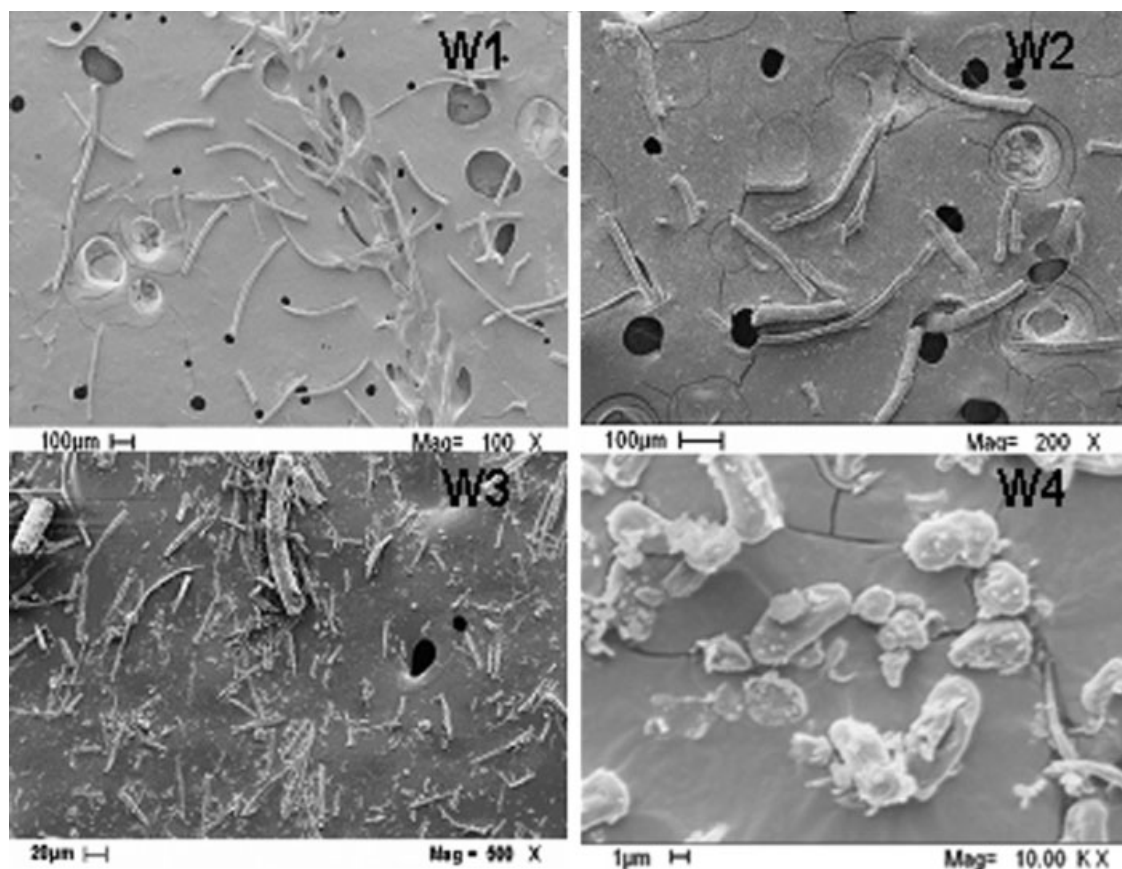


Figure 1 SEM images of wool samples.

were 122.1 and 136.5 keV for ^{57}Co , 511 keV for ^{64}Cu , and 88.0 keV for ^{109}Cd . Analytical standard solutions of CuCl_2 (0.01M) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1M) were supplied by Riedel de Haen and CoCl_2 (0.01M) by Sigma-Aldrich.

Preparation of wool powders

Chopped fibre (W1)

W1 (or control) was prepared by chopping merino wool top (20.4 μm in mean fibre diameter) into small snippets using a Frisch Pulverisette 19 rotary chopper. This material was then used to produce three wool powders (W2, W3, and W4). The production procedure is summarized below and detailed elsewhere.²⁵

Wool sample (W2)

W1 was further ground into smaller fragments using a rotary ceramic mill to prepare W2. Thirty passes were used until a point was reached, where it was judged that the powder was not becoming any finer.

Wool powder (W3)

W3 was produced by treating W2 with 4% of the sodium salt of dichloroisocyanuric acid (DCCA), and then passing 10 times through an air-jet mill (OM2,

Micronizer[®], Sturtevant) with a grinding pressure of 90 PSI and a feed pressure of 40 PSI.

Wool powder (W4)

The treated W2 with 4% DCCA (sodium salt) was passed through a commercial air-jet mill in Australia under proprietary conditions to prepare W4. SEM images of wool samples are given in Figure 1.

Brunauer, Emmett, Teller surface area analysis

Approximately 0.5 g of each wool sample was placed in a glass analysis tube and conditioned under vacuum at 50°C for 16 h. The samples were checked on the conditioning rig to confirm that the surface is cleaned of any adsorbents and therefore ready for analysis. The analysis tubes were then weighed and vacuum tested before analysis by the Brunauer, Emmett, Teller (BET) nitrogen adsorption technique.

Positron annihilation lifetime spectroscopy analysis

The lifetime spectra of positrons were measured using a conventional lifetime system with BaF_2

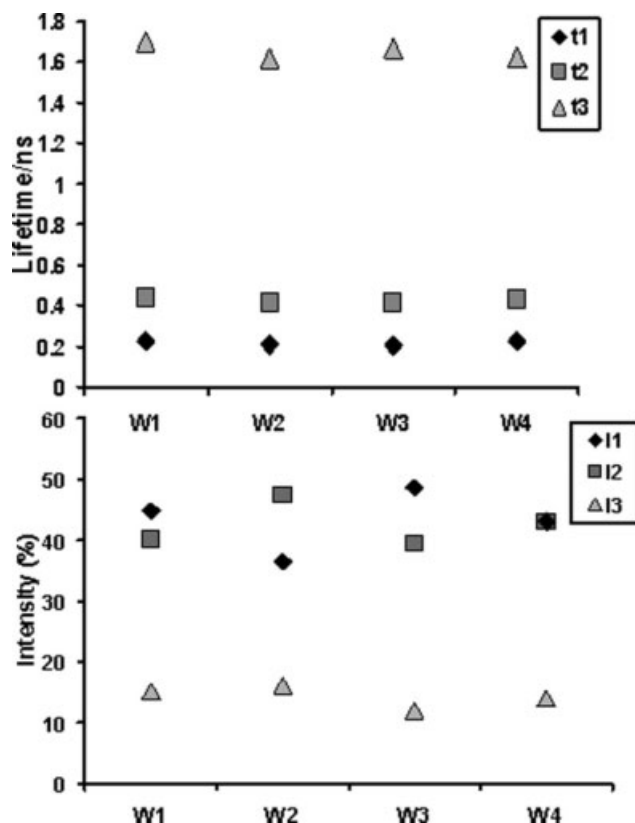


Figure 2 The lifetime (ns) and relative intensities of nanopores in the wool samples.

scintillators attached to H3378 (Hamamatsu Photonics) photomultiplier tubes and digital oscilloscope.²⁶ Each spectrum contained about 6×10^6 counts. The lifetime spectrum of positrons in amorphous materials can be represented in a continuous decay form:

$$S_{LT}(t) = \int_0^{\infty} \lambda \alpha(\lambda) \exp(-\lambda t) d\lambda \quad (1)$$

where λ is an inverse of the positron lifetime ($=1/\tau$) and $\alpha(\lambda)$ is the probability density function (PDF) of the annihilation rate. The measured spectra were analyzed with a time resolution (full width at half-maximum) of approximately 200 ps by a numerical Laplace inversion technique developed by Gregory.²⁷ Results from this analysis are given in Figures 2 and 3.

The effect of pH on metal binding

The binding affinity and rate of uptake of metal ions by the wool powders were monitored over the pH range 3–9 using various buffer solutions; 0.1M glycine/0.1M NaCl for pH 3; 0.1M sodium succinate for pH 4; 0.1M 4-morpholinoethanesulfonic acid for pH 5; 0.1M sodium phosphate dibasic for pH 6, 7, and 8; 0.1M glycine/0.1M NaCl for pH 9. A typical pro-

cedure involved incubating approximately 10 mg (accurately weighed in quadruplicate) of wool powder in the appropriate buffer ($\sim 900 \mu\text{L}$). An aliquot (100 μL) of the relevant metal ion (Co^{2+} , Cu^{2+} , or Cd^{2+} at 10^{-4}M) doped with radioisotope (^{57}Co , ^{64}Cu or ^{109}Cd , respectively) was added to this suspension. The final volume of the reaction mixture was adjusted to 1 mL with buffer. The mixture was then vortexed and left to rotate at 60 rpm. At set intervals ($t = 15, 30, 45, 60$ min, and 24 h), the mixture was centrifuged (5000 rpm for 15 min) and the supernatant sampled (triplicate of 20 μL). The radioactivity in each aliquot was measured in a gamma counter and the moles of metal ion associated with the sorbent calculated in the following manner,

$$M = \frac{\%A \times C}{W} \times V \quad (2)$$

where M , Moles of metal ion absorbed per mg of sorbent; $\%A$, Percent of metal ion absorbed onto the sorbent; C , Concentration of carrier (nonradioactive metal ion) in moles per litre; W , Weight of sorbent in milligram; V , Total volume of mixture in litres.

Distribution coefficient or binding coefficient (K_d) for each metal ion and sorbent was determined using the following formula,

$$K_d = \frac{\%A_{\text{sor}}/W}{\%A_{\text{sol}}/V} \quad (3)$$

where $\%A_{\text{sor}}$, Percent of metal ion on sorbent; $\%A_{\text{sol}}$, Percent of metal ion in solution; W , Weight of sorbent in grams; V , Total volume of mixture in millilitres.

Selected data are illustrated in Figures 4–8.

Recovery of bound metal ion on wool powders

Based on results of absorption study, selected wool samples were tested for reversibility of metal ion

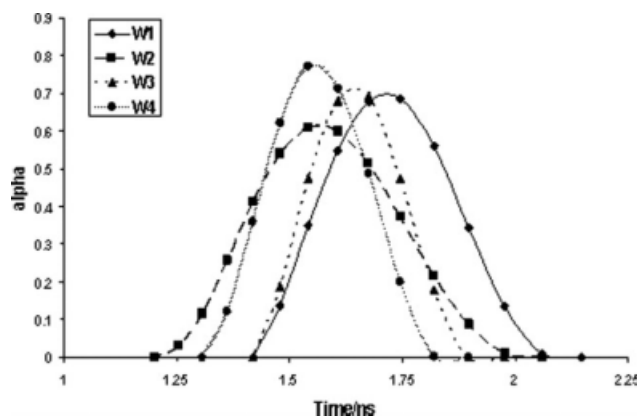


Figure 3 Probability density function (PDF = alpha) analysis for the wool samples.

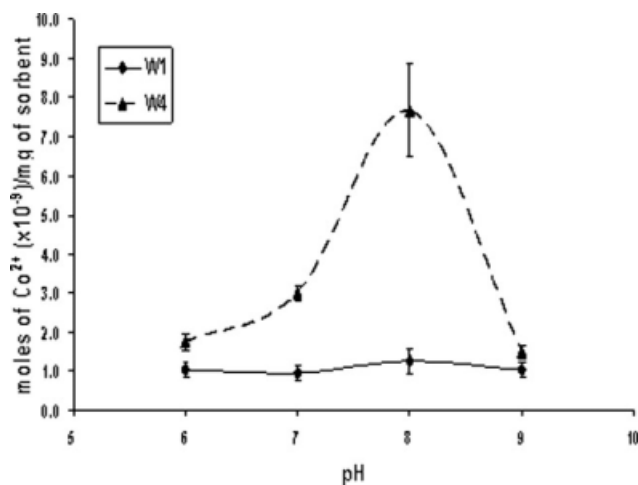


Figure 4 Co^{2+} absorbed onto fibre (W1) and powdered (W4) wool at 15 min, pH 6–9, ambient temperature (23°C , $n = 12$).

(Co^{2+} , Cu^{2+} , and Cd^{2+}) binding. Typically at the end of binding study, metal doped W3 samples (at pH 8) were centrifuged (5000 rpm for 15 min) and the supernatant was removed. Then 1 mL of pH 3 buffer was added to a sample. To another equivalent sample, pH 8 buffer (1 mL) was added. The mixtures were allowed to rotate and the supernatant was sampled ($20\ \mu\text{L} \times 3$) at 10 min and 21 h. The radioactivity in each $20\ \mu\text{L}$ aliquot was measured in a gamma counter and the percent of metal ion released for each wool sample was calculated. Selected data are illustrated in Figure 9.

Metal ion loading capacity of wool powders

The loading capacity of wool sorbents was monitored over a range of metal ion concentrations

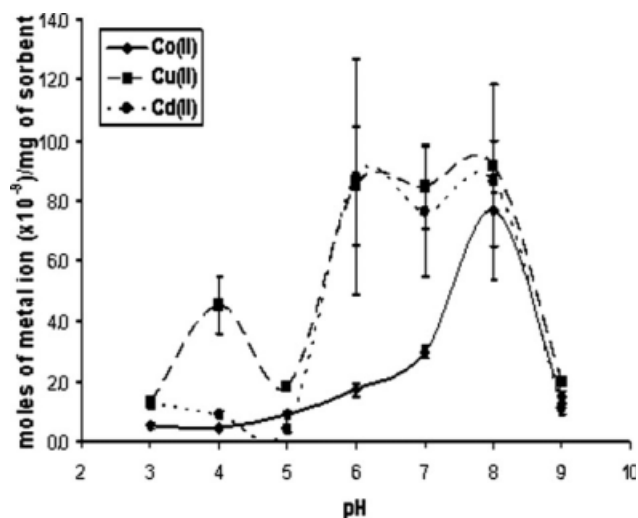


Figure 5 Comparison of Co^{2+} , Cu^{2+} , and Cd^{2+} absorption on W4 over a range of pH after 15 min incubation at ambient temperature (23°C , $n = 12$).

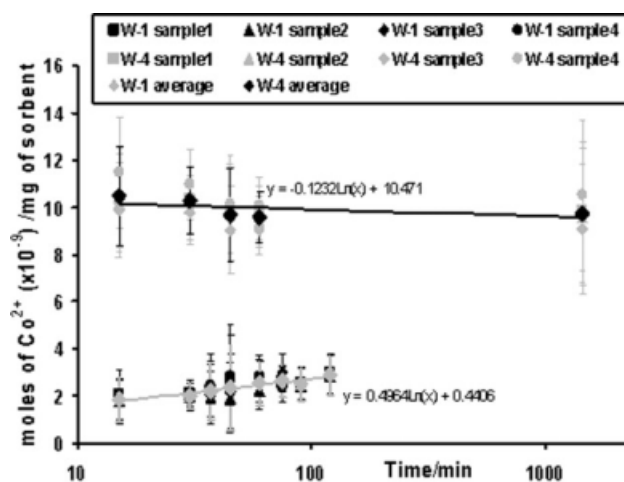


Figure 6 Comparison of Co^{2+} absorbed (at pH 8) on W1 compared to W4 over time at ambient temperature (23°C).

(10^{-3} – 10^{-6}M) at pH 4 and 8 for Co^{2+} and Cd^{2+} , and at pH 4 and 7 for Cu^{2+} . A typical procedure involved exposing the sorbents (approximately 10 mg in quadruplicate) to 1 mL mixture of buffer of appropriate pH and metal ion of correct concentration doped with respective tracer. The samples were allowed to rotate and supernatant liquor was sampled at 30 min and at 24 h. The radioactivity of each aliquot was measured and the associated moles of metal ion was calculated. Selected data are illustrated in Figure 10.

RESULTS AND DISCUSSION

Wool powder production and characterization

Wool fibres are very soft and long (several cm), requiring several mechanical milling processes to generate a fine powder. For this study merino wool fibres, with a mean diameter of $20.4\ \mu\text{m}$, were first chopped into shorter fibres (W1) generally $500\ \mu\text{m}$

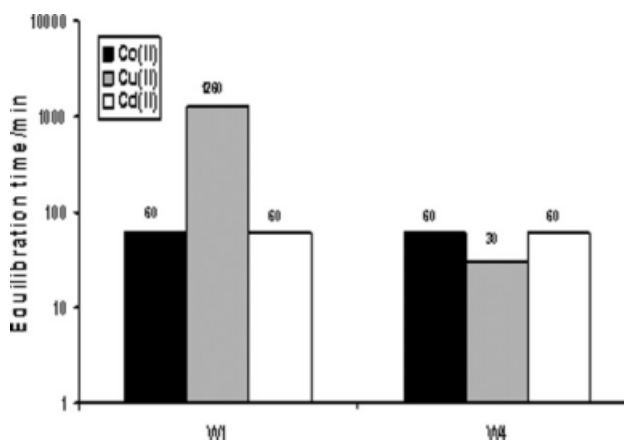


Figure 7 Time required for W1 and W4 to reach equilibrium in the absorption of Co^{2+} , Cu^{2+} , and Cd^{2+} in pH 8 buffer at ambient temperature (23°C , $n = 12$).

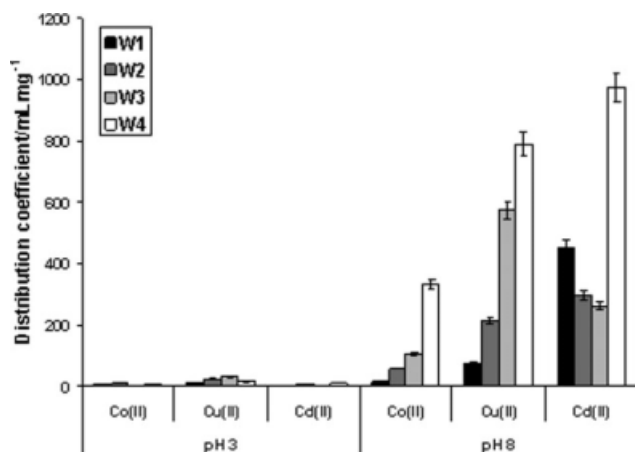


Figure 8 The distribution coefficients (K_d) for each metal ion ($[M^{2+}] = 10^{-4}$) with various wool samples at pH 3 and 8 at 15 min (23°C , $n = 12$).

length. The scanning electron micrograph of W1 (Fig. 1) confirms that they were intact fibre snippets $\sim 500 \mu\text{m}$ in length. Although this material was largely fibrous in nature, its properties are different from those of the original fibre, due to the relatively high frequency of exposed fibre ends. W1 was further ground into smaller fragments (W2) illustrated in Figure 1. Though small in size the W2 is still considered fibrous with a length of $\sim 150 \mu\text{m}$ (measured from SEM image). The W2 sample wool underwent chlorination, which resulted in further breakdown of the wool substrate to facilitate the air-jet milling process. A finer product, W3 (Fig. 1) was produced, powder-like in appearance with particles that are fibroid in shape. Its mean particle size was determined to be $15.1 \mu\text{m}$ on a volume basis. A fourth wool sample W4 was produced using a similar method to that employed for W3, except a commercial air-jet milling process was used. W4 was the finest of the three powders (Fig. 1), with a mean particle size of $4.6 \mu\text{m}$ on a volume basis. Although there is still a small amount of fibrous matter present in

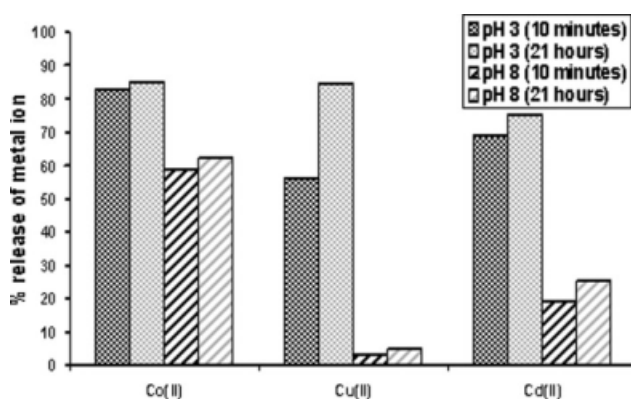


Figure 9 Percentage of metal ion released from metal loaded on W3 over time at pH 3 and 8 ($n = 3$).

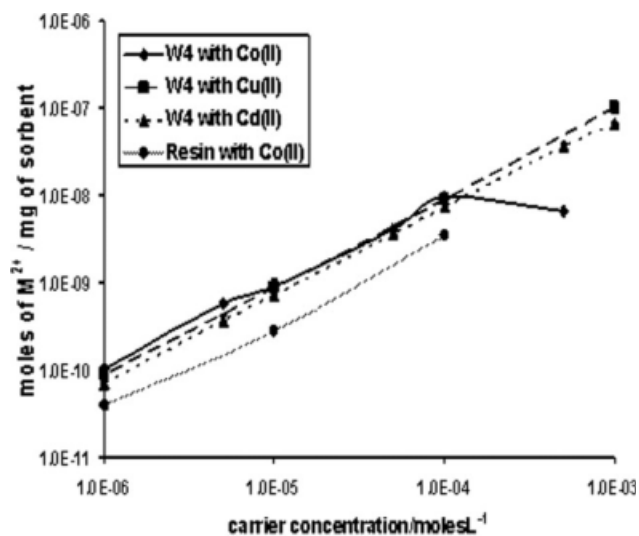


Figure 10 Comparison of loading capacities of Co^{2+} , Cu^{2+} , and Cd^{2+} on W4 and a cation exchange resin as a function of metal ion concentration at pH 8 (23°C , $n = 3$).

W4, the material is largely particulate in nature; the structure of the outer cuticle has been very severely modified, readily exposing the inner cortex. In this study, the properties of short wool fibre (W1) were used as a control, and compared with the fibrous wool particles (W2, W3, and W4). The BET surface area analysis of the samples showed that the processing did not cause any significant changes in the sample surface area of W4 as compared with control W1. The positron annihilation lifetime spectroscopy (PALS) study provides information about the nanoporosity of these materials. The positron lifetimes were analysed using the Laplace inversion technique and fitted assuming three annihilation modes or three components (i.e. free positron, parapositronium, and orthopositronium). The third component, associated with the pickoff annihilation of orthopositronium (o-Ps), is used to determine the lifetime and relative intensities or concentration of the nanopores in the wool powders (Fig. 2). From these lifetimes the size of the nanopores are calculated using eq. (1) given in the experimental.

The data show that the size (i.e., 0.5 nm) of the nanopores in each wool sample is similar; however their relative intensity varies with the different processing methods. Further analysis using the PDF of the annihilation rate obtained through the numerical Laplace inversion technique for the wool samples is illustrated in Figure 3. This analysis shows that all samples have a slight reduction in free pore volume compared with W1. However, the change in the nanoporosity of wool materials is not significant. Collectively the BET and PALS data indicate that the processing of the wool fibres does not appear to change the basic internal protein structure of the wool.

TABLE I
Comparison of Moles of Co²⁺, Cu²⁺, and Cd²⁺ Absorbed at Equilibrium on Wool

Wool	Moles ($\times 10^{-9}$) absorbed/mg of sorbent at equilibrium ^a		
	Co(II)	Cu(II)	Cd(II)
W1	3.9 \pm 0.8	9.7 \pm 1.8	9.3 \pm 2.1
W2	5.1 \pm 0.8	8.7 \pm 2.5	9.7 \pm 6.2
W3	5.4 \pm 0.4	8.4 \pm 1.4	9.0 \pm 1.6
W4	7.7 \pm 1.2	9.1 \pm 0.9	8.6 \pm 3.2

^a Time to reach equilibrium changes for each wool sample and each metal ion; ranging from 15 min to >24 h.

Metal binding affinity and rate of uptake

The absorption of Co²⁺, Cu²⁺, and Cd²⁺ onto W1 and the wool powders (W2, W3, and W4) was investigated over the pH range 3–9 and at metal ion concentration ranging from 10⁻³ to 10⁻⁶M, at ambient temperature (23°C). Each metal solution was doped with appropriate radioisotope (⁵⁷Co, ⁶⁴Cu, and ¹⁰⁹Cd, respectively), in quadruplicate.

Buffer conditions employed were used to ensure the metal ion did not form colloids and therefore were available for exchange with the wool sample. The binding affinity and rate of uptake of each metal ion varied significantly between the powders and the control W1. However, between batches and within sets of experiments the data show good correlation suggesting the bulk of the wool samples are consistent in nature. All wool samples (W1–W4) showed an absorption peak at pH 8 for Co²⁺ binding. Selected data for W1 and W4, illustrated in Figure 4 clearly show a seven fold increase in Co²⁺ absorption on W4 compared to W1 at 15 min.

The absorption profiles for Cu²⁺ and Cd²⁺ on W1–W4 were also similar. Figure 5 compares a typical absorption curves for Co²⁺, Cu²⁺, and Cd²⁺ on W4. Results show two peaks in the absorption profile for Cu²⁺ at pH 4 and then at pH 6–8. While Cd²⁺ optimum binding occurs only between pH 6–8. A comparison of total amount of metal ion adsorbed on the wool samples at equilibrium (i.e., varying from minutes to hours) is summarized in Table I and shows there is little change in total amount of Cu²⁺ and Cd²⁺ absorbed on processing the wool powders. In contrast, the absorption of Co²⁺ was significantly enhanced on processing the wool powders into small particles.

While the total amount of Cu²⁺ absorbed on W1, W2, W3, and W4 is similar there is a dramatic increase in rate of absorption with processing of these powders. This behaviour tended to correlate with particle size. For example, W1 which is fibre like, requires >21 h to reach equilibrium. In contrast, finer sorbents, W2 (also fibre like but smaller than

W1) and W3 (15.1 μ m) took only 60 min to reach equilibrium. W4, with the finest particle size (4.6 μ m) reached absorption equilibrium rapidly (within 30 min) under the same conditions. Comparison of the rate of Co²⁺ absorbed by W1 and W4 over time (Fig. 6) show that equilibrium for both is established within 1 h.

Absorption of Cd²⁺ is comparatively slower than that of Co²⁺ and Cu²⁺ for both W2 and W3 samples. In contrast, the absorption equilibrium reached a similar rate (60 min) for both W1 and W4. Overall the rate of uptake for both Co²⁺ and Cd²⁺ appears to be independent of the particle size of the material.

Figure 7 compares the time required to reach absorption equilibrium under the conditions investigated for the W1 and W4 for the three metal ions. The dramatically enhanced uptake of Cu²⁺ by W4 compared with W1 is in stark contrast to the negligible improvement in the rate of uptake of Co²⁺ and Cd²⁺.

Distribution or binding coefficients K_d at 15 min were also calculated for each metal ion. Figure 8 summarizes the data and shows a good binding affinity at pH 8 for all metal ions. The comparatively low K_d values at pH 3 for each metal ion indicate how readily the metal ions may be removed from the sorbents. The higher binding affinity for Cd²⁺ to these wool powders compared with Cu²⁺ suggest that the complexing donor groups for the former are different and perhaps the thiol or by-products of the sodium dichloroisocyanurate are contributing to this behavior.

Reversibility of metal binding to wool powders

To test reversibility of binding of metal ions to wool samples, W3 was loaded with metal ion (Co²⁺, Cu²⁺, and Cd²⁺, respectively) at pH 8, and after equilibrium was established the mixture was centrifuged and the supernatant removed. The wool samples were then incubated in either pH 3 or 8 solutions. The release of metal ion was monitored after 10 min and after 21 h. Percentage of metal ion lost from the wool samples is given in Figure 9. Data shows how rapidly (within minutes) both Co²⁺ and Cd²⁺ are released and how quickly (within 10 min) equilibrium is established at pH 3. In comparison, only 55% of the Cu²⁺ is released after 10 min at pH 3 and it continues to be released upto 80% over the next 21 h. In moderately basic conditions (pH 8), the release of Cu²⁺ is minimal (<10%) over an equivalent timeframe compared to that of Cd²⁺ (~30%) and Co²⁺ (~60%). This indicates that the binding of Co²⁺ is considerably weaker than Cd²⁺ and Cu²⁺. However, the slower release of the Cu²⁺ tends to suggest a different mechanism of binding for Cu²⁺ to the wool compared with the Cd²⁺ and Co²⁺ ions.

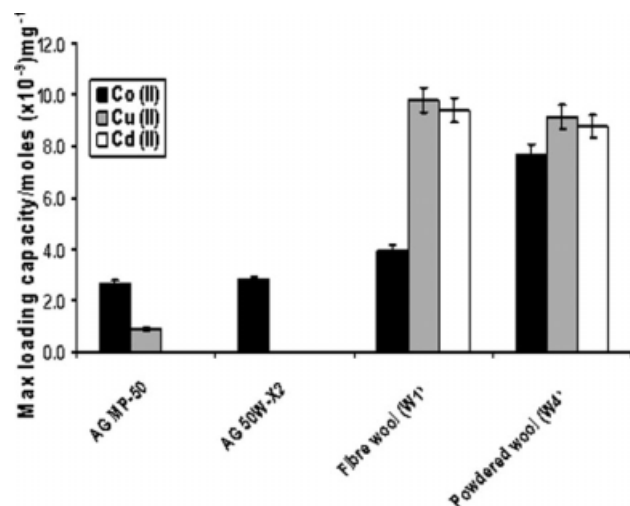


Figure 11 Comparison of W1 and W4 maximum loading capacities for Co^{2+} , Cu^{2+} , and Cd^{2+} with commercial resins (AG MP-50 and AG 50W-X2) at pH 8 (metal ion concentration 10^{-4} M , 23°C , $n = 3$).

The loading capacity for each metal ion with W4 was investigated by incubating 10 mg of wool powder in 1 mL solution of metal ion at varying concentrations (10^{-6} – 10^{-3} M). The moles of metal ions absorbed per mg of wool powder (or loading capacity) at each concentration are illustrated in Figure 10. The results show a linear relationship between loading capacity and the concentration of the Cu^{2+} and Cd^{2+} ions in solution. In contrast, the linear relationship for Co^{2+} binding only holds for Co^{2+} concentrations upto 10^{-4} M . These loading capacities were compared to those of commercial resins (AG MP-50 and AG 50W-X2) determined under similar conditions (Fig. 11). Both resins studied were Polystyrene/divinyl benzene sulfonic acid cation exchange resins. These resins are used for water purification, solute concentration and analytical determination of mixed cationic solutions. Such applications require a high and rapid absorption of metal ions to the resin to be effective. The data in Figure 11 clearly shows that metal binding of the wool powder presented in this work is significantly higher than the commercial resins (>2 fold for Co^{2+} and 9 fold for Cu^{2+}).

CONCLUSIONS

This study clearly illustrates the potential of milled wool in the recycling and recovery of metal ions. The powders were readily produced in bulk and were easy to handle. BET analysis did not show any significant changes in surface area on processing. PALS shows that nanoporosity remained the same with slight variation in concentration of nanopores

as the particles sizes were reduced. Insoluble in water and stable against chemical and physical attack, the basic structure and chemical properties of the wool powders appeared to maintain the unique characteristics of the wool fibres.

In general, the wool sorbents show highest absorption at pH 6, 7, and 8 with Cu^{2+} and Cd^{2+} . For Co^{2+} , the wool sorbents absorb best at pH 8. Selectivity for the metal ions could be enhanced on processing due to the increase in rate of uptake. However the total amount of Cu^{2+} and Cd^{2+} absorbed on the wool samples did not change on processing. Interestingly the Co^{2+} , with weak binding affinity for wool fibre, showed considerably enhanced binding, suggesting similar trends may be possible with other weak binding metal ions.

Furthermore the reversible binding of the transition metal ions and the higher loading capacity of these materials for the transition metal ions compared to commercial resins supports the application of wool powders in the recovery and recycling of metal ions from industrial effluents and contaminated waterways. The study of metal binding properties using radiotracers proved to be a rapid and cost effective method of analysis, which is adaptable for high throughput screening of the chemistry of novel materials.

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