NRC7 - SEVENTH INTERNATIONAL CONFERENCE ON NUCLEAR AND RADIOCHEMISTRY
Budapest, Hungary 24-29 August 2008

Metal Binding Properties of Processed Wool

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Abstract – A preliminary investigation of the heavy metal ion absorption of processed wool fibers for potential application in the removal and recycling of metal ions from industrial effluents and the environment is reported. Absorption kinetics and metal ion loading capacity of the wool samples over pH 3-9 at 23°C were investigated using radiotracers. The studies show the uptake of metal ions by the wool samples was rapid and highly dependent on pH. The powdered wool showed significantly higher loading capacity compared to the chopped wool.

Keywords – wool, wool powder, radiometal ions, metal adsorption, ion exchange.

I. INTRODUCTION

Increasing awareness by the public and government has encouraged industry to develop environmentally friendly composite materials, using renewable resources such as wool powders. Because of the various reactive groups present within the wool fibres they are able to adsorb a variety of chemicals, such as metal ions, dyes and surfactants[1-3]. Metal binding properties have been further improved by chemically modifying the wool fibers[4, 5]. Recently, milling wool fibers into powders was demonstrated to significantly enhance the uptake of dyes by these materials[5].

Generally, the uptake of metal ions by materials is monitored using Ion Coupled Plasma Mass Spectrometry (ICP MS). However this method is not easily adapted to fast throughput analysis (seconds), small samples (μL) or can tolerate high concentrations of electrolytes without considerable processing of the samples. In contrast, the use of radiotracers to monitor the metal ion uptake can be a highly specific and significantly more sensitive (up to 10^{-14}M) tool that is independent of media. A particularly attractive aspect of the use of radiotracers is the ability to analyze metal ion uptake with in seconds using very little (μL of the solutions or μg to mg of adsorbent) of the test sample with minimal sample preparation. A wide array of samples can be analyzed in varied reaction conditions using high throughput screening techniques.

This article investigates the heavy metal ion binding properties of physically and chemically treated wool powders and their potential as ion exchange materials. The absorption of Co^{2+}, Cu^{2+} and Cd^{2+} ions was monitored using radiotracers (^{57}Co, ^{64}Cu and ^{109}Cd, respectively) over the pH range 3 to 9 and metal ion concentration range of 10^{-3} to 10^{-6}M, at ambient temperature (23°C). A high throughput analysis was developed that could be used to screen materials for application in immobilization and recovery of metal ions from waste streams.

II. MATERIALS AND METHODS

All reagents and solvents used (without further purification) were of analytical grade and obtained from commercial sources. All water used was Milli-Q grade. Radioisotopes ^{57}Co (typical SA[1] = 185 GBq/mg), ^{64}Cu (typical SA = 500 GBq/mg) and ^{109}Cd (typical SA = 0.12GBq/mg) were purchased from MDS Nordion, ANSTO Radiopharmaceuticals and Industrials and Perkin Elmer, respectively. Analytical standard solutions of copper (II) chloride (0.01M) and cadmium (II) nitrate tetrahydrate (1M) were supplied by Riedel de Haen and Cobalt (II) chloride (0.01M) by Sigma-Aldrich.

A. Preparation of wool powders

W-1: Merino wool chopped into snippets (d_{mean}[2] = 20.5μm).
W-2: W-1 stone ground, chlorinated with DCCA, then commercially air-jet milled in Australia (d_{mean} = 1.2μm).

B. Metal Binding Studies

Effect of pH

The binding affinity and rate of uptake were monitored over pH range 3 to 9. A typical procedure involved incubating ~10 mg accurately weighed (x4) wool powder in appropriate buffer with the relevant metal (Co^{2+}, Cu^{2+}, Cd^{2+}) ion (10^{-4}M) doped with radioisotope (^{57}Co, ^{64}Cu, ^{109}Cd, respectively). The mixture was vortexed and left to rotate. At set intervals (t =15, 30, 45, 60 min and 24 hrs), the mixture was centrifuged (5000rpm for 15 min) and the supernatant sampled (20μL x 3). The radioactivity in each aliquot was measured in a gamma counter and the associated moles of metal ion calculated.

Loading capacity

The loading capacity of wool sorbents was monitored over a range of metal ion concentrations (10^{-3}M to 10^{-6}M) at pH 4 and 8 for Co^{2+}, Cd^{2+} and at pH 4 and 7 for Cu^{2+}. A typical procedure involved suspending the sorbents (~10mg, x4) in buffer of appropriate pH and then adding metal ions doped with their respective radioisotope at concentrations of 10^{-6}M

[1] Specific activity (radioactivity of given isotope per unit mass)

[2] Mean particle diameter

to 10^{-3}M. The samples were allowed to rotate and supernatant was sampled (20µL x 3) at 30 min and 24 hours. The radioactivity of each aliquot was measured and the associated moles of metal ion calculated.

Selected results from these studies are presented in figures 1-4.

III. RESULTS

The scanning electron microscopy (SEM) images in Figure 1 show the morphology of wool samples that have undergone different physical and/or chemical treatment.

The binding affinity and rate of uptake of each metal ion varied significantly for processed (W-2) compared to unprocessed (W-1) wool. Figure 2 illustrates the effect of pH on the binding of Co^{2+} to W-1 and W-2. At optimum pH the rate of metal ion binding also varied significantly. The equilibrium was established within minutes for both Co^{2+} and Cu^{2+} on processed wool compared to hours for wool fiber. In contrast there was no difference in the rate of uptake of Cd^{2+} for both wool samples.

Comparison of Co^{2+}, Cu^{2+} and Cd^{2+} binding at pH 8 is illustrated in Figure 3. The data show a significant enhancement of Co^{2+} binding with processed wool as compared to the unprocessed. But no such increase is observed for Cu^{2+} and Cd^{2+} under the conditions tested. However, the rate of Co^{2+} and Cu^{2+} uptake was shown to be about 100 fold higher for processed wool compared to the unprocessed wool.

The loading capacity of each metal ion on the wool samples is illustrated in Figure 4. The data clearly show a linear relationship between the moles absorbed/mg and concentration of metal ion for both Cu^{2+} and Cd^{2+}, for the entire concentration range investigated. For Co^{2+}, however, the loading capacity limit is reached at 10^{-4} moles/mg under the same conditions.

IV. DISCUSSION AND CONCLUSION

The pH greatly affects the metal ion binding properties of the wool samples. In general the binding of Cu^{2+} was significantly higher than Co^{2+} but comparable to Cd^{2+}. The rate of Cu^{2+} uptake appears to be inversely proportional to the surface area of the wool samples. Interestingly the rate of Cu^{2+} and Co^{2+} binding was fast, establishing equilibrium within 2 hours under the conditions studied. While both wool samples continued to absorb the Cd^{2+} over 24 hours, the final amount of Cu^{2+} and Cd^{2+} absorbed onto both the processed and unprocessed wool samples was comparable at equilibrium (i.e. 2 hour and 24 hour, respectively). In contrast, the milling of the wool fiber resulted in enhancement (about 2 fold) in its ability to adsorb the Co^{2+}.

Attempts to remove the metal ions loaded on to the wool samples at pH 8, using pH 3 buffer solutions showed both Co^{2+} and Cd^{2+} could be removed (80% with single wash) fast (within 30 minutes). However, the removal of the Cu^{2+} required incubation in low pH buffer for longer periods of time (hours) indicating stronger binding of this metal ion.

The processed wool was demonstrated to have unusually high loading capacity for Co^{2+}, Cu^{2+} and Cd^{2+} (about 10^{-5} moles/mg). Comparison with commercial resins, such as PVP and Dowex, shows that processed wool has about a 100 fold higher loading capacity[6, 7].

Wool is estimated to be made from 170 different proteins heterogeneously distribute throughout the fiber[8], bound together by covalent as well as non-covalent bonds. The high absorption of Co^{2+}, Cu^{2+} and Cd^{2+} between pH 6 to 8 is not surprising given the isoelectric point (pI) of the amino acids, such as alanin, glycine, histidine, and valine[9], which are most likely to complex with metals ions in pH range investigated. The binding affinity and extent of metal binding reversibility agree with the Lewis acidity strength of the three metal ions under investigation, $Cu^{2+} > Cd^{2+} > Co^{2+}$[10].

This study clearly shows the variation in complexation kinetics of the metal ions with the wool powders at ambient temperatures. This could form the basis for selective extraction of one metal ion from another in solutions. Binding of the heavy metals to the wool powders was found to be reversible and could provide an opportunity for the recycling of the same. However, particular characteristic of the wool powders that makes them attractive for clean up of toxic metals from industrial effluents and environment is their extraordinarily high loading capacity for metal ions compared to commercial resins.

Future work will study effects of various processing techniques on manufacturing wool powders, which could further enhance their metal binding ability.

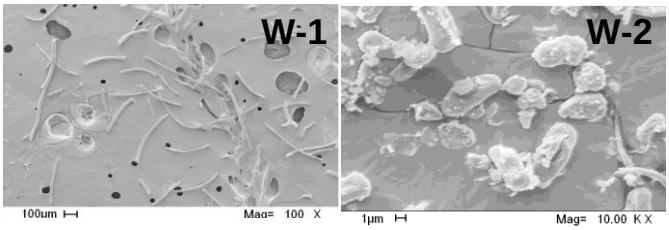

Figure 1. SEM images of wool powders (Leica S440, 5kV acceleration voltage, Au coating for 40 seconds).

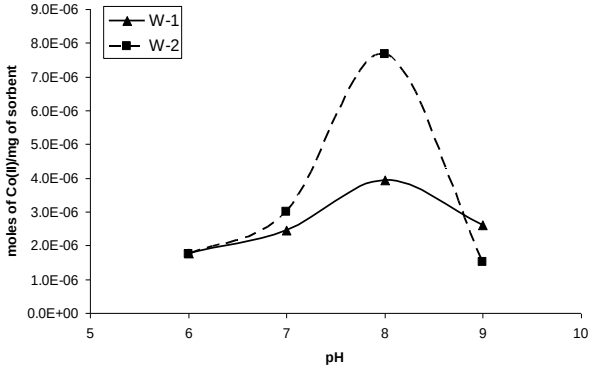

Figure 2. Cobalt (II) absorbed onto processed and unprocessed wool powders, pH 6-9, 23°C.

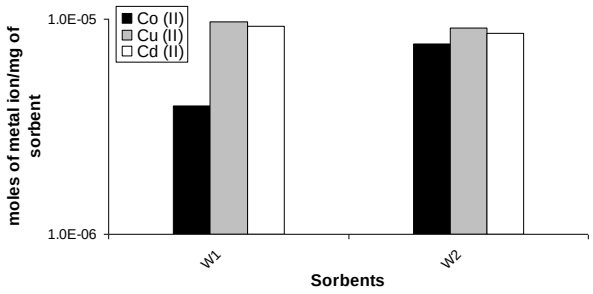

Figure 3. Comparison of moles of Co^{2+}, Cu^{2+} and Cd^{2+} absorbed per mg of wool sorbent.

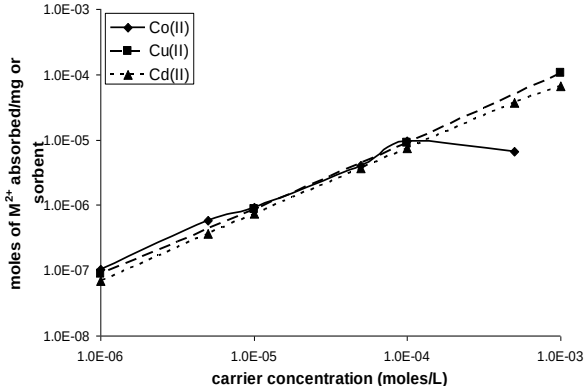

Figure 4. Comparison of loading capacities for processed wool with Co^{2+}, Cu^{2+} and Cd^{2+} as a function of carrier concentration, 23°C

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Metal binding properties of powdered wool

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Introduction

Wool fibres can adsorb a variety of chemicals (metal ions, dyes, surfactants).[1-3] These binding properties can be significantly enhanced when the wool fibre is chemically treated or modified [4] or milled [5] to produce wool powders. These wool powders have also been shown to rapidly absorb dyes at room temperature. Such behaviour shows promise for applications in the separation, recovery and recycle of heavy metals from industrial effluents. The high sensitivity of radiotracers and their rapid detection makes them ideal tools for high through-put analysis of materials. We are interested in using radio-metal ions for the analysis of the heavy metal binding properties of engineered wool powders. The ability to detect gamma signals in the presence of complex media from solids and liquids, provides for greater accuracy of metal binding properties as it does not require additional processing of solutions prior to analysis.

Results and Discussion

Morphology of Wool Powders

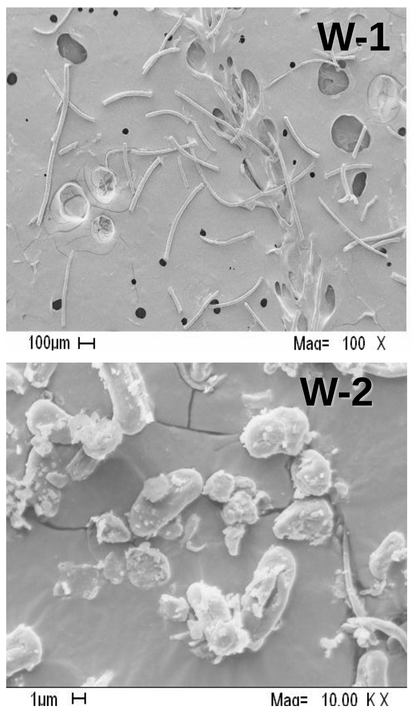

Figure 1. SEM images of wool powder (Leica S440, 5kV acceleration voltage, gold coating for 40 seconds).

Figure 1 illustrates the change in morphology of the wool after it has undergone processing. Particle size is dramatically altered after chemical processing and milling.

W-1: Merino wool chopped into snippets (d_{mean}=20.5µm).
W-2: W-1 stone ground, chlorinated, commercially air-jet milled (d_{mean}=1.2µm).

Reduction in size increases the surface area (W-1 = 0.94m^2/g, W-2 = 6.13m^2/g) of these materials and therefore the kinetics of metal binding.

Metal binding Properties

Figure 2 shows the increase in Co^{2+} absorption for processed (W-2) wool compared to unprocessed (W-1) wool.
The peak in absorption at pH correlates well with the type of amino acids (e.g. Histidine) present in the wool powders.

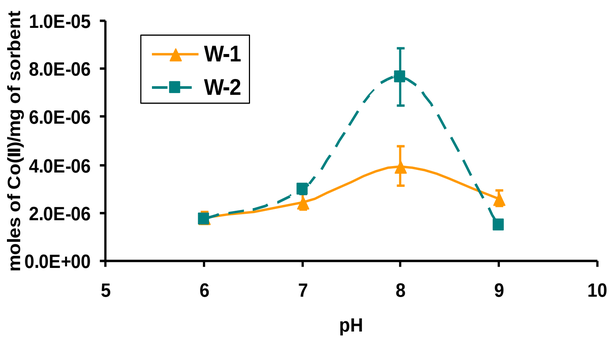

Figure 2. Co^{2+} absorbed onto processed (W-2) and unprocessed (W-1) wool powders (pH 6-9, t = 15 min for W-2, 1440 min for W-1, 23°C).

Figure 3 shows how processing of wool fibre into powders can dramatically enhances the rate of uptake of Co^{2+} and Cu^{2+}.

Surprisingly the rate of uptake of Cd^{2+} is not changed.

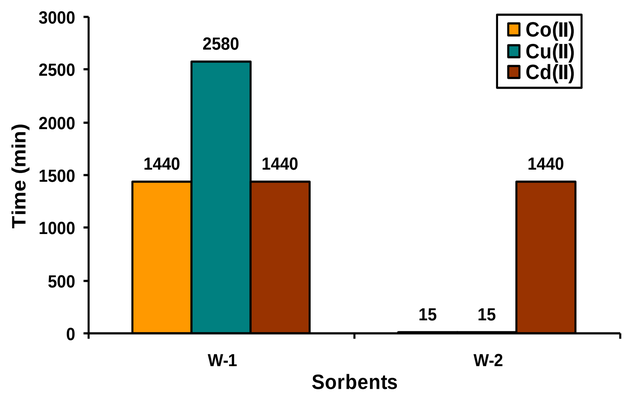

Figure 3. Rates of uptake for Co^{2+}, Cu^{2+} and Cd^{2+} on unprocessed (W-1) and processed (W-2) wool powders at optimum binding pH 8, 23°C .

Reclaiming bound metal ion

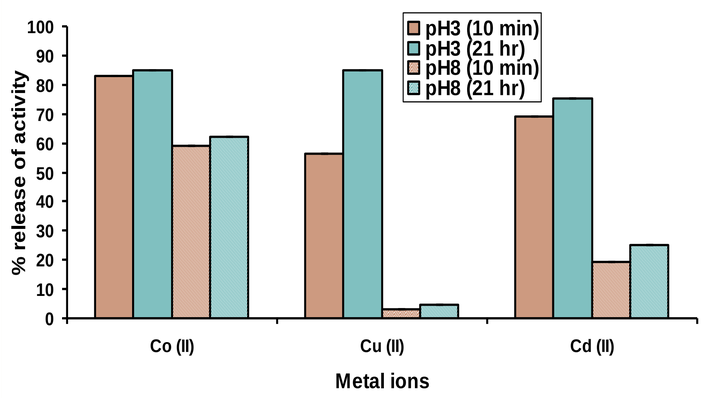

Figure 4. Percent release of activity (absorbed at pH 8) from processed wool (W-2) over time, when exposed to buffers of pH 3 and 8, at 23°C.

Metal ions (Co^{2+}, Cu^{2+} and Cd^{2+}) absorbed on wool samples were re-exposed to fresh solutions of buffers at pH 3 and pH 8.

Figure 4 shows the proportion of metal ions released at 10 minutes and at 24 hours after incubation in pH 3 and pH 8 buffer.

The Co^{2+} and Cd^{2+} establish equilibrium rapidly, releasing over 70% of metal ion within 10 minutes at pH 3. in contrast the release of Cu^{2+} was considerably slower at pH 3.

The pH 8 buffer is a poor eluent for removing Cu^{2+} and Cd^{2+} from the wool powders.

Loading capacity

Figure 5 illustrates the metal ion loading on wool powders.

The absorption of Cu^{2+} and Cd^{2+} on 10 mg of powder over the concentration range 10^{-6} to 10^{-3}M was found to be linear.

In contrast the wool powder becomes saturated in the presence of 10^{-4}M Co^{2+}.

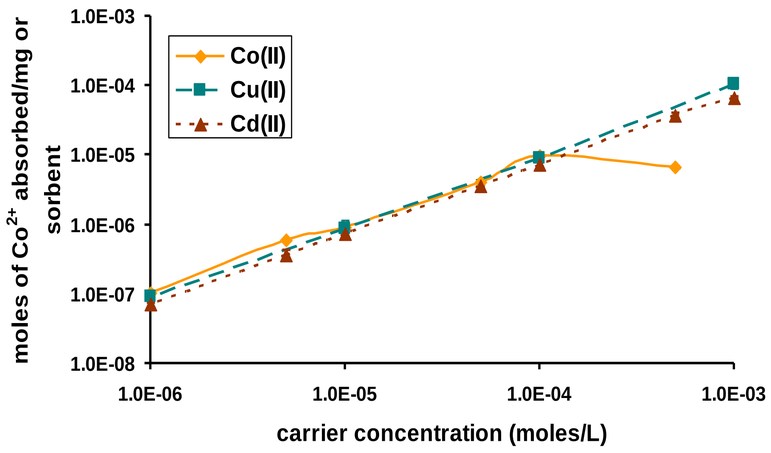

Figure 5. Comparison of Co^{2+}, Cu^{2+} and Cd^{2+} loading on wool powder (W2) at various metal ion concentrations.

Conclusion

This study shows the transition metal binding properties of wool powders are dependent on pH. The rate of absorption as well as the total amount of metal ion absorbed can be enhanced by the powdering process. For example, the rate of uptake for Cu^{2+} and Co^{2+} is increased by > 90 fold compared to wool fibres. Interestingly, once loaded on the wool powder, the rate of desorption is fast (minutes) only for Co^{2+} and Cd^{2+}, compared to Cu^{2+} which can be hours. A comparison of the metal binding properties of wool powders to commercial ion exchange resins [6,7] we find a ~ 7 fold increase in absorption. Such characteristics show promise for the selective extraction of metal ions from solutions and recycling of the precious metals from industrial effluents and environment.

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