

Metal binding properties of wool powders vs commercial resins

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Because of the various reactive groups present within the wool fibres, they can absorb a variety of chemicals, such as metal ions, dyes and surfactants. These metal binding properties have been improved by chemically modifying the wool fibers [1]. Milling wool fibers into powders has also shown significant enhancement in the uptake of dyes by these materials [2]. The present study compares the metal ion (Co²⁺, Cu²⁺ and Cd²⁺) binding properties of powdered wool with commercial resins over a range of pH values, using radiotracers (⁵⁷Co, ⁶⁴Cu and ¹⁰⁹Cd, respectively). The potential application of wool powders in the removal and recovery of metal ions from industrial effluents and the environment is investigated.

Merino wool top (mean fibre diameter = 20.4 µm) was cut into 2 mm snippets, then chemically treated and air-jet milled (mean particle size = 1.40 µm) to produce powdered wool. The positron annihilation lifetime spectroscopy (PALS) analysis of the powders shows no change in the nanoporosity (suggesting no change in basic structural framework) of the powdered samples as compared to fibres.

Powdered wool samples (~10 mg x 4) were exposed to varying concentrations (~10⁻³ to 10⁻⁶ M) of metal ion doped with respective radiotracer under various buffer (pH 3 – 9) conditions at 23°C. The uptake of metal ions was rapid (15 to 60 minutes) and the metal ions were easily removed on lowering the pH. Figure 1 compares the Co²⁺ and Cu²⁺ loading capacity of powdered wool to that of commercial ion exchange resins under the same conditions. The data show the loading capacity of wool powder was ~3 fold and ~10 fold higher for Co²⁺ and Cu²⁺, respectively, compared to the commercial products. This study demonstrates the potential of wool powders for the recovery and recycling of metal ions.

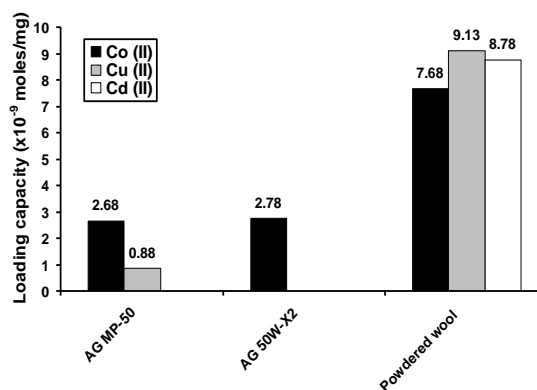


Figure 1. Metal ion loading capacity of powdered wool compared with commercial ion exchange resins at 10⁻⁴ M after equilibration at room temperature and at pH 8 (n = 12,)

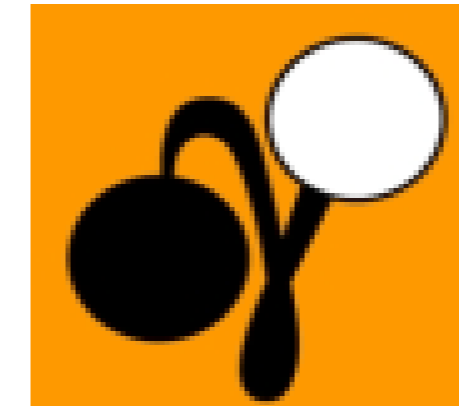
References

- [1] Y. F. Cheng, C.W. M. Yuen, Y. Li, S.K.A. Ku, C. W. Kan, J. Y. Yu, *Journal of Applied Polymer Science*, **2007**, *104*, 803.
- [2] G. Wen, P.R. Brady, J.A. Rippon, X.G. Wang, X. Liu and P.G. Cookson, *The Fiber Society Spring 2008 Conference*, **2008**.





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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 modified⁴ or milled⁵ to produce wool powders. 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 illustrates the morphology of wool powder, obtained by SEM imaging.

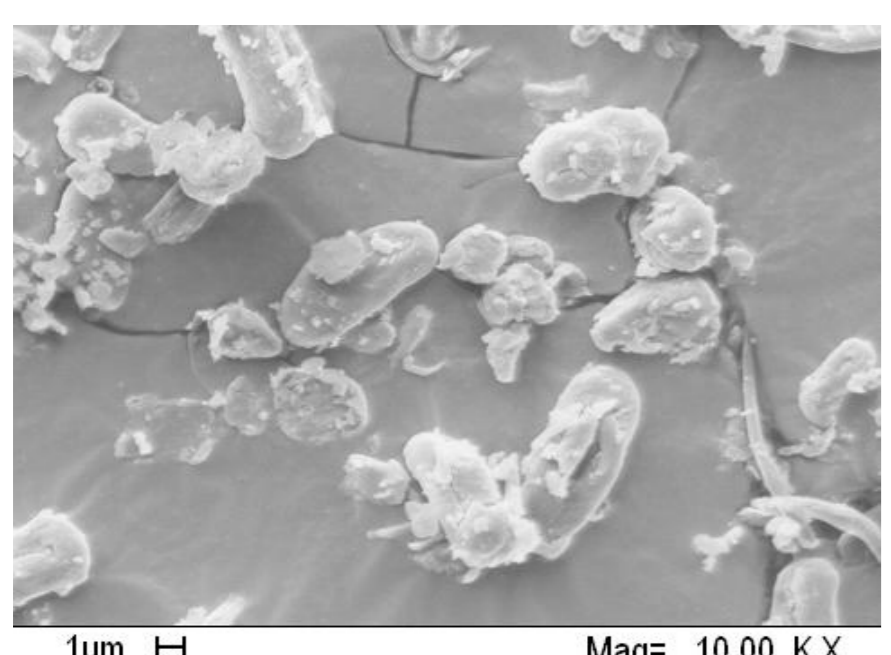


Figure 1. SEM image of wool powder (Leica S440, 5kV acceleration voltage, gold coating for 40 seconds).

- Wool fibre was stone ground, chlorinated, commercially air-jet milled ($d_{\text{mean}}=1.2\mu\text{m}$).
- Reduction in size increases the surface area (fibre = $0.94\text{m}^2/\text{g}$, powder = $6.13\text{m}^2/\text{g}$) of these materials and therefore the rate of kinetics of metal binding.

Metal binding Properties

Figure 2 shows the pH dependence of metal binding to powdered wool.

- The uptake is rapid (> 30 minutes) for Co^{2+} and Cu^{2+} . In contrast, Cd^{2+} requires up to 24 hours.
- Absorption maxima for metal ions investigated (pH 8 for Co^{2+} and pH 6-8 for Cu^{2+} and Cd^{2+}) correlate well with the type of amino acids (e.g. alanine, glycine, histidine, valine) present in the wool powders.

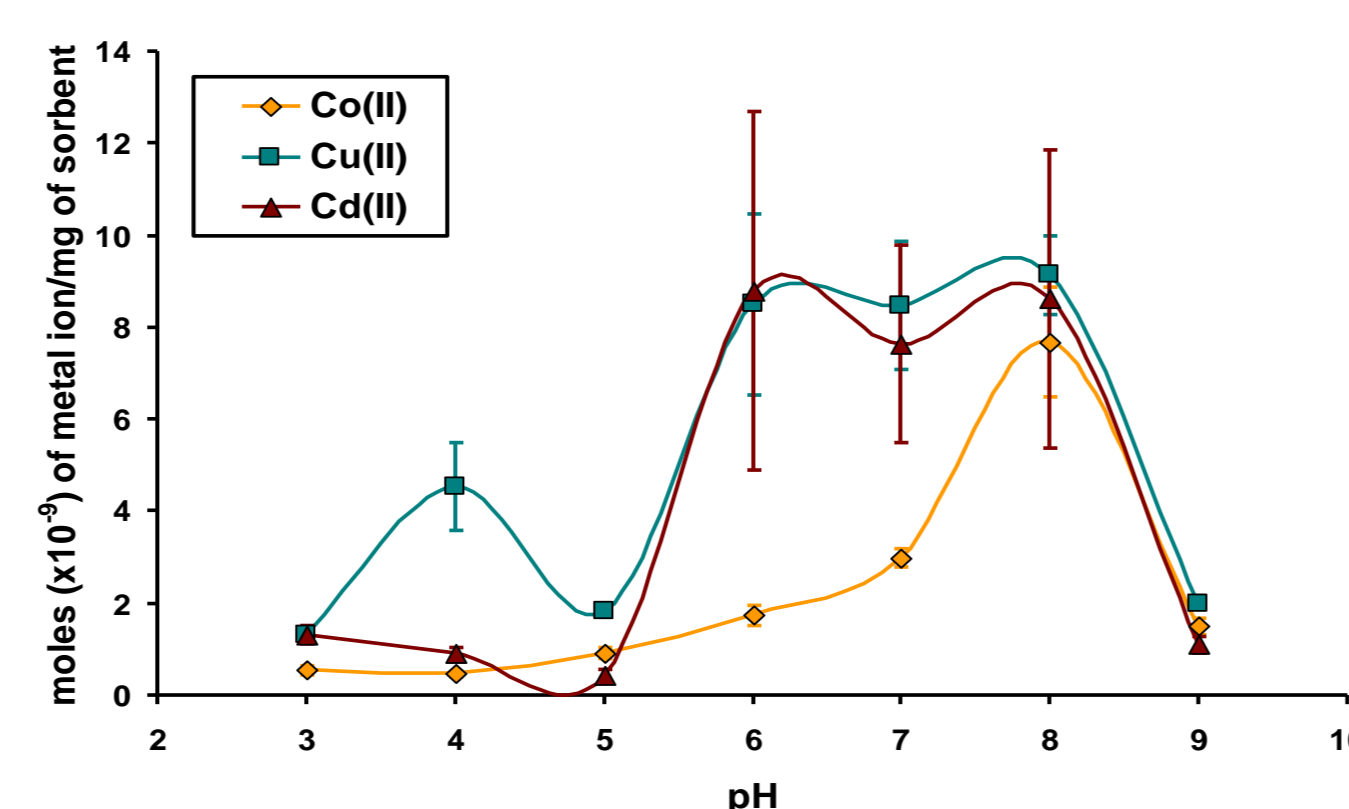


Figure 2. Metal ions absorbed onto processed wool powder (pH 3-9, at equilibrium, 23°C).

Reclaiming bound metal ion

Figure 3 shows the percent of absorbed metal ions (Co^{2+} , Cu^{2+} and Cd^{2+}) released at 10 minutes and at 24 hours after incubation in pH 3 and pH 8 buffer.

- Over 70% of Co^{2+} and Cd^{2+} were rapidly (<10 minutes) released at pH 3. In contrast, the release of Cu^{2+} was considerably slower.
- The pH 8 buffer is a poor eluent for removing Cu^{2+} and Cd^{2+} from the wool powders.

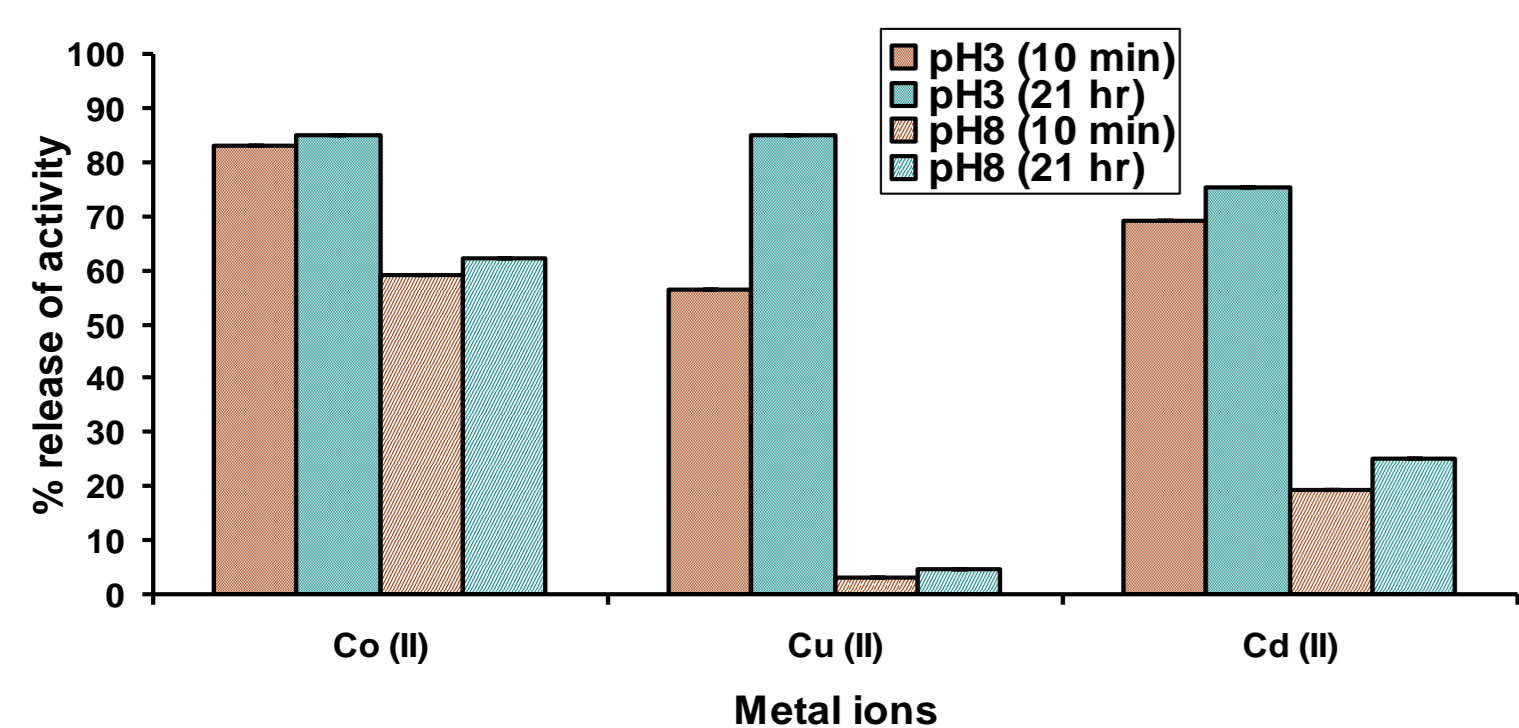


Figure 3. Percent release of activity (absorbed at pH 8) from wool powder over time, when exposed to buffers of pH 3 and 8, at 23°C.

Loading capacity vs. commercial resins

Figure 4 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+} .

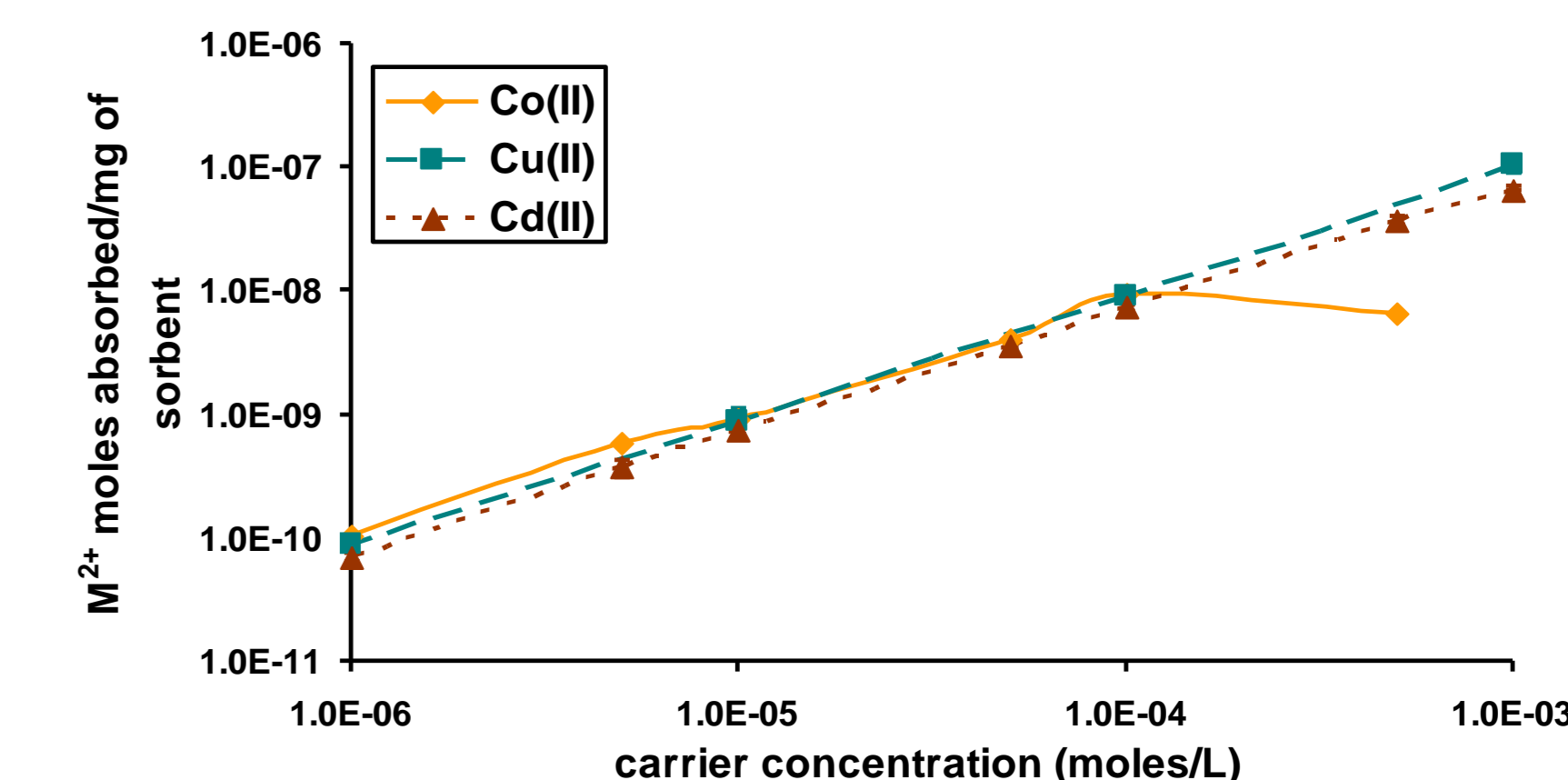


Figure 4. Comparison of Co^{2+} , Cu^{2+} and Cd^{2+} loading on wool powder at various metal ion concentrations.

The Co^{2+} and Cu^{2+} loading capacity of powdered wool was compared to that of commercial ion exchange resins under the same conditions.

- Both resins studied were Polystyrene/divinyl benzene sulfonic acid (figure 5) cation exchange resins.
- Used for water purification, solute concentration and analytical determination of mixed cationic solutions.

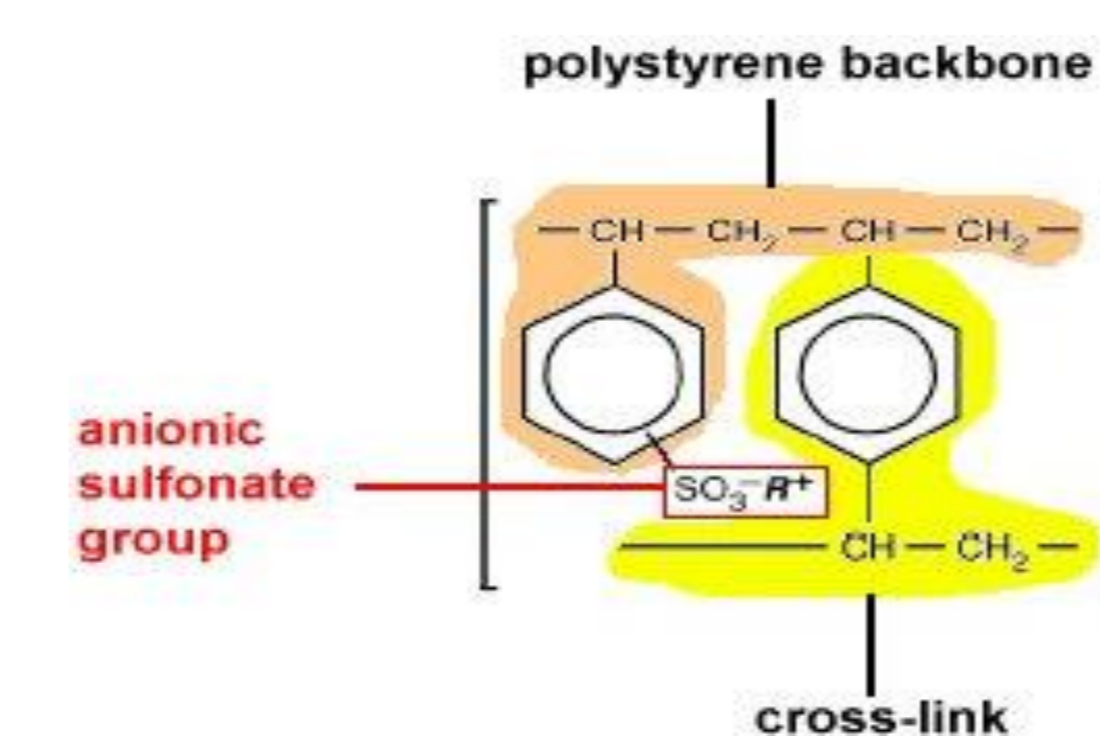


Figure 5. Structure of a polystyrene/divinyl benzene sulfonic acid resin.

Figure 6 summarises the results obtained.

- The data show the loading capacity of wool powder was ~3 fold and ~10 fold higher for Co^{2+} and Cu^{2+} , respectively, compared to the commercial products.

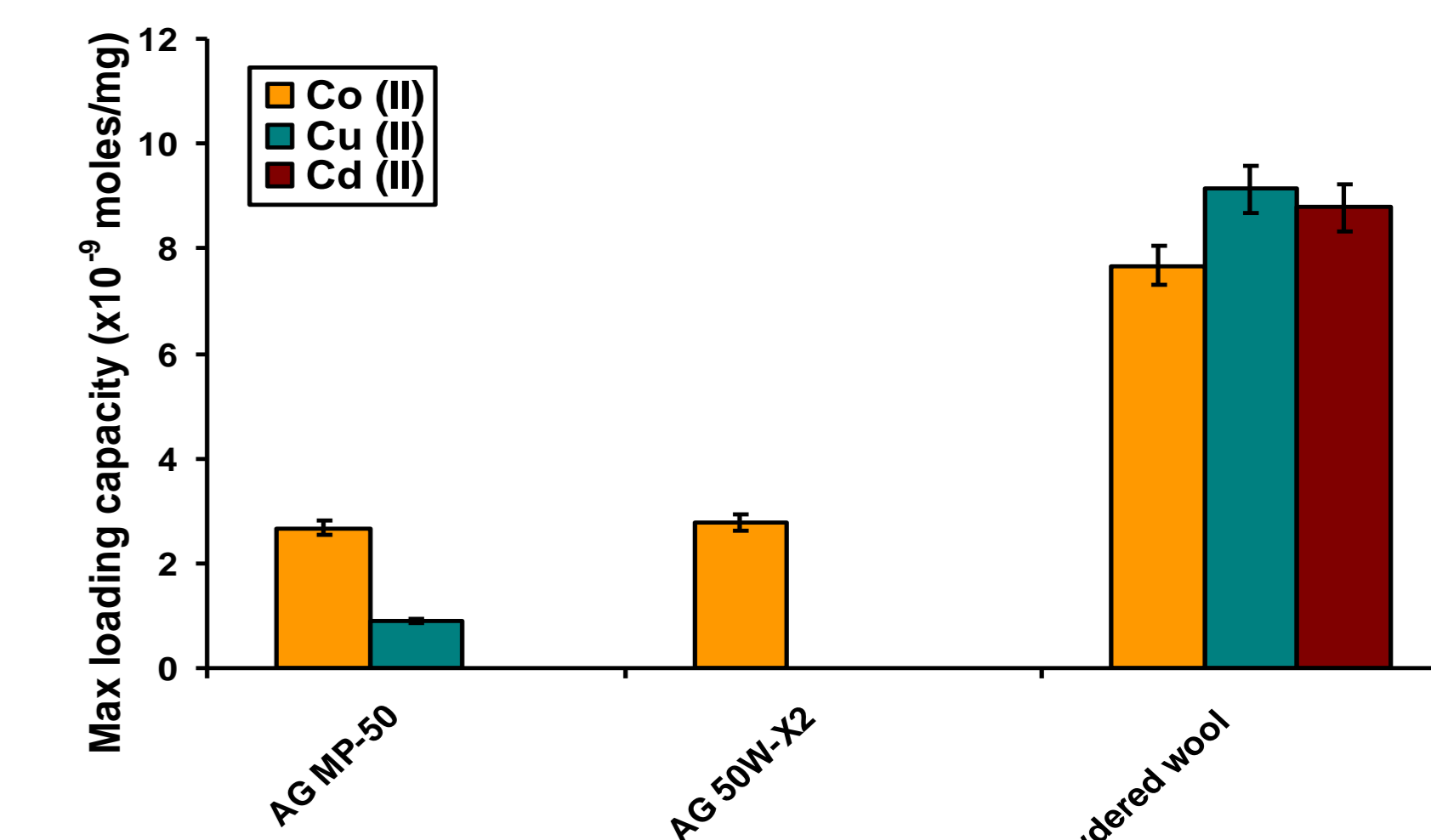


Figure 6. Metal ion loading capacity of powdered wool compared with commercial ion exchange resins at 10^{-4}M after equilibration at room temperature and at pH 8 (n = 12)

Conclusion

- This study shows the transition metal binding properties of wool powders are dependent on pH. 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 we find a 3 to 10 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.
- Future directions would include incorporating these wool powders into composite materials.

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