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Metal absorption on eri and mulberry silk powders: a comparative study

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Silk powders are readily employed in commercially available cosmetic products and nutritional foods. Their applications in coating, fibre treatment, fillers in films, wound care, enzyme immobilisation, composite scaffold for cell growth and drug delivery have also been reported.[1,2] Recently, fine and sub-micron scale silk powders have been fabricated from different silk varieties using standard milling devices.[2] These powders retain the crystallinity and water insolubility of fibroin particles, which are required in applications such as metal absorption. The present investigation compares the metal (Co^{2+}, Cu^{2+} and Cd^{2+}) binding properties of such milled silk powders, over a range of pH (3-9).

Eri and mulberry cocoons were degummed using different concentrations of alkali and temperatures, then chopped into snippets and milled into fine powders using attritor and/or jet mill. The SEM images of these powders revealed the difference in the morphology of the powders originating from the two varieties of silk. These powders (~10 mg in quadruplicate sampled; n=12) were exposed to 10^{-4}M of Co^{2+}, Cu^{2+} and Cd^{2+} doped with radiotracer (^{57}Co, ^{64}Cu and ^{109}Cd) respectively under various buffer (pH 3–9) conditions at 23°C. The results in Figure 1 show that the metal ion binding properties were quite different depending on the varieties of silk. Over the pH range 3-9, the Mulberry silk powder shows two absorption peaks (pH 4-5 and 8) for all the metal ions studied, whereas the Eri silk powder shows absorption maximum at pH 8 for Co^{2+} and a broad absorption peak for Cu^{2+} and Cd^{2+} over pH 6-8.

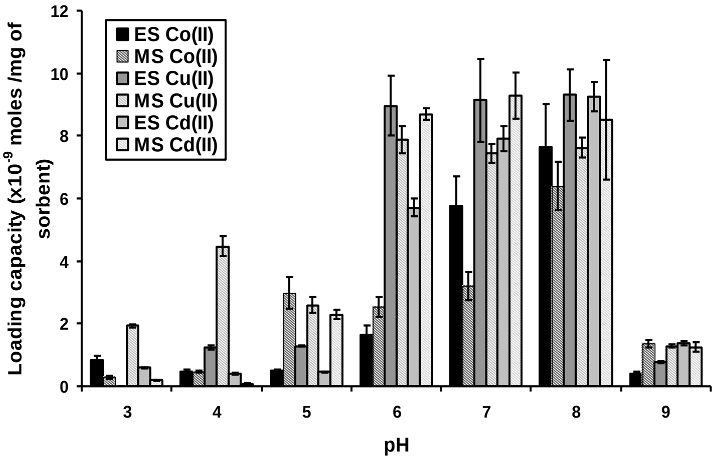

Figure 1. Comparative metal binding properties of Eri and Mulberry silk powders ([M^{2+}] = 10^{-4}M, pH 3-9, 23°C, Sample size for each bar: n = 12; ES: Eri silk powder, MS: Mulberry silk powder).

The significant differences in the metal binding profiles between the eri and mulberry silk powders suggests substantial differences in amino acid composition and fine structure of these silk varieties. Such silk powder performance supports further exploration in selective recovery of metals and also incorporation of these materials in composites applications such as controlled drug release.

References

[1] X. Wang, E. Wenk, A. Matsumoto, L. Meinel, C. Li, D.L. Kaplan, *Journal of Controlled Release*, **2007**, 117 (3), 360.

[2] R. Rajkhowa, L. Wang, X. Wang, Powder Technology, **2008,** 185 (1): 87.

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Metal binding and porosity of Eri and Mulberry silk powders: a comparative study

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IC 08, Christchurch, 16/12/2008

Applications and Properties of Silk Powders

Applications [1-3]

- Cosmetic products
- Nutritional foods
- Fibre treatment, Fillers in films
- Wound care, Enzyme immobilisation
- Composite scaffold for cell growth
- Drug delivery

Properties [4-8]

- Biocompatible, biodegradable
- Ease of processing
- Good mechanical properties

[1] X. Wang, E. Wenk, A. Matsumoto, L. Meinel, C. Li, D.L. Kaplan, *Journal of Controlled Release*, **2007**, 117 (3), 360. [2] R. Rajkhowa, L. Wang, X. Wang, *Powder Technology*, **2008,** 185 (1): 87. [3] E. Wenk, A. Wandrey, H. Merkel, L. Meinel, *Journal of Controlled Release*, **2008** (accepted for publication) [4] Hakimi, O., D.P. Knight, F. Vollrath, P. Vadgama, Composites Part B: Engineering Bio-engineered Composites 2007, 38, (3), 324-337. [5] Minoura, N., S.-I. Aiba, M. Higuchi, Y. Gotoh, M. Tsukada, Y. Imai, Biochemical and Biophysical Research Communication 1995, 208, (2), 511-516. [6] Tsubouchi, K., T. Ninagawa, Patent 11104228, 1999. [7] Tsubouchi, K. Patent 123683, 2004. [8] Wang, Y., H.-J. Kim, G. Vunjak-Novakovic, D.L. Kaplan, Biomaterials 2006, 27, (33), 6064-6082.

Processing of Silk powders

Silk powder is prepared from silk fibroin:

- Regeneration from solution
- Mechanical attrition

- Advantages of Mechanical attrition,
  - ➢ Uniform
  - ➢ Water insoluble
  - ➢ Retain β crystalline structure
  - ➢ Short processing time
  - ➢ Lower cost

Varieties of Silk powder

- Eri silk

Samia ricini

- Mulberry silk

Bombyx mori

Different morphology

And

Amino acid composition

Silk powder preparation for this study

- Eri silk
  - Cocoons degummed (Na_2CO_3/100°C)
  - Chopped into snippets
  - Mechanical attrition (ball-mill, air-jet mill)
  - Spray dried
- Mulberry silk
  - Commercial product used without further processing

Aim

How does the variety of silk effect:

- Metal binding (Co^{2+}, Cu^{2+}, Cd^{2+})
    - ➢ Effect of pH
    - ➢ Rate of uptake
    - ➢ Loading capacity

    } Radiotracer

- Porosity
    - ➢ SEM (Scanning elelctron microprobe)

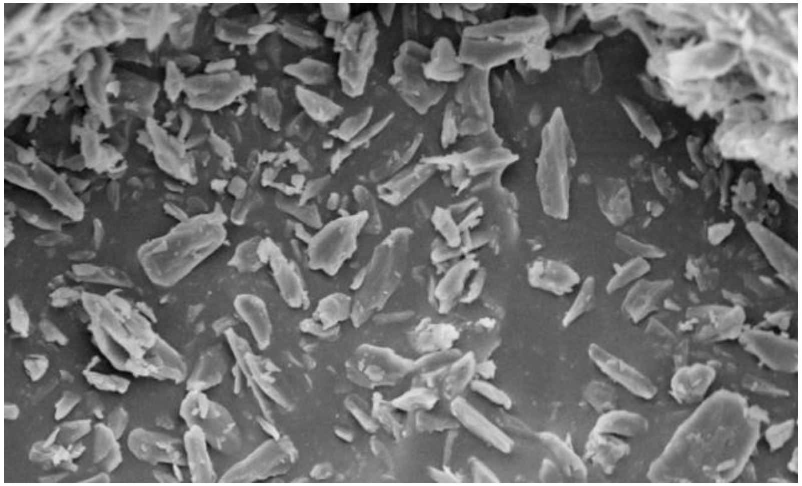
      >50nm (macropore)
    - ➢ BET (Brunauer, Emmett, Teller) gas absorption

      10-50nm (mesopore)
    - ➢ PALS (Positron annihilation lifetime spectroscopy)

      0.1-10nm (micropore)

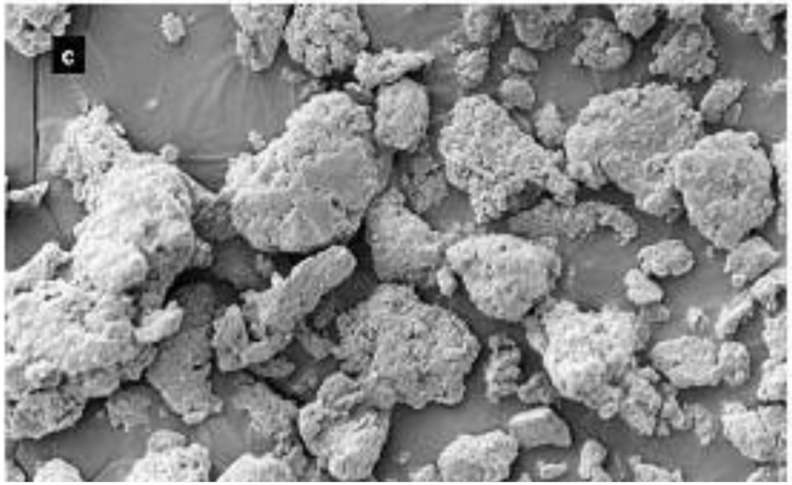
SEM (Scanning Electron Microscope) imaging

Eri: degumming, ball & air-jet mill, spray dry
4.5µm



10µm

Mulberry: commercial, without further processing
5µm



10µm

Particle size = Median of volume based particle size distribution

PALS

(Positron annihilation lifetime spectroscopy)

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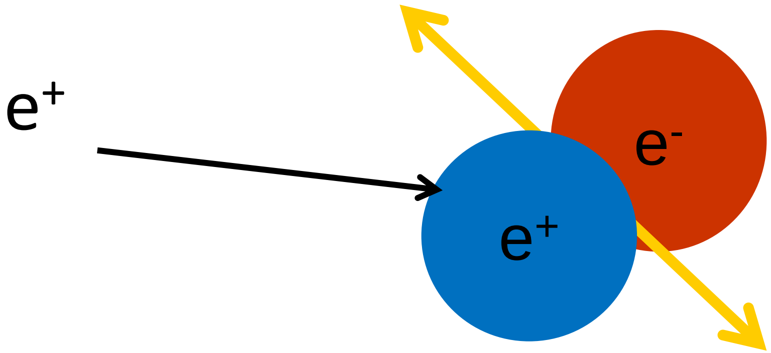
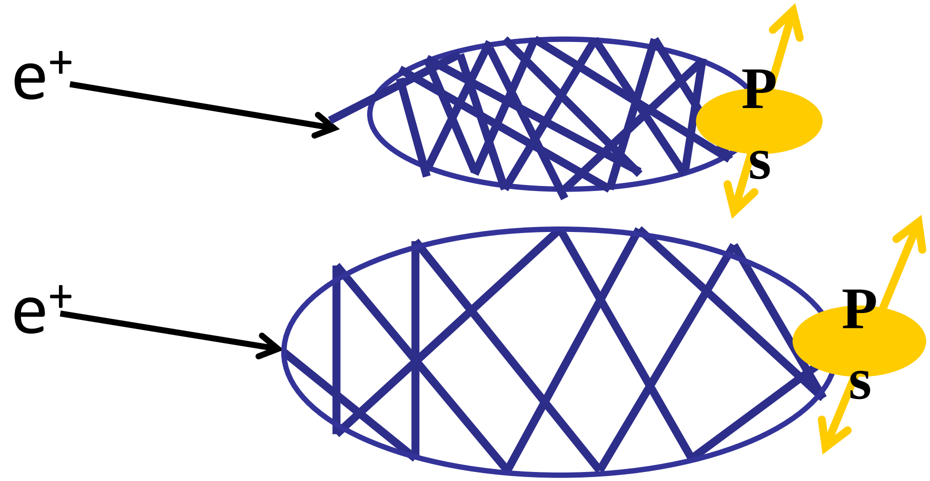


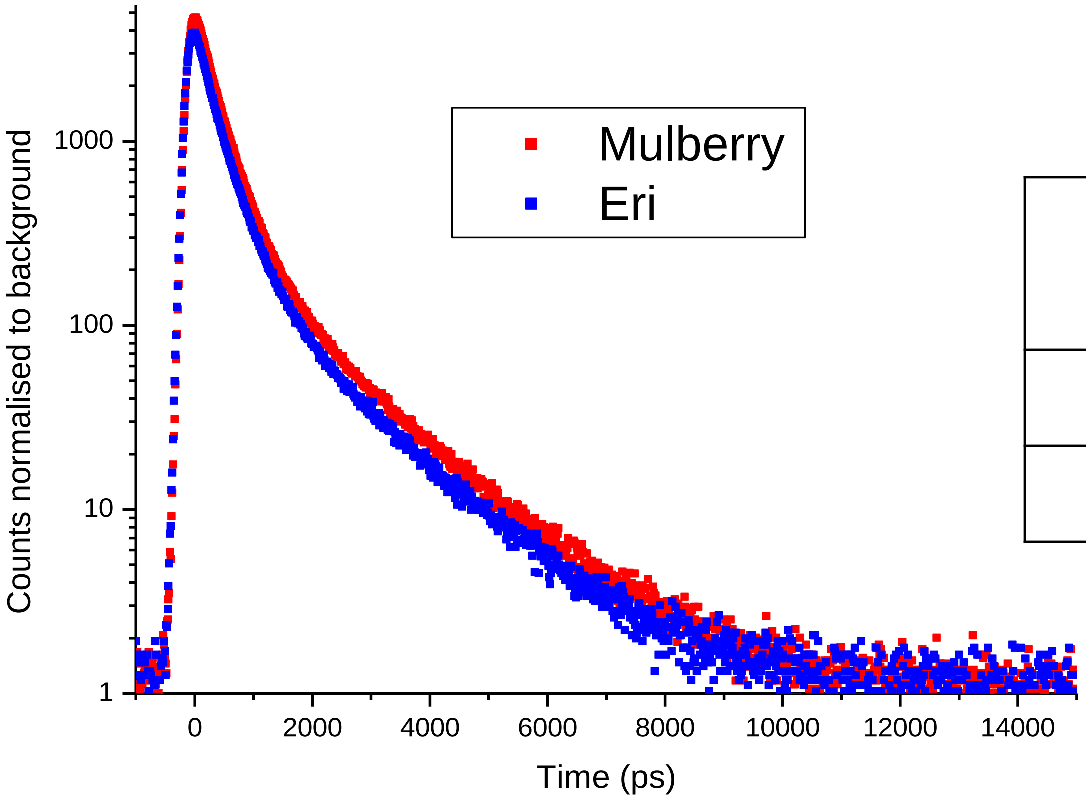
Positronium:
25% p-Ps (singlet, short-lived)
75% o-Ps (triplet, longer-lived)

- Positron lifetime (τ) is a function of the electron density at the annihilation site.

- Larger pore volume leads to longer lifetime



Porosity



Silk sample analysed	Pore size (nm)
Eri	0.48
Mulberry	0.47

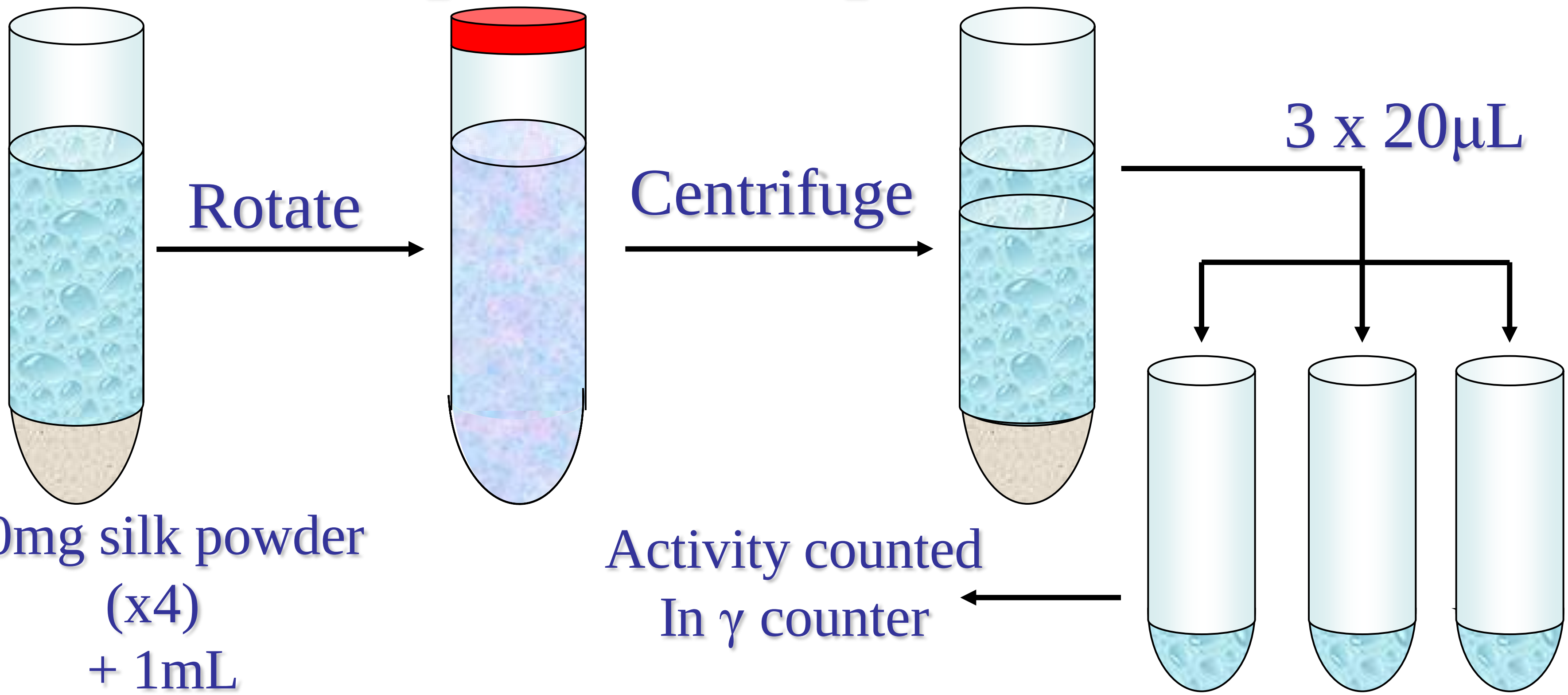
- PALS shows no change in microporosity.
- BET shows only slight change in surface area.

Basic protein structure appears to be conserved

Experimental conditions

- $^{64}Cu/Cu^{2+}$, $^{57}Co/Co^{2+}$, $^{109}Cd/Cd^{2+}$
- pH: 3 to 9
- Temperature: 23°C
- $[M^{2+}] = 10^{-3}$ to 10^{-6}M

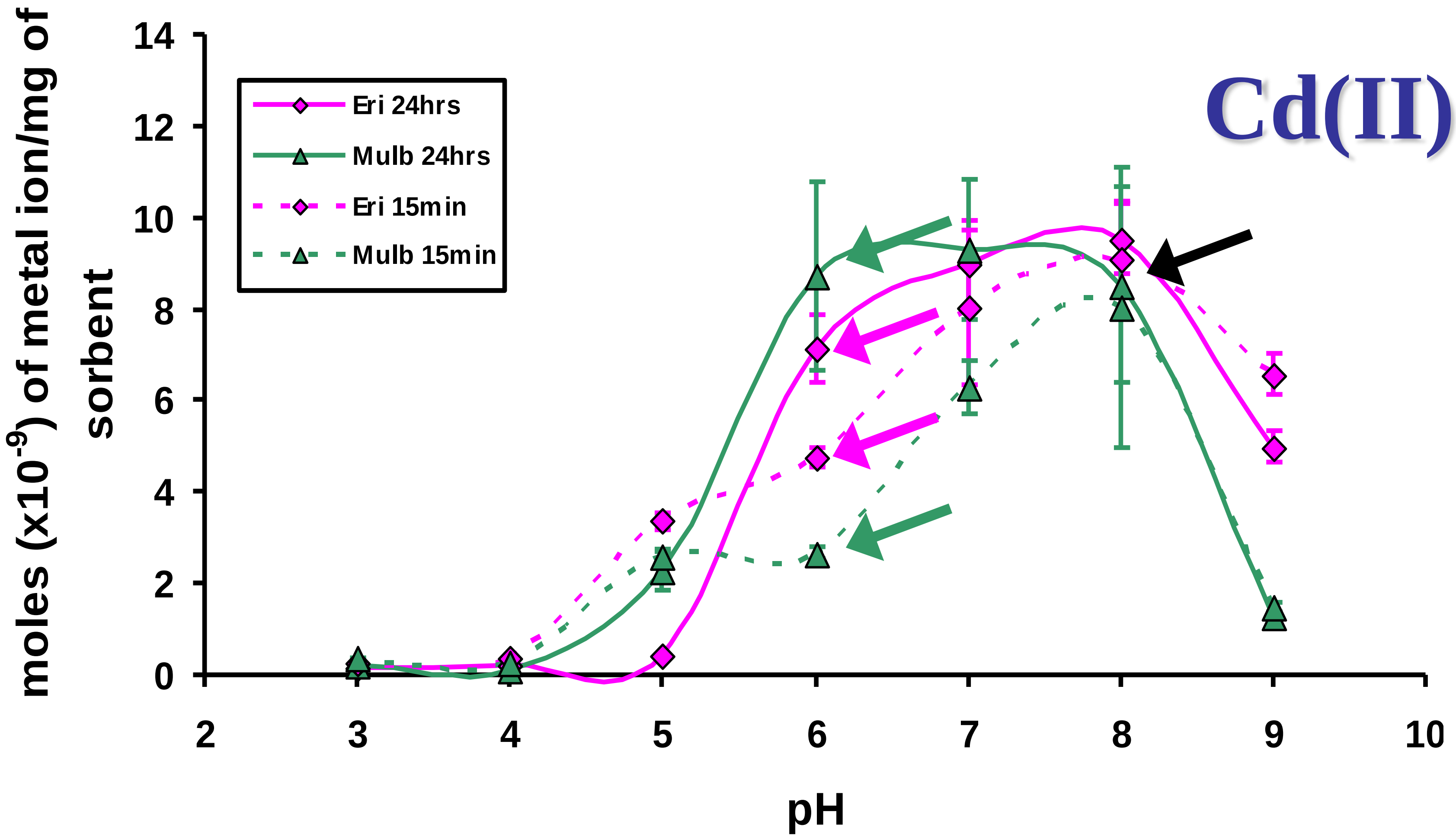
Experimental procedure



~10mg silk powder
(x4)
+ 1mL
(metal ion +
radiometal ion +
buffer)

- Fast (10 sec), sensitive (10^{-3} ppb), small volume (μL)
- High throughput (~800 readings)
- Independent of media

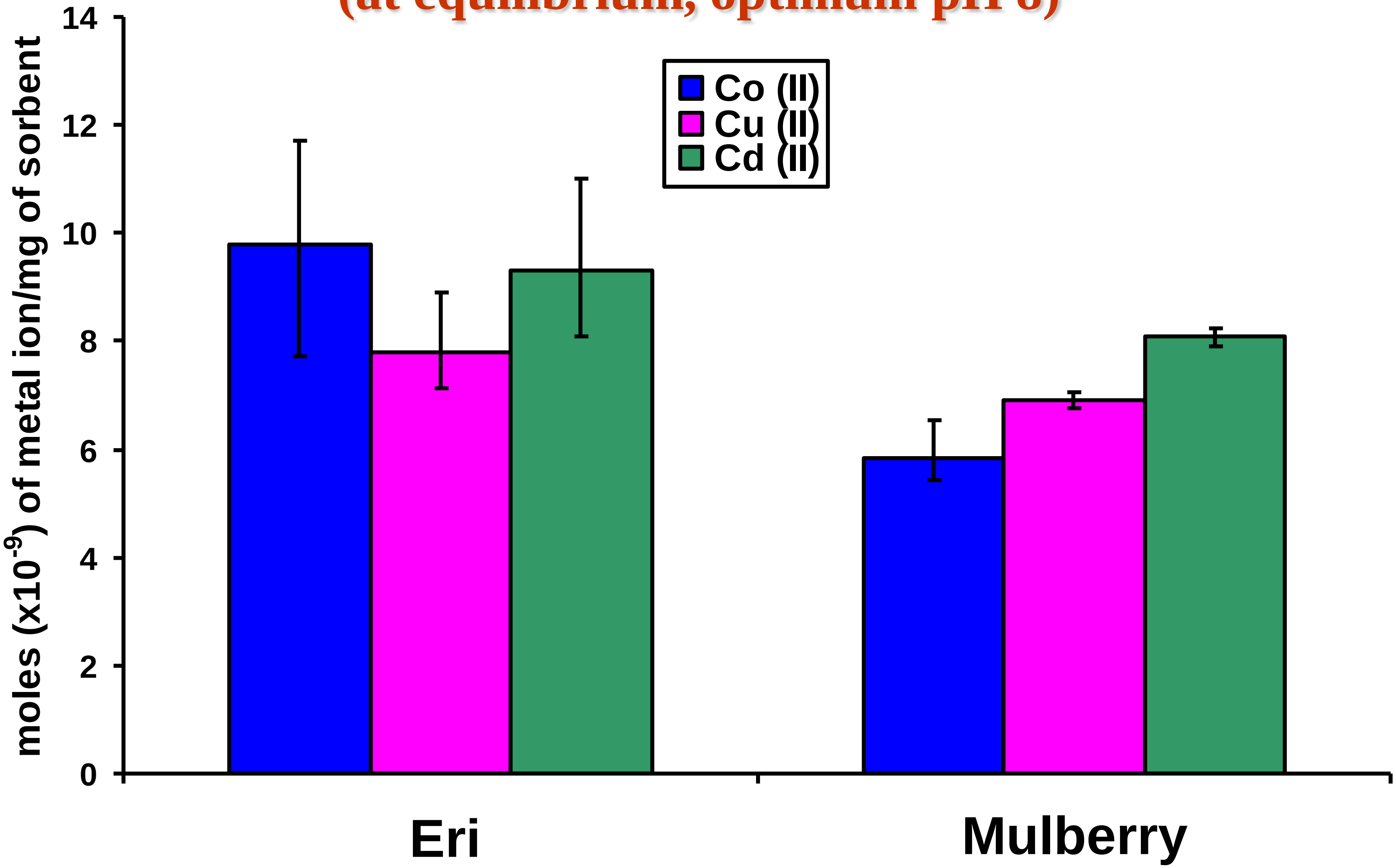
Effect of pH on Metal Binding



$[M^{2+}] = 10^{-4}M$; powder 10 mg; Temp.23°C; Total Vol: 1.0 mL; centrifuge; 5000 rpm

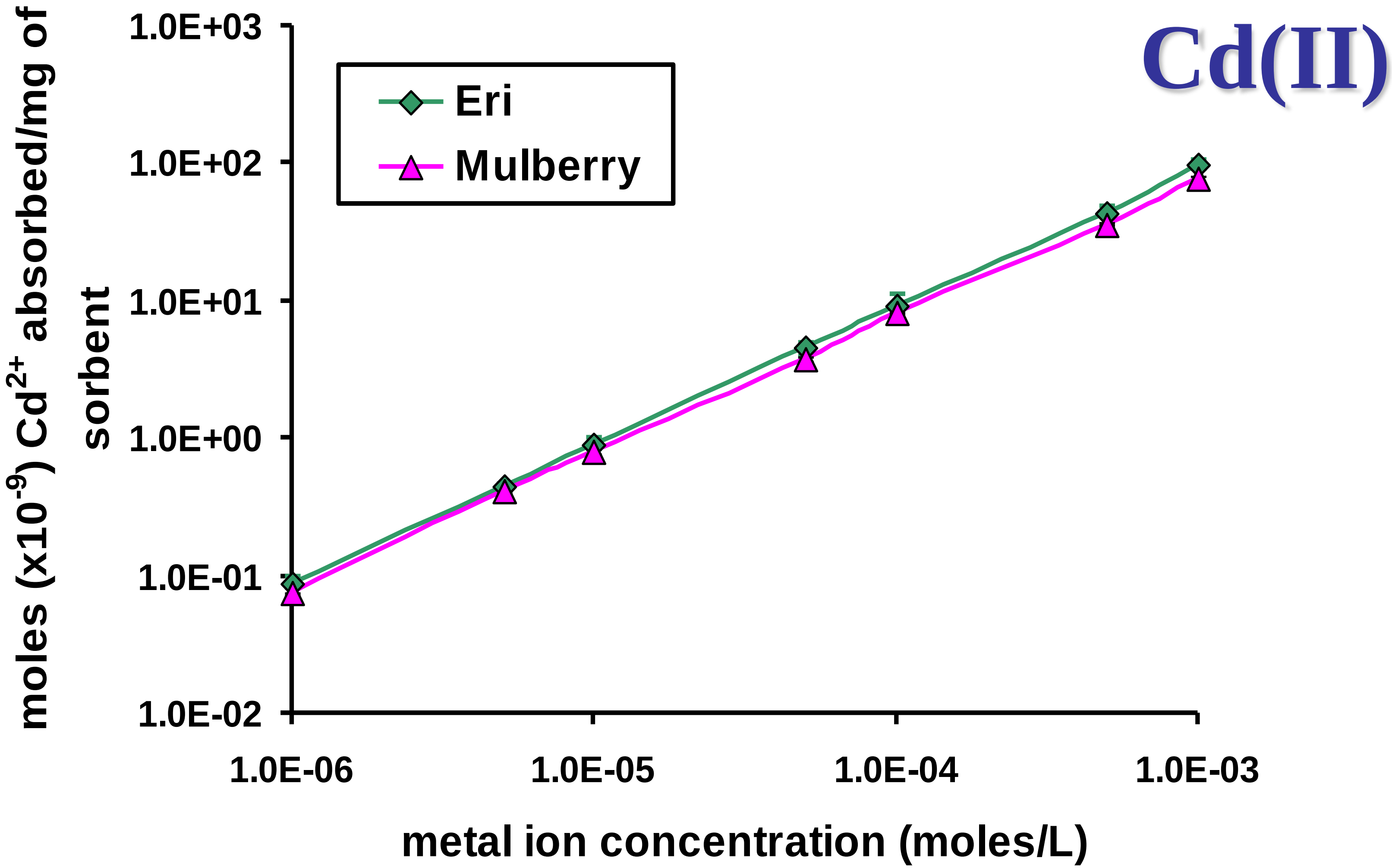
Metal binding affinity

(at equilibrium, optimum pH 8)



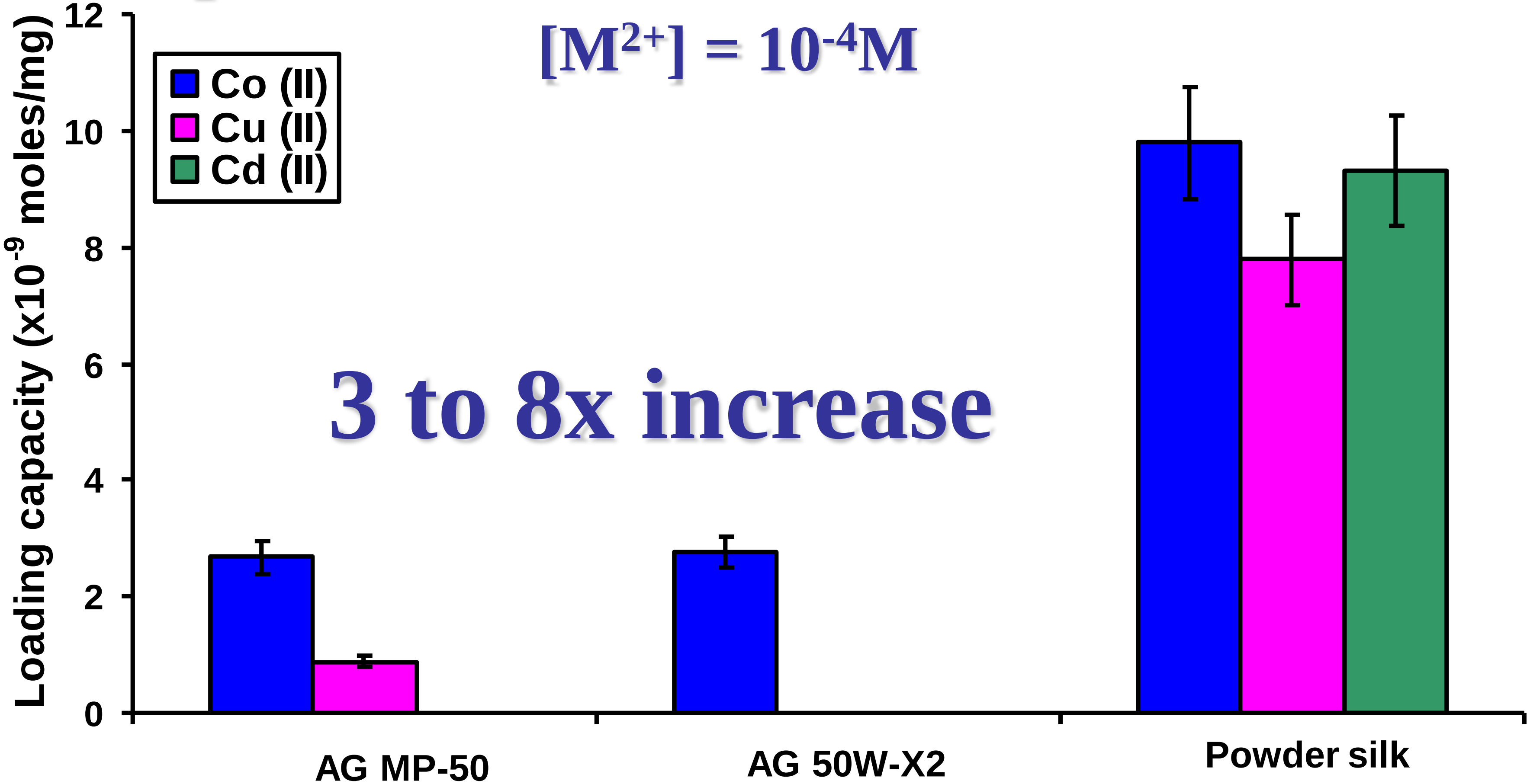
$[M^{2+}] = 10^{-4}$M; powder 10 mg; Temp.23^{o}C; Total Vol: 1.0 mL; centrifuge; 5000 rpm

Loading capacity (at equilibrium, optimum pH 8)



$[M^{2+}] = 10^{-3}$ to 10^{-6}M; powder 10 mg; Temp.23^{o}C; Total Vol: 1.0 mL; centrifuge; 5000 rpm

Comparison of metal loading on silk powders with commercial resins



cation exchange resins;
used in water purification

powder 10 mg; Temp.23°C; Total Vol: 1.0 mL; centrifuge; 5000 rpm

Conclusion

- Basic protein structure and porosity independent of silk variety.
- Use of radiotracers allowed rapid, sensitive and high-throughput analysis.
- Metal binding varies significantly with pH; slightly with silk variety.
- Higher (3 to 8x) loading capacity than commercial resins.
- Possible application in removal and recovery of metal ions and controlled drug delivery.

Future directions

• Incorporate into composite material; evaluate performance (selectivity, loading capacity).

• Evaluate the effect of binding with larger molecules (e.g.: proteins, drugs) with radioactive mimics.

Acknowledgements

Nuclear Probes, ANSTO:

- Dr. Suzanne Smith
- Dr. Dharmaprakash
- Sabrina Hureau

Australian Government

ansto

Deakin University:

- Rangam Rajkhowa
- Prof. Lijing Wang
- Prof. Xungai Wang

DEAKIN UNIVERSITY

University of WA:

- Prof. Jim Williams
- Paul Guagliardo
- Dr. Tony Sergeant

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University of Tsukuba:

- Prof. Akira Uedono

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