Comparative Study of Metal Ion Adsorption and Gold Reduction by Cross-linked and Non Cross-linked Sericin

Kaoru Ohe*, Yudai Yamaguchi, Tatsuya Oshima
Faculty of Engineering, University of Miyazaki, 1-1 Gakuen Kibanadai-Nishi Miyazaki, 889-2192, Japan

Email:okaoru@miyazaki-u.ac.jp, hn21355@student.miyazaki-u.ac.jp, oshimat@miyazaki-u.ac.jp
*Corresponding Author

Abstract

Sericin is an underutilized biomass of hydrophilic protein removal during the refining process of silk yarn. Processing abundant functional groups such as hydroxyl, carboxyl, amide, and amino groups, sericin exhibits affinity for metal ions, making it a promising biosorbent. This study investigated the adsorption behavior of metal ions using sericin and glutaraldehyde-crosslinked sericin(Glu-sericin). Glu-sericin selectively adsorbed precious metals over Cu(II) in 0.01 M HCl. In contrast, sericin showed a red color change after Au(III) adsorption from 0.01 M and 0.1 M HCl, indicating the reduction of Au(III) to Au(0). These results show that sericin non-crosslinked treatment, both adsorption and reduction functions, making it a unique biomass material for gold recovery.

Keywords: sericin, crosslinking, metal ions, adsorption, reduction

1. Introduction

The presence of heavy metals in the environment adversely affects plants and aquatic organisms due to increased emissions and toxicity. The sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and the fertilizer industry[1]. Excessive intake of copper results in an accumulation in the liver. It is also toxic to aquatic organisms even at very low concentrations in natural water[1]. Furthermore, the recovery of precious metals has become a critical issue due to soaring gold prices. Methods for separating and adsorbing metals from aqueous solutions include ion exchange, adsorption, and precipitation[2], [3]. Adsorption is the most effective and widely used method. Commercially available polymer resins are expensive, making the development of low-cost alternatives a focus of researchers in this field.

Bioadsorption using biologically derived materials is gaining attention as a novel technology for treating metal-containing wastewater. Silkworm cocoons consist of two main proteins: fibroin (ca. 75%) and sericin (ca.25%). Sericin is a soluble, hydrophilic biopolymer in hot water or weak alkaline aqueous solutions. Sericin is a hydrophilic protein contained in silkworm cocoons, typically discarded during raw silk refining. Composed mainly of the amino acids Ser (approximately 30%), Gly (approximately 20%), and Asp (approximately 20%) [4], sericin is gaining attention in biomedical and cosmetic fields due to its biocompatibility. Sericin has abundant amide, hydroxyl, amino, and carboxyl groups, and, due to its many functional groups capable of interacting with metal ions, it is expected to be useful as a metal-ion separation adsorbent. However, there are few comparative examples between cross-linked sericin and non cross-linked sericin regarding metal ion adsorption. Therefore, this study evaluated the metal adsorption characteristics of two types of sericin, investigating the effects of adsorption time course, pH, acid concentration, and metal concentration on metal ion adsorption.

2. Experimental

2.1. *Synthesis of cross-linked sericin*

Sericin was purchased from Takada Seiren Co., Ltd (non cross-linked sericin). The procedure was performed almost identical to that described by Guibal *et al.* [5]. Add 1.50 g of sericin to 15 mL of dimethylformamide (DMF), swell at 60°C for 1 hour, then add 0.15 g of glutaraldehyde and react for 24 hours (Siff based sericin). Add 1.13 g of sodium borohydride to the sample and stir at 60°C for 24 hours under a nitrogen atmosphere. Wash the sample with DMF and distilled water, then air-dry (cross-linked sericin). The cross-linked sericin did not dissolve in 0.1 M NaOH.

2.2. *Adsorption tests*

All adsorption experiments were conducted using the batch method. Fifty milligrams of crosslinked sericin were added to 15 mL of 0.1 M metal solution and shaken at 30°C for 24 hours (120 rpm). The metal concentration in the filtrate was analyzed using an atomic absorption spectrophotometer. The adsorption rate A% (Eq. (1))and adsorption capacity q (mmol/g)(Eq. (2)) were calculated using the following equations.

$$A\% = 100 \times (C_e - C_i) / C_i \quad (1)$$

$$q = (C_e - C_i) \times V / W \quad (2)$$

Here, C_i is the initial metal concentration (mM), C_e is the equilibrium metal concentration (mM), V is the volume of the metal solution (mL), and W is the amount of adsorbent (mg).

Adsorption isotherm was evaluated by Langmuir equation Eq. (3) and Freundlich equation Eq. (4).

$$q = K_L\, q_{max}\, C_e / (1 + K_L C_e) \quad (3)$$

$$q = K_F\, C_e^{1/n} \quad (4)$$

Here, K_L Langmuir constant (L/mmol), q_{max} is the maximum adsorption capacity (mmol/g), K_F Freundlich constant, and 1/n is coefficient.

3. Results and Discussion

3.1. Cross-linked sericin

FT-IR analysis results for three types of sericin (non cross-linked, Schiff base, cross-linked sericin) obtained by the KBr tablet method are shown in Figure 1. Cross-linked sericin showed increased absorption peaks at 1400 cm^{-1} (C-N stretching vibration) [6]. Schiff base sericin exhibited azomethine group (C=N) absorption peaks at 1600-1640 cm^{-1}[6]. Thus, sericin cross-linked with glutaraldehyde was successfully synthesized.

3.2. Cu(II) Adsorption

Figure 2 shows the time-dependent changes in Cu(II) adsorption by crosslinked sericin (initial pH=3.0). The equilibrium reaching time for Cu(II) was within 15 minutes, which is significantly faster than the adsorption of Cu(II) by the commercially available iminodiacetic acid chelating resin Diaion CR11 (12 hours), confirming that Cu(II) adsorption occurred rapidly. The adsorption isotherms of Cu(II) using cross-linked and non-cross-linked sericin are shown in Figure 3 (initial pH 3.0, w=50 mg, v=15 mL). The adsorption behavior was determined by calculating the maximum adsorption capacity q_{max} from a linear plot of C_e/q versus C_e, derived from a modified Langmuir adsorption equation (Eq. (2)). The correlation coefficient $r > 0.98$ indicated that the Langmuir equation well-fitted the Cu(II) adsorption onto both cross-linked and non-cross-linked sericin. The Cu(II) saturation adsorption capacity of cross-linked sericin was 0.147 mmol/g, representing a 65% reduction in Cu(II) adsorption capacity compared to non-cross-linked sericin. Cross-linking treatment reduces adsorption performance by decreasing the number of free amino groups and reducing accessibility to internal adsorption sites.

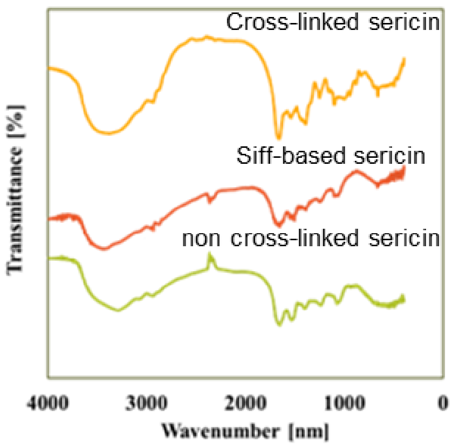


Figure 1 FT-IR spectra of cross-linked, Siff-based, non cross-linked sericins.

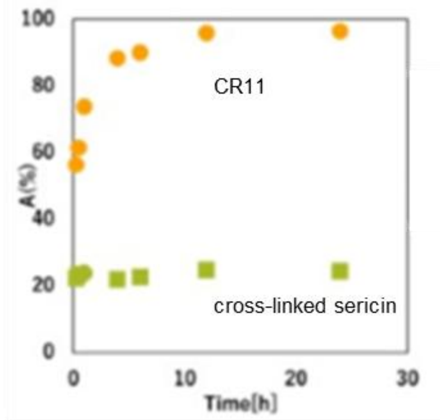


Figure 2 Time course of Cu(II) adsorption with crosslinked sericin and CR11.

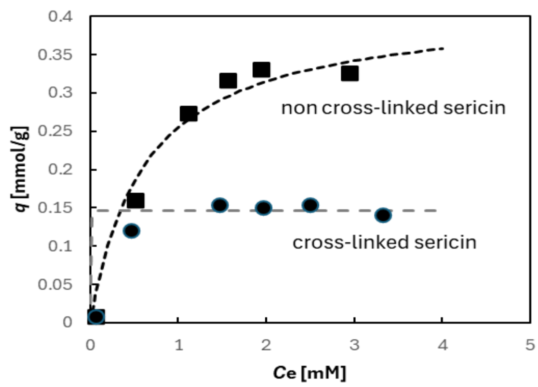


Figure 3 Adsorption isotherms of Cu(II) with crosslinked and non cross-likned sericin(303K)

3.3. Au(III) adsorption/reduction from HCl solution

Figure 4 shows the effect of hydrochloric acid concentration on the adsorption of Au(III), Pt(IV), Pd(II), and Cu(II) by cross-linked sericin. At 0.01–0.1 M HCl, the adsorption rates for Au(III), Pt(IV), and Pd(II) were high, while Cu(II) showed hardly adsorption. The chemical species of the adsorbed precious metal chloride complexes are the anions $AuCl_4^-$[7], $[PdCl_3(H_2O)]^-$[8], and $PtCl_5^-$[9], whereas Cu(II) is the cation $CuCl^+$[10]. This result indicates the potential for selective separation of precious metals from the base metal Cu(II) in low concentration HCl solutions.

Next, we investigated the adsorption of Au(III) from hydrochloric acid solutions using cross-linked sericin, non-cross-linked sericin, and chitosan (a biomass polymer with amino groups) (Figure 5(b)). Cross-linked sericin exhibited a decrease in the Au(III) adsorption percentage at hydrochloric acid concentrations above 0.1 M HCl, with adsorption behavior similar to that of chitosan. Au(III) adsorption by chitosan from acidic chloride solutions is due to electrostatic attraction with protonated amino groups. Above 1M HCl, adsorption of the precious metal chloride complex ions decreased, likely due to competitive adsorption by coexisting Cl^-.

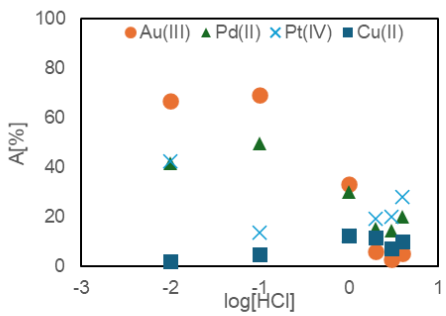
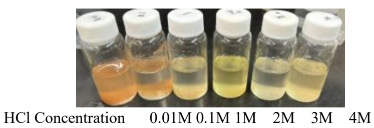


Figure 4 Effect of HCl concentration of Au(III) cross-linked sericin (303K)

(a)



(b)

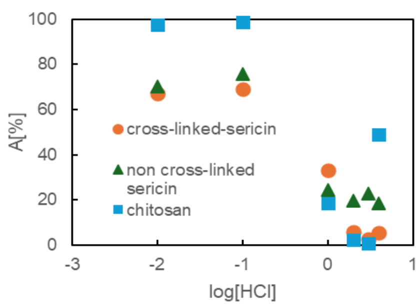


Figure 5 (a) Photos of samples after Au(III) adsorption from 0.01M-4.0 M HCl using non cross-linked sericin, (b)Au(III) adsorption from HCl solution using cross-linked sericin, non cross-linked sericin and chitosan

Here, for non-crosslinked sericin, the adsorbent turned colored after Au(III) adsorption with 0.01 M and 0.1 M HCl, as shown in Figure 5(a) After filtration, the adsorbent was air-dried, followed by XRD analysis and UV/Vis analysis. Figure 6 shows a broad peak around $2\theta = 20°$ for sericin before Au(III) adsorption, indicating its amorphous structure. The XRD diffraction pattern after Au(III) adsorption showed sharp diffraction peaks at 2θ=38° (111) and 45° (200), consistent with the JCPDS file number 4-0784 for Au(0) nanoparticles[11]. The broad peak observed around 550 nm in the post-adsorption UV/Vis spectrum (Figure 7) is interpreted as arising from the excitation of plasmon resonance in the Au nanoparticles[12].

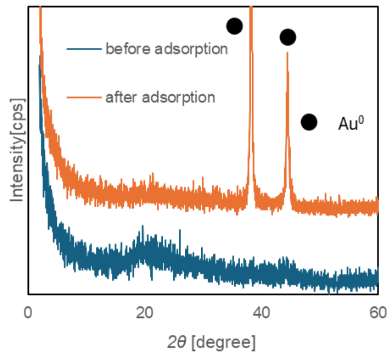


Figure 6 XRD of sericin before and after Au(III) adsorption from 0.1 M HCl.

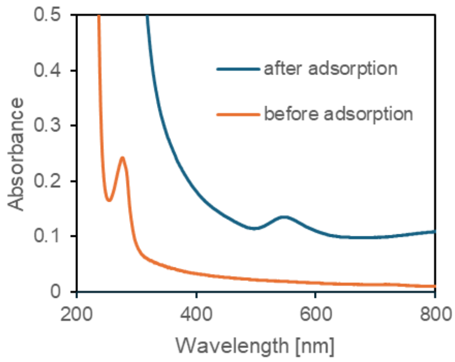


Figure 7 UV/Vis spectra of sericin before and after Au(III) adsorption from 0.1 M HCl.

4. Conclusion

This study revealed sericin's potential as a unique biomass material for gold recovery due to its dual functionality in adsorption and reduction processes. The color change observed when non cross-linked sericin adsorbed Au(III) indicates the reduction of Au(III) to Au(0). Furthermore, cross-linked sericin was found to selectively adsorb gold, platinum, and palladium over Cu(II) in hydrochloric acid. Furthermore, while cross-linked sericin exhibited faster Cu(II) adsorption rates than commercial chelating resins, its Cu(II) maximum adsorption capacity reduced significantly to non cross-linked sericin. These results suggest the need to investigate cross-linking agents that do not affect interactions with metal ions.

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Authors Introduction

Dr. Kaoru Ohe

She received her Ph.D. degrees from University of Miyazaki, Japan, in 2014. Currently she is an Associate Professor of Center for Science and Engineering Education, Faculty of Engineering. Her researches are separation engineering especially adsorption hazardous heavy metals and oxyanions.

Mr. Yudai Yamaguchi

He received Bachelor's degree in Engineering in 2025 from Faculty of Engineering, University of Miyazaki in Japan.

Prof. Dr. Tatsuya Oshima

He received his Ph.D. degrees from Kyushu University, Japan, in 2001. Currently he is an Professor of the Department of Applied Chemistry, Faculty of Engineering. His researches are separation engineering (especially solvent extraction for precious metal ions) and formulation techniques for poorly water-soluble drugs and nutrients.