Adsorption Properties of Au(III) and Cu(II) from Aqueous Solution Using Chemically Treated Sheep Wool

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Abstract Au(III) and Cu(II) adsorption from aqueous solution were carried out using sheep wools with chemical treatments, by NaOH, Na_2S, $NaHSO_3$, and $NaBH_4$ aqueous solution. The fibrous wool was transformed into a film like structures after the chemical treatment using Na_2S. The sheep wool and the chemically treated sheep wool adsorbed selectively Au(III) from Au-Cu binary aqueous solution and the presence of copper ion had no effect on the Au(III) adsorption. Au(III) adsorbed substantially at low pH range. The kinetic experimental data fitted well with the pseudo-second-order kinetic model and the adsorption amount of Au(III) increased with time and reached a plateau after 12 h. The kinetic analysis suggests that rate determining step of Au adsorption would be chemisorption due to the formation of a monolayer on the wool surface. Sheep wool is a low cost, eco-friendly material, and has a high capacity of adsorption, and could be used as a biosorbent for precious and heavy metals by modification of appropriate chemical treatment.

1 Introduction

Biomaterials are widely used for heavy metal and precious metals adsorption because it's cost effectiveness. Regarding study by Han *et al*. (2017), some mining and industrial effluents contain both of the precious and heavy metals. Therefore, high selective biosorbent materials are appropriate for the precious metal adsorption from the mining and industrial effluents. The biosorption mechanism is complicated and is still not fully explored. Wen *et al*. (2010) and Enkhzaya *et al*. (2017) have been studied interaction between metal ion and wool. In the past years, biosorption of heavy metals has been studied by modified sheep wool due to its large number of functional groups (Freddi *et al*., 2001; Naik *et al*., 2010).

Carbon, nitrogen, oxygen, hydrogen, sulfur, and trace elements make up wool. In its natural state, wool usually contains mainly proteins and structural lipids. The wool is extraordinary because it contains sulfur (disulfide bridge) and the amount of sulfur is higher than other proteins (Simpson and Crawshaw, 2002).

Sheep wool has been widely studied and precious metal adsorption was done using modified sheep wool. Keratin-based materials of wool for removal of Au, Ag, and Hg have been investigated (Ghosh and Collie, 2014). Chicken feather powder was prepared and used to remove Ag, Pd, and Pt (Suyama *et al*., 1996). Wool powder was applied to adsorption of gold nanoparticles (Tang *et al*., 2017). AuCN removal was carried out using chicken feather (Ishikawa and Suyama, 1998).

This work investigates adsorbents, sheep wool and chemically treated sheep wool for Au(III) and Cu(II) adsorption from aqueous solution.

2 Materials and Methods

2.1 Materials

All chemicals used for chemical treatment of the sheep wool were provided from Wako Pure Chemical Corporation. Sheep wool (SW) was collected from Erdenet city which is the northern part of Mongolia.

2.2 Preparation of sheep wool biosorbent

Sheep wool was treated by 1.0 M of NaOH, Na_2S, $NaHSO_3$, and $NaBH_4$ solution. 1 g sheep wool was immersed in the 100 ml chemicals under 323 K for 1 h. Chemically treated sheep wool were washed with distilled water and air-dried at room temperature for further analysis.

2.3 Characterization of sheep wools

All chemically treated sheep wools were analyzed using Scanning Electron Microscopes model of Hitachi,

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Japan, "SU3500". Before studying morphology and chemical characterization, the sheep wool samples were coated with gold.

The IR spectroscopy was carried out Infrared Spectrometer (JASCO 6600 Infrared-Raman Spectrometer, Japan) for the chemically treated samples to understand the functional group change. The spectroscopy was performed on the full range of 400 – 4000 cm^{-1}, the scan number of 80 and a resolution of 4 cm^{-1}.

2.4 Adsorption experiments of Au (III) and Cu(II) by sheep wools

Biosorption experiments for Au(III) and Cu(II) were conducted by treated sheep wool, in the batch adsorption system. 15 ml of aqueous metal solution was prepared at a specific concentration and 10 mg of the treated sheep wools was added to the solution. Biosorption was conducted for 48 hours with agitation at 303K. The adsorption amounts of the metal ion were calculated from the remaining concentration in the aqueous solutions measured by Inductively-coupled plasma atomic emission spectrometer (Shimadzu ICPS-8100, Japan).

In order to investigate the kinetic study of biosorption, the adsorption was performed at 0.5, 1, 2, 3, 4, 6, 12, 24, and 48 hours.

3 Results and Discussions

3.1 Morphology of sheep wool and chemically treated sheep wools

NaOH, Na_2S, $NaBH_4$, $NaHSO_3$ at 1.0 M solution were used for treatment of sheep wool. The SEM images are shown in Figure 1.

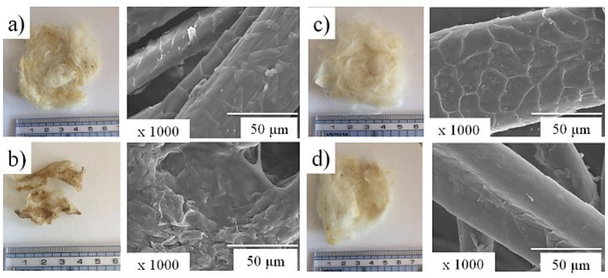

Figure 1. Morphology observation by SEM a) NaOH treated SW, b) Na_2S treated SW, c) $NaHSO_3$ treated SW, d) $NaBH_4$ treated SW

During the treatment of wool, the solution color changed transparent to yellow regarding the dissolution of sheep wool. In Na_2S treatment of wool, weight loss was large as about 75%, compared with other treatment chemicals. There is no color change was observed in the $NaBH_4$ treatment of wool whereas, the color change observed after 40 minutes in the NaOH and $NaHSO_3$ treatment.

3.2 FTIR Spectroscopy analysis of wool

FTIR analysis of the sheep wools was performed to understand the interaction between the metal ion and functional groups of the sheep wool. The spectra of chemically treated sheep wools and Au and Cu adsorbed sheep wools are shown in Figures 2 and 3.

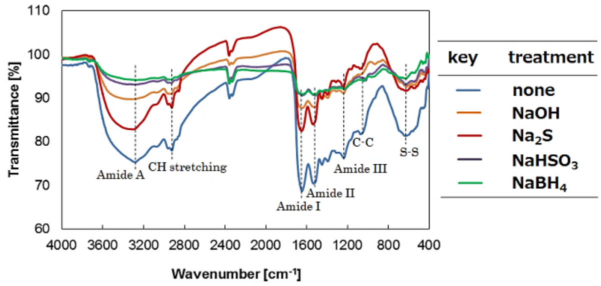

Figure 2. FTIR spectra of wool and chemically treated wool

Sheep wool contained reactive groups of amino, carboxyl, hydroxyl and disulfide crosslinks. The amide A and amide I, II, and III bands were assigned as the main amino acid of keratin fiber.

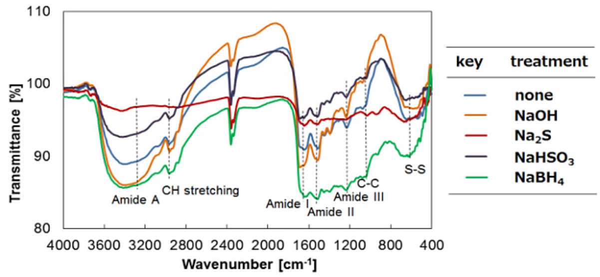

Figure 3. FTIR spectra of wool and chemically treated wool after Au and Cu adsorption

The peak bands were assigned as: 3252 cm^{-1} (the amide A band of N-H stretching peak (Chican *et al.*, 2017); 2897 and 2905 cm^{-1} (CH stretching of $-CH_3$ and $-CH_2$- asymmetric and symmetric modes); 1217 cm^{-1} (Amide III of complex vibration contains N-H bending, C-N stretching, and C=O stretching); 1481 – 1508 cm^{-1} (Amide II of C-N stretching/NH bending); and 1606 – 1619 cm^{-1} (Amide I of 80% C=O stretch and small contribution from NH bend).

In FTIR spectra of gold and copper adsorbed onto sheep wool, the change in intensity at 3252 cm^{-1} was identified. The chemical interaction of Au(III) with amino groups was shown by this observation.

3.3 Effect of pH on the adsorption

The effects of pH on the biosorption of the chemically treated sheep wools for Au(III) and Cu(II) are shown in Figures 4, and 5, respectively.

The pH value of an aqueous solution is one of the most important parameters which affect the biosorption process. The metal speciation in the solution and the biosorbent surface speciation influence by the pH of the solution. The metal adsorption was strongly related to the pH of the aqueous solution as shown in the result.

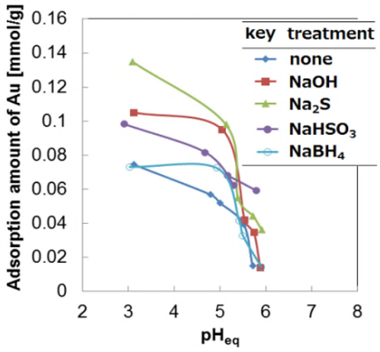

Figure 4. Effect of pH on the biosorption of the chemically treated sheep wools for Au(III) (Experimental condition: *w*: 10 mg, *v*: 15cm^3, C_{ini}:10 mg/l)

Increasing pH value, Au adsorption was decreased and greatly decreased at pH>5.0. The gold was highly adsorbed by the Na_2S treated sheep wool when equilibrium pH was 1.9 – 4.5. That value was two times higher than the untreated sheep wool samples.

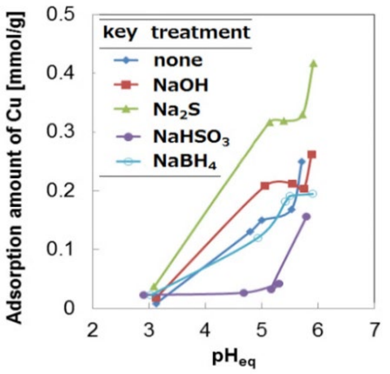

Figure 5. Effect of pH on the biosorption of the chemically treated sheep wools for Cu(II) (Experimental condition: *w*: 10 mg, *v*: 15cm^3, C_{ini}:10 mg/l)

The adsorption amount of Cu(II) was high at pH of 5–6 for all chemically treated sheep wools. Also, the highest adsorption amount of 0.42 mmol/g was obtained for the Na_2S treated sheep wool.

3.4 Adsorption Isotherm of Au(III)

The mechanism of biosorption and attraction between wool-heavy metal aqueous solution systems can be explained by the isotherm model. Langmuir isotherm models were used for this study;

$$q_e = \frac{Q_{\max} K C_e}{1 + K C_e} \quad (1)$$

Q_{max}: maximum adsorption capacity [mmol/g],
C_e: heavy metal concentration at equilibrium [mg/L],
q_e: equilibrium adsorption capacity [mmol/g],
K: Langmuir adsorption constant [L/mg], respectively.

The experimental result of the adsorption of Au(III) was analyzed using Langmuir isotherm which is shown in Figure 6. Langmuir adsorption isotherm model fitted well to the result of Au adsorption.

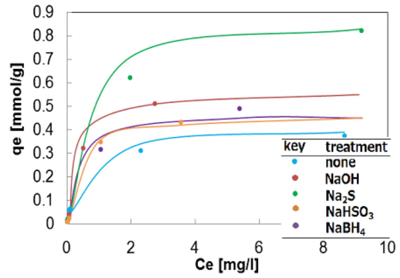

Figure 6. Langmuir isotherm model for the biosorption (experimental and calculated values) of Au(III) (Experimental condition: *w*: 10 mg, *v*: 15cm^3, C_{ini}:1-100 mg/l)

3.5 Adsorption Kinetics of Au(III) and Cu(II)

Pseudo-first and second-order kinetic models were used to clarify the binding mechanism (Ho *et al*., 1999). Pseudo-second-order model is appropriate and it can be used to explicate well interaction between heavy metal ions and sheep wool. Pseudo-second-order kinetic model is calculated by using Equation (2);

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

q_t: amount of metal ion adsorbed at the time per weight of adsorbent [mmol/g],
q_e: amount of metal ion adsorbed at the equilibrium per weight of adsorbent [mmol/g],
t: time [min],
k_2: pseudo-second-order kinetic rate constant [g/mmol min], respectively.

The time course of Au(III) and Cu(II) adsorption by the treated sheep wools are shown in Figures 7 and 8. The Pseudo-second order kinetic constant and other parameters determined were summarized in Table 1.

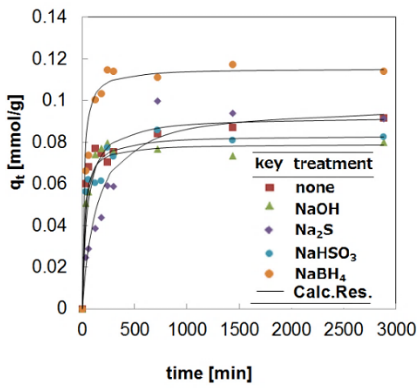

Figure 7. Time course of Au(III) adsorption by the chemically treated sheep wools (Experimental condition: *w*: 10 mg, *v*: 15cm^3, C_{ini}:10 mg/l, pH=2)

The pseudo-second-order kinetic model fitted well to the experimental data and it can theorize for monolayer formed on the surface of chemically treated wool during Au(III) and Cu(II) adsorption (Ho *et al*., 1999).

Therefore, the adsorption of Au(III) by the chemically treated sheep wools can be determined chemisorption due to the formation of a chemical bond between the Au(III) and sheep wool (Tang *et al*., 2017).

Table 1. Kinetic constants of Pseudo-second-order model for Au(III) and Cu(II) adsorption with the treated sheep wools

Metal	Chemical treatment	Pseudo-second-order kinetic constants		
		k_2 [g/mmol·min]	q_e [mmol/g]	R^2
Au(III)	none	0.2318	0.0923	0.9991
	NaOH	0.6243	0.0792	0.9985
	Na_2S	0.0740	0.0978	0.9931
	$NaHSO_3$	0.4186	0.0833	0.9993
	$NaBH_4$	0.5669	0.1154	0.9996
Cu(II)	none	0.8867	0.0014	0.9997
	NaOH	0.8626	0.0016	0.9994
	Na_2S	0.0729	0.0005	0.9842
	$NaHSO_3$	0.1439	0.0004	0.9912
	$NaBH_4$	0.6434	0.0021	0.9988

Treatment condition: 1 hour treatment with chemicals at 50^0C

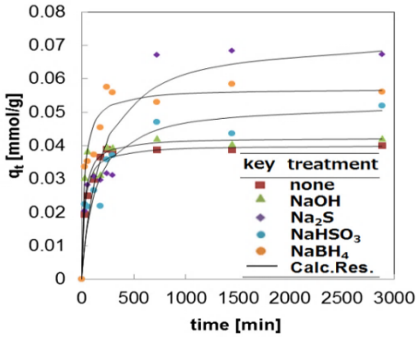

Figure 8. Time course of Cu(II) adsorption by the chemically treated sheep wools (Experimental condition: *w*: 10 mg, *v*: 15cm^3, C_{ini}:10 mg/l, pH=2)

The adsorpiton mechanism is considered as follows. Wool contains a substantial amount of cystine, glutamic acid, and serine. The side chain of these amino acids which were thiol, amine, and hydroxyl groups are defined as highly reactive with metal ions. Au(III) can be selectively adsorbable when positively charged metal ions (Cu^{2+} etc.) could not be adsorbed at low pH because of the positive charge of $–NH_3^+$.

4 Conclusions

Sheep wool is keratin based biosorbent and it was easily treated with chemicals. Sheep wool has a high capacity to adsorb heavy metals and adsorption amounts were increased after chemical treatment. Amino group is determined as the main binding site for Au(III) by FTIR analysis. The adsorption of Au(III) was high at pH lower than 5 and the presence of copper ion had no effect on the Au(III) adsorption. The experimental data fitted well with the model of pseudo-second-order kinetic. It is seen that chemical treatment is an easy and cost-effective method for precious and heavy metal adsorption and it has potential applications in industrial wastewater treatment.

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