Chromium adsorption on sodium sulfide treated sheep wool

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Abstract. Chromium adsorption from the aqueous phase was evaluated using Mongolian sheep wool as a biosorbent. The wool was chemically treated with sodium sulfide to enhance the adsorption capacity. The surface of the wool was analyzed by SEM, EDX and FTIR were also used for the analysis of differences in the wool after chromium adsorption. Chromium was detected in the wool after adsorption by EDX analysis. FTIR data indicated the intensity change in amide A and amide I, which shows chromium may be adsorbed to the amino and carboxyl groups of the wool. The sodium sulfide treated wool showed better adsorption capacity of chromium(III) than the untreated wool. In the case of chromium(III), the adsorption amount increased with the pH increased, while for chromium(VI), the adsorption value increased with the pH decreased. Kinetic analysis of the adsorption indicated that the removal of chromium followed pseudo-second order kinetic model for the whole contact time range. Langmuir isotherm model was used for the analysis of adsorption equilibrium and the adsorption followed well Langmuir isotherm. This study demonstrates the sodium sulfide treated wool is an effective and low-cost biosorbent for heavy metal adsorption.

1. Introduction

Environmental contamination with heavy metal is increasing due to the rapid development of industry. Industrial wastes contain various heavy metals, such as chromium. Chromium-containing wastewater is a major source of environmental pollution. Chromium(III) and chromium(VI) are common oxidation states of chromium [1]. Excessive intake of chromium can negatively affect fertility, the respiratory tract and can lead to cancer [2-4]. The elimination of chromium pollution in the aquatic environment is essential for human health and the environment. Recently, special attention has been given to keratin-based materials because of its cost-effective and biodegradable properties. Sheep wool was selected as adsorbent, and it has a high capacity to remove heavy metals from aqueous solutions regarding its high content of functional groups [5]. Chemically treated sheep wool is high effective adsorbent in gold, copper, lead, and cadmium adsorption. The adsorption mechanism of heavy metal on sheep wool can be interpreted in a previous study [6]. In this study, chromium(III) and chromium(VI) adsorption was performed using wool treated with sodium sulfide.
2. Materials and methods

2.1 Chemicals
High purity reagents (FUJIFILM Wako Pure Chemical Corporation, Japan) were applied in this study. Sodium hydroxide and hydrochloric acid were alternatively used for solution pH adjustment for the adsorption experiment. Sodium sulfide was applied as a modifying agent for sheep wool.

2.2 Preparation of adsorbent
The sheep wool sample was dried after cleansed by detergent. The sheep wool was simply treated with sodium sulfide (Na₂S) solution. The sheep wool chemical modification flow chart is shown in Figure 1. Chemical reactions on disulfide bonds are shown below [7]:

\[ R - S - S - R + H_2S \to R - SH + H_2S_2 \]

![Figure 1. Sheep wool modification by sodium sulfide](image)

2.3 Adsorption experiments
Heavy metals adsorption studies with sheep wool were carried out using batch adsorption experiments. Adsorption amount for detection decreases or increases due to external effects when conducting adsorption. The adsorption amounts of heavy metals were affected by many factors, such as solution temperature, concentration, pH, adsorbent size and dosage, mixing speed, and the effect of the co-existing ions [8].

Sheep wool was treated with sodium sulfide and added 5-10 mg to every 15 ml of chromium solution. The chromium concentration of the solution was determined after 48 hours of adsorption. The effect of concentration, contact time, and pH of chromium solution was executed in the adsorption study.

3. Results and discussion

3.1 Surface morphology
SEM analysis was carried out to understand the adsorbent morphology. The result is presented in Figure 2. As a result of chemical modification by sodium sulfide (0.05 M), the wool loses its fibrous structure and becomes a thin layer.
Figure 2. SEM image of a) sheep wool, b) sodium sulfide (0.05 M) treated sheep wool

3.2 Adsorption behaviors

3.2.1 Effect of pH The adsorption of chromium(III) and chromium(VI) was evaluated in a specific pH range. The initial pH of the chromium solution affected both trivalent and hexavalent chromium adsorption, the metal ions states are causes this difference. Chromium uptake is enormously different between chromium(III) and chromium(VI) depending on solution pH. As the pH increased (Figure 3a), the adsorption value increased. The highest adsorption occurred at pH 5.0-6.9 for the adsorbents.

Figure 3. Effect of pH a) chromium(III); b) chromium(VI) adsorption
(Experimental condition: V: 15cm³, Cini: 0.1 mmol/l, pHini=1.0-7.0)

Chromium(VI) was adsorbed in the low pH range; no adsorption was observed at the high pH range, especially at pH 5.8-8.5. The amount of adsorption was increased with increasing initial chromium concentration in Gao et al. study [9].

3.2.2 Effect of chromium concentration The adsorption of chromium(III) and chromium(VI) was evaluated in specific chromium concentrations. Figures 4 and 5 show the chromium adsorption results. The adsorption amounts were increased by increasing the initial metal concentration.
Figure 4. The adsorption isotherm of chromium(III) by sheep wool (Experimental condition: V: 15cm³, C_{ini}:0.019-1.923 mmol/l, pH_{eq}=5.4)

Langmuir adsorption models were applied to the adsorption result [10]. All the isotherm constants and parameters are obtained and summarized in Table 1. The experimental data of the adsorption of chromium on sheep wool, chromium(III) had very consistent with the Langmuir adsorption model.

Figure 5. The adsorption isotherm of chromium(VI) by sheep wool (Experimental condition: V: 15cm³, C_{ini}: 0.019-1.923 mmol/l, pH_{eq}=2.1)

Additionally, adsorption of chromium(VI) results were also consistent with the Langmuir adsorption model. With a high correlation coefficient value. The adsorption capacity of chromium(III) significantly increased after sodium sulfide treatment, which can be defined as hydrogen and peptide bond disruption on the sheep wool.
### Table 1. Adsorption capacities and adsorption equilibrium constant

| Metal  | Chemical treatment | $q_{\text{max}}$ (mmol/g) | $K$ (L/mmol) | $R^2$   |
|--------|-------------------|---------------------------|--------------|---------|
| Cr(III)| none              | 0.045                     | 0.95         | 0.8558  |
|        | Na$_2$S           | 2.388                     | 0.02         | 0.9835  |
| Cr(VI) | none              | 0.796                     | 0.14         | 0.9818  |
|        | Na$_2$S           | 0.845                     | 0.12         | 0.9935  |

3.3 Adsorption kinetics

The adsorption of chromium(III) and chromium(VI) was evaluated at different times. The adsorption values of chromium(III) are determined differently for untreated wool and sodium sulfide modified wool. The adsorption amount increased 4-5 times after sodium sulfide treatment. The equilibrium was reached in 12 hours for both sheep wool, and sodium sulfide treated wool, shown in Figure 6.

![Figure 6. Effect of contact time on the chromium(III) adsorption](image)

The adsorption of the chromium(VI) into adsorbents at the different contact time is shown in Figure 7. From the results, there is no difference observed for adsorption amount in sodium sulfide modified sheep wool. Untreated wool and sodium sulfide modified sheep wool, both show the same adsorption capacities and reaches the equilibrium in 6 hours.
Figure 7. Effect of contact time on the chromium(VI) adsorption

In this study, the kinetic parameters and correlation coefficients were well fitted with the pseudo-second-order kinetic model. It indicates that chromium was adsorbed on sheep wool by chemisorption.

Figure 8. EDX analysis of wool crosssection after a) chromium(III), b) chromium(VI) adsorption by sheep wool, c) chromium(III), d) chromium(VI) adsorption by sodium sulfide treated sheep wool
3.4 EDX analysis
EDX analysis of chromium adsorbed sheep wool sample results are shown in Figure 8. All the sheep wool and sodium sulfide modified wool comprise carbon, nitrogen, oxygen, sulfur, and chromium after chromium adsorption. The amount of chromium(VI) was defined as high, 10.5 wt% in the crosssection of sheep wool, and 24.3 wt% in sodium sulfide treated wool comparing with the chromium(III) adsorption.

3.5 FTIR results
The amide A band of N-H stretching peak was determined at 3267 cm⁻¹, following 2 weak bands (-CH₃ and –CH₂- asymmetric and symmetric modes) of CH stretching at 2889 and 2904 cm⁻¹ in adsorbent of sheep wool. The peaks of 1215 cm⁻¹, 1506 cm⁻¹, and 1618 cm⁻¹ are defined as the main amino acid of amide III, amide II, amide I, respectively (Figure 9).

![Figure 9. FTIR measurements of sheep wool (SW) after chromium adsorption.](image)

![Figure 10. FTIR measurements of sodium sulfide modified sheep wool (SW).](image)
The disulfide bridge of the S-S bond was discriminated at 571 cm\(^{-1}\) for the untreated sheep wool sample (Figure 10). Weak broadband of 1030-1180 cm\(^{-1}\) represents cysteine, and different intensities were observed for the sodium sulfide treated wool samples. It indicates that some part of the disulfide bond was disrupted due to the treatment.

The main functional groups of the sheep wool had changed after chromium adsorption. The transition had occurred in amide A and amide I groups. It indicates that the functional group of amino and carboxyl groups are the main attraction site of chromium(III) and chromium(VI).

4. Conclusion
Expeditious technique and technology development have resulted in harmful effects on the environment due to industrial production. Therefore, the adsorption of chromium by sodium sulfide treated sheep wool system was investigated. Batch experiments for chromium(III) and chromium(VI) removal were varied due to the pH value. Chromium(III) had the highest adsorption amount at pH of 5-7, while chromium(VI) had the highest removal value at pH of 2-4. The chromium adsorption mechanism was evaluated by EDX and FTIR analysis. In EDX analysis, after chromium adsorption, the content of chromium was detected on the crosssection of the sheep wool. The FTIR result was approved that chromium is attached to the carboxyl group and amino group of the sheep wool. Sheep wool is a cheap, eco-friendly material and has a high capacity of adsorption, which is expected to be applied to mining and industrial wastewater treatment in the near future.

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