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A study on the heavy metal adsorption of Mongolian livestock biomass

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Abstract

Mongolia has a problem of heavy metal pollution around mining area and there is necessity to investigate a new removal technology of heavy metals. Adsorption materials of Mongolian livestock biomasses were prepared and heavy metal removal performances were investigated by this study. Sheep manure, sheep wool and sheep fats were used to make adsorption of Cu (II), Pb (II) and Cd (II). Alkaline treatment made on sheep wool sample. Structure and morphology of adsorption materials were determined by using SEM, EDAX and FTIR analysis. The adsorption studies were made under various conditions and determined using ICP-MS. Sheep wool, sheep manure, and sheep fat were determined as possible to remove heavy metals from aqueous solution. The adsorption amounts of heavy metals of Cu (II), Pb (II) and Cd (II) were increased after the alkaline treatment of wool. It was concluded that the wool adsorbent treated by Na_2S and NaOH would use as an adsorbent for removal of heavy metals from contaminated water.

Keywords: Bio-adsorption, livestock biomass, heavy metals

1. INTRODUCTION

Mongolia riches many natural resources such as coal, copper, gold and oil. Boroo gold mining area and Erdenet copper mining area located in northern part of the Ulaanbaatar, the capital city of the Mongolia. Tamsagbulag petroleum industry locates on Dornod province about 856 km east part of the Ulaanbaatar city. Oyu-Tolgoi gold-copper mining area and Tavan Tolgoi coal mining area located in Umnugovi province about 235 km south part of the Ulaanbaatar city.

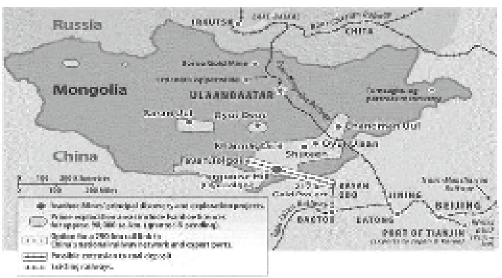

Fig.1 Mining map of Mongolia [4]

Source of the heavy metal pollution: Small scale gold mining area, there has called Ninja (people) are living for extracting gold and selling to the speculators. They are using very dangerous method such as mercury method to extract gold from the soil illegally [9]. Around mining area, river and land polluted by toxic substances and heavy metals by mining operation. Rehabilitation is necessary to the environment after mining operations [4].

Mongolian animal husbandry is one of the major part of agriculture sector and the number of Mongolian livestock reached 66.2 million in 2017 [7]. Almost half of the total livestock is sheep and herders got many wastes such as sheep manure, sheep wool and sometimes sheep fat from animal husbandry. Sheep manure, wool and fat comprise from protein and many kinds of functional groups which are applicable to make heavy metal adsorption from the wastewater. Wool fibers have effective characteristics for removing heavy metals by their large specific surface area and high adsorption capacities [6].

2. MATERIALS AND METHODS

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2.1 Materials

The chemical substances used this study were purchased from Wako Pure Chemical Industries Ltd (Japan). Sheep wool, sheep manure and sheep fat was collected from the animal husbandry of the Erdenet (Mongolia), the northern part of Ulaanbaatar city.

2.2 Methods

2.2.1 Preparation of sheep wool, manure and fat

Mongolian livestock biomasses, sheep wool, sheep manure were washed with distilled water and dried at room temperature. Sheep fat was used as adsorbents after cutting.

Alkaline dissolution mechanism of sheep wool: Wool from amino acid chains, basically settled on the crosslinkages of cystine [10].

Na_2S treatment: The treatment of Na_2S is used for the separate wool from hide in the industry for a long time. Hydrogen bond of wool is broken by the treatment of sodium sulfide. Furthermore, disulfide bonds break while dispersion by sodium sulfide into the wool [11]. Only epicuticle and some resistant cortical elements rest after alkaline treatment [9]. Sheep wool was put into Na_2S (0.5 M) solution (pH=10-13) for 6 hours at 30^0C [5]. Wool was washed with distilled water and dried at room temperature.

$$2R - X + Na_2S \leftrightarrow R_2S + 2NaX$$

NaOH treatment: Alkali treatment made cleavages of disulfide bond in the wool. Random coil and α-helix would be lost the structure in the sheep wool proteins, furthermore hydrogen bonds cleaved by the treatment of alkaline. Adsorption capacities increased by increasing in the treatment time of sodium hydroxide and heavy metals adsorbed on adsorptive sites of the alkaline treated wool [4]. Wool treated in NaOH (0.1 M) solution for 1, 10 and 20 hours at 50^0C. Wool was washed with distilled water and dried [8].

$$R - S - S - R + OH^- \rightarrow R - SOH + R - S^-$$

2.2.2 Heavy metals adsorption analysis

Adsorption analysis of Cu, Pb and Cd was made by the heavy metal solution with the adsorbent and shaking. Their adsorption performances were measured with by ICP-AES. The adsorption capacity of the heavy metal ions was calculated by equation (1):

$$q_e = \frac{C_0 - C_a}{m} \cdot V \qquad (1)$$

q_e – amount of heavy metal ions adsorbed at equilibriums per weight of adsorbent, [mg g^{-1}]
C_0, C_a – heavy metal ion concentration for initial and after adsorption, [mg l^{-1}]
V – volume of the solution, [l]
m – amount of adsorbent, [g]

3. RESULTS AND DISCUSSIONS

3.1 Adsorption behavior of Mongolian biomass of livestock

Fig. 2 shows heavy metal removal percentage of livestock biomasses, is represents all of the biomasses adsorbents are possible to make adsorption from heavy metal solution. The removal efficiency of the heavy metals was determined as 62.28 % and above in the sheep manure, 79.63 % and above in the sheep wool, 97.68% and above in the sheep fat samples.

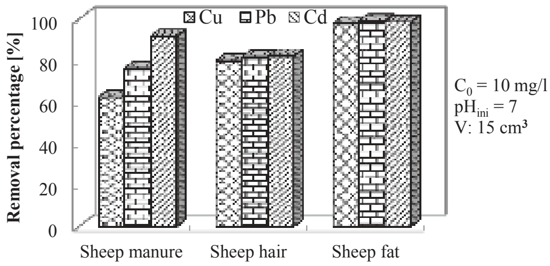
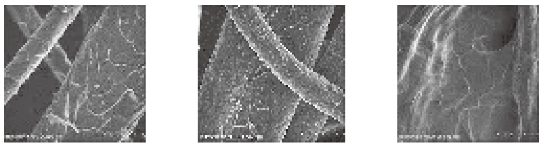


Fig. 2 Removal percentage of heavy metals by livestock biomasses

3.2 Alkaline treated sheep wool

3.2.1 Morphology analysis of alkaline treated sheep wool

The surface of the wool fiber has cuticle cells. Cuticle cells were broken in the NaOH treatment. In Na_2S treatment, the wool surface was dissolved and changed smooth as shown in Fig. 3.



a. b. c.

Fig. 3 Morphology of wool surfaces. a: Untreated sheep wool, b: NaOH treated sheep wool, c: Na_2S treated sheep wool

3.2.2 EDAX analysis

The morphologies of alkaline treated sheep wool samples were analyzed after Cu, Pb, Cd adsorption by the Energy Dispersive X-ray spectroscopy where Scanning Electron Microscopes is in operation. After adsorption of heavy metals, all of the NaOH treated wool samples were mainly comprises of C, N, O, Na, Sr and S elements. The amount of heavy metals was defined as 4.15 % of Cu, 2.63 % of Pb and 2.47 % of Cd in the surface of sheep wool samples.

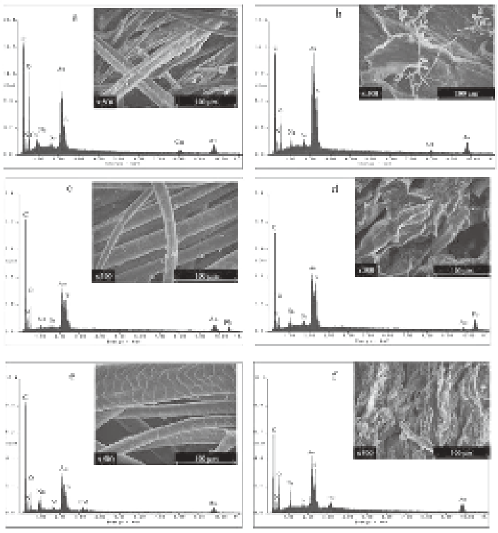


Fig. 4 EDAX analysis of alkaline treated wools. a: NaOH treated wool after adsorption of Cu, b: Na_2S treated wool after adsorption of Cu, c: NaOH treated wool after adsorption of Pb, d: Na_2S treated wool after adsorption of Pb, e: NaOH treated wool after adsorption of Cd, f: Na_2S treated wool after adsorption of Cd

After adsorption of heavy metals, all of the Na_2S treated wool samples mainly comprising of C, N, O, Na, Sr and S elements. The amount of heavy metals was defined as 2.42 % of Cu, 3.32 % of Pb and 2.56 % of Cd in the surface of sheep wool samples.

3.2.3. Fourier transform infrared spectroscopy (FTIR) measurements of wool

The sheep wool and the alkaline treated sheep wool samples were prepared and interfold into pellets using KBr sheet by the hand press. The wave number was 400 – 4000 cm^{-1}, the scan number is 80 and resolution was 4 cm^{-1} and results shown in Fig. 5.

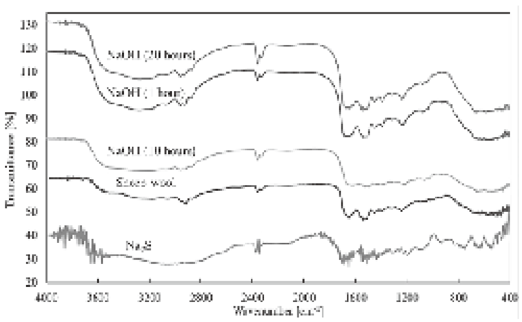


Fig. 5 FTIR analysis of alkaline treated wools

The amide (N – H) bonds III, II, I reflected on FTIR analysis in in 1229 – 1301 cm^{-1}; 1498 – 1559 cm^{-1} and 1509 – 1654 cm^{-1} band range for untreated and alkaline treated wool samples. The untreated wool samples and alkaline treated samples were defined as FTIR analysis for 2850 – 2958 cm^{-1} is attributed C – H aliphatic stretch; 1074 – 1079 cm^{-1} is C – O stretch and 2959 – 3293 cm^{-1} is O – H stretch.

3.2.4 Adsorption behavior of alkaline treated sheep wool

Fig. 6 shows the heavy metal adsorption amounts of wool and alkaline treated wool.

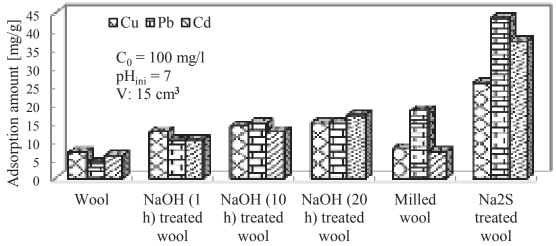


Fig. 6 Removal of heavy metals by livestock biomasses

The adsorption amount of heavy metals was determined as 7.15 mg/g Cu in wool, which increased to 26.04 mg/g in Na_2S treated wool. Wool adsorbed 4.30 mg/g Pb, 6.26 mg/g Cd, which amounts defined as 43.72 mg/g Pb, 37.35 mg/g Cd in Na_2S treated wool samples. Milled wool adsorbed high amount of heavy metals comparing to the untreated wool.

3.2.4.1 Effect of treatment time of sheep wool by NaOH solution

Heavy metal removal by NaOH treated wool was measured with different time as shown in Fig. 7. NaOH (0.1 M) treatment was made for 1, 10, 20 hours at 50^0C. The initial concentrations of heavy metals were set at 100 mg/l.

By increasing treatment times, the adsorption amount of heavy metal was increasing [9]. Wool treated with NaOH for 20 hours, adsorption amount was defined as 15.19 mg/g of Cu, 15.15 mg/g of Pb and 17.32 mg/g of Cd at initial concentration of 100 mg/l.

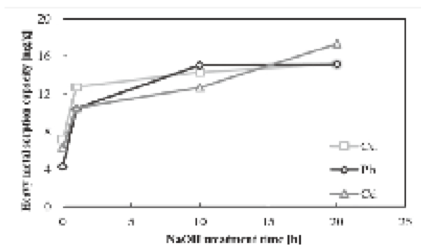


Fig. 7 Effect of treatment time of heavy metal sorption of alkaline treated wool

3.2.4.2 Effect of pH

The removal effects of the Cu, Pb, Cd by alkaline treated wool on effect of pH for 3, 5, 6, 8 are shown in Fig. 8. Removal efficiency of Cu defined as 59.91 % and above, except Cu removal by NaOH and Na_2S treated wool for the pH_{eq} at 3.3 – 3.7. Removal efficiency was defined as 73.02 % and above for Pb solutions, 81.36 % and above, except Cd removal by NaOH treated wool for the pH_{eq} at 3.6.

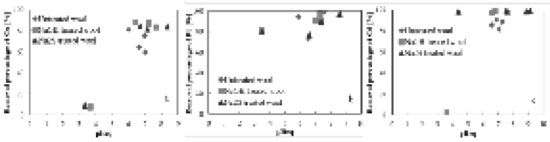


Fig. 8 a: Removal percentage of Cu in pH difference, b: Removal percentage of Pb in pH difference, c: Removal percentage of Cd in pH difference

4. CONCLUSIONS

This study evaluated the adsorption of heavy metals removal using low cost sorbents such as livestock biomasses of Mongolia. Sheep manure, sheep wool and sheep fat were defined as effective adsorbent for heavy metal after alkaline treatment of wool adsorption the amounts of heavy metals increased. The removal efficiency was determined as quite high at low initial concentration. The removal efficiency was determined as 62.28 % and above in sheep manure, 79.63 % and above in sheep wool, 97.68% and above in sheep fat samples. The Na_2S and NaOH treated wool adsorbent adsorbed high amount of heavy metals rather other adsorbents in this study. The adsorbent materials of wool treated with NaOH and Na_2S are used as filter for sheet and film formation for removal of heavy metals from contaminated water in further study.

5. REFERENCES

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