Adsorption of Cesium Ion on Silk Fibroin in Aqueous Solution

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The adsorption behaviors of cesium ion on silk fibroin (SF) fibers in aqueous solution were investigated for applications to purify the contaminated water by radioactive cesium ion. The ability of adsorption of cesium was smallest among the other metal ions compared. Tendency of such adsorption was explained in terms of the stability of the combination between the ions and the SF. The optimal condition for adsorption of cesium ion was searched. The thermodynamic adsorption behavior was discussed using the Langmuir and the Freundlich equilibrium adsorption models.

Key words: adsorption, silk fibroin, cesium ion, Langmuir model, Freundlich model

1. INTRODUCTION

The silk fibroin obtained from the silkworm, *Bombyx mori*, has been used as materials of a textile fabric for a long time. Nowadays, many kinds of investigations for its applications in various fields, such as surgical sutures [1], food additives [2], cosmetics [3], and drug-release materials [4, 5] and so on, have been extensively carried out. Applications for adsorption of metal ions from aqueous solutions have been attempted as a special interest for environmental problems. Since the biomass polymers such as silk can be biological decomposed in a nature, there is advantage in volume decreasing the wasted adsorbents compared with other adsorbents such as zeolites and activated carbons. The filament of the natural silk fiber is constituted of silk fibroin (SF) and a water-soluble protein glue, silk sericin (SS). It has been reported that the SF has the capability to adsorb some metal ions on its specific chemical structures [6-8]. The amino acid structure of the SF provides the ability to adsorb metal ions at oxygen atoms or nitrogen atoms of amide group (CONH). In addition, the amino (NH₂) and carboxyl groups (COOH) at the terminals of the protein macromolecule can be ionized in water at over isoelectric point (pH > 3.7) and form ammonium (NH₃⁺) and carboxylate ions (COO⁻), respectively. They can be thought that the carboxylate ions also attract the metal ions. At higher pH (>5), the amino groups also can attract the metal ions [7]. The schematic mechanism of adsorption is shown in Figure 1. In this study, we first compared adsorption ability in some metal ions, cesium (Cs⁺), palladium (Pd²⁺), copper (Cu²⁺), and cerium (Ce³⁺) in the aqueous solutions. In particular, we focus on the details of adsorption behavior of Cs⁺. The adsorption of Cs⁺ from water have been received much attention, because purification of water polluted by radioactive Cs⁺ induced by the accidents in nuclear power plant in Japan is urgent subject. So far, adsorption behavior of Cs⁺ on the SF has not been reported. We attempt to make interpretations

Figure 1. Adsorption mechanism of metal ions to SF. Adsorption to (a) amide structure, and (b) terminals of the SF.

for adsorption of Cs⁺ from the viewpoints of thermodynamic models such as the Langmuir and the Freundlich models.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of silk fibroin

The raw silk kindly supplied by MATUOKA Co., Inc. Japan was boiled with an aqueous solution of 5 % Na₂CO₃ for 1 hour to remove SS, and then to be suction filtrated separated to obtain SF. The SF obtained was washed by distilled water and dried at 45 °C for more than 24 hrs

under the atmosphere. The SF was immersed to the saturated CaCl_2 aqueous solution. The solution of CaCl_2 destroy aggregation of the SF fibers and increase surface areas of contact with solutions. Then the dialysis of SF was carried out by distilled water to remove Ca^{2+} and Cl^- , and then was freeze dried. Thus, the fibrous SF (SF-Ca) was obtained.

2.2 Adsorption of each metal ion

The solutions of metal ion of 50 mg/L were prepared by diluting the original solutions of CsCl , PdCl_2 , $\text{Cu}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3$ with a concentration of 1000 mg/L. These solutions as an analytical grade were purchased from Kanto Chemicals Co., Inc. The 0.5 g of the SF-Ca prepared was added into 50 ml of the solution and then added 30 mL of the buffer solution. The buffer solution was prepared by mixing the 5 g of 0.1 M solution of acetic acid and 40.8 g of 0.6 M solution of sodium acetate. The value of pH was controlled at 6.9. The adsorption experiments were carried out under shaking for 8 hrs in the water bath controlled at 40 °C [6-8]. After that, SF was removed from the solution by filtration. The concentrations of the ions of Pd^{2+} , Cu^{2+} and Ce^{3+} were measured by ICP analysis (Inductively Coupled Plasma, Hitachi High-technologies SPS3500DD) and the Cs^+ was AAS analysis (Atomic Absorption Spectrometry, Hitachi High-technologies Z-5010). Each adsorption experiments were carried out at least three times and the average values of the concentrations were determined. The removal efficiency can be calculated according to the following equation:

$$RE [\%] = \frac{C_i - C_f}{C_i} \quad (1)$$

where RE is the removal efficiency of metal ions, C_i and C_f are the initial and the final concentrations of metal ions (mg/L), respectively. The amount of ions adsorbed on 1 g of the SF was calculated according to the following equation:

$$q_e [mg/g] = \frac{(C_i - C_f)V}{m} \quad (2)$$

where q_e is the adsorption capacity, V is the volume of the solution (L) and m is the weight of the SF (g).

2.3 Optimization of adsorption conditions of Cs^+

(a) Effects of adsorption disturbance by the other ions

In order to clarify the effects of adsorption disturbance by the Ca^{2+} from CaCl_2 , the SF without immersion in CaCl_2 (SF-n) was used in adsorption experiments. In addition, to confirm the disturbance by Na^+ from the buffer solution, the CsCl solution without addition of the buffer solution was employed in the experiments.

(b) Effects of contact time and initial concentration

The values of RE for the SF-n at the various contact times from 3 to 480 min were obtained under initial concentration of CsCl fixed to 10 mg/L. Next, initial concentrations were changed from 5 to 100 mg/L for up to 120 min of contact time.

2.4 Adsorption isotherm of Cs^+

In order to obtain the adsorption isotherm of Cs^+ for the SF-n, the q_e at various c_e , equilibrium concentration of Cs^+

(mg/L), at 40 °C for 120 min were obtained.

3. RESULTS AND DISCUSSIONS

3.1 Removal efficiency for each metal ion

The results of adsorption experiments were shown in Figure 2. The value for Pd^{2+} was the highest among the ions employed. While for the Cs^+ was 4 %, *i. e.*, Cs^+ hardly adsorbs on the silk fibroin. The tendency of removal efficiency was in the order of $\text{Pd}^{2+} \gg \text{Cu}^{2+} > \text{Ce}^{3+} > \text{Cs}^+$. Results of removal efficiency were considered from the viewpoints of ionic radius, charge number of ions, pair anion, and the HSAB (hard and soft acids and bases) rules. The favorite situations for adsorption are small size of positive ion, large number of electric charge, and small size of pair anion under suiting the HSAB rule. The ionic radius of Cs^+ , Pd^{2+} , Cu^{2+} and Ce^{3+} were 1.81, 1.00, 0.87 and 1.15 Å, respectively. The pair anions probably accompany around the metal ion and may play a role of spatial hindrance in adsorption. The HSAB rule has been established as a semi-empirically rule to predict the affinity about the metal ions (Lewis acid) to the ligand (Lewis base) [9]. The hard acid and base refer to what have small polarizability. On the other hand the soft acid and base large polarizability. The hard acids exhibit affinity to the hard bases, and the soft acids to the soft bases. Cs^+ and Pd^{2+} belong to soft acid, and Cu^{2+} and Ce^{3+} are middle and hard acid, respectively. Amino group (NH_2), and carboxylate ion (COO^-) at the molecular terminals are the hard bases. These accomplish great influence in adsorption [6]. The structure of C=O and NH at amide group are soft and hard bases, respectively. It should be mentioned that the contribution of the amide groups on adsorption might be restrictive, because most of amide groups associate each other by hydrogen bonds and form β -sheet structure in fibers. It can be understood that the lowest tendency of adsorption for Cs^+ is due to large of cation size, the charge number (+1), and the HSAB rule. On the other hand, the reasons for the highest adsorption tendency of Pd^{2+} are the charge number, sizes of cation and the pair anion (Cl^-) and C=O , although the combination of Pd^{2+} with COO^- , NH_2 and NH are not in agreement with the HSAB rule. Lower results for Cu^{2+} and Ce^{3+} may be attributed to large size of pair anion (NO_3^-).

Figure 2. Results of removal efficiency of each metal ion by using the SF-Ca.

3.2 Effect of adsorption disturbance by Ca^{2+} and Na^+

In Figure 3 (a) and (b), three types of SF, *i. e.*, the raw silk fiber (coated with SS), the SF-Ca and SF-n were

compared. As shown in (a), the results demonstrated that addition of the buffer solution was not effective for Cs^+ adsorption. However, Figure 3 (b) showed that certain improvement of adsorption was observed at no buffer solution system. In particular, for the SF-n the value for RE reached about 40%. The value of pH for CsCl solution of 50 ppm was 7.6, which satisfied the conditions of ionizations of COO^- and NH_2 . Changes of the values of pH were not recognized through the experiments. As shown in Figure 2, the adsorption of Pd^{2+} was not disturbed by Ca^{2+} and Na^+ . This may be attributed to that Pd^{2+} ion can exchange with Ca^{2+} and Na^+ since the order of ionization tendency is $\text{Cs}^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Cu}^{2+} > \text{Ce}^{3+}$. Thereafter, the adsorption experiments employed the solution without buffer solution and the SF-n.

Figure 3. Influence of the state of adsorbents on removal efficiency. (a) with buffer solution, (b) without buffer solution. A: raw silk, B: SF-n, C: SF-Ca.

3.3 Effects of contact time and initial concentration

First, effect of contact time on the adsorption efficiency was discussed. As shown in Figure 4, the RE reached about 65 % at 3 min, which implies the adsorption proceeds rapidly at an early stage. After that the RE value somewhat decreased, which implies the occurrence of desorption. This phenomenon is based on the adsorption equilibrium. From above result, we assumed that the equilibrium is realized for contact time of 120 min. Effect of initial concentration of Cs^+ on adsorption was shown in Figure 5. From the figure maximum of RE was also attained in 3 min except for the initial concentration of 100 mg/L.

3.4 Adsorption isotherm of Cs^+

In this study two of the most commonly used isotherm equations were employed, namely, the Langmuir type [10] and the Freundlich type [11] of equilibrium isotherms. The Langmuir equation, initially derived from kinetic considerations, was based on the assumption that there are energetically equivalent numbers of sorption sites on the

Figure 4. Effect of time on the removal efficiency for cesium ions ($N = 3$) using the SF-n. The initial concentration was 10 mg/L.

Figure 5. Effect of initial concentration on removal efficiency for cesium ions using the SF-n.

sorbent surface. The binding of adsorbates to the sorption sites can be classified either chemical or physical, but it must be sufficiently effective to prevent displacement of the adsorbates on neighboring sites. Figure 6 shows the isothermal adsorption curve of cesium ion to the SF. As shown in the figure, the value of q_e monotonically increases with C_e .

Figure 6. Adsorption isotherm of Cs^+ for the SF-n.

The equation for the Langmuir model as follows:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (3)$$

Where q_m and K_L are corresponding to the maximum adsorption capacity of ions (mg/g) under monolayer sorption and the Langmuir constant (L/mg), respectively. K_L means the ratio of rate constants of adsorption to desorption. Equation 4 was derived as follows:

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (4)$$

If the experimental data is applied to the equation as single straight line, the value for q_m can be derived from the intercept of the plot. The value of K_L was calculated from the slope of the plot. However, Figure 7 shows that the plots would be expressed by combination of two straight lines. This suggests that the kinds of adsorption sites might be extended such as NH_2 , $\text{C}=\text{O}$, NH , as well as COO^- . Such situation was realized as the pH become larger than the isoelectric point of the SF. The value of pH was 7.6 in this system, which was applicable to such situation. It would be suggested that the occasion for repulsion between metal ions on adsorption sites increases as the adsorption sites were extended at pH more than the isoelectric point [6]. In another suggestion, it is expected that adsorption has taken place at the sites with large of binding energy in low concentration. This implies that the energy of adsorption changes with adsorption sites like COO^- , NH_2 , $\text{C}=\text{O}$, and NH .

Figure 7. Adsorption isotherm of Cs^+ for the SF-n using the Langmuir model.

On the other hand, the Freundlich model is an empirical equation which can express the heterogeneous mixture and is expressed as follows:

$$q_e = K_f C_e^{1/n} \quad (5)$$

where K_f is a constant related to the adsorption capacity and the energy of adsorption, and n is an empirical parameter related to the adsorption intensity. The following equation can be formulated as

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (6)$$

Figure 8 shows the plots for $\log C_e$ vs. $\log q_e$. K_f can be

determined from the intercept of the plot and n from the

Figure 8. Adsorption isotherm of Cs^+ for the SF-n using the Freundlich model.

slope of the plot. As shown in the figure, the experimental data can fit linearity implying applicable to the Freundlich model. The values of K_f and n are 0.166 and 1.11, respectively, and correlation coefficient (r^2) was 0.9896. The Freundlich parameters were compared with those of reported using the other adsorbents, e. g., Ni/hexacyanoferrate-sericite ($K_f = 6.125 \text{ mg/L}$, $n = 2.54$, $r^2 = 0.991$) [12], and prussian blue ($K_f = 70.4$, $n = 2.63$, $r^2 = 0.9351$) [13]. From the above comparison, the adsorption capacity and energy for Cs^+ towards the SF are resulted to be small.

SUMMARY

The removal efficiency of metal ions Cs^+ compared with Pd^{2+} , Cu^{2+} , and Ce^{3+} by adsorbing to the SF fibres were investigated. The efficiency for Cs^+ was lowest in those ions. These behaviour were explained by means of ionic radius, charge number of ions, pair anions, and HSAB rule. It was found that adsorption of Cs^+ was improved by avoiding Na^+ and Ca^{2+} , which play a role of disturbance. The adsorption of Cs^+ to the SF was suggested that existence of multiple adsorption site on the SF structure.

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