Article**Bacterial Cellulose for Adsorption of Antimony**

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Abstract

As the thickness of bacterial cellulose (BC) microfibrils is two orders of magnitude smaller than that of plant cellulose (PC), BC is expected for increasing adsorption for various adsorbates. Therefore, in this study, adsorption behavior of Sb(III) on BC was evaluated and compared with that on PC. The adsorption capacity for Sb(III) on BC was slightly greater than that on PC, however, the initial reaction rate of adsorption of Sb(III) on BC was much faster than that on PC. The result suggested that BC is superior to PC in rapid adsorption of Sb(III), on the basis of the large surface area.

Key words: bacterial cellulose, antimony, adsorption, microfibrinous structure

1 Introduction

There has been a growing demand for antimony in the production of industrial materials such as clarificant, flame retardant and catalyst. Sb(III) is contained in wastewater from these producing processes. Sb(III) causes a bad influence on human body. Inhalation exposure to antimonials has been reported to produce pneumonitis, bone marrow damage and carcinonitis. The LD₅₀, a measure of antimony toxicity, is 100 mg kg⁻¹ in rats. The WHO guideline provides that for drinking water quality, the antimony level should be 0.005 mg dm⁻³ [1]. Therefore, it is necessary to establish techniques for removal of antimony from the wastewater.

In recent years, many researchers have been developing adsorbents for Sb(III). Deorkar et al. [2] synthesized pyrogallol-attached silica-gel ceramics with a functional group density of 0.26 mmol g⁻¹, in order to separate Sb(III), Cu(II) and Pb(II) from aqueous solutions using a column mode. Saito et al. [3] investigated adsorption of Sb(III) using polyol-ligand-containing porous hollow-fiber membranes introducing *N*-methylglucamine. Cellulose, which is the most abundant biopolymer on earth and representative of microbial extracellular polymers, is also available for adsorption of Sb(III) as shown in a paper by Uezu et al. [4]. Cellulose after mercerization or digestion by cellulase was found increasing adsorption capacity for Sb(III) compared to the native cellulose. Namely, fibrous structure of cellulose would affect on the adsorption behavior for Sb(III).

In the present study, we focused on bacterial cellulose (BC) for adsorption of Sb(III). BC belongs to specific products of primary metabolism by some bacteria and is composed of microfibrils, which is a ribbon-like structure [5]. Therefore, the thickness of BC is much smaller than that of PC. The microfibrinous structure of BC was expected increasing adsorption capacities for various adsorbates as well as increasing adsorption rate. In this work, adsorption behavior of Sb(III) on BC was compared to that of commonly used PC.

2 Experimental

2.1 Materials

Aqueous Sb(III) solution was prepared using a standard solution of SbCl_3 , purchased from Wako Pure Chemical Industries, Japan. Cellulose powder as PC originating from a plant source was purchased from AdvantecToyo Kaisha, Ltd., Japan and used as received. BC was prepared from “*nata de coco*”, by grinding, washing with distilled water, and freeze-drying. After grinding, BC was obtained as white powder. All other chemicals were of analytical grade or higher and were used as received.

2.2 Characterization

PC and BC were observed using a scanning electron microscope (HITACHI S-4100). The specific surface areas of cellulose were determined by N_2 -BET method using a volumetric adsorption measurement instrument (BEL Japan BELSORP mini). Furthermore, the specific surface areas of those were also derived from the maximum amounts of adsorption of Congo red in the similar manner shown in a previous paper [6]. Under the assumption that each Congo red molecule adsorbs parallel to the cellulose molecule, the surface area of cellulose was calculated by determining the area occupied by one molecule of Congo red.

2.3 Adsorption Tests

Adsorption experiments were carried out using a batchwise method. An aqueous solution (15 cm^3) containing 15 mg dm^{-3} of Sb(III) was prepared and the pH was adjusted using NaOH. A portion (15 cm^3) of the aqueous solution and 50 mg of PC or BC were mixed in a stoppered 30 cm^3 glass flask and shaken (120 rpm) in a thermostat-regulated water bath at 293 K for 24 hours. Thereafter, the mixture was filtrated with PTFE membrane filter. The initial and equilibrium concentrations of Sb(III) in the filtrate were analyzed using ICP spectrometer (Shimadzu ICPS-7000) to determine the percent adsorption. Equilibrium pH in the aqueous solutions was determined with pH meter (TOA HM-30G).

3 Results and Discussion

3.1 Characterization of PC and BC

SEM photographs of PC and BC were shown in Fig.1. As shown, fibrous structures of PC from a plant source and BC produced by bacteria are quite different: The microfibrillar structure of BC is apparently observed and the thickness of the ribbons of BC is around $0.1 \mu\text{m}$. The microfibrillar structure of BC is found to be two orders of magnitude smaller than that of PC.

Fig. 1 SEM photographs of cellulose adsorbents at 10,000 magnification: (a) PC and (b) BC.

The specific surface areas of cellulose adsorbents calculated from N₂-BET method were 1.0 m² g⁻¹ for PC and 27.3 m² g⁻¹ for BC, respectively. On the other hand, the specific areas obtained from Congo red adsorption were 36 m² g⁻¹ for PC and 151 m² g⁻¹ for BC, respectively: The maximum adsorption capacities were 33.3 mg g⁻¹ for PC and 138.9mg g⁻¹ for BC. The difference of the specific surface areas is likely because of the difference of the multilayer adsorption of N₂ gas and the monolayer adsorption of Congo red. Anyhow, the specific surface area of BC is much larger compared to that of PC in the both methods.

3.2 Adsorption Tests

Figure 2 shows the distribution of chemical species of Sb(III) [7, 8]. The neutral species Sb(OH)₃ is the principal species over a wide range. The anionic species Sb(OH)₄⁻ is present under basic condition. Figure 3 displays the effect of pH on the adsorption of Sb(III) on PC and BC. As shown in the figure, adsorption percent of Sb(III) increases with increase of pH. Sb(III) seems to be adsorbed as Sb(OH)₄⁻ on cellulose because the adsorption profile agrees with the distribution profile of Sb(OH)₄⁻. Maximum adsorptions of Sb(III) on PC and BC were shown around pH 13. Adsorption of Sb(III) on BC was approximately twice higher than that on PC around pH 10-11. Figure 4 shows the relationships between amount of adsorbent (PC or BC) and adsorption percent of Sb(III). Adsorption of Sb(III) appeared a remarkable increase with increasing amount of cellulose. BC exhibits the higher adsorption of Sb(III) than PC.

Fig.2 Distribution of chemical species of Sb(III) [7, 8].

Fig.3 Effect of pH for adsorption percentage of Sb(III) on BC and PC: volume; 15 cm³, adsorbent; 50 mg, [Sb(III)]_{ini}=15 mg dm⁻³.

Fig.4 Relationships between the amount of adsorbent and adsorption of Sb(III): volume; 15 cm³, [Sb(III)]_{ini}=10 mg dm⁻³, pH_{ini}; 11.0.

The adsorption isotherms of Sb(III) onto PC and BC at varying equilibrium concentration are shown in Fig. 5. The results were correlated with the Langmuir isotherm model and the theoretical curves were drawn in the figure. The amount of adsorption for Sb(III) on BC was slightly greater than that on PC at pH_{ini} 13. The maximum

values of Sb(III) adsorption were 4.8 mg dm^{-3} for PC and 5.2 mg dm^{-3} for BC, respectively. In general, Sb(III) is considered to be adsorbed on polyol adsorbents by complexation with hydroxyl groups through dehydration condensation. Therefore adsorption of Sb(III) should increase with increasing the number of available hydroxyl groups which can participate in complexation with Sb(III). The specific surface areas of BC obtained from N_2 -BET method and adsorption of Congo red were much larger than those of PC, however, the adsorption capacity for Sb(III) on BC was slightly greater than that on PC. Thus the microfibrinous structure of BC is not so efficient for enhancing adsorption capacity of Sb(III) ion.

Time courses of Sb(III) adsorption on cellulose adsorbents were investigated in order to compare the adsorption rates for Sb(III) on PC and BC (Fig. 6). It should be noted that the adsorption rate for Sb(III) on BC was much faster than that on PC. The initial reaction rate of adsorption of Sb(III) on BC was 2.7 times greater than that on PC. Adsorption capacity of BC at equilibrium state is not so larger than that of PC, however, the initial rate of Sb(III) adsorption on BC would be much faster than that on PC due to the large specific surface area. Namely, BC is superior to the commonly used PC in view of rapid uptake of Sb(III) from aqueous solution.

Fig.5 Adsorption isotherms of Sb(III) on PC and BC: volume; 15 cm^3 , adsorbent; 10 mg , pH_{ini} ; 13, $[\text{Sb(III)}]_{\text{ini}} = 5\text{-}50 \text{ mg dm}^{-3}$.

Fig.6 Time courses of amount of Sb(III) adsorption on BC and PC: volume; 200 cm^3 , adsorbent; 100 mg , pH_{ini} ; 13, $[\text{Sb(III)}]_{\text{ini}} = 10 \text{ mg dm}^{-3}$.

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