Article

Adsorption of Rare-Earth Metal Ions on Natural Banana Fiber

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(Manuscript received April 6, 2018; accepted June 14, 2018)

Abstract

The adsorption properties of banana fibers for rare-earth metal ions (La^{3+} , Gd^{3+} , Tm^{3+} , Pr^{3+} , Tb^{3+} , Yb^{3+} , Nd^{3+} , Dy^{3+} , Lu^{3+} , Sm^{3+} , Ho^{3+} , Eu^{3+} , and Er^{3+}) were investigated, and the concentrations of metal ions were measured by using an inductively coupled plasma optical emission spectrometer. The pH value of the aqueous phase was measured using a pH meter equipped with glass electrodes. Over 70% of all the metal ions were adsorbed on non-treated banana fiber at pH values ranging from 2.0 to 6.0. On the other hand, using alkali-treated banana fiber, the adsorption ratio for rare-earth metal ions increased with pH. The reaction equation for the alkali-treated banana fiber system was investigated by the slope analysis between logarithmic distribution ratio and pH. The results suggest that not only the hydroxy groups originated from the interaction between cellulose and metal ions but also other negative ions might be involved in the ion-exchange reaction in the alkali-treated banana fiber. Such distinct behavior raises the possibility of the utilization of banana fibers in the separation and adsorption of metal ions.

Keywords: Banana fiber, Rare-earth, Ion exchange, Metal ion adsorbent

1. Introduction

Since over a billion banana stalks are thrown away every year, banana fiber has recently attracted attention as an abundant inedible natural resource, and its effective reuse as a valuable biomass resource has been studied¹⁻³⁾. Additionally, the investigation of banana fibers as an adsorbent for dyes has been reported. Thus, Gupta et al. described the use of banana fibers as an adsorbent for the removal of malachite green dye⁴⁾, and Haris and Sathasivam reported the removal of methyl red from aqueous solutions using banana fibers^{5,6)}. However, to the best of our knowledge, the investigation of banana fibers or chemically modified banana fibers as an adsorbent for various metal ions has not been reported to date. For the removal and

separation of metal ions, several methods are available, including ion exchange and solvent extraction. In this context, the development of environmentally friendly ion-exchange methods and the use of chelate materials for the collection and separation of metal ions are attracting growing attention from many researchers⁷⁻¹¹⁾. Recently, we evaluated the adsorption properties of modified banana fiber for transition metal ions¹²⁾ and rare metal ions¹³⁾. The adsorption of cesium and strontium ions was studied using banana fibers as adsorbents¹⁴⁾.

Rare and rare-earth metals are important in many fields of advanced materials science; moreover, their applications in material industries have significantly increased. In the present study, the adsorption properties of banana fibers for rare-earth

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metal ions were evaluated. The reaction equation in alkali-treated banana fiber system was investigated by the slope analysis between logarithmic distribution ratio and pH. From the results obtained, banana fibers can be envisaged as good candidates for the adsorption of metal ions.

2. Experimental

2.1 Materials

Banana fiber was obtained from the Republic of the Philippines. Standard solutions for each metal ion and other chemicals were purchased from Wako Pure Chemical Industries Co., Ltd, Osaka, Japan and used without further purification.

2.2 Alkali-treated banana fiber

About 7 g of the banana fiber was packed into a 200 mm long column of 10 mm diameter. Alkali treatment was performed by pumping 2 mol dm⁻³ sodium hydroxide solution into the column at a flow mass of 1.5 dm³.

2.3 Adsorption of rare-earth metal ions on banana fibers

Individual aqueous solutions containing 5.0×10^{-5} mol dm⁻³ of the metal ions La³⁺, Gd³⁺, Tm³⁺, Pr³⁺, Tb³⁺, Yb³⁺, Nd³⁺, Dy³⁺, Lu³⁺, Sm³⁺, Ho³⁺, Eu³⁺, and Er³⁺, 1.0×10^{-2} mol dm⁻³ sodium sulfate, and 1.0×10^{-2} mol dm⁻³ acetic acid, chloroacetic acid, or 2-morpholinoethanesulfonic acid monohydrate (MES) were prepared. Next, 10 cm³ of each solution was put into plastic tubes along with 0.1 g of the metal ion adsorbent. These tubes were shaken for 48 hour at room temperature. After the reaction was complete, the mixed solutions were filtered. The concentration of the metal ions was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES). The pH value of the aqueous phase was measured using a pH meter equipped with glass electrodes.

3. Results and Discussion

3.1 Adsorption properties of non-treated and alkali-treated banana fibers for rare-earth metal ions

Adsorption experiments were performed using non-treated and alkali-treated banana fibers.

The adsorption ratios of the rare-earth metal ions are shown in Fig. 1 and Fig. 2. Over 70% of all the metal ions were adsorbed at pH values ranging from 2.0 to 6.0 using non-treated banana fiber. On the other hand, the adsorption ratios of the rare-earth metal ions using alkali-treated banana fiber increased up to a pH value of about 5.0. From 45% to 99% of all the metal ions were adsorbed at pH values below 2.0; however, not all the metal ions were adsorbed up to this point using alkali-treated banana fiber (Fig. 3 and Fig. 4). These results demonstrate the feasibility of the use of banana fibers for rare-earth metal ion adsorption; however, the rare-earth metal ions could not be separated from each other by either non-alkali or alkali-treated banana fibers.

Fig. 1 Effects of pH on the adsorption of La³⁺, Nd³⁺, Eu³⁺, Tb³⁺, Ho³⁺, Tm³⁺, and Lu³⁺ using non-treated banana fiber.

Fig. 2 Effects of pH on the adsorption of Pr³⁺, Sm³⁺, Gd³⁺, Dy³⁺, Er³⁺, and Yb³⁺ using non-treated banana fiber.

In general, banana fibers are composed of approximately 9% lignin, 39% hemicellulose, and 43% cellulose, among other compounds^{15,16}. The alkali treatment removed the lignin and hemicellulose present in the non-treated banana fiber. In our previous study, we reported the SEM images of the surfaces of the banana fibers before and after being subjected to alkaline treatment¹³. The smooth surfaces of the banana fibers were found to adopt a wavy morphology after alkali treatment, which was indicative of the presence of more hydroxy groups stemming from the cellulose on the surfaces of the banana fibers. Furthermore, lignin could be identified in the banana fibers by using FT-IR. The C=C groups of lignin were found to give rise to different bands around 1620 cm⁻¹ in the spectra of non-

treated and alkali-treated banana fibers. Since lignins, along with other functional groups, are considered the adsorption sites of metal ions in the banana fibers, and most all the lignin content was removed by sodium hydroxide treatment¹⁷⁾, the difference in the lignin content could be invoked to explain the observed differences in the adsorption behavior of non-treated and alkali-treated banana fibers.

Fig. 3 Effects of pH on the adsorption of La^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , Ho^{3+} , Tm^{3+} , and Lu^{3+} using alkali-treated banana fiber.

Fig. 4 Effects of pH on the adsorption of Pr^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} using alkali-treated banana fiber.

3.2 Behavior of alkali-treated banana fiber in the adsorption of rare-earth metal ions

The half-adsorption pH values ($\text{pH}_{1/2}$), defined as the pH at which 50% of the metal ion content is adsorbed using alkali-treated banana fiber, are shown in Table 1. Here, the equation

Table 1 Half-adsorption pH values and slopes

	$\text{pH}_{1/2}$ value	Slope
La^{3+}	- ^a	1.85
Pr^{3+}	3.84	1.51
Nd^{3+}	3.75	1.10
Sm^{3+}	3.67	1.34
Eu^{3+}	3.76	1.54
Gd^{3+}	4.15	1.89
Tb^{3+}	4.37	1.63
Dy^{3+}	4.62	1.56
Ho^{3+}	4.82	1.91
Er^{3+}	4.82	1.94
Tm^{3+}	4.83	1.74
Yb^{3+}	4.49	1.42
Lu^{3+}	4.49	1.43

^aLess than 50% adsorption.

of the reaction between rare-earth metal ions and alkali-treated banana fiber can be expressed as

where R-OH represents the hydroxy group originated from the cellulose. The selectivity coefficient (K) was calculated from Eq. (1) as follows:

$$K = [(\text{R-O})_n\text{M}^{(n-3)+}][\text{H}^+]^n / [\text{M}^{3+}][\text{R-OH}]^n \quad (2)$$

$$K = D([\text{H}^+]^n / [\text{R-OH}]^n) \quad (3)$$

$$(D = [(\text{R-O})_n\text{M}^{(n-3)+}] / [\text{M}^{3+}])$$

where $[\text{M}^{3+}]$ represents the moles of metal ion per 1 cm^3 of aqueous solution. From Eq. (3), the reaction equation in the alkali-treated banana fiber system was investigated by the slope analysis between the logarithmic distribution ratio ($\log D$) and pH.

$$\log K = \log D + n \log [\text{H}^+] - n \log [\text{R-OH}] \quad (4)$$

$$\log D = np\text{H} + \text{constant} \quad (5)$$

where *constant* represent $\log K + n \log [(\text{R-OH})] + np\text{H}$ under constant pH. The results of the slope analysis between $\log D$ and pH for the adsorption of Pr^{3+} , Eu^{3+} , Dy^{3+} , Yb^{3+} , Ho^{3+} , and Gd^{3+} on alkali-treated banana fiber are shown in Fig. 5 as representative examples. In all plots, straight lines with slopes between 1.10 and 1.94 were obtained, which suggests that, in the ion-exchange reaction with alkali-treated banana fiber, not only the hydroxy groups originated from the interaction between cellulose and metal ions might be involved, but also other negative ions such as sulfate (Fig. 6). To confirm this hypothesis, further studies on the exact adsorption behavior of alkali-treated banana fiber for metal ions are required.

On the other hand, we observed in our previous study on the adsorption and desorption of Cs^+ and Sr^{2+} by batch method using non-treated banana fiber that the desorption reaction and site of monovalent Cs^+ and divalent Sr^{2+} were different¹⁴⁾. The adsorption behavior of non-treated banana fiber for rare-earth metal ions will be the focus of future studies.

Fig. 5 Plots of $\log D$ of metal ions as a function of pH in the alkali-treated banana fiber system.

Fig. 6 Adsorption behavior of alkali-treated banana fiber and metal ions.

4. Conclusion

Over 70% of all the metal ions were adsorbed at pH values ranging from 2.0 to 6.0 using non-treated banana fiber. In contrast, the adsorption ratios using alkali-treated banana fiber increased up to a pH value of about 5.0.

The reaction equation of rare-earth metal ions and alkali-treated banana fiber was investigated. Straight lines with slopes between 1.10 and 1.94 were obtained, which suggests that not only the hydroxy groups originated from the reaction between cellulose and metal ions but also other negative ions such as sulfate might be involved in the ion-exchange reaction.

Although the rare-earth metal ions could not be separated from each other by either non-alkali or alkali-treated banana fibers, the results obtained in this work demonstrate the potential of banana fibers as adsorbents of rare-earth metal ions.

Acknowledgment

This research was supported by the Environment Research and Technology Development Fund (3K143003) of the Ministry of the Environment, Japan.

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