Article

Synthesis of a Metal Ion Adsorbent from Banana Fibers and Its Adsorption Properties for Rare Metal Ions

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Abstract

The synthesis of metal ion adsorbents from modified banana fibers comprising a Schiff base was investigated. The adsorption properties of a metal ion adsorbent were evaluated, and banana fiber (BF)-*g*-(glycidyl methacrylate)(GMA)(BF-GMA) were synthesized. A Schiff base 2,2'-{iminobis[ethane-2,1-diyl(nitrilo(E)methylidene)]}bisphenol was synthesized via a reaction of diethylenetriamine and 5-bromo-salicylaldehyde in methanol. A metal ion adsorbent (BF-GMA(Br)) was synthesized via a reaction of the Schiff base with BF-GMA. Over 90% of La³⁺, Gd³⁺, Tm³⁺, Pr³⁺, Tb³⁺, Yb³⁺, Nd³⁺, Dy³⁺, Lu³⁺, Sm³⁺, Ho³⁺, Eu³⁺, and Er³⁺ were adsorbed in a pH range of 6.0–6.6 by the synthesized metal ion adsorbent. Almost 100% of In³⁺ at a pH value of 3.0–4.0 and 95% of Ga³⁺ at a pH value of 3.9 were absorbed, thereby showing the maximum adsorption percentage. Almost 15% and 25% of In³⁺ was adsorbed at a pH value of 1.4–1.6 and 1.8, respectively. Adsorption of Ga³⁺ was barely observed in the pH range of 1.4–1.8. These results show that banana fibers can be utilized as metal ion adsorbents.

Keywords: Banana fiber, Schiff base, Rare metal, Rare earth, Metal ion adsorbent

1. Introduction

In recent years, banana fibers have drawn attention as a renewable source of materials for industrial applications. Banana is an environment-friendly food material and its cultivation does not take a toll on farmlands. Therefore, effective reuse of banana fibers has been studied as a valuable biomass resource^{1,2)}. In our previous study, banana fiber and poly(butylene succinate) composites were investigated using hexamethylene di-isocyanate as a reactive compatibilizer³⁾. Upon the addition of hexamethylene di-isocyanate, alkali-treated banana fibers were found to improve adhesion between banana fibers and poly(butylene succinate). Therefore, it is desirable to explore other useful characteris-

tics of banana fibers.

Several methods for collecting and separating metal ions, including ion exchange and solvent extraction, have been reported. Environment-friendly ion exchange and the use of chelate materials for collection and separation of metal ions have been investigated by many researchers^{4–8)}. Additionally, investigation of banana fibers as an adsorbent for dyes has been reported. Gupta *et al.* reported the use of banana fibers in the removal of malachite green dye⁹⁾. Haris and Sathasivam reported that banana fibers can be used as adsorbents for removing methyl red from aqueous solutions^{10,11)}. However, to the best of our knowledge, investigation of banana fibers (or chemically modified banana fibers) as

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adsorbents for various metal ions has not been reported. In our recent study, adsorption of Cs and Sr ions was studied using banana fibers as adsorbents¹²⁾. The adsorption of transition metal ions using modified banana fiber has also been evaluated¹³⁾; however, the mechanism of metal ion adsorption and the metal ions has not been analyzed in detail. Thus, a re-examination of the synthetic conditions for metal ion adsorbents is necessary.

Rare metals are important in many fields of advanced materials science; moreover, their applications in material industries have significantly increased. In the present study, the synthesis of a metal ion adsorbent from modified banana fibers comprising a Schiff base was investigated in detail. In addition, adsorption properties for the rare metal ions of the metal ion adsorbent were evaluated.

2. Experimental

2.1 Materials

Banana fibers were obtained from the Republic of the Philippines. Glycidyl methacrylate (GMA), diethylenetriamine, 5-bromo-salicylaldehyde (Tokyo Chemical Industry, Co., LTD., Tokyo, Japan), di-ammonium cerium(IV) nitrate (Nakarai Tesque, INC., Kyoto, Japan), and all other chemicals were purchased and used without further purification. Deionized water was prepared by MILIPORE Elix Advantage 3 and used throughout.

2.2 Alkali-treated banana fibers

Banana fibers (100 g), shown in Fig. 1, were treated with 3.0 dm³ of a 20-wt% NaOH aqueous solution (aq) at room temperature for 2 h¹³⁾. The resulting alkali-treated banana fibers (BFs) were washed with water and dried overnight in a vacuum oven at 70°C. Strands from the BFs were cut into 5-mm-long pieces (Fig. 2).

Fig. 1 Banana fibers.

2.3 SEM Observation

Surface morphologies of the banana fibers were observed using a scanning electron microscope (SEM).

2.4 Synthesis of Schiff base

A Schiff base 2,2'-{iminobis[ethane-2,1-diyl]nitrilo(E)methylidene]]bisphenol, which introduced a -Br group into the phenyl rings, was synthesized via a reaction of 10.3 g of diethylenetriamine and 40.2 g of 5-bromo-salicylaldehyde at room temperature for 5 days in 1000 cm³ of methanol (Fig. 3)¹⁴⁾. The obtained product was a yellow powder. After washing several times with methanol, this powder was dried overnight in a vacuum oven at 50°C. The Schiff base was identified using ¹H nuclear magnetic resonance (NMR)

Fig. 2 Alkali-treated banana fibers. The strands of the fibers were cut into lengths of 5 mm.

Fig. 3 Synthesis of the Schiff base.

spectroscopy. Yield: 31.1 g (66.4%); mp: 60.0–62.0°C; ^1H NMR (acetone- d_6): 2.9 ppm ($-\text{CH}_2-$, 4H), 3.7 ppm ($-\text{CH}_2-$, 4H), 6.8 ppm ($-\text{CH}=\text{N}-$, 2H), 7.4 ppm–8.5 ppm (C_6H_3 , 6H), and 13.6 ppm ($-\text{OH}$, 2H).

2.5 Synthesis of banana fiber (BF)-g-(glycidyl methacrylate)(GMA)(BF-GMA)

Banana fiber (BF)-g-(glycidyl methacrylate)(GMA) (BF-GMA) was synthesized via a reaction of 10.0 g of BF and 4.0 g of glycidyl methacrylate with 0.1 g of di-ammonium cerium(IV) nitrate and 0.5 g of nitric acid at 60°C for 25 min under a nitrogen atmosphere in 200 cm^3 of pure water

(Fig. 4)¹⁵. The product was dried overnight in a vacuum oven at 70°C, after which 13.0 g of BF-GMA was obtained. BF-GMA was identified using FT-IR spectroscopy. FT-IR: 1719 cm^{-1} (carbonyl group), 849 cm^{-1} (epoxide group).

2.6 Synthesis of the metal ion adsorbent

A metal ion adsorbent (BF-GMA(Br)), which introduced the $-\text{Br}$ group onto the phenyl rings, was synthesized via a reaction of 10.0 g of 2,2'-[iminobis(ethane-2,1-diyl nitrilo(E) methylidene)]bisphenol and 5.0 g of BF-GMA for 1 day in 200 cm^3 of methanol (Fig. 5). The obtained material was dried overnight in a vacuum oven at 70°C, after which 8.0 g

Fig. 4 Synthesis of BF-GMA.

Fig. 5 Synthesis of metal ion adsorbent (BF-GMA(Br)).

of the metal ion adsorbent was obtained. The metal ion adsorbent was identified using FT-IR spectroscopy. FT-IR: 1718 cm^{-1} (carbonyl group), 818 cm^{-1} (aromatic group).

2.7 Adsorption of rare-earth metal ions by the metal ion adsorbent

Individual aqueous solutions containing $2.0 \times 10^{-5}\text{ mol dm}^{-3}$ of the 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+} and $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ sodium perchlorate, $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ acetic acid, and $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ 2-morpholinoethanesulfonic acid monohydrate (MES) were prepared. Next, 20 cm^3 of each solution with 0.2 g of the metal ion adsorbent was put into plastic tubes. These tubes were shaken for 14 days 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 argon plasma atomic emission spectrometer (ICP-AES). The pH value of the aqueous phase was measured via a pH meter equipped with glass electrodes.

2.8 Adsorption of In^{3+} and Ga^{3+} ions by the metal ion adsorbent

Individual aqueous solutions containing $1.0 \times 10^{-4}\text{ mol dm}^{-3}$ of In^{3+} and Ga^{3+} ions, $1.0 \times 10^{-1}\text{ mol dm}^{-3}$ of sodium perchlorate, and $1.0 \times 10^{-2}\text{ mol dm}^{-3}$ of acetic acid were prepared. A 30 cm^3 aliquot of each solution with 0.3 g of the metal ion adsorbent was put into plastic tubes. These tubes were shaken at room temperature for five days. This reaction was performed for the purpose of comparison with a previous unpublished work of ours. After the reaction was complete, the mixed solutions were filtered. The concentration of the metal ions was then determined using ICP-AES. The pH value of the aqueous phase was measured via a pH meter equipped with glass electrodes.

3. Results and Discussion

3.1 Alkali-treated banana fibers

The SEM images of the surfaces of the banana fibers (BFs) with and without alkaline treatment are shown in **Figs. 6** and **7**. The BFs purchased from the Republic of the Philippines were virtually untreated. They were only washed with soap and water, leaving much of the lignin and hemicellulose intact. BFs comprise approximately 9% lignin, 39% hemicellulose, 43% cellulose, and many other compounds^{16,17}. The smooth surfaces of the banana fibers transformed into a wavy morphology after alkali-treatment; the lignin and hemicellulose that originated from the BFs were removed by this treatment. Consequently, more reactive groups that originated from the cellulose existed on the surfaces of the BFs.

Fig. 6 SEM image of the surface of a non-alkali-treated banana fiber. Smooth surfaces on the banana fibers were observed.

Fig. 7 SEM image of the surface of an alkali-treated banana fiber. After alkali-treatment, the smooth surfaces of the banana fibers transformed into a wavy morphology.

3.2 Synthesis of BF-GMA(Br)

In the present study, BF-GMA(Br) was synthesized. The monomer reaction percentage (%) and grafting percentage (%) were determined as:

$$\text{Monomer reaction (\%)} = \frac{(W_a - W_b)}{W_c} \times 100$$

$$\text{Grafting (\%)} = \frac{W_a}{W_b} \times 100$$

where W_a and W_b represent the weights of the BFs after and before the grafting process, respectively. Additionally, W_c represents the weight of the monomer (GMA). During the

Fig. 8 Effects of pH on the adsorption of rare-earth metal ions.

synthesis of BF-GMA, the monomer reaction percentage (%) of GMA was 75% and the grafting percentage (%) was 130%.

The reaction of the Schiff base with BF-GMA resulted in 0.3 g of BF-GMA(Br), incorporating 2.4×10^{-4} moles of the Schiff base.

When introducing an electron-withdrawing group such as $-\text{Br}$, the acid dissociation constant of BF-GMA(Br) was enhanced compared to a $-\text{H}$ group or an electron-donating group such as $-\text{CH}_3$ or $-\text{OCH}_3$. Therefore, BF-GMA(Br) can be more readily chelated with metal ions in comparison to introduction of a $-\text{H}$ group or an electron-donating group such as $-\text{CH}_3$ and $-\text{OCH}_3$ ¹³⁾.

3.3 Adsorption properties of BF-GMA(Br) for rare-earth metal ions

An adsorption experiment was performed using BF-GMA(Br). The adsorption percentages of the rare-earth metal ions are shown in Fig. 8. Over 90% of the all the metal ions were adsorbed at pH values ranging from 6.0 to 6.6. These results demonstrate the strong possibility for utilization of banana fibers as adsorbents of rare-earth metal ions; however, the rare-earth metal ions were not separated from each other by BF-GMA(Br).

3.4 Adsorption properties of BF-GMA(Br) for In^{3+} and Ga^{3+}

The adsorption percentages of In^{3+} and Ga^{3+} (shown in Fig. 9) increased up to a pH value of 3 and decreased at pH values higher than 4; this was probably because of hydrolysis. Approximately 20% of In^{3+} ions were adsorbed at pH values below 1.9; however, no Ga^{3+} was adsorbed up to this point, indicating the possibility that In^{3+} can be separated from Ga^{3+} using this method. Although the adsorption percentage

Fig. 9 Effects of pH on the adsorption of In^{3+} and Ga^{3+} ions.

of In^{3+} was not significant at these pH values, increasing the number of GMA chains and the amount Schiff base may improve In^{3+} adsorption.

4. Conclusion

Over 90% of 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 adsorbed at pH values of 6.0–6.6 using BF-GMA(Br).

Almost 100% of In^{3+} was adsorbed at pH values of 3.0–4.0, and 95% of Ga^{3+} was adsorbed at a pH value of 3.9; these are the maximum adsorption percentages obtained in this study. Almost 15% of In^{3+} was adsorbed at pH values in the range of 1.4–1.6 and 25% was adsorbed at a pH value of 1.8. Conversely, Ga^{3+} was barely adsorbed at these pH values. These results show the possibility for utilization of banana fibers as metal ion adsorbents.

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