Note

Oxidative Adsorption of Arsenic by *N*-Methylglucamine-modified Chelate Fiber and Manganese Dioxide

Atsushi KURAOKA, Toshiyuki UMEBAYASHI, Syouhei NISHIHAMA
and Kazuharu YOSHIKAZUKA *

Department of Chemical Engineering, The University of Kitakyushu, Hibikino 1-1, Kitakyushu 808-0135, Japan

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Abstract

We investigated removal of arsenic (As) from water using a combination of adsorption on a *N*-methylglucamine-modified chelate fiber and oxidation of As(III) to As(V) by manganese dioxide. Batch experiments revealed that the chelate fiber had high selectivity for As(V) over As(III), especially in the acidic pH region, because of differences in the species distribution of As in an aqueous solution. Oxidative and selective adsorption of As(III) was achieved when manganese dioxide was added to the adsorption system with the chelate fiber. The oxidative adsorption could be performed using the connected columns of the manganese dioxide and the chelate fiber. As(III) in the aqueous feed solution was oxidized to As(V) as it passed through the manganese dioxide column, and this was followed by adsorption of As(V) in the chelate fiber column. This method provides a simple removal method of As, as both As(III) and As(V), from water.

Keywords: Arsenic, Oxidative adsorption, *N*-Methylglucamine, Manganese dioxide

1. Introduction

Arsenic (As), a well-known toxic element, mainly exists as a sulfide ore (As_2S_3 and As_3S_4) or sulfate ore (FeAsS) in nature¹⁾. From these ores, it can leach into groundwater and diffuse into the environment. Most As in water is present as As(III) or As(V). The toxicity of As(III) is 25 to 60 times that of As(V)²⁾. The World Health Organization has established a limit of 0.01 mg/L for As in drinking water. As contamination in groundwater is problematic worldwide, and removal of As from water is required. Several methods have been reported for removal of As from water, including coprecipitation³⁾, reverse osmosis⁴⁾, and adsorption. Coprecipitation results in precipitation of a chemically unstable form of As, and separation of the precipitate and water is complicated⁴⁾. Reverse osmosis has high energy consumption and requires complicated sample processing.

The adsorption method is an excellent method for removal of As because it is safe, inexpensive, simple, and creates only

small quantities of waste. Several adsorbents for As have been reported, including activated alumina⁵⁾, iron oxide⁶⁾, titanium oxide⁷⁾, and ion exchange resins⁸⁾. The activated alumina, iron oxide, and titanium oxide adsorbents have high adsorption affinities for As(III), whereas ion exchange resins have high adsorption affinities for As(V). Recently, adsorbents modified with a *N*-methylglucamine group have attracted attention because the ligand selectively adsorbs As(V). The chelate fiber Chelest fiber GRY-HW is an adsorbent modified with a *N*-methylglucamine group on the surface of its cellulose fibers. This fiber provides removal of As(V), but further processing of the water is required for removal of As(III).

Oxidation of As(III) during adsorption is a promising method for the complete removal of As from water. Several oxidizing reagents, including potassium permanganate⁹⁾, potassium peroxodisulfate¹⁰⁾, ozone¹¹⁾, and hydrogen peroxide¹²⁾, have been reported for As(III), but they are expensive.

* Corresponding author

E-mail: yoshizuka@kitakyu-u.ac.jp

In the present work, we investigated oxidative adsorption of As from water using Chelest fiber as the adsorbent and manganese dioxide as an oxidizing reagent. Adsorption of As(III) and As(V) with the Chelest fiber was investigated first, and then oxidative adsorption of As(III) was conducted a batch experiments. Finally, oxidative adsorption of As in a chromatography adsorption system was investigated using connected columns containing manganese dioxide and the Chelest fiber.

2. Experimental

2.1 Reagents

Chelest fiber GRY-HW (Chelest Co., Osaka) was used as an adsorbent. The fiber was conditioned by washing twice with hydrochloric acid and deionized water in sequence. Manganese dioxide ($\text{Li}_{1.5}\text{Mn}_2\text{O}_4$, JGC Catalysts and Chemicals Ltd., Kanagawa) was washed twice with hydrochloric acid and deionized water in sequence. Aqueous solutions of As were prepared by dissolving NaAsO_2 (Wako Pure Chemical Industries) or $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Alfa Aesar) in deionized water.

2.2 Batch adsorption experiments

Batch adsorption experiments were carried out by shaking an As solution (10 mL) with Chelest fiber (20 mg) for 24 h. The pH of the aqueous solution was adjusted with either hydrochloric acid or sodium hydroxide solution. The total concentration of As remaining in the aqueous solution was determined by ICP-AES (Shimadzu ICPE-9000).

2.3 Column adsorption experiments

In the column system, manganese dioxide was granulated with alumina binder (Cataloid AP-1, JGC Catalysts and Chemicals). An aqueous feed solution containing both As(III) and As(V) ($[\text{As(III)}] + [\text{As(V)}] = 0.1 \text{ mmol/L}$) was continuously supplied to connected columns containing the granulated manganese dioxide and Chelest fiber. The space velocity of the solution was 20 h^{-1} for the manganese dioxide and 27 h^{-1} for the Chelest fiber. After reaching adsorption saturation, the Chelest fiber column was eluted with 2 mol/L hydrochloric acid. The concentration of metal ions in the eluate was determined by ICP-AES.

3. Results and Discussion

3.1 Batchwise adsorption of arsenic with Chelest fiber

Batchwise adsorption of As(III) and As(V) with Chelest fiber from separate solutions was investigated first. The effect of pH on the amounts (q) of As(III) and As(V) adsorbed was evaluated (Fig. 1). For As(III), almost no adsorption was observed at $\text{pH} < 6$ and minimal adsorption occurred at $\text{pH} > 6$. For As(V), high adsorption was observed at $\text{pH} < 6$, and the adsorption amount decreased at $\text{pH} > 6$. Next, we investigated the species distribution of As(III) and As(V) in the aqueous solution (Fig. 2)¹³. For As(III), the predominant species at pH

< 6 was neutral H_3AsO_3 , and anionic H_2AsO_3^- appeared at $\text{pH} > 6$. For As(V), the predominant species at $\text{pH} < 6$ was monovalent H_2AsO_4^- , and divalent HAsO_4^{2-} appeared at $\text{pH} > 6$. Therefore, the Chelest fiber shows affinity for monovalent anionic species, and the difference in the adsorption amounts between As(III) and As(V) could be attributed to the distribution of As species in the aqueous solution.

Fig. 1 Effect of pH on the amounts of As(III) and As(V) adsorbed by Chelest fiber.

Fig. 2 Distributions of (a) As(III) and (b) As(V) species in aqueous solution¹³.

3.2 Oxidative adsorption of As(III)

We then investigated oxidative adsorption of As(III) with Chelest fiber and manganese dioxide and compared it with conventional adsorption of As(V) with only the Chelest fiber (Fig. 3). Oxidation of As(III) to As(V) with manganese dioxide was successful, and the As(V) produced was adsorbed on the fiber. Therefore, the oxidative adsorption of As(III) was almost

Fig. 3 Comparison of oxidative adsorption of As(III) with manganese dioxide and conventional adsorption of As(V) with Chelest fiber.

the same as the adsorption of As(V). The oxidative adsorption system with manganese dioxide and Chelest fiber shows potential for effective removal of As from water.

3.3 Oxidative adsorption of As with the connected column system

Finally, we investigated the oxidative adsorption using the column system. In this system, columns of granulated manganese dioxide and Chelest fiber were connected in series. Then, a mixture of As(III) and As(V) was supplied to the connected columns. Breakthrough and elution curves of As were recorded (Fig. 4). Oxidative adsorption of As was achieved even in the chromatographic adsorption system, and As could be completely adsorbed until the bed volume was approximately 10,000. Elution of the adsorbed As from the Chelest fiber was also achieved. The amount adsorbed was 0.672 mmol/g, and the amount eluted was 0.647 mmol/g, which gave an elution yield of 96.2 %. Therefore, the oxidative

Fig. 4 (a) Breakthrough curve and (b) elution curve of As. Adsorption behavior of As(III) and As(V) by oxidative adsorption with manganese dioxide and Chelest fiber.

adsorption method using manganese dioxide and Chelest fiber can provide complete removal of As, as both As(III) and As(V), from water.

4. Conclusions

We evaluated Chelest fiber and manganese dioxide for oxidative adsorption of As. Chelest fiber has high adsorption ability for As(V) at pH < 6, but almost no adsorption of As(III) occurs. This difference in adsorption ability is caused by the species present in the aqueous solution. Manganese dioxide can successfully oxidize As(III) to As(V), and oxidative adsorption of As(III) is achieved with a combination of manganese dioxide and Chelest fiber. The oxidative adsorption of As can be conducted by connecting columns containing the different components in series.

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