



Simultaneous treatment of both As(III) and As(V) with Iron-Coated Sand (ICS) and Manganese-Coated Sand (MCS)

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INTRODUCTION

From the natural geochemical process and anthropogenic activities such as mining wastes, petroleum refining, and agricultural chemicals, surface and groundwater are widely contaminated with arsenic (Bhumbla and Keefer, 1994). Inorganic arsenic is commonly present as arsenite and arsenate depending on the aquatic redox systems. In anoxic systems such as groundwater, the stable form of arsenic is As(III) which is more toxic and mobile than As(V). Although several methods such as activated alumina, coagulation, membrane or electrolysis have been identified as promising techniques in the treatment of As(V) (Chen *et al.*, 1999), these processes were partly effective to treat As(III), requiring a highly effective and economic technique on the oxidation of As(III) to As(V) as a pre-treatment. In this study, as a promising technique for the treatment of both As(III) and As(V) at the same time in a single reactor, reactor systems containing both manganese-coated sand (MCS) and iron-coated sand (ICS) were used to investigate the oxidation kinetics of As(III) and adsorption of As(V) with variation of the configuration of MCS and ICS in column experiments.

MATERIALS AND METHODS

Preparation of MCS and ICS

Joomoonjin sand, one of Korean standard sands, having particle size ranging from 0.5 to 1.2 mm was used as supporting material. In order to prepare MCS, $\text{Mn}(\text{NO}_3)_2$ solution (100 mL of 0.1 M) previously adjusted to pH 8 with NaOH solution was mixed with Joomoonjin sand (100 g) in a rotary evaporator. By rotating the rotary evaporator

at 30 rpm in water bath maintained at 70°C, water in the suspension mixed with manganese and sand was continuously removed by applying vacuum until approximately 10% of water was remained in the suspension. After then the sand was dried at 150°C for 1-hr. To remove trace of uncoated manganese on the sand, dried sand was rinsed with distilled water several times and then dried again at 105°C. In the preparation of ICS, FeCl₃ solution (100 mL of 0.1 M) previously adjusted to pH 12 with NaOH solution was mixed with Joomoonjin sand (100 g) in a rotary evaporator. And then same procedure used in the preparation of MCS was followed. Manganese and iron coated on the sand were stripped by using an acid digestion method (U.S.EPA 3050B). After filtration, the dissolved concentration of manganese and iron was measured using an induced coupling plasma (ICP).

Experimental methods

As(III) removal was conducted in a 1.0 cm diameter glass column at room temperature (23°C~25°C) and constant initial pH 4.5. In a column, 5.0 grams of each ICS and MCS were packed with three different configurations; homogenized, two-staged, and four-staged column. The arsenite solution (1 mg/L) with a constant ionic strength at 0.01 M NaNO₃ was pumped upward through the bottom of the column using Acuflo Series II high-pressure liquid chromatography at a flow rate of 0.4 mL/min. Effluent samples were then received using Spectra/Chrom CF-1 Fraction Collectors. After the samples were filtered with 0.45 μm syringe filters, a portion of sample was applied in a modified anion exchange method (Wilkie and Hering 1998) in order to quantify As(III) and As(V). The dissolved total and As(III) was measured with ICP.

RESULTS AND DISCUSSION

MCS and ICS used in this study had approximately 4,000 mg Mn and 6,000 mg Fe, respectively, on the sand. In homogenized system, arsenic breakthrough was occurred after 200 pore volumes (V/V_o) and then reached 80% breakthrough after 700 pore volumes. After breakthrough of arsenic, concentration of As(III) in the effluents was below 20 ppb over the entire reaction period and most arsenic was identified as As(V) due to near complete conversion of As(III) to As(V) by MCS. From the reaction of MnO₂ coated on the sand with As(III), soluble Mn²⁺ was produced. At the initial reaction time, the soluble Mn²⁺ was approximately 0.9 mg/L and then slightly decreased as reaction proceeded (0.6 mg/L after 700 pore volumes). Input concentration of As(III) and soluble Mn²⁺ in the effluent at initial reaction time was 1.33×10^{-5} M and 1.64×10^{-5} M, respectively. This result suggests near equimolar reaction between MnO₂ and As(III) such as $\text{H}_3\text{AsO}_3 + \text{MnO}_2 \rightleftharpoons \text{HAsO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$ suggested by Driehaus *et al.* (1995). In other wise, soluble Fe was below 10 ppb. The pH of effluents was around 5.5 over all reaction time. In two-staged and four-staged

columns, arsenic breakthrough was occurred after 100 pore volumes. Most arsenic in the effluents was also identified as As(V) in both two-staged and four-staged columns. However, compared to homogenized system, concentration of As(III) in the effluents was slightly greater and showed 40 ppb in average. Soluble Mn^{2+} and Fe in both two-staged and four-staged columns were also greater compared to homogenized system.

CONCLUSIONS

From this research, MCS and ICS was identified as a good filter material on the oxidation of toxic As(III) and removal of total arsenic although oxidation and removal capacity slightly depending on the configuration of ICS and MCS in columns. By considering oxidation of As(III), removal of total arsenic, and dissolution of Mn^{2+} and Fe, homogenized system was identified as better configuration in the removal of As(III). However, further studies such as convenience of regeneration and adjustment of the ratio of ICS and MCS are needed to decide which configuration is more efficient in real application.

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