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Oxidation of As(III) with MnO_2-Coated Sand

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INTRODUCTION

Inorganic arsenics originated from natural geochemical process and anthropogenic activities (Bhumbla and Keefer, 1994) are commonly present as arsenate and arsenite 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). To treat arsenic in the water system, activated alumina, coagulation, membrane or electrolysis have been used (Chen *et al.*, 1999). However, as these processes are partly effective to treat As(III), a highly effective and practical technique on the oxidation of As(III) to As(V) is highly required. In this study, as a promising technique for the treatment of As(III), manganese-coated sand (MCS) synthesized with $Mn(NO_3)_2$ and Joomoonjin sand widely used in Korea were used to investigate the oxidation kinetics of As(III) with variation of solution pH and dosage of MCS as well as removal efficiencies of arsenic in batch and column experiments.

MATERIALS AND METHODS

Preparation of MCS

Joomoonjin sand having particle size ranging from 0.5 to 1.2 mm was used as supporting material. MCS was prepared at different conditions such as baking time, temperature and ratio of Mn(II)solution to sand. $Mn(NO_3)_2$ solution (100 mL of 0.01 M) previously adjusted to pH 8 with NaOH solution was mixed with sand (200 g) in a rotary evaporator. By rotating the rotary evaporator at 30 rpm in water bath maintained at 70^{o}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 with different baking temperature and time. To remove trace of uncoated manganese on the sand, dried sand was rinsed with distilled water several times and then dried again at 105^{o}C. Amount of manganese coated on the sand was measured by using an acid digestion method (U.S.EPA 3050B). Manganese content was measured using induced coupling plasma (ICP).

Experimental Methods

In order to study oxidation kinetics of As(III) onto MCS, four polyethylene bottles were used. In each bottle, 0.1, 1.0, 2.0, 4.0 g of MCS was mixed with As(III) solution (45 mL of 10.0 mg/L) with a constant ionic strength (0.01 M $NaNO_3)$. After the solution pH was adjusted to 4.5, the bottles were placed in a shaker maintained a constant temperature (25^{o}C) and allowed to equilibrate for the specified time. 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) to separate As(III) and As(V). Finally total arsenic and As(V) in solution was measured with ICP.

Oxidation kinetics of As(III) (45 mL of 10.0 mg/L) at different pH were studied with variation of solution pH ranging from 3 to 8.5 with 0.5 g MCS. The bottles were then also placed in the shaker maintained 25^{o}C and allowed to 35 hours. After filtration and separation of As(III) and As(V), the dissolved arsenic was also measured with ICP.

Column experiments were conducted in a 1.0 cm diameter glass column at room temperature (23^{o}C$\sim$25^{o}C). In a column, MCS was packed with 5.0 and 7.5 g depending on experiment. The arsenite solution (1 mg/L) was pumped upward through the bottom of the column using Acuflow Series II high pressure liquid chromatography at a flow rate of ranging from 0.04 to 1.6 mL/min. Effluent samples were then received using Spectra/Chrom CF-1 Fraction Collectors. The arsenic concentration of the effluent samples was then determined using the ICP after separation of As(III) and As(V) as mentioned above.

RESULTS AND DISCUSSION

Coated amount of Mn(II) on the sand was approximately 4,000 mg Mn(II)/kg sand and was quite similar over the entire baking temperature above 150^{o}C with 1 hour baking time. In order to apply MCS as an oxidizing catalyst in the treatment of arsenite, MCS should have a sufficient oxidizing capacity. From the batch experiment on the oxidation of As(III) by MCS prepared at different conditions, it was identified that oxidation of As(III) gradually increased and reached a maximum (45%) as baking time increased up to 300^{o}C, while severe reduction (below 10%) was observed at 600^{o}C. As the initial dosage of Mn(II) increased from 0.01 to 1.6 Mn(II) mol/kg sand, coated amount of Mn(II) on to sand continuously increased. Oxidation of 10 ppm As(III) by MCS, at pH 4.5 and 0.5g MCS, also gradually increased as the initial dosage of Mn(II) increased up to 0.4 Mn(II) mol/kg sand and after then no more increase was noted. In order to find an optimum preparation condition, normalized oxidation of As(III) was calculated based on the unit amount of Mn(II) coated on the 1 kg sand. This calculation suggests that maximum conversion of As(III) to As(V), conversion of 1 ppm As(III) to As(V) with 1.0 g of Mn(II), was possible at the initial dosage of 0.1 Mn(II) mol/kg sand.

From the oxidation of As(III) with variation of solution pH ranging from 3 to 8.5, oxidation gradually decreased as pH increased, suggesting acid-catalyzed reaction of As(III) with Mn(II). Oxidation kinetics of 10 ppm As(III) performed with variation of the dosage of MCS at pH 4.5 indicated that initial oxidation rate increased as the dosage of MCS increased.

From oxidation of 1 ppm As(III) in the column packed 5 g of MCS at pH 4.5 with different flow rates ranging from 0.2 to 1.6 ml/min and 10 g of MCS at different flow rates ranging from 0.04 to 0.16 ml/min, near complete oxidation of As(III) as well as the least breakthrough of total arsenic was observed above 30 minutes retention time. After breakthrough of arsenic, concentration of As(III) in the effluents was below 20 ppb over the entire reaction period. This result suggests that MCS is a good catalyst in the oxidation of toxic As(III).

CONCLUSIONS

From this research, oxidation of As(III) onto MCS followed an acid-catalyzed reaction and initial oxidation rate increased as the dosage of MCS increased. From the complete conversion of As(III) to As(V) above 30 minutes retention time, MCS was identified as a good filter material on the oxidation of toxic As(III).

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