

Utilization of Layered Double Hydroxide to Remove Arsenic and Suppress pH Decrement During Ultrasound Oxidation of Arsenious Acid

亜ヒ酸の超音波酸化過程における pH 低下の抑制を目的としたヒ素吸着剤 LDH の利用

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1. Introduction

Arsenic (As) is used for semiconductor and supports our computer community. However, it is toxic for human body. Therefore, it is necessary to treat arsenic in industrial effluent before discharge. Values of effluent standard in Japan are < 0.1 ppm of As and pH 5.8 to 8.6.¹ Commonly, As is removed by coprecipitation method. The forms of As are arsenious acid [As(III)] and arsenic acid [As(V)] and removal ratio of As(V) using coprecipitation method is much higher than that of As(III). Therefore, it is crucial to efficiently oxidize As(III) to As(V). Oxidants and bacteria are used to oxidize As(III). Recently, the oxidation method using radicals generated by ultrasound irradiation is studied. Hosokawa et al. performed As(III) removal using combination of ultrasound oxidation and adsorption of ferric hydroxide.² They could remove 99.2% of As from 10 ppm of As(III) solution in O₂ atmosphere. However, in air atmosphere, removal ratio of As was decreased. This reason is the dissolution of ferric hydroxide by pH decrease of the solution. It is well known that nitrous acid and nitric acid are generated by ultrasound irradiation. The drawback of As(III) treatment using ultrasound irradiation is pH decrease. Therefore, we focused on combination utilization of layered double hydroxide (LDH) and ultrasound irradiation. LDH can remove As(V) by ion-exchange capacity and surface adsorption capacity.³ In addition, LDH has pH buffer ability. Furthermore, LDH changes from hydroxide to oxide by calcination. Calcined LDH generates OH⁻ at rehydration process. In this study, we investigated change of pH and removal ratio of As by the addition of calcined LDH into the solution irradiated by ultrasound for 1 h in air.

2. Experiment

LDH was prepared by the co-precipitation using raw materials of Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and NaOH. Synthesized LDH was analyzed by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) at a heating rate of 5°C/min

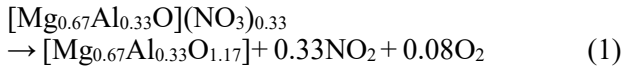
in air from 30°C to 600°C.

As(V) adsorption capacity and pH buffer ability of calcined LDH samples were investigated. Calcined LDH (50 mg) was added into As(V) solution (74 ppm, 100 mL, pH3) and stirred at 200 rpm for 2 h. As(V) adsorption capacity of calcined LDH was evaluated by measuring the As(V) concentration in the filtrate. Secondly, As(III) solution (10 ppm, pH5, 50 mL) was oxidized using ultrasound (200 kHz, 200 W) for 1 h under air flow (100 mL/min). 10 mL of the treated solution was used to analyze concentration of As(V) by colorimetric method using ultraviolet visible absorption spectroscopy (UV-vis). Total As concentration, As(III) + As(V), in the solution was analyzed using inductively coupled plasma (ICP). The residual solution was used for As(V) removal experiment. As(V) removal experiment was conducted using calcined LDH (52.7 mg) for the solution (40 mL) under stirring (200 rpm) for 2 h. Removal ratio of As was confirmed by measuring the As concentration in the filtrate using ICP.

3. Results

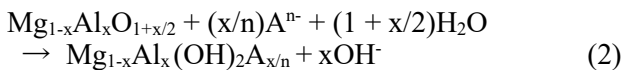
Synthesized sample was identified as LDH of [Mg_{0.67}Al_{0.33}(OH)₂](NO₃)_{0.33}·0.5H₂O from peaks of x-ray diffraction (XRD). TGA and DTA curves of LDH are shown in Fig. 1. From the TG curve, we can distinguish four stages by weight loss: stage I 30-120°C, II 120-300°C, III 300-380°C, and IV 380-600°C. Stage I is 3.8% of mass loss and it corresponds to the evaporation amount of surface adsorbed water. Stage II and III are 19.3% and 33.7% of mass loss respectively. These values of mass loss correspond to dehydroxylation from layer containing Al and Mg in LDH. Stage IV is 48.5% of mass loss and it corresponds to elimination of NO₃. XRD charts of LDH calcined at various temperatures are shown in Fig. 2. These XRD patterns of calcined LDH at 150°C and 300°C are similar to that of uncalcined LDH. According to curves of TGA and DTA, dehydroxylation of Al(OH)₂⁺ in LDH layer was occurred. However, dehydroxylation of Mg(OH)₂ was not occurred. Therefore, LDH

calcined at 150°C and 300°C were considered to maintain the structure of LDH. XRD peaks of calcined LDH at 400°C showed oxidized magnesium (MgO). LDH calcined at 400°C was also confirmed to become oxide from hydroxide by TGA and DTA. The formation of Mg-Al oxide is represented by the following reaction.



We considered that LDH calcined at 340°C is an intermediate between hydroxide and oxide³.

As adsorption capacity and pH buffer ability of calcined LDH samples (50 mg) were investigated using As(V) solution (74 ppm, 100 mL, pH3). Relationship calcination temperature and As(V) adsorption capacity of LDH shows Fig. 3. The value of pH of the treated solution using LDH calcined at 400°C showed pH7.7. Calcination temperature becomes higher, pH value of the solution becomes higher. Oxide generates OH⁻ by rehydroxylation reaction. Rehydroxylation reaction reported is represented by following reaction.



Calcined LDH generates OH⁻ and increases pH. Therefore, pH value of the treated solution using calcined LDH is higher than that of the solution using LDH (25°C). On the other hand, removal ratio of As(V) using LDH calcined at > 300°C is lower than that using LDH calcined at < 150°C.

Secondly, 100% of As(III) in the solution (10 ppm, 50 ml, pH5) was oxidized using ultrasound irradiation in air for 1 h. The value of pH of the treated solution by ultrasound changed from 5.0 to 3.2. This decrease comes from HNO₃ and HNO₂ generated by ultrasound irradiation. LDH calcined at 400°C was added into 40 mL of the solution irradiated. Additional amount of LDH without calcination and LDH with calcination at 400°C was 52.7 mg and these molar ratio of LDH/As(V) were 124 and 154 respectively. 100% of As(V) in the solution was removed by addition of LDH calcined at 400°C. Furthermore, LDH calcined at 400°C showed higher value of pH 7.4 than pH 6.5 of LDH without calcination.

References

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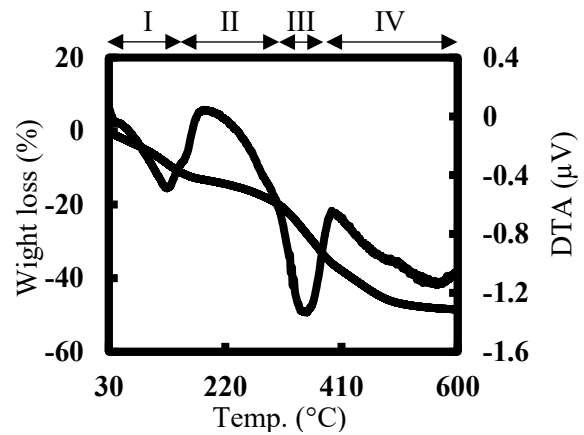


Fig. 1 TG-DTA curves of LDH synthesized in air.

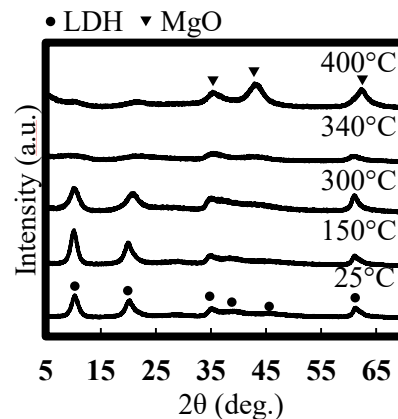


Fig. 2 XRD patterns of samples calcined at different temperatures.

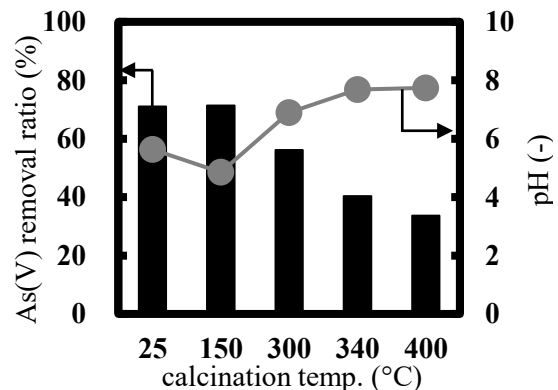


Fig. 3 Removal ratio of As(V) and change of pH value of the solution treated using LDH calcined at different temperatures. Initial pH of the solution was adjusted at pH3.