

## Attempt of Arsenic Removal in Wasted Water by Inorganic Materials

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Fe<sup>3+</sup> substituted hydrotalcites (Fe<sup>3+</sup>-HT) were synthesized in order to remove As ions in wasted water and also evaluated its removal ability for As in solution. Synthesis of Fe<sup>3+</sup>-HT with formula  $[\text{Mg}(\text{II})_6\text{Fe}(\text{III})_2(\text{OH})_{16}]^{2+} [\text{CO}_3 \cdot y\text{H}_2\text{O}]^{2-}$  was carried out by a co-precipitation method. Products obtained by this co-precipitation method were characterized by powder X-ray diffraction analysis (XRD) and Fourier transform infrared spectroscopy (FT-IR). From XRD results, lattice parameter of a-axis in Fe<sup>3+</sup>-HT was slightly larger than that of hydrotalcite (HT). These results suggested that Al<sup>3+</sup> ions in HT were replaced by Fe<sup>3+</sup> ions. According to results of As removal measurements, Fe<sup>3+</sup>-HT had high removal ability in compared to HT.

### 1. Introduction

Recent, water pollution problem due to arsenic (As) has attracted considerable attention. It is considered that the main source of its pollution was outflow of mining water and geothermal water into rivers. Since As is an element of strong toxic, influence of its element on living things is anxiety. Therefore, the development for removal method of As in wasted water is required.

Some researchers have reported about As removal with various adsorbents, such as iron oxides [1] and activated carbon [2]. Iron oxides have high affinity for As adsorption, since most of As in natural environment exist on surface of iron oxides. Activated carbons have high adsorption ability due to its porous structure. However, it is difficult to remove As in wasted water with some ppm pollution using those adsorbents, because iron oxides have low adsorption ability and activated carbons do not have affinity for As adsorption. Therefore, the adsorbent, which have higher adsorption ability of iron oxides, is desired for As removal in wasted water.

Here, We focused on hydrotalcite (HT) as material for As removal. Hydrotalcite consist of brucite (Mg(OH)<sub>2</sub>) layers, in which a part of divalent cations are isomorphously substituted by trivalent cations. At inter layer between brucite layers, exchangeable anion and crystal water exist because of compensating for excess positive charge of the brucite layers resulting from substitution (Fig.1). From layered structure of HT and presence of adsorption [3] and anion exchange [4]. Chemical formula of HT is described as  $[\text{M}(\text{II})_{1-X}$

$\text{M}(\text{III})_X(\text{OH})_2]^{X+} [(\text{A}^{n-})_{X/n} \cdot y\text{H}_2\text{O}]^{X-}$ , where M(II) is a divalent cation (e.g. Mg, Ni, Co Zn), M(III) is a trivalent cation (e.g. Al, Fe, Cr, Ga), and A<sup>n-</sup> is an interlayer anion (e.g. CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) [5-9]. The value of X (X=M(III)/M(II)+M(III)) ranges between 0.2 and 0.33. A number of HT with a wide variety of M(II)-M(III) cation pairs and with different anions in the interlayer have been synthesized and their physicochemical properties have been reported.

Thus, HT has received much attention due to their potential application in various fields as anion exchangers, adsorbents, ionic conductors, catalysis and catalysis supports. We focused on easy design of the developments of synthesis processing for various type of HT. It is well known that iron oxides have affinity for As adsorption, as above mentioned. In this study, Fe<sup>3+</sup> substituted HT was synthesized by co-precipitation method and investigated its microstructure, and measured the As removal ability for substituted HT.

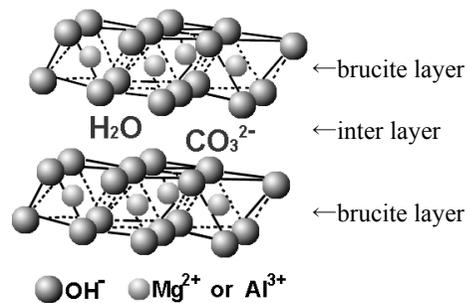


Fig.1. Crystal structure of hydrotalcite with formula  $[\text{Mg}(\text{II})_{1-X}\text{Al}(\text{III})_X(\text{OH})_2]^{X+} [(\text{CO}_3^{2-})_{X/2} \cdot y\text{H}_2\text{O}]^{X-}$

## 2. Experimental Procedures

### 2.1. Synthesis of various HT

Figure 2 shows the flow chart for synthesis procedure of  $\text{Fe}^{3+}$  substituted hydrotalcites ( $\text{Fe}^{3+}$ -HT).  $\text{Fe}^{3+}$ -HTs were synthesized by co-precipitation method. First, Aqueous solutions with  $\text{Mg}^{2+}/\text{Fe}^{3+}$  molar ratio of 2, 3 or 4 were prepared by mixing of 0.1 M- $\text{FeCl}_3$  solution and 0.1 M- $\text{MgCl}_2$  solution. Next, aqueous solution was titrated down to vigorous stirred 0.1 M- $\text{NaHCO}_3$  solution. The co-precipitation reaction was always performed at room temperature and at solution pH of 10 using 0.1 M – NaOH solution. After the co-precipitation, products obtained by co-precipitation were aged for 24 h at room temperature under mixing with a stirrer. Subsequently, the products obtained by co-precipitation method were filtrated and washed using ion exchanged water. Obtained products were air dried at 100 °C in for 24 h and then dried samples were crashed. Products were named  $\text{Mg}^{2+}/\text{Fe}^{3+}=2, 3$  or 4 after molar ratio.

### 2.2. Evaluation

Crystal structure and lattice parameters of obtained products were analysed by X-ray powder diffraction (XRD: Rint 2500, Rigaku, Japan) using Ni filtered  $\text{CuK}\alpha$  radiation at 40 kV and 50 mA. Absorption bands were observed with FT-infra red spectroscopes (FT-IR: winspec 50, JOEL, Japan) to know bonding patterns of products.

Removal ability of obtained products for As was evaluated as follows. As solution (initial concentration of 10 ppm) was prepared by dissolving arsenious acid ( $\text{As}_2\text{O}_3$ ) into ion exchanged water. Value of initial pH of As solution was adjusted to 8 using 0.05 M- $\text{NaOH}$ . Powder product (0.3g) and As solution (30ml) were put into a glass tubes. After the immersion of powder products into As solution for appointed time, As solution was separated. Atomic concentration of As in separated solution was determined by inducted coupled plasma analysis (ICP).

## 3. Results and Discussion

### 3.1. Characterization of brucite layer of $\text{Fe}^{3+}$ -HT

Figure 3 shows X-ray diffraction patterns (XRD) of the products obtained by the co-precipitation method with various  $\text{Mg}^{2+}/\text{Fe}^{3+}$  molar ratios. XRD profiles of the products were composed of several diffraction peaks that are due to crystal structure of HT. Lattice parameter of a-axis in HT and various  $\text{Fe}^{3+}$ -HT are summarized in Table 1. The value of lattice parameter of a-axis in  $\text{Fe}^{3+}$ -HT

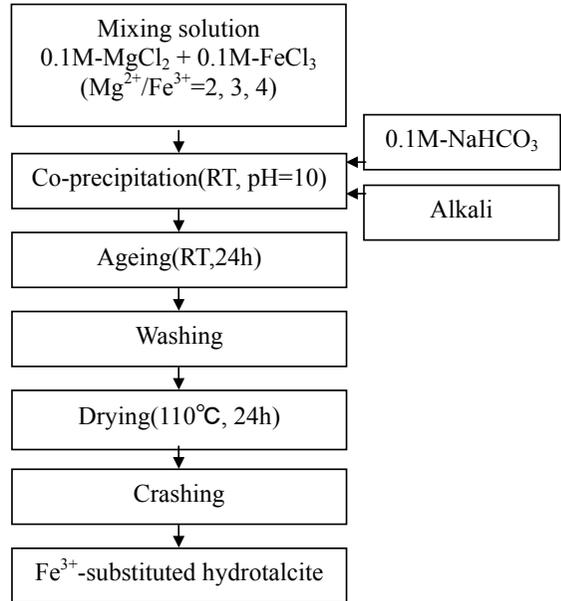


Fig.2. Synthesis procedure of  $\text{Fe}^{3+}$  substituted HT.

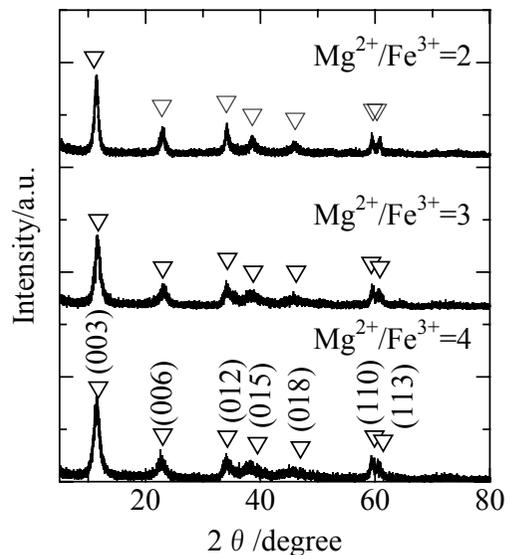


Fig.3. XRD patterns of HT and products obtained by co-precipitation.

Diffraction peaks marked by open triangle(▽) show crystal structure of HT.

Table 1. Values of lattice parameter of a-axis in HT and in Fe<sup>3+</sup>-HT.

Molar ratio	Lattice parameter a-axis / nm
Mg <sup>2+</sup> /Fe <sup>3+</sup> =2	0.310
Mg <sup>2+</sup> /Fe <sup>3+</sup> =3	0.311
Mg <sup>2+</sup> /Fe <sup>3+</sup> =4	0.311
Mg <sup>2+</sup> /Al <sup>3+</sup> =4	0.308

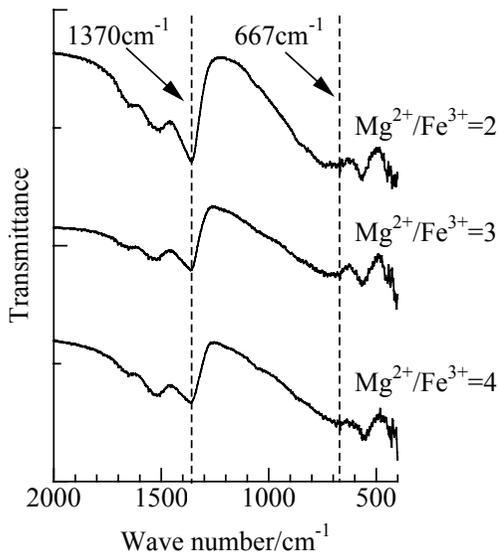


Fig.4. FT-IR spectrum of Fe<sup>3+</sup>-HTs with various Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratios. Absorption band appeared around 1370 and 667 cm<sup>-1</sup> are due to asymmetric vibration CO<sub>3</sub><sup>2-</sup> ions.

is slightly long compared to that of HT. It is considered that the expansion of a-axis was caused by substitution of Fe<sup>3+</sup> ions in brucite layer. In the comparison of three Fe<sup>3+</sup>-HTs that were prepared with Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of 2, 3 or 4 respectively, Value of a-axis get smaller with a increase of Fe<sup>3+</sup> ions (namely, decrease of Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio) in Fe<sup>3+</sup>-HT. HT consists of brucite layers, which is composed of divalent and trivalent cations. Ionic radius of Fe<sup>3+</sup> and Mg<sup>2+</sup> are 0.550 and 0.720 Å, respectively. It is considered that the decrease of lattice parameter with increase of Fe<sup>3+</sup> ions in Fe<sup>3+</sup>-HT was caused by the increase of ratio of Fe<sup>3+</sup> ions to Mg<sup>2+</sup> ions in brucite layer. These results of

XRD and lattice parameter measurements show that Fe<sup>3+</sup> ions substitutes for Al<sup>3+</sup> ions in brucite layer of HT.

### 3.2. Characterization of inter layer anions in

Figure 4 shows Fourier transform infrared spectrum (FT-IR) of Fe<sup>3+</sup>-HTs with various Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratios. FT-IR profiles of Fe<sup>3+</sup>-HT showed two absorption bands due to asymmetric vibration of carbonate (CO<sub>3</sub><sup>2-</sup>) ions at around 1370 and 667 cm<sup>-1</sup>. Kolprogge reports that absorption bands of free CO<sub>3</sub><sup>2-</sup> ions in solution appear at 1415 and 680 cm<sup>-1</sup>, and they are observed at slightly higher wave numbers than those in HT [9]. A reason for these shifts of the absorption bands of CO<sub>3</sub><sup>2-</sup> ions in Fe<sup>3+</sup>-HT would be due to the interaction of CO<sub>3</sub><sup>2-</sup> ions into inter layer of Fe<sup>3+</sup>-HT. From these results of FT-IR, it is confirmed that CO<sub>3</sub><sup>2-</sup> ions are located in inter layer of Fe<sup>3+</sup>-HT.

As shown in Fig.4, the absorption bands due to CO<sub>3</sub><sup>2-</sup> ions get stronger with an increase of Fe<sup>3+</sup> ions (namely, decrease of Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio) in Fe<sup>3+</sup>-HT. The inter layer of HT is composed of the anions and water molecules because the neutralization of excess positive charges of the brucite layer results from the substitution. It is considered that the increase of absorption due to CO<sub>3</sub><sup>2-</sup> ions with an increase of Fe<sup>3+</sup> ions in Fe<sup>3+</sup>-HT occurs by the increase of CO<sub>3</sub><sup>2-</sup> ions intercalated into inter layer. From results of FT-IR, it is considered that CO<sub>3</sub><sup>2-</sup> ions exist at inter layer of Fe<sup>3+</sup>-HT.

From these results of both XRD and FT-IR, it is obvious that products obtained by co-precipitation were HT-like compounds, which contain Fe<sup>3+</sup> ions in its brucite layer and CO<sub>3</sub><sup>2-</sup> ions at its inter layer.

### 3.3. Evaluation of arsenic (As) removal ability of HT and Fe<sup>3+</sup>-HT

Table 2 shows As removal of HT and Fe<sup>3+</sup>-HT with various Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratios. HT and Fe<sup>3+</sup>-HT rapidly remove As in solution. Fe<sup>3+</sup>-HT prepared with Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of 4 removes a large quantity of As in solution compared to HT synthesized with Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of 4. Although there is a difference in cation of brucite layer between HT and Fe<sup>3+</sup>-HT, Fe<sup>3+</sup>-HT has the same anion exchange capacities as those of HT. Both HT and Fe<sup>3+</sup>-HT with same value of M<sup>2+</sup>/M<sup>3+</sup> molar ration possess the same anion exchange capacities. Some papers have reported that the mobility of As in natural environment depends on the presence of metal oxides, especially, iron oxides[2]. It is considered that high As removal ability of Fe<sup>3+</sup>-HT compared to HT is caused by outbreak of As affinity resulting from substitution

Table 2. Time dependence of As concentration after immersion time for various HTs.

Molar ratio	Atomic concentration of As /ppm			
	0h	1h	4h	18h
Mg <sup>2+</sup> /Fe <sup>3+</sup> =2	10	0.13	0.11	0.098
Mg <sup>2+</sup> /Fe <sup>3+</sup> =4	10	2.48	1.23	0.95
Mg <sup>2+</sup> /Al <sup>3+</sup> =4	10	2.56	3.94	3.38

of Fe<sup>3+</sup> ions in brucite layer of Fe<sup>3+</sup>-HT.

With increase of Fe<sup>3+</sup> ions in Fe<sup>3+</sup>-HT, As removal ability of Fe<sup>3+</sup>-HT get higher. HT consists of brucite layer and inter layer. Its brucite layer is composed of Mg<sup>2+</sup> and Al<sup>3+</sup> ions with wide range of Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio. The anion exchange capacity of HT gets increase with a decrease of Mg<sup>2+</sup>/Al<sup>3+</sup> molar ratio (namely, increase of Al<sup>3+</sup> ions in brucite layer of HT). Therefore, the anion exchange capacity of Fe<sup>3+</sup>-HT also increases with a decrease of Mg<sup>2+</sup>/Fe<sup>3+</sup> ions in brucite layer of Fe<sup>3+</sup>-HT. As mentioned above, iron oxides have affinity for As adsorption, because most of As in natural environment exist on surface of iron oxides. It is considered that increase of Fe<sup>3+</sup> is caused by the increase of anion exchange capacity and As affinity.

#### 4. Conclusion

In this study, Fe<sup>3+</sup> substituted hydrotalcites (Fe<sup>3+</sup>-HT) with formula [Mg(II)<sub>6</sub>Fe(III)<sub>2</sub>(OH)<sub>16</sub>]<sup>2+</sup>[CO<sub>3</sub> · yH<sub>2</sub>O]<sup>2-</sup> were synthesized by a co-precipitation method in order to remove As ions in wasted water. XRD and FT-IR results for obtained products showed that Fe<sup>3+</sup> ions substitute for Al<sup>3+</sup> ions in brucite layer, and CO<sub>3</sub><sup>2-</sup> ions locate at inter layer of Fe<sup>3+</sup>-HT. Fe<sup>3+</sup>-HT prepared with Mg<sup>2+</sup>/Fe<sup>3+</sup> molar ratio of removed a large quantity of arsenic in solution compared to HT synthesized with Mg<sup>2+</sup>/Al<sup>3+</sup> molar ratio of 4.

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