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# Characteristics of a novel adsorbent Fe–Mg-type hydrotalcite and its adsorption capability of As(III) and Cr(VI) from aqueous solution

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ABSTRACT

In the present study, we prepared a newly adsorbent, Iron–Magnesium-type hydrotalcite (FHT), at different molar ratios (FHT3.0; $Mg^{2+}/Fe^{3+} = 3.0$ and FHT5.0; $Mg^{2+}/Fe^{3+} = 5.0$) for removing heavy metal ions. Characteristics of FHT and arsenite (As(III)) and hexavalent chromium (Cr(VI)) adsorption capability onto that were evaluated. Amount adsorbed of As(III) and Cr(VI) increased with raising temperatures. Amount adsorbed of heavy metal ions onto FHT in the single liquid phase was smaller than that in the mixed liquid phase, which suggests that the amount adsorbed was affected by the adsorbent properties, interlayer space, and solution pH.


## Introduction

IARC reported that arsenic was listed in a Group I carcinogen. Excessive drinking and exposure to arsenic containing water leads to the different types of cancer (skin cancer etc.), as well as pigmentation [1,2]. In general, organic arsenic compounds are less toxic than inorganic one, and arsenate (As(V)) is the most abundant anion in the aerobic surface water and arsenite (As(III)) is the most common species present in groundwater [3–5]. The USEPA in 2001 adopted a new standard for As in drinking water with a limit of 10 ppb, replacing the old standard of 50 ppb [5]. In addition, wastewater including Cr(VI) is discharged from a lot of factories (electroplating textiles etc.). In liquid phase hexavalent chromium ion exists in the form of highly toxic and soluble chromate ions, more saw than any other species. Since it is difficult for degradation of Cr(VI) by a microorganism and Cr(VI) has a tendency to multiply in living organisms, it causes many adverse effects to humans [6–8]. Various methods were reported for the removal of arsenic ion and hexavalent chromium ion in liquid phase, such as membrane treatment, ion exchange method, adsorption process, and coagulation or precipitation treatment [9–19]. The adsorption method has been reported to be more effective than other methods [20].

Hydrotalcites ($[H_{1-y}{}^{2+}H_y{}^{3+}(OH)_2](M^{n-})_{y/n}\cdot mH_2O$) are composed of layered metal double hydroxides ($H^{2+}$ and $H^{3+}$ show the divalent and the trivalent cations, $M^{n-}$ shows the anion, and $y$ is defined as the $H^{3+}/(H^{2+}+H^{3+})$ ratio). These materials have positively charged brucite layers ($Mg(OH)_2$), which are balanced by water molecules ($H_2O$) and anions ($CO_3{}^{2-}$, $NO_3{}^-$, $Cl^-$, etc.) in the intermediary region. The large interlaying area coupled with many exchangeable anions, make hydrotalcites ideal for applications like adsorbents and ion-exchangers [21–24].

Recently, many adsorbents (Mg–Al hydrotalcite-supported kaolin clay, Fe-hydrotalcite-supported magnetite nanoparticles, nano-hydrotalcite/$SiO_2$ composite, and calcined nano-Mg/Al hydrotalcite) were reported for arsenite ion and hexavalent chromium ion removal in liquid phase [6,9,10,21]. Presently, only limited research exists on As(III) and Cr(VI) adsorption onto Fe-hydrotalcite from aqueous solution. The affinity of hydrotalcites for these ions is influenced by the anion size or charge ratios and also by the temperatures. Therefore, the $H^{2+}/H^{3+}$ molar ratio strongly affects the As(III) and Cr(VI) removal in liquid phase [25–28].

The purpose in the present study is to elucidate the adsorbent (FHT) characteristics at two different molar ratios of $Mg^{2+}/Fe^{3+}$, 3.0 and 5.0. In addition, the physicochemical characteristics of FHT, adsorption isotherms, and effect of contact time, temperature and pH in solution were investigated. These results provide the useful information about the development of high-performance FHT for heavy metal removal in water phase.

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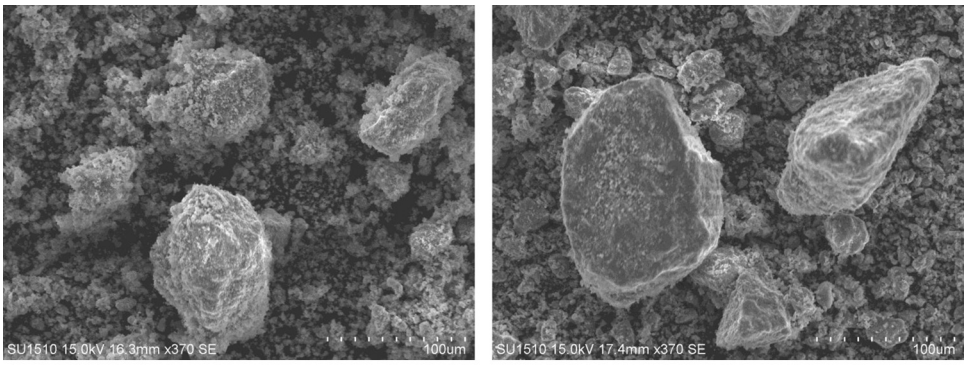


**Fig. 1.** SEM images of FHT3.0 and FHT5.0.

## Experimental

### *Materials*

The FHT was obtained from Tomita Pharmaceutical Co., Ltd., Japan (FHT3.0; $Mg^{2+}/Fe^{3+} = 3.0$ and FHT5.0; $Mg^{2+}/Fe^{3+} = 5.0$). As(III) and Cr(VI) standard solutions were purchased as $As_2O_3$ and $K_2Cr_2O_7$, respectively (Wako Pure Chemical Industries. Ltd., Japan). The specific surface area and morphology analysis were performed by a NOVA4200*e* (Yuasa Ionics, Japan) and by SU1510 (SEM; Hitachi Ltd., Japan), respectively. X-ray diffraction (XRD) patterns were measured using a Mini Flex II (Rigaku, Japan). The distribution of As (III) and Cr(VI) analysis on the adsorbent was performed by JXA-8530F (EPMA; JEOL, Japan).

### *Adsorption of heavy metal ions in single solution system*

The 0.01 g of FHT was added to an As(III) or a Cr(VI) solution (0.1–10 mg/L, 50 mL). In the case of evaluating the difference in pH, an As(III) or a Cr(VI) solution were adjusted to the pH range from 2 to 10 by the addition of HCl or NaOH solution using the glass pH electrode (F-73, HORIBA, Ltd., Japan). The suspensions were shaken for 24 h at 100 rpm (Temperatures is 5, 25, and 45 °C). Subsequently, the sample solution was then filtered through a 0.45 μm membrane. The filtrate concentration was measured by ICP-7500 (Shimadzu Co., Japan). The amount adsorbed of heavy metal ions was calculated by Eq. (1):

$$A = (M_0 - M_e)S/W \quad (1)$$

where $A$ is the amount adsorbed of heavy metal ions (mg/g), $M_0$ and $M_e$ are the concentration before and after adsorption process (mg/L), $S$ is the solvent volume (L), and $W$ is the FHT weight (g). The data values provided are taken from the average of three experiments.

### *Amount of As(III) and Cr(VI) adsorbed in binary solution system*

The 0.01 g of FHT was added to an As(III) and a Cr(VI) binary solution (1, 5, and 10 mg/L, 50 mL). The adsorbed amount was measured by above-mentioned.

## Results and discussion

### *Characteristics of adsorbent*

The SEM images of FHT are shown in Fig. 1. We could observe the different particle sizes; FHT did not show perfectly rounded particles. This indicates a poor amount of crystallinity, which is typical of hydrotalcite-like layered metal double hydroxides [29–32]. The XRD patterns of FHT3.0 and FHT5.0 are shown in Fig. 2. As expected, FHT consisted of hydrotalcite-like layered double hydroxides. We could confirm the stacking of the brucite-like sheets by the (003) and (006) peak reflections [9], reemphasizing that the intermediary area depends upon the size or radius of metal ion and anion, the $H^{2+}/H^{3+}$ molar ratio, and the degree of hydration. Therefore, the ferric iron (the large radius) affects the d-spacing in FHT [21,33]. Additionally, the hydromagnesite structure was confirmed in FHT5.0, because the content ratio of magnesium in FHT5.0 was greater than that in FHT3.0. Therefore, the degree of crystallinity in the hydrotalcite-like layered double hydroxide (FHT5.0) was lower than that in FHT3.0. These results agree with an earlier study by Hirahara et al. [34]. In addition, the specific surface area of FHT3.0 and FHT5.0 was 22.4 and 13.1 $m^2/g$, respectively. Previous studies have reported that the specific surface area of other hydrotalcites were 1.5 or 6.9 $m^2/g$ [9,29]. It is notable that FHT had a larger surface area, which is probably as a result of the presence of ferric iron in hydrotalcite.

### *Adsorption isotherms in single solution*

Adsorption isotherms in single solution are shown in Figs. 3 and 4, respectively. The number of heavy metal ions adsorbed onto FHT increased with elevating temperatures (the number of Cr(VI)

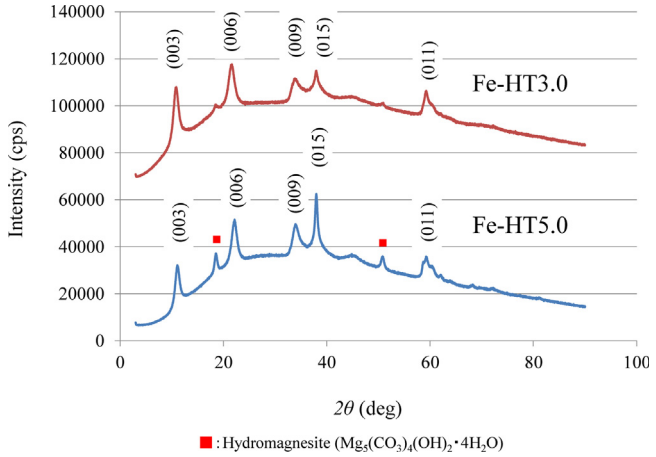


**Fig. 2.** XRD patterns of FHT3.0 and FHT5.0.
■:Hydromagnesite.

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