

# CLARIFICATION FOR HG (II) REMOVAL MECHANISM IN FERRIHYDRITE CO-PRECIPTAION PROCESS BY XAFS ANALYSIS

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**Abstract-** Inorganic mercury is known as one of the toxic elements and strictly regulated by Japanese effluent standard that need to be under 0.005 mg/dm<sup>3</sup> for discharged water. This value is the lowest among other inorganic toxic elements regulated in Japan. As a result, high quality method has been required for Hg(II) wastewater treatment. Objective of this study is to clarify Hg(II) removal mechanism using ferrihydrite in co-precipitation process. Isotherm drawing, X-ray diffraction (XRD) and X-ray Adsorption Fine Structure (XAFS) analysis were conducted for both co-precipitation and adsorption processes to investigate the immobilization mechanism at pH 4. These experimental results suggested that the sorption mechanism of Hg(II) with ferrihydrite was almost the same between co-precipitation and adsorption processes, but it involved not only surface complexation but also three dimensional uptakes such as surface precipitation.

**Index terms-** XAFS, Co-precipitation, Hg(II) removal, Ferrihydrite, Isotherm

## I. INTRODUCTION

Inorganic mercury (Hg(II)) is known as one of the toxic elements and regulated by Japanese effluent standard to be under 0.005 mg/dm<sup>3</sup> in discharged water. This value is the lowest among other inorganic toxic elements regulated in Japan, therefore a high quality method has been required for Hg(II) wastewater treatment. Additionally, more efficient treatment method in which amount of sludge generation after wastewater treatment is reduced has been desired.

Most popular methods for Hg(II) wastewater treatment is coagulation-sedimentation method using sulfide precipitation<sup>[1]</sup>. However, in this method, re-dissolution of Hg(II) from the sludge after treatment has become concern in oxidative atmosphere. Furthermore, additional Chemical Oxygen Demand (COD) treatment is generally required after Hg(II) treatment. On the other hand, it is widely known that ferrihydrite can remove many kinds of inorganic toxic elements including Hg(II) by co-precipitation method. Therefore, if Hg(II) treatment method using co-precipitation with ferrihydrite can be established, simultaneous treatment of several inorganic toxic elements including Hg(II) become possible. However, the mechanism of Hg(II) uptake by ferrihydrite during co-precipitation process was not clearly understood.

The objective of this study is focused on the clarification of Hg(II) removal mechanism using ferrihydrite in co-precipitation process, to enable optimum design of treatment processes for large amounts of wastewater. To accomplish this, the sorption mechanism of Hg(II) on ferrihydrite in co-precipitation and adsorption processes was investigated experimentally by sorption isotherm drawing and X-ray diffraction (XRD) and X-ray Adsorption Fine Structure (XAFS) analysis.

## II. MATERIALS AND METHODS

All chemicals and solutions used were of analytical grade and were purchased from Kanto Chemicals Inc., Tokyo, Japan & Wako Pure Chemical Industries, Tokyo, Japan. The Hg(II) and Fe(III) solutions were prepared from Hg(NO<sub>3</sub>)<sub>2</sub> · H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, respectively. Throughout the experiments, the pH and ionic strength were adjusted by addition of 0.1 M HNO<sub>3</sub>, KOH and KNO<sub>3</sub>. The ionic strength was fixed at 0.05. All experiments were conducted at temperature of 25 °C.

The co-precipitation experiments involved the formation of ferrihydrite in the presence of Hg(II) ions. Fe(III) and Hg(II) solutions were initially combined at pH 2 to maintain the ionic states of both Fe(III) and Hg(II). The pH and ionic strength were then adjusted to the target level and maintained for 1 h with agitating. The pH was kept at the target value within ± 0.5 range by the addition of a few drops of 0.1 M KOH during agitation. After agitation, the suspension was filtered through a 0.1 μm membrane filter, and the filtrate was analyzed using ICP-AES (Seiko Instruments, SPS-7800, Chiba, Japan) to achieve the concentration of Fe(III), and cold vapor atomic absorption spectrophotometry (Japan Instruments, RA-3, Tokyo, Japan) to achieve the concentration of Hg(II). The initial Hg(II) concentration was fixed at 10 or 25 mg/dm<sup>3</sup> (0.05 or 0.12 mmol/dm<sup>3</sup>), and the Fe(III) concentration was varied to give initial Hg/Fe molar ratios from 3 to 11. Adsorption experiments were conducted using the same conditions as for the co-precipitation experiments, but ferrihydrite suspensions and Hg(II) solutions were prepared separately at twice the initial concentrations of Hg(II) and Fe(III). The pH values and ionic strengths of both solutions were ready adjusted to the target levels, and equivalent amounts

of the solutions were then combined and agitated for 1h. The pH was kept at the target value within  $\pm 0.5$  by the addition of a few drops of 0.1 M KOH during agitation, After agitation, Fe(III) and Hg(II) concentration in filtrate were analyzed using the procedure described as above. In all the adsorption experiments, freshly precipitated ferrihydrite was used to avoid changes caused by aging.

The filter residues from the co-precipitation and adsorption experiments were analyzed using XRD (RINT Ultima III, Rigaku Inc., Tokyo, Japan) and XAFS in Aichi synchrotron. For these analysis, the initial Fe(III) concentration was adjusted to  $10 \text{ mg/dm}^3$  and initial Hg(II) concentration was varied according to the target Hg/Fe molar ratio. The filter residues from the co-precipitation and adsorption experiments were freeze-dried at  $-45^\circ\text{C}$  and 10 Pa at least for 24 h to avoid crystallization or mineralogical transformation.

Powder XRD patterns were obtained using a copper target (Cu-K $\alpha$ ), a crystal graphite monochromator and a scintillation detector. The X-ray source was operated at 40 kV and 30 mA with step scanning from  $2\theta$  values of  $2 - 80^\circ$ , in increments of  $0.02^\circ$ . A crystal sample holder was used the patterns were not corrected for background diffraction.

Powder XAFS patterns were obtained using a transmission method. All sample's spectrum were obtained by EXAFS analysis. Thus, these were analyzed by Fe and Hg absorption edge. After XAFS analysis, XAFS spectrum was analyzed by REX2000 ver2.5, Athena and Artemis software.

### III. HG (II) REMOVAL BY FERRIHYDRITE

The Hg(II) removal properties incorporating ferrihydrite in co-precipitation and adsorption processes at different pH values were shown in Figure. 1. In these experiments, the initial concentration of Hg(II) and Fe(III) was set at  $10 \text{ mg/dm}^3$  and  $100 \text{ mg/dm}^3$ , respectively. Chemical equilibrium calculation showed that Hg(II) precipitates as mercury hydroxide at over pH 4 when Hg(II) concentration is above  $50 \text{ mg/dm}^3$ . Since the purpose of this study is to know the removal amount of Hg(II) by sorption to ferrihydrite not by its own precipitation. So, these experiments were conducted under  $50 \text{ mg/dm}^3$ . In these experiments was conducted within the wide variety of pH range starting from 3 to 12, in which Fe(III) precipitates as ferrihydrite.

Figure. 1 clearly showed that the best pH condition for Hg(II) removal by ferrihydrite is pH 4. In addition, there is no significant difference of Hg(II) removal amount between in co-precipitation and adsorption processes.

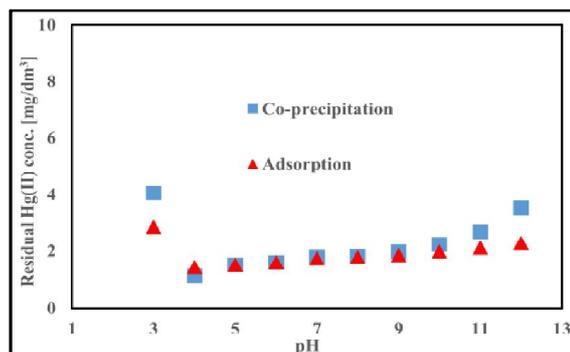


Figure. 1 Relationship between pH and residual Hg(II) concentration obtained from co-precipitation/adsorption experiments; Initial Hg(II) concentration =  $10 \text{ mg/dm}^3$ , initial Fe(III) concentration =  $100 \text{ mg/dm}^3$

### IV. ISOTHERM DRAWING

The relationship between Hg(II) removal amount and Fe(III) dosage obtained from adsorption and co-precipitation experiments were shown in Figure. 2. In these experiments, the initial concentration of Hg(II) was set at  $25 \text{ mg/dm}^3$  and pH was fixed at 4.0 as it is the suitable pH to remove Hg(II) from solution. Based on the results shows in Figure. 2, there was no significant difference for Hg(II) removal between co-precipitation and adsorption processes could be also confirmed.

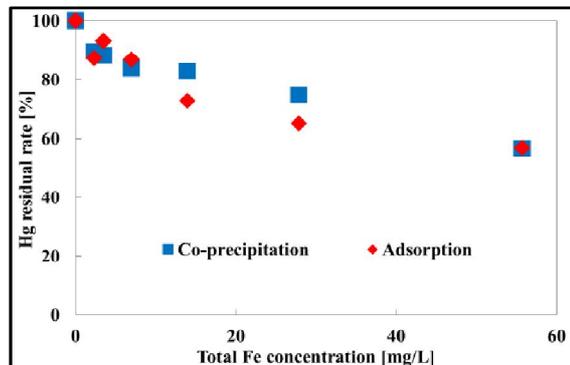


Figure. 2 Relationship between Fe(III) concentration and Hg(II) residual rate obtained from co-precipitation/adsorption experiments at pH 4; Initial Hg(II) concentration =  $25 \text{ mg/dm}^3$ , Hg/Fe molar ratio = 0.125- 3

The sorption isotherms obtained in the co-precipitation and adsorption experiments at pH 4.0 were presented in Figure. 3 that Fig. 3 indicate the initial Hg/Fe molar ratios. In both co-precipitation and adsorption processes, the sorption density became larger at lower Fe dosages and higher initial Hg/Fe molar ratios.

Both in co-precipitation and adsorption processes, the sorption isotherm was not saturated similar to Brunauer-Emmett-Teller type. This trend suggests that Hg removal mechanism in both co-precipitation and adsorption processes involves more than simple

adsorption, especially at 0.125 – 0.5 of initial Hg/Fe molar ratios, at which the Hg sorption density increased substantially.

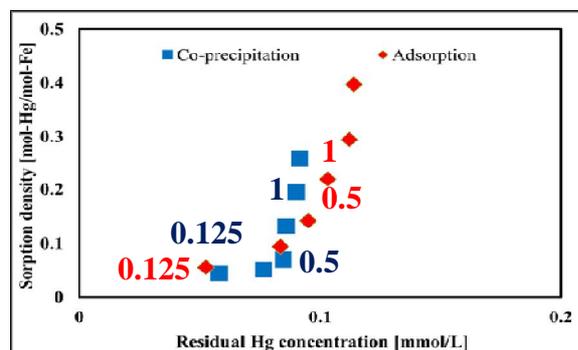


Figure. 3 Sorption isotherm obtained from co-precipitation/adsorption experiments at pH 4; Initial Hg(II) concentration = 25 [mg/dm<sup>3</sup>], Hg/Fe molar ratio = 0.125 - 3

## V. X-RAY DIFFRACTION (XRD) ANALYSIS

The XRD patterns of the Hg(II) co-precipitated and adsorbed precipitates in various initial molar ratios of Hg/Fe were shown in Figures. 4 and 5. The XRD spectrum of ferrihydrite, which was prepared from 20 mg/dm<sup>3</sup> of Fe(III) solution at pH 9 by applying a similar procedure in the co-precipitation experiments, was also shown in the figure as a reference material. The XRD pattern of the prepared ferrihydrite had broad peaks at 34° and 61° of 2θ values, which correspond to 2-line poorly crystalline ferrihydrite. Figures. 4 and 5 indicated that the XRD patterns of the precipitates obtained in both co-precipitation and adsorption experiments were almost the same to those with poorly crystalline ferrihydrite when Hg/Fe molar ratio was less than 0.125. These results suggested that the main mechanism of Hg(II) uptake was simply Hg(II) adsorption on poorly crystalline ferrihydrite by surface complexation when Hg/Fe molar ratios was low in both co-precipitation and adsorption processes. On the other hand, the XRD patterns of the precipitates gradually changed when the initial Hg/Fe molar ratio was greater than 0.125, the XRD patterns had broad peak at about 25° of 2θ. These results suggested that ferrihydrite was transformed into another form of precipitate when more Hg(II) was uptaken to it. These should be a possibility of surface precipitation when the initial Hg/Fe molar ratio was more than 0.125 in both co-precipitation and adsorption processes.

From above mentioned results, the main mechanism of Hg(II) by ferrihydrite should be surface complexation of Hg(II) with poorly crystalline ferrihydrite at initial Hg/Fe molar ratios less than 0.125, whereas surface precipitation should be involved at higher molar ratios.

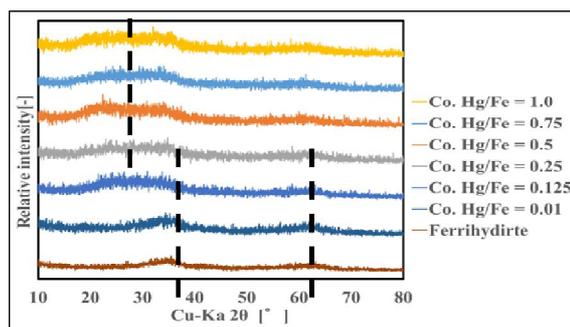


Figure. 4 XRD patterns of precipitates obtained in co-precipitation process at pH 4; Hg/Fe molar ratio = 0.01 – 1.0, Initial Fe(III) concentration = 10 mg/dm<sup>3</sup>

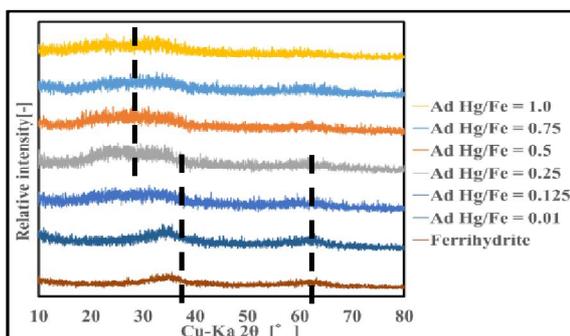


Figure. 5 XRD patterns of precipitates obtained in adsorption process at pH 4; Hg/Fe molar ratio = 0.01 – 1.0, Initial Fe(III) concentration = 10 mg/dm<sup>3</sup>

## VI. X-RAY ADSORPTION FINE STRUCTURE (XAFS) ANALYSIS

The Fe K-edge and Hg L3-edge XANES pattern of the Hg(II) co-precipitated precipitates of various initial molar ratios of Hg/Fe was shown in Figures. 6 and 7, respectively<sup>[2]</sup>. In Figures. 6 and 7, reference samples are ferrihydrite, HgO (yellow) and HgO (red). Initial Hg(II) concentration that initial Hg/Fe molar ratio is 3.0 and 5.0 is over 50 mg/dm<sup>3</sup>. Thus, these samples are possible to form its own hydroxide by chemical equilibrium calculation. 0.01 Hg/Fe molar ratio do not exist in Figure. 7, because the Hg concentration in sample is very low not to analyze by Hg L3-edge XAFS.

As shown in Figure. 7, it was confirmed that the peak position changed from 12283 eV to 12281 eV after Hg/Fe molar ratio is 0.5. And, reference samples also had the peak in 12281 eV. So, the peak position in 12281 eV suggested that Hg contained in precipitates after 0.5 Hg/Fe molar ratio existed as solid phase. This trend is almost the same as isotherms and XRD analysis. Moreover, the peak of HgO (yellow) and HgO (red) in 12290 eV could not be confirmed samples of the Hg(II) co-precipitated precipitates. This results suggested that Hg(II) contained in precipitates do not exist as crystalline of HgO (yellow) or HgO (red). Thus, it is possible to exist as non-crystalline of HgO or mercury hydroxide.

On the other hand, it found that no significant different from the results of Fe K-edge XANES pattern of the Hg(II) co-precipitated precipitates of various initial molar ratios of Hg/Fe.

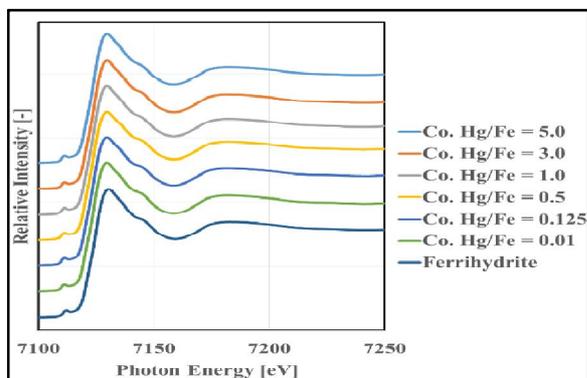


Figure. 6 Fe K-edge XANES pattern of precipitates obtained in co-precipitation process at pH 4; Hg/Fe molar ratio = 0.01 – 5.0, Initial Fe(III) concentration = 10 mg/dm<sup>3</sup>

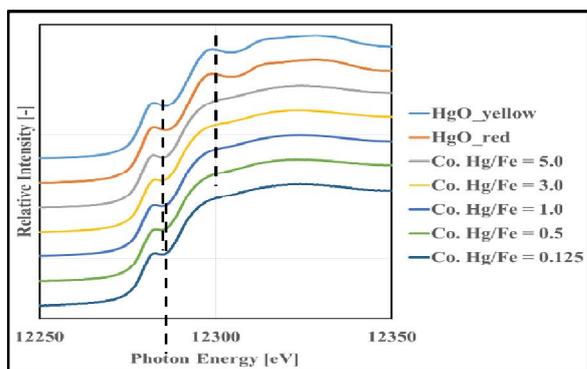


Figure. 7 Hg L3-edge XANES pattern of precipitates obtained in co-precipitation process at pH 4; Hg/Fe molar ratio = 0.125 – 5.0, Initial Fe(III) concentration = 10 mg/dm<sup>3</sup>

## CONCLUSION

The Hg(II) removal mechanisms in treatments using ferrihydrite were experimentally investigated by comparing the co-precipitation and adsorption processes.

Hg(II) removal by ferrihydrite was preeminent at pH 4.0. Therefore, co-precipitation and adsorption experiments were separately conducted at pH 4.0 and the results were compared using isotherms, XRD analysis, to investigate the Hg(II) removal mechanisms. It was found that Hg(II) removal with ferrihydrite mainly involved surface complexation in both co-precipitation and adsorption processes. However, in both process, surface precipitation was also observed when the initial Hg/Fe molar ratio was greater than 0.125 – 0.5.

From XAFS analysis, it was confirmed same trend of isotherms and XRD analysis. Hence, Hg(II) contained in precipitates do not exist as crystalline of HgO (yellow) or HgO (red). It might be exist as non-crystalline of mercury Oxide or mercury hydroxide.

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