

# Porous Iron Oxyhydroxide Having Dual Adsorption Site for Efficient Removal of Anions in Wastewater

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## 1. Introduction

Runoff that contains excessively supplied phosphorus and nitrate nitrogen flows into rivers and lakes. The emission of phosphorus and nitrate nitrogen causes eutrophication, that is, growth of waterbloom, and depletion of dissolved oxygen. Treatment methods of effluent including phosphorus and nitrate nitrogen have been studied during the past few decades. Typical removal methods for effluent including high concentration phosphorus are biological treatments such as the conventional activated sludge process, chemical treatments such as precipitation with Fe and Ca, and a combination of both treatments. However, for the runoff of a low phosphorus concentration such as stormwater, biotreatment and precipitation are ineffective. Instead, fixed-bed processes using adsorption methods are recommended as the most effective removal process for the treatment of waste water including phosphorus of low concentrations. In addition, the multipurpose adsorbent for various ions should be developed for economical recovery of resources from wastewater.

The adsorption of anion is governed both by the physical properties of adsorbent such as pore diameter and the physico-chemical properties of active site such as hydrogen bonding. From this viewpoint, iron oxyhydroxide is a promising candidate of adsorbent because the pore structure and the hydrogen bond property can be easily changed by calcination. In this study, we tried to prepare an efficient adsorbent having a large amount of micropores and hydrogen bonds by combining the precipitation of  $\text{Fe}^{3+}$  ion with alkali and the air-drying. The removal performance of phosphoric acid ion by the prepared adsorbent was discussed from the viewpoint of the structure.

## 2. Experimental Section

### 2.1 Sample Preparation

Porous iron oxyhydroxide was prepared in a beaker (at 28 °C) by hydrolysis of a spared 0.5 M  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Wako Co.) solution. An automatic titration system was used to add the 2M NaOH at a constant rate up to pH = 4. After filtration of the precipitate and washing several times with distilled water, it was dried for 24 h at 50 °C.

### 2.2 Thermal treatment

To control pore size distribution of porous iron oxyhydroxide powders, we need to remove the crystalline water molecules. We calcinated the synthesized powders from 50 °C to 350 °C.

## 2.3 Analyses of adsorbent

The pore structure of the sample was characterized by nitrogen adsorption-desorption at 77K using Bellsorp-mini (Bell Japan Ltd.). Specific surface area was determined from gas-adsorption using the multi-point Brunauer-Emmett-Teller (BET) method. We also measured *In-situ* FT-IR spectrum using a diffused reflection method (JEOL, SPX60) as follows. The samples were equilibrated at 30 °C in a flowing nitrogen stream. Then they were heated at the rate of 5 K/min up to 400 °C during which ultra high purity nitrogen was continually supplied at the rate of 100 cc/min in order to maintain the temperature. A BaF<sub>2</sub> disc was put on the pinhole from where the light passes through. The light source was a heated Ni-Cr wire and the detector was MCT (mercury cadmium-tellurium). FT-IR spectrum was collected by acquisition of 100 scans at every 50 °C of interval. Moreover, particle size of the ample was determined using a laser scattering particle-size distribution analyzer (HORIBA, LA-920).

## 2.4 Adsorption experiment

To examine the capacity of each adsorbent for the removal of PO<sub>4</sub><sup>3-</sup>, AsO<sub>3</sub><sup>3-</sup>, F<sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, we measured the equilibrium adsorption. Adsorbent of 0.1 g was put into the aqueous solution contained those ions, and stirred for 24 h at 28 °C. The concentration of those ions in the solution was measured using plasma luminescence analysis equipment, ICP, (Shimadzu, ICPS-750) and a liquid chromatograph with a CDD detector using an ion-exchange column (Shimpak). The fixed-bed adsorption test was also conducted in 15.7 ml mini-column. All test work used synthetic solutions of PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, flow rate of 5 ml/min(19 SV/h). The concentration of those ions in the solution was measured using plasma luminescence analysis equipment, ICP and a liquid chromatograph.

## 3. Results and discussion

### 3.1 X-ray diffraction

Fig. 1 shows the XRD patterns of the porous iron oxyhydroxide calcinated from 25 °C to 300 °C for 1 h in a flowing nitrogen stream. XRD patterns of samples of under 200 °C representing the diffraction peaks was weak and amorphous structure can be indexed as akaganeite structure<sup>1-3</sup>). At the temperature above 300 °C, the structure transformed to hematite, which coincides with the phase transformation process of β-FeOOH to α-Fe<sub>2</sub>O<sub>3</sub> by heating<sup>3,4</sup>).

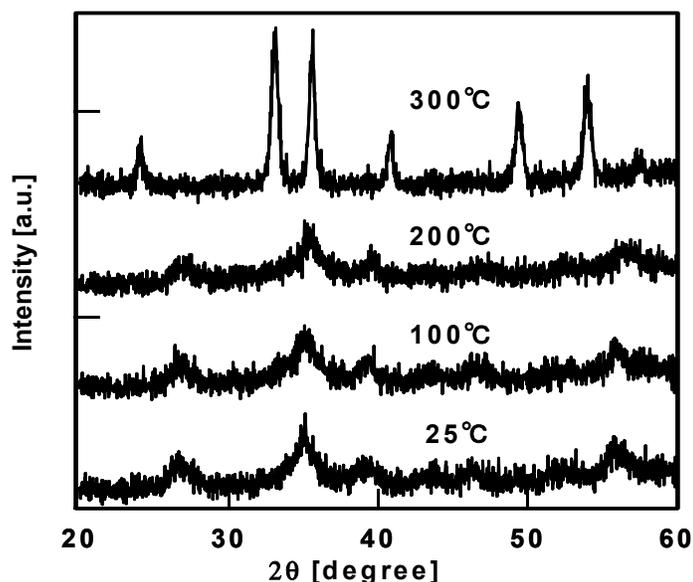


Fig. 1 X-ray diffraction patterns of the iron oxyhydroxide calcinated from 25 °C to 300 °C.

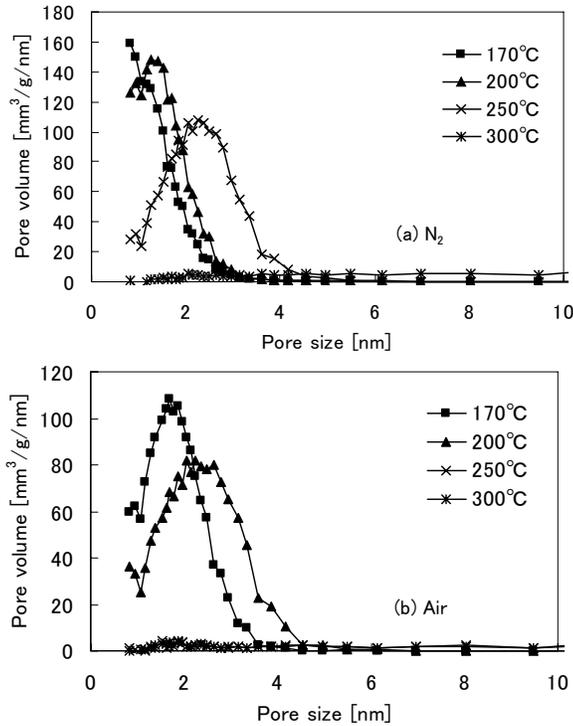


Fig. 2 Pore size distribution of calcinated iron oxyhydroxide.

**Table 1 Mean pore peak determined by BJH method and BET surface area of samples.**

[°C](1hour)	Air	N <sub>2</sub>	Air	N <sub>2</sub>
140		254.6		0.83
170	179.6	260.8	1.70	0.83
200	145.8	260.2	2.04	1.28
250	22.0	163.4	41.85	2.25
300	18.7	35.1	41.85	21.19

<sup>a</sup> BET specific surface area.

<sup>b</sup> Mean pore peak determined by BJH method.

### 3.2 Controlled pore size distribution

Fig. 2 shows the pore size distribution curves calculated from the adsorption branches of the isotherms by BJH method of porous iron oxyhydroxide and Table 1 shows the BET surface area of sample. The BET surface area of calcination at 170 °C in N<sub>2</sub> atmosphere reached up to the value of 260.8 m<sup>2</sup>/g. On the other hand, The BET surface area of calcination at 170 °C in air atmosphere is 179.6 m<sup>2</sup>/g. Even in N<sub>2</sub> atmosphere, the peak of the pore size distributions shifted toward large diameter, but the surface areas decreased with increasing the calcination temperature, and finally the surface area was rapidly reduced to the value of 22.0 m<sup>2</sup>/g by the complete collapse of the mesostructure caused during the transformation into hematite over 250 °C.

### 3.3 Hydrogen bond distribution of adsorbent

Fig. 3 shows the IR spectra ranging from 2400 to 3800  $\text{cm}^{-1}$  of porous iron oxyhydroxide. Porous iron oxyhydroxide has a large amount of hydrogen bond of 3410  $\text{cm}^{-1}$ , which is the peak of OH-OH hydrogen bond, and the bond dissociation energy was 20  $\text{kJ/mol}$ <sup>5</sup>. The peak of IR spectra of the porous iron oxyhydroxide with calcination at over 250  $^{\circ}\text{C}$  decreased for the wide range of wave number. From the thermogravimetric analysis data, the weight loss from 50  $^{\circ}\text{C}$  to 200  $^{\circ}\text{C}$  is attributed to the loss of surface adsorbed water. The weight loss in the range of over 250  $^{\circ}\text{C}$  is due to the removal of the crystalline water molecules, which indicates the transformation into hematite as mentioned above.

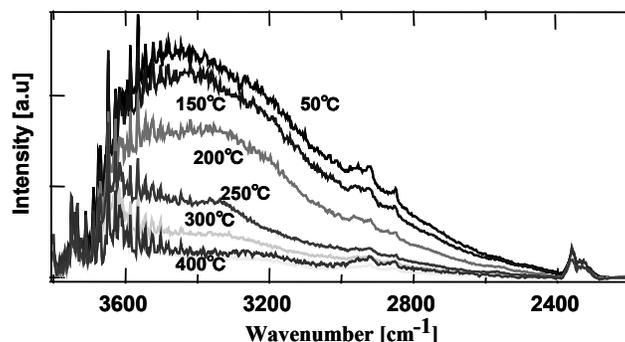


Fig. 3 Temperature-resolved IR spectra show a decrease in the intensities of the OH bands.

## 4. Adsorption performance

### 4.1 Batch operation test

We successfully prepared porous iron oxyhydroxide. We then examined its adsorption capacity from the equilibrium adsorption experiment. The equilibrium amounts of adsorbed phosphoric acid ion were measured under various concentrations of phosphoric acid at 28  $^{\circ}\text{C}$ , and then the adsorption isotherms was constructed. Fig. 4 compares the adsorption isotherms among the prepared porous iron oxyhydroxide, pure FeOOH, the calcined FeOOH from pure FeOOH, and the conventional adsorbent having high capacity<sup>6</sup>. At first, all adsorption isotherms were correlated by the Freundlich equation. The slopes of correlation lines of the four porous iron oxyhydroxide were almost equal, indicating that the affinity of phosphoric

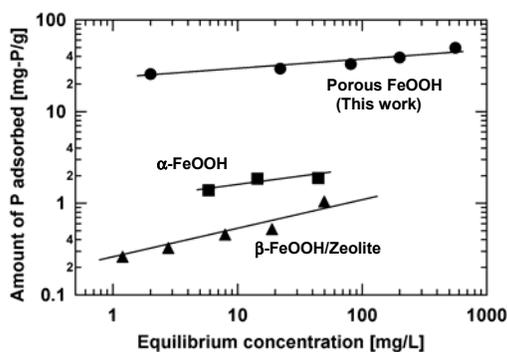


Fig. 4 Adsorption isotherms of various adsorbents for phosphoric acid.

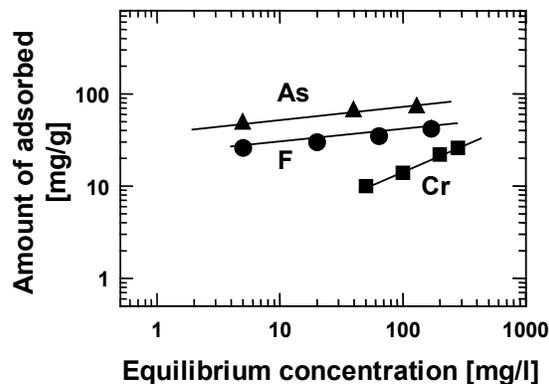


Fig. 5 Adsorption isotherms of various adsorbents for As, F and Cr.

acid ion and adsorption site is the same. This also shows that the data are reasonable; thus, we can estimate the equilibrium capacity in the light of the amount of adsorption site. Comparing each line, the capacity of the developed FeOOH had a high performance for the removal of phosphoric acid ion. The equilibrium amounts of phosphoric acid ion reached to 70 mg/g-FeOOH in the 2 mg/l solution. The value was several tenfold higher than that of pure FeOOH and the conventional adsorbent. This caused by the high surface area and a large amount of hydrogen bond. On the other hand, we also examined the desorption ability of the developed porous iron oxyhydroxide. Almost all the phosphoric acid ions were desorbed under alkali condition. Thus, it was shown that the developed porous iron oxyhydroxide has extremely high performance for the removal of phosphoric acid ion.

Next, we examined the applicability of the developed adsorbent to other ions. Especially, we paid a great attention to the removal of  $F^-$  ion, because  $F^-$  ion is difficult to remove by conventionally used adsorbents. Fig. 5 shows the absorption isotherm of each ions used porous iron oxyhydroxide. It was found that  $F^-$  ion was successfully adsorbed at high capacity. From these results, we can conclude that the developed porous iron oxyhydroxide has extremely high performance for the removal of many kinds of ions such as  $AsO_3^{3-}$ ,  $F^-$ ,  $CrO_4^{2-}$  and  $NO_3^-$  ions.

#### 4.2 The fixed-bed adsorption test

The fixed-bed adsorption test was conducted in 15.7 ml mini-column to examine the validity of the developed adsorbent for practical use. All test work used synthetic solutions of  $PO_4^{3-}$ ,  $F^-$ , and  $NO_3^-$ , flow rate of 5 ml/min (19 SV/h). Fig. 6 shows the break through curves for each ion of  $PO_4^{3-}$ ,  $F^-$ , and  $NO_3^-$  and shows the concentration of  $Cl^-$

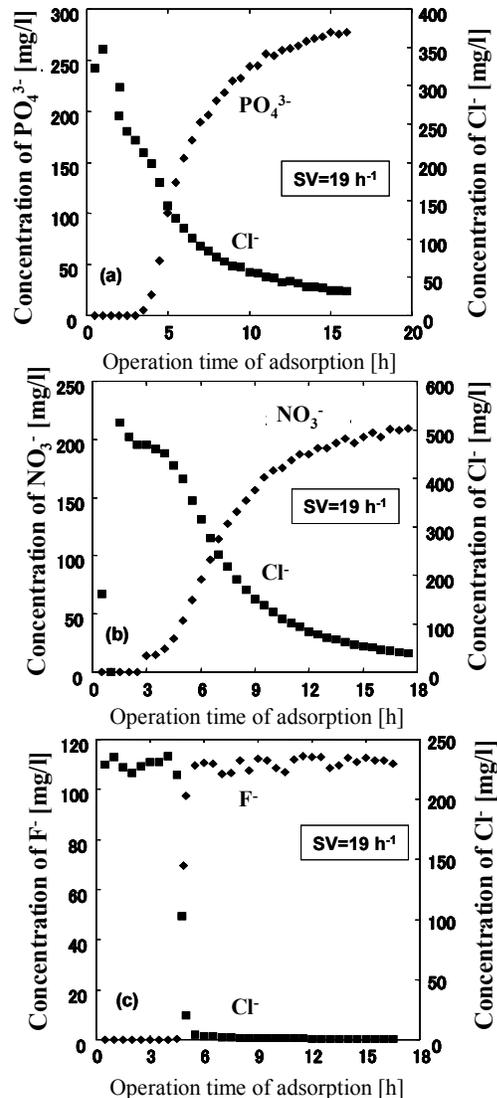


Fig. 6 The break through curves for each ion of  $PO_4^{3-}$ ,  $F^-$ , and  $NO_3^-$ , and shows the concentration of  $Cl^-$ .

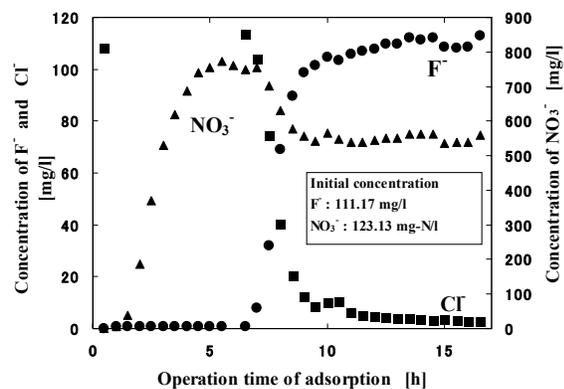


Fig. 7 The break through curves of mixed two ions.

$\text{Cl}^-$ . The adsorption mechanism of porous iron oxyhydroxide was the ion exchange of  $\text{Cl}^-$ .

As mentioned above, many kinds of ions can be treated by the developed adsorbent. To clarify the mechanism to adsorb each ion, we conducted fixed-bed adsorption test for binary ions. Fig. 7 shows the breakthrough curves when treating the aqueous solution containing both  $\text{F}^-$  and  $\text{NO}_3^-$ . At first,  $\text{NO}_3^-$  was broken through at 1 h, then  $\text{F}^-$  was broken through at 6 h. The break through curves of the  $\text{NO}_3^-$  greatly exceeded an initial concentration of feed solution. This indicates that the adsorption site is the same to  $\text{F}^-$  and  $\text{NO}_3^-$  ion. The adsorption site of  $\text{F}^-$  (2.7 Å) and  $\text{NO}_3^-$  (3.6 Å) ion is tunnel site (3.7 Å) of  $\text{Cl}^-$ . However, because the ionic diameter of  $\text{PO}_4^{3-}$  (6 Å) is large, the adsorption site is not a tunnel site, but an amorphous site of large surface area. Thus, it was clarified that the porous iron oxyhydroxide developed is an attractive adsorbent having two different types of adsorption sites. The presence of two sites of different pore sizes suggests the possibility of simultaneous adsorption of binary ions such as the mixture of  $\text{PO}_4^{3-}$  and  $\text{F}^-$ .

## 5. Conclusion

We have developed a new efficient adsorbent of anion based on the control of hydrogen bonding and controlled pore size distribution in FeOOH. The FeOOH precipitated at pH = 4 and dried at 50 °C had a high capacity for the adsorption of  $\text{PO}_4^{3-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{F}^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{NO}_3^-$ . This was caused by high surface area of 260.8  $\text{m}^2/\text{g}$  as well as a large amount of hydrogen bonds. The equilibrium adsorption capacity of the developed FeOOH was several tenfold larger than those of conventional adsorbents. We also found that the adsorption site of tunnel site and OH hydrogen site. On the other hand, the phosphoric acid adsorbed in FeOOH was completely desorbed by adding alkali. Therefore, we can conclude that the proposed adsorbent was effective for the recovery of the  $\text{PO}_4^{3-}$ ,  $\text{AsO}_3^{3-}$ ,  $\text{F}^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{NO}_3^-$  ion in wastewater.

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