



pH-Dependent improvement of pyrophosphate removal on amorphous ferric hydroxide by incorporating Ca^{2+}

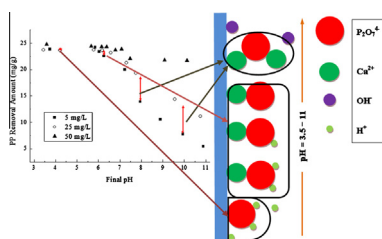
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HIGHLIGHTS

- A pH-dependent improvement of PP removal by Ca^{2+} was observed on $\text{Fe}(\text{OH})_3$.
- The formation of $\equiv\text{FeO}^+$ was responsible for PP removal at $\text{pH} < 7.5$.
- The removal amount of PP was increased at $\text{pH} \geq 7.5$ due to the precipitation of $\text{Ca}_2\text{P}_2\text{O}_7$.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction of calcium and pyrophosphate (PP) on the surface of amorphous ferric hydroxide (AFH) was investigated at $\text{pH} 3.5\text{--}11.0$. Zeta potential analysis of solid samples after PP removal indicates that the removal of PP by Ca^{2+} on the AFH was relative to the interaction of Ca^{2+} with different species of PP. The reduction of PP removal amount with the pH increasing was observed in all cases at the initial PP concentration ranging from 5 to 50 mg/L. The lowest PP removal amount at the initial PP concentration of 25 mg/L was 5.0, 11.1 and 21.7 mg/g with the initial $[\text{Ca}^{2+}]$ of 0, 25 and 50 mg/L, respectively. Moreover, this improvement of the PP removal in the presence of Ca^{2+} was pH-dependent. At $\text{pH} < 7.5$, the formation of surface complex $\equiv\text{FeO}^+$ was supposed, which is expected to absorb and remove PP. This resulted in a Ca/P ratio ranging from 2.5 to 25.6 in the solid sample. In contrast, the precipitation of $\text{Ca}_2\text{P}_2\text{O}_7$ was responsible for the increasing of PP removal amount in basic solution, which resulted in the reduction of Ca/P in the solid sample to 2.0 at $\text{pH} \geq 7.5$. The Ca/P molar ratio higher than 1.0 in $\text{Ca}_2\text{P}_2\text{O}_7$ indicates extra Ca^{2+} adsorbed in the sample during the precipitation. Therefore, our results suggest an improved treatment of PP wastewater through the adsorption on AFH with a small Ca addition at low pH.

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1. Introduction

Iron oxide/hydroxide (such as goethite, ferrihydrite and AFH) is one of efficient adsorbents for the removal of aqueous anions, such as F^- and PO_4^{3-} [1–4]. The adsorption process is relative to the predominant complexes ($\equiv\text{FeOH}_2^+$, $\equiv\text{FeOH}$ and $\equiv\text{FeO}^-$) on the surface of the iron oxide/hydroxide, which leads to different removal efficiency of anions. The distribution of these surface complexes depends on $[\text{H}^+]$. In the case of high $[\text{H}^+]$, both $\equiv\text{FeOH}_2^+$ and $\equiv\text{FeOH}$

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are responsible for the anion adsorption as the reaction between these surface complexes and anions yields $\equiv\text{FeOH}$ -anion and $\equiv\text{FeO}$ -anion complexes [5,6]. In contrast, at $\text{pH} > \sim 6.0$, the deprotonation of $\equiv\text{FeOH}_2^+$ and $\equiv\text{FeOH}$ occurs to form the negatively charged $\equiv\text{FeO}^-$ [7]. This results in the reduction of anions adsorption as the repulsion between $\equiv\text{FeO}^-$ on the surface and anions in the bulk solution. In this case, the presence of binary cation (such as Ca^{2+} and Pb^{2+}) is supposed to improve the removal anions on the surface with negative $\equiv\text{FeO}^-$ as the cation interacts with both $\equiv\text{FeO}^-$ and anions [2,8,9]. Such a ternary system (FeO-cation-anion) could work in solution at $\text{pH} > 6.0\text{--}7.0$.

Among the species of phosphates, pyrophosphate (PP, $\text{P}_2\text{O}_7^{4-}$) has attracted much attention as it leads to eutrophication as plant roots preferentially absorb PP instead of orthophosphate [10–14].

The precipitation of calcium pyrophosphate was the common approach to the removal of aqueous PP [15–17]. On the other hand, PP is a strong ligand bonding to cations at neutral and alkaline pH [16,18–20], which inhibits the precipitation of Ca-PP through forming soluble calcium pyrophosphate complexes such as $\text{CaP}_2\text{O}_7^{2-}$ [15,16]. This inhibition effect depends on the pH and the molar ratio of Ca/PP in the solution. It was revealed that the formation of $\text{CaP}_2\text{O}_7^{2-}$ was improved at high pH and low initial Ca/PP [21,22]. In such case, more Ca addition was suggested to promote the precipitation of Ca-PP for high efficiency of PP removal. However, the addition of excessive Ca^{2+} always results in high pH value of the final solution, which increases the cost of wastewater treatment.

Recently, we reported pyrophosphate (PP, $\text{P}_2\text{O}_7^{4-}$) removal by Fe-based layered double hydroxide (LDH), in which PP was removed through both precipitation and adsorption [23]. These two processes were attributed to the dissolution of LDH that produced Ca^{2+} and amorphous iron hydroxide (AFH) [24]. It was proposed that 27–50% of PP was removed via adsorption on the AFH surface. As the releasing of Ca^{2+} from LDH, the adsorption of PP in our previous work seems related to the formation of FeO-cation-anion ternary system. Compared to the precipitation, this system was supposed to improve the PP removal with lower amount of Ca^{2+} at low pH value (i.e. $\text{pH} > 6.0$). However, the practical effect of Ca^{2+} on the PP removal at various pHs was not clear.

Herein, the objectives of the current study were to investigate the formation of the surface complex of AFH-Ca as well as the interaction of this complex and PP. For this purpose, the following work was carried out: (1) PP and calcium ion adsorption on the AFH surface; (2) the removal of PP by AFH in the presence of Ca^{2+} at various pHs; (3) the interactions between PP and Ca^{2+} on the AFH surface by the zeta potential analysis. We observed the enhancement of PP removal in the presence of Ca^{2+} at various pH values. This result provides the potential approach to the efficient PP removal at relative low pH and less Ca addition, compared to the precipitation of PP.

2. Materials and methods

2.1. Pyrophosphate removal on AFH with or without Ca

Pyrophosphate solutions were prepared from $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (99.0%, AR) with the initial total phosphorus concentrations ([P]) of 5, 10, 25 and 50 mg/L, respectively. The ion strength was controlled by 0.001 M of NaNO_3 . The removal of PP was carried out by adding 1 g/L of AFH in a thermostatic water bath at 25 ± 1 °C with shaking for 24 h. In order to keep the final pH of solution after the experiment in the range of 3.5–11.0, the initial pH was adjusted by 0.1 M NaOH or HNO_3 . The amount of PP removed was expressed by the total phosphorus amount.

The improvement effect of Ca^{2+} was performed in the PP solution of 25 mg/L (as total P concentration, [P]) with initial $[\text{Ca}^{2+}]$ ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.0%, AR)) of 5, 25 and 50 mg/L, respectively. The experiment was conducted in the same way as in the case of Ca^{2+} absence. All experiments were carried out in triplicate with the reproducibility within 5%.

After the experiment, the solution was filtered through 0.22 μm filter membrane. The solid was washed by deionized water and dried at 60 °C for further characterization.

2.2. Ca adsorption on AFH and Ca-pyrophosphate precipitation

The Ca adsorption on AFH was carried out in the similar way above in which PP was absent. Moreover, the precipitation of Ca-PP was conducted in the PP solution of 25 mg/L (as total P

concentration) at various initial Ca concentrations. These two processes above are denoted as Ca-AFH and Ca-PP precipitation, respectively, to distinguish the process of PP removal on AFH with Ca^{2+} (Ca-PP-AFH).

2.3. Characterization

The pH of all solution was read by a Mettler Toledo pH meter (FE20) with a combined glass electrode (LE438). The inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, Leeman Co.) was used to determine Ca concentration. The total P concentration was determined by spectrophotometric method (4800UV/VIS, 700 nm) after the digestion of liquid sample at 120 °C in the autoclave for 30 min with 5% (w/w) $\text{K}_2\text{S}_2\text{O}_8$.

Zeta potential was measured on Zetasizer (Malvern 3000HSA Instruments) by dispersing the sample in deionized water by 24 h agitation in water bath at 25 ± 1 °C.

X-ray Photoelectron Spectroscopy (XPS, Krato Axis ULTRA, Physical electronics) was performed with monochromatic Al K α radiation under constant neutralization using an electron flood gun with Ar ion energy at 10 eV. The carbon standard with the binding energy of C (1 s) at 284.6 eV was used to calibrate the binding energy of instrument.

3. Results and discussion

3.1. Characterization of surface property

The surface charge of solid samples was characterized by zeta potential (ZP). Fig. 1 shows that ZP of AFH decreased from 38.0 to -47 mV with pH increasing from 3.0 to 11.0, in which process the pH at zero charge point was around 7.0. This demonstrates that $[\text{H}^+]$ reduction allowed the exposure of negative $\equiv\text{FeO}^-$. With Ca^{2+} adsorbed, the ZP of AFH-Ca kept positive regardless of pH increasing, indicating that $\equiv\text{FeOCa}^+$ surface complex was predominant on the AFH surface as expected [8,9].

Moreover, ZP of those samples in the presence of PP (25 mg/L) was all negative and decreased with pH increasing. This represents that the amount of PP anions adsorbed was much more than that of positive charge on the AFH surface. Due to the multi-step dissociation of $\text{H}_4\text{P}_2\text{O}_7$ [25], the decreasing of ZP was contributed to the negative charge of PP anions at various pH. For instance, the dominant $\text{HP}_2\text{O}_7^{3-}$ at $\text{pH} > 6.7$ gives more negative ZP than $\text{H}_2\text{P}_2\text{O}_7^{2-}$ at $\text{pH} < 6.7$. As a result, the reduction of the PP removal amount on

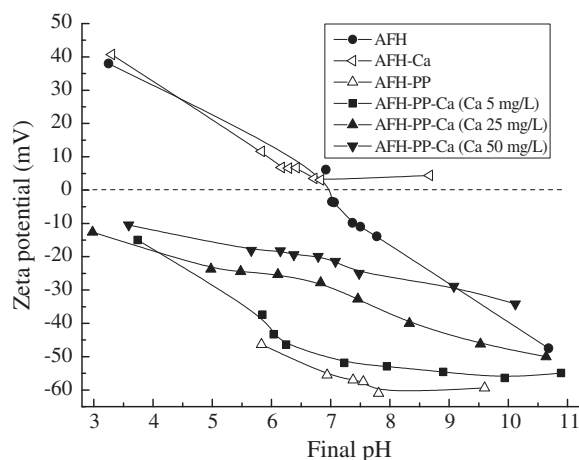


Fig. 1. Zeta potential of AFH sample as a function of pH during the removal of pyrophosphate (25 mg/L) on AFH with and without Ca^{2+} addition.

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