Effect of pH and aging temperature on the phosphorus removal properties of layered hydroxide synthesized from zinc acetate

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ABSTRACT
Zinc hydroxide acetate (ZHA) is a promising material for anion exchange applications because it has a layered structure with intercalating $\text{CH}_3\text{COO}^-$ and $\text{H}_2\text{O}$. ZHA can be synthesized through a direct precipitation method by adding sodium hydroxide solution to a $\text{Zn(OOCCH}_3)_2$ solution. In this study, ZHAs were synthesized under various conditions and tested as phosphorous removal agents. The ZHA precipitates were obtained at pH 6, 7, and 9. They were then aged at 25°C, 60°C, 90°C, and 120°C under hydrothermal conditions. At pH 6, nearly pure single-phase ZHAs were obtained regardless of the aging temperature. On the other hand, most of the ZHAs that were prepared at higher pH and aged at higher temperature were transformed to $\text{ZnO}$. For the phosphorous removal experiments, the single-phase ZHA precipitates removed approximately 99% of the phosphate ions in a 100 mg L$^{-1}$ phosphorous solution, and the phosphorous removal efficiency decreased with increasing amounts of $\text{ZnO}$. Therefore, ZHAs that were prepared at lower pH and aged at lower temperatures contained little to no $\text{ZnO}$, thereby showing high phosphorous removal capabilities.

1. Introduction
The eutrophication of lakes and inner bays is a worldwide problem that causes high phytoplankton production with severe implications on both ecological health and drinking water quality. The main cause of this problem is an excessive loading of nutrients into the lakes and bays from artificially influenced sources. In particular, phosphate (P) is considered one of the key nutrients for the phytoplankton plague; thus, a reduction of P input is essential to improve water quality and ecological health [1–3]. Because of eutrophication concerns caused by wastewater discharge, considerable effort is now being devoted toward the advanced P removal at national scale [4]. Recently, P removal was achieved through an anoxic/oxic process (A/O process) and a chemical precipitation process [5,6]. The A/O process is one of the activated sludge processes, which alternately repeats aerobic agitation for biochemical oxygen demand oxidation and nitrification, and anaerobic agitation for denitrification. The A/O process utilizes advantages from both biological and chemical methods for the removal of phosphorus. However, the treatment and disposal of excess sludge accounts for approximately 50–60% of the total cost of wastewater treatment. Conventional disposal methods, such as landfilling or ocean dumping, may cause secondary pollution problems and are strictly regulated in many countries [5–7]. For chemical precipitation process, the high sludge production and the associated disposal problems are also common concerns [8]. Alternatively, adsorption/ion exchange methods are promising, because they are simple economical, and minimize the disposal problem associated with sludge production. Furthermore, these methods would be the most suitable for small water supplies contaminated by P because of its simplicity, effectiveness, P selectivity in the presence other ions, easy recovery of P, and relatively low cost [9,10].

Layered zinc compounds (formula: $\text{Zn}_x(\text{OH})_{10-x}(\text{A}^{3+})_{y/m}\cdot n\text{H}_2\text{O}$) belong to the family of metal hydroxide salts (MHS) with the general formula: $\text{M}_n(\text{OH})_b(\text{A}^{3+})_{(2a-b)/c}\cdot n\text{H}_2\text{O}$, where $\text{M} = \text{Zn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+}$, etc. Structurally, MHS consist of positively charged brucite-like layers of metal hydroxides that require the presence of interlayer anions to maintain the overall charge neutrality. These interlayer anions can be $\text{Cl}^-$, $\text{CO}_3^{2-}$, $\text{CH}_3\text{COO}^-$, and $\text{SO}_4^{2-}$. MHS with layered structures have been widely studied for ion exchange applications in catalysis, bio-sensing, drug delivery, nanofillers, UV protection, and mixed metal oxides precursors. Layered zinc hydroxides are promising materials for application in anion exchange and can be synthesized by direct precipitation methods, through adding sodium hydroxide to aqueous solutions of zinc salts [11–13]. Therefore, layered zinc hydroxides are expected to function as ion exchange agents that can effectively remove P from wastewater [14–16].

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In this study, to develop hydroxides of zinc hydroxide that have high phosphorus removal capacity, layered zinc hydroxide acetate (ZHA) was synthesized by direct precipitation by adding sodium hydroxide solution to \( \text{Zn(OCOCH}_3\text{)}_2 \) solutions. ZHA precipitates were obtained at various pH and aged at various temperatures under hydrothermal conditions. The resulting ZHA precipitates were physically characterized and analyzed for phosphorous removal capacity and the phosphorous removal mechanism.

\[
P \text{removal ratio} (%) = \left( \frac{P \text{ residual concentration (mgL}^{-1})}{P \text{ initial concentration (mgL}^{-1})} \right) \times 100
\]  

\[(1)\]

2. Materials and methods

\( \text{Zn(OCOCH}_3\text{)}_2\cdot2\text{H}_2\text{O} \) (Guaranteed Reagent, Nacalai Tesque, Inc.) and \( \text{NaOH} \) (Guaranteed Reagent, Nacalai Tesque, Inc.) were separately dissolved in distilled water to prepare 1 mol \( \text{L}^{-1} \) solutions.

The 1 mol \( \text{L}^{-1} \) \( \text{NaOH} \) solution was added with a burette, to the 100 mL \( \text{Zn(OCOCH}_3\text{)}_2 \) solution until the prescribed pH (6, 7, and 9) were indicated under \( \text{N}_2 \) bubbling. The precipitate-containing solutions were enclosed in Teflon-lined autoclaves and aged at room temperature (25°C), 60°C, 90°C, and 120°C for 24 h. In the preliminary experiment, when the precipitate was aged for 24 h or more, ZHA easily transformed to zinc oxide, therefore the aging time was fixed to 24 h. After aging, Teflon-lined autoclaves were cooled for 24 h. The precipitates were centrifuged at 10,000 rpm for 20 min, decanted, and washed with distilled water. This procedure was repeated three times sequentially. The final products used as the ZHA samples were obtained as powders after freeze-drying.

The crystalline phases of the ZHAs were identified using powder X-ray diffraction analysis (XRD) (RINT2000, Rigaku Co.) with the following parameters: \( \text{Cu Kα radiation, tube power 1.6 kW (40 kV at 40 mA), scan speed 4° min}^{-1} \), and scan angle 5°–65°. The morphologies of the ZHA precipitates were investigated with a field emission scanning electron microscope (S-800 Hitachi, LTD). An accelerating voltage of 20 kV was used with a 6–20-μm aperture. The specific surface area of the ZHA precipitates was evaluated using a nitrogen gas adsorption method (Gemini 2375, Shimadzu Co.). Thermogravimetric-differential thermal analyses (TG-DTA) were conducted using a Thermoplus Tg8120 (Rigaku Co.) instrument with a heating rate of 10°C min\(^{-1}\) in an air atmosphere.

\( \text{KH}_2\text{PO}_4 \) (0.4934, Guaranteed Reagent, Nacalai Tesque, Inc.) was dissolved in 1000 mL distilled water to obtain a 100 mg \( \text{L}^{-1} \) solution of \( P \) (\( P \) solution). ZHA samples (0.2 g each) were immersed and stirred in 25 mL \( P \) solution with a magnetic stirrer for 10 min. After stirring, the filtrates and ZHA sample powders were separated by filtration. The residual \( P \) concentration was measured with an inductively coupled plasma spectroscope (ICPE-9800, Shimadzu Co.), and the phosphorus removal ratios were calculated using Equation (1):

Fourier-transform infrared spectroscopy measurements (FTIR) measurements before and after the \( P \) removal experiment with 100 mg \( \text{L}^{-1} \) and 1000 mg \( \text{L}^{-1} \) \( P \) solutions were carried out with ZHA powders obtained at pH 6 and 7 and aged at 60°C using an AVATR370DTGS (Thermo Fisher Scientific, Inc.) spectrometer.

3. Results and discussions

Figure 1 shows the powder XRD patterns of the precipitates obtained at pH 6, 7, and 9 and aged at various temperatures. The diffraction peaks, except for these of \( \text{ZnO} \), were assigned to \( \text{Zn(OH)}_8\) (\( \text{OCOCH}_3\))\(^2\)\( \text{H}_2\text{O} \) (ZHA). The diffraction peak marked with ▼ was assigned to ZHA containing a different number of crystallized water molecules, but has not been clearly identified. As shown in Figure 1(a), \( \text{ZnO} \) diffraction peaks were rarely observed for the precipitates obtained at pH 6. On the other hand, sharp diffraction peaks from \( \text{ZnO} \) appeared in the patterns of ZHA samples obtained at pH 7 and 9 [17–19]. A portion of the precipitates prepared at pH 7 and aged at over 90°C transformed to \( \text{ZnO} \). However, the precipitates obtained at pH 9 already began transformation to \( \text{ZnO} \) upon aging at 60°C. Furthermore, the amount of \( \text{ZnO} \) increased with increasing aging temperature at pH 9.

Figure 2 shows the SEM images for the ZHAs obtained at pH 6 (a), 7 (b), and 9 (c); aged at 25°C (1), 60°C (2), 90°C (3), and 120°C (4). For the precipitates obtained at pH 6, thin plate-like crystals overlapped with each other, and the morphology of the crystals changed from thin plate to rectangular columnar as the aging temperatures increased. For the pH 7 and 9 ZHAs, the morphologies of the precipitates aged at 25°C were also thin plate-like crystals, similar to the precipitates obtained at pH 6. However, the morphologies changed to hexagonal...
Figure 1. X-ray diffraction patterns of ZHAs synthesized from Zn(OCOCH$_3$)$_2$ solution obtained at various pH: (a) pH6, (b) pH7, (c) pH9 and aged at 25°C, 60°C, 90°C, 120°C, respectively.

Figure 2. SEM images of the ZHAs synthesized from Zn(OCOCH$_3$)$_2$ solution obtained at various pH: (a) pH6, (b) pH7, (c) pH9 and aged at 25°C, 60°C, 90°C, 120°C, respectively.
columnar, as shown in Figure 2 (b3), (b4), (c3), and (c4) with increasing aging temperature. These hexagonal columnar crystals were deduced to be ZnO by contrasting the SEM observations and XRD patterns of precipitates obtained at pH 7 and pH 9 (Figure 1).

The pyrolysis of ZHA occurs under the hydrothermal conditions and the nucleation of ZnO occurs on the outer sides of the hexagonal column [18–20]. However, although ZnO peaks were observed in the XRD pattern of the precipitates obtained at pH9 and aged at 60°C, the hexagonal columnar crystals of ZnO were not seen in Figure 2. This suggests that the amount of ZnO crystals present in this precipitate were lower and the crystal growth of ZnO was imperfectly; thus, the ZnO particles were not identified to be the hexagonal column crystals.

The pyrolysis processes of ZHAs were also examined by TG-DTA and summarized in Figure 3. Considering the DTA curves, the two endothermic peaks at 90–150°C suggest that the water molecules physically adsorbed to ZHA and the intercalating crystal water molecules desorbed [21]. The endothermic process at 60–90°C is associated with a 7–8% weight loss and the process at 90–150°C is associated with an approximately 10% weight loss. This combined weight loss of about 17–18% is close to the theoretical weight loss (17.5%) ascribed to the release of six water molecules from the formula unit and the two associated reactions can be described by reaction formulae (2) and (3).

![Figure 3. TG-DTA curves of the ZHAs synthesized from Zn(OCOCH₃)₂ solution obtained at various pH: (a) pH6, (b) pH7, (c) pH9 and aged at various temperature.](image-url)
Zn$_5$(OH)$_8$(OCOCH$_3$)$_2$·2H$_2$O
→ Zn$_5$(OH)$_8$(OCOCH$_3$)$_2$ + 2H$_2$O \hspace{1cm} (2)

Zn$_5$(OH)$_8$(OCOCH$_3$)$_2$
→ 4ZnO + Zn(OCOCH$_3$)$_2$ + 4H$_2$O \hspace{1cm} (3)

The evolution of Zn(OCOCH$_3$)$_2$ occurs at over 147°C, but the processes involved after reaction (3) are not straightforward. The decomposition of Zn(OCOCH$_3$)$_2$ upon heating is sensitive to the humidity of the surrounding atmosphere.

In this study, the weight loss observed by TG between 147°C and 200°C can be mainly assigned to processes that form ZnO through reaction (4). However, in highly humid atmospheres, Zn(OCOCH$_3$)$_2$ can react with H$_2$O to form ZnO and acetic acid, as shown in reaction formula (5).

\[ \text{Zn(OCOCH}_3\text{)}_2 \rightarrow \text{ZnO} + (\text{CH}_3\text{CO})_2\text{O} \quad (4) \]

\[ \text{Zn(OCOCH}_3\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{CH}_3\text{COOH} \quad (5) \]

Zn(OCOCH$_3$)$_2$ can also be converted to Zn$_4$O(OCCOCH$_3$)$_6$ and acetone at over 250°C in dry atmospheres, and Zn$_4$O(OCCOCH$_3$)$_6$ may subsequently decompose to ZnO and acetate according to reaction (6).

\[ \text{Zn}_4\text{O(OCCOCH}_3\text{)}_6 \rightarrow 4\text{ZnO} + 3\text{CH}_3\text{COCH}_3 + 3\text{CO}_2 \quad (6) \]

In this study, there was a further approximately 3% weight loss between 250°C and 400°C. This was assigned to the release of volatile materials from the zinc-bearing materials [22–24]. The ZHAs, including ZnO, such as the powders obtained at pH 9 aged at 90°C and 120°C, showed no or very small endothermic peaks. For the TG curves, the ZHAs that contained a large amount of ZnO showed much lower weight loss than the theoretical weight loss value (about 38%) [15].

The P removal ratios of the ZHAs were shown in Figure 4. The ZHAs obtained at pH 6 showed approximately 99% P removal, regardless of the aging temperature. The P removal ratios for the ZHAs at pH 7 aged at 25°C and 60°C were over 99%. However, upon aging at over 90°C, this decreased with increasing aging temperature. The P removal ratio of ZHA obtained at pH 9 started to decrease on aging at 60°C. Taking the XRD and TG-DTA results into account, the ZHAs containing large amounts of ZnO showed the lower P removal ratios, but the removed P amount is not small. We consider that hydroxyls of the Zn(OH)$_2$ produced on ZnO surface by hydration in water formed hydrogen bonds to P ions so that the ZHAs containing large amount of the ZnO adsorbed about half amount of phosphate ions than the pure ZHA sample. As observed above, highly pure ZHAs can remove approximately 99% of the phosphate ions from a 100 mg L$^{-1}$ P solution.

Figure 5 shows the FT-IR spectra of ZHAs before and after the P removal experiments with 100 and 1000 mg L$^{-1}$ P solutions. For each spectrum, three adsorption bands, due to the acetate group, were observed in the 1600–1300 cm$^{-1}$ range, the band at 1548 cm$^{-1}$ was assigned to the COO$^-$ antisymmetric stretching, and the band at 1392 cm$^{-1}$ was assigned to the COO$^-$ symmetric stretching [19,25–27]. The bands due to the deformation mode of CH$_3$ appeared at 1336 cm$^{-1}$ [17]. After immersing the ZHA sample synthesized at pH 7 and aged at 60°C into the 100 mg L$^{-1}$ P solution, the characteristic bands for P–OH bond appeared at 1016 and 937 cm$^{-1}$. After immersing into the 1000 mg L$^{-1}$ P solution, three bands at 1021, 1002, and 937 cm$^{-1}$ appeared. These bands are also attributed to the P–OH bond [28]. Furthermore, the band at 1108 cm$^{-1}$ was attributed to the P=O stretching vibration. For FT-IR measurements, the ZHA powders were washed with distilled water and dried after immersing into the P solutions; thus, the above FT-IR measurements suggest that the phosphate ions are absorbed between the layers through an anion exchange mechanism, not through surface adhesion. For the 1000 mg L$^{-1}$ P solution, compared to 100 mg L$^{-1}$ P solution, the adsorption bands due to the phosphate ions were stronger, likely due to the loss of more acetate ions. If all acetate ions between layers are exchanged with phosphorus ions, the ZHAs can remove phosphorus ions up to 804 mg L$^{-1}$ P theoretically. In this study, we use 100 mg L$^{-1}$ P solution. The ZHAs after the phosphorus removal experiment have not only phosphorus ions but acetate ions between the layers. Thus, the adsorption bands assigned to COO$^-$ appeared after the
phosphorus removal experiment. In respect of 1000 mg L$^{-1}$ P solution, the bands due to COO$^-$ appeared. The acetate ions in the inner layers are difficult to be exchanged for phosphorus ions physically, so the COO$^-$ bands due to acetate ions in the inner layers remain in the FT-IR spectrum. These results indicate that more phosphate ions are intercalated between the layers on immersing the ZHA in 1000 mg L$^{-1}$ P solution. Furthermore, from the preliminary experiment, there is no change in the XRD patterns for the ZHAs after the P removal experiment compared to before. The SEM images and TG-DTA curves also remained unchanged after the P removal experiment.

4. Conclusions

This work describes a novel method to efficiently remove phosphate from aqueous solutions using layered zinc hydroxides, a promising material for improving water quality. The phosphorus removal capacity of the ZHA synthesized from Zn (OCOCH$_3$)$_2$ solutions using direct precipitation under various conditions was investigated.

At pH 6, nearly single-phase ZHAs were obtained regardless of the aging temperature. The ZHAs obtained at pH 7 and aged at 25°C and 60°C mainly consisted of ZHA; however, ZnO was formed when the precipitates were aged at over 90°C. On the other hand, the ZHAs obtained at pH 9 started to transform to ZnO on aging at 60°C, and most of the ZHAs were transformed to ZnO at over 90°C. These results indicate that the production ratio of ZnO increases with increasing pH and aging temperature.

For the phosphorus removal experiment, highly pure ZHA could remove approximately 99% of the phosphate ions in a 100 mg L$^{-1}$ phosphorus solution. On the other hand, ZHAs containing large amounts of ZnO showed lower phosphorus removal capacities. Therefore, ZHAs prepared at lower pH and aged at lower temperatures are of high purity and show higher phosphorus removal efficiency.

Disclosure statement

No potential conflict of interest was reported by the authors.

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