



Influence of calcination on the adsorptive removal of phosphate by Zn–Al layered double hydroxides from excess sludge liquor

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ABSTRACT

The influence of calcination of Zn–Al layered double hydroxides (LDHs) on their phosphate adsorption capacity was studied in order to improve phosphorus removal from an excess sludge liquor. Powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), thermogravimetry-differential scanning calorimetry (TG–DSC) and nitrogen adsorption–desorption were employed to characterize the raw Zn–Al and the calcined products. The results reveal that the Zn–Al LDHs evolved to a phase of mixed metal oxides with the calcination temperature increasing to 300 °C and finally to spinel ZnAl₂O₄ at 600 °C. When the Zn–Al was calcined at 300 °C, the interlayer carbonate ions were removed and the greatest BET surface area of 81.20 m²/g was achieved. The tested phosphate adsorption capacities of the raw and calcined Zn–Al were closely related to the evolution of physicochemical properties of the LDHs during the calcination. The Zn–Al-300 (Zn–Al LDHs calcined at 300 °C) exhibited the highest P uptake of 41.26 mg P/g in 24 h. The phosphate adsorption by the raw Zn–Al and the Zn–Al-300 both follows a pseudo-second-order kinetic model; the adsorption isotherms show a good fit with a Langmuir-type equation.

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1. Introduction

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds or anionic clays, have attracted considerable attention in recent years due to their application as precursors for heterogeneous catalysts [1], electrode surface modifiers [2], anion adsorbents [3–5] and new functional materials [6]. Their general formula can be expressed as $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} \cdot yH_2O$, where M^{2+} and M^{3+} represent di- and tri-valent metal cations, A^{n-} is the intercalated anion and x normally ranges from 0.17 to 0.33 [7]. The high charge density of the sheets from the isomorphous substitution of M^{2+} by M^{3+} and the exchangeability of interlayer anions make LDHs excellent and cheap adsorbents for removing anion pollutants from aqueous environments [3–5].

Phosphate removal from waste streams has been extensively studied and put into practice since people realized that the excess input of phosphorus would accelerate eutrophication of the receiving waters [8,9]. The widely applied methods include chemical precipitation and crystallization [10,11], enhanced biological phosphorus removal (EBPR) processes [12], constructed wetlands [13] and adsorption [14–16]. Adsorptive removal of phosphorus from wastewaters is a cost-effective and environment-friendly technol-

ogy, by which the chemical sludge production is small and the adsorbed P can be easily recovered. The main challenge for this method is to find or develop a material with a high adsorption capability. Researchers have investigated many different adsorbents, such as industrial byproducts [15], minerals [17], metal oxides/hydroxides [18], ion exchange resins [19], etc.

LDHs have been studied in recent years to remove phosphorus from simple electrolytes [20–24], seawater [25], drain effluents [16], etc. The phosphate adsorption capacity of LDHs varied significantly due to their great diversity in metal precursors, intercalated anions, and preparation methods [21,25,26]. A great number of studies were performed to explore the influencing factors of the adsorption capability of LDHs [27]. Many of the authors reported that calcination markedly improved the anions uptake by LDHs [4,5,25]. The improvement was extensively explained by the rehydration of the calcined LDHs in water, “memory effect”, and the increased specific surface area after calcination. However, the relationship among the treatment conditions, the structure of resulted LDHs and their adsorptive properties of anions, especially phosphate, has not been addressed in detail as needed. The mechanisms of phosphate adsorption onto calcined LDHs, therefore, are still not clear.

In the present work, we examined the phosphate adsorption by a raw Zn–Al and the Zn–Als calcined at different temperatures. The structural evolution of the LDHs during the calcination was studied to help explain the variation of phosphate adsorption capacity of

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the resulted Zn–Al and subsequently to explore the mechanisms of the phosphate uptake. Sludge liquor from a municipal wastewater treatment was used as the P-rich stream due to its potential for large-scale P recovery in the future.

2. Materials and methods

2.1. Preparation of raw and calcined Zn–Al LDHs

Zn–Al layered double hydroxides were synthesized by coprecipitation method. A 200-mL solution of mixed chloride containing 0.5 M Zn²⁺ and 0.25 M Al³⁺ was prepared in a 500-mL beaker. Under magnetic stirring at 80 °C in a high-purity N₂ atmosphere, the pH of the mixture was adjusted to 9.0 ± 0.2 by dropwise adding 20% NaOH. The resulted slurry was aged at the same temperature for 18 h, then filtered and washed thoroughly with deionized water. The precipitate was dried at 80 °C overnight and ground to ~100-μm particles. The obtained Zn–Al LDHs were calcined at different temperatures from 150 to 600 °C in high-purity nitrogen for 4 h, denoted as Zn–Al-*T*, where *T* stands for the calcination temperature.

2.2. Adsorbent characterization

Chemical analyses for Zn and Al in the synthesized Zn–Al LDHs were conducted by an inductively coupled plasma optical emission spectrometry (ICP-OES) system (Optima 5300DV, PerkinElmer) after dissolving the samples in 0.5 M HCl solutions. Thermogravimetry-differential scanning calorimetry (TG-DSC) measurements of the LDHs were carried out on a NETZSCH STA449C instrument. 4.675 mg of the raw Zn–Al was heated up to 1000 °C (10 °C/min) in an Ar atmosphere at a flow rate of 30 mL/min. Powder X-ray diffraction (XRD) analyses of the samples were conducted using a Rigaku X-ray diffractometer (D/Max-RB) with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 45 mA. XRD patterns were collected over a 2θ from 10° to 90° with a scan rate of 5° (2θ)/min. Fourier-transform infrared (FTIR) spectra were taken using a PerkinElmer Spectrum one FTIR in the wavenumber range of 400–4000 cm⁻¹. The samples in powder form were mixed with dried KBr powders at 1/99 ratio and pressed into specimens for spectra collection. The surface morphology of the Zn–Al LDHs was identified by scanning electron microscopy (HITACHI S4700). Samples were coated with gold (~20 nm) before observation. The surface area, total pore volume and pore size were measured by the N₂ adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) method on an ASAP 2020 instrument (Micromeritics) after the powder sample was out-gassed overnight under vacuum (10⁻⁵ Torr) at 80 °C.

2.3. Phosphate adsorption onto Zn–Al LDHs

The P adsorption capacities of the Zn–Al LDHs and the calcined products were estimated by batch assays in a thermostatic shaker at room temperature. 0.02 g of sample was added into 50 mL of sludge liquor in 117-mL serum bottles. The sludge liquor was from Taiping municipal wastewater treatment plant in Harbin, China (the water composition shown in Table 1). After 24 h of contact (almost equilibrate according to our previous study), the supernatant was filtered through a 0.45- μ m membrane and the residual P concentration was measured by the molybdate blue method [28]. LDHs-free controls were performed to observe the non-adsorption degradation of phosphate in the sludge liquor. Kinetics of P adsorption was investigated using the raw Zn–Al and the Zn–Al-300 as the adsorbents. 0.1 g of LDHs sample was added to 250 mL of sludge liquor, and the soluble phosphate concentration was monitored for 72 h. Adsorption isotherms were obtained by mixing known amounts of adsorbents with 250 mL of sludge liquor and testing the equilibrium phosphate concentrations after 72 h of contact at

Table 1
Characteristics of the sludge liquor.

Parameter	Sludge filtrate
pH	6.80 ± 0.00
SS, mg/L	3.82 ± 0.00
COD, mg/L	514.62 ± 6.24
PO ₄ ³⁻ , mg-P/L	20.00 ± 4.10
NO ₂ ⁻ , mg/L	ND ^a
NO ₃ ⁻ , mg/L	ND ^a
SO ₄ ²⁻ , mg/L	112.53 ± 0.42
Cl ⁻ , mg/L	81.44 ± 0.50
NH ₄ ⁺ , mg/L	84.34 ± 4.82
Na ⁺ , mg/L	83.65 ± 0.19
K ⁺ , mg/L	44.66 ± 0.05
Al ³⁺ , mg/L	0.06 ± 0.00
Ca ²⁺ , mg/L	105.80 ± 0.60
Cu ²⁺ , mg/L	ND ^a
Fe, mg/L	0.24 ± 0.00
Mg ²⁺ , mg/L	27.22 ± 0.09
Mn ²⁺ , mg/L	1.34 ± 0.01
Zn ²⁺ , mg/L	0.01 ± 0.00

^a ND: non-detectable.

room temperature. All the adsorption assays were performed in triplicate.

3. Results and discussion

3.1. Characterization of the Zn–Al and the calcined products

Zn–Al layered double hydroxides were synthesized as illustrated by XRD patterns with the characteristic reflection peaks for (0 0 3) and (0 0 6) planes (Fig. 1). The pattern could be indexed to a hexagonal cell ($a = 3.081 \text{ \AA}$ and $c = 23.405 \text{ \AA}$). The tested Zn/Al molar ratio (1.94:0.97) corresponded approximately to that in the starting metal solution, indicating an efficiently coprecipitation. Additional

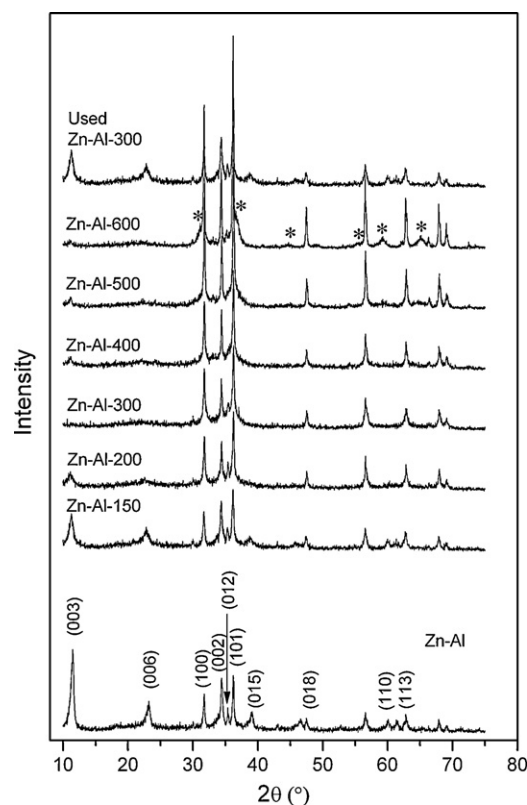


Fig. 1. X-ray diffractograms of the raw Zn–Al and the calcined Zn–Al samples at different temperatures. (*) ZnAl₂O₄.

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