



Performance of layered double hydroxides intercalated with acetate as biodenitrification carbon source: The effects of metal ions and particle size

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ABSTRACT

In situ synthesis of layered double hydroxides (LDHs) is an effective way to extract short chain fatty acids (SCFAs) from anaerobic fermentation liquid to be used as carbon source for biodenitrification, but the slow release performance need to be improved. Three layered double hydroxides with different metal cations (Mg-Al, Ni-Al, Ni-Fe) intercalated with acetate (Ac) were successfully prepared in the present study. The release rates decreased in the order of MgAl-LDH > NiAl-LDH > NiFe-LDH, meaning that NiFe-LDH-Ac showed the best slow release performance. The release rate of LDHs decreased greatly along with the increase of particle size. Batch denitrification tests showed that the carbon source utilization efficiency of NiFe-LDH-Ac was 79.9%, which was much higher than that of CH₃COONa (48.8%) as control. These results indicate that NiFe-LDH-Ac could be successfully employed as slow release carbon source for biodenitrification.

1. Introduction

Biological heterotrophic denitrification involves the sequential microbial reduction of nitrate or nitrite to nitrogen gas, which requires an available carbon source as the terminal electron acceptor (Rezania et al., 2007; Sage et al., 2006). Many researches have proved that fermentative short-chain fatty acids (SCFAs) via organic wastes fermentation process, as a type of environment-friendly and economical production, are a promising and effective external carbon source to enhance biological nitrogen removal rate (Cao et al., 2013; Kim et al., 2016; Liu et al., 2016). But there are heavy metals and a large amount of NH₄⁺-N in anaerobic fermentation liquid of organic wastes, which could cause toxicity to microorganism and enhance the nitrogen load of the system (Jiang et al., 2013; Nwoba et al., 2017). At the same time, the dosage of this kind of carbon source is hard to be controlled accurately (Boley et al., 2000; Xu et al., 2011).

In Jiang's previous study, SCFAs were successfully extracted from anaerobic fermentation liquid via in situ synthesis of layered double hydroxides (LDHs). The synthesized LDHs was then used as a slow release carbon source of biodenitrification, being free of metal ions (Jiang et al., 2017). However, slow release performance determines the utilization efficiency of carbon sources and nitrogen removal efficiency. If it is possible to achieve controlled release of carbon source, utilization

efficiency of carbon sources and nitrogen removal efficiency may be improved.

Controlled release is closely related to particle size of LDHs and metal type of laminates (Rives et al., 2013; Saha et al., 2017). It has been reported that larger particles appear much slower release properties than small ones (Zhang et al., 2014). In addition, it was found that different metal cations had a great influence on release performances (Williams and O'Hare, 2006). This was also proved by Ding et al, founding that the poverty of LDHs was affected by different metals laminates because of different charge densities, resulting in different attractive forces between hosts and guests of LDHs (Ding et al., 2010). In general, the electrostatic attraction between positively charged metal hydroxide layer and the negatively charged host is enhanced with the increase of the metal charge density and electronegativity of interlayer anions (Aisawa et al., 2001; Leroux and Taviot-Gu  ho, 2005). Differently, strong or weak hydrogen bonds between the metal hydroxide layer and anions guest (with O atoms), may be formed for different metal layer (Manoara and Kamath, 2010). Moreover, in the release process, a small amount of metal will be released, different metals may cause favorable or unfavorable influence on microbes (Imran et al., 2016). Many researchers have indicated that trace metals can effect on microbial respiration, biomass, and microbial community structure (Magalh  es et al., 2007). The effect of trace metals (Fe, Mn, Cu, Zn and

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Mo) on the denitrification activity has been explored, and found that iron had a great effect to the increase of denitrification rate (Labbe et al., 2003). Ni-containing nanoparticles has been used for denitrification, resulting in a high nitrogen removal efficiency (An et al., 2010). Mg and Al are the most commonly used divalent and trivalent metal ions for the synthesis of LDHs; Ni and Fe could give a better release performance of LDH-Ac, and could promote denitrification activity and denitrification rate (Labbe et al., 2003). Thus, LDHs of different metal laminates (Mg-Al, Ni-Al, Ni-Fe) and particle sizes with acetate (Ac) will be synthesized and eventually used as a carbon source of slow release for denitrification.

Some studies have revealed that, among SCFAs, the acetic acid showed a higher denitrification rate, since acetic acid has a simple biodegradation pathway, it could be directly used by the β -oxidation process forming acetyl-CoA in the denitrifying bacteria system (Elefsiniotis and Li, 2006; Xu, 1996). In the alkaline anaerobic fermentation process, acetic acid was the most dominant product with a fraction of 50–67% (Duan et al., 2016; Yuan et al., 2006). So acetate anion has been chosen as interlayer anions of LDHs (LDH-Ac). The objectives of this study were: 1) to examine the feasibility of MgAl-LDH-Ac NiAl-LDH-Ac and NiFe-LDH-Ac synthesis by coprecipitation method; 2) to evaluate the slow release performance of LDH-Ac with different metal ions and particle sizes; 3) to investigate the nitrogen removal performance and utilization efficiency of carbon source with NiFe-LDH as an external carbon source.

2. Materials and methods

2.1. Preparation of LDH-Ac

MgAl-LDH, NiAl-LDH and NiFe-LDH were synthesized by co-precipitation method. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water with molar ratio of 3:1 ($\text{Mg}^{2+}/\text{Al}^{3+}$, $\text{Ni}^{2+}/\text{Al}^{3+}$ and $\text{Ni}^{2+}/\text{Fe}^{3+}$). Then, the mixed salt solution was dropwise added to NaOH solution and Ac solution with vigorous agitation under a nitrogen atmosphere. The pH value was then adjusted to 10.0 by adding NaOH solution (2 M). The reaction mixture was subsequently heated at 80–90 °C for 24 h. The precipitates was then washed for three times with deionized water, and dried at 60–70 °C for 24 h.

2.2. Characterization and analytical methods

Powder X-ray diffraction (XRD) data between 5° and 80° were recorded on the Germany Bruker D8ADVANCE using Cu-K α radiation ($\lambda = 0.15418$ nm) at a scan rate of 4°/min and the instrument operated at 40 kV and 40 mA, which were used to determine the phase structures of the LDHs samples. Fourier transform infrared (FTIR) spectra were collected using a Germany Bruker NICOLET 380 FTIR and pressed pellets containing approximately sample and KBr of 1:300. Each FTIR spectrum was recorded as an average of 40 scans in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} .

All samples were filtered using 0.45 μm filter. COD, NO_3^- -N, NO_2^- -N and mixed liquid suspend solid (MLSS) were measured according to Standard Methods (APHA-AWWA-WEF, 2005). That is, COD was determined using Potassium dichromate oxidation titrimetric method; NO_3^- -N was determined by UV spectrophotometer (Shimadzu UV-2310II) at 220 and 275 nm; NO_2^- -N assayed by N-(1-naphthyl)-ethylene diammonium spectrophotometry method; MLSS was determined by heating weighing method. pH were routinely measured with pH electrode (Thermo Toledo FE20).

2.3. Release performance experiment

MgAl-LDH-Ac, NiAl-LDH-Ac, and NiFe-LDH-Ac (all taking 0.25 g) with particle size of 80 mesh were added to Erlenmeyer flasks,

respectively, followed by the addition of deionized water (100 mL). The flasks were continuously oscillated for 8 h at constant temperature 25 °C under vibration rate of 100 times/min. Samples for chemical oxygen demand (COD) measurements were extracted at 20 min intervals before 1 h, and 1 h intervals after 1 h. The release percentage of COD was calculated by Eq. (1).

$$\text{Release percentage of COD} = \text{COD}_{\text{release}}/\text{COD}_{\text{total in LDHs}} \quad (1)$$

NiFe-LDH-Ac (0.25 g) with particle size of 28, 55, 80 mesh were added to Erlenmeyer flasks, respectively. Release performance experiment was completed as described above.

2.4. LDH-Ac as carbon source of denitrification

Denitrifying seed sludge was collected from a municipal WWTP in Shanghai, China. The collected sludge was concentrated by settling at 4 °C for 24 h, and the supernatant was discarded. Seed sludge was firstly cultured for domestication about 20 days in a reactor, using sodium Ac as carbon source and nitrate as nitrogen source, potassium dihydrogen phosphate as phosphorus source, and supplemented trace element for microbial growth (Jiang et al., 2017). Denitrifying sludge was then put into batch reactors with volume of 1 L until final effluent with less than 1 mg/L of nitrate and none of nitrite (Ge et al., 2012). The concentrations of denitrifying sludge (MLSS) were controlled with concentration of around 1700 mg/L (Fig. S1). The initial nitrate concentration of the reactors was 50 mg N/L with addition of KNO_3 (AR), then CH_3COONa and NiFe-LDH were taken as external carbon source giving the COD/N ratio of 4:1 and 6:1 by adjusting the influent concentration of external carbon source, respectively. Nitrogen gas was pumped into the reactor to provide an anaerobic environment. The denitrification was carried out at room temperature for 8 h. Samples for COD and NO_3^- -N measurements were taken at 20 min intervals before 1 h, then 1 h intervals after 1 h.

3. Results and discussion

3.1. Characterization of LDH-Ac

Fig. S2a shows the XRD patterns of as-synthesized MgAl-LDH-Ac, NiAl-LDH-Ac and NiFe-LDH-Ac, which displayed a series of characteristic diffractions of LDHs materials, and no impurity phases were observed (Yu et al., 2014). Due to the size of acetate anion (0.35 nm \times 0.27 nm), arrangement of Ac can form the vertical (single layer or bilayer), parallel or tilted in the interlayer. Correspondingly, the basal spacing of LDH-Ac was estimated to be among 1.2–1.28 nm, which was considered the bilayer arrangement of acetate anions in the interlayer (Prevot et al., 2005). Some researchers also indicated the interlayer spacing of LDH-Ac was about 0.75–0.854 nm, corresponding to the monolayer arrangement of the acetate anion in the interlayer (Huang & Cheng, 2014; Wang et al., 2014b). In this study, the interlayer spacing of MgAl-LDH-Ac, NiAl-LDH-Ac and NiFe-LDH-Ac were 0.804 nm, 0.808 nm and 0.818 nm, respectively, all were between 0.75 and 0.85. Considering the thickness of the gibbsite layer of 0.48 nm (Gerds et al., 2012), the gallery spacing is approximately 0.32 ~ 0.338 nm, indicating that the acetate anion lay parallel or tilted to the gibbsite layers.

The FTIR spectroscopy also confirms the intercalation of acetate anion within the interlamellar region, which are shown in Fig. S2b. The sharp peak at 3450 cm^{-1} , which could be attributed to the O–H stretching vibration from the hydroxide layer and the interlayer water (Chiang and Wu, 2011; Wang et al., 2014a). Respectively, the asymmetric and symmetric stretching vibrations of the carboxylate anion appeared at 1695 cm^{-1} and 1430 cm^{-1} (Benito et al., 2009; Xu and Braterman, 2010). In the low-frequency region, the band was observed at 554 cm^{-1} , which was attributed to O–M–O lattice vibration modes (Gerds et al., 2012). The FTIR results further indicated the existence of

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