Bioresource Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Selective release of phosphorus and nitrogen from waste activated sludge with combined thermal and alkali treatment

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HIGHLIGHTS

- Thermal-alkali treatment released 94%, 76%, and 49% of T-P, T-N, and COD from sludge.
- Release rate increased with NaOH concentration.
- Temperature increased release rate only at low NaOH concentration.
- The ratio of T-N and COD to T-P that released were 0.6–0.9 and 0.2–0.6.
- NaOH created cavities on sludge, and these cavities reduced P selectivity.

ARTICLE INFO

Article history:
Received 25 December 2014
Received in revised form 24 January 2015
Accepted 27 January 2015
Available online xxxx

Keywords:
Phosphorus recovery
Phosphorus release
Alkali treatment
Thermal treatment
Waste activated sludge

ABSTRACT

Selective release characteristics of phosphorus and nitrogen from waste activated sludge (WAS) were investigated during combined thermal and alkali treatment. Alkali (0.001–1.0 N NaOH) treatment and combined thermal-alkali treatment were applied to WAS for releasing total P(T-P) and total nitrogen(T-N). Combined thermal-alkali treatment released 94%, 76%, and 49% of T-P, T-N, and COD, respectively. Release rate was positively associated with NaOH concentration, while temperature gave insignificant effect. The ratio of T-N and COD to T-P that released with alkali treatment ranged 0.74–0.80 and 0.39–0.50, respectively, while combined thermal-alkali treatment gave 0.60–0.90 and 0.20–0.60, respectively. Selective release of T-P and T-N was negatively associated with NaOH. High NaOH concentration created cavities on the surface of WAS, and these cavities accelerated the release rate, but reduced selectivity. Selective release of P and N from sludge has a beneficial effect on nutrient recovery with crystallization processes and it can also enhance methane production.

1. Introduction

Phosphorus (P) is an indispensable and irreplaceable element that produced by neutralization of phosphoric acid from phosphate rock. Cooper et al. (2011) reported that terrestrial phosphate rock reservoir is estimated to be exhausted in about 100 years, considering the current consumption rate of phosphate rock (176×10^6 ton/year). Therefore, recovery and recycling of P is critical for a sustainable world. Most of the used P flows into wastewater and accumulates in waste sludge during wastewater treatment, hence P recovery from wastewater and waste sludge has attracted a lot of attention in the last decade.

Even though waste sludge has a high P content, it cannot be directly applied to agricultural land as a fertilizer, because it is usually contaminated with pathogens, heavy metals or other pollutants (Babel and Dacera, 2006). Phosphorus is often released from sludge with hydrolysis and recovered with crystallization as hydroxyapatite ($Ca_5(PO_4)_3OH$) or struvite ($MgNH_4PO_4$) (Doyle and Parsons, 2002).

Sludge treatment has been intensively investigated for the increase of soluble chemical oxygen demand (COD) with sludge hydrolysis, which accelerates and enhances anaerobic sludge digestion. Nevertheless, only a few studies have been focused on P release with sludge pre-treatment (Kuroda et al., 2002; Takiguchi et al., 2007; Tao and Xia, 2007; Wang et al., 2010). Kuroda et al. (2002), Takiguchi et al. (2007) reported the release of P with low-temperature (50–90 °C) treatment from laboratory grown P accumulating organisms (PAO). Tao and Xia (2007), Wang et al. (2010) investigated the release characteristics of P, nitrogen (N), and organic (measured as COD) compounds with thermal and ultrasonic treatment, respectively. Recently, Bi et al.

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http://dx.doi.org/10.1016/j.biortech.2015.01.106
0960-8524/

(2014) recovered P and NH_4^+ as struvite with alkaline hydrolysis of sludge.

Most recent studies focused on the solubilization of P, N, and organic compounds, but not on their selective release. Mechanical sludge treatment, such as ultrasound, was not effective for the selective release of P, N and organic compounds, given that the composition of the supernatant was similar to that of sludge (Wang et al., 2010). However, recent research revealed that the release percentages of P and N were much higher than organic compounds when thermal treatment was used (Kim, 2014).

In this study, selective release of P and N compounds over COD from waste activated sludge (WAS) was investigated with low-temperature (50–80 °C) thermal and alkali treatment. Total phosphorus (T-P), inorganic phosphate (Pi), and polyphosphate (poly-P) contained in the supernatant were analyzed to understand the releasing mechanism of P from WAS and to develop an effective recovery method of P. Total nitrogen (T-N) and COD in the supernatant were also measured to investigate the release characteristics of nitrogenous and carbonaceous compounds from WAS and to compare them with those of P. Scanning electron microscopy was used to observe changes in the morphology of WAS and identify whether compounds are released with cell hydrolysis or transportation through cell membranes and walls. The objectives of this study were (1) to investigate the effect of temperature and alkali concentration on the release of P, N, and COD, and (2) to identify the most effective treatment conditions for selective release of P and N compounds.

2. Methods

2.1. Sludge preparation and thermal-alkali treatment

WAS was taken from the aeration basin of a municipal wastewater treatment plant in Chuncheon, Korea, which uses biological nutrient removal. Sludge was packed in an ice-box and transported to the laboratory, where it was placed in a 2-L cylinder for 30 min. The characteristics of sludge were as follows: pH 6.8, sludge volume index 135, 183 mg L^{-1} T-P, 553 mg L^{-1} T-N, 6131 mg L^{-1} COD, 6970 mg L^{-1} mixed liquor suspended solids (MLSS), and mixed liquor volatile suspended solids (MLVSS)/MLSS ratio of 0.695.

For the alkali treatment of WAS, 30-mL samples were placed into 50-mL glass tubes, where the initial NaOH concentration was adjusted at 0.001, 0.005, 0.075, 0.01, 0.02, 0.1, and 1.0 N. All tubes were incubated in a temperature-controlled shaking water-bath (WSB-45, Daihan Scientific, Korea) at 25 °C for 120 min. For the combined thermal and alkali treatment of WAS, 30-mL samples were placed into 50-mL glass tubes, where the initial NaOH concentration was adjusted at 0.001, 0.005, 0.075, 0.01, 0.02, 0.1, and 1.0 N and incubated in a temperature-controlled shaking water-bath at 50, 60, 70, and 80 °C for 120 min. Then 2-mL samples were taken from the tubes for analysis. The samples were centrifuged at 6000×*g* for 10 min (Mega 17R, Hanil Science Industry, Korea) and filtered using GF/C™ glass fiber filters (Whatman, USA) for chemical analysis to measure Pi, poly-P, T-P, T-N, and COD in the supernatant. All sludge treatments were repeated three times and the average values were used for analysis.

2.2. Chemical analysis

Pi was determined with ascorbic acid method (APHA, 2005). T-P was measured as Pi after digestion of the sample with ammonium persulfate at 121 °C for 30 min. Poly-P was measured as Pi after hydrolyzing the supernatant in 1 N H_2SO_4 at 95 °C for 15 min (Harold, 1960) and calculated by subtracting Pi amount in the supernatant before acid hydrolysis from that measured after acid hydrolysis. Analyses of COD and T-N were performed according to standard methods as described in APHA (2005). For scanning electron microscopy (SEM), sludge samples were fixed in 2% glutaraldehyde and 2% paraformaldehyde with 0.1 M sodium cacodylate for 1 h at 25 ± 2 °C. Samples were washed with phosphate-buffered saline, treated with 1% osmium tetroxide for 1 h at 25 ± 2 °C, and then dehydrated in graded ethanol solution. Dehydrated samples were treated with CO_2 for critical point drying, sputter coated, and observed with a low vacuum-SEM (S-3500N, Hitachi Sciences Systems, USA).

3. Results and discussion

When the sludge was treated with different NaOH concentrations, pH gradually decreased from the initial value with treatment time in all the cases due to alkalinity consumption. However, the pH variation was low when NaOH concentration was high. The pH variations were 7.7–9.0 (0.001 N NaOH), 9.1–10.3 (0.005 N NaOH), 10.6–11.5 (0.01 N NaOH), 12.3–12.4 (0.02 N NaOH), 13.0–13.1 (0.1 N NaOH), and 13.2–13.6 (1.0 N NaOH) while the intact WAS had pH within 6.6–6.8. Release characteristics during the alkali treatment were monitored by measuring P, N, and organic compounds in the supernatant. T-P, Pi, poly-P, T-N, and COD were monitored for the analysis and they were expressed as percentage (%) of the compound in WAS.

3.1. Effect of alkali treatment on P, N, and COD release from WAS

Fig. 1 shows the release characteristics of P compounds (A, B, C), T-N (D), and COD (E) during alkali treatment. Even though the amount of released T-P was less than 1%, the release rate of T-P and Pi was much increased for the initial 10 min when 0.001 N NaOH was used. Additionally, the amount of released poly-P was very low; almost close to 0%, when 0.001 N NaOH was used. As NaOH concentration increased to 0.005 N, about 17% T-P, 13% Pi, and 3% poly-P were released as shown in Fig. 1A–C. When 0.0075 N NaOH was applied to sludge, a maximum of 26% T-P, 20% Pi, and 6% poly-P were released. As NaOH concentration further increased to 0.01 N, about 35% T-P, 26% Pi, and 6% poly-P were released (Fig. 1A–C). When NaOH concentration was 0.02, 0.1, and 1.0 N, 64%, 86%, 90% T-P was released, respectively (Fig. 1A). At the same NaOH concentrations of 0.02, 0.1, and 1.0 N, the ratios of released Pi were 21%, 17%, and 16% (Fig. 1B), respectively, and those of released poly-P were 26%, 49%, and 51% (Fig. 1C). The release of poly-P increased with NaOH concentration, while the release of Pi remained almost constant at 20%.

Fig. 1D and E show the release characteristics of T-N and COD during the alkali treatment at 25 ± 2 °C, respectively. The release of T-N and COD was mostly occurred in the initial 10 min regardless of the NaOH concentration. The release of T-N and COD was positively associated with NaOH concentration. T-N release ratio increased from 1% when 0.001 N NaOH was used to a maximum of 69% when 1 N NaOH was used, while COD increased from 0.5% to 45% at the same NaOH concentrations, respectively.

Fig. 2 shows the effect of NaOH concentration on the distribution of released P compounds (Pi and poly-P) in the supernatant. Both ratios of Pi and poly-P to T-P determined after 2 h. The ratio of poly-P to T-P increased steadily with NaOH concentration until 0.1 N and then reached a plateau until 1 N. On the other hand, the ratio of Pi maintained in the 70–80% range until 0.01 N NaOH and it decreased rapidly until 0.1 N NaOH. The ratio maintained at about 20% when higher than 0.1 N NaOH was used.

Fig. 3 shows the effect of NaOH concentration on the release percentages of T-P, T-N, and COD and the ratio of released T-N

Please cite this article in press as: Kim, M., et al. Selective release of phosphorus and nitrogen from waste activated sludge with combined thermal and alkali treatment. Bioresour. Technol. (2015), http://dx.doi.org/10.1016/j.biortech.2015.01.106