Bioresource Technology 217 (2016) 233–238

Contents lists available at ScienceDirect

Bioresource Technology

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

Phosphorus extraction and sludge dissolution by acid and alkali treatments of polyaluminum chloride (PAC) treated wastewater sludge

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HIGHLIGHTS

- P release characteristics of PAC treated wastewater sludge were studied.
- Highest P release was found with 2 N HCl and 1 N NaOH concentrations at 2 h.
- Kinetic studies of P release and sludge dissolution follow the first order reaction.
- Sequential extraction with NaOH/HCl give maximum P release (91.7%).

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form 3 February 2016
Accepted 4 February 2016
Available online 9 February 2016

Keywords:
Phosphorus release
Sludge dissolution
Polyaluminium chlorides
Wet chemical

ABSTRACT

Phosphorus (P) leaching characteristics of polyaluminium chlorides (PAC) treated wastewater sludge was investigated by wet chemicals (acid and alkali). Sludge fractionation showed non-apatite inorganic P was the dominant P (90.9% of TP) while apatite P only accounted for 3.7%. After 2 h extraction with 1 N NaOH or 2 N HCl, 80.5% and 77.9% of total P was leached, while sludge dissolution reached 72.7% and 75.6%, respectively. Kinetic study with HCl and NaOH showed that P release and sludge dissolution follow first order reaction with rate constants of 0.50 and 0.35 min^{-1} (P release) and 0.47×10^{-2} and 0.15×10^{-2} min^{-1} (sludge dissolution), respectively. Sequential extraction by NaOH/HCl leached 91.7% of the total P. This study will help in understanding the P release behavior of the PAC treated wastewater sludge.

1. Introduction

It is estimated that phosphate rock reserves may be exhausted in 60–80 years (Hong et al., 2005; Rittmann et al., 2011). Phosphorus (P) is an irreplaceable elemental resource and the phosphate rock mines are regionally confined to only a few countries. Therefore, it is necessary to establish a permanent sustainable P recovery technology from wastewater to reduce the consumption of phosphate rock.

Large quantity of P is spread on farmland for agricultural production and it causes eutrophication and an environmental nuisance in the receiving water body via domestic wastewater and agricultural runoff. In order to solve the problem, biological and chemical approaches have been widely used in wastewater treatment plants to reduce P in the effluent. Biological sludge has a high P bioavailability and it has been extensively studied for P recovery (O'Connor et al., 2004; Usman et al., 2012). But, P in chemical sludge has a low bioavailability in many cases and it was the drawback of P recovery. However, stringent P regulation in the wastewater effluent induces chemical P treatment process. Therefore, chemical sludge production has been increased significantly and an appropriate P recovery technology needs to be developed.

In a conventional WWTP, Al^{3+} or Fe^{3+} based salts, such as $Al_2(SO_4)_3$ (alum), polyaluminum chlorides (PAC), and $FeCl_3$, are widely used for P removal. PAC have a polymeric structure ($(Al_n(OH)_mCl_{(3n-m)})_x$) and it is a preferred coagulant over alum due to lower alkalinity consumption and less metal content in the sludge (Gebbie, 2001). Moreover, PAC produces larger and stronger flocs than alum and provides more space for adsorption (Gregory and Dupon, 2001). Kim et al. (2002) also proposed that PAC can remove phosphates and particulate matters by the mechanism of precipitation and adsorption because of ionic state of Al in PAC.

Since the disposal of P rich sludge is a P loss, the sludge needs to be treated properly for P recovery. Hybrid processes of low pressure wet oxidation/nanofiltration (Blocher et al., 2012) and wet chemical extraction/thermochemical method have been tested to recover P from sludge (Gorazda et al., 2013). Wet chemical extraction methods are based on acid and alkali leaching. The main char-

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http://dx.doi.org/10.1016/j.biortech.2016.02.017
0960-8524/

acteristics of the acidic leaching is the dissolution of heavy metals as well as Ca and Al combined P (Ca–P, Al–P) while it dissolves Fe–P a little (Petzet et al., 2012). Heavy metals are undesirable in a recovered P and strictly regulated when used as a fertilizer. On the other hand, alkaline leaching dissolves amphoteric Al and Fe bound P but does not dissolve Ca–P and heavy metals (Levlin, 2005; Petzet et al., 2012).

Sludge leaching efficiency of P with acid and alkali depends upon several factors such as the composition of sludge, type and concentration of the extractant, pH and treatment time (Gorazda et al., 2013). Many different types of acid have been used for P leaching; H_2SO_4 (Franz, 2008), HCl (Schaum et al., 2007), HNO_3 (Sano et al., 2012), citric acid and oxalic acid (Biswas et al., 2009) while only NaOH was used for alkali treatment (Levlin, 2007; Sano et al., 2012).

P is bound with metals such as Ca, Al, and Fe. These metal bound P (Me-P) cannot be completely dissolved with a single extractant (acid or alkali) because Me-Ps have different solubility depending on extractant (Wang et al., 2013). Ca–P and Fe–P easily dissolve in acid while Al–P dissolves in both acid and alkali up to some degree (Sano et al., 2012; Schaum et al., 2007). Therefore, sequential extraction by acid and alkali is necessary to dissociate most of the Me–Ps (Levlin, 2005; Petzet et al., 2011). Literature survey showed that few studies have been carried out on P recovery from wastewater chemical sludge (Sano et al., 2012; Takiguchi et al., 2007). Moreover, P recovery from PAC treated sludge has not been reported yet even though the PAC treated sludge occupies a significant portion. In addition, most of the previous studies focused on P release from sludge but did not pay any attention on dissolution of sludge. Sludge is usually disposed in landfill and it continuously reduces available landfill capacity (Adam et al., 2009). To cope with the issue sludge reduction is necessary before disposal. The objective of this study was to investigate the release characteristics of P with acid and alkali for P recovery from the PAC treated sludge. For the purpose, P release and dissolution kinetics from the PAC treated sludge were studied.

2. Methods

2.1. Sludge collection and preparation

PAC treated sludge was collected from a municipal wastewater treatment plant in Chuncheon, Korea. The PAC treated sludge was first filtered with hardened ashless filter paper (Cat No. 1541-240, Whatman, USA) in order to remove any dissolved P in the liquid. After filtration the sludge was dried in a convection oven at 105 °C for 48 h. After drying, the sludge was ground and pulverized with mortar to a mesh size <500 μm before acid and alkali leaching.

2.2. Characterization and analysis of PAC treated sludge

The PAC treated sludge was characterized after the sample preparation. All the analytical methods were based on the Standard Methods unless stated otherwise (APHA, 2005). Total phosphorus (TP) was measured after calcination at 450 °C for 3 h and then extracted with 3.5 N HCl for 16 h. Sludge fractionation was based on the Standard Measurement and Testing (SMT) method (Ruban et al., 1999). Inorganic phosphorus (IP) was extracted with 1 N HCl for 16 h and residues of this extraction was calcined for 3 h at 450 °C and then again extracted with 1 N HCl for organic phosphorus (OP). Non-apatite inorganic phosphorus (NAIP) associated with oxides and hydroxides of Fe, Al or Mn (Fe/Al–P) was extracted with 1 N NaOH for 16 h and then some part of this extract was treated with 3.5 N HCl. The residues of this extraction was extracted for apatite phosphorus (AP) associated with Ca (Ca–P) with 1 N HCl for 16 h. The extracted solution was measured for TP analysis.

Crystallization pattern of the prepared PAC treated sludge was studied by X-ray diffraction (XRD) spectrometer (XRD, D/Max-2500V, Rigaku, Japan). Elemental composition of the PAC treated sludge was analyzed by ICP-OES spectrometer (iCAP 6300, Thermo, USA) after digesting the sludge by HNO_3 and *aqua regia* (Andersen and Kisser, 2004). For the HNO_3 digestion 1 g PAC treated sludge sample and 20 mL of 7 N HNO_3 was mixed and autoclaved at 121 °C for 30 min. The sample was cooled at room temperature and filtered with 0.45 μm PTFE membrane filter (Cat No. MTF045047H, Chm, Spain). The filtrate was analyzed by ICP-OES after dilution. In case of *aqua regia*, 3 g of the PAC treated sludge sample was mixed with 1 mL of distilled water and treated with 21 mL of HCl followed by 7 mL of HNO_3. All the PAC treated sludge leaching experiments were carried out in triplicate and the average values were used for the analysis.

2.3. Phosphorus release and dissolution of PAC treated sludge

In this study, five different concentrations of the HCl and NaOH were used for sludge treatment: 0.1 N, 0.2 N, 0.5 N, 1.0 N and 2.0 N. For leaching, 10 g dried PAC treated sludge was mixed with 100 mL of acid or alkali (*L*/*S* ratio 10) in 300 mL flask for P extraction. After P extraction, the solution was immediately centrifuged at 10,000*g* for 10 min and the supernatant was separated. The residual solid was washed by the respective extractant again in order to leach any remaining P and the TP in the supernatant was measured. Sludge residue was weighed after drying at 105 °C for the calculation of sludge dissolution after acid/alkali leaching. The pH was also checked before and after the leaching. Sequential P extraction was carried out in order to measure the acid and alkali releasable fraction of P. In a sequential extraction, dried PAC treated sludge residue after acid treatment was treated with alkali, and *vice versa*, for extracting the remaining P in the sludge residue. The sludge dissolution was measured by Eq. (1).

$$\text{Sludge dissolution } (\%) = \frac{S_f}{S_i} \times 100 \tag{1}$$

where S_f = sludge dry weight (g) after leaching, S_i = sludge dry weight (g) before leaching.

The kinetics of P release (Eq. (2)) and sludge dissolution (Eq. (3)) were analyzed with the first order kinetic model. The rate constants (k_1, k_2) were calculated by statistical data analysis and scientific graphic software (SigmaPlot, V. 10).

$$C_t = C_o(1 - e^{-k_1 t}) \tag{2}$$

$$C'_t = C'_o e^{-k_2 t} \tag{3}$$

where C_t = concentration of solid (mM) at time t, C_o = initial concentration of P (mM), C'_t = concentration of sludge in TS solid (g/L) at time t, C'_t = initial concentration of sludge in TS solid (g/L), k_1 = P release rate constant at room temperature, k_2 = sludge dissolution rate constant at room temperature.

3. Results and discussion

3.1. Characteristics of PAC treated sludge

The dried PAC treated sludge (pH 6.4 ± 0.08) had a total suspended solids (TSS) of 11.73 ± 0.74 g/L and volatile suspended solids (VSS) of 6.16 ± 0.23 g/L. Inorganic elemental composition of dried PAC treated sludge was obtained by ICP-OES spectrometry and the fractions of major elements are shown in Table 1. The