Benefits of Controlled Struvite Precipitation during Anaerobic Digestion

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INTRODUCTION
Controlled phosphate precipitation during anaerobic digestion could reduce inorganic scaling and clogging in the sludge downstream processes, and the phosphate load in the reject water that is returned to sewage wastewater treatment (STP) plant inlet (Wu and Bishop 2004). This could significantly reduce operational cost for the treatment plant associated with acid flushing and overhauling shutdowns (Shu et al. 2006). Currently, phosphate precipitation is mostly applied to centrate or reject water post anaerobic sludge dewatering (Mehta et al. 2015). However, the uptake of this technology is sluggish due to requirement for a crystallizer, chemical cost and low value fertilizer products (struvite or calcium phosphate) recovered from the process. The phosphate precipitation before dewatering has the additional advantage such as improvement in sludge dewaterability (Bergmans et al. 2014), possibly due to presence of excess Mg. An improvement in dewaterability would reduce the volume of the dewatered sludge (low moisture content) and polymer requirement, hence additional savings through reduce polymer consumption and transport/disposal cost of the sludge. Previous work has reported influence of MgCl₂ on controlled struvite formation of the digested wastewater sludge at different Mg dosing and pH conditions (Bergmans et al. 2014). But, there is a lack of information on precipitation kinetics and influence of Mg(OH)₂ as Mg source. Hence, further studies are required to validate benefits of this technology for STP operators. The aim of this work was to investigate influence of pH, aeration and Mg source on phosphate precipitation in the digested sludge and test dewatering of the precipitated sludge.

METHODS
Batch experiments were performed using existing 1 L reactor in a temperature controlled water bath (30°C). The sludge pH was raised through aeration or CO₂ stripping using submerged air stone. Three different aeration rates (200, 400 and 800 ml min⁻¹) were tested and solution pH was recorded. Mg was dosed as MgCl₂ and magnesium hydroxide liquor (MHL or Mg(OH)₂) in the aerated sludge at three different dosing rates, soluble Mg:P molar ratio of 0.5, 1 and 1.5 and at three pH conditions, 7.4, 7.7 and 8.0. Each precipitation experiment was conducted for 24 hrs, with sampling at fixed intervals. An acid dosing system was installed to control setpoint pH and avoid influence low mechanical mixing causing pH increment. The elements (P, K, Mg and Ca) were analysed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and P-PO₄ and N-NH₄ were measured using Flow Injection Analyser (FIA). The dewatering test was performed on the control and the precipitated sludge using centrifuge technique.

RESULTS AND DISCUSSION
Aeration of the digested sludge stripped the dissolved CO₂ and increased the pH (Fig. 1). The pH rise from 7.0 to 8.3 for all three aeration rates, with maximum pH in the range of 8.2 and 8.3. Linear effect of aeration was observed, time required to achieve pH 8.2 reduced from 200, 100 and 50 min as the aeration rate increased from 200, 400 and 800 ml min⁻¹ respectively using 1 L sludge.
Fig 1: Increment in pH of 1L digested sludge at different aeration rate, 200, 400 and 800 ml/min.

Phosphate (soluble P) concentration reduced with increase in pH due to aeration without added Mg (Fig. 2), and it was further reduced by adding of excess Mg (soluble Mg:P ratio >1.0 mol/mol). Soluble P concentration around 10 mg/l was achieved at pH 8.0 and equimolar Mg:P ratio, that is more than 80% removal of phosphate from the digested sludge. The removal was almost half at Mg:P ratio 0.5, while no difference was observed at 1 and 1.5 molar ratios. Instantaneous drop in phosphate concentration (within 10 min) was observed with addition of MgCl$_2$ (Fig. 2). For all the solutions, equilibrium condition was achieved within experimental period, such crystallisation kinetics had been observed in previous work (Mehta and Batstone 2013). The phosphate removal was comparatively lower with MHL at similar dosing rate and pH conditions (Fig. 2), suggesting lower solubility and slower dissolution of MHL. The soluble Mg concentration in the MHL treated sludge increased over 24 hr operation and was found dependent on sludge pH (dissolved Mg concentration from MHL at pH 7.4>pH 7.7> pH 8.0). The MHL is less expensive compared to MgCl$_2$, but it is insoluble in water and require longer disassociation times (Zeng and Li 2006). Hence, there is possibility of high proportion of un-dissociated MHL during struvite precipitation where it is used as Mg source due to basic pH conditions. The soluble calcium concentration reduced above pH 7.4, suggesting formation of calcium phosphates along with struvite (data not shown). During struvite crystallization, presence of Ca$^{2+}$ above 30 ppm in the wastewater have been reported to react with soluble P to form different forms of calcium phosphates (Le Corre et al. 2005).
An increase in pH without magnesium addition had no effect on the sludge dewaterability. At a constant pH of 8.0, achieved by CO\textsubscript{2} stripping, the addition of magnesium led to an improvement in dewaterability compared to the sludge without any treatment (Fig. 3). This could be due to increase in cation concentration in the effluent, leading to improvement in sludge dewatering (Higgins and Novak 1997). However, there was no significant difference in dewaterability at different Mg:P ratio. This is contrary to previous study where improvement in sludge dewaterability was observed due to a decrease in orthophosphate concentration or by precipitant formation (Bergmans et al. 2014).

At present, phosphate precipitation is economical feasible for wastewater with a P-PO\textsubscript{4}\textsuperscript{3-} concentration above 100 mg L\textsuperscript{-1}, as it has the potential to reduce operating costs by reducing energy and chemical consumption and minimizing nuisance phosphate precipitants formation in piping/equipment. It is reasonable to assume that a sewage treatment plant can recover 1 kg of struvite from 100 m\textsuperscript{3} d\textsuperscript{-1} of wastewater, and that would cost AUD 1.4 d\textsuperscript{-1} (Shu et al. 2006). Based on that following financial benefits can be achieved (Shu et al. 2006): reduced chemical requirement
(AUD 1.3 d⁻¹ as alum); reduced sludge handling and disposal cost (AUD 1.1 d⁻¹); reduced cleaning cost of deposits (AUD 7.8-39.1 d⁻¹); and reduced cost of sludge landfilling (AUD 0.003 d⁻¹).

CONCLUSIONS
Phosphate concentration in the digested sludge reduced with increment in pH and Mg-dosing. The phosphate concentrated can be reduced to 10 mg/l at pH 8.0 using excess Mg. Mg released was slower from MHL compared to MgCl₂ and the MHL remained insoluble at alkaline conditions. Hence, for similar P removal at pH 8.0, excess amount of MHL will be required compared to MgCl₂. Mg dosing improved dewatering by 5-7% compared to control. Hence, there is a significant savings from recovery of phosphate from sewage digested wastewater.

REFERENCES