Removal of ammonium and phosphate from the supernatant of anaerobically digested waste activated sludge by chemical precipitation

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1. Introduction

Sustainable treatment of wastewater and development of sustainable technologies have become the focus of wastewater management as a result of increasing concerns of limiting resources (water, energy, reserves, etc.) and of environmental pollution problems. Therefore, wastewater treatment plants are being assessed in terms of their performance in removing contaminants, potential impact of effluent discharge on receiving waters and their implementation of recovery and reuse of potential value added products. One of the most valuable products of a wastewater treatment plant is sludge since it contains high amounts of energy (biogas) and nutrients, and its value as a fertiliser. Sustainable management of sludge urges the recovery of phosphorus not only from an environmental point of view but also based on the limited reserves of phosphorus rocks. Economics of the technologies to recover phosphorus from sludge are yet uncertain (Daveelaar, 2007).

The most common technique to stabilize waste activated sludge (WAS) produced in wastewater treatment plants is anaerobic digestion. The concentrations of ammonium ($NH_4^+$) and phosphate ($PO_4^{3-}$) ions in the effluent of anaerobic digesters are usually very high due to high N and P loading to the digester (Stabinikova et al., 2005; Nandakumar et al., 1998) and the release of nutrients during anaerobic digestion (Cheng and Liu, 2002; Demirer and Chen, 2005a, b). Supernatant of anaerobically digested sludge are usually returned to plant input (upstream of primary clarifiers) or further treated hence increasing the loading onto the treatment plant and the total cost of wastewater treatment (Battistoni et al., 2001). One of the techniques to remove $NH_4^+$ and $PO_4^{3-}$ from wastewater is their precipitation as magnesium ammonium phosphate (MAP, commonly named struvite) (Doyle and Parsons, 2002). Since MAP can be used as a fertilizer, this technique allows not only removal but also the recovery of the nutrients.

There are many studies focusing on the removal of nitrogen (N) and phosphorus (P) from wastewaters rich in $NH_4^+$ and $PO_4^{3-}$, such as, swine waste (Burns et al., 2001; Jaffer et al., 2001; Celen et al., 2007), effluents from the anaerobic treatment of the baker’s yeast factory (Altinbas et al., 2002), of molasses (Turker and Celen, 2007), of piggery waste (Wang et al., 2005), of dairy manure (Uldug-Demirer et al., 2005) and of human urine (Ganrot et al., 2007) by the formation of MAP. In addition, the supernatant produced during the anaerobic digestion of enhanced biological phosphorus removal sludges has been found to be appropriate for the recovery of phosphorus by the crystallization of MAP (Pastor et al., 2008; Marti et al., 2008a, b).

The formation constant of MAP (or struvite) is $1.41 \times 10^{13}$ according to the reaction of

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

(1)

involving molar concentration ratio of Mg:$NH_4$:PO$_4$ as 1.0:1.0:1.0 (Buchanan et al., 1994). In other words, MAP can form and...
precipitate in solutions if the product of Mg\(^{2+}\), NH\(_4^+\), and PO\(_4^{3-}\) activities exceeds ion activity product at equilibrium (IAP\(_{eq}\)), that is

\[
IAP_{eq} = \{Mg^{2+}\} \cdot \{NH_4^+\} \cdot \{PO_4^{3-}\} = 7.08 \times 10^{-14}
\]  

(2)

Therefore, in planning for and optimisation of the formation and precipitation of MAP all factors affecting the activity of ions should be considered, particularly pH being the most important factor. This is simply due to changes in free concentrations of Mg\(^{2+}\), NH\(_4^+\), and PO\(_4^{3-}\) ions with pH change. The concentrations of free Mg\(^{2+}\) and NH\(_4^+\) ions decrease with increase in pH as a result of formation of Mg\(^{2+}\) hydroxide complexes (MgOH\(^+\), Mg(OH)\(_2\), etc.) and volatilization in the form of NH\(_3\)\(_(g)\) (Eqs. (3a) and (3b)), respectively. On the other hand, the concentration of free PO\(_4^{3-}\) ion is expected to increase as solution becomes more basic. In addition, pH controls the solubility of MAP, which is reported to be the minimum in a pH range of 9.0–10.7 (Nelson et al., 2003; Doyle and Parsons, 2002).

\[
NH_4^+ \rightarrow NH_3 (aq) + H^+
\]  

(3a)

\[
NH_3 (aq) \rightarrow NH_3 (g)
\]  

(3b)

Ionic strength of solution, presence of metal complexing agents, presence of other cations forming species especially with PO\(_4^{3-}\) and temperature are among the other factors affecting the activities of the ions and equilibrium constants. Because the characteristics of wastewater deviate from those for pure water considerably, the MAP formation potential and estimation of chemical dosages to add have to be investigated in laboratory for each type of wastewater or predicted by using equilibrium models (Celen et al., 2007).

The formation of other species, in addition to MAP, in the presence of high concentrations of Mg\(^{2+}\) and PO\(_4^{3-}\) is very critical since it may use up additional Mg\(^{2+}\), which means extra cost, and also it may affect the purity of the precipitate as a result of formation of other insoluble species. Species other than MAP that may form in solutions with high concentrations of Mg\(^{2+}\) and PO\(_4^{3-}\) are magnesium phosphates\(^+\), such as, MgHPO\(_4\) \(\cdot\) 3H\(_2\)O (newberyite), Mg\(_3\)(PO\(_4\))\(_2\) \(\cdot\) 2H\(_2\)O (bobierite). The presence of Ca\(^{2+}\), which is one of the most commonly encountered cations in wastewater, can lead to the formation of other species, for instance, Ca\(_3\)(PO\(_4\))\(_2\)\(_2\)OH (hydroxyapatite), Ca\(_2\)(PO\(_4\))\(_2\) (whitlockite), Ca\(_9\)(HPO\(_4\))\(_2\)(PO\(_4\))\(_2\) \(\cdot\) 5H\(_2\)O (octacalcium phosphate), CaHPO\(_4\) (mononite), CaHPO\(_4\) \(\cdot\) 2H\(_2\)O (brushite). In addition Mg\(_2\)O\(_2\) (magnesite), Mg\(_2\)O\(_2\) \(\cdot\) 3H\(_2\)O (nésquehonite), CaMg(CO\(_3\))\(_2\) (dolomite), CaMg(CO\(_3\))\(_3\) (hunite) and Mg(OH)\(_2\) (brucite) may form in the solutions. Geochemical equilibrium models (e.g. MINEQL, MINTEQ and PHREEQC) can be used to find out thermodynamically possible species forming in the solutions containing Mg\(^{2+}\), NH\(_4^+\), and PO\(_4^{3-}\). The chemical equilibrium model, Visual Minteq 2.23, has been trialled for predicting required chemical dosages, considering all species which may form due to presence of the major cations in wastewater (Mg\(^{2+}\) and Ca\(^{2+}\)) and PO\(_4^{3-}\), for the removal of phosphorus from liquid swine manure by MAP precipitation (Celen et al., 2007). The XRD results from this study have indicated the formation of MAP, mononite, and brushite in the liquid swine manure dosed by MgCl\(_2\).

Among the species listed above, there is one specie, containing NH\(_4^+\) in its composition and that is MAP. Hence the observed removal of NH\(_4^+\) in systems with high concentrations of Mg\(^{2+}\) and PO\(_4^{3-}\) ions can be counted to occur due to two major mechanisms as follows:

\[
[\text{NH}_4^+]_{\text{total\ removal}} = [\text{NH}_4^+]_{\text{removal\ by\ MAP\ formation}} + [\text{NH}_4^+]_{\text{removal\ by\ volatilization}}
\]  

(4)

Most of the studies published in literature reported results of considerable removal of NH\(_4^+\) and PO\(_4^{3-}\) by adding the limiting reactants (Mg\(^{2+}\) and PO\(_4^{3-}\) in general) for MAP formation at equilibrium conditions for different wastewaters (Burns et al., 2001; Jaffar et al., 2001; Celen et al., 2007; Altinbas et al., 2002; Uludag-Demirer et al., 2005). The prevalence of equilibrium conditions in the wastewater solutions regarding MAP formation is necessary to find out maximum removal of the ions at specified conditions and to check the predictability of results using available geochemical equilibrium models. However, kinetics of MAP formation is also important for estimation of the time required to establish equilibrium conditions as well as for finding out the rate of removals of MAP-forming ions from the wastewater. The kinetic parameters calculated for MAP formation in different wastewaters are listed in Table 1 and there are differences in these studies in terms of initial molar concentration ratio of Mg\(^{2+}\):NH\(_4^+\):PO\(_4^{3-}\), pH, type of wastewater and ion selected to analyse the kinetics of MAP formation.

As seen in Table 1, the results indicate that first order rate constants based on PO\(_4^{3-}\) concentration between pH of 8.3 and 8.7 are similar as estimated in two independent studies (Ohlinger et al., 2000 and Nelson et al., 2003), while the reaction kinetics studied at pH 8.5 based on Mg\(^{2+}\) concentration was second order with a much higher rate constant in another study by Turk et and Celen (2007). In another independent study by Rahaman et al. (2008), the removal of PO\(_4^{3-}\) from a synthetically prepared solutions has been reported as first-order with increasing rate constants as the Mg:P ratio increases. It is interesting to note that the kinetics of MAP formation has not been investigated based on removal of NH\(_4^+\), which may be probably due to its volatilization at basic solutions. However, studying the kinetics of MAP formation based on decrease in Mg\(^{2+}\) and PO\(_4^{3-}\) concentrations may overestimate the reaction rate, since they may form other species than MAP. To be able to investigate the kinetics of MAP formation more accurately, it is proposed to look at rate of volatilization of NH\(_4^+\) at pH of solution as well as to measure concentrations of the three ions remaining in wastewater solution at certain reaction times and compare the rates of removals of each ion in this study.

This study focuses on removing NH\(_4^+\) associated with the removal of PO\(_4^{3-}\) by the formation of MAP from the supernatant of anaerobic digester. The supernatant was obtained from the anaerobic digester in domestic wastewater treatment plant in Melbourne, Australia, in which waste activated sludge (WAS) and primary clarifier sludge are substrates. Currently high concentration of NH\(_4^+\) in the supernatant is reduced to acceptable levels by aeration and there is no unit for the removal of PO\(_4^{3-}\). The main goal of the research was to find out a combination of chemical dosage and pH which lead to maximum removals of NH\(_4^+\) and PO\(_4^{3-}\), in different wastewater compositions in terms of Mg\(^{2+}\) and PO\(_4^{3-}\) concentrations aiming complete removal of PO\(_4^{3-}\) associated with partial removal of NH\(_4^+\) and complete removal of NH\(_4^+\) and PO\(_4^{3-}\) at equilibrium conditions. However, prior to investigation of the conditions yielding the maximum removal of NH\(_4^+\) and PO\(_4^{3-}\) at equilibrium, the removal of NH\(_4^+\) by volatilization and MAP formation was studied to find out total removal of NH\(_4^+\) by these mechanisms. Furthermore, the kinetics of MAP formation was studied based on the disappearance rate of the ions from the solution with reaction time.

2. Methods

The domestic wastewater plant has an anaerobic digester in which WAS is part of the influent to the digester. The anaerobic sludge is then sent to sludge drying pans, where the solid liquid separation is accomplished. The supernatant of sludge is aerated in lagoons to remove NH\(_4^+\) (aq) in the form of NH\(_3\) (g).
The supernatant of anaerobic sludge was collected from the sludge drying pans and its composition was determined in the first 16 h of sample collection except for measurements of metals concentrations. For metals concentrations the samples were acidified by HNO₃ and kept at about 4 °C until measured.

The supernatant was greenish in colour and contained low concentration of solids (TS = 1995 mg/L). The dissolved total N (277 mg NH₄⁺/L) and total P (193 mg PO₄³⁻/L) concentrations are slightly higher than NH₄⁺ (273 mg NH₄⁺/L) and PO₄³⁻ (168 mg PO₄³⁻/L) concentrations, which indicates that majority of the total N and P in the solution exist in the form of NH₄⁺ and PO₄³⁻ ions. The pH of the supernatant was 7.95 and Mg²⁺ concentration was measured as 11 mg/L. To be able to store the supernatant without changing its initial composition, the samples were filtered and then centrifuged at 4000 rpm for 15 min (Eppendorf Centrifuge 5701). The solid-free solution was then acidified using H₂SO₄ (1 mL/L) and stored at 4 °C in refrigerator for later use in the experiments.

### 3. Analytical measurements

The measurement of pH was made using calibrated pH meter (ThermoOrion, Model 550A). The total solids (TSs) and total suspended solids (TSSs) were measured gravimetrically according to the Standard Methods (APHA, 1998). Soluble components of the supernatant were measured after filtration and centrifugation to be consistent with the sample pre-treatment before storage. Moreover, it was tested that adopting only filtration or centrifugation as a pre-treatment technique for the samples did not affect the measurements of NH₄⁺ and PO₄³⁻ concentrations in the solution. The measurements of COD, total P, total N, PO₄³⁻, and NH₄⁺ were made by colorimetric techniques using HACH Spectrophotometer (DR/4000). There are two methods to measure NH₄⁺ concentration using HACH reagents, one by using powder pillows and the other by using vials for high range. It was found more reliable to use vials, not only because of high concentration of NH₄⁺ in the solution, but also because of the of interference caused by PO₄³⁻ and Mg²⁺ based substances when using powder pillows. The measurement of Mg²⁺ concentration was made using AAS (Varian SpectraAA-600), while K concentration measurement was made in a commercial laboratory.

### 4. Experimental

#### 4.1. Effect of aeration on the removal of NH₄⁺ at pH = 9.0

A 100 mL sample from the supernatant solution was placed in a beaker with pH (Mettler Toledo M 700c) and dissolved oxygen (DO) (Mettler Toledo O₂ 4050e) probes. Following up the measurement of initial pH level and DO concentration, pH of the sample was raised to 9.0 by adding NaOH (3 M) under continuous mixing at 300 rpm and aeration at a rate of 4.0 mL/s. Air flow rate was measured by a flow meter (Porter Instrument Company) and was kept constant during the experiment by maintaining a constant DO concentration. The flow rate of 4 mL/s is much lower than the typical air flow rate for NH₃ (aq) removal by aeration. This level of airflow was sufficient in illustrating an extreme case of NH₃ removal by volatilization for the experimental conditions specified in the study as there was no aeration of the solutions during experimentation. Samples of 1 mL were withdrawn at 10, 20, 30, 50, and 60 min and were analysed immediately following filtration to measure NH₄⁺ concentrations.

Another experiment was carried out to assess the effect of aeration on the removal of NH₄⁺ and PO₄³⁻ by MAP formation. A sample of 100 mL was used. The initial molar concentration of Mg²⁺ was raised to 1.52 × 10⁻² M by adding MgCl₂ (technical grade). The pH of solution was raised to about 9.14 while aerating continuously at 4 mL/s. The formation of solid particles was fast and they remained suspended in the solution as a result of continuous mixing (300 rpm) and aeration. Similar to the first set of experiments in this part, samples were taken at 10, 20, 30, 50, and 60 min and analysed immediately after filtration for NH₄⁺. Concentration of PO₄³⁻ in the solution was measured only in the samples taken at t = 0 and t = 60 min.

#### 4.2. Kinetics of MAP formation

The kinetics of MAP formation was studied using samples containing 87.6 mg Mg²⁺/L (3.65 × 10⁻³ M), 273 mg NH₄⁺/L (1.52 × 10⁻² M), and 168 mg PO₄³⁻/L (1.77 × 10⁻³ M) initially. The concentration of Mg²⁺ was increased using MgCl₂ (technical grade) and pH of solution was adjusted to 8.76 by NaOH (3 M) prior to that. Sampling started immediately after the addition of MgCl₂ and repeated at certain time intervals during the reaction time of 36 min. The samples were filtered through glass fibre (Advantec) and cellulose acetate membrane filter (Advantec) installed in series in 15–20 s and analysed in the first 20 min of sampling to measure the remaining concentrations of Mg²⁺, NH₄⁺, and PO₄³⁻ in the solution. The pH of solution changed from 8.76 to 8.58 during the course of experimentation probably due to acidic nature of MgCl₂.

#### 4.3. Removal of NH₄⁺ and PO₄³⁻ by MAP formation at equilibrium conditions

On the basis of the initial composition of the supernatant solution, Mg²⁺ and PO₄³⁻ concentrations, 4.62 × 10⁻¹ and 1.77 × 10⁻³ M, respectively, were required to be increased to desired levels as they were both limiting for the removal of existing NH₄⁺ by MAP formation. The concentration of NH₄⁺ was kept constant at its original level (1.52 × 10⁻² M) in all experimental runs. The experimental design consisted of three different levels for three variables (Mg²⁺, PO₄³⁻ concentrations and pH level) corresponding to 27 experiments (3³ factorial). The concentration levels of Mg²⁺ and PO₄³⁻ were decided so that the addition of chemicals can be kept as minimum as possible, while achieving considerable amounts of removal of NH₄⁺ and PO₄³⁻. Therefore minimum level of concentration (level 1) consisted of [Mg²⁺] = 1.77 × 10⁻³ M (42.5 mg/L)
aiming for complete PO$_4^{3-}$ removal and partial removal of NH$_4^+$. Level 3 (maximum level) was to simulate MAP formation stoichiometry in the solutions and therefore it was equal to initial NH$_4^+$ concentration of 1.52 \times 10^{-2} M (273 mg/L) to provide enough Mg$^{2+}$ and PO$_4^{3-}$ for high removal of NH$_4^+$. Level 2 was decided as the mid-point between levels 1 and 2 corresponding to 8.5 \times 10^{-3} M concentration for each ion to assess the effect of Mg$^{2+}$ and PO$_4^{3-}$ concentrations on the removal of NH$_4^+$ and PO$_4^{3-}$. The pH levels tested were 8.0, 8.5, and 9.0.

The experiments were undertaken in Erlenmeyer flasks using 100 mL of solution. The pH of solution was raised to 4.0–5.0 using NaOH (3 M) before adjusting the composition of wastewater. MgCl$_2$ (technical grade, BDH Chemicals) and Na$_3$PO$_4$ - 12H$_2$O (analytical grade, BDH Chemicals) were used as Mg$^{2+}$ and PO$_4^{3-}$ providing chemicals, in powder form, and they were added to provide the desired initial molar concentration counting the initially existing amounts in the wastewater. The pH level of the solution was raised and then kept at the adjusted level using 1 M HCl and 3 M NaOH solution. Since the volumes of HCl and NaOH added were very small, dilution effect was neglected. The flasks were stirred continuously at 300 rpm. It was noted that once pH is fixed, the particles form quickly; growing bigger in size and the pH of the solution remained constant afterwards. The reaction was not terminated until after 10 min of observing constant pH and then a 45 mL sample was withdrawn into a centrifuge tube. The sample was centrifuged at 4000 rpm for 20 min. The chemical analyses of the solid-free solution were made immediately in the first 30 min after centrifugation to measure the concentrations of NH$_4^+$ and PO$_4^{3-}$.

The precipitate from the experiment conducted using a supersaturated solution with equal concentrations of Mg$^{2+}$, NH$_4^+$, and PO$_4^{3-}$ (1.52 \times 10^{-2} M) ions at pH 9.0 was collected by centrifugation of the entire volume of solution in the reactor and air dried to be able to analyse its compositional structure using X-ray diffraction (XRD) technique. For this, wide angle XRD instrument (Bruker AXS D8 Advance) with Cu tube was employed and analyses were made in a range of 5°–90° angle. The experiment was repeated to prepare duplicate samples for XRD measurements.

There were control experiments to quantify the removal of NH$_4^+$ by volatilization as a result of mixing continuously at 300 rpm at the pH levels tested in this study. These experiments were carried out similar to NH$_4^+$ and PO$_4^{3-}$ removal testing experiments at equilibrium except the addition of chemicals. There was no chemical addition except NaOH (3 M) to adjust the pH of solution. Samples, which are pre-treated following the same procedure, were analysed immediately to find out any removal of NH$_4^+$ and PO$_4^{3-}$.

5. Results and discussion

5.1. Effect of aeration on NH$_4^+$ removal by MAP formation

There are two major mechanisms for the removal of NH$_4^+$ from the wastewater solution under the conditions tested in this study. These are, (i) by volatilization and (ii) MAP formation (Eq. (4)). To be able to determine the effect of volatilization on NH$_4^+$ removal, two experiments were conducted. The first experiment was made using original wastewater, which is aerated and mixed (at 300 rpm) at the same time at the pH level of 9.0. The airflow rate set to the level of 4 mL/s, which is relatively smaller than the typical airflow rate (1.2–1.6 L/min; Liao et al., 1995) applied in aeration systems for NH$_4^+$ removal. The concentration of NH$_4^+$ remaining in the solution decreased with time almost at a constant rate of 0.99 mg/L s during 1 h of aeration. The final concentration of NH$_4^+$ corresponded to 19% removal of NH$_4^+$ by volatilization. There was a small amount of solid formation observed in the solution, but it was unlikely to observe MAP formation in considerable amounts because of very low Mg$^{2+}$ concentration (4.62 \times 10^{-4} M). The removal of NH$_4^+$ could have been higher by increasing the air flow rate, pH and aeration time as studied by Liao et al. (1995), but this was out of the scope of this study.

In the second experiment, the aeration was provided with the same air flow rate complementary to the removal of NH$_4^+$ by MAP formation. The initial composition of the wastewater was modified to increase the level of Mg$^{2+}$ from 4.62 \times 10^{-4} to 1.52 \times 10^{-2} M to initiate the formation of MAP. The pH of the solution was adjusted and kept at 9.14 during the experiment. The formation of solid particles was observed immediately after the addition of Mg$^{2+}$ ion and they remained suspended in solution during the experimentation. The initial removal of NH$_4^+$ was fast and out-competed the removal of NH$_4^+$ by aeration. There was a continuous but slight decrease in the concentration of NH$_4^+$ after 10 min of reaction with a rate similar to the rate of removal of NH$_4^+$ by aeration. The total removal of NH$_4^+$ at the end of an hour was calculated as 38% under the specific conditions defined here. The results obtained in this part proved that the MAP formation rate is much faster than the rate of NH$_4^+$ removal by volatilization, which can therefore be neglected especially in the first 10 min of reaction time. In fact, after the equilibrium conditions established regarding MAP formation, there was a further removal of NH$_4^+$ with a rate similar to removal rate by aeration, which can be recognized as an asset. However, no further research was made on this since it is out of the scope of the study. The removal of PO$_4^{3-}$ ion was found to be considerably high at 85% under the conditions specified in this part.

5.2. Kinetics of MAP formation

The kinetics of MAP formation was studied to find out time for equilibrium as well as removal rate of each ion involved in the formation of MAP. The decrease in dissolved concentrations of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ with reaction time was observed for an initial molar concentration ratio of Mg:PO$_4$ as 2.0:1.0, which indicates that the solution has Mg$^{2+}$ and PO$_4^{3-}$ ions limiting the MAP formation to some extent while NH$_4^+$ is in excess. This composition was used to be able to slow down the reaction rate, which is otherwise in the saturated concentrations of the three ions. The samples taken at certain time intervals were analysed to measure the concentrations of Mg$^{2+}$, NH$_4^+$ and PO$_4^{3-}$ and the data obtained showed that the equilibrium conditions were established in the solution after 300 s (5 min) (Fig. 1). There was no significant change in the concentrations during the rest of the experiment, which continued another half an hour.

The results obtained during first 140 s of reaction time were used to fit first, second, and third order rate model equations to Fig. 1. Kinetics of MAP formation at room temperature (pH = 8.58–8.76).
estimate the best kinetic model. Interestingly there was no single superior model over others based on $R^2$ values and data showed statistically acceptable fits to all models. The calculated kinetic parameters for different rate equations and prediction of initial concentrations are given in Table 2. As seen from the kinetic parameters calculated (Table 2), the removal rate constants of Mg$^{2+}$ ion was higher than those for NH$_4^+$ and PO$_4^{3-}$ ions with the exception that it was of similar magnitude to the first order rate constant of PO$_4^{3-}$. This is not surprising since Mg$^{2+}$ ion is involved in many reactions forming species other than MAP. The best model describing the relation between Mg$^{2+}$ ion concentration remaining in the solution and reaction time was determined as third order based on the $R^2$ value and prediction of initial concentration, which is different from the kinetic study accomplished by Turker and Celen (2007) (see Table 1). The rate constant of NH$_4^+$ ion removal was consistently the smallest in all three models considered, which can be explained by the fact that this ion is not as reactive as Mg$^{2+}$ or PO$_4^{3-}$ in the solution. The major removal mechanisms for this ion are MAP formation and volatilization. The rate of NH$_4^+$ removal was described statistically well in all three models being best fit to the third order rate model on the basis of $R^2$ value and initial concentration prediction. However, the removal of PO$_4^{3-}$ was found to be clearly first order based on the prediction of the model for initial concentration of PO$_4^{3-}$ similar to the outcome of the kinetic studies carried out by Ohlinger et al. (2000), Nelson et al. (2003), and Rahaman et al. (2008). The rate constant for PO$_4^{3-}$ removal was determined as 25.2 h$^{-1}$, which is much higher than the published rate constants in the literature. This difference could be due the differences in the compositions of the wastewaters studied in independent studies especially in terms of ions forming MAP.

5.3. Removal of NH$_4^+$ and PO$_4^{3-}$ by MAP formation at equilibrium

Initial composition of the supernatant from anaerobic digester contained a molar concentration ratio of 4.62 x 10$^{-3}$:1.52 x 10$^{-2}$:1.77 x 10$^{-3}$ of Mg:NH$_4$:PO$_4$ indicating that Mg$^{2+}$ ion is the limiting reactant for NH$_4^+$ and PO$_4^{3-}$ removal by MAP formation. Therefore, it had to be added in all experimental runs to initiate MAP formation. Similarly, the concentration of PO$_4^{3-}$ was not adequate for higher removals of NH$_4^+$ and it was necessary to add PO$_4^{3-}$ ion to improve NH$_4^+$ removal. The removal of both NH$_4^+$ and PO$_4^{3-}$ was tested at three concentration levels of 1.77 x 10$^{-3}$, 8.50 x 10$^{-3}$, and 1.52 x 10$^{-2}$ M representing conditions of limiting reactant(s) as well as saturation. The experimental design allowed observing the effects of Mg$^{2+}$ and PO$_4^{3-}$ concentrations at constant NH$_4$:PO$_4$ and Mg:NH$_4$ ratios respectively on the removal of ions at pH levels of 8.0, 8.5, and 9.0.

5.3.1. The effect of Mg$^{2+}$ concentration on the removal of NH$_4^+$ and PO$_4^{3-}$ at equilibrium

One of the major ions in MAP formation is Mg$^{2+}$ and it is usually lowest in concentration compared to NH$_4^+$ and PO$_4^{3-}$ concentrations in many wastewaters (Doyle and Parsons, 2002). Therefore, the addition of Mg$^{2+}$ ion has been necessary to remove and recover NH$_4^+$ and PO$_4^{3-}$ in the form of MAP. The concentration of Mg$^{2+}$ ion was increased in all experimental runs to make it equal with PO$_4^{3-}$ at a minimum and varied as 43, 204, and 365 mg/L. The highest molar concentration of this ion was the same as of NH$_4^+$. The removal of NH$_4^+$ and PO$_4^{3-}$ was tested at pH levels of 8.0, 8.5, and 9.0 in the solutions containing different levels of Mg$^{2+}$. The results from these experiments are shown in Fig. 2 for different NH$_4$:PO$_4$ ratios. The horizontal lines on the plots show the removal of the ions in the control experiments, in which no chemical was added to observe the effect of pH and mixing on the removal of the ions. The removal of the ions did not change significantly in the pH range studied and averaged as 9.0% for NH$_4^+$ and 2.5% for PO$_4^{3-}$ in the control reactors. Additional experiments were conducted using wastewater solutions containing higher concentrations of Mg$^{2+}$ as 1.5 and 2.0 times of the initial molar concentration of NH$_4^+$ and NH$_4$:PO$_4$ ratio of 8.6:1.0 and 1.0:1.0 at pH 9.0 (Fig. 2).

As expected, pH 9.0 was the level of higher removal of the ions regardless of NH$_4$:PO$_4$ molar concentration ratio and Mg$^{2+}$ concentration. The significance of pH as a factor diminished as the molar ratio of NH$_4$:PO$_4$ increased. This is because of investigating the removal of NH$_4^+$ and PO$_4^{3-}$ by MAP formation in a small range of pH and as the solution becomes more saturated with respect to the ions forming MAP, the change in free ion concentrations becomes less effective in the pH range studied.

Fig. 2a shows the results from the experiments conducted using wastewater solution with original NH$_4^+$ and PO$_4^{3-}$ concentrations. The trend of removal of ions indicated a proportional relationship with Mg$^{2+}$ concentration. The significant difference between NH$_4^+$ and PO$_4^{3-}$ removals for this wastewater at all pH levels was probably due to removal of PO$_4^{3-}$ ion by other mechanisms as discussed before. Additional experiments conducted using this wastewater solution loaded by Mg$^{2+}$ concentration equal to 1.5 and 2.0 times of NH$_4^+$ concentration at pH 9.0 showed that removal of NH$_4^+$ can be improved up to 46% while PO$_4^{3-}$ removal levels out at about 90%, which is considerably high, regardless of increase in Mg$^{2+}$ concentration. This is because of the limiting concentration of PO$_4^{3-}$ in the solution beyond the point of Mg$^{2+}$ concentration of 365 mg/L (1.5 x 10$^{-2}$ M).

The results from the experiments conducted using wastewater with a NH$_4$:PO$_4$ molar concentration ratio of 1.8:1.0 (Fig. 2b) showed that the removal of ions could be improved as solution became more saturated in Mg$^{2+}$ and PO$_4^{3-}$ ions. It can also be seen from the plots that percent removals of ions have become similar, which might indicate MAP formation as the major removal mechanism in this wastewater. A similar observation is true for the results from the experiments accomplished using wastewater with NH$_4$:PO$_4$ ratio of 1.0:1.0 (Fig. 2c). The results from XRD analyses for the precipitate collected from the reactor containing wastewater solution simulating the MAP formation stoichiometry.

### Table 2

<table>
<thead>
<tr>
<th>Ion measured</th>
<th>$C_0$ (mg/L)</th>
<th>$k$ (L/mg s)</th>
<th>$R^2$</th>
<th>Predicted $C_0$ (mg/L)</th>
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<td></td>
<td>First</td>
<td>Second</td>
<td>Third</td>
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<td>Mg$^{2+}$</td>
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<td>1 x 10$^{-4}$</td>
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<td>NH$_4^+$</td>
<td>273</td>
<td>2 x 10$^{-3}$</td>
<td>1 x 10$^{-5}$</td>
<td>5 x 10$^{-5}$</td>
</tr>
<tr>
<td>PO$_4^{3-}$</td>
<td>168</td>
<td>7 x 10$^{-3}$</td>
<td>8 x 10$^{-5}$</td>
<td>9 x 10$^{-7}$</td>
</tr>
</tbody>
</table>

*a* $\ln(C_p)$ = $\ln(C_0) - kt$.

*b* $\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_2}$.

*c* $\frac{1}{k_1} = \frac{1}{k_3} + \frac{1}{k_4}$. 
(Mg:NH₄:PO₄ = 1.0:1.0:1.0) at pH 9.0 showed clearly that the precipitate is basically MAP. The pattern of the sample and MAP (which was retrieved from the data base in the software installed to the equipment) match almost exactly showing also the purity of MAP is high. Results were similar for the precipitate collected from duplicate experiments. More detailed XRD analysis was carried out to estimate any impurities in the precipitate and trace amounts of newberyite, bobierrite, brushite, monetite, and brucite were detected.

The average percent removals of the ions observed in triplicate experiments were 64% and 63% for NH₄⁺ and PO₄³⁻, respectively in this wastewater solution at pH 9.0 with Mg:NH₄:PO₄ molar ratio of 1.0:1.0:1.0. The additional experiments conducted to improve the removal of ions by adding 1.5 and 2.0 times more Mg²⁺ than NH₄⁺ molar concentration yielded very high and similar removals of NH₄⁺ (92%) and PO₄³⁻ (94%), which again pointing out MAP formation as the major mechanism for removing the ions. Although the percent removals of the ions are high, it should be noted that effluent still has considerably high concentration of PO₄³⁻ (86 mg/L at [Mg²⁺] = 2[NH₄⁺] initially and pH 9.0) since it was added into the wastewater to simulate MAP formation stoichiometry. The concentration of NH₄⁺ decreased from 273 to 15 mg/L under the same conditions.

5.3.2. The effect of PO₄³⁻ concentration on the removal of NH₄⁺ and PO₄³⁻ at equilibrium

The experimental design was such that the effect of PO₄³⁻ concentration on the removal of ions could be observed at three different levels of Mg:NH₄ ratios, which are 1.0:8.6, 1.0:1.8 and 1.0:1.0. The results are given in Fig. 3. The average removals of NH₄⁺ and
PO$_4^{3-}$ in the control reactors are shown in the plots as horizontal lines. The ratio of Mg:NH$_4$ indicates the saturation level of Mg$^{2+}$ compared to NH$_4^+$ in solution and their molar concentrations are equal in the solution with Mg:NH$_4$ ratio of 1.0:1.0. The concentration of PO$_4^{3-}$ was changed as 168 mg/L, 808 mg/L to 1444 mg/L, so that the lowest concentration represents original composition of the solution while the highest is equal to NH$_4^+$ concentration. All experimental runs using similar wastewater compositions were made at pH levels of 8.0, 8.5, and 9.0. In other words, except the last data point shown in Fig. 3c, formation of MAP is limited either by concentration of Mg$^{2+}$ or PO$_4^{3-}$ or both. As seen from Fig. 3, the removal of ions was usually superior at pH 9.0 than at pH 8.0 and 8.5. Even though the effect of pH on the performance of the process was investigated in a narrow range, it was interesting to observe that pH level became an insignificant factor as Mg:NH$_4$ ratio increased. This means that the saturation of the solution in terms of the ions has become more significant factor than pH level of the solution in the removal of NH$_4^+$ and PO$_4^{3-}$ at the specified conditions of the study.

The removal of NH$_4^+$ and PO$_4^{3-}$ increased as Mg:NH$_4$ ratio increased for the same concentration of PO$_4^{3-}$ and pH. This supports the importance of Mg$^{2+}$ concentration as a factor in removing both ions in the form of MAP as discussed before. It is also seen from the results that increasing PO$_4^{3-}$ concentration improves NH$_4^+$ removal considerably under the conditions of unsaturated or saturated concentrations of Mg$^{2+}$ ion. The highest removal of NH$_4^+$ was about 60–70% at Mg:NH$_4$:PO$_4$ ratio of 1.0:1.0:1.0 corresponding an effluent with NH$_4^+$ concentration between 70 and 99 mg/L and PO$_4^{3-}$ concentration between 490 and 660 mg/L at pH range of 8.0–9.0 (54–67% removal). The concentration of PO$_4^{3-}$ in the effluent was very high because it was added in to the solution to increase its concentration up to 1.52$\times 10^{-2}$ M. The percent removal of PO$_4^{3-}$ was usually found to be higher than NH$_4^+$ removal and the effect of pH on the removal disappeared as PO$_4^{3-}$ concentration and Mg:NH$_4$ ratio increased. At Mg:NH$_4$ ratio of 1.0:8.6, the removal of PO$_4^{3-}$ was lower than 50% in all experimental runs including those with the equal molar concentrations of Mg$^{2+}$ and PO$_4^{3-}$ (1.77$\times 10^{-3}$ M). This is due to the deficiency of
free Mg$^{2+}$ ion in the solution as it becomes more basic and formation of other species containing Mg$^{2+}$. For the molar ratio of Mg:NH$_4$ of 1.0:1.8, higher removals of PO$_3^{4-}$ was measured. The removal of PO$_3^{4-}$ was as high as 90% in the Mg$^{2+}$ concentration range between 8.50 \times 10^{-3} and 1.52 \times 10^{-2} M. The addition of PO$_3^{4-}$ to bring up a concentration higher than 8.50 \times 10^{-3} M did not increase the removal efficiency of PO$_3^{4-}$ although this concentration of PO$_3^{4-}$ is lower than the initial concentration of NH$_4$ in the wastewater. This is mainly due to the limiting concentrations of cations, which form insoluble species with PO$_3^{4-}$, in the wastewater, such as Mg$^{2+}$ and Ca$^{2+}$.

As a result of comparing the removal of ions in wastewater with different Mg$_{\text{wastewater}}$:NH$_4$:PO$_4$ ratios, it was found out that Mg$^{2+}$ concentration was the most significant factor in the removal of NH$_4$ and PO$_3^{4-}$ compared to pH as a factor in the range considered and PO$_3^{4-}$ concentration. However, it was clear from the results that PO$_3^{4-}$ concentration controls the removal of NH$_4$ significantly. This is because the major removal mechanism of NH$_4$ was by MAP formation, while PO$_3^{4-}$ removal is by the formation of several insoluble species including MAP. Similar results have been reported in the study by Uludag-Demirer (2008) using statistical methods to determine the significance of factors (concentration of MAP forming ions and pH) on the removal of NH$_4$ and PO$_3^{4-}$ ions using design of experiments approach of Taguchi.

By changing the initial concentrations of Mg$^{2+}$ and PO$_3^{4-}$ in the supernatant solution, the effects of Mg$^{2+}$ and NH$_4$:PO$_4$ ratios on removing NH$_4$ and PO$_3^{4-}$ were analysed. There were two extreme compositions of supernatant solution as one corresponding to the original composition of solution with NH$_4$:PO$_4$ ratio of 1.52 \times 10^{-2}:1.77 \times 10^{-3} (8.6:1.0) and the other simulating MAP formation stoichiometry in the solution with NH$_4$:PO$_4$ ratio of 1.52 \times 10^{-2}:1.52 \times 10^{-2} (1.0:1.0). The two different compositions also indicate the use of MAP formation for different purposes. The maximum removals of the ions along with the initial molar composition of the solution, composition of the effluent, advantages and disadvantages of the technique for each case are summarized in Table 3.

As seen from Table 3, if the concentrations of NH$_4$ and PO$_3^{4-}$ are kept as in the original wastewater, which is preferred over the addition of PO$_3^{4-}$, the concentration of NH$_4$ can be reduced to 147 mg/L in a solution containing Mg$^{2+}$ molar concentration equal to 2 times of initial NH$_4$ molar concentration at pH 9.0 by MAP formation. The same conditions, however, yielded considerably high removal of PO$_3^{4-}$ ion by reducing its concentration to 22 mg/L. As discussed before, the difference between the removal of NH$_4$ and PO$_3^{4-}$ may indicate the formation of other species containing PO$_3^{4-}$, which lowers the purity of MAP. This is why in cases where NH$_4$ and PO$_3^{4-}$ ions are desired to be recovered in the form of MAP, PO$_3^{4-}$ concentration should be higher to not to limit MAP formation. Since NH$_4$ removal is not high in this case, there will be post treatment of this ion down in the stream to meet the regulations. Therefore, MAP formation in wastewater composition with excess Mg$^{2+}$ and limiting PO$_3^{4-}$ can be used to remove PO$_3^{4-}$.

On the other hand, the percent removal of NH$_4$ and PO$_3^{4-}$ in the wastewater with equal molar concentrations of Mg$^{2+}$, NH$_4^+$, and PO$_3^{4-}$ was almost the same as 64% and 63%, respectively. The precipitate collected from these experiments was analysed using XRD and results showed the formation of almost pure MAP. It was also shown that overloading the solution with Mg$^{2+}$ increases both NH$_4$ and PO$_3^{4-}$ removals significantly and effluent has considerably lower concentrations of both ions (Table 3). Since the composition of wastewater was changed by adding PO$_3^{4-}$, the concentration of PO$_3^{4-}$ in effluent is still high although the percent removal of the ion is significant.

Removal and recovery of both ions, NH$_4$ and PO$_3^{4-}$, by MAP formation seem to be possible only for wastewaters containing equal molar concentrations of Mg$^{2+}$, NH$_4^+$, and PO$_3^{4-}$ and the performance of the process can be increased by adding more Mg$^{2+}$ ion. Recycling of the effluent can be beneficial in terms of not losing high PO$_3^{4-}$ content of the effluent in a continuous system.

### 6. Conclusions

The supernatant from the anaerobic digester, in which WAS was the substrate, was used in this study mainly because it is one of the richest streams in the treatment plant in terms of NH$_4$ and PO$_3^{4-}$. The experimental program was designed to establish the kinetics of MAP formation and to investigate the removal of NH$_4$ and PO$_3^{4-}$ under varying concentrations of Mg$^{2+}$ and PO$_3^{4-}$ ions and levels of pH. The results obtained showed the followings:

- Removal of NH$_4$ by MAP formation was much faster than by volatilization at pH 9.0, which means the amount of NH$_4$ lost via volatilization can be ignored during the period of experimentation and under the specified conditions.
- MAP formation was fast and achieving equilibrium state after the first 5–10 min of reaction time based on disappearance of each ion forming MAP. The formation rate of MAP was tested in terms of concentrations of the ions remaining in solution and the results showed rate of removals of Mg$^{2+}$, PO$_3^{4-}$, and NH$_4$ in descending order.
- Removal of NH$_4$ and PO$_3^{4-}$ was sensitive most to the Mg$^{2+}$ concentration and PO$_3^{4-}$ concentration controls NH$_4$ removal by MAP formation. pH was another parameter controlling the process.

### Acknowledgements

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### Table 3

Maximum removals of NH$_4$ and PO$_3^{4-}$ by MAP formation at pH=9.0 and analysis of the technique.

<table>
<thead>
<tr>
<th>Wastewater Composition</th>
<th>[NH$_4^+$]$_0$ (mg/L)</th>
<th>[PO$_3^{4-}$]$_0$ (mg/L)</th>
<th>Mg$_{\text{wastewater}}$:NH$_4$:PO$_4$ (molar ratio)</th>
<th>[NH$_4^+$]$_0$ (mg/L)</th>
<th>[PO$_3^{4-}$]$_0$ (mg/L)</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original with excess Mg$^{2+}$</td>
<td>273</td>
<td>168</td>
<td>172:8:6.1:0</td>
<td>147.0</td>
<td>22.0</td>
<td>No PO$_3^{4-}$ addition, high removal of PO$_3^{4-}$</td>
<td>Purity of MAP is high</td>
<td>Only for PO$_3^{4-}$ removal</td>
</tr>
<tr>
<td>Simulating MAP stoichiometry</td>
<td>273</td>
<td>1444</td>
<td>1.0:1:0:1:0</td>
<td>82.0</td>
<td>530.0</td>
<td>Addition of Mg$^{2+}$ and PO$_3^{4-}$ in effluent</td>
<td>Addition of Mg$^{2+}$ and PO$_3^{4-}$ in effluent</td>
<td>For removing NH$_4$ and PO$_3^{4-}$ with recirculation of the effluent</td>
</tr>
<tr>
<td>Simulating MAP stoichiometry with excess Mg$^{2+}$</td>
<td>273</td>
<td>1444</td>
<td>2.0:1:0:0:1</td>
<td>15.0</td>
<td>86.0</td>
<td>Purity of MAP is high, higher removal of NH$_4$ and PO$_3^{4-}$</td>
<td>Purity of MAP is poor, Mg$^{2+}$ addition, low removal of NH$_4$</td>
<td>For removing NH$_4$ and PO$_3^{4-}$ with recirculation of the effluent</td>
</tr>
</tbody>
</table>
References


