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ORIGINAL PAPER

Investigating techniques to determine magnesium addition requirements for the operation of a struvite crystallization process

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Abstract The recovery of phosphorus from wastewater has gathered strength due to its acceptance as a sustainable method for solving wastewater treatment plant struvite problems and the low global reserves of phosphorus ore. Although the chemistry and successful operation of phosphorus recovery plants are well documented, there still exists opportunity to reduce and optimize the use of external resources, such as magnesium, that is required for the nutrient recovery. One of the primary operational costs arises from the need for external magnesium addition, and therefore, the proper (and timely) detection of the element is necessary. In this study, methods were tested which could provide information, on-site, on the rate of application of the element and its concentration in the various water matrices. A method was developed that utilizes the combined use of pH and conductivity to determine the amount of external magnesium that needs to be added to a water sample. The amount required was determined by locating a transition point in the pH–conductivity—external magnesium added graph and the phosphate concentration in the water. For each mole of phosphorus removed, the molar ratio of Mg:P was 1.3–2.0 at the transition point. The magnesium concentration in the water matrix was also determined by the hardness test method; this method was found to be suitable for quick, on-site testing.

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Introduction

Phosphorus precipitation as struvite (magnesium ammonium phosphate hexahydrate, MAP) requires equimolar concentrations of phosphorus and magnesium. In wastewater treatment systems, magnesium is normally the limiting ion for the recovery of phosphorus by struvite precipitation, and it is commonly supplemented by adding an external magnesium source. Determining the concentration of magnesium in a struvite crystallization process is important because of its influence on the compound's solubility product and the associated operational cost. An insufficient magnesium addition limits phosphate removal, while excess addition results in higher concentration in the effluent; this, in turn, increases struvite formation potential downstream of the P-recovery system (in a wastewater treatment plant).

Common methods of determining the concentration of magnesium in a water matrix involve the use of expensive and time-consuming methods, such as use of atomic absorption (AA) or inductively coupled plasma (ICP). In a continuous process, such as in a struvite crystallizer, methods that provide results quickly are needed to reduce the lag time between sampling and analysis. For efficient process control and optimal product quality, it is imperative that the magnesium concentration in the crystallizer, process feed, and effluent be known in real time or at least be measured by a process that requires less time. Although the determination of magnesium is important because of its widespread use, little work has been reported on the development of ion-selective electrodes (ISEs) for magnesium (Gupta et al. 2002). Of the few electrodes that have been reported, the reliability in measuring in-line magnesium is reduced, due to interference from other metals, especially calcium and potassium (Gunzel and Schlue 2002).

In the absence of a suitable and reliable online analyzer for the determination of magnesium, the quantity of magnesium required for suitable struvite growth can be determined indirectly. This can be accomplished by introducing the concept of pH and electrical conductivity changes, in accordance with the struvite reaction. Conductivity is a direct measurement of the ions in solution and is proportional to the type and number of ions (Shepherd et al. 2009). Since formation of struvite reduces the number of ions, this in turn is expected to reduce the conductivity of the solution. The relationship between ionic concentrations and specific conductivity, κ, can be calculated from Eq. 1 (Shepherd et al. 2009).

$$\kappa = v * N/1000 \tag{1}$$

where $N =$ normality of the solution (eq/L), $\kappa =$ specific conductivity (S/cm), $v =$ equivalent conductance of the solution (S cm^2/mol)

For simplicity, the theoretical conductivity of the present system was assumed to originate mostly from magnesium, chloride, ammonium, and phosphate ions (Eq. 2). The initial theoretical conductivity was corrected to correspond to the actual conductivity of centrate, so that both theoretical and practical conductivity values had the same starting point.

$$\kappa = \left[\mathrm{Mg}^{2+}\right] v_0^{\mathrm{Mg}^{2+}} + \left[\mathrm{Cl}^-\right] v_0^{\mathrm{Cl}^-} + \left[\mathrm{PO}_4^{-3}\right] v_0^{\mathrm{PO}_4^{-3}} + \left[\mathrm{NH}_4^+\right] v_0^{\mathrm{NH}_4^+} \tag{2}$$

where $\kappa =$ specific conductivity (S/cm), $v_0 =$ Molar (equivalent) conductance of the solution at infinite dilution (Sc m^2/mol). Values were taken from Lide (1991).

The MAP reaction with magnesium chloride ($MgCl_2$) is obtained from Eq. 3. The hypothesis behind this indirect determination is outlined. When $MgCl_2$ is added to centrate (or crystallizer constituents), electric conductivity should increase as the chloride and magnesium ions' concentrations increase. However, the increase in conductivity should theoretically be slow (due to the removal of magnesium ion) up to the completion of the MAP reaction; at this point, all phosphate has been removed and magnesium does not participate in any subsequent reactions. After the equivalence point, the point where theoretically all the phosphate has been precipitated, this increase should be more rapid. As a result, there exists a transition point (Fattah 2010) when equivalence is reached. On the other hand, since hydroxide ion is consumed during the reaction, the pH should decrease as the MAP reaction proceeds. That is, there should be an existence of a similar bending point for pH. Thus, by determining the bending points for completion of the MAP reaction, the practical amount of magnesium needed can be determined.

In order to apply this approach, it would be necessary to determine the location of the bending point and then calculate the magnesium concentration required. One advantage of this method is that there is no need to measure the individual magnesium or phosphorus concentrations in the wastewater (feed and effluent) and the matrix present in the reactor. Therefore, this method could offer a quick and practical technique in the operation of the crystallizer.

$$\mathrm{Mg}^{2+} + 2\mathrm{Cl}^- + \mathrm{NH}_4^+ + \mathrm{PO}_4^{-3} + 6\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{MgNH}_4\mathrm{PO}_4 \cdot 6\mathrm{H}_2\mathrm{O} + 2\mathrm{Cl}^- \tag{3}$$

Magnesium can also be determined indirectly by calculating the water hardness, assuming that the hardness is mainly a function of divalent calcium and magnesium ions. By determining the total hardness and calcium hardness, magnesium hardness can then be estimated, which, in turn, can then be used to estimate the actual magnesium concentration. This technique for magnesium concentration determination had not previously been used in the context of a struvite crystallization process.

Laboratory experiments for this study were carried out at the University of British Columbia, Vancouver, BC, Canada.

Objectives of the study

This study aimed to use both conductivity and pH as a means of determining a relationship between changes in the conductivity and pH of the system and the required magnesium concentration.

Since the conductivity–pH method does not measure the actual concentration of magnesium in the system (rather it determines the quantity of standard magnesium chloride that needs to be added to the system for efficient struvite precipitation), a method to determine the concentration of magnesium was tested. This method involved the use of hardness tests to indirectly determine magnesium concentrations in wastewater centrate feed.

Methods and materials

Determination of magnesium usage for struvite precipitation—use of pH and conductivity

Several experiments, using synthetic water and centrate from Lulu Island wastewater treatment plant (LIWWTP) in Metro Vancouver, B.C., Canada, were carried out to determine the applicability of using conductivity and pH for magnesium requirements during struvite precipitation. The synthetic water was prepared by adding ammonium dihydrogen phosphate ($NH_4H_2PO_4$), ammonium chloride (NH_4Cl), and magnesium chloride ($MgCl_2 \cdot 6H_2O$), for a final solution having phosphate, ammonium, and magnesium concentrations of 300, 180, and 180 ppm, respectively. The phosphate concentration was deliberately set high so that it would not be a limiting ion during the precipitation process. A magnesium standard of 3,000 ppm was prepared in water using $MgCl_2$.

All experiments were carried out in well-mixed, 1-L Nalgene beakers using 500 mL of water sample. The prepared magnesium chloride standard was added to the solution in 0.5 mL increments every minute; conductivity and pH were logged 1 min after chloride addition. Conductivity was measured using a Hanna Instruments HI9033 multi-range conductivity meter, while pH was measured with an Oakton® pH meter.

Determination of magnesium usage for struvite precipitation—use of hardness

Hardness tests were carried out according to Standard Methods (APHA et al. 1995) for both calcium (Method 3500-Ca D) and total hardness (Method 2340 C). The magnesium concentration was calculated based on the difference between total and calcium hardness, assuming that the hardness was derived primarily from Ca^{2+} and Mg^{2+} ions. Due to low concentrations usually found in wastewater centrate (Fattah et al. 2012), the presence of interfering cations such as cadmium, zinc, iron, nickel, and cobalt was ignored. The interference due to aluminum was reduced by adding a magnesium salt of 1, 2-cyclohexanediaminetetraacetic acid (MgCDTA).

Sample preparation

Centrate samples were first centrifuged and filtered onsite with 0.45-micron membrane filter papers, before being preserved according to Standard Methods (APHA et al. 1995). Analytical measurements of phosphorus were carried out in the laboratory using colorimetric flow injection analysis (model LaChat QuikChem® 8000). Magnesium and calcium ions were analyzed using flame atomic absorption spectroscopy (AA) (model Varian Inc. SpectrAA220®). For each condition, two samples were taken and analyzed according to Standard Methods (APHA et al. 1995).

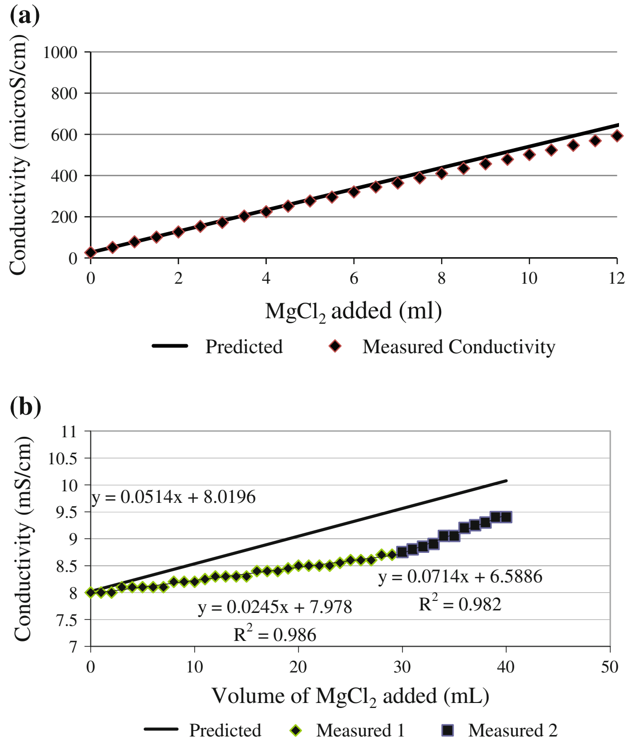

Fig. 1 Influence of magnesium chloride addition on the conductivity: **a** predicted versus measured in distilled water (with no P and N), and **b** predicted versus measured in centrate sample

Results and discussion

Prediction of magnesium requirements from conductivity–pH measurements

Theoretical versus practical change in conductivity

In the present study, experiments were carried out in the laboratory to predict (using Eq. 2) the conductivity increase with the addition of external magnesium chloride and then to compare this value to the actual change in conductivity. As illustrated in Fig. 1a, the actual conductivity in distilled water could be predicted according to this equation, with a high degree of accuracy. However, when the same principle was used to predict the conductivity increase in real centrate solution, the values did not increase as predicted (Fig. 1b). This was assumed to be due to the formation of struvite and removal of other ions through secondary reactions. The initial (Measured 1 in Fig. 1b) rate of change in conductivity was lower compared to the latter part, indicating that the rate of increase in ionic concentrations was lower. After 30 mL (Measured 2 in Fig. 1b) of magnesium chloride addition, the rate of conductivity increase changed and actually increased relative to the start of the test. The location of the ‘increased rate of change’ was then assumed as the bending/transition

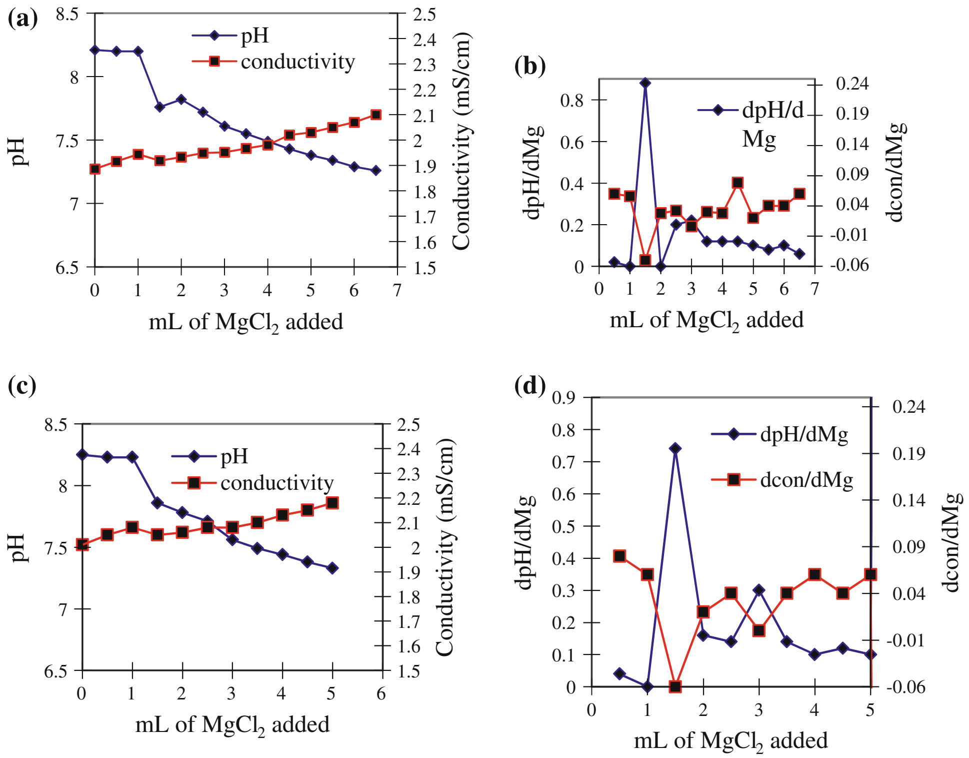

Fig. 2 **a**, **c** Influence of magnesium chloride addition on pH and conductivity of a synthetic wastewater and **b**, **d** change in pH and conductivity as a function of magnesium chloride addition for different runs

point where all available phosphate is expected to have precipitated out as struvite. The process of locating the bending point is further explained in the following section.

Experimental runs to determine the transition point for magnesium addition

The objective of this part of the study was to validate the presence–absence of a bending or transition point in the conductivity and pH trends, when magnesium chloride is added to the water matrix.

Figures 2 and 3 illustrate the influence of magnesium chloride additions on the conductivity and pH in experimental runs with synthetic and LIWWTP centrate, respectively. By using the first derivatives of pH and conductivity, a more graphic and 'easy-to-comprehend' location of the transition point can be determined. The transition point is the location where the dpH/dMg ratio is highest, while the dcon/dMg ratio is lowest. This corresponds to 1.5 mL of $MgCl_2$ in Fig. 2. Figure 4 is an expanded format to provide an explanation of the phenomena occurring and the method to detect the bending point.

In this experiment, three conductivity zones were distinguishable—the initial rapid increase in conductivity, the middle low conductivity rise, and a final increased rate of conductivity change. By theory, the slope of the conductivity curve in the final section should be higher than that at the beginning, but as was found from the tests, this was not the case. This may indicate that not all of the reactions were completed and some magnesium ion (and/or chloride ion) is still being consumed. However, determining these possible "other" reactions was not part of the current study.

Three zones in the pH–magnesium chloride addition were also noticeable—the initial slow pH change, the rapid pH decrease, and the final slow pH decrease. The addition of magnesium chloride to water would normally increase the pH of the system into which it is added. However, since struvite formation is accompanied by a lowering of the pH, the end of the middle section was hypothesized as the end of struvite formation. Since the final pH section did not show an increase in pH, as expected, due to the continued addition of magnesium chloride, it could be hypothesized that certain reactions, which reduces the pH of the system, were still occurring. The equations shown in the figure are based on linear trend lines of the three distinguishable zones.

Several tests were carried out to determine whether the process of finding the transition point could be replicated, and each time the same transition location was found. Upon determining the molar concentrations at the transition points, it was found that, for each mole of phosphate removed, the Mg:P molar ratio was between 1.3 and 2.0. This ratio, also suggested by other studies (Jaffer et al. 2002; Munch and Barr 2001), is important; although it does

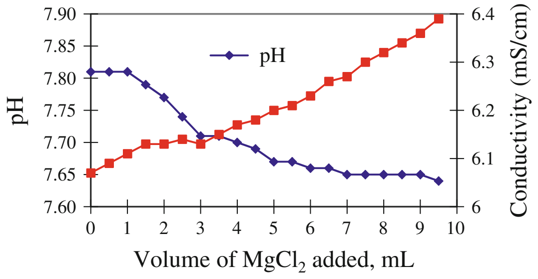

Fig. 3 Influence of magnesium chloride addition on pH and conductivity in centrate

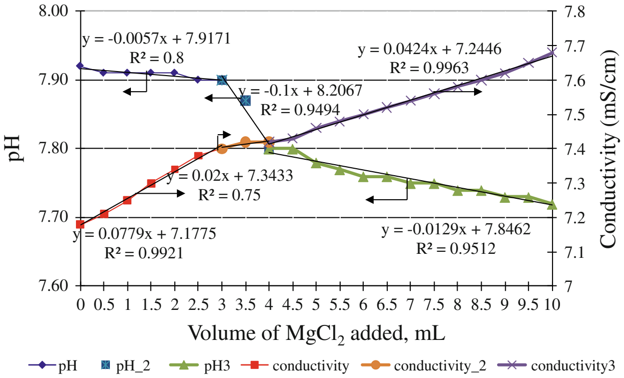

Fig. 4 Influence of magnesium chloride addition on conductivity and pH of centrate—determination of transition point

not signal the end of the reaction, it determines the quantity of magnesium chloride required to remove one mole of phosphate. By knowing the phosphate concentration through use of online analyzers, the amount of magnesium required to completely precipitate phosphate out as struvite can then be calculated more easily. That is, the phosphate molar concentration would be multiplied by a factor of 1.3–2.0 to get the required magnesium dosages. This method can provide the basis for developing a more accurate crystallizer operation (with respect to magnesium addition) and control operating costs.

Although pure struvite crystallization occurs at a Mg:P molar ratio of 1:1, the Mg:P molar ratio determined here can be explained in terms of the activity and concentration of $MgCl_2$ in the standard. Normal detection of magnesium, by AA, provides values for the total magnesium concentration. However, the portion of the measured magnesium that actually takes part in the reaction is represented by the activity of soluble magnesium ion, which, with most ions concerned with struvite precipitation, is lower than the actual concentration. Therefore, this technique provides a better estimate of the dosages required. Conductivity changes, due to magnesium chloride addition on swine manure slurries by Shepherd et al. (2009), found that an inflection point occurred around 50 % of the stoichiometric magnesium demand. However, they were unable to use their data to provide any ratio or estimate the rate of magnesium addition that would provide for optimized application.

Hardness test results

The hardness method for determining the magnesium concentration required the determination of both total hardness and Ca-hardness. The result for calcium detection has been included in this section to illustrate the use and efficiency of the method in determining the concentration of the metal.

From the Ca-hardness test, the calcium concentration was calculated and compared with values determined by the AA. Figure 5a illustrates that, in most instances, the hardness method gave higher than actual values; the average absolute error in the values was only 3.8 mg/L. Given that hardness test results, by themselves, have limitations (such as in detecting the end point), the predictability of this method was deemed acceptable.

Similar to the calcium values, it was found that, on most occasions, magnesium concentrations determined by the hardness test method were higher than those measured by the AA (Fig. 5b); the absolute average error between the two tests was only 2.0 mg/L. The relatively higher

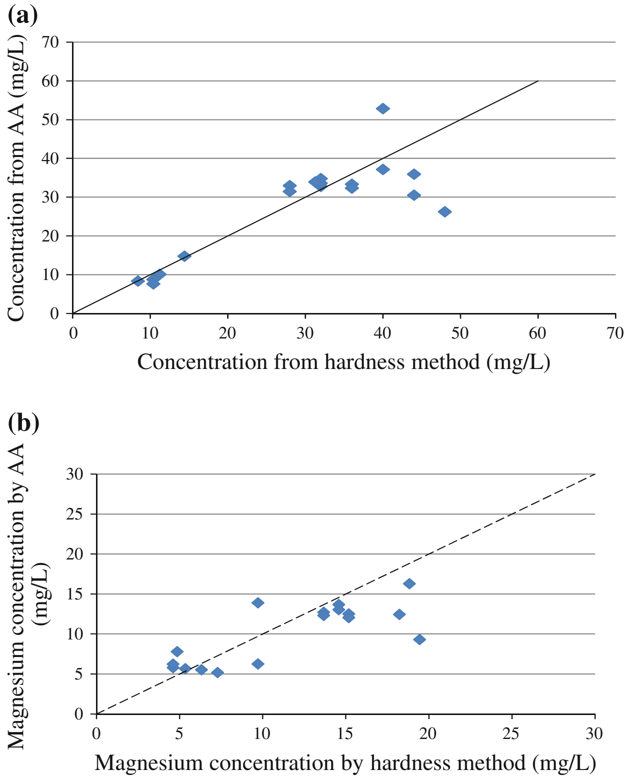

Fig. 5 Comparison of **a** calcium and **b** magnesium concentrations via hardness method and AA. The *line* depicts the equivalence line

experimental values can probably be attributed to (in addition to titration limitations/errors) the addition of MgCDTA inhibitor, during the hardness test. Forrest et al. (2008) used a modified hardness test method to determine the magnesium concentration and found a relative standard deviation of 4.5 %. Tests carried out to determine the magnesium concentration in a parallel study found an absolute error of 3.9 mg/L (Dirk, B. pers. comm. 2009).

It is important to note that the accuracy of prediction is higher at the lower concentration end (0–7 mg/L). This is important because the typical magnesium concentration in wastewater centrate at LIWWTP was only 0–6 mg/L. Therefore, although not 100 % accurate, this method provides a good estimate of the Mg^{2+} concentrations in the sample; also, the method can be performed on site and is much quicker and cheaper than employing AA or ICP.

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