



Nutrient Enrichment of the Anaerobic Sludge by Co-Precipitating N and P in the Mesophilic Anaerobic Digester

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Summary

Copper One of the techniques used for the stabilization of sewage sludge is anaerobic digestion. The effluent from anaerobic digesters usually requires further treatment since they contain high concentrations of N and P as a result of volatile solids destruction. In this study, a control was developed over the nutrient ions within the anaerobic digester by using substrate with high concentration of Mg^{2+} ion. The amount of Mg^{2+} ion added was determined based on the release rate of N and composition of magnesium ammonium phosphate. The results showed 50% removal of NH_4^+ and PO_4^{3-} can be achieved without compromising the performance of the reactor in COD and VSS removal and biogas formation.

Keywords: anaerobic digestion, magnesium ammonium phosphate, nutrient removal, sewage sludge

Introduction

New and innovative ways to extract valuable product(s) from anaerobic sludge are still under investigation to reduce the impacts of treatment processes on the environment. Anaerobic sludge is viewed as a resource for its use in agricultural activities although its application on land is still limited due to uncertain levels of pathogen removal during anaerobic digestion and quality of anaerobic sludge as a fertilizer.

To be able to enrich the composition of anaerobic sludge, the removal of nutrients, i.e., NH_4^+ and PO_4^{3-} ions, is considered to take place in the anaerobic digesters by using a chemical precipitation technique. The nutrient removal integrated with anaerobic digestion can serve to the purpose of recovery of N and P from wastewater as well to protect the receiving water bodies from eutrophication, to reduce the use of non-renewable phosphorus (P) reserves and the energy consumption during the production of nitrogen (N) based fertilizers. One of the techniques for the removal and/or recovery of N and P from wastewater is the formation of magnesium ammonium phosphate (MAP) or struvite. MAP is a valuable product. It is a slow release fertilizer with a market value. The formation of MAP and its consequent precipitation in the anaerobic digester may increase the fertilizer value of the anaerobic sludge.

The production of MAP from a wastewater is economically and technically feasible in Mg^{2+} and nutrient rich and slightly alkaline solutions. Anaerobic digesters in domestic wastewater treatment plants usually possess these conditions, except Mg^{2+} concentration level. The concentration of Mg^{2+} is gener-

ally lower than the nutrient concentration. However, there is still enough of Mg^{2+} ion to observe uncontrolled formation and accumulation of MAP in the hydraulic works and reactors in the anaerobic digestion unit, which may cause significant maintenance problems and replacements (Doyle et al., 2003).

In this study, the co-precipitation of N and P is aimed in the anaerobic digesters following the addition of Mg^{2+} ion. While the performances of the digesters were checked regularly, the N and P contents of the anaerobic sludge were investigated. The anaerobic digesters were operated in semi-continuous mode. The Mg^{2+} ion was supplied along with the substrate, a mixture of primary settlings (PS) and waste activated sludge (WAS). The effect of Mg^{2+} ion on the performance of the digesters was observed by measuring the biogas formation (or COD removal) and its composition and controlling the microbial diversity using molecular techniques. The methanosaeta and methanosarcina population in the samples was determined by quantitative polymerase chain reactions (qPCR) method. The removal of N and P was observed based on the concentrations of NH_4^+ and PO_4^{3-} ions in the solution. In addition, the anaerobic sludge mixed with MAP was analyzed in its N and P content using the solubility test.

Experimental Study

ATA Test for Mg^{2+} : A series of batch reactors was prepared with the liquid volume of 60 ml consisted of 50 ml of seed (anaerobic culture). Each assay was prepared in triplicates. The inoculum was obtained from the anaerobic digester operating in a local

wastewater treatment plant. Two controls, seed and feed, were prepared to understand the inhibition of Mg^{2+} on the production of biogas. The feed was Caacetate (CaAc) (stock solution with 150 g/l concentration), which was added (1 ml = 0.15 g CaAc/reactor and 0.65 g COD/g CaAc) to provide 1.6 g COD/l initially in the reactors. The Mg^{2+} ion in the form of $MgCl_2 \cdot 6H_2O$ was added to obtain initial concentrations of 0.038 and 0.077 M. The remaining volume was completed to 60 ml using sterilized tap water. The reactors were purged with N_2 and CO_2 mixture for a minute to mix the contents and strip the dissolved oxygen. Then, the reactors were sealed by septa and kept mixed using a shaker and at 35–37°C. The volume of the biogas and its composition were measured daily for 11 days.

Operation of anaerobic reactors: Three semi continuous glass reactors with the effective volume of 6.0 l received the mixture of waste activated sludge and primary settlings daily. The volumetric ratio of activated sludge and primary settlings in the mixture had a fixed total solids content of 3.5% (dry weight). The hydraulic and solids retention time was the same as 15 days. The temperature was in the 35–37°C range. The volume of the biogas produced was measured by wet-tip meters connected to a counter (Rebel Point Wet-Tip Gas Meter Co., Nashville, TN). The reactors were mixed continuously at 600 rpm using a shaft with 2 blades. One of the three digesters was the control reactor, which received only the substrate during the study. The other two digesters were fed by Mg^{2+} ($MgCl_2 \cdot 6H_2O$) containing substrate. The amount of $MgCl_2 \cdot 6H_2O$ to add was calculated based on the molar concentration of NH_4^+ in aqueous phase and the release rate of N from VS destruction. The reason of using NH_4^+ molar concentration is to make sure the Mg^{2+} ion does not become a limiting reactant in the formation of MAP during the process.

Two different strategies were used to add Mg^{2+} into the reactors. Reactor A received Mg^{2+} ion to precipitate all NH_4^+ in the reactor by a single dose. The amount added was also enough for the NH_4^+ released from the destruction of volatile solids during a week long period. The other reactor, Reactor B, received Mg^{2+} every day according to the rate of NH_4^+ release in the reactor. The rate of NH_4^+ release was calculated using the destruction rate of the volatile solids assuming the approximate composition of the new cells as $C_5H_7NO_2$ neglecting P (Metcalf and Eddy, 2004). The destruction of volatile solids was determined by the measurement of volatile solids concentration in the feed and effluent periodically.

Analytical Measurements: The biogas composition was analyzed for CH_4 and CO_2 by a Hewlett

Packard™, Model 6890 gas chromatograph equipped with a thermal conductivity detector. An eight meter long HayeSep® Q, 80/100 packed column was used to separate CH_4 and CO_2 (Alltech Associates Inc, Deerfield, IL). Helium was the carrier gas with a flow rate of 25 ml/min. The concentration of NH_3 was measured using ammonia ion-selective electrode (Cole-Parmer, Vernon Hills, IL). The concentrations of ortho- PO_4^{3-} and COD were measured using HACH kits (colorimetric method) while solids content of the effluent was measured gravimetrically according to the standard methods (APHA, 1995). The identification of and quantification of *Methanosarcina* and *Methanosaeta* were made by PCR and real time quantitative PCR respectively in the samples taken directly from the digesters. The details of the molecular techniques can be found in a recently published article by Uludag-Demirer *et al.*, 2012.

Results and Discussion

The effect Mg^{2+} on the biogas formation (ATA test): The results obtained from the ATA showed that Mg^{2+} ion concentration up to the concentration of 0.077 M is not inhibitory on the production of CH_4 . The upper limit for Mg^{2+} concentration was decided based on the maximum concentration of NH_3 (or NH_4^+) in the anaerobic digesters. The cumulative CH_4 formed in the reactors was the same in feed control and Mg^{2+} added reactors, which means the recovery of all COD added in the form of acetate was observed (Fig. 1).

Performance of the anaerobic digesters: The performance of the digesters was observed based on the volume of CH_4 produced per day (Fig. 2). The volume of CH_4 in the control reactor varied between 3500 and 4500 ml/day (at 35°C and 1 atm). There may be several reasons for measuring the volume of CH_4 with high variation, for example, variance in the characteristics of the feed sludge during the storage and samplings, which were made several times in the course of the study. The average daily COD added to the reactors was 50,000 mg/l and it decreased down to 18,700–19,000 mg/l in the effluent of the both Reactors A and B before the addition of Mg^{2+} containing substrate. The removal of COD was around 62%, which is close to the range of COD removal of 56–77% for the mesophilic anaerobic digestion of municipal biosolids with the retention time of 15 days (Metcalf and Eddy 2004). This COD removal is expected to yield 5,000 ml of CH_4 at 35°C theoretically, which has not been observed during the operation period of the reactors (Figure 2). It is not unusual to observe such discrepancies between the measured and calculated volume of CH_4 due to the variation in the COD of the feed since it was prepared every day.

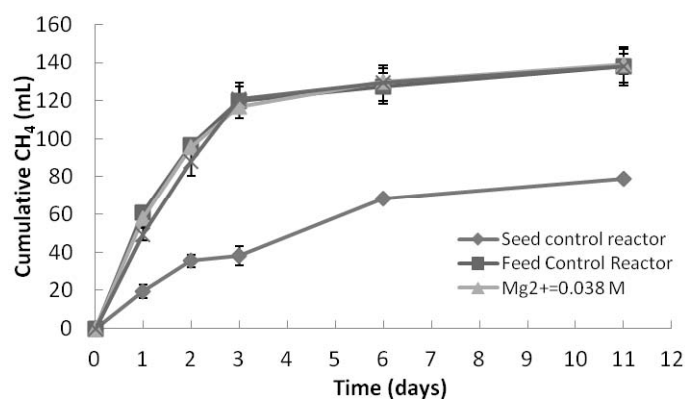


Fig. 1. The cumulative CH₄ formation in the ATA study for Mg²⁺ ion
Rys. 1. Zbiorcza formacja CH₄ w badaniu ATA dla jonu Mg²⁺

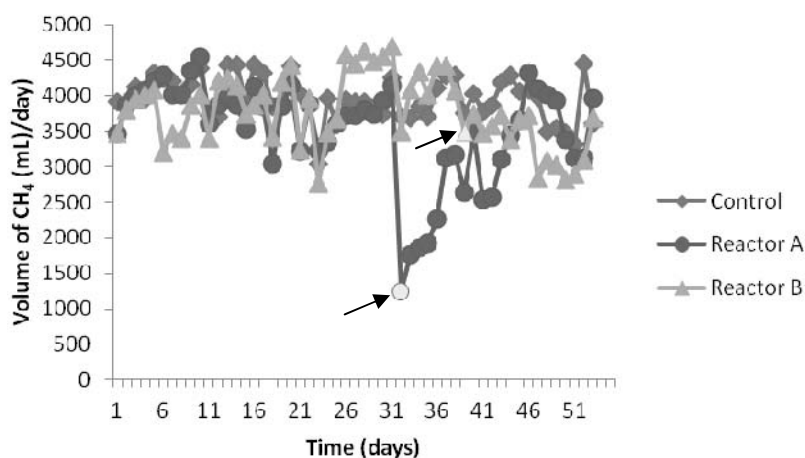


Fig. 2. The volume of CH₄ produced daily in the semi-continuous reactors.
The data points filled by the arrows indicate the addition of Mg²⁺ into the Reactors A and B
Rys. 2. Objętość CH₄ wyprodukowanego w ciągu dnia w reaktorze półciągłym.
Strzałki wskazują dodatek jonów Mg²⁺ do reaktorów A i B

The production of CH₄ in Reactor A decreased to the levels of 1,000 ml immediately after the addition of 0.135 M Mg²⁺ at once, but started recovering the following day. In about 20 days, the volume of CH₄ achieved similar levels of CH₄ volume that is produced in the control reactor (Fig. 2). As a result of a significant decline in the performance of A, another addition of Mg²⁺ into this reactor was not made during the study. The reactor B was dosed by Mg²⁺ everyday at the level of 0.085 mol/l. day, which is decided based on the destruction rate of VS. The amount of Mg²⁺ added into the reactor B is similar to the concentration level adopted in ATA study (0.077 M), which also yielded no effect on the production of CH₄ as compared to the control reactor.

The investigation of changes in the biological diversity as a result of the presence of Mg²⁺ using molecular techniques showed that there was no significant difference in the number of *Methanosaeta* (formerly known as *Methanothrix*) and *Methanosarcina* in the control reactor and reactors received

Mg²⁺. The average *Methanosaeta* gene copy was 5.66×10^7 (average of three samples) in the control reactor while the average *Methanosarcina* gene copy was 5.63×10^4 in the same reactor. Similar differences were observed in the reactors that received Mg²⁺ along with the substrate. Analyses showed that *Methanosaeta* was the predominant species compared to *Methanosarcina* in all of the reactors confirming their optimum conditions to be mesophilic and their dominance in low acetate concentrations. It is typical that *Methanosaeta* dominates in low acetate concentration and mesophilic conditions while *Methanosarcina* prefer the higher concentration of acetate and thermophilic conditions (Chapman and Krugel, 2008).

The removal of nutrients: During the operation of the reactors, the concentrations of NH₃ and PO₄³⁻ in the effluent of the reactors were monitored to understand and quantify the effect of excess Mg²⁺ on the removal of nutrients. The removal of NH₃ was significant after the addition of Mg²⁺ into the reactors A and

B in day 31 and day 39 respectively. Addition of excess Mg^{2+} (0.135 M) at once into the Reactor A (day 31) proved to be high enough to precipitate all NH_3 in the reactor and NH_3 released from VS degradation during a week. A gradual decrease in the concentration of NH_3 during the first 5 days was followed by a more stable concentration around 0.04 M corresponding to about 50% removal of NH_3 . The addition of Mg^{2+} was discontinued so that the microbial population within the reactor was not disturbed further and any possible changes in the biodiversity following the recovery of CH_4 production level could be assessed. The removal of NH_3 was more gradual in the Reactor B, which received Mg^{2+} of 0.085 mol/L .day. The removal increased up to a maximum removal of 50% over the operation period. It seemed that the continuous addition of Mg^{2+} helped to control NH_3 concentration without affecting the formation of CH_4 , which is a great advantage over the shock addition of Mg^{2+} as tested in Reactor A. The removal of PO_4^{3-} in the reactors A and B was determined by measuring the concentration of the ion in the control reactor and Reactors A and B periodically. During the operation of the control reactor, the concentration of PO_4^{3-} was around 0.0015 M, which was reduced to 0.0008 M after the addition of Mg^{2+} regardless of the type of dosing the reactor, i.e., slug and continuous dosing. This decrease in concentration corresponds to about 47% removal of PO_4^{3-} .

Changes in the characteristics of the anaerobic sludge: The solids content of the anaerobic sludge in the reactors changed during the course of the study. Following the addition of Mg^{2+} ion into the Reactors A and B increase total solids content of the anaerobic sludge as expected as a result of minerals formation, such as MAP (Fig. 3). In reactor

A, the TS level started to decrease since the addition of Mg^{2+} was made one time (day 31) during the operation of the reactor. The TS concentration became closer to that in the control reactor toward the termination of Reactor A. The concentration of VS in Reactor A was higher after the addition of Mg^{2+} ion (Fig. 4). This definitely points at a reduction in the performance of the reactor in VS destruction by controlling the overall rate of biotransformation reactions. The smaller sized mineral particles may act as a nucleus for the agglomeration of the organisms causing to wash out the VS from the reactor in larger quantities. However, this needs more research for its clarification.

The concentration of TS in the Reactor B increased gradually with time, indicating an accumulation of the precipitate as Mg^{2+} addition continued (Fig. 3). The destruction of VS declined up to a level that there was no measurable removal of VS in the system (Fig. 4). Again this could be due to the precipitate formed and accumulated on the solids, which may be acting as a physical barrier. There is certainly a need to study the performance of such a digester for a longer period of time to understand how the system recovers from this obstacle.

Conclusions

The MAP formation via continuous Mg^{2+} addition to anaerobic treatment processes can be an option for the recovery of nutrients, N and P, without affecting the performance of the digesters significantly. The experimental results also show that NH_4^+ and PO_4^{3-} were removed higher than their molar ratios in struvite suggesting their removal mechanisms other than struvite formation which should be investigated in detail to overcome the limitations of the forced nutrient recovery.

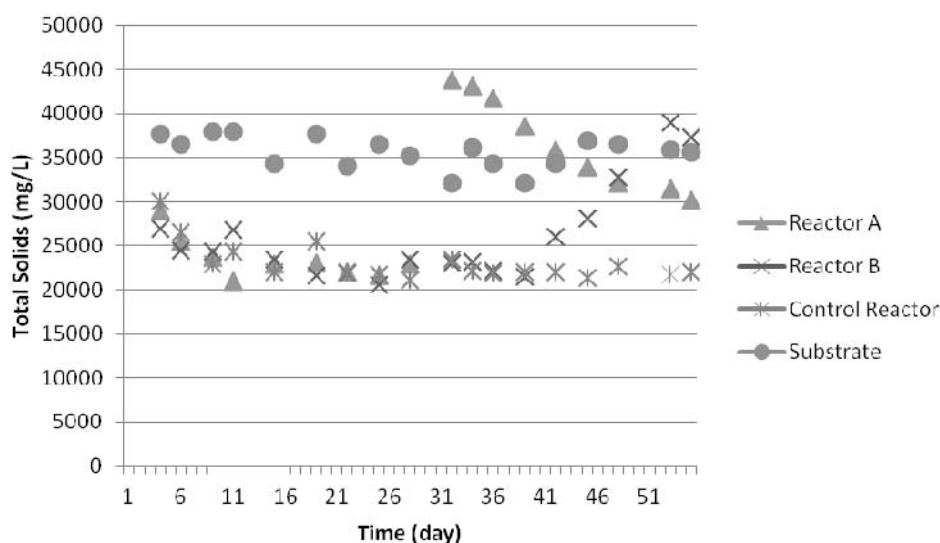


Fig. 3. The concentration of total solids (TS) in the anaerobic digesters

Rys. 3. Całkowite stężenie substancji stałych w beztlenowych komorach fermentacyjnych

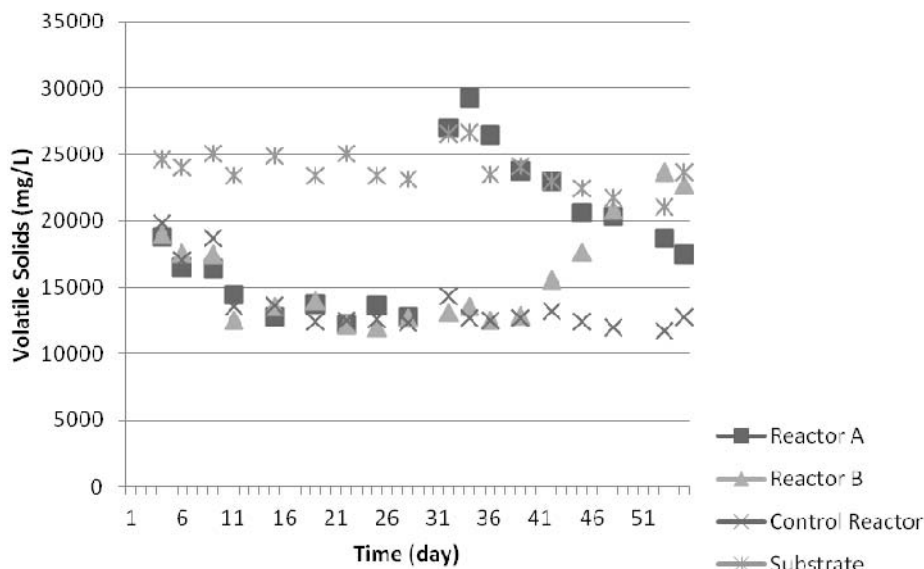


Fig. 4. The concentration of volatile solids (VS) in the anaerobic digesters

Rys. 4. Stężenie suchej masy organicznej w beztlenowych komorach fermentacyjnych

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Wzbogacanie pożywki anaerobowych osadów ściekowych przez współstrącanie N i P w mezofilowym fermentatorze anaerobowym

Jedną z technik użytych do stabilizacji osadów ściekowych jest fermentacja beztlenowa. Ścieki z komór fermentacyjnych zwykle wymagają dalszej obróbki ze względu na fakt, że zawierają wysokie stężenia N i P jako rezultat rozkładu substancji stałych. W referacie zamieszczono wyniki kontroli nad jonami substancji odżywczych w obrębie komory fermentacyjnej przez użycie substratu o wysokim stężeniu jonów Mg^{2+} . Ilość dodanych jonów Mg^{2+} określono na podstawie stopnia uwolnienia N i składu fosforanu amonowo-magnezu. Wyniki pokazują 50% usuwalność NH_4^+ i PO_4^{3-} co może być osiągnięte bez kompromisu pomiędzy wydajnością reaktora COD a usuwalnością VSS i tworzeniem biogazu.

Słowa kluczowe: fermentacja beztlenowa, fosforan amonowo-magnezowy, usuwanie substancji odżywczych, osady ściekowe