

Sludge digestion enhancement and nutrient removal from anaerobic supernatant by $Mg(OH)_2$ application

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Abstract Anaerobic sludge digestion is a widely adopted process for sludge stabilization. Phosphate removal from anaerobic supernatant is necessary to limit the phosphate returned to the head of the treatment plant, thereby improving the overall treatment efficiency. In this study, magnesium hydroxide ($Mg(OH)_2$) was used to improve the sludge digestion efficiency and to remove phosphorus from anaerobic supernatant. The anaerobic sludge digestion experiment was conducted at a pilot scale, and the results showed that applying $Mg(OH)_2$ to anaerobic sludge digester resulted in a larger reduction in SS and COD, a higher biogas production rate, a lower level of phosphate and ammonia nitrogen concentrations in the sludge supernatant and an improved sludge dewaterability. Research results at both lab scale and pilot scale on phosphorus removal from anaerobic supernatant using $Mg(OH)_2$ showed that a high removal of phosphorus can be achieved through the addition of $Mg(OH)_2$. The required reaction time depends on the initial phosphorus concentration and the $Mg(OH)_2$ dosage.

Keywords Anaerobic supernatant; magnesium hydroxide; nutrient removal; phosphorus; sludge digestion

Introduction

In conventional activated sludge wastewater treatment plants, there are two side waste streams that must be properly addressed: anaerobic digester supernatant and waste activated sludge. Both streams contain a very high concentration of phosphorus and nitrogen compared to the incoming wastewater. Through mathematical modeling, recycle of phosphorus loads from anaerobic digestion can be estimated (Wild *et al.*, 1997). Removing the nutrients from anaerobic supernatant or fixing them inside the digester will not only reduce the nutrient backload to the headworks of the treatment plant but will also help to minimize struvite (magnesium ammonium phosphate) formation, which can cause major problems for plant operation, such as pipe and pump clogging. Struvite is commonly formed in anaerobic sludge digester and post digestion sludge handling facilities, e.g. belt presses and centrifugation facilities. Some research has been done to control the formation of struvite, e.g. dosing with ferric chloride (Mamais *et al.*, 1994).

Chemical phosphorus removal in wastewater treatment plant is usually realized through the addition of Fe and Al salts. However, this practice has two major drawbacks: one is that the chloride or sulfate concentration in wastewater is increased and the other is that phosphorus recovery from either ferric or aluminium phosphate is nearly impossible. Addition of magnesium hydroxide, on the other hand, has the advantage of being not only able to increase the pH to favor the precipitation but also able to generate more usable phosphate salts, e.g., struvite. This is particularly true if magnesium hydroxide is added to anaerobic digester supernatant, as this side waste stream contains a high concentration of phosphate and ammonium.

Phosphorus fixation in anaerobic supernatant through chemical precipitation or crystallization has been addressed by several researchers; it has proved to be a very promising process (Joko, 1984; Giesen, 1999; Battistoni, 1997a, 1997b, 2000).

Magnesium hydroxide occurs in nature as brucite, which is composed of white, pale green, blue or gray trigonal crystals with a white streak. It is a white, very fine, bulky powder or slurry. It has a very low solubility in water, with a solubility constant of $10^{-7.4}$.

Dravo Lime Co. has, for several years, supplied a magnesium-containing lime for use in wet flue gas desulfurization (FGD) systems. This lime contains 3 to 6% MgO. Dravo Lime Co. and Cincinnati Cinergy have demonstrated that $\text{Mg}(\text{OH})_2$ can be successfully recovered from the FGD system (Smith *et al.*, 1995). The recovered $\text{Mg}(\text{OH})_2$ is about 2/3 the production cost of commercially available $\text{Mg}(\text{OH})_2$ product.

The objective of this research was to investigate the effect of $\text{Mg}(\text{OH})_2$ in enhancing anaerobic sludge digestion and removing nutrients, primarily phosphorus, from anaerobic supernatants. This paper presents part of the research results; further research is still under way.

Methods

The experiments were divided into two parts: 1) investigation of the effect of $\text{Mg}(\text{OH})_2$ on enhancing anaerobic sludge digestion, and 2) research on the use of $\text{Mg}(\text{OH})_2$ in removing nutrients from sludge handling liquors, i.e. anaerobic supernatant.

Materials

Reagent grade $\text{Mg}(\text{OH})_2$ was purchased from Fisher Scientific. The reclaimed $\text{Mg}(\text{OH})_2$ product was supplied by Dravo Lime Co. In order to investigate the effect of Mg^{2+} on phosphorus removal from anaerobic supernatant, reagent grade MgCl_2 obtained from Fisher Scientific was also used. The anaerobic supernatant was supplied from the sludge dewatering facility (both centrifuge and belt-press) at the Mill Creek Wastewater Treatment Plant (WWTP), Cincinnati, OH, USA. Two pilot-scale sludge digesters, each with a volume of 32 L, were operated in batch mode. One reactor was used as a control digester and $\text{Mg}(\text{OH})_2$ was added to the other. Digested sludge from the Cincinnati Mill Creek WWTP was used as the anaerobic inoculum for the anaerobic sludge digesters; dissolved air flotation (DAF) sludge was fed to the reactors.

Analysis

In the anaerobic sludge digestion experiments, samples were periodically taken for analysis of pH, alkalinity, acetate, total COD (TCOD), soluble COD (SCOD), total suspended solids (TSS), volatile suspended solids (VSS), sulfate, ortho-phosphate, ammonium nitrogen, Mg^{2+} and Ca^{2+} . Analysis of pH, alkalinity, COD and SS were carried out in accordance with the *Standard Methods* (APHA, 1995). Sulfate, ortho-phosphate, ammonium nitrogen, Mg^{2+} and Ca^{2+} were analyzed using a Dionex ion chromatograph. Sludge dewaterability was measured in terms of capillary suction time (CST).

In the experiments evaluating phosphorus removal from anaerobic supernatant, analysis of pH, alkalinity, phosphate and ammonium-nitrogen were conducted. Powdered X-ray diffraction (XRD) analysis was used to study the mineral phases of the formed precipitate.

Equipment

For the anaerobic sludge digestion experiments, two pilot-scale reactors, each with a volume of 32 L, were used. The schematic diagram of the reactors is shown in Figure 1.

For the nutrient removal experiments, both lab scale and pilot scale equipment were employed. In the lab scale experiments, plastic bottles and a water bath/shaker were used. Pilot-scale column equipment was used for the pilot experiment. The column is made of plexiglass. There are 3 removable segments for easy transportation and assembly. The column is 30 cm in ID and 3 m in overall height. Sampling ports, with a spacing interval of 25 cm, are arranged along the column height. An air compressor provides the air required for mixing and CO_2 stripping. The whole unit – the column, the pump and the air compressor – are fixed onto a movable steel cart.

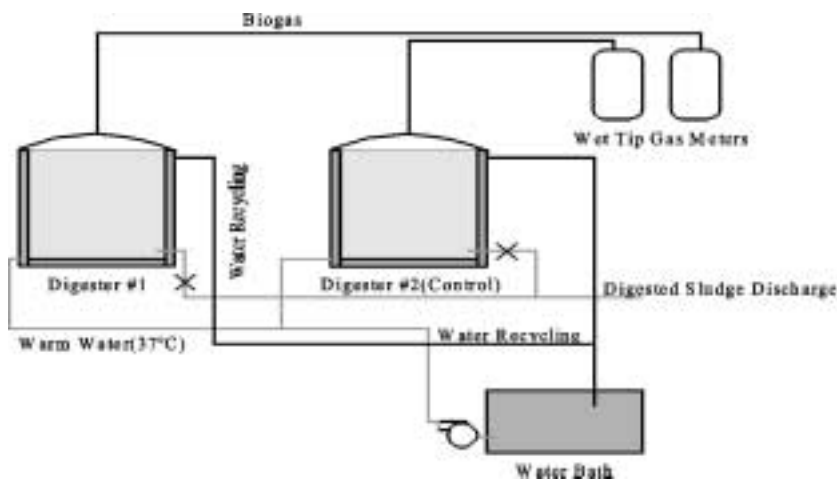


Figure 1 Schematic diagram of the pilot scale sludge digesters

Results and discussion

Mg(OH)₂ enhanced anaerobic sludge digestion experiment

Temperature was kept at $35 \pm 1^\circ\text{C}$ in both reactors. Two experimental runs were conducted: Run #1 lasted 18 days and Run #2 lasted 17 days. Mg(OH)₂ dosage was 300 mg/L for both runs. Results of COD and CST changes during digestion for Run #1 are shown in Table 1. The complete results for Run #2 are summarized in Table 2.

From Tables 1 and 2, it can be seen that: 1) the Mg(OH)₂ treated digester had a larger reduction in TSS, VSS, TCOD and SCOD than the control reactor; 2) with Mg(OH)₂ addition, the phosphate and ammonia nitrogen concentrations in the sludge supernatant were much lower than that of the control reactor, which implies the nutrient load to the head of the treatment plant would be greatly reduced; and 3) sludge digestion normally results in a deterioration of the sludge dewaterability, but with Mg(OH)₂ addition there was almost no change in sludge dewaterability before and after sludge digestion. Results on the gas production rate (data not shown) showed that the Mg(OH)₂ amended digester had a higher gas production rate than the control digester.

The above results can be explained by the following rationale: 1) dissolution of Mg(OH)₂ can neutralize the volatile fatty acids produced by the Acidogens, resulting in a better pH environment for the Methanogens; 2) light metal cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) are stimulatory to the anaerobic sludge digestion process. At the Mg(OH)₂ dosage of 300 mg/L, the Mg²⁺ released into the bulk solution (124 mg/L) falls within the stimulatory range, which is 75–150 mg/L (Grady *et al.*, 1999); and 3) Mg²⁺ released from the dissolution of Mg(OH)₂ and the enhanced polyphosphate hydrolysis, and degradation of organic solids, can react with phosphate to form struvite or a mixture of struvite and other

Table 1 COD and CST changes during sludge digestion – Run #1

Date	Control reactor			Reactor with Mg(OH) ₂ addition		
	TCOD (mg/L)	SCOD (mg/L)	CST (sec)	TCOD (mg/L)	SCOD (mg/L)	CST (sec)
Day 1	32605	3239	473	30170	3366	316
Day 3	24346	5642		20005	7368	
Day 6	18417	6796		16723	3535	
Day 9	15346	4489		13228	2318	
Day 12	16828	2615		16299	2180	
Day 15	16723	2562		14817	1937	
Day 18	19581	2159	573	17252	1640	340

Table 2 Summary of experimental data for sludge digestion – Run #2

	pH	Alkalinity (mg/L, CaCO ₃)	TSS (mg/L)	VSS (mg/L)	Acetate (mg/L)	PO ₄ ³⁻ -P (mg/L)	NH ₃ -N (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)
Control reactor									
Day 1	6.3	950	53943	33604	384	59.0	296	28	104
Day 2	5.5	909	29597	17753	1441	122	468	42	132
Day 5	5.6	1563	24873	13840	2180	196	726	60	172
Day 8	6.0	1950	25013	13530	2143	242	805	59	146
Day 11	7.1	3650	40530	21383	456	149	809	10	69
Day 14	7.2	4100	32123	16217	503	162	1332	17	81
Day 17	7.2	5150	29670	14497	424	168	1815	0	119
Reactor with Mg(OH)₂ addition									
Day 1	6.3	1125	53330	33164	350	55.0	204	28	114
Day 2	6.2	1250	19850	12240	1278	30.5	398	92	118
Day 5	6.3	1925	17850	10160	1755	84.0	602	102	132
Day 8	6.9	2500	21410	11606	790	80.0	688	63	95
Day 11	7.4	3650	23315	12439	156	27.0	855	40	87
Day 14	7.3	3900	22563	11713	291	19.4	996	36	108
Day 17	7.3	5150	22500	11087	118	18.4	477	15	52

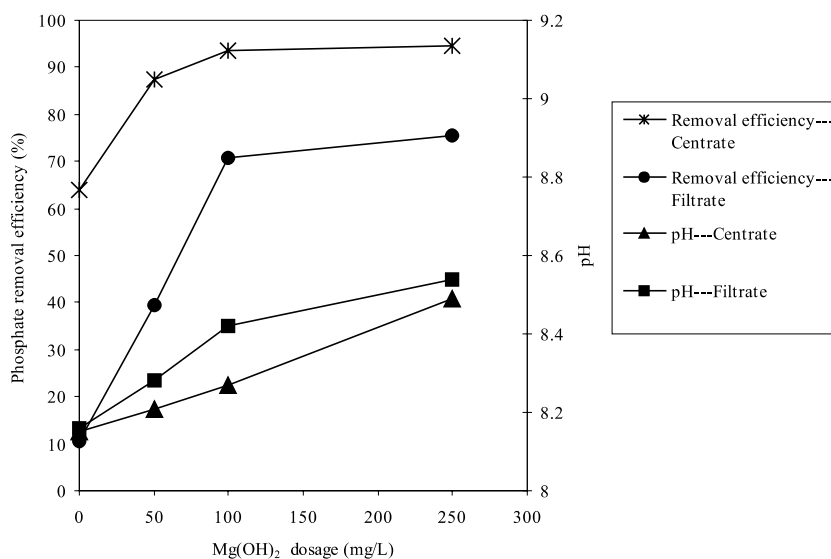
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phosphate salts, thereby lowering the level of nutrient concentrations in the bulk solution of the Mg(OH)₂ amended sludge digester.

Experiments on phosphate removal from anaerobic supernatant

A series of experiments were carried out at both bench scale and pilot scale for phosphate removal from centrate and filtrate generated in the sludge dewatering facility at the Mill Creek WWTP. Figure 2 shows the treatment efficiency in one of the lab scale experiments. The initial pHs of the centrate and filtrate were 7.65, 7.91; initial phosphorus concentrations were 107.6 mg/L and 33.3 mg/L, respectively. It can be seen that, with a magnesium hydroxide dosage of only 100 mg/L, as much as 93% and 71% of the phosphorus could be removed from centrate and filtrate, respectively.

Centrate from the sludge centrifuge at Mill Creek WWTP was used in the pilot experiments on phosphorus removal using Mg(OH)₂. The centrate was pumped into the column to the height of 1.8 m. Then the centrate was aerated for 60 min and then allowed 60 min of

**Figure 2** Phosphate removal efficiency vs Mg(OH)₂ dosage (mg/L)

quiescent settling. Both MgCl_2 and $\text{Mg}(\text{OH})_2$ were used in the experiments. The results are shown in Figure 3.

The reaction time to get the desired level of phosphate removal depends on the initial phosphate concentration and the chemical dosage. At low dosage and in a control experiment, after 60 min aeration and 60 min sedimentation, the phosphate concentration continues to decrease, which implies longer aeration or sedimentation time is needed for the precipitation/crystallization reaction to reach its equilibrium. The higher the dosage and the higher the initial phosphate concentration, the larger the concentration product for insoluble phosphate salts (struvite, magnesium phosphate, calcium phosphate and hydroxyapatite, etc.), hence the larger the driving force for the completion of the reaction. It can be seen that with 400 mg/L $\text{Mg}(\text{OH})_2$, the phosphate level quickly decreases within 30 min aeration to the level of 1.6 mg/L from 33.0 mg/L. It was also noticed that aeration is a very important step in speeding up the reaction. This can be explained by the fact that aeration can provide both adequate mixing and stripping of CO_2 , resulting in a pH increase which favors nucleation and crystal growth. This can be seen from the fact that even by simple air stripping for 60 min followed by 60 min sedimentation, more than 60% phosphate removal can be achieved.

A series of comparison experiments for phosphorus removal from centrate using reagent grade and reclaimed magnesium hydroxide was carried out. The difference between the two chemicals is their purity and particle size. The reclaimed product contains about 5% calcium sulfate and has a smaller particle size than the reagent grade chemical. The same dosage (based on magnesium hydroxide) was used for the two chemicals. As suggested by the previous experiments, two hours aeration followed by 1 hour sedimentation was employed for the control and the 50 mg/L $\text{Mg}(\text{OH})_2$ dosage experiments. But for the rest of the experiments, 1 hour rather than 2 hours aeration time and 1 hour sedimentation were used because no obvious further reaction was observed after one hour aeration. The results are tabulated in Table 3. It is evident that the reclaimed product produces a higher phosphorus removal efficiency than the reagent chemical. This can be explained by the fact that the calcium sulfate impurity present in the reclaimed product is helpful for the formation of calcium phosphate salt, and the reclaimed magnesium hydroxide product can dissolve faster due to its smaller particle size.

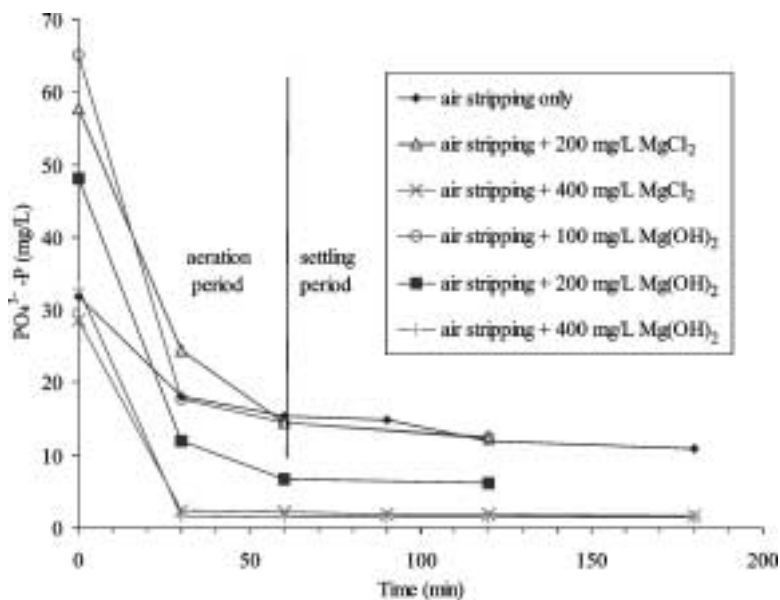


Figure 3 Phosphorus change with reaction time under different reaction conditions

Table 3 Comparison study results between reagent grade and Dravo reclaimed magnesium hydroxide for phosphorus removal from centrate

Mg(OH) ₂ dosage (mg/L)	Mg(OH) ₂ source	Initial PO ₄ ³⁻ -P concentration (mg/L)	Final PO ₄ ³⁻ -P concentration (mg/L)	Removal efficiency (%)
Control	No chemicals added	30.6	13.4	56
50	Reagent grade	38.9	17.2	56
	Dravo reclaimed product	30.0	9.9	67
100	Reagent grade	46.9	19.4	59
	Dravo reclaimed product	47.2	12.1	74
200	Reagent grade	57.4	10.1	82
	Dravo reclaimed product	59.4	9.8	84
400	Reagent grade	54.1	4.5	92
	Dravo reclaimed product	55.6	3.8	93

Conclusions

This research investigated the potential applications of magnesium hydroxide in enhancing anaerobic sludge digestion efficiency and in removing nutrients from anaerobic supernatant. The following conclusions can be reached.

1. Mg(OH)₂ can speed up the anaerobic sludge digestion process. Larger reductions in TSS, VSS, TCOD and SCOD are achieved in the Mg(OH)₂ amended sludge digester.
2. With Mg(OH)₂ application, the dewaterability of the digested sludge can be improved.
3. With Mg(OH)₂ addition, the nutrient level in the final sludge supernatant can be greatly reduced.
4. Mg(OH)₂ is very effective in removing phosphorus from anaerobic supernatant. To achieve the desired level of phosphate, considerations should be given to the initial phosphate concentration, time period for the mixing and CO₂ stripping, and time for sedimentation.

Overall, if the production cost for Mg(OH)₂ can be reduced, as with recovered magnesium hydroxide from the flue gas desulfurization process, the potential application of Mg(OH)₂ in municipal wastewater treatment plants is very promising.

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