

Use of magnesit as a magnesium source for ammonium removal from leachate

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Abstract

Using magnesit (MgCO_3) as a low cost source of magnesium ions in the struvite precipitation for the removal of high ammonium content of leachate was evaluated. Optimum molar concentration and pH conditions were analyzed to minimize the struvite solubility. Since solubility of magnesit in water is low, HCl was used to obtain soluble Mg. Maximum soluble Mg was obtained for the addition of 2 M HCl to the 1 M MgCO_3 . Struvite precipitation with magnesit was effective for the removal of ammonium, suspended solid, phosphate and turbidity. Economical evaluation was made comparing the costs of two magnesium sources, MgCl_2 and MgCO_3 . The economical analysis has shown that operation cost of struvite precipitation can be reduced about 18% by using MgCO_3 instead of MgCl_2 . High salt concentration after struvite precipitation has no inhibitory effect on the anaerobic reactor performance.

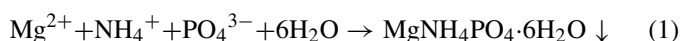
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1. Introduction

Landfill leachate contains high concentrations of ammonium which poses a major problem in wastewater treatment. Among alternative treatment methods, struvite precipitation has been proved more effective for the removal of high ammonium concentrations from leachate because of its high reaction rate and removal efficiency [1–3]. Additionally, nitrogen, phosphorus and magnesium constituents of struvite and low solubility in pH neutral solutions make it a valuable product to be used as fertilizer [4–6].

Struvite is a white crystalline compound consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$). Struvite precipitation occurs virtually and struvite crystals can be easily separated from the water phase. Struvite forms according to the reaction shown below.



Since magnesium and phosphate tends to be low relative to concentrations of ammonium in municipal landfill leachate, the cost of adding magnesium salts is a major economic constraint to application of struvite crystallization for struvite precipitation [7,8]. Similarly, researchers indicated that high operating cost of struvite precipitation of leachate is created by addition of chemicals [9,10]. Various low-cost materials have been used as an alternative source of magnesium ions, such as, MgO-containing by-products [11,12] bittern [8], seawater [13]. In our best knowledge, there is no study focused on the chemical, economical and environmental feasibility of using natural magnesit mineral (MgCO_3) for the purpose of providing magnesium ions to the struvite precipitation. Abundant natural deposits and low cost of magnesit makes it to be an important source for magnesium ion. In Kutahya region, Turkey has abundant magnesit mineral deposits having high content of magnesium.

The objective of this study was to investigate the feasibility of magnesit mineral as a source of magnesium ion for struvite precipitation of ammonium from leachate. Some parameters effecting on the struvite precipitation were investigated and ammonium removal from leachate was conducted at optimal

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conditions. Struvite precipitation was used as a pre-treatment step and effect of salts produced during struvite precipitation on anaerobic treatment of leachate was investigated. Finally, economical comparison of alternate magnesium sources was made.

2. Materials and methods

2.1. Materials

Landfill leachate was taken from the Odayeri Sanitary Landfill Site located in the European Side of Istanbul in Turkey. Approximately daily 1000 ton of leachate is produced in the landfill site and the composition of leachate sample is shown in Table 1 [14]. Leachate has high contents of organics (COD and BOD₅) and ammonium. Total phosphorus was 43 mg/l and pH was around neutral conditions. TKN was measured 2950 mg/l and about 90% of TKN was composed of ammonium nitrogen. The leachate samples were kept at 4 °C in refrigerator before usage.

Magnesit used as magnesium source was obtained from Kütahya Magnesit Co. In the experiments, magnesit having the diameter lower than 0.1 mm was used. The composition of magnesit is given in Table 2. Magnesit is composed of mainly MgCO₃ and the content of Mg is about 30%.

Synthetic ammonium solution was prepared using NH₄Cl and MgCl₂·6H₂O chemicals. Magnesit and phosphoric acid (H₃PO₄) were used as magnesium and phosphate sources for struvite precipitation. Bulk solution of MgCO₃–H₃PO₄ was prepared to obtain the soluble form of magnesium. The solubility of Mg was increased by HCl addition and the pH of struvite solution was adjusted using 10 M NaOH.

2.2. Experimental procedure

The experiment trials were carried out at room temperature with jar test apparatus. Two hundred milliliters leachate and

Table 1
Composition of leachate sample

Parameter	Value
pH	7.3
COD (mg/l)	20400
BOD ₅ (mg/l)	15000
NH ₄ (mg/l)	2700
TKN (mg/l)	2950
Total phosphorus (mg/l)	43
Suspended solid, (mg/l)	400
Turbidity (NTU)	2900
Mg (mg/l)	680
Alkalinity (mg/l CaCO ₃)	16500

Table 2
Chemical composition of magnesit

Composition	MgCO ₃	CaO	Fe ₂ O ₃	SiO ₂
%	98	1	0.3	0.7

sources of magnesium and phosphate sources were mixed into 250 ml beaker. Rapid mixing of bulk solutions was performed for 5 min and slow mixing was continued 15 min following pH adjustment using NaOH.

Optimum molar ratio and pH experiments were carried out using synthetic solutions. After determining optimum conditions, additional struvite experiments were carried out using leachate. Magnesit and phosphoric acid (H₃PO₄) were used for magnesium and phosphate sources. Since only soluble forms of magnesium is used for struvite formation and solubility of MgCO₃ in water is low, firstly bulk solution of MgCO₃–H₃PO₄ was prepared to obtain soluble form of Mg. HCl was added to the bulk solution in order to increase the solubility of MgCO₃. Suspension was filtered through a 0.45 μm filter (S&S ME25) and the resulting clear solution was used for the analysis of soluble magnesium. The results of struvite experiments were evaluated using ammonium removal efficiencies.

The effluent of struvite precipitation was fed to the biological reactor in order to investigate the effect of salt produced during struvite process on the performance of anaerobic treatment of leachate. Anaerobic treatment of leachate was performed in a laboratory scale upflow anaerobic sludge blanket reactor (UASB). UASB reactor was seeded with granular sludge obtained from an anaerobic reactor treating alcohol wastewater. The UASB reactor was operated at mesophilic conditions (35 °C) and start-up period continued for 120 days. The performance of UASB was monitored using the results of COD and BOD₅ values of effluent.

Following struvite formation and sludge sedimentation, the supernatant was used for the analysis of ammonium, phosphate, magnesium, turbidity and suspended solid. Magnesium experiments were performed using atomic absorption spectrophotometer (Unicam 929A). COD analysis was made according to Closed-Reflux method. All experiments were performed according to Standard Methods [15].

3. Results and discussion

3.1. Optimum conditions for struvite precipitation

In the experimental studies, optimum conditions for the struvite precipitation such as, pH and molar concentrations of struvite constituents were determined using synthetic solutions. pH is the main driving force behind struvite precipitation and variation of pH effects the solubility or formation of struvite crystals [16]. Minimum solubility of struvite crystal produces the maximal potential for its formation. The effect of pH was investigated as a function of solubility of struvite crystal. Prior to experiments, struvite sludge produced from synthetic solution at stoichiometric ratio was dried at 35 °C for 24 h. Struvite suspension (2 g/l) was prepared using dried struvite and diluted water, and solubility of Mg, NH₄ and PO₄ ions was monitored as a function of pH. As is clear from the data in Fig. 1, all struvite crystals were dissolved in acidic pH values. In contrast, decrease in solubility of struvite was observed as a result of pH increase. Consequently, the minimum solubility of stru-

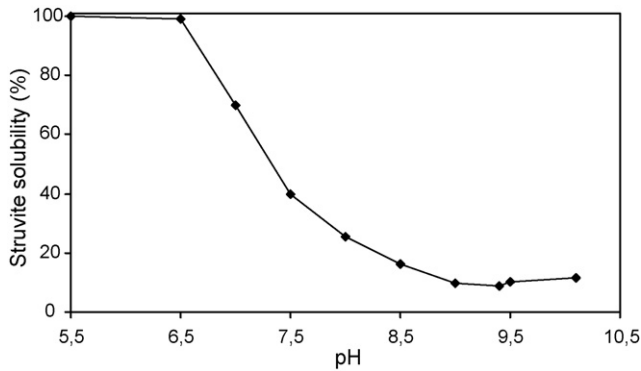


Fig. 1. Effect of pH on the solubility of struvite crystal ($\text{Mg}:\text{NH}_4:\text{PO}_4 = 1:1:1$).

vite was observed in the range of pH 8.8–9.4 and solubility began to increase above pH of 9.5. Similarly, pH of minimum struvite solubility was reported in the range of 9–10.7 [17].

The struvite precipitation also depends on molar ratio of struvite constituents, such as magnesium, phosphate and ammonium. Preliminary experiments were carried out to determine the optimum amount of magnesium ions to obtain maximum struvite precipitation. During the experiments, ammonium concentration of synthetic solution was maintained as 2413 mg/l, the NH_4/PO_4 ratio was 1/1 and pH was kept as 8.6 to avoid the negative effect of ammonia stripping on the struvite precipitation.

The variation of residual ions as a function of molar ratio of magnesium is shown in Fig. 2. Remaining soluble magnesium concentration increased with the addition of magnesium source but phosphate concentration decreased gradually. In all cases, ammonium has the lowest concentration in the supernatant and it has not changed for the magnesium values higher than 0.95 M. Total residual ions was minimized at the stoichiometric ratio ($\text{Mg}:\text{NH}_4:\text{PO}_4 = 1:1:1$) and about 97% of ammonium was removed by struvite precipitation. In order to obtain maximum removal efficiencies subsequent experiments were performed at stoichiometric ratio and pH of 8.6.

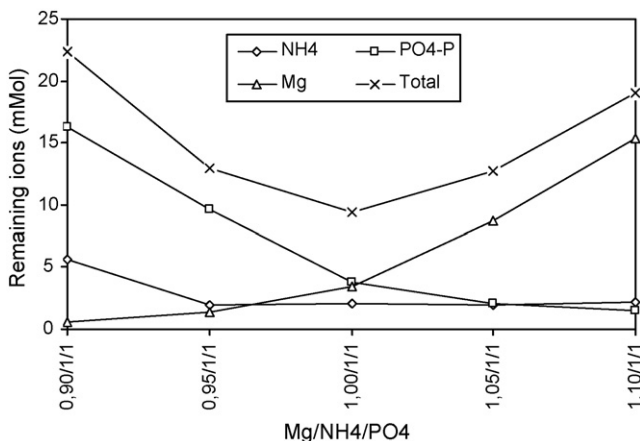


Fig. 2. Effect of molar ratio on the struvite precipitation (pH = 8.6).

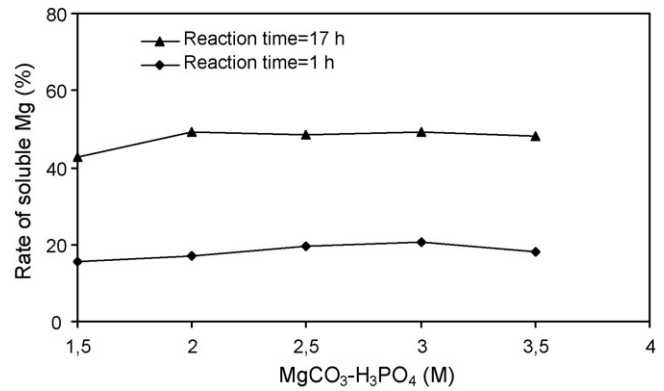


Fig. 3. Effect of $\text{MgCO}_3\text{-H}_3\text{PO}_4$ concentration on the Mg solubility ($\text{Mg}:\text{PO}_4 = 1:1$).

3.2. Solubility of magnesit

In this study, struvite formation was achieved using soluble forms of magnesium, ammonium and phosphate ions according to reaction in Eq (2).



Following experiments were conducted to dissolve the MgCO_3 since only soluble form of Mg reacts by struvite precipitation. In these experiments, soluble Mg obtained from MgCO_3 and H_3PO_4 were used as magnesium and phosphate sources for struvite precipitation. Bulk solution of $\text{MgCO}_3\text{-H}_3\text{PO}_4$ was prepared in order to obtain soluble form of magnesium. The degree of solubility of Mg was investigated as a function of bulk concentration solution and reaction time.

Variation of Mg solubility with the composition of bulk solution and reaction time was shown in Fig. 3. The solubility of magnesium increased with increase in concentration of bulk and reaction time. The highest amount of soluble Mg was achieved at 3 M concentration of bulk solution for all cases. The solubility rate was 20% at the reaction time of 1 h and it was increased to 50% at the reaction time of 17 h.

3.3. Struvite precipitation of leachate

Experiments were conducted for the removal of ammonium from leachate using $\text{MgCO}_3\text{-H}_3\text{PO}_4$ bulk solution. As shown above, the amount of soluble Mg remained very little even in very high reaction time. Therefore, addition of HCl to the bulk solution was performed in order to increase the solubility of MgCO_3 , hence the removal rate of ammonium from leachate. Different amounts of HCl were added to the bulk solution of 3 M $\text{MgCO}_3\text{-H}_3\text{PO}_4$ and the results are shown in Fig. 4. The lowest ammonium removal rate was obtained in the case of no addition of HCl due to low amount of soluble magnesium in the solution. During addition of HCl, amount of soluble Mg increased and nearly all Mg (99.4%) was dissolved when 6 M HCl was added to the 3 M $\text{MgCO}_3\text{-H}_3\text{PO}_4$ bulk solution. Therefore, addition of HCl to the bulk solution was performed in order to increase the solubility of MgCO_3 and to improve the removal rate of ammonium from leachate. The 90.9% removal efficiency by leachate

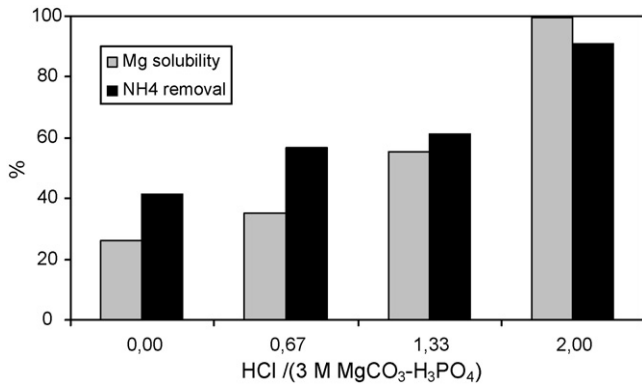


Fig. 4. Effect of HCl addition on Mg solubility and the NH₄ removal from leachate (pH = 8.6, Mg:NH₄:PO₄ = 1:1:1).

was very close to the efficiency of 97% by synthetic experiments and it is expected that the slight difference occurred by the effect of other ion content of leachate. From these results, it can be said that 2 M HCl should be added to the 1 M MgCO₃ to dissolve all Mg content of MgCO₃.

The removal efficiencies of some parameters for the struvite precipitation of leachate using MgCO₃ are shown in Fig. 5. Ammonium has the maximum removal rate and the lowest removal was obtained for COD after struvite precipitation. 91% of ammonium content of leachate was removed by struvite precipitation but organic nitrogen removal could not be achieved.

Moreover, struvite process lowered significantly the amount of suspended solid, alkalinity and turbidity in the effluent of leachate. On the contrary, struvite precipitation caused the increase of salinity and conductivity in the effluent. After struvite precipitation, chloride concentration of leachate increased sharply from 4500 mg/l to 18,500 mg/l and conductivity increased from 30 mS/cm to 52 mS/cm.

3.4. Economical evaluation

In the scope of this study, a comparative economic evaluation of using magnesit as magnesium source instead of MgCl₂ has been performed. In Fig. 6, cost distributions of

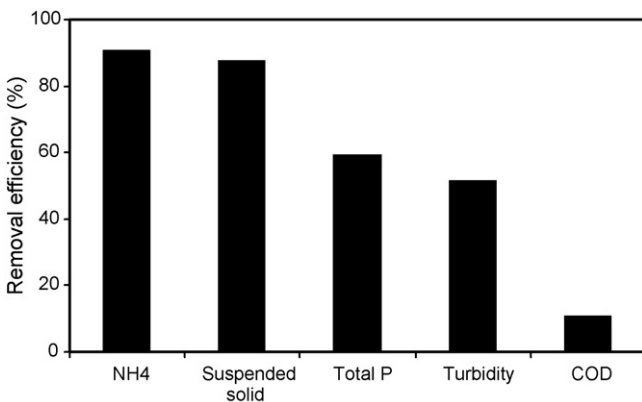


Fig. 5. Removal efficiencies of struvite precipitation of leachate (pH = 8.6, Mg:NH₄:PO₄ = 1:1:1).

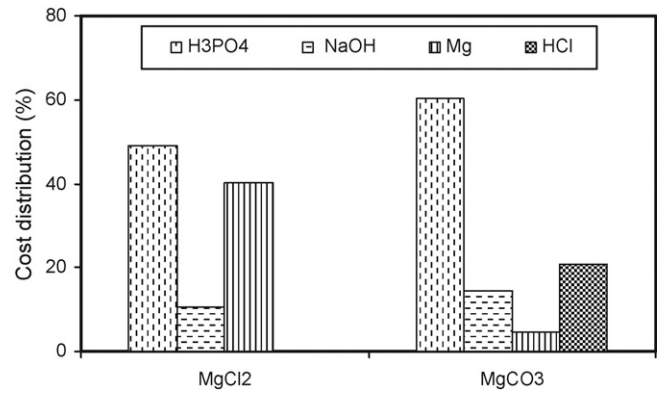


Fig. 6. Economical comparisons of alternate Mg sources.

each constituent were given for two cases and total operation cost were compared. Using magnesit as Mg source reduced the costs of struvite process from 28.1 \$/m³ to 22.9 \$/m³ leachate, which is about 18.3% lower than MgCl₂. When magnesit was used, contribution of Mg cost to the total operation cost decreased from 40.2% to 4.4% and rate of NaOH was calculated as 10.7% for MgCl₂ and 14.5% for MgCO₃, respectively. Since H₃PO₄ has highest cost in two cases, more investigations are needed for finding cheaper phosphate source to reduce the operation cost of struvite precipitation.

3.5. Effect of struvite precipitation on the anaerobic treatment of leachate

In the literature, it is speculated that high concentration of salt formed during struvite precipitation may inhibit microbial activity in a following biological treatment process and cause decrease in the COD removal efficiency [18–20]. Following experiments were conducted for the investigation of effect of struvite pretreatment on the anaerobic treatment of leachate. For this purpose, anaerobic treatment of leachate was operated without and following struvite precipitation and the effluent quality of two cases was compared.

Although struvite pretreatment caused high salt concentration in the influent of anaerobic reactor, it is clear from Table 3 that inhibition was not observed on the removal performances of COD and BOD₅, but a somewhat improvement was obtained for the removal of organics. Approximately 86% of COD and 94% of BOD₅ content of leachate was treated by only anaerobic treatment and struvite precipitation slightly decreased concentration of effluent organics of anaerobic reactor. Moreover, struvite pretreatment improved removal efficiencies of suspended solid, turbidity and alkalinity of leachate. As expected, struvite precipitation was effective mainly on the removal of ammonium and alkalinity. On the other hand, very small content of TKN was removed by anaerobic degradation and struvite precipitation has no effect on the removal efficiency of organic nitrogen. These results revealed that struvite precipitation provided improvements in the effluent water quality of anaerobic treatment.

Table 3

Evaluation of struvite pretreatment on the anaerobic treatment of leachate (pH = 8.6, Mg:NH₄:PO₄ = 1:1:1)

Parameter	Raw leachate	Only anaerobic treatment	Struvite + anaerobic treatment
COD (mg/l)	20400	3000	2950
BOD ₅ (mg/l)	15000	950	900
NH ₄ (mg/l)	2700	2680	238
TKN (mg/l)	2950	2930	473
Suspended solid (mg/l)	400	450	80
Turbidity (NTU)	2900	3000	1500
Alkalinity (mg/l CaCO ₃)	16500	17000	5500
Conductivity (mS/cm)	31	30	52

4. Conclusions

The present study evaluated the feasibility of magnesit mineral as a low-cost source of magnesium ions in the struvite precipitation. Additionally, effect of salt produced during struvite precipitation on the performance of anaerobic treatment was investigated. As a result of experiments, the lowest struvite solubility was obtained at stoichiometric molar ratios of struvite constituents and pH range of 8.6–9.4. It was found that, solubility of magnesit with H₃PO₄ was very low and adding two-fold HCl to the bulk solution MgCO₃–H₃PO₄ is required to dissolve all the magnesium content of magnesit. Struvite precipitation with MgCO₃ lowered significantly the amount of ammonium, phosphate, suspended solid and turbidity from leachate but salinity content of leachate effluent increased sharply. Struvite precipitation was applied as a pretreatment step and it was observed that struvite effluent with high salt content did not inhibit the COD and BOD₅ removal of anaerobic treatment. Although addition of HCl for increasing the solubility of magnesit has negative effect on total operation cost, economical comparing showed that cost of struvite precipitation with MgCO₃ is 18.3% cheaper than with MgCl₂. When MgCO₃ is used, the rate of Mg cost decreased about 90% and H₃PO₄ has highest rate in total operation cost.

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