



## The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester

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### ABSTRACT

The formation of struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) in wastewater treatment plants can lead to scaling and thus operational problems reducing the treatment efficiency. However, struvite has significant commercial value as an agricultural fertilizer. Therefore, controlled struvite formation in wastewater treatment plants not only presents an opportunity to recover nutrients but also corresponds to the valorization of wastes.  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  removal and recovery from the effluent of a full-scale sewage sludge anaerobic digester via controlled struvite precipitation were investigated in this study. The effect of the residual heavy metal and micropollutant content of the formed struvite on fertilizer quality was also evaluated. Removal efficiencies of  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  and COD were 89.35%, 95% and 39.78% when Mg:N:P molar ratio was 1.5:1:1 and pH was 9.0. Mercury, nickel, zinc and chrome concentrations derived from struvite precipitation were below the regulatory limit for fertilizer usage in Turkey. The precipitate did not contain polychlorinated biphenyls (PCB). X-ray diffraction (XRD) analysis conducted on the precipitate indicated a struvite formation.

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### 1. Introduction

Stabilization of sludge at large wastewater treatment plants is usually carried out by anaerobic digestion. During anaerobic digestion of sewage sludge, part of the phosphorus and nitrogen present in the organic matter is released. Sewage sludge refers to residues generated at centralized wastewater treatment plants as a result of the treatment of wastes released from a variety of sources, including homes, industries, medical facilities, street runoff and businesses. Struvite deposition is a recognized operational problem for waste treatment plants, especially in anaerobic digesters, as a result of high concentrations of struvite forming ions,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  and high pH [1]. Struvite is magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4$ ) and forms a hard crystalline deposit when the molar ratio of Mg:N:P is greater than 1:1:1. Struvite deposits foul pumps and cause pipe blockages, leading to a significant increase in the cost of sludge management operations [2]. Although unintentional struvite formation can be a problem in wastewater treatment plants, controlled formation has also been proposed as a method to recover  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  in the form of struvite, which is valuable fertilizer [3]. Struvite can be used as slow release fertilizer or in other industrial products (cleaning products,

chemicals, fire retardants) [4]. Further, when struvite is used as a fertilizer, mining of phosphate rocks can be reduced [5].

Much of the phosphorus and part of the ammonium of the supernatant obtained after centrifuging the sludge that comes from a biological treatment plant can be used for struvite production [6]. This permits the phosphorus and ammonium to be recovered as struvite through the struvite formation process. The removal of  $\text{PO}_4\text{-P}$  has been mostly studied in struvite precipitations derived from the effluent of anaerobic sludge digesters [7–10]. However, the present study examined the removal of  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$  and COD combination.

Sewage sludge usually contains a number of metals, including Cd, Cu, Cr, Ni, Pb, Zn and organic micropollutants (polychlorinated biphenyls (PCBs) and polynuclear aromatic hydrocarbons (PAHs)) [11]. Precipitate acquired from struvite can be used as an agricultural fertilizer, but the heavy metal and micropollutant content is an important factor in this application. The presence of such pollutants in fertilizer is strictly regulated and excessive amounts can result in the fertilizer being banned from use in agriculture [12]. Despite the potential benefits of struvite recovery and the need to ensure a consistent product, there are only a limited number of previous studies on the quality evaluation, in terms of heavy metal and micropollutant content, of fertilizer derived from struvite precipitation formed in the effluent of anaerobic sludge digesters [9].

In recent years, PCBs are of great environmental concern because of their high persistence, lipophilic properties, bioaccumu-

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lation, and toxicity to the ecosystem and human health [13]. Due to these properties, PCBs have been banned in the USA and Europe since the end of 1970s and have been listed as serious threats to health and the environment by the Stockholm Convention (May 22, 2001). For these reasons, the concentrations, transport, fate and environmental risk of PCBs in various environmental media have been extensively studied [13,14]. Due to their lipophilic nature, PCBs preferentially partition onto sludge during wastewater treatment. Sewage sludge presents a typical PCB content of 1–10 mg/kg with an elevated proportion of highly chlorinated PCBs [15]. Therefore, PCB was chosen as the representative type in determining the micropollutants in the struvite in the present study.

The aims of the present studies are as follows: (1) characterization of the effluent of a full-scale sewage sludge anaerobic digester and the liquid phase in terms of nutrient, metal and PCB content; (2) investigating of the removal efficiency of  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$  and COD by struvite precipitation at different pH and Mg:N:P molar ratios; (4) identifying the constituent compounds of the formed struvite with X-ray diffraction (XRD) analysis, and; (5) assessing the quality of the formed struvite for use as fertilizer by analyzing its heavy metal and PCB content.

## 2. Materials and methods

### 2.1. Struvite precipitation experiments

The struvite precipitation experiments were conducted using liquid phase of effluent of a sewage sludge anaerobic digester. 250 mL of sample was first poured into 400 mL beaker. The amounts of  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  ions to be added were calculated considering initial concentrations of the ions in samples. The chemicals used to add the required ions into the reactors were  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 85%  $\text{H}_3\text{PO}_4$  to provide  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$ , respectively. The samples were stirred continuously on a magnetic stirrer (Heidolph, MR Hei-Mix L) at standard rotation speed (250 rpm) for about 30 min until an equilibrium state in terms of stable pH was reached. During the struvite reaction, the pH of samples was adjusted to desired value by the gradual addition of 20% NaOH. The pH of the experiment solution was measured continuously (Hanna Instruments, HI 8314) and NaOH (20%) solutions were used to keep the pH at the desired level after adding the required chemicals. The pH of solution was monitored until observing a constant pH at the adjusted level [16]. All the runs were carried out at ambient laboratory temperature of about 20 °C. Prior to any analyses done, all samples were allowed to settle for 1 h in a beaker in order to separate the crystallized precipitate from bulk liquid. Precipitates were filtered using a coarse filter. Metals, orthophosphate and ammonium–nitrogen concentrations of the filtrate were measured. Filtered precipitate was dried in a 35 °C oven for 24 h. Each experiment was performed twice to be able to calculate the variance of the results.

### 2.2. Analytical procedures

The pH of wastewater samples was measured by a pH meter (Hanna Instruments, HI 8314) and a probe (Hanna Instruments, HI 1230). Total solids (TS), total suspended solids (TSS), total volatile suspended solids (TVSS), total kjeldahl nitrogen (TKN) (standard code: 4500-Norg B), total phosphorus (TP) (standard code: 4500-P E), ammonium nitrogen ( $\text{NH}_4\text{-N}$ ) (standard code: 4500-NH<sub>3</sub> C), total chemical oxygen demand (TCOD) and soluble chemical oxygen demand (SCOD) (standard code: 5220 B) were conducted by the procedure described in the Standard Methods [17]. Orthophosphate ( $\text{PO}_4\text{-P}$ ) was measured colorimetrically using multiphotometer (Aqualytic, PCMulti Director). SCOD and  $\text{PO}_4\text{-P}$  were determined by filtering the sample through 0.45  $\mu\text{m}$  What-

man GF/C filter. Absorbance values were recorded at 880 nm by using a spectrometer (Pharmacia Biotech Novaspec II) for TP analysis. Al, As, Hg, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn were measured using an atomic absorption spectrometer (Perkin Elmer, AAnalyst 400). K and Na were measured using a flame photometer (Jenway, PFP7). The detection limits for the metals are (in mg/L): Al 0.1, As 0.001, Hg 0.003, Ca 0.003, Cd 0.002, Co 0.03, Cr 0.02, Cu 0.01, Fe 0.02, Mg 0.0005, Mn 0.01, Ni 0.02, Pb 0.05, Zn 0.005, K 0.005, Na 0.002. All the samples were analyzed immediately after sampling.

#### 2.2.1. Polychlorinated biphenyls (PCB) analyses

Primarily the samples were deep freeze at  $-20^\circ\text{C}$ . Then, their moisture content was removed by using Christ Alpha 1–4 freeze drier ( $\approx 0.006$  mbar,  $-45^\circ\text{C}$  condenser temperatures). After pulverizing the dried samples, <1 mm sized particles were used in experiments. In PCB extraction from samples, American Environment Agency (US EPA) methods were adopted (Method 3540). In order to remove the sulphur content of samples, acid activated granule copper was added to soxhlet flask (Method 3630). The extracted volume was dried in  $\text{Na}_2\text{SO}_4$  (at  $400^\circ\text{C}$  4 h of purification) column and by using Kuderna–Danish (KD) apparatus, it was concentrated to 10 ml. Organics that colouring and attempting in extract were removed by using 1:1 concentrated  $\text{H}_2\text{SO}_4$  (Method 3660). Later on, the isolated PCBs (Method 3630) by using 3 g of silica (0.063–0.1 mm) which deactivated in the ratio of 3.3% were concentrated to 1 ml by applying KD process once again and then gassing nitrogen. PCB analyses, by using Varian CP3800 branded Gas Chromatograph (GC)/Electron Capture Detector (ECD), WCOT fused silica capillary were done by column (30 m length  $\times$  0.32 mm internal diameter, 0.25  $\mu\text{m}$  film thickness). In the system that helium and nitrogen gasses were used as conveyor and make-up, by rising the furnace temperature which was  $100^\circ\text{C}$  (wait for 2 min) primarily to  $160^\circ\text{C}$  at  $8^\circ\text{C}/\text{min}$  velocity, then to  $250^\circ\text{C}$  at  $3^\circ\text{C}/\text{min}$  velocity (wait for 10 min) and finally to  $290^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$  velocity (wait for 5 min), PCB was detected. Injector and detector temperatures were  $250^\circ\text{C}$  and  $350^\circ\text{C}$ , respectively.

The amount of PCB in samples was determined on Aroclor 1016/1260 composition basis and reported as total PCB. In the system of 5 point calibration curve ( $r^2 > 0.995$ ,  $\text{RSD} \leq 20\%$ ) set in the basis of signal/noise ratio 3, the instrumental measuring limit was calculated as  $0.5 \mu\text{g}/\text{l}$  ( $n = 7$ ).

#### 2.3. Dried precipitate analyses

For metal determinations, microwave (Berghof, MWS-2) digestion was applied by the addition of nitric acid and hydrochloric acid to 0.5 g of solid sample in pressure-resistant Teflon tubes. Dried precipitate produced in the experiments were examined and identified as struvite by X-ray diffractometer (Philips, X Pert Pro MPD). The data were collected over the two theta range of  $5\text{--}75^\circ$  using step size  $0.05^\circ$ .

PCB analysis in dried struvite precipitate was done as mentioned in (Section 2.2.1) article of analytical procedures.

## 3. Results and discussion

### 3.1. Characterization of effluent of a full-scale sewage sludge anaerobic digester and liquid phase

Effluent of a full-scale sewage sludge anaerobic digester was provided by the Ankara Metropolitan Municipality Waste Water Treatment Facility. Characterization of the effluent of a sewage sludge anaerobic digester is given in Table 1. As can be seen from Table 1, the effluent of a sewage sludge anaerobic digester includes high concentration of  $\text{NH}_4\text{-N}$  and an intermediate concentration

**Table 1**  
Characteristics of the sewage sludge anaerobic digester effluent and liquid phase.

Parameter	Sewage sludge anaerobic digester effluent	Liquid phase
TS (mg/L)	25365 ± 243.79	nd <sup>a</sup>
TVSS (mg/L)	11520 ± 72.11	nd <sup>a</sup>
TSS (mg/L)	22910 ± 296.98	580 ± 56.57
TCOD (mg/L)	25881 ± 1912.54	936.36 ± 12.856
SCOD (mg/L)	398.11 ± 30.92	nd <sup>a</sup>
TP (mg/L)	391.8 ± 2.84	nd <sup>a</sup>
PO <sub>4</sub> -P (mg/L)	21.4 ± 0.02	51 ± 4.24
TKN (mg/L)	1043 ± 19.8	nd <sup>a</sup>
NH <sub>4</sub> -N (mg/L)	949.76 ± 11.85	749 ± 19.79
Total PCB (ng/g)	4.69 <sup>b</sup>	nd <sup>a</sup>
Ca (mg/L)	1049.575 ± 56.713	107.950 ± 2.4042
K (mg/L)	74.451 ± 4.528	115.8851 ± 7.233
Na (mg/L)	175.370 ± 8.198	285.41 ± 15.655
Mg (mg/L)	193.550 ± 1.462	20.975 ± 1.237
Al (mg/L)	90.848 ± 10.085	<0.1
Fe (mg/L)	318.618 ± 32.51	0.256 ± 0.0184
Mn (mg/L)	3.596 ± 0.099	<0.01
As (mg/L)	0.0507 ± 0.00	0.004 ± 0.0001
Cd (mg/L)	0.059 ± 0.004	<0.002
Co (mg/L)	0.143 ± 0.004	<0.03
Cr (mg/L)	11.232 ± 0.764	0.198 ± 0.00
Cu (mg/L)	4.021 ± 0.091	<0.01
Ni (mg/L)	2.993 ± 0.018	0.265 ± 0.0035
Pb (mg/L)	0.83 ± 0.08	<0.05
Zn (mg/L)	50.998 ± 5.374	0.063 ± 0.0035
Hg (mg/L)	8.79 ± 0.87	0.426 ± 0.056
NH <sub>4</sub> -N (mM)	67.84	53.5
PO <sub>4</sub> -P (mM)	0.69	1.645
Mg (mM)	8.065	0.874
Ca (mM)	26.188	2.694
Mg:N:P	11.69:98.32:1	1:61.22:1.88
Ca:Mg	3.25:1	3.08:1
pH	7.60	7.88

<sup>a</sup> nd: not determined.

<sup>b</sup> The PCB concentration depicts the mean concentrations of the duplicate analysis.

of PO<sub>4</sub>-P. It was reported in various studies that the total PCB concentration in fresh sewage sludge is in the range of 0.19–72.5 ng/g [18,19]. Therefore, the total PCB concentration value of 4.69 ng/g in treated sewage sludge in the present study (Table 1) is relatively high.

Magnesium, potassium, and calcium are present in wastewaters [20] in organic or inorganic forms, and so they can be found in sewage sludge. During anaerobic digestion, part of the organic K, Mg and Ca are released as a consequence of decomposition of organic matter [2]. It is therefore necessary to determine the organic content of K, Mg and Ca in the effluent from the sewage sludge anaerobic digester (Table 1).

Prior to the struvite precipitation experiment, the effluent of the sewage sludge anaerobic digester was centrifuged at 4000 rpm for 15 min with a Hettich Rotofix 32 A model centrifuge in order to distinguish the liquid–solid phase. The liquid phase separated via the centrifuge process was used during struvite precipitation experiments. Characterization of the liquid phase is given in Table 1. High concentrations of ammonium and dissolved phosphate are required for struvite precipitation. Other important requirements are low concentration of TSS and a pH value higher than 7.5 [21]. Schuiling and Andrade [22] reported that TSS concentrations above 1000 mg/L interfere with the precipitation process. The presence of TSS in large amounts is an indication that the organic matter content is also high and hence gives way to inevitable precipitation of these solids in favour of the components of struvite, thus inhibiting the formation of struvite [23]. The data in Table 1 indicate that the liquid phase where struvite precipitation is going to be realized meets these requirements. While ammonium content in the sewage sludge anaerobic digester liquid phase is generally

700–800 mg/L, it was reported that P concentration in liquid phase varies significantly [9]. Münch and Barr [9] reported that NH<sub>4</sub>-N concentration was 790 ± 30 mg/L and PO<sub>4</sub>-P concentration was 61 ± 5 mg/L in the sewage sludge anaerobic digester liquid phase. These results are similar to the results obtained in the present study (Table 1).

Molar ratios of the main compounds, such as phosphorus, ammonium, magnesium, calcium and potassium have a significant effect on struvite crystallization [24]. Phosphorus can precipitate as metal phosphates by reacting with metals present during the struvite precipitation [8,25]. This can cause reduced phosphorus concentration, which is formed as struvite [26]. In case of high Ca/Mg molar ratios, calcium phosphate precipitation occurs [24], which inhibits struvite precipitation. Hwang and Choi [27] and Le Corre et al. [28] indicated that the molar ratio of Ca:Mg should be below 1 for effective struvite formation. In the present study, the molar ratio of Ca:Mg in the liquid phase was 3.08 (Table 1), indicating that, in order to provide the necessary stoichiometric conditions between magnesium, ammonium and phosphate, magnesium should be added to the media. In this way, the molar ratio of Ca:Mg also decreases. Siegrist et al. [29] also emphasized that a high molar ratio of Mg is necessary for the removal of phosphorus in the form of magnesium ammonium phosphate. Iron and aluminium phosphate precipitation were deemed impossible in the scope of the present study due to the very low iron and aluminium concentration values in the liquid phase (Table 1). A similar case was reported by Marti et al. [30]. Various studies [22,31] indicate that potassium struvite (K-MAP, KMgPO<sub>4</sub>·6H<sub>2</sub>O) precipitates instead of ammonium struvite (MAP) in very low ammonium concentrations. In the present study, the liquid phase has 749 mg/L (Table 1) ammonium concentration, which is not considered low. Accordingly, the possibility of potassium precipitation instead of struvite precipitation is relatively low. Due to such inhibition effects of the main compounds on struvite formation, PO<sub>4</sub>-P, NH<sub>4</sub>-N, Mg, Ca and K concentrations and molar ratios in were determined in the liquid phase (Table 1). Moreover, heavy metals can be incorporated into the crystal lattice or sorbed onto the surface of struvite, reducing the purity of the product [32]. Thus, it is important to know the concentrations of the heavy metals in the wastewater subjected to struvite precipitation experiments. Although struvite precipitation has been widely studied by many researchers as an established and promising method for NH<sub>4</sub><sup>+</sup> or PO<sub>4</sub><sup>3-</sup> removal from derived from the effluent of anaerobic sludge digesters, no study in the literature has been performed on the heavy metal content in the effluent of sewage sludge anaerobic digester. The heavy metal content of the sewage sludge anaerobic digester effluent and liquid phase are given in Table 1. As shown in Table 1, heavy metals (Fe, As, Cr, Ni, Zn and Hg) present in the liquid phase. According to Directive 76/464/EU, metals and metal compounds belong to group II of substances extremely dangerous for water environment.

Molar ratios of Mg, NH<sub>4</sub>-N and PO<sub>4</sub>-P in the liquid phase are shown in Table 1. The molar ratios of Mg:N:P ions necessary for struvite formation were found to be 1:61.22:1.88 (Table 1). Struvite forms when the molar ratio of Mg<sup>2+</sup>:NH<sub>4</sub><sup>+</sup>:PO<sub>4</sub><sup>3-</sup> is greater than 1:1:1 [8]. When the necessary stoichiometric conditions for struvite precipitation are not achieved, ions limiting the precipitation are incorporated into the media [7,16,33–35]. Under these conditions, in order to provide necessary stoichiometric conditions for struvite precipitation (Table 1), ions of Mg<sup>2+</sup> and PO<sub>4</sub><sup>3-</sup> were added to media in the present study.

### 3.2. The effect of pH

In order to remove struvite from water by precipitation, the pH value of the wastewater should be in the range (pH 8.0–9.0) where struvite solubility is minimal [3]. According to previous studies,

**Table 2**Effect of pH on  $\text{NH}_4\text{-N}$  and COD removals, residual  $\text{PO}_4\text{-P}$  concentration, and ammonia volatilization.

pH	Residual $\text{PO}_4\text{-P}$ concentration (mg/L)	$\text{NH}_4\text{-N}$ removal (%)	COD removal (%)	Ammonia volatilization (%)
8.0	108 ± 2.828	85.42	12.62	3.55
8.5	58 ± 5.656	89.16	21.23	4.67
9.0	27 ± 1.414	88.79	27.18	6.17

the solubility of struvite gradually decreases towards pH 9.0 and increases above pH 9.0 [3]. Based on the results of previous studies [23,36], the effect of pH was researched in the present study which was conducted batch test at Mg:N:P molar ratio of 1:1:1.

The present study examined the effect of pH on nutrient removal with struvite precipitation under conditions in which the molar ratio was 1:1:1 and pH values were 8.0, 8.5 and 9.0. The results according to variations in pH value are given in Table 2. There was no significant difference in terms of  $\text{NH}_4\text{-N}$  removal efficiency at pH 8.5 and 9.0. Following struvite precipitation, there was higher orthophosphate concentration in liquid phase when compared with influent concentrations at pH 8.0 and 8.5; however, there was lower orthophosphate concentration ( $27 \pm 1.414$  mg/L) when compared with the influent value when operating at pH 9.0. This was the lowest  $\text{PO}_4\text{-P}$  concentration. Maximum COD removal was 27.18%, recorded at pH 9.0 (Table 2). It was seen that the optimum pH value obtained in the present study is consistent with the values obtained in other studies. Where the effect of pH was investigated within the range 4.45–11 in the batch test when Mg:N:P molar ratio was 1:1:1, it was found that maximum  $\text{NH}_4\text{-N}$  and COD removal efficiencies were obtained when pH value was 9.0 [36]. When the effect of pH was investigated within the range 8.0–11.5 in the batch test when Mg:N:P molar ratio was 1.2:1:1 [35], it was found that the best  $\text{NH}_4\text{-N}$  removal efficiency (78%) was obtained at pH 9.2. It was found that removal efficiency decreased when pH was higher than 9.4. In the batch study conducted by Uludag–Demirer [16], it was reported that maximum  $\text{NH}_4\text{-N}$  and  $\text{PO}_4\text{-P}$  removal efficiencies were obtained at a pH value of 9.0.

Ammonium volatilization is predicted based on mixing period and pH increase [36,37]. As detailed in the experimental procedure (Section 2.1) of struvite precipitation, the mixing process continued for 30 min after fixing pH. The possible effect of pH on ammonium volatilization was determined at pH 8.0, 8.5, and 9.0 during the 30 min mixing (Table 2). According to Table 2, the effect of pH on ammonium volatilization is negligible. Similarly, a previous study on the removal of ammonium with struvite precipitation at pH 9.0 [36] indicated that ammonium volatilization did not have a significant effect on  $\text{NH}_4\text{-N}$  removal during 15 min mixing in a magnetic stirrer and ammonium volatilization was neglected in the study.

### 3.3. The effect of molar ratio of Mg:N:P

Previous studies demonstrate the importance of molar concentration of  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ions in struvite formation and indicate that this ratio should be experimentally determined in order to maximize struvite formation [38]. The effect of molar

ratios of Mg:N:P on residual  $\text{PO}_4\text{-P}$  concentration,  $\text{NH}_4\text{-N}$  and COD removal efficiency at pH 9.0 is given in Table 3.

It has been noted in previous studies that ammonium and phosphate removal was generally affected by the amount of magnesium added to the struvite precipitation [8,39–41]. The findings of many previous studies [9,16,42] emphasize that supplementary Mg concentration is necessary for maximum  $\text{PO}_4\text{-P}$  removal. In the present study, magnesium was found to be the limiting reagent in the formation of struvite from the liquid phase (Table 1); thus, it was necessary to supplement the media with magnesium.

Although the increase in the molar ratio of  $\text{Mg}^{2+}$  ion did not have a significant effect on  $\text{NH}_4\text{-N}$  removal, residual  $\text{PO}_4\text{-P}$  concentration in water decreased to  $2.55 \pm 0.071$  mg/L (Table 3). High magnesium concentrations lead to low phosphate concentrations in effluent. Accordingly,  $\text{PO}_4\text{-P}$  removal was 95% when compared with influent concentration. It was also reported by Yetilmezsoy and Sapci-Zengin [36] that excessive Mg doses do not have any significant effect on  $\text{NH}_4\text{-N}$  removal. In the study, it was found that, while  $\text{NH}_4\text{-N}$  removal efficiency was 85.4% when pH value was 9.0 and Mg:N:P molar ratio was 1:1:1, the efficiency increased to 89.3% when Mg:N:P molar ratio was 1.5:1:1. In a study where Mg:P molar ratio increased from 1:1 to 3:1 [42], it was reported that the efficiency of  $\text{PO}_4^{3-}$  removal increased from 47.4% to 92.1%. In another study [8], it was stated that 95% of the total phosphorus could be removed when Mg:P molar ratio was 1.05:1. A decrease in the molar ratio of  $\text{Mg}^{2+}$  ion caused a significant increase in residual  $\text{PO}_4\text{-P}$  concentration in the water (Table 3). Accordingly, there was a higher level of  $\text{PO}_4\text{-P}$  concentration in the water when compared with the influent value. Münch and Barr [9] stated that the efficiency of  $\text{PO}_4\text{-P}$  removal decreased rapidly when the added magnesium was below a certain concentration. When molar concentrations of Mg and  $\text{PO}_4\text{-P}$  were below 1, removal efficiencies of  $\text{NH}_4\text{-N}$  and COD decreased (Table 3). Similarly, in a study where Mg and  $\text{PO}_4\text{-P}$  molar ratio were below 1 [36],  $\text{NH}_4\text{-N}$  and COD removal efficiencies decreased and COD removal efficiencies varied within a small range.

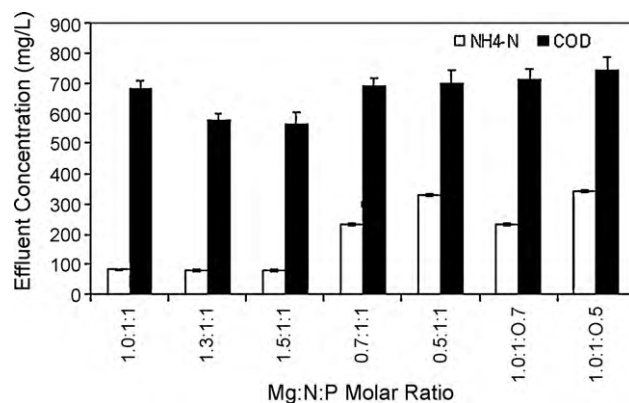
When only Mg was added and supplementary phosphorus was not added to the media (values were not given in the table), struvite did not form (molar ratios of Mg:N:P were 1:1:0.0307). Ammonium removal was only 11.21%. In a study where only magnesium was added [9], ammonia removal was 6%. If ammonium removal is desired besides phosphorus, supplementary phosphorus is required, as reported by Münch and Barr [9], Ryu et al. [35], Stefanowicz et al. [43], and He et al. [44]. The effect of increasing concentrations of phosphorus on struvite precipitation has been investigated by many studies [16,34,35]. However, the effect of decreasing phosphorus levels has been investigated by fewer stud-

**Table 3**Effect of different Mg:N:P molar ratios on  $\text{NH}_4\text{-N}$ , COD and Mg removals, and residual  $\text{PO}_4\text{-P}$  concentration.

Molar ratio (Mg:N:P)	Residual $\text{PO}_4\text{-P}$ concentration (mg/L)	$\text{NH}_4\text{-N}$ removal (%)	COD removal (%)	Mg removal (%)
1:1:1	27 ± 1.414	88.79	27.18	93.66
1.3:1:1	3.85 ± 0.071	89.35	38.17	81.63
1.5:1:1	2.55 ± 0.071	89.35	39.78	76.31
0.7:1:1	793.75 ± 44.194	68.97	25.82	99.99
0.5:1:1	1140 ± 0.00	56.26	25.20	99.99
1:1:0.7	1.80 ± 0.141	68.97	23.51	73.41
1:1:0.5	1.1 ± 0.11	54.39	20.33	70.02

**Table 4**  
Metal concentrations in the effluent of struvite precipitation, in different molar ratios of Mg:N:P.

Metal/heavy metal concentration (mg/L)	Molar ratio of Mg:N:P						
	1:1:1	1.3:1:1	1.5:1:1	0.7:1:1	0.5:1:1	1:1:0.7	1:1:0.5
Mg	82.4 ± 7.07	310.6 ± 5.37	462 ± 3.39	< 0.0005	< 0.0005	345.8 ± 40.73	389.9 ± 5.233
Ca	9.47 ± 0.141	17.34 ± 0.134	46.87 ± 0.248	7.76 ± 0.02	5.96 ± 0.587	11.59 ± 0.863	31.96 ± 0.644
K	90.13 ± 0.453	78.18 ± 0.91	87.22 ± 3.67	79.92 ± 7.11	86.31 ± 3.81	88.67 ± 4.29	86.31 ± 3.81
Na	3393.75 ± 130.89	3293.70 ± 232.64	3227.30 ± 339.84	2891.1 ± 221.04	2608.8 ± 267.43	2408.4 ± 15.98	2465.05 ± 32.17
Fe	0.129 ± 0.008	0.077 ± 0.002	0.075 ± 0.007	0.136 ± 0.016	0.098 ± 0.003	0.125 ± 0.011	0.123 ± 0.009
As	0.0014 ± 0.00015	0.0016 ± 0.0002	0.00158 ± 0.00017	0.0030 ± 0.00011	0.0033 ± 0.00013	0.0034 ± 0.00002	0.0030 ± 0.00013
Hg	0.219 ± 0.015	0.235 ± 0.02	0.218 ± 0.011	0.387 ± 0.017	0.277 ± 0.013	0.173 ± 0.014	0.397 ± 0.013
Zn	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Cr	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Ni	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02



**Fig. 1.** Effect of Mg:N:P molar ratio on NH<sub>4</sub>-N and COD effluent concentration.

ies [36]. As can be seen from Table 3, the present study investigated the effects of both increased and decreased concentrations of phosphorus on struvite precipitation. While NH<sub>4</sub>-N removal efficiency was 88.79% when Mg:N:P molar ratio was 1:1:1, this decreased significantly to 54.39% when Mg:N:P molar ratio was 1:1:0.5. It was also stated in the study by Ryu et al. [35] that the amount of added PO<sub>4</sub>-P significantly affected NH<sub>4</sub>-N removal.

When molar ratios of Mg:N:P were 1:1:1, 1.3:1:1 and 1.5:1:1, Mg removal efficiencies were 93.66%, 81.63% and 76.31% (Table 3). When Mg concentration decreased and Mg:N:P molar ratios were 0.7:1:1 and 0.5:1:1, Mg removal efficiency was 99.99%. However, residual PO<sub>4</sub>-P concentration significantly increased (Table 3). In Mg concentrations of less than 1:1:1 Mg:N:P the potential for struvite formation decreased, as phosphorus in the media was less reactive with magnesium. It was reported in the study by Jaffer et al. [8] that phosphorus cannot be removed only as struvite when the applied Mg dose below 3.4 mL<sup>-1</sup>.

NH<sub>4</sub>-N removal efficiency decreased with decreasing phosphorus and magnesium concentrations. Maximum COD removal efficiency (39.78%) was observed when the molar ratio of Mg:N:P was 1.5:1:1 at pH 9.0 (Table 3).

NH<sub>4</sub>-N and COD concentrations in effluent water following struvite precipitation at different molar ratios of Mg:N:P are given in Fig. 1. As can be seen from Fig. 1, when the molar ratios of Mg:N:P were below 1:1:1, NH<sub>4</sub>-N and COD concentration increased in effluent water following struvite precipitation. Consequently, a reduction in the molar ratios of magnesium and phosphorus negatively affected NH<sub>4</sub>-N removal efficiency. This finding is emphasized by Yetilmezsoy and Sapci-Zengin [36].

Other ions in the media can affect the precipitation of struvite and dissociation form from water [24]. Calcium is one ion that can inhibit the formation of struvite by forming calcium phosphate, depending on the pH value of the media and the concentration of Ca<sup>2+</sup> ions. Calcium ions compete with magnesium ions to react with phosphorus. In the event that the molar ratio of the Ca<sup>2+</sup> ion is high, most of the phosphorus is removed as calcium phosphate [8]. As can be seen from Table 4, the increase of Mg molar ratio from 1 to 1.5 corresponded with an increase in Ca concentration in the liquid phase from 9.47 mg/L to 46.87 mg/L. Accordingly, the increase in Mg molar ratio causes more magnesium to react with phosphorus than calcium. This was also reported by Musvoto et al. [45]. Similarly, it was found in the study by Jaffer et al. [8] that phosphorus is probably removed as struvite when a high dose of Mg is applied. XRD analysis performed in precipitation is compatible with that result. Intensive struvite formation with the increase of Mg molar ratio was shown (data not shown).

Heavy metal elimination via struvite precipitation has been investigated by fewer studies [32]. Metal and heavy metal concen-

**Table 5**

Allowable limits for key contaminants in fertilizer (Turkey regulations) and results obtained for dried precipitate produced in this study (Mg:N:P molar ratio is 1.5:1:1 at pH 9.0).

Compound	Results	Legal limit
Ni (mg/kg)	<1.29	120
Cr (mg/kg)	<1.35	270
Zn (mg/kg)	13 ± 1.7	1100
Hg (mg/kg)	4.23 ± 0.38	5
As (mg/kg)	<0.125	Not identified
Total PCB (ng/g)	0	Not identified

tration values in effluent water following struvite precipitation at different molar ratios of Mg:N:P are given in Table 4. The all struvite experiments show that struvite precipitation processes reduced the heavy metal content (As, Cr, Ni, Fe, Zn and Hg) when compared with influent concentration. 70.70% of Fe, 60.50% of As and 48.83% of Hg were reduced by struvite precipitation when the molar ratio of Mg:N:P was 1.5:1:1 at pH 9.0. As shown in Table 4, Zn, Cr and Ni concentrations in the effluent were below the minimum measurement limit at all Mg:N:P molar ratios following struvite precipitation. Thus, heavy metal elimination via struvite precipitation was carried out. The high reduction efficiencies of these heavy metals indicated their precipitation together with struvite. Similar observation was recorded by Ronteltap et al. [32], who illustrated that the metals can be incorporated into the crystal lattice or sorbed to the surface of struvite decreasing the purity of the product. Accordingly, the heavy metals were stored in struvite precipitation. For this reason, this situation is analyzed in the evaluation of struvite precipitation (Section 3.4).

#### 3.4. Evaluation of struvite precipitation products

To assess the possible agricultural use of the struvite precipitation product, impurities content must be analyzed and compared to legal limits. Heavy metal and PCB contents were analyzed in order to determine the suitability of the struvite precipitation for use as agricultural fertilizer. Heavy metal and PCB levels in struvite when Mg:N:P molar ratios were 1.5:1:1 at pH 9.0 are summarized in Table 5. The results were compared with regulatory limits for fertilizer-use in Turkey [46] as shown in Table 5.

As can be seen from Table 5, the heavy metal analysis indicated that As, Ni and Cr concentrations were below the minimum measurement limit when Mg:N:P molar ratios were 1.5:1:1. Hg and Zn concentrations were below the regulatory limit. PCB was not detected in struvite precipitation. PCBs in the effluent of the anaerobic sludge digester were not transferred to struvite precipitant. The use of experimentally derived struvite precipitant as fertilizer seems possible, since it meets regulatory limits for heavy metal content. In a study which was conducted on the effluent of a sewage sludge anaerobic digester [9], only the heavy metal content of struvite was determined for the use of struvite as fertilizer. It was reported that cadmium, lead and mercury concentrations were below the legal limits for fertilizers in Australia.

The results of XRD analysis of dry precipitate indicated the formation of the struvite. Intensive struvite peaks were observed with the increase of Mg molar ratio (data not shown).

#### 4. Conclusions

The present study investigated the potential for removal and recovery of nutrients by struvite formation from the effluent of a full-scale sewage sludge anaerobic digester. Both ammonium and phosphorus removal were achieved by adding necessary amounts of Mg and P to the liquid phase struvite precipitation experiments. Both pH and Mg:N:P molar ratio affected the nutrient removal effi-

ciency and recovery process. Increased Mg molar ratio significantly decreased residual PO<sub>4</sub>-P concentration. When Mg:N:P molar ratios were 1.5:1:1 at pH 9.0, NH<sub>4</sub>-N removal efficiency was 89.35%, COD removal efficiency was 39.78% and Mg removal efficiency was 76.31%. Residual PO<sub>4</sub>-P concentration was 2.55 ± 0.071 mg/L in effluent water. PO<sub>4</sub>-P removal was 95% when compared with influent concentration. When molar concentration of phosphorus decreased and molar ratios of Mg:N:P were 1:1:0.7 and 1:1:0.5, NH<sub>4</sub>-N removal efficiencies were 68.97% and 54.39%. Even when the amount of additional phosphorus was reduced, significant NH<sub>4</sub>-N removal efficiency was achieved.

Heavy metal elimination via struvite precipitation was carried out. The all struvite experiments show that struvite precipitation processes reduced the heavy metal content (As, Cr, Ni, Fe, Zn, Hg, Zn, Cr and Ni). The high reduction efficiencies of these heavy metals indicated their precipitation together with struvite. When molar ratios of Mg:N:P were 1.5:1:1 at pH 9.0, As, Cr and Ni concentrations in the struvite precipitation were below the minimum measurement limit and Hg and Zn concentration values were below the legal limit. Only some of the heavy metals precipitated and they did not exceed the regulatory limit. According to PCB analysis in this molar range, the precipitate did not include PCB. Heavy metal and PCB analysis indicated that the material derived from struvite precipitation was suitable for use as an agricultural fertilizer. XRD analysis conducted on the precipitate indicated a struvite formation.

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