Recovery of ammonium nitrogen from the effluent of UASB treating poultry manure wastewater by MAP precipitation as a slow release fertilizer

Kaan Yetilmezsoy*, Zehra Sapci-Zengin

Department of Environmental Engineering, Yildiz Technical University, 34349 Yildiz, Besiktas, Istanbul, Turkey

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ABSTRACT

Magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$, MAP) precipitation was studied on up-flow anaerobic sludge blanket (UASB) pretreated poultry manure wastewater in a lab-scale batch study. To recover high strength of ammonium nitrogen ($NH_4^+-N = 1318$ mg/L) from UASB effluent, three combinations of chemicals including $MgCl_2 \cdot 6H_2O + KH_2PO_4$, $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$, and $MgO + 85\% H_3PO_4$ were first applied at the stoichiometric ratio ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$) and at different pH levels ranging from 4.45 to 11. Preliminary test results indicated that maximum NH_4^+-N removal, as well as maximum chemical oxygen demand (COD) and color reductions, were obtained as 85.4%, 53.3% and 49.8% at pH 9.0 with the addition of $MgCl_2 \cdot 6H_2O + KH_2PO_4$, respectively. The paired experimental data obtained from batch studies were statistically evaluated by a non-parametric Mann–Whitney test and a two-sample *t*-test. Based on the previous results, another batch experiments were then performed at pH 9.0 using $MgCl_2 \cdot 6H_2O + KH_2PO_4$ for different molar ratios applied as overdose (1.2:1:1, 1.5:1:1, 1:1:1.2, 1:1:1.5) and underdose (0.5:1:1, 0.8:1:1, 1:1:0.5, 1:1:0.8). In the final step, the fertility of the MAP precipitate as struvite was also tested on the growth of three test plants including purslane (*Portulaca oleracea*), garden cress (*Lepidum sativum*) and grass (*Lolium perenne*). Findings of this experimental study clearly confirmed the recovering of NH_4^+-N from UASB pretreated poultry manure wastewater by MAP precipitation, and also the application of recovered MAP sludge as a valuable slow release fertilizer for agricultural use.

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1. Introduction

The growing demand for poultry and livestock production in both developed and developing coutries has lead to the accumulation of large volumes of animal wastes in limited areas. Haga [1] has reported that the total amount of animal wastes in Japan has remained at around 90 million ton per year. Likewise, the daily excrement production in Germany (16 million cattle, 26 million pigs, 114 million poultry and about 4 million horses and sheep) has been reported to be 57,500 tons organic dry substance in year 2001 [2]. Similarly, the yearly production of poultry and livestock waste on centralised farms in Russia has been reported to exceed 700 million m³ [3]. Atuanya and Aigbirior [4] have stated that the poultry production is the fastest growing cottage industry in both urban and rural areas in most developing countries, and the solid waste annually produced in poultry farms has been estimated at millions of tons in Nigeria. Moreover, Gungor-Demirci and Demirer [5] indicated that the production of cattle and poultry manure was approximately 20 million tons dry matter in Turkey in year 2000.

Improperly managed poultry manure can result in nuisance consequences to environment, which are very difficult to control using traditional practices. Therefore, urgent treatment and disposal solutions are needed to manage the huge amount of wastes produced particularly in concentrated areas. Recently, several treatment processes are used to treat poultry and livestock wastes. Among them, anaerobic digestion technology has become a technology of growing importance and a highly competivive alternative, especially for highly polluted wastewaters [6,7]. A number of studies conducted on the anaerobic treatment of animal manure wastewaters using different anaerobic process configurations have been reported in a comprehensive literature study elaborated by Sakar et al. [8].

Yetilmezsoy and Sakar [9] have reported that the poultry manure wastewater can be succesfully pretreated by means of high-rate anaerobic processes, however, compliance with the effluent discharge standards in terms of final organic and nutrient loads may not be met. Therefore, to meet strict laws on environmental protection, there is a need to install effective post-treatment methods, after undergoing anaerobic processes treating heavily contaminated waste streams, such as poultry manure wastewater [5,7]. Although the conventional approaches of nutrient management for animal wastewater include some farm-based applications, such as spreading of nutrient-rich wastewater on cropland and dumping

* Corresponding author. Tel.: +90 212 3833033; fax: +90 212 2619041.
E-mail address: yetilmez@yildiz.edu.tr (K. Yetilmezsoy).

of this into receiving waters, increasing nutrient loads sometimes limit these approaches due to the eutrophication of surface water-bodies, burning of roots, and devastation of aquatic life [10]. Ali [10] has suggested that one of the proposed solutions to this problem is to recover nutrients using crystallization. The key feature of this recovery technique is the combined removal of ammonium (NH_4^+), phosphate (PO_4^{3-}) and magnesium (Mg^{2+}) from super-saturated solutions. The by-product of this method is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$), which is commonly known as struvite. Struvite or MAP usually precipitates as a stable white orthorhombic crystals at the stoichiometric ratio ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$) according to following reaction [10–12]:

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad (1)$$
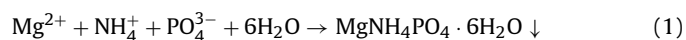
However, crystalization experiments have shown that the precipitation of struvite reduces the pH of the solution, and therefore HPO_4^{2-} will take place in the reaction rather than PO_4^{3-} as follows [13]:

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^+ \qquad (2)$$
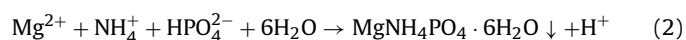
Li et al. [12] have reported that since the molecular weight of $MgNH_4PO_4 \cdot 6H_2O$ is 245 g/mol, 17.5 g $MgNH_4PO_4 \cdot 6H_2O$ should be theoretically formed as precipitated MAP sludge, when 1 g of NH_4^+-N is removed (Eq. (2)). The success of MAP precipitation depends on two main factors: $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ ratio and the pH of the solution [14]. In a given solution, struvite precipitates if the product of Mg^{2+}, NH_4^+, PO_4^{3-} activities exceed the equilibrium ion-activity product [11] or the thermodynamic solubility product [13,15]. Although H^+ concentration does not directly enter the ion-activity product equation, $MgNH_4PO_4 \cdot 6H_2O$ precipitation is highly pH dependent because the activities of both NH_4^+ and PO_4^{3-} are pH dependent [11]. Similarly, Marti et al. [15] have reported that the struvite solubility decreases when the pH increases. Therefore, Burns and Finlayson [16] have suggested that the minimum pH of the solution should be 7.0 to obtain a favourable struvite precipitation. Depending on the studied experimental conditions, Ohlinger et al. [17] and Tunay et al. [18] obtained the minimum struvite solubility between pH 10.3–10.7 and pH 8–10, respectively. Some published values for struvite solubility products (pK_S) ranging from 9.94 to 13.26 can be found in the previous work of Shin and Lee [19].

In recent years, several papers have addressed the recovery of NH_4^+ or PO_4^{3-} as struvite from various types of wastewaters (mostly leachate and piggery wastewaters) such as landfill leachate [12,20–24], swine wastewater [25–28], source-separated human urine [29,30], industrial wastewater [13,31], anaerobically pretreated domestic wastewater [32], slaughterhouse wastewater [33], filtered pig manure wastewater [34], anaerobic swine lagoon liquid [11], and supernatant of anaerobically digested sludge [35]. Compared with these studies, Lei et al. [36] have emphasized that there is an advantage for applying struvite precipitation process to anaerobic effluents due to predominance of struvite constituent ions, NH_4^+-N and $PO_4^{3-}-P$, in the methane fermentation effluent, thereby minimizing the need to add chemicals. Although struvite precipitation has been widely studied by many researchers as an established and promising method for NH_4^+ or PO_4^{3-} removal from various types of wastewaters, however, there are almost no papers in the literature specifically devoted to a study of the applicability of MAP precipitation for the post-treatment of anaerobically pretreated poultry manure wastewater. So far, most of studies on nutrient removal from animal wastewaters by struvite precipitation/crystallization have been mainly focused on piggery wastewaters. Moreover, only a few of studies [20,31] dealing with this problem have earlier addressed the fertilizing value of the MAP precipitate using plant studies. Even though a number of investigations have been conducted on nutrient recovery from various waste

Table 1
Characteristics of the mixed UASB effluent.

Constituent	Mixed UASB effluent (mean ± S.D.)
Total chemical oxygen demand, TCOD (mg/L)	1800 ± 90
Biological oxygen demand, BOD_5 (mg/L)	370 ± 50
Soluble chemical oxygen demand, SCOD (mg/L)	1060 ± 80
Total solids, TS (mg/L)	2030 ± 170
Volatile solids, VS (mg/L)	1140 ± 190
Total suspended solids, TSS (mg/L)	1130 ± 90
Volatile suspended solids, VSS (mg/L)	970 ± 110
Total Kjeldahl nitrogen, TKN (mg/L)	1580 ± 100
Ammonium nitrogen, NH_4^+-N (mg/L)	1318 ± 70
Total phosphorus, TP (mg/L)	370 ± 30
pH	7.95 ± 0.10
Alkalinity (mg $CaCO_3$/L)	2440 ± 160
Color (Hazen)	1750 ± 50

streams by struvite precipitation, every special process needs to be given a particular attention for investigation. Therefore, clarification of the place of struvite precipitation in the treatment scheme for anaerobically pretreated poultry manure wastewater is important for contribution to the literature in this field.

The specific objectives of this study were: (1) to precipitate NH_4^+-N from UASB pretreated poultry manure wastewater using different types of magnesium and phosphate sources; (2) to appraise the performance of MAP precipitation on residual COD and color removals for the present application; (3) to optimize the effects of operating parameters such as type of chemical combination, reaction pH, and $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio; (4) to examine the physical properties of the MAP product; (5) to demonstrate the combination of a two-stage system on the treatability of poultry manure wastewater using an UASB process followed by MAP precipitation; and (6) to evaluate the fertilizing potential of MAP precipitate by greenhouse experiments.

2. Materials and methods

2.1. Characteristics of UASB effluent used in MAP precipitation

Anaerobic treatability studies on high strength poultry manure wastewater were fully investigated in our previous studies [6,7,9]. The anaerobically pretreated poultry manure wastewater samples were periodically obtained from effluents of two ongoing mesophilic UASB reactors in Environmental Engineering Laboratory at Yildiz Technical University (Istanbul, Turkey), and collected in a 15-L plastic container for further physico-chemical treatability studies. Because the collected wastewater contained different volumes of effluents from UASB reactors operated with different organic and hydraulic loading conditions, preliminary analyses were conducted on the mixed wastewater to determine final organic pollutant contents prior to MAP precipitation experiments.

Some wastewater characteristics of the mixed UASB effluent are given in Table 1. As seen in Table 1, the mixed UASB effluent showed a low biodegradability index with a low BOD_5/TCOD (5-day biological oxygen demand/total chemical oxygen demand) ratio of about 0.21, and a low $TCOD/NH_4^+-N$ ratio of about 1.37. The mixed effluent sample also appeared dark brown in color and contained a high NH_4^+-N concentration. Therefore, the mixed UASB effluent was found to be recalcitrant to a possible further biodegradation.

2.2. MAP precipitation tests

In each MAP precipitation test, 400 mL of UASB pretreated poultry manure wastewater was first poured into 500 mL beaker and then chemicals used as magnesium and phosphate sources were added as required dosages. Effluent samples were stirred conti-
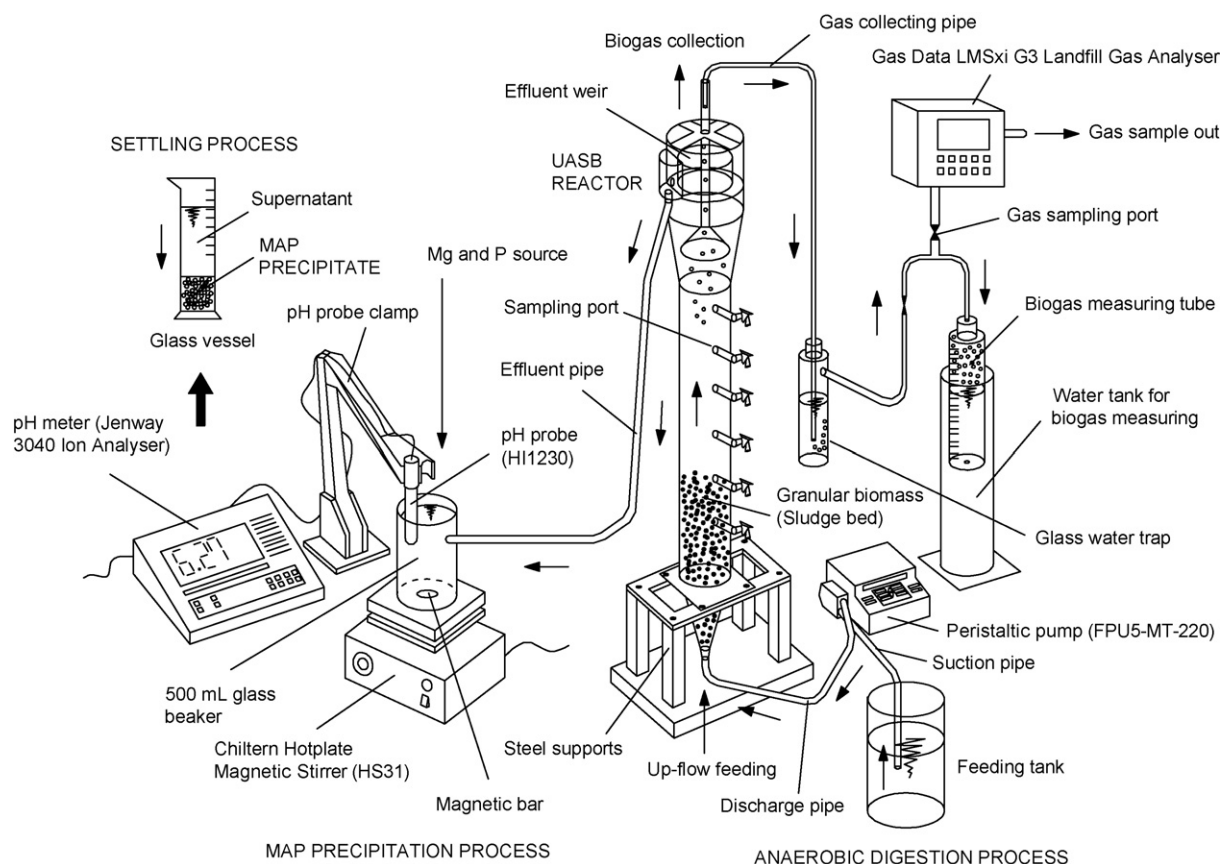
Fig. 1. A detailed schematic of the experimental set-up.

nously on a magnetic stirrer (Chiltern Hotplate Magnetic Stirrer, HS31) for about 15 min until an equilibrium state in terms of a stable pH was reached. During the MAP reaction, the pH of samples was adjusted to desired value by the gradual addition of 1N and 6N NaOH. All the runs were performed at a stable temperature of about 25 °C. Prior to any analysis done, all samples were allowed to settle for 30 min in a graduated glass vessel in order to separate the crystallized precipitate from bulk liquid. About 100 mL of supernatant sample was then collected for NH_4^+–N, COD and color analysis after the settling process.

Three combination of chemicals including $MgCl_2 \cdot 6H_2O$ + KH_2PO_4, $MgSO_4 \cdot 7H_2O$ + $NaHPO_4 \cdot 7H_2O$, and MgO + 85% H_3PO_4 were employed to select the best combination and also to optimize the pH in terms of NH_4^+–N, COD and color removals from UASB effluent. Based on preliminary test results, subsequent experiments were then carried out at the optimum pH (as found in the previous step) using the most efficient chemical combination. Besides the stoichiometric ratio, eight different Mg^{2+}:NH_4^+–N:PO_4^{3-}–P molar ratios were applied as overdose (1.2:1:1, 1.5:1:1, 1:1:1.2, 1:1:1.5) and underdose (0.5:1:1, 0.8:1:1, 1:1:0.5, 1:1:0.8) to investigate the influence of molar ratio on NH_4^+–N removal, as well as on COD and color reductions. A detailed schematic of the experimental set-up is depicted in Fig. 1.

2.3. Plant growth tests

The fertility of the MAP precipitate was investigated in a set of greenhouse experiment. Three quick-growth test plants including purslane (*Portulaca oleracea*), garden cress (*Lepidum sativum*) and grass (*Lolium perenne*) were selected for the present agricultural study. Garden soil and sand samples were used as raw solid media for germination and growth of the selected plants. Based on the

dimensions of conical plastic pots (height of 90 mm, upper diameter of 135 mm, bottom diameter of 95 mm), about 1.14 kg of garden soil and sand samples were separately filled in each pot. The characterization of the investigated raw solid samples were pH 7.5, electrical conductivity (EC) 0.70 mS/cm and total carbon (TC) 49.4 g/kg for garden soil, and pH 6.47, EC 0.41 mS/cm and TC 5.36 g/kg for sand, respectively.

The growth of each plant species was tested in four different conditions using two types of solid media (garden soil or sand): (1) garden soil only as control (without fertilizer); (2) garden soil with addition of MAP precipitate; (3) sand with addition of KCl only as control; (4) sand with addition of KCl and MAP precipitate. Therefore, a total of 8 pots were set up for the present plant growth tests.

Required dosages of macro elements (N, P, K) for fertilizer applications for Turkish vegetable growth has been recommended as 150–1000 mg N/L (of fertilizer solution), 100–400 mg K/L, and 50–100 mg P/L [37]. When the lower limits of the suggested ranges for K and N were considered, the required dosages of KCl and the MAP precipitate in 1.14 kg of solid media were determined to be about 218 mg and 3 g, respectively. A schematic of the present greenhouse experiment is illustrated in Fig. 2.

In the cultivation of plants, following steps were implemented as described by Li and Zhao [20]: (1) each plastic pot was filled with the selected solid media samples (garden soil or sand); (2) about 2 cm of top layer was removed from the pots; (3) pre-weighted chemicals (KCl and the MAP precipitate) were mixed into the packed media prior to planting; (4) 100 mL of tap water was added evenly over the surface of each pot; (5) pre-weighted plant seeds (each of 1 g) were laid evenly on the excavated surface; (6) plant seeds were covered with the removed solid media samples, and surfaces of the backfilled media were then gently compressed by the reverse side
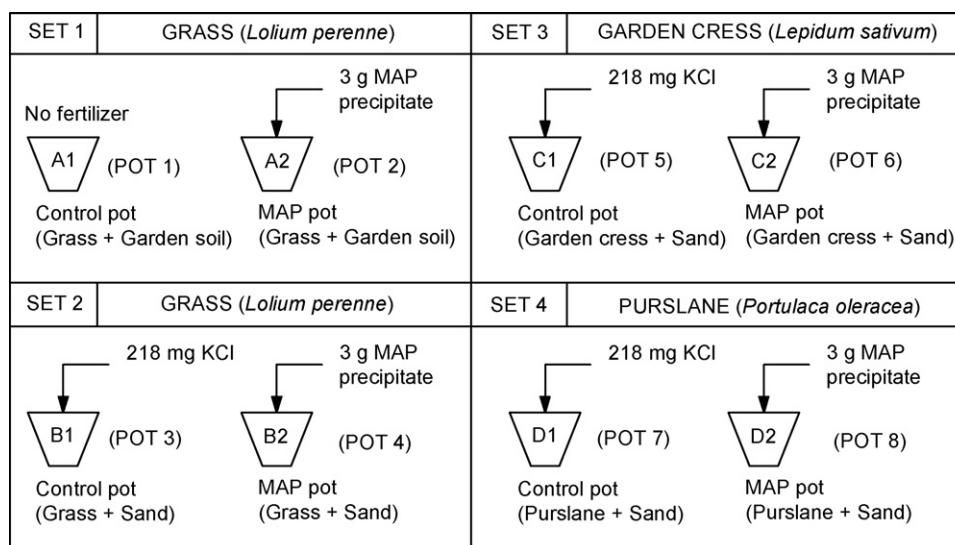
Fig. 2. Schematic of the greenhouse experiment.

of a tablespoon; (7) a second 100 mL of tap water was added evenly over the planted and covered surface.

Pots were randomly placed in an artificially illuminated growth chamber at about 25 °C under suitably sterile conditions. In the chamber, ultraviolet radiation was continuously provided by a modulated fluorescent lamp (Panlight daylight lamps, 3011 T8 36W). Based on the humidity of the ambient air, pots were irrigated with the required volume of tap water by using a graduated glass vessel to ensure equal watering to all plants during the agricultural process.

2.4. Analytical procedure

The pH of wastewater samples was measured by a pH meter (Jenway 3040 Ion Analyser) and a pH probe (HI1230, Hanna Instruments). Soluble chemical oxygen demand (SCOD) was determined by filtering the sample through 0.45 μm Whatmann GF/C filter. Ammonium nitrogen (NH_4^+–N), total COD, total solids (TS), total suspended solids (TSS), volatile solids (VS), 5-day biological oxygen demand (BOD_5), alkalinity, ammonia nitrogen (NH_3–N), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) were conducted by the procedures described in the Standard Methods [38]. Samples were ignited at 550 °C by using an ashing furnace (Lenton) for VS and volatile suspended solids (VSS) analyses. Absorbance values were recorded at 690 nm by using a spectrophotometer (Pharmacia Biotech LKB Novaspec® II) for TP analysis. Color of wastewater samples was measured with a Merck photometer (SQ 118) and determined as Hazen color unit according to method number of 138 [39].

In the greenhouse experiments, test plants were dried at 60 ± 5 °C in an orbital incubator with thermostat (Gallenkamp) prior to measuring dry weights. Fresh and dry weights of plants were measured with an electronic sensitive scientific balance (Avery Berkel). Total carbon (TC) values of raw solid growing media (sand or garden soil) were determined by using IL 550 TOC-TN analyser (Hach Lange Ltd.). The electrical conductivity (EC) and pH analyses for raw solid growing media were conducted by using a multiparameter instrument (WTW® Oxi 330i) after dilution with ultra pure water (1:2.5), as described by Allen [40]. Both deionized and ultra pure water used in the experiments were supplied from a TKA-GenPure water purification system (Niederelbert, Germany). Stability of the treatment process and components of wastewater samples were monitored in Environmental Engineering Laboratory at Yildiz Technical University in Istanbul, Turkey.
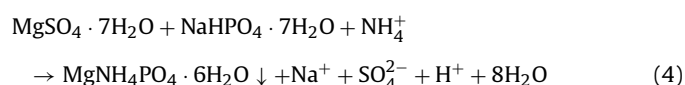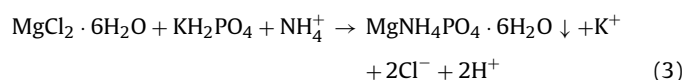
2.5. Statistical analysis

Each experiment was performed in triplicate and repeated at least three times to observe the reproducibility, and experimental results were reported as the mean value of each parameter with standard deviation. All standard deviations reported in this study were calculated using the statistical functions in spreadsheets of Microsoft Excel® 2000 or DataFit® scientific software (version 8.1.69, Copyright© 1995–2005 Oakdale Engineering) used as ODBC (Open Database Connectivity) data sources. A non-parametric Mann–Whitney (or Wilcoxon rank-sum) test and a two-sample t-test were also performed to evaluate the relationship between paired experimental data using Minitab® 15.1.1 statistical software package. An alpha (α) level of 0.05 was used to determine the statistical significance in all analyses. Results were assessed with test statistics (W or t value), p values and values of degrees of freedom (df) to reflect the statistical significance between paired groups.

3. Results and discussion

3.1. $MgNH_4PO_4 \cdot 6H_2O$ precipitation

In the first step of MAP precipitation tests, three combination of chemicals including $MgCl_2 \cdot 6H_2O + KH_2PO_4$, $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$, and $MgO + 85\%$ H_3PO_4 were conducted to precipitate an average NH_4^+–N concentration of 1318 mg/L from the anaerobically pretreated poultry manure wastewater. According to stoichiometric calculation ($Mg^{2+}:NH_4^+$–N$:PO_4^{3-}$–P = 1:1:1), required dosages of chemicals to precipitate the residual NH_4^+–N in the form of struvite is given in Table 2. The chemical reactions for the struvite (MAP) precipitation are given in Eqs. (1)–(3) as follows:

$$MgCl_2 \cdot 6H_2O + KH_2PO_4 + NH_4^+ \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + K^+$$
$$+ 2Cl^- + 2H^+ \quad (3)$$

$$MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O + NH_4^+$$
$$\rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + Na^+ + SO_4^{2-} + H^+ + 8H_2O \quad (4)$$

Table 2
Dosages of chemicals in 400 mL of the mixed UASB effluent at the stoichiometric ratio ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$).

Amount of NH_4^+-N in 400 mL UASB effluent (g)	Mg and $PO_4^{3-}-P$ sources	Molecular weight of chemicals (g/mol)	Amount of chemicals added (g)	Purity of chemicals
0.527	$MgCl_2 \cdot 6H_2O$	203.30	7.66	Analytical grade
	KH_2PO_4	136.09	5.12	Analytical grade
0.527	$MgSO_4 \cdot 7H_2O$	246.47	9.28	Analytical grade
	$NaHPO_4 \cdot 7H_2O$	268.03	10.09	Analytical grade
0.527	MgO	40.30	1.52	Analytical grade
	H_3PO_4	97.99	3.69	85% H_3PO_4

$$MgO + 85\%H_3PO_4 + NH_4^+ \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H_2O \qquad (5)$$

In MAP precipitation tests, it was observed that the initial pH 7.95 of the mixed UASB effluent dropped immediately to 5.77, 6.68 and 4.45 as soon as the chemicals were added at the stoichiometric ratio for the corresponding chemical reactions, respectively. To explore the effect of pH on NH_4^+-N removal from the UASB pretreated effluent, the decreased pH of the medium was raised and gradually set to the desired value by adding 6N and 1N NaOH, respectively.

As the pH was increased above its initial value, the removal percentage of the residual NH_4^+-N significantly increased and reached its maximum value at pH 9.0 for each chemical combination (Fig. 3a). In these tests, the effluent quality in terms of the residual COD and color were also determined. As seen in Fig. 3b and c, experimental results showed that not only did MAP precipitation help to remove 85.4% of NH_4^+-N from the UASB effluent, but also achieved maximum removal efficiencies of about 54% for total COD and about 50% for biologically recalcitrant color with the addition of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ at the stoichiometric ratio. Ozturk et al. [21] reported similar values with a maximum NH_4^+-N removal of 89% and a total COD reduction of about 50% at pH 9.2 for anaerobically pretreated raw landfill leachate effluent used in a MAP precipitation study.

As seen in Fig. 3a and b, total COD reductions were not so high as compared to the corresponding NH_4^+-N removals in the experiments, which implies that MAP precipitation technique has a significant selectivity to particularly remove NH_4^+-N from the wastewater, as similarly reported by Li et al. [12]. Therefore, the removal of COD during the precipitation of MAP may be attributed to the co-precipitation of struvite together with side-products and other impurities present in the raw UASB effluent. Because the total COD was not significantly reduced during the MAP precipitation, a biological treatment process may need to be followed to remove residual COD.

The growth of MAP crystals were observed to be improved above pH 6.5, and the amount of precipitate at the bottom of beaker increased when the pH of the solution was gradually raised to 11. The MAP product was formed rapidly and settled quickly at the bottom of the beaker after stopping magnetic stirring for the present application. With the addition of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ at the stoichiometric ratio ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$), about 90 mL of MAP precipitate (22.5% of the working volume) at pH 9.0 was collected at the bottom of the beaker after 30 min of quiescent settling. However, the amount of MAP precipitate decreased substantially to about 15 mL (3.75% of the working volume) at pH 5.77 ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$). Basakcilardan-Kabakci et al. [29] and Diwani et al. [31] observed similar phenomena for the precipitation of $MgNH_4PO_4 \cdot 6H_2O$ from the source-separated human urine and industrial wastewater, respectively.

The experimental results indicated that combinations of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ were found to be more effective in terms of NH_4^+-N removal, as well as in terms of COD and color reductions compared to values obtained by using $MgO + 85\% H_3PO_4$. As seen in Fig. 3a–c, the

addition of $MgO + 85\% H_3PO_4$ showed the poorest performance among three combination of chemicals. This phenomenon can be attributed to the fact that since MgO has a limited solubility in the water phase, its very slow dissolution in the UASB effluent sample resulted in a low efficiency. Li and Zhao [20] obtained similar results for the comparison of chemical combinations employed for removing NH_4^+-N from landfill leachate by MAP precipitation. They reported that $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$ was found to be most efficient combination in terms of NH_4^+-N removal from the leachate compared to removals obtained with the addition of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\% H_3PO_4$, respectively. The authors also concluded that at pH 9.0 nearly 92% of NH_4^+-N
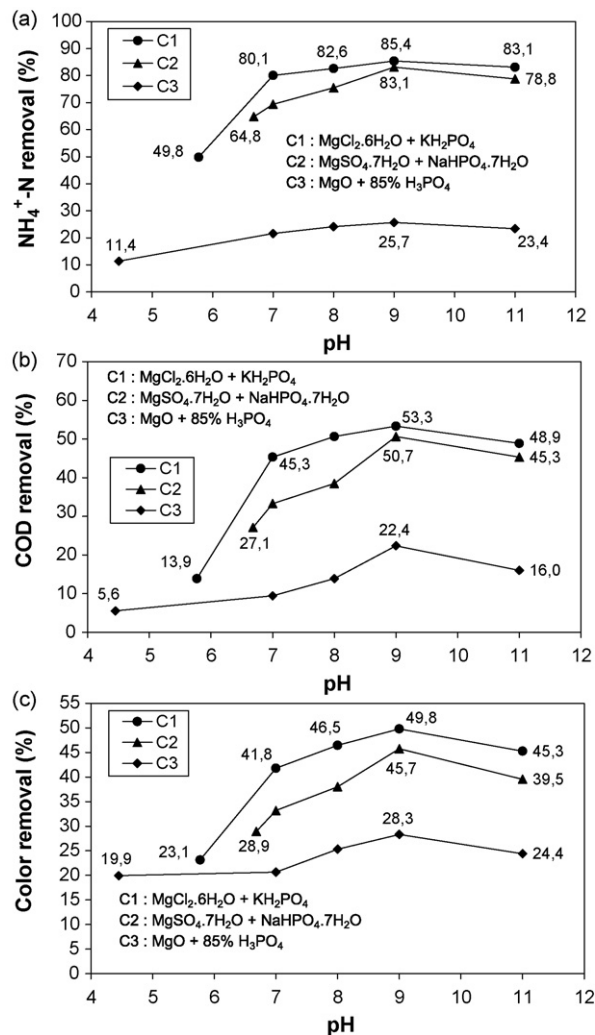
Fig. 3. Effect of pH on NH_4^+-N, COD and color removals from the UASB pretreated poultry manure wastewater for different chemical combinations (initial $NH_4^+-N = 1318$ mg/L, initial COD = 1800 mg/L, initial color = 1500 Hazen, initial pH 7.95, $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$).

was effectively removed from the local landfill leachate by adding the chemical combination of $MgCl_2 \cdot 6H_2O + Na_2HPO_4 \cdot 12H_2O$ at the stoichiometric ratio ($Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$).

For the present application, the Mann–Whitney test showed that there was no statistically significant difference between NH_4^+-N removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ ($W = 32.5$, $p = 0.347$). However, there was a significant difference between NH_4^+-N removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 ($W = 40$, $p = 0.01$). In this case, because the p value is less than the chosen α level of 0.05, the null hypothesis (H_0) was rejected in favor of alternative hypothesis (H_a). Similarly, the difference between NH_4^+-N removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 was found to be significant ($W = 40$, $p = 0.01$), and therefore H_0 was rejected. Besides the Mann–Whitney test, a two-sample t-test was also performed to evaluate the relationship between paired experimental data, as well as to prove statistical results. Two-sample t-test indicated that there was no sufficient evidence for a significant difference between NH_4^+-N removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ (t value $= 0.25$, $p = 0.806$, df $= 8$). As similarly found in the Mann–Whitney test, there was a significant difference between NH_4^+-N removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 (t value $= 7.72$, $p = 0.00$, df $= 8$). Likewise, there was a sufficient evidence for a significant difference between NH_4^+-N removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 to reject H_0 (t value $= 12.82$, $p = 0.00$, df $= 8$).

The Mann–Whitney test concluded that there was insufficient evidence for a significant difference between COD removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ ($W = 32$, $p = 0.40$). On the contrary, a significant difference was found between COD removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 ($W = 38$, $p = 0.03$). Also, there was a significant difference between COD removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 ($W = 40$, $p = 0.01$), and therefore we rejected H_0. Furthermore, two-sample t-test revealed that no sufficient evidence was found for a significant difference between COD removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ (t value $= 0.41$, $p = 0.69$, df $= 8$). However, there was a significant difference between COD removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 (t value $= 3.71$, $p = 0.006$, df $= 8$). Moreover, two-sample t-test concluded that there was a sufficient evidence for a significant difference between COD removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 to reject H_0 (t value $= 5.03$, $p = 0.001$, df $= 8$).

The Mann–Whitney test was also used to appraise the relationship between paired color removal data obtained from experiments. The statistical evaluation of the experimental data resulted that there was no significant differences between color removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ ($W = 33$, $p = 0.29$). However, a sufficient evidence was found for a significant difference between color removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 ($W = 37$, $p = 0.05$), and therefore H_0 was rejected. Similarly, there was a statistically significant difference between color removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 to reject H_0 ($W = 40$, $p = 0.01$). Furthermore, two-sample t-test showed that there was no sufficient evidence for a significant difference between color removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ (t value $= 0.76$, $p = 0.467$, df $= 8$). As obtained in the Mann–Whitney test, a significant difference was determined between color removals of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgO + 85\%$ H_3PO_4 resulting to the rejection of H_0 (t value $= 3.54$, $p = 0.008$, df $= 8$). Finally, a sufficient evidence was obtained for a significant difference between color removals of $MgSO_4 \cdot 7H_2O + Ca(H_2PO_4) \cdot H_2O$ and $MgO + 85\%$ H_3PO_4 (t value $= 4.51$, $p = 0.003$, df $= 8$), and therefore we rejected H_0.

Based on the statistical evaluation for the present paired experimental data, both $MgCl_2 \cdot 6H_2O + KH_2PO_4$ and $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$ were proven to be more effective in terms of NH_4^+-N removal, as well as in terms of COD and color reductions compared to the combination of $MgO + 85\%$ H_3PO_4. However, from an aesthetic point of view, experimental results indicated that the addition of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ was more suitable to achive highest efficiencies particularly in terms of COD and color removals in addition to NH_4^+-N. Therefore, $MgCl_2 \cdot 6H_2O + KH_2PO_4$ may be proposed as the best option to achieve the maximum removal of NH_4^+-N from the anaerobically pretreated poultry manure wastewater at pH 9.0. Considering the highest removal efficiencies, subsequent batch experiments were conducted at pH 9.0 with $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 to investigate the effects of different molar ratios on the NH_4^+-N removal efficiency, as well as on residual COD and color removals from the UASB pretreated effluent.

It is well known that ammonia removal is higher at higher pH than that at lower pH, because the proportion of volatile NH_3 of NH_4^+-N is a function of pH and temperature [36]. As temperature increases, more of the ammonia is converted to free ammonia gas because of the temperature dependence of the acid dissociation constant. For instance, at a pH level of 7, under standard conditions (i.e., temperature is 25 °C and pressure is 1 atm), 0.56% of ammonia present is in the form of free ammonia. When the temperature increases to 60 °C, the percentage of free ammonia present at pH 7 increases to 4.90%. Therefore, it can be noted that as temperature increases, the dominant ammonia removal mechanism becomes volatilization.

Air flow also plays an important role in ammonia-nitrogen volatilization. As air is introduced, it begins to agitate the solution, creating a removal pathway for dissolved free ammonia to volatilize and leave the solution. In addition, air flow dilutes the concentration of gas-phase ammonia-nitrogen, increasing the driving force for dissolved ammonia-nitrogen to partition to the gaseous phase. Therefore, tendency for ammonia volatilization increases with increasing temperature and with increasing surface area between the liquid and the air provided by increasing aeration rate. For a constant ammonia concentration in the liquid, ammonia volatilization would be expected to increase with increased aeration rate. For this purpose, a sufficient aeration time should be provided to achieve high removal efficiencies. Instead of this, experiments can also be carried out without aeration, however, longer stirring times up to 24 h may be needed to obtain high removals. For instance, Lei et al. [36] obtained an ammonia removal efficiency of about 60.2% with an aeration rate of 0.6 L/min in a reaction time of 4 h. They also achieved the same removal efficiency in a reaction time of 24 h, but without aeration (only stirring). However, in the study, about 93.4% of removal efficiency was obtained with an aeration rate of 0.6 L/min in a reaction time of 24 h. They also found that for 1 L wastewater, ammonia removal rate almost reached maximum 95.3% after 12 h with an aeration rate of 10 L/min.

Comparing to above, no additional aeration was specifically supplied through diffusers for the ammonia removal in the present study. Although stirring was performed directly open to air, however, the stirring time in our study was only about 15 min. This was relatively low as compared to other studies [21,36] in which very long reaction times up to 24 h were applied for ammonia volatilization. Furthermore, at a pH level of 9, under standard conditions (25 °C and 1 atm), only about 36.2% of ammonia present is in the form of free ammonia. On the basis of the present experimental procedure (without aeration and only 15 min of stirring time) and also other findings in the literature [21,36], it can be concluded that ammonia volatilization is not expected to have a significant impact on the removal of NH_4^+-N from the UASB effluent, as compared to MAP precipitation performed in the present study.

Table 3
Dosages of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ in 400 mL of the mixed UASB effluent at different $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratios (initial $NH_4^+-N = 1318$ mg/L, reaction pH 9.0).

$Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio	Amount of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ added (g + g)
0.5:1:1	3.83 + 5.12
0.8:1:1	6.13 + 5.12
1:1:0.5	7.66 + 2.56
1:1:0.8	7.66 + 4.10
1:1:1	7.66 + 5.12
1.2:1:1	9.19 + 5.12
1.5:1:1	11.49 + 5.12
1:1:1.2	7.66 + 6.14
1:1:1.5	7.66 + 7.68

3.2. Effect of $Mg^{2+}:NH4^+-N:PO_4^{3-}-P$ molar ratio

Effects of different $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratios on NH_4^+-N removal, as well as on COD and color reductions were investigated for eight molar concentrations ranging from 0.5 to 1.5. Based on previous results, $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 were used in subsequent batch experiments, and the final pH of the effluent samples was adjusted to 9.0. For the investigated molar concentrations, required dosages of $MgCl_2 \cdot 6H_2O + KH_2PO_4$ to precipitate the residual NH_4^+-N from the mixed UASB effluent are summarized in Table 3.

As seen in Fig. 4, batch experimental results showed that although the removal percentage of residual color could be increased up to about 56.1% at the $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio of 1.5:1:1, however, no striking improvement was observed in the residual NH_4^+-N removal with the increase of Mg^{2+} dosage. Similar results were obtained when the initial molar concentration of $PO_4^{3-}-P$ was in excess. With the increase of $PO_4^{3-}-P$ dosage, the removal percentage of residual color was increased from 49.8 to 55.4%, whereas the NH_4^+-N removal efficiency was increased a little with a rise of about 2.1% at the $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio of 1:1:1.5. In both cases of overdose conditions, initial molar concentrations of Mg^{2+} or $PO_4^{3-}-P$ were not found to have considerable effects on the further removal of residual COD from the anaerobically pretreated effluent as much as other investigated parameters.

Another set of batch experiments were conducted at four different molar ratios (0.5:1:1, 0.8:1:1, 1:1:0.5, 1:1:0.8) to explore the effects of underdose conditions on the removal efficiencies. Experimental results showed that when the molar concentrations of Mg^{2+} or $PO_4^{3-}-P$ were lower than 1, percentages of NH_4^+-N, COD and color removals also demonstrated lower levels compared to values obtained with higher molar concentrations (Fig. 4). With
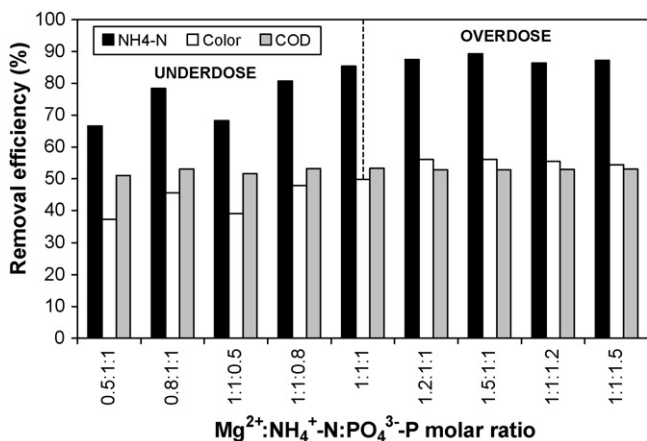
Fig. 4. Effects of different $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratios on NH_4^+-N, COD and color removals.
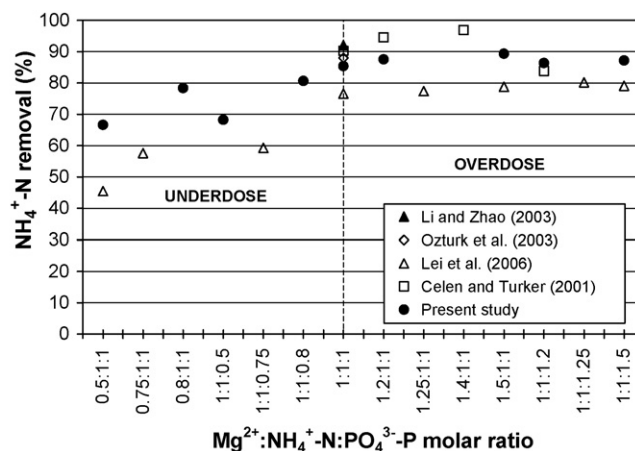
Fig. 5. Performance of different MAP precipitation tests conducted at pH 9.0 with $MgCl_2 \cdot 6H_2O$ as magnesium source.

the decrease of Mg^{2+} or $PO_4^{3-}-P$ dosages, the percentage of COD removal kept almost same tendency within a narrow range of 51–53.2%, as similarly found in overdose experiments.

Experimental findings indicated that the removal percentage of the residual NH_4^+-N can be increased up to only 89.3% or 87.2% at the corresponding $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratios of 1.5:1:1 or 1.1:1.5, respectively. Based on the wastewater characteristics and selected operating conditions, it can be possible to enhance the recovery of NH_4^+-N with the excess concentrations of Mg^{2+} or $PO_4^{3-}-P$. However, this application may be limited in practice due to possible high levels of residual chemicals after precipitation, as recommended by other researchers [29,33,36].

Experimental results showed that NH_4^+-N removal reached almost maximum at the stochiometric ratio for the present application. Excess dosages of Mg^{2+} or $PO_4^{3-}-P$ did not provide striking benefits on both NH_4^+-N and organic matter removals. These results agreed with the findings of several previous studies [12,33,36]. Therefore, taking into account both present results and those previously obtained, a $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio of 1:1:1 was considered to be enough for the residual NH_4^+-N removal from UASB pretreated poultry manure wastewater by MAP precipitation. Furthermore, from an engineering point of view, it may be practical to control the $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P$ molar ratio at 1:1:1 when the NH_4^+-N is required to be precipitated from the anaerobically pretreated poultry manure wastewater. Li et al. [12] has reported similar results for the NH_4^+-N removal from landfill leachate by MAP precipitation.

On the basis of the performance data obtained from the present application, experimental results were compared with those of other studies in terms of the effects of various molar ratios on the NH_4^+-N removal. In order to make a comparable evaluation of our data, results of MAP precipitation tests conducted at similar experimental conditions (pH = 9.0, magnesium source: $MgCl_2 \cdot 6H_2O$) using anaerobically digested effluents were particularly included in the comparison. In Fig. 5, the performance of the present application is compared with other experimental data reported in the literature [13,20,21,36]. The comparison of results shows that the present results are close to or superior than those reported by others. However, it is noted that differences are probably due to the characteristics of studied wastewaters and other operating conditions such as total mixing time, settling time and also types of phosphate sources (Table 4).

With the proposed experimental conditions of the present investigation (pH = 9.0, $Mg^{2+}:NH_4^+-N:PO_4^{3-}-P = 1:1:1$, $MgCl_2 \cdot 6H_2O + KH_2PO_4$), the anaerobically pretreated effluent having an average NH_4^+-N concentration of 1318 mg/L was

Table 4
Several experimental data of different MAP precipitation tests.

Component	Present study	Lei et al. [36]	Celen and Turker [13]	Ozturk et al. [21]	Li and Zhao [20]
Wastewater type	UASB pretreated poultry manure wastewater	Methane fermentation effluent	Anaerobically pretreated molases-based industrial wastewater	Anaerobically pretreated young landfill leachate	Aging methanogenic landfill leachate
Initial COD (mg/L)	1800	1720	3240	2420	3720
Initial NH_4^+–N (mg/L)	1318	1160	1354	2240	2750
Initial PO_4^{3-}–P (mg/L)	28	84	24	23.4	NS
Initial pH	7.95	7.55	7.90	7.70	8.50
Magnesium source	$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$	$MgCl_2 \cdot 6H_2O$
Phosphate source	KH_2PO_4	$NaHPO_4 \cdot 12H_2O$	H_3PO_4	$NaHPO_4 \cdot 2H_2O$	$NaHPO_4 \cdot 12H_2O$
Reaction pH for MAP	9.0	9.0	9.0	9.0	9.0
Reaction time (min)	TMT = 15; ST = 30	TMT = 15; ST = 30	TMT = 40; ST = NS	TMT = 35; ST = 30	TMT = 15; ST = 15

UASB, up-flow anaerobic sludge blanket; COD, chemical oxygen demand; MAP, magnesium ammonium phosphate hexahydrate; TMT, total mixing time; ST, settling time; NS, not specified.

reduced to about 192 mg/L by MAP precipitation. The remaining NH_4^+–N concentration in the final water may be further removed in a proper biological treatment step, which is also necessary for the removal of the residual COD, as recommended by other investigators [12,41]. In other words, MAP precipitation may be used as a pre-treatment process to minimize ammonia toxicity before biological treatment [12]. Some experimental studies on the biological treatability of MAP precipitation effluents can be found in the literature [33,42].

3.3. Agricultural experiments

The present greenhouse study showed that test plants sprouted for about 3 days. It was observed that the plants in the MAP pots grew much faster than those in the control pots, but all plants grew at different rates depending on their species and growing media (Fig. 6). To explore the ameliorative effect of the collected MAP sludge ($MgCl_2 \cdot 6H_2O + KH_2PO_4$, pH 9.0, Mg^{2+}:NH_4^+–N:PO_4^{3-}–P = 1:1:1) on the plant growth, all plants were harvested on the 11th day after seeding. Prior to harvesting, the plants in the pots were sprayed with deionized water to wash the dust off, as conducted by Li and Zhao [20]. After drying in ambient conditions, the three tallest plant individuals in each pot were selected to compare their fresh heights, as shown in Fig. 7c. Thereafter, the cut plant samples were weighed before and after drying at $60 \pm 5\,^\circ$C to determine their fresh and dry weights, respectively (Fig. 7a and b).

Results of the agricultural experiments revealed that after about two weeks rates of increase in fresh and dry weights of grass (*Lolium perenne*) grown in garden soil were determined to be about 257% and 402% for MAP as compared with control, respectively. Likewise, rates of increase in fresh and dry weights of grass grown in
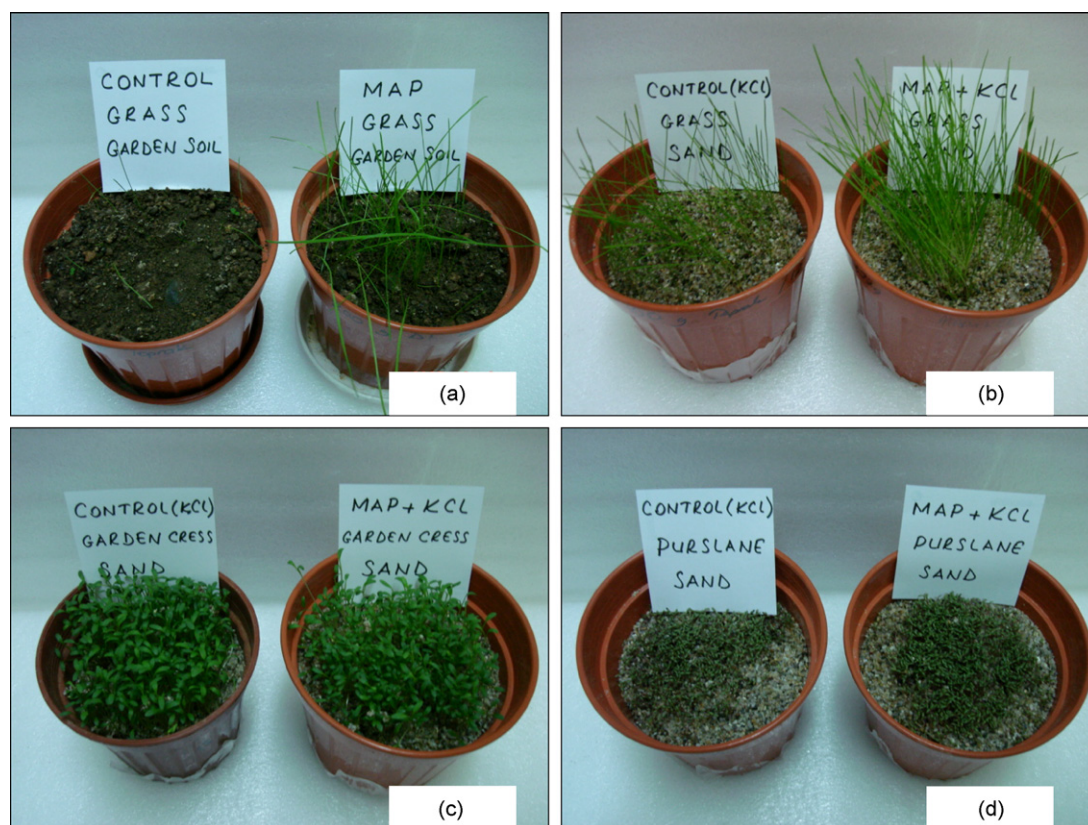
Fig. 6. Photos of three plants at different cultivation conditions after 11 days growth (control pots at left-hand side and MAP pots at right-hand side); (a) grass (*Lolium perenne*) growing in garden soil, (b) grass (*Lolium perenne*) growing in sand, (c) garden cress (*Lepidum sativum*) growing in sand, (d) purslane (*Portulaca oleracea*) growing in sand.
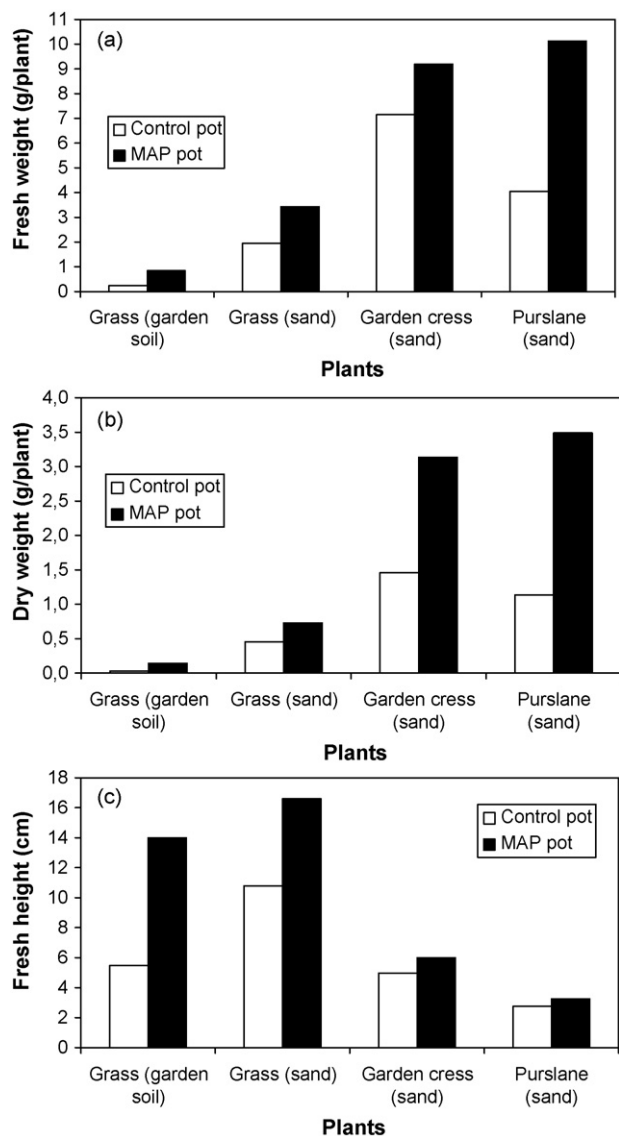
Fig. 7. Average fresh and dry weights and fresh heights of three plants at different cultivation conditions after 11 days growth.

depends on its reaction of different sources of inorganic compounds (N, P and Mg) with binding sorbing sites on the exchange complex to form stable complexes. Therefore, it can be concluded that the investigation of ameliorative effects of various types of MAP sludges produced in different operating conditions (such as magnesium and phosphate sources, types of wastewaters entering the process, etc.) seems to be worthy of investigation by future studies. Furthermore, different plant species amended with MAP sludge should be tested for scientific purposes to develop an agricultural database for farm-based applications.

4. Conclusions

The applicability of MAP precipitation process for the recovery of high strength of NH_4^+–N from UASB pretreated poultry manure wastewater effluent was investigated using three combinations of chemicals: $MgCl_2 \cdot 6H_2O + KH_2PO_4$, $MgSO_4 \cdot 7H_2O + NaHPO_4 \cdot 7H_2O$, and $MgO + 85\%$ H_3PO_4. Preliminary test results showed that $MgCl_2 \cdot 6H_2O + KH_2PO_4$ was selected as the most efficient combination in terms of NH_4^+–N removal, as well as in terms of COD and color reductions compared to other chemical combinations studied. The maximum NH_4^+–N removal was achieved as 85.4% at a pH of 9.0 with the addition of $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 at the stoichiometric ratio (Mg^{2+}:NH_4^+–N:PO_4^{3-}–P = 1:1:1). Besides, maximum removal efficiencies of about 54% for total COD and about 50% for residual color were obtained with the same experimental conditions.

Subsequent batch experiments conducted at pH 9.0 with $MgCl_2 \cdot 6H_2O$ and KH_2PO_4 resulted that when the initial molar concentration of Mg^{2+} was in excess (Mg^{2+}:NH_4^+–N:PO_4^{3-}–P = 1.5:1:1), removal percentages of NH_4^+–N and residual color could be increased up to 89.3% and 56.1%, respectively. However, taking into account both cost of chemicals consumed and possible high levels of residual Mg^{2+} and PO_4^{3-}–P in the final water, a Mg^{2+}:NH_4^+–N:PO_4^{3-}–P molar ratio of 1:1:1 was proposed to be sufficient for NH_4^+–N removal from UASB pretreated poultry manure wastewater by MAP precipitation. Initial molar concentrations of Mg^{2+} or PO_4^{3-}–P did not show a considerable effect on the further removal of residual COD from the anaerobically pretreated effluent. It was found that COD removal efficiencies remained almost unchanged (51–53.3%) within the investigated molar concentration range of 0.5–1.5. Therefore, a proper biological treatment process followed by MAP precipitation is suggested to remove remaining COD and NH_4^+–N in the MAP process effluent.

In the final step, the fertility of the MAP precipitate as struvite was tested on the growth of three test plants including purslane (*Portulaca oleracea*), garden cress (*Lepidum sativum*) and grass (*Lolium perenne*). Results of agricultural experiments clearly indicated that the addition of struvite as a slow fertilizer significantly increased both fresh and dry weights of the test plants depending on their species and growing media in the ranges of 28–257% and 60–402%, respectively. Furthermore, rates of increase in fresh heights of test plants were found in the range of 18–156% for MAP sludge as compared with control. Consequently, findings of this experimental study clearly confirmed the recovering of NH_4^+–N from UASB pretreated poultry manure wastewater by MAP precipitation, and also the application of recovered MAP sludge as a valuable slow release fertilizer for agricultural use.

sand were found as about 76% and 60% for for MAP as compared with control, respectively. Experimental results indicated that after about two weeks rates of increase in fresh and dry weights of garden cress (*Lepidum sativum*) grown in sand were determined to be about 28% and 115% for MAP as compared with control, respectively. For other studied test plant, purslane (*Portulaca oleracea*) grown in sand, rates of increase in fresh and dry weights were obtained as about 150% and 207%, respectively. Findings of the present agricultural experiments clearly showed that the addition of struvite as a slow fertilizer significantly increased both fresh and dry weights of the test plants.

In the present greehouse study, fresh heights of the test plant were also compared to explore the fertilizing potential of struvite on the plant growth. Experimental results showed that after about two weeks rates of increase in fresh heights of grass grown in garden soil, grass grown in garden sand, garden cress grown in sand, and purslane grown in sand were found to be about 156%, 54%, 21% and 18% for MAP as compared with control, respectively. However, it is noted that differences in rates of increase are probably due to the species of studied plants and also types of growing media. Diwani et al. [31] have reported that the ameliorative effect of struvite mainly

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