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Struvite solubility equilibria calculations for the recovery of nutrients from uasb reactor effluent treating municipal wastewater

Cálculos del equilibrio de solubilidad de la estruvita para la recuperación de nutrientes del efluente de un reactor uasb usado en el tratamiento de aguas residuales municipales

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Abstract

This study aimed to evaluate the nutrient recovery potential as struvite from the UASB reactor effluent used to treat municipal wastewater through chemical equilibrium calculations. pH and Mg^{2+}, NH_4^+, and PO_4^{-3} concentrations were obtained from a pilot-scale UASB reactor treating actual municipal wastewater. This reactor operated for six months under environmental temperature and two hydraulic retention times (HRT): 8 and 12 hours and 150-day solids retention time (SRT). The conditional solubility product (Ps) for struvite and the reaction quotients (Qs) in the UASB effluent were calculated using solubility equilibria equations. Results revealed that UASB effluent was undersaturated regarding Mg^{2+}, NH_4^+, and PO_4^{-3} concentrations, and pH was around 7.5. Thus, spontaneous struvite precipitation is unlikely due to the disparity among the molar concentrations of nutrients in UASB effluent. The proposed strategies of adjusting the pH to 8.5 and adding magnesium and phosphorus ions to achieve struvite precipitation would be necessary to fulfill environmental regulations for phosphate and ammonium discharges. Before implementing experiments on a laboratory or full-scale basis, it is imperative to thoroughly evaluate the influence of calcium ions on struvite precipitation. This fact is particularly crucial due to the elevated alkalinity concentrations in the UASB reactor, which have the potential to impede struvite precipitation.

Keywords: Nutrient recovery, Solubility Product, Struvite, UASB effluent.

Resumen

El objetivo de este trabajo fue evaluar el potencial de recuperación de nutrientes, en forma de estruvita, del efluente de un reactor UASB utilizado para tratar aguas residuales municipales a través de cálculos de equilibrio químico. El pH y las concentraciones de Mg^{2+}, NH_4^+ y PO_4^{-3} se obtuvieron de un reactor UASB a escala piloto que trató aguas residuales municipales. El producto de solubilidad condicional (Ps) para la estruvita y los coeficientes de reacción (Qs) se calcularon utilizando ecuaciones de equilibrio de solubilidad. Los resultados mostraron que el efluente del reactor estaba insaturado con respecto a las concentraciones de Mg^{2+}, NH_4^+ y PO_4^{-3}, y el pH estuvo alrededor de 7.5, por lo que la precipitación espontánea de estruvita no ocurrió. Así, de acuerdo con los cálculos de equilibrio, sería necesario ajustar el pH a 8.5 y añadir iones de magnesio y fosfato para conseguir la precipitación de estruvita y cumplir de las regulaciones ambientales para las descargas de fosfato y amonio. Antes de una aplicación real, es crucial analizar el impacto de los iones de calcio, ya que el reactor UASB tenía altas concentraciones de alcalinidad que podrían dificultar el proceso.

Palabras clave: Efluente reactor UASB, Estruvita, Producto de solubilidad, Recuperación de nutrientes.

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1 Introduction

The increasing demand for materials to produce commodities and other valuable products, driven by population growth and higher living standards, has resulted in the over-exploitation of natural resources worldwide. Even agriculture follows this trend, as it relies on a heavy extraction of phosphorus from non-renewable geological deposits to produce increasing amounts of fertilizer (Alewell *et al*., 2020), resulting in the shortage of natural non-renewable sources and the massive transport of nutrients to aquatic ecosystems, an environmental global problem that exceeds the safe limits for sustainable human development (Carpenter and Bennett, 2011).

Human activities commonly discharge nutrients such as nitrogen and phosphorus into wastewater. When treated wastewater is employed for irrigation, these nutrients can enhance cropland growth. However, this practice can lead to them reaching nearby water bodies and causing adverse effects such as eutrophication, toxicity in the roots, and harm to aquatic life (Ali and Schneider, 2008).

Indeed, eutrophication is a global environmental issue, significantly deteriorating the quality of natural waters and rendering them unsuitable for human activities. Its impact on the development of diverse species of flora and fauna in aquatic ecosystems is profound (Catone *et al*., 2021). Moreover, it is one of the leading environmental impacts of wastewater treatment plants (WWTP), associated with the emissions of nutrients to water bodies. The severity of eutrophication in effluents from anaerobic systems cannot be understated due to their lower nutrient removal than aerobic treatments (Mainardis *et al*., 2020). Hence, prioritizing their recovery from these effluents is crucial.

The circular economy proposes sustainable production methods based on efficient resource management by designing processes to leverage waste in the production system (Catone *et al*., 2021; Ubando *et al*., 2020). In WWTP, a novel reconceptualization is proposed, seeing wastewater as a source of several valuable products, such as energy and commodities, instead of a cause of pollution.

Multiple biological and physicochemical nutrient removal or recovery processes have been developed in recent decades. Nonetheless, struvite precipitation stands out as a sustainable and efficient alternative for nutrient recovery, yielding a relatively pure precipitate from treated wastewater (Siciliano *et al*., 2020).

Struvite precipitation as a method for nutrient recovery, especially phosphorus, has gained interest in recent years due to the depletion of phosphorous natural sources. The peak of phosphatic rock extraction is expected to reach in the following decades, leading to a significant decrease in phosphorous sources in the coming century (Desmidt *et al*., 2015).

Struvite comprises magnesium, phosphate, and ammonium in a 1:1:1 molar ratio (NH_4^+:Mg^{2+}:PO_4^{-3}), so it can be used as a fertilizer. At the same time, its production reduces the nutrient concentrations in WWTP effluents, promoting savings in the resources used (Moragaspitiya *et al*., 2019). This way, adding $MgCl_2$ and a slight pH increase in wastewater constituted a method for recovering phosphorous and nitrogen as struvite from treated wastewater (Monballiu *et al*., 2018), a salt with a low k_{sp} that tends to precipitate in the reactor. Its precipitation is controlled by temperature, molar ratios, pH, and competitive ions (Siciliano *et al*., 2020).

In recent decades, studies on recovering ammonium and phosphates have mainly employed landfill leachates (Di Iaconi *et al*., 2010; Kim *et al*., 2007; Li and Zhao, 2003; Ramaswami *et al*., 2016; Siciliano, 2016). These researchers used a sequencing batch reactor (SBR) reactor for struvite precipitation and maintained pH between 8.5 and 9 by adjusting it with NaOH. They also reported stoichiometric ratios close to 1:1:1, with Di Iaconi *et al*. (2010) finding a stoichiometric ratio of Mg^{2+}: NH^{+4}: PO_3^{-3} = 2:1:1. The removal efficiencies for phosphate ranged between 86 and 100%, while for ammonium, they were between 72 and 95%.

Several studies have also utilized synthetic wastewater; for example, Stratful *et al*. (2004) and Pastor *et al*. (2008) used SBR to obtain struvite while Adnan *et al*. (2015), Guadie *et al*. (2014), Jordaan *et al*. (2013), Rahaman *et al*. (2008), and Shih *et al*. (2017) used fluidized bed reactors. In these works, $MgCl_2.6H_2O$ was added for phosphate removal, resulting in higher efficiencies than 80%. The pH was adjusted between 7.9 and 9.5.

However, few studies employed the effluent from anaerobic systems for struvite precipitation even though these effluents have great potential for struvite recovery since, as a result of anaerobic metabolism, ammonium and phosphates concentrations are higher in the final effluent than in wastewater (Cárdenas-Medina *et al*., 2020; Cervantes-Zepeda et al., 2011).

Studies with anaerobic treatments were carried out with potato and dairy effluents (Moerman *et al*., 2009), fermented sludge from municipal WWTP (Pastor *et al*., 2010), supernatants (Huang *et al*., 2006; Xavier *et al*., 2014), digested manure (Brown *et al*., 2018), digested centrates (Bhuiyan *et al*., 2008; Iqbal *et al*., 2008), and swine slurries (Taddeo & Lepistö, 2015).

For its part, studies that consider the struvite precipitation in the effluent of up-flow anaerobic sludge blanket (UASB) reactors are scarce. These reactors, used globally for municipal wastewater treatment due to their high loading capacity and low sludge production, can produce energy in the form of methane. However, they are known to have a limited effect on nutrients (nitrogen and phosphorus) and micro-pollutants (Mainardis *et al.*, 2020), potentially significantly increasing the eutrophication of receiving water bodies.

In this regard, the obtention of struvite represents a sustainable way to recover the nutrients contained in municipal wastewater, producing a biofertilizer with the potential to reduce the over-exploitation of non-renewable phosphorous resources as well as the eutrophication potential of UASB effluent, highlighting the attributes reported for these reactors. Thus, the current study aimed to evaluate the potential of nutrient recovery as struvite from the UASB reactor effluent used to treat municipal wastewater through chemical equilibrium calculations.

2 Methodology

2.1 Experimental setup

The data on pH and nutrient concentrations were obtained from a pilot-scale UASB reactor (700 L volume, PVC) treating municipal wastewater from the National University of Mexico and the surrounding neighborhoods. This reactor was inoculated with sludge from a brewery treatment plant and had an acclimation period of two months. Wastewater was pumped using a peristaltic pump (Masterflex 77410-10, 0.35 HP, Cole-Parmer, USA). The UASB reactor operated for six months under room temperature and two hydraulic retention times (HRT): 8 and 12 hours and 150-day solids retention time (SRT).

2.2 Analytical methods

Effluent samples from the UASB reactor were collected three times per week. pH, ammonium, and phosphate analysis were carried out according to the Standard Methods (American Public Health Association, 2018). Magnesium was analyzed in an ion chromatograph equipped with a conductivity cell (Model ICS-1000, DIONEX, USA) and a 100 μL injection loop.

The isocratic separation of Mg^{2+} cations was carried out on a medium-capacity cation exchange column with carboxylate functional groups, which had a 250-mm length and a 4-mm internal diameter (IonPac CG12A, DIONEX, USA). The eluent employed was methanesulfonic acid (MSA) at a flow rate of 0.9 mL min^{-1}.

2.3 Struvite precipitation calculations

The conditional solubility product (Ps) of struvite was calculated with Equation 2.1, proposed by Stumm and Morgan (1995):

$$Ps = \frac{Kps\ (MgNH_4PO_4)}{\propto_{Mg}\propto_{NH_4}\propto_{PO_4}} \tag{2.1}$$

Where:

$Kps_{(MgNH4PO4)}$ = Struvite solubility product (pKps = 12.60)

Mg, NH_4, and PO_4 = Fractions of magnesium, ammonium, and phosphate, respectively, available for struvite precipitation.

These fractions depend on pH, as Equations 2.2 to 2.4 indicate:

$$\propto Mg = \left(1 + \frac{*K_1}{[H^+]}\right)^{-1} \tag{2.2}$$

$$\propto NH_4 = \left(1 + \frac{K_{1N}}{[H^+]}\right)^{-1} \tag{2.3}$$

$$\propto PO_4 = \left(1 + \frac{[H^+]}{K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]^3}{K_1K_2K_3}\right)^{-1} \tag{2.4}$$

Where:

pK_1 = 11.4, pK_{1N} = 9.24, pK_1 = 2.1, pK_2 = 7.2, and pK_3 = 12.3.

The reaction quotients (Qs) in the UASB effluent were estimated with equation 2.5:

$$Q_{s_{UASB}} = C_{T\ Mg} * C_{T\ NH_4} * C_{T\ PO_4} \tag{2.5}$$

Where:

$C_{T\ Mg}$, $C_{T\ NH4}$, and $C_{T\ PO4}$ are the molar concentrations of magnesium, ammonium, and phosphate ions in the UASB effluent.

The values of Qs and Ps were compared to determine if struvite precipitation occurred. Hence, if Qs < Ps, struvite did not precipitate; if Qs = Ps, struvite was in equilibrium. If Qs was slightly greater than Ps, partial precipitation takes place. If Qs was 0.6 units greater than Ps, struvite precipitation was optimal (Stumm and Morgan, 1995).

3 Results and discussion

Figure 3.1 depicts the struvite conditional solubility product (Ps, Eq. 2.1) and the reaction quotients (Qs, Eq. 2.7) of UASB effluent as pH function.

In Figure 3.1, the solid line shows the conditional solubility product of struvite as a pH function, indicating that as pH increases, Ps diminishes until an inflection point in pH 10.25. This line also represents the equilibrium in struvite precipitation, where Qs and Ps are equal. If Qs is greater than Ps, it will be a

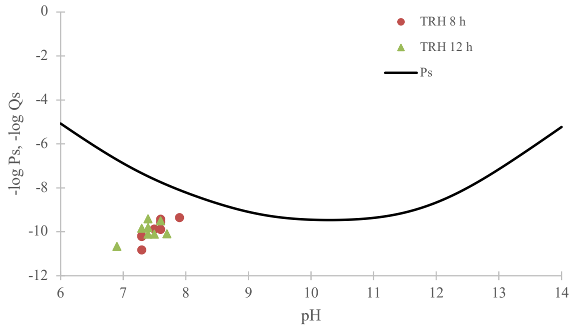

Figure 3.1. Struvite conditional solubility product (Ps) and reaction quotients (Qs) of UASB effluent as pH function.

supersaturation scenario, indicating that the struvite precipitated; otherwise, if Qs is less than Ps, it will be an undersaturation scenario, and precipitation will not occur.

The circles and triangles in Figure 3.1 correspond to the Qs obtained for 8 and 12h HRT, respectively. These results show that UASB effluent was undersaturated regarding ammonium, phosphate, and magnesium ions, as Ps < Qs for all samples. Thus, spontaneous struvite precipitation is unlikely to occur in this UASB effluent.

Struvite precipitation implies the simultaneous removal of ammonium, phosphate, and magnesium ions from supersaturated solutions when these ions are in a stoichiometric ratio of 1:1:1. Therefore, the molar concentration of these ions is a crucial factor in the struvite precipitation, which occurs according to the following reaction (Le Corre *et al.*, 2009):

$$Mg^{2+} + NH^{+4} + PO_4{}^{-3} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow \qquad (3.1)$$

However, struvite precipitation diminishes pH, and $HPO_4{}^{2-}$ will be in solution rather than $PO_4{}^{-3}$ ions:

$$Mg^{2+} + NH_4{}^{+} + HPO_4{}^{2-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \downarrow + H^{+} \qquad (3.2)$$

Besides the stoichiometric ratio of ions that form struvite (Table 3.1), pH is another critical factor for its precipitation since the presence of ammonium and phosphate ions is highly dependent on this variable. Degryse *et al.* (2017) and Moragaspitiya *et al.* (2019) established a pH range for struvite precipitation between 8.5 and 9. If pH increases above 9, struvite precipitation can be prevented because the ammonium/ammonia equilibrium will shift to produce ammonia gas, while phosphate ions in the solution will notably rise (Siciliano *et al.*, 2020).

However, Shin and Lee (1998) reported pK_{sp} values for struvite ranging from 9.94 to 13.26, and Siciliano *et al.* (2013) found an optimal pH of 10 for struvite precipitation from landfill leachates. These differences can be explained by wastewater composition influencing the ionic strength and activity, which, in turn, affected the precipitation potential of struvite. However, it can be concluded that struvite precipitation mainly occurs at moderate basic pH.

Table 3.1. Nutrient concentrations in the UASB effluent.

HRT (h)	Sample	pH	Nutrient concentration						Stoichiometric ratio
			mg/L			M			
			NH_4^+	PO_4^{-3}	Mg^{2+}	NH_4^+	PO_4^{-3}	Mg^{2+}	NH_4^+:PO_4^{-3}:Mg^{2+}
8	1	7.6	53.2	9.9	14.2	0.0029	0.00010	0.00041	2.9:1.0:4.1
	2	7.3	18.2	5.8	12.7	0.0010	0.00006 0.00006	0.00024	1.7:1.0:4.0
	3	7.3	40.6	7.9	11.6	0.0023	0.00008	0.00032	2.9:1.0:4.0
	4	7.5	57.4	9.7	18.3	0.0032	0.00010	0.00040	3.2:1.0:4.0
	5	7.3	30.8	9.5	12.5	0.0017	0.00010	0.00039	1.7:1.0:3.9
	6	7.6	84.0	13.5	18.3	0.0047	0.00014	0.00056	3.4:1.0:4.0
	7	7.6	86.8	11.5	16.1	0.0048	0.00012	0.00047	4.0:1.0:4.0
	8	7.9	86.8	14.6	14.8	0.0048	0.00015	0.00060	3.2:1.0:4.0
Average		**7.51**	**57.2**	**10.3**	**14.8**	**0.0032**	**0.00011**	**0.00042**	**--**
12	1	7.7	22.4	12.2	16.2	0.0012	0.00012	0.00050	1.0:1.0:4.2
	2	7.4	86.8	13.6	17.1	0.0048	0.00014	0.00055	3.4:1.0:3.9
	3	7.3	58.8	10.0	6.9	0.0033	0.00011	0.00041	3.0:1.0:3.7
	4	7.6	81.2	12.7	13.8	0.0045	0.00013	0.00052	3.5:1.0:4.0
	5	6.9	19.6	6.7	12.8	0.0011	0.00007	0.00028	1.6:1.0:4.0
	6	7.4	46.2	8.3	18	0.0026	0.00008	0.00034	3.2:1.0:4.2
	7	7.4	61.6	10.3	17.9	0.0034	0.00011	0.00042	3.1:1.0:3.8
	8	7.5	46.2	8.3	16.2	0.0026	0.00008	0.00034	3.2:1.0:4.2
Average		**7.4**	**52.8**	**10.2**	**14.9**	**0.0029**	**0.00011**	**0.00042**	**--**

Regarding the UASB effluent in the present study, all of the above factors still need to be met. From the results of UASB effluent characterization presented in Table 3.1, the stoichiometric ratio (Mg^{2+}: NH_4^+: PO_4^{-3}) was characterized by a higher molar ratio of ammonium and magnesium than phosphates, while pH was between 6.9 and 7.9; that is, the conditions in UASB effluent were not adequate to promote struvite precipitation.

The significant difference in the molar concentrations of magnesium, ammonium, and phosphate in UASB effluent was a consequence that effluents derived from anaerobic processes have higher ammonium concentrations in comparison to phosphate due to ammonium ions generated in the anaerobic digestion by protein deamination, increasing its concentration in the UASB effluent. This fact makes struvite precipitation more expensive due to the reagent addition to reach the stoichiometric ratio Mg^{2+}: NH_4^+: PO_4^{-3} = 1:1:1 (Siciliano *et al*., 2020).

Altinbas¸ *et al.* (2002) reported struvite precipitation in a UASB effluent from municipal wastewater, achieving a decrease of 10 mg/L in ammonium concentration with an influent concentration of 35 mg/L without adding any reagent. Although this ammonium concentration was lower than those in the present study (Table 3.1), these authors reported a stoichiometric ratio of Mg^{2+}: NH_4^+: PO_4^{-3} = 1:1:1 at a pH of 9.2. These results confirm the importance of the stoichiometric ratio of magnesium, phosphorus, and ammonium ions, as well as the pH in the effluent of the UASB reactor, to achieve struvite precipitation.

As previously mentioned, struvite precipitation removes phosphorus and ammonium from wastewater. However, this process can be more expensive as it requires adding magnesium and phosphorus reagents to reach the stoichiometric molar ratio of 1:1:1 if ammonium ions are in excess, as occurs in anaerobic effluents. Alternatively, Siciliano *et al.* (2020) suggested that struvite precipitation can be used exclusively for phosphorus recovery, making it a more sustainable process. In this way, only magnesium addition is required, and the process mainly depends on the Mg^{2+}: PO_4^{-3} molar ratio.

Magnesium oxide or hydroxide can increase pH and provide the necessary Mg^{2+} ions for struvite nucleation. However, their low solubility requires them to be dissolved in acids, complicating the precipitation process and making it impossible to control pH adjustment and Mg^{2+} addition separately. To address this issue, NaOH is often used as an alkaline reagent for struvite precipitation. It can quickly and effectively adjust pH, providing the pH necessary for successful struvite precipitation (Siciliano *et al*., 2020).

Thus, the amount of sodium hydroxide (NaOH) that would need to be added to increase the pH of the UASB reactor effluent to 8.5 was calculated. Then, the molar concentration of magnesium ions to achieve precipitation was determined, considering that Stumm and Morgan (1995) stated that optimal struvite precipitation occurs when Qs is 0.6 units higher than Ps. The molar concentration of magnesium ions required for precipitation was calculated according to Equation 3.3.

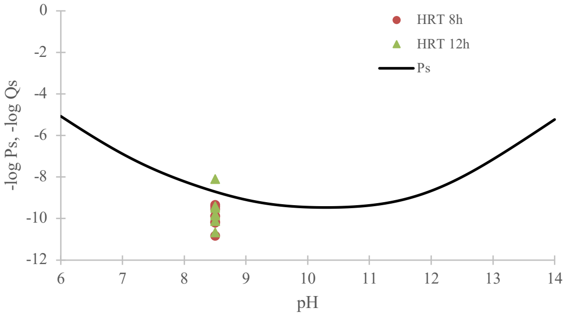

Figure 3.2. Struvite conditional solubility product (Ps) and reaction quotients (Qs) of UASB effluent as pH function after pH adjustment to 8.5.

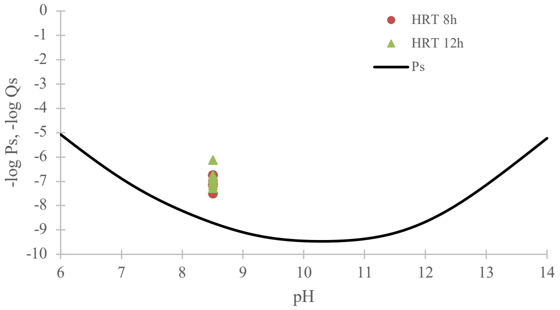

Figure 3.3. Struvite conditional solubility product (Ps) and reaction quotients (Qs) of UASB effluent as pH function after pH adjustment to 8.5 and Magnesium ions addition.

$$\left[Mg^{2+}\right] = \frac{Ps_{pH=8.5} + 0.6}{[NH_4^+]\left[PO_4^{3-}\right]} \tag{3.3}$$

Where:

$[Mg^{2+}]$, $[NH_4^+]$, and $[PO_4^{3-}]$ are the molar concentrations of magnesium, ammonium, and phosphate ions, respectively.

$Ps_{pH=8.5}$ = Struvite conditional solubility product at pH = 8.5

The molar concentration of magnesium ions added was calculated as the difference between results from Equation 3.3 and magnesium ions in UASB effluent (Table 3.1). Figures 3.2 and 3.3 depict the struvite Ps and Qs of UASB effluent as pH function after pH adjustment to 8.5 (Figure 3.2) and magnesium addition (Figure 3.3).

Figure 3.2 shows that after adjusting UASB effluent pH to 8.5 with NaOH, Qs did not substantially increase, and struvite precipitation was not likely to occur. Hence, adding magnesium ions to UASB effluent would be necessary to achieve struvite precipitation.

After pH adjustment and adding magnesium ions (Figure 3.3), Qs for all samples were greater than Ps at pH 8.5, so struvite precipitation could occur in UASB effluent. Therefore, to achieve struvite precipitation in the UASB effluent, it would be necessary first to adjust the pH to 8.5 with NaOH and then to add magnesium ions, such as magnesium chloride.

Table 3.2 shows the NaOH and Magnesium ion molar theoretical concentrations required for struvite precipitation in UASB effluent.

Lime, as $Ca(OH)_2$ or CaO, is commonly used to increase the pH level in wastewater. However, it is not advisable to use lime in UASB effluent because calcium ions can hinder struvite precipitation. This occurs because calcium ions compete with ammonium and magnesium ions to form apatite and hydroxyapatite instead of struvite when the pH is above 10. As a result, phosphate ions are not available for struvite formation (Capdevielle *et al*., 2014; Ryu *et al*., 2014).

Magnesium salts like $MgSO_4$ and $MgCl_2$ are commonly used as sources of magnesium in kinetic studies and full-scale applications. These salts are easy to manage and highly soluble, making it easy to recover a high-purity precipitate. However, their use also increases the sulfate and chloride concentration in the final effluent, which can be problematic (Siciliano *et al*., 2020).

The theoretical percentage of phosphorus and nitrogen removal after struvite precipitation in the UASB effluent was calculated considering the required magnesium concentrations (Table 3.2). The limiting reactant was phosphate, which had the lowest molar proportion relative to the other ions. Then, the theoretical amount of ammonium that did not react and its removal percentage were calculated. Results are presented in Table 3.3.

Results in Table 3.3 show that as the limiting reactant was phosphate, it would be removed entirely from the UASB effluent and recovered through struvite precipitation. This result concords with (Huang *et al*., 2006), who analyzed the struvite crystallization process from anaerobic digester supernatants. These authors employed $MgCl_2.6H_2O$ to reach a molar ratio Mg^{2+}:PO_4^{-3}=3.3:1, and pH was adjusted to 7.6 – 8.4, finding phosphates removals higher than 80%.

Diverse reports (Iqbal *et al*., 2008; Moerman *et al*., 2009; Pastor *et al*., 2010; Xavier *et al*., 2014) researched phosphate recovery from anaerobic effluents in various wastewaters, including centrates, potato, and dairy industries, and supernatants of anaerobic sludge stabilization. By adjusting the pH to above 8.0 and introducing magnesium ions, these authors achieved phosphate removal rates ranging from 40% to 95%. These findings also emphasize the role of the Ca^{2+}/PO_4^{3-} molar ratio and the molar concentration of Ca^{2+}, highlighting how calcium ions can affect struvite precipitation.

The calculations in this study suggest that achieving high phosphate removals and recovering struvite from a UASB reactor treating domestic wastewater treatment is possible. However, before actual application, it is necessary to analyze the potential impact of calcium ions on struvite precipitation. This is particularly relevant in anaerobic reactor effluents with high alkalinity concentrations since carbonate and bicarbonate ions can react with ammonium and magnesium to form stable aqueous phases of $MgCO_3$, $Mg(HCO_3)_2$, and NH_4HCO_3, preventing struvite precipitation (Huang *et al*., 2017).

Table 3.2. NaOH and Magnesium concentrations required for struvite precipitation.

HRT (h)	Sample	Initial Qs	NaOH pH=8.5 (M)	Mg^{2+} for precipitation (M)	Mg^{2+} added (M)
8	1	1.25E-10	1.59E-06	0.0255	0.0250
	2	1.47E-11	1.70E-06	0.1270	0.1268
	3	6.10E-11	1.70E-06	0.0418	0.0415
	4	1.30E-10	1.64E-06	0.0241	0.0237
	5	6.69E-11	1.70E-06	0.0458	0.0454
	6	3.68E-10	1.59E-06	0.0118	0.0113
	7	2.76E-10	1.59E-06	0.0134	0.0130
	8	4.45E-10	1.36E-06	0.0106	0.0100
12	1	8.02E-11	1.53E-06	0.0491	0.0486
	2	3.86E-10	1.67E-06	0.0114	0.0108
	3	1.41E-10	1.70E-06	0.0228	0.0224
	4	3.15E-10	1.59E-06	0.0130	0.0125
	5	2.12E-11	1.77E-06	0.1021	0.1018
	6	7.66E-11	1.67E-06	0.0350	0.0346
	7	1.57E-10	1.67E-06	0.0211	0.0207
	8	7.66E-11	1.64E-06	0.0350	0.0346

Table 3.3. Theoretical ammonium concentration and removal after struvite precipitation.

HRT (h)	Sample	NH_4^+ (M)	PO_4^{3-} (M)	Mg^{2+} (M)	Limiting reactant	NH_4^+ Remnant (M)	NH_4^+ Remnant (mg/L)	NH_4^+ removal (%)
8	1	0.0029	0.00010	0.0255	PO_4^{3-}	0.0029	51.32	3.53
	2	0.0010	0.00006	0.1270	PO_4^{3-}	0.0010	17.10	6.04
	3	0.0023	0.00008	0.0418	PO_4^{3-}	0.0022	39.10	3.69
	4	0.0032	0.00010	0.0241	PO_4^{3-}	0.0031	55.56	3.20
	5	0.0017	0.00010	0.0458	PO_4^{3-}	0.0016	29.00	5.85
	6	0.0047	0.00014	0.0118	PO_4^{3-}	0.0045	81.44	3.05
	7	0.0048	0.00012	0.0134	PO_4^{3-}	0.0047	84.62	2.51
	8	0.0048	0.00015	0.0106	PO_4^{3-}	0.0047	84.03	3.19
						Average	**55.27**	**3.88**
12	1	0.0012	0.00012	0.0491	PO_4^{3-}	0.0011	20.09	10.32
	2	0.0048	0.00014	0.0114	PO_4^{3-}	0.0047	84.22	2.97
	3	0.0033	0.00011	0.0228	PO_4^{3-}	0.0032	56.90	3.22
	4	0.0045	0.00013	0.0130	PO_4^{3-}	0.0044	78.79	2.96
	5	0.0011	0.00007	0.1021	PO_4^{3-}	0.0010	18.33	6.48
	6	0.0026	0.00008	0.0350	PO_4^{3-}	0.0025	44.63	3.41
	7	0.0034	0.00011	0.0211	PO_4^{3-}	0.0033	59.65	3.17
	8	0.0026	0.00008	0.0350	PO_4^{3-}	0.0025	44.63	3.41
						Average	**50.90**	**4.49**

Table 3.4. Theoretical ammonium and phosphate concentrations and removals after struvite precipitation with $Mg^{2+}:PO_4^{3-}$ = 1:1.

HRT (h)	Sample	NH_4^+ (M)	PO_4^{-3} (M)	Mg^{2+} (M)	Limiting reactant	NH_4^+ remnant (M)	NH_4^+ remnant (mg/L)	NH_4^+ removal (%)	PO_4^{3-} remnant (M)	PO_4^{-3} remnant (mg/L)	PO_4^{-3} removal (%)
8	1	0.0029	0.0016	0.0016	$\mathbf{PO_4^{3-}}$	0.0013	23.9	55.1	0.0000	0.0	100.0
	2	0.0010	0.0028	0.0028	$\mathbf{NH_4^+}$	0.0000	0.0	100.0	0.0010	95.0	50.0
	3	0.0023	0.0019	0.0019	$\mathbf{PO_4^{3-}}$	0.0004	7.0	82.7	0.0000	0.0	100.0
	4	0.0032	0.0016	0.0016	$\mathbf{PO_4^{3-}}$	0.0016	29.2	49.2	0.0000	0	100.0
	5	0.0017	0.0021	0.0021	$\mathbf{NH_4^+}$	0.0000	0.0	100.0	0.0003	28.5	85.0
	6	0.0047	0.0013	0.0013	$\mathbf{PO_4^{3-}}$	0.0034	60.7	27.8	0.0000	0.0	100.0
	7	0.0048	0.0013	0.0013	$\mathbf{PO_4^{3-}}$	0.0035	63.8	26.4	0.0000	0.0	100.0
	8	0.0048	0.0013	0.0013	$\mathbf{PO_4^{3-}}$	0.0035	63.8	26.4	0.0000	0.0	100.0
						Average	**31.1**	**58.5**	**0.0002**	**15.4**	**91.9**
12	1	0.0012	0.0025	0.0025	$\mathbf{NH_4^+}$	0.0000	0.0	100.0	0.0008	76.0	60.0
	2	0.0048	0.0013	0.0013	$\mathbf{PO_4^{3-}}$	0.0035	63.8	26.4	0.0000	0.0	100.0
	3	0.0033	0.0015	0.0015	$\mathbf{PO_4^{3-}}$	0.0017	30.9	47.4	0.0000	0.0	100.0
	4	0.0045	0.0013	0.0013	$\mathbf{PO_4^{3-}}$	0.0032	57.5	29.2	0.0000	0.0	100.0
	5	0.0011	0.0027	0.0027	$\mathbf{NH_4^+}$	0.0000	0.0	100.0	0.0009	85.0	55.0
	6	0.0026	0.0017	0.0017	$\mathbf{PO_4^{3-}}$	0.0008	14.7	68.1	0.0000	0.0	100.0
	7	0.0034	0.0015	0.0015	$\mathbf{PO_4^{3-}}$	0.0019	34.4	44.2	0.0000	0.0	100.0
	8	0.0026	0.0017	0.0017	$\mathbf{PO_4^{3-}}$	0.0008	14.7	68.1	0.0000	0.0	100.0
						Average	**27.0**	**60.4**	**0.0002**	**20.1**	**89.4**

In turn, calculated ammonium removal percentages were only 3.88% and 4.49% for 8 and 12h HRT, respectively. These removal percentages were much lower than those reported by (Altinbaş, *et al.*, 2002; Yetilmezsoy and Sapci-Zengin, 2009). With molar ratios of 1:1:1 and pH 9.0, they obtained 68% and 84% ammonium removal percentages, respectively. This result highlights the importance of correctly adjusting the pH and the $Mg^{2+}:NH_4^+:PO_4^{3-}$ stoichiometric ratio.

To comply with discharge regulations for ammonium established in NOM-001-2021-SEMARNAT (28 – 35 mg/L), simply adjusting the pH with $Mg(OH)_2$ and adding magnesium ions as $MgCl_2.6H_2O$ in UASB effluent could not be enough. Therefore, changing the $Mg^{2+}:PO_4^{3-}$ molar ratio to 1:1 in UASB effluent may also be necessary. Calculations are presented in Table 3.4.

Magnesium and phosphate molar concentrations in Table 3.4 were calculated considering Qs = 7.84E-9, greater than Ps at pH 8.5, to guarantee struvite precipitation. These results indicate that adjusting pH at 8.5 and $Mg^{2+}:PO_4^{3-}$ molar ratio to 1:1 in UASB effluent could increase ammonium removal to 83.5 % and 91.5% for 8 and 12h HRT, respectively. This would also achieve high phosphate removals if it remains the limiting reactant. However, if ammonium were the limiting reactant, phosphate could be as high as 95 mg/L. Therefore, it is crucial to dose the reagents precisely to avoid excess nutrient concentrations in the final effluent.

Altinbas *et al.* (2002) reported 71% ammonium removal in raw wastewater after struvite precipitation with a stoichiometric ratio of Mg^{2+}: NH_4^+: PO_4^{3-} = 1:1:1 at a pH of 9.2. Xavier *et al.* (2014) found that the best cost-effective alternative for struvite precipitation from the supernatant of sludge anaerobic digestion was $MgCl_2$ addition in a Mg^{2+}:PO_4^{3-} molar ratio of 1:1 at pH 10, obtaining removals of 90.6 and 29.0% for phosphate and ammonium, respectively. These studies suggest that adjusting pH at 8.5 and Mg^{2+}:PO_4^{3-} molar ratio to 1:1 in UASB effluent could be a feasible strategy to remove ammonium and phosphates by producing struvite.

Moreover, the recovered struvite must not contain hazardous elements that can cause harmful effects on the environment or public health. In this sense, the NOM-004-SEMARNAT-2002 (SEMARNAT, 2002) establishes the following maximum permissible limits of heavy metals for sludge and biosolids use and final disposal: Cadmium (39 mg/kg dry matter), Chrome (1200 mg/kg dry matter), Mercurium (17 mg/kg dry matter), Niquel (420 mg/kg dry matter), Lead (300 mg/kg dry matter), Arsenic (41 mg/kg dry matter), Cupper (1500 mg/kg dry matter), and Zinc (2800 mg/kg dry matter). Therefore, it is essential to recover a struvite precipitate with limited amounts of hazardous elements.

In this regard, struvite derived from municipal WWTP that used anaerobic digesters for sludge management (Munch & Barr, 2001; Uysal *et al.*, 2010) and semiconductor WW (Ryu *et al.*, 2012) presented mercury, nickel, zinc, arsenic, lead, and chrome concentrations below the regulatory limits.

Conclusion

The struvite solubility equilibria calculations presented in this research showed that the UASB reactor treating municipal wastewater was under-saturated regarding struvite, and precipitation is unlikely to occur spontaneously. The equilibrium calculations also indicated that it is necessary to adjust the pH to 8.5 and add magnesium and phosphate ions to achieve struvite precipitation and, at the same time, fulfill environmental regulations for phosphate and ammonium discharges due to the existing disparity in the effluent of the UASB reactor of these nutrients.

Struvite precipitation in UASB effluent can remove high amounts of phosphates and ammonium, diminishing eutrophication in water-receiving bodies. However, before lab or real-scale application, it is essential to analyze the potential impact of calcium ions on struvite precipitation, as the UASB reactor had high alkalinity concentrations.

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