

Article

Simulations and Laboratory Tests for Assessing Phosphorus Recovery Efficiency from Sewage Sludge

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Abstract: Phosphorus is a potential environmental pollutant, which could lead to the eutrophication of water bodies. For this reason, wastewater treatment plants worldwide are often designed and operated to eliminate phosphorous from effluents, at substantial cost. At the same time, phosphorus is an essential nutrient for agriculture and, consequently, human life. Data seem to suggest that the world will run out of phosphorus by around 2300, in the best case scenario, although even shorter estimates exist. This situation evokes the need for more efficient phosphorus recovery technologies, in order to meet current water quality requirements and—at the same time—critical future phosphorous needs. Chemical precipitation is the main process for achieving a phosphorus-containing mineral suitable for reuse as a fertilizer, where Struvite is an example of such a product. In this study chemical equilibrium of struvite precipitation was simulated using US Geological Survey (USGS) PHREEQC model, and results were compared to laboratory precipitation tests to evaluate struvite recovery efficiency under various conditions. pH had the most significant effect on the results and P recovery of >90% was achieved at pH = 9.5. Simulations indicated that struvite precipitation is affected by the presence of Amorphous Calcium Phosphate (ACP) and calcite in the final product of the process. The model showed great potential for predicting equilibrium conditions, and could be very helpful for future optimization of the process.

Keywords: mineral phosphorous; scarcity; wastewater; precipitation modeling; struvite

1. Introduction

Potential environmental effects of phosphorous in surface waters are well known: the most important is eutrophication, that is, the excessive growth of aquatic plants, algae and photosynthetic bacteria such as cyanobacteria (often incorrectly called blue-green algae), most often controlled by the high concentration of this nutrient in a water body. In addition to the aesthetic damage, eutrophying organisms may produce toxic or taste-and-odor compounds into sources of drinking water, requiring additional treatment [1]. Dead photosynthetic biomass will settle, leading to accumulation of organic matter and phosphorus storage into sediments, which could contribute to future sediment oxygen demand (SOD), or cycle between water column and sediments in a phenomenon known as internal loading, which could maintain excessive phosphorus levels in a water body even after external pollution sources have been eliminated [2–4]. Large daily swings in dissolved oxygen (DO) concentrations and pH (due to complementary swings in dissolved carbon dioxide concentrations) could also be due to excessive amounts of floating photosynthetic biomass. Lakes are the water bodies most frequently affected by this phenomenon [5–8]. In aquatic environments, based on relatively low concentrations of Al, Fe and Ca ions, P is much more available than in soils, where the soluble fraction represents a very small part of total P (TP), but is the only form of phosphorus (free orthophosphate

ions PO_4^{3-}) that plants are able to assimilate for growth. Since this amount is quantitatively negligible, TP in soils consists almost solely of the adsorbed and organic fractions of the mineral. Where mandated, removal of N & P from wastewater discharges can occur both with physicochemical and biological processes [9,10]. This process is costly, and perhaps not completely necessary in view of the new paradigms on wastewater management, stressing resources recovery principles [11–13]. In this study, chemical equilibrium modeling of struvite precipitation was conducted to evaluate its behavior in the presence of constituent ions, the presence of Ca^{2+} as a competitive ion and variable pH and compared to laboratory experiments.

2. The Phosphorus Resources Issue

In a recent paper, Daneshgar et al. [14] summarized and commented on the most recent information about P use trends and resources forecasting. About 95% of all phosphorous production in the world is used in the agricultural sector, mainly in fertilizers: aside from P, only nitrogen has such an important role in the inorganic fertilizers industry. Almost the totality of Phosphate is taken out of the ground as ore, which, after processing to remove impurities (sand, clay etc.) is called phosphate rock (PR). PR typically contains 13–14% P by weight.

World total PR production in 2014 was around 197 Mt, which, assuming nominal contents, would correspond to about 26 Mt P [15]. World total PR reserves in 2014 (Table 1) were reported as 68,776 Mt (about 9000 Mt as P) with a 73% share stored in geological deposits located in Morocco and Western Sahara. Estimated total global phosphate resources, on the other hand, are more than 300 billion tonnes [16], the great part of which are not suitable for extraction under current economic and technological conditions, since they are located in the continental shelves of the Atlantic and Pacific Oceans, with no economically profitable method for their exploitation. It should be noted that, in addition to the specific issues examined in this paper, the high geographical concentration of these resources is also liable to create issues related to the security of their supply in case of sudden sociopolitical changes.

Table 1. Phosphate rock (PR) production and reserves as beneficiated PR, 2014 data ([14]).

Source	Production		Reserves		R/C
	(Mt/year)	(%)	(Mt)	(%)	(years)
Morocco & Western Sahara	30	13	50,000	73	1667
China	100	45	3700	5.4	37
United States	25.3	12	1100	1.6	40
MENA-M/WS *	25.7	12	8166	12	318
Rest of the world	37.2	17	5810	8	156
World total	218		68,776		315
As P **	28.6		9005		

Mt = megatonnes = million metric tonnes = Tg. ** Assuming PR is 30% P_2O_5 . * Middle East and North Africa not including Morocco and Western Sahara.

Phosphate rock seems thus to be a finite, irreplaceable, nonrenewable resource. The question is therefore whether (and when) it will be totally depleted in the future, although overall data indicate that a crisis in phosphorus resources is not yet imminent. According to some researchers from the International Fertilizer Development Center (IFDC) the current ratio of “serves to consumption” stands now at almost 300 years [17], however, if population growth rate continues at the current rate (as forecasted in the UN “high” population estimate), they could only last until 2170 [18].

P scarcity, whether decades or centuries from now, would be catastrophic. Such a risk suggests that mankind should begin immediately to modify current wasteful practices concerning phosphorus resources management, especially since many of these practices result in environmental problems seriously affecting us today. Humanity, in fact, intervenes in the global P cycle in many disrupting ways: the anthropogenic P cycle, while resembling the natural one (Figure 1), induces a more intense

use of this resource, with a flux that is about three times the natural one [19], and a negligible fraction actually recycled. In addition the cycle, mainly targeted to the production of food for human/animal consumption, shows significant “leaks” of material (e.g., erosion and leaching from cropland, improper animal waste disposal, food waste, etc.) along the way, resulting in only about 16% of the original quantities being put to effective use. Efforts at reducing P wastage could potentially increase the duration of existing reserves by a factor of up to six.

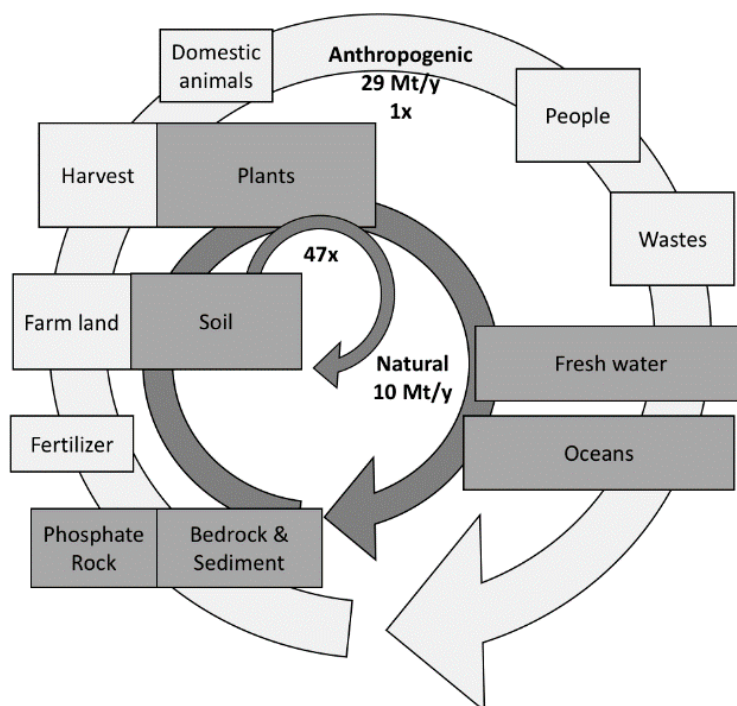


Figure 1. The natural and anthropogenic (agricultural) phosphorus cycles.

Phosphorous Waste Reduction and Recovery

The issue is clearly double-edged: it concerns P resources depletion and environmental pollution due to its excessive dispersion in the environment. As mentioned, there are a number of interventions that could conserve phosphorus, reduce its dispersion, or both. Reduction of food waste could potentially help in conserving it in significant amounts. Reducing losses from agricultural land would also be an important goal, though more difficult to implement, as this is currently mandated to voluntary Best Management Practices (BMPs) aimed at the control of nutrients leaching into surface waters. Losses via animal waste could be reduced either by reducing the incidence of meat consumption in the human diet, or by more effective recycling strategies for animal waste. Recycle could be applied to other parts of the cycle, such as crop waste, harvest waste, food waste, and human (bodily) waste.

Recycling the P fraction contained in human wastes will affect, however, only about 16% of mined phosphorus, even if 100% recycling of this stream could be achieved. Raw wastewater contains somewhere in the range of 4.0–16.0 mg P/L. About 20–30% of this is removed during conventional biological treatment, which would leave a nominal 3.0 to 12.0 mg P/L in treated effluents. Enhanced chemical precipitation, combined with filtration, could achieve effluent concentrations as low as about 0.05 mg P/L [20], resulting, however, in a form of precipitated P bound in a sludge that would necessitate complex post-treatment to make it recoverable and reusable. It would therefore seem reasonable to modify processing technologies and direct these sludges to P (and energy) recovery in the form of products such as struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), a mineral which can be utilized for fertilizer production.

3. Phosphorus Recovery Technologies

The most important difference between P-removal and P-recovery processes is that the former aim at obtaining phosphorus-free wastewater treatment plant (WWTP) effluents, while the latter is focusing on creating P-containing by-products, which can then be reused for other purposes, mainly in the fertilizers' industry. P-recovery technologies are mainly applied to industrial and urban wastewater, while there are few available methods applicable to livestock manure [21,22]. Recovery rate from liquid phase wastes can reach up to a maximum of 40–50%, while in sludge phase rates close to 90% could be achieved [21]. Figure 2 shows different possible locations for P-recovery processes within a wastewater treatment plant. Table 2 summarizes commercially available technologies, organized by type of waste treated and technology.

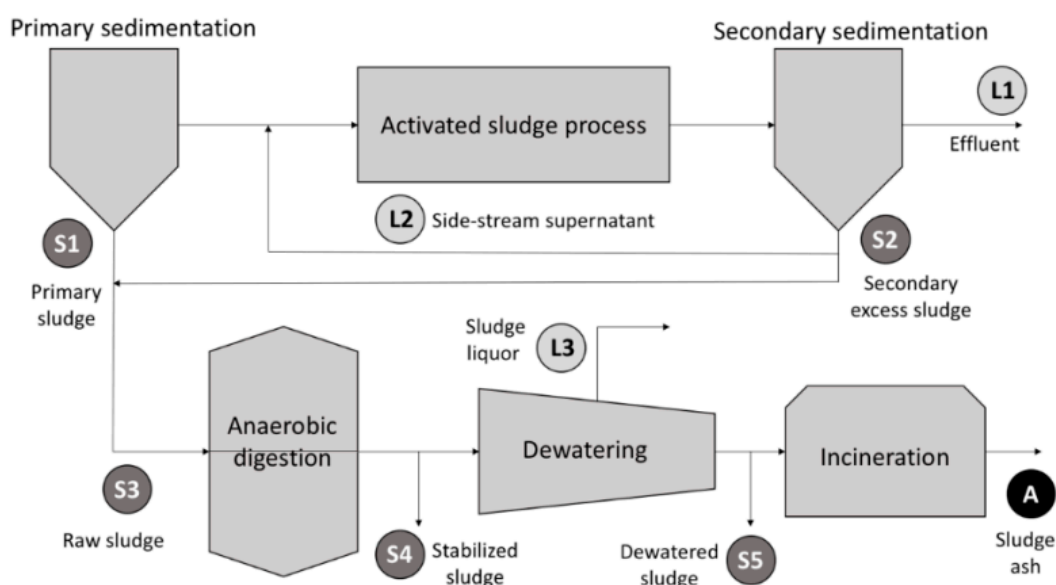


Figure 2. Possible phosphorus recovery locations in a conventional wastewater treatment plant (WWTP) (based on [21,23]).

Accumulated polyphosphates in bacterial cells performing an Enhanced Biological Phosphorous Removal (EBPR) process can be released under anaerobic conditions, so phosphorus could be recovered from the supernatant of the side-stream recycle to the activated sludge process (L2), the effluent after sedimentation (L1), or from the dewatering process after sludge digestion (L3). P recovery from wastewater streams may be achieved by precipitation/crystallization processes: struvite (magnesium ammonium phosphate hexahydrate) crystallization is one of the current leading technologies for P recovery. Recovery from the solid phase could also be achieved from primary sludge (S1), excess secondary sludge (S2), the raw sludge prior to anaerobic digestion (S3) and sludge before and after dewatering (S4, S5). Struvite and calcium phosphate may also be alternatively obtained from sewage sludge or sludge ash: as an example, it is possible to recover P from incinerated sludge ash (A, in Figure 2). This is actually the technology that will yield the most concentrated form of phosphorus: 4–11% by weight, comparable to PR (about 13% P) [24].

Chemical precipitation methods and in particular, the struvite precipitation process, are variably efficient methods for recovery of P from wastewater. Precipitation may produce a high-quality mineral that could be further used as a fertilizer, and generally has low metal content compared to raw sludge. However, some disadvantages in this method are present as well. The process may need substantial amounts of Mg^{2+} added to the system, since this element is usually present at insufficient concentrations in typical wastewater streams [25,26], and that would significantly increase costs. In addition, also the cost of added NaOH, necessary to control the pH level, may be considerably

high [26]. Although struvite would have an added value as a fertilizer product, the offset in costs may not be yet high enough to justify process implementation at large scale, under current conditions [26]. At the moment, in fact, there are only a handful of full-scale plants worldwide using this technology. Furthermore, obtaining pure struvite as a final product could still be a challenge, as shown by the experimental results of this study, and specific regulations must be met for a struvite product to be used as a fertilizer. Struvite could in fact still contain some unwanted contaminations due to the presence of heavy metals, pathogens and pharmaceutical residues [27–29].

Table 2. Some commercially available technologies for P recovery (from [14]).

Sludge Type	Process Name	Method	Products	Operational Scale
Sludge liquor	P-ROC	Adsorption	CaP, CaP on CSH	Semi-industrial
	RECYPHOS	Adsorption	FeP	Semi-industrial
	PHOSIEDI	Adsorption	CaP	Lab scale
	PHOSTRIP	Precipitation	CaP	Full scale
	PRISA	Precipitation	Struvite	Semi-industrial
	CRYSTALACTOR	Pellets	CaP, struvite	Full scale
Digested sludge	PEARL	Pellets	Struvite	Full scale
	BERLINER VERFAHREN	Without leaching	Struvite	Full scale
	FIX-PHOS	Without leaching	CaP on CSH	Lab scale
	SEABORNE	With leaching	Struvite	Full scale
	STUTTGARTER VERFAHREN	With leaching	Struvite	Full scale
	LOPROX/PHOXAN	With leaching	Phosphoric acid	Full scale
	CAMBI	With leaching	FeP, AlP, CaP	Lab scale/Full scale
	AQUA RECI	With leaching	FeP, AlP, CaP	Lab scale/Full scale
	K REPO	With leaching	FeP	-
	SEPHOS	With leaching	AlP, CaP	Lab scale
	SESAL-PHOS	With leaching	CaP	Lab scale
	P ASCH	With leaching	Struvite	Semi-industrial
	BIOLEACHING	With leaching	Struvite	Lab scale
	BIO CON	With leaching	Phosphoric acid	Semi-industrial
Sludge ash	MEPHREC	Thermal treatment	CaP	Semi-industrial
	ASH DEC	Thermal treatment	Fertilizer	Semi-industrial
	THERMPHOS	Thermal treatment	Elemental phosphorus	Industrial process
	PHOSPHORUS INDUSTRY	Thermal treatment	Fertilizer	Industrial process

Other technologies that could be applied to P recovery have also been proposed recently. Assimilation is an example, consisting of the adsorption of phosphate by algae. Usually, microalgae are good candidates for this process, applied through an old technology, such as the so-called aerobic pond. However, due to the non-optimized biomass production in aerobic ponds, P recovery rate with this method is limited, and maxima of up to around 60% of P recovery could be achieved in practice [30]. A major advantage of the assimilation concept, however, is the production of high-value biomass that can be further used in different industries (biofactories/biorefineries) [31].

Lately, the use of membrane technology was proposed as another method for P recovery. This could be used in combination with chemical precipitation, since membrane media might promote precipitation by concentrating the necessary ions in their retentate [32]. Osmotic membrane bioreactors (OMBRs), in particular, are part of a newly developed technology that could be applied to P recovery. While so far it has been applied mostly for P recovery in the form of Amorphous Calcium Phosphate (ACP) [28], this method has a potential for P recovery up to 95% [33]. Recovered ACP appears to have potential as a fertilizer source without further chemical processing, such as the acid treatment typically used to process phosphate rock. Plants fertilized with recovered ACP showed P uptake responses almost as good as for triple superphosphate (TSP, one of the first P-based fertilizers widely used in the 20th century, $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$, now less popular in use than other fertilizers). As systems' performance may be affected by many environmental factors such as salinity, membrane fouling, hydraulic load, and so on [34], their assessment is still under progress.

Struvite Crystallization

Struvite can form under controlled conditions in crystallization reactors, from where it is removed as small, fairly pure pellets. It might also take place spontaneously in different locations of a wastewater treatment facility with undesired consequences (i.e., clogging of pumps, pipes and valves) [35]. The initial concentration of P determines whether struvite formation is possible, due to its limited solubility product. The process of crystallization is based on the following stoichiometric equation:



However, phosphate in solution could also be present in HPO_4^{2-} and H_2PO_4^- forms that can contribute to struvite formation according to Equations (2) and (3):



In practice, Equation (2) is dominant in the favorable pH range 7–11 for struvite formation [36]. Solution's pH influences P forms and dominant crystal type. Struvite crystal are possible at the above pH value range, otherwise, at a higher values $\text{Mg}_3(\text{PO}_4)_2$ or $\text{Mg}(\text{OH})_2$ could be formed. All reactions, and in particular the reaction of HPO_4^{2-} , should be taken into account while examining struvite precipitation. Important factors affecting this process are pH, concentrations of mineral constituents and presence of competitive ions, most notably Ca^{2+} that could reduce the size of struvite, modify crystal growth, or delay the nucleation rate and the growth rate of crystals [37].

The mechanism of crystallization can be divided into three steps: nucleation (formation of small crystals of struvite), crystal growth (development of the small sized crystal into larger ones), and aggregation (a number of crystals come together and forming clusters) [38]. Studies on the kinetics of struvite precipitation suggested that the three steps above can all be formulated empirically as a function of supersaturation ratio of struvite [38]. This is basically the ionic activity product (IAP) of constituent ions in the solution, over its equilibrium solubility product or K_{sp} . A solution is supersaturated when ionic concentration is above its equilibrium level, and consequently struvite precipitation may occur to bring back the system into equilibrium conditions. Equation (4) formulates the "Saturation Index (SI)" concept, which is the logarithm of a system's supersaturation ratio [39]:

$$\text{IAP} = \left\{ \text{Mg}^{2+} \right\} \left\{ \text{NH}_4^+ \right\} \left\{ \text{PO}_4^{3-} \right\} \quad (4)$$

$$\text{SI} = \log \left(\frac{\text{IAP}}{K_{sp}} \right) \quad (5)$$

Struvite solubility product is in the range of 9.4–13.26 [40], and it can precipitate in the pH range of 7–11 [41]. An increase in pH will decrease struvite solubility. One of the key obstacles on the way of obtaining pure struvite precipitation is the presence of competitive ions, and particularly calcium (Ca^{2+}), which could lead to the presence of impurities in the final precipitates (calcium phosphate salts).

4. Materials and Methods

For this study, sludge samples were collected from the Nosedo (Milan, Italy) wastewater treatment plant (WWTP), the main one among those serving the city of Milan, with capacity of 1.25 million p.e. and an annual dewatered sludge production of about 50,000 tons/year. The estimated phosphorus content of this sludge is at least 240 tons/year. The facility does not have a traditional anaerobic digestion phase for sludge treatment, but relies on an extended aeration process, followed by dewatering and thermal drying to limit disposable volume. A large part of dewatered sludge is normally disposed to agricultural land, while a smaller part is thermally dried and then used as solid recovered fuel into cement kilns.

Samples were taken from one of the activated sludge system oxidation tanks, where a higher P concentration is normally observed, due to its release in the preceding anaerobic stage, therefore creating higher potential for struvite precipitation. Table 3 summarizes the main characteristics of the samples in terms of relevant ionic content for struvite crystallization.

Table 3. Wastewater sludge characteristics.

Ion	Concentration (mg/L)
Ca ²⁺	101
Mg ²⁺	26.4
P	40.3
NH ₄ ⁺	32.6

Investigation of the thermodynamics and kinetics of struvite precipitation was tested both experimentally on the samples collected, and theoretically assessed with application of chemical equilibrium modeling. The advantage of using verified modeling tools over experiments, besides the faster and time efficient process, lies in their capability to predict equilibrium conditions and ion speciation, based on initial conditions. In this study, the PHREEQC model, an established geochemical modeling tool developed by US Geological Survey (USGS) was used [42]. PHREEQC is capable of performing a wide variety of aqueous equilibria calculations, such as ion speciation batch-reactions, and saturation index (SI) values calculations based on solution characteristics (ionic concentrations, pH, etc.) as input. Version 3.0 of the software was used herein to model the chemical equilibria of the struvite precipitation process. Results were then validated by comparing them with actual laboratory precipitation tests.

4.1. Model Description

PHREEQC contains multiple databases that include different chemical species, their corresponding reactions, and the solid phase products that could precipitate as final outcome. The default model database was used in this work, however, as this was not initially optimized for the study of struvite precipitation; it needed modification to describe specific reactions. First of all, struvite itself, for instance, was not defined as a default possible final solid phase reaction product, and hence needed to be explicitly included. Table 4 summarizes the final list of possible solid phases that may precipitate in such systems, with their corresponding K_{sp} values. Some of these were added to the initial database, others needed to be removed, as they were highly unlikely to precipitate in the foreseen experimental conditions (e.g., pH levels). For example, magnesium phosphate compounds, other than struvite, were removed from the database, as well as transformations that are known to be extremely slow compared to the operating conditions timescale, and thus also unlikely to precipitate, such as tricalcium phosphates and hydroxyapatite (HAP). Octa-calcium phosphate (OCP) was also removed due to the low pH level (5–6) required for its precipitation [43]. ACP and monetite were the only two calcium phosphate compounds kept in the database. Two main carbonate compounds could form in the system; calcite (CaCO₃) and magnesite (MgCO₃). Calcite was maintained in the database, however magnesite was removed due to the high pH (>9.5) required for its precipitation in substantial amounts [44].

Key operating factors in struvite formation are pH level, magnesium concentration and presence of other competing ions, especially calcium. In most cases, the limiting agent in wastewater streams is magnesium, therefore it could be added to the process in the form of MgCl₂, Mg(OH)₂ or MgO to ensure its stoichiometrically correct concentration. In addition to stoichiometry, the solution must possess an appropriate pH level. For this, addition of sodium hydroxide (NaOH) is the most common approach. Using added MgO or Mg(OH)₂ as a source of magnesium could also provide sufficient pH adjustment to the solution (due to oxides' alkalinity) but their low level of solubility should also be considered.

Table 4. List of solid phases and reactions present/added to the PHREEQC database.

Solid Phase	Representative Reaction	Operating Condition	pK _{sp} at 25 °C
Struvite ^(A)	$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} + 6\text{H}_2\text{O} \leftrightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	7 < pH < 11	13.26
Newberyite ^(A)	$\text{Mg}^{2+} + \text{HPO}_4^{2-} + 3\text{H}_2\text{O} \leftrightarrow \text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	High Mg^{2+} / P, pH < 6	5.8
Bobierite ^(A)	$3\text{Mg}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O} \leftrightarrow \text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Days to precipitate	25.2
Hydroxyapatite (HAP)	$10\text{Ca}^{2+} + 6\text{PO}_4^{3-} + 2\text{OH}^- \leftrightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Slow formation from ACP, DCPD	44.3
Tricalcium phosphate (TCP)	$3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2$	Slow formation from ACP, DCPD	32.63
Octacalcium phosphate (OCP) ^(A)	$8\text{Ca}^{2+} + 2\text{HPO}_4^{2-} + 4\text{PO}_4^{3-} \leftrightarrow \text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4$	Hydrolysis of DCPD at pH = 5–6	36.48
Monetite (DCP) ^(A)	$\text{Ca}^{2+} + \text{HPO}_4^{2-} \leftrightarrow \text{CaHPO}_4$	Fast formation from ACP, DCPD	6.81
Brushite (DCPD)	$\text{Ca}^{2+} + \text{HPO}_4^{2-} + 2\text{H}_2\text{O} \leftrightarrow \text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	pH < 7	6.6
Amorphous calcium phosphate (ACP) ^(A)	$3\text{Ca}^{2+} + 2\text{PO}_4^{3-} + x\text{H}_2\text{O} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$	pH > 6	25.46
Calcite	$\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$	Stable at 25°C and atmospheric P	8.42–8.22–8.48
Magnesite	$\text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{MgCO}_3$	Stable at pH < 10.7	7.46–8.2
Brucite	$\text{Mg}^{2+} + 2\text{OH}^- \leftrightarrow \text{Mg}(\text{OH})_2$	pH > 9.5	11.16
Ca(OH) ₂	$\text{Ca}^{2+} + 2\text{OH}^- \leftrightarrow \text{Ca}(\text{OH})_2$	pH > 9.5	5.2

^(A) Added to original database.

4.2. Experimental Setup

Chemical precipitation tests were performed in triplicate in the laboratory using 200 mL mixed beakers in a jar test apparatus. A NaOH solution was used to adjust the beakers' content to the required pH. MgCl₂ and NH₄Cl were used as additional sources of magnesium and ammonium, respectively. Phosphorus concentrations were measured according to the colorimetric method (EPA 365.3) using UV-Vis spectroscopy. 15 separate experiments were performed in total, combining pH and different relevant ionic concentrations: Ca, Mg, NH₄ and P. Precipitates obtained in each test were collected after 20 hr in order to allow completion of process equilibrium, results from equal-conditions tests were mixed and filtered with 0.45 µm paper filters, washed with deionized water, and dried at room temperature. Analysis of precipitates was conducted using Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer 1600 series, Waltham, MA, USA) in order to determine the presence of different solid phases.

Concentrations of all available ions were then fed to the PHREEQC model as inputs. The output of the model consisted of ion speciation conditions, and values of saturation index (SI) for each of the solid phases in the database. Speciation data were used to calculate the theoretical phosphorus removal percentage for each of the experiments.

5. Results and Discussion

Results of experimental tests and PHREEQC modeling are summarized in Table 5. Ion speciation and removal yields were determined for all numerical tests and runs, struvite saturation index (SI) values, only for numerical simulations. SI values were all positive, indicating that struvite precipitation could actually occur in the system under the simulated conditions. Some of these values were, however, very low (e.g., 2nd and 9th run), indicating that the possibility of precipitation was low. Furthermore, the range of SI values obtained during the whole cycle of simulations was not excessively high (all values were <1), in contrast with most literature results generally reporting higher values (>1) for

this parameter. This is likely due to the fact that most studies have dealt with anaerobic sludges with considerably higher initial phosphorus concentrations (usually 300–500 mg/L) compared to the aerobic extended-aeration sludge from the Nosedo plant (where P is around 40 mg/L) of this study. Fang et al. [45] suggested that, as the initial phosphorus concentration increases, SI value will also increase, up to P concentrations of around 1000 mg/L, after which it would decrease.

Table 5. Results of experimental tests and PHREEQC modeling.

Run	Ca (mg/L)	Mg (mg/L)	NH ₄ (mg/L)	P (mg/L)	pH	P removed Predicted (%)	P removed Measured * (%)	P precip. Predicted (mg)	P precip. Measured * (mg)	SI Predicted
1	101	84	35	40	9	82.46	84.27	33.23	31.24	0.48
2	101	26	35	40	9	72.76	82.99	29.32	30.85	0.17
3	101	84	82	40	9	82.15	82.05	33.11	29.77	0.84
4	101	26	82	40	9	72.20	82.21	29.10	30.07	0.54
5	101	84	59	40	8.5	70.28	54.72	28.32	23.60	0.54
6	101	26	59	40	8.5	58.03	61.43	23.39	24.14	0.21
7	101	84	59	40	9.5	92.08	91.93	37.11	34.66	0.60
8	101	26	59	40	9.5	86.33	89.28	34.79	33.65	0.32
9	101	40	35	40	8.5	62.40	68.47	25.15	25.74	0.13
10	101	40	82	40	8.5	61.60	62.36	24.83	24.74	0.49
11	101	40	35	40	9.5	88.59	92.15	35.70	34.09	0.22
12	101	40	82	40	9.5	88.29	87.62	35.58	33.65	0.58
13	101	40	59	40	9	75.86	85.74	30.57	31.37	0.52
14	101	40	59	40	9	75.89	82.31	30.58	30.84	0.52
15	101	40	59	40	9	75.89	84.13	30.58	30.78	0.52

* from triplicate tests.

The phosphorus removal percentage and amount of total phosphorus precipitated, both calculated based on the result of PHREEQC modeling, were compared to the measured values in the laboratory precipitation tests to assess the model potential in predicting accurately equilibrium process conditions. Such comparison is in fact essential for understanding the ability of the model to correctly predict new experimental outcomes without implementing all the individual tests in the lab. Results are also shown in Table 5. Notwithstanding some inevitable inaccuracies and small measurement errors in the comparison between calculated and observed values, some of them attributable to laboratory procedures, it could still be concluded that the model had a more than acceptable performance overall in reproducing laboratory experiments.

Analysis of the precipitates using Fourier Transform Infrared (FTIR) spectroscopy confirms the presence of struvite and calcium phosphate compounds in the solid phase final products of precipitation tests. Figure 3 compares the FTIR spectra of final precipitates at different pH levels and different components' molar ratios. It can be clearly seen that all the spectra follow the same pattern, with the main difference between them being the intensity of the peaks. Peaks associated with PO₄^{3−} and H₂O groups, at 1000–1100, and 2200–3800 cm^{−1}, respectively, can be identified in all the spectra obtained, and can be attributed to the presence of struvite and calcium phosphate compounds in the final solid phases [46]. However, FTIR spectra within the range of 1200 to 1900 cm^{−1} indicate no direct evidence of the presence of struvite since visible peaks could be typical of carbonate groups (around 1440 and 1650 cm^{−1}) and also of ACP water molecules (at around 1600–1650 cm^{−1}). This suggests that, in all the laboratory experiments, precipitates obtained were in fact a mix of struvite, ACP and calcite. Comparing the intensity of FTIR peaks, it could be concluded that as pH increases there will be more phosphate groups in the final precipitates, and thus higher phosphorus removal from the system. However, as expected, final precipitates could also be highly affected by the presence of calcium as a competitive ion in the solution, thus allowing formation of high amounts of calcium phosphate compounds (mainly ACP) at the highest values of pH.

Although the main objective of this study is to assess the possibility of P recovery in the form of struvite, in a form as pure as possible, the presence of ACP and calcite in the precipitate seems to be inevitable in experimental conditions. One important aspect to mention is that the presence of ACP

still represents a more favorable situation than that of calcite. Due to its P content, in fact, ACP can still be considered an acceptable fertilizer, although not as good as struvite. It is therefore important, in practice, not to move below a pH value of 9.0 in the tested conditions, as after this point there would be considerably more potential for calcite precipitation in the system.

Laboratory tests on extended aeration sludge show that the level of pH significantly affects P removal yields from the system, and that more than 90% P removal can be achieved at $\text{pH} > 9$. Nonetheless, due to the relatively low initial phosphorus concentration in the Nosedo sludge, the possibility of obtaining a significant amount of struvite in the final precipitates is low, unless adequate quantities of Mg and NH_4 additives could be introduced into the system to improve struvite crystallization and extraction.

Finally, Figure 4 shows the theoretical SI values calculated from the simulation results for Struvite, ACP and calcite in solution. These values suggest that in all cases, under present conditions, the final precipitates will be a mixture of struvite, ACP and calcite. As can be seen, in experiments 7, 8, 11, and 12 where pH reached 9.5, values of SI for calcite are higher, which is not an optimal situation for P recovery. The best result was obtained in experiment 3, where pH was 9 and concentrations of Mg and NH_4 at the highest levels. Addition of both these ions is therefore essential for achieving higher struvite precipitation in the solution at hand.

The next steps of the study will include additional tests on the extended aeration sludge, to investigate conditions under which more significant amounts of struvite precipitation could be obtained. Addition of higher molar ionic ratios will be tested, and the possibility of using $\text{Ca}(\text{OH})_2$ as an economic pH adjustment additive (instead of NaOH) will also be investigated.

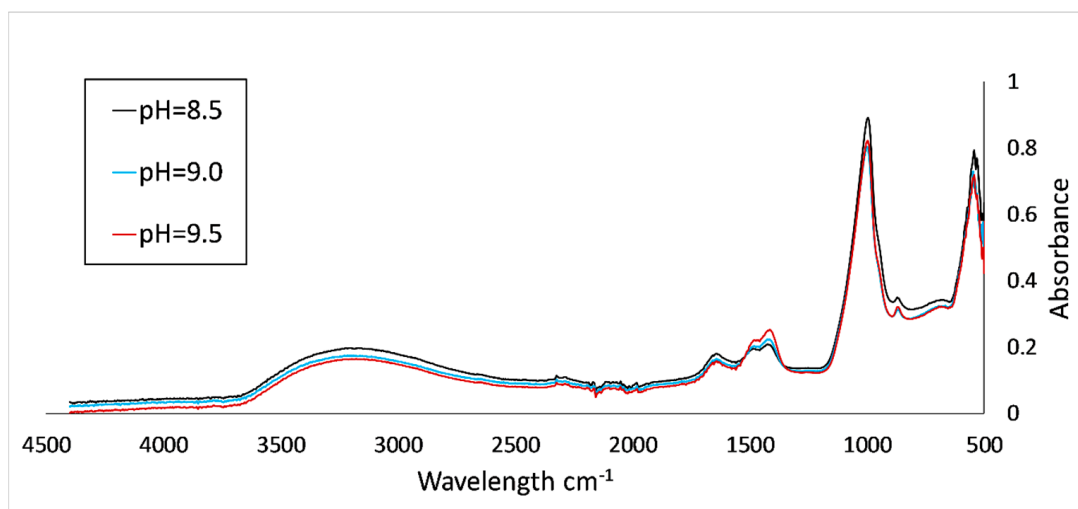


Figure 3. Fourier Transform Infrared (FTIR) spectra of the precipitates obtained at different levels of pH.

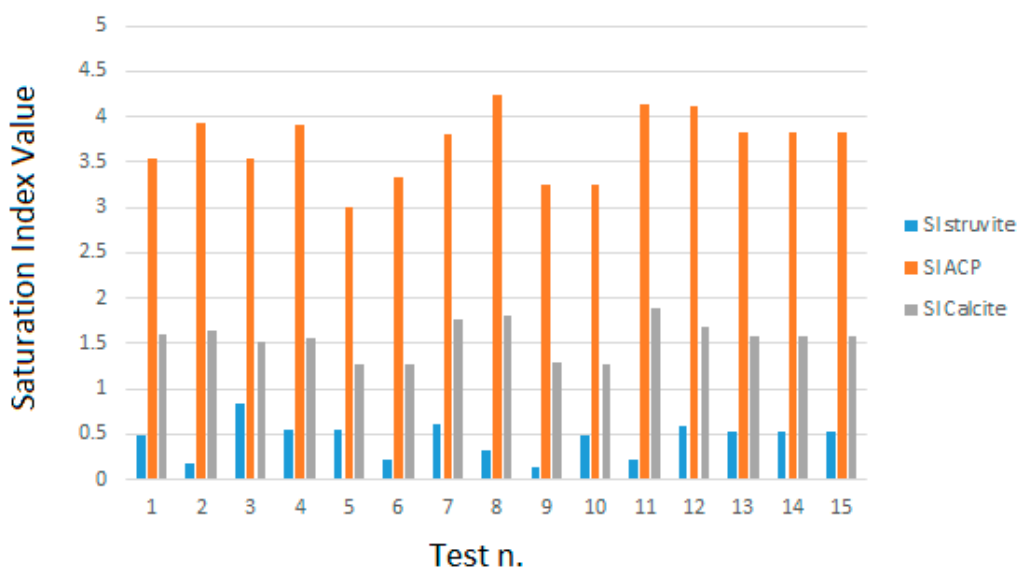


Figure 4. Theoretical saturation index (SI) values calculated by PHREEQC for possible solid phases.

6. Conclusions

In this study, a chemical equilibrium modeling tool was used, in combination with real laboratory precipitation tests, in order to investigate conditions under which high phosphorus recovery, in the form of struvite, could be achieved from the urban sewage sludges produced by the WWTP facility in Nosedo (Milan, Italy). Values of the struvite saturation index (SI) calculated by the chemical equilibrium model, showed that limited precipitation of this mineral is possible under present circumstances, due to wastewater characteristics, and estimated phosphorus removal efficiency was compared to laboratory results. As solution pH increases above 9, very high phosphorus removal percentages (>90%) could be achieved, but the possibility of achieving high recovery (pure struvite precipitation) is diminished. The presence of low P concentration in the wastewater sludge, in addition to relatively high Ca^{2+} content will lead to achieve a less desirable mix of struvite, ACP and calcite in the final precipitates. Results suggest that in order to obtain higher SI values for struvite, both magnesium and ammonium need to be added to the system in high amounts (as in experiment 3) in order to compete efficiently in precipitation with the presence of Ca^{2+} . Chemical equilibrium modeling showed great potential for predicting achievable equilibrium conditions by further ion addition to the solution, which could be pursued to achieve increased struvite precipitation. Modeling results in terms of P removal percentage and mass confirm a very good fit to the laboratory tests. Hence, model performance is confirmed by experimental evidence and, as such, the model could be a valuable tool for the optimization of the process and the development of a pilot-scale struvite precipitation system.

On the practical side, it was observed that struvite crystallization was hindered by small particle size and slow crystal growth, and therefore, modification of reactors' structure, compared to the laboratory's beakers used herein, and optimization of process parameters to enhance particle size, or minimize loss of crystals should be considered as possible methods to enhance the settleability of this mineral in real scale applications. Although, at the moment, struvite is the product of choice for P recovery, ACP may also have an appeal as final product for similar purposes. Precipitates purity and their market value will have to be compared to evaluate the economic sustainability of either product.

Considering the certainly limited, but uncertain extent of residual global phosphorus resources, development and enhancement of P recovery processes, which could allow recovery of this element, should be pursued, with the aim of extending the useful life of confirmed global reserves while maintaining sustainable levels of production of phosphorus compounds for use in agriculture. Chemical precipitation, in spite of having its own drawbacks, is still the most efficient and common

approach for P recovery. Equilibrium modeling of such a process could considerably help in predicting and achieving the best conditions under which highly efficient struvite precipitation can be obtained.

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