



Phosphorus recovery from sewage sludge – phosphorus leaching behavior from aluminum-containing tertiary and anaerobically digested sludge

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ABSTRACT

Systematic investigations of the acidic dissolution of phosphorus (P), aluminum (Al), iron (Fe), and calcium (Ca) from Al-containing tertiary sludge were carried out in this work. The results were compared with the dissolution behavior of Al-containing anaerobically digested sludge to evaluate the P recovery potential in the form of struvite from tertiary sludge versus anaerobically digested sludge. Additional investigations of synthetically produced Al sludge served as a comparison for the dissolution behavior of P and Al without the influence of other contaminants (metals, biomass). In addition, the acid consumption was analyzed as a function of the target pH during the dissolution. The dissolution efficiency of ortho-phosphate in tertiary and anaerobically digested sludge after acid treatment at pH 2 was ~90%. The dissolution efficiency of Al and Ca in tertiary sludge was also ~90% at pH 2, while the release efficiency of Al and Ca in anaerobically digested sludge was lower, ~70% at pH 2. In tertiary sludge, about 75% of Fe was found dissolved at pH 2, whereas in anaerobically digested sludge this value was higher, ~90%. Based on the experimental data, it can be concluded that significant dissolution of phosphorus from Al-containing tertiary sludge can take place at pH < 3. The highest sulfuric acid consumption for P dissolution was observed in the case of tertiary sludge at pH 2.

Key words | acid consumption, acidic leaching, anaerobically digested sewage sludge, phosphorus recovery, post-precipitated tertiary sludge

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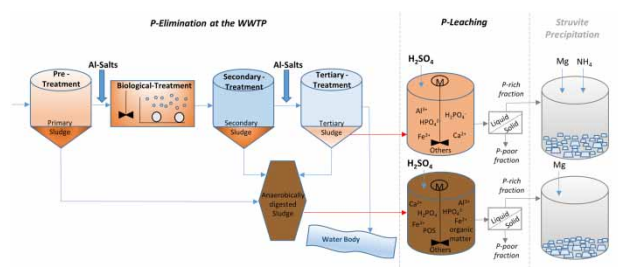
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HIGHLIGHTS

- Dissolution efficiency of ortho-phosphate ($\text{PO}_4\text{-P}$) in tertiary and anaerobically digested sludge at pH 2 was ~90%.
- The optimal pH for the leaching of $\text{PO}_4\text{-P}$ depended strongly on the composition of the sludge.
- For aluminum phosphate sludge, pH < 3 is most efficient for $\text{PO}_4\text{-P}$ dissolution.
- For P recovery as struvite, external source of magnesium (Mg) is required for the digested sludge leachate, and of both Mg and ammonium-nitrogen for the tertiary sludge leachate.

GRAPHICAL ABSTRACT



INTRODUCTION

In addition to potassium (K) and nitrogen (N), phosphorus (P) is one of the most important nutrients for agriculture and cannot be replaced by other substances. Nevertheless, phosphate rock is a non-renewable resource that is becoming increasingly scarce, the availability of P-rock is estimated at around 300 years (Cordell & White 2015). The production of mineral fertilizers is based on P-rock, which are increasingly contaminated with impurities such as cadmium (Cd) and uranium (U), resulting in higher production costs (Pizzol *et al.* 2014) and contamination of the soil with heavy metals. In addition, the overproportional global distribution of P-rock leads to an almost complete import dependency of countries with resource deficits.

An analysis of phosphorus flows in the European Union in 2005 showed that 2,392 Gg P were imported, about half of which accumulated in agricultural soils and about half was lost as waste, in which the largest P sink was municipal waste water (van Dijk *et al.* 2016). If P is recovered from municipal wastewater, it would theoretically be possible to replace about 50% of the P demand in Central Europe from secondary sources (Egle *et al.* 2016).

The direct agricultural use of sewage sludge is controversial because sewage sludge contains not only nutrients, but also heavy metals, persistent organic pollutants (Rorat *et al.* 2019), and pathogens (Goberna *et al.* 2018). Moreover, in September 2017 Germany adopted the amended sewage sludge ordinance, making P recovery mandatory from sewage sludge with P content >20 g P/kg dry mass or mono-incinerated sewage sludge ash for all wastewater treatment plants (WWTP) >50,000 population equivalents (PE). This new federal law provides a transition period of 12–15 years for the WWTP operators to prepare a concrete P recovery plan before the legislation comes into force by 2032 (AbfklärV 2017).

Complying with the strict effluent discharge P-limit values requires either chemical or enhanced biological phosphorus

removal (EBPR), or a combination of biological and chemical P elimination. Chemical P precipitation is more common in Germany. A large variety of coagulants salts such as aluminum (Al) salts, iron (Fe) salts, sodium aluminate ((NaAl(OH)₄)) or hydrated lime are used for the chemical P elimination from wastewater. The most commonly used Al salts are aluminum chloride (AlCl₃), polyaluminium chloride (Al(OH)₃-xCl_x)_y, where 'y' is the degree of polymerization, and aluminum sulphate (Al₂(SO₄)₃). Sodium aluminate (NaAl(OH)₄) is used for alkaline precipitation, which increases the pH and the acid capacity of the medium. Furthermore, mixed products such as aluminum–iron(III) sulphate (Al₂(SO₄)/Fe₂(SO₄)₃·H₂O) or aluminum–iron chloride (AlCl₃/FeCl₃) are also used. The advantage of these products is the simultaneous control of floating sludge. Most precipitants are often by-products from the aluminum, steel or chemical industries, which also may contain other undesirable heavy metals (Baumann 2003).

The P recovery following simultaneous chemical P elimination in the biological treatment stage requires the use of acid or base for the dissolution of the chemically and/or biologically bound P. The efficiency of P recovery depends on several factors, such as sludge composition, type and concentration of the leaching agent, pH, and contact time (Gorazda 2013). When the collected mixed excess sludge (activated sludge + chemical sludge) is exposed to acidic or alkaline leaching, the P released from the sludge follows different mechanisms. In the acidic pH range, first the chemically bound P is released into solution, while in the alkaline range it is the opposite where normally the biologically bound P is dissolved first (Weideler 2010; Ali & Kim 2016; Xu *et al.* 2018).

Digested sewage sludge (wet or dewatered) and sewage sludge ash (mono-incinerated) are the preferred streams

for P recovery within a WWTP due to their high P recovery potential (max. 90% of the WWTP inflow P). However, the enforced leaching of P from the sludge leads to simultaneous undesirable dissolution of metals and organic pollutants, which can subsequently precipitate in the recovered P-product (e.g. struvite). Alternatively, post-precipitated chemical sludge, so-called tertiary sludge, is produced during the post-precipitation of P with metal salts after the secondary clarification, without mixing it with the biomass in the aeration tanks. The advantages of chemically precipitated tertiary sludge are significantly lower volume and less contamination with undesirable pollutants (Wiechmann *et al.* 2013) compared to mixed activated and chemical sludge. These are a major beneficial reasons for subsequent P recovery.

Previous studies investigated the dissolution behavior of primary, activated, or digested sewage sludges under the influence of different parameters such as molar concentrations of acid or base, temperature, and reaction time (Zou *et al.* 2017; Lee *et al.* 2018; Xu *et al.* 2018; Bashir *et al.* 2019; Toor *et al.* 2019). Few studies have performed systematic comparative investigations of phosphorus leaching from sewage sludge (Güney *et al.* 2008; Weideler 2010; Ali & Kim 2016; Meyer *et al.* 2018; Quist-Jensen *et al.* 2018). However, they all compare the P-leaching behavior between sludges of the same type (e.g. primary, activated, or digested sludge), even if the sludge samples come from different sewage treatment plants. According to our knowledge, except for our own recent work (Monea *et al.* 2020) there are no other published studies that compare systematically the leaching behavior between different sludge types and against a reference ideal synthetic sludge.

The P dissolution from post-precipitated tertiary sludge has only been reported in a few studies so far (Reuna & Väisänen 2018; Rossi *et al.* 2018; Toor & Kim 2019; Monea *et al.* 2020). In this work we investigated the P dissolution from Al-containing sludges in the acidic range for pH values 7.5, 5.0, 4.0, 3.5, 3.0, 2.5, and 2.0. The simultaneous release of Al, Fe, and Ca was also studied. Subsequently, P recovery from tertiary versus anaerobically digested sludge was considered. Additionally, the chemical consumption for each pH was analyzed in detail.

MATERIALS AND METHODS

General information and overview of sludge substrate

Three different sludges were tested in this work: post-precipitated tertiary sludge, anaerobically digested sewage

sludge, and synthetically precipitated chemical sludge. The post-precipitated tertiary and anaerobically digested sludge came from the same wastewater treatment plant, where the chemical P elimination was carried out using polyaluminum chloride (PAC). The synthetic sludge was freshly synthesized at laboratory scale before every new experiment, always using the same procedure, as detailed later. The composition of the synthetically precipitated chemical sludge is listed in Table 2. The P in synthetic sludge was precipitated with AlCl_3 and also with PAC. Comparable results were obtained, which are shown in Table S1 in the Supplementary material.

The experiments were carried out in duplicate and the results are given as average values. The standard deviation of the single values was within 10% in all tests. The total number of measurement for the respective sludge examined is shown in Table S2 in the Supplementary material.

Post-precipitated tertiary sludge and anaerobically digested sludge from a wastewater treatment plant

The sludge samples were collected from the WWTP Überlinger See, Uhlidingen in Germany. Überlinger See is part of the Lake Constance region used for recreation as well as for drinking water supply, and there is a strict discharge limit value for the lake.

The capacity of WWTP Überlinger See is 68,000 PE. The mixture of domestic and industrial wastewater undergoes mechanical and biological (activated sludge) treatment. In order to comply with the strict discharge limit value for P of 0.3 mg/L (annual mean value), a two-stage P elimination is required. After P precipitation in the activated sludge tank, the post-precipitation (second-stage P precipitation) takes place at the end of the treatment process in an existing retrofitted secondary clarifier before discharging the WWTP effluent. The excess sludge is anaerobically digested together with the primary sludge and then thermally incinerated. The tertiary sludge is removed from the system approximately once a week and also anaerobically digested. During the P post-precipitation in dry weather, an over-stoichiometric ratio of 4 ($\text{Al}/\text{P} \approx 4$) was set to compensate for competing reactions. For example, simultaneous formation of aluminum hydroxide may happen in parallel with the precipitation of aluminum phosphate (AlPO_4) (de-Bashan & Bashan 2004). Moreover, the high stoichiometric ratio during precipitation of metal phosphates is necessary to overcome the chemical reaction thermodynamic limitations due to the low P concentration in the pre-treated wastewater (Mayer *et al.* 2013).

Post-precipitated tertiary sludge and anaerobically digested sludge were sampled and their chemical composition was systematically analyzed (Table 1). The dark, almost black color of the tertiary sludge and the pungent

Table 1 | Composition of post-precipitated tertiary and anaerobically digested sludge

	Tertiary sludge		Anaerobically digested sludge	
DM ^a (%)	2.5		2.2	
LOI ^b (wt%)	42		60	
pH	7.5		7.5	
Parameter	(mmol/L)	(% of DM)	(mmol/L)	(% of DM)
Total P	39.7	5.0	22.6	3.2
PO ₄ -P	0.1	–	0.07	–
TKN	36.1	2.0	140	9.0
NH ₄ -N	4.1	–	63.5	–
Total ^c Al	162	16.9	38.5	4.8
Dissolved ^d Al	0.02	–	0.1	–
Total ^c Fe	0.7	0.1	3.7	0.8
Dissolved ^d Fe	0.01	–	0.1	–
Total ^c Ca	11.3	2.2	34.2	6.3
Dissolved ^d Ca	2.0	–	2.2	–

^aDry mass.

^bLoss on ignition.

^cMeasured in the homogenized sample.

^dMeasured after membrane filtration at 0.45 µm.

Note: The symbol '–' means 'not applicable', i.e. the parameter does not apply to the designated category.

odor may indicate the formation of hydrogen sulfide (H₂S) due to anaerobic microbial activity. This could not be excluded because of the relatively long settling time of about one week. The unexpectedly high content of organic matter in the tertiary sludge was confirmed by the high loss on ignition value (LOI = 42%), which is most likely caused by the microbial activity and the co-precipitation of organic matter due to the high stoichiometric ratio.

The results, presented as concentrations in mmol/L, are plotted as average values in Figure 1.

Synthetically precipitated chemical sludge

The synthetic sludge was prepared under laboratory conditions always using the same procedure. It was freshly prepared before each experiment. For this purpose, ~1,000 mg/L ortho-phosphate (PO₄-P) stock solution was prepared by adding 85 wt% orthophosphoric acid (H₃PO₄) in deionized water and mixed in 10 L volume. Subsequently, the precipitant AlCl₃ was added by hand under vigorous mixing conditions, while the stoichiometric value Al/P ≈ 1.5 was retained in all experiments. The stoichiometric ratio Al/P = 1.5 was purposefully lower than in the post-precipitated tertiary sludge from WWTP Überlinger See (Al/P ≈ 4). The synthetic chemical sludge used in this study had a relatively high P concentration (approximately 33 mmol/L), which was thermodynamically favorable and required a lower Al dosage for the P precipitation reaction. Furthermore, in the synthetic sludge there are no competing ions or other

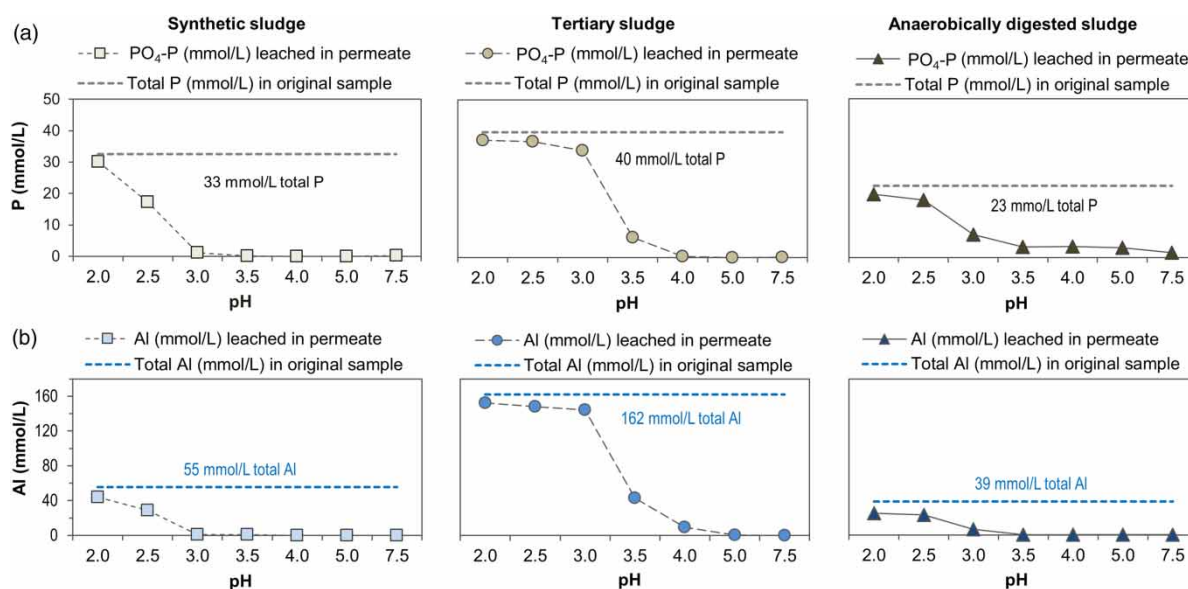


Figure 1 | Measured concentrations (mmol/L) in leached permeate and original sample of (a) phosphorus and (b) aluminum in synthetic, post-precipitated tertiary and anaerobically digested sludge.

interfering substances, which justified the lower stoichiometric ratio $\text{Al/P} = 1.5$ as sufficient to achieve high P-removal efficiency. The pH 7.5 was kept constant by adding 20 wt% sodium hydroxide (NaOH). After the addition of AlCl_3 , a contact time of 30 min was maintained to ensure the precipitation reaction was completed. The concentrations of P and Al were measured in the homogenized (total concentration) and $0.45\ \mu\text{m}$ membrane-filtered (dissolved concentration) sample. Very low dissolved concentrations of P and Al (Table 2) indicate a high precipitation rate of Al-phosphate.

Subsequently, the leaching experiments were carried out with the addition of 37 wt% sulfuric acid (H_2SO_4). A solid-liquid separation was not performed, i.e. the leaching experiments were carried out directly in the prepared solution. The experiments were carried out in duplicate and the results, in mmol/L, were plotted as average values (deviation within 7%) in Figure 1.

The synthetic sludge was specifically prepared to contain only Al-phosphates in order to investigate the dissolution behavior of this compound without the influence of organic matter or other mineral phosphorus compounds, such as Fe-phosphates or Ca-phosphates.

Chemical reagents and analytical methods

Orthophosphoric acid (85 wt% H_3PO_4), sodium hydroxide (20 wt% NaOH) and 37 wt% H_2SO_4 were supplied by Merck KGaA, Darmstadt. AlCl_3 was ordered from VWR Chemicals Deutschland.

The total concentrations of all parameters were measured in the homogenized samples (original samples) without further processing. The dissolved concentrations in the soluble phase were analyzed in the supernatant after solid-liquid separation (laboratory centrifuge Hettich Rotanta/P) and subsequent membrane filtration ($0.45\ \mu\text{m}$). Dry mass (DM) was determined following DIN 38409 1 01/1987 and the LOI based on DIN 38409-1 01/1987 (German Institute for

Standardization 1987). Total P was performed according to the German standard DIN-EN-ISO-6878 (German Institute for Standardization 2004) and $\text{PO}_4\text{-P}$ was analyzed according to DIN-EN-ISO 6878/2004 (German Institute for Standardization 2004). Total Kjeldahl nitrogen (TKN) was determined in compliance with DIN-EN-25663 11/1993 (German Institute for Standardization 1993) and ammonium-nitrogen ($\text{NH}_4\text{-N}$) according to DIN-38406 5-2-10/1983 (German Institute for Standardization 1983). The Al, Fe, and Ca concentrations were analyzed after acid digestion in nitric acid/hydrogen peroxide using the NexION 350X instrument from PerkinElmer for inductively coupled plasma mass spectrometry according to DIN-EN-ISO 17294-1 (German Institute for Standardization 2007). The pH was measured with a mobile standard instrument pMX-3000 from WTW.

Experimental procedure and equations

All leaching tests were carried out on a laboratory scale. The release of P, Al, Fe, and Ca was investigated only under the influence of H_2SO_4 . For the dissolution of P, which is strongly bound to Al, the addition of a strong acid is necessary (Ali & Kim 2016). The use of H_2SO_4 is a practical choice of acid because it is not expensive and can be produced easily and in large quantities.

The plexiglass reactors used for the experiments had a total volume of 15 L, whereas the leaching tests were carried out in 10 L scale. The H_2SO_4 (37 wt% H_2SO_4) was dosed with a membrane pump up to the target pH value. The addition of H_2SO_4 as a function of pH was regulated by an automatic controller. The specific volume and ratio of added H_2SO_4 for adjusting the target pH values are available in Table S3 in the Supplementary material. After reaching the desired pH value, a contact time of 30 min was maintained and then a sample was taken for the chemical analysis. A contact time of 30 min was defined as sufficient through preliminary tests. The results of the preliminary tests are available in Table S4 in the Supplementary material. Subsequently, the solid phase was separated from the liquid phase, the supernatant was filtered ($0.45\ \mu\text{m}$), and the dissolved fraction was measured.

The dissolution efficiency (%) was calculated according to the following formula:

$$E_{\text{Diss}} = \frac{C_{\text{diss, mf}} - C_0}{C_{\text{total}} - C_0} \times 100\ (\%) \quad (1)$$

where $C_{\text{diss, mf}}$ (mmol/L) is the dissolved concentration of the respective element in the membrane-filtered sample after dissolution, C_0 (mmol/L) is the already dissolved background

Table 2 | Composition of synthetically precipitated chemical sludge

	Synthetic sludge
pH	7.5
Parameter	(mmol/L)
Total P	32.6
$\text{PO}_4\text{-P}$	0.3
Total Al	55.4
Dissolved Al	<0.00005

fraction in the homogenized sample (original sample) before treatment with H_2SO_4 , and C_{total} (mmol/L) is the total concentration of the element, including the dissolved and solid fraction, in the homogenized original sample.

RESULTS AND DISCUSSION

Dissolution of phosphorus and aluminum from sludge samples

The concentrations of $\text{PO}_4\text{-P}$ and Al, in mmol/L, of all investigated sludge samples in the pH range between 7.5 and 2.0 are shown in Figure 1. The calculated dissolution efficiency of $\text{PO}_4\text{-P}$ and Al, in %, of all tested sludge samples is presented in Figure 2.

For all sludge types, concentrations of $\text{PO}_4\text{-P}$ in the homogenized samples at pH 7.5 were measured below 1.5 mmol/L, with the lowest concentration in the post-precipitated tertiary sludge (0.1 mmol/L). The probability of a significant spontaneous dissolution of $\text{PO}_4\text{-P}$ after chemical P elimination during the wastewater treatment process is considered to be low. In the neutral pH range, AlPO_4 has a low solubility defined by the equilibrium constant $\log K = -21$ (Stumm & Morgan 1996), corresponding to 1.38×10^{-8} g/L (Kotz & Treichel 1999). If biological P elimination takes place simultaneously, $\text{PO}_4\text{-P}$ can be released during anaerobic treatment of the sewage sludge because the polyphosphate accumulating organisms tend to release phosphate spontaneously under anaerobic conditions through their metabolic activity (Baumann 2003).

Between pH 5 and 4 the synthetic- and post-precipitated tertiary sludge did not show any significant release of $\text{PO}_4\text{-P}$. The dissolved P in the homogenized samples was below 1%. Even down at pH 3 the synthetic sludge did not show any

significant changes for $\text{PO}_4\text{-P}$ dissolution. Here a $\text{PO}_4\text{-P}$ dissolution efficiency of about 3% was observed.

In the post-precipitated tertiary sludge at pH 3.5 and pH 3.0, 15% and even 85% $\text{PO}_4\text{-P}$ was released. This corresponds to approximately 6 mmol/L and approximately 34 mmol/L of released $\text{PO}_4\text{-P}$, respectively. The highest dissolution efficiency of about 93% was observed at pH 2. A low $\text{PO}_4\text{-P}$ release of approximately 7% was observed in the anaerobically digested sludge at pH 5. At pH 3 the dissolution rate in anaerobically digested sludge was approximately 30%, whereas at pH 2 about 90% $\text{PO}_4\text{-P}$ was released. All three investigated sludge samples showed a dissolution rate of $\text{PO}_4\text{-P}$ of approximately 90% at pH 2, but the dissolution efficiency along the pH spectrum was different (Figure 2). The results obtained in this work comply with data from literature, in which dissolution efficiency of about 90% at $\text{pH} < 2.0$ was reported (Güney *et al.* 2008; Meyer *et al.* 2018).

The curves of Al dissolution in the investigated sludge samples follow a similar trend as the $\text{PO}_4\text{-P}$ dissolution curves (Figure 2). This is related to the application of the Al salts used for P elimination at the WWTP. A significant leaching of Al in the synthetic and anaerobically digested sludge at pH 3 was not observed, whereas at pH 2.5 more than 50% of Al was released in both sludge samples. The molar concentrations were about 30 mmol/L in the synthetic sludge at pH 2.5 and about 23 mmol/L in the anaerobically digested sludge. At pH 2, 44 mmol/L was measured in the synthetic and 25 mmol/L in the anaerobically digested sludge. This corresponds to a dissolution rate of about 80 and 70%, respectively. Similar dissolution behavior has been found in literature. A significant release of Al from anaerobically digested sludge is reported for pH values < 3 (Meyer *et al.* 2018). At $\text{pH} < 2.0$ Weideler *et al.* (2020) indicates Al-dissolution $> 90\%$ (Weideler *et al.* 2020).

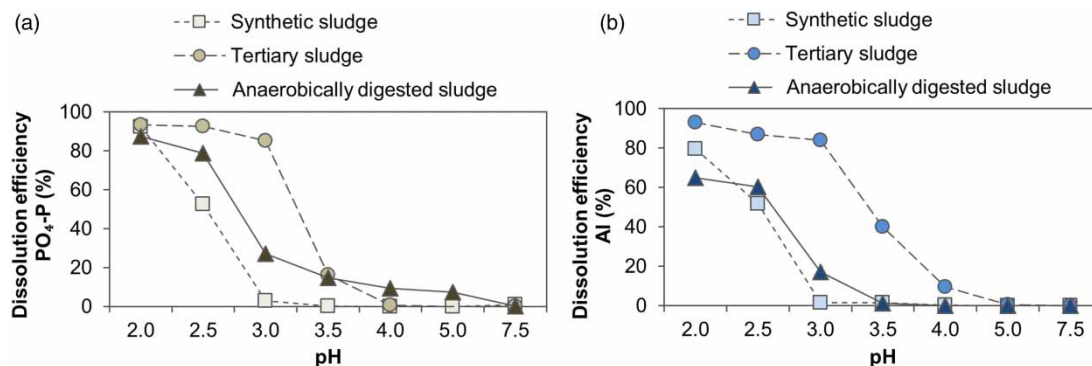


Figure 2 | Dissolution efficiency (%) of (a) phosphorus and (b) aluminum from synthetic, post-precipitated tertiary and anaerobically digested sludge.

The leaching behavior of the post-precipitated tertiary sludge was untypical. The high release of Al (40%) at pH 3.5 was not expected considering the relatively low solubility of AlPO_4 (variscite) at this pH (Stumm & Morgan 1996, p. 407). Various reasons were given for this phenomenon. First, the over-stoichiometric ratio $\text{Al/P} \approx 4$ during $\text{PO}_4\text{-P}$ precipitation could have an influence. The high stoichiometric ratio was necessary to overcome the thermodynamic and kinetic limitations of the chemical reaction due to the low $\text{PO}_4\text{-P}$ concentration in the pre-treated wastewater (Mayer *et al.* 2013). Low phosphate concentrations are unfavorable for the P precipitation process due to the slow reaction rate. This can be compensated with higher dosage of Al salt to accelerate the process kinetics and improve the P precipitation efficiency. The overdosed Al was probably adsorbed onto the organic substances in the wastewater (e.g. humic substances), which might have caused the earlier release during acidification. The humic substances contain different functional groups and are generally negatively charged, therefore they have a high affinity for the adsorption of metal ions (Murano *et al.* 2018; Zhang *et al.* 2019). The consumption of coagulants is always higher for post-precipitation than for simultaneous precipitation of $\text{PO}_4\text{-P}$ to ensure sufficient flocculation for P elimination (Maher *et al.* 2015). On the other hand, during chemical P precipitation with Al-salts, in addition to AlPO_4 , the formation of Al(OH)_3 may occur, which could be responsible for this Al-leaching behavior. As a result of the acidic treatment, both Al compounds are dissociated, where Al is released from the Al(OH)_3 compound at a higher pH compared to the AlPO_4 compound (Xu *et al.* 2018).

Figure 3 shows the molar ratios of Al/P in synthetic, post-precipitated tertiary and anaerobically digested sludge in the original homogenized sample and in the leached permeate of the acidified sample at pH 2 for comparison. During the preparation of the synthetic sludge AlCl_3 was

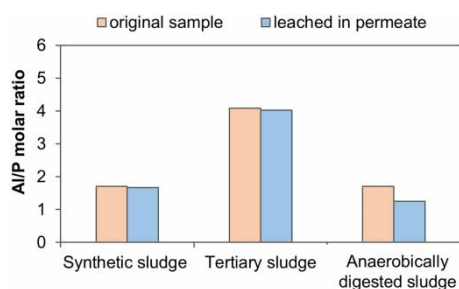


Figure 3 | Molar ratios of Al/P in the original homogenized sample (pH 7.5) and in the leached permeate at pH 2.0 for synthetic, tertiary and anaerobically digested sludge.

added in a theoretical stoichiometric ratio to $\text{PO}_4\text{-P}$ of $\text{Al/P} = 1.5$. However, the measured concentrations showed a slightly higher actual stoichiometric ratio of $\text{Al/P} = 1.7$. The deviation from the original value could be due to analytical and statistical errors during the experimental process. At pH 2 the starting molar ratio $\text{Al/P} = 1.7$ of the original sample was obtained in the leached permeate of the synthetic sludge (Figure 3). This indicates an almost complete dissolution of $\text{PO}_4\text{-P}$ and Al. The calculated molar ratio in the original homogenized tertiary sludge sample was $\text{Al/P} = 4.1$. After acid treatment at pH 2, the initial stoichiometric ratio was almost reached ($\text{Al/P} = 4.0$). The anaerobically digested sludge had a molar ratio $\text{Al/P} = 1.3$ at pH 2, which was slightly lower than the stoichiometric initial ratio $\text{Al/P} = 1.7$ of the original sample. A high stoichiometric ratio at pH 2 indicates a high simultaneous dissolution of P and Al. Stoichiometric ratio >1 is necessary because during the simultaneous $\text{PO}_4\text{-P}$ precipitation in the aeration tank competing reactions take place. Often only AlPO_4 is formed, but other compounds such as Al(OH)_3 can sometimes be formed. Al can also form complexes with the constituents present in the sludge. Ideally, if the compound formed by chemical precipitation during $\text{PO}_4\text{-P}$ elimination is AlPO_4 , the theoretical stoichiometric ratio Al/P after acidification at highly acidic pH should be close to 1. All literature sources concluded that in the acidic range the most significant $\text{PO}_4\text{-P}$ dissolution occurs between pH 2 and 3 (Güney *et al.* 2008; Weideler *et al.* 2010; Meyer *et al.* 2018; Toor & Kim 2019). This is in compliance with the results obtained in this study. However, it should be noted that the composition of the sludge and the operation of the treatment plant play an important role in the leaching efficiency of P and Al from the sludge.

Dissolution of Fe and Ca from sludge samples

The acidic leaching of sludge may lead to the dissolution of other elements besides P and Al, such as Fe and Ca (Petzet *et al.* 2012). Depending on the sludge composition, Mg and heavy metals may also be released (Quist-Jensen *et al.* 2018). In this work, the simultaneous dissolution of Fe and Ca in the post-precipitated tertiary and anaerobically digested sludge was also investigated. Studies with other sludges have shown that after P and Al, mainly Fe and Ca are leached from anaerobically digested sludge. The composition of different anaerobically digested sludges can be found in Figure S1 in the Supplementary material.

Post-precipitated tertiary sludges are considered chemical P sludges, i.e. in this case chemical Al-phosphate sludge. However, the investigations showed that the presence of Fe and Ca cannot be excluded, although the concentration of Fe in the tertiary sludge was very low (Table 1). The Fe and Ca concentrations (in mmol/L) in the original samples and leached permeates of tertiary and anaerobically digested sludge are shown in Figure 4. In addition, the dissolution efficiencies (%) for both Fe and Ca are plotted in Figure 5.

If not directly used in the wastewater treatment process, other potential sources of Fe and Ca can come from industrial production processes or occur naturally in the drinking water. It has to be mentioned that in Germany, the presence of Fe in the drinking water is limited to 0.2 mg/L by legislation (TrinkwV 2001).

For the post-precipitated tertiary sludge, the concentration of Fe in the homogenized sample was 0.7 mmol/L (Figure 4(a), left), whereas the dissolved part was negligible. The anaerobically digested sludge had a 3.7 mmol/L total Fe concentration in the homogenized sample, and already dissolved (as part of total Fe) was 0.1 mmol/L (Figure 4(a), right). Thus, the already dissolved Fe content in the anaerobically digested sludge was below 0.1%. The lower Fe

concentration in the tertiary sludge was probably due to the sludge formation in the last step of the wastewater treatment process. Most of the Fe has probably already been removed with the excess sludge from the wastewater treatment process. The higher Fe concentration in anaerobically digested sludge supports this assumption.

The dissolution of Fe in the spectrum pH 2.0–7.5 showed a similar behavior in both investigated sludge samples. At pH 5 about 10% and at pH 3.0 about 60% Fe were released in tertiary and anaerobically digested sludge (Figure 5(a)). At pH 3 this corresponds to 0.4 mmol/L Fe in tertiary sludge and 2.3 mmol/L in anaerobically digested sludge (Figure 4). More than 90% Fe was transferred in the soluble phase in the anaerobically digested sludge at pH 2, whereas the tertiary sludge revealed a lower dissolution of approximately 75% at the same pH value. This corresponded to a concentration of 0.5 mmol/L. The early leaching of Fe in both samples, already at pH 5, indicates the presence of Fe(II) compounds. Earlier research on the dissolution behavior of Fe in different sludge types showed that Fe(III)-phosphates are only transferred into solution at pH < 2. In contrast, Fe(II)-phosphates are already in solution at pH 5 (Monea *et al.* 2020). Although the P

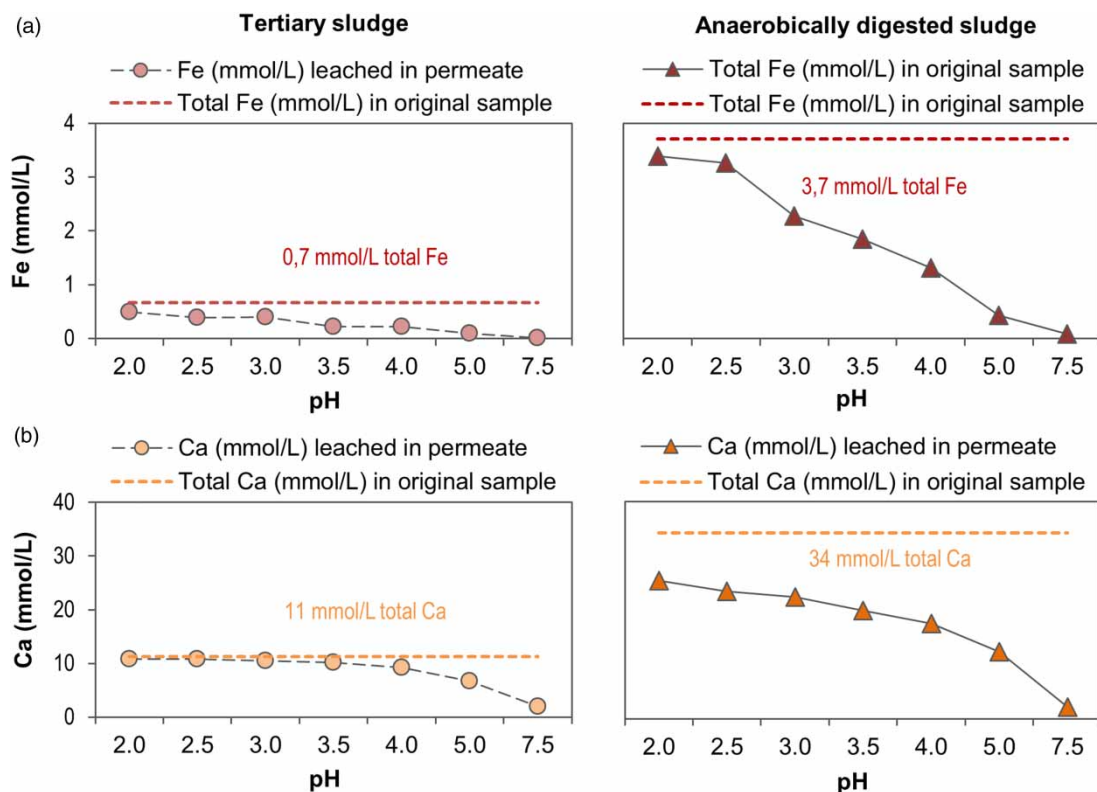


Figure 4 | Measured concentrations (mmol/L) in leached permeate and original sample of (a) Fe and (b) Ca in post-precipitated tertiary and anaerobically digested sludge.

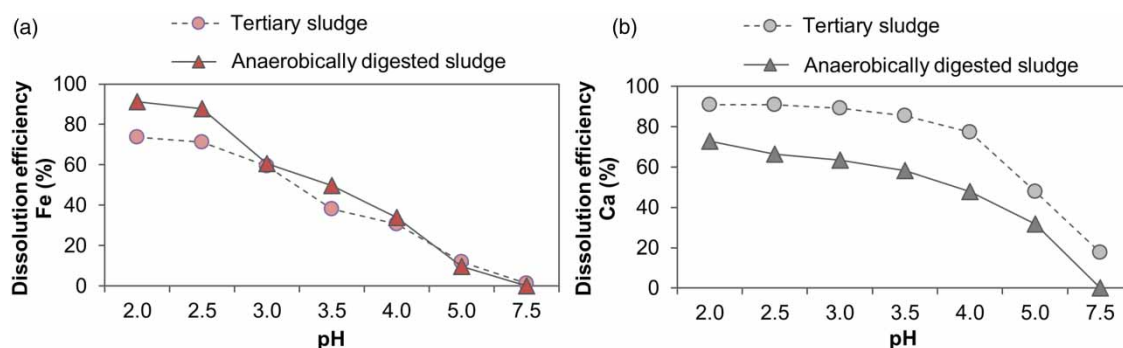


Figure 5 | Dissolution efficiency (%), of (a) Fe and (b) Ca from post-precipitated tertiary and anaerobically digested sludge.

elimination took place using Al salts, the formation of Fe-phosphate compounds cannot be excluded. Fe has a high biological importance by being an essential trace element for living organisms. In medicine, medications containing Fe are used to treat Fe deficiency. In the food industry, Fe is sometimes added to food. Thus, Fe can enter the WWTP via direct discharge through human excreta or through production processes. The Fe present in the wastewater is then incorporated into the sewage sludge. The Fe-reducing bacteria can reduce Fe(III) to Fe(II) compounds (Piepenbrock *et al.* 2014). As a result, Fe can be released during leaching with H_2SO_4 at higher pH values at pH 5. Nevertheless, it should be noted that the Fe concentrations measured in both sludge samples were lower than 4 mmol/L.

The concentrations (mmol/L) and dissolution efficiencies (%) of Ca for the investigated range pH 2.0–7.5 are shown in Figure 4(b), left and right, and Figure 5(b). In both sludge samples a similar curve was observed with respect to the Ca dissolution efficiency, whereas the post-precipitated tertiary sludge showed a higher dissolution rate than the anaerobically digested sludge throughout the whole pH spectrum. In the tertiary sludge at pH 5 approximately 50% Ca was already released, whereas the anaerobically digested sludge showed approximately 30% Ca dissolution. This corresponds to a Ca concentration of about 7 mmol/L and 12 mmol/L, respectively. The dissolution of Ca in tertiary sludge at pH 3 (approximately 90%) showed no significant difference to pH 2. In anaerobically digested sludge, 73% Ca ions were transferred to the soluble phase at pH 2, about 5% more compared to pH 3.0 (Figure 5(b)). This corresponds to a concentration at pH 2 of about 11 mmol/L in tertiary sludge and about 26 mmol/L in anaerobically digested sludge. Similar dissolution behavior of Ca has been observed in literature as a result of

acidic treatment. Weideler observed a significant release of Ca ions already at $\text{pH} \leq 5$ (Weideler 2010).

Due to the P elimination via addition of Al salts, it can be assumed that the Ca compounds found in the sludge are not in the form of Ca-phosphates. Nevertheless, the presence of Ca-phosphates cannot be excluded. Further possible Ca compounds can be Ca-sulphates or Ca-carbonates, where the main Ca source can be drinking water. The drinking water in Uhldingen is extracted from Lake Constance with a water hardness in the medium hardness range (CaCO_3 concentration 1.63 mmol/L); the water is supplied to the customers without previous softening. Industrial sources of Ca discharge are not excluded.

Ca-phosphates can be present in various forms in sewage sludge, including dicalcium phosphate dehydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, brushite), dicalcium phosphate anhydrate (CaHPO_4 , monetite), hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), or amorphous Ca-phosphate ($\text{Ca}_x\text{H}_y(\text{PO}_4)_z \cdot n\text{H}_2\text{O}$). The amorphous Ca-phosphates are more soluble than the crystalline phosphates (Valsami-Jones 2001; Dorozhkin 2010). Investigations in the medical field showed a high release of Ca ions at pH 6 (Rodgers *et al.* 2006). Other possible Ca compounds in the sludge, such as the Ca-carbonates, also show a good solubility at pH 5 (Kurdowski 2012).

Figure 6 compares the molar concentrations of $\text{PO}_4\text{-P}$ against the sum of Al, Fe, and Ca leached in the permeate at pH 2 for the tertiary and anaerobically digested sludge. In the tertiary sludge, the sum of Al, Fe, and Ca concentrations ($\sum \text{Al, Fe, Ca} = 164 \text{ mmol/L}$) was about 4.5 times higher than the molar concentration of $\text{PO}_4\text{-P}$ (37 mmol/L). In comparison, for the anaerobically digested sludge this ratio was lower, i.e. $\sum \text{Al, Fe, Ca} / \text{PO}_4\text{-P} = 2.7$. Thus, it becomes evident that the sum of Al, Fe, and Ca in the tertiary sludge was about three times higher than in the anaerobically digested sludge. Nevertheless, the highest portion of the three metals was for Al, due to the necessary

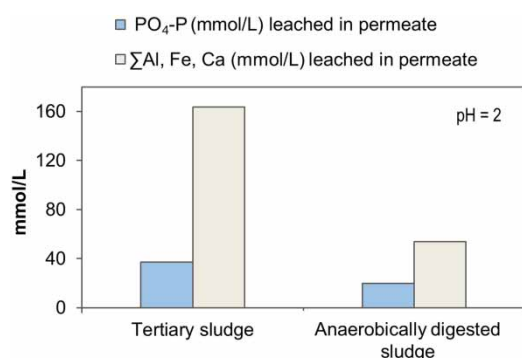


Figure 6 | Comparing the molar concentrations of PO₄-P against the sum of metals (ΣAl, Fe, and Ca) leached in the permeate at pH 2 for post-precipitated tertiary and anaerobically digested sludge.

over-stoichiometric dosing for P elimination after the secondary clarifier.

The molar PO₄-P concentration was lower than the concentration of the sum of Al, Fe, and Ca for both sludge samples. This indicates that the investigated metals were not introduced into the wastewater as a result of the chemical P elimination. Other research has shown that the acidic leaching of sewage sludge generated from EBPR also leads to metals dissolution (Weideler et al. 2010).

Phosphorus recovery potential as struvite from post-precipitated tertiary and anaerobically digested sludge and full-scale implications

The P content in relation to DM was 1.5 times higher in the tertiary sludge than in the anaerobically digested sludge (Table 1). The tertiary sludge contained 5.0% P DM while the anaerobically digested sludge had 3.2% P DM. Therefore, it is theoretically possible to recover more P from the post-precipitated chemical sludge than from the mixed biomass/chemical anaerobically digested sludge.

P recovery in the form of struvite after acidic leaching of digested sewage sludge has already been successfully tested on a pilot-scale in the 'Stuttgart process', achieving a P precipitation rate >95% in the final struvite product (Meyer et al. 2018). With a 90% P dissolution and 95% P precipitation efficiency, it would theoretically be possible to recover 8.7 kg struvite per m³ of post-precipitated tertiary sludge. Under the same assumptions, about half of this P may be recovered from the anaerobically digested sludge, i.e. 4.6 kg struvite per m³ sludge. The detailed calculation of the struvite precipitation mass balance can be found in the Supplementary material. Thus, in the context of P recovery, it would be meaningful to change the WWTP

operation to P elimination via chemical post-precipitation after the secondary clarification step. Nevertheless, it must be taken into account that in the struvite (magnesium ammonium phosphate) precipitation process, the reaction partner NH₄-N is not present in large enough quantities in the effluent wastewater, i.e. in the tertiary sludge (Table 1) to achieve high P precipitation efficiency through the struvite formation. Therefore, the external addition of NH₄-N is indispensable. A possible on-site alternative source of NH₄-N could be the ammonium-rich internal flows at the WWTP, such as the sludge dewatering centrate. Moreover, external addition of Mg would be necessary for both sludges considered in this work.

The proportion of metal ions present in the leached permeate also plays an important role for the formation and purity of the struvite crystals. In the 'Stuttgart process', metal ions are complexed with citric acid (C₆H₈O₇) to avoid possible metal co-precipitation in the final product (P recycle in the form of struvite). Citric acid is added in a stoichiometric ratio of 1 to the sum of the metals Al, Fe, Ca (C₆H₈O₇/ΣAl, Fe, Ca = 1). This means that higher amounts of citric acid for metals complexation would be necessary for the treatment of tertiary sludge compared to anaerobically digested sludge. From an economic point of view, citric acid is more expensive than the other resources used in the P recovery process (Meyer et al. 2018).

The replacement of citric acid with a cheap and equally effective alternative complexing agent would make the process more economically viable. Nevertheless, there is still a need for further research of this aspect. It is important to mention that pH is one of the key parameters for efficient struvite precipitation. Based on numerous studies published so far, the most beneficial pH for struvite precipitation is in the range pH 8–9 (Desmidt et al. 2013; Munir et al. 2017, 2019; Meyer et al. 2018). Another possibility for P elimination and simultaneous P recovery from leached permeate of post-precipitated tertiary sludge is the use of selective ion exchangers. A good example is the use of composite magnetic particles coated with a P-selective ZnFeZr sorbent, which can reversibly adsorb phosphate, desorbed it using an alkaline solution and then recover it as struvite or other phosphate-containing fertilizers (Drenkova-Tuhtan et al. 2017).

H₂SO₄ consumption for the P leaching from the various sludge types

The results regarding the consumption of 37 wt% H₂SO₄ as a function of the target pH and of the achieved PO₄-P, Al,

Fe, and Ca molar concentrations, are summarised in Figure 7.

The H_2SO_4 consumption for pH adjustment was dependent on the type of sludge. In the case of the synthetic sludge, 5.8 mmol/L H_2SO_4 was required for acidification to pH 5, while the anaerobically digested sludge consumed 12 times more acid (72.3 mmol/L) to reach the same pH (Figure 7(a)). This can be explained with the different buffer capacities of the sludge (Quist-Jensen et al. 2018). During the addition of acid to the anaerobically digested sludge, foaming could also be observed due to degassing of CO_2 . An additional 1 h leaching time was needed to reach pH 5 compared to the synthetic and post-precipitated tertiary sludge.

The acid consumption of the tertiary sludge at pH 3 was notable (200 mmol/L), and was 11 times more than for the synthetic sludge and about twice as much as for the anaerobically digested sludge. The highest H_2SO_4 consumption,

however, was observed for the tertiary sludge at pH 2, approximately 234 mmol/L. The reason for this is probably the high stoichiometric ratio $\text{Al}/\text{P} \approx 4$. In contrast, approximately 150 mmol/L H_2SO_4 was required for the synthetic sludge and approximately 76 mmol/L for the anaerobically digested sludge.

The release of $\text{PO}_4\text{-P}$, Al, Fe, and Ca (in mmol/L) as a function of the dosed amount of H_2SO_4 is shown in Figure 7(b)–7(e), respectively. In the case of synthetic sludge, approximately 80 mmol/L of H_2SO_4 (pH 2) caused the release of ~ 30 mmol/L of $\text{PO}_4\text{-P}$ and ~ 40 mmol/L of Al. This corresponds to a dissolution efficiency of over 80% for both parameters. In contrast, the anaerobically digested sludge required a higher H_2SO_4 consumption, ~ 150 mmol/L (pH 2), for the release of ~ 20 mmol/L $\text{PO}_4\text{-P}$ (leaching efficiency $\sim 90\%$) and ~ 25 mmol/L Al (leaching efficiency $\sim 70\%$). The highest H_2SO_4 consumption was observed for the tertiary sludge: ~ 230 mmol/L

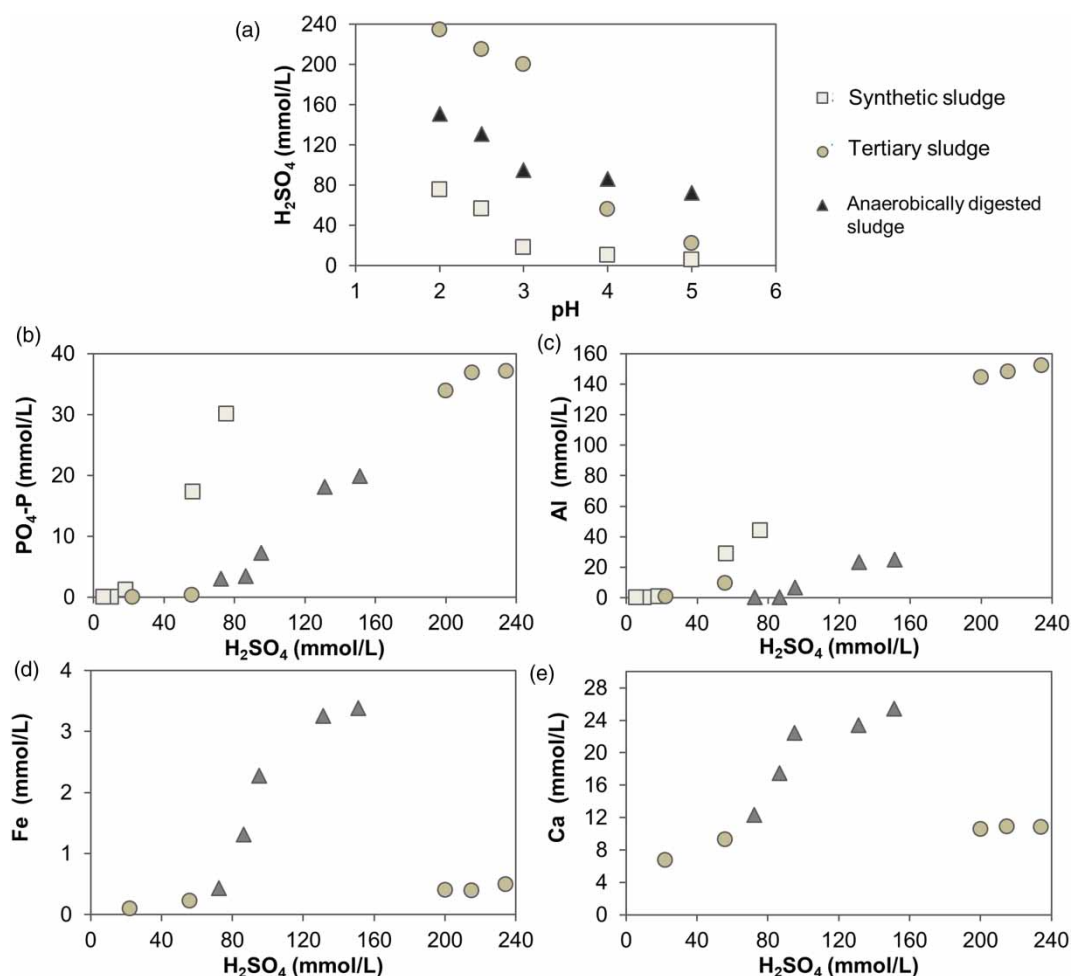


Figure 7 | H_2SO_4 (37 wt%) consumption as a function of (a) target pH value and achieved molar concentrations of (b) $\text{PO}_4\text{-P}$, (c) Al, (d) Fe, and (e) Ca.

acid was required to transfer ~90% PO₄-P (37 mmol/L) and ~90% Al (152 mmol/L) into the dissolved phase.

In summary, it should be noted that the highest specific H₂SO₄ consumptions were observed in the treatment of tertiary sludge.

CONCLUSIONS

This work investigated the P dissolution of Al-containing sludges (post-precipitated tertiary sludge, anaerobically digested sewage sludge, and synthetically precipitated chemical sludge) in the pH range of 2.0–7.5 using H₂SO₄ (37 wt%). The simultaneous leaching of Al, Fe, and Ca was also considered. In addition, the H₂SO₄ consumption was analyzed in detail as a function of the target pH for dissolution. The theoretical P recovery potential from tertiary sludge versus anaerobically digested sludge was also compared.

The optimal pH for the leaching of PO₄-P depended strongly on the composition of the sludge. For sludges containing mainly AlPO₄, a pH < 3 is recommended for the dissolution of PO₄-P. More than 60% of Al and >70% of Fe and Ca were released at pH 2.

For P recovery in the form of struvite, Mg had to be added as an external source, whereas NH₄-N was required as an external addition to the tertiary sludge.

At pH 4, the highest consumption of H₂SO₄ was for the leaching of the anaerobically digested sludge. In contrast, at pH 2 the highest H₂SO₄ requirement was observed in the case of tertiary sludge.

Nevertheless, it should be taken into account that the post-precipitated tertiary sludge has a more compact volume compared to anaerobically digested sludge and, with regard to P release, could offer a higher P yield.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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