

Comparative Evaluation of Pre-treatment Methods to Enhance Phosphorus Release from Digestate

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Abstract This paper aims to evaluate various pre-treatment methods to improve the release of phosphorus (P) in the liquid fraction after solid–liquid separation of digestate (input: (dairy) manure and organic biological by-products provided by the food industry). As such, the P recovery potential from the liquid fraction as concentrated fertilizer product can be increased, whereas soil organic carbon can be maintained through local recycling of the resulting thickened fraction. Four different mechanical pre-treatments (microwave heating, conventional heating, ultrasonic treatment, and orbital shaking) were tested in combination with the chemical dosing of three different acids (citric acid, formic acid, and HCl) down to pH 4, 5, and 6. The pre-treatments released 13–28 % soluble ortho-P relative to total P. When balancing the recovery efficiency with the acid costs, the addition of HCl down to pH 4 under microwave heating was most feasible. Nevertheless, if no pasteurization is required for fertilizer marketing,

then orbital shaking (mixing in practice) with HCl addition may be more attractive.

Keywords Anaerobic digestion · Bio-based fertilizers · Nutrient recovery · Residuals management · Struvite · Waste (water) treatment

Introduction

The recovery and efficient use of phosphorus (P) has become an important challenge in light of natural P resources that are rapidly depleting and the increasingly strict legislative standards for P application to agricultural soils. The latter results from the observed P accumulation in many soils worldwide caused by excessive manure (and sludge) application. Previous field studies have shown that the P use efficiency (PUE) in animal manure may be increased through anaerobic (co-)digestion [25, 26, 28]. Indeed, during digestion, struvite precipitation may occur, as well as calcium (Ca) and magnesium (Mg) phosphate formation, which both end up in the digestate, thereby improving its slow-release properties [9, 10]. However, due to legislative constraints, processing of digestate is required (especially in high-nutrient regions) in order to obtain exportable end products, concentrated mineral fertilizers (=chemical fertilizer substitutes), or environmentally neutral compounds.

As such, current digestate processing practices mostly involve a solid–liquid separation step. In P saturated regions, the thickened fraction is then transformed into an organic end product fit for export, and hence valuable nutrients (P, Ca, Mg) and organic carbon (OC) are eliminated from the local agricultural cycle [27]. As a consequence, soil organic carbon depletion has become an

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important issue worldwide [1, 17]. This leads to the suggestion to enhance the release of soluble orthophosphates (i.e. inorganic soluble $\text{PO}_4\text{-P}$) in the liquid fraction during solid–liquid separation (after or prior to digestion) in order to obtain: (1) a stabilized carbon-rich soil conditioner with increased local marketing potential, and ii) a P-rich liquid fraction with increased potential for P recovery as high-purity struvite, Ca/Mg–P precipitates, or a concentrated P-solution. A local market for the latter products may exist in the horticultural sector, for crops with high P demand, and/or for industrial purposes.

Methods that have been used to improve the P release from (digested) manure and/or sludge mainly consist of microwave heating, advanced oxidation, and acidification to around pH 4 [3, 11, 13, 14, 21, 31, 32]. Microwave heating would help in digesting organic P and polyphosphates, i.e. salts or esters of polymeric oxyanions formed from tetrahedral PO_4 , that are often available in animal manure [14, 21]. However, Pan et al. [20] have shown that additional acidification is required in order to effectively improve the P release from dairy manure, which is not the case for sewage sludge [15]. Acidification followed by solid–liquid separation concerns a potential low-cost option to concentrate P ions in the liquid fraction for direct use in the horticultural sector as concentrated P-solution, or for subsequent precipitation as pure struvite or Ca/Mg–P precipitates. Both organic acids, such as citric acid [24] and formic acid [4], and mineral acids, as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) [19, 24], have been used for this purpose.

Although the potential of some of the above techniques to improve the P release in the liquid fraction has already been shown at lab-, pilot-, and even full-scale (e.g. acidification of digested sludge in the Seaborne process; [19], limited research comparing (combinations of) various pre-treatment methods for P release has been conducted to date, definitely not for the treatment of digestate. As such, the application of efficient and cost-effective pre-treatments is still limited, as there is no common basis comparing the P release efficiency in relation to the costs of the pre-treatment methods involved. Moreover, on top of the above methods, ultrasonic treatment is gaining importance to improve the bio-degradability and/or dewatering of manure or sludge [22, 30]. Also conventional heating is often applied for product (digestate/manure/sludge) pasteurization [22, 27]. Nevertheless, studies on the P release when applying these pre-treatments (whether or not in combination with acidification) are lacking in literature, though relevant because of their increasing use.

This paper aims to compare (combinations of) promising pre-treatment methods (acidification + mechanical treatment) to improve the P release from digestate. The selected mechanical pre-treatments involve microwave

heating, conventional heating, ultrasonic treatment, and orbital shaking (i.e. mixing in practice), whereas the chemical pre-treatments concern the addition of the organic acids, citric acid and formic acid, and the mineral acid, HCl. The heat treatments were applied so as to respect the European standards for product pasteurization, i.e. 1 h heating at 70 °C according to the regulation EG 1069/2009 (formal 1774/2002; [5, 6]). A comparative economic evaluation of the various treatments based on the chemical cost as function of the P release efficiency is also presented.

Materials and Methods

Experimental Set-up

Digestate (20 L) was collected at Wittevrongel Eneco Energy, Aalter, Belgium, and transported to the laboratory within 1 h, carried in cooler boxes filled with ice. It concerns a mesophilic (35 °C) anaerobic (co-)digestion plant (capacity: 60,000 ton y^{-1} , 3.033 MW_{el}), with an input feed mainly consisting of (dairy) manure, additionally supplied with organic biological by-products provided by the food industry (percentage depends on the availability). The sample was stored at a temperature of 4 °C before use. Prior to the pre-treatment, the digestate was homogenized and physicochemically analyzed as described in “Physicochemical analysis” section. The product characteristics are given in Table 1.

Table 1 Physicochemical characteristics of the digestate used for the various pre-treatments (mean \pm standard deviation; $n = 2$)

Parameter	Value
pH	7.8 \pm 0.0
EC (mS cm^{-1})	30 \pm 0
Density (g L^{-1})	1047 \pm 5
Dry weight (%)	7.4 \pm 0.0
OC (% on DW)	31 \pm 0
Alkalinity ($\text{g HCO}_3 \text{L}^{-1}$)	17 \pm 0
Total P (mg L^{-1})	422 \pm 24
Soluble ortho-P (mg L^{-1})	48 \pm 7
Inorganic P (mg L^{-1})	244 \pm 12
Organic P (mg L^{-1})	178 \pm 31
$\text{NH}_4\text{-N}$ (g L^{-1})	3.0 \pm 0.0
Total Ca (mg L^{-1})	338 \pm 80
Total Mg (mg L^{-1})	117 \pm 10
Total K (g L^{-1})	4.5 \pm 0.0
Total Na (g L^{-1})	2.3 \pm 0.1

DW dry weight, EC electrical conductivity, OC organic carbon

An overview of the experimental set-up can be found in Fig. 1.

Homogenized subsamples were taken for pre-treatment. Four mechanical pre-treatments were used, each in combination with three different acids and adjusted to three different pH values (4, 5, and 6). For each treatment, 5 g of digestate was weighted on an electronic balance (CP8201, Sartorius, Göttingen, Germany) and 30 mL of milli-Q (i.e. ultrapure) water was added to the sample. The latter was necessary for correct pH-adjustment and to avoid foaming. The samples were adjusted to pH 4, 5, and 6 by addition of the acid (2 M) using a micropipette and a pH-meter, during continuous stirring on a magnetic stirrer (Cenco Instruments b.v., Breda, the Netherlands). The amount of acid required was recorded. In addition, for each treatment, a control (=no acid addition) was prepared, resulting in a total of 48 different pre-treatments (4 mechanical treatments, 3 acids, 3 pH-values, 12 controls). All pre-treatments were prepared in triplicate (=total of 144 treatments).

For the microwave and conventional heating pre-treatments, the samples were weighted before and after the treatments. The water lost through evaporation was added to each sample. All treated samples were transferred to centrifuge tubes (45 mL) and decanted using a laboratory centrifuge (Heraeus megafuge 1.0, Kendro Laboratory Products, Hanau, Germany) at 3000 rpm for 1 min. The liquid fractions were separated from the solid fractions, filtered through 0.45 μm pores, diluted with distilled water in 50 mL volumetric flasks, and manually transferred to test tubes for physicochemical analysis of soluble ortho-P (“Physicochemical analysis” section).

Organic acids (formic acid, 90 % CH_2O_2 and citric acid, 100 % $\text{C}_6\text{H}_8\text{O}_7$, each 2 M) and mineral acid (hydrochloric acid, 37 % HCl , 2 M) were used. These chemicals were applied to the digestate samples to adjust the pH down to 4, 5, and 6 before using the mechanical pre-treatments. The duration and temperature of the mechanical pre-treatments

that involve heat were chosen in line with the European requirements for product pasteurization, i.e. 1 h heating at 70 °C or a proven equivalent [5, 6]. As such, the subsequent recovered products (concentrated P-solution, struvite, or Ca/Mg–P precipitates) could be recognized as a valuable chemical fertilizer substitute for horticultural purposes (strict hygienic requirements) and/or for export. Also the remaining organic thickened fraction is pasteurized in this way. The following mechanical pre-treatments were applied:

1. A time-controlled orbital shaker (GFL 3015, Gesellschaft für Labortechnik mbH, Burgwedel, Germany): All samples were shaken at 200 rpm during 60 min in 250 mL erlenmeyer flasks;
2. A conventional heating plate (HT22, Harry Gestigkeit GmbH, Düsseldorf, Germany): The temperature was adjusted to 70 °C and the power was adjusted to 100 W to maintain a constant temperature. The samples were treated for 60 min in an erlenmeyer flask;
3. A temperature-controlled ultrasonic bath (Bandelin Electronic 12207, Berlin, Germany), with a basket to keep the samples away from the tank base: The basket was filled with distilled water up to the minimum water requirement for use (± 15 cm water height). The temperature was adjusted to 25 °C (no heat treatment) and the samples were treated for 15 min in 100 mL erlenmeyer flasks;
4. A microwave oven (CEM MARS 5, Drogenbos, Belgium): It includes an open microwave digester, equipped with a rotating microwave diffuser for homogenous microwave distribution. The system is capable of accommodating up to 36 volumetric flasks at one run. Centrifuge tubes of 45 mL were used, consisting of a control cap with a vent tube. A temperature sensor was inserted through a hole on top of the microwave oven into the sealed tubes. The

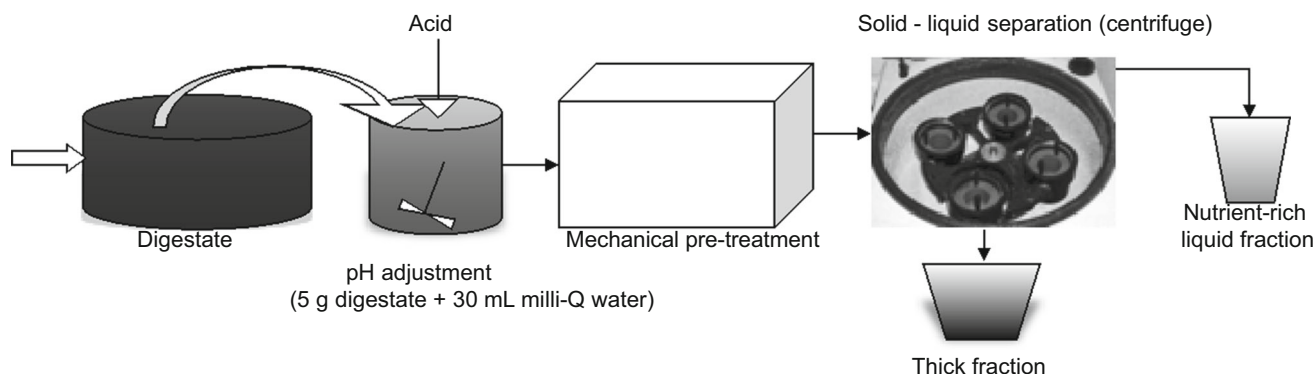


Fig. 1 Overview of the experimental set-up for pre-treatment (acidification + mechanical treatment) of digestate to improve the P release efficiency in the liquid fraction after solid–liquid separation

temperature was fixed at 70 °C and the power output was adjusted to 600 W to maintain a constant temperature. The samples were treated for 1 h.

Note that these treatments can be applied on liquid waste streams both prior or after anaerobic digestion. In this study, it was aimed to test the treatments on the non-degraded digestate. This is of increasing interest as the thickened fraction after pre-treatment and solid–liquid separation can (partially) be fed back into the anaerobic digester for further improved degradation and organic waste stabilization [16]. Indeed, during anaerobic digestion only a part of the available organic matter is transformed into biogas. The digestate hence still contains a large fraction of organic matter that potentially can be converted. By application of a disintegration technique (pre-treatments above) on the digestate and subsequent recirculation to the digester, the overall degradation potential could be significantly increased, while reactor dimensions can be reduced and a more stabilized soil conditioner is obtained [16, 19, 23]. All this may come on top of the potential improved P recovery when applying a pre-treatment. Yet, important is the finding of Jin et al. [14] that H₂SO₄-based pre-treatments result in a low anaerobic digestability due to sulfur (S) inhibition, unlike HCl. Moreover, it leads to high concentrations of hydrogen sulfide (H₂S) in the biogas, which are unwanted in terms of corrosion risks in subsequent piping and equipment. H₂S is also highly toxic to humans, even at low concentrations, and odorous when escaping from the system. Therefore, HCl was selected as mineral acid for the purpose of this study.

Physicochemical Analysis

The DW content was determined as residual weight after 72 h drying at 80 °C in an oven (EU 170, Jouan s.a, Saint Herblain, FR). Organic carbon (OC) was determined after incineration of the dry samples during 4 h at 550 °C in a muffle furnace (Nabertherm, Lilientahl, DE). The loss of ignition (=weight loss after incineration) was divided by a conversion factor of 1.72 to calculate OC, hence assuming that organic matter contains 58 % OC [29]. Electrical conductivity (EC) and pH were determined potentiometrically using a WTW-LF537 (Wissenschaftlich Technischen Werkstätten, Weilheim, DE) electrode and an Orion-520A (Orion Research, Boston, USA) pH-meter, respectively. Ammonium (NH₄) was determined using the Kjeltec-1002 distilling unit (Gerhardt Vapodest, Königswinter, DE) after addition of magnesium oxide (MgO) to the sample and subsequent titration [29]. The initial total P content in the digestate sample was determined using the colorimetric method of Scheel (1936; [29] after wet digestion using nitric acid (HNO₃) and hydrogen peroxide (H₂O₂). The

initial amount of inorganic P was determined by the method of Møberg and Petersen [18], while organic P was computed by the difference between total P and inorganic P. Soluble ortho-P was analyzed using the method of Scheel (1936) in the liquid fraction after centrifugation and filtration (0.45 µm pores). The absorbance at 700 nm of samples and standards was determined using a Jenway 6400 spectrophotometer (Barloworld Scientific T/As Jenway, Felsted, UK). Total calcium (Ca), magnesium (Mg), and potassium (K) were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista MPX, Palo Alto, CA, USA; [29] after wet digestion in HNO₃ and H₂O₂. Bicarbonate (HCO₃⁻) alkalinity was determined by the titration method described by Van Ranst et al. [29].

Statistical Analysis

Statistical analyses were conducted using SAS 9.3. A one-way ANOVA model ($\alpha = 0.05$) was used to compare the effect of the various pre-treatments (i.e. the independent variable, between-groups factor) on the amount of P released (i.e. the dependent variable). For each mechanical treatment, significant differences between the three applied acids were evaluated per pH value. Moreover, for each acid used, the effect of the mechanical pre-treatment was checked at each pH value under study. The condition of normality was verified using the Kolmogorov–Smirnov test and QQ-plots, whereas equality of variances was checked with the Levene Test. When homoscedascity was found, significance of effects was tested by use of an *F* test and post hoc pair-wise comparisons were conducted using Tukey's honestly significant difference (HSD) test ($\alpha = 0.05$). When no homoscedascity was found, a Welch *F* test combined with a post hoc Games-Howell test was used ($\alpha = 0.05$). When the condition of normality was not fulfilled, the non-parametric Kruskal–Wallis test was applied instead of the one-way ANOVA.

Results

Acid Requirements

The amount of acid (mol L⁻¹ digestate) required to reach pH 4, 5, and 6 is presented in Fig. 2. The initial pH of the solution (5 g digestate + 30 mL milli-Q water) was about 8.3.

It can be seen that for the same amount of acid, the obtained pH decreased from formic acid to HCl and citric acid. Hence, the amount of acid needed to obtain a certain pH increased reversely.

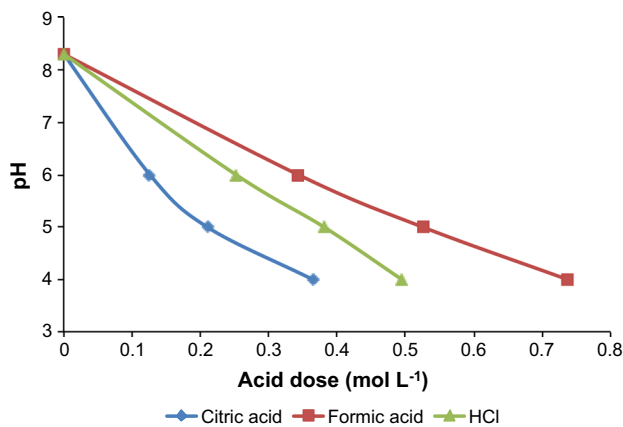


Fig. 2 Amount of acid (citric acid, formic acid, HCl) used (mol acid L⁻¹ digestate) to reach the required pH (4, 5, or 6) for the pre-treatment. Initial pH (5 g digestate + 30 mL milli-Q water) = 8.3

Orthophosphate Release

The amount of orthophosphate released from digestate (mg P L⁻¹) as function of the pre-treatment is presented in Fig. 3. The ortho-P release without any pre-treatment (no mechanical treatment and no acidification) was 48 ± 7 mg L⁻¹ or about 11 % of the initial total P (Table 1). Especially for the microwave and conventional heating pre-treatments, occasionally large standard deviations on the results were obtained. These can be attributed to dilution errors when adding water to replace water lost through evaporation (see “[Experimental set-up](#)” section).

All pre-treatments resulted in a significant effect ($p < 0.05$) on the ortho-P release as compared to the control (no acid addition) and to the untreated digestate, except for orbital shaking in combination with HCl and formic acid at pH 6. Citric acid generally released more soluble ortho-P ions into the liquid fraction as compared to the other acids, which was significant ($p < 0.05$) at pH 6 for all mechanical pre-treatments and at pH 5 for microwave treatment, orbital shaking, and conventional heating. At pH 4, no significant differences ($p > 0.05$) between the different acids per mechanical treatment were found, except for orbital shaking, where the use of citric acid again resulted in the highest ortho-P release. For the ultrasonic treatment, the use of formic acid also resulted in a significantly higher ortho-P release as compared to HCl at pH 6.

Using the same molar concentration of acid (hence the same pH) for all mechanical pre-treatments, no statistically significant difference ($p > 0.05$) between the mechanical pre-treatment methods in releasing soluble ortho-P ions was found with citric acid. For formic acid at pH 6, the ultrasonic treatment showed a significantly higher P release than all other mechanical pre-treatments, while conventional heating also released significantly more P than

orbital shaking. These effects disappeared at lower pH values. At pH 4, the microwave treatment showed a significantly higher P release than orbital shaking. No other significant differences between the various mechanical pre-treatments at pH 4 and 5 were observed using formic acid. The P release for HCl at pH 6 was significantly higher for conventional heating and ultrasonic treatment as compared to the microwave treatment, which showed significantly higher values than orbital shaking. Nevertheless, these effects disappeared at lower pH values, and at pH 4 the microwave treatment showed again a significantly higher effect than all other mechanical pre-treatments under study.

For each mechanical pre-treatment, the maximum obtained ortho-P release (mg L⁻¹) using the different acids can be derived from Fig. 3. Interestingly, for citric acid under microwave and conventional heating pre-treatments, the maximum amount of ortho-P released was found at pH 5. For the other acids, the maximum release was found at pH 4, independently of the mechanical treatment. The highest average ortho-P release was found for the combination of citric acid and microwave treatment at pH 5 (143 ± 26 mg L⁻¹), which was comparable to that of HCl and microwave treatment at pH 4 (133 ± 12 mg L⁻¹). The maximum obtained ortho-P release with formic acid was in average slightly lower, i.e. 117 ± 6 mg L⁻¹ under microwave heating at pH 4.

Discussion

All physicochemical pre-treatments used resulted in higher concentrations of soluble ortho-P ions in the liquid fraction as compared to the control (no acidification) and to the untreated digestate, except for orbital shaking in combination with HCl and formic acid at pH 6. Hence, the combination of the applied mechanical instruments and acids were found to be effective in increasing the release of ortho-P in the liquid fraction of digestate, although orbital shaking at pH 6 was only of interest with addition of citric acid.

It should be remarked that the mechanical treatments alone were not effective in improving the release of ortho-P in the liquid fraction, similar as was previously observed by Pan et al. [20] for microwave digestion of dairy manure. Little to no hydrolysis would occur without acidification. These authors attributed this inconvenience to the inherent characteristics of manure. The phosphorus in manure exists in many forms, such as inorganic residual P, acid-soluble organic P, and lipid P, which are neither very soluble nor easily hydrolysed. This was likely also the case for the digestate under study, which was mainly produced from dairy manure. Indeed, in the case of livestock residues, the hydrolysis step in anaerobic digestion is restricted by the

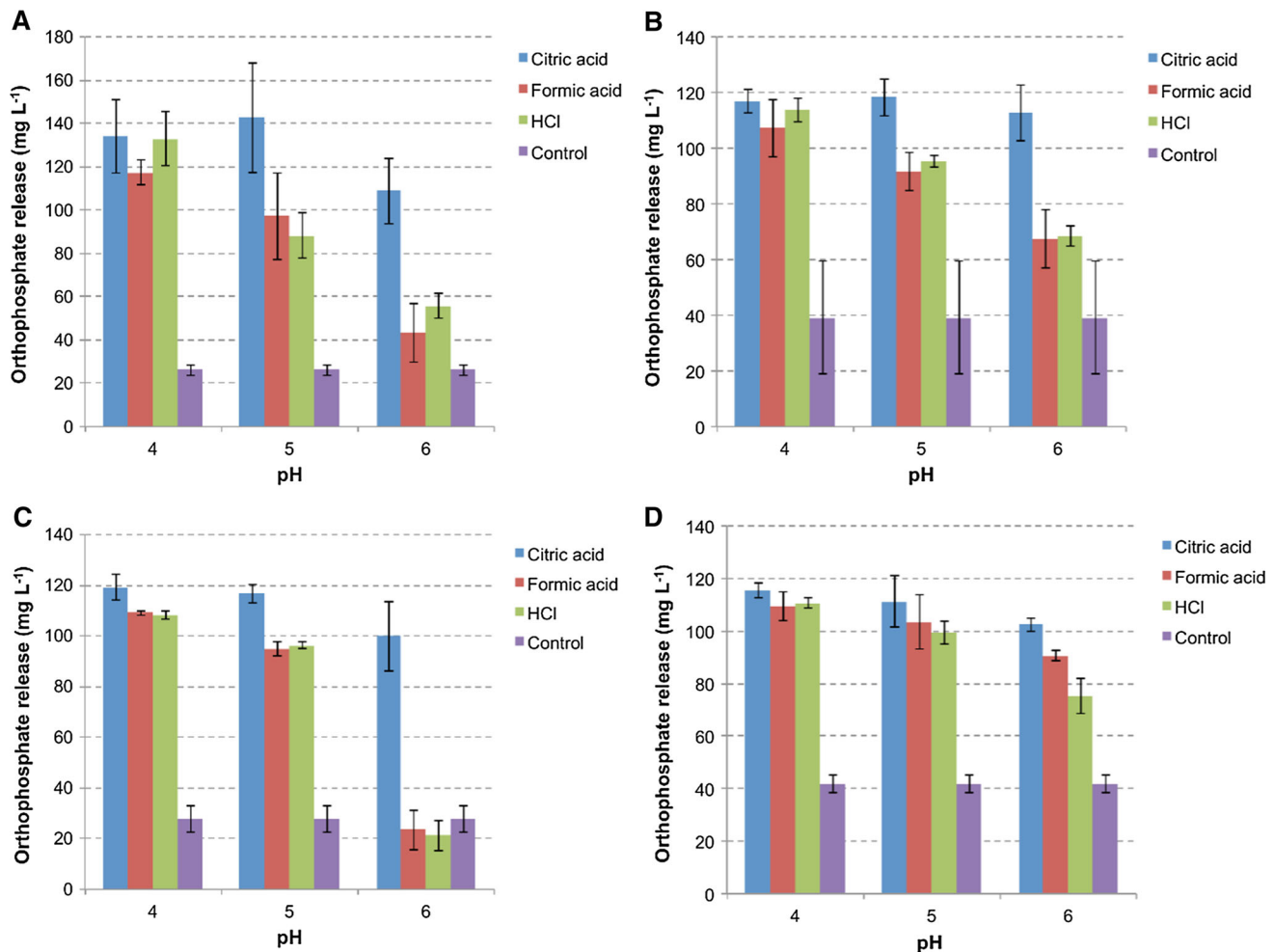


Fig. 3 Concentration of orthophosphate released from digestate (mg P L^{-1} digestate; mean \pm standard deviation; $n = 3$) after pre-treatment at pH 4, 5, and 6 as function of the chemical (citric acid, formic acid, HCl) and mechanical treatment used: **a** microwave

heating, **b** conventional heating, **c** orbital shaking, and **d** ultrasonic bath. *Control* no acidification. *Note* initial ortho-P concentration without pre-treatment = $48 \pm 7 \text{ mg L}^{-1}$

presence of fibers, resulting in a low anaerobic degradation, and hence high digestate fiber concentration [8, 34]. In this study the synergetic effect of acidification and mechanical treatment was the most expressed for microwave heating, which at lower pH (4), hence higher acidification, showed a significantly higher P release than the other mechanical treatments when using formic acid or HCl. Looking at all three acids, the ultrasonic treatment seems to be the most capable mechanical pre-treatment for releasing ortho-P from digestate at a higher pH (6). Literature evidence to support this finding is lacking for digestate. However, Saha et al. [23] found that ultrasonic treatment was more effective than microwave heating (without acidification) for COD (chemical oxygen demand) solubilization of various sewage sludges. This may support the improved P release found in this study at relatively high pH (6) for HCl and formic acid under the ultrasonic treatment. Interestingly, when using

citric acid, all mechanical pre-treatments were very effective at pH 6 (see below).

The maximum P release efficiency (%) provoked by the various pre-treatment methods was calculated as the difference between the maximum amount of ortho-P release achieved with the pre-treatment at the respective pH (Fig. 3) and the ortho-P release without pre-treatment ($48 \pm 7 \text{ mg L}^{-1}$), relative to the total initial amount of P in the digestate (Table 1). The pre-treatments maximally released 13–28 % soluble ortho P. Alternatively, the absolute (maximum) P release compared to total P (hence not correcting for the untreated control) ranged from 25 to 40 %, which is about 2.3 to 3.6 times higher as compared to not applying a pre-treatment at all (11 %). Note that the latter value corresponds well to values obtained at full-scale during solid–liquid separation, e.g. $\pm 9 \%$ of the total P ended up in the liquid fraction in Vaneeckhaute et al. [27].

Table 2 Acid dose (mol L⁻¹ digestate), estimated acid cost (€ m⁻³ digestate), and additional ortho-P released from digestate under the various pre-treatments (g m⁻³ digestate) relative to the P released without pre-treatment (48 ± 7 g m⁻³)

Acid	pH	Acid dose (mol L ⁻¹)	Acid cost (€ m ⁻³)	Average additional P release (g m ⁻³) compared to no pre-treatment			
				Microwave heating	Conventional heating	Orbital shaking	Ultrasonic bath
HCl	6	0.25	0.35	8.0	21	0	27
	5	0.38	0.53	40	47	48	51
	4	0.49	0.69	85	66	60	63
Citric acid	6	0.13	16.39	61	64	52	54
	5	0.21	27.31	95	70	69	63
	4	0.36	47.34	86	69	71	67
Formic acid	6	0.34	6.86	0	19	0	43
	5	0.53	10.50	49	44	47	55
	4	0.74	14.73	69	59	61	61

Acid prices: HCl: € 0.0014 mol⁻¹, citric acid: € 0.13 mol⁻¹, formic acid: € 0.02 mol⁻¹ (Brenntag NV, 2012). € 1 ≈ 1.415 CAD (November 2014)

Looking at the maximum obtained P release efficiencies, among the mechanical pre-treatments, the microwave treatment was generally most effective in releasing ortho-P. The obtained ortho-P release efficiencies are in line with Jin et al. [14], who reported values in the range of 13–30 % using microwave digestion and various chemicals (NaOH, CaO, H₂SO₄, HCl) for the treatment of dairy manure. Moreover, the P release obtained in this study was similar to that in Pan et al. [20] using a closed vessel microwave with addition of H₂SO₄ (1:50-ratio) at 60 °C for dairy manure treatment (115 ± 3 mg P L⁻¹ or 40 % of total P). Differences can be attributed to the different chemicals used, the heating temperature, the pH, the microwave system used (open system for this study), and differences in initial P content and animal diet [12, 24], next to the fact that in this study the manure was subjected to anaerobic (co-)digestion prior to the microwave treatment.

The improved P release may be attributed to the ability of microwave digestion to convert other forms of P, such as polyphosphates and organic phosphates, into orthophosphates via hydrolysis at 70 °C as compared to mesophilic anaerobic digestion at 35 °C [14, 21]. The fact that microwave digestion was able to release more ortho-P than conventional heating is likely due to an increased solubilization of lignocelluloses under microwave heating at low pH. Also Jin et al. [14] previously observed this effect. Orbital shaking and ultrasonic treatment, both without imposed heat supply, showed similar maximum release efficiencies as conventional heating at low pH. Hence, from a technical point of view, if pasteurization is targeted, microwave heating may be preferred above conventional heating in order to simultaneously maximize the P release efficiency, at least when working at low pH.

The differences between the three acids can be attributed to the strength and individual properties of the acids. Citric acid generally released more soluble ortho-P ions into the liquid fraction under all pre-treatments (Fig. 3). Even at high pH (6), high ortho-P release efficiencies were obtained under all mechanical treatments. Moreover, less acid was required to reach a certain P release and pH as compared to the other chemicals under study (Figs. 2, 3). The improved P release is probably caused by complex formation of citrate with cations in the solution (Ca²⁺ and Mg²⁺), which reduced the availability of Ca²⁺ and Mg²⁺ as free cations to precipitate with P [7, 33]. Formic acid showed a lower P release, likely because formic acid is a monodentate (only one atom in the ligand can bind to the metal), whereas citric acid is a multidentate [7]. Citric acid also generally released more P than HCl from digestate, which is in line with the findings of Szogi et al. [24] for poultry litter. Overall, in this study, HCl and formic acid showed similar release efficiencies at the same pH. However, less acid was required when using HCl to obtain a particular pH. HCl also seems to be more effective when heat (microwave or conventional heating) is involved, though this could statistically not be evidenced.

Although citric acid seems the most interesting chemical to use, the choice of the acid also depends on its price. The estimated acid cost for each pre-treatment is presented in Table 2. It was calculated from the cost price of the used acids, as offered by the chemical provider [2]. Also the average amount of additional ortho-P release above that obtained without pre-treatment (48 ± 7 mg L⁻¹) is presented.

Although the combination of microwave treatment and citric acid at pH 5 resulted in the highest average ortho-P

release, the cost of this treatment (only for the acids) was about 50 times higher as compared to the use of HCl. In this respect, it seems more interesting to use HCl down to pH 4 (hence more acid required), which still resulted in high P release efficiencies under the various mechanical pre-treatments, though significantly reduced the acid costs. Moreover, if no pasteurization is required for effective fertilizer marketing, then orbital shaking may be considered as mechanical treatment (in combination with HCl addition down to pH 4), due to its generally lower operational cost and energy use, but still relatively high P release efficiency. In practice, this pre-treatment can easily be realized by addition of the acid into a continuously stirred tank reactor, for example, a digestate storage tank. The choice and cost of the mechanical treatment will also depend on the local availability of (recovered) heat.

Although the above estimated costs seem fairly high, the results are comparable to the findings of Daumer et al. [4] for the treatment of raw pig slurry using formic acid down to pH 5, i.e. € 8 m⁻³, only taking in account the acid costs. Hence, the findings were believed to be realistic. Looking on a phosphorus base, the costs are even more discouraging, ranging from € 8 (microwave heating, HCl, pH 4) to ±€ 700 (ultrasonic bath, citric acid, pH 4) per extra kg of P released as compared to not applying a pre-treatment at all. To this, the costs for a Mg-source will have to be added if struvite is to be produced, next to the costs for the mechanical treatment. On the other hand, a reduction in transport costs (estimated at € 1.2 ton⁻¹ km⁻¹; [4] can be obtained as the resulting organic thickened fraction should have increased local valorization potential (higher C:P-ratio). Moreover, the thickened fraction may (partially) be recycled to the anaerobic digester prior to marketing in order to enhance biogas production and further stabilize the organic amendment. It should, however, be remarked that the fertilizer value and characteristics of such organic thickened fractions remain to be explored. The carbonate content, for example, may be reduced during acidification.

Revenues can also be obtained from (local) struvite fertilizer marketing, ranging from ±€ 45 to 1400 ton⁻¹ anno 2014 [25]. On top of that, the production and transport costs for chemical P fertilizers may be reduced or even eliminated. Hence, the economic feasibility of implementing a pre-treatment will have to be evaluated for each specific case.

Next to the costs and technical performance, another important factor influencing the chemical choice is related to the acid composition. Mineral acids supply anions (chloride in this case) at high concentrations. These soluble anions increase the salinity of the final effluent. On the other hand, organic acids increase the easily degradable carbon content of the effluent [4]. Hence, the acid to be preferred will also depend on the required effluent quality.

Note that when simultaneously applying a mechanical treatment, further COD degradation is expected to occur. Also pathogens can be further killed off during the pre-treatment. Moreover, next to P, (heavy) metals can be released, which could be recovered prior to struvite precipitation, meanwhile improving the struvite purity and effluent quality [19]. The Ca/Mg-dose needed for P precipitation may also be reduced, due to the potential improved Mg release. Yet, the pH will have to be increased after the pre-treatment to allow for precipitation to occur. Finally, acids of reduced quality could be used, which may significantly reduce the acid costs, but again impact on the fertilizer and effluent quality. These aspects were out of scope of the present study, but should be taken in account when selecting the technically and economically most feasible pre-treatment for each particular case.

Conclusions and Perspectives

The phosphorus release potential of various combinations of mechanical (microwave, ultrasonic, heating, mixing) and chemical (addition of HCl, citric acid, formic acid) pre-treatments was studied at pH 4, 5, and 6. All pre-treatments were effective in increasing the release of P from digestate, although orbital shaking at pH 6 was only of interest using citric acid. The chemical costs as function of the P release efficiency were high for all pre-treatments. Further substantive case studies are required so as to conclude on the economic feasibility of implementing such treatments for P release from digestate at full-scale.

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