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Abstract

Solid residues from thermal treatments of sewage sludge (SS) represent a valuable source of phosphorus (P) for the fertilizer production. This study aims at evaluating the P recovery potential from solid residues obtained from wet air oxidation of SS under subcritical water conditions (WAO residues). A series of P extraction experiments was performed by acidic and alkaline leaching at different liquid to solid ratios. Hot chemical extractions and P fractionations were also carried out to characterize the chemical composition of the WAO residues. The main objectives of this work were to determine the best operating conditions for P extraction, and to describe and understand the kinetics and the main mechanisms leading to P release. The results obtained in this study indicate that 1 M citric acid and 1 M HCl at the liquid to solid ratio of 10 L/kg can extract 61% and 65% of the total P content after 2 h of contact time at room

temperature, thus giving P extraction capacities of 81 and 86 g P/kg WAO residues, respectively. The analysis of kinetic data indicates that P extraction with 1 M HCl is faster, but 1 M citric acid can give higher P extraction efficiencies at the equilibrium. The molar ratios of Ca to P of the leachates suggest that P extraction from WAO residues was primarily due to the dissolution of a mixture of various Ca-P complexes.

Keywords: phosphorus recovery; sewage sludge; wet air oxidation residue; acidic leaching; kinetic model.

1 Introduction

Nowadays, industrial production of chemical fertilizers strongly depends on non-renewable phosphorus (P) sources such as natural deposits of phosphate minerals (*e.g* apatite rocks), and the evaluation of alternative renewable resources for fertilizer production today represents a critical research topic for ensuring the future global food security (Cordell et al., 2011; Desmidt et al., 2015). Indeed, the demand of chemical fertilizers for food production is rising rapidly due to the increase in world population, and recent prospective studies have indicated that a peak of P extraction from apatite rocks will occur at around 2020, and then P is likely to become a critical resource by 2050 (Cordell et al., 2011; Desmidt et al., 2015; Sørensen et al., 2015). There is therefore an urgent need to identify alternative renewable P sources for the fertilizer production.

Currently, there is a general consensus among researchers that P recovery from wastewater may represent a promising way to overcome the shortage of natural resources (Cieślik and Konieczka, 2017; Cordell et al., 2011; Herzel et al., 2016; Melia

et al., 2017). Moreover, the removal of P from wastewater can significantly reduce the supply of this nutrient to sensitive aquatic ecosystems, thus reducing the risk of eutrophication. The results of Cordell et al. (2011) indicate that more than 25% of the P demand in 2100 can be met by recovering P from agricultural and municipal wastewater. In particular, sewage sludge (SS) from municipal wastewater treatment plants (WWTPs) shows one of the most interesting potentials for P recovery, due to their relatively high and constant content in P (Melia et al., 2017).

A large number of processes have been proposed by researchers and practitioners to recover P from SS, such as the direct reuse as fertilizers in the fields, the precipitation of struvite and hydroxyapatite from the sludge leachates, and the extraction of P from the solid residues (*e.g.* char and ashes) that are obtained after thermal treatments of SS (Cieślik and Konieczka, 2017). Among these different techniques, P recovery from char and ashes presents several advantages compared to the other recovery techniques, as thermal treatments of SS usually provide: (i) the destruction of pathogens; (ii) a significant reduction in the volumes (70-80%); (iii) the accumulation and the concentration of the P content in the solid residues (Cieślik and Konieczka, 2017). Indeed, total P contents of char and ashes are usually comprised between 5 to 11% (dried mass), which is 1.2 to 2.6 times higher than the average P content of untreated SS (Herzel et al., 2016).

Several studies have investigated the potential of P recovery from char and ashes produced by incineration, gasification, and pyrolysis of SS (Atienza–Martínez et al., 2014; Donatello et al., 2010; Gorazda et al., 2018; Kleemann et al., 2017; Ottosen et al., 2013; Petzet et al., 2012; Xu et al., 2012). Most of these studies have focused on P extraction via acidic or alkaline leaching, and then P was recovered from the leachates

by chemical precipitation. However, many studies have focused only on equilibrium capacities, and further experiments are needed to model kinetics and mechanisms of P extraction. Moreover, only a few studies have dealt with P recovery from solid residues obtained by supercritical water gasification, supercritical water oxidation, and hydrothermal carbonation (Acelas et al., 2014; Huang and Tang, 2015; Stark et al., 2006), and there is a lack of data in the literature on P recovery from solid residues obtained by wet air oxidation of SS. Therefore, further experiments are needed to achieve a complete overview of P recovery potential of SS residues derived from the different current technologies.

This study aims at evaluating the potential of P recovery from solid residues obtained from wet air oxidation of SS under subcritical water conditions (WAO residues). A series of experiments of P extraction was performed by acidic and alkaline leaching at different liquid to solid ratios. Also, hot chemical extractions and P fractionations were carried out to characterize the chemical composition of the WAO residues. The main objectives of this study were (i) to determine the best operating conditions for P extraction, (ii) to determine the rate constants and maximum equilibrium capacities of P extraction, and (iii) to describe the main mechanisms leading to P extraction from the WAO residues. To the best of our knowledge, this paper represents the first complete study on capacity, kinetics, and mechanisms of P extraction from WAO residues. Knowledge and understanding of the kinetics and the main mechanisms of P extraction is indispensable to improve the design and the operation of the extraction process.

2 Material and methods

2.1 *Samples collection and preparation*

Solid residues used in this study derived from high temperature (235 °C) and pressure (4.5 MPa) wet air oxidation (WAO technology Athos, VEOLIA, France) of SS produced in the domestic WWTP of La Pioline (capacity 175000 population equivalent), located in Aix-en-Provence (France). The WAO residues were milled using a ceramic mortar to obtain particles with a size less than 0.5 mm and dried at 45 °C overnight to reduce their water content before the experiments. The temperature of 45 °C was selected in order to reduce the risk of changes in the mineralogical composition during drying. The total water content of residues was determined after heating at 105 °C until constant weight. This was done to determine the correct amount of WAO residue, based on dried mass equivalent, to be used in the different experiments.

2.2 *Chemical characterization and P fractionation*

A series of chemical extractions and elemental analyses were performed to investigate the chemical composition and quantify the different forms of P in the samples.

Aqua regia extractions were performed according to standard methods (EN 13346, 2000; EN 13657, 2003) to investigate the elemental composition of the WAO residues. *Aqua regia* dissolves metal oxides, hydroxides, carbonates, and metal phosphates. Organic matter is digested and carbon is lost as CO_2, while P and S are oxidized to phosphates and sulfates. A mixture of 1 g of WAO residue (dried mass equivalent) and 28 mL of *aqua regia* was heated to 110 °C for two hours. Then, the mixture was filtered (0.45 µm filters) before elemental analyses. *Aqua regia* extractions were performed in duplicate. For each experiment, element extraction capacities q (mg/g) were determined

using equation (1), where C is the element concentration in the leachates (mg/L), V is the volume of extractant solution (L), and m is the dried mass of WAO residue (g).

$$q = C \cdot L/m \quad (1)$$

A sequential extraction protocol, adapted by Tiessen and Moir (1993), was followed to quantify the fractions of P bound to different mineral compounds in the residues. Four fractions of P were sequentially extracted from 1 g of WAO residue (dried mass equivalent):

i. Bicarbonate extractable P was extracted in 20 mL of 0.5 M $NaHCO_3$. This fraction is defined as weakly bound P, since the chemical changes introduced are minor and P extraction is mainly due to washing and ion exchange;

ii. Hydroxide extractable P was extracted in 20 mL of 0.1 M NaOH. This fraction is primarily related to dissolution of Al and Fe bound P compounds that are soluble at high, but insoluble at low pH;

iii. Diluted acid extractable P was extracted in 20 mL of 1 M HCl. This fraction is defined as Ca bound P, since Al and Fe bound P compounds that might remain after NaOH extraction are insoluble in acid;

iv. Hot concentrated acid extractable P was extracted in 12 mL of 10 M HCl in a 20 min water bath at 80 °C. This fraction represents P in stable residual compounds that need much more energy to be dissolved.

The fractions (i), (ii) and (iii) were determined after 16 h of rotary agitation at 5 r/min (rotary agitator STR4, Stuart, UK) at room temperature. After each extraction, the solid residues were washed with 20 mL of 1 M KCl to recover P re-adsorbed on the residue surface, and the KCl washes were added to the supernatant solution. Liquid samples

from each extraction were filtered (0.45 µm filters) before elemental analyses. Then, for each step, P extraction capacities were determined by using equation (1). Sequential extractions were performed in duplicate.

Scanning electron microscopy observations coupled with energy dispersive X-ray spectroscopy analyses (SEM/EDX) were also performed to investigate the morphology and chemical composition of the residues. SEM/EDX analyses were carried out using a S-3000N scanning electron microscope model (Hitachi, Japan). All samples were dried at 45 °C overnight before SEM/EDX analyses.

2.3 *P extraction experiments*

2.3.1 P extraction efficiency

P extraction experiments (adapted from EN 12457-1 and 2, 2002) were performed using four different extractant solutions (1 M HCl, 1 M citric acid, 1 M acetic acid, and 0.1 M NaOH) at four different liquid to solid ratios (L/S) of 2, 5, 10, and 20 L/kg. The main objective was to establish the best extractant solution and L/S ratio for the P extraction. For each experiment, 100 mL of extractant solution were added into a series of four 200 mL plastic bottles containing 5, 10, 20, and 50 g of WAO residues (dried mass equivalent). Then, the bottles were rotary agitated at 5 r/min at room temperature, and liquid samples were taken from each bottle after 24 h of agitation. All liquid samples were filtered (0.45 µm filters) before elemental analyses. For each experiment, the 24 h element extraction capacities q (mg/g) were determined by using equation (1), as already described in the previous section. Element extraction efficiencies were then calculated as shown in equation (2), where q is the 24 h element extraction capacity by

159 acidic or alkaline leaching (mg/g), and $q_{a.r.}$ is the element extraction capacity with *aqua*
160 *regia* (mg/g).

161 $$Efficiency\ (\%) = 100 \cdot q/q_{a.r.} \quad (2)$$

162 *2.3.2 P extraction kinetics*

163 A series of batch kinetic experiments was carried out to determine the maximum
164 equilibrium capacities and the rate constants of P extraction from WAO residues.

165 Kinetic experiments were performed using 1 M citric acid and 1 M HCl at the L/S ratio
166 of 10 L/kg. These operating conditions were selected based on the results of the
167 comparative experiments (section 2.3.1). For each experiment, 700 mL of extractant
168 solution were added into 1 L plastic bottles containing each 70 g of WAO residues
169 (dried mass equivalent). Then, the bottles were rotary agitated at 5 r/min under room
170 temperature, and liquid samples were collected from each bottle after 15, 30, 60, 120,
171 180, and 240 min. Kinetic experiments were performed in duplicate. All the liquid
172 samples were filtered (0.45 µm filters) before elemental analyses, and for each sample
173 element extraction capacities were determined by using equation (1). Experimental
174 extraction capacities were then modelled using the integrated form of the pseudo second
175 order kinetic equation as proposed by Ho and McKay (1998) (equation 3), where q_t is
176 the extraction capacity at time t (mg/g), q_e is the extraction capacity at the equilibrium
177 (mg/g), and k_2 is the constant rate of the pseudo second order (g/(mg·min)).

178 $$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (3)$$

179 According to Ho and McKay (1998), the pseudo second order kinetic model efficiently
180 describes a process primarily controlled by chemisorption (or chemidesorption) rather

than diffusion, with the concentration of one or more reagents that may become limiting the rate of the reaction over time.

2.4 *Analytical methods*

Elemental analyses (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Pb, Se, Si, V, and Zn) of liquid samples were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a spectrometer Jobin Yvon Horiba Ultima-C (Horiba, Japan). For each set of analyses, limits of detection and limits of quantification were determined by analysis of blanks. All chemicals used were of analytical grade.

3 Results and discussion

3.1 *Chemical characterization and P fractionation*

The results of *aqua regia* extractions indicated that Ca, Fe, P, Mg, and Al represent at least 49.5% of the total mass of dried WAO residues (Table 1). Ca, Fe, P, Mg, and Al extraction capacities with *aqua regia* were 170 ± 2 mg Ca/g WAO residue, 150 ± 1 mg Fe/g WAO residue, 132 ± 1 mg P/g WAO residue, 22.9 ± 0.1 mg Mg/g WAO residue, and 19.8 ± 0.2 mg Al/g WAO residue, respectively (average values ± standard deviation from duplicate experiments). Ca and Mg in WAO residues were most probably primarily related to the Ca and Mg contents of wastewater and biomass, whereas Fe and Al likely derived from the use of Fe and Al salts to improve P removal from wastewater by chemical precipitation in the WWTP. Moreover, *aqua regia* extractions indicated a significant presence of K (3.0 ± 0.2 mg/g), Cu (2.5 ± 0.1 mg/g), and Zn (2.08 ± 0.02 mg/g), which are essential micronutrients for biomass growth and they are classically present in little amounts among the components of SS. Furthermore, the results in Table 1 suggest that other elements such as Ba, Cd, Co, Cr, Mn, Ni, Pb, Se, and V were

present only in trace in WAO residues, and their concentrations in the *aqua regia* leachates were often very close to the limits of quantification for the analyses.

Sequential extraction experiments indicated that the main fraction of P in WAO residues was Ca bound P, representing the 86.3% of the total mass of P extracted, followed by P in stable compounds (8.9%), and Al and Fe bound P (3.5%) (Figure 1). In the literature (Barca et al., 2014; Drizo et al., 2002; Tiessen and Moir, 1993), Ca bound P is mainly attributed to amorphous Ca phosphates and/or less stable Ca phosphates, such as dicalcium phosphate (DCP), octacalcium phosphate (OCP), and tricalcium phosphate (TCP), which can be dissolved with diluted acids (*e.g.* 1 M HCl), whereas the residual P in stable compounds can be referred to more thermodynamically stable Ca-P crystals (*e.g.* hydroxyapatite) and/or P from stable organic matter that is not alkaline extractable (Drizo et al., 2002; Thomsen et al., 2017; Tiessen and Moir, 1993).

A large number of studies have investigated the P composition of SS residues derived from various types of thermal treatments (Table 2). The data indicate that the total P content of SS residues may vary into a large range of values, from 27 to 119 g P/kg (Stark et al., 2006; Xu et al., 2012), depending on the type of the thermal process, on the temperature and pressure conditions of the process, and on the initial P composition of SS (Kleemann et al., 2017; Tan and Lagerkvist, 2011; Thomsen et al., 2017). During SS incineration at temperatures ranging between 800-900 °C, organic P volatilizes to form volatile oxides that re-condense upon temperature decreases at 400-600 °C, and it is recovered as inorganic Ca, Al, and/or Fe phosphates in the fly ashes (Cieślik and Konieczka, 2017; Magdziarz et al., 2016; Niu and Shen, 2018), while inorganic Fe-P and Al-P pools are oxidized to new P complexes (mainly Ca phosphates) and residual pools of Fe and Al oxides (Atienza–Martínez et al., 2014; Li et al., 2017; Parés Viader

et al., 2017b; Thomsen et al., 2017). The addition of CaO during SS incineration may promote the transformation of inorganic Fe-P and Al-P pools to Ca-P complexes and residual Fe and Al oxides, as demonstrated by Li et al. (2017). As a result of these mineralogical changes, inorganic Ca-P pools often represent the main P fraction in solid residues from SS incineration (Donatello et al., 2010; Li et al., 2017, 2015; Magdziarz et al., 2016). Similar trends were also observed for SS residues from gasification and pyrolysis processes (Acelas et al., 2014; Kleemann et al., 2017; Parés Viader et al., 2017b; Thomsen et al., 2017).

The results of this study indicate that the P content of WAO residues is higher than the average P content of SS residues tested in previous studies (Table2), and P in WAO residues is mainly present as Ca bound P. Most probably, the relatively lower temperature (235 °C) and higher pressure (4.5 MPa) conditions of the WAO process had the effect of (i) avoiding the volatilization of organic P and (ii) promoting its conversion to inorganic Ca-P complexes, thus leading to a significant increment in the P content of the residues. The results of SEM/EDX indicated that WAO residues are primarily composed of O, Ca, P, and Fe (Figure 1S, supplementary material), and elemental maps confirmed the presence of Ca-P pools covering the full surface of the samples (Figure 2S, supplementary material). Furthermore, SEM observations revealed that WAO residues are composed of amorphous aggregates with rare crystalline phases, suggesting that Ca-P complexes are mainly present as amorphous phases. There is a large discrepancy in the literature concerning the main crystalline and amorphous phases that are present in the residues from thermal treatments of SS. Overall, many studies have indicated that quartz (SiO_2), calcite ($CaCO_3$), and hematite (Fe_2O_3) are the prevalent crystalline phases, whereas Ca-P pools are often present as amorphous or

252 poorly crystallized aggregates (Atienza–Martínez et al., 2014; Donatello et al., 2010;
253 Magdziarz et al., 2016).

254 3.2 *P extraction efficiency*

255 Figure 2 shows the P extraction efficiencies observed after 24 h of contact time as a
256 function of the liquid to solid ratio (L/S) for the different extractant solutions that were
257 tested. The results clearly indicated that the best extractants for P extraction were 1 M
258 citric acid and 1 M HCl at the L/S ratio of 10 L/kg. Indeed, 1 M citric acid and 1 M HCl
259 at the L/S ratio of 10 L/kg extracted 86.4 mg P/g WAO and 92.0 mg P/g WAO,
260 respectively, representing 65% and 70% of the total mass of P extracted with *aqua regia*
261 (Table 1). A further increase in L/S ratio to 20 L/kg did not lead to a significant increase
262 in P extraction efficiencies (Figure 2).

263 The lowest P extraction efficiencies (< 2.5%) were observed when using 0.1 M NaOH
264 as solvent. This is in good agreement with the findings of previous studies (Biswas et
265 al., 2009; Stark et al., 2006; Xu et al., 2012), which have indicated that NaOH is not an
266 effective solvent for P extraction from SS residues.

267 The pH values of the leachates after 24 h of extraction ranged between 1.1-2.8 for 1 M
268 HCl, 2.2-2.8 for 1 M citric acid, 3.3-4.0 for 1 M acetic acid, and 10.2-12.4 for 0.1 M
269 NaOH (Table S1, supplementary material). These results seem to confirm that Ca bound
270 P represents the main fraction of P in WAO residues, and that P extraction was
271 primarily due to dissolution of Ca-P complexes under acidic conditions. Indeed,
272 solubility of Ca phosphates drastically increases with decreasing pH below 4 (Stumm
273 and Morgan, 2012), and they are much more soluble under acidic rather than alkaline
274 conditions. According to the supposed mechanism of P extraction, the higher pH values

275 of the leachates for 1 M acetic acid may account for its lower P extraction efficiency
276 compared to those of 1 M citric acid and 1 M HCl (Figure 2).

277 Figure 3 shows the evolution of P concentrations and pH values of the leachates after 24
278 h of contact time as a function of the L/S ratio when using 1 M citric acid and 1 M HCl
279 as extractant solutions. The results seem to confirm that the L/S ratio of 10 L/kg was the
280 optimum operating condition for combining high P extraction efficiencies (> 60%) with
281 high P concentrations in the leachates (> 8 g P/L). Moreover, the results shown in
282 Figure 3 indicate that 1 M citric acid may give higher P concentrations than those
283 obtained with 1 M HCl at similar pH values of the leachates, especially when using a
284 L/S ratio lower than 10 L/kg. This was most probably due to the metal chelating
285 properties of citric acid, which may have the effect of preventing the precipitation of
286 metal phosphates after P extraction, thus improving the effective solubility of P in the
287 leachates.

288 Table 1 summarizes the element extraction capacities and efficiencies using 1 M citric
289 acid and 1 M HCl at the L/S ratio of 10 L/kg after 24 h of contact time compared to
290 *aqua regia* extractions. The highest extraction efficiencies were observed for Ca (>
291 78%) and P (> 65%), whereas the extraction efficiencies of the other elements that are
292 present in greater amounts in the composition of WAO residues (Al, Fe, and Mg) were
293 always lower than 24% for Al, 28% for Fe, and 55% for Mg. These results seem to
294 indicate a higher affinity of 1 M citric acid and 1 M HCl for the dissolution of Ca-P
295 complexes rather than Al and/or Fe complexes, as already found in previous studies
296 (Biswas et al., 2009; Petzet et al., 2012), most probably because: (i) Fe oxides produced
297 during thermal treatments of SS (*e.g.* hematite) are usually acid-insoluble (Thomsen et

298 al., 2017), and (ii) Ca phosphates are several orders of magnitude more soluble than Al
299 and Fe phosphates at pH lower than 4 (Stumm and Morgan, 2012).

300 As shown in Table 1, 1 M HCl has shown a P extraction capacity 1.06 times higher than
301 1 M citric acid, while 1 M citric acid has shown Zn and Cu extraction capacities 1.47-
302 1.70 times higher than 1 M HCl. This was most probably due to the metal chelating
303 properties of citric acid that may have favored extraction of Zn and Cu from WAO
304 residue, as already observed in comparative studies that tested the use of weak organic
305 acids to extract heavy metals from polluted soils (Wasay et al., 2001).

306 It should be also noticed that 1 M citric acid and 1 M HCl have shown very higher Si
307 extraction capacities than *aqua regia*. Indeed, silicate minerals are usually recalcitrant to
308 dissolution by *aqua regia* and they remain in solid form (Chen and Ma, 2001).
309 However, P extraction capacities with 1 M citric acid and 1 M HCl were lower than
310 those observed with *aqua regia* (Table 1), and they were in good agreement with the
311 findings of P fractionation (Figure 1). This suggests that the amount of P extracted by
312 dissolution of silicate minerals was negligible compared to the amount of P extracted by
313 dissolution of Ca-P compounds.

314 Table 2 summarizes the optimum operating parameters and the main experimental
315 results of recent studies that have investigated the P extraction from various types of SS
316 residues. As shown in Table 2, it is difficult to compare the results of the different
317 studies because of the large variety on the origin and chemical compositions of the
318 residues, and the discrepancy between the experimental parameters that were
319 established for the extractions. Many studies have focused on ashes from incineration,
320 and only a few have dealt with SS residues from gasification, pyrolysis, and
321 supercritical water processes. Most of the studies have indicated optimum extraction

conditions with inorganic acids (HCl, H_2SO_4, HNO_3) at concentrations ranging from 0.05 to 2.7 M and L/S ratios from 2 to 150 L/kg. Only two studies have tested organic acids (oxalic acid)(Acelas et al., 2014; Atienza–Martínez et al., 2014), and only one study has found high extraction efficiency (> 70%) with an alkaline solvent (1 M NaOH), but this after an acidic pretreatment of the residues to promote the mobilization of Ca bound P (Petzet et al., 2012). The main mechanism of P extraction was attributed to the dissolution of various P compounds (mainly Ca phosphates) that are soluble under acidic conditions (Donatello et al., 2010; Kleemann et al., 2017; Li et al., 2015). Therefore, a high fraction of Ca bound P is considered as a positive predictive factor when evaluating the potential of P recovery from a residue. Overall, there is a good agreement in the literature concerning the optimum contact time for P extraction from SS residues, and usually the extraction efficiencies stabilize around a value ranging between 80% and 90% after 2 h of contact time (Table 2).

As shown in Table 1 and 2, P extraction efficiencies of this study were lower, while P extraction capacities were higher than those observed in previous studies. This seems to indicate that WAO residues contain a higher fraction of P that is recalcitrant to acidic leaching compared to the other types of SS residues. This fraction may be primarily attributed to more thermodynamically stable Ca-P crystals (*e.g.* hydroxyapatite) and to P in stable residual organic compounds, as already suggested by the results of P fractionation (Figure 1). Indeed, P bound to residual organic compounds is usually inert to acidic and basic leaching (Acelas et al., 2014). The higher fraction of P recalcitrant to acidic extraction in WAO residues was probably related to the relatively lower temperature of the WAO process, which may have led to an incomplete conversion of organic P. Indeed, comparative experiments of supercritical water gasification (SCWG)

346 of SS have confirmed that the higher the SCWG temperature, the more organic P is
347 converted into inorganic leachable P (Acelas et al., 2014).

348 3.3 *P extraction kinetics*

349 Kinetic experiments of P extraction were carried out using 1 M HCl and 1 M citric acid
350 at the L/S ratio of 10 L/kg, which represent the optimum extraction conditions that were
351 established by the previous experiments (section 3.2). Figure 4 shows the evolution of
352 experimental extraction capacities of Ca and P as a function of the time for the
353 experiments performed with 1 M HCl (Figure 4A) and 1 M citric acid (Figure 4B). The
354 results indicate that a pseudo-equilibrium in P extraction was achieved after 1 h for 1 M
355 HCl and after 2 h for 1 M citric acid, with P extraction capacities stabilizing around a
356 value of 80 mg P/g WAO residue. These results are in good agreement with the finding
357 of previous studies (Table 2), which have shown optimum contact times of around 2 h.

358 Table 3 summarizes the main results of modelling experimental extraction capacities of
359 Ca and P by the use of the pseudo-second order kinetic equation of Ho and McKay
360 (1998). The very high coefficients of correlation ($R^2 > 0.998$) indicate that the model
361 describes the experimental data very well. Moreover, the equilibrium extraction
362 capacities of Ca and P obtained by the model (Table 3) were in good agreement with the
363 experimental capacities observed after 24 h of contact time (Table 1), thus confirming
364 the validity of the model. Furthermore, the kinetic constants k_2 of Ca and P extractions
365 with 1 M HCl were 4-5 times higher than those obtained with 1 M citric acid (Table 3),
366 confirming that P extraction using 1 M HCl is faster than using 1 M citric acid.
367 However, despite P extraction with 1 M HCl being faster, the results shown in Figure 4
368 and Table 3 suggest that maximum P extraction capacities at the equilibrium may be
369 higher when using 1 M citric acid as solvent. This was probably due to the metal

370 chelating properties of citric acid which may have improved (i) the capacities of metal
371 bound P extraction at the equilibrium, and (ii) the effective solubility of P in the
372 leachates, as already discussed in the previous sections.
373 Overall, the experimental and modelled results seem to indicate a clear correlation
374 between Ca and P extraction from WAO residues, whereas no correlations were found
375 between P extraction and the extraction of Fe and Al. This appears to further confirm
376 that P extraction was mainly due to dissolution of Ca-P complexes under acidic
377 conditions.

378 3.4 *P extraction mechanisms*

379 According to Ho and McKay (1998), if the pseudo-second order model well describes
380 the kinetic data, this may indicate that P release from the WAO residues was primarily
381 controlled by the chemical reaction rather than diffusion, with one or more reagents that
382 can become limiting the rate of the extraction over time. However, recent studies have
383 shown that a good mathematical description of experimental data is not sufficient
384 enough to validate the underlying mechanisms of the model, and more caution should
385 be paid to the analysis of kinetic data (Simonin, 2016).

386 For these reasons, experimental data were further analyzed in order to fully understand
387 the main mechanisms leading to P extraction from WAO residues. As shown in Figure
388 5, a very good direct correlation between moles of Ca extracted and moles of P
389 extracted was observed during kinetic experiments. The molar ratios of Ca to P
390 extracted were 1.34 Ca/P and 1.31 Ca/P when using 1 M HCl and 1 M citric acid,
391 respectively. These molar ratios were in the range of molar ratios Ca/P of the most
392 common Ca phosphates in wastewater treatment systems (Table 4), and this appears to

393 confirm that P extraction was primarily due to the dissolution of a mixture of various
394 Ca-P complexes.

395 Table 4 summarizes formula, molar ratios Ca/P, and solubility constants of various Ca
396 phosphates. Among the crystalline forms, the most soluble are dicalcium phosphates
397 (DCP) and tricalcium phosphates (TCP). Solubility of amorphous calcium phosphates
398 (ACP) is variable, but usually they are more soluble than crystalline phases (Valsami-
399 Jones, 2001). The findings of this study seem to indicate that dissolution of ACP was
400 the most probable mechanism leading to P extraction, as SEM observations revealed
401 that WAO residues were predominantly composed of amorphous aggregates. Moreover,
402 experimental molar ratios of Ca/P extracted (1.31-1.34) were very consistent with the
403 theoretical molar ratio of Ca/P for the dissolution of a mixture of various ACP (Table
404 4).

405 Overall, the results of this study seem to confirm that P extraction from WAO residues
406 was a process primarily controlled by the dissolution of Ca phosphates, with Ca
407 phosphates that can become limiting the rate of the extraction over time. This
408 hypothesis is further supported by the very good agreement between the amount of Ca
409 bound P on WAO residues (Figure 1) and the equilibrium capacities of Ca and P
410 extraction (Table 3), which indicate that Ca phosphates were no longer available for
411 dissolution after 4 h of contact time.

412 **4 Closing remarks and perspectives**

413 The results of this study have indicated a high potential for P recovery from WAO
414 residues using 1 M citric acid and 1 M HCl as extractant solutions. Despite HCl shows a
415 faster P extraction kinetic, the use of citric acid presents several advantages compared to

HCl, as (i) citric acid is a bio-sourced product that can be produced in large amounts in bioreactors by cultivation of microorganisms (*e.g. Aspergillus niger*), and (ii) it is highly biodegradable, thus facilitating the treatment and management of the effluents from the process.

However, as shown in Table 1, significant amounts of heavy metals (in particular Fe, Al, Cu, and Zn) were extracted from WAO residues, whose presence in the leachates is unbeneficial as it may affect the purity and quality of the P recovered. A large variety of separation techniques have been proposed in the literature to recover and concentrate P from the leachates of acidic extractions. Among the different techniques, sequential precipitation with increasing step by step the pH of the leachates was one of the most employed to recover P in the form of pure Ca-phosphates (Kaikake et al., 2009; Kalmykova and Fedje, 2013; Petzet et al., 2012). Other authors have proposed the use of cation exchange resins to remove heavy metals from the leachates and hence obtain metal free solutions (Donatello et al., 2010; Franz, 2008; Xu et al., 2012). Biswas et al. (2009) obtained good efficiencies of P recovery from the leachates by selective adsorption on orange waste gel.

Thermochemical pre-treatments of SS residues may also represent a suitable alternative solution to remove metals from the residues and improve P bioavailability and/or leachability (Adam et al., 2009; Havukainen et al., 2016; Krüger and Adam, 2015). Adam et al. (2009) indicated that a thermal pretreatment of ashes at temperatures of about 1000 °C can effectively remove heavy metals by volatilization due to their high vapor pressures, while P bound to stable mineral phases is transformed to more soluble Ca and Mg phosphates.

In recent years, the development of membrane-based electrodialytic processes for simultaneous separation of P and heavy metals from the leachates has received increasing attention from the scientific community (Ebbers et al., 2015; Guedes et al., 2016; Parés Viader et al., 2017a; Villen-Guzman et al., 2018). Parés Viader et al. (2017a) indicated that the recovery of Al- and Fe-free P from Al- and Fe-rich ashes can be increased by a factor of two with a sequential electrodialytic process that alternates a first step of acidic extraction followed by a second step of alkaline extraction.

According to the data published in the literature, sequential precipitation appears to be the most robust technique to recover pure Ca-P precipitates from the leachates due to the simplicity and relatively low operating costs of the process. Nevertheless, it should be noted that metal chelating properties of certain organic acids and residual organic compounds may inhibit and/or alter the stability of Ca-P precipitation (Valsami-Jones, 2001), thus affecting kinetics and efficiency of the process. Therefore, the use of membrane-based and electrically-driven processes such as electrodialysis seems to be more appropriate to achieve efficient separation of phosphates and heavy metals from the leachates, especially when using 1 M citric acid as extractant solution.

However, despite numerous studies have demonstrated the effectiveness of these separation techniques at the laboratory scale, today the number of pilot and industrial scale applications is still scarce (Krüger and Adam, 2015). A comparative study on life cycle assessment (LCA) and life cycle cost analysis (LCC) for the different processes, based on the results of full scale applications, would be required to thoroughly identify the advantages and limitations of each technique.

5 Conclusions

The results of this study confirm that SS residues of WAO are a promising secondary P source for fertilizer production. *Aqua regia* extractions and P fractionation experiments revealed a total P content of WAO residues of about 132 ± 1 g P/kg, with P mainly present as Ca bound P. Optimum conditions for P extraction were observed when using 1 M citric acid and 1 M HCl at L/S ratio of 10 L/kg as extractant solutions at room temperature. After 2 h of contact time, P extraction efficiencies were 61% and 65%, giving P extraction capacities of 81 and 86 g P/kg of WAO for 1 M citric acid and 1 M HCl, respectively. The kinetic analysis of experimental data by the use of the pseudo-second order kinetic model indicates that P extraction with 1 M HCl is faster, but 1 M citric acid may give higher capacities of P extraction at the equilibrium. Molar ratios of Ca to P extracted from WAO residues ranged around 1.31-1.34 mol Ca/mol P, suggesting that P extraction was primarily due to dissolution of a mixture of various Ca-P complexes (most probably amorphous Ca phosphates) under acidic conditions. Al and Fe extraction efficiencies have been always lower than 28%, and no correlations were observed between the extraction of these metals and the extraction of P, thus indicating that 1 M citric acid and 1 M HCl have a higher affinity for the dissolution of Ca phosphates rather than Al and Fe complexes.

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Supplementary material

Figure S1. SEM/EDX analysis: elemental spectrum for WAO residues.

Figure S2. SEM/EDX analysis: elemental maps of Ca (A) and P (B) for the same sample of WAO residue.

Table S1. pH values and P concentrations of the leachates after 24 h of extraction as a function of the liquid to solid ratio (L/S) for different extractant solutions.

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633 Table 3. Main results of modeling experimental extraction capacities of Ca and P by
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637

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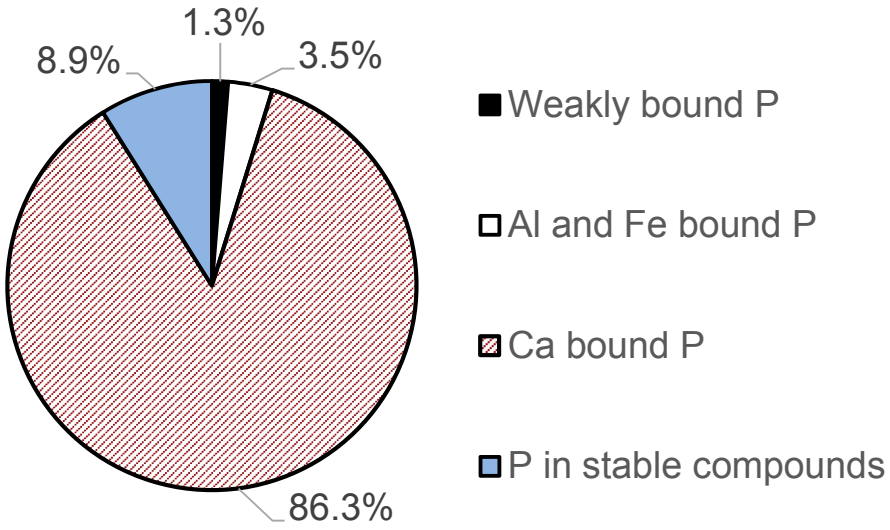
655



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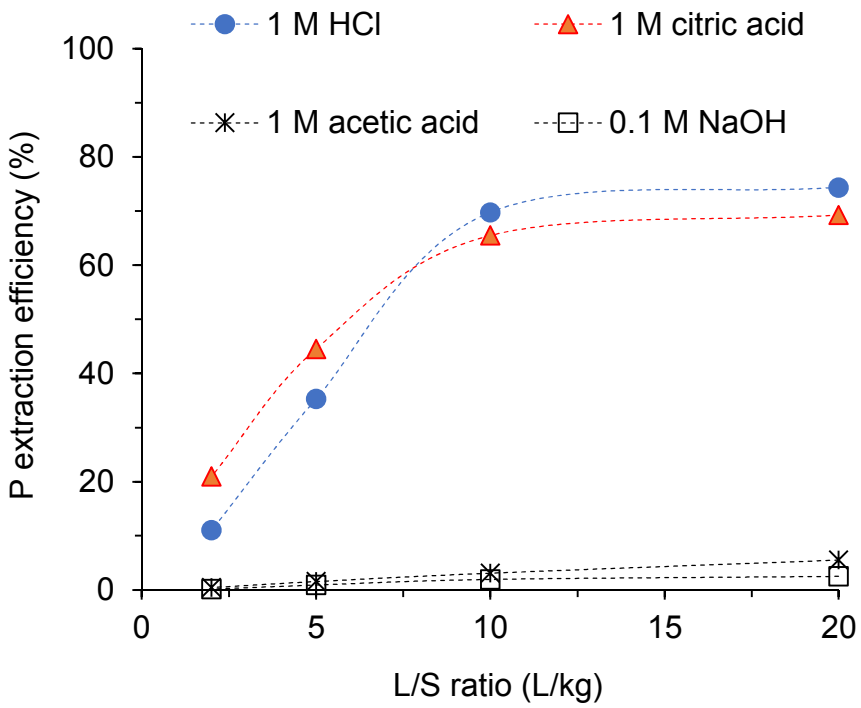

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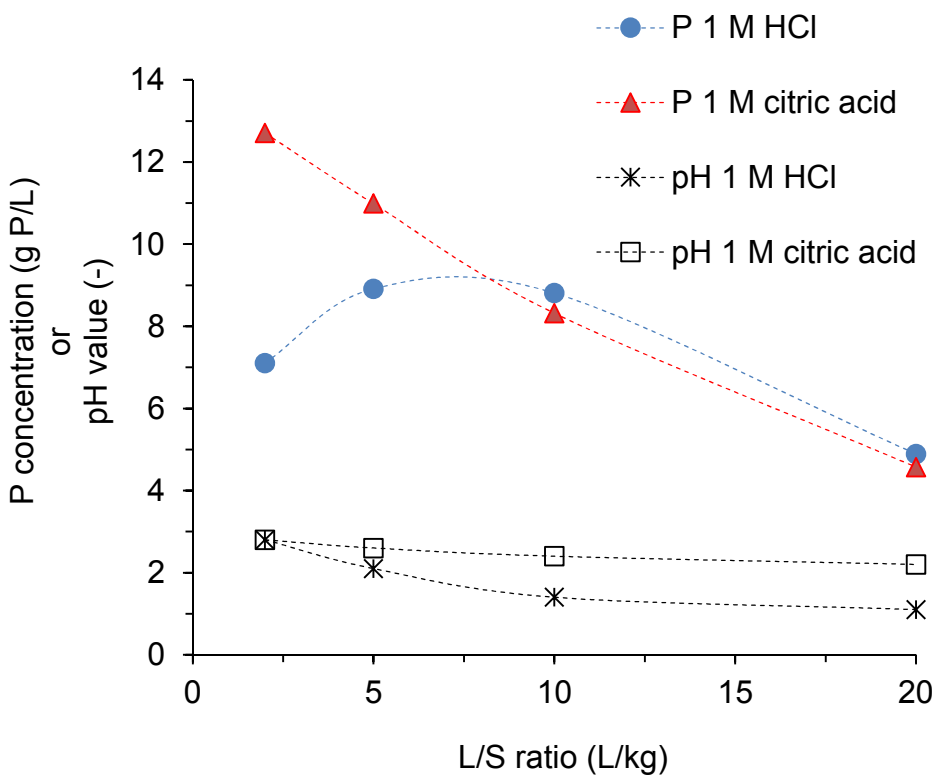

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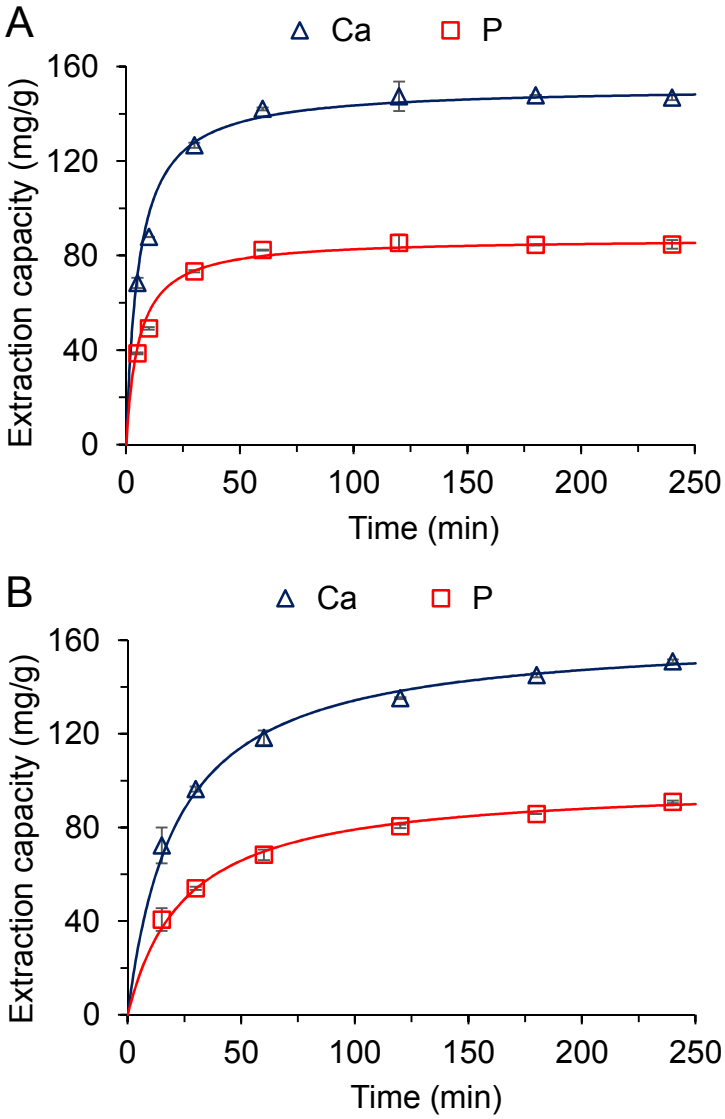

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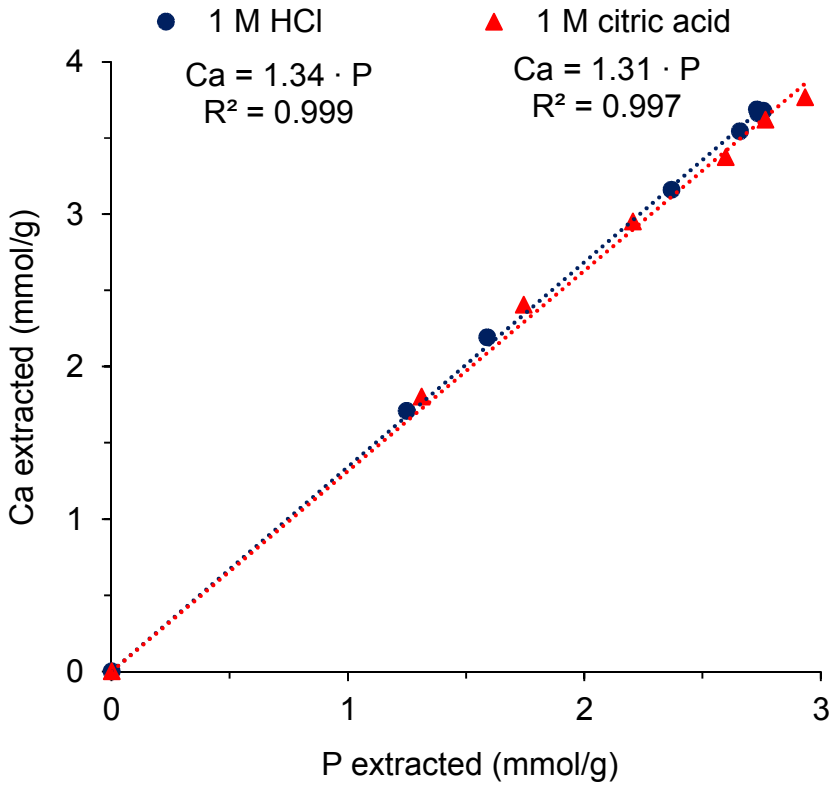

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Table 1. Element extraction capacities and efficiencies using 1 M citric acid and 1 M HCl after 24 h of contact time compared to *aqua regia* extraction capacities.

Element	*Aqua regia* extraction capacity[a] (mg/g)	1 M citric acid extraction at L/S ratio 10 L/kg		1 M HCl extraction at L/S ratio 10 L/kg	
		Capacity (mg/g)	Efficiency[b] (%)	Capacity (mg/g)	Efficiency[b] (%)
Al	19.8 ± 0.2	3.99	20	4.79	24
Ba	1.2 ± < 0.1	0.46	38	0.047	4
Ca	170 ± 2	132	78	149	88
Cd	0.016 ± 0.001	0.0032	20	0.0028	18
Co	0.012 ± < 0.001	0.0028	23	0.0024	20
Cr	0.14 ± < 0.01	0.026	19	0.027	19
Cu	2.5 ± 0.1	1.3	52	0.74	30
Fe	150 ± 1	42.0	28	31.9	21
K	3.0 ± 0.2	1.5	50	0.92	31
Mg	22.9 ± 0.1	11.3	49	12.6	55
Mn	0.44 ± < 0.01	0.26	59	0.16	36
Ni	0.066 ± 0.001	0.0095	14	0.011	17
P	132 ± 1	86.4	65	92.0	70
Pb	0.20 ± < 0.01	0.020	10	0.057	28
Se	0.066 ± 0.014	0.023	35	0.012	18
Si	0.272 ± 0.058	3.17	1160	2.64	970
V	0.015 ± 0.001	0.0075	50	0.0039	26
Zn	2.08 ± 0.02	1.09	52	0.774	37

[a]Average values ± standard deviation from duplicate experiments.

[b]Compared to *aqua regia* extraction.

Table 2. Main results of recent studies that have investigated P extraction from solid residues derived from thermal treatments of SS: ISS = incineration SS; PSS = pyrolysis SS; GSS = gasification SS; HTC = hydrothermal carbonization; SCWO = supercritical water oxidation; SCWG = supercritical water gasification.

Study	Residue tested			Optimum parameters and main results of P extraction			
	Type of residue	Process temperature and pressure	P content (g/kg)	Extractant solution	L/S ratio (L/kg)	Reaction time (h)	P extraction efficiency (%)
Stark et al., 2006	SCWO residue	> 374 °C, > 22 MPa	27-80	0.1 M HCl	50	2	80-100
Franz, 2008	ISS ash	830-850 °C	92	1.4 M H_2SO_4	2	0.167	90
Biswas et al., 2009	ISS ash	N.A.	88	0.1 M HCl or 0.05 M H_2SO_4	150	4	~ 100
Donatello et al., 2010	ISS ash	800-900 °C	54-76	0.5 M H_2SO_4	20	2	91
Petzet et al., 2012	ISS ash	N.A.	79-110	1 M NaOH[a]	10	24	70-77
Xu et al., 2012	ISS ash	850 °C	66-119	0.5 M HCl	50	2	95
Ottosen et al., 2013	ISS ash	850	70-99	0.19 M H_2SO_4	20	2	~ 100
Acelas et al., 2014	SCWG residue	400 °C, 24.6 MPa	83	pH 2[b]	1000	8	84
		500 °C, 37.0 MPa	87				86
		600 °C, 49.6 MPa	94				95
Atienza–Martínez et al., 2014	ISS ash	600 °C	78	0.06 M oxalic acid	150	2	93
		750 °C	79				98
		900 °C	81				96
Huang and Tang, 2015	PSS char	250-600 °C	40-100	0.25 M NaOH + 0.05 M EDTA	20	16	40-65
	HTC char	225 °C	70-80				50-55
Kleemann et al., 2017	ISS ash	850-950 °C	72-75	0.6 M H_2SO_4	10	0.5	88-90
	PSS char	850 °C	56	0.8 M H_2SO_4			89
Gorazda et al., 2018	GSS char	800-1000 °C	87.6	2.7 M HNO_3	~ 2.5	2	82
This study	WAO residue	274 °C, 4.5 MPa	132	1 M citric acid	10	2	61
				1 M HCl		1	62

[a] After acid pretreatment; [b] Continuously controlled by addition of oxalic acid.

Table 3. Main results of modeling experimental extraction capacities of Ca and P by using the pseudo-second order kinetic equation.

Element	Extractant (L/S = 10)	Main results of the pseudo-second order model		
		R^2	q_e[a] (mg/g)	k_2[a] (g/(mg · min))
Ca	1 M HCl	0.999	151 ± 1	0.00120 ± 0.00022
P	1 M HCl	0.999	87.3 ± 0.7	0.00206 ± 0.00046
Ca	1 M citric acid	0.999	163 ± 1	0.000288 ± 0.000022
P	1 M citric acid	0.999	99.0 ± 1.1	0.000402 ± 0.000036

[a] Estimate parameters ± standard errors.

Table 4. Formula, molar ratios Ca/P, and solubility constants of various Ca phosphates (adapted from Valsami-Jones, 2001).

Name	Formula	Molar ratio Ca/P	Solubility constant (mol/L)
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4 \bullet 2H_2O$	1	$2.49 \cdot 10^{-7}$
Dicalcium phosphate anhydrous (DCPA)	$CaHPO_4$	1	$1.26 \cdot 10^{-7}$
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3 \bullet 2{,}5\ H_2O$	1.33	$1.25 \cdot 10^{-47}$
Tricalcium phosphate (TCP)	$Ca_3(PO_4)_2$	1.5	$1.20 \cdot 10^{-29}$
Hydroxyapatite (HAP)	$Ca_5(PO_4)_3OH$	1.67	$4.7 \cdot 10^{-59}$
Amorphous calcium phosphates (ACP)	variable	1-1.5	variable