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Investigation of phosphorus desorption from P-saturated alum sludge used as a substrate in constructed wetland

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Abstract

Phosphorus (P) desorption from P-saturated alum sludge, which was used as main substrate in a novel constructed wetland for wastewater treatment, was studied. Groups of batch experiments were designed and conducted to explore the efficiencies of P extraction using different acids (HCl, HNO_3, H_2SO_4) and bases (NaOH, KOH). The results showed that either acid or base is efficient for P-extraction and the efficiency relied mainly on the concentrations of H^+/OH^-, not the type of acid or base. Considering the efficiency, price and safety of the acids and bases tested, H_2SO_4 was chosen as most suitable reagent for P-extraction. A Box-Behnken experimental design based on the response surface methodology (RSM) was applied to evaluate the optimum of H_2SO_4 extraction. The optimal condition for the mass of sludge, H_2SO_4 concentration and volume was 0.8 g, 0.063 M and 142 ml, respectively. At such optimal condition, the maximum P-extraction efficiency of 98.2 % was achieved. Additionally, most of the main components of the saturated sludge, such as metals (Al, Ca, Mg, Fe), TOC (total organic carbon) and nitrogen can also be extracted. Overall, the results supported that H_2SO_4 seems to be an efficient and cost-effective reagent among all the reagents tested for P-saturated alum sludge treatment.

Keywords: phosphorus, desorption, acid, base, alum sludge, RSM, constructed wetland

1. INTRODUCTION

In contemporary society, phosphorus (P) is a crucial element for agricultural and numerous industrial activities. It is very severe that P is a non-regenerative resource and the known reserves are estimated to last only about 100 years with the present utilization rate [1]. At the same time, significant amount of P is consumed via various industrial- and daily life activities, thus making P being one of the main contaminants in various wastewaters. The main processes of P removal from wastewaters are chemical precipitation by metal salts, biological removal in bioreactors, constructed wetlands and enhanced biological phosphorus removal (EBPR) etc. [2]. In line with sustainable wastewater treatment technologies which are environmentally friendly, more and more efforts have been made in recent years, towards recovering phosphorus from wastewater and the sludge generated inevitably during the wastewater treatment [3-5].

On the other hand constructed wetland as a less energy-intensive, easy to operate and cost-effective technology is increasingly employed worldwide for various wastewater treatments. In the past five years, great efforts have been made at the University College Dublin, Ireland, towards developing a novel constructed wetland system for wastewater, especially the P-rich wastewater, treatment [6-8]. The novel constructed wetland lies in the use of the dewatered aluminium-based drinking-water treatment sludge (termed as alum sludge) as a substrate and a P-removing material for wastewater treatment. Such reuse of alum sludge in wetland is quite attractive. The concept is also sustainable as the objective of its utilization is not merely to dispose the alum sludge as a waste or find an alternative disposal route, but to utilize it for the purpose of enhancing wastewater treatment (particularly P removal) in constructed wetland. It has been demonstrated that more than 90% of

phosphorus can be absorbed by alum sludge cakes [7]. Previous study [9] has showed that the P adsorption capacity of the same alum sludge determined using batch isotherm tests would be 14.3 mg P/g dried sludge, implying that the lifetime of the alum sludge used in the constructed wetland for domestic wastewater treatment could be 9–40 years [8]. Even in the case of high P effluent of animal farm wastewater treatment tested, the lifetime of alum sludge can be estimated as 2.5– 3.7 years.

After use or saturation of such substrate (dewatered alum sludge), the investigation of desorption or extractability of P retained in the substrate is very crucial regarding the p-recovery as a resource. Recently, studies on P recovery technologies by the application of the solvent-extraction method have attracted considerable attention [10]. However, these methods not only use a large amount of organic solvent such as butyl-alcohol or tri-butyl phosphate to extract P but also require a very complicated procedure.

Therefore, the objective of this study was to investigate effectiveness of acids or bases extraction of phosphorus from saturated alum sludge which was adopted as a substrate in a laboratory scale constructed wetland for P immobilization from an animal farm effluent containing COD (chemical oxygen demand) of 213 ± 127 mg/l, BOD_5 (biochemical oxygen demand) of 110 ± 69 mg/l, phosphorus of 28 ± 15 mg/l (PO_4^{3-}–P), SS (suspended solids) of 72 ± 66 mg/l and pH of 6.8 ± 0.4 [8]. The farm possesses about 2000 livestock units of sheep, pigs, cattle and horses. The animal farm effluent is derived from all the activities on the farm and it undergoes some form of primary sedimentation before being pumped to the treatment wetland system [8]. After the preliminary

94 investigation, the study was focused on selecting the most suitable reagent for P desorption and
95 optimizing the factors like mass of sludge, concentration and volume of reagent using response
96 surface methodology (RSM) to achieve the most optimal and economical conditions. The
97 accompanying changes of other main components of sludge such as metals, nitrogen, TOC (total
98 organic carbon) under the optimal desorption conditions were also examined.
99
100 **2. MATERIALS AND METHODS**
101 **2.1 Origin of P-saturated alum sludge**
102 The P saturated alum sludge used in this study was obtained from a laboratory scale
103 constructed wetland system which uses dewatered alum sludge (collected from Ballymore Eustace
104 Water Treatment Works in Southwest Dublin, Ireland) as the substrate for a P-rich animal farm
105 wastewater treatment. After a long time operation, the alum sludge was almost saturated with
106 marginal P adsorption ability. The sludge was dried at room temperature and then ground and sieved
107 to diameter <0.3 mm to provide the test samples. By using inductively coupled plasma-mass
108 spectrometry (ICP-MS) (for testing Al, Ca, Fe, Mg and P), Eltra CS800 carbon/sulfur determinator
109 (for testing TOC) and Kone Analyser (for testing nitrite and nitrate), the characteristics of the
110 P-saturated sludge are listed in Table 1. As a comparison, the characteristics of the air-dried fresh
111 alum sludge before the wetland use are jointly listed in Table 1.
112 [Table 1 here]
113
114 **2.2 Experimental procedure**
115 The experiments were conducted in room temperature and the procedure was as follows. Initially,

the efficiencies of P extraction by acid and base under varied extraction time were examined. A batch of 0.8 g pre-weighed sludge samples was put into a series of 250 ml flasks. Then, 150 ml of acid (HCl) or base (NaOH) with different concentrations up to 0.1 M was added to the samples, thereafter the flasks were placed on a orbital shaker (SSL1, Bibby Sterilin LTD, UK) at 225 rpm for 1-6 hours for P extraction. During the extraction period, pH was not controlled although it was occasionally monitored and the pH was slightly increased along with the extraction process. After extraction, the samples were filtered using 0.45 μm Millipore filter paper (Millipore) before the phosphate (PO_4-P) analysis, which was conducted following the standard method using a Hach spectrophotometer (DR/2400).

The second set of experiments was conducted to examine the effect of different acid (H_2SO_4, HNO_3, HCl) or base (NaOH, KOH) with different concentrations from 0.01 M to 0.1 M on P extraction at fixed extraction time of 60 min following the same procedure described above.

The third set of experiments was designed using RSM method to optimize the H_2SO_4 extraction. RSM is a collection of mathematical and statistical techniques which can be used for studying the effect of several factors at different level and their influence on each other [11]. A Box-Behnken design [12] was chosen to evaluate the combined effect of the three independent variables, i.e. mass of alum sludge (X_1), concentration (X_2) and volume of acid solution (X_3) with extraction time being fixed as 60 min. The full experimental plan with respect to the values of the parameter in actual and coded form is listed in Table 2.

[Table 2 here]

Subsequently, P-extraction of the wetland used sludge with H_2SO_4 under the optimal conditions was conducted. In such experiment, the characteristics of the leachate were examined to evaluate the release/extraction of other components in the sludge by H_2SO_4.

Finally, a series of 100 ml H_2SO_4 leachate were tested by adding 4 M NaOH at pH range of 4-10.5 and stirred 30 min to form the aluminum phosphate precipitations. This is expected as the process for P recovery.

3. RESULTS

3.1 Phosphorus extraction by acid and base

Results of phosphorus extraction from P-saturated alum sludge by HCl or NaOH at different extraction time are presented in Fig. 1. The results showed that both the HCl and NaOH can be the efficient reagents for P extraction. Relatively, acid (HCl) is better than base (NaOH) since more than 90% phosphorus can be extracted by 0.1M HCl while 70% P extraction was obtained with the same concentration when NaOH was used. Concentration of HCl or NaOH seems to be an important factor to affect the extraction efficiency with high P extraction being achieved at strong acid or base. From Fig. 1, it can be seen that P was mostly extracted in the initial stage and the equilibrium can be reached within 60 min for both HCl and NaOH extraction.

[Fig. 1 here]

Yang *et al.*[13] studied the P-adsorption by alum sludge and claimed that the phosphorus and aluminum can form the complex compounds through chemical reaction and precipitation. The

160 P-adsorption is dominated by the significant amount of reactive functional groups, such as –OH,
161 –Cl, $–SO_4$ and humic substances in the sludge surface via the ligand exchange mechanism.
162 Therefore, it is expected that the P extraction via leaching to the acid or base solution from the alum
163 phosphate can be expressed with chemical equations shown below.

164 $$AlPO_4 + 3H^+ \rightarrow Al^{3+} + H_3PO_4 \quad (1)$$

165 $$AlPO_4 + 4OH^- \rightarrow Al(OH)_4^- + PO_4^{3-} \quad (2)$$

166 Based on the kinetic fitting using the experimental data derived from this study, the P extraction in
167 the initial stage was found to follow a first-order reaction, which could be described as follows:

168 $$\log (C_t/C_0) = -(\kappa/2.303)t \quad (3)$$

169 where C_t=residual P concentration in the sludge (mg/g) at extraction time t, C_0=initial P
170 concentration in the sludge (mg/g) (at t=0), κ=rate constant (min^{-1}), t=extraction time (min). At 20
171 ^oC, the correlation coefficients and the rate constants κ of different solutions were calculated and
172 showed in Table 3.

173 [Table 3 here]

174

175 Fig. 2 illustrated P extraction using different acids (HCl, HNO_3, H_2SO_4) or bases (NaOH, KOH)
176 with different concentrations at extraction of 60 min. From the results, there is no obvious
177 difference of extraction abilities between different acids or bases. The extraction efficiencies
178 exhibited an increased trend with concentrations of H^+ or OH^- but no significant increasing between
179 0.075 and 0.1 M. As all the acids and bases used are strong types and they are all completely
180 ionized in solution, dissolution of $AlPO_4$ is fully dependent on H^+ or OH^- (see Eq. (1), (2)), thus no
181 striking difference within acids and bases is understandable.

[Fig. 2 here]

Interestingly, it is noted from Fig. 2 that in low concentrations under 0.05 M, P extraction is more efficient by using base than that of using acid, but in high concentrations, acids are more powerful than bases. For example, P extraction efficiency by 0.075 M HNO_3 and NaOH was 90% and 65% respectively. The possible reasons for this may be the $Al(OH)_3$ inside the alum sludge, which was formed during the flocculation in water treatment process. The residual $Al(OH)_3$ might consume some acid or base when the sludge were treated/extracted by lower concentration. The reaction can be described as follows.

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \qquad (4)$$

$$Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O \qquad (5)$$

Obviously, more acid was used for dissolving $Al(OH)_3$. As a result, the acids exhibited the less efficiency for P extraction in the low concentration range. On the contrary, when concentrations are high enough, the reactions mainly follow the equation (1) and (2) and humic acid in sludge is thus easily released by base. As a result, the acids displayed the higher efficiency than the bases. Overall, it is a rather complicated reaction because of the complexity of components in alum sludge. Stark *et al.* [14] studied the P extraction from different sludges (collected from an incineration plant and a waste water treatment plant located in Sweden) by acid or base and claimed that the use of acid gave a higher P extraction for all samples. Keep in mind of this, by considering the cost of HNO_3, HCl and H_2SO_4 for the reagents for P extraction, H_2SO_4 was chosen for the subsequent experiments since H_2SO_4 extraction is much cheaper than HNO_3 and HCl, as shown in Table 4. In addition, considering the convenience and safety of operation, H_2SO_4 is better than the others as well because

204 HNO_3 and HCl are both high volatile acids with dangerous acid mist.

205 [Table 4 here]

206

207 **3.2 Optimization of H_2SO_4 extraction**

208 The sludge mass, H^+ concentration and volume of solution were selected as factors in the screening
209 test, to determine their significance in maximizing the solubilization of phosphate from used alum
210 sludge under H_2SO_4 extraction. According to a Box-Behnken design, the three-level experiments
211 were carried out and the results of experimental and predicted P extraction efficiencies are presented
212 in Table 5.

213 [Table 5 here]

214

215 The following second-order fitting polynomial equation was then obtained after the data fitting.

216 $$E\ (\%)=88.04-15.9X_1+13.33X_2+12.83X_3-6.75X_1^2-9.62X_2^2-8.06X_3^2+11.66X_1X_2+13.56X_1X_3-10.83X_2X_3 \quad (6)$$

217 (R^2=99.8 %; adj R^2=99.4 %)

218 Where E (%) is the P extraction efficiency and R^2 is the coefficient of determination. The average
219 values of efficiency and SD (standard division) obtained from the triple experiments and the
220 responses predicted via Eq. (6) are jointly shown in Table 5. Obviously, a good agreement of the
221 data between the experimental and the predicted is obtained. This can be confirmed with coefficient
222 R^2 value of 0.998. R^2 is defined as the ratio of the explained variation to the total variation and is a
223 measure of the degree of fit [15]. If R^2 value is higher than 0.8, it indicates that the model explained
224 the reaction well [16].

225

Minitab-14 was used to determine optimum conditions of the operating variables. The maximum efficiency of P extraction obtained is 97.4 %, correspondingly the maximum values of the process variables in coded values were given as follows: X_1=-1.00, X_2=0.167 and X_3=-0.16. According to relation between X_i and ψ_i, the actual values of tested variables are shown in Table 6. To validate the modeled results, three additional experiments using the optimum operation conditions (Table 6) were conducted. The replicate experiments yielded an average P extraction efficiency of 98.2 %. This clearly demonstrated that this model is effective to optimize the H_2SO_4 extraction.

[Table 6 here]

3.3 Extraction of other chemical components of the sludge by H_2SO_4

Table 7 presents the results of the extraction of aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), nitrite and nitrate in the P-saturated alum sludge by H_2SO_4 under the optimal operational conditions. It is very clear that all of them can be extracted via the release into solution except for the iron, implying that H_2SO_4 has a high leachability not only for phosphorus but also for other main chemical components of the sludge such as metals, nitrogen and TOC. Therefore, it is confident to claim that the wetland used sludge after H_2SO_4 extraction can be disposed without a risk for environment.

[Table 7 here]

3.4 P recovery by deposition

The H_2SO_4 extraction makes it possible for both $PO_4^{3-}$and Al^{3+} being released from the sludge to the

248 acidic solution. The molar ratio of Al^{3+}/ PO_4^{3-} is 2, which is suitable to form $AlPO_4$ by deposition.
249 Therefore, through adjusting pH of extraction solution by adding NaOH and keeping gentle mixing
250 for 30 min, the precipitates were formed. Such results are showed in Fig. 3. By monitoring the P
251 concentrations in H_2SO_4 extraction solution before and after NaOH adjustment to form $AlPO_4$
252 deposition, the P reduction in proportion of P concentration before NaOH adjustment was expressed
253 as $AlPO_4$ deposition efficiency in percentage, showing in Fig. 3. It is seen from Fig. 3 that the
254 suitable pH range is 5 to 7, allowing over 98% P being deposited.

255 [Fig. 3 here]

256

257 **4. DISCUSSION**

258 In Ireland, due to the nature of the geographic distribution of residents, there is huge potential of
259 application of small wastewater treatment systems. In line with the development of a novel
260 constructed wetland system of reuse dewatered drinking water treatment sludge as wetland substrate
261 for P-rich wastewater treatment, P extraction from the wetland used/saturated alum sludge was
262 studied. It has been noted in the literature that P extraction from P-rich sludges using different
263 methods has been reported. However, these sludges or sludge ash are mainly derived from
264 wastewater treatment processes. For example, Takahashi *et al*.[17] have found that phosphorus and
265 various heavy metals in the incinerated wastewater treatment sludge can be extracted when the pH
266 of the ash fell below 2.0 by adding sulfuric acid. Hong *et al*.[10] revealed that phosphorus in the
267 waste-activated sludge incinerator ash was completely extracted by 1 M HCl at the $L_{acid}S$ ratio of
268 6.4:1. Liao *et al.*[18,19] have reported that by using microwave treatment for only 5 min, about
269 80% of total phosphorus in the sewage sludge could be released into solution. However, it is not the

case for P-saturated alum sludge since it has been demonstrated that microwave treatment is weak for P extraction according to our previous study [20]. The knowable reason for this lies in that the main type of phosphorus in sewage sludge is organic-phosphorus, which can be easily released by microwave heating. Comparing with sewage sludge, alum sludge has a strong affinity with P due to its nature of abundant aluminum, which serves as coagulant in the main process of water treatment system. Ippolito *et al.* [21] studied the P retention mechanisms of a WTR and they rejected the hypothesis that P-loaded WTR will readily release P to solution. Therefore, it is more difficult to get P being released/extracted. Nevertheless, this study mainly focuses on trying to explore a simple, efficient, cost-effective alternative to address the puzzle of P extraction from the wetland used alum sludge. From the results of this study, H_2SO_4 extraction is demonstrated to be a suitable method.

However, it should be pointed out that the optimal condition for H_2SO_4 extraction determined by response surface methodology in this study may prove inadequate to even partially extract a significant portion of total P from the substrate-WTR in real and field situation since the pH-buffering capacity of the wastewater in the wetland may be much greater than the current testing system that simply utilizes air-dried WTR in contact with an acidic solution.

Actually, H_2SO_4 extraction adopted in this study for the special case of P extraction from substrate-WTR is a solvent-extraction approach. As shown in Tables 6 and 7, approximately 100% of the total P and the metal-Al which seems to be the backbone of the WTR particles are extracted from the WTR, suggesting that near complete dissolution and not extraction is taking place upon the use of the strong sulfuric acid. Fortunately, both P and Al released from the sludge are suitable to form $AlPO_4$ by deposition, as illustrated in Fig. 3. According to the studies of Makris *et al.* [22, 23], the immobilized P by WTR was at least in the form of an organo (TOC)-Al-P amorphous moiety

which involved adsorption mechanism of intraparticle phosphorus diffusion [24]. Thus, the extraction of P along with all other elements in the saturated WTR including metal and TOC are understandable.

Regarding the application of WTR as raw material for wastewater treatment, it should bear in mind that the characteristics of the WTR may vary significantly due to the differences in the quality of the raw water and the varied treatment chemicals and processes in practice [23,25]. Therefore, caution should be paid to use such the material for difference wastewater treatment.

5. CONCLUSIONS

In relation to the beneficial reuse of dewatered alum sludge as main substrate in constructed wetland for P-rich wastewater treatment, studies of P desorption from P-saturated alum sludge was described in this paper. Different acids (HCl, HNO_3, H_2SO_4) and bases (NaOH, KOH) as P extraction reagent have been tested. The results indicated that both acid and base were efficient for P-extraction and the efficiency mainly relied on the concentrations of H^+/OH^-, not the type of acid or base. H_2SO_4 was then chosen as most suitable reagent for P-extraction. According to the response surface methodology, which was applied to optimize the extraction process, the optimal condition for the mass of sludge, H_2SO_4 concentration and volume of 0.8 g, 0.063 M and 142 ml, respectively, could be determined. At such optimal condition, the maximum P-extraction efficiency of 98.2 % was achieved. Additionally, most of the main components of the saturated sludge, such as metals (Al, Ca, Mg, Fe), TOC and nitrogen can also be extracted, thus providing an environment-safe sludge for final disposal.

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FIGURES

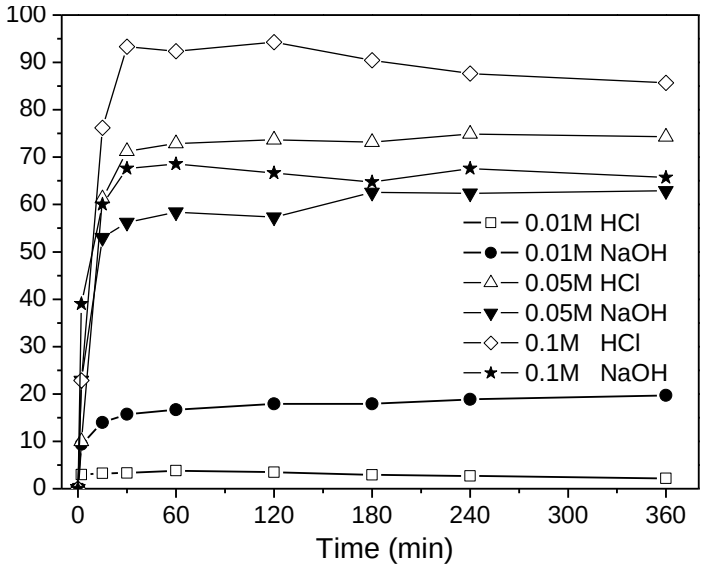

Fig. 1 P extraction by HCl or NaOH extraction at different time

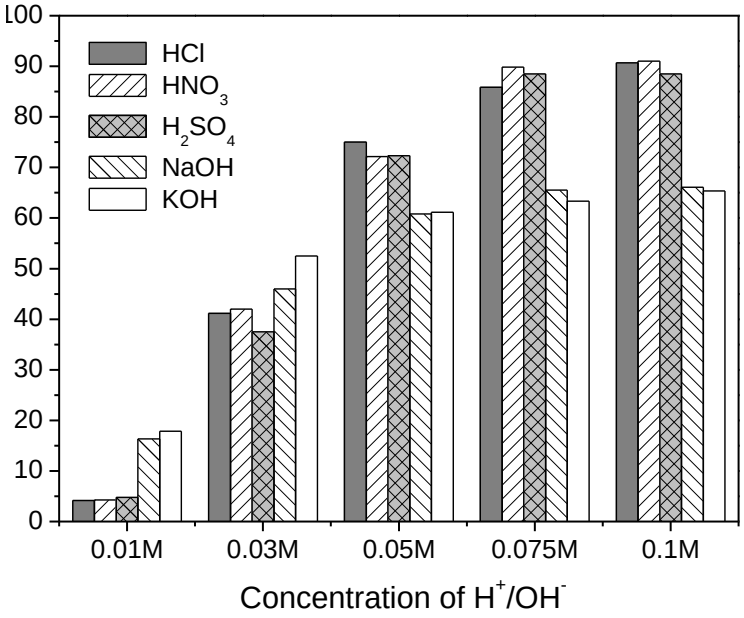

Fig. 2 P extraction by different acid or base with different concentrations

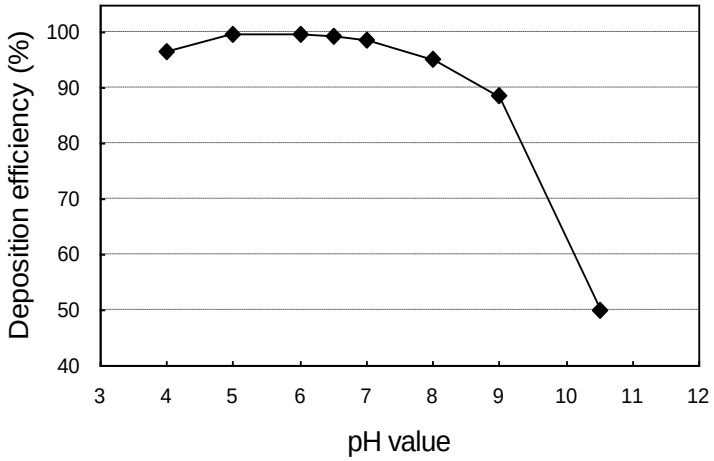

Fig. 3 Mean values of P deposition efficiency under different pH

TABLES

Table 1 The chemical components of the alum sludge (*DM denotes dry mass)

Chemical composition	Unit	Fresh alum sludge	P-saturated alum sludge
Total organic carbon (TOC)	% in DM*	12.8	6.9
H_2O (moisture content)	% in DM	22.64	21.46
Aluminum (Al)	mg/kg DM	42,880	63,020
Calcium (Ca)	mg/kg DM	1,964	16,460
Iron (Fe)	mg/kg DM	2,465	3,758
Magnesium (Mg)	mg/kg DM	46	2,377
Phosphorus (P)	mg/kg DM	154	38,590
Nitrate as NO_3	mg/kg DM	42	366
Nitrite as NO_2	mg/kg DM	0.4	3.2

Table 2 Range and levels of actual and corresponded coded variables for RSM

Variables	Symbols		Levels		
	Actual	Coded	-1	0	1
Mass of alum sludge (g)	ψ_1	X_1	0.8	1.6	2.4
Concentration of H_2SO_4 (M)	ψ_2	X_2	0.04	0.06	0.08
Volume of H_2SO_4 solution (ml)	ψ_3	X_3	100	150	200

Note: $X_1=(\psi_1-1.6)/0.8$, $X_2=(\psi_2-0.06)/0.02$, $X_3=(\psi_3-150)/50$

Table 3 Correlation coefficients (R^2) and rate constants (κ) of reactions

	HCl			NaOH		
	0.01 M	0.05 M	0.1 M	0.01 M	0.05 M	0.1 M
R^2	0.6091	0.9819	0.9877	0.8801	0.9858	0.9854
κ (min^{-1})	0.0006	0.0159	0.1243	0.0007	0.0030	0.0277

Table 4 Cost estimation for P extraction with different acids

Acid	Price (Euro/tone)	Cost (Euro/g P)
HNO_3	214	7.21×10^{-3}
HCl	51	2.17×10^{-3}
H_2SO_4	32	7.06×10^{-4}

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Table 5 RSM for the three experimental variables in coded units and its experimental and predicted response

Run no.	Coded factors			P extraction efficiency (%)	
	X_1	X_2	X_3	Experimental	Predicted
1	-1	-1	0	87.42	85.90
2	-1	1	0	88.34	89.24
3	1	-1	0	31.68	30.78
4	1	1	0	79.25	80.76
5	0	-1	-1	31.73	33.37
6	0	-1	1	79.91	80.69
7	0	1	-1	82.48	81.69
8	0	1	1	87.33	85.69
9	-1	0	-1	90.00	89.86
10	1	0	-1	31.68	30.94
11	-1	0	1	87.67	88.40
12	1	0	1	83.59	83.72
13	0	0	0	87.33	88.04
14	0	0	0	88.18	88.04
15	0	0	0	88.61	88.04

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Table 6 Optimum value of the process parameter for maximum P extraction efficiency

Parameters	Optimum values
P extraction efficiency (%)	97.4
Mass of alum sludge (g)	0.8
Concentration of H_2SO_4 (M)	0.063
Volume of solution (ml)	142

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Table 7 Extraction of other components of the sludge by H_2SO_4

Chemical components	H_2SO_4 leachate	Release efficiency
Aluminum (Al)	346.4 mg/L	99.62 %
Calcium (Ca)	74.8 mg/L	82.35 %
Iron (Fe)	8.984 mg/L	43.34 %
Magnesium (Mg)	10.88 mg/L	82.94 %
Nitrate as NO_3	1.7 mg/L	100 %
Nitrite as NO_2	＜0.05 mg/L	100 %
TOC	378.9 mg/L	99.53 %

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