

Demonstration of ion exchange technology for phosphorus removal and recovery from municipal wastewater

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Abstract

Orthophosphate (PO₄-P) removal and recovery from municipal wastewater were investigated in a 10 m³/day hybrid anion exchanger (HAIX) demonstration plant. To date, HAIX resins have been investigated for PO₄-P removal at laboratory scale with promising results but there is a need to investigate the application of the technology at larger scale, over extended operation whilst establishing an efficient regenerant management solution. The HAIX removed an average of 6 mg PO₄-P /L to >0.3 mg PO₄-P/L, within 430 bed volumes, with a capacity of 4.1 mg PO₄-P/g resin. To manage the regenerant (NaOH 2%) efficiently, this was reused up to 8 times, reaching 785 mg PO₄-P/L, but the adsorption capacity was compromised, and it decreased to 1.5 mg PO₄-P/g resin. By adding calcium hydroxide to the saturated NaOH, 95% of the PO₄-P was recovered as hydroxyapatite, and at the same time the regeneration effectiveness was re-established, as <0.3 mg PO₄-P/L was reached again in the effluent. The treated NaOH was reused as regenerant solution, ensuring high effluent quality of <0.2 mg PO₄-P/L. This study confirmed the capability of HAIX technology to remove and recover PO₄-P from wastewater offering a solution which ensures both a high effluent quality and a circular economy approach.

Keywords: Phosphorus removal, ion exchange, regenerant management, circular economy, resource recovery

1. Introduction

Orthophosphate ($\text{PO}_4\text{-P}$) concentrations in municipal wastewater range between 4 and 12 mg $\text{PO}_4\text{-P/L}$ [1]. This $\text{PO}_4\text{-P}$ needs to be removed to ensure that stringent discharge limits imposed by the Water Framework Directive, enforcing phosphorus (P) concentration as low as <0.1 mg/L in effluent [2], are met. Different technologies can be applied in wastewater treatment plants (WWTPs) to remove $\text{PO}_4\text{-P}$ [3] but the overall increasing demand for P [4] has moved the attention towards technologies that can allow for both removal and recovery of P [5]. To evaluate the applicability of such technologies many factors need to be considered, including operational and maintenance costs, final effluent quality, sludge production, chemical consumption, purity of the recovered product and environmental impact of the technology such as greenhouse gas emissions. One type of technology which can meet the tighter consents limit for P discharge [6] with low energy consumption and moderate environmental impact [7,8] is based on using ion exchange resin (IEX). Ion exchange technologies have been applied to remove a wide range of chemicals such as nitrate [9], ammonium [10], arsenic [11], phosphorus [7] from water and wastewater [12]. In particular, $\text{PO}_4\text{-P}$ can be selectively removed from wastewater using resins [13,14], such as inorganic ion exchangers, polymeric hydrogels or polymeric ligand exchanger [1]. Most of these resins can be regenerated after reaching saturation, commonly using a high pH brine solution (such as NaOH), thus restoring their initial capacity [15].

A selective IEX resin that has been widely used for the efficient $\text{PO}_4\text{-P}$ removal is composed of a hybrid polymeric base [12] where hydrated ferric oxide nanoparticles (HFO-NP) have been dispersed, usually referred to as hybrid anion exchanger (HAIX) [7,16]. Due to the Donnan membrane exclusion effect, the polymeric anion exchanger allows enhanced permeation of anions, such as $\text{PO}_4\text{-P}$, within the polymer phase due to its high concentration of fixed positive charges of FeOH_2^+ [17]. In particular, previous studies have confirmed that 90% of the capacity of the resin for phosphorus is due to the ferric nanoparticles with the other 10% is related to the exchange component [18]. The process for the preparation of the HAIX was developed at Lehigh University and it has since been commercialized by Layne Christensen and Purolite Company in the US [17]. The previous work conducted on HAIX describes $\text{PO}_4\text{-P}$ removal from municipal wastewater [6,19], surface waters with high concentration of natural organic matter [20], urban wastewater treatment plant sludge liquor [6], primary and secondary effluent wastewater [18] (Table 1). In these laboratory scale experiments, the HAIX removed up to 95% of the $\text{PO}_4\text{-P}$ present in wastewater with high affinity for the $\text{PO}_4\text{-P}$ in presence of competitive ions compared to other selective resins [20] with a capacity up to 14.4 mg P/g resin according to the initial $\text{PO}_4\text{-P}$ concentration [6] (Table 1). HAIX effectively removed $\text{PO}_4\text{-P}$ within a pH range of 6-8 [12] where the divalent anion HPO_4^{2-} and the monovalent anion H_2PO_4^- are present and can therefore create an inner sphere complexed with HFO-NP via Lewis acid (metal oxides)-base (orthophosphate anion) interactions [16,21].

Regeneration is a key part of any IEX process that must be completed as effectively and economically as possible. An alkaline solution can be used to deprotonate the HFO-NP whereas polymeric base requires brine regeneration as with common IEX processes [18], usually 2% NaOH / 2% NaCl [13] (Table 1). The regeneration of the HAIX resin concentrates >90% of the adsorbed PO₄-P into the regenerant solution by reusing the same regenerant solution multiple times [6,15,22]. The multiple reuses of the regenerant also contributes to reduce the environmental impact of the IEX process by decreasing the chemical consumption needed for the regenerant production.

The saturated regenerant solution can be further processed for PO₄-P recovery [15]. Despite the use of the recovered P as fertilizer, there is a raise high-value phosphorus-based materials being developed for a range of applications, such as black phosphorene used in electronics and sensing applications [23]. Struvite crystallisation is often applied for PO₄-P recovery from different wastewaters and it has been widely studied [24,25,26]. However, the successful crystallization depends on the pH, Mg²⁺ and NH₄⁺ concentrations, temperature, and mixing energy [25,27], and regenerant solutions do not often have the suitable characteristics for struvite formation. Recently, the recovery of calcium phosphate has gained attention due to the lower cost and simplicity of the process [26,28].

Table 1. Laboratory scale experiments using HAIX for the removal of PO₄-P from synthetic and real wastewater.

HAIX resin supplier	Treated solution	Initial PO ₄ -P conc.	Adsorption capacity (mg P/g resin)	Regen. efficiency	Experiment scale	Ref.
Solmetex Co., Massachusetts	Sludge liquor, municipal WW	350 mg/L	14.2-14.4	95% (1M NaOH)	Batch test; Packed bed column test (45 HX1.5D cm glass column)	[6]
	Real and synthetic WW	4.8 mg/L	0.29-0.51 (13% of the exhaustive capacity)	88% (2-5% NaCl and 2-5% NaOH)	Batch test; Fixed-bed columns (20H x 1.5D cm)	[7]
	Municipal WW	4 mg/L	3.4-6.3	N/A (NaCl-NaOH)	Fixed-bed columns (0.03-1.0m H X 15 and 500 mm D)	[19]
Layne Christensen Company, Texas	Secondary WW effluent	100 mg/L	7-9.7	90% (4% NaOH)	Fixed-bed columns (2.5 cm D)	[18]
	Synthetic solution	5 mg/L	N/A	>90% (2% NaCl and 2% NaOH)	Batch experiments	[21]
	Organic-rich surface water	132-250 µg/L	N/A	80% (NaCl-NaOH)	Fixed-bed column (50H X 10D mm glass column)	[20]

WW: wastewater; H: Height; D: Diameter.

Depending on the operational conditions different forms of calcium phosphate can be obtained, namely hydroxyapatite (Ca₅(PO₄)₃(OH)) [29], octa calcium phosphate (Ca₄H(PO₄)₃·3H₂O) [26], tricalcium phosphate (Ca₃(PO₄)₂) [26],

monotite (CaHPO_4) or brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) [30]. According to Ansari *et al.* [28], the efficiency of the recovery mainly depends on the initial P concentration in the treating solution with higher concentration resulting in higher recovery. This makes the process suitable for the management of the IEX regenerant solution as the NaOH saturated with $\text{PO}_4\text{-P}$ can be used to recover calcium phosphate.

To date, HAIX resins have been investigated for P removal at laboratory scale [15,16,22] with promising results (Table 1), but there is a need to investigate the application of the technology in WWTP at larger scale, over extended operation whilst establishing an efficient regenerant management solution. This is the first study on an ion exchange technology that investigates both phosphorus removal and recovery from municipal secondary effluent wastewater, that considers factors such as long-term operation, regenerant reuse and recovered product quality, at near full-scale. Hence, this study investigates changes in $\text{PO}_4\text{-P}$ adsorption capacity over an extended period of operation (under fixed conditions to establish the consistency of performance), regenerant reuse and calcium phosphate recovery in a demonstration IEX plant fed with $10 \text{ m}^3/\text{day}$ of secondary treated municipal wastewater over a period of 2 years.

2. Materials and methods

2.1. Resin and secondary wastewater

The resin, HAIX-LayneRT (HAIX), was purchased from Layne Christensen Company, Texas, United States. It is a commercially available resin mainly used for arsenic removal from contaminated groundwater [11,31]. The HAIX base material is a strong base anion exchange resin (macroporous, with a quaternary

ammonium functional group [31]), within which hydrated ferric oxide nanoparticles have been dispersed to enhance the selectivity for phosphorus [13]. The average particle diameter was 0.69 μm [19]. The secondary treated wastewater originated from Cranfield University WWTP, after preliminary, primary and secondary treatment that ensured solids and chemical oxygen demand (COD) removal.

The demonstration plant was manufactured to the required specifications by MionTec GmbH (Germany) and assembled on site (Figure 1). It consisted of a drum filter, a compressed air diaphragm pump with float flow measurement and air flow regulator to adjust the pump's flow rate, a PVC-U column, two manometers to measure pressure loss and sampling points. The IEX column had an internal diameter of 22 cm and a height of 158 cm and it was filled with 35L of HAIX (24 kg), up to a height of 95 cm, 60% of the total height, to allow for resin expansion during backwash and regeneration procedures.

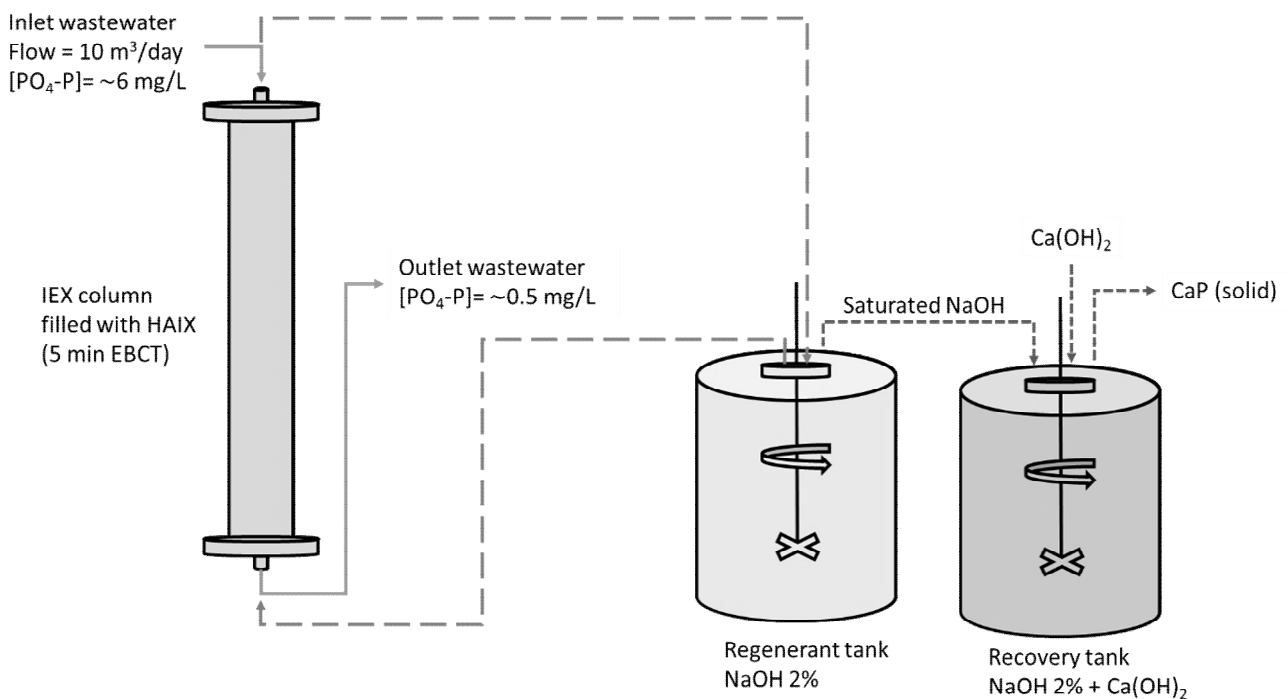


Figure 1. Schematic representation of demonstration plant.

The IEX column was fed with wastewater in downflow operation at a flow rate of 10 m³/day (417 L/h) equivalent to an empty bed contact time (EBCT) of 5 minutes, that was suggested as the optimal in previous studies [32]. The PO₄-P concentration at the influent and effluent was monitored daily by taking samples from the designated valves. The regeneration of the resin was performed with 10 bed volumes (BV) of NaOH 2% (W/V) solution in upflow operation at 400 L/h. The column was drained before and after the regeneration started. The regenerant was kept homogenous by a mixer installed on the regenerant storage tank. At the end of the regeneration, the total volume of the regenerant was collected in the storage tank (Figure 1) to be reused and the column was backwashed with tap water for 30 minutes before a new adsorption cycle was started.

2.2. Operating parameters

Considering the bed volume, BV (L), and the flow rate in the bed, F (L/min), it was possible to calculate the empty bed contact time (EBCT), according to Equation 1 [33]:

$$EBCT = BV/F \quad \text{Equation 1}$$

The orthophosphate adsorption capacity (Q, mg PO₄-P/g resin) and desorption (Q_{reg}, mg PO₄-P/g resin) of the HAIX in each cycle was calculated as in Equations 2 [34] and 3 [35]:

$$Q = \frac{\int_{V=0}^{V^{fin}} (C_{in} - C_{out}) dV}{M} = \frac{\sum_0^n [(C_0 - C_n) * (V_n - V_{n-1})]}{M} \quad \text{Equation 2}$$

$$Q_{reg} = \frac{[C_{r.i} - C_{r.f}] * V_{reg}}{M} \quad \text{Equation 3}$$

where C_{in} and C_{out} are the initial and final orthophosphate concentration in wastewater (mg PO_4 -P/L); M is the mass of resin (g); V is the volume of the wastewater treated in each cycle (L); $C_{r.i}$ and $C_{r.f}$ are the orthophosphate concentrations in the regenerant at the beginning and at the end of each regeneration cycle (mg PO_4 -P/L); V_{reg} is volume of regenerant (L).

The adsorption and regeneration efficiencies (AE and RE, respectively) were calculated following Equations 4, 5 and 6 [36].

$$M_{ret} = M_{fed} - M_{out} \quad \text{Equation 4}$$

$$AE = \frac{(M_{fed} - M_{out})}{M_{fed}} * 100 \quad \text{Equation 5}$$

$$RE = \frac{M_{reg}}{M_{ret}} * 100 \quad \text{Equation 6}$$

where, M_{fed} , M_{out} are the mass of PO_4 -P in the wastewater the influent and effluent of the IEX demonstration plant (g), respectively; M_{ret} and M_{reg} are the mass of PO_4 -P retained by the HAIX and recovered during the regeneration phase (g), respectively. Considering that the regenerants were reused multiple times, to accurately calculate the regeneration efficiency, the orthophosphate concentration from previous cycles was taken into account.

2.3. Investigation of the accumulation of organics on the resin

To test the effect of organic matter on the adsorption capacity of the HAIX, 4 g of resin were taken from the top of the column. The resin was regenerated with 400 mL of 2% NaOH for 1 hour, mixing at 100 rpm orbital shaker (SSL1, STUART, UK). Successively 2 g of the regenerated resin were treated with 5% NaCl (1 hour at 100 rpm), adding 100 mL/g resin. The regenerated resin (both 2% NaOH and 2% NaOH + 5% NaCl) was used to treat wastewater with an initial concentration of 4.3 mg PO₄-P/L in a batch test. For this, 1 gram of resin was added to 100 mL of wastewater and left in agitation at 100 rpm overnight. The orthophosphate concentration and the chemical oxygen demand (COD) were analysed in the regenerants (NaOH and NaCl) before and after the regeneration and in the wastewater, before and after the adsorption.

2.4. Recovery process

The PO₄-P saturated regenerant solution (2% NaOH) was used to test the recovery process at two different Ca:P ratios. A calcium hydroxide (Ca(OH)₂) solution (300 g/L) was added to 600 mL of saturated regenerant to achieve Ca:P molar ratios of 2 and 3, based on the reaction stoichiometry. The solutions were mixed at 75 rpm (Phipps and Bird PB-700 jar tester, Richmond, USA) at room temperature (18°C) for 6h. Samples were taken after 1, 2, 4 and 6h. After 1 hour of settling, the samples were filtered using filter syringes (Sartorius 0.2 µm retention syringe filter, 26 mm diameter) and the PO₄-P concentration was measured in each sample. The experiment was conducted in triplicate.

The recovery of $\text{PO}_4\text{-P}$ from the IEX demonstration scale plant was done in batch. Fifty litres of saturated regenerant solution were mixed with a solution of 300 g/L of $\text{Ca}(\text{OH})_2$ at a Ca:P ratio of 3. The solution was mixed for 24h and the samples were taken after each hour. The precipitate was successively filtered (polypropylene filter bags, 50 μm), washed with deionized water and dried in the oven overnight at 100°C.

2.5. Chemical analysis

During adsorption phase, samples of the effluent were collected using an ISCO autosampler (3700 Standard Portable Sampler, Teledyne Isco) while manual sampling three times a day was used for the influent wastewater. The samples were filtered using Whatman Filters (22 μm pores diameter) before all the analysis were performed to remove any solids in solution. If storage was needed, the samples were kept refrigerated at 4°C. Orthophosphate, pH, temperature and chemical oxygen demand (COD) were monitored regularly. During regeneration (desorption phase), samples of NaOH were taken before and after the regeneration and pH, calcium and $\text{PO}_4\text{-P}$ concentrations were measured.

Orthophosphate concentration was analysed using the Smartchem200 (AMS Alliance, Frépillon, France) which performs a colorimetric analysis (phosphate determination by molybdenum blue in compliance with EPA 365.3). Analysis of pH and temperature were performed using pH and temperature portable meters (Jenway 3510 pH and conductivity meter, Camlab, UK), used on site. Calcium and COD were analysed using Spectroquant® Cell Test kit (Merk Millipore) according to manufacture protocol. Anions and cations in wastewater were

analysed following standard colorimetric analysis [37]. Metals were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) [38]. Analysis of the total suspended solids (TSS) was performed according to Standard Methods (Standard Methods 2540D). The recovered product was weighted and analysed with a scanning electron microscope (SEM, Tescan Vega 3, large chamber, Kohoutovice, Czech Republic) and X-ray diffraction (XRD, Siemens D5000 powder diffraction set-up, theta/2 theta configuration, Munich, Germany) for chemical characterization.

3. Results and discussion

3.1. Wastewater characterisation

The secondary wastewater fed to the IEX demonstration plant presented an average orthophosphate ($\text{PO}_4\text{-P}$) concentration of around 6 mg $\text{PO}_4\text{-P/L}$ and total phosphorus (TP) of 6.6 mg TP/L ; it contained 75 mg $\text{SO}_4\text{-S/L}$, 141 mg $\text{NO}_3\text{/L}$ and 76 mg Cl/L (Table 2). The pH was stable at around 7.1 ± 0.2 while the COD was 54 ± 5.7 mg/L.

Table 2. Characterisation of the secondary treated wastewater fed to the IEX demonstration plant.

Pollutant	$\text{PO}_4\text{-P}$	TP	$\text{SO}_4\text{-S}$	$\text{NH}_4\text{-N}$	Na	K	Ca	Cl	$\text{NO}_3\text{-N}$
Conc.	5.9	6.6	75.4	8.1	60.0	16.9	69.0	75.6	141.0
(mg/L)	±0.1	±0.2	±6.2	±2.0	±14.6	±0.1	±14.0	±9.6	±4.9

The chemical characterisation presented in Table 2 confirmed the typical composition of secondary effluent wastewater, where competing ion such $\text{SO}_4\text{-S}$, NO_3 and Cl are usually present in higher concentration than $\text{PO}_4\text{-P}$ [32,39]. In

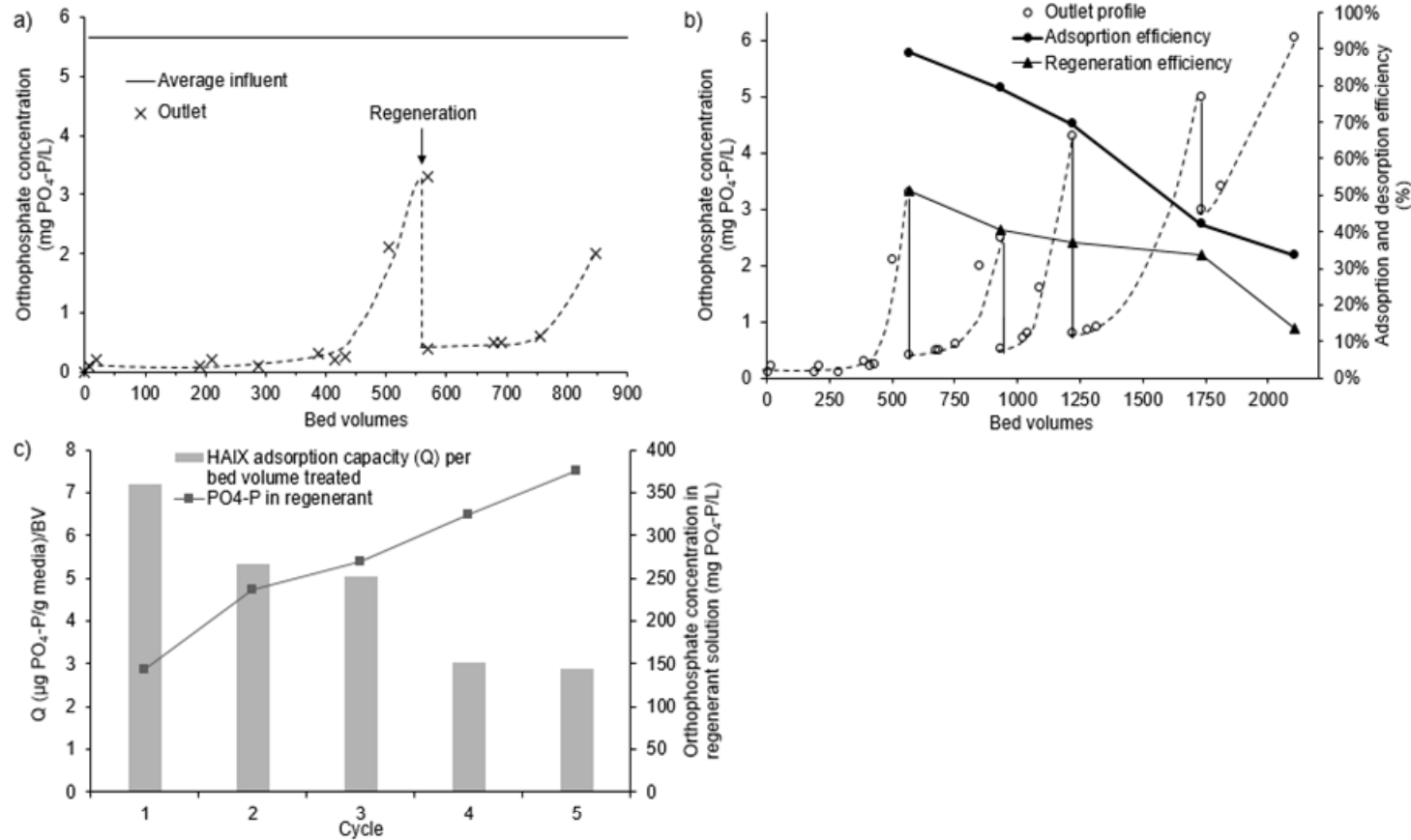
particular, $\text{SO}_4\text{-S}$ can act as strong competitor for the $\text{PO}_4\text{-P}$ adsorption due to the similarity in atomic weight and valence between the two molecules [1,16]. In a study completed by Muhammad et al [18] it was demonstrated that sulphate removals of 4-9% reached an equilibrium after the 7 cycle of operation, but values of 56% were recorded for the first cycle. For this reason, there is a need of an adsorptive resin with high selectivity for $\text{PO}_4\text{-P}$.

3.2. Orthophosphate removal from wastewater

When operating the demonstration plant with fresh HAIX resin at 5 min EBCT, the effluent $\text{PO}_4\text{-P}$ concentration was kept below 0.3 mg $\text{PO}_4\text{-P/L}$ for 430 bed volumes (Figure 2a). The HAIX resin removed up to 90% of the $\text{PO}_4\text{-P}$, yielding an adsorption capacity of 4.1 mg $\text{PO}_4\text{-P/g}$ resin. This is in agreement with previous studies completed with EBCT of 4 min (capacity up to 3.8 mg $\text{PO}_4\text{-P/g}$) [19]. The high selectivity of the HAIX is related to the quaternary ammonium groups on the polymeric base and the hydrated ferric oxide nanoparticles dispersed on the resin [17]. According to literature, the HAIX adsorption capacity can range from 0.29 to 14.4 mg $\text{PO}_4\text{-P/g}$ resin, depending on the initial $\text{PO}_4\text{-P}$ concentration wastewater [6,7,18].

About 51% of the adsorbed $\text{PO}_4\text{-P}$ was recovered in the regenerant solution, corresponding to a Q_{des} of 2.1 mg $\text{PO}_4\text{-P/g}$ resin. In previous studies conducted at laboratory scale [1,7,16], the regeneration of the HAIX resin allowed for the recovery of 65-80% of the phosphorus adsorbed on the resin. In these studies, the regeneration was performed with a combination of NaOH (2-4% wt) and NaCl (2-5% wt) to allow for both the regeneration of the polymeric base as well as the

hydrated ferric oxide nanoparticles. On the other hand, in this work the regeneration of the HAIX was obtained with NaOH 10%. Possible reasons for the reduced regeneration efficiency could be linked to the need of the treatment with NaCl as well the limited EBCT which did not allow enough contact time between the regenerant and the resin and the fouling of the resin with organic matter. Furthermore, the same regenerant was reused for the following four cycles and the adsorption capacity gradually decreased down to 1.5 mg PO₄-P/g resin (33% adsorption efficiency) in the fifth cycle (Figure 2b). The efficiency of the regeneration decreased to 13% in cycle 5 (Figure 2b) due to a reduction of the available adsorption sites. The bed volumes treated before breakthrough decreased from 430 BV in cycle 1 to 83 BV in cycle 5, showing that both the resin and the regenerant reached saturation. To indicate, the effluent PO₄-P concentration was 0.4 mg PO₄-P/L in the second cycle and was kept below 0.6 mg PO₄-P/L for 186 BV. However, the effluent was 3 mg PO₄-P/L at the beginning of the fifth cycle (Figure 2b). At the same time, the PO₄-P concentration in the regenerant solution increased from 144 mg PO₄-P/L after the first cycle up to 375 mg PO₄-P/L in the fifth cycle (Figure 2c). Consequently, a loss in capacity from 7.2 µg PO₄-P/g resin/BV to 2.9 µg PO₄-P/g resin/BV after the fifth reuse of the regenerant was detected (Figure 2b).



12 Figure 2. a) Orthophosphate removal from municipal wastewater ($C_{in} = 5.7 \text{ mgPO}_4\text{-P/L}$) using fresh hybrid anion exchanger (HAIX) and
 13 regeneration with NaOH 2% (10 bed volumes); b) impact of reusing the same regenerant solution multiple times upon HAIX adsorption
 14 capacity (Q), regeneration cycle is indicated with vertical lines; c) Q per bed volume (Q/BV) of wastewater treated and increase in
 15 concentration of the regenerant solution after each regeneration cycle.

3.5. Long-term operation of the IEX technology

The longevity and robustness of the IEX technology was investigated by reusing the HAIX resin over an extended period of time. Figure 3a presents the C_t/C_0 (effluent concentration at time t /influent concentration at time $t=0$) during entire period of operation of the demonstration plant (63 cycles) and the increase in the concentration $PO_4\text{-P}$ in the regenerant. The NaOH was reused up to 8 times reaching a concentration of 785 mg $PO_4\text{-P/L}$. When the efficacy of the regeneration fluid was no longer apparent, the solution was stored for the recovery process and re-used or a new solution was prepared (Figure 3a). Figure 3b presents the breakthrough curves of cycles 1, 17, 32, 42 after regeneration with fresh regenerant. After the regeneration with fresh regenerant solution, the adsorption cycles were initiated and the C_t/C_0 was below 0.1 (Figure 3b). Nevertheless, the prolonged use of the HAIX resin decreased the amount of bed volumes treated before breakthrough. In fact, while for cycle 1 the C_t/C_0 was kept below 0.1 for almost 450 BV, the same C_t/C_0 was reached after 108 BV in cycle 42 indicating a loss in the adsorption capacity over time (Figure 3b). This indicated that the resin lifespan was reduced when subjected to intensive operation, which was further investigated and discussed in the sections below,

as other studies indicate that the HAIX resin is expected to have an operational life of seven years [1].

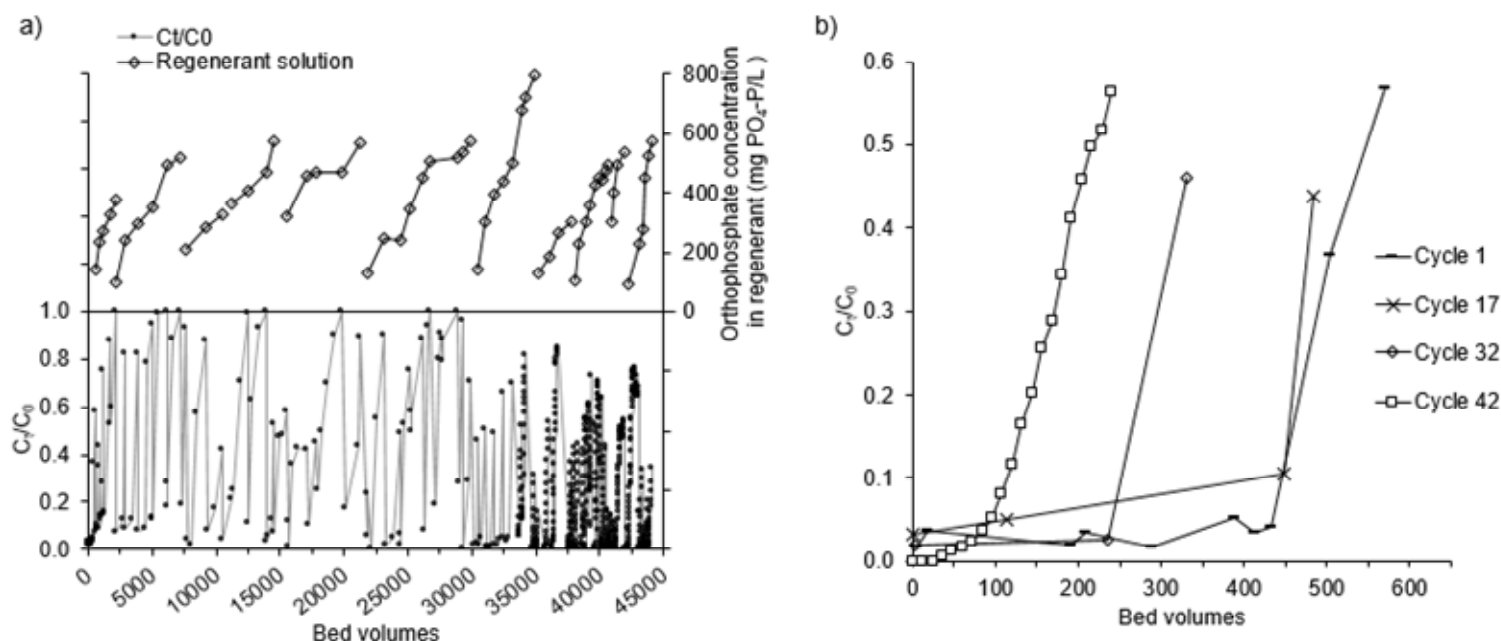


Figure 3. C_t/C_0 for all the cycles performed at demonstration scale (63 cycles) and increase in orthophosphate concentration in the regenerant solution (NaOH) obtained by multiple reuse (a); impact of reusing the same HAIX resin multiple times upon number of bed volumes treated between breakthroughs for cycle 1, 17, 32 and 42 (b).

3.6. Investigation of the accumulation of organics on the resin

The HAIX was also observed to remove around $26 \pm 10\%$ of the influent COD during the entire period of operation. This corroborates with previous studies [18] and highlights the importance of taking into consideration the accumulation of organic matter on the resin surface. This, in fact, can occupy the sorption sites and, at the same time, limit the mass transfer on the resin surface and, when not removed, will eventually foul the HAIX and result in loss of capacity [17]. To demonstrate the impact of organics on resin capacity, a laboratory scale

experiment was performed. When the resin was regenerated with 2% NaOH, about 13.28 ± 0.33 mg $\text{PO}_4\text{-P/L}$ and 71.8 ± 2.4 mg COD/L were desorbed and released in the regenerant. When the resin was regenerated with 5% NaCl, an additional 0.06 ± 0.03 mg $\text{PO}_4\text{-P/L}$ and 387 ± 17 mg COD/L were released. The higher amount of organic matter in solution was confirmed by the evident brown colour of the NaCl solution after regeneration. As a result, the resin regenerated with NaOH and NaCl presented adsorption efficiency of 0.43 ± 0.0 mg $\text{PO}_4\text{-P/g}$ resin, 16% higher of the capacity of the resin regenerated with only NaOH (0.35 ± 0.02 mg $\text{PO}_4\text{-P/g}$ resin). This aligned with the study from SenGupta [17] that suggests the soaking of the resin in NaCl at slightly high temperature (40°C) facilitates the desorption of organics. Successively, the NaCl brine and the organics can be separated by nanofiltration, electrodialysis or ion exchange technologies [40,41]. This would ensure the recovery of the brine for its use and allow for the recovery of natural organic matter (NOM) (i.e. humic acids and low molecular weight (LMW) organics, [40]. In particular, there is a recent interest in the recovery of humic substances for their application in the agricultural industry due to their beneficial effects on soil quality and plant growth [42]. Additional studies on the possibility to recover organics from saturated IEX brine should be performed as well as their recovery as valuable products.

The IEX process was proved adequate for wastewater treatment thanks to its simplicity of operation, no need of start-up time, resilience towards any fluctuation of the influent concentrations while others also refer to advantages related with low environmental impact [8] related to lack of greenhouse gas (GHG) emission and low energy demand. The electricity consumption of the IEX demonstration

plant was monitored during the operation (ENERWATER Wellness TechGroup©) and resulted in an average of 1.17 ± 0.068 kWh/day, i.e., 0.12 ± 0.01 kWh/m³, compared with average values of 0.6 kWh/m³ for BNR processes [43]. This is of particular relevance moving forward towards an environmentally sustainable circular economy, the reduction in GHG emission (namely CO₂, NO₂ and CH₄) is a crucial advantage of the IEX process compared to conventional biological processes.

3.7. Phosphorus recovery from saturated HAIX solution

Reusing the same regenerant for 8 cycles increased the orthophosphate concentration up to 785 mg PO₄-P/L. The disposal of saturated regenerant as hazardous waste represents a cost (typically £65/ton) and environmental concern [8,16]. For this reason, the recovery of the regenerants is critical to ensure sustainability and economic feasibility of the IEX process. The addition of Ca(OH)₂ to a molar Ca:P ratio of 3 allowed for the recovery of 98% of the mass of PO₄-P, after 1 hour of mixing (Figure 6a). In comparison, 69% of the orthophosphate present in solution was recovered after the addition of Ca(OH)₂ to a Ca:P ratio of 2, while a maximum recovery of 80.5% was obtained after 6h of mixing (Figure 4a).

The concentration of PO₄-P in the NaOH regenerant decreased to 19.4 ± 2.2 mg PO₄-P/L and 106.5 ± 3.5 mg PO₄-P/L after the recovery with Ca:P ratios of 3 and 2, respectively. The pH of the regenerant solution before the recovery was 12.74 and final values of 12.75 and 12.83 were registered after the recovery with Ca:P of 3 and 2, respectively. Following the experiment to investigate the Ca:P ratio,

batches of 50L of saturated regenerant were treated with $\text{Ca}(\text{OH})_2$ at a Ca:P ratio of 3. As presented in Figure 4b, a plateau was reached after 6h of mixing (94% of recovery) and the $\text{PO}_4\text{-P}$ concentration decreased from $684 \pm 16 \text{ mg PO}_4\text{-P/L}$ to $42 \pm 2 \text{ mg PO}_4\text{-P}$. At the same time, the calcium concentration in the regenerant solution was $0.4 \pm 0.01 \text{ mg Ca}^{2+}/\text{L}$ indicating that almost the total mass of calcium added as $\text{Ca}(\text{OH})_2$ had precipitated.

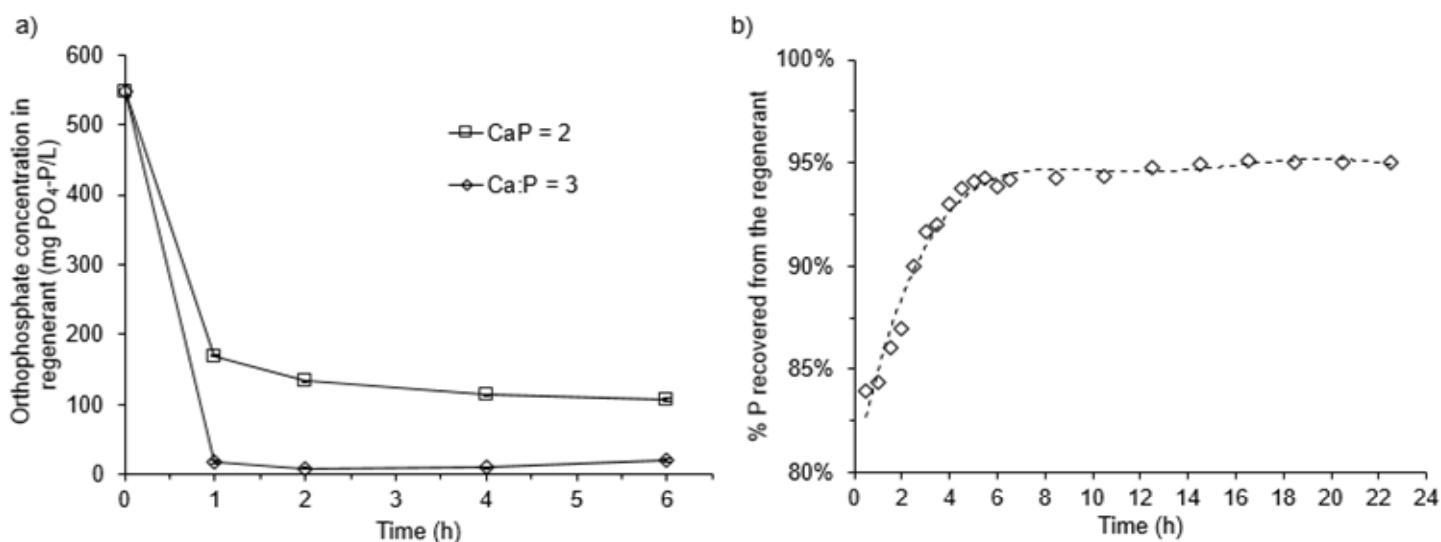


Figure 4. a) Decrease in concentration of the regenerant solution (NaOH) following addition of calcium hydroxide to saturated NaOH at Ca:P molar ratio of 2 and 3 and b) phosphorus (P) recovery from 50 L batch from saturated NaOH solution following addition of calcium hydroxide up to a Ca:P molar ratio of 3.

The scanning electron microscope (SEM) analysis revealed an amorphous crystal structure (Figure 5a) and the EDX indicated a composition of 5.7% P, 15.1% Ca (in wt%). The Ca:P ratio was 2.7, very close to dosed Ca:P ratio of 3. The XRD analysis showed that the recovered precipitate was similar to hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as shown by the comparison against the standard from literature [44] (Figure 5b). Nevertheless, is also possible that other

forms of CaP precipitated as there was difference between the dosed and recovered product Ca:P ratios. The recovered hydroxyapatite was also analysed for impurities and showed no pathogens (total coliforms and *Escherichia coli* <0 cfu/g), low concentrations of metals and the investigated organic pollutants were below the detection limits (Table 3).

A total of 0.45 kg of precipitate was recovered from 50 L of saturated regenerant. Depending on the quantity of the recovered product, niche applications for the hydroxyapatite can be found, especially in market sectors interested in investing in circular economy. In particular, the hydroxyapatite can be used as agricultural and ornamental crop fertilizer [8]. However, particular attention needs to be put on the level of metals such as cadmium, chromium, copper, lead, mercury, nickel and zinc, which are regulated at different limits depending on the country [45]. When comparing the metals content of the recovered product with known regulation limits for fertilizers, the metals concentration in the precipitate were found to comply with regulations for product use as fertilizers in China [46], Turkey [45] and the new proposed European Union (EU) limits [47]. Additionally, hydroxyapatite has been used for the remediation of water and soils contaminated with heavy metals such as zinc, lead as well as cadmium [48,49]. The recovery of the calcium phosphate allowed for the reuse of the NaOH as regenerant solution for the HAIX at demonstration scale (Figure 6). In particular, as presented in Figure 6c, after the recovery, it was possible to regenerate the resin to keep $C_t/C_0 < 0.2$ for 230-240 bed volumes. The recovery was repeated after four regeneration cycles (final concentration of NaOH of 539 mg PO₄-P/L). The NaOH treated twice for the recovery was again reused as regeneration

solution for the following six regeneration cycles maintaining a C_i/C_0 below 0.2 for up to 228 bed volumes (Figure 6). However, it is important to highlight that the multiple reuse of the regenerant solution after the recovery of the hydroxyapatite can have an impact on the purity of the recovered product. To indicate, additional studies on the hydroxyapatite obtained from the NaOH recovered twice, revealed an increase in the concentration of heavy metals (namely chromium, copper, nickel, potassium and zinc) up to 78% compared to the concentration in the hydroxyapatite recovered from the NaOH treated once which could limit the implementation of the product in the fertilizer industry.

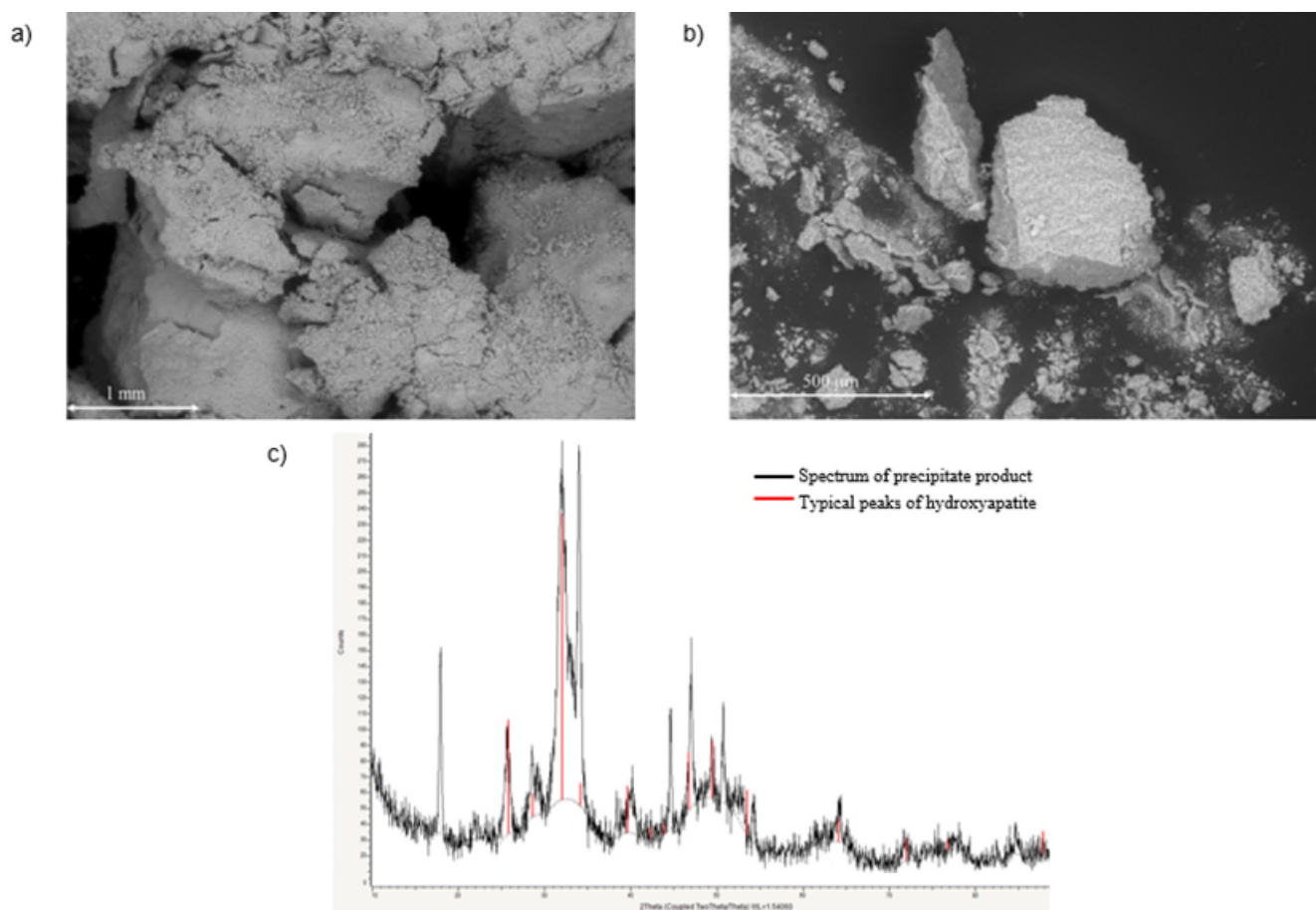


Figure 5. a-b) Scanning electron microscope pictures of recovered product, identified as hydroxyapatite; c) X-ray diffraction spectrum of calcium phosphate precipitate from saturated NaOH treated with calcium hydroxide (Ca:P=3) compared to hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$).

Table 3. Element composition (wt%) and purity analysis of calcium phosphate (hydroxyapatite) recovered from saturated NaOH treated with calcium hydroxide.

Elemental composition (wt%)									
O	Ca	C	P	Na	Si	Mg	S		
63	15.1	12.7	5.7	2.6	0.4	0.2	0.2		
±0.5	±1.1	±1.0	±0.0	±0.2	±0.0	±0.1	±0.0		
Pathogens (µg/g)									
Total coliform	Escherichia coli								
0	0								
Metals (µg/g)									
Al	Cd	Cr	Cu	Fe	Pb	Hg	Ni	K	Zn
4.0	2.4	8.0	3.6	9.2	2.4	4.0	1.2	7.2	7.2
×10 ⁵	×10 ⁴	×10 ³	×10 ⁴	×10 ⁵	×10 ³	×10 ²	×10 ⁴	×10 ⁵	×10 ⁴
Organic pollutants (µg/g)									
Benzene	Other organics *								
4×10 ⁵	Below detection limit (<4×10 ⁴)								

*Acenaphthene, Acenaphthylene, Anthracene, Benzo (a) anthracene, Benzo (g,h,i) perylene, Benzo (a) pyrene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Chrysene, Dibenz (a,h) anthracene, Fluoranthene, Fluorene, Indeno (1,2,3) cd pyrene, Naphthalene, Phenanthrene, Pyrene, PAH, 4-n-Nonylphenol, 4-Nonylphenol

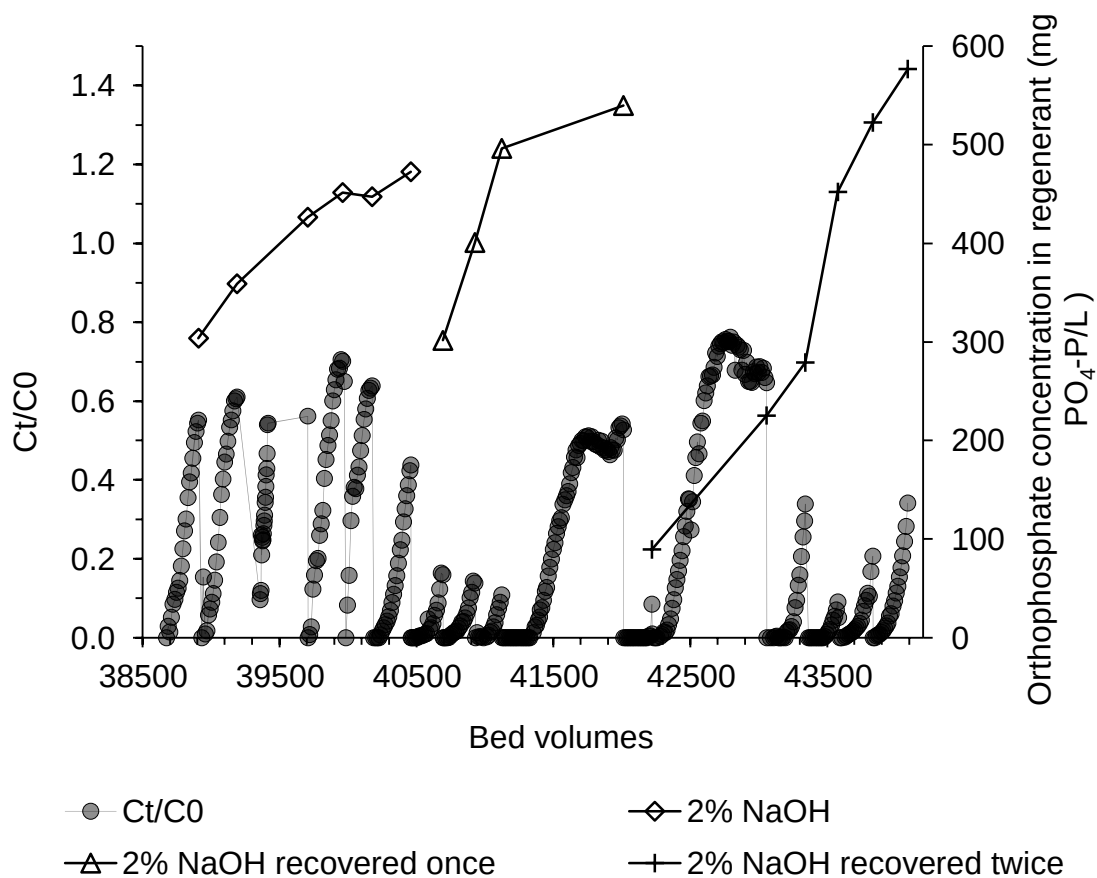


Figure 6. Reusability of the recovered NaOH as regenerant solution at demonstration scale.

3. Conclusions

The results from this work confirmed the feasibility of IEX for the treatment of wastewater for long-term operations. This technology offers a route to efficiently remove orthophosphate from wastewater and recover it in with a sustainable circular approach which is not found in conventional biological (EBPR) processes [8]. This work demonstrated that the HAIX is suitable for long-term operation of IEX technology and high effluent quality <0.3 mg PO₄-P/L can be maintained for a significant number of bed volumes. However, an efficient regeneration of both the hydrated ferric oxide nanoparticle (with NaOH) and the polymeric base of the

resin (with NaCl) is needed to ensure the long-term applicability the process and avoid the reduction of the adsorption capacity and lifespan of the resin. Additionally, it was proved that more than 95% of the orthophosphate in municipal wastewater can be recovered as hydroxyapatite from the saturated regenerant solution (NaOH) by adding calcium hydroxide to a Ca:P molar ratio of 3 in less than 6h. Future studies are needed to provide an in-depth analysis of the HAIX media before, during and after the P removal cycles. Also, the study of the impact of multiple uses of the saturated brine on the hydroxyapatite recovered quality and potential heavy metal leaching, needs further investigation. The recovered product can be applied by the chemical and fertiliser industries; however, these applications will need to be further explored and documented. Finally, the afterlife of the HAIX resin and its disposal need to be considered to obtain a safe final product with minimum waste volume.

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Demonstration of ion exchange technology for phosphorus removal and recovery from municipal wastewater

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