PHOSPHATE REMOVAL AND RECOVERY: USING CONTINUOUS ION EXCHANGE FOR A CIRCULAR ECONOMY SOLUTION

Olga Yahorava ¹, Adam Fischmann ¹, Emma Baillie ¹, Will McLean ¹ 1. Clean TeQ Water, Melbourne, VIC

KEYWORDS

Phosphate polishing, phosphorus recovery, nutrient removal, ion exchange, circular economy

ABSTRACT

Clean TeQ Water's PHOSPHIX[®] process utilises continuous ion exchange to efficiently remove phosphate from wastewater and recover it as hydroxyapatite (14% PO₄-P). A successful pilot study demonstrated phosphate removal to <1 mg/L from MBR effluent while optimizing reagent consumption and operating costs. The recovered hydroxyapatite offers potential reuse in agriculture, supporting circular economy principles. Economic analysis indicates cost-efficient operation, with further optimization possible through reagent recycling and hydroxyapatite valorization. The study validated the technology's effectiveness in treating complex feedwaters, and provided the confidence to progress to a 2.1 MLD full scale plant.

INTRODUCTION

Phosphorus (P) is essential for natural ecosystems and industrial processes, but its excessive discharge into water bodies causes environmental concerns, particularly eutrophication. In response, regulatory bodies worldwide have tightened phosphorus discharge limits to protect water quality and promote sustainable management (Kardos, et al., 2025). These stricter regulations have pushed industries to improve phosphorus removal technologies to comply with evolving standards. At the same time, concerns about global phosphorus scarcity are growing. Phosphorus is a finite resource, primarily extracted from phosphate rock, with major reserves concentrated in a few countries. As demand for phosphorus in agriculture and industry continues to rise, the depletion of highquality reserves presents a long-term sustainability challenge. To address this, some governments are implementing mandatory phosphorus recycling laws, requiring industries and wastewater treatment plants to recover and reuse phosphorus from waste streams. These regulations aim to reduce reliance on mined phosphate, improve resource efficiency, and create circular economy solutions for phosphorus management.

Chemical precipitation using iron (Fe) and aluminium (Al) salts remains the most widely used phosphorus removal method. However, as discharge limits are tightened to 0.5 mg/L, this approach faces increasing challenges. At low phosphorus concentrations (1–10 mg/L as PO₄-P), Fe- and Albased precipitation becomes less efficient, requiring higher chemical dosages, resulting in increased sludge production, and greater operational costs. Additionally, metal salt usage can lead to secondary contamination and complicate phosphorus recovery and sludge disposal, driving interest in alternative, more sustainable PO_4 -P removal technologies.

Clean TeQ Water (Australia) has developed the PHOSPHIX $^{\mbox{\tiny B}}$ process (see Figure 1), a novel



Figure 1: The PHOSPHIX process

phosphorus (PO₄-P) removal and recovery system. The process involves PO₄-P adsorption onto a selective resin, resin regeneration, PO₄-P transfer into a desorption solution, and finally precipitation as hydroxyapatite using lime.

The system integrates Clean TeQ Water's continuous ion exchange technology (Zontov, 2006), which enhances efficiency by operating as a counter-current moving bed rather than a traditional fixed-bed. This reduces fouling in feeds containing solids and organics and minimises chemical consumption (salt, caustic, and water) during desorption.

Previous applications of P-specific resins have been directed towards polishing low levels of P from low TDS municipal waters (Blaney, et al., 2007), (Guida, et al., 2021), (Pinelli, et al., 2022). These applications all use fixed bed ion exchange on relatively clean drinking water feeds, however, these fixed bed systems are prone to fouling in wastewater environments. The continuous nature of ion exchange in PHOSPHIX allows ion exchange to be considered for more challenging water treatment tasks, including feed waters with higher fouling potential and in applications where relatively frequent resin regeneration is required.

P-selective resins are hybrid anion exchange materials that combine a strong-base anion with hydrous exchange resin iron oxide nanoparticles. At neutral pH, P (present as H₂PO₄and HPO42-) is loaded onto the resin via both electrostatic attraction to the guaternary ammonium groups of the resin matrix and by inner-sphere coordination to the hydrous iron oxide (Clark, et al., 2024). Desorption is achieved by raising the pH and providing salt. The higher pH converts the iron oxide surface to a negative charge (unfavourable for P coordination), and chloride displaces PO₄-P and other anions from the anion exchange resin sites.

 PO_4 -P precipitation from the resulting eluate as hydroxyapatite rather than other calcium precipitates is preferred due to its low solubility, which enables efficient phosphate removal. Hydroxyapatite can also be used as a slow release fertilizer, as an input for fertilizer production, as a supplement in animal feed, or can be easily disposed of to landfill.

The following proof-of-concept studies were undertaken at a laboratory scale where the process was tested and customised to treat the discharge water at an industrial site in Europe. The current paper presents the results of the PHOSPHIX process customisation for polishing P from industrial wastewater exiting a membrane bioreactor (MBR) system.

METHODOLOGY

The PHOSPHIX process was tested for its ability to reduce phosphate levels below 1 mg/L PO_4 -P in wastewater from an industrial manufacturing plant,

where influent concentrations ranged from 3 to 20 mg/L PO $_4$ -P.

The study involved:

- Analysis of the historical water quality trends to define optimal operating conditions for the treatment plant.
- Assessing the resin's performance in polishing PO₄-P to meet discharge limits while maintaining loading capacity over multiple adsorption/desorption cycles.
- Piloting the adsorption, desorption, and washing circuits using a 2 L moving bed column (Figure 2).
- Precipitating PO₄-P as hydroxyapatite from the spent desorption liquor and characterizing the precipitate.
- Optimizing process parameters for improved efficiency.

Objectives of the research campaign were to:

- Determine solution-to-resin flow ratios under maximum phosphorus loading.
- Assess reagent consumption during resin regeneration.
- Evaluate lime requirements for efficient phosphate precipitation.
- Analyse the properties and quality of the precipitated solids.
- Generate reliable process design parameters, by spiking wastewater samples from the site with critical impurities at maximum design levels to simulate real-world conditions.

The P-selective resin used was a commercially available, iron-impregnated strong-base resin chosen for its mechanical durability and suitability for deployment in a moving bed system.

Bench-scale testwork

Equilibrium adsorption tests were performed using standard operating procedures (Helfferich, 1962). Adsorption/desorption testwork was done in a fixed bed column (25 mL in volume, 1 cm diameter). An adsorption/desorption cycle consisted of the loading of the same resin sample by passing 200 bed volumes (BVs) of P-containing wastewater at 4 BVs/hr flow rate, its desorption using 10 BVs of 1% NaOH+5% NaCI solution and washing with 10 BVs of water.

Fixed bed column desorption studies were conducted by passing 10 BVs with various compositions of the desorption solutions (i.e. 1, 2 and 4% NaOH in 5% NaCl) at 1 BV/hr flowrate and analysis of the effluent solutions for PO₄-P, Cl, SO₄ and OH.

Piloting the PHOSPHIX process

The piloting of the PHOSPHIX process (Figure 1) was conducted in a batch-continuous mode. The adsorption circuit was tested on-site in Europe, after which the loaded resin was shipped to Australia for desorption and washing trials. Hydroxyapatite

precipitation was carried out using the spent desorption solution generated during these trials.

The moving bed column operated through a countercurrent flow of solution and resin, with process details summarised in Table 4.

The column (Figure 2) was loaded with resin (fresh, loaded, or unwashed), while the solution (feed water, desorption solution, or wash water) was pumped in from the bottom for a set cycle time. After each solution flow cycle, the solution flow was stopped, and approximately 0.2 L (10% of the column volume) of resin was added to the top. Then, an equal portion was drained from its bottom (5 min per resin transfer/ movement). This cycle was then repeated. A sketch of the desorption trial is presented in Figure 3.



Figure 2: Sketch of moving bed 2 L column



Figure 3: Resin regeneration pilot sequence

The spent desorption solution containing PO₄-P, NaOH, NaCl, and organics was collected and treated in four batches. The procedure followed is shown in Figure 4. Lime slurry (10% w/w) was added to precipitate hydroxyapatite. The precipitate was filtered, dried, and assayed.



Figure 4: Batch co-current precipitation of hydroxyapatite

During the pilot testing, solution samples were analysed for PO4-P using benchtop photometry, using either the vanadomolybdophosphoric acid colourimetric method (Standard Methods for the Examination of Water and Wastewater, 20th edition, 4500-P C) or the amino acid method (Standard Methods for the Examination of Water and Wastewater, 18th edition, Amino Acid method). Sulphate was analysed by the barium chloride turbidometric method, chloride by titration with AgNO₃ and K₂CrO₄, and alkalinity by titration with strong acid using phenolphthalein and methyl orange indicators. Selected samples were retained for confirmatory analysis by a commercial laboratory for PO₄-P , sulphate, chloride, total organic carbon (TOC), and alkalinity.

RESULTS AND DISCUSSION

Phosphate removal trials

Analysis of the historical data on the wastewater composition revealed that the PO₄-P levels approached 20 mg/L in the worst-case scenario. The other main anions present in the water were sulphate (maximum concentration of 1.5 g/L), bicarbonate (0.6-0.8 g/L), and chloride (0.5 g/L). TOC levels usually peaked at ~10 mg/L, and pH ranged from 8.0 to 8.5.

Wastewater at pH 8.0-8.5 was spiked with impurities and PO₄-P to create a representative "worst case" scenario feed and used to generate the adsorption equilibrium isotherm presented in Figure 5.



Figure 5: Phosphorus adsorption equilibrium isotherm

Adsorption and desorption cycles were conducted using daily wastewater samples and various composites collected over five days. The water contained PO₄-P in the range of 10–15 mg/L, sulphate at 1200–1600 mg/L, chloride at 500–600 mg/L, and the pH was 7.9-8.6. As shown in Figure 6, the resin maintained its capacity throughout the cycles, indicating no short-term detrimental effects on resin performance from the water constituents. Polishing of the PO₄-P to below 1 mg/L was achieved at the beginning of every adsorption cycle.



Figure 6: Change in PO₄-P loading with cycles

The PO_4 -P adsorption breakthrough curve presented in Figure 7 provided information regarding the kinetics of the PO_4 -P adsorption by the resin, which was critical for the pilot operation and final commercial design.



Figure 7: PO₄-P adsorption breakthrough curve generated at 4 BV/hr flowrate

During the adsorption campaign, wastewater was fed to the 2 L moving bed column at 8 L/hr flowrate and resin was removed at 0.1 L/hr flowrate. PO₄-P was constantly removed from 20 mg/L to <0.2 mg/L and resin loading varied between 1.5 to 1.7 g/L, in line with the equilibrium adsorption and desorption curves. While the P-selective resin also removed organics present in the feed at ~10 mg/L levels, their concentration in the feed should be minimised to avoid long-term impact on the resin.

In total, 2 m³ of wastewater was treated, and ~20 L of loaded resin was generated for the subsequent desorption/precipitation studies.

P-selective resin regeneration trials

Selection of the desorption liquor composition was made based on column elution testwork results presented in Figure 8.

The difference between PO₄-P desorption efficiency using 1%, 2%, and 4% NaOH mixture with 5% NaCI was negligible. All three solutions could desorb PO₄-P, and approximately 25 g NaOH and 55 g NaCI were required to regenerate 1 L of resin.

The counter-current desorption process generally enhances reagent efficiency compared to fixed-bed applications. Therefore, an assessment was conducted to determine whether 20 g NaOH per L of resin would suffice for resin regeneration despite fixed-bed tests indicating a requirement of 25–26 g NaOH per L of resin.

A mixture of 1% NaOH and 5% NaCl was selected as a desorption solution for the pilot plant. Desorption solution-to-resin flows of 2.0 BV/BV were trialled, providing 20 g NaOH and 100 g NaCl per L of resin.

The counter-current desorption pilot trial was conducted following the sequence shown in Figure 3. The streams with compositions outlined in Table 1 were generated.



Figure 8: Column desorption profiles (a) effect of NaOH concentration on PO₄-P desorption (with 5% NaCl) (b) behaviour of major loaded components (with 1% NaOH & 5% NaCl)

Table 1: Composition of streams (g/L) entering and exiting desorption CIX column

Component	Resin IN	Eluate IN	Resin OUT	Eluate OUT*	Reagent consumption
PO ₄ -P	1.6	-	0.02	0.56	N/A
SO ₄	33	-	0	11.8	N/A
тос	0.5	-	0.08	0.15	N/A
NaCl	N/A	50	N/A	21	41
NaOH	N/A	10	N/A	0.6	18

* includes water transfer volume

Over 98% of PO₄-P loaded onto the resin was desorbed into the spent desorption liquor. The solution contained >0.5 g/L PO₄-P and had a pH of ~12.5. Lower reagent demand for resin regeneration than expected from the fixed bed tests was verified.

2 BVs of water provided for the resin wash in the CIX column were adequate for the recovery of entrained reagents, which was confirmed by the conductivity and pH of the water transferred with the resin taken

at the bottom of the column (i.e. 0.3 mS/cm and 10.5). Spent wash water contained recovered NaCl and NaOH units and was used to make the desorption solution.

A sample of regenerated and washed resin was used for the PO_4 -P readsorption test (see Figure 7). Adsorption curves achieved with a fresh resin and a sample that went through the full cycle of adsorption and regeneration coincided, indicating that the regeneration regime was adequate for restoring resin properties.

Hydroxyapatite (HA) precipitation

Phosphate removal from spent desorption solution by precipitation with calcium is more economically attractive due to its low solubility, cost-effectiveness, and sustainability, as it produces valuable byproducts like hydroxyapatite. Additionally, it meets stringent regulatory requirements, offers efficient phosphorus removal, and is easier to manage than other chemical methods. The recovery efficiency mainly depends on the initial PO₄-P concentration in the treating solution, with higher concentrations resulting in higher recovery (Muhammad, et al., 2019).

Five possible calcium phosphates can be produced, but the least soluble product is hydroxyapatite, which forms according to Eq. (1): (Machiela, et al., 2018):

$$10Ca(OH)_2 + 6PO_4^{3-} \to Ca_{10}(PO_4)_6(OH)_2 + 18OH^-$$
(1)

The precipitation rate of calcium phosphate decreases as the pH increases, and seed crystals are desirable because they make the slow nucleation of new crystal grains unnecessary.

HA precipitation studies were conducted using a batch co-current approach, as shown in Figure 4. The calcium-to-phosphorus ratio required to bring PO_4 -P concentration down from around 580-600 to <1 mg/L per precipitation batch is shown in Figure 9.



Figure 9: Hydroxyapatite precipitation from the spent desorption solution

Precipitation of PO₄-P as HA with lime as a source of calcium required on average a \sim 30% stoichiometric excess of calcium relative to the PO₄-P concentration to bring the residual concentration to <1 mg/L PO₄-P. The solids were a mixture of calcium phosphate and unreacted lime (see Table 2). Elevated sulphate and chloride levels were due to entrained spent desorption solution and can be minimised by more thorough precipitate washing.

Table 2: Composition of the hydroxyapat	ite, %	% w/w
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Total P	SO_4	CI	тос
14.26	2.5	1.5-1.6	0.2
SiO ₂	Fe	Ca	Na
0.12	0.02	36.8	3.9

The testwork demonstrated that PO₄-P polishing to below 1 mg/L with subsequent immobilisation as hydroxyapatite is technically viable. Independent analysis confirmed that the solids should pass European landfill waste acceptance criteria limits after limited washing.

Economic analysis and opportunities for OPEX improvement

Analysis of the OPEX for the PHOSPHIX process was based on the composition of the specific wastewater tested during this study. A preliminary economic analysis was undertaken for a typical water flow of 2.1 MLD, and has been converted from EUR to AUD and summarised in Table 3.

Values used to calculate the OPEX were as follows:

- Power cost: 0.2 AUD/kWh
- NaOH (as 100 wt.%): 1.28 AUD/kg
- Ca(OH)₂ (as 100 wt.%): 0.16 AUD/kg
- NaCl (as 100 wt.%): 0.08 AUD/kg
- Sulphuric acid (as 100 wt.%): 0.16 AUD/kg
- Resin top-up: ~ 5% p.a.
- Plant operation labour is excluded

Scenario	Nominal	Maximum	Unit
Feed flow	2.1		MLD
Operation hours	8,500		per year
PO ₄ -P in the feed	5	20	mg/L
PO ₄ -P flow	3.72	14.88	
HA flow (100% mass basis)	20	80	t/vr
HA-rich sludge (dry mass basis)	27	106	591
NaOH cost	0.07	0.15	
Ca(OH) ₂ cost	0.01	0.03	
NaCI cost	0.02	0.03	
H ₂ SO ₄ cost	0.01	0.03	AUD/m ³
Resin cost	0.03	0.08	
Reagent total	0.14	0.32	
Power cost	0.014	0.055	
	0.16	0.37	AUD/m ³
TOTALOPEA	116,136	275,313	AUD/yr
Sale price of HA required to offset the OPEX	6.2	3.48	AUD/kg

Table 3: PHOSPHIX economic assessment

Reagent costs are the primary economic factor in selecting processes for the water treatment industry. In the PHOSPHIX process, reagent demand per cubic meter of treated water depends on how often the resin needs to be regenerated. The water's composition influences this regeneration frequency—particularly PO₄-P concentration, pH, and critical impurities such as sulphate. Municipal wastewaters, for example, typically have a sulphate concentration far below 1,500 mg/L, which can significantly reduce the overall operational costs.

Every 1 kg of HA precipitated regenerates 0.7 kg of NaOH, and as shown in Table 1, the eluate still contains 2.1% w/w of NaCl. Recycling the solution after precipitation of HA can therefore reduce the consumption of NaOH and NaCl. In this application, additional treatment of the eluate would be required to remove the sulphate and organics prior to recycling.

Another option to improve the process economics is to offset the treatment costs by selling HA. HA with $14\% PO_4$ -P content is comparable to phosphate rock commonly used in fertilisers, making it a potential raw material for phosphorus-based fertiliser manufacturers.

Lime contamination in HA, a byproduct of the PHOSPHIX process, could provide benefits as a soil amendment, particularly in acidic soils. As a result, HA could serve a dual purpose—supplying phosphorus while acting as a liming agent to neutralise soil acidity.

To offset power and reagent costs for the case presented in the current paper, selling HA to the agricultural industry would require a market price of 3.4–6.2 AUD per kilogram, depending on the mass of phosphorus removed.

CONCLUSION

The PHOSPHIX process developed for PO₄-P removal and fixation in the form of hydroxyapatite was evaluated for treating industrial wastewater (MBR effluent) with a complex composition (i.e., 1.5 g/L SO₄, 0.6-0.8 g/L HCO₃, 0.5 g/L Cl, 10 mg/L TOC, and 0.02 g/L PO₄-P).

The process was proven to polish PO₄-P to <1 mg/L. An efficient regeneration procedure using a combination of NaOH and NaCI ensured resin efficiency was maintained over several adsorptiondesorption cycles.

Piloting of the resin regeneration step in countercurrent moving bed columns established the water and reagents requirements as:

- 20 g NaOH per L of resin
- 100 g NaCl per L of resin
- 2.0-2.6 L of water per L of resin

Subsequent phosphate fixation via precipitation with lime as hydroxyapatite was possible, with every kg

of PO₄-P removed from the wastewater generating ~10 kg of hydroxyapatite (dry mass basis). Only 30% of stoichiometric excess of lime was required to bring the PO₄-P concentration to <1 mg/L. The product is classified as non-hazardous waste and can be sold as an additional revenue stream to offset the water treatment costs.

Overall PO₄-P removal costs estimated for the water composition tested were determined as 0.16 AUD/m^3 for the base case scenario and 0.37 AUD/m^3 for the worst case.

The PO₄-P concentration and composition of the feed solution governs the process economics, and using the process in typical municipal applications with much lower sulphate concentrations is expected to significantly improve the OPEX. Reagent recycling following precipitation of hydroxyapatite can also decrease reagent demands.

To offset power and reagent costs for the case presented in the current paper, selling HA to the agricultural industry would require a market price of 3.4–6.2 AUD per kilogram for the worst-case and base-case scenarios.

The study validated the effectiveness of PHOSPHIX for treating complex wastewaters, and provided the confidence to progress to a 2.1 MLD full scale plant. PHOSPHIX effectively achieves stringent PO_4 -P discharge limits that are challenging for conventional chemical precipitation methods, while also minimising sludge generation, reducing disposal costs. There is significant potential to apply PHOSPHIX for phosphate polishing and P recovery at municipal water treatment plants, allowing users to protect the environment and support circular economy principles.

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Table 4: Moving bed column operation in different modes

Function	Adsorption	Desorption	Washing
Solution IN	Feed water	Desorption solution	Wash water
Solution OUT	Effluent water	Spent desorption solution	Spent wash water
Resin IN	Fresh/ regenerated resin	Loaded resin	Desorbed unwashed resin
Resin OUT	Loaded resin	Desorbed unwashed resin	Washed/ regenerated resin
Solution flowrate (net), L/hr	8	0.66	0.8
Resin flowrate, L/hr	0.1	0.33	0.4
Cycle time, hrs	2.0	0.6	0.5