

Phosphorus Recovery in Wastewater Treatment: Moving from Lab to Pilot Scale

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Abstract -Domestic and industrial wastewaters are relatively rich in phosphorous, nitrogen, and carbonaceous contaminants that are essential nutrients for the growth of plants. Several treatment methods have been developed in order to remove phosphorus from wastewaters. However, new, innovative designs and technologies are needed, which will focus on the recovery of resources, such as the nutrients content of wastewaters. Thus, it seems that phosphate recovery from wastewaters, e.g. as calcium or magnesium phosphate salts, due to their possible applications as fertilizers, would be an attractive option. Batch adsorption experiments were conducted for PO_4^{3-} removal at a temperature of 20 ± 1 °C and pH= 7.0, by using iron oxy-hydroxides (FeOOH) as the adsorbent. Rapid Small Scale Column Tests (RSSCTs) were subsequently applied in lab-scale experiments for the treatment of secondary effluent from wastewater treatment, indicating an adsorption capacity of 5 mg PO_4^{3-} /g, using AquAsZero as the iron based adsorbent. The laboratory columns were made from glass with a height of 40 cm and diameter 1.1 cm, having EBCT (Empty Bed Contact Time) \approx 3-4 min, filling with 20-25 g of adsorbent with particle size 0.25-0.5 mm and hydraulic loading (flow) 0.4 L/h, simulating the pilot scale process, which will follow. Better regeneration of adsorbent was achieved by the addition of NaOH solution (\approx 0,015 N) at pH 12.6. The recovery of phosphorous accomplished from the outflow of adsorbent's regeneration by adding Ca^{2+} for phosphorous precipitation (75% recovery). Following this information, a regeneration procedure was designed, simulating a larger-scale system, in which the NaOH solution was continuously recirculated in the saturated adsorbent column. Finally, a pilot-plant working in continuous flow mode was designed and built to treat 100-300 L/h of the treated effluent from a convenient municipal wastewater treatment plant, operating by the activated sludge process. The first results from the pilot plant for AquAsZero-FeMn were satisfactory and comparable to those of RSSCTs. The regeneration solution was enriched in phosphates (\sim 50 mg P- PO_4^{3-} /L).

Keywords: Adsorption, desorption, iron oxy-hydroxides, phosphorus recovery, pilot plan, wastewater

1. Introduction

Phosphorus is an essential, yet limited resource, which cannot be replaced by any other element. Removal of phosphorous from municipal and industrial wastewater is a crucial aspect in limiting the water pollution problem of eutrophication, which can result in an excessive growth of photosynthetic

organisms, and therefore unbalancing the natural water ecosystems (Dueñas et al. 2003). This is why there are increasing efforts to remove or recycle phosphorus contained in wastewater, which it involves the separation of phosphates from other co-existing substances and, normally, the recovery of phosphorus. Large-scale wastewater treatment is an inevitable consequence of contemporary societies. Wastewater is usually dangerous to human populations and to the environment and must be appropriately treated prior to disposal into streams, lakes, seas, or land surfaces.

Before discharging wastewater into water bodies, the efficient removal of phosphate is usually obligatory, even though in many cases it is not performed, and leads to major eutrophication problems on a worldwide level. The wastewater treatment industry presently uses several methods to remove phosphorus (Dueñas et al. 2003), such as enhanced biological phosphorus removal processes, coagulation/flocculation, chemical precipitation, membrane purification, or adsorption (Nur et al. 2014). In all these cases, phosphorus is removed by converting the phosphorus to insoluble salt precipitate. However, new and innovative designs and technologies are needed, which will focus on the recovery of resources, such as the nutrients content of wastewaters. Thus, it seems that phosphate recovery from wastewaters, e.g. as calcium or magnesium phosphate salts, due to their possible applications as fertilizers, would be an attractive option (Sawsan et al., 2009)

Water treatment based on the adsorption of contaminants from solution is considered as useful and cost effective method for phosphate removal. Adsorbents are selected mostly having a porous structure and large internal surface area. Iron oxide–hydroxides (FeOOH) and iron oxide magnetic nanoparticles have been intensively studied as adsorbents since several years for the purification of drinking water, groundwater and even of industrial wastewater (Chitrakar et al. 2006, Nowack and Stone 2006, Zelmanov and Semiat 2014).

The interaction of phosphate with FeOOH is important also for controlling phosphate in the environment, as well as in industrial and engineering processes. Generally, iron-based adsorbents are useful due to their economic and safety merits. Iron oxy-hydroxide is known to occur commonly as goethite (α -FeOOH), akaganeite (β -FeOOH), and lepidocrocite (γ -FeOOH). It has been reported that new iron oxides, i.e. schwertmannite (Bigham et al. 1996, Tresintsi et al. 2012), have a tunnel structure like that of akaganeite, where sulphate also co-exist, but these materials undergo transformation to more stable goethite.

The aim of this study was to investigate the removal and recovery of phosphates from the secondary effluent of the wastewater treatment plant (WWTP) “AINEIA”, which is located in Aggelochori, Thessaloniki, Greece. AINEIA is a conventional treatment plant, which was started-up in 1997 and nowadays, receives about 8,000 m³ of influent per day. However, the sludge processing units (thickening and anaerobic digestion) was put into operation in October of 2014. The plant consists of a combination of conventional preliminary, primary, secondary treatment and ozone disinfection. Preliminary treatment includes coarse screening, grit and sand removal. There are two primary and secondary sedimentation tanks. One primary tank is used as equilibration/homogenization tank of domestic septage waste. The effluent from primary treatment is further treated by aerobic biological processes, (“carousel”-type aerators) after which the effluent is ozonated (for disinfection) and discharged into the sea, Thermaikos Gulf. The primary and the secondary sludge are thickened by gravity thickeners. After that, all sludge is treated in anaerobic digester, where the sludge is stabilized, the sludge volume is reduced and biogas is produced. Finally, the sludge is dewatered in belt filters and eventually it can be used as soil amendment product. Secondary effluent usually contains 3-5 mg P- PO₄³⁻/L, which exceeds the upcoming phosphorus discharge limit of 1 mg P- PO₄³⁻/L. It must be underlined that the disposal regulation limit for phosphates in case of AINEIA is 12 mg P-PO₄³⁻/L.

This study’s challenging part was to scale-up the appropriate recovery treatment schema of phosphorous, from lab to full-scale. Batch adsorption experiments were conducted for PO₄³⁻ removal at a temperature of 20±1 °C and pH= 7.0, by using FeOOH adsorbents.

The recovery of phosphorous accomplished from the regeneration solution by adding CaCl₂ for phosphorous precipitation. Following these data, a pilot-plant working in continuous flow mode was designed and built to treat 100-300 L/h of the treated effluent from the WWTP “AINEIA”. The

regeneration procedure of pilot plant was designed to simulate a larger-scale system, in which the NaOH solution was continuously recirculated in the saturated adsorbent column.

2. Materials and Methods

2. 1. Adsorption Experiments

In order to investigate the adsorption capacity of FeOOH, dynamic continuous flow adsorption experiments were conducted for PO_4^{3-} removal at a pH value 7.0, by implementation of Rapid Small Scale Column Tests (RSSCTs). RSSCTs were performed using laboratory glass columns of diameter 1.1 cm and height 40 cm with PTFE valves/caps and a glass frit at the base. The tests were designed for a full-scale adsorption column with an empty bed contact time (EBCT) equal to 3-4 min at 20 °C, particle size 0.25-0.50 mm, hydraulic loading 0.4 L/h. Columns filled with granules of adsorbent at a bed height of 20 cm were fed with secondary effluent from wastewater treatment plant “AINEIA” containing 4-6 mg $\text{P-PO}_4^{3-}/\text{L}$. The iron based adsorbent used in this study, as exhibit from preliminary experiments, was *AquAsZero* supplied by *Loufakis Chemicals S.A.*, nominally consisting of schwertmannite (Mitrakas et al., 2012).

The stannous chloride method was applied for the photometric determination of phosphates concentration, which is more suited for the range between 0.01 to 6 mg P/L, according to Standard Methods for the Examination of Water and Wastewater (Greenberg et al. 1992).

2. 2. Regeneration Process

The regeneration procedure was designed, simulating a larger-scale system, in which the NaOH 0.015 N solution was continuously recirculated through the saturated adsorbent column. The process adsorption-desorption/regeneration-precipitation was continuous aiming for every adsorbent to be regenerated more than once. Further on, phosphates were precipitated as calcium phosphate salt by the addition of calcium hydroxide CaCl_2 solution in the enriched in phosphates regeneration solution.

3. Results and Discussion

3. 1. Adsorption-Desorption/Regeneration-Precipitation Experiments

The phosphate removal from the secondary effluent by adsorption onto iron oxy-hydroxide (FeOOH) resulted in final concentrations significantly lower than the respective regulation limit. Breakthrough curves from the RSSCTs revealed an adsorption capacity of: 5 mg $\text{P-PO}_4^{3-}/\text{g}_{\text{FeOOH}}$ for *AquAsZero*, at breakthrough concentration equal to upcoming discharge limit (1 mg $\text{P-PO}_4^{3-}/\text{L}$). However, this adsorption capacity was gradually stabilized to 3 mg $\text{P-PO}_4^{3-}/\text{g}$ FeOOH for *AquAsZero* after 4 regeneration cycles, as shown in Fig. 1.

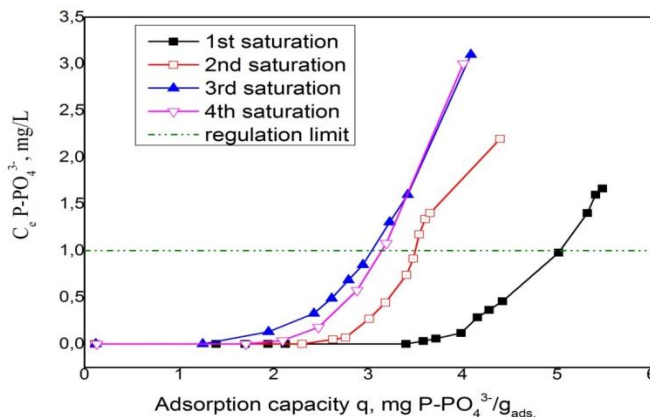


Fig. 1. Breakthrough curves of RSSCTs for 4 sequential cycles of *AquAsZero*.

The regeneration at pH value 12.5 resulted in the efficient phosphate recovery within 2h, as shown in Fig. 2, which in turn favours its subsequent chemical precipitation and recovery by the addition of Ca^{2+} . The phosphate content in the recovered solids was $48 \pm 4\%$ w/w. The precipitation of calcium phosphate is favoured by the high pH values of regeneration solution.

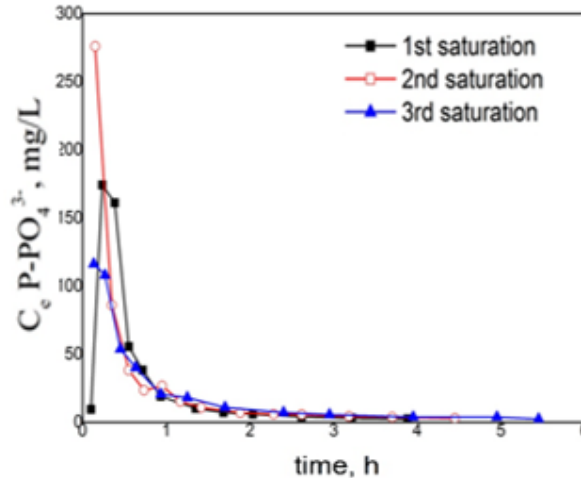


Fig. 2. Profile of P-PO_4^{3-} concentration in regeneration solution by the addition of (alkaline) NaOH solution.

3. 2. Pilot-Plant

Following the RSSCTs experiments, a pilot-plant, working in continuous flow mode, was designed and built to treat 100-300 L/h, as illustrated in Fig. 3. This pilot plant consists briefly of the following processing units:

- Feed of the pilot plant with a flow rate of 185-215 L/h secondary effluent and microfiltration by hollow fibres membranes for retaining the solids.
- Phosphate adsorption onto FeMnOOH is taken place by using a fixed bed working with a range of Empty Bed Velocity (EBV) 7.4-8.6 m/h and a range of Empty Bed Contact Time (EBCT) 8.9-10 min.
- Phosphate recovery from the regeneration stream is performed by adding chemical reagents (CaCl_2) to form precipitate. The separation of precipitate (as calcium phosphate solids) is performed by microfiltration membranes, following by the dehydration of precipitate. The regeneration process works on 9-10 m/h EBV and pH in the range 12.5–13.
- The design of the pilot plant enables the alternative operation of the unit without the operation of the 1st stage of the adsorption bed. In this case Fe(III) is added to precipitate iron phosphate, which is subsequently separated by the microfiltration membranes and dewatered.

The description of the pilot plant is as follows:

The pump PUG01 sucks the secondary effluent from wastewater treatment plant “AINEIA” containing 1.3-8 mg $\text{P-PO}_4^{3-}/\text{L}$ (average value: 3.0) and follows the discharge in tank TOP01, 384L, which feeds tank TOM01, 144 L. In tank TOP01 hollow fibres membranes are installed. Filtration through membranes is effected by a peristaltic-type pump (PPD01), which has a speed controller (VSD01) and can operate in reverse to wash the membranes. From tank TOM01 filtered water is sucked by peristaltic pump (PPD02), which has a speed controller (VSD02), for feeding the adsorption bed with filtered water.

The adsorption bed (LFA01) is made of polypropylene and contains 32 L adsorbent and 3 L quartz sand to cover diffusers (DFC03). Column filled with granules of 23 kg adsorbent, particle size 0.2 - 2 mm (mean, 0.63 mm), specific surface area: 150-250 m^2/g at a bed height of 120 cm and surface of 0.0025 m^2 were fed with secondary effluent. The iron based adsorbent used is *AquaZeroFeMn (FeMnOOH)* supplied by *Loufakis Chemicals S.A.*

Special mixer (MIS01) of PVC for mixing chemicals with the liquid during the regeneration phase of the bed, and a spiral mixing device (MIS02), length 25 m polyethylene for the alternative operation of the unit without the operation of the adsorption bed, are installed. For chemical solution preparation there are three (3) reservoirs TOM03, TOP03 with an agitator (MIX01/02) each and TOP04. The above chemical solutions are metered using dosing pumps (PUP01/02/03). For separation of precipitate a tank TOM02, 736 L, with conical bottom is installed. In a part of the tank low speed stirrer (MIX03) is established for the completion of the reaction, pH adjustment and aggregation of solids. In the other part of the tank microfiltration membranes are installed. Peristaltic pumps (PPD03, PUG02/03) are installed for the suction of the filtered water through membranes and discharge into tank TOP02, for the process of regeneration of the adsorption bed with alkaline water and for recirculation and removal of sediment from the settling tank, respectively.

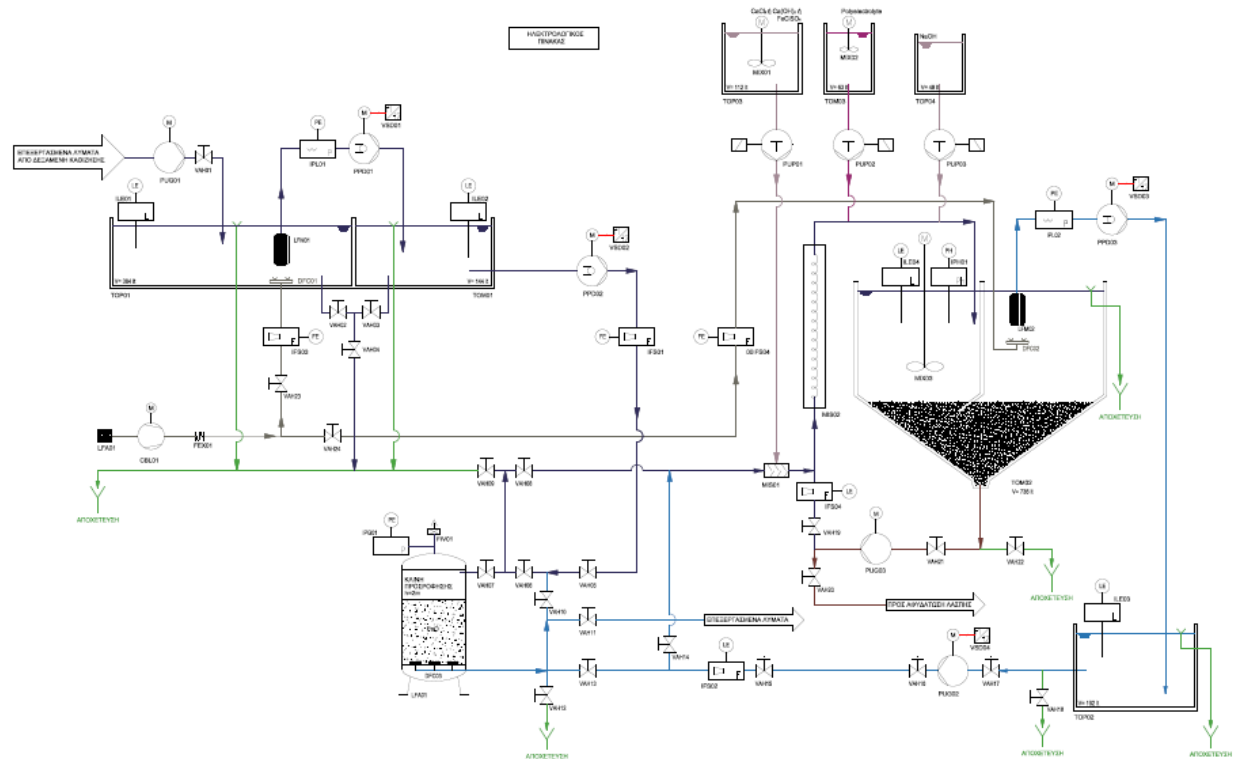


Fig. 3. Pilot-plant working in continuous flow mode.

In Fig. 4 the pilot-plant established in “AINEIA” is illustrated where is shown the basic parts of the followed procedure. It is noteworthy to highlight the automated operation of the pilot-scale: the operation of all peristaltic pumps, the addition of chemicals, the level sensors and the pH controllers, the automatic backwashing of the membranes and all the aforementioned functions are controlled by a programmable logic controller (PLC).

The breakthrough curves for the FeMnOOH adsorbent are presented in Fig. 5. The first results from the pilot plant for *AquAsZeroFeMn* were satisfactory and comparable to those of RSSCTs. The FeMnOOH at pilot scale showed satisfactory adsorption capacities. The curves revealed a range of: 2.0-4.1 mg P-PO₄³⁻/g_{FeMnOOH} at breakthrough concentration equal to upcoming discharge limit (1 mg P-PO₄³⁻/L). The first breakthrough curve revealed an adsorption capacity of 7.3 mg P-PO₄³⁻/g_{FeMnOOH}. It lasted 20 d and interrupted before the residual concentration reached 1 mg P-PO₄³⁻/L. It was decided to interrupt the phosphate loading of the column to optimize the process of regeneration.

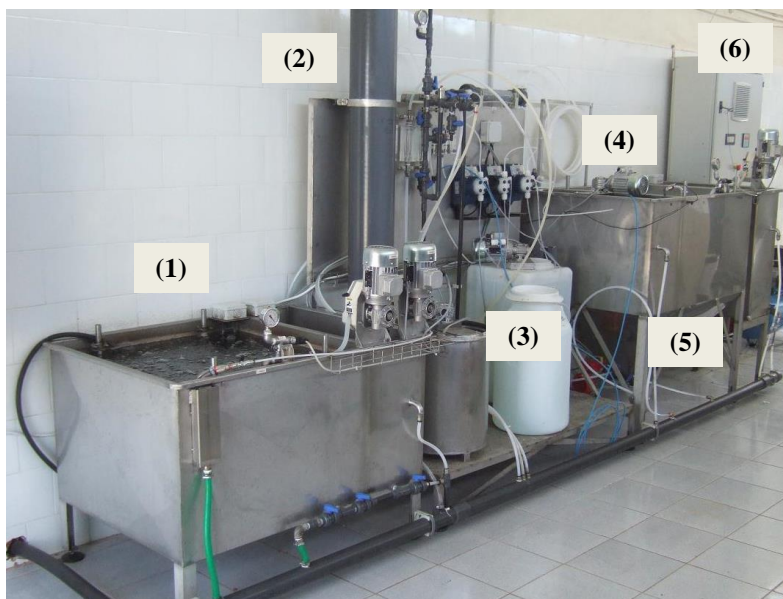


Fig. 4. Pilot-plant illustration established in “AINEIA WWTP”. 1. Membrane Filtration, 2. Fixed Bed, 3. Chemical dosing, 4. Chemical regeneration/precipitation, 5. Precipitate collection, 6. PLC controller.

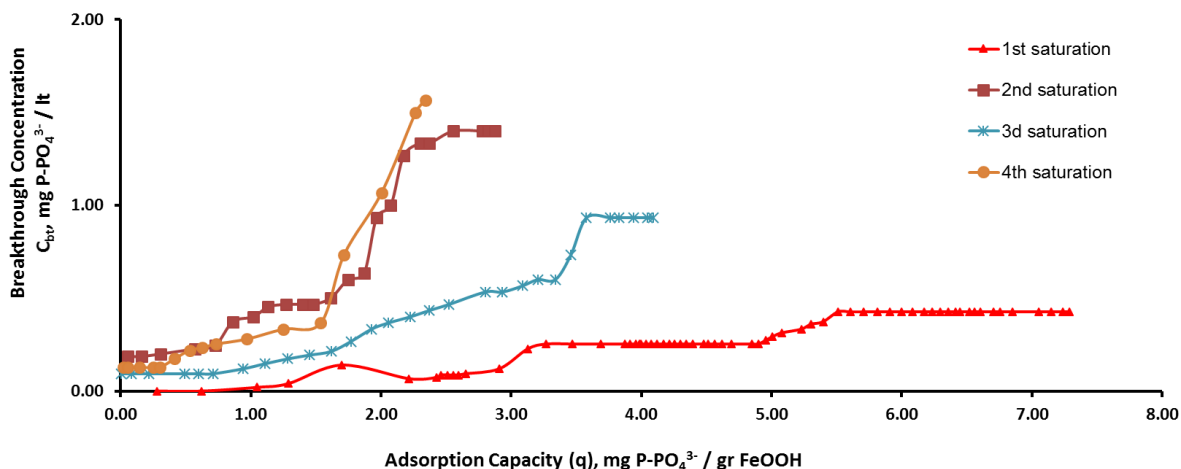


Fig. 5. Adsorption capacity of iron manganese oxy-hydroxide (FeMnOOH-AquAsZero) adsorbent used for phosphate removal by continuous feeding of secondary treated wastewater effluent from the WWTP “AINEIA”.

After the saturation of the bed with phosphates (Fig. 5), the regeneration step was started (Fig.6). Phosphates were desorbed by alkaline solution of about 0.015 N NaOH ($\text{pH} \approx 12.6$) and the column was ready for reuse. The process adsorption-desorption/regeneration-precipitation was continuous. According to Fig. 6 desorption took place much longer than the 2 h regeneration step of RSSCTs for the iron oxy-hydroxides. The results of the first regeneration were not listed because of the optimization of the regeneration process (flow rate adjustment of dosing pump PUP01 and peristaltic pumps PPD03, PUG02). The same problems were faced in the second and third regeneration. In the fourth regeneration the desorption conditions were appropriate and was completed in approximately 6 h, time that will further be eliminated. Although we would expect that the adsorbent would have its adsorption capacity lower after each regeneration process, this was not observed because the regeneration process was never completed.

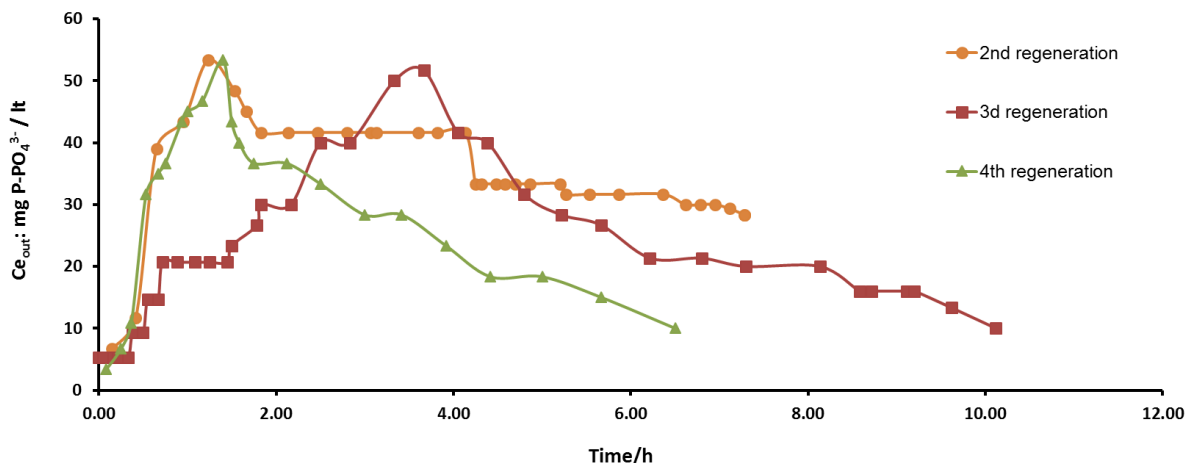


Fig. 6. Profile of P-PO₄³⁻ concentration in regeneration solution by the addition of (alkaline) NaOH solution in the phosphate recovery content from the pilot-plant in WWTP “AINEIA”.

4. Conclusion

In this study, the secondary effluent of AINEIA’s municipal WWTP, established in N. Michaniona-Thessaloniki, in Northern Greece, was treated for phosphates removal and recovery. RSSCTs adsorption experiments were conducted for P-PO₄³⁻ removal at pH= 7.0, by using FeOOH, such as *AquAsZero*. The regeneration solution was enriched in phosphates (>100 mg P-PO₄³⁻/L) and phosphates were precipitated as calcium phosphate by the addition of CaCl₂ solution. Phosphate adsorption onto FeOOH, which is a low-cost adsorbent, seems to be a promising process, considering the pre-requirement for phosphate removal below regulation limit of 1 mg PO₄³⁻/L and their efficient regeneration and phosphate recovery.

Following the RSSCTs experiments a pilot-plant, working in continuous flow mode, was fed with a flow rate of 185-215 L/h secondary effluent. The adsorption bed is working with a range of EBV 7.4-8.6 m/h and a range of EBCT 9-10 min. The first results from the pilot plant for *AquAsZeroFeMn* were satisfactory and comparable to those of RSSCTs. The FeMnOOH at pilot scale showed respectable adsorption capacities. The curves revealed a range of: 2.0 - 4.1 mg P-PO₄³⁻/g_{FeMnOOH} at breakthrough concentration equal to upcoming discharge limit (1 mg P-PO₄³⁻/L).

Phosphates were desorbed by alkaline solution of about 0.015 N NaOH (pH≈ 12.6) and the column was ready for reuse. The regeneration solution was enriched in phosphates (~50 mg P-PO₄³⁻/L) and phosphates were precipitated as calcium phosphate salt by the addition of CaCl₂ solution.

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