

Chemical Precipitation of Phosphorus in Water and Wastewater Samples: the Role of Water Components

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Abstract

The present study aims to investigate the feasibility of phosphate removal and recovery from the secondary effluent of wastewater treatment plant "AINEIA", Thessaloniki – Greece, which usually contains 3-5 mg P-PO₄³⁻/L. Chemical precipitation by the addition of commercial reagents NaOH, Ca(OH)₂, MgO, CaMg₃(CO₃)₄, illustrated that for reducing phosphate below the regulation limit of 1 mg P-PO₄³⁻/L, pH value higher than 10 should be maintained. Moreover, NaOH proved as the cost effective reagent, since Ca²⁺ and Mg²⁺ concentrations of wastewater are high enough for PO₄³⁻ precipitation, as the corresponding salts. However, the major drawbacks of this precipitation route are the low PO₄³⁻ content of produced solids, along with the subsequent demand to decrease (again) the pH <9 for final wastewater disposal. In contrast, by the addition of Fe(III) or Al(III) salts, PO₄³⁻ concentration below the regulation limit can be achieved in pH 7–8, which is commonly encountered in wastewaters, while the PO₄³⁻ content in the produced solids was 29 and 16 %w/w, respectively.

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 Rapid Small Scale Column Tests (RSSCTs) revealed an adsorption capacity of Q₁=6.5 mg P-PO₄³⁻/g FeOOH at breakthrough concentration equal to regulation limit (1 mg P-PO₄³⁻/L). However, this adsorption capacity was gradually stabilized to 3.5 mg P-PO₄³⁻/g FeOOH after 4 regenerations. The regeneration at pH value 12.5 resulted in the efficient phosphate recovery within 2 h, which in turn favors its subsequent chemical precipitation and recovery by the addition of either Ca²⁺, or Mg²⁺. The phosphate content in the recovered solids was 48±4% w/w for calcium and 20±2 % w/w for magnesium, while both produced solids presented good phosphorus bioavailability. Another important observation is that at the end of regeneration process, the equilibrium PO₄³⁻ concentration was practically zero and therefore, the regeneration solution could be recycled in the next cycle. Further on, the challenging part is to scale-up from lab to full-scale.

Results and Discussion

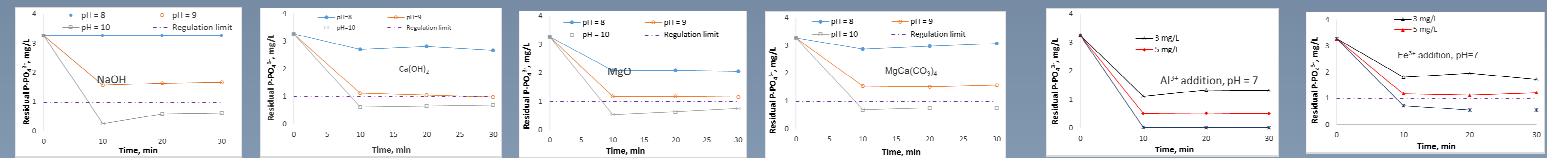


Figure 1: Effect of pH on precipitation of PO₄³⁻ with the addition of commercial salts in wastewater samples.

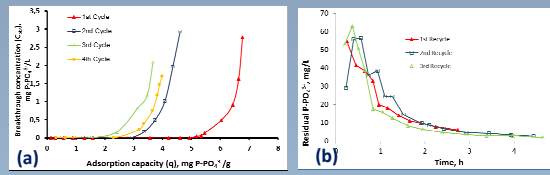
Figure 2: Precipitation of PO₄³⁻ with Fe(III) and Al(III) salts

The PO₄³⁻ content (% w/w) of produced solids was as follows: NaOH 9.3, Ca(OH)₂ 1.2, MgO 1.5, CaMg₃(CO₃)₄ 1.3, Fe(III) 29, Al(III) 16.

Rapid Small Scale Column Tests (RSSCTs)



Figure 3: Continuous configuration of Rapid Small Scale Column Tests (RSSCTs)



GFH and AquaAsZero sorbents showed similar results for phosphates

Figure 4: (a) Breakthrough curves of RSSCTs for 4 sequential cycles of SORB, and (b) profile of PO₄³⁻ concentration in regeneration solution.

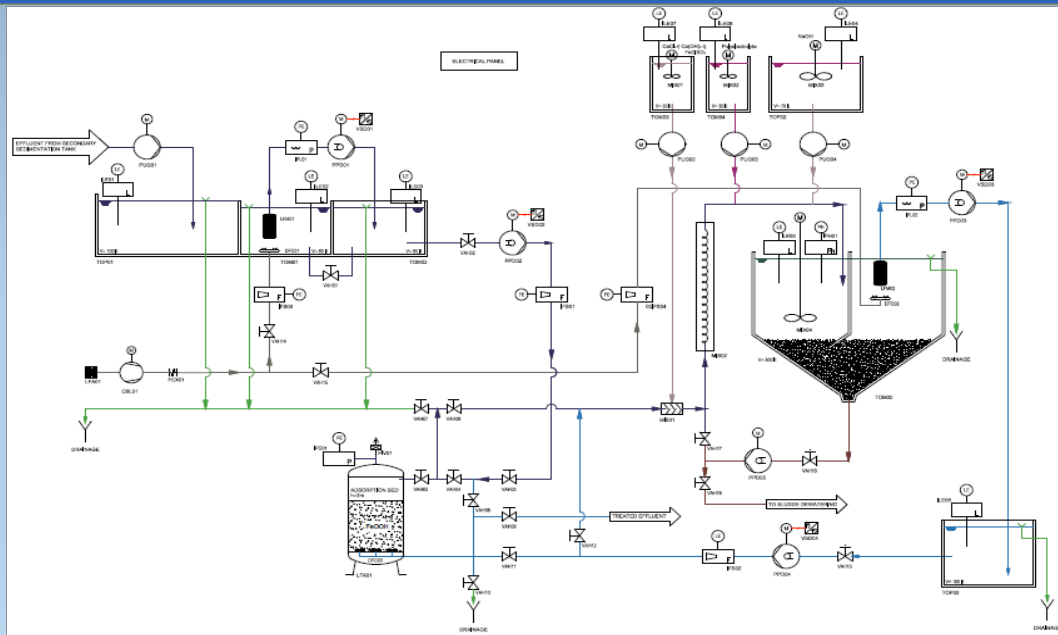
Pilot Plant

Phosphate adsorption onto FeOOH solids seems to be a promising process, considering the pre-requirement for their regeneration and phosphate recovery.

Following the RSSCTs experiments a pilot-plant, working in continuous flow mode, was designed and built to treat 100-300 L/h.

This pilot plant consisted of two major parts:

- The adsorption bed is working for Empty Bed Velocity (EBV) 5-20 m/h and for Empty Bed Contact Time (EBCT) 3-10 min.
- The regeneration part works on 10 m/h EBV, pH 12.5–13 and incorporates also the phosphates recovery part. Calcium or magnesium phosphate solids will be further separated by membrane filtration.



Conclusions

- ❖ By increasing the pH of secondary effluent above 10, PO₄³⁻ were effectively removed, due to their adsorption onto precipitated CaCO₃ or Mg(OH)₂ solids.
- ❖ NaOH proved the cost effective reagent for pH control (increase) and PO₄³⁻ removal from the secondary effluent.
- ❖ PO₄³⁻ were almost stoichiometrically precipitated at pH range 7-8, as Fe(III) or Al(III) salts.
- ❖ RSSCTs using FeOOH at pH 7 showed effective PO₄³⁻ removal. FeOOH was efficiently regenerated with NaOH solution, and PO₄³⁻ recovered as Ca or Mg salts.
- ❖ Following the results from RSSCTs, a continuous flow pilot-scale plant was designed and built to recover PO₄³⁻ from the secondary effluent of "AINEIA".

Acknowledgements

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