



Article

Holistic Approach to Phosphorus Recovery from Urban Wastewater: Enhanced Biological Removal Combined with Precipitation

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Abstract: Combined phosphorus (P) removal and recovery from wastewater is a sensible and sustainable choice in view of potential future P-resource scarcity, due to dwindling primary global reserves. P-recovery from wastewater, notwithstanding the relatively small fraction of total global amounts involved (less than 1/5 of total global use ends up in wastewater) could extend the lifespan of available reserves and improve wastewater cycle sustainability. The recovery of the resource, rather than its mere removal as ferric or aluminum salt, will still allow to achieve protection of receiving waters quality, while saving on P-sludge disposal costs. To demonstrate the possibility of such a recovery, a strategy combining enhanced biological phosphorus removal and mineral P-precipitation was studied, by considering possible process modifications of a large treatment facility. Process simulation, a pilot study, and precipitation tests were conducted. The results demonstrated that it would be possible to convert this facility from chemical -precipitation to its biological removal followed by mineral precipitation, with minimal structural intervention. Considerable P-recovery could be obtained, either in form of struvite or, more sustainably, as calcium phosphate, a mineral that also has possible fertilizing applications. The latter would present a cost about one order of magnitude lower than the former.

Keywords: nutrients; phosphorus; wastewater; bio-P process; modeling; P-recovery; precipitation; struvite; calcium sulphate

1. Introduction

Phosphorus (P) and nitrogen are the primary elements used for inorganic fertilizer production. Phosphorous minerals, in addition, find applications in the production of animal-feed additives, and therefore this element is essential to the provision of adequate food supplies for the world population: about 95% of all P-production is used in agriculture, mainly as industrial fertilizers. The remaining 5% is used in wide range of applications, such as: additives (e.g., polyphosphates, soft drink ingredients) in the food sector, or in household or industrial products (e.g., detergents and cleansers, metal surface treatment, corrosion inhibitors).

Unlike nitrogen that makes up about 78% of the earth's atmosphere, phosphorous is present on the planet in much lower amounts: its only primary source being phosphate rock (PR), which is found in accessible form only in specific areas on the globe (most in Morocco and Western Sahara, with minor deposits in China), is a finite, irreplaceable, nonrenewable resource. In 2006, the CEO of the Morocco Phosphate Company, the largest world supplier of phosphate rock stated: "With the anticipated requirements for phosphate for agricultural and industrial uses, the world is likely to run out in the

near future of low-cost recoverable phosphate rock" [1]. If the current level of PR production pro capita is applied to the median United Nations world population projection, in fact, current reserves would last until the year 2315. If, unfortunately, the population should grow as forecasted by the UN under the "high" population growth estimate, however, the same reserves would only last until the year 2170 [2].

In the phosphorus anthropogenic cycle, mainly targeted to food production, significant "leaks" (erosion and leaching from crop fields, uncollected animal waste and food waste) of this element occur along the way, resulting in only about 16% of the mined phosphorus being effectively assumed in human diet. Therefore, even if 100% human waste recycling could be attained, dependence on mined P would be reduced at most by that percentage. Nevertheless, even such relatively small amount of recovery could be an important step in reducing future humankind dependence on PR and extend the lifespan of available reserves.

Man has created an artificially accelerated and intensive phosphorus cycle, unbalancing the natural one. The natural P-cycle in fact mobilizes 10 Mt P/year, with intensive recycle between non-crop plants and soil, while the manmade cycle mobilizes an estimated 29 Mt P/year with negligible internal recycle [3]. As a consequence, P-containing wastes are discharged into rivers, lakes and seas, causing huge problems in aquatic and marine ecosystems, in primis through the eutrophication phenomenon. Raw wastewater contains about 4.0–16.0 mg P/L, of which 20%–30% is removed by conventional biological treatment, leaving 3.0–12.0 mg P/L in treated effluents. Environmental regulations, such as the European Water Framework Directive [4], limit admissible released P-levels at 1–2 mg/L. It is also expected that these limits may be lowered in the near future.

The difference between P-removal (mandated by regulations) and P-recovery is that the former aims at obtaining almost P-free effluents, while the latter focuses on obtaining suitably reusable P-rich by-products. Among the methods used for P-removal in wastewater treatment plants (WWTPs), enhanced biological phosphorus removal (EBPR) is gradually becoming an almost standard procedure, where needed, in lieu of chemical precipitation with ferric or aluminum salts, which implies the production of a mostly unusable chemical sludge that needs costly disposal and huge addition of precipitation chemicals. EBPR relies on specific polyphosphate-accumulating organisms (PAOs) to concentrate P in biomass by "luxury uptake". The feasibility of EBPR was discovered independently in the 1960s by two research groups [5,6] who observed increased P-uptake under aerobic conditions and its release under anaerobic conditions in an activated sludge process (ASP) (Figure 1). By appropriately alternating these conditions, P is removed from the solution and stored in the biomass. The first practical EBPR process, called PhoStrip, was described in [6] and evolved later in the Bardenpho process, which is the basis of most such plants operating today [7]. The adoption of EBPR may be further supported by the relative ease of integrating in it P-recovery through struvite (magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$) or calcium phosphate precipitation, or by composting waste activated sludge (WAS) directly. In fact, EBPR is typically used to achieve P-removal from treated wastewater, producing a biological excess sludge rich in P. In this case, the idea is to exploit the uptake/release mechanism to achieve a P-enriched sludge from which it could then be released and mineral P precipitated in readily reusable form.

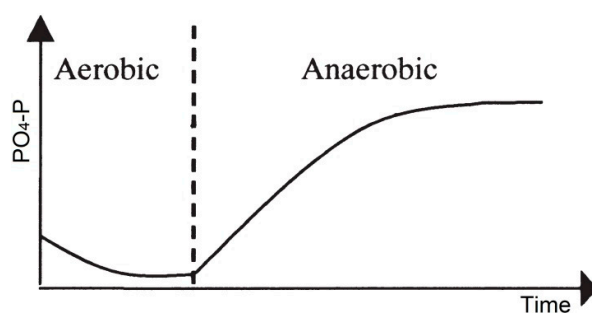


Figure 1. Solute P in the enhanced biological phosphorus removal (EBPR) aerobic–anaerobic sequence.

This paper deals with a case study in which the combined implementation of EBPR, with subsequent P-mineral precipitation, in a large municipal WWTP in Italy is considered, similarly to what proposed by Oleszkiewicz and Barnard [8]. The facility is currently employing P-precipitation with ferric chloride and aerobic WAS stabilization. Simulations of EBPR application and experimental tests of mineral-form P compounds were conducted in order to formulate an intervention proposal to enhance resource recovery at the facility. The area adjacent to the plant is an intensive agricultural area with potential to absorb the recovered fertilizer products without the need for long-distance transport. At the moment, the facility's WAS, rich in carbon, nitrogen, and phosphorus (the latter in the range 2%–2.5%), is reused directly in agriculture after dehydration and conditioning. However, political and public opinion pressures have been mounting locally for some time to restrict such practices, which are likely to be severely curtailed in the next future. Suitable alternative solutions are therefore needed. With an estimated excess sludge P-content of around 1400 tons/year, this facility would provide a suitable application case for integrated P-removal and recovery according to new paradigms advocating urban water management according to sustainability and conservation principles [9]. Almost the totality of published studies on P-recovery relate to traditional APS followed by anaerobic digestion. The recovery of fertilizer P from aerobically stabilized sludge is rarely the object of investigation.

The outcome of this study shows that a paradigmatic change in wastewater treatment could be achieved in this and many other similar cases, effectively converting WWTPs in WRRFs (Water and Resources Recovery Facilities) [10] thus achieving long-term sustainability of this sector by implementing saving or recovering resources and energy schemes.

2. Case Study Materials and Methods

2.1. Reference Facility

A municipal WWTP in Italy with a rated capacity of 1.25 million P.E., average flow rate of over 425,000 m³/day, and an annual dewatered sludge production of about 50,000 tons/year, was chosen as the object of this study. Wastewater is processed according to a traditional ASP nitrification/denitrification scheme with chemical precipitation of phosphorous by ferric salts. The average inlet flow rate to the facility may vary three-fold, between 5 m³/sec during normal dry weather, and 15 m³/sec in wet weather conditions. Plant effluent, on average 150 million m³/year of treated wastewater, is regenerated to a quality suitable for nearby irrigation of an area of about 4000 hectares, essentially devoted to the production of corn, alfalfa, cereals, and rice.

The facility operates on four equal parallel lines, defined by the design parameters illustrated in Table 1. The integration of EBPR into this conventional wastewater treatment scheme could allow reduction of operating costs by lowering chemical additives consumption for P-precipitation, reduction of hard-to-dispose chemical sludge production, and increase of P-concentration in the sludge (up to 30%–40% on dry weight). Thus, several advantages could be achieved, not least the possible subsequent implementation of mineral P-precipitation, in the form of struvite, a magnesium ammonium phosphate, which is considered an ideal fertilizer, or other similarly usable mineral P-forms [11].

Table 1. Design characteristic of each treatment line units.

Unit/Parameter	Variable [Units]	Value
Denitrification (anoxic)	V1 [m ³]	12,500
Nitrification-carbon oxidation (aerobic)	V2 [m ³]	38,000
Final clarification	A [m ²]	8700
Influent flow rate	QF [m ³ /d]	115,000
COD	SF [mg/L]	290
Total nitrogen	MF [mg/L]	26
Nitrous and nitric nitrogen	NF [mg/L]	1
Total phosphorus	PF [mgP/L]	4

Table 1. Cont.

Unit/Parameter	Variable [Units]	Value
Biomass concentration in return line	XR [mg/L]	5300
WAS rate	QW [m ³ /d]	1120
Mixed liquor recycle ratio	Ra	0.728
Sludge recycle ratio	Rb	1.05

2.2. EBPR: Plant Configuration and Dynamic Analysis

The approach adopted for this study was to hypothesize a new configuration of the facility under analysis that would allow EBPR support with minimal changes compared to present condition.

The software ASCAM (Activated Sludge Computer Aided Modeling), which allows direct evaluation of the process units volumes, was applied for this purpose, then the new configuration thus determined was tested for steady state and dynamic analysis with the software WEST (Wastewater treatment plant Engine for Simulation and Training).

ASCAM is a WWTP design software registered by the Water Research Institute (IRSA) of the Italian National Research Council (CNR) based on a mechanistic mathematical model, with empirical components [12]. ASCAM can be used for active sludge treatment plant design and simulation in steady state and dynamic conditions. The software allows to easily determine the dimensional characteristics of process units of a WWTP and a series of other operational process parameters, given influent properties, values of kinetic and stoichiometric parameters and operating conditions, under predetermined requirements of removal efficiency of key quality parameters (COD, N, P). A classic EBPR scheme, illustrated in Figure 2, was referred as the basis for the design and subsequent simulations.

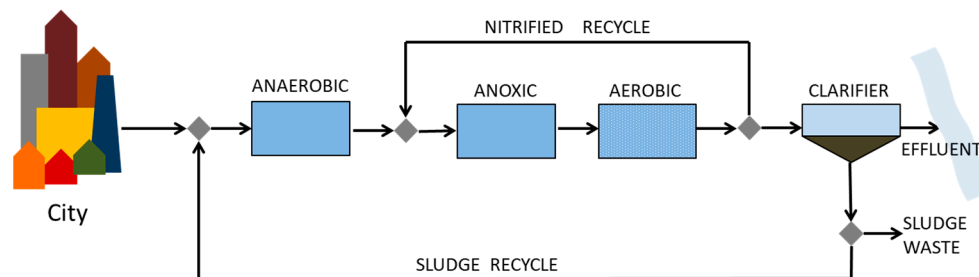


Figure 2. Proposed scheme for the new, EBPR-supporting plant configuration.

The second tool applied, WEST is a modeling environment specific for dynamic simulation of wastewater treatment plants providing a user-friendly platform to easily test the expected performance of such facilities under a series of different hypotheses [13]. WEST is based on the ASM (Activated Sludge Model) series of models [14] and, compared to ASCAM, is characterized by a more detailed fractionation of substrates and biomass fractions. Within WEST, several simulations were conducted selecting the ASM2d model to test the new configuration scheme under dynamic operating conditions, using actual past observed operating data provided by the plant operator.

2.3. Pilot Scale Study

Following this phase, a pilot model of the plant in 1:10⁶ physical scale was set-up and operated in steady state, closely resembling the scheme illustrated in Figure 2, as summarized in Table 2, using actual influent and sludge from the original facility as feed and biomass inoculum respectively. The flow and internal recycles were maintained by peristaltic pumps. Analyses of quality parameters (COD, TKN, TP) were carried out every other day (three days across weekends) by photometric method (HANNA Instruments HI83399 and relevant reagent kits). The pilot was run in steady state for over 30 days after sufficient PAO biomass stabilization had been achieved, and this allowed confirming the

expected results given by the simulations in terms of effluent quality and P-accumulation in sludge during EBPR.

Table 2. Characteristics of the pilot plant.

Process Unit/Parameter	Variable [Units]	Value
Denitrification (anoxic)	V1 [L]	8.5
Nitrification-carbon oxidation (aerobic)	V2 [L]	35.0
P-release (anaerobic)	V3 [L]	1.0
Influent flow	Q [L/d]	110
Mixed Liquor Recycle	QMLR [L/d]	80

2.4. Precipitation Tests

Precipitation tests were conducted on the influent to the aerobic unit of the pilot plant, where higher P-concentration in sludge is normally observed due to its release in the previous anaerobic stage, and on the aerobic mixed liquor of the original facility. A 10 L semi-continuous reactor (Figure 3), with automated pH control system, was used for these tests.

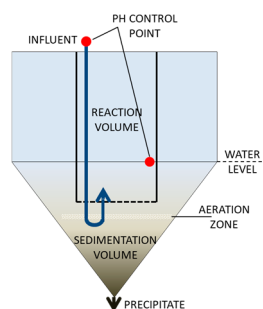


Figure 3. Precipitation reactor scheme.

Average chemical composition observed in the samples of the pilot plant was: $\text{Ca}^{2+} = 95 \text{ mg/L}$, $\text{Mg}^{2+} = 28.8 \text{ mg/L}$, $\text{P} = 40.3 \text{ mg/L}$ and $\text{NH}_4^+ = 35.2 \text{ mg/L}$, thus suitable for P-recovery as struvite.

P-concentration in samples from the oxidation tank of the full scale facility ranged from 7.0–9.2 mg/L, while other parameters had median values similar to the former sample, that is, $\text{Ca}^{2+} = 101 \text{ mg/L}$, $\text{Mg}^{2+} = 32 \text{ mg/L}$ and $\text{NH}_4 = 32 \text{ mg/L}$. In this case, P-concentration is too low for achieving effective precipitation, thus, according to the method suggested by Tykesson and La Cour Jansen [15], a pre-conditioning anaerobic treatment at variable retention times, up to 36 hours, was applied.

While struvite is perhaps the most “popular” and sought P-precipitated mineral, many other (over a dozen), mineral forms of precipitated P exist, with variable fertilizer recovery value [16]. Different factors affect struvite (as well as other mineral precipitates) crystallization, such as: solution pH, constituent ions (Ca^{2+} , Mg^{2+} , PO_4^{3-} and NH_4^+) molar ratios, agitation rates, process retention time, etc. Optimal precipitation conditions were determined with the PHREEQC model, an established geochemical modeling tool developed by US Geological Survey (USGS) according to a procedure reported in a previous study [17]. Corresponding values of the operating parameters were: at pH = 9, $\text{Ca/Mg} = 0.8$ and $\text{NH}_4/\text{P} > 3.5$, at pH = 9.5, $\text{Ca/Mg} = 1.2$, $\text{NH}_4/\text{P} = 2$. It was also shown that the maximum struvite content in the precipitates was achieved for $\text{Ca/Mg} < 1$ and pH close to 9. At higher pH levels, high P-recovery (>90%) could still be achieved, although producing precipitates with lower struvite content [18].

Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and ammonium chloride (NH_4Cl) addition was required to achieve the ideal $\text{Mg}:\text{NH}_4:\text{P}$ molar ratios in solution indicated by PHREEQC simulations

(5:5:1 and 3:3:1), with mixed liquor adjusted to pH = 9. NaOH was used as buffer agent. Precipitates were examined as described in [18].

Further tests were subsequently conducted on both liquid media at their original components' molar ratios, with no chemicals addition. Moreover, the expensive NaOH buffer solution was substituted by the much less costly reagent $\text{Ca}(\text{OH})_2$, that can be purchased at about 1/10th of the price of the former, to control pH at the values of 8.5 and 9.0 [16].

2.5. Analytical Methods

Analyses of quality parameters (COD, TKN, NH_4 , TP, etc.) were carried out in triplicate every other day (three days across weekends) by photometric method (HANNA Instruments HI83399 and relevant reagent kits), according to methods USEPA 410.4 for COD, Nessler D1426-92-ASTM for ammonia, chromothropic for TN, EPA 365.2 for TP, calmagite for Mg, ossalate for Ca. pH was measured with HANNA HI 98191 handheld probe. Characterization of final precipitates with identification of their components was performed with Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer 1600 series, Waltham, MA, USA), thermal gravimetric analysis (TGA) (Mettler Toledo TGA 1 STARe System, Columbus, OH, USA) combined with Quadrupolar Mass Spectroscopy (MS) and X-ray Diffraction (XRD) (Bruker D5005, Billerica, MA, USA). Evaporates from TGA were checked by MS for components. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for quantitative measurement of Ca^{2+} , Mg^{2+} , and P in precipitates.

3. Results

This section presents results obtained from the design and operational modeling simulations of the designed EBPR full-scale facility, the pilot study, and the laboratory studies on optimized precipitation.

3.1. Design and Operational Modeling

ASCAM simulations showed that the new system configuration would both fulfill the required effluent discharge standards (total N \leq 10 mg/L, COD \sim 0 mg/L, total P \sim 0 mg/L) and achieve consistent EBPR needed for the creation of an anaerobic PAO selection/enrichment step (for each treatment line). The calculated anaerobic unit volume was $V_{\text{anaer}} = 800 \text{ m}^3$ (positioned as in Figure 1), dimensionally much smaller than present volumes. Volumes of anoxic and aerobic tanks were, respectively, 8500 m^3 and 35,000 m^3 , also lower than those already available. It follows that the present configuration could be easily modified to simultaneous biological removal of C, N and P by adapting the currently existing anoxic tank, with volume of 12,500 m^3 , partly for the anaerobic biomass-selection unit (800 m^3), and partly for denitrification (needed $V_{\text{anox}} = 8500 \text{ m}^3$, available 11,700 m^3). This volume distribution still leaves a large volumetric margin of safety (3200 m^3 , i.e., more than 37% of the one actually needed). The existing aerobic nitrification/oxidation unit would remain unmodified with a safety margin close to 8%. The configuration of the original WWTP would make such changes relatively easy and relatively inexpensive to implement.

Assuming for the new configuration the values of anaerobic, anoxic and aerated volumes thus obtained, steady-state simulations were then performed with the WEST tool. Steady-state simulation results related to achievable effluent concentrations are shown in Table 3.

Table 3. Simulated steady-state effluent concentrations obtained with the WEST model.

Parameter	Units	Value
BOD	mg/L	2.5
COD	mg/L	43.6
TKN	mg/L	1.7
TP	mg/L	1.4
TSS	mg/L	13.6

Dynamic simulation analysis was subsequently performed with the same model to assess the effects of time variability of influent flow rates and concentrations. Operator-provided past observed time series of daily inflows and corresponding influent parameters concentrations were used, as shown in Figures 4 and 5.

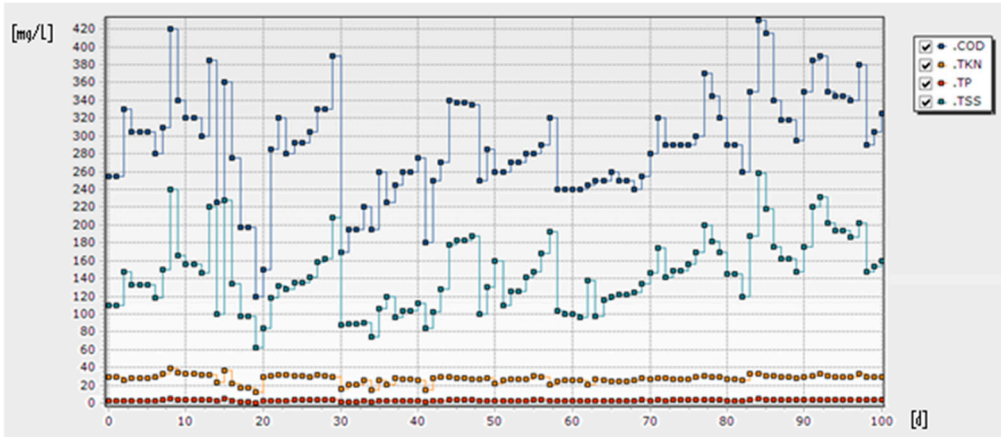


Figure 4. Observed influent quality parameters time series.

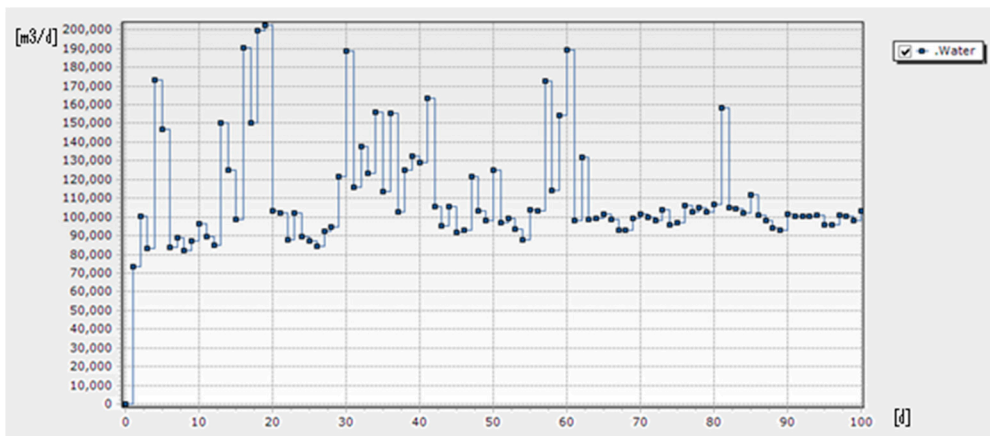


Figure 5. Observed influent flow time series.

With the above model input load curves over a simulation period of 100 days, dynamic simulation of the new EBPR-enabled facility was carried out. Results are shown in Figure 6, where the average daily concentrations of effluent parameters expressed in mg/L are summarized.

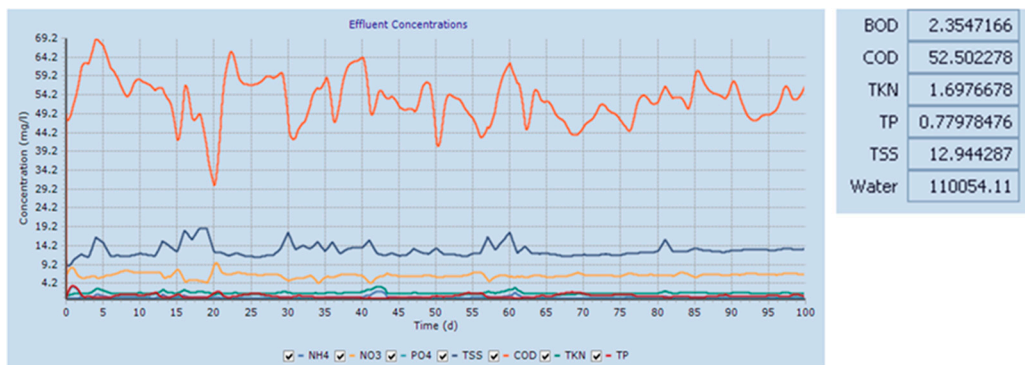


Figure 6. Continuous and average (right box) effluent concentrations of quality parameters from a 100-day WEST-based dynamic simulation of the new EBPR configuration.

In the simulated conditions, all effluent parameters are well below the Italian standards for effluent discharge [19]. Of particular relevance is the very low effluent P-concentration, consequent to the effects of the EBPR process. In these conditions, chemical P-precipitation with ferric salt could safely be eliminated from normal wastewater processing, perhaps keeping it as a stand-by, emergency treatment option in case of EBPR failure due to unexpected inhibition or mechanical failure. The high P-content of the sludge in the presence of the biological P-removal process, furthermore, could allow maximization of P-recovery by precipitation as discussed below.

3.2. Verification of Design Conditions by Pilot Plant

The pilot plant was inoculated with actual WAS from the original facility and fed with influent flow aliquots taken from the original WWTP every week. After it reached a condition closely resembling EBPR steady state, it was then monitored during a 33-day running period. During that period the influent flow main characteristics, reported in Table 4, were relatively stable and quite similar to the actual design values adopted for the ASCAM model. Operating conditions were made to reproduce as closely as possible the design operating parameters determined through ASCAM in the previous study phase.

Table 4. Influent wastewater characteristics during pilot study.

Parameter [mg/L]	1st Week	2nd Week	3rd Week	4th Week
COD	295	320	340	260
TKN	33	35	32	28
TP	6.3	4.2	4.5	5.1

The pilot plant performance results are summarized in Figure 7. It should be noted that, notwithstanding the influent variability during the test period and the uncertainties related to the operation of a pilot-scale plant of this size and the analytical imprecision due to the use of spectrometric analytical kits for parameters determination, the scaled installation performed close to expectations, confirming the findings of the previous theoretical study phase. In addition, its operation allowed to actually determine values of expected P-concentration in the mixed liquor after the anaerobic release phase

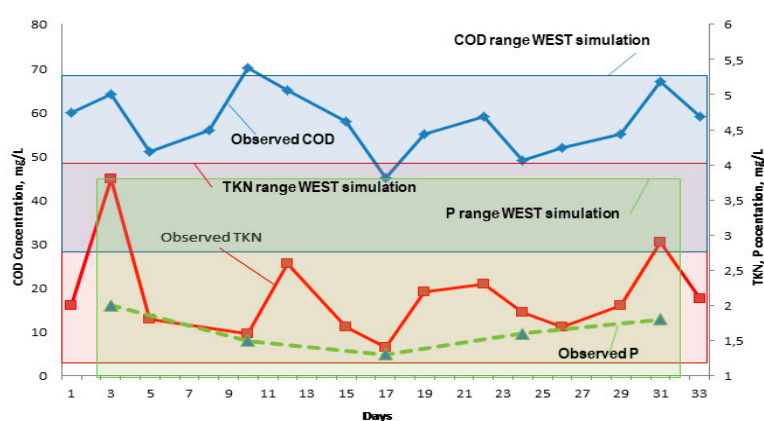


Figure 7. Observed effluent quality parameters from the pilot plant (lines) and their ranges from dynamic WEST simulation (boxes).

3.3. P-precipitation Preliminary Study and Laboratory Tests

Results achieved from EBPR pilot plant mixed liquor indicated that to achieve significant struvite precipitation, high levels of Mg^{2+} and NH_4^+ addition would be needed in case of anaerobic sludge to reach the ideal $Mg:NH_4:P$ constituent ratios for struvite precipitation identified by precipitation

modeling as 5:5:1 and 3:3:1. In preliminary tests, the former originated better precipitation yields and was hence adopted for all subsequent experiments. In addition, tests confirmed that the optimal pH range for struvite precipitation lies in the range 8.5–9.0, and that at pH > 9.0, the possibility of struvite precipitation is significantly diminished, compared to the other P-salts. P-recovery from the solution reached maximum values at 80%–85% (at pH = 9), with final precipitates consisting of a variable mix of struvite, amorphous calcium phosphate (ACP), and calcite. Precipitates analytical characterization was described in detail elsewhere by Daneshgar et al. [18]. A test conducted at pH = 9.5 showed that high P-removal was still possible (up to 94%) using NaOH as pH buffer, but precipitates obtained were mostly in the form of calcite. Although P-removal in these conditions was higher, this should be considered an undesirable outcome, as calcite is not a favorable product for reuse as fertilizer. These conditions were therefore excluded from further consideration.

In samples from the oxidation tank of the full scale plant, the phenomenon of secondary P release in the absence of electron acceptors was observed at long retention times (>24 h), as described by Barnard [20]. Although very slowly, secondary release increased P-concentration in the conditioned mixed liquor, from 7.0–9.2 mg/L to almost 18 mg/L, and led to satisfactory results in terms of P-precipitation, with specific efficiency (78%–88%) closely comparable to the ones observed in the former tests, although absolute recovered amounts were lower due to lower solute concentration. The lower P-concentrations achieved in this case and the long residence time required are most likely due to the lower fraction of PAOs biomass present in the full-scale facility, which lacks an anaerobic zone biomass selector, which ultimately limits the possibility of substantial alternate P-uptake and release. It should be noted that the availability of excess volumes from the old denitrification and aeration sections combined and properly modified, could allow the implementation of an anaerobic unit required for enhancement of P-release. The required HRT values, however, would be compatible with P-removal only from a fraction (10%–15%) of the incoming flow in this case, while under the EBPR configuration, the entire flow could be treated [15]. Table 5 summarizes observed results.

Table 5. Summary of precipitation tests.

Molar Ratio	pH Buffer	pH Value	P-Recovery (%) EBPR Samples	P-Recovery (%) Full-Scale Samples
Mg:NH ₄ :P = 5:5:1 (adjusted)	NaOH	8.5	77.4–81.2	75.7–78.2
		9.0	80.1–84.8	78.2–87.7
As sampled	Ca(OH) ₂	8.5	72.3–76.6	68.2–73.6
		9.0	85.7–88.4	81.3–86.4

Implementability of either solution, however, is affected by the high cost of chemicals (magnesium chloride hexahydrate and ammonium chloride) and of the pH buffer (NaOH) needed.

Tests with no chemical addition resulted in P-recoveries efficiencies quite analogous to the previous case, in the range 72%–77% at pH = 8.5 and 86%–88% at pH = 9.0, with similar mass dosages of buffering agent (in the range of 90–98 mg/L and 7–125 mg/L for NaOH and Ca(OH)₂ respectively). In this case, recovered P was mostly in the form of ACP (Ca₃(PO₄)₂), and not of struvite (due to low concentration of Mg and NH₄ in solution), which may also be employed directly as fertilizer or as main ingredient in commercial fertilizers' production.

In an actual implementation at real-scale, such precipitation unit would be operated as a side-stream process of the main liquid treatment (Figure 8). As confirmed by the ASCAM model, the facility conversion to EBPR support under listed design conditions (Tables 1 and 2) would allow conversion of existing excess volumes for this purpose, since all or part of the excess denitrification and aeration volumes available (3200 and 3000 m³ respectively, as determined by the model) could be converted into such side-stream precipitation unit by appropriate in-plant modifications.

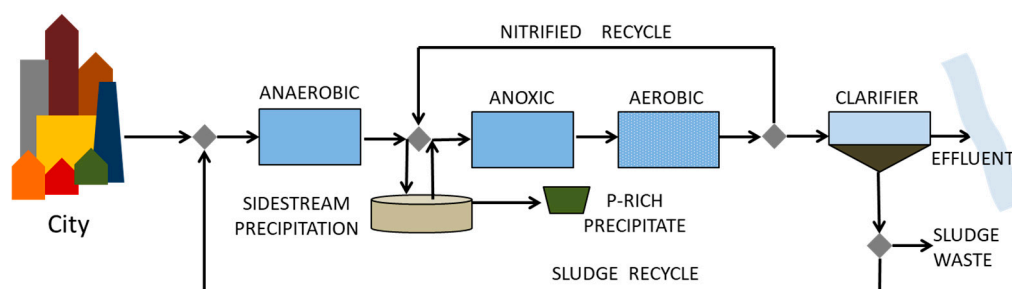


Figure 8. New facility configuration with side-stream precipitation reactor.

4. Discussion

Simulation using available operational time series, and additional preliminary pilot tests studies conducted on a small-scale model of the new proposed plant configuration confirm that conversion to EBPR of the examined facility could be possible and would be able to operate effectively. Existing volumes are in excess of calculated requirements for EBPR operation and the biological units could be converted to the new process scheme with a good degree of safety. Part of the excess volume available could be converted to a side-stream precipitation reactor for P-recovery.

Obtaining a pure struvite product, no matter how high dissolved P-concentration, might not be the best, nor the most economically feasible or advantageous option due to the potentially high (depending on solution's composition) need of expensive chemicals' addition (i.e., Mg, NH₄) and pH buffer requirements (NaOH) to achieve optimal ionic molar ratios for its precipitation. This may also be the case in commercial patented P-recovery processes applications, such as Ostara® and Struvia™, which effectiveness may be undermined by these drawbacks. The commercial cost of chemicals normally used as sources of Mg and NH₄, magnesium chloride hexahydrate (MgCl₂·6H₂O) and ammonium chloride (NH₄Cl) is in fact relevant: under the described facility influent conditions and calculated optimal molar ratios, Mg and NH₄ addition would cost, on average, around 0.12 and 0.05 Euro/m³ treated, respectively. Dosage of NaOH for pH adjustment would further increase the treatment price tag by 0.04–0.07 Euro/m³ at pH = 8.5 and 9.0, respectively, with total cost under tested conditions between 0.21–0.24 Euro/m³.

ACP precipitation could instead be obtained under no chemical addition, using Ca(OH)₂ for pH adjustment, with a more affordable price tag, due to the lower cost of that sole buffering agent, calculated in the order of 0.003–0.006 Euro/m³ treated, that is, two orders of magnitude lower than under the former option of struvite recovery. Under tested conditions, similar P-removal and recovery efficiencies as the previous method were achieved with ACP precipitation. In addition, under either option, costs for P chemical precipitation with ferric or aluminum salts would be avoided, as well as costs for the final disposal of those residues [21]. Liquid-phase P-recovery would also reduce the overall energy demand and related GHG emissions of a treatment facility [22], by cutting requirements for chemical sludge handling, providing replacement P-containing products (extraction of P of from PR requires approximately 2 kWh/kg P [23]) and renewed resources. It was estimated that the introduction of P-recovery may lower the cumulative energy demand of a WWTP by 17.7% on average [24].

Under either option, precipitation tests of both pilot and real plant mixed liquor (the latter after anaerobic conditioning) yielded very similar specific P-recovery efficiencies (i.e., P-recovery as a fraction of solute-P) in the range of 72%–88%. These results compare favorably with those reported in an EBPR pilot plant study recording P-precipitation efficiency between 83%–91% with recovery efficiency at slightly lower values (76%–83.9%), the latter attributed to the formation of fine crystals that could not be recovered. Struvite content of precipitates ranged between 35.4% and 72.6% [25]. Similar recovery values were also observed for struvite precipitation from aerobically digested sludge filtrates from four small WWTPs in north Florida (USA), ranging from 41%–61% recovered P, which could be improved to over 90% by Mg salt additions. In that case study, however, WWTP-wide P-load reduction estimates ranged only from 3%–43% as these facilities did not rely on EBPR in the treatment train [26].

These results compare favorably with those of the currently adopted chemical precipitation, achieving an average of 80% P-removal with FeCl at Fe:P ratio >1.5. Of course, in the pilot mixed liquor, where EBPR was implemented, the absolute yield was higher due to the higher concentration in solution. Mineral precipitation from the real plant mixed liquor (without implementation of EBPR) would be partially effective to recover some P-minerals, but may not meet discharge requirements.

EBPR implementation should however carefully consider possible inhibitory factors affecting the process performance, including long-term organic and nutrient loading rates that could affect the PAO microbiome development, possible occurrence of dissolved toxic substances and variations of reactor operation parameters that could influence the stability and reliability of the EBPR system. These effects were not fully considered in the WEST modeling simulation, although dynamic simulation under observed data was performed, and were not detected in the limited pilot study. All these factors should be analyzed in a more detailed pre-implementation study, including long-term operation of a larger-scale, onsite, pilot plant study capable of fully capturing the natural seasonal variability of influent flow, conditions and parameters, in order to reproduce and better understand the likely behavior of a full-scale EBPR process implementation more precisely.

5. Conclusions

As many other service sectors, the sewerage sector has recently embraced the quest for greater sustainability and recovery of wastewater embedded resources. Phosphorus is an essential resource of finite availability, and one that is contained in wastewater in considerable amounts and from which it must be removed under current environmental regulations. Recovery of reusable mineral P, rather than its mere removal from effluents, would make wastewater treatment processes more environmentally sustainable.

This study has shown that, by combining EBPR and P-precipitation under appropriately favorable conditions, as those presented by the examined treatment facility, a great percentage of P in solution could be recovered as struvite or, more economically, as ACP, a fertilizing-value product that can be reused in agriculture.

Author Contributions: M.C.T. coordinated the modeling study and interpreted its results; V.S. implemented the West model, run the ASCAM and WEST simulations and contributed to results interpretation; S.D. conducted literature analysis and carried out experimental work on P precipitation; A.G.C. designed the study, coordinated the pilot plant work, contributed to the analysis of results and wrote the main body of the draft paper. All authors discussed and contributed to the manuscript outline. All authors have read and agreed to the published version of the manuscript.

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