Review

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Review

Post-Removal of Phosphorus from Biologically Treated Wastewater and Recovering It as Fertilizer. A Pilot-Scale Attempt—The Project PhoReSe

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Abstract: The major issue of raw materials depletion and more specifically of phosphorous (an important fertilizer) has currently become an emergent aspect, due to expected depletion problems, needing immediate handling. This was the reason for the implementation of PhoReSe project that aimed to remove and recover phosphorus from the secondary (biologically treated) effluent of a municipal wastewater treatment plant (WWTP "AINEIA", located near Thessaloniki, N. Greece), treating the wastewaters of the nearby touristic area. Regarding the phosphorous supplementary removal and recovery treatment options, two methods mainly examined, initially in laboratory scale (batch experiments), i.e. (1) the adsorption of phosphorous, and (2) the chemical precipitation of phosphorus. Both methods further applied in pilot-scale, by performing initially the adsorption of phosphorous onto the AquAsZero commercial sorbent, which is a mixed manganese iron oxy-hydroxide, followed by the chemical precipitation of phosphorous, implemented after the de-sorption process of previously saturated adsorbent. The final precipitate of this procedure examined as an alternative/supplementary fertilizer, returning with this way phosphorus into the natural cycle. These experiments, as applied successfully in pilot-scale, set the basis for the larger-scale relevant application for similar WWTP facilities.

Keywords: phosphorus recovery; sustainability; fertilizer; secondary (treated) effluent; adsorption; chemical precipitation; wastewater management

1. Introduction

Even though the Life Cycle Assessment (LCA) method and the concept of Circular Bio/Economy have dynamically entered the industrialized optimization processes, nevertheless the linear use of materials is still quite widely applied, resulting in the loss or the unnecessary disposal of useful raw materials [1]. Apart from the sustainability aspects, the increased processing costs for the achievement of the even stricter disposal limits, as imposed by the respective regulation norms, to avoid potential environmental problems, usually require the further potential exploitation of used end-of-life materials, such as phosphorus (P), to reduce the respective costs [2]. Phosphorus is among the important nutrients, pointing out the recycled/recovered options during each step of wastewater treatment process, due to its significance for the growth of plants and living organisms, as well as since is not considered as a convenient renewable material in nature [3, 4]. The crystallization of struvite (i.e. MAP, $MgNH_4PO_4{\cdot}6H_2O$) during certain wastewater treatment processes, regarding the P-rich streams (usually after the anaerobic digestion of sludge), once considered as a serious operational problem, but nowadays is mainly used to retrieve phosphorus from these streams, when the existing conditions (i.e. mainly Mg and nutrients' content, pH and temperature) allow its formation, since it can be subsequently effectively applied as a potential fertilizer; therefore, enabling the recovery of phosphorus from wastewaters and its environmental reuse [5,6].

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Phosphates gradual depletion due to overuse of fertilizers (expected to be from 7.5 to 12.5 Tg/year during 2005-2050) results in a high phosphorous footprint, which can be related also to methane production (being an important part (around 13-20%) of the total Greenhouse Gases effects), due to the potential creation of algae blooms in water bodies, caused by the resulting eutrophication problem from the respective mismanagement/disposal, and following their death, which can produce methane under anaerobic conditions; hence, overall affecting seriously the climate change [7, 8]. If not recycled, phosphorus scarcity will result in the future in the "phosphogeddon" phenomenon, affecting apart from the climate change, the food production and quality as well [9]. Phosphorus is an essential element for agriculture and cannot be substituted, making very important the identification of potential strategies to secure sufficient phosphorous supply and to avoid the expected deficiency by 2035 [10, 11]. These strategies must be implemented worldwide towards the exploitation and recovery of phosphorous from several waste streams [12].

Initially, the respective treatment processes, regarding phosphorous, aimed to remove it from wastewater to avoid the adverse environmental effects of its disposal. However, nowadays, the problems of phosphorous depletion have led to practices that promote the closing of P-cycle by implementing processes to recover and recycle it instead [13]. Noting also that most of current studies are focusing on the recovering/recycling of P from P-rich streams (e.g. from food production wastes, from municipal wastewater treatment plants (anaerobically treated sewage sludge) and from aqueous sewage liquors, from animal wastes etc.) [14-18]. The European Sustainable Phosphorus Platform (ESPP) updates annually the nutrient recovery technologies catalogue, reporting the applied technologies for phosphorus mostly in the forms of struvite, hydroxyapatite, calcium phosphates and phosphoric acid. Anong the 53 technologies in the respective 2023 report only one reported for the recovery of phosphorus from lower concentrated steams [19, 20]. Bearing in mind the serious economic consequences, which will be negatively affected by the "phosphogeddon" depletion effect, but also the respective environmental benefits, the scientific community is oriented to achieve the P-recovery not only from the P-rich streams (which are mainly in the form of inorganic phosphates/PO_4^{3-}), but also from the lower concentrated P-streams, such as the secondary (treated) wastewater treatment effluents, as well as the meat industry and the steelmaking slag etc. [13, 21].

Since phosphorus scarcity is one of major issues that must be dealt with during the 21st century, the realization of PhoReSe project held within the framework of circular economy and sustainable development framework, targeting the environmental achievement of closing the phosphorus loop and deficiency, and preventing its foreseen elimination as a raw material source [22-25]. The importance of PhoReSe project lies beyond the state of the art of other relevant studies, as it has produced an applicable solution for the recovery of phosphorus from the stream of treated municipal wastewater, before its disposal in the receiving water bodies, producing primarily an environmentally valuable product that enables the re-entering/reuse of phosphates as a nutrient source, while at the same time avoiding the eutrophication phenomena, caused by its disposal to rivers, lakes or even to the sea [26].

2. Materials and Methods

For the realization of this research, it is important to examine the stability of wastewater treatment process, and to determine the phosphorus concentration that can be potentially recovered. For this reason, the statistical variations of secondary (biologically treated) effluent from a WWTP, handling about $8x10^3$ m^3/d of influent, consisting of $7x10^3$ m^3/d of municipal wastewater and $1x10^3$ m^3/d of domestic septage waste, examined for the period of 12 months. The mean higher phosphorus concentrations in this effluent are the determinant values for the design of experimental tests [23], because it is crucial for the recovery process to be able to effectively treat the whole range (min.-max.) of respective phosphorus concentrations [27]. The statistical variation of main parameters conducted, by using the SPSS software package.

To achieve the required residual concentrations, being lower than the commonly applied legislation limit for PO_4^{3-} (i.e. 1 mg total-P/L, or 3 mg PO_4^{3-}/L) the continuous recovery of phosphorus, disposed with the treated secondary effluents, examined [28]. The municipal WWTP of "AINEIA" is

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treating wastewaters produced from the nearby touristic areas of Thessaloniki, which usually contain (mean) phosphorus concentration 4-6 mg P-PO_4^{3-}/L [22-25]. The PhoReSe experimental investigation includes the examination of chemical precipitation of phosphorus, with the addition of commercial forms of inorganic salts, i.e. magnesia (MgO), calcium hydroxide ($Ca(OH)_2$), huntite ($Ca.Mg_3(CO_3)_4$), ferric chloro-sulfate ($FeClSO_4$) and sodium aluminate ($NaAlO_2$), in various water matrixes, i.e. aquatic solutions of potable or distilled water and of biologically treated wastewater (secondary effluent), containing an initial concentration of about 5 mg P-PO_4^{3-}/L. These salts examined as Ca^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+} sources to form the respective insoluble precipitates of phosphorus [29]. According to the relevant speciation diagram that corresponds to a phosphate concentration of 10 mg/L in the National Sanitation Foundation (NSF) water matrix which is used as a typical element concentration in natural waters, the respective calcium and magnesium salts can be formed at pH values >6 at 293 K with the negatively charged phosphate anions [25, 30]. The chemical precipitation experiments conducted in three different matrixes, i.e. distilled, potable and treated wastewater after the secondary (biological) wastewater treatment, and the main characteristics are shown in Table 1. The phosphate stock solution prepared by using anhydrous KH_2PO_4 (supplied by Panreac, >98.0% purity).

The phosphorus adsorption experiments contacted by using certain hydrous iron oxyhydroxides, either commercially available (i.e. GEH, Bayoxide, and AquAsZero), or produced in the laboratory (schwertmannite and lepidocrocite), as well as the organic resin PuroliteA200 EMBCL, aiming to examine whether the disposal of phosphorus effluent is achievable below the regulation limit and can be further recovered. Regarding the recovery of phosphorus, the preliminary desorption at alkaline environment of the P-loaded sorbent investigated, followed by the subsequent chemical precipitation, by using certain salts as coagulant agents [24]. The respectively produced precipitated phosphate salts examined further as potential fertilizers, by checking their phosphate content and their soil bioavailability [22].

Table 1. Main **c**hemical characteristics (parameters) of Thessaloniki's tap (potable) water, NSF water, and of the WWTP AINEIA secondary treated effluent used in the experiments.

Parameter	Potable	NSF Water	WWTP treated Effluent
pH	7.5±0.1	-	7.4±0.3
ConductivityμS/cm	590±10	-	4400±200
Hardness	30±1	-	750±50
HCO_3^-mg $CaCO_3$/L	341.6±5	138	500±50
NO_2^- mg/L	ND	ND	0.45±0.1 m
NH_4^+ mg/L	ND	ND	0.6±0.2
PO_4^{3-} mg/L	0.055	0.04	12-17
Ca^{2+} mg/L	50.2±2	40	120±10
Mg^{2+} mg/L	28.1±1	12.7	100±10
Na^+ mg/L	8.1±0.5	88.8	585±10
K^+ mg/L	2.4±0.5	ND	37±5

The coagulation/precipitation procedure investigated initially by batch experiments, adding the respective coagulant doses to phosphate solutions, and examining the optimum phosphate removal, as well as the required dosages and treatment time. The used chemical agents investigated during this project as "coagulants" for the eventual precipitation of PO_4^{3-} were the following inorganics:

- magnesia (MgO) (supplied by Grecian Magnesite SA, Greece, with >94.0% purity),
- calcium hydroxide ($Ca(OH)_2$) (supplied by CaO Hellas, with >90% purity),
- huntite ($Ca.Mg_3(CO_3)_4$) (supplied by Sibelco Ellas, Greece, with >95% purity),
- ferric chloro-sulfate ($FeClSO_4$) (supplied by Feri-Tri SA, Greece, with 12,5% w/w content), and
- sodium aluminate ($NaAlO_2$) (supplied by Loufakis Chemicals S.A., Greece, with content 25%w/w as Al_2O_3).

The adsorption experiments evaluated by the batch isotherms, thermodynamics, and pH effect in which a quantity of adsorbent placed in the phosphate solution and examined for the respective adsorption capacity; also, by using the Rapid Small Scale Column Tests (RSSCTs) the adsorption

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capacity examined in continuous flow. The examined commercially available adsorbents were the following:

- GEH (supplied by GEH Wasserchemie GmbH & Co.KG, Osnabrück, Germany), consisting mainly form akaganeite.
- Bayoxide (supplied by Lanxess, Cologne, Germany), consisting mainly of goethite.
- AquAsZero (supplied by Loufakis Chemicals S.A., Greece), consisting mainly of tetravalent manganese feroxyhyte.
- the organic resin PuroliteA200 EMBCL (supplied by Purolite).

In addition, two laboratory-synthesized iron oxyhydroxides examined, prepared under intensive oxidative conditions after the oxidation and precipitation reaction of $FeSO_4{\cdot}H_2O$ (supplied by Loufakis Chemicals S.A., Thessaloniki, Greece, with >99.0% purity), producing as final products, i.e. schwertmannite and lepidocrocite, but only in the experiments examining the temperature effect [31].

The relevant thermodynamic adsorption study conducted in the NSF water matrix, simulating potable water, as shown in Table 1. The water matrix preparation based on the guidelines provided by the National Sanitation Foundation (NSF) standard and prepared by using chemical grade reagents, i.e. $NaHCO_3$ (supplied by Merck, with >99.5% purity), $NaNO_3$ (supplied by Merck, with >99.5% purity), $NaH_2PO_4{\cdot}H_2O$ (supplied by Sigma-Aldrich, with >98.0% purity), NaF (supplied by Merck, with >99.0% purity), $NaSiO_3{\cdot}5H_2O$ (supplied by Loufakis Chemicals S.A., with >99.0% purity), $CaCl_2{\cdot}2H_2O$ (supplied by Riedel-de Haen, with >99.0 purity), and $MgSO_4{\cdot}7H_2O$ (supplied by Panreac, with >98.0% purity) [24]. The desired pH values for the experiments adjusted by the addition of NaOH (supplied by Loufakis Chemicals S.A., Greece, as 50% w/w solution), or by HCl addition (supplied by Chemlab, as conc. 37% a.r.), and 2 mM of N, N-Bis(2-hydroxyethyl)-2-amino-ethane-sulfonic acid reagent (denoted as BES and supplied by Alfa Aesar, with >99.0% purity), which used to stabilize pH at the desired value, as a buffer [25].

The resulting chemical precipitates of phosphorus in the alkaline effluent after the desorption procedure, investigated in terms of phosphorus bioavailability in acidic and alkaline soil samples by the extraction of phosphorus with the Mehlich-3 solution (consisting from 0.001 M EDTA, supplied by Merck, with >99.0% purity; 0.015 M NH_4F, supplied by Merck, with >98.0% purity; 0.2 M CH_3COOH, supplied by Merck, with >99.8% purity; 0.25 M NH_4NO_3; 0.013 M HNO_3, supplied by Merck, as 65.0% a.r.), or with the Olsen solution ($NaHCO_3$ 0.5 M) for the acidic or alkaline samples, respectively. Moreover, the assessment of soil samples phytotoxicity conducted, by using the commercially available toxicity bioassay ''Phytotox kit micro-biotest''.

The sustainability aspect was the main target of PhoReSe project, aiming to engage phosphorus from the secondary treated wastewater effluent back into the phosphorus environmental cycle [32]. The promising results obtained from the laboratory-scale experiments led to the design, construction, and operation of a relevant pilot-plant, put in operation in the WWTP of AINEIA. The pilot plant set-up also included a membrane pre-filtration unit for the efficient removal of residual suspended solids, an adsorption-desorption column, and a final chemical precipitation tank, alongside the fully automation panel for remote controlling the whole recovery process [24, 33]. The respective materials and methods explained with more details in the previous relevant publications [22-25].

3. Results

The results' evaluation of adsorbents efficiencies showed the superiority of iron-based adsorbents, as compared to the lower adsorption/ion exchange capacity of Purolite A200 EMBCL material. Figure 1 presents the data fittings by applying the Freundlich and Langmuir isotherm models and shows the major findings, regarding the high iron-based adsorbents removal efficiencies. The obtained data fitted better the Freundlich model, due to the presence of heterogeneous adsorption sites, while it is obvious that the AquAsZero adsorbent material presents the optimum adsorption capacity (Q), with Q_{max} 60 mg PO_4^{3-}/g_{ads}, whereas the Q_3, which is calculated to comply with the regulation limit of 3 mg PO_4^{3-}/L, found as 57.4 mg PO_4^{3-}/g_{ads}. It is remarkable that the adsorption favored by the co-existing ions, showing better adsorption capacity, when the adsorbents dispersed in the

NSF water matrix. For the better evaluation of AquAsZero the effect of different pH values also examined, i.e. pH 6, 7, and 8, with the adsorption optimum results shown for the lower pH value [24]. Moreover, the effect of temperature for the adsorption of phosphate onto the iron-based adsorbents thoroughly examined and an exothermic process reported, when the adsorption took place in the distilled water matrix, while an endothermic process found for almost all examined iron-based adsorbents, except of Bayoxide, when the matrix was the NSF water. The difference in thermodynamics can be attributed to the co-existing ions in the NSF water matrix that favor the adsorption of phosphates onto the iron-based adsorbents. Higher temperatures seem to favor the phosphate removal by adsorption onto the iron oxyhydroxides, with 90% removal occurring after 1 h of contact time [25].

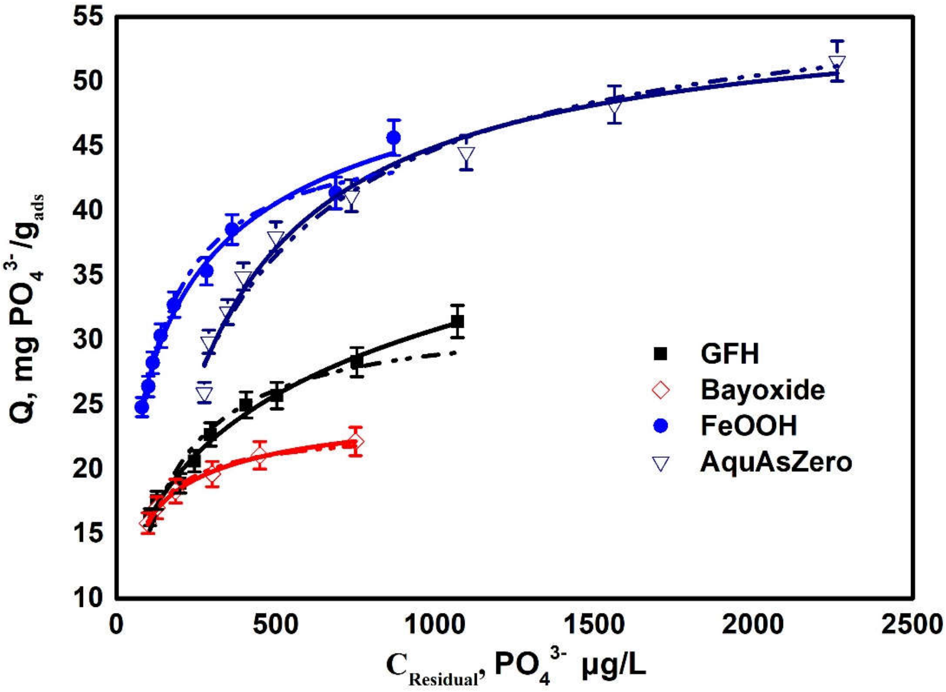

Figure 1. Comparison of phosphates' adsorption efficciency using several adsorbents in NSF water matrix at pH 7 and 20° C.

The removal/separation of phosphates by adsorption onto the iron-based adsorbents investigated also with the continuous running Rapid Small Scale Column Tests (RSSCTs) that can simulate more efficiently the full-scale applications, than the previous batch tests, by using as matrix the secondary treated effluent from the WWTP "AINEIA", which according to the statistical variation results of Table 1 can contain about 12-17 mg PO_4^{3-}/L. The breakthrough curves for the 1st cycle of adsorption resulted in 34, 31, 19, and 15 mg PO_4^{3-}/g_{ads} for the materials AquaAsZero, FeOOH, Bayoxide, and GEH, respectively, as calculated for the regulation discharge limit of 3 mg PO_4^{3-}/L. As expected, the different chemical content of this aqueous matrix is negatively affecting the adsorption procedure.

The examined phosphate concentration for the preliminary chemical precipitation experiments was approximately 10 mg PO_4^{3-}/L. The chemical precipitation of phosphorus, resulting by the addition of magnesia (MgO), calcium hydroxide ($Ca(OH)_2$), or huntite ($Ca.Mg_3(CO_3)_4$), requires alkaline environment; hence, pH greater than 10 applied to achieve the required efficient capture/removal of phosphorus, and the residual concentration to be lower than the set regulation limit of 3 mg/L, by using all examined water matrixes, i.e. potable or distilled water and wastewater (secondary effluent). For the same matrix, the addition of 5 mg Al^{3+}/L at pH range 6–8 can achieve removals lower than the required regulation limit of 3 mg PO_4^{3-}/L, which however increased significantly for even higher pH values, due to the corresponding increase of aluminum solubility. Moreover, this also occurs for the addition of 7.5 mgFe^{3+}/L and the reaction ratio of 0.5:1 for Al^{3+}:PO_4^{3-}

and 0.75:1 for Fe^{3+}:PO_4^{3-} as estimated for the optimum removal at pH 7 (Figure 2). Additionally, the temperature also affects the PO_4^{3-} removal, as shown in Figure 2, with the temperature increase to favor slightly the removals for the cases of $Ca(OH)_2$, or $Ca.Mg_3(CO_3)_4$ additions, while slightly decreasing the removal for the rest of examined chemical agents. In addition, the formed precipitates contain almost 50.1% PO_4^{3-} for the case of $Ca(OH)_2$ addition, whereas only 1.2% PO_4^{3-} for the case of $Ca.Mg_3(CO_3)_4$, and 19.0% $PO_4^{3-}$for MgO, 8.7% $PO_4^{3-}$for $NaAlO_2$, 27.3% $PO_4^{3-}$for $FeClSO_4$, when the experimental matrix was distilled water.

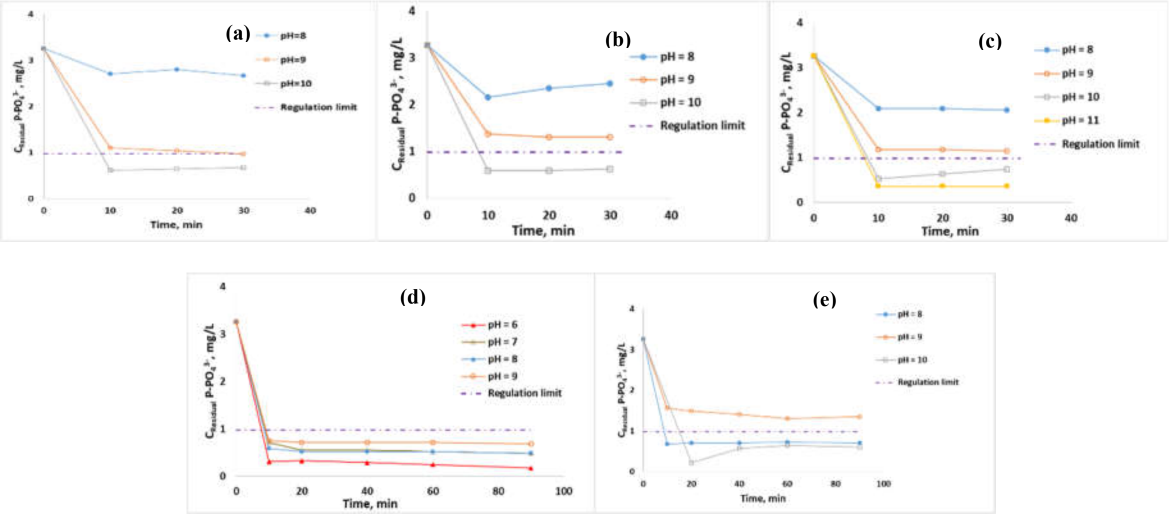

Figure 2. pH effect on phosphate removal for the initial concentration 10 mg PO_4^{3-}/L and after the addition of (a) 50 mg $Ca(OH)_2$/L, (b) of 100 mg $Ca.Mg_3(CO_3)_4$/L, (c) 75 mg MgO/L, (d) 7.5 mgFe^{3+}/L (from $FeClSO_4$), and (e) 5 mg Al^{3+}/L (from $NaAlO_2$).

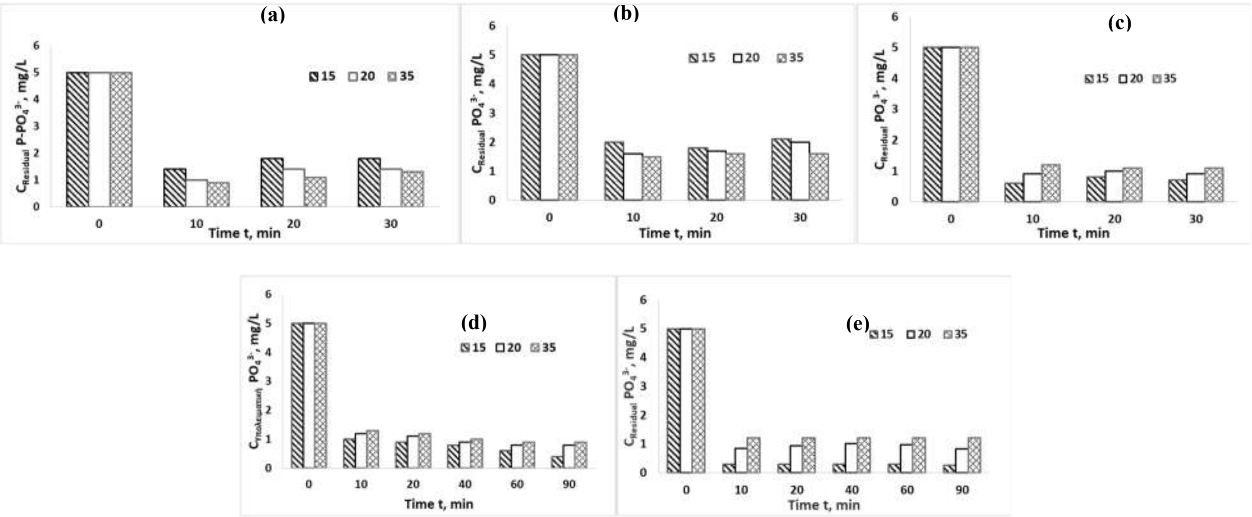

Figure 3. Temperature effect on phosphate removal for the initial concentration 5 mg PO_4^{3-}/L and after the addition of (a) 75 mg $Ca(OH)_2$/L at pH 10, (b) 100 mg$CaMg_3(CO_3)_4$/L at pH 10, (c) 10 mg MgO/Lat pH 10, (d) 5 mgFe^{3+}/L (from $FeClSO_4$) at pH 7, and (e) 3 mg Al^{3+}/L (from $NaAlO_2$) at pH 7.

Similar to the RSSCTs results, an adsorption capacity of 32 mg PO_4^{3-}/g_{ads}, as calculated for the regulation discharge limit of 3 mg PO_4^{3-}/L, reported for the following pilot-scale implementation (Figure 4), by using AquAsZero as the adsorbent medium. The pilot-plant successfully processed the secondary treated effluent from the WWTP "AINEIA" both in the adsorption process with an Empty Bed Velocity (EBV) 10 m/h, as well as in the desorption mode with an EBV 5-20 m/h (7 adsorption and 6 desorption cycles for the pilot-plant performed), where the continuous adsorption-desorption cycles with a loss of adsorption sites (and efficiency) of approximately 20% between the 1st and the 2nd cycle and 10% more loss between the subsequent adsorption cycles noticed. This capacity loss can be attributed to the strongly bound phosphates onto the iron oxy hydroxides' adsorption sites that cannot be easily desorbed during the subsequent treatment cycle [22, 24, 32, 34]. More specifically, even though during the RSSCTs experiments, the desorption succeeded by applying the NaOH solution at the pH 12.5±0.2 achieved in approximately 3 h to complete the adsorbents' regeneration, permitting the reuse of adsorbent, for the pilot-plant operation the requirement of regeneration optimization process is reflected on the non–expected reduction of adsorption capacity during the subsequent operation cycles, as shown in Figure 5. Even higher pH value (12.8±0.2) applied in the pilot-plant to optimize the regeneration process at the 4th regeneration cycle, favoring the adsorption capacity after the 5th operation cycle. Beside the loss of adsorption capacity, the regeneration process is vital for the economic viability of the overall recovery process [35].

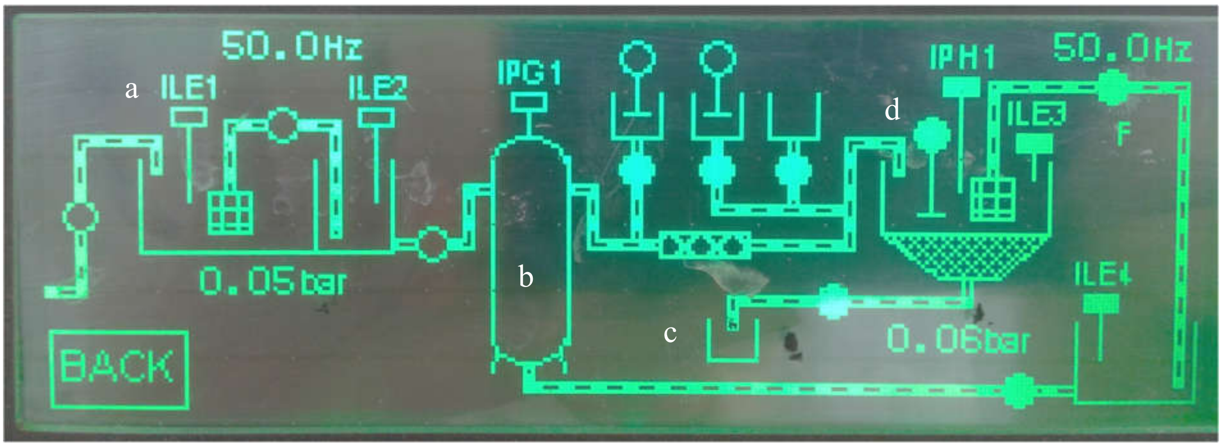

Figure 4. The pilot plant plc operation; (a)pre-treatment tank with hollow-fiber commercial membranes for the preliminary TSS removal, (b) the adsorption-desorption column, (c) the solution tanks (containing NaOH and $CaCl_2$), and (d) the precipitation tank.

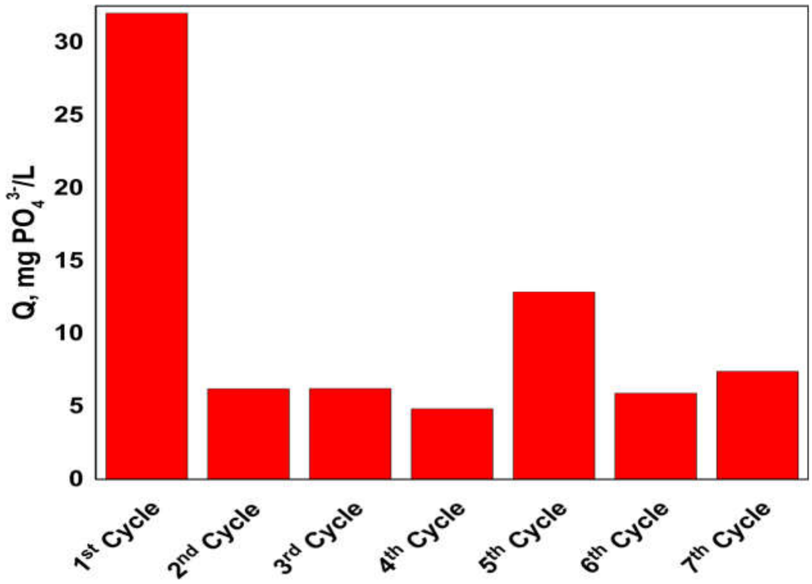

Figure 5. Adsorption capacity of phosphorus for the pilot-plant experiments after the subsequent operation cycles.

The alkaline solution from the desorption process collected in the sedimentation tank, as shown in Figure 4, where according to the preliminary chemical precipitation experiments, the contained

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phosphates can be best precipitated and separated with the presence of Ca^{2+} or Mg^{2+} addition of salts. Since the precipitate intended to be finally used as fertilizer, the maximum PO_4^{3-} content in the precipitate is desired; therefore, Ca^{2+} selected for this process. The non-toxic precipitate as collected from the pilot-plant application (Figure 6) for the 6 adsorption/desorption cycles was approximately 5 kg, and presents high phosphate content (35.4 wt.%) that can be easily subsequently applied as a phosphate-based fertilizer, mostly in acidic soils, where the phosphate release is expected to be better, while at the same time no adverse effects, regarding the plants' growth, may be caused, as reported during the phytotoxicity investigation [22, 24].


(**a**) (**b**)

Figure 6. Collected Ca-phosphate precipitate; (a) collection in basket filters, (b) dried fertilizer.

4. Discussion

The eutrophication problem of water resources is accelerated by anthropogenic activities that include the disposal of municipal (not-sufficiently treated) wastewaters. The increase of nutrients into water bodies and more specifically of nitrogen and phosphorus, can result in severe algal blooms, as well as to the presence of potentially harmful cyanobacterial species that could produce in turn dangerous cyanotoxins [36, 37]. Being a global issue, eutrophication must be mitigated by implementing efficient treatment strategies that will allow both the removal, as well as the recovery and re-entering of phosphorus into its natural bio-geo-environmental cycle. Since there is a tendency to increase the total phosphorus content in raw wastewaters the target should be to obtain low residual concentration levels (<1 mg/L) in the treated effluents disposed in the water bodies; hence, eliminating the eutrophication undesirable phenomena [38]. During the PhoReSe project the statistical results showed that notable variations reported, regarding the phosphorus content, especially during the summer period in the secondary treated wastewater effluent, indicating the need for additional post-treatment [23].

The relevant mitigation techniques may include chemical, physical and biological processes. P-rich streams in the wastewater treatment process, when the phosphorus recovery is required, usually include the urine influent (when separated), the secondary wastewater treated effluents (as in the PhoReSe project), the anaerobic digester supernatant of sewage sludge treatment, and the specifically incinerated sewage sludge ash [39]. The wet chemical (hydrometallurgical) method is a simple technique that allows the recovery of phosphorus mainly from the sewage sludge ash, or from the anaerobic digester supernatant in the form of high purity products, such as struvite, presenting though a relatively high operating cost, due to the added chemical reagents and the operational procedures [40]. The sewage sludge ash can be also treated with more complex and higher energy-consuming thermal methods to recover phosphorus, producing high purity products and minimum pollutant content. Diverse technologies, such as pyrolysis and electrochemistry, can be also applied to sewage sludge to recover phosphorus. Even though pyrolysis shows high recovery rate, the main problems are the potential dioxin and furans gases produced during this process. The electrochemical methods are still under investigation, but mostly in laboratory-scale [41, 42].

On this other side, adsorption is an easy handling process, showing high selectivity for the removal of phosphorus and can be applied in the aqueous phase streams; usually a proper pre-treatment step for the enhanced separation of suspended solids is required. This method is also highly dependent on the applied sorbent material's capacity for capturing phosphorus [24,43].

To achieve the phosphorus removal and recovery from the treated secondary wastewater effluents, being the P-stream that PhoReSe has examined, several chemical agents can be added, such as lime, aluminum, or iron salts. However, due to the cost and the required quantities of these agents the process can become viable economically, but only for the P-reach streams, while at the same time a secondary treatment to eliminate the remaining potential microbial etc. pollutant load may be commonly required [44, 45]. On the other hand, the application of biological processes cannot handle constantly and with high removal efficiency the phosphorus content, being around 70% treatment efficiency for most of the relevant cases and being also a highly temperature-dependent process [46, 47]. Moreover, the alternative application of micro- or ultra-filtration membrane specific processes, apart from the rather high implementation costs, can also result in a supernatant that still contains quite high quantities of phosphorus; hence, contributing to secondary pollution problems, when disposed of, or requires additional post-treatment [36, 48]. Currently, pilot, and full-scale applications are oriented also to the combination of adsorption and precipitation processes, such as those examined in the PhoReSe project [24, 49].

Comparing PhoReSe with the relevant REM NUT® process that also use adsorption onto the Cu-form resin Dowex M-4195, which is rather expensive adsorbent, and using as matrix in the respective pilot-plant the secondary effluent from Massafra (S.E. Italy) Wastewater Treatment Plant, it becomes obvious that the AquAsZero adsorbent can treat greater volumes of the secondary wastewater, noting that both comparatively examined effluents contain similar concentration of phosphates; hence, PhoReSe is presenting in this way a lower cost for the whole treatment process [50]. Like the PhoReSe project, the secondary wastewater effluent from another municipal sewage treatment plant has been treated at pilot-scale, by applying phosphate adsorption onto the ZnFeZ material, which also subsequently subjected to desorption and finally, phosphorus precipitated as struvite. Even though the obtained results in this case study seem quite promising, nevertheless the operational cost is elevated, due to the additional magnetic separator required, whereas that process is operated in batch mode (another disadvantage) [51]. Additionally, a similar adsorption process reported, using the HAIX-Layne RT (HAIX) resin for the phosphate anion exchange from the secondary treated wastewater with a removal capacity of 4.1 mg PO_4^{3-}/g_{resin}, which is significantly lower, than the capacity found for AquAsZero (32 mg PO_4^{3-}/g_{ads}) [52].

Phosphorus content in the municipal waste streams corresponds to the largest percentage (approximately 23.6%) of the whole lost phosphorus from the respective cycle of use, being at the same time the most promising recovery option from secondary sources [53]. The effective circulation from the wastewater streams to finally reach (and fertilize) the soil is of high importance, since the phosphorus deposits are being quickly depleted worldwide [54, 55]. Therefore, sustainable strategies based on the best available technique should be applied to recover the disposed phosphorus from the secondary wastewater treated effluents as an added-value material (fertilizer) that will release phosphorus again in the agricultural soil, closing partially in this way the respective material balance and reducing the actual phosphorus needs from virgin (mineral) sources [56].

The future work should be oriented to the optimization of fertilizer production by reducing the $CaCO_3$ content in the precipitate. Moreover, the combination of proper materials, such as the serpentinized solid wastes from the Grecian Magnesite SA mining operations could be also used as Mg^{2+} sources, recycling with this way two different types of wastes, and belonging in the general context of sustainability [57]. A supplementary addition that can be also made in the pilot set-up is that of a second adsorption column that will operate in parallel to the first one, treating the effluent continuously, even when one of these columns is being under the regeneration mode.

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5. Conclusions

The global demand for phosphorus, due to depletion problems, considered as finite resource, alongside with the ecological vulnerability of receiving water bodies towards the presence of excess phosphorus, causing eutrophication problems, has led to the investigation of post-treatment for the secondary effluents from a municipal WWTP, considering both the phosphorus removal and recovery options. Initially, the statistical variation of phosphorus content through an operation year determined as 12-17 mg PO_4^{3-}/L. During the performed (preliminary) chemical precipitation experiments, it is noticeable that the removal of phosphorus can be enhanced by the co-presence in the water to be treated of wastewater common ions; the precipitation process can be also positively influenced (after the desorption/regeneration process) by the increase of alkalinity, rather than by the excess addition of chemical reagents. Calcium and magnesium compounds can effectively remove phosphates, when the solution pH value is greater than 9, whereas iron and aluminum salts can effectively remove phosphorus at the pH range 6-9.

The adsorption evaluation in laboratory-scale experiments pointed out that the AquAsZero material presents the optimum adsorption capacity of 34 mg PO_4^{3-}/L, an efficiency verified also during the subsequent pilot-scale experiments (32 mg PO_4^{3-}/L), as calculated for the current disposal regulation limit of 3 mg PO_4^{3-}/L; hence, indicating the proper design of the examined process and implying its suitability for full-scale application at the operating pH around 7. Both the (small) columns (at laboratory-scale) and the larger ones at the pilot-plant can be effectively regenerated, by using the NaOH solution at pH >12.5, resulting to an enriched PO_4^{3-} solution that could be further treated by adding Ca^{2+} as the chemical agent to precipitate phosphorus, producing the respective fertilizers that can contribute to the phosphorous sustainable/proper management.

Summarizing, the PhoReSe project achieved the effective phosphorus recovery from the small-concentrated treated wastewater effluent (in the range of few mg/L) in the form of a fertilizer that can re-introduce phosphorus in the agricultural cropland. It is of high importance that the circular economy loop of phosphorus can be (partially) closed, a fact that presents important benefits, such as the increased availability of phosphorus-based fertilizers that nowadays face severe scarcity issues, reducing also the respected high fertilizers' cost, as well as the potential to prevent eutrophication problems, since the load of phosphorus in the disposal of post-treated effluents can be significantly lower. As presented, the PhoReSe project showed high removal capacity (32 mg PO_4^{3-}/g_{ads}) and recovery efficiency (>95%), resulting to the superiority of examined treatment process in comparison with other (relevant) pilot-scale plants, as presented in the literature. The significance of this project is the potential of its implementation for the treated secondary wastewater effluents from municipal WWTPs, a fact that is of great environmental importance, as it complies with the current regulation limits, and it is considered as economically feasible, unlike most of the other implemented technologies. The realization of the project is in accordance also with the green chemistry and engineering principles, as well as with the sustainable environmental management techniques, by using and producing materials being environmentally friendly.

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