

Supplementary Materials

Recovery of Phosphorus from Waste Water Profiting from Biological Nitrogen Treatment: Upstream, Concomitant or Downstream Precipitation Alternatives

Albert Magrí ^{1,*}, Mar Carreras-Sempere ², Carmen Biel ² and Jesús Colprim ¹

¹ LEQUIA, Institute of the Environment, University of Girona, Campus Montilivi, Carrer Maria Aurèlia Capmany 69, E-17003 Girona, Catalonia, Spain; jesus.colprim@udg.edu

² IRTA, Institute of Agrifood Research and Technology, Sustainable Plant Protection Program, Ctra. de Cabrils, km 2, E-08348 Cabrils (Barcelona), Catalonia, Spain; mar.carreras@irta.cat (M.C.-S.); carmen.biel@irta.cat (C.B.)

* Correspondence: albert.magri@udg.edu; albert.magri@gmail.com; Tel.: +34-972-419-542

Received: 19 June 2020; Accepted: 14 July 2020; Published: 18 July 2020

Table S1. Relevant words included (or discarded) in the multi-term topic search assessed via the Web of Science Core Collection (Clarivate Analytics, USA).

| Topic | Words |
|-----------------------------------|---|
| <i>Included</i> | <i>Included</i> |
| Core element under study | "ortho-phosphate*" OR "orthophosphate*" OR "phosphate*" OR "phosphorous" OR "phosphorus" |
| Management strategy | "*recover*" OR "recycl*" |
| Technological process | "crystal*" OR "formation" OR "*minerali*" OR "precipitat*" OR "production" |
| Product formed | "*apatite*" OR "bobierrite" OR "brushite" OR "monenite" OR "newberyite" OR "*struvit*" OR "vivianite" |
| By-products to be processed | "biosolid*" OR "centrate*" OR "digestate*" OR "dung" OR "effluent*" OR "filtrate*" OR "leachate*" OR "liquor*" OR "manure" OR "residu*" OR "sewage" OR "sludge*" OR "slurr*" OR "stream*" OR "supernatant*" OR "urine" OR "waste*" OR "WWTP*" |
| <i>Discarded</i> | <i>Discarded</i> |
| P-related chemicals and compounds | "acetyl phosph*" OR "*adenosin*" OR "*alanin*" OR "arginine phosph*" OR "carbonate apatite*" OR "cellulose phosphate" OR "chloro-phosph*" OR "dinucleotide*" OR "fluorophosphoric" OR "hypoxanthine*" OR "ketone*" OR "lipid-phosphate" OR "molybdopho*" OR "monobasic potassium phosphate" OR "nitrophosphate" OR "organo-phosph*" OR "organophosph*" OR "pentose phosph*" OR "peptide" OR "phosphate-buffered" OR "phosphate buffer" OR "phosphate cement*" OR "phosphate ceramic*" OR "phosphate group*" OR "phosphate transporter*" OR "*phosphine*" OR "*phosphinite*" OR "*phosphite*" OR |

| | |
|---|---|
| | <p>"phosphogypsum" OR "*phosphomannos*" OR "phosphomolyb*" OR "*phosphonate*" OR "*phosphopeptid*" OR "phosphoric ester" OR "*phosphorite*" OR "phosphoryl" OR "*phosphoserin*" OR "pyridoxal" OR "pyrophosphate" OR "sulphonate" OR "tributyl phosphate*" OR "tricresyl phosphate*"</p> |
| Biomedical studies | <p>"analgesic*" OR "antibiotic*" OR "antibod*" OR "antigenic*" OR "arthritis" OR "blood" OR "*bone*" OR "calculi" OR "cancer*" OR "cartilage*" OR "catheter*" OR "cisplatin" OR "*clampsia" OR "clinical*" OR "coronary" OR "cortisol" OR "creatine*" OR "crystalluria" OR "cystoplast*" OR "cytophatic" OR "dental" OR "dentin*" OR "disease*" OR "disinfect*" OR "enamel*" OR "endocrine" OR "fetal" OR "heart*" OR "hepatitis" OR "holmium" OR "immunoassa*" OR "implant*" OR "inflammator*" OR "inositol" OR "kidney*" OR "*kinase*" OR "laser-induced damage" OR "lincomycin" OR "lithostatine" OR "liver*" OR "loperamide" OR "lung*" OR "lysozyme*" OR "mammal*" OR "mammary-gland" OR "mucos*" OR "mutagen*" OR "nephro*" OR "nucleotide*" OR "orthopaedic*" OR "pericardium" OR "*polyoma" OR "precipitation of protein*" OR "prostat*" OR "*protease*" OR "renal*" OR "salivar*" OR "*stanniet*" OR "*synaptic*" OR "tendinopath*" OR "testosterone" OR "therap*" OR "tooth" OR "urolithiasis" OR "urothelial*"</p> |
| Natural history, ecosystems, mineralogy and other related studies | <p>"archaeobotany" OR "archaeologist*" OR "amphibian*" OR "*antarctic*" OR "boreal" OR "chlorspodioside" OR "diamond*" OR "lentic ecosystem*" OR "lotic ecosystem*" OR "magma*" OR "metamorphism" OR "mimetite" OR "paleocen*" OR "prehistoric*" OR "pollen" OR "*pyrite*" OR "riparian" OR "*silicate*" OR "soil structure"</p> |
| Radioactivity and chemical studies | <p>"actinide*" OR "antimony" OR "barium" OR "cesium" OR "erbium" OR "fission" OR "lanthanide*" OR "lanthanum" OR "lithium" OR "neodymium" OR "nuclear waste*" OR "plutonium" OR "production of HF" OR "radioactive material*" OR "radioactive waste*" OR "radionuclide*" OR "scandium" OR "strontium" OR "technogenic waste*" OR "thorium" OR "uranium" OR "vanadium"</p> |
| Alternative P management alternatives | <p>((("4-phosphate" OR "6-phosphate" OR "adsorbent*" OR "agricultur*" OR "Al and Fe" OR "Al/Fe" OR "Al:Fe" OR "*alkanoate*" OR "alum*" OR "ash*" OR "BNR" OR "clogging" OR "*coagula*" OR "combustion*" OR "electrodialy*" OR "Fe and Al" OR "fertili*" OR "*floccul*" OR "incinerat*" OR "ion exchange" OR "iron*" OR "membrane*" OR "osmosis" OR "P removal" OR "phosphate discharge*" OR "phosphate removal" OR "phosphorous discharge*" OR "phosphorus discharge*" OR "phosphorous removal" OR "phosphorus removal" OR "polyphosphate*" OR "removal of phosphate*" OR "removal of phosphorous" OR "removal of phosphorus" OR "scale" OR "scaling" OR "soil*" OR "*sorption*" OR "sediment*" OR "wetland*")) NOT ("apatite*" OR "bobierrite" OR "brushite" OR "calci*" OR "magnesi*" OR "monenite" OR</p> |

"newberyite" OR "recover*" OR "*struvit*" OR "vivianite")) OR
 "alumina recovery" OR "EBPR recovery" OR "phytoremediation" OR
 "production of available phosphorus from rock phosphate" OR
 "recovered by backwashing" OR "recovering alloy steels" OR
 "recovery of normal operation" OR "rhizofiltrat*"

Others
 "cheese quality" OR "D2EHFA" OR "DBDECMP" OR "flame" OR
 "glass-ceramics" OR "LDH" OR "LUKE" OR "parenteral
 nutrition" OR "resilon" OR "silicon" OR "thermal ionization" OR
 "titanium" OR "u-th-ra" OR "water-ethanol"

Table S2. Summary of experiences integrating chemical precipitation aiming at P recovery followed by biological N oxidation, or removal (upstream precipitation).

| Waste water source ¹ | Precipitation performance ² | Bioprocess performance | Precipitate characteristics | Reference |
|--|--|--|--|-----------|
| <i>NDN as the bioprocess following chemical P precipitation</i> | | | | |
| Hydrolysed urine Composition: pH 9.1, ALK 19692, COD 5868, TN 5280, NH ₄ ⁺ -N 5193, TP 280, Mg & Ca not detected | MgP precipitated in lab tests simultaneously to vacuum thermal stripping (+acid absorption) at 25–65°C using MgCl ₂ 3 h batch stripping tests at 60°C and 21.3 kPa → 80% infl. N recovery; solids produced: 25.3 g/L _{urine} [(NH ₄) ₂ SO ₄ + NH ₄ HSO ₄ : 85.5 + 13.9 wt%] | NDN via nitrite in a continuous-flow AS AO MBR (2.4 L) Increased COD/N (4.7) and ALK/NH ₄ ⁺ -N (4.4) mass ratios after precipitation favoured NDN NLR 0.37 g N L ⁻¹ d ⁻¹ , NRE >80%; higher efficiency limited by ALK shortage | MgP mostly precipitated as MAP (>90 wt%) according to XRD and chemical analysis of the solid Composition of the precipitate: 13.1% P, 8.2% Mg, 5.3% N | [68] |
| | Mg/P adjusted to 1.2/1 → PUE >95%; solids produced: 1.5 g/L _{urine} | Global performance: >95% N and P reduction | | |
| Anaerobically digested sludge dewatering centrate from a municipal WWTP | MgP precipitated in a lab batch reactor (3.5 L) MgCl ₂ added, pH 8.5 (NaOH), reaction time 10 min 16% NH ₄ ⁺ and 73% PO ₄ separated; | Nitrification in a fixed-film aerated reactor (0.4 L), denitrification in a MFC-cathode (0.1 L); MFC-anode fed with raw waste water (270 mg COD L ⁻¹) NRE 52%; power generation 0.3 | No data available for the precipitate | [105] |

| | effluent with TN 1530 mg L ⁻¹ | mW/m ² –ref. anodic surface– | | |
|--|--|---|--|-------|
| Anaerobic lagoon digester supernatant in a swine farm | MgP precipitated in lab batch tests (in beakers) | NDN in a SBR (4.5 L); pH adjusted to 7.0 (influent) | MgP precipitated mostly as MAP according to XRD and SEM-EDS | [106] |
| Composition: pH 8.1, COD 266, TN 607, NH ₄ ⁺ -N 598, PO ₄ -P 22, Mg 31 | Raw vs. (organically) fermented superphosphate fertiliser [Ca(H ₂ PO ₄) ₂] used as P source; fermentation increased 15% water-soluble P and provided extra bCOD | COD/TN mass ratio raised (0.4 → 1.8) by adding fermented superphosphate favouring NDN (COD 598, NH ₄ ⁺ -N 328, mg L ⁻¹) | Effectiveness of the precipitate as fertiliser demonstrated in a pot test (increased crop yield) | |
| | MgSO ₄ supplied at pH 9.0 (NaOH), reaction time 30 min; process optimisable at pH 9.5 | NRE 71% (lower if fermented superphosphate not used) | | |
| | 41–50% (up to 55%) NH ₄ ⁺ separated | Global performance: 72% COD, 89% N and 98% P reduction | | |
| Side-stream sludge fermenter effluent from an EBPR system treating low-strength synthetic waste water | CaP precipitated in a SBR at 20°C | EBPR in a continuous-flow AS A ² O system (10 L), HRT 0.5 d | Composition of the precipitate: 13.8% P | [107] |
| Composition of synthetic waste water: pH 7.0–8.0, COD 340, TN 48, NH ₄ ⁺ -N 23, PO ₄ -P 7 | Ca(OH) ₂ added at pH 10 | Fermentation of purged sludge followed by precipitation of released P lead to improved simultaneous P uptake and N removal in the mainstream (NRE 80%) | | |
| | PUE >99% (65% influent P recovered) | | | |
| Urine | PO ₄ precipitated in a lab stirred system using RO brine (from a reclaimed WWTP in a thermal power | NDN via nitrite in a continuous-flow AS AO MBR (10.4 L); influent COD 2500–4000, TN 1800–3200, mg L ⁻¹ ; HRT 2 d | Precipitates produced at different brine/urine mixture ratios (0/1–1/1) with 10–15% P | [108] |
| Composition: pH 6.2–7.9, TN 4670–7630, NH ₄ ⁺ -N 315–2250, TP 330– | | | | |

| | | | | |
|---|---|--|--|-------|
| 654, PO ₄ -P 283–585, Mg 31–65, Ca 68–128 | plant) as Me ions source at 20°C Brine/urine mixture adjusted to 1/1 vol., pH 9.0 (with NaOH), reaction time 30 min PUE >90% | NRE 45% (with internal COD), increased to 92% when using methanol as external COD source Global performance: >90% COD, N and >99% P reduction | Depending on the amount of brine added (Mg+Ca/P molar ratio 0.2–2.3), Mg in the solid decreased from 7 to 2.5%, and Ca raised from 8 to 25% Low K, Na and Si content (sum <5%); no hazardous compounds (e.g. HMs) | |
| Ultrafiltered permeate from an(aerobically) digested sludge dewatering centrate in a municipal WWTP Composition: pH 8.8, COD 2694, TN 2024, NH ₄ ⁺ -N 1717, TP 420, PO ₄ -P 326 | MgP precipitated in lab batch tests (in beakers) at 20°C Mg/NH ₄ /PO ₄ adjusted with MgCl ₂ + K ₂ HPO ₄ , pH increased with NaOH, reaction time 2 min, MgP deposits used as seeding material Mg/NH ₄ /PO ₄ adjusted to 1.0/1.0/1.0 and pH to 9, 65% NH ₄ ⁺ and 95% PO ₄ separated Mg and PO ₄ supply favoured NH ₄ ⁺ separation; addition of seeding material did not enhance N & P precipitation efficiency (but favoured chemical sludge settling); presence of HMs could negatively affect MAP precipitation | NDN in a continuous-flow AS A ² O system (24 L) (+settler) for treating raw sewage plus MgP precipitation effluent Mixing of precipitation effluent with raw sewage decreased COD and N removal efficiency NLR >0.13 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ (mixture ratio >1/1 vol.) triggered NO ₂ ⁻ accumulation (hypothesised by nitrification inhibition) | MgP precipitated mostly as MAP according to XRD Quality of the MgP precipitated potentially compromised by the HM content | [109] |
| Urine-seawater mixture | PO ₄ precipitated in a lab continuous-flow reactor (0.84 L) incl. a | Nitrification in a continuously aerated SBR (for subsequent in- | MgP precipitated mostly as MAP according to XRD and chemical | [110] |

| | | | | |
|--|---|--|---|-----------|
| Composition (depending on the mixture ratio, 25–50% urine): pH 6.6–6.7, TN 1750–3470, NH_4^+ -N 143–462, TP 104–187, Mg 545–826, Ca 274–374 | concentric cylinder differentiating hydrolysis-precipitation zone and settling-separation zone PUE >91% regardless HRTs (1.5–6 h) and urine mixture ratio (25–50%); P recovery enhanced with HRT and urine fraction; effluent with <10 mg TP/L Urea hydrolysis almost completed in all cases (84–94%) | sewer denitrification) with 25% urine fraction ALK added as NaHCO_3 based on pH set-point Complete nitrification albeit high Cl^- (13 g L^{-1}) 4–5 mg P g^{-1} NH_4^+ oxidised needed for stable nitrification (when necessary achieved by ~1% urine bypass) NLR 0.75 g $\text{L}^{-1} \text{d}^{-1}$, NCE 90% (NH_4^+) | analysis of the solid formed; calcite also detected; higher purity MAP obtained with higher urine content Precipitate with similar NH_4^+/P (0.8), Mg/P and Ca/P molar ratios (Mg/P slightly greater than NH_4^+/P); Mg+Ca/P of 1.5–2.0 | |
| Low-strength synthetic waste water Composition: pH 6.4, COD 250–325, TN 60–75, NH_4^+ -N 45–55, PO_4 -P 10–12, Mg 22*, Ca 12* (*calculated) | MgP precipitated in a lab FBR (9.5 L) at 20°C pH adjusted with NaOH (7.5 → 9.5); PO_4 separation improved from 43% to 94% At pH 9 and HRT 2h; >80% PO_4 and <40% NH_4^+ (<30% COD) separated pH 9.5 favoured NH_3 loss from FBR | NDN in a MBR (8.4 L) intermittently aerated P-recovery in FBR enhanced SND and COD, NH_4^+ and PO_4 removal in MBR (NRE 99%, PUE 93% at pH 9, HRT 6 h and aeration on/off 45/15 min); final effluent with <1 mg PO_4 -P/L Membrane fouling was mitigated when the FBR-MBR system run at optimal conditions | MgP precipitate mostly as MAP according to XRD and SEM-EDS Precipitate with molar ratios of Mg/P 1.1 and Ca/P 5 10^{-3} <i>Anhydrous</i> precipitate with 23.5% P, 19.8% Mg, 0.5% K, 0.1% Ca (EDS analysis reported as not sensible to N) | [111] |
| Low-strength synthetic waste water Composition: COD 250–300, NH_4^+ -N 30–45, PO_4 -P 5–15 | CaP precipitated in a lab up-flow reactor at 20°C CaCl ₂ added after the anaerobic stage of a EBPR system and CO ₂ stripping | EBPR in a continuous-flow AS A ² O system for N & P removal (~300 L) Chemical P precipitation | CaP precipitate mostly as HAP (or precursors) according to XRD and SEM-EDS Composition of the precipitate: 8–13% P | [112–113] |

| | | | | |
|---|--|---|---|-------|
| | by aeration (5% NH_3 loss), calcite used as seeding material | favoured EBPR (PUE > 99%) regardless COD/P mass ratio (20–67); final effluent with <1 mg $\text{PO}_4\text{-P/L}$ | Precipitate with Ca/P molar ratio >1.67 due to carbonate co-precipitation; high P release in the anaerobic stage favoured HAP crystallisation | |
| Side-stream sludge fermenter effluent from an EBPR system treating low-strength synthetic waste water | MgP precipitated in batch (in flasks) using MgO at room temperature | EBPR in a SBR alternating AO phases also involved partial N removal through NDN (NRE 25%) | | |
| Composition of synthetic waste water: COD 300, $\text{NH}_4^+\text{-N}$ 30, $\text{PO}_4\text{-P}$ 10 | Mg/ NH_4/PO_4 adjusted to 1.5/2.7/1.0 | Fermentation of purged sludge followed by precipitation of the released N and P, plus reintroduction of VFAs formed into EBPR system, lead to higher P separation efficiency (P in the effluent reduced by >65%) and complete nitrification | MgP precipitate mostly as MAP according to supernatant analysis and XRD | [114] |
| Swine waste water | MgP precipitated in a lab CSTR (10 L) at 27°C, MgP precipitate recovered from an external settler | NDN in a 2-stage continuous flow intermittently aerated AS system (+ settler) (20 L; air on/off 1/1 h), pH adjusted to that of raw waste water (HCl) | MgP precipitate partly as MAP according to XRD and EDS | |
| Composition: pH 7.3–7.9, COD 5117–6705, TN 959–1120, $\text{NH}_4^+\text{-N}$ 733–922, TP 106–222, $\text{PO}_4\text{-P}$ 31–56 | Mg/ NH_4/PO_4 adjusted to 1.0/1.0/1.0 by adding MgCl_2 and K_2HPO_4 ; pH increased to 9 with NaOH; MgP precipitate partly recycled to the reaction tank as seeding material | COD/TN mass ratio increased from 4.8–6.1 to 13.0–19.8 favouring NDN, COD/TP mass ratio increased from 35– | Anhydrous precipitate with 25.3% P, 18.3% Mg, 7.1% N, 5.4% K, 2.5% Ca | [115] |
| | | | Quality of the precipitate potentially compromised by the organic content (35 wt% as COD) | |

| | | | | |
|--|---|---|---|-------|
| | 78–92% NH_4^+ , 84–93% PO_4 (besides 74% TSS, 47% COD) separated | 50 to 267–430 favouring EBPR MgP precipitation enhanced nitrification and ARE due to a reduced OLR and NLR once fixed HRT, low NH_3 levels in bioreactors (eventually toxic triggering NO_2^- accumulation) OLR 4.5 g COD $\text{L}^{-1} \text{d}^{-1}$, NLR 0.18 g N $\text{L}^{-1} \text{d}^{-1} \rightarrow \text{NRE} > 90\%$ (NH_4^+) | | |
| Anaerobically digested landfill leachate Composition: pH 7.5–8.1, ALK 11120, Cl^- 2000, COD 12000, BOD_5 4250, NH_4^+ -N 2800, TP 14 | MgP precipitated in a lab stirred system using MgCl_2 and PO_4 $\text{Mg}/\text{NH}_4/\text{PO}_4$ adjusted to 0.7/1.0/0.7, pH 9, reaction time 2 h 70% NH_4^+ separated | NDN in a SBR (10 L), pH adjusted to 7.5 (influent) $\text{BOD}_5/\text{NH}_4^+$ -N mass ratio increased from 1.5 to 6.5 favouring NDN, 6-fold Cl^- raise (12 g L^{-1}) The higher MgCl_2 addition the higher NH_4^+ separation as MAP, but $\text{Cl}^- > 12 \text{ g L}^{-1}$ limited nitrification (triggering NH_4^+ accumulation in the bioreactor) | Composition of the MgP formed not determined analytically | [116] |
| Rare-earth smelting waste water Composition: pH 0.77, COD 1088, NH_4^+ -N 1540, La^{3+} 200, Eu^{3+} 78 | MgP precipitated in lab batch tests (in beakers) at 20°C $\text{Mg}/\text{NH}_4/\text{PO}_4$ adjusted with $\text{MgSO}_4 + \text{Na}_2\text{HPO}_4$ (among other P-sources), pH increased with KOH | SND in a batch system using immobilised microorganisms COD/ NH_4^+ -N mass ratio increased from 0.7 to 7.2 favouring NDN (COD 566, NH_4^+ -N 79, mg L^{-1}) | MgP precipitate mostly assumed as MAP. Composition: 15.6% P, 9.3% N, 8.3% Mg Quality of the MgP precipitated compromised by the rare metal content | [117] |

| | | | | |
|--|---|--|---|----------|
| | Mg/NH ₄ /PO ₄ adjusted to 1.2/1.0/1.3, pH 11.1–11.2, reaction time 1.5 h | Rare metal ions removed from the liquid phase favouring biological treatment | When Ca dosed instead of Mg, CaP formed hypothesised as Ca-struvite. Composition: 18.3% Ca, 13.6% P, 6.5% N | |
| | 95% NH ₄ ⁺ separated | NLR 0.13 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ , NRE 86% (NH ₄ ⁺) | | |
| | Using CaO (not KOH) and Ca ₃ (PO ₄) ₂ (not MgSO ₄ , Na ₂ HPO ₄) → ~80% NH ₄ ⁺ separated | | | |
| | MgP precipitated in lab batch tests (in beakers) | NDN in a fill-and-draw system under intermittent aeration (air on/off 1/1 h) | | |
| Raw swine waste water obtained by centrifugation | Mg/NH ₄ /PO ₄ adjusted with MgCl ₂ + KH ₂ PO ₄ , pH increased with NaOH | BOD/TN increased from 1.6 to 7 enhancing NDN (BOD 8200, TN 1166, mg L ⁻¹) | Composition of the MgP not determined analytically | [66,118] |
| Composition: pH 8.5, BOD 9500, TN 5930, NH ₄ ⁺ -N 2500, TP 360, PO ₄ -P 302 | Mg/NH ₄ /PO ₄ adjusted to 0.9/1.0/0.6, pH 7.5, temperature 25°C, reaction time 1 h | NLR 0.97 g N L ⁻¹ d ⁻¹ , NRE 91% w/o detecting TP removal | | |
| | 79–87% NH ₄ ⁺ , 40–88% P separated | Additional 60% PO ₄ precipitated as CaP by adding CaCl ₂ once biotreatment ended | | |
| <i>PNA as the bioprocess following chemical P precipitation</i> | | | | |
| Digester sludge thickening lagoon supernatant in a municipal WWTP | MAP precipitated by the Ostara® process at full-scale; PO ₄ -P reduced to 32 mg L ⁻¹ | PNA in a IFAS-SBR (6 L) with intermittent aeration | No data available for the precipitate | [69] |
| Composition: pH 8.0, ALK 3180, TSS 344, | | NLR 0.31 g N L ⁻¹ d ⁻¹ , NRE improved from 55% to 88% when PO ₄ was decreased | | |

| | | | | |
|---|--|--|---|-------|
| COD 644, NH ₄ ⁺ -N 892, PO ₄ -P 235 | | High PO ₄ inhibited anammox bacteria, higher tolerance to PO ₄ stress when biomass grew as biofilm rather than forming flocs | | |
| Anaerobically digested sludge dewatering centrate in a municipal WWTP Composition: pH 8.0–8.8, TIC 681–893, COD 410–510, NH ₄ ⁺ -N 1081–1177, PO ₄ -P 260–351 | MgP precipitated in a lab CSTR (10 L) at 10°C with MgO | PNA as 2-step process (PO ₄ precipitated after PN) and also as 1-step process (with intermittent aeration) using SBRs (3.5 L) | Composition of the MgP formed not determined analytically | [119] |
| | Mg/P adjusted to 1, reaction time 2.5 h; PO ₄ -P reduced to 31 mg L ⁻¹ MgP formation (incl. eventual NH ₃ stripping) resulted in 8% NH ₄ ⁺ separation | NRR ~0.3 g N L ⁻¹ d ⁻¹ for both configurations 45–50% anammox activity drop at ~300 mg P L ⁻¹ Lower sensitivity to PO ₄ -P was estimated in short-term experiments (IC ₅₀ : 650 mg L ⁻¹ at 35°C, pH 6.5) | | |
| Anaerobically digested industrial (potato) waste water Composition (anaerobic effluent 2-fold diluted): pH 7.9, TIC 396, NH ₄ ⁺ -N 203, PO ₄ -P 57, Mg 39 | MgP precipitated in a lab mixed reactor (4 L) with MgCl ₂ | PNA as 2-step process (20 L CSTR w/o sludge retention + 3.7 L UFBR) and also as 1-step process (UFBR) at 35°C | MgP precipitate mostly as MAP according to XRD | [120] |
| | pH adjusted to 7.8 (NaOH) Urea (1.5%) added to the crystallisator as N source (in presence of anaerobic sludge), HRT 6–7 h TIC/NH ₄ ⁺ -N decreased from 2.3 to 1.9 favouring PNA (TIC 421, NH ₄ ⁺ -N 261, mg L ⁻¹); PUE 83% (PO ₄) | NLR 0.1–0.25 g N L ⁻¹ d ⁻¹ Global performance (2-step process): 86% N, 83% PO ₄ reduced | | |

| | | | | |
|--|---|---|---|-----------|
| Anaerobically digested industrial (potato) waste water from a UASB reactor + anaerobically digested sludge dewatering centrate in a municipal WWTP | MAP precipitated by the PHOSPAQ™ process at full-scale (2*300 m ³), aeration supplied for bCOD degradation and CO ₂ stripping | PNA as 1-step process (600 m ³) with granular sludge and dynamically controlled continuous aeration at 37°C | MAP with low HM content with respect to EU standards for fertilisers | |
| Composition: COD 565, NH ₄ ⁺ -N 372, PO ₄ -P 73 | MgO dosed and pH adjusted to 8.2–8.3; PUE ~67% (feasible >80%) | NLR 1.5 g N L ⁻¹ d ⁻¹ Global performance: ca. 56% COD, 73% TN, 91% NH ₄ ⁺ , 76% TP reduced | Precipitate fertilising effectiveness demonstrated in field tests (= performance as commercial fertilisers) | [121–122] |
| Anaerobically co-digested sludge dewatering supernatant in a municipal WWTP | MgP precipitated in a CSTR (50 L) using MgCl ₂ or MgCO ₃ Solids >0.8 mm removed before precipitation Mg/P adjusted to 1.3, reaction time 24 h; PO ₄ -P reduced to 18 mg L ⁻¹ MgP formation (incl. eventual NH ₃ stripping) resulted in 4.5% NH ₄ ⁺ separation | PNA as 2-step process: MBBR (7.4 L) + SBR (30 L) PN: NLR 1 g N L ⁻¹ d ⁻¹ , NCE 50% (at 30°C) Anammox: PO ₄ -P increase from 30 to 55 mg L ⁻¹ implied SAA loss of 45% (in 7 days); by decreasing PO ₄ -P to <20 mg L ⁻¹ activity was recovered (SAA ≤100 mg N ₂ g ⁻¹ VSS d ⁻¹ , at 35°C); anammox activity was potentially limited at pH 7 and TIC <24 mg L ⁻¹ | Composition of the MgP formed not determined analytically | [67] |
| Composition: NH ₄ ⁺ -N 651, PO ₄ -P 75 | | | | |

Abbreviations: A²O, anaerobic-anoxic-oxic; ALK, alkalinity (as CaCO₃); anammox, anaerobic ammonium oxidation; AO, anaerobic-oxic; AS, activated sludge; BOD, biochemical oxygen demand; CaP, calcium phosphate; COD, chemical oxygen demand (b-, biodegradable; s-, soluble); CSTR, continuous stirred tank reactor; EBPR, enhanced biological P removal; EDS, energy dispersive X-ray spectroscopy; FBR, fluidised bed reactor; HM, heavy metal; HRT, hydraulic residence time; IC₅₀, half maximal inhibitory concentration; IFAS, integrated fixed film AS; MAP, magnesium ammonium phosphate; MBR, membrane bioreactor; MBBR, moving bed bioreactor; Me, metal; MFC, microbial fuel cell; MgP, magnesium phosphate; N, nitrogen; NCE, N conversion efficiency; NLR, N loading rate; NDN, nitrification-denitrification; NRE, N removal efficiency; NRR, N removal rate; OLR, organic loading rate; P, phosphorus; PNA, partial nitrification-anammox; PUE, P uptake efficiency; RO, reverse osmosis; SAA, specific anammox activity; SBR, sequencing batch reactor; SEM, scanning electron microscope; SND, simultaneous NDN; TIC, total inorganic carbon; TN, total N; TP, total P; TSS, total suspended solids; UASB, upflow anaerobic sludge blanket; UFBR, upflow fixed bed reactor;

VFA, volatile fatty acids; VSS, volatile suspended solids; WWTP, waste water treatment plant; XRD, X-ray diffraction.

¹ Composition, concentrations expressed in mg L⁻¹.

² Ca/P, Mg/P and other component ratios expressed in molar units.

Table S3. Summary of experiences integrating biological N oxidation, or removal, and mineral precipitation aiming at P recovery inside the bioreactor (concomitant precipitation).

| Waste water source ¹ | Experimental conditions | Bioprocess performance | Precipitate characteristics | Reference |
|--|--|---|---|-----------|
| <i>Nitrification as the bioprocess concomitant to P precipitation</i> | | | | |
| Synthetic urine Composition: TN 7780, NH ₄ ⁺ -N 400, PO ₄ -P 890 | Long-term nitrification in trickling filters (6 L) partially packed with pumice & mussel shells (CaCO ₃ content: ~75 vol%) Process at 29°C considering urine solutions at different concentrations Urine concentration did not influence filter performance in terms of stability and nitrate production rate | PO ₄ precipitation induced by Ca released from mussel shells Mussel shells also provided carbonate needed for buffering the system (the higher the concentration of urine the higher the CaP formed and the buffering capacity released) | Composition of the CaP formed not determined analytically | [168] |
| Synthetic waste water mimicking anaerobic digester dewatering centrate Composition: HCO ₃ ⁻ 4700, COD 480, NH ₄ ⁺ -N 470–590, PO ₄ -P 100, Mg 45, Ca 115 | PN in aerated SBR (10 L) vs. SBBR (16 L) packed with polyethylene particles Process at 30°C and pH 7.5 Only 25–60% of the TSS as VSS in the SBR (SRT 30 d) and 27–40% in the SBBR (SRT 20 d) | SBR: NLR 0.19 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NCE 95%, PLR 0.04 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 40–90% (depending on NH ₄ ⁺ availability within the reactor), faster start-up SBBR: NLR 0.35 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NCE 40%, PLR 0.07 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 70%, more stable facing disturbances in | Mineral crystals identified in the sludge when observed at the microscopy Suspended solids containing 9–10% P Complementary work in the SBR transforming PN into NDN [169] showed (using XRD) that PO ₄ precipitated in different form depending on pH (7–8.5): mainly as HAP at | [71] |

| | | | | |
|---|---|---|---|------|
| | | dissolved oxygen conditions | pH >7.5 and partly as MAP (potentially associated to CaCO ₃) at pH >8.0 | |
| Anammox as the bioprocess concomitant to P precipitation | | | | |
| | | NLR 5 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 87%; PLR 0.21 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 66%; Granule size 1.3–1.7 mm | | |
| Synthetic waste water mimicking effluent from a PN reactor | Anammox process in an EBR with internal recirculation | Complementary work [170] in an attached film EBR (35°C) reached NLR 50 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 90% + PLR 0.55 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 72% | CaP recovered as HAP according to chemical analysis of the solid formed (Ca/P molar ratio 1.67) | |
| | Composition: pH 7.4, TIC 71, NH ₄ ⁺ -N 135, NO ₂ ⁻ -N 178, PO ₄ -P 13, Ca 85 | Complementary work [171] in an attached film EBR (35°C) reached NLR 10 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 77% + PLR 0.15 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 68% (CaCl ₂ added in recirculation) | Granules with 83% mineral content, 28.9% Ca, 13.4% P, 0.9% N, 0.5% Mg | [72] |
| | Reactor (5 L) at 33°C and pH 8.6 with 43.9–70.3 g VSS L ⁻¹ (17% of the TSS) | Complementary work [172] in an EBR (25°C) reached NLR 20 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 84% + PLR 1.32 g PO ₄ -P L ⁻¹ d ⁻¹ and PUE 94% (CaCl ₂ added in recirculation) | The core of the granule contained more Ca than the external part (30% vs. 27%) probably due to the formation of CaCO ₃ or type-B carbonate apatite | |
| PNA as the bioprocess concomitant to P precipitation | | | | |
| Anaerobically digested sludge dewatering centrate in a municipal WWTP | PNA process as 1-stage | | CaP recovered as HAP according to XRD and chemical analysis of the solid formed (Ca/P molar ratio 1.64) | |
| | SBR (10 L) at 25°C and pH ~7.2 with 1.45 g VSS L ⁻¹ (62% of the TSS) | NLR 0.31 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ and NRE 66% | Granules purged with 71% mineral content, | [70] |

| | | |
|---|---|--|
| Composition: pH 8.1, ALK 4401, NH ₄ ⁺ -N 966, PO ₄ -P 57, Ca 79, Mg 14 | No addition of chemicals (w/o pH control) | 33.5% Ca, 15.8% P, 0.2% Mg HMs content complied with EU standards for P fertilisers and requirements from P industry |
|---|---|--|

Abbreviations: ALK, alkalinity (as CaCO₃); anammox, anaerobic ammonium oxidation; COD, chemical oxygen demand; EBR, expanded bed reactor; HAP, hydroxyapatite; HM, heavy metal; N, nitrogen; NCE, N conversion efficiency; NLR, N loading rate; NRE, N removal efficiency; P, phosphorus; PLR, P loading rate; PN, partial nitrification; PNA, PN-anammox; PUE, P uptake efficiency; SBBR, sequencing batch biofilm reactor; SBR, sequencing batch reactor; SRT, solids retention time; TIC: total inorganic carbon; TSS, total suspended solids; VSS, volatile suspended solids; WWTP, waste water treatment plant; XRD, X-ray diffraction.

¹ Composition, concentrations expressed in mg L⁻¹.

Table S4. Summary of experiences integrating biological N oxidation, or removal, followed by chemical precipitation aiming at P recovery (downstream precipitation).

| Waste water source ¹ | Bioprocess performance | Precipitation performance ² | Precipitate characteristics ² | Reference |
|---|--|--|---|-----------|
| <i>Nitrification as the bioprocess preceding chemical P precipitation</i> | | | | |
| Anaerobically digested swine waste water from a UASB reactor Composition: pH 7.6 (7.0), ALK 3231 (428), TOC 636 (154), NH ₄ ⁺ -N 882 (160), PO ₄ -P 33 (98), s-Ca 98 (204) | Nitrification in a continuous aerated system at pilot-scale Similar tests also conducted considering NDN and PNA as the bioprocess preceding P precipitation (less satisfactory results obtained according to PUE and Ca/P ratio); as far as ALK availability increased P content in precipitate decreased | CaP precipitated in lab batch tests (in beakers) using hydrated lime [10% Ca(OH) ₂] Lime injected under stirring up to pH 9 (24 h settling); PUE >90% (PO ₄) with Ca/P 2 Similar results previously given in [205] | Field tests under equivalent conditions also performed; sludge formed contained 30.0% Ca, 5.7% P, 2.5% Mg; the high Ca/P ratio (~4.6) indicated co-precipitation | [74] |
| Anaerobically digested industrial (potato) waste water from a UASB reactor | Nitrification in an aerated CSTR (3.6 L + settler) with NCR 0.26 g NH ₄ ⁺ -N L ⁻¹ d ⁻¹ | CaP precipitated in a lab CSTR (3.6 L + settler) with CaCl ₂ ; pH 7.8–10.5 and Ca/P 0.7–1.5; tests at room temperature | CaP precipitated mostly as HAP according to XRD and chemical analysis of the solid formed | [206] |

| | | | |
|---|--|---|--|
| <p>Composition: pH 8.1 (7.9), TIC 587 (77), NH₄⁺-N 293 (9), NO₃⁻-N 0 (304), PO₄-P 50 (55), Mg 30 (29), Ca 47 (46), K 1213 (1239)</p> | | <p>PUE 70% PO₄ at pH 7.8 with CaP yield depending on Ca ions availability; high pH and Ca/P initiated co- precipitation of carbonates and MgP</p> <p>Nitrification reduced Ca(HCO₃)₂ inhibition and carbonate precipitation making Ca available for CaP precipitation</p> | <p>Composition: Ca/P/Mg ratio as 1.5/1.0/0.1</p> |
| | | <p>CaP precipitated in lab batch tests (in beakers), 1 h reaction time</p> | |
| <p>Anaerobically digested industrial (potato) waste water previously processed for urease-induced partial phosphate removal</p> <p>Composition: pH 7.5 (8.5), TIC 455 (32), NH₄⁺-N 180 (0), NO₃⁻-N 0 (180), PO₄-P 36 (12), Mg 43 (115), Ca 121 (74), K 997 (997)</p> | <p>Nitrification in an aerated MBR (25 L)</p> <p>Mg content and pH increased due to preliminary ureolytic phosphate removal</p> <p>Ca/P molar ratio increased from 2.6 to 4.8 (66% PO₄ reduction)</p> | <p>Several chemicals used (NaOH, Ca(OH)₂, Na₂CO₃) to raise pH (8.5– 9.0) and test effect of TIC</p> <p>TIC decrease due to nitrification (>90%) implied shorter dosage of NaOH for raising the pH; NaOH supply w/o nitrification may lead to MgP & CaCO₃ formation</p> <p>pH increase with Ca(OH)₂ favoured PO₄ precipitation due to extra Ca dosage</p> <p>pH increase with Na₂CO₃ hampered Ca and PO₄ precipitation</p> | <p>Composition of the precipitate not determined analytically</p> <p>Similar results than in [207] where P uptake was assessed as a function of reaction time, pH, Ca/P and presence of competitive ions; optimal TIC/NH₄⁺ molar ratio before nitrification ~2</p> |

[124]

| | | | | |
|--|--|---|--|-------|
| Surface lagoon liquids from swine farms | <p>Nitrification in fluidised bed reactors (1.2 L) with sludge immobilised in supporting porous medium (3–5 mm cubes) at 30°C with NCR 0.26 g $\text{NH}_4^+\text{-N L}^{-1} \text{ d}^{-1}$</p> <p>Ca/P molar ratio of 0.3–2.7 for the influent waste water</p> <p>>90% ALK reduction and prevention of NH_3 emission</p> | <p>CaP precipitated in lab batch tests (in glass tubes), 1 min mixing</p> <p>pH 6–12 and Ca/P 1–10 tested; Ca(OH)_2 added as precipitant (hydrated lime suspended in water)</p> <p>pH increased to ≥ 9.5 for optimum P precipitation; PUE >90% TP</p> <p>Similar field test in [73] (reactor vol. 379 L, hydrated lime injected after nitrification until pH 9.0–10.5); P in effluent adjustable for on-farm use according to crop needs (N/P ratio)</p> | <p>Composition of the precipitate: 2.5–10% P; nitrification favoured P availability in the precipitate; the recovered material can be exported from the farm and reused as P-fertiliser</p> <p>The high pH value applied in the precipitation process destroys pathogens</p> <p>For the field test [73] composition of the precipitate was 24.6% Ca, 6.9% P, 1.2% Mg, 0.5% K</p> | [208] |
| <i>NDN as the bioprocess preceding chemical P precipitation</i> | | | | |
| Fertiliser industry waste water | <p>NDN in a continuous flow AS AO system at pilot-scale (760 L)</p> <p>NLR 0.6–1.3 g N $\text{L}^{-1} \text{ d}^{-1}$; nitrification partially inhibited; denitrification achieved by adding methanol</p> | <p>MgP precipitated in a continuous pilot-scale unit (320 L + settler); NLR 48–72 g N $\text{L}^{-1} \text{ d}^{-1}$</p> <p>Mg/$\text{NH}_4/\text{PO}_4$ adjusted to 1.5–1.8/1.0/1.5–1.8 with $\text{MgCl}_2 + \text{H}_3\text{PO}_4$; pH 11–12 (NaOH)</p> <p>Mg and PO_4 recovered from the precipitate by heating (while NH_3 stripped out) allowing the recycling within the process (>90 wt%)</p> | <p>Composition of the precipitate after drying: 24.0% P, 16.6% Mg, 1.1% N</p> | [209] |

| | | | |
|---|--|--|--|
| Residual PO ₄ removed from the water line electrochemically | | | |
| Global performance: 88% TN, 87% NH ₄ ⁺ , 92% NO ₃ ⁻ reduction | | | |
| Subfloor slurry from a pig farm, liquid separated by a rotary press | NDN in a continuous flow AS AO system at full-scale (504- m ³) | CaP precipitated in a continuous full- scale unit, well- mixed and with conical bottom (300 L); hydrated lime [12% Ca(OH) ₂] injected to pH 9.5 | Composition of the precipitate not determined analytically |
| Composition: pH 7.8 (8.0), ALK 5469 (1422), TSS 1254 (227), NH ₄ ⁺ -N 1213 (124), NO ₃ ⁻ - N 0 (221), PO ₄ ⁻ P 82 (76), Mg 44 (16), Ca 106 (39), K 1551 (1420) | Influent waste water with Ca/P molar ratio 0.4 74% ALK, 87% COD, 90% NH ₄ ⁺ , 7% PO ₄ reduction | PUE 75% PO ₄ | 0.67 and 0.39 log ₁₀ reductions for total faecal coliforms and enterococci, respectively |
| [99] | | | |
| MPP precipitated in: | | | |
| (1) lab experiments lasting 2–3 h at room temperature (2) pilot plant running as CSTR (2-m ³ + settler); MgO added as Mg source; reaction time 0.5 h; TSS may interfere if >1 g L ⁻¹ (3) full-scale plant (3 CSTRs + settler); MgO added as Mg source achieving <30 mg P L ⁻¹ in the effluent | | | |
| Calf manure | NDN running at full-scale | | Lab: Fine-grained elongated crystals with a maximum diameter of several tens of microns |
| | | | Pilot-plant: the recovered product contained 12.5% P, 10.7% Mg, 11.4% K, 1.3% Ca, 0.7% N (5.5% organic-C) |
| [210] | | | |
| PNA as the bioprocess preceding chemical P precipitation | | | |
| Anaerobically digested sludge dewatering centrate from two municipal WWTPs –with chemical vs. | PNA as 1-step process at lab- (10 L) and pilot- scale Centrate with 59 (chemical) vs. | MgP precipitated in lab batch tests (in beakers) pH 8–12 (adjusted with NaOH), Mg/P 0.75–1.75, (adjusted | MgP precipitated as MAP & MPP according to XRD and chemical analysis |
| | | | At pH 11, precipitate composition: 11.4% P, |
| [76] | | | |

| | | | |
|--|---|--|---|
| biological P removal in the mainstream– | 222 (biological) mg PO ₄ -P L ⁻¹ ; Mg/K/P molar ratio: 0.02–0.3/1.2–3.9/1 | with MgCl) and temperature 20–40°C | 9.2% Mg, 4.3% K, 3.5% N, 0.9% Ca |
| Composition: pH 7.8–8.0 (7.5–7.7), ALK 3276–3407 (327–752), NH ₄ ⁺ -N 949–963 (109–228), PO ₄ -P 59–222 (53–233), Mg 4–12 (4–14), Ca 21–54 (21–33), K 251–327 (261–367) | Ca. 90% ALK, 85% NH ₄ ⁺ reduction | K uptake from water line positively correlated with the pH value up to pH 11 | |
| Anaerobically digested manure centrate | After biological treatment, Mg/K/P molar ratio adjusted to ca. 2.0/4.5/1.0 | MgP precipitated in lab batch tests (in beakers) targeting MPP recovery | MgP precipitated mostly as MPP with co-precipitation of other salts according to XRD |
| Composition: TSS (500), NH ₄ ⁺ -N (8), PO ₄ -P (108), Mg (163), Ca (36), K (609) | | Different dilutions rates (0–90%) tested to decrease interference by TSS (K and PO ₄ adjusted using chemicals); pH 9–12, 38°C | High dilution (90%) favoured co-precipitation of Mg ₃ (PO ₄) ₂ and Mg(OH) ₂ ; low dilution (0–50%) favoured recovery of all PO ₄ as MPP, but with co-precipitation of Mg(OH) ₂ |
| | | Up to 80% PO ₄ recovery at pH 10 and 90% dilution | Suspended particles acted as nuclei for heterogeneous nucleation favouring aggregation of crystals as star-asterisk forms |

[75]

Abbreviations: ALK, alkalinity (as CaCO₃); anammox, anaerobic ammonium oxidation; AO, anoxic-oxic; AS, activated sludge; CaP, calcium phosphate; CSTR, continuous stirred tank reactor; HAP, hydroxyapatite; MAP, magnesium ammonium phosphate; MBR, membrane bioreactor; MgP, magnesium phosphate; MPP, magnesium potassium phosphate; N, nitrogen; NCR, N conversion rate; NDN, nitrification-denitrification; P, phosphorus; PNA, partial nitrification-anammox; PUE: P uptake efficiency; TIC, total inorganic carbon; TOC, total organic carbon; TP, total P; TSS, total suspended solids; UASB, upflow anaerobic sludge blanket; WWTP, waste water treatment plant; XRD, X-ray diffraction.

¹ Composition, concentrations expressed in mg L⁻¹; values after biological N treatment in brackets.

² Ca/P, Mg/P and other component ratios expressed in molar units.

