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Phosphorous removal and recovery from urban wastewater: current practices and new directions

Authors: Francesco Di Capua^a, Simona de Sario^a, Alberto Ferraro^a*, Andrea Petrella^a, Marco Race^b, Francesco Pirozzi^c, Umberto Fratino^a, Danilo Spasiano^a

Affiliations:

^a Department of Civil, Environmental, Land, Building Engineering and Chemistry, Polytechnic University of Bari, Via E. Orabona 4, Bari, 70125, Italy

^b Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via di Biasio 43, Cassino, 03043, Italy

^c Department of Civil, Architectural and Environmental Engineering, University of Naples "Federico II", Via Claudio 21, 80125, Naples, Italy

* Corresponding author: <u>alberto.ferraro@poliba.it</u>

1 Abstract

2 Phosphate rocks are an irreplaceable resource to produce fertilizers, but their availability will not be 3 enough to meet the increasing demands of agriculture for food production. At the same time, the 4 accumulation of phosphorous discharged by municipal wastewater treatment plants (WWTPs) is one of the main causes of eutrophication. In a perspective of circular economy, WWTPs play a key 5 role in phosphorous management. Indeed, phosphorus removal and recovery from WWTPs can both 6 7 reduce the occurrence of eutrophication and contribute to meeting the demand for phosphorus-based fertilizers. Phosphorous removal and recovery are interconnected phases in WWTP with the former 8 9 generally involved in the mainstream treatment, while the latter on the side streams. Indeed, by reducing phosphorus concentration in the WWTP side streams, a further improvement of the overall 10 phosphorus removal from the WWTP influent can be obtained. Many studies and patents have been 11 12 recently focused on treatments and processes aimed at the removal and recovery of phosphorous from wastewater and sewage sludge. Notably, new advances on biological and material sciences are 13 constantly put at the service of conventional or unconventional wastewater treatments to increase 14 the phosphorous removal efficiency and/or reduce the treatment costs. Similarly, many studies have 15 been devoted to the development of processes aimed at the recovery of phosphorus from 16 wastewaters and sludge to produce fertilizers, and a wide range of recovery percentages is reported 17 as a function of the different technologies applied (from 10-25% up to 70-90% of the phosphorous 18 19 in the WWTP influent). In view of forthcoming and inevitable regulations on phosphorous removal 20 and recovery from WWTP streams, this review summarizes the main recent advances in this field to provide the scientific and technical community with an updated and useful tool for choosing the 21 best strategy to adopt during the design or upgrading of WWTPs. 22

23 Keywords: phosphorus removal; phosphorus recovery; sewage sludge; urban wastewater; WWTP.

24

25 List of abbreviations

AD	Anaerobic digestion
AGS	Aerobic granular sludge
A ² O	Anaerobic/anoxic/oxic
AOB	Ammonium oxidizing bacteria
AP	Acidification potential
BOD	Biological oxygen demand
CAS	Conventional activated sludge
CED	Cumulative energy demand
CFR	Continuous-flow reactor
COD	Chemical oxygen demand
CSTR	Completely stirred tank reactors
DO	Dissolved oxygen
DPAO	Denitrifying PAO
EBPR	Enhanced biological phosphorous removal
EU	European Union
FBR	Fluidized-bed reactor
GWP	Global warming potential
HM	Heavy metal
HRAP	High-rate algal pond
HRT	Hydraulic retention time
IA	Intermittent aeration
IFAS	Integrated fixed activated sludge
MBBR	Moving bed biofilm reactor
MBR	Membrane bioreactor
MLE	Modified Ludzak Etlinger
MLSS	Mixed liquor suspended solids
MUCT	Modified University of Cape Town
NF	Nanofiltration
NOB	Nitrite oxidizing bacteria
PAO	Phosphorous accumulating organisms
PHA	Polyhydroxyalkanoates

Poly-P	Polyphosphates
PR	Phosphate rocks
RAS	Recirculated activated sludge
S2EBPR	Side-stream EBPR
SBR	Sequencing batch reactor
SCWO	Supercritical water oxidation
SDG	Sustainable Development Goal
SND	Simultaneous nitrification denitrification
SRT	Sludge retention time
SSM	Sidestream MLSS fermentation
SSR	Side-stream reactor
TN	Total nitrogen
TP	Total phosphorus
TRL	Technology readiness level
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UCT	University of Cape Town
UMIF	Unmixed in-line MLSS fermentation
VFA	Volatile fatty acids
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant

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1. Introduction

Phosphorous (P) plays a key role in the global food supply because, together with nitrogen (N) and 47 potassium (K), is a biolimiting nutrient for plants and, for this reason, is largely used to produce 48 chemical fertilizers. P is a relatively limited resource (Wellmer and Scholz, 2015) and almost 85% 49 50 of P used in agriculture derives from the extraction and processing of PR (Geissler et al., 2015). To meet the agricultural demand, from 1993 the global consumption of elemental P deriving from PR 51 52 raised by almost 3-4% per year (Chen and Graedel, 2016). Global PR reserves amount to almost 65×10^3 Tg, and they could reach 290×10^3 Tg hypothetically considering deposits and unprocessed 53 rock of varying quality (Van Kauwenbergh, 2010). In fact, according to the last summary of the 54 U.S. Geological Survey, the worldwide PR reservoirs amount to 71×10^3 Tg, while the excavated PR 55 amount equaled 223 Tg in 2020 (U.S. Geological Survey, 2021). Furthermore, to reach the target 56 2.3 of the Sustainable Development Goal of United Nations (doubling the productivity of 57 smallholder farms) by 2030, the need for an increase of P application by 39% (126 Tg) has been 58 estimated (Langhans et al., 2021). According to this, the constant increase of P demand provides a 59 growing concern over long-term security of P supply (Desmidt et al., 2015). Indeed, it has been 60 estimated that global PR reserves will last 3-4 centuries, but excluding Morocco, which holds 61 almost 75% of global PR reserves (Jasinski, 2010), all the other countries will deplete their share 62 63 within the next century (Cooper et al., 2011).

Moreover, the price of PR used to produce fertilizers influences the cost of food, as in the case of cereals, and consequently the world hunger. Consequently, many countries are dealing with this topic to overcome the problems generated by the sudden increase in the cost of PR, as happened in 2008 (Neset and Cordell, 2012). Specifically, the 5Rs strategy (Realign P inputs in agriculture, Reduce P losses in the hydrosphere, Recycle P in bio-resources, Recover P from waste, and Redefine the food system) has been suggested to EU countries in the past few years (Withers et al., 2015). As a result, the EU has welcomed these suggestions and is trying to put them into practice.

For instance, the European Parliament has recently proposed the promotion of "large scale fertilizer 71 72 production in the EU from domestic organic or secondary raw materials" (European Parliament, 2016). Ott and Rechberger (2012) highlighted that almost 20% of the P used for food, feed and non-73 food products, such as detergents, by the EU15 former countries ends up in industrial and urban 74 wastewater treatment plants (WWTPs). As reported by the authors, 70% of P comes out from 75 WWTP in the form of sludge, not always reused in agriculture, while the remaining 30% ends up 76 directly in the hydrosphere. Additionally, part of the P contained in fertilizer and WWTP sludge 77 reused in agriculture is washed away by rain, with a consequent migration of P to surface waters 78 (Ball Coelho et al., 2012). Another study on the EU27 countries highlighted that 27% of P imported 79 80 during 2005 (655 Gg) was lost after the consumption of commercial goods (i.e., food and 81 detergents) mainly in wastewater (55%), food waste (27%), and pet excreta (11%) (van Dijk et al., 82 2016).

As a result, in 2013 the yearly amount of P from anthropogenic pollution that reaches the sea has 83 been evaluated to be equal to 37.9 Tg, which represents more than the 50% of the global annual P 84 consumption, i.e., 68.7 Tg (Chen and Graedel, 2016). In particular, the accumulation of P, derived 85 from WWTPs and runoff, in small lakes, rivers or backwaters is the main cause of eutrophication 86 87 (Huser et al., 2016), which generates serious problems to the environment and human activities. 88 Indeed, eutrophication causes turbidity, hypoxia and malodor in surface waters, leading to a serious burden on the aquatic ecosystem (Conley et al., 2009). Moreover, blue-green algae (cyanobacteria) 89 may excrete toxins that are dangerous to humans and animals (Dittmann and Wiegand, 2006). 90

In this context, WWTPs play a key role in the reduction of eutrophication phenomena, since many treatments, some being still under investigation, could be adopted to reduce the P concentration in WWTPs effluents. For instance, under the guidelines of the EU Urban Wastewater Directive, the achievement of lower P concentrations in UK wastewater reduced the average annual total P concentration in rivers from 0.27 to 0.1 mg P/L during the 1974-2012 period (Worrall et al., 2016).

Despite this, according to van Puijenbroek et al. (2019), numerical calculation on a global scale 96 97 showed a discharge in wastewater equal to 1.5 Tg of P in 2010 and estimated values up to 1.6-2.4 Tg of P expectable by 2050. Indeed, this clearly highlights the necessity to achieve very high P 98 removal efficiency within WWTPs. However, the increasing efficiency of P removal from 99 100 wastewater concurrently leads to the nutrient accumulation in sewage sludge. Then, the scientific community is striving to enhance P recovery from wastewater and sewage sludge. By performing 101 102 both P removal (on the mainstream line) and recovery (on the side streams) within the WWTP is possible to implement a strategy consistent with the principles of circular economy (Geissdoerfer et 103 al., 2017; Sauvé et al., 2016). This also meets the measures foreseen by the EU and other countries 104 105 to counteract the negative effects of a predictable P scarcity and excessive release in the 106 hydrosphere.

In line with this, many studies and patents have been devoted to the development of treatments and processes to remove and/or recover P from urban and industrial wastewater (Desmidt et al., 2015), leading to significant advances on this topic in recent years. Some technologies have already been implemented in WWTPs and are currently being optimized, while many have been tested only in laboratory reactors or pilot-scale installations. The present review provides a critical perspective of the existing P removal and recovery systems from WWTP streams with a focus of full-scale technologies and indicates the new research directions based on recent studies on this topic.

114

2. Phosphorous removal from municipal wastewater

The average TP concentrations in municipal wastewater typically ranges between 6 and 12 mg/L (Rittmann and McCarty, 2012; US EPA, 2007). The typical phosphorous forms present in urban wastewaters are orthophosphates (PO_4^{3-}) and polyphosphates (Poly-P) which turn to PO_4^{3-} after slow hydrolysis (Park et al., 2016). Secondary treatment involving only aerobic biological treatment displays a TP removal efficiency ranging from 20 to 30%, resulting in effluent concentrations from 3-4 to 8-10 mg P/L, being higher than typical TP standard in protected watershed, i.e., 1 mg/L (Daneshgar et al., 2018). Therefore, supplemental TP removal should be provided in WWTPs toavoid eutrophication of the surface water (Lürling and Oosterhout, 2013).

Generally, phosphorus removal from WWTP influent is carried out during mainstream wastewater treatment, while recovery is performed via side-stream processes, e.g., in the sludge streamline. In mainstream WWTP treatment, phosphorus can be removed upstream, within and downstream the biological phase. The first and third approaches are commonly carried out via chemical methods, while the second one via biological treatment, although addition of chemical for P precipitation within the biological treatment is also reported in literature (Carolina et al., 2011; Ma et al., 2020).

Calcium, magnesium, aluminum and iron ions are commonly employed as precipitators in the 129 130 primary wastewater treatment (pre-precipitation), in the post-precipitation treatment (after 131 secondary biological treatment) or in the co-precipitation treatment (contemporary to the biological treatment) (Magrí et al., 2020). In the first system, 65-80% removal efficiency can be achieved with 132 a relatively low P concentration in the final effluent (~1 mg/L) and wastewater alkalinity can 133 134 influence reactant dosage (Metcalf & Eddy Inc. et al., 2014). In the post-precipitation treatment, it is possible to achieve lower P concentration (from <0.1 to 0.5 mg P/L for sludge separation by 135 filtration and sedimentation, respectively) in the final effluent (Kroiss et al., 2011). These final 136 effluent concentrations can be obtained due to a more efficient chemical action ascribed to the 137 conversion of the organic phosphates to orthophosphates during the biological step. The post-138 precipitation system is more expensive than pre-precipitation as additional treatment basins are 139 required. In the co-precipitation treatment, which is suitable for activated sludge reactors, chemical 140 141 consumption is reduced because of the combined effect operated by the sludge recirculation and the 142 sorption and precipitation processes, and no additional basins are needed. For these reasons, this system is less expensive than the post-precipitation treatment also because tanks of moderate size 143 are required, but chemical and biological sludges are not differentiated. In the present case, 144 145 aluminum and iron ions are commonly employed as precipitators and phosphorous removal efficiency can reach values up to 93-99% (Costa et al., 2019; Filali-Meknassi et al., 2005). Although chemical precipitation remains an established and highly efficient solution for phosphorus removal and is applied in many WWTPs, current research is producing significant effort in enhancing biological phosphorus removal with the aim to limit the consumption of chemicals, reducing treatment costs and guaranteeing a higher process sustainability. In the following sections, both well-assessed and innovative biological treatments are critically described.

152

2.1 Biological P removal in mainstream wastewater treatment

Biological P removal is based on the accumulation of phosphorus in microbial cells forming 153 secondary sludge, which is subsequently removed from the water. In a CAS system, phosphorus is 154 taken up by microorganisms for their metabolic reactions. However, the amount of TP removed in 155 CAS is only 7-18 g per kg of removed organic matter expressed as COD, resulting in a 20-30% 156 reduction of the influent TP concentration (Henze et al., 1997). To increase the efficiency of 157 phosphorus removal, several biological processes characterized by the presence of suspended or 158 attached biomass (chemo- or photo-synthetic) have been developed. The main operating 159 characteristics and TP removal efficiency of several full-scale WWTPs adopting these technologies 160 161 are reported in Tables 1-3.

162

163 Table 1. Full-scale applications of suspended biomass biological systems for phosphorus removal.

164 **2.1.1** Biological P removal by suspended biomass processes

165 In the second half of the seventies, intermittent anaerobic/aerobic conditions and the development of enriched cultures of PAO were proposed to obtain P removal up to 90% (Barnard, 1974). This 166 process, known as EBPR, is mainly facilitated by some specialized microorganisms such as 167 168 Tetrasphaera- and Accumulibacter-related bacteria, which respectively constitute the 27-35% and 3-24% of the total biomass volume in EBPR systems (Cydzik-Kwiatkowska and Zielińska, 2016; 169 Stokholm-Bjerregaard et al., 2017). The behavior of these microorganisms is a controversial topic, 170 and it is still being studied. However, the bio-chemical reactions that seem to be recognized by the 171 whole scientific community are reported below and depicted in Figure 1. Under anaerobic 172 conditions, Tetrasphaera-related microorganisms can assimilate some rapidly biodegradable 173 substrates, such as glucose, glutamate, aspartate and glycine, to ferment them and synthetize 174 glycogen and new cells (Marques et al., 2017). The required energy is obtained from both 175 176 fermentation of rapidly biodegradable substrates and degradation of Poly-P, with a consequent release of phosphates and low molecular weight organic compounds such as lactate, acetate, and 177 succinate (Nguyen et al., 2011). Meanwhile, the low molecular weight organic compounds, also 178 produced from the metabolism of Tetrasphaera-related microorganisms, are taken up and stored as 179 PHA in the cells of Accumulibacter-type bacteria thanks to the energy derived from both the 180 hydrolysis of Poly-P and the glycolysis of intracellular glycogen (He and McMahon, 2011). Like 181 Tetrasphaera-related microorganisms, also bacteria associated to Accumulibacter release 182 phosphates during the anaerobic step due to the hydrolysis of Poly-P. During the subsequent aerobic 183 and/or anoxic phase, due to the scarcity of exogenous energy and carbon sources being already 184 depleted during the anaerobic phase, the stored glycogen and PHA are oxidized aerobically and/or 185 anoxically to provide carbon and energy required for the production of new cells as well as for 186 phosphate assimilation and the consequent restoration of the Poly-P reserve (Kristiansen et al., 187 2013). Phosphate uptake under aerobic conditions exceeds the amount released during the anaerobic 188

phase, resulting in a net P uptake also defined as *luxury* uptake. Bacteria capable of anoxic 189 190 oxidation of stored carbon compounds are known as DPAO and include both Tetrasphaera- and Accumulibacter-related microorganisms, although Tetrasphaera has shown lower anoxic P uptake 191 compared to Accumulibacter (Margues et al., 2018). Tetrasphaera and Accumulibacter contributed 192 for the 24-70% of the TP removed, corresponding to 14.84-37.52 mg P/g TSS, in eight different 193 WWTPs performing EBPR, the rest being attributed to the activity of unknown PAO and chemical 194 precipitation (Fernando et al., 2019). P content in the biomass of EBPR systems can reach up to 100 195 mg P/g TSS (150 mg P/g VSS), which is 6.7 times higher than that typically found in CAS sludge, 196 i.e., around 15 mg P/g TSS (20 mg P/ g VSS) (Henze et al., 2008). 197

198

199 Figure 1. A brief description of *Tetrasphaera*- and *Accumulibacter*-related microorganisms in an EBPR system.

200

EBPR in WWTPs is commonly achieved in concomitance with N removal. To this purpose, several
configurations can be applied (Figure 2).

203

Figure 2. WWTP cycles for combined biological P and N removal from wastewater.

205

Among these, the A^2O configuration is the easiest, as it simply adds an anaerobic basin, which receives the recycle sludge from the secondary settler, to the classical pre-denitrification system. In literature, some successful A^2O applications are reported, although they indicate variable TP removal efficiencies. For instance, TP removal of almost 96% was reported in a full-scale A^2O system characterized by an average SRT of 12.7 d and a biomass concentration of 3-4 g/L (Wang et al., 2014). On the contrary, a significantly lower TP removal (43%) was reported for a A^2O system operated at a similar SRT (12 d) but lower biomass concentration in the tanks, according to the TSS

concentration in the sludge (2.9 g/L) (Lanham et al., 2013). For this application, influent 213 characteristics were almost equal to 253 mg/L for the average COD, 81 mg/L of suspended solids, 214 43 mg-N/L (average N), 33 mg-N/L (average NH₃), 5 mg-P/L (average TP) with a resulting 215 COD:N:P ratio of 51:9:1. A drawback of the A²O configuration is that the NO₃⁻ contained in the 216 recycle sludge can be used by denitrifying bacteria to oxidize part of the COD destined to the 217 synthesis of PHA (Accumulibacter) and glycogen (Tetrasphaera) and limit the subsequent aerobic 218 P uptake. Therefore, an alternative configuration avoiding NO₃⁻ contamination of the anaerobic 219 process should be preferred. At this aim, the 5-stage Bardenpho scheme involves the addition of 220 two further stages (anoxic and aerobic, respectively) downstream the aerobic stage. Specifically, the 221 222 new anoxic stage is aimed at further lowering NO_3^- concentration from the previous aerobic tank using endogenous carbon. Then, the final aerobic stage is useful for the minimization of phosphates 223 release in the secondary clarifiers. Effluent PO₄³⁻-P concentrations <0.5 mg/L and P removal 224 efficiencies >95% have been reported in a full-scale WWTP configured with a 5-stage Bardenpho 225 process and treating wastewater containing 240–360 mg BOD₅/L and 10 mg PO₄³⁻-P /L (Meyer et 226 al., 2006). 227

The scheme proposed by the University of Cape Town, namely UCT process, is another strategy to 228 229 overcome high NO_3^- concentrations in the anaerobic tank by recycling sludge to the anoxic basin 230 and mixed liquor from the anoxic to the anaerobic basin (Rittmann and McCarty, 2012). In this way, NO_3^{-1} is mostly reduced under anoxic conditions before entering the anaerobic basin. The 231 MUCT scheme further optimizes this configuration by dividing the anoxic basin in two 232 compartments: the first, which recycles liquor to the anaerobic basin, receives only recycle sludge 233 (which has limited NO_3^- levels), further limiting NO_3^- concentration in the stream feeding the 234 anaerobic bacteria, while the other receives the nitrified liquor from the aerobic phase. As a result, a 235 study by Beer et al. (2006) on real WWTPs (with influent P concentrations ranging from 7.5 to 12 236 mg/L and operating temperatures from 16°C to 25°C) in Australia reported a TP removal efficiency 237

after MUCT treatment in the range of 52-98%. An alternative to MUCT is the Johannesburg
process, in which RAS is denitrified in an anoxic tank before being recirculated to the anaerobic
basin.

Besides the schemes illustrated in Figure 2, alternative configurations have been designed with the 241 scope to improve the stability of the EBPR process. Among these, the S2EBPR scheme implies that 242 a portion of RAS or anaerobic mixed liquor is maintained in a SSR for a period of 16-48 h, enabling 243 VFA production via sludge fermentation and consequent PO_4^{3-} release and carbon uptake by PAO. 244 This configuration can be further modified by feeding the SSR with supplemental carbon from the 245 primary sludge fermenter. Other S2EBPR configurations include the SSM, in which part of the 246 247 anaerobic MLSS is diverted to a SSR, and the UMIF, in which an unmixed zone is introduced in the cycle to favour MLSS fermentation (Onnis-Hayden et al., 2020). An anoxic SSR was also 248 implemented in the BiodenitroTM process, which consists of two tanks where anoxic and aerobic 249 250 conditions are alternated. This has the aim of partially degrade the RAS (HRT = 20-30 h) and recirculate the previously fermented stream into the BiodenitroTM tank operating under anoxic 251 conditions (Lanham et al., 2013; Vollertsen et al., 2006). In the two examples reported by Lanham 252 et al. (2013), high TP removal efficiencies, i.e., 94 % and 96 %, were observed, despite the high 253 differences between of operating conditions, i.e., influent TP concentration equal to 4 and 10 mg/L, 254 influent COD concentration of 198 and 636 mg/L, average flow rate of $49 \cdot 10^3$ and $17 \cdot 10^3$ m³/d, and 255 SRT maintained at 19 and 30 d, respectively. However, since the authors reported that FeCl₃ was 256 added as a polishing step for P removal, it is not possible to determine the contribution of the sole 257 BiodenitroTM configuration, combined with an anaerobic SSR, in the achievement of the 258 overmentioned TP removal efficiencies. Another interesting side-stream configuration was tested 259 by Wang et al. (2019), who modified a A²O system moving the anaerobic compartment (continuous 260 stirring and HRT = 1.6 h) from the mainstream to the side-stream line with consequent influent inlet 261 into the anoxic compartment. At the same time, RAS was conveyed into the side-stream anaerobic 262

reactor together with primary sludge to provide a supplemental carbon source. With TP and COD concentrations in the influent equal to 3.7 mg/L and 254 mg/L, respectively, a TP removal efficiency equal to 84% was obtained. However, the TP removal efficiency was further enhanced (93%) by adopting an intermittent mixing of the anaerobic compartment. In fact, the intermittent mixing condition led to the sedimentation of a part of the sludge, thus increasing the SRT in the anaerobic compartment and enhancing the hydrolysis/fermentation of RAS.

Recent research is moving towards the implementation of more compact systems allowing more 269 efficient and sustainable removal of organic carbon, N and P in one single reactor through the 270 alternation of different oxygen conditions. In this direction, Roots et al. (2020) combined P and 271 272 shortcut N removal from real municipal wastewater in a pilot-scale (56 L) SBR with a cycle set on 273 an anaerobic period followed by IA and without the addition of exogeneous carbon. Aeration was set to target a DO level of 1 mg/L (duration 4-5 minutes), followed by pump shutdown and up to 3-274 min long anoxic period. Influent characteristics were approximately 2.8 mg N/L (TKN), 1.7 mg N/L 275 (NH₄⁺), 1.4 mg P/L (PO₄³⁻), 2.2 mg P/L (TP), 150 mg total COD/L, 94 mg filtered COD/L, 72 mg 276 TSS/L, and 4.7 meq/L of alkalinity. Average TP, total nitrogen (TN) and COD removal at 20°C 277 were 83%, 81% and 70%, which resulted in effluent TP concentrations ≤ 0.3 mg/L (on average). 278 279 Candidatus Accumulibacter was the most abundant PAO representative in the reactor with relative 280 abundances up to 12%, while *Tetrasphaera* remained always below 0.3%.

281

2.1.2 Biological P removal by microbial biofilm-based/granular sludge processes

In the last years, research has also focused on technologies able to simplify plant operation and strongly limit the number of basins and recycles required for EBPR while reducing investment and operational costs. In particular, the use of the SBR has gained increasing interest as SBR allows a full control of operational conditions and, by alternating aeration and non-aeration phases, the complete removal of P, N and C in a single basin. To allow the simultaneous growth of AOB, NOB, PAO and DPAO, biofilm processes are advantageous compared to suspended-growth systems, as
mass transport limitations within the biofilm create ecological niches allowing the coexistence of
different types of bacteria.

AGS has been successfully applied in recent years for P removal from both municipal and industrial wastewaters and typically develops in a SBR system. AGS granules have a core which stays anaerobic under the non-aeration phase (feast) and turns partially to aerobic/anoxic during the aeration phase (famine) due to oxygen penetration and nitrifying activity. Indeed, nitrifiers (AOB and NOB) develop on the external layer of the granules where oxygen is more available, resulting in the production of NO_x^- diffusing to the internal layers of the granule (**Figure 3**).

296

Figure 3. Main phosphorus, nitrogen and carbon transformation and layer distribution in an AGS granule during aerationand non-aeration phases.

299

300 Recent applications of the AGS technology have focused on the combined removal of phosphorus, nitrogen and carbon from domestic wastewater. Campo et al. (2020) investigated the C/N/P removal 301 performance of AGS treating real domestic wastewater with low C/N as well as the impact of high 302 SRT on the process in a lab scale reactor. High PO4³⁻-P removal (96%) combined to C and N 303 removal of 84% and 71% in respective order was obtained when treating wastewater with C/N of 304 3.8, resulting in effluent PO_4^{3-} -P concentrations <0.1 mg/L (on average). Moreover, the long SRT of 305 61 d led to low sludge yield (0.21 gCOD_{biomass}/gCOD_{removed}). Similar P removal (95%) and higher N 306 removal efficiency (87%) were observed in a full-scale AGS reactor in Poland (Świątczak and 307 308 Cydzik-Kwiatkowska, 2018) operated with a SRT of 30 d (Table 2). Nonetheless, a recent study on a full-scale AGS application displayed a lower P removal efficiency (69%) (Oliveira et al., 2020). 309 It is worth highlighting that nearly all full-scale AGS systems reported in Table 2 were operated 310 311 with mixed wastewater (domestic and industrial), resulting in influent P concentrations often above

10 mg P/L. In particular, the industrial wastewater fractions (generally around 30-40% of the 312 influent) originated from different sources depending on the reported study (such as dairy industries 313 and slaughterhouses) (Giesen et al. 2013, Świątczak and Cydzik-Kwiatkowska 2018, Ortega et al. 314 2021). Despite a significant percentage of industrial wastewater in the plant influents, results from 315 these studies displayed very high P removal efficiency (82-98%), highlighting the good 316 performances achievable through the AGS technology. Further supporting the high AGS efficiency, 317 a case of study from Giesen et al. (2016) reported a P removal efficiency equal to almost 95% for a 318 plant treating a mix of domestic, septic tank and industrial wastewaters and characterized by 319 prolonged periods of industrial peak load. 320

In terms of energy consumption, it was reported that the SBR-AGS system can achieve electricity demand reduction equal to 23%, 35%, and 50-70% compared to activated sludge with EBPR, IFAS, and MBR systems, respectively (Bengtsson et al., 2018). As a consequence, operating costs decrease can be expected through AGS system also highlighting the beneficial investment achievable through its application.

The new direction in developing the AGS technology is towards the design of CFRs capable to 326 cultivate the granules, being able to treat higher flow rates and easier to implement in municipal 327 WWTPs than SBR systems, as WWTPs receive wastewater to be treated continuously. The main 328 329 challenge of continuous-flow AGS systems relates to the stability of the granules, as the absence of a settling phase promotes the retention of filamentous flocs, being commonly washed out in SBRs 330 during the short settling phase. The outgrow of filamentous bacteria in the system can undermine 331 332 the long-term stability and integrity of the granules. Additionally, the settling phase consists also in a starvation period enabling the feast/famine regime (Kent et al., 2018). To assure granules 333 retention and limit the proliferation of filamentous bacteria in the systems, several continuous-flow 334 AGS configurations providing aerobic, anoxic and anaerobic zones have been tested at laboratory 335 scale, including bubble columns with baffles, serial multiple chambers, and systems coupled to 336

clarifiers or submerged membranes for granules retention. Nevertheless, no full-scale 337 implementation of these technologies has been completed up to date (Rosa-Masegosa et al., 2021). 338 Indeed, removal of filamentous bacteria is not always effective in CFRs especially at high organic 339 loadings (Li et al., 2016), which is detrimental for P removal, as granule destruction would 340 inevitably disrupt the alternation of feast/famine phases providing PAO and DPAO with a 341 competitive advantage for organic uptake over other heterotrophic bacteria. Despite these 342 challenges, further improvement of AGS-based CFRs in terms of granule stability could promote 343 their application in WWTPs in the near future. 344

Similar to AGS, the moving bed biofilm reactor (MBBR) allows the formation of a multi-layered 345 346 biofilm including nitrifiers, denitrifiers, PAO and DPAO. The simultaneous removal of carbon and 347 nutrients can be achieved by coupling SND to EBPR by operating the MBBR in SBR mode to allow the alternation of aerobic and anaerobic phases (Ferrentino et al., 2018). Recently, lab-scale 348 MBBRs have been applied in continuous-flow mode for the combined removal of P, N and C under 349 stable microaerobic conditions (Iannacone et al., 2019) or by alternating aerobic and microaerobic 350 phases (Iannacone et al., 2021, 2020). The highest P removal efficiency, i.e., 83-86% (on average), 351 coupled to complete C and >80% N removal via shortcut SND was achieved when alternating DO 352 concentrations between 0.2 and 3 mg/L at stable HRT of 1 day and feed C/N and C/P of 3.6 and 11, 353 354 respectively (Iannacone et al., 2021). Microbial characterization of the MBBR biofilm strongly suggested that P uptake was mainly carried out by bacteria belonging to the genus 355 Hydrogenophaga, which dominated the biofilm microbiome under IA conditions. Previous studies 356 357 reported that bacteria related to Hydrogenophaga have the ability to take up P under aerobic conditions at a rate comparable to those observed in full-scale EBPR systems when acetate is used 358 as source of organic carbon (Iannacone et al., 2020). P removal under IA conditions was higher 359 when coupled to shortcut SND than to complete SND under similar operating conditions, which 360 suggests that the organic carbon saved by denitratation (NO_3^- reduction to NO_2^-) can support P 361

uptake under low COD conditions typical of domestic wastewaters (Campo et al., 2020; Chai et al.,
2019).

The results obtained by Iannacone et al. (2021, 2020) confirm that the anaerobic phase is not 364 mandatory for biological P removal from wastewater. Full-scale experiences had already shown that 365 high-efficiency P removal was achieved in conventional CAS and MLE configurations lacking the 366 anaerobic stage in which P release and denitrification occurred under anoxic conditions in the same 367 basin (Qiu et al., 2019). It was suggested that, if enough organic carbon is available for 368 denitrification, PAO can release P under anoxic conditions as in the anaerobic phase and perform 369 luxury uptake in the subsequent aerobic phase. This was confirmed by the relatively high 370 371 abundance of *Ca. Accumulibacter* ($\geq 2\%$) and *Tetrasphaera* (0.4-1.8%) in the microbial community of the CAS and MLE sludges (Qiu et al., 2019). Besides, EBPR has been reported also under 372 complete aerobic conditions by using a synthetic wastewater containing 250 mg/L of acetic acid 373 (Pijuan et al., 2006). 374

375 Although EBPR can occur under complete aerobic conditions, the presence of an anaerobic phase could promote VFA production from complex organic matter typical of real wastewater. VFA 376 levels in the feed of most laboratory-scale studies are not representative of those typically occurring 377 in real WWTP influents (<100 mg COD/L) (Barajas et al., 2002) and, therefore, scale-up of the 378 379 studied processes and the use of real domestic wastewater is recommended to assess the actual P 380 removal efficiencies. It is worth mentioning a further configuration represented by the IFAS system, which is a hybridization of the MBBR in which carrier-attached and suspended biomass coexist. 381 Some studies on full-scale WWTPs integrating the IFAS technology to EBPR reported TP removal 382 383 from 48% to >80% for influents characterized by TP concentration ranging from 2.9 to 8.5 mg/L (Kwon et al., 2010; Onnis-Hayden et al., 2011) (Table 2). It is wort mentioning that the lower 384 removal percentage (48%) was observed for an influent characterized by 120.5 mg BOD/L, 124.4 385 mg TSS/L, 32.2 mg N/L, 2.9 mg P/L, and a WWTP operated at HRT of 5.9 h and average 386

temperature of 23°C (Kwon et al., 2010). On the contrary, higher P removal efficiency was reported 387 388 for a WWTP operating at an average mixed liquor SRT of 3.78 d and a recycle flow relative to the influent flow of 40% and 60% for activated sludge and mixed liquor, respectively. Moreover, the 389 390 WWTP influent was characterized by average concentrations of 8.5, 35.2, and 6 mg/L for TP, ammonia and NO_x, respectively (Onnis-Hayden et al., 2011). A previous study also highlighted the 391 highest cost effectiveness of IFAS-EBPR (93.82 \$/kg of P removed) compared to MBR (135.31 392 \$/kg of P removed) and five-stage Bardenpho systems (102.24 \$/kg of P removed), while a similar 393 value was observed compared to the MUCT process (93.89 \$/kg of P removed) (Bashar et al., 394 2018). 395

396

397 Table 2. Biofilm-based applications for full-scale phosphorus removal.

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399 **2.1.3 Mi**

Microalgae integration into WWTP to enhance P removal

The use of P as a nutrient for photosynthetic organisms has been exploited through the development 400 of microalgae-based P removal bioprocesses. Similar to PAO, microalgae can uptake P in excess of 401 growth requirement (*luxury uptake*) as orthophosphate, which can be also produced by solubilizing 402 organic P via the enzyme phosphatase, and store it inside the cell as Poly-P granules (Bunce et al., 403 2018). The use of microalgae for P removal from wastewater may lead to several advantages 404 compared to bacterial-based systems. Microalgae can combine efficient P removal and recovery to 405 CO₂ sequestration, energy generation (e.g., through production of biofuels) and production of 406 organic fertilizer (Badgujar et al., 2020; Suleiman et al., 2020). Very high removal efficiencies have 407 408 been observed in lab-scale studies on microalgae-based wastewater treatment. For instance, Rasoul-Amini et al. (2014) carried out lab-scale tests on the simultaneous removal of N and P from 409 secondary wastewater effluents in 250 mL batch photobioreactors. In this case, Chlamydomonas 410 sp., *Chlorella* sp. and *Oocystis* sp were tested by adopting the following experimental conditions: 411 pH=9, constant illumination (4150 lux), T=25 °C, 190.7 mg NO₃⁻-N/L, and 19.11 mg PO₄³⁻-P/L. As 412 reported by the authors, within 14 d the minimum and maximum P removal were 82% and 100% 413 for Chlorella sp. and Chlamydomonas sp., respectively. Similar P removal efficiencies were 414 observed in a study reporting the treatment of the primary effluent of a WWTP by 11 different 415 416 microalgae strains (Chawla et al., 2020). Specifically, the batch experiments were performed in 250 mL flasks at 25°C and intermittent illumination of 12 h light (50 µmol/m²·s) and dark. In this 417 conditions, effluent P concentrations ranging from 0.1 and 3.2 mg PO₄³⁻-P/L compared to an 418 influent concentration of 15.5 PO₄³⁻-P/L. Compared to the very high removal efficiencies observed 419 at lab-scale experiences, a lower performance for pilot and full-scale applications can be expected 420 due to the difficulty of maintaining stable operating conditions (temperature, irradiation) which can 421 be easily set in laboratory experiments. 422

Although the application of microalgae in WWTP has been shown as a promising opportunity, only 423 a few full-scale microalgae-based systems have been operated so far. The majority of microalgae-424 based systems applied at pilot and full scale for P removal (Table 3) consist in open suspended-425 growth systems such as the HRAP (Chatterjee et al., 2019) and waste stabilization ponds (Brown 426 and Shilton, 2014). In particular, HRAP are generally characterized by lower electrical energy 427 consumption for mixing (50-110 kWhe/ML) compared to conventional activated sludge (230-960 428 kWh_e/ML) (Craggs et al., 2011). However, despite the well-assessed technology, further process 429 optimization is fundamental in order to achieve higher nutrient uptake rate as well as cost effective 430 microalgal biomass harvesting (Sturm and Lamer, 2011; Sutherland et al., 2017). Another 431 432 interesting strategy for microalgae-based treatment is represented by the use of a microalgal 433 biofilms which can allow an easy harvesting from the support material (e.g., flat panels or rotating biological contactors) or by collecting the gel matrixes in which they are embedded. However, 434 microalgae biofilms also present some challenges, as their application requires high surface areas 435 for biofilm development and high capital costs for purchasing the support material (Mohsenpour et 436 al., 2021). 437

The latest research in this field has focused on incorporating microalgae into bacterial systems 438 typically operated in WWTPs. The main advantage of this strategy is that microalgae can contribute 439 440 to meet the oxygen need of aerobic heterotrophs degrading the influent organic substrates, which can significantly reduce the energy costs for aeration and mixing (Wang et al., 2015). On the other 441 hand, microalgae can capture the CO₂ produced by the oxidation of organic matter which turns into 442 443 higher production of energy and P-rich microalgae biomass (Cai et al., 2019). Moreover, microalgae-bacteria systems do not require a transition between different operating environments 444 for simultaneous carbon and nutrient removal as microalgae directly assimilate both N and P for 445 cell growth and metabolic functions, thus reducing the complexity of the treatment configuration. 446

To establish a successful microalgae-bacteria symbiosis, the microalgae culture and physical-447 chemical conditions should be accurately selected and maintained inside the system. Microalgae 448 belonging to Chlorella and Scenedesmus, as well as diversified consortia, have been successfully 449 applied for P removal from urban wastewater after primary treatment (concentrations of 3.8-7.5 mg 450 PO₄³⁻-P/L, 147-473 mg NH₄⁺/L, <0.5-0.9 mg NO₃⁻-N/L, 101-147 mg COD/L, and pH ranging from 451 8.21 to 8.34) (Gouveia et al., 2016). In this work, removal efficiencies up to 100% for P and 98% 452 453 for N were achieved in a pilot-scale photobioreactor (150 L) operating in fed-batch mode over three months (September-November) with average air temperatures from 11°C to 23°C (Gouveia et al., 454 2016). 455

Regarding the operating parameters, the illumination period and intensity are fundamental to 456 enhance microalgae growth and consequently avoid an increasing bacteria/algae ratio. Although P 457 removal seems less affected, low light intensity (such as 40 μ E/m²·s) may cause the proliferation of 458 nitrifying bacteria, causing NO₃⁻ and NO₂⁻ accumulation in the system and reducing TN removal 459 (González-Camejo et al., 2018). The optimal pH range to sustain the growth of both microalgae and 460 bacteria is between 7 and 9. Higher values may occur due to CO₂ consumption by microalgae and 461 impair bacterial growth, resulting in less CO₂ supporting the growth of microalgae and, 462 subsequently, lower P removal from wastewater. Although optimal temperatures of 28-30°C have 463 464 been indicated for the growth of microalgae (Park et al., 2011), significant P removal from waste liquid streams (90%) has been reported also at temperatures as low as 15°C (Filippino et al., 2015) 465 and 5°C (38%) (Chatterjee et al., 2019) with cultures of Chlorella and Scenedesmus, respectively. 466

467 Although promising outcomes have been shown at laboratory and pilot scale, integration of algal 468 and bacterial microorganisms for P removal from wastewater has not been successfully tested at full 469 scale. However, recent studies recently focused on demonstrating the economic feasibility of 470 applying microalgae-bacteria consortia in open systems for the treatment of WWTP streams. 471 Mantovani et al. (2020) showed that the application of a pilot-scale open raceway pond for the sidestream treatment of the centrate (244 mg NH₄⁺-N/L, 0.2 mg NO₃⁻-N /L, 0.4 mg NO₂⁻-N /L, 5.7 mg PO₄³⁻-P/L, 83 mg TSS/L, 112 mg COD/L, pH of 8.2 and conductivity of 1492 μ S/cm) produced from a WWTP sludge streamline led to P and N removal >70% (on average) and nearly satisfied oxygen demand for nitrification. Moreover, the process results in extra energy production by sending additional biomass to AD. Overall, integrating a side-stream raceway pond to the WWTP would result in a net energy saving of around 0.4 W/m².

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Table 3. Algae-based biological systems for phosphorus removal at full and pilot scale.

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3. Phosphorus recovery from WWTP streams

As biological and chemical P removal WWTP treatments have the primary goal to reduce P 482 concentration of the influent wastewater within the mainstream treatment by incorporating it into 483 biomass or precipitates, all removed P ends up in the sludge streamline. Consequently, phosphorous 484 485 recovery is typically performed from liquid/solid side streams of the WWTP (Figure 4a), and it is expected to improve when EBPR or chemical P removal are implemented in the WWTP 486 487 mainstream line. The presence of a hydrolysis/AD step in the sludge streamline can also help to enhance the subsequent P recovery by promoting mineralization of organic P contained in the 488 sludge and the biological P release from PAO. A fundamental aspect of this practice lies in the 489 potential benefits derived from the recovery of removed phosphorous and its consequent reuse. 490 491 Many patented treatment systems for phosphorous recovery are nowadays reported in the literature, 492 and some of them have reached a technology readiness level (TRL) of 9 (Table 4), meaning successful implementation at full scale. These processes mainly differ from one another according 493 494 to the matrix representing the P source. In the following sub-sections, P recovery systems will be reviewed by distinguishing the treatments related to the recovery from sludge-derived aqueous 495 496 streams (digester supernatant, sludge dewatering liquor) and (semi)solid phases (i.e., digestate and sludge ash). Only technologies sufficiently tested with real municipal WWTP streams are discussed. 497

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Figure 4. Schematics of phosphorus recovery in the WWTP sludge streamline (a) and of applicable patented technologies for
P recovery from digester centrate (b), dewatered sludge (c) and sludge ashes (d).

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502 **3.1** Systems for phosphorous recovery from liquid streams

P-loaded liquid streams within a municipal WWTP typically refer to the liquid fraction of anaerobically digested or hydrolyzed sewage sludge obtained post dewatering, e.g., centrate or filtrate. P recovery in the liquid fraction can be enhanced by applying sludge disintegration technologies prior to AD, e.g., thermal hydrolysis with Cambi (Di Capua et al., 2020), which enhance P solubilization and subsequent recovery in the sludge liquor.

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3.1.1 Crystallization technologies

One of the main processes applied for phosphorus recovery from the liquid phase is represented by 509 510 crystallization, which commonly occurs in fluidized systems (Chrispim et al., 2019). An example is provided by the Crystalactor[®] water treatment technology of Royal HaskoningDHV, which was 511 initially developed to remove hardness from drinking water (Desmidt et al., 2015). This system 512 provides the crystallization of a determined component in a FBR. During the crystallization process, 513 the size of the material constituting the fluidized bed increases, and the resulting heavier material 514 settles to the reactor bottom. Suitable dosage of reagents (e.g., lime and Mg(OH)₂) should be 515 provided during the process for adequate crystallization rate in order to achieve phosphorus 516 517 recovery in the final forms of calcium phosphate, magnesium phosphate or struvite 518 (NH₄MgPO₄·6H₂O), the latter being an appreciated slow-release fertilizer (Di Capua et al., 2020). 519 Indeed, the relative fertilizer efficiency of struvite can be 100% for acidic soils but lower for alkaline ones (Amann et al., 2018). The latter values are more beneficial when compared to calcium 520 521 phosphate providing lower P uptake when used in slight acidic and neutral soils (Johnston and Richards, 2003). The main advantage of Crystalactor[®] is the combination in one stage of the 522

conventional steps constituting the precipitation process (i.e., coagulation, flocculation, separation 523 524 of the produced sludge and its dewatering). Water-free pellets can be produced leading to the elimination of dewatering treatment and related costs. P recovery from the digester supernatant 525 through Crystalactor[®] can reach values up to 40% with respect to the WWTP influent, while typical 526 ranges are from 10% to 25% of the influent P for recovery technologies from the digester 527 supernatant (Egle et al., 2016). However, the higher efficiency observed with the Crystalactor® 528 529 technology can be achievable if enhanced biological phosphorous removal process is applied in the WWTP. 530

Recovery percentage from 10% to 30% are also reported for another crystallization system 531 represented by the patented Ostara Pearl® technology (Chrispin et al., 2019). In this case, 532 phosphorous is recovered solely as struvite in the "Pearl" reactor, a FBR in which crystallization of 533 struvite is controlled through the addition of magnesium salts and, if required, NaOH to adjust the 534 pH. The system recycles part of the treated effluent from the top to the bottom of the reactor to 535 control the product size (Figure 4b). Once the struvite seeds have reacted the desired size (>0.5 536 mm), they are commercialized under the name of Crystal Green® (Gysin et al., 2018). In the 537 Multiform Harvest[™] process, which has been acquired by Ostara in 2019 and already applied in 538 small WWTP and farms, a cone-shaped FBR is used for struvite crystallization through the addition 539 540 of NaOH and MgCl₂.

As an alternative to the fluidized systems, the application of the fixed-bed reactor and CSTR also proved feasible P recovery from supernatant digester. The P-RoC[®] process is based on a fixed-bed configuration (Berg et al., 2007) where crystallization is achieved using calcium silicate hydrate or synthesized pellets of tobermorite. The obtained product displayed a P total yield of 10-11%, which is comparable to the common values for a commercial NPK 12-24-12 fertilizer (TP equal to 10.5%) as well as natural P-rocks (Green, 2015). Differently, the NuReSys[®] process is carried out in two CSTRs, i.e., a stripper for pH and scaling control and a reactor with MgCl₂ addition to promote

active formation of struvite pellets (Bio-Stru[®]). NuReSys[®] has been successfully applied at full 548 549 scale selectively on centrate and digested sludge (5-6% TS) of municipal WWTP as well as on both streams sequentially through a hybrid configuration, resulting in P recovery >86% (Dewaele, 2015). 550 The PHOSPAQTM process, developed by Paques, combines biological COD removal to chemical P 551 removal in an aerated CSTR. Aeration provides oxygen for biological COD oxidation to CO₂, 552 which strips and raises the pH to 8.2-8.3, promoting struvite formation through the addition of 553 554 magnesium oxide (MgO). Struvite pellets (0.7 mm) are harvested from the bottom of the reactor by means of a hydrocyclone followed by a screw press (Driessen et al., 2018). The process has been 555 successfully applied for the removal of phosphorus on sludge dewatering liquors at municipal 556 557 WWTPs and on industrial effluents, showing reliable full-scale performances. Additionally, this process has been successfully combined with the anammox process in a municipal WWTP for 558 simultaneous removal of PO₄³⁻-P (80%) and NH₄⁺-N (90%) from the effluents of an UASB reactor 559 560 treating potato processing wastewater. The overall process produced biogas from COD conversion into the UASB and fertilizer-grade struvite, and allowed the WWTP to respect the effluent 561 standards for nutrients (Remy et al., 2013). 562

An example of mainstream phosphorous recovery is represented by the REM-NUT® technology. In 563 this case, phosphate is removed from the effluent of secondary treatment through a selective ion-564 565 exchange, and then recovered from the spent regeneration liquid of the ion-exchange with chemical precipitation as struvite. The REM-NUT[®] has been developed only at pilot scale but never been 566 applied at full scale, which could be related to the selection of proper ion-exchangers for selective 567 removal of phosphorus and to the high cost of ion exchangers. Besides REM-NUT®, other studies 568 focusing on combined P removal and recovery from WWTP mainstream line have been carried out 569 at laboratory scale. For instance, Zou and Wang (2016) tested an EBPR coupled with a 570 crystallization step aimed at recovering P as hydroxyapatite from synthetic wastewaters (SRT = 20571 d; T = 16-21 °C; 5 mg PO₄³⁻-P/L). Results showed that PO₄³⁻-P removal efficiency was 87.5% and 572

573 59.3% of P compared to the influent concentration. In another study, concurrent P removal and 574 recovery was achieved combining anammox biological treatment and hydroxyapatite precipitation 575 in an expanded bed reactor maintained at 33°C (Ma et al., 2018). In particular, TP removal 576 efficiency equal to 66%, with an influent P concentration of 13 mg/L, was achieved in a 5 L reactor, 577 while a volumetric removal capacity equal to 0.14 kg P/m³·d was estimated.

Despite the majority of P recovery processes have the goal of recovering phosphorus as struvite, 578 which can be used as slow-release fertilizer, it is noteworthy to mention that P recovered in the form 579 580 of other compounds, such as hydroxyapatite or amorphous calcium phosphate, can have a broader scope than fertilization. Indeed, calcium phosphates are the main constituents of PR, which are 581 582 mined not only to produce fertilizers, but also for the production of detergents, food additives, 583 phosphoric acid and much more (Chen and Graedel, 2016). Recently, the production of calcium phosphates was attempted from the effluent of a UASB reactor. Specifically, by introducing a 584 nitrification step of the UASB effluents, the production of struvite is by-passed due to the 585 586 conversion of ammonia to nitrates, and the concentration of dissolved inorganic carbon, which both inhibits calcium phosphate precipitation and leads to the contamination of the phosphate with 587 carbonate, is reduced (Monballiu et al., 2018a). This strategy was tested with the UASB effluents 588 collected at a potato processing plant in a two pilot-scale CSTRs connected in series (HRT of 25-27 589 590 h): the first was operated as a nitrification reactor, while the second was used for the precipitation of 591 calcium phosphates. The influent to the first reactor was characterized by approximately 293 mg N/L (as NH4⁺), 50 mg P/L (as PO4³⁻) while Ca²⁺/P and Mg²⁺/NH4⁺/P molar ratios were equal to 592 0.7/1.0 and 0.8/13.0/1.0, respectively. Accounting for the influent of the second reactor, 593 concentrations equal to 9 and 55 mg/L were respectively observed for NH₄⁺-N and PO₄³⁻-P, while 594 values of 0.6/1.0 and 0.7/0.4/1.0 were reported for the Ca²⁺/P and Mg²⁺/NH₄⁺/P molar ratios. In this 595 study, a satisfactory phosphate recovery of 70%, mainly in the form of hydroxyapatite, was reached 596 at neutral pH (Monballiu et al., 2018b). 597

598 **3.1.2** Adsorption

Adsorption represents another possible strategy that can be applied for P recovery from urban 599 wastewaters and liquid fraction of sewage sludge. This process is driven by Van der Waals and 600 electrostatic forces, and is favored by low temperatures. Also, it is reversible and not site-specific 601 (multi-layer formation). Important parameters of the process are the pH of the solution, which 602 controls the absorption capacity, the contact time, the affinity to the sorbent surface, and the 603 604 increase of sorbent dosage (Ajmal et al., 2018; Kumar and Viswanathan, 2018). Phosphate ions can be effectively removed from water and wastewater through a double step mechanism based on 605 sorption and precipitation. Generally, adsorption occurs via an ion-exchange mechanism between 606 607 calcium and magnesium compounds present at the surface of adsorbent materials, e.g., cement/concrete, and phosphate in solution, while the partial dissolution of Ca⁺² and Mg²⁺ ions 608 from the adsorbent triggers phosphate precipitation, which is favored by the increase of pH detected 609 after ion dissolution (dos Reis et al., 2020; El Bouraie and Masoud, 2017). 610

Current research is moving towards the use of industrial by-products as sorbents for the removal of 611 phosphate from wastewater, promoting the reuse of secondary raw materials for recovery purposes 612 (Sellner et al., 2019; Hashim et al., 2021). These sorbents are chemically constituted by oxides, 613 hydroxides, Si, Fe, Al, Mg, Ca, and Ti carbonates and may have different origins, e.g., power plant, 614 615 mining and steel industry (fly ash, red mud, slags) (Goscianska et al., 2018; Guo et al., 2018; Kim et al., 2000). Phosphate removal can be also obtained by iron oxides from mineral processing 616 industry (Ajmal et al., 2018) or by wollastonite from the mining of this calcium meta-silicate 617 618 mineral (Obradović et al., 2017). Ligand exchange and surface precipitation are the predominant sorption mechanisms with removal capacities depending on the by-product composition, size, 619 porosity and on the experimental methodology adopted. 620

Among organic sorbents, ion-exchange resins have largely replaced the use of zeolites and arewidely used in various chemical engineering applications, particularly in the water demineralization

processes also as phosphate sorbent. Different ion exchange resins have been employed to remove 623 phosphate from wastewater such as Purolite A500P, Purolite A520E, Purolite FerrIX A33E, 624 Amberlite IRA910Cl and Amberjet 1200Na, Dowex 21K XLT (Nur et al., 2014, 2012), or magnetic 625 ion exchange and hybrid anion exchange resins (Nur et al., 2012; Sowmya and Meenakshi, 2013). 626 These resins are structurally characterized by a polymeric matrix with grains in the range of few 627 mm and exchangeable ions. The regeneration of the exhausted resins can be obtained by NaCl, 628 NaOH, CaCl₂, HCl, and Na₂CO₃ (Loganathan et al., 2014) or their mixtures. Involvement of 629 calcium or magnesium salts for resins regeneration leads to precipitation phenomena advantageous 630 for possible phosphorus recovery and reuse as fertilizer. As an alternative, activated carbons are 631 632 characterized by low cost, easy availability, high porosity, high specific surface area, and can be 633 used for phosphate removal from water and wastewater (Khalil et al., 2017; Yao et al., 2018).

Agricultural wastes have been proven low-cost biological sorbents to remove phosphate from 634 wastewater. The surface properties and the porosity of these materials can be improved after 635 chemical modification of the structure. Specifically, efficient anion exchangers are obtained by 636 grafting amine groups onto wheat straw (Xu et al., 2010), whereas chemical treatments may 637 increase the porosity and the number of functional groups as in the case of saw dust from 638 woodworking operations (Benyoucef and Amrani, 2011). Organic wastes with quantitative presence 639 640 of iron showed good retention capacities of the phosphates (Field et al, 2019, Zou et al, 2017). In recent years, biochar obtained by thermal degradation (pyrolisis) of a biomass of animal or 641 vegetable origin has been increasingly applied on municipal wastewater as phosphate sorbent. 642 643 Modification of biochar surface with functional additives such as AlCl₃, MgCl₂, and Fe₃O₄ can be performed to enhance phosphate removal efficiency (Zheng et al., 2020). Zheng et al. (2019) 644 645 applied biochar modified with colloidal and nanosized aluminum oxyydroxide (AlOOH) and produced through direct pyrolysis of wood chips pretreated with Al salt to recover P from real 646 secondary treated wastewater, showing promising results both in terms of P recovery and 647

application of P-loaded biochar as fertilizer. Indeed, (modified) biochar may in the future be applied for nutrient removal and recovery from WWTP liquid streams through a biofiltration step. Trials with real municipal wastewater have shown a 78% TP reduction after passing through a biochar filter with a surface area of 1000 m²/g and loading of 1 g/L (Manyuchi et al., 2018), demonstrating potential for full-scale implementation for phosphorus recovery.

653

3.1.3 Electrochemical precipitation

Electrochemical precipitation represents a newly explored and economically sustainable solution for 654 655 P recovery from municipal wastewater, as it does not require chemicals for pH increase and stoichiometric requirements (struvite precipitation), nor for surface modification of sorbent 656 materials (adsorption). In electrochemical systems, water electrolysis at the cathode generates a 657 658 local pH increase, driving the precipitation of calcium phosphate, e.g., as hydroxyapatite (Ca₅(PO₄)₃OH). Subsequently, the formed precipitate can be harvested from the cathode without the 659 need of a separation step. A recent investigation by Lei et al. (2018) with municipal wastewater 660 showed that the efficiency of selective P precipitation on the cathode strongly depends on the 661 cathode size and Ca/P ratio in wastewater, the latter being generally much higher than the 662 stoichiometric ratio for hydroxyapatite formation in real wastewater (1.67 mol/mol). This leads to 663 the co-precipitation of by-products such as calcite (CaCO₃) and brucite (Mg(OH₂)), which reduce 664 the purity of the obtained P precipitate. However, the extent of by-product precipitation can be 665 666 limited by reducing the current intensity and/or through the addition of external P (which anyway would offset the advantage of no chemical utilization). Trials with raw domestic wastewater showed 667 that less than 50% P removal could be achieved with this strategy, being significantly lower than 668 those observed with crystallization and absorption technologies. Further development is needed for 669 potential implementation of electrochemical systems for P recovery in municipal WWTP. 670 Additionally, it should be noted that hydroxyapatite is considered a less valuable P-based product 671

672 for agricultural utilization compared to struvite, although it can be used as a platform chemical for P673 extraction.

674 **3.2** Systems for phosphorous recovery from raw and digested sewage sludge

Higher phosphorous recovery from sludge can be expected compared to the influent wastewater as 675 up to 95% of P removed from the WWTP influent is estimated to be transferred to the sewage 676 sludge (Cornel and Schaum, 2009). This could promote the strategy of sewage sludge reuse for land 677 fertilization purposes. This practice is allowed in many countries and represents a convenient and 678 679 sustainable option for P recycling from sewage sludge (Di Costanzo et al., 2021). Indeed, sewage sludge can be spread to land if complies with required quality standards and after appropriate 680 681 hygienization, e.g., through thermophilic AD in centralized plants collecting dewatered sewage 682 sludge on regional/national scale (Di Capua et al., 2020). This practice enables the maximum exploitation of sewage sludge nutrient potential, as most of the P contained in the sludge is bound to 683 the solid phase. The issue about agricultural reuse of sewage sludge is the potential presence of 684 685 pollutants (e.g., HMs, pharmaceuticals and pesticides) at high concentrations, including emerging contaminants being nowadays of increasing concern. Also, depending on the pollutant, the AD 686 process can display effective (such as for polychlorinated biphenyl) or ineffective degradation 687 efficiency, consequently not assuring a suitable sludge quality standard for agricultural reuse 688 (Fijalkowski et al., 2017). From this perspective, many countries worldwide adopt different 689 690 restrictive regulations to discipline sludge agricultural reuse (Christodoulou and Stamatelatou, 2016). Besides the presence of organic pollutants, elevated concentrations of HMs within the sludge 691 often limit sludge application in agriculture, and therefore alternative strategies for exploiting the P 692 content of sewage sludge should be undertaken. Accordingly, the technologies applied for 693 phosphorous recovery from sludge also aim at limiting HMs content in the recovered product to 694 provide a safe fertilizer. 695

696 Strategies for P recovery from sewage sludge include struvite crystallization (e.g., MagPrex[®]), wet-697 chemical extraction (e.g., Gifhorn and Stuttgart), wet-oxidation (e.g., LOPROX), supercritical 698 water-oxidation (e.g., Aqua Reci[®]), metallurgic smelt gassing process (MEPHREC[®]) and magnetic 699 separation of Fe-P precipitates. These technologies can reach 40-70% recovery of the P contained in 690 the WWTP influent, being significantly higher than that obtained from the sludge liquid fraction 691 and discussed in section 3.1.

The MagPrex[®] system (formerly AirPrex[®]) developed by Berliner Wasserbetriebe involves 702 digestate treatment in an air-lift reactor in which air is recycled for CO₂ stripping and consequent 703 704 pH increase (from 7 to 8). Then, subsequent addition of MgCl₂ allows the formation of struvite 705 crystals that sink to the bottom of the reactor when reaching a certain size. Full-scale plants operating with this system were reported to achieve phosphate recovery from the digestate >80%. 706 707 For instance, two WWTPs (in Wassmannsdorf and Amsterdam west) characterized by similar influent dissolved PO₄³⁻-P concentrations equal to 387 and 400 mg/L and SRT for all reactors of 708 10.5 and 8 h displayed a $PO_4^{3-}P$ precipitation efficiency up to 87% and 95%, respectively. In these 709 full-scale applications, higher precipitation efficiency was achieved by dosing 1.9 mol Mg/mol P as 710 MgCl₂, while dosing 1.7 mol Mg/mol P resulted in the lower precipitation efficiency (Zhou et al., 711 2019). However, only 40-50% of the produced struvite is recovered in the air-lift reactor, as the rest 712 713 ends up in the solid fraction in the following dewatering phase (CNP Cycles GmbH, 2015).

The Gifhorn process is carried out by a first wet-chemical extraction of the P bound in the biomass through the addition of sulfuric acid. Afterwards, the dissolved metals are precipitated as sulfides by dosing Na₂S and adjusting the pH with NaOH. Finally, the addition of Mg(OH)₂ leads to phosphorous precipitation and recovery as a mix of struvite and calcium phosphates (Rashid et al., 2020). The wet-chemical extraction step applied in the Gifhorn process is a general key-point for strategies involved in the phosphorous recovery from sewage sludge. Indeed, the Stuttgart process is performed through a first acidification step of the sludge similar to the Gifhorn approach, but metal ion separation is achieved through complexation by means of chelating agent (such as citric acid) addition before the struvite precipitation step (Meyer et al., 2019). The whole process efficiency depends on the chemicals involved and pH conditions for phosphorous dissolution. In fact, the initial acid leaching step at pH 3 can lead to final phosphorous recovery from Stuttgart process higher than 65% in struvite form with low metal content (Meyer et al., 2019).

A different approach is displayed by the Aqua Reci[®] process in which a SCWO step is employed 726 727 before the acid or alkaline leaching phase (Figure 4c). The SCWO phase provides both the mineralization of the total organic matter and the oxidation of toxic metals and phosphorus 728 respectively to their maximum valency and P₂O₅ (Stendahl and Jäfverström, 2004). The resulting 729 730 ash from the SCWO can further undergo alkaline leaching to extract phosphorous as sodium 731 phosphate that can be easily precipitated as calcium phosphate by lime addition. Alternatively, acid leaching could be involved and precipitation can occur through three neutralization steps gradually 732 raising the pH and recovering ferric phosphate, aluminum, iron, and HMs (Stendahl and 733 Jäfverström, 2004). Despite the overall system can lead to sludge volume reduction, which is 734 beneficial in terms of operating costs, it should be also taken into account that previous life cycle 735 analyses highlighted significant energy consumption related to the process (Amann et al., 2018). 736

737 Low pressure wet oxidation at temperature ranging between 160°C and 220°C, pressure of 11.8-738 27.6 atm and acidic conditions (pH=1.5) can be used for sludge oxidation in presence of pure oxygen. This oxidation treatment is identified as the LOPROX system, and is followed by two 739 740 membrane filtration phases to recover phosphorous from sludge (Blöcher et al., 2012). The first 741 membrane step (ultrafiltration) aims at removing suspended solids from the LOPROX effluent, while the second step, i.e., NF, aims at recovering phosphorus in the membrane permeate. 742 743 Specifically, the recovery rate is strictly related to the ion rejection effects of the NF membrane on phosphorous. Indeed, higher phosphorus recovery is expected with decreasing rejection achievable 744 through an acidic wash of the NF membrane (Blöcher et al., 2012). Finally, the MEPHREC[®] 745

metallurgic process allows, compared to the other recovery processes applied on sludge, the highest
recovery percentage in terms of WWTP influent (up to 75%) in the form of a final P-rich slag where
P is present as calcium silicon phosphate (Amann et al., 2018; Günther et al., 2018). Nonetheless,
some difference in terms of depollution efficiency can be expected during the process due to
possible metals behavior variation (Egle et al., 2016).

An interesting research direction that is emerging in the last years is the recovery of the mineral 751 752 vivianite (Fe₃(PO₄)₂·8H₂O) from sewage sludge produced in WWTPs performing chemical P precipitation with iron. Indeed, this mineral has been reported as the most abundant P precipitate in 753 digested sludge when iron is dosed in the mainstream line to remove P from wastewater (Wilfert et 754 755 al., 2018). At this stage, only lab-scale experiments have been carried out on real sewage sludge with magnetic separation concentrating the vivianite by a factor of 2-3, but significant amount of 756 organic matter, quartz and metals remained in the magnetic concentrate (Prot et al., 2019). Indeed, 757 758 this technology is still at early stage and further research is required towards optimization of separation efficiency and quality of the concentrate. However, vivianite extraction from sewage 759 sludge is promising as it could be applied directly as a slow-release fertilizer in iron-poor soils or 760 used as a platform compound for P extraction, while reducing the amount of sludge to be disposed. 761

762

3.3 Systems for phosphorus recovery from sludge ash

Technologies recovering P from sludge ash include wet-chemical extraction (RecoPhos[®] and
Fertilizer Industry), wet-chemical leaching (e.g., PASCH and LEACHPHOS[®]), thermo-chemical
treatments (e.g., AshDec[®] and Thermophos[®]). These technologies can reach P recovery efficiencies
of 70-90% related to WWTP influent.

Acidic wet leaching has been widely used as the main step of several systems aimed at phosphorous recovery from sludge ashes. However, sludge ash contains elevated concentrations of HMs, primarily Fe, Zn and Cu, which should be separated from the recovered P for its safe utilization in agriculture (Di Costanzo et al., 2021). Examples of acidic wet leaching for P recovery are provided
by PASCH e LEACHPHOS[®] processes which aim at re-solubilizing the P contained in the ashes 771 772 after the incineration process. For PASCH, a liquid-liquid HMs removal step is also performed in 773 order to achieve a higher purification of the recovered P (Egle et al., 2016). Nonetheless, both the PASCH and LEACHPHOS[®] processes have been applied only at laboratory and pilot scale. In 774 processes such as RecoPhos[®] and Fertilizer Industry, a P recovery equal to 85% of that contained in 775 the WWTP influent can be achieved in the form of mineral fertilizer through acid-wet chemical 776 extraction. Although no selective HMs extraction step is performed, the obtained RecoPhos® ash-777 derived fertilizer has shown compliance with the German Fertilizer Ordinance as well as conformity 778 to conventional fertilizers in terms of HM content and effect on crops (Weigand et al., 2013). 779 Various final recovered products are instead achieved by EcoPhos[®], which has been implemented at 780 full scale despite the plant being not currently in operation (Ploteau et al., 2021). In this case, the 781 technology leads to the production of fertilizer-grade phosphoric acid and/or production of 782 783 dicalcium phosphate. Ashes are first leached using phosphoric acid and the leach liquor is subsequently decontaminated from HMs by passing through multiple ion-exchange modules. If HCl 784 is used instead of H₃PO₄ as leaching agent, phosphate in the leachate is chemically precipitated and 785 recovered as dicalcium phosphate (Takhim et al., 2019). 786

A further approach for the recovery of phosphorus from sewage sludge ashes is provided by thermal 787 788 processes. The AshDec® system, which has been tested at pilot scale, represents a well-assessed solution in which sludge ashes, mixed with potassium and/or sodium compounds, and a reducing 789 agent (preferably dry sewage sludge), are treated in a rotary kiln at 900-950°C for 15-20 min 790 791 (Figure 4d). Potassium and sodium ions replace calcium ions in the phosphates and form soluble P and PK fertilizers. Simultaneously, HMs evaporate and, as soon as the process gas cools down, the 792 particles condensate and are removed by means of electrostatic precipitators (Hermann and Schaaf, 793 2019). 794

At high temperatures (1500-1600°C) achieved through coke burning or electric heating it is possible 795 796 to recover phosphorous as elemental white phosphorus (P_4) . The latter approach is followed in the Thermphos[®] process, which indeed can be considered as a highly energy demanding strategy. 797 However, the pure (99.99%) product recovered can be suitably reused in the production of several 798 P-based chemicals (such as P2O5, NaH2PO2, PCl3, PH3, etc.), while the calcium-silica slag 799 remaining in the furnace can be employed in road construction (Jupp et al., 2021). In addition, 800 Thermphos[®] produces dust rich in HMs, which is precipitated electrostatically and recycled into the 801 process. However, the presence of high iron levels in the ashes lowers P recovery efficiency, as Fe 802 can be reduced to FeP and FeP₂, reducing P₄ yield. Volatile HMs can partly evaporate, precipitate 803 804 on dust, and build up in the system through dust recycling, requiring periodical purging. A fullscale Thermphos[®] plant was run in The Netherlands from 2007 until 2012, when the company 805 declared bankruptcy apparently due to excessive market competition for P₄ commercialization 806 807 (BSR WATER, 2021).

3.4 Environmental impact of P recovery technologies applied in WWTPs

809 An environmental assessment of the existing technologies applied in WWTP for P recovery has been carried out by Amann et al. (2018) through a life cycle assessment which also considers the 810 impacts of energy production and waste disposal of each technology. The analysis has been carried 811 out based on three indicators: CED, GWP and AP. Technologies recovering P from the liquid 812 fraction of sewage sludge generally feature negative values of the three indicators, indicating low 813 environmental impact. In this regard, an exception is represented by Crystalactor[®], which features a 814 CED of 41 kWh per population equivalent per year due to the high energy demand of this process, 815 as well as positive GWP and AP values. Another positive aspect of these technologies is that the 816 materials recovered from the liquid phase of sewage sludge are generally safe, as they contain 817 extremely low concentrations of HMs, micropollutants and pathogens. 818

Despite the high energy demand of incineration, technologies recovering P from sewage sludge ashes can also feature negative values of the three indicators due to reduced production of P fertilizers using PR and industrial chemicals, being partially replaced by recovered P-rich products such as H₃PO₄ and P₄. However, materials recovered from sludge ashes can present high levels of HMs and, although incineration destroys pathogens and micropollutants, it can also generate toxic contaminants such as dioxins and furans.

In contrast, technologies recovering P from sewage sludge, such as wet-oxidation processes, generally feature positive CED, GWP and AP due to the high demand of energy intense chemicals. Materials recovered from sewage sludge, e.g., through the Gifhorn and Struttgart processes, can feature low contamination levels if decontamination steps for the removal of HMs are carried out. Although some organic micropollutants can be detected, they are generally at lower concentrations than in the untreated sewage sludge (Amann et al., 2018).

3.5 Overall economics of the P recovery processes applied in WWTPs

832 Annual costs for technologies aimed at phosphorous recovery from post-digestion supernatants are generally around 8-10 \in per kg of recovered P (**Table 4**). The NuReSys[®] technology is reported as 833 the cheapest technology on the market, resulting in operational cost of $\leq 3 \notin$ per kg of recovered P 834 (Desmidt et al., 2012; Dewaele, 2015), which promotes the use of CSTR as a more convenient 835 alternative to conventional fluidized-bed columns for P crystallization. In comparison, the 836 attractiveness of a fixed-bed technology such as the P-RoC[®] may be limited by higher annual costs 837 (around $6 \notin \text{per kg}$ of recovered P) (Egle et al., 2016) and by calcium phosphate as the end-product, 838 being less bioavailable to plants than struvite especially in neutral and alkaline soils (Amann et al., 839 2018). However, some studies suggest the use of refractory calcium phosphates, such as calcium 840 hydrogen phosphate, calcium pyrophosphate, and hydroxyapatite, as substitute of PR (Berg et al., 841 2006; Monballiu et al., 2020) or for the production of nanostructured P fertilizers (Tang and Fei, 842 2021). Overall, the benefit of implementing these technologies at full scale relates primarily to a 843

reduction of maintenance operations and related costs, as struvite incrustation may severely impact
the WWTP piping and pumping systems. Also, struvite precipitation and harvesting significantly
reduce P backflow to the mainstream treatment with the digester supernatant, reducing the burden
for P removal.

848

Table 4. Full-scale (TLR 9) technologies for P recovery from solid/liquid WWTP streams (Corona Encinas, 2020; Desmidt et
al., 2012; Dewaele, 2015; Egle et al., 2016; Val del Río et al., 2016).

851

The involvement of chemicals (such as acids and/or basis) for phosphorous recovery can lead to a 852 significant increase of the operating costs. Indeed, the REM-NUT[®] technology, which recovers P 853 854 directly from the WWTP effluent, results in the most expensive approach with annual costs (excluding savings and revenues) as high as 28 € per kg of recovered P due to the high requirement 855 of resins and reagents (Egle et al., 2016). Additionally, the powdery/dusty struvite obtained by 856 REM-NUT[®] is not directly applicable and marketable, needing a further granulation/classification 857 step prior to be sold. Approaches for phosphorous recovery from sludge through wet-oxidation also 858 859 result in operating burden due to the high energy demand and annual costs (e.g. 23-27 € per kg of recovered P for the Aqua Reci[®] system) (Egle et al., 2016; Law and Pagilla, 2019). Similarly, 860 considering the recovery systems from sludge ashes, high costs and energy consumption can be 861 862 expected especially referring to thermochemical treatments. An example is provided by the AshDec[®] system which is significantly energy demanding due to the heat required to separate 863 phosphates and HMs (Ye et al., 2017). 864

Capital and operational costs may be substantially reduced by considering the potential revenues and savings from 1) the commercialization of the obtained P-rich products, 2) reduced sludge disposal volumes, 3) improved dewaterability of the digestate due to aeration and leaching of the sludge with acids and 4) heat recovery from thermal P-recovery processes (Egle et al., 2016).

However, some criticalities exist regarding the low market value of the obtained P-rich secondary 869 870 material (0-100 € per ton) and uncertainties on their safety for agricultural use related to the potential presence of pathogens (Mayer et al., 2016). The latter issue is a further limitation to the 871 use of digestate-derived struvite, since it has been observed to contain more pathogens compared to 872 struvite from the dewatering liquor of digestate (Muys et al., 2021). Despite the high operational 873 costs of thermal treatments for P recovery from sludge, these technologies allow to recover heat and 874 energy and convert the sludge to disposable inert waste, which can considerably decrease the 875 overall treatment cost. However, uncertainties regarding the economic impact of thermal treatments 876 exist, since these technologies have only been implemented at pilot scale (Egle et al., 2016). 877 878 According to this, the identification of a suitable approach aimed at maximizing the overall benefits, in terms of process economics and valuable product recovery, should consider several aspects. This 879 clearly highlights that specific assessments should be singularly distinguished in order to properly 880 select the optimal technical solution characterized by: (i) significant process efficiency, (ii) 881 economic affordability and (iii) environmental sustainability. 882

883

4. Conclusions

Innovations and practices on P removal from WWTP influents are moving towards the 884 implementation of compact and more efficient biological systems such as AGS and carrier-based 885 886 biofilm systems both in SBR and continuous-flow configurations for the combined removal of P, N 887 and C from urban wastewaters through alternation of aeration phases activating microbial groups with diverse metabolic functions. Although successful operation of these system has been shown up 888 to TRL 9, uncertainties regarding long-term stability remain due to their operational and biological 889 890 complexity. Therefore, further optimization at full scale is still needed to enhance the stability and promote the application of these systems in modern WWTPs. Similarly, integration of microalgae 891 to bacterial systems might help improving the efficiency and sustainability of P removal in 892 WWTPs, but full-scale experience is required the confirm long-term stability of algae-bacteria 893

consortia and assess their response to changing of influent characteristics, physical conditions, 894 degree of toxicity and microbial community composition. Simultaneous removal and recovery of P 895 is the new trend in modern WWTPs, although incentives from national governments to promote the 896 use of struvite and sludge-derived fertilizers would significantly encourage this practice. 897 Technologies for P recovery from sludge liquors are the readiest for implementation at full-scale, as 898 they offer a high level of technical maturity and are less complex and costly than those recovering P 899 from sludge and sludge ash. Moreover, the high P content of dewatered sewage sludge can be 900 exploited in agriculture when sludge quality and local legislation allow this practice. Coupling P 901 recovery from wastewater/sludge liquors in WWTP and digestate application to land would allow a 902 903 nearly complete P recycling from waste streams and improve the overall P removal efficiency of the WWTP. In this direction, performing an hydrolysis step in the WWTP sludge streamline may help 904 P solubilization in the sludge liquor (and its subsequent recovery) as well as methanogenesis in 905 906 centralized AD, being hydrolysis the limiting step of high-solid AD of sewage sludge (Di Capua et al., 2020; Morello et al., 2021). When agricultural utilization is not applicable, thermochemical P 907 recovery from sludge ash offers a promising alternative to P recovery from aqueous streams, based 908 on high recovery efficiencies, safety and the possibility of savings based on heat recovery and 909 910 cheaper disposal of the inert residue. Direct recovery from the sludge is not yet considered 911 convenient for full-scale implementation due to lower quality of the obtained P-based products, low environmental sustainability, and high costs. 912

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1471 Figure 1. A brief description of *Tetrasphaera-* and *Accumulibacter-*related microorganisms in an EBPR system.





1481 Figure 2. WWTP cycles for combined biological P and N removal from wastewater.



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a)

Sludge from EBPR DEWATERING SLUDGE ASH DIGESTION UNIT INCINERATION (d) DEWATERED SLUDGE (c) CENTRATE (b) b) To head of Ostara Pearl® WWTP water flow Supernatant recirculation PO_4^{3} NH_4^+ Mg^2 Struvite NaOH and MgCl₂ Centrate dosage c) Dewatered • CO₂, N₂, O₂ Separator sludge Aqua Reci® To head of Thickener WWTP Hydroxyapatite Lime t Supercritical Wet Oxidation T > 370 °C; P > 220 bar; RT = 60 s ↓ Chemical sludge + Energy + Oxygen +NaOH Gas treatment d) ---T AshDec[®] Venturi/cyclone system i for Na2SO4/K2SO4 I I heating -! Air ı Na2SO4 Post K2SO4 1 combustion I CO rich gas Gas treatment ----Binder Hot Na2SO4/K2SO4 **Rotary kiln** T > 900 °C; TR > 15 min Ash Gas Air Cooling Granulation PK fertilizer screw drying

- 1508 Figure 4. Schematics of phosphorus recovery in the WWTP sludge streamline (a) and of applicable patented technologies for
- 1509 P recovery from digester centrate (b), dewatered sludge (c) and sludge ashes (d).

1510 List of Tables

1511

1512 Table 2. Full-scale applications of suspended biomass biological systems for phosphorus removal.

Process configuration	Location	Flow rate (m ³ /d)	Feed P (mg/L)	C:P	Removal efficiency (%)	Reference	
A ² O	Moscow (USA)	11,000	2.58- 21.54	0-49.23 (mol/mol)	91.2-99.1	Coats et al. (2017)	
MUCT	Madison (USA)	158,000	4-7	-	>75	Zilles et al. (2002a)	
Orbal	Mazomanie (USA)	2,190	6.1-7.1	34-44 ^a	87.3	Zilles et al. (2002b)	
A ² O	Thorneside (Australia)	7,500	11	50 ^b	72.7	Pijuan et al.	
5-stage Bardenpho	(Australia)	12,000	10	24-36 ^a	>95	(2008)	
A ² O	(China)	225,000	-	-	96-96.8	Wang et al.	
Inverted A ² O	(China)	225,000	-	-	95.4-97	(2014)	
MUCT	(Australia)	80,000	9.4	-	52		
3-stage Bardenpho	(Australia)	25,000	13.5	-	96		
Carousel/UCT	(Australia)	60,000	12	-	99.2	_	
3-stage Bardenpho	(Australia)	32,000	10	-	88		
MUCT	(Australia)	44,000	7.5	-	97.3	Beer et al. (2006)	
Carousel/UCT	(Australia)	25,000	6	-	75		
MUCT	(Australia)	120,000	10	-	<80	-	
MUCT	(Australia)	30,000	12	-	98.3		
MUCT	(Australia)	60,000	12	-	83.3		
Side-stream RAS	Apex (USA)	19,700	7.1±0.1	39 a	94.4		
Side-stream RAS plus carbon	West Kelowna (Canada)	9,800	6.8±1	38.4 ª	97.1	Onnis-Hayden	
Modified Johannesburg with SSM	Cedar Creek (USA)	13,600	2.7±5.4	102 a	67	et al. (2020)	
Johannesburg with UMIF	Henderson (USA)	11,400	5.7±0.8	46.5 ^a	91.6		
Carousel MUCT	Hardenberg (The Netherlands)	6,000	11±1	25 ª	94.5	López-	
Carousel MUCT	Deventer (The Netherlands)	8,800	7±1	33.3 ^a	87.1	(2008)	

Carousel A ² O	Katwoude (The Netherlands)	8,200	9±2	25 ª	95.6	
Carousel A ² O	Hoek van Holland (The Netherlands)	22,000	7±1	16.7 ^a	92.9	
Carousel A ² O	Venlo (Netherlands)	71,400	10±4	20 a	97	
A ² O	Waarde (The Netherlands)	10,800	6±3	25 ª	90	
Sidestream P-stripping	Haarlem Waarderpolder (The Netherlands)	36,900	6±2	11.1 ^a	95	
5-stage step feeding	(Singapore)	361,000	5.53– 6.52	5.8-11.2 (g/g)	80.7	
A ² O	(Singapore)	205,000	6.02– 8.19	7.8-11.6	100	Qiu et al. (2019)
Inverted A ² O	(Singapore)	68,000	3.48– 6.37	10.8-25	76.8	
A ² O	Lisbon (Portugal)	48,000	5±0.9	51 ^b	43	
A ² O	Setúbal (Portugal)	12,000	5±3	206 ^b	85	
A ² O	Hjørring (Denmark)	13,000	4±1	50 ^b	92	Lanham et al.
Biodenitro [®] configuration with side-stream RAS	Aalborg (Denmark)	49,000	10±5	63 ^b	94	(2013)
Biodenitro [®] configuration with side-stream RAS	Aalborg (Denmark)	17,000	10±6	40 ^b	96	
A ² O plus primary sludge fermentate	Hillsboro (USA)	24,628	3.7±0.5	68.6 ^b	82	
Side-stream RAS plus primary sludge fermentate (S2EBPR) with continuous mixing	Hillsboro (USA)	24,453	3.7±0.5	68.6 ^b	84	Wang et al. (2019)
Side-stream RAS plus primary sludge fermentate (S2EBPR) with intermittent mixing	Hillsboro (USA)	20,177	3.8±0.3	76.8 ^b	93	
sludge termentate (S2EBPR) with intermittent mixing	Hillsboro (USA)	20,177	3.8±0.3	76.8 0	93	

1513 ^a as BOD₅/P 1514 ^b as COD/P

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1517 Table 2. Biofilm-based applications for full-scale phosphorus removal.

Process configuration	Location	Population equivalents (flow rate)	Feed P (mg/L)	C:P	Removal efficiency (%)	Reference
AGS	Garmerwolde (The Netherlands)	(28,600 m ³ /d)	1.9-9.7	75 ^a	86.6	Pronk et al. (2015)
AGS	Lubawa (Poland)	15,000 PE (3,200 m ³ /d)	19.5±2.1	66.7 ª	95	Świątczak and Cydzik- Kwiatkowska (2018)
AGS	Epe (Netherlands)	35,000 PE (5,000 m ³ /d)	8-13	101-117 a	98	Ortega et al. (2021)
AGS	Gansbaai (South Africa)	(4,000 m ³ /d)	19	66.6 ^a	82	Giesen et al. (2013)
AGS	Ryki (Poland)	38,600 PE (5,320 m ³ /d)	12.6	57.1 ^a	94.7	Giesen et al. (2016)
IFAS-EBPR	Denver (USA)	(17,280 m ³ /d)	4–16.5	8.4–30 ^b	>88	Onnis-Hayden et al. (2011)

	IFAS-EBPR	(China)	(50,000 m ³ /d)	2.2–4.5	60.9 ^a	81	Bai et al. (2016)
	IFAS-EBPR	Guri (South Korea)	(160,000 m ³ /d)	2.9	41.4 °	48.3	Kwon et al. (2010)
	biofilm carriers - A ² O	Xi'an (China)	(48,000 m ³ /d)	8.27±2.8	55.2 ª	97	Xiao et al. (2016)
1518 1519 1520	^a as COD/P ^b as biodegradable C ^c as BOD ₅ /P	OD/P					
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Table 3. Algae-based biological systems for phosphorus removal at full and pilot scale.

Process configuration	Location	Flow rate (m ³ /d)	Feed P (mg/L)	C:P	Removal efficiency (%)	Reference
HRAP	Christchurch (New Zeland)	486-796	0.9-3.9 ^a	28-290 ^b	22-49	Sutherland et al. (2014)
HRAP	Cambridge (New Zeland)	1500	3.8–7.8 ^a	18.1 c	32.7-51.9	Sutherland et al. (2017)
HRAP	Rabat (Morocco)	60	7.45	14.8 d	66	El Hamouri (2009)
algal pond	Thessaloniki City (Greece)	33-48	3.06	45.5-73.1	26-65	Papadopoulos et al. (2014)
algal pond	Lawrence (USA)	4.7	3.2±0.9	-	<90.6	Sturm and Lamer (2011)

^a as dissolved reactive phosphorus
^b as VSS/P
^c as BOD₅/P
^d as COD/P

1531 1532 1533

1544 Table 4. Full-scale (TLR 9) technologies for P recovery from solid/liquid WWTP streams (Corona Encinas, 2020; Desmidt et

1545 al., 2012; Dewaele, 2015; Egle et al., 2016; Val del Río et al., 2016).

Technology	Application	Type of reactor	Number of active plants	Annual costs (€/kg P recovered)	Product	Form of product	P recovery efficiency (%)
Crystalactor®	Wastewater/ supernatant (>25 mg P/L)	FBR	4	5-8	Struvite, CaP, MgP	Pellet	<40)
Ostara Pearl®	Digester and thickener supernatants	FBR	8	9-10	Crystal green®	Pellet (0.9-3 mm)	10-25
Multiform Harvest TM	Digester supernatant	cone-shaped FBR	2	n.a.	Struvite	Pellet	n.a.
NuReSys®	Digestate, filtrate and centrate of WWTP	CSTR	7	1.31-3	Bio-Stru®	Pellet	n.a.
PHOSPAQ™	Municipal sludge reject liquors	CSTR	11	n.a.	Struvite	Pellet (0.7 mm)	n.a.
MagPrex®	Digestate	Air-lift	7	7-8	Struvite	Coarse- grained	10-15

1546 n.a. = not available.