1-1-2013

Enhanced biological phosphorus removal and its modeling for the activated sludge and membrane bioreactor processes

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Keywords

bioreactor, processes, phosphorus, removal, its, modeling, enhanced, activated, biological, sludge, membrane

Disciplines

Engineering | Science and Technology Studies

Publication Details

Enhanced Biological Phosphorus Removal and its Modeling for the Activated Sludge and Membrane Bioreactor Processes

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Abstract

A modified activated sludge process (ASP) for enhanced biological phosphorus removal (EBPR) needs to sustain stable performance for wastewater treatment to avoid eutrophication in the aquatic environment. Unfortunately, the overall efficiency of the EBPR in ASPs and membrane bioreactors (MBRs) is frequently hindered by different operational/system constraints. Moreover, although phosphorus removal data from several wastewater treatment systems are available, a comprehensive mathematical model of the process is still lacking. This paper presents a critical review that highlights the core issues of the biological phosphorus removal in ASPs and MBRs while discussing the inhibitory process requirements for other nutrients' removal. This mini review also successfully provided an assessment of the available models for predicting phosphorus removal in both ASP and MBR systems. The advantages and limitations of the existing models were discussed together with the inclusion of few guidelines for their improvement.

Keywords: Enhanced biological phosphorus removal, Membrane bioreactor, Mathematical modeling, Activated sludge process.

Nomenclature

A$_2$N	Anaerobic-anoxic/nitrifying	NPFMBR	Nearly Plug Flow MBR
A$_2$O	Anaerobic-anoxic-oxic	n_{qPAO}	Reduction factor for denitrifying processes
AEI	Aerobic/extended-idle	n_{iPAO}/η_{PAO}	Reduction factor for anoxic growth of X$_{PAO}$
ASM	Activated sludge model	OHOs	Ordinary Heterotrophic Organisms
ASP	Activated Sludge process	P	Phosphorus
bio-P	Biological Phosphorus	PAOs	Phosphate Accumulating Organisms
BNR	Biological Nutrient removal	PHA	Polyhydroxyalkanoates
BNRAS	BNR system	PHB	Polyhydroxybutyrate
BNRM1	BNR Model 1	PO$_4$-P	Phosphate-P
b_{PAO}	Endogenous respiration rate of X$_{PAO}$	poly-P	Polyphosphate
b_{PP_PO4}	Rate constant for Lysis of X$_{PP}$	q_{Gly}	Rate constant for formation of X$_{GLY}$
b_{Stor_VFA}	Rate constant for respiration of X$_{Stor}$	$q_{PAO,PO4\_PP}/q_{pp}$	Rate constant for storage of X$_{PP}$
C	Carbon	q_{PAO,SB_Stor}	Rate constant for S$_A$ uptake rate (X$_{PHA}$ storage)
CAS	Conventional Activated Sludge	$q_{PAO,VFA\_PHA,An}$	Rate constant for S$_A$ uptake rate (X$_{PHA}$ storage) (anaerobic)
COD	Chemical Oxygen Demand	$q_{PAO,VFA\_PHA,Ax}$	Rate constant for S$_A$ uptake rate (X$_{PHA}$ storage) (anoxic)
DPAOs	Denitrifying PAOs	q_{PAO,VFA_Stor}	Rate constant for S$_A$ uptake rate (X$_{PHA}$ storage)
EBPR	Enhanced biological phosphorus removal	q_{PHA_PAO}	Rate for X$_{PHA}$ consumption (X$_{PAO}$ growth)
EPS	Extra-polymeric Substances	S_A	Fermentation product (Volatile Fatty Acids)
F/M	Food to Microorganism ratio	S_{ALK}	Alkalinity (HCO$_3^-$)
FCASM1	Fully Coupled ASM1	SBMBR	Sequencing Batch MBR
$f_{Gly\_PAO,Max}$	Maximum ratio of X$_{GLY}$/X$_{PAO}$	SBR	Sequencing Batch Reactor
$f_{PP\_PAO,Max}$/K$_{max}$	Maximum ratio of X$_{PAO,PP}$/X$_{PAO}$	SMP	Soluble Microbial products
$f_{SU\_PAO,lys}$	Fraction of S$_I$ generated in X$_{PAO}$ decay	S_{N2}	Dissolved nitrogen gas
$f_{XU\_PAO,lys}$	Fraction of X$_I$ generated in X$_{PAO}$ decay	S_{NH}	Ammonium and ammonia nitrogen (NH$_4$ + NH$_3$)
GAOs	Glycogen Accumulating Organisms	S_{NO}	Nitrate and nitrite (NO$_3$ + NO$_2$) (considered to be NO$_3$ only for stoichiometry)
HRT	Hydraulic Retention Time	S_O	Dissolved oxygen
K_2PO_4	Dipotassium Phosphate	S_{PO4}	Soluble inorganic phosphorus
$K_{Alk,PAO}$	Half-saturation coefficient for S$_{ALK}$	SRT	Sludge Retention Time
K_{fGly_PAO}	Half-saturation coefficient for X$_{GLY}$/X$_{PAO}$	S_S	Soluble biodegradable organics
K_{fPHA_PAO}	Half-saturation coefficient for X$_{PHA}$/X$_{PAO}$	SSMBR	Sponge Submerged MBR
K_{fStor_PAO}	Saturation constant for X$_{PHA}$/X$_{PAO}$	TOC	Total Organic Carbon
$K_{fStor\_PAO,Plim}$	Half-saturation coefficient for X$_{PHA}$/X$_{PAO}$ (P limit)	TP	Total Phosphorus
$K_{Gly,PAO}$	Half-saturation coefficient for X$_{GLY}$	TSS	Total Suspended Solids
K_{I,fPP_PAO}	Half-inhibition coefficient for X$_{PP}$/X$_{PAO}$	VFA	Volatile Fatty Acid
$K_{NHx,PAO}$	Half-saturation coefficient for S$_{NH}$	WWTP	Wastewater Treatment Plant
$K_{NOx,PAO}$	Half-saturation coefficient for S$_{NO}$	X_{GLY}	Stored glycogen in PAOs
$K_{O2,PAO}$	Half-saturation coefficient for S$_o$	X_I	Particulate undegradable organics
$K_{PHA,PAO}$	Half-saturation coefficient for X$_{PHA}$	X_{MeOH}	Metal hydroxide compounds
$K_{PO4,PAO,lys}$	Half-saturation coefficient for X$_{PHA}$ lysis (phosphorus continuity)	X_{MeP}	Metal phosphate compounds
$K_{PO4,PAO,nut}$	Half-saturation coefficient for S$_{PO4}$ as nutrient (X$_{PAO}$ growth)	X_{PAO}	Phosphorus accumulating organisms
$K_{PO4,PAO,upt}$	Half-saturation coefficient for S$_{PO4}$ uptake (X$_{PP}$ storage	X_{PHA}	Storage compound in PAOs
$K_{PP,PAO}$	Half-saturation coefficient for X$_{PP}$	X_{PP}	Stored polyphosphates in PAOs
K_{S,fPP_PAO}	Maximum ratio of X$_{PP}$/X$_{PAO}$	X_{STO}	Storage compound in OHOs
$K_{SB,PAO}$	Half-saturation coefficient for S$_S$	Y_{H2}	Yield for ohs growth(aerobic)
$K_{VFA,PAO}$	Half-saturation coefficient for S$_A$	Y_{NADH_ATP}	ATP produced per NADH or P/O ratio
MBR	Membrane Bioreactor	Y_{PAO}	Yield for X$_{PAO}$ growth per X$_{PHA}$
MEBPR	Membrane EBPR	$Y_{PAO,Ax}$	Yield for X$_{PAO}$ growth per X$_{PHA}$(Anoxic)
MLSS	Mixed Liquor Suspended Solids	$Y_{PAO,Ox}$	Yield for X$_{PAO}$ growth per X$_{PHA}$ (Aerobic)
MLVSS	Mixed Liquor Volatile Suspended Solids	$Y_{PAO\_Gly,Ax}$	Yield for formation of X$_{GLY}$ (Anoxic
$m_{PAO,An}$	Maintenance rate for X$_{PAO}$ (Anaerobic)	$Y_{PAO\_Gly,Ox}$	Yield for formation of X$_{GLY}$ (Aerobic)
$m_{PAO,Ax}$	Maintenance rate for X$_{PAO}$ (Anoxic)	$Y_{PAO\_PP,Ax}$	Yield for X$_{PP}$ formation per X$_{PAO}$ (Anoxic)
$m_{PAO,O2}$	Observed oxygen consumption for	$Y_{PAO\_PP,Ox}$	Yield for X$_{PP}$ formation per X$_{PAO}$ (Aerobic)

	maintenance		
$m_{PAO,Ox}$	Maintenance rate for X_{PAO} (Aerobic)	$Y_{PHA\_PAO,Ax}$	Yield for consumption of X_{PHA} per X_{PAO} formation (Anoxic)
$m_{PAO,Stor}$	Rate constant for respiration of X_{PHA}	$Y_{PHA\_PAO,Ox}$	Yield for consumption of X_{PHA} per X_{PAO} formation (Aerobic)
N	Nitrogen	$Y_{PP\_PHA,PAO,An}$	Yield for X_{PP} requirement (S_{PO4} release) per X_{PHA} stored (S_A utilized) (Anaerobic)
N_2O	Nitrous oxide	$Y_{PP\_PHA,PAO,Ax}$	Yield for X_{PP} requirement (S_{PO4} release) per X_{PHA} stored (S_A utilized) (Anoxic)
n_{bPP_PO4}	Reduction factor for anoxic lysis of X_{PP}	$Y_{PP\_Stor,PAO}/ Y_{PO4}$	Yield for X_{PP} storage (S_{PO4} uptake) per X_{PHA} utilized
NDEBPR	Nitrification Denitrification EBPR	$1/Y_{Stor\_PP}$	Yield for X_{PP} storage (S_{PO4} uptake) per X_{PHA} utilized
NITs	Nitrifiers	$Y_{PP\_Stor,PAO}$	Yield for X_{PP} requirement (S_{PO4} release) per X_{PHA} stored (S_A utilized)
n_{KNOx}	Reduction factor for K_{NO} for X_{PP} formation	$Y_{Stor\_PP,Ax}$	Yield for X_{PP} storage (S_{PO4} uptake) per X_{PHA} utilized (Anoxic)
n_{KO2}	Reduction factor for $K_{O2,PAO}$ for X_{PP} formation	$Y_{Stor\_PP,Ox}$	Yield for X_{PP} storage (S_{PO4} uptake) per X_{PHA} utilized (Aerobic)
n_{mPAO}	Reduction factor for anoxic endogenous respiration of X_{PAO}	$Y_{VFA\_PHA,PAO,An}$	Yield for X_{PHA} storage per S_A (Anaerobic)
$n_{mPAO,Stor}$	Reduction factor for anoxic respiration of X_{PHA}	$Y_{VFA\_PHA,PAO,Ax}$	Yield for X_{PHA} storage per S_A (Anoxic
$NO_{(x)}$	Nitrite/Nitrate	$i_{PAO,Max}$	Maximum growth rate of X_{PAO}
NO_3-N	Nitrate-N	$i_{PAO,Max,Plim}$	Maximum growth rate of X_{PAO} (when P is limiting)

1. Introduction

Controlling phosphorous (P) discharge has become a global issue in preserving surface water quality since it has been identified as the key element responsible for eutrophication in the aquatic environment. The modification of activated sludge systems for phosphorus removal (P-removal) was notably introduced through the enhanced biological phosphorus removal (EBPR) system in the late 1950s (Wentzel et al., 2008). Since then, several modifications to the EBPR systems have been proposed in the literature (Peng and Ge, 2011; Yuan and Oleszkiewicz, 2011). In the EBPR treatment system, the phosphate accumulating organisms (PAOs) of the bacterial community are enriched to accumulate large quantities of polyphosphate (poly-P) in their cells and thus enhance the biological phosphorus removal (bio-P-removal) from wastewater. The PAOs have a strict requirement of cyclic anaerobic, anoxic and aerobic conditions which consequently makes the bio-P-removal process from wastewater a more complex one compared to the nitrogen (N) and chemical oxygen demand (COD) removal.

Biological nutrient removal (BNR) efficiencies of activated sludge processes (ASPs) and the improved variations thereof suffer from critical sensitivity to various system parameters such as sludge retention time (SRT), hydraulic retention time (HRT), alkalinity and pH, temperature and various other factors. Since MBR is a modified version of ASP with the secondary clarifier of conventional ASP replaced by the membrane separator, it also tends to suffer from the similar bioprocess system constraints of ASPs affecting its nutrient removal efficiency. Although a better overall nutrient removal efficiency of MBRs over that of the ASPs has been reported (Daigger et al., 2010; Lesjean et al., 2003), the typically longer SRT and higher Membrane Liquor Suspended Solids (MLSS) concentration frequently hinder the P-removal efficiency of the MBR treatment system. Application of MBR systems in order to meet effluent quality targets for P-removal is possible if the biological processes particularly related to P-removal could be completely understood and linked to other biological process parameters.

The inherent complexity of the bio-P-removal process makes the mathematical modeling of this process tedious. Several models, such as activated sludge model 2: ASM2 (Henze et al., 1995), ASM2d (Henze et al., 1999), the Technical University of Delft Phosphorus model (TUDP model) (Meijer, 2004; van Veldhuizen et al., 1999), ASM3-bioP model (Rieger et al., 2001), UCTPHO$^+$ (Hu et al. 2007a) are typically suitable for the mathematical description of the bio-P-removal processes and their application to full-scale wastewater treatment plant (WWTP). However, the application of these models has yet to yield satisfactory results to describe completely the observed behavior of bio-P-removal processes.

Hauduc et al. (2013) recently presented a critical review of seven mathematical models (ASM1, ASM2d, ASM3, ASM3-bioP, TUDP, Barker & Dold model and UCTPHO[+]). Although it provided a deep insight into the process chemistry and the conceptual development of the models, the limitations of the models for practical modeling applications are not exposed in the review. Naessens et al. (2012a, b) reviewed different biokinetic, hydrodynamic and integrated mathematical models for the MBR systems, and mentioned some adjustments of the biokinetic and stoichiometric conversion parameters were required for their applications to the MBRs, especially regarding the specificities of the MBR for the EBPR process and its mathematical modeling.

This review, therefore, is aimed at presenting a mini-review of the state-of-the-art in bio-P-removal by conventional ASP and MBR treatment systems. Among other factors affecting the bio-P-removal, the nitrification and denitrification processes that may inhibit the P-removal efficiency of a treatment system under various operating conditions has been discussed as one of the major concerns and the challenges to overcome for simultaneous N and P-removal are outlined in the paper. The advantages and limitations of the existing mathematical models are discussed and guidelines for the potential application of these models are given for improved mathematical modeling of the bio-P-removal processes of the activated sludge treatment systems.

2. Fundamentals of biological phosphorus removal

Phosphorus can be removed from the wastewater either by precipitation and/or adsorption, or by uptake (Radjenovic et al., 2008). Only a small amount of phosphorus is naturally removed by cell synthesis (1-2% of the total suspended solids (TSS) mass in the mixed liquor) (Lesjean et al., 2003). P-removal from wastewater, therefore, greatly

needs enhancement of its biological treatment processes or the adaption of a chemical treatment process. Besides, the removal of phosphates by precipitation and adsorption requires an appropriate pH, the presence of iron or calcium ions, etc. which is very difficult to be maintained precisely in a biological WWTP.

2.1 EBPR treatment mechanism

In biological WWTPs, the state-of-the-art development of P-removal is the EBPR where the PAOs can remove phosphorus beyond its anabolic requirements by accumulating intracellular poly-P reserves. The classical treatment configuration for the EBPR in the ASP is the introduction of an anaerobic phase in the wastewater/treatment line ahead of the aerobic phase and recycling of sludge through the intermittent anaerobic and aerobic phase (Smolders et al., 1995). During the EBPR process, measurable chemical transformations occur both in the wastewater and within sludge biomass (Gebremariam et al., 2011). Organic carbon can be removed from wastewater under anaerobic conditions and stored as intracellular polyhydroxyalakanoates (PHAs) within the cell while intracellular glycogen and poly-P are codegraded, and phosphate is excreted into the wastewater. On the other hand, phosphate taken up from the wastewater can be stored in the form of intracellular poly-P under aerobic or denitrifying conditions and intracellular glycogen reserves restored as PHAs are oxidized. Because the amount of phosphate excreted during the anaerobic phase is less than the amount taken up during the aerobic or denitrifying phase, net phosphorus is taken up into the organisms, and phosphorus can be removed readily from the wastewater by wasting phosphorus-rich sludge (Mino et al., 1998; Oehmen et al., 2007).

The microorganisms in the EBPR sludge are generally classified by their ability or inability to accumulate phosphorus as PAOs or non-PAOs. Some PAOs are further classified as denitrifying PAOs (DPAOs) as they respire nitrate. Among non-PAOs, glycogen-accumulating organisms (GAOs) are notable in the published literature for chemical oxygen demand (COD) removal (Oehmen et al., 2007; Seviour and McIlory, 2008), because they are able to recycle carbon in similar fashion as PAOs and aerobically accumulate glycogen instead of polyphosphate.

Generally, PAOs act differently comparing with other microorganisms. In anaerobic conditions, they mainly take up carbon sources such as volatile fatty acids (VFAs) and store them intracellularly as PHAs. The cleavage of poly-P and release of phosphate from the cell supply the required energy for the bio-transformations. Moreover, the glycolysis of internally stored glycogen also can provide reducing power for PHA formation (Mino et al., 1998). However, the metabolic pathways of both the PAOs and GAOs are still unclear to some extent, so is the indirect role that GAOs play in P-removal.

2.2 Factors affecting the EBPR and constraints

Successful operation of the EBPR process depends on various environmental and/or operational factors. Disturbances and prolonged periods of insufficient P-removal have been observed at full-scale plants on numerous occasions even under seemingly favorable conditions for the EBPR (Oehmen et al. 2007). One of

Table 1

Factors	Remarks	References
	The imposition of the anaerobic stress alone was observed to be insufficient to select for the PAOs and other environmental and/or operational conditions could play the important role.	Okada et al. (1987)
Dynamic stress state	The capacity for the substrate uptake by the aerobic EBPR bacteria was eventually influenced by its capacity to overcome anaerobic stress. The imposition of anaerobic stress was thought as a sufficient and necessary condition to select for organisms that accumulate poly-P, because other organisms would lack the energy to compete for substrate under anaerobic	Gebremariam et al. (2011)

conditions.

Feed composition	Complete anaerobic carbon uptake with no phosphorus release was observed in a reactor fed with a mixture of acetate and glucose where the reactor sludge was dominated by a group of G-bacteria. Glucose was found to enhance GAO proliferation and impede EBPR.	Cech and Hartman (1990)
	An optimum glucose/acetate mixture of 50/50% was found to achieve significantly higher P-removal over that of 100% acetate in a sequencing batch reactor (SBR). The P-removal deteriorated with a further increased feed of glucose/acetate (75/25%).	Gebremariam et al. (2012)
	When the COD/P feed ratio was low, the anaerobic-anoxic/nitrifying (A_2N) process was unstable in attaining the required minimum total P concentrations in the effluent.	Kapagiannidis et al. (2012)
Presence of nitrate and oxygen	Recycled nitrate and oxygen reduced the mass of VFAs available to the PAOs for storage, which could hinder the phosphorus release, uptake and removal.	Wentzel et al. (2008)
	The allocation of COD for denitrification could increase the bio-P removal. The DPAOs played an important role to remove up to 40% of P along with N.	Lee et al. (2009)
	In a sequencing batch reactor, aerobic PAOs' P-uptake was more sensitive to nitrite inhibition than the process of anaerobic P-release. Partial nitrification coupled with the supply of sufficient VFAs was the key to achieve 98% EBPR. The inhibition due to the presence of nitrite in the aerobic phase may depend on the treatment process, wastewater characteristics and biomass properties.	Yuan and Oleszkiewicz (2011)
	Nitrite seriously deteriorated the performance of a granule-based EBPR system as the excretion of inhibited polysaccharides led to the instability and disintegration of the granules. Nitrite affected the microbial community structure against which the GAOs had stronger resistibility and higher recovery rate than that of the PAOs.	Zheng et al. (2013)
Competition between GAOs and PAOs	High COD/P ratios may result in P-limited conditions favoring the proliferation of GAOs, thereby leading to EBPR failure.	Liu et al. (1996)
	Acetate-COD/P ratio of ($\approx$) 10 was required to achieve high P-removal.	Schuler and Jenkins (2003)
	GAOs appeared to gain dominance over PAOs with increasing temperatures.	Whang and Park (2006)
	GAOs proliferation has been identified as the root cause for the impairment of the EBPR .	Thomas (2008)
	The COD must have a sufficient portion of VFAs. Increasing pH could give an advantage to PAOs, while alkaline conditions inhibited GAO proliferation without affecting PAO metabolism.	Gebremariam et al. (2011) and Liu et al. (1996)
	Detrimental effect of nitrite/free nitrous acid (FNA) on the anaerobic metabolism of the PAOs was observed in a study of the EBPR in a SBR. FNA decreased the acetate uptake, PHA production to VFA uptake and the rate of glycogen degradation, while the phosphate release to acetate uptake by the PAOs was substantially increased due to the competitive advantage of GAOs over the PAOs.	Ye et al. (2013)
SRT	A decreased P-removal at longer SRT (> 20 days) was attributed to the possibility that PAOs did undergo competitive conditions with GAOs.	Yoon et al. (2004)
	High SRTs along with the low F/M ratio as a result of high suspended solids in the oxic tank led to the decrease of bio-P removal efficiency.	Ersu et al. (2010)
	For the SRT maintained at 30 days, P-removal efficiency was found higher at 20 °C (> 90%) than at 30 °C (60%). The treatment efficiency could be increased by removing excess sludge equally throughout the sludge bed.	Bassin et al. (2012)
Internal recycling time mode and HRT	As the anoxic/anaerobic time ratio increased, N-removal rate increased but P-removal rate decreased. The organic substrate was consumed more for denitrification rather than phosphorus release in the limited condition of readily biodegradable substrate. Decreasing HRT increased both N and P-removal efficiency due to the increased F/M loading ratio which enhanced the biological capacity and activity of denitrifying bacteria.	Song et al. (2009)

the major constraints of sustaining EBPR system operation is perhaps

maintaining the favorable aerobic/anaerobic stress state for the EBPR bacteria. The

capacity for the substrate uptake by the aerobic EBPR bacteria is eventually influenced

by its capacity to overcome anaerobic stress. The appropriate feed composition to maintain a stable COD/P ratio can also be crucial for the successful operation of EBPR (Kapagiannidis et al., 2012). Moreover, the inhibition of the P-removal by the presence of nitrate and oxygen has also been widely studied specially in cases where simultaneous removal of the nitrogen and phosphorus is desired (Lee et al., 2009; Yuan and Oleszkiewicz, 2011).

In addition, although the nature of competition between PAO and GAO and its role in EBPR deterioration have not been elucidated fully yet, to control competition between PAOs and GAOs has been considered as the major challenge for the deterioration of P-removal in EBPR plants (Gebremariam et al. 2011). As the environmental and/or operating process parameters (e.g. temperature, pH, carbon type, COD/P ratio, sludge age, etc.) stimulating the PAO-GAO competition can result in the competitive advantage of GAOs over the PAOs, they have been identified as the influential factors for the proliferation of GAOs. Table 1 summarizes the major findings of factors and constraints affecting the successful operation of EBPR.

Table 1: Factors and constraints affecting the EBPR

2.3 Recent studies on inducing mechanism for bio-P-removal

It was reported that the bio-P-removal could be achieved in an ASP system using both glucose and acetate as the sole carbon source if the idle period is suitably extended (Wang et al., 2008). Recently, Wang et al. (2012) proposed an inducing mechanism for poly-P accumulation by introducing the concept of the aerobic/extended-idle (AEI) process. In the AEI process, an idle P-release accompanied by a low idle PHA production was observed to induce some cells to effectively uptake phosphorus in excess of the metabolic requirement. With the increase of idle P-release,

P-removal efficiency linearly increased. The results also showed that a long idle period with a low level of intracellular glycogen could significantly increase P-release contents, thus remarkably enhancing P-removal performances.

Podedworna and Sudol (2012) evaluated two different operating strategies through the application of such operating conditions in a sequencing batch reactor (SBR) that would enable the achievement of the highest possible share of denitrifying P-removal in nutrient removal. The common feature of both of these strategies was a forced anoxic phase in the SBR treatment cycle. The first one was based on an intermittent aeration, which led to periodic occurrence of anoxic conditions when the uptake of phosphate could occur. The second strategy was based on mimicking the (anaerobic/anoxic/oxic-A_2O) process and forcing an anoxic phase straight after an anaerobic phase. The reactor with the first operating condition did not allow the achievement of significant denitrifying P-removal although DPAO/PAO ratio was equal to 50.5%. It was reported in the study that almost the entire load of orthophosphates was removed in aerobic conditions right after the anaerobic phase, even though that aerobic period lasted only 20 minutes. On the contrary, the highest share of denitrifying P-removal (above 80%) in the total removal of phosphorus was guaranteed in the second strategy for a SBR with a forced anoxic phase occurring after an anaerobic phase where the highest DPAO/PAO ratio was 82.8%.

3. Specific aspects of phosphorus removal by MBR treatment processes

The EBPR in MBR treatment system is not easily achievable especially with weak sewage and with longer SRT which are common operating conditions in MBR (Lee et al., 2009). The specificities of MBR systems such as the solid-liquid separation by membrane, the high MLSS or MLVSS concentration and the high SRT may induce

significant differences in the sludge properties and dynamic behavior of MBR systems as compared to the well-known conventional ASPs. In addition, the competition between PAOs and other heterotrophs would limit available carbon and energy for anaerobic P-release in weak wastewater (Lee et al., 2009). Ersu et al. (2010) attributed the decrease of bio-P removal efficiency to possible increase in lysis of microbial cells at high SRTs along with the low F/M ratio as a result of high suspended solids in the oxic tank. Possible nitrate recycle to the anaerobic zone may also reduce P-release when internal sludge recycle is used. However, the MBR treatment system may achieve significantly better P-removal under conditions that provide suitable environment for the proliferation of PAOs (Silva et al., 2012). Also, the membrane may completely retain the PAOs whose size is typically larger than microfiltration membrane pores (0.2 μm) (Radjenovic et al., 2008). However, the MBR system serve the purpose of other biological nutrient removal for which several interventions such as chemical addition, reconfiguration of the basic treatment systems are made. These may positively or negatively influence the performance of a particular system for the bio-P-removal.

3.1 Effects of chemical addition

P-removal in MBRs has been successfully achieved at lab-scale and full-scale studies through either exclusively by biological treatment or by combination of biological and chemical addition (Adam et al. 2003; Daigger et al. 2010; Liu et al. 2011). A very low effluent TP concentration (0.032mg P/L) was achieved in a pilot plant MBR (Liu et al., 2011) through biological removal with a limited chemical addition in which the chemical addition did not affect other biological processes. However, simulation results for the calibration period indicated that the excessive chemical addition might negatively impact the bio-P-removal.
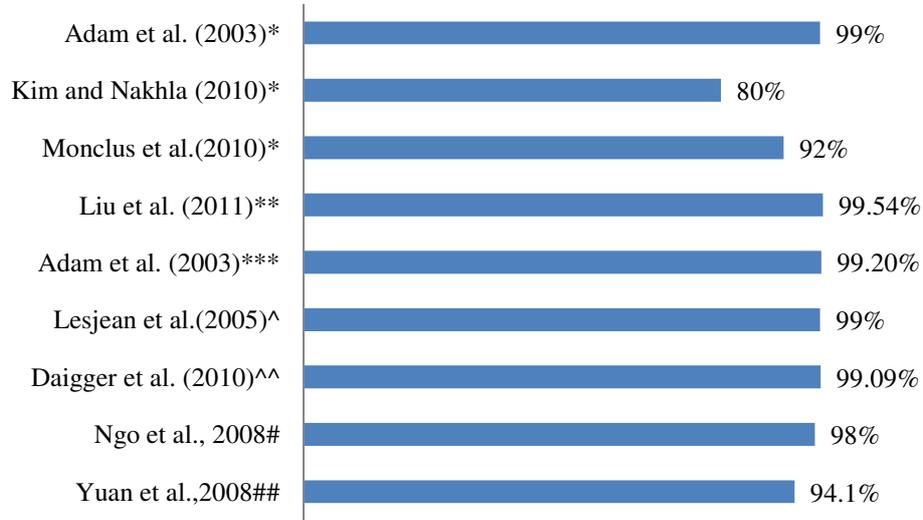
Fig. 1

Fig.1- Comparative chart of P-removal studies in MBR ([*] Biological Process; [**] Biological process + chemical process; [***]Post denitrification; ^ Pre/Post de-nitrification+ chemical process; ^^ Pre + Post de-nitrification+ chemical process; [#] Alternating anaerobic and anoxic

3.2 Effects of the change of treatment sequence

Designs catering for intermittent aerobic and anoxic conditions have also been introduced into different MBR systems which provide more control in order to maintain the conditions favorable for P-removal by the MBRs. Notable among them is the introduction of intermittent aeration methods in several submerged MBR systems. Zhang et al. (2006) examined a sequencing batch membrane bioreactor (SBMBR) in alternating aerobic and anoxic/anaerobic condition for enhancing N and P-removal up to approximately 90%. A sponge submerged MBR (SSMBR) at lab-scale was demonstrated to achieve high simultaneous N and P-removal (Ngo et al., 2008).The SSMBR system achieved 98% of P-removal efficiency which was ascribed to the fact that the sponge provided a good anoxic condition around the surface of the sponge and

anaerobic condition inside the sponge. After assessing two full-scale MBR, Daigger et al. (2010) provided guidelines for the design of MBR to achieve total P-concentration as low as 0.05 mgP/L, viz.: (1) direct the membrane recirculation flow to the aerobic zone; (2) provide intense mixing at the inlets of the anaerobic and anoxic zones; (3) control internal recirculation rates to maintain the desired MLSS distribution; and (4) control supplemental metal salt addition in proportion to the residual P after bio-P-removal. A comparative chart shown in Fig. 1 indicates several MBRs' performance efficiency in terms of P-removal after different manipulations of its basic configuration.

In order to reduce the impact of the products of nitrification on the P-removal processes, a very unconventional combination of post-denitrification and enhanced bio-P-removal (Fig. 2) in MBR could be an option even without supplementary carbon source (Kraume et al., 2007). Adam et al. (2003) studied the performance of a bench scale submerged MBR under two different EBPR configurations. 99% and 99.2% TP reduction were achieved with pre- and post-denitrification mode, respectively. In another study, Lesjean et al. (2005) found 90% P-removal in both the pre and post-denitrification modes but improved N-removal was achieved in the post-denitrification method. In addition to post-denitrification, other concepts like nitrification denitrification enhanced bio-P-removal (NDEBPR) and nearly plug flow membrane bioreactor (NPFMBR) could be cost-effective and environmentally sound where simultaneous COD, N and P-removal are required. Most recently, Sibag and Kim (2012) investigated NDEBPR in an alternating hypoxic/oxic MBR based on the findings that a defined anaerobic condition was not a prerequisite of high P-removal in MBRs because of the anaerobic micro-niches within the sludge flocs (Silva et al., 2012). It was
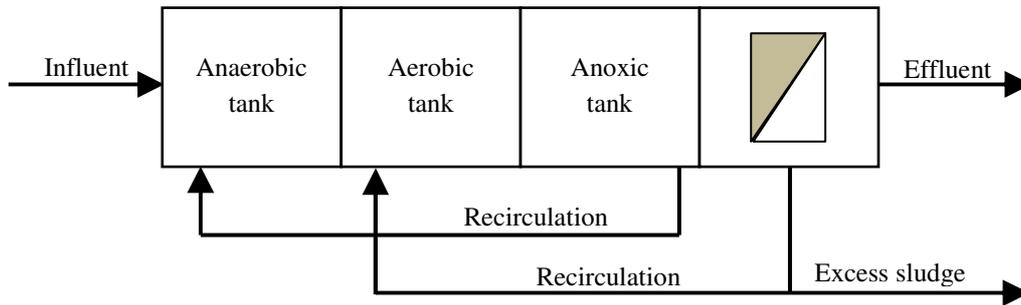
Fig. 2

Fig.2- Flow sheet for MBR with enhanced biological phosphorus removal and post-dentrification (adapted from Kraume et al. 2007)

Fig. 3- Flow diagram of anaerobic storage and aerobic growth of PAOs in ASM2 and ASM3-bio-P model (ASM2 adapted from Ng and Kim 2007; TUDP model adapted from van Loosdrecht et al. 2008)

concluded that strict anaerobic or anoxic maintenance of the system and process susceptibility to low organic loading were major concerns in NDEBPR. Results of long-term observations (Meng et al., 2012a) showed that average removal degrees of COD, TN and TP reached 95%, 85%, and 89% respectively at the steady operation period of NPFMBR.

Figure 2: Flow sheet for MBR with enhanced biological phosphorus removal and post-dentrification (adapted from Kraume et al. 2007)

4. Mathematical models for the EBPR processes in ASP and MBR

The EBPR process has been typically described by two basic types of mathematical models, namely the metabolic models and the activated sludge models (ASM). Both of these two models are composed of sets of stoichiometric and kinetic

expressions that describe the biochemical transformations of the EBPR process and other relevant biological nutrient removal processes of ASPs and MBR systems (Oehmen et al., 2007). They have also been combined in some models in order to simulate the behavior of full-scale and laboratory-scale EBPR plants.

Although metabolic models have been employed to investigate the competition between PAOs and GAOs and the optimization of P-removal performance in EBPR systems, as neither PAOs nor GAOs have been obtained in pure culture, the reactions of the metabolism can only represent the reaction stoichiometry based on assumed biochemical pathways. Hence, substrate, energy and reducing power balances, minimizing the need for site-to-site parameter calibration are the key points to obtain the yield coefficients in metabolic models theoretically. In addition, the comparison of experimentally determined stoichiometry with the theoretical model predictions has allowed better understanding of the EBPR processes in many cases (Oehmen et al., 2007; Yagci et al., 2003).

Normally, ASM1 (Henze et al., 1987) and ASM3 (Gujer et al., 1999) are mainly used to simulate COD and N-removal processes. To simulate full-scale EBPR processes, the ASM2 (Gujer et al., 1995; Henze et al., 1995) and ASM2d (Henze et al., 1999) have been most widely used. Being an updated model of ASM2, ASM2d comprises the denitrification capability of PAOs. All the ASM models can describe the bulk biochemical transformations of soluble and particulate compounds in the sludge through a set of stoichiometric and kinetic expressions. Nevertheless, determining the yield coefficients experimentally rather than theoretically distinguish the ASM models from the metabolic models. In all ASM models, PAOs take up acetate as the sole carbon source, while PHA (more specifically, PHB) is the sole carbon storage polymer cycled

by PAOs. Although the existence of GAOs is not considered in these models, some modified versions of ASM2 have been formulated to incorporate glycogen as a separate storage polymer in addition to PHA, as well as the growth and activity of GAOs (Mino et al., 1995; Oehmen et al., 2007).

The combination of metabolic and ASM models offers an approach to solve the problem of the model complexity due to recent

Table 2

Models	ASM2 (Henze et al., 1995)	ASM2d (Henze et al., 1999)	ASM3-bio-P (Rieger et al., 2001)	TUDP (e.g. Meijer 2004)	UCTPHO+ (Hu et al., 2007a)
Major processes involved with the phosphorus accumulating organisms	Storage of X_{PHA} Storage of X_{PP} Lysis of X_{PAO} Lysis of X_{PP} Lysis of X_{PHA} Aerobic growth of X_{PAO} on X_{PHA} Precipitation of S_{PO4} Redissolution of S_{PO4}	Storage of X_{PHA} Aerobic Storage of X_{PP} Anoxic Storage of X_{PP} Anoxic growth on X_{PP} Lysis of X_{PAO} Lysis of X_{PP} Lysis of X_{PHA} Precipitation of S_{PO4} Redissolution of S_{PO4} Aerobic growth of X_{PAO} on X_{PHA}	Storage of X_{PHA} Aerobic storage of X_{PP} Anoxic storage X_{PP} Aerobic lysis of X_{PP} Anoxic lysis of X_{PP} Anoxic growth on X_{PHA} Anoxic respiration of X_{PHA} Aerobic growth of X_{PAO} on X_{PHA} Aerobic respiration of X_{PHA} Aerobic endogenous respiration of X_{PAO} Anoxic endogenous respiration of X_{PAO}	Aerobic storage of X_{PP} Anoxic storage of X_{PP} Anoxic storage of S_A Aerobic, anaerobic and anoxic maintenance Aerobic X_{PHA} consumption Aerobic X_{GLY} formation Anoxic X_{GLY} formation Anaerobic Storage of S_A Anoxic X_{PHA} consumption	Aerobic growth of X_{PAO} on X_{PHA} with S_{NH4} Aerobic growth of X_{PAO} on X_{PHA} with S_{NO3} Heterotrophic decay but S_{PO4} limited Conversion of S_f to S_A but S_{PO4} limited Anoxic growth of X_{PAO} on X_{PHA} with S_{NH4} Aerobic growth of X_{PAO} on X_{PHA} with S_{NO3} Aerobic decay X_{PP} lysis on anaerobic decay X_{PHA} lysis on anaerobic decay X_{PP} cleavage for anoxic maintenance X_{PP} cleavage for anaerobic maintenance Sequestration of S_A by X_{PAO}
EBPR	Yes	Yes	Yes	Yes	Yes
Chemical P-removal	Yes	Yes	No	No	No
Fermentation	Yes	Yes	No	Yes	Yes
Reactions	19	21	23	22	35
State variables	19	19	17	17	16
Full-scale	CAS Yes	Yes	Yes	Yes	BNRS

application	MBR	No	Yes	No	No	No

improvements in modeling and makes the model easy to use in practice. In full-scale WWTPs, metabolic models have been coupled with ASM models to model N and P-removal. The TUDP model developed at the Technical University of Delft, which combined metabolic model and ASM2d model, has been successfully applied to domestic WWTPs with numerous configurations such as UCT (University of Cape Town Process) reactor, modified UCT and A_2N (Oehmen et al., 2007; Meijer et al., 2001; van Veldhuizen et al., 1999). Considering the relevance of a particular model including kinetics of bio-P removal, the following models are discussed briefly regardless of their classification under the metabolic or ASM model families or the combination of both. Table 2, 3 and 4 give comparison of the some of the basic mathematical model parameters, their default stoichiometric and kinetic values respectively which are typically used for the modeling of bio-P-removal in ASP and MBR.

Table 2: Comparison of different mathematical models for bio-P-removal (updated from Garnaey et al., 2004)

Table 3: Stoichiometric parameters and their default values for PAOs of different models reviewed in the study (Hauduc et al., 2010)

Table 4: Kinetic parameters and their default values for PAOs of different models reviewed in the study (Hauduc et al., 2010)

4.1 ASM2 /ASM2d model for modeling phosphorus removal in ASPs

The mathematical modeling to describe EBPR system has been started with the ASM2, which is the extension of ASM1 incorporating EBPR process variables and chemical P-removal via precipitation. The model incorporates PAOs to the biomass consisting of heterotrophs and autotrophs. In the ASM2 model, the PAOs are capable of accumulating P under aerobic conditions and storing them in the form of cell internal poly-P and PHA. However, it is assumed in the model that the PAOs are incapable of any denitrifying activity and can only grow on stored PHA of the cell using energy derived from the hydrolysis of poly-P, which leads to the release of soluble phosphates (S_{PO4}) (Ng and Kim, 2007). Growth of PAOs occurs only under aerobic conditions and on cell internal organic material in the model. Storage is not dependent on the electron acceptor conditions, but is only possible when fermentation products such as acetate are available. For the lyses of PAOs, separate process rates are provided in the model. Phosphate precipitation and redissolution are also modeled by considering that S_{PO4} reacts with metal hydroxides to form a metal phosphate precipitate. The ASM2d model builds on the ASM2 model, adding the denitrifying activity of PAOs so as to allow a better description of the generation and accumulation of phosphate and nitrate. Retaining other details of ASM2, the model additionally assumes that the PAOs can use internal cell organic storage products for denitrification and thus grow under anoxic conditions leading to the addition of two rate processes to ASM2 processes: the storage of polyphosphates and growth of PAOs under anoxic conditions (Ng and Kim, 2007).

The default model parameters and assumptions made in the basic ASM2d model have also been modified in different ASM2/2d based models in order to validate some relevant features of nitrification/denitrification associated with bio-P-removal. Penya-Roja et al. (2002) calibrated and validated ASM2d model with data obtained from pilot

plant treating municipal wastewater from the city of Valencia (Spain). Differences between the values of calibrated model parameters and default values of those in ASM2d were explained. The calibration of the model was done by changing Y_{PO4}, Y_{PAO}, and K_{MAX} and the model simulation could reproduce the experimental results of P-release and uptake. Swinarski et al. (2012) expanded ASM2d to incorporate a new readily biodegradable substrate (ethanol or fusel oil), which is not available for PAOs under anaerobic conditions but can support growth and denitrification by PAOs under anoxic conditions. In comparison with ASM2d, the new model better predicted COD, NO_3-N, and PO_4-P behaviors in batch experiments under anaerobic, anoxic, and aerobic conditions with ethanol and fusel oil. However, for model simulations of the addition of ethanol to the anoxic zone of a full-scale BNR facility, both models predicted similar effluent NO_3-N and TN concentrations.

4. 2 The TUDP model

The research group at the Delft University of Technology associated with IWQW task group presented the TUDP (Meijer 2004; van Veldhuizen et al., 1999) model to describe EBPR of the ASPs. The model combined the total metabolism of PAOs with the heterotrophic, hydrolytic and autotrophic reactions of ASM2d. According to the mechanism described in the model, PAOs store X_{PHA} under anaerobic condition with the consumption of cell internal glycogen (X_{GLY}) and X_{pp} releasing a large amount of phosphate into the bulk liquid. X_{PHA} is oxidized in the subsequent aerobic (or anoxic) condition and the energy generated in this phase is mostly used to restore X_{GLY} and X_{pp}. PAO's take up phosphate from the bulk liquid to restore X_{pp} and the remaining energy is used for growth and maintenance. The TUDP model uses the maintenance instead of the

Table 4

Notation[*]	Unit	Value (T= 20^{0}C)			
		ASM2d (Henze et al., 1999)	TUDP (Meijer 2004)	ASM3-BioP (Rieger et al., 2001)	UCTPHO+ (Hu et al., 2007a)
q_{PAO,VFA_Stor}	g X_{STO}·g X_{PAO}^{-1}·d^{-1}	3			6.0
$q_{PAO,VFA\_PHA,An}$	g X_{PHA}·g X_{PAO}^{-1}·d^{-1}		8		
$q_{PAO,VFA\_PHA,Ax}$	g X_{PHA}·g X_{PAO}^{-1}·d^{-1}		1.2		
q_{PAO,SB_Stor}	g X_{STO}·g X_{PAO}^{-1}·d^{-1}			6	
$q_{PAO,PO4\_PP}$	g X_{PP}·g X_{PAO}^{-1}·d^{-1}	1.5	0.1	1.5	
q_{PHA_PAO}	g X_{PHA}·g X_{PAO}^{-1}·d^{-1}		5.51		
q_{Gly}	g X_{GLY}·g X_{PAO}^{-1}·d^{-1}		0.93		
K_{S,fPP_PAO}	g X_{PP}·g X_{PAO}^{-1}	0.01		0.05	
K_{I,fPP_PAO}	g X_{PP}·g X_{PAO}^{-1}	0.02		0.05	
K_{fStor_PAO}	g X_{STO}·g X_{PAO}^{-1}	0.01		0.1	0.18
$K_{fStor\_PAO,Plim}$	g X_{STO}·g X_{PAO}^{-1}				0.18
$K_{VFA,PAO}$	g S_A·m^{-3}	4	4.0		1
$K_{O2,PAO}$	g S_O·m^{-3}	0.2	0.2	0.20	0.002
$K_{NOx,PAO}$	g S_{NO}·m^{-3}	0.5	0.5	0.5	0.2
$K_{NHx,PAO}$	g S_{NH}·m^{-3}	0.05	0.05	0.05	0.01
$K_{Alk,PAO}$	mol HCO_3^-·m^{-3}	0.1	0.01	0.1	
$K_{PO4,PAO,upt}$	g S_{PO4}·m^{-3}	0.2	1	0.20	0.25
$K_{PO4,PAO,nut}$	g S_{PO4}·m^{-3}	0.01	0.02	0.01	
$K_{PO4,PAO,lys}$	g S_{PO4}·m^{-3}				0.1
$K_{PP,PAO}$	g X_{PP}·m^{-3}				1
$K_{SB,PAO}$	g S_S·m^{-3}			10	
$K_{PHA,PAO}$	g X_{PHA}·m^{-3}		0.01		
$K_{Gly,PAO}$	g X_{GLY}·m^{-3}		0.01		
K_{fGly_PAO}	g X_{GLY}·g X_{PAO}^{-1}		0.01		
K_{fPHA_PAO}	g X_{PHA}·g X_{PAO}^{-1}		0.2		
$f_{PP\_PAO,Max}$	g X_{PP}·g X_{PAO}^{-1}	0.34	0.01	0.2	
$f_{Gly\_PAO,Max}$	g X_{GLY}·g X_{PAO}^{-1}·d^{-1}		0.5		
$\mu_{PAO,Max}$	d^{-1}	1		1.0	1.2
$\mu_{PAO,Max,Plim}$	d^{-1}				0.42
$n_{\mu PAO}$	-	0.6		0.6	0.35
n_{qPAO}	-		0.8		
n_{mPAO}	-			0.33	
n_{bPP_PO4}	-			0.33	
n_{KO2}	-		0.22		
n_{KNOx}	-		0.22		
$m_{PAO,Stor}$	d^{-1}			0.2	
$n_{mPAO,Stor}$	-			0.33	
$m_{PAO,O2}$	g S_O·g X_{PAO}^{-1}·d^{-1}		0.096		
$m_{PAO,Ox}$	d^{-1}		0.06		
$m_{PAO,Ax}$	d^{-1}		0.09		
$m_{PAO,An}$	g P·g X_{PAO}^{-1}·d^{-1}		0.05		
b_{PAO}	d^{-1}	0.2		0.33	0.04
b_{PP_PO4}	d^{-1}	0.2		0.20	0.03
b_{Stor_VFA}	d^{-1}	0.2			

[*]According to the standardized notation rules by Corominas et al. (2010)

decay concept, and it is assumed that the bio-P-organisms always have internal substrate X_{PHA} available to satisfy the requirement for the maintenance of cell structure (van Veldhuizen et al., 1999).

The integrated metabolic model (TUDP model) was first applied for the validation on a full-scale WWTP Holten in Netherlands (van Veldhuizen et al., 1999). However, the appropriate methods for model calibration could not be suggested. Meijer et al. (2004) modified the model to solve the kinetic problems of the model, and concluded that operational conditions greatly influenced the WWTP operation. They also indicated that steady state conditions were not suitable to calibrate model kinetics since the growth of PAO's was mainly determined by the glycogen formation rate. Furthermore, it was mentioned that the temperature changes should be modeled as PAO concentration was strongly influenced by preceding (seasonal) temperature changes.
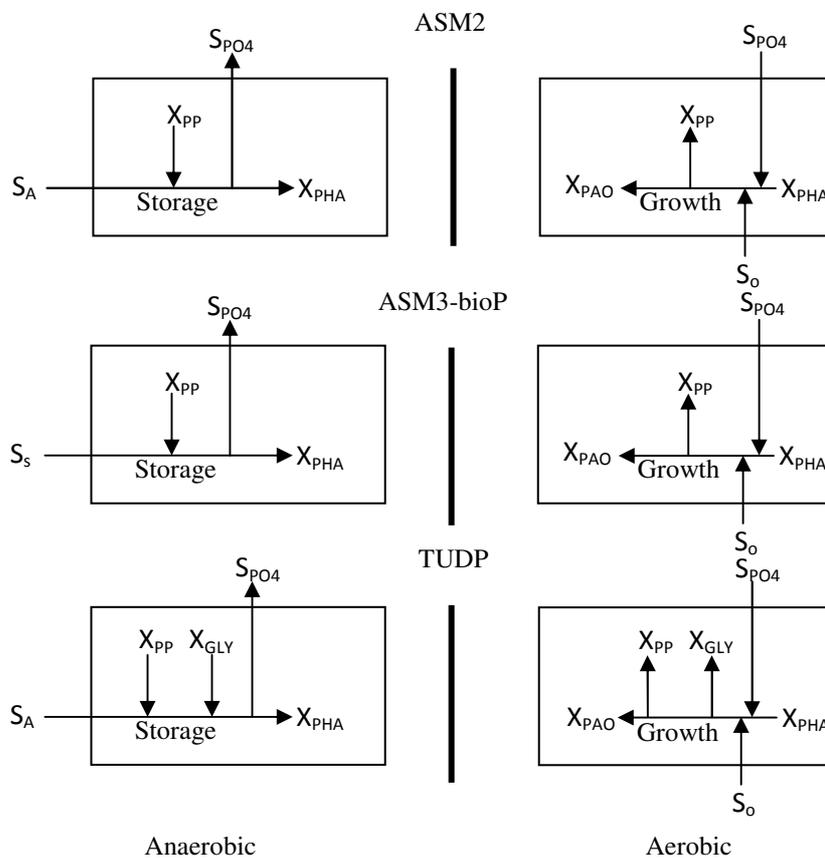
4.3 ASM3-bioP model

The ASM3-bioP model (Rieger et al., 2001) integrated the bio-P-removal to ASM3 (Gujer et al., 1999) including both the EBPR by the PAOs and the P-uptake during the growth of organisms. The model has four specific state variables (S_{PO4}, X_{PAO}, X_{PHA}, X_{PP}) identical to ASM2d as well as 13 components of ASM3. The main limitation of the ASM3-bioP model is that no reliable characterization methods are suggested for some important parameters such as poly-P and glycogen. The model cannot be validated for a low resolution of COD, N and P and it also has limitation to accurately describe P-removal in all growth phases. The model does neither consider the decreasing phenomena of storing and response of PHA under anoxic condition nor does it include the anaerobic decay and chemical precipitation. In addition, fermentation is not considered in ASM3-bio-P model and hydrolysis is considered as a rate-limiting step. Thus, this can be a major limitation of the model especially in cases where hydrolysis is no longer the rate limiting step (Hauduc et al., 2013). Although the model could successfully predict the process behavior in a pilot-scale reactor, reliable prediction of N

and phosphate variations caused by changing of operating conditions in the full-scale plants would confirm its practical applicability.

Sun and Song (2009) proposed an advanced model based on the ASM3-bioP model considering the effects of competition among microorganisms for organic carbon, nitrate and ammonia. In the so called Fully Coupled Activated Sludge Model No. 1 (FCASM1), they added two equations into the kinetic expression to show the restraint on the nitrifier growth and the storage of X_{PHA}.

Fig. 3

However, the representation of interaction mechanism among the microorganisms cannot adequately describe the competition among them for oxygen, ammonia and nitrogen. Although the model seems to be more practical than the ASM3-

bioP model, it still needs calibration by using observations at full-scale WWTPs. Ni et al. (2010) expanded ASM3-bioP model incorporating the two-step nitrification, the anoxic phosphorus uptake, and the associated two-step denitrification by PAOs. The database used for simulations done by Ni et al. (2010) originates from a full-scale BNR municipal WWTP. Simulation results indicate that the calibrated model is capable of predicting the microbial growth, COD removal, nitrification and denitrification, as well as aerobic and anoxic P-removal. Trutnau et al. (2011) presented a TOC-based variant of ASM3-bioP model for the bio-P-removal, and the batch test-based calibrations showed a good match with experimental data, following modifications of the model to account for the anaerobic volumes and retention times applied in the tests.

It is evident from the above discussion that there are significant differences among the assumptions and kinetics involved in the three basic mathematical models that are typically applied to describe the EBPR processes. Although the models were subsequently developed to overcome the limitations of the previous models, neither of the models could be fully validated at modeling the observed behavior of lab-scale/full-scale wastewater treatment processes. Fig. 3 shows a schematic of the process kinetics involved for bio-P-removal in three basic mathematical models discussed above.

Fig. 3- Flow diagram of anaerobic storage and aerobic growth of PAOs in ASM2 and ASM3-bio-P model (ASM2 adapted from Ng and Kim 2007; TUDP model adapted from van Loosdrecht et al. 2008)

4.4 UCTPHO$^+$ model

In order to model the biological behavior for carbonaceous material removal, nitrification, denitrification and biological excess phosphorus removal (BEPR) for an activated sludge system with external nitrification, Hu et al. (2007a) developed a kinetic

model called UCTPHO$^+$. This model is a combination of metabolic and ASM2/2d models which has been derived from the UCTPHO model (Wentztel et al., 1992) but with modifications to address some of the deficiencies of the model ASM2/2d and Barker and Dold model (Barker and Dold, 1997). The basic UCTPHO model represented kinetics for ordinary heterotrophic organisms (OHOs) and nitrifiers as well as for the PAOs. The model also included the kinetics and stoichimetric behaviors of this three group of organisms under anaerobic, anoxic and aerobic conditions. The modified UCTPHO model, namely UCTPHO$^+$ model, was comprised of anoxic growth of PAO with associated anoxic uptake/denitrification/death/maintenance of PAO, provision for a separate reduced anoxic growth yield coefficient (Y_{H2}) for OHO growth, and the linkage of the organic N and P fractions/transformation to the corresponding COD fractions/transformation (Henze et al., 1995). It was assumed in the model that the PAOs (X_{PAO}) grow only on stored PHA (X_{PHA}) and as a result, the two PAO aerobic growth processes from UCTPHO (with ammonia and nitrate as N source) were included unmodified. Sequestration of S_A (fermentation product such as VFAs) and associated P-release were also taken unmodified from UCTPHO. Additionally, two processes were included for the aerobic PAO growth on PHA (X_{PHA}) under P-limiting (S_{PO4}) conditions: (1) The aerobic PAO growth processes are duplicated for anoxic conditions to accommodate PAO anoxic growth, but with the process rates multiplied by the reduction factor (η_{PAO}); and (2) nitrate was used as terminal electron acceptor instead of oxygen which could explain more accurately the denitrification and anoxic P uptake by PAOs (Hu et al., 2007a). In this case, poly-P (X_{pp}) could supply phosphate for the PAO synthesis while phosphorus uptake ceases, In addition, a new anoxic poly-P cleavage process was encompassed with the rate proportional to the fraction of PAOs unable to

denitrify. In this formulation, the P-release due to poly-P cleavage is assumed to be directly proportional to the S_A uptake. Thus, the model has been evaluated against a large number of experimental data sets under anaerobic, anoxic, and aerobic conditions and been successfully used to simulate a wide variety of conventional BNRAS systems (Hu et al., 2007b). Simulation results have demonstrated that the model is capable of predicting COD removal, nitrification and denitrification as well as aerobic and anoxic/aerobic P-uptake in EBPR with appropriately calibrated parameters.

However, the model considers the hydrolysis process simultaneously with growth but without taking into account the anaerobic hydrolysis which may cause limitation in its usage as it is important for bio-P models to make substrate available for storage. Besides, like the above-mentioned models discussed, as denitrification and nitrification were modeled as one-step and the same decay rate under all electron acceptor conditions is not consistent with experimental observations, the model is also not suitable to predict nitrite accumulation or N_2O production (Hauduc et al., 2013).

In addition, the models mentioned are also based on the crude assumption that all processes including N and P-removal are independent, thereby having no interactions among those processes. Therefore, due to the complexity of interaction (the coexistence of PAOs, autotrophic and heterotrophic organism) together with the asymmetry of aeration and hydraulics (no absolute area of anaerobic, aerobic and anoxic reaction) in activated sludge system, all the models discussed in the review can only partially reflect the real processes and the application of the models are limited by factors such as temperature, toxicity and alkalinity.

4.5 Application of CAS models for phosphorus removal in MBR systems

Only a few studies have evaluated the bio-P-removal performance of MBR systems using the default ASM2d model parameters. Jiang et al. (2008) used ASM2d in a simultaneous study of MBR fouling and biological nutrient removal. As the model overestimated nitrate concentration and underestimated P-concentration with the default ASM2d parameters, the model was calibrated simultaneously reducing biodegradable acetate (S_A) production in the anaerobic compartment and the aerobic/anoxic phosphorous uptake rate by trial and error (Fenu et al., 2010). In another study, Monclus et al. (2010) evaluated the performance of an MBR pilot plant for BNR during 210 days of operation using ASM2d. During the course of the experiment, P-removal efficiencies sequentially increased and a bio-P-removal efficiency of 92% was achieved eventually. However, the modeling of the observed removal of other nutrients could not be completely validated. Fenu et al. (2011) studied a full scale MBR adding the SMP fractions within the framework of a calibrated version of ASM2d. However, the removal of neither of the nutrients (N and P) could be modeled well during the model simulation. Naessens et al. (2012a) reported that the application of the ASM2d was better based to account for the activity of the PAOs with little calibration requirement for the parameters of the model.

The TUDP model was found sufficient to describe the process behavior of UCT-type membrane enhanced biological phosphorus removal (MEBPR) process (Al-Atar, 2007). The trend of the measured concentration profiles were reasonably predicted, but the exact concentration for the anoxic nitrate and the effluent ortho-phosphate were not predicted by the model. Simulation studies showed that the sludge mass distribution in the bioreactor zones of the anaerobic and the aerobic zone were critical for the bio-P-removal and the nitrification process, respectively. Recently, an integrated MBR

mathematical model has been proposed by Cosenza et al. (2013) which has been developed to describe the BNR process in addition to SMP modeling and fouling predictions in a UCT-MBR pilot plant fed with real wastewater. The ASM2d-SMP hybrid model was first introduced by Jiang et al. (2008) for the BNR description in MBR. Nevertheless, the concept of including SMP into the model considerably increased the model complexity and also varied the calibrated model parameters from default ASM2d values. Cosenza et al. (2013) found a higher value of the co-efficient of q_{pp} than that was found in the published literature. This was attributed to the fact that orthophosphate assimilation took place not only in the aerobic tank but also in the anoxic one. The model simulation took into account the increasing storage rate during the period of K_2PO_4 dosing and unmodeled release of phosphorus due to possible anaerobic conditions occurring inside the cake layer on the membrane surface which might be another reason for the higher value of q_{pp}.

The influence of enhanced BNR process depending on sludge characteristics (e.g., EPS/SMP) and its consequence on membrane fouling, occurrence of nitrification, denitrification and P-removal possibly impact the generation and utilization of EPS/SMP (Meng et al., 2012b) within the bioreactor. The study of the role of membrane rejection on the metabolism of microorganisms responsible for N and P-removal are currently at a rudimentary level. However, the longer SRTs typically employed in the MBR treatment and also the higher MLSS and MLVSS concentration may induce competitive advantage of GAOs over the PAOs. In this backdrop, different configurations of MBR controlling the SRT or feed composition have provided partial success of simultaneous N and bio-P-removal. The mathematical modeling of such specificities of MBR systems is yet to be implemented by state-of-the-art mathematical

modeling tools. The fundamental differences between the conventional ASPs and MBR need to be taken into account while applying the mathematical modeling for simulating the behavior of MBR systems for bio-P-removal. The following key points are re-emphasized in this regard

- The longer SRT, especially in case of an MBR fed with weak sewage may induce significant differences in the capabilities of PAOs for the storage of PHA and its further consumption. The competition between PAOs and other heterotrophs may limit available carbon and energy for anaerobic P-release in weak wastewater (Lee et al., 2009). This needs to be taken into consideration in the modeling application by adjusting the reaction stoichiometry for the PAOs and GAOs with reasonable assumption of their reaction rate as well as that for the relevant yield coefficients.

- Unlike the fate of PAOs in the conventional ASPs, significant amount of PAOs are retained in the bioreactor due to their increased size compared to the microfiltration pore sizes of MBRs. The PAOs thus retained has obviously other associated influences on the bioprocesses of MBR as compared to the same of ASPs. Therefore, this warrants revision of PAOs' associated model parameters and rate processes for mathematical modeling of MBR system.

5. Conclusion

The EBPR in a WWTP cannot be treated as a discrete issue as it is critically sensitive to system's operating/environmental conditions, such as SRT, HRT, pH, temperature, alkalinity, COD/P ratio, intermittent aerobic/anoxic operation and other associated factors. The various configurations of ASPs/MBRs may also affect the removal kinetics of other nutrients. Therefore, the bio-P-removal model should have provisions for the periodic adjustment of factors such as stoichiometric reaction rates

for the PAOs and GAOs and the relevant yield coefficients. An optimized configuration of a treatment system for bio-P-removal is desired without compromising the treatment quality targets for other nutrients.

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