

### 5.1.3 Model of biological phosphorus removal

#### 5.1.3.1 Enhanced cultures

Based on the concepts presented in the previous section, a model was developed at the university of Cape Town (UCT) to describe the processes involved in biological phosphorus removal, including the release of phosphorus in the anaerobic zone and the excess phosphorus absorption in the subsequent aerobic zone. This model is an extension to the general activated sludge model and includes the presence of the PAO. To investigate the behaviour of PAO, Wentzel et al (1986) operated activated sludge systems using acetate as the only source of COD in the influent, resulting in a culture enhanced with PAO. Based on experimental observations it was concluded that:

- In the anaerobic zone there is a proportional relationship between the absorbed concentration of acetate and the concentration of released phosphate. This constant  $f_{pr}$  has a value of  $0.5 \text{ mg P.mg}^{-1} \text{ COD absorbed}$ ;
- The PHB generated in the anaerobic zone will be completely utilised in the subsequent aerobic zone;
- The absorption of phosphorus in the anoxic- and aerobic zones by the PAO produces polyphosphate, which is internally stored. Depending on the amount of acetate present in the influent (and thus on the amount of PHB formed), this can result in a maximum phosphorus content of 38% in the active biomass.

When comparing the PAO with the normal micro-organisms present in activated sludge systems, the following differences can be observed (apart from the increased phosphorus content):

#### (1) Release of phosphate in the anaerobic zone

Under anaerobic conditions and the presence of an adequate substrate (VFA such as acetate), the PAO transforms internally stored polyphosphate into phosphate, a process that liberates the energy required for the absorption of the VFA. The release of phosphate is described as:

$$P_r = f_{pr} \cdot S_{VFA} \quad (5.1)$$

Where:

$P_r$  = phosphate concentration released to the liquid phase ( $\text{mg P.l}^{-1}$ )

$S_{VFA}$  = concentration of volatile fatty acids ( $\text{mg COD.l}^{-1}$ )

$f_{pr}$  = phosphorus release constant =  $0.5 \text{ mg P.mg}^{-1} \text{ COD}$ )

#### (2) Decay rate of PAO

The decay rate of PAO is significantly less than that of the other (heterotrophic) bacteria in activated sludge. The value for the decay rate constant  $b_p$  was determined experimentally to be  $0.04 \text{ d}^{-1}$  at  $20^\circ\text{C}$ .

### (3) Quantity and composition of activated sludge and the endogenous residue

It was determined that 25 percent of the bacterial mass remained as endogenous residue after decay:  $f_{ep} = 0.25$ . However, the endogenous residue does not contain the high poly-P content of the active PAO bacterial mass. Instead the phosphorus content was equal to that of normal biomass: i.e. 2.5 percent. Thus, when PAO decay, the stored polyphosphate is released into the liquid phase.

### (4) Ratio VSS/TSS

Due to the large inorganic fraction in PAO (mainly stored polyphosphate), the ratio between VSS and TSS ( $f_{vp}$ ) is equal to  $0.46 \text{ mg VSS.mg}^{-1} \text{ TSS}$ . This is significantly smaller than the  $f_v$  value of normal activated sludge, which typically is between 0.70 to 0.85  $\text{mg VSS.mg}^{-1} \text{ TSS}$ . The amount of excess sludge produced is therefore much higher in systems with PAO sludge than in conventional systems.

### (5) Denitrification

Wentzel et al (1986) observed that the denitrification rate of the PAO in an anoxic environment is very small and for all practical purposes can be ignored. In the first version of the Activated Sludge Model II, which included bio-P removal, PAO are therefore modelled as being incapable of denitrification. However, since in practice a significant rate of phosphate uptake is observed in the anoxic zones of full-scale bio-P removal plants, it can be concluded that this is not correct.

An explanation for the observation of Wentzel et al (1986) on the absence of denitrification capability of the PAO can be derived from the data reported by Kuba et al (1995). The cytochrome oxidation enzyme required for aerobic oxidation is always present in the heterotrophic PAO, even when the organisms have been cultivated under strictly anaerobic/anoxic conditions. However, this is not the case for the equivalent enzyme required for anoxic oxidation (nitrate reductase).

When denitrifying PAO are cultivated under anaerobic/aerobic conditions, a large part of the nitrate reductase is lost and the denitrification capacity decreases accordingly. Once anoxic conditions are established, it takes significant time for the denitrification capacity to recover. As the experimental work of Wentzel et al (1986) was done on anaerobic/aerobic systems, the (temporary) absence of denitrification can thus be explained.

Comparing the aerobic- and anoxic P-uptake of sludge from two full-scale waste water treatment plants operating in UCT configuration, Kuba et al (1994) estimated the fraction of denitrifying PAO at a value between 40 and 50% of the total PAO biomass. He did however not compensate for the 40% reduction of growth rate observed under anoxic conditions (resulting from the lower ratio between ATP formed/NADH<sub>2</sub> used, refer to Section 5.1.1). The determination was repeated later by Janssen et al (2004) at 11 full-scale bio-P removal systems in the Netherlands: six with dedicated anoxic zones and five aeration circuits (carrousel). The average ratio between anoxic- and aerobic P-uptake was 0.54 for the systems with separate anoxic zones and 0.63 for the carrousel.

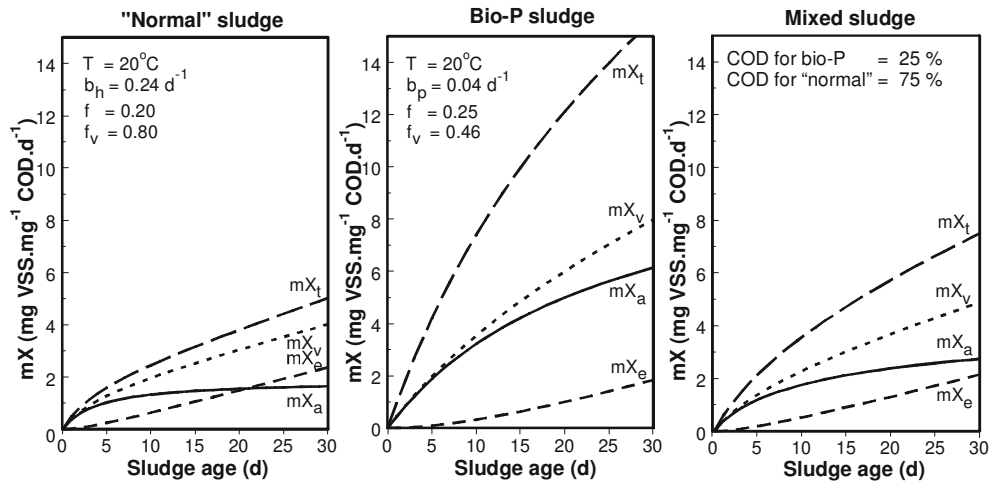
When it is taken into account that the growth rate of biomass under anoxic conditions is about 40% lower as compared to the growth rate under aerobic conditions, it can be concluded that in an activated sludge process specifically designed for combined nitrogen- and biological phosphorus removal, probably all PAO are capable of denitrification. In practice this fraction may be lower due to adverse conditions or sub-optimal design, resulting in loss of denitrification capacity, probably due to inactivation of part of the enzymes used in the denitrification process as explained above.

Therefore for design purposes a more conservative estimate might be used. For instance, from the values reported by Kuba et al. (1994), the anoxic PAO fraction of the two WWTP investigated can be estimated as  $0.4/0.6 = 0.67$  and  $0.5/0.6 = 0.83$  respectively. In Table 5.2 the values of some key characteristics of PAO as compared to those of "conventional" micro-organisms in activated sludge systems are summarised.

**Table 5.2 Parameters of PAO compared to regular heterotrophic organisms (at 20 °C)**

Parameter	Symbol	PAO	non-PAO	UoM
Phosphorus content	$f_p$	0.38	0.025	mg P.mg <sup>-1</sup> VSS
Decay constant	$b$	0.04	0.24	d <sup>-1</sup>
Endogenous residue	$f$	0.25	0.20	(-)
P-fraction end.. residue	$f_p$	0.025	0.025	mg P.mg <sup>-1</sup> X <sub>e</sub>
Ratio VSS/TSS	$f_v$	0.46	0.80	mg VSS.mg <sup>-1</sup> TSS
Denitrifying fraction	$f_{pd}$	0.6 - 1.0	1.0	(-)
Denitrification rate	$K_2/K_3$	0.10 / 0.08	0.10 / 0.08	mg N.mg <sup>-1</sup> X <sub>a</sub> .d <sup>-1</sup>
Anaer. phosphate release	$f_{pr}$	0.5	---	mg P.mg <sup>-1</sup> COD

In Fig. 5.4 the total sludge mass of the different types of sludge in a conventional activated sludge system, an enhanced PAO culture and a mixed activated sludge system are shown as a function of the sludge age. The mixed culture is based on a division of influent COD in which 25 % of the influent COD is available for PAO and 75% for the conventional organisms. In the next section it will be demonstrated that this is approximately the ratio that can be expected for domestic sewage.



**Figure 5.4 Comparison of the sludge mass and -composition in a conventional, an enhanced PAO and a mixed culture activated sludge system**

In Fig. 5.4 it can be observed that:

- The active sludge mass fraction in systems with PAO is much higher than in conventional systems, due to the slow decay rate of PAO while simultaneously the endogenous residue mass fraction of PAO is much lower;
- The total suspended solids content of the sludge containing PAO will be much higher due to the high inorganic mass fraction (predominantly poly-P) in the PAO.

### 5.1.3.2 Mixed cultures

In many municipal waste water treatment plants, the organic fraction in the influent is not in the form required by the PAO, i.e. present as volatile fatty acids. In general the fraction of VFA in domestic waste waters is less than 10% of the total COD concentration, even when the residence time in the sewer system is long and some fermentation has occurred (which produces VFA). Wentzel (1985) demonstrated that in an anaerobic environment, the conventional bacteria present in activated systems are able to convert the easily biodegradable material into VFA, which then can be absorbed by the PAO. The PAO themselves are not capable of converting the easily biodegradable material into VFA. So in those cases where the waste water does not contain sufficient VFA, the presence of conventional bacteria is a necessity to generate sufficient substrate for the PAO. Therefore, in bio-P removal systems there will always exist a mixed culture of conventional micro-organisms and PAO. Wentzel et al (1990) developed a model to describe the behaviour of an activated sludge system with such a mixed culture, based on the UCT configuration.

- (1) If nitrate is introduced into the anaerobic zone, the concentration of easily biodegradable material is reduced according to the following expression (see Eq. 4.46):

$$S'_{bsi} = S_{bsi} - r \cdot N_{nc} \cdot 2.86 / (1 - f_{cv} \cdot Y) \cdot K_1 / (K_1 + K_2) \quad (5.2)$$

Where  $S'_{bsi}$  = influent concentration of easily biodegradable material after correction for denitrification in the anaerobic zone

The factor  $K_1/(K_1+K_2)$  reflects the proportion of easily- versus slowly biodegradable organic material that is used for nitrate reduction.

- (2) In an anaerobic environment the easily biodegradable material will be fermented into VFA. Assuming there is no VFA present in the influent, Wentzel et al (1990) proposed the following expression:

$$dS_{VFA}/dt = K_c \cdot X_{a,an} \cdot S_{bs} \quad (5.3)$$

Where:

$K_c$  = fermentation constant = 0.06 litre.mg<sup>-1</sup>VSS.d<sup>-1</sup>

$X_{a,an}$  = concentration of active (non PAO) sludge in the anaerobic zone

In an UCT configuration,  $X_{a,an}$  will be less than  $X_a$  in the other reactors, as the thickened sludge from the settler is not returned to the anaerobic reactor. The dilution factor equals  $r/(r+1)$ . For a completely mixed reactor the following expression can be derived for the residual concentration of the easily biodegradable material in the effluent of the anaerobic reactor:

$$S_{bs} = [S'_{bsi}/(1+r)] / [1 + (f_{an} \cdot K_c \cdot MX_a/Q_i)/(r+1)] \quad (5.4)$$

And for a series of N equally sized anaerobic reactors:

$$S_{bsN} = [S'_{bsi}/(1+r)] / [1 + (f_{an} \cdot K_c \cdot MX_a/Q_i)/(N \cdot (1+r))]^N \quad (5.5)$$

Where:

$f_{an}$  = anaerobic sludge mass fraction  
 $MX_a$  = total active sludge mass in the system

- (3) All fermented organic material (plus any VFA present in the influent) will be taken up by the PAO and stored as PHB (this is a relatively rapid process). Therefore the concentration of organic material sequestered by the PAO is given as:

$$MS_{seq} = Q_i \cdot S'_{bsi} - (1+r) \cdot Q_i \cdot S_{bsN} \quad (5.6)$$

- (4) In the aerobic zone, the sequestered material is used by the PAO for growth and for the absorption of phosphate from the liquid phase for the production of intracellular polyphosphate. The residual organic material in the liquid phase of the aerobic reactor will be utilised by the non-PAO organisms only. Therefore the total sludge mass of the PAO and non-PAO organisms can be expressed as:

$$MX_{ap} = Y \cdot R_s / (1 + b_p \cdot R_s) \cdot MS_{seq} \quad (5.7)$$

and

$$MX_a = Y \cdot R_s / (1 + b_h \cdot R_s) \cdot (MS_{bi} - MS_{seq}) \quad (5.8)$$

The formulas presented above do not yet supply the information required to calculate the performance of an activated sludge system with biological phosphorus removal. For this it will be necessary to determine the residual concentration of easily biodegradable material in the anaerobic zone. This concentration can be calculated using the iterative procedure outlined below:

- (1) Assume that the conversion of easily biodegradable material in the anaerobic zone is complete

$$S_{bsN} = 0 \text{ and}$$

$$MX_a = Y \cdot R_s / (1 + b_p \cdot R_s) \cdot (MS_{bi} - MS'_{bsi});$$

- (2) Using the value calculated above for  $MX_a$ , calculate the new value for  $S_{bsN}$ ;  
 (3) Using the value of  $S_{bsN}$  from step (2), recalculate the new value for  $MX_a$  using Eq. (5.8);  
 (4) Repeat steps (2) and (3) until the values of  $S_{bsN}$  and  $MX_a$  are stable.

Once the concentration of the influent biodegradable organic material that will be sequestered by the PAO is known, all other important system parameters can be calculated.

The model of Wentzel et al (1990) described above has been validated extensively in a series of experimental studies where all the important factors were varied:

- Configuration type: Phoredox, modified Bardenpho, UCT, modified UCT and Johannesburg;
- Operational conditions: sludge age, recirculation factors, anaerobic-, anoxic- and aerobic sludge mass fractions;
- Waste water characteristics: temperature, concentration and composition of the organic material, ratio TKN/COD and ratio P/COD.

It was verified that all parameters determined experimentally did have close correlation with the simulated model values. Therefore the model may be considered to be a reliable instrument to estimate the removal of phosphorus for a specific system configuration and for a specified set of operational conditions and waste water characteristics.

### 5.1.3.3 Denitrification of bio-P organisms

As discussed before, an aspect that was not clear from the model by Wentzel (1990) is the denitrification rate in the anoxic zone following the anaerobic zone. While the pure culture of PAO did not display a significant denitrification capacity, in the mixed culture denitrification did exist, in fact even at a higher rate than in the conventional system designed for nitrogen removal. Clayton (1989, 1991) investigated this issue and presented the following findings:

- In activated sludge systems with an anaerobic zone, the denitrification rate can still be described with the following generic equation:  $r_D = k \cdot X_a$ ;
- The primary denitrification phase in the pre-D reactors is much reduced or does not exist at all, which signifies that the concentration of easily biodegradable organic material in the effluent of the anaerobic zone is low. This is of course a result of the processes observed in the anaerobic zone, such as the absorption of VFA and the release of phosphorus, which remove a large part of the available easily biodegradable organic material;
- The value of denitrification constant  $K_2$ , corresponding to the utilisation of slowly biodegradable material in the pre-D reactor, is about 2.5 times higher than the value in conventional nitrogen removal systems. The value of denitrification constant  $K_3$  is about 1.5 times higher;
- Clayton hypothesised that a possible reason for the increase of the denitrification constants might be an increase in the rate of hydrolysis of the slowly biodegradable organic material as a result of the inclusion of an anaerobic zone.

However, the existence of denitrifying PAO was not considered in this hypothesis, which meant that the calculation of the denitrification rates was based only on the active non-PAO biomass. However, as will be demonstrated in Example 5.3, the observed increase in denitrification rate per unit mass  $X_a$  can be fully explained when the PAO biomass is taken into account. Thus the values of the denitrification constants  $K_2$  and  $K_3$  in bio-P removal systems are comparable to those in activated sludge systems designed for nitrogen removal. The denitrification capacity in a bio-P removal system can be described by adapting Eqs. (4.62 and 4.63) and differentiating into nitrate removal due to PAO and due to non-PAO organisms:

$$\begin{aligned} D_{c1} &= N_{ds} + N_{dp} = N_{dsp} + N_{dsh} + N_{dpp} + N_{dph} \\ &= [f_{dn} \cdot (f_{bsp} \cdot f_{pd} + f_{bsh}) \cdot f_{sb} + K_2 \cdot f_{x1} \cdot (C_{rh} \cdot f_{bh} + C_{rp} \cdot f_{bp} \cdot f_{pd})] \cdot S_{bi} \end{aligned} \quad (5.9)$$

Where:

$N_{dsp}$  and  $N_{dpp}$  = nitrate removal due to easily and slowly biodegradable COD by the PAO  
 $N_{dsh}$  and  $N_{dph}$  = nitrate removal due to easily and slowly biodegradable COD by the non-PAO

$$\begin{aligned} MD_{c1} &= f_{dn} \cdot (f_{bsp} \cdot f_{pd} + f_{bsh}) \cdot f_{sb} \cdot MS_{bi} + K_2 \cdot f_{x1} \cdot MX_{ah} + K_2 \cdot f_{x1} \cdot f_{pd} \cdot MX_{ah} \text{ or} \\ &= f_{dn} \cdot f_{sb} \cdot MS_{bi} + K_2 \cdot f_{x1} \cdot MX_a \text{ for } f_{pd} = 1 \end{aligned} \quad (5.10)$$

$$D_{c3} = K_3 \cdot f_{x3} \cdot (C_{rh} \cdot f_{bh} + C_{rp} \cdot f_{bp} \cdot f_{pd}) \cdot S_{bi} \text{ and} \quad (5.11)$$

$$\begin{aligned} MD_{c3} &= K_3 \cdot f_{x3} \cdot MX_{ah} + K_3 \cdot f_{x3} \cdot f_{pd} \cdot MX_{ah} \text{ or} \\ &= K_3 \cdot f_{x3} \cdot MX_a \text{ for } f_{pd} = 1 \end{aligned} \quad (5.12)$$

Where:

$f_{bsp}$  = fraction of  $S_{bsi}$  sequestered by PAO =  $S_{bsp}/S_{bsi}$   
 $f_{bsh}$  = fraction of  $S_{bsi}$  consumed by normal heterotrophs ( $f_{bsh} + f_{bsp} = 1$ ) =  $S_{bsh}/S_{bsi}$   
 $f_{bp}$  = fraction of  $S_{bi}$  sequestered by PAO =  $S_{bsp}/S_{bi}$   
 $f_{bh}$  = fraction of  $S_{bi}$  consumed by normal heterotrophs ( $f_{bh} + f_{bp} = 1$ ) =  $(S_{bi} - S_{bsp})/S_{bi}$   
 $f_{pd}$  = fraction of PAO capable of denitrification  
 $MX_{ah/ap}$  = total active non PAO- respectively PAO sludge mass in the system

From Example 5.3 it can be concluded that the inclusion of anoxic PAO into the simplified steady state model leads to a very good description of the two observed phenomena: i.e. phosphate uptake in the anoxic zone and the (perceived) increased denitrification rate when based on  $X_{ah}$  only. It also confirms that, when conditions are favourable, the fraction of PAO capable of denitrification will be high.

A typical domestic waste water with a COD concentration of  $500 \text{ mg.l}^{-1}$  will have a TKN concentration between 40 and  $55 \text{ mg N.l}^{-1}$ , of which about  $15 \text{ mg N.l}^{-1}$  will be used for the production of excess sludge ( $N_f$ ) at the short sludge age typical for P removing systems. Therefore the expected nitrification capacity is between 25 to  $40 \text{ mg N.l}^{-1}$ . It is concluded from this example that the denitrification capacity that can be created in a bio-P activated sludge system is approximately equal to the expected nitrification capacity. Therefore for such a waste water, the degree of nitrogen removal can be high and the production of an effluent with a low level of both nitrogen and phosphorus is possible.

#### 5.1.3.4 Discharge of organic phosphorus with the effluent

The total effluent phosphorus concentration  $P_{te}$  is composed of two fractions: soluble inorganic phosphate ( $P_{pe}$ ) and organic phosphorus ( $P_{oe}$ ). The organic phosphorus fraction  $P_{oe}$  consists of a soluble fraction ( $P_{oes}$ ) and a particulate fraction, which is part of the volatile suspended solids in the effluent:

$$P_{oep} = f_p \cdot X_{ve} = f_p \cdot f_v \cdot X_{te} \quad (5.13)$$

The value of  $P_{oes}$  is often low (typically between 0.1 and  $0.2 \text{ mg P.l}^{-1}$ ) and cannot be influenced by process conditions. The fraction  $P_{oep}$  is actually a part of  $P_1$ , the organic phosphorus discharged with the excess sludge. However, due to imperfections in the solid-liquid separation process in the final settler,  $P_{oep}$  will leave the system with effluent rather than with the excess sludge.

For activated sludge systems without bio-P removal (assuming  $f_p = 0.025 \text{ g P.g}^{-1} \text{ VSS}$ ), a secondary clarifier that performs well can produce an effluent with 4 - 12 mg VSS.l<sup>-1</sup>, which will result in an effluent concentration of about 0.1 to 0.3 mg P.l<sup>-1</sup> of organic particulate phosphorus. This is a significant contribution to the value of  $P_{te}$ , especially given the trend towards stricter effluent phosphorus limits (< 1 mg total-P.l<sup>-1</sup>).

When bio-P removal is applied in the activated sludge system, the contribution to  $P_{oep}$  to  $P_{te}$  will be even larger, as the phosphorus content of the bio-P bacteria may reach a maximum of 0.38 mg P.mg<sup>-1</sup> VSS. For a bio-P removal system, the average  $f_p$  value of the combined volatile biomass will be in the range of 0.04 to 0.08 g P.g<sup>-1</sup> VSS.

This results in typical values for  $P_{oep}$  between 0.4 and 0.8 mg P.l<sup>-1</sup> for bio-P removal systems. If no more specific data is available for the design of municipal waste water treatment systems, the following default values could be adopted: 0.2 mg P.l<sup>-1</sup> for conventional activated sludge systems and 0.6 mg P.l<sup>-1</sup> for bio-P removal systems.

In the steady state model, the value of  $P_{oe}$  includes both  $P_{oes}$  and  $P_{oep}$ . For those cases where phosphorus removal is not required,  $P_1$  is not corrected for the loss of organic phosphorus with the effluent and is therefore slightly overestimated. This results in an equal underestimate of the concentration of phosphate in the effluent, as this is calculated according to:

$$P_{pe} = P_{ti} - P_1 - P_{oe} = P_{ti} - P_1 - P_{oes} - P_{oep}$$

When an activated sludge system is designed for phosphorus removal, this might result in a design where the amount of phosphorus to be removed is underestimated and the effluent phosphorus limit is not met. Therefore in the case of biological- or chemical phosphorus removal, the value of  $P_1$  will have to be corrected (refer also to similar discussion about particulate organic nitrogen in the effluent in Appendix 5). The phosphorus concentration discharged with the excess sludge is equal to:

$$P_{lex} = P_1 - P_{oep} \tag{5.14}$$