

5.1.1 Mechanisms involved in biological phosphorus removal

Phosphorus is only partly removed in conventional activated sludge processes. The mechanism responsible is the production of excess sludge as the phosphorus mass fraction in volatile sludge is about 2.5% of the VSS concentration. For a municipal nitrogen removal activated sludge system operating at an average sludge age of 8 to 12 days, the excess sludge production is around $0.25 \text{ mg VSS} \cdot \text{mg}^{-1} \text{ COD}$ (refer to Fig. 3.10). The phosphorus removal will be approximately $0.25 \cdot 0.025 = 0.006 \text{ mg P} \cdot \text{mg}^{-1} \text{ COD}$. Thus for sewage with a P/COD ratio between 0.01 and $0.02 \text{ mg P} \cdot \text{mg}^{-1} \text{ COD}$, an effluent concentration between 0.004 and $0.014 \text{ mg P} \cdot \text{mg}^{-1} \text{ COD}$ can be expected. This amounts to 2 to $7 \text{ mg P} \cdot \text{l}^{-1}$ for municipal sewage with a COD concentration of $500 \text{ mg} \cdot \text{l}^{-1}$. In Chapter 3 an expression was developed to determine the concentration of phosphorus in the influent that is removed as part of the excess sludge (Section 3.2.3):

$$P_1 = mP_1 \cdot S_{ti} = f_p \cdot mE_v \cdot S_{ti} = f_p \cdot (1 - f_{np} - f_{np}) \cdot [(1 + f \cdot b_h \cdot R_s) \cdot C_r / R_s + f_{np} / f_{cv}] \cdot S_{ti} \quad (3.62)$$

Generally, it will be required to lower the effluent phosphorus concentration to a value $\leq 1 \text{ mg P} \cdot \text{l}^{-1}$. However, when discharge of organic phosphorus in the excess sludge is the only mechanism of phosphorus removal, this is only possible under favourable conditions (i.e. a low P/COD ratio combined with a short sludge age). In waste waters with a higher level of nutrients and/or activated sludge systems operating at a higher sludge age, additional methods of phosphorus removal will be necessary.

Initially the techniques used for phosphorus removal were all based on physical-chemical treatment methods, especially the addition of metal salts (FeCl_3 , FeSO_4) or lime. This results in the precipitation of metal-phosphorus complexes such as ferric phosphate (FePO_4), calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), apatite ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3$) and struvite (NH_4MgPO_4). There are two important disadvantages associated to this strategy: (1) a certain overdosing of metal salts is necessary to obtain the required low effluent phosphorus values, resulting in high costs of chemicals and a significant increase of excess sludge production and (2) the accumulation of ions (increased salt content) may seriously restrict the reuse possibilities of the effluent.

For these reasons, research on the subject of phosphorus removal became focused on biological removal methods. In the last two decades the knowledge about biological phosphorus removal processes and feasibility and optimisation of this process has increased enormously. Nowadays, in modern municipal waste water treatment plants for which phosphorus removal is to be achieved, physical-chemical treatment methods will only be auxiliary to biological methods. For nutrient removal plants (where removal of both nitrogen and phosphorus is required), the main reason to apply physical-chemical treatment is the restricted availability of easily biodegradable COD that is required to simultaneously achieve the objectives of nitrogen- and phosphorus removal. In Section 5.3, the use of chemical precipitation as the principal method to remove phosphorus will be discussed.

The removal mechanism involved in biological excess phosphorus removal (or bio-P removal) is the so-called luxury phosphorus uptake. Under appropriate operational conditions a sludge mass will develop that contains a significantly increased phosphorus content, compared to the 2.5% normally found in conventional activated sludge processes. Using artificial substrate (acetate), phosphorus mass fractions up to 38% weight have been reached. In systems designed for bio-P removal, a mixed population will develop with "normal" sludge mass with 2.5% phosphorus content and "enriched" bio-P sludge mass containing 38% phosphorus.

An average phosphorus mass fraction between 8 to 10 mg P.mg⁻¹ VSS can be expected, depending on the concentration and composition of the organic material in the influent, the operational conditions and the configuration of the sewage treatment plant. The mechanism involved in the removal of luxury phosphorus is complex. However it has been determined that the following conditions are fundamental in order for the luxury phosphorus uptake to occur:

- (1) The most important finding was that the inclusion of an anaerobic zone in the process configuration (i.e. a zone without oxygen or nitrate present) resulted in an increase of the mass fraction of phosphorus in the biomass. Many researchers established that the biomass in this anaerobic environment released phosphate to the liquid phase of the sludge, e.g. Barnard (1975), Comeau et al (1985), Wentzel et al (1988). In the subsequent anoxic- and aerobic zones, the uptake of phosphorus by the biomass was such that the phosphorus fraction in the biomass in a system containing an anaerobic zone in general was much higher than in conventional activated sludge systems. This process is called luxury phosphorus uptake. The increased phosphorus fraction in the sludge results in a higher degree of phosphorus removal (through disposal with the excess sludge).
- (2) To create an anaerobic environment in activated sludge systems, Barnard (1975) suggested a modification of his Bardenpho system, in which an anaerobic zone is installed upstream of the pre-D reactor. In this zone an anaerobic environment will be established when the nitrate removal in the Bardenpho system is complete or virtually complete. If not, then first all nitrate recycled to the anaerobic zone will have to be removed by denitrification.
- (3) Siebritz and Marais (1982) demonstrated that exposing the activated sludge to an anaerobic environment was necessary, but this condition alone was not sufficient to induce the process of phosphate release and absorption. It was established that the phosphorus fraction in the sludge was dependent on the concentration of easily biodegradable material in the anaerobic zone. A minimum concentration of 25 mg COD.l⁻¹ is required to induce phosphate release, which explains why phosphate release in an anaerobic reactor is not always observed. Thus the nature and concentration of the organic material in the anaerobic reactor play an important part as well.
- (4) The presence of nitrate in the anaerobic reactor will result in partial or complete removal of the easily biodegradable material. To protect the anaerobic zone against a contamination with nitrate the UCT configuration was developed: an activated sludge system consisting of three reactors (anaerobic/anoxic/aerobic). The a- and s-recycles are returned to the anoxic zone, where a low concentration of nitrate is maintained by manipulation of the a-recycle.

An additional r-recycle is introduced, returning mixed liquor from the anoxic zone to the anaerobic zone. This ensures minimal introduction of nitrate in the anaerobic zone. It should be noted that the sludge concentration in the anaerobic reactor will only be a fraction $r/(1+r)$ of the sludge concentration in the other reactors.

- (5) Wentzel et al (1986) demonstrated that the organic material responsible for triggering the release of phosphate in the anaerobic zone was largely composed of volatile fatty acids (mainly present in the form of acetate). Using a synthetic feed containing acetate, Wentzel et al (1986) managed to cultivate a sludge mass containing a phosphorus mass fraction of up to 38%. *Acinobacter* spp. was identified as a one of the dominant species of so-called phosphate accumulating organisms (PAO) or bio-P organisms.

(6) A scientific model was developed to explain the observed empirical phenomenon of excess phosphorus accumulation:

- a. The presence of a sufficient amount of volatile fatty acids in the anaerobic reactor upstream of the anoxic/aerobic reactors triggers the development of a bacterial population that normally is not encountered in an activated sludge system: the bio-P organisms or PAO;
- b. In this anaerobic environment, the non PAO organisms are not able to use the available substrate, as they lack a suitable electron acceptor such as dissolved oxygen or nitrate.

However, the PAO have the option to absorb the volatile fatty acids in their cells in the form of internal polymers such as polyhydroxy-butyrates (PHB). To supply the energy required for this process, the PAO use the energy of previously stored polyphosphate, which is split into orthophosphate (PO_4^{3-}) and then released from the cell.

In the anoxic and oxic conditions encountered in the subsequent reactors, the PHB is used by the PAO as a source for energy supply and bacterial growth. Part of the released energy is used to regenerate the polyphosphate released in the anaerobic reactor. In this process, phosphate is absorbed from the liquid phase by the PAO;

- c. Due to the capability of the PAO to “harvest” organic material in the anaerobic phase and store it internally, they gain a competitive advantage over the regular micro-organisms present in an activated sludge system. Thus it is possible to establish a sludge rich in PAO, with a phosphorus level much higher than the fraction of $0.025 \text{ mg P.mg}^{-1} \text{ VSS}$ found in conventional activated sludge systems.
- d. The maximum phosphorus level is dependent on the composition of the waste water (phosphorus and volatile fatty acids content), but will not exceed the maximum value of $0.38 \text{ mg P.mg}^{-1} \text{ VSS}$ as measured in enhanced cultures;
- e. As it is vital for the growth of PAO that volatile fatty acids are present in the anaerobic reactor, it is of crucial importance that the return of nitrate to the anaerobic reactor is avoided, as the volatile fatty acids will then be used for denitrification by non-PAO organisms.

After extensive research by the research group of van Loosdrecht and Heijnen in the Netherlands, Smolders et al (1994) presented a detailed metabolic model explaining the phenomena observed above on the level of cell microbiology:

- PAO organisms contain three internal cell storage products relevant for excess phosphorus removal: (1) polyphosphate, (2) polyhydroxy-alkanoates (mainly present as PHB) and (3) glycogen;
- Under anaerobic conditions, volatile fatty acids are taken up from the liquid phase and stored as PHB. An important intermediate in this process is NADH_2 , an energy carrier released during the formation of PHB from glycogen. The energy required comes from the hydrolysis of polyphosphate and the subsequent formation of ATP;
- Under anoxic or aerobic conditions, the stored PHB will be oxidised to CO_2 , releasing energy in the form of NADH_2 . This will be used to create ATP, which in turn will allow the PAO organism to grow and restock with polyphosphate and glycogen. This process is graphically displayed in Fig. 5.1;
- The main difference between the metabolism of PAO under anoxic and aerobic conditions is the ratio between ATP formed/ NADH_2 used: this ratio is about 40% lower under anoxic conditions. This explains the lower growth rate observed under anoxic conditions and also applies to “normal” heterotrophic organisms.

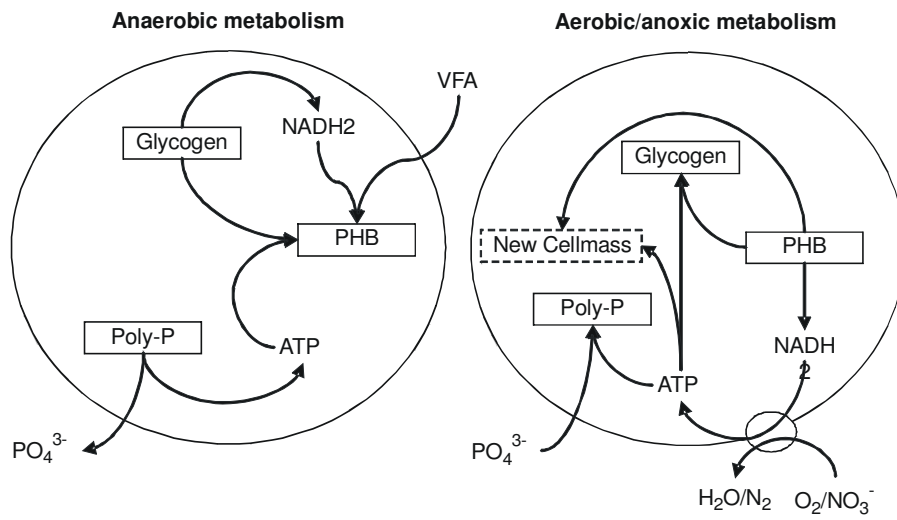


Figure 5.1 Metabolism of PAO under anaerobic and oxic conditions, Smolders et al (1994)