



Περιβαλλοντική Βιοτεχνολογία- Environmental Biotechnology

Ενότητα 7: Removal of Phosphorus

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Phosphorus removal processes

Phosphorus is an essential macronutrient that spurs the growth of photosynthetic algae and cyanobacteria, leading to accelerated eutrophication of lakes. Wastewater discharges that reach lakes sensitive to eutrophication often require phosphorus removal over and above that normally taking place in primary and secondary treatment. **Conventional primary** sedimentation and secondary activated sludge reduce the effluent total P to about **6 mg/L**. However, a typical effluent standard for a protected watershed is **1 mg P/L**. Therefore, additional phosphorus removal is necessary. Phosphorus can be removed from wastewater prior to biological treatment, as part of biological treatment, or following biological treatment.

Three phenomena can be exploited to remove phosphorus as part of a microbiological treatment process:

- Normal phosphorous uptake into biomass
- Precipitation by metal-salts addition to a microbiological process
- Enhanced biological phosphorus uptake into biomass



Biological removal of phosphorus

The biomass that develops normally in an aerobic biological process, such as activated sludge, contains 2 to 3% P in its dry weight. The stoichiometric formula for biomass can be modified to include this amount of P. The formula $C_5H_7O_2NP_{0.1}$ has a formula weight of 116 g/mol, of which P is 2.67 percent. Sludge wasted from the process removes P in proportion to the mass rate of sludge VSS wasted ($Q^w X_v^w$). A steady-state mass balance on total P is:

$$0 = QP^0 - QP - Q^w X_v^w (0.0267 \text{ g P / g VSS})$$

in which P^0 and P are the influent and effluent total P concentrations, and Q is the influent flow rate. Above equation can be solved for the effluent total P concentration,

$$P = \frac{QP^0 - Q^w X_v^w (0.0267)}{Q} = P^0 - \frac{Q^w X_v^w (0.0267)}{Q}$$



Biological removal of phosphorus

The rate of sludge wasting is proportional to the BOD removal (ΔBOD_L) and the observed yield (Y_n):

$$Q^w X_v^w = Y_n Q(\Delta BOD_L)$$

The **net yield** depends on the SRT (θ_x), the true yield (Y), the endogenous decay rate (b), and the biodegradable fraction of the new biomass (f_d):

$$Y_n = Y \frac{1 + (1 - f_d)b\theta_x}{1 + b\theta_x}$$

The relationship describing how the effluent P concentration depends on the influent P concentration, the BOD_L removal, and the SRT:

$$P = P^0 - \frac{(0.0267)Y(1 + (1 - f_d)b\theta_x)(\Delta BOD_L)}{1 + b\theta_x}$$



Biological removal of phosphorus

**Effects of SRT and BOD_L removal on the effluent P concentration
when the influent P concentration is 10 mg P/L**

BOD_L removal mg BOD_L /L	Effluent PO_4-P concentration, mg/L			
	3 d	6 d	15 d	30 d
100	9.0	9.1	9.4	9.5
300	7.0	7.4	8.1	8.5
500	5.0	5.7	6.8	7.5
1,000	0	1.4	3.6	5.1

For domestic sewage, which is best represented by the BOD_L removal of 300 mg/l, the effluent P concentration is well above 1 mg P/l, and the need for advanced treatment is obvious.

In many cases, N removal must accompany P removal. Thus, the large SRTs needed for nitrification reduce sludge wasting and normal P removal.

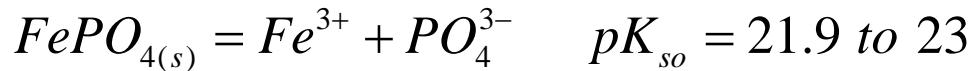
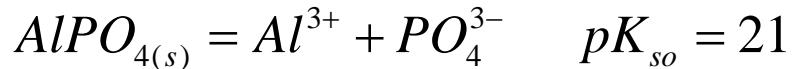
On the other hand, a wastewater having a low P: BOD_L ratio may not require advanced treatment if the SRT is carefully controlled to keep a low, but positive P concentration.



Chemical sedimentation of phosphorus

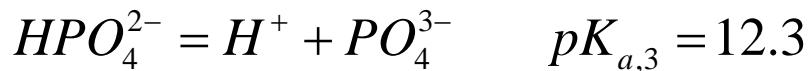
Aluminum and ferric cations precipitate with the orthophosphate anion at pH values that are compatible with microbiological treatment. Therefore, salts of Al^{3+} or Fe^{3+} can be added directly to the wastewater as it enters or leaves the bioreactor. Precipitates form, are incorporated into sludge, and are removed from the system by sludge wasting.

The key precipitates are $\text{AlPO}_{4(s)}$ and $\text{FePO}_{4(s)}$. Their standard dissolution reactions and solubility products (pK_{so}) are:



Chemical sedimentation of phosphorus

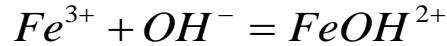
Although the solubility products are very small, the conditional solubility of phosphates is not necessarily minuscule, because Al^{3+} , Fe^{3+} , and PO_4^{3-} undergo competing acid/base and complexation reactions. For phosphate, the key competing reactions are acid/base ones that result in the formation of protonated species. The acid/base reactions and pKa values are:



At near neutral pH, HPO_4^{2-} and H_2PO_4^- , not PO_4^{3-} , are the dominant species. For example, at pH = 7.0, PO_4^{3-} comprises about 0.00025 percent of the total dissolved orthophosphates. **Higher pH gives a greater fraction as PO_4^{3-} .**



Chemical sedimentation of phosphorus



$$pK_1 = 11.8$$



$$pK_2 = 10.5$$



$$pK_3 = 7.7$$



$$pK_4 = 4.4$$



$$pK_1 = 9.0$$



$$pK_2 = 9.7$$



$$pK_3 = 8.3$$



$$pK_4 = 6.0$$

The acid/base nature of the hydroxy complexes means that the iron or aluminum speciation is pH dependent. At neutral pH, the dominant species are $Fe(OH)_2^+$, $Fe(OH)_3^0$, and $Al(OH)_3^0$. Al^{3+} and Fe^{3+} are tiny fractions of the total aluminum and iron. **Lower pH is required to give greater fractions of Al^{3+} or Fe^{3+} .**

Due to the opposing pH trends for the precipitating anion (PO_4^{3-}) versus the precipitating cations (Al^{3+} or Fe^{3+}), an optimal pH exists. Based on the reactions shown above, the pHs of minimum solubility are **near 6 for $AlPO_4(s)$ and near 5 for $FePO_4(s)$** . In principle, stoichiometric additions of the cations can drive the total phosphate concentration to well below 1 mg P/l near these optimal pH values.



Chemical sedimentation of phosphorus

Problems:

1. Phosphate forms competing complexes, such as CaHPO_4 , MgHPO_4 , and FeHPO_4^+ . Thus, the fraction of total phosphate that is present as PO_4^{3-} is less than predicted by acid-base chemistry alone.
2. Aluminum and iron form other complexes, particularly with organic ligands, or precipitate as $\text{Al(OH)}_{3(s)}$. These reactions reduce the available Al^{3+} and Fe^{3+} .
3. Some of the total phosphorus is not orthophosphate, but is tied up in organic compounds.
4. The optimal pH for precipitation may not be compatible with the optimal microbiological activity. The pH cannot be changed so much that metabolic activity is significantly inhibited.
5. The precipitation reaction may be kinetically controlled and not reach its maximum extent, which occurs at equilibrium.

Typically, the metal-salts dosage is 1.5 to 2.5 times the stoichiometric amount.



Chemical sedimentation of phosphorus

Problems:

An important consideration for metal-salts addition is that the added metals behave as acids and consume alkalinity as they precipitate with PO_4^{3-} or complex with hydroxide.

For low alkalinity waters, pH depression is a major risk. In such cases, a base, such as lime (CaO), can be added to supplement the alkalinity. Another alternative is to dose sodium aluminate (NaAlO_2), which dissolves in water to give



This dissolution reaction is a net generator of alkalinity: one base equivalent/mol Al. Another alternative is to dose ferrous iron (Fe^{2+}), which is oxidized to Fe^{3+} in a reaction that produces 1 base equivalent per mole of Fe^{2+} oxidized:



Chemical sedimentation of phosphorus

Problems:

Precipitation of $\text{AlPO}_{4(\text{s})}$ or $\text{FePO}_{4(\text{s})}$ creates significant quantities of inorganic sludge that is retained within the biological process and ultimately wasted.

The stoichiometric production ratios are 3.9 g $\text{AlPO}_{4(\text{s})}$ /g P and 4.9 g $\text{FePO}_{4(\text{s})}$ /g P. For example, removal of 8 mg P/l produces 39 mg $\text{FePO}_{4(\text{s})}$ /l of plant flow. If an activated sludge process has an SRT (ϑ_x) of 6 d and a hydraulic reaction time of 0.25 d (ϑ), the concentration factor (ϑ_x/ϑ) is 24, which means the concentration of $\text{FePO}_{4(\text{s})}$ built up in the mixed liquor is **935 mg/l**. Clearly, **phosphate precipitation increases the sludge to be wasted and significantly enriches it in inorganic solids.**



Enhanced biological removal of phosphorus

When enhanced biological phosphorus removal is successful, the biomass contains **2 to 5 times the P content of normal biomass.**

$$P = P^0 - \frac{(0.0801)Y(1 + (1 - f_d)b\theta_x(\Delta BOD_L))}{1 + b\theta_x}$$

The effluent P concentration for a BOD_L removal of 300 mg/l and an influent P concentration of 10 mg/l then becomes 4.2 mg/l for $\vartheta_x = 15$ d and 2.2 mg/l for $\vartheta_x = 6$ d. These values approach a typical P standard of 1 mg/l. Increased poly P enrichment or a higher BOD_L :P ratio in the influent make the effluent goal achievable.



Enhanced biological removal of phosphorus

1. The influent wastewater and recycle sludge must mix and first enter an **anaerobic bioreactor**. Electron acceptors-particularly O_2 and NO_3^- must be excluded to the maximum degree possible so that BOD oxidation is insignificant in this reactor. Due to the high mixed-liquor biomass level, hydrolysis and fermentation steps occur, but the electron equivalents in the influent BOD are not transferred to a terminal electron acceptor.
2. The mixed liquor flows from the anaerobic tank to the main activated sludge bioreactor or bioreactors. Depending on the system's SRT, nitrification and denitrification may not occur. Ample electron acceptors are available through aeration, which directly supplies O_2 and allows generation of NO_3^- if nitrification occurs. These electron acceptors make it possible for the heterotrophic bacteria to oxidize electron donors, gain energy, and grow.
3. The sludge that was most recently in the main bioreactor is wasted to control the SRT and to remove the biomass when it is enriched in poly P.



Enhanced biological removal of phosphorus

4. The mixed liquor exiting the main bioreactor is settled, and most of it is recycled back to the head of the process, where it mixes with the influent and enters the anaerobic tank. This recycling ensures that all of the biomass experiences **alternating anaerobic and respiring conditions**.

In the past, **Bio-P bacteria** were identified as belonging to the genus *Acinetobacter*. Further research has shown that *Acinetobacter* is only one genus of Bio-P bacteria and often is not the dominant genus. Bio-P bacteria also are found among the *Pseudomonas*, *Arthrobacter*, *Nocardia*, *Beyerinkia*, *Ozotobacter*, *Aeromonas*, *Microlunatus*, *Rhodocyclus*, and others.



Enhanced biological removal of phosphorus

Although the biochemical and ecological foundation for enhanced biological phosphorus removal by Bio-P bacteria now seems to be firmly established, some evidence supports the concept that chemical precipitation plays a role, at least in some instances. The main candidate for the solid phase is **$\text{Ca}_5(\text{OH})(\text{PO}_4)_{3(s)}$, or hydroxyapatite**. Its solubility product is $pK_{\text{so}} = 55.9$, which suggests that moderately hard waters could drive the orthophosphate below 1 mg P/l for pH values greater than about 7.5. **Struvite (MgNH_4PO_4)** is another possibility when Mg^{2+} and NH_4^+ concentrations are elevated. Strong denitrification produces base that can increase the pH, particularly inside a floc or biofilm, and foster precipitation of hydroxyapatite or struvite. Very high aeration rates, which strip CO_2 from solution, also raise the pH and can foster precipitation of hydroxyapatite.



Enhanced biological removal of phosphorus

Sequencing batch reactors (SBRs) also can be used for enhanced biological phosphorous removal, as well as nitrogen removal.

Carryover of settled sludge from the previous cycle always contains some NO_3^- . Once the NO_3^- is denitrified during an unaerated fill period, anaerobic conditions can be established and lead to poly P and PHB cycling.

Biofilm processes can be used for enhanced biological phosphorous removal if the biofilm is exposed to alternating anaerobic and respiratory periods, Characteristic responses of phosphate release during the anaerobic phase and phosphate uptake during the respirator phase occur. Oxygen or NO_3^- could be used as the terminal electron acceptor. Cycle times of around 6 h are workable, but further research is needed to optimize these processes for N and P removal.



References

The images where their origin is not mentioned are derived from the book:
Environmental Biotechnology : Principles and Applications,
Bruce E. Rittmann and Perry L. McCarty,
McGraw-Hill Series in Water Resources and Environmental Engineering



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