

Technologies to Remove Phosphorus from Wastewater

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This brief literature review examines treatment technologies available for wastewater treatment plants to remove phosphorus. Although it is not meant to be exhaustive or complete, it does include some of the newest available reports on P removal.

Treatment technologies presently available for phosphorus removal include:

Physical:

filtration for particulate phosphorus
membrane technologies

Chemical:

precipitation
other (mainly physical-chemical adsorption)

Biological

assimilation
enhanced biological phosphorus removal (EBPR)

The greatest interest and most recent progress has been made in EBPR, which has the potential to remove P down to very low levels at relatively lower costs. Membrane technologies are also receiving increased attention, although their use for P removal has been more limited to date. The question of sludge handling and treatment of P in side streams is also being addressed.

A. Physical Treatment

1. Filtration for particulate P

Assuming that 2-3% of organic solids is P, then an effluent total suspended solids (TSS) of 20 mg/L represents 0.4-0.6 mg/L of effluent P (Strom, 2006b). In plants with EBPR the P content is even higher. Thus sand filtration or other method of TSS removal (e.g., membrane, chemical precipitation) is likely necessary for plants with low effluent TP permits (Reardon, 2006).

2. Membrane technologies

Membrane technologies have been of growing interest for wastewater treatment in general, and most recently, for P removal in particular. A recent 3 day national Water Environment Research Foundation (WERF) workshop on achieving low effluent nutrient levels devoted an entire session (4 papers) to this topic (WERF, 2006). In addition to

removing the P in the TSS, membranes also can remove dissolved P. Membrane bioreactors (MBRs, which incorporate membrane technology in a suspended growth secondary treatment process), tertiary membrane filtration (after secondary treatment), and reverse osmosis (RO) systems have all been used in full-scale plants with good results. Reardon (2006) reported on several plants achieving <0.1 mg/L TP in their effluent, and suggested the current reliable limits of technology are 0.04 mg/L for MBRs and tertiary membrane filtration, and 0.008 mg/L for RO.

B. Chemical Treatment

1. Precipitation

Chemical precipitation has long been used for P removal. The chemicals most often employed are compounds of calcium, aluminum, and iron (Tchobanoglous et al., 2003). Chemical addition points include prior to primary settling, during secondary treatment, or as part of a tertiary treatment process (Neethling and Gu, 2006). Song et al. (2002), using thermodynamics, modeled the effects of P and Ca concentration, pH, temperature, and ionic strength on theoretical removal. Researchers (e.g., Hermanowicz, 2006) generally agree, however, that the process is more complex than predicted by laboratory pure chemical experiments, and that formation of and sorption to carbonates or hydroxides are important factors. In fact, full-scale systems may perform better than the 0.05 mg/L limit predicted (Neethling and Gu, 2006). Takács (2006) suggests the limit is probably 0.005-0.04 mg/L.

A major concern with chemical precipitation for P removal continues to be the additional sludge that is produced. This can be dramatic, especially if the method selected is lime application during primary treatment (Tchobanoglous et al., 2003). Use of alum after secondary treatment can be predicted to produce much less sludge, but the increase could still be problematic (Strom, 2006a).

2. Other

The precipitation methods described above rely in part on sorption to achieve the low concentrations observed. Möller (2006) reported on an iron reactive filtration system achieving <0.01 mg/L TP at a 1.2 MGD (average flow) plant. Woodard (2006) described a magnetically enhanced coagulation process that may achieve <0.03 mg/L TP based on long term pilot tests.

Gas concrete (produced from mixtures of silica, sand, cement, lime, water, and aluminum cake) waste was used to remove phosphate from pure aqueous solutions (Oguz et al., 2003). High phosphate removal ($> 95\%$ in 10 min, batch system) was obtained from a 33 mg/L P solution, but direct applicability to wastewater treatment (lower concentrations, possible interferences) was not investigated. The gas concrete's removal efficiency can be regenerated at low pH, with the resulting concentrated phosphate solution potentially a source of recycled phosphate. Similarly, iron oxide tailings were found to be effective for phosphorus removal from both pure solutions and liquid hog manure (Zeng et al., 2004).

C. Biological Treatment

1. Assimilation

Phosphorus removal from wastewater has long been achieved through biological assimilation – incorporation of the P as an essential element in biomass, particularly through growth of photosynthetic organisms (plants, algae, and some bacteria, such as cyanobacteria). Traditionally, this was achieved through treatment ponds containing planktonic or attached algae, rooted plants, or even floating plants (e.g., water hyacinths, duckweed). This continues to be an area of research (e.g., Awuah et al., 2004), although less so in the northeastern USA. Land application of effluent during the growing season has also been used, and constructed wetlands are now an established practice as well. In all of these cases, however, it is necessary to remove the net biomass growth in order to prevent eventual decay of the biomass and re-release of the P (Strom, 2006a). Interestingly, assimilation was not discussed at the WERF (2006) workshop.

2. EBPR

As indicated in the introduction, the greatest recent and present interest has been in enhanced biological phosphorus removal. This is because of its potential to achieve low or even very low (<0.1 mg/L) effluent P levels at modest cost and with minimal additional sludge production. Removal of traditional carbonaceous contaminants (BOD), nitrogen, and phosphorus can all be achieved in a single system, although it can be challenging to achieve very low concentrations of both total N and P in such systems.

A detailed review of EBPR microbiology is given in Mino et al. (1998). Mulkerins et al. (2003) also have reviewed the process. To summarize (Strom, 2006a and 2006b), phosphate accumulating organisms (PAOs) store polyphosphate as an energy reserve in intracellular granules. Under anaerobic conditions, in the presence of fermentation products, PAOs release orthophosphate, utilizing the energy to accumulate simple organics and store them as polyhydroxyalkanoates (PHAs) such as poly- β -hydroxybutyrate (PHB). Under aerobic conditions, the PAOs then grow on the stored organic material, using some of the energy to take up orthophosphate and store it as polyphosphate. Thus PAOs, although strictly aerobic, are selected for by having an up-front anaerobic zone in an activated sludge type of biological treatment process. The PAOs are able to compete with other aerobes under these conditions because of their ability to sequester a fraction of the available organic material under the initial anaerobic conditions, while out-competing the anaerobes because of the much higher energy yield from aerobic vs. fermentative metabolism.

The phosphate in EBPR is removed in the waste activated sludge, which might have 5% or more P (dry weight) as opposed to only 2-3% in non-EBPR sludges. EBPR has been demonstrated in several systems (Tchobanoglous et al., 2003), such as the various Bardenpho processes (also remove N), the A/O and A/A/O or A2O (removes N) processes, sequencing batch reactors (SBRs), and the PhoStrip process (which combines EBPR with phosphate stripping and chemical removal). Simultaneous biological nutrient removal (SBNR) has also been observed in treatment systems, such as the Orbal™

oxidation ditch, not specifically designed for nutrient removal. SBNR recently has been examined in some detail (Littleton et al., 2000, 2001, 2002a, 2002b, 2003a, 2003b, accepted I, accepted II; Strom et al., 2004)

James Barnard (2006), developer of the Bardenpho process, recently moderated a session on the capabilities and constraints of EBPR, and discussed the requirements for achieving effluent P concentrations <0.1 mg/L. He emphasized the need for production of volatile fatty acids by fermentation in order to assure their availability for the PAOs. Some of the factors contributing to the difficulty of achieving very low levels of both N and P simultaneously were pointed out, including secondary release of P in anoxic zones. The need to select for PAOs over the competing glycogen accumulating organisms (GAOs) was also discussed, with the following factors favoring GAOs: high sludge age, high temperature, longer un-aerated detention times, stronger wastes with low organic N, polysaccharides fed to the anaerobic zone, and low pH.

Neethling et al. (2005) examined the factors that influence the reliability of EBPR in full-scale plants. They concluded that P “concentrations <0.1 mg/L can be achieved for extended periods (more than a month), 0.03 mg/L for a week, and even below 0.02 mg/L for several sequential days. Excursions above these levels are common.” A sufficient BOD/P ratio ($>25:1$) is one requirement for reliable high removal efficiencies. This might be achieved by BOD augmentation through fermentation or addition of a fermentable substrate. Control of recycle streams is also necessary, so that they do not bring too much P back to the EBPR process. They also concluded that while GAOs can be problematic, their presence does not preclude good P removal.

Randall (2006) also discussed the use of carbon augmentation in EBPR. Short chain volatile fatty acids (VFAs), particularly acetic and propionic acids, are most desirable. Some carbon sources, such as some sugars and alcohols, may lead to production of GAOs, bulking, or excessive exocellular polymer production. VFAs may be generated in the sewer system, arise from industrial discharges, be added directly, or be generated on-site. For many plants, on-site generation in the anaerobic zone may be sufficient. Alternatively, fermentation of the primary sludge, primary effluent, or some of the activated sludge might be practiced. In the PhoStrip process, fermentation also occurs in the stripping tank.

Cold weather can provide a challenge for many biological treatment processes. However, the Kalispell, Montana, wastewater treatment plant has maintained a long-term average effluent phosphorus concentration of 0.11 mg/L (Emrick, 2006) with a Bardenpho process modification (UCT). This area has only 91 frost-free days per year, with average winter high and low temperatures of 30 and 15°F, respectively.

Akin and Ugurlu (2003) examined nutrient removal in a laboratory sequencing batch reactor (SBR) system with a new operational mode: simultaneous feeding and decanting. The synthetic wastewater contained glucose and acetate as carbon sources, and 20 mg/L P (COD/P ratio = 20). Filtered effluent P concentrations below 1 mg/L (and as low as 0.1 mg/L) were achieved under some operational conditions.

Converting a non-P removing activated sludge to EBPR by acclimatization to alternating anaerobic and aerobic conditions takes 40-100 days, but many EBPR systems experience start-up failure or breakdown (Dabert et al., 2005). Bioaugmentation (inoculating with previously adapted microorganisms) was found to speed up the process for a laboratory SBR by about 15 days compared to a non-augmented control.

Optimization of dissolved oxygen, sludge age, and nitrate-N concentration for efficient phosphorus removal were tested at an A2O wastewater treatment plant in Guilin, China, (Li et al., 2005). Results showed that DO must be controlled in the anaerobic phase, nitrate-nitrogen concentration must be decreased in the anaerobic section, and a sludge age of 8-10 days was preferable to 15 days.

Kuba et al. (1997) examined the role of denitrifying phosphorus removing bacteria (DPB) in wastewater treatment plants using batch tests with activated sludge from two plants in the Netherlands. DPBs appeared to be of little importance in one plant, but contributed substantially to P removal in the other.

D. Sludges and Side Streams

There is some concern about the effects of solids management processes and return side streams on the ability to remove P to low levels. Processes that destroy organic material (such as digestion) have the potential to release the particulate organic-P present as soluble organic or inorganic P. In particular, anaerobic conditions are likely to release soluble P from EBPR sludges and iron precipitates (ferrous phosphate is much more soluble than ferric phosphate). Any released P may then be returned to the main wastewater treatment process in high concentrations through recycle side streams, thus requiring removal a second time. Non-continuous processes may also lead to variable loadings from side streams. A number of these issues were discussed by Narayanan (2006).

In some cases, these problems, particularly with anaerobic digestion, have not been as severe as originally anticipated, or could be controlled (deBarbadillo, 2006). This appears in part to be related to the formation of the mineral struvite, $MgNH_4PO_4$. Struvite has long been known for its potential to cause clogging in anaerobic digesters (Vaccari et al., 2006), where ammonium and phosphate are released as the organic matter is degraded. However, it appears that formation of this mineral in digesters at EBPR plants may lead to its precipitation as small granules that remain with the sludge, rather than the release of soluble P to the supernatant where it would be recycled. This is apparently enhanced by the liberation of Mg^{2+} by PAOs as a major associated cation during phosphate release (Liao et al., 2003).

Another approach is to remove the P from the recycle stream. Britton et al. (2005) demonstrated treatment of anaerobic digester supernatant in pilot scale using a fluidized bed reactor. Phosphate was recovered in the form of struvite through the addition of magnesium chloride and pH adjustment. Liao et al. (2003) looked at release of P directly from EBPR sludge by several methods for possible P recovery. Takiguchi et

al. (2004) tested thermal (70°C) treatment followed by precipitation with Ca in a lab-scale.

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