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**Removal Techniques Of Phosphorus From Waste Water To Enhance Its Reuse
Potential To Meet The Water Crises**

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Abstract

Wastewater contains high levels of nutrients like nitrogen and phosphorus depending on industrial sources, water conservation, or whether a detergent ban is in place. Excessive release of these to the environment can lead to a buildup of nutrients, called eutrophication, which can in turn lead to the overgrowth of weeds and algae. Chronic symptoms of over-enrichment include low dissolved oxygen, fish kills, murky water, and depletion of desirable flora and fauna. In addition, the increase in algae and turbidity increases the need to chlorinate drinking water, which, in turn, leads to higher levels of disinfection by-products that have been shown to increase the risk of cancer. The removal of organics and nutrients from wastewater is required by many regulatory agencies based on issues of toxicity, oxygen demand, and eutrophication effect. Many wastewater treatment plants have been designed or upgraded to remove nitrogen and phosphorus by biological and chemical means. To achieve lower effluent limits, facilities have to look beyond conventional treatment technologies. To control eutrophication in receiving water bodies, biological nutrient removal (BNR) of nitrogen and phosphorus has been widely used in wastewater treatment practice, both for the upgrade of existing wastewater treatment facilities and the design of new facilities. However, implementation of BNRAS systems presents challenges due to the technical complexity of balancing influent COD for both biological phosphorus and nitrogen removal. Sludge age and aerated/unaerated mass fractions are identified as key parameters for process optimization. Emerging concerns about process sustainability and the reduction of carbon footprint are introducing additional challenges in that influent COD, N and P are increasingly being seen as resources that should be recovered, not simply removed.

In light of this emerging paradigm of “sustainability” which includes environmental, social and economic costs as factors determining process selection, it is useful to understand the relevant factors which differentiate competing BNR technologies. To address this need, this paper overviews key factors in BNR technologies which impact operational cost, greenhouse gas (GHG) emissions (carbon footprint reduction) and the ability to recover nutrients as fertilizer.

Keywords: Biological nutrient removal, eutrophication, treatment process, sewage treatment plant.

Introduction

Wastewater may contain high levels of the nutrients nitrogen and phosphorus. Excessive release to the environment can lead to a build up of nutrients, called eutrophication, which can in turn encourage the overgrowth of weeds, algae, and cyanobacteria (blue-green algae). This may cause an algal bloom, a rapid growth in the population of algae. The algae numbers are unsustainable and eventually most of them die. The decomposition of the algae by bacteria uses up so much of oxygen in the water that most or all of the animals die, which creates more organic matter for the bacteria to decompose. In addition to causing deoxygenation, some algal species produce toxins that contaminate drinking water supplies. Different treatment processes are required to remove nitrogen and phosphorus.

Phosphorus: Total phosphorus (TP) in domestic wastewater typically ranges between 4 and 8 mg/L but can be higher depending on industrial sources, water conservation, or whether a detergent ban is in place. Sources of phosphorus are varied. Some phosphorus is present in all biological material, as it is an essential nutrient and part of a cell's energy cycle. Phosphorus is used in fertilizers, detergents, and cleaning agents and is present in human and animal waste.

Phosphorus in wastewater is in one of three forms:

- Phosphate (also called Orthophosphate PO₄³⁻)
- Polyphosphate, or
- Organically bound phosphorus.

The orthophosphate fraction is soluble and can be in one of several forms (e.g., phosphoric acid,

phosphate ion) depending on the solution pH. Polyphosphates are high-energy, condensed phosphates such as pyrophosphate and trimetaphosphate. They are also soluble but will not be precipitated out of wastewater by metal salts or lime. They can be converted to phosphate through hydrolysis, which is very slow, or by biological activity. Organically bound phosphorus can either be in the form of soluble colloids or particulate. It can also be divided into biodegradable and non-biodegradable fractions. Particulate organically bound phosphorus is generally precipitated out and removed with the sludge. Soluble organically bound biodegradable phosphorus can be hydrolyzed into orthophosphate during the treatment process. Soluble organically bound non-biodegradable phosphorus will pass through a wastewater treatment plant. A typical wastewater contains 3 to 4 mg/L phosphorus as phosphate, 2 to 3 mg/L as polyphosphate, and 1 mg/L as organically bound phosphorus [12].

Phosphorus content in wastewater can be measured as

- Orthophosphate
- Dissolved orthophosphate
- Total phosphorus
- Total dissolved phosphorus (i.e., all forms except particulate organic phosphorus).

Phosphorus removal is important as it is a limiting nutrient for algae growth in many fresh water systems. It is also particularly important for water reuse systems where high phosphorus concentrations may lead to fouling of downstream equipment such as reverse osmosis. EPA classifies advanced treatment as “a level of treatment that is more stringent than secondary or produces a significant reduction in conventional, non-conventional, or toxic pollutants present in the wastewater” [13].

Removal Of Phosphorus

Phosphorus can be removed biologically in a process called enhanced biological phosphorus removal. In this process, specific bacteria, called polyphosphate accumulating organisms (PAOs), are selectively enriched and accumulate large quantities of phosphorus within their cells (up to 20 percent of their mass). When the biomass enriched in these bacteria is separated from the treated water, these biosolids have a high fertilizer value.

Phosphorus removal can also be achieved by chemical precipitation, usually with salts of iron (e.g. ferric chloride), aluminum (e.g. alum), or lime [1]. This may lead to excessive sludge production as hydroxides precipitates and the added chemicals can be expensive. Chemical phosphorus removal requires significantly smaller equipment footprint than biological removal, is easier to operate and is often

more reliable than biological phosphorus removal. Another method for phosphorus removal is to use granular laterite.

Once removed, phosphorus, in the form of a phosphate-rich sludge, may be stored in a landfill or resold for use in fertilizer.

Barriers to Implementing Nutrient Removal:

There are a number of barriers that may impact forward progress in implementing nutrient removal processes and achieving reductions in aquatic ecosystems beyond that which is currently being achieved, including:

- Costs
- Limitations on physical expansion
- State resources
- Increased carbon footprint
- Advanced operations and control

Nutrient removal comes at a cost to municipal wastewater treatment facilities and their ratepayers. A second factor affecting the cost of nutrient removal at wastewater facilities is limitations on physical expansion of wastewater treatment facilities. Some plants are located in urban areas and do not have any way to obtain the physical space necessary to expand. Space limitations can severely limit the type of approaches that can be used to reduce nutrients. Two potentially negative environmental impacts of employing advanced technologies to remove nutrients from wastewater are the increase in the carbon footprint and quantity of bio-solids requiring disposal. The increased carbon footprint will result not only from the nitrogen removal process but also from the increased energy usage necessary to power the technology needed to achieve the proposed nutrient reduction levels. The level of process control is much greater than for BOD₅ and TSS removal. In addition, these processes are susceptible to wet weather, cold weather, and inhibitory substances entering the plants. Despite the challenges associated with nutrient removal, new research and information are steadily becoming available.

Chemical: Deep-bed down-flow two-media filters were used in pilot plant studies with filtration of secondary settled wastewater. FeSO₄ or FeCl₃ was applied as a precipitation agent and NaAc·3H₂O was chosen as a carbon source when denitrification was desired. The concentration of PO₄-P in the filtrate from the pilot plant study never exceeded 0.05 mg PO₄-P/l when iron salts were dosed. The total nitrogen reduction over the filter bed increased from an average of 2.3 mg (NO₃+NO₂)-N/l at the beginning of each experiment to an average of 4.3 mg (NO₃+NO₂)-N/l towards the end of the test. When only secondary settled wastewater, suspended solids, primary settled wastewater, iron salts, or sodium acetate was added, at a hydraulic load of 10

m/h, the time before clogging became 100 h, 10 h, 10 – 15 h, 20 – 40 h, and 20 – 40 h, respectively. Almost the entire pressure drop was located on the surface of the filter bed and 0.25 metre down in the expanded clay layer. [4]. The enhanced biological phosphorus removal (EBPR) method is widely adopted for phosphorus removal from waste-water, yet little is known about its microbiological and molecular mechanisms. Therefore, it is difficult to predict and control the deterioration of the EBPR process in a large-scale municipal sewage treatment plant. In this study authors used a novel strain isolated in the laboratory, *Pseudomonas putida*, which had a high phosphate accumulating ability and could recover rapidly from the deteriorated system and enhance the capability of phosphorus removal in activated sludge. Strain GM6 marked with *gfp* gene, which was called GMTR, was delivered into a bench-scale sequencing batch reactor (SBR) of low efficiency, to investigate the colonization of GMTR and removal of phosphorus. After 21 days, the proportion of GMTR in the total bacteria of the sludge reached 9.2%, whereas the phosphorus removal rate was 96%, with an effluent concentration of about 0.2 mg L⁻¹[5]. A series of jar tests using iron (III) chloride were carried out to identify factors affecting phosphorus removal. Mixing conditions and the extent of iron hydrolysis prior to reaction with phosphate ions were explored using crude sewage as a medium. Total phosphorus removal of 80% was achieved at a dose of 1.48:1 molar ratio Fe:P. When a mixture of pre-hydrolysed iron and iron chloride was added, 80% total phosphorus removal was achievable at a dose of 1.86:1 molar ratio Fe:P. Metal hydroxides have the capability to remove phosphorus by absorption but less efficiently [6].

Wollastonite, a calcium metasilicate mineral mined in upstate New York, is an ideal substrate for constructed wetland ecosystems for removing soluble phosphorus from secondary wastewater. Design parameters, required for designing a full-scale constructed wetland, were measured in vertical upflow columns with hydraulic residence times varying from 15 to 180 h. Secondary wastewater was pumped vertically upward through eleven soil columns, 1.5 m in length and 15 cm in diameter and influent and effluent concentrations of soluble phosphorus were monitored for up to 411 days. Greater than 80% soluble phosphorus removal (up to 96%) was observed in nine out of 11 columns and effluent concentrations of ranged from 0.14 to 0.50 mg/l (averaging 0.28 mg/l) when the residence time was >40 h. [7]

Column experiments were conducted to examine the removal of phosphorus and nitrogen from sewage

effluent by passage through sand amended with bauxite refining residue (red mud). Red mud was neutralized with 5% gypsum. An average of 24% nitrogen removal was obtained with 30% red mud, 9% removal with 20% red mud and very little removal with 10% red mud. An average of 91% phosphorus removal was obtained with 30% red mud, 63% removal with 20% red mud and 50% removal with 10% red mud. The decrease in phosphorus and nitrogen removal with decreasing red mud content was caused by a decrease in the adsorption capacity of the soil and an increase in the infiltration rate [8]. The choice of chemical dose used depends on the stability of process required, which increases with increasing dose, capital available and the EC limits imposed on the effluent to be discharged. T. Clark (1997) investigated the following:

1. Chemical dosing onto a BAF using ferrous sulphate heptahydrate is a highly effective method for the removal of phosphorus from wastewater, and it required a very low chemical consumption.
2. To meet EU phosphate discharge standards, the optimum dose of iron (II) is 1:1.25 (weight ratio of P: Fe).
3. Nitrification appeared to be significantly affected by the presence of the chemicals.

Chemical Dose And Phosphorus Removal Efficiency

In all observations on chemical removal of phosphorus, the percent phosphorus removal increases and effluent phosphorus concentration decreases as the molar chemical dose for metal salts increases, but the incremental removal diminishes with increased dosages (Sedlak 1991, Szabo et al. 2008, WEF and ASCE 2009). Smith et al. (2007) found that for typical influent phosphorus concentrations, ferric doses above 1.5 to 2.0 Medose/Pini ratios are sufficient to remove 80 to 98 percent of soluble phosphorus. Reaching very low effluent TP concentrations, i.e. below 0.10 mg/L, requires significantly higher ratios of about 6 or 7 Medose/Pini. A similar dose was reported for 75 to 95 percent phosphorus removal from wastewater using alum (WEF and ASCE 2009). For similar phosphorus removal efficiencies using pre-polymerized salts such as PACl or sodium aluminate, a higher dose is needed. Factors that influence dose and removal efficiency may include pH, alkalinity, competing substances in the wastewater, initial mixing conditions and flocculation.

Mixing at dosage point: Mixing at the dosage point is necessary to ensure that the metal and phosphate molecules react. Mixing intensity can be represented by the velocity gradient, G , in units of seconds⁻¹. Smith et al. (2007) reported that the reactions of phosphates at the surface of the hydrous ferric oxides depend highly on the mixing conditions. Rapid mixing means that the surface sites are available, whereas with slower mixing, many of the metal oxides would form in the absence of phosphate and render internal oxygen atoms unavailable for binding. Bench-scale kinetic experiments by Szabo et al. (2008) revealed that a majority of phosphate will react with iron in the first 10 to 20 seconds under ideal mixing conditions ($G = 425 \text{ second}^{-1}$). The authors recommend that plants attempt to achieve a very high mixing intensity at the dosage point. Mixing time, at high energy are generally in the range of 10 to 30 seconds.

After the initial rapid kinetics, phosphorus removal can continue with slow reaction kinetics between the phosphate and iron over many hours and even days.

Flocculation: After rapid mixing at the dosage point, gentle mixing is needed to form flocs that can be settled or removed through a solids separation process. This is critical for meeting low effluent phosphorus requirements. Often, movement of the wastewater through the treatment plant is sufficient for floc formation (USEPA 2008b). Flocculation can be limited by insufficient time or conditions that disrupt floc formation such as pumping and aeration.

pH and Alkalinity: The highest removal efficiency for chemical precipitation is within a pH range of 5.5 to 7.0 (Szabó et al. 2008). Between pH 7 and 10, phosphorus removal efficiency declines because the surfaces of metal hydroxides are more negatively charged, and soluble iron hydroxides begin to form. At low pH values, the solubility of the precipitant is reduced, and at extremely low pH values, metal hydroxide precipitation is limited. Szabó et al. (2008) reported similar relationships between phosphorus removal efficiency and pH for both alum and ferric chloride.

COD and TSS in Raw Wastewater: The efficiency of metal salt addition in the primary treatment step can be affected by the wastewater characteristics. Based on the results of jar tests using municipal wastewater, Szabo et al. (2008) observed a relationship between organic content and efficiency of phosphorus removal using metal salts. Between chemical oxygen demand (COD) values of 300 to 700 mg/L, the phosphate removal efficiency decreased with increasing COD. Similar results were observed for total suspended solids (TSS), with lower phosphorus removal efficiency at higher TSS concentrations. In addition to reduced efficiency

during primary treatment, organic content can reduce the efficiency of metal salt removal of phosphorus in activated sludge reactors. Iron and aluminum ions can react with humic and fulvic acid substances to form insoluble complexes with the metal ions and their mineral oxides, thereby blocking the reactive sites for phosphate precipitation (WERF 2009).

When to remove P: The removal of carbonate alkalinity and phosphorus by lime prior to biological treatment can have a negative impact on nitrification processes (WEF and ASCE, 1998). Previous studies showed that the hydroxide alkalinity can be balanced by the hydrogen ions produced during nitrification. Sludge recalcification can be used to achieve high removal efficiencies using lime in tertiary treatment.

One potential advantage to adding chemicals during primary treatment instead of tertiary treatment is reduced capital costs and space requirements as a result of removing additional BOD and TSS and reducing the load to downstream processes, thereby reducing the size of the subsequent activated sludge basins and the amount of oxygen transfer needed. Bench-scale and pilot scale tests are often used to determine the correct mixing rate for a given composition of wastewater and chemicals used, including polymer (USEPA, 1999a). Direct addition of metal salts to activated sludge processes followed by conventional clarification can typically remove TP to effluent levels between 0.5 and 1.0 mg/L (Bott et al., 2007).

Conclusion

To meet the water crises and to increase the potential for water reuse nutrient removal is necessary to increase the categories of reuse. Biological nutrient removal is an established technology and has been widely and successfully used in practice. However to overcome the disadvantages, chemical methods to remove phosphorus is an attractive method with optimum dose of coagulant and time.

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