Phosphorus Removal From Wastewater via Chemical Process With Stoichiometric and pH Solubility Control

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Phosphorus is a significant pollutant in wastewater and has proven difficult to remove to low levels in a practical and economical manner. However, a chemical process for removing phosphorus from water through control of equilibria and solubility has been developed and demonstrated at a laboratory through pilot scale via continuous-mode on-site testing at municipal water resource recovery facilities and lakes. The process is based on coagulation and precipitation and utilizes conventional water treatment chemicals and equilibrium-based chemistries to a heretofore previously unpracticed level of control. It uses traditional solid/liquid separation technology, making it a readily deployable, cost-effective, and safe technique to bring total phosphorus concentrations to below 100 parts per billion (ppb) extremely economically with one stage, and to below 20 ppb with two-stage processing. Furthermore, the process provides sanitary beneficiation and significantly reduces biochemical oxygen demands (BODs) and coliform bacteria by 33 percent and 99 percent, respectively.

Water commonly contains soluble ions as impurities resulting from natural processes, such as dissolution of natural minerals and materials and from human activities, including agriculture, mining, manufacturing, chemical processing, and domestic and industrial water use. Dissolved ions are potentially disruptive to the normal steady-state of ecological systems, such as encouraging the undesired overgrowth of cyanobacteria (algae), encouraging eutrophication, and causing deleterious effects on the systems that extend beyond the water systems themselves, as well as being undesirable for ecological release and human use in potable water systems.

The U.S. Environmental Protection Agency (EPA) currently regulates phosphorus discharge on a concentration-emitted basis. Permits are generally issued on a site basis and vary widely across the United States. Some states have no regulated limits, whereas others have implemented regulations in the sub-100, sub-75, or sub-50 ppb range. There is a clear, concerted ongoing effort to reduce phosphorus emissions through

regulation, and regulations are tightening and are expected to continue to tighten as phosphorus-removal technology and cost efficiencies for removal improve and are thereby more readily deployable to reduce the directly assignable impacts of phosphorus on the environment.

Efficient, economical means of removal of dissolved ions are sought to provide cleaner water for the sustainment of ecological systems, prevention of human activity-induced environmental changes, eutrophication, and negative toxicological effects, as well as for further clean potable water use. There are no known documented economically viable full-scale processes by which <20 ppb total phosphorus is practically attainable due to cost constraints. Various means of phosphorus reduction are commonly practiced and have been for decades, including chemical treatment by Al and Fe chemicals (Bowker and Stensel, 1990); however, the levels achieved do not approach those described here.

Equilibria for the various species in solution have been previously studied (Stumm and Morgan, 1996), and the relationships are complex and made more so by the variability of composition of the dissolved ions in solution. Removal of phosphorus and other nutrients and impurities by coagulation and flocculation has been extensively investigated, reported, and practiced (Edzwald, 2011). Research progress has not resulted in a process suitable for large-scale deployment, and work has suggested that adsorption, rather than coagulation, may play a more significant role in phosphorus removal (Yang et al, 2010) in the current deployed processes.

There is no prior technological deployment that uses the specific control of pH as a specified means of control of the process and utilizes a process-controlled two-stage process with potentially different complexation agents in each stage that effectively removes phosphorus (not exclusively orthophosphate, but oligomeric organic/inorganic phosphorus, present in suspended solids and dissolved species). There is no reported or implemented process that achieves the level of removal to <20 ppb phos-

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phorus, regardless of the influent composition and concentration, as does this process. Furthermore, this process provides multiple stages of complexation and controlled pH adjustment to remove impurities based on solubility to achieve heretofore unprecedented levels of nutrient and impurity removal.

Methodology

It is well established that ionic salts of phosphorus, primarily phosphate, have pH-dependent solubilities, and have equilibria dependent on the other dissolved species concentration and composition in solution. The pH dependence can be exploited in two ways: first, with appropriate water-safe, EPA-approved reagents, the pH regions of highest solubility can be used to provide the largest amount of dissolved phosphorus; and second, the solubility minima can be used to remove the largest fraction of precipitated phosphorus solids. The processes reported here utilize the adjustment of pH, the control of specific pH gradients in solution, and the conventional-based water treatment chemicals to affect the pH and the formation of phosphorus complexes as precipitate.

In terms of solids removal, and therefore solids produced, this resultant product can be dewatered and distributed as a soil nutrient enhancement, further refined via chemical processing to a salable product, amended to an aggregate, or landfilled. The fate of the solid is largely contingent upon the impurities present in the influent to the process.

To evaluate the phosphorus removal process, streams of water were passed through the system via a positive displacement pump, and the exit stream was decanted from an overflow clarifier. The system employs chemicals
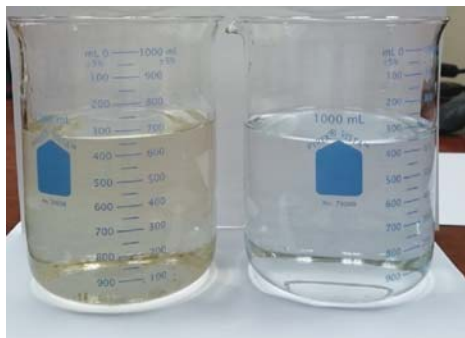
Figure 1. Water Recovery Facility Effluent, Pre-treatment and Post-Treatment

containing aluminum, calcium, magnesium, flocculating polymer, and pH-adjusting acid. Total phosphorus concentrations were determined using the EPA acid persulfate digestion method from the *Standard Methods for the Examination of Water and Wastewater*, 4500-P-B and E, as Hach Method 8190. Independent laboratory results from a contracted third-party laboratory are reported (Foundation Analytical Laboratory; Cherokee, Iowa). Secondary confirmation, as well as minor impurities, were detected via inductively coupled plasma optical emission spectrometry (ICP-OES) and confirmed through a third-party laboratory (Spec-

tro Analytical Instruments, Ametek Materials Analysis Division; Mahwah, N.J.).

Results and Discussion

The process provides water cleaning, sanitization, and phosphorus removal. The effluent from a water recovery facility, properly operating well within discharge limits, is shown in Figure 1 on the left. A similar sample of water was continuously processed by this phosphorus removal process and the effluent is shown on the right; the water is water-white, odorless, and colorless.

The results of several demonstrations of the process for illustration are presented: two water resource recovery facilities (WWTP1 and WWTP2) and a retention pond requiring remediation (Pond1). The phosphorus concentration results are depicted in Figure 2 for the influent (influent for the WWTPs only), effluent (the effluent of the WWTPs, or the pumped effluent from the pond), for a conventional alum addition (at Al = 10 x P), and for the water produced by the process described.

Figure 3 indicates the results, with y-axis to scale to allow visualization of the effluent phosphorus levels from the described process. The results suggest that the pH-controlled solubility equilibrium of phosphorus complexes formed as the result of the coagulant addition provides removal to <20 ppb of all detectable phosphorus species results that cannot be obtained through conventional treatment alone.

Table 1 contains the observed results of the effluents from one of the water resource recovery facilities and the results of the phosphorus-removal process. The intended phosphorus removal was achieved, as was sanitary beneficiation. Coliform bacteria was significantly reduced to levels <1 percent of the original levels. Interestingly, the level of BOD was reduced by >33 percent as well, indicating that the coprecipitation/clarification process captures additional molecules.

Conclusions

This new process demonstrates that there is a readily deployable, cost-effective, and safe technique to bring total phosphorus concentrations to below 100 ppb, as well as reduction of BODs by >33 percent and coliform bacteria by 99 percent. Future work will provide information relating to the expected impact of the process on removing other impurities and nutrients. Additional demonstrations and studies will be conducted to evaluate its applicability to different influent compositions and to demonstrate the economics and how the process can be incorporated into existing wastewater and industrial site operations.
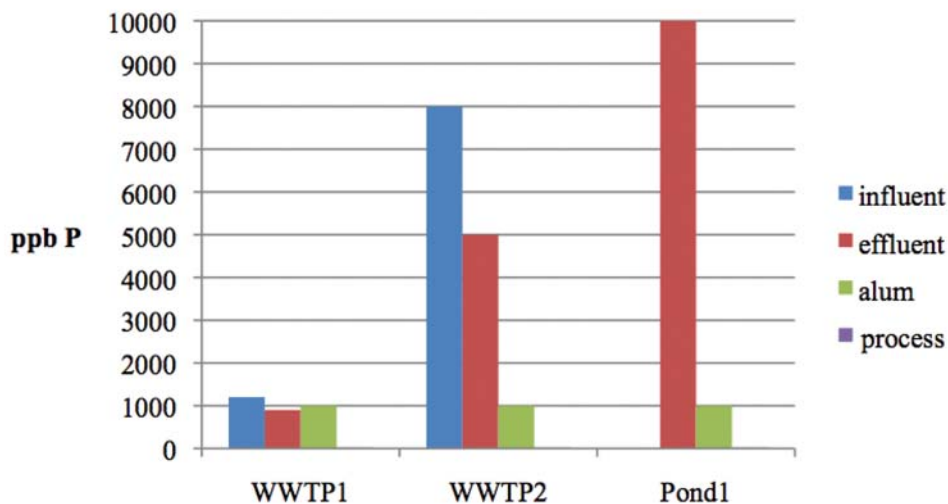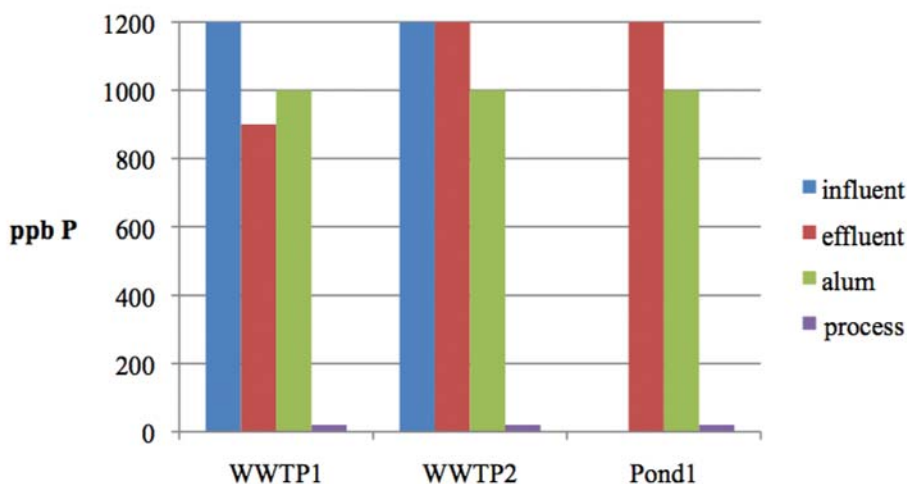

Figure 2. P Concentration

Figure 3. P Concentration (y-axis truncated to show low values)

References

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Table 1. Effluent Results

Test	Units	Influent	ONE stage	TWO stage
Total Phosphorus	ug/L, ppb	4300	110	20
Nitrate as N	mg/L, ppm	24.3	24.1	23.4
BOD[1]	mg/L, ppm	12.1	7.6	8.0
COD[2]	mg/L, ppm	23.6	12.4	12.4
TSS[3]	mg/L, ppm	9	3.5	9.5
TDS[4]	mg/L, ppm	949	1205	1471
TOC[5]	mg/L, ppm	8.43	5.04	4.81
Coliform	MPN/100mL	48100	2419	435
E. coli	MPN/100mL	33400	142	22
pH	pH units	7.4	7.3	7.4
Hardness	mg/L, ppm	464	598	634
Conductivity	uS/cm	1540	1792	1981

[1]Biochemical oxygen demand
[2]Chemical oxygen demand
[3]Total suspended solids
[4]Total dissolved solids
[5]Total organic carbon