Significance of Design and Operational Variables in Chemical Phosphorus Removal

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ABSTRACT: Batch and continuous experiments using model and real wastewaters were conducted to investigate the effect of metal salt (ferric and alum) addition in wastewater treatment and the corresponding phosphate removal from a design and operational perspective. Key factors expected to influence the phosphorus removal efficiency, such as pH, alkalinity, metal dose, metal type, initial and residual phosphate concentration, mixing, reaction time, age of flocs, and organic content of wastewater, were investigated. The lowest achievable concentration of orthophosphate under optimal conditions (0.01 to 0.05 mg/L) was similar for both aluminum and iron salts, with a broad optimum pH range of 5.0 to 7.0. Thus, in the typical operating range of wastewater treatment plants, pH is not a sensitive indicator of phosphorus removal efficiency. The most significant effect for engineering practice, apart from the metal dose, is that of mixing intensity and slow kinetic removal of phosphorus in contact with the chemical sludge formed. Experiments show that significant savings in chemical cost could be achieved by vigorously mixing the added chemical at the point of dosage and, if conditions allow, providing a longer contact time between the metal hydroxide flocs and the phosphate content of the wastewater. These conditions promoted the achievement of less than 0.1 mg/L residual orthophosphate content, even at lower metal-to-phosphorus molar ratios. These observations are consistent with the surface complexation model presented in a companion paper (Smith et al., 2008). *Water Environ. Res.,* **80,** 407 (2008).

KEYWORDS: adsorption, chemisorption, chemical phosphorus removal, kinetics, precipitation, co-precipitation.

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Introduction

Chemical phosphorus removal using metal salts is an important technology for achieving very low residual phosphorus concentrations in wastewater treatment plant effluents. Despite its widespread use, the actual complex mechanism, likely consisting of iron and phosphate complexation through an oxygen atom, precipitation of hydroxides, co-precipitation of phosphate, chemisorption/adsorption, diffusion, and coagulation and flocculation processes, has not been studied sufficiently. In practice, this

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typically leads to high (''safe'') doses and consequently unnecessarily high chemical costs and sludge production.

It is well-known that, in chemical phosphorus removal, solids that contain variable ratios of metals and phosphate are formed (WEF, 1998). Measured residual phosphate concentrations, both in plants (i.e., Takács et al., 2006) and in experiments shown in this paper, are highly variable. Therefore, pure component, chemical-equilibrium-based models, which predict fixed equilibrium residual phosphorus concentration, are not suitable to calculate chemical sludge formation and residual phosphorus concentration. Equilibrium models also assume ideal mixing and instant reactions. The effect of mixing on phosphorus removal was documented by Sagberg et al. (2006). To develop a comprehensive model that is able to describe these complex processes, an extensive measurement program was carried out as the first step.

The objectives of the research project initiated by the Washington D.C. Water and Sewer Authority were to

(1) Determine the most important design and operating factors influencing phosphorus removal; and
(2) Investigate the potential chemical, physicochemical, and physical mechanisms and their consequences on engineering design and operation of these systems.

A large number of laboratory batch and a series of continuous-flow tests were used to establish the effect and role of initial and residual phosphorus, metal dose, pH, alkalinity, chemical oxygen demand (COD) and solids concentration, kinetics, mixing, time, chemical solids formation, and the mechanism of chemical phosphorus removal. Experimental results and conclusions are presented in this paper.

In the companion paper by Smith et al. (2008), some of these variables (dose, pH, and floc age) are investigated in more detail, to develop a conceptual model for phosphate removal. The developed model is based on phosphate complexation—active oxygen sites bonding iron and phosphorus atoms according to chemical equilibrium principles—and can predict phosphate removal under well-controlled laboratory conditions.

This paper is divided into subsections including jar test methodology and results and continuous-flow-test methodology and results.

Jar Test Methodology

Environmental and operational conditions influencing phosphorus removal processes were investigated in laboratory experiments.

Coagulation-flocculation jar tests were carried out with model and real wastewater. More than 1500 model wastewater samples and 600 real wastewater samples were analyzed. Model wastewater
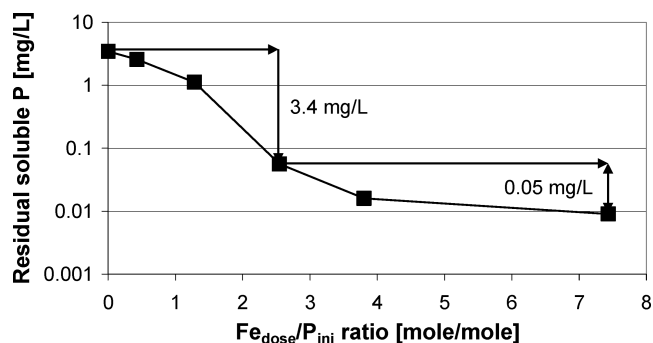
Figure 1—Residual soluble phosphorus in terms of initial Fe/P molar ratio (phosphorus solution, ferric chloride, $pH_{ini} = 6.5$, $P_{ini} = 3.5$ mg/L, and $Alk_{ini} = 125$ mg $CaCO_3$/L).

contained a phosphate solution prepared from tap water and dipotassium hydrogen orthophosphate (KH_2PO_4); raw wastewater was collected from municipal wastewater treatment plants in Hungary. All experiments were performed in 1-L glass cylinders with a Kemira flocculator device (Kemira Kemi AB, 1990). In the first set of tests (examining the effects of dose, pH, initial phosphorus concentration, alkalinity, and organics), coagulant was added to a 1-L sample during intensive stirring (350 r/min, $G = 425$ second^{-1}). The intensity of mixing is characterized in this work using the mean velocity gradient, G (Grady et al., 2007). A calibrated relationship between the propeller speed and mean velocity gradient provided by the manufacturer of the flocculator device was used to calculate the G values reported. After initial rapid mixing, the flocs were allowed to grow for at least 10 minutes, while the sample was gently mixed (20 r/min, $G = 6$ second^{-1}). In the case of raw wastewater, samples were settled for 20 minutes. The pH was set before each experiment, but it was not readjusted during or after coagulation. Model systems (phosphorus solutions) were buffered by the natural alkalinity of tap water or by addition of sodium bicarbonate ($NaHCO_3$). Most of the wastewater experiments were carried out at the original pH without pH control. Samples were taken at different times and were filtered immediately through a membrane filter, with 0.45-µm nominal pore size (Sartorius Stedim Biotech, Göttingen, Germany). Phosphate was analyzed according to the ascorbic acid photometric method, with a detection limit of 10 µg-P/L.

Coagulant types used in the experiments were ferric chloride, ferric sulfate, aluminum sulfate, and pre-polymerized aluminum chloride.

Investigating Kinetics

Laboratory experiments to optimize chemical phosphorus removal from wastewaters are typically performed with fast mixing ($G = 300$ to 1000 second^{-1}), providing optimal removal efficiency in short-term experiments. In wastewater treatment plants, mixing at the dosage point is typically poor ($G = 20$ to 100 second^{-1}), and flocculation is hindered by insufficient flocculation time and several processes that disrupt floc formation, including pumping, aeration, and phase separation. To gain a better understanding of phosphorus removal kinetics, the effect of mixing intensity (as measured by the mean velocity gradient, G) and floc aging in the process of chemical dosing were investigated in laboratory experiments.

In certain experiments, the phosphorus removal capacity of ferric hydroxide flocs was investigated (similarly to earlier experiments

[Licskó, 1976]). Ferric hydroxide flocs were preformed in the absence of phosphate ions. This simulates the effect of dosage on plants with insufficient mixing, in which these flocs are forming without coming into contact with the soluble phosphorus content of the wastewater. Subsequently, some of the preformed flocs were used immediately for phosphorus removal, while others were aged for various lengths of time, and their soluble phosphorus removal (adsorption) capacity was tested in jar tests.

Jar Test Results

The jar test results are divided into 11 subsections that will investigate the relevant issues.

Influence of Metal-to-Phosphorus Molar Ratio. The metal-to-phosphorus (Me/P) molar ratio is one of the main factors determining phosphorus removal efficiency. The Me/P molar ratio can be expressed in various forms. The three frequently used expressions are as follows:

(1) Initial Me/P molar ratio (moles of metal dosed divided by moles of soluble phosphorus initially present, Me_{dose}/P_{ini}).
(2) The Me/P molar ratio in the solid co-precipitate (Me_{prec}/P_{prec}).
(3) Moles of metal dosed per moles of soluble phosphorus removed (Me_{dose}/P_{prec}). For typical pH values, this latter is very similar to (Me_{prec}/P_{prec}), because most metal dosed will be incorporated to the co-precipitate.

Initial Metal-to-Phosphorus Ratio. For a given wastewater, applying higher coagulant doses (Me_{dose}/P_{ini} ratio) results in a lower residual soluble phosphorus (PO_4-P) concentration. In the case of small coagulant doses (and relatively high residual phosphorus), the relationship between dose and the residual phosphorus is close to linear; however, specific phosphorus removal decreases with increasing coagulant dose (Figure 1). For the typical concentration ranges (initial soluble phosphorus concentration between 0.5 and 6.0 mg/L), to achieve 80 to 98% soluble phosphorus removal efficiency, doses above 1.5 to 2.0 Me_{dose}/P_{ini} are required, even in "pure" phosphorus solutions and among the most favorable environmental circumstances (efficient mixing, optimal pH range, etc.). Reaching a low (<0.1 mg-P/L) residual PO_4-P concentration requires metal doses far in excess of the stoichiometric 1 moleMe/moleP ratio.

Metal-to-Phosphorus Ratio in the Precipitate. The amount of phosphorus incorporated to the precipitate (P_{prec}) can be calculated as the difference of initial phosphorus (P_{ini}) and residual soluble phosphorus concentration (P_{res}) (i.e., $P_{ini} - P_{res}$). In the same way, the amount of metal in the solid precipitate is $Me_{dose} - Me_{res}$. According to laboratory experiments carried out by addition of ferric chloride to phosphorus solution, above pH 5, the residual soluble iron (Fe_{res}) (measured by the standard phenanthroline method) is generally less than 0.1 mg/L and generally insignificant compared with the dose (Figure 2). At low pH, residual iron is high because the formation of soluble ferric complexes is dominant. In Figure 2, the lower Fe_{res} values at low pH may be attributed to ferric phosphate ($FePO_4$) (a solid) formation. The $FePO_4(s)$ is only expected to form at low pH values (Smith et al., 2008).

The amount of iron precipitated can be estimated by the amount added, as practically all the added iron precipitates in the typical operating pH range. Consequently, the iron-to-phosphorus ratio in the co-precipitate depends on the initial iron-to-phosphorus ratio. For $Me_{dose}/P_{ini} > 1.0$ mole/mole, the higher the initial molar ratio, the higher the Me_{prec}/P_{prec} will be in the co-precipitate (Figure 3). The slope on the bottom is the practical boundary and applies in
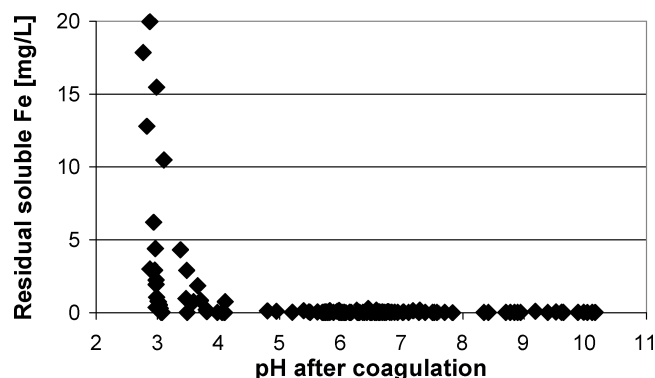
Figure 2—Residual soluble iron (Fe) concentration versus pH after the coagulation (phosphorus solution, ferric chloride, P_{ini} = 0.5 to 12.5 mg/L, pH_{ini} = 3.0 to 10.2, Fe_{dose} = 0 to 50 mg/L, and Alk_{ini} = 0 to 250 mg $CaCO_3$/L).

those cases when almost no residual phosphorus is left behind (Me_{dose}/P_{ini} = Me_{prec}/P_{prec}). This is the optimal case. Points further from this boundary show data where environmental conditions (pH, organic concentration, mixing, etc.) were not optimal for phosphorus removal.

Influence of Coagulant Type. The aluminum (Al^{3+})- and ferric iron (Fe^{3+})-containing coagulants show similar efficiencies (on a molar basis) for phosphate removal, both in model and real wastewaters. Figure 4 shows the results of several experiments with raw wastewater treated by different coagulants. The scatter in the data is the result of the significantly different raw wastewater composition of many samples (initial PO_4-P, total suspended solids [TSS], COD concentration, pH, etc.). Figure 5 shows the results of a specific experiment using the same raw wastewater.

Ferric and aluminum chemistry, the various ionic species formed, and their ionization constants differ significantly for iron and aluminum ions. However, the most important reaction directly affecting phosphate removal is the formation of metal hydroxides (hydrous metal oxides, or specifically in the case of iron, hydrous ferric oxides), which is the dominant process in the case of both metals at typical plant pH values (National Institute of Standards and Technology, 2001). The phosphate complexation properties of these metal hydroxides were only investigated in detail for
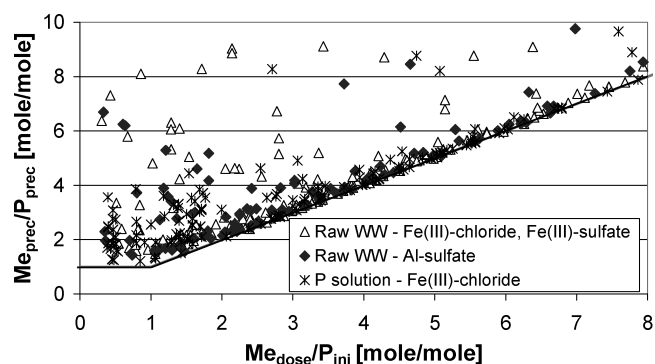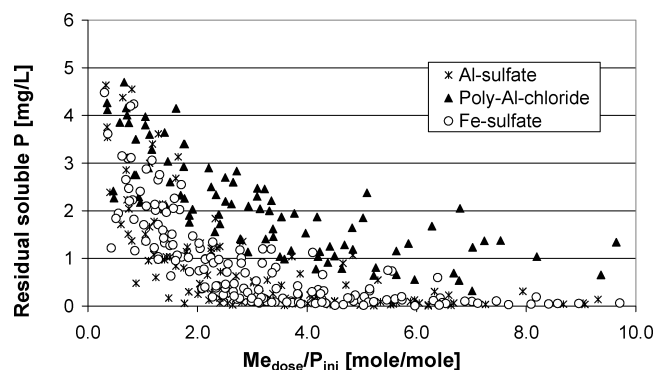

Figure 4—Residual soluble phosphorus applying different types of coagulants (different raw wastewater samples; pH_{ini} = 6.8 to 8.7, P_{ini} = 0.9 to 7.4 mg/L, TSS_{ini} = 50 to 2050 mg/L, and COD_{ini} = 200 to 4000 mg/L; 500 samples).

ferric ions (Smith et al., 2008); however, based on the results of these jar tests, they must be similar for aluminum.

Pre-polymerized salts are less efficient in removing PO_4-P, as shown in Figures 4 and 5, in agreement with the works of Fettig et al. (1990), Gillberg et al. (1996), and Ratnaweera et al. (1992). Because precipitate formation decreases with increasing basicity (hydroxide-to-metal ratio or degree of polymerization), the higher the basicity, the lower the phosphate removal efficiency will be (Gillberg et al., 1996; Ratnaweera et al., 1992).

Influence of pH. Full-scale and laboratory data show that, if conditions are favorable, very low soluble phosphorus residuals (P_{res}) can be achieved in the chemical phosphorus removal process in a wide pH range, for both model water (phosphorus solution) and raw wastewater. Figure 6 contains full-scale plant data from the Noman Cole (Fairfax, Virginia) and Blue Plains (Washington D.C.) wastewater treatment plants. The plants have been able to achieve very low (0.01 to 0.05 mg-P/L) soluble phosphorus concentrations in the majority of effluent samples in a wide range of pH conditions (6.0 to 7.5).

In laboratory experiments using tap water with initial soluble phosphorus concentrations (P_{ini}) of 0.5 to 12 mg/L, residual PO_4-P <25 μg/L was achieved at pH 3.5 to 8.5, if other environmental conditions (i.e., mixing) were favorable and the coagulant dose was

Figure 3—Metal-to-phosphorus molar ratio in the precipitate, in terms of initial Me/P ratio (P_{ini} = 0.5 to 12.5 mg/L and pH_{ini} = 3 to 10).
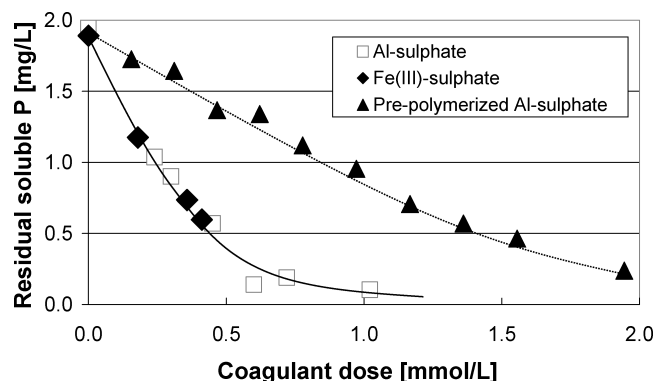

Figure 5—Residual soluble phosphorus in one raw wastewater sample, using different types of coagulants (P_{ini}=1.9 mg/L and pH_{ini} = 7.1).
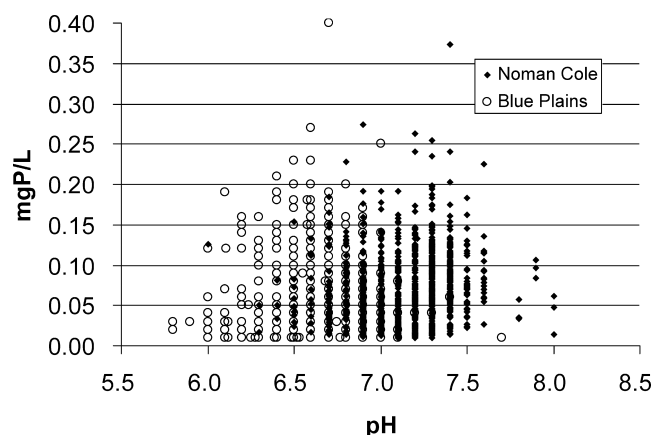
Figure 6—Effluent soluble phosphorus data for 3 years, in two large plants in the Eastern United States.

Figure 8—Residual soluble phosphorus concentration in terms of pH after coagulation (phosphorus solution, aluminum sulfate, and ferric sulfate; P_{ini} = 3.6 to 4.0 mg/L).

high enough (Figure 7). Similar residual PO_4-P concentrations could be reached in raw wastewater (COD_{ini} = 250 to 1000 mg/L and TSS_{ini} = 50 to 550 mg/L) between pH 5.0 and 7.0 without pH control (the detection limit for the colorimetric phosphate method is 10-µg/L phosphorus; some of the measured values were below the detection limit, and these are shown to be 10-µg/L phosphorus). However, to achieve such low PO_4-P concentrations in the treated water, high metal doses were required, even if other conditions were favorable. To assure P_{res} = 0.1 mg/L, at least Me_{dose}/P_{ini} = 2.5 mole/mole was needed, and Me_{dose}/P_{ini} = 5.0 mole/mole was necessary to obtain P_{res} = 0.01 mg/L in these experiments. In cases when environmental conditions were not optimal, the above residual phosphorus concentrations could not be reached. Figure 7 includes these cases and the data without chemical dosage and using small coagulant doses. These laboratory results cannot be directly applied to predict full-scale plant effluent phosphorus concentrations, as mixing and hydraulics will play a large role at these low concentrations (typically in the negative sense, increasing residuals).

In the WEF model (WEF, 1998), the lowest soluble phosphorus concentration possible is 46 µg/L, and 0.1 mg-P/L is achievable between pH values of 6.5 and 7.3 only. In some of our experiments, lower residual phosphorus concentrations were observed in a wider

pH range than predicted by this chemical equilibrium model. This may be attributed to optimal experimental conditions, which are not always achievable in full-scale plants; new, more sensitive analytical techniques; and a more extensive dataset available.

At extremely low or high pH values, the minimum achievable P_{res} and thus the efficiency of phosphorus removal depends on pH. At acidic pH values, the precipitation of metal hydroxide is limited, and mostly soluble phosphate complexes form. Even the already precipitated phosphate will redissolve when decreasing the pH, by adding more coagulant to the system (despite the higher coagulant dose).

At alkaline pH values (pH 7 to 10), the surface of the metal hydroxides is more negatively charged, and soluble iron hydroxide complexes [i.e., $Fe(OH)_4^-$] start to form (National Institute of Standards and Technology, 2001). Thus, the phosphorus removal efficiency decreases with increasing pH. At pH values greater than 10, the PO_4-P can form a precipitate with the magnesium and calcium ions available in most wastewaters (Fettig et al., 1990), and reduction of the soluble phosphorus concentration can take place without iron or aluminum coagulant addition.

Phosphorus removal has the highest efficiency between pH 5.5 and 7.0. Within this pH range, which occurs most of the time in practice after metal salt addition, the effect of pH is not very important in co-precipitation and coagulation reactions. Both the molar ratio in the precipitant and the residual phosphorus concentration are not significantly affected by pH within this interval (Figure 8). These results are in contradiction with earlier studies (Fettig et al., 1990; Jenkins et al., 1971; Lijklema, 1980), in which strong pH dependency was found between pH 5 and 8, for both adsorption and co-precipitation of phosphorus, both for iron and aluminum coagulants.

The results show that aluminum and ferric salts remove phosphorus with similar efficiency, and the pH dependency of residual phosphorus concentration is comparable (Figure 8). Therefore, the choice between iron and aluminum salts should depend on other factors, such as availability, price, and sludge handling possibilities. In this paper, all of the other results and references relate to ferric salts, not alum.

Influence of Alkalinity. Jar tests with model wastewater showed that phosphorus removal efficiency is influenced by the alkalinity of the raw wastewater. In the same pH range (though without pH control), higher alkalinity resulted in slightly higher
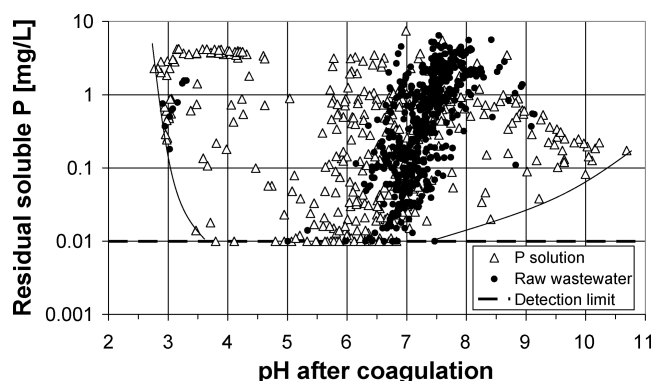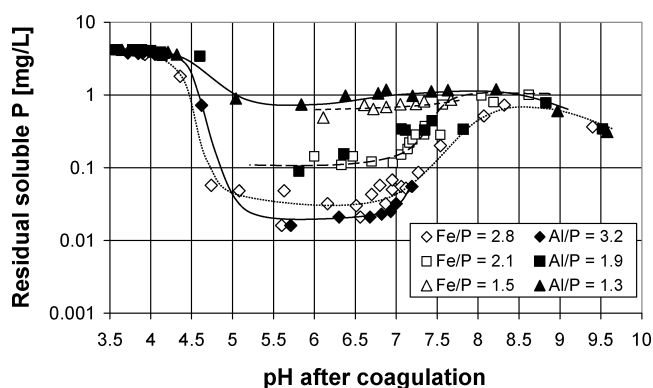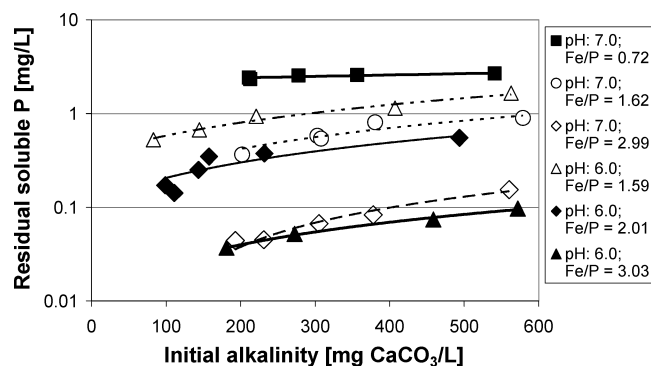

Figure 7—Residual soluble phosphorus concentration versus pH (model and real wastewater experiments, different types and doses of coagulants, and P_{ini} = 0.5 to 12.5 mg/L).

Figure 9—Residual soluble phosphorus concentration in terms of initial alkalinity (phosphorus solution and ferric chloride; P_{ini} = 3.9 to 4.3 mg/L).

Figure 11—Residual soluble phosphorus concentration, in terms of the initial Fe/P ratio (phosphorus solution in tap water and ferric chloride).

residual soluble phosphorus concentrations (Figure 9). This phenomenon is currently not well-understood. In waters with higher alkalinity, the formation of metal hydroxides can be significantly faster, because the hydrogen ion (H^+)-capturing capacity is higher. This creates a better chance (kinetic advantage) for fast precipitation of metal hydroxides and a lower probability for co-precipitation of phosphate and metal hydroxides. It is also possible that competition exists between the bicarbonate (HCO_3^-) ions and phosphate (HPO_4^{2-}) ions for the active sites. However, this phenomenon requires further investigation and confirmation.

Influence of Initial Phosphate-Phosphorus Concentration. Phosphorus removal efficiency depends on the soluble phosphorus concentration of the raw wastewater. The higher the initial phosphorus concentration, the lower the Me_{prec}/P_{prec} ratio will be (Figure 10). This can approach approximately 1, though this is not necessarily an indication of the formation of a pure metal phosphate precipitate. In phosphorus solution, the ratio typically goes below 2.0 mole/mole at small relative doses (Me_{dose}/P_{ini} <2.0 mole/mole), if the initial phosphorus concentration is higher than 2 mg-P/L and the pH is in the optimal range (5.5 to 7.0). A similar tendency was found in experiments done with raw wastewater; however, phosphorus removal efficiency was generally lower (and the Me_{prec}/P_{prec} ratio was higher) than in "pure" systems. The difference between the results gained in phosphorus solution and wastewater was more significant when the initial soluble phosphorus concentration was lower (<4 mg-P/L).
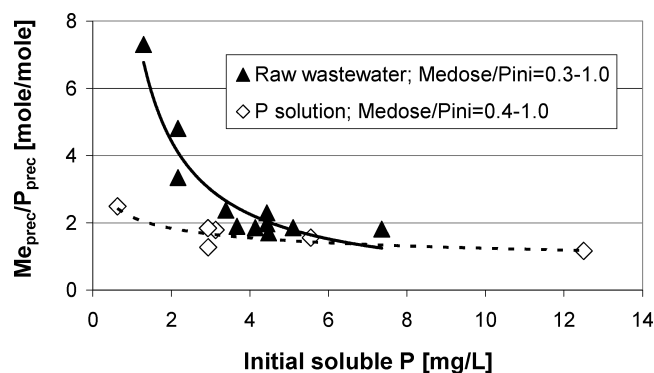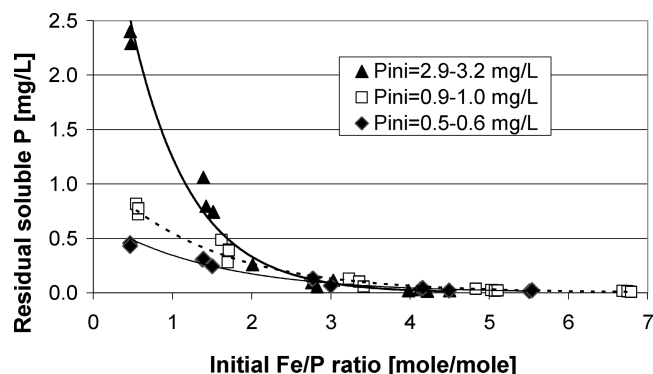
Although the relative efficiency of phosphorus removal increases with increasing initial soluble phosphorus concentration (low Me_{prec}/P_{prec} ratios were observed when the initial phosphorus concentration was higher), to reach a certain residual phosphorus concentration, a higher relative coagulant dose (Me_{dose}/P_{ini}) is needed when the P_{ini} is higher (Figure 11).

Influence of Raw Wastewater Chemical Oxygen Demand Concentration. Based on jar tests carried out with municipal wastewater, it was found that the amount of organic material present in raw wastewater significantly influences the phosphorus removal efficiency (Figure 12). With increasing raw wastewater COD concentration, chemical pretreatment will result in higher residual soluble phosphorus concentration (applying the same dose). Phosphorus removal efficiency can be negatively affected by both particulate and dissolved organic materials. In these experiments, the two effects could not be separated, as a higher dissolved COD concentration most often occurred with a higher particulate organic matter concentration.

Parallel to higher initial COD concentration, the TSS concentration of the raw wastewater was also higher. At higher TSS concentrations, less efficient phosphorus removal was observed. Although the effects of COD and TSS cannot be separated, the observed tendency agrees with results found by other authors (Fettig et al., 1990).
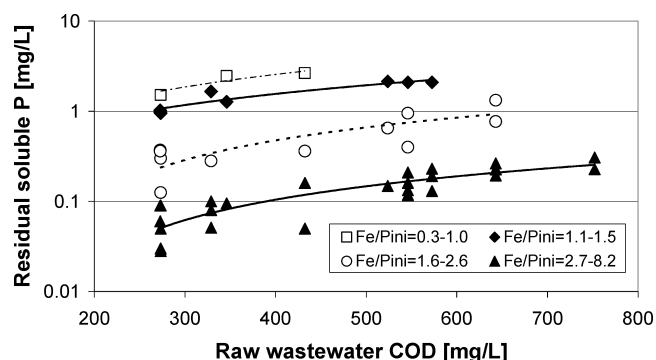

Figure 10—Me/P ratio in the precipitate, in terms of initial soluble phosphorus concentration.

Figure 12—Residual soluble phosphorus concentration, in terms of raw wastewater COD concentration (raw wastewater; pH_{ini} = 7.5 to 8.5, PO_4-P_{ini} = 3.1 to 5.2 mg/L, and TSS_{ini} = 80 to 260 mg/L).
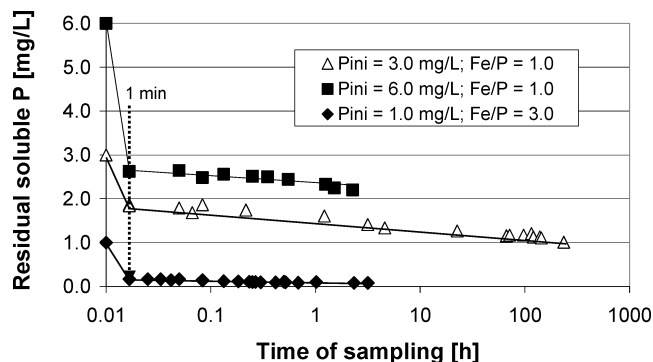
Figure 13—Kinetics of phosphorus removal (phosphorus solution, ferric chloride, Me$_{dose}$/P$_{ini}$ = 1.0 to 3.0 mole/mole, and G = 425 second^{-1}).

A phosphate complexation model (Smith et al., 2008) is consistent with the observation that the presence of organic materials decreases removal efficiency. The mechanism could be that carboxylic and phenolic groups on the organic matter compete with phosphate for binding sites on the surface of the metal hydroxides.

Influence of Time (Kinetics) on Phosphorus Removal. Several parameters were investigated that have an effect on or relationship with kinetics or general, time-dependent reactions. The first one discussed in this section is the time-dependent reaction rate itself. In the following two sections, mixing (as measured in inverse time units, G second^{-1}) and age of preformed flocs are investigated more closely.

The reaction rate (kinetics) of phosphate removal was investigated in traditional jar tests, in which the change in residual PO$_4$-P concentration was followed in time. Typical kinetics of phosphorus removal are shown in Figure 13. There is an initial fast removal of phosphorus occurring in less than 1 minute, or likely even in a much shorter timeframe (referred to as *instantaneous phosphorus removal*). However, significant further removal can occur after a few hours or days (termed *slow phosphorus removal*). The following parameters were investigated concerning their effect on the rate of phosphorus removal: initial Me/P ratio, mixing conditions, and age of hydroxide flocs.

The importance of kinetic reactions resulting in slow phosphorus removal under typical plant conditions should be taken in context of Figure 1, where the removal of an additional 0.05 mg/L residual
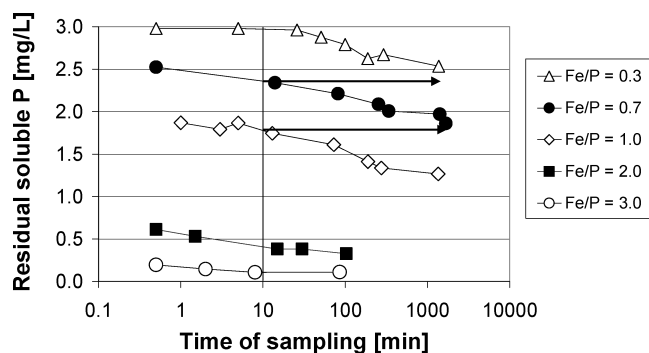

Figure 14—Kinetics of phosphorus removal (phosphorus solution, ferric chloride, P$_{ini}$ = 3.0 mg/L, Fe$_{dose}$/P$_{ini}$ = 0.3 to 3.0 mole/mole, and G = 425 second^{-1}).

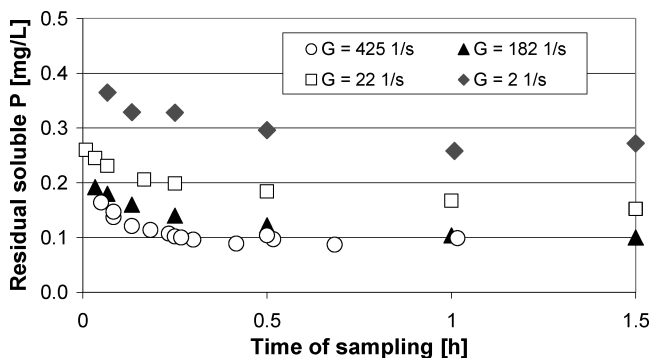**Figure 15—Phosphorus removal kinetics at different G values (phosphorus solution, ferric chloride, P$_{ini}$ = 1.0 mg/L, and Fe$_{dose}$/P$_{ini}$ = 3.0 mole/mole).**

phosphorus required a significant increase in molar ratio (5.0 extra mole coagulant/mole phosphorus). Figure 14 shows the kinetics of phosphorus removal by different Fe/P ratios, starting at a similar initial phosphorus concentration (P$_{ini}$ = 3.0 mg/L). As an example, 1.8 mg/L residual soluble phosphorus was reached by Me$_{dose}$/P$_{ini}$ = 1.0 mole/mole dosage in 10 minutes. However, if the reactions are allowed to proceed for 30 hours, the same PO$_4$-P concentration can be reached by a dose of Me$_{dose}$/P$_{ini}$ = 0.7 mole/mole only. Although the absolute phosphorus removal by the slow reaction is smaller when a higher dose is applied, achieving an additional small removal of residual phosphorus can be reached by allowing slow processes to occur, rather than by adding massive dosages of excess metal salts. Allowing for slow reactions can thus remove these small amounts of phosphates without a large dose requirement.

Influence of Mixing Intensity. There is a significant "instantaneous" reduction (very fast reduction, which is observed as a result of practical sampling limitations in a 0.5- to 1.0-minute timeframe) of phosphorus concentration under ideal mixing conditions (G = 425 second^{-1}, in this case). The majority of phosphorus removal (close to 90%) occurs within 10 to 20 minutes, and further removal occurs in the next few hours. When the intensity of initial mixing is low (G = 2 to 22 second^{-1}) during coagulant addition, the "instantaneous" removal efficiency is impaired (residual phosphorus = 0.2 to 0.3 mg/L after 10 to 20 minutes). However, phosphorus removal continues even after several hours as a slow process (Figure 15). In both cases, the main phosphorus removal process is very fast; however, slow phosphorus removal provides a further decrease ("polishing") in soluble phosphorus concentration. The extent of the two different processes depends on mixing intensity. Ideally, a very high mixing intensity should be achieved at the chemical dose point in full-scale plants— a G value higher than 200 to 300 second^{-1}, similar to jar testing conditions.

Residual phosphorus concentration in a similar experimental series is shown in Figure 16 as a function of G value. Instantaneous phosphate removal is more efficient when metal hydroxides are being formed under high G conditions, which provides ample opportunity for contact between ferric and phosphate ions. This is the case when the metal salt is added to wastewater before the biological treatment step (pre-precipitation) or after biological treatment and phase separation (postprecipitation) under good mixing conditions. If preformed metal hydroxide flocs come in contact with phosphate ions (because of inefficient or incomplete mixing or because pre-polymerized metal salts are used), initial
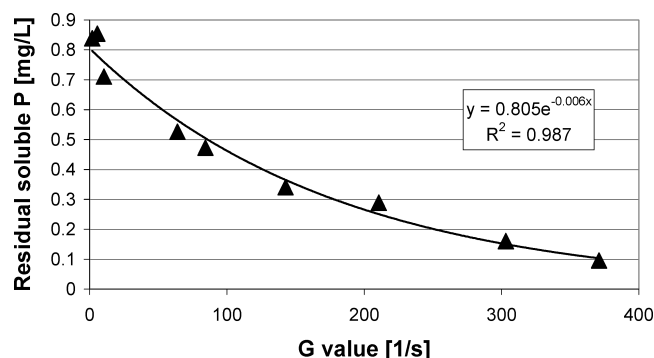
Figure 16—Effect of *G* value on phosphorus removal (ferric chloride, P_{ini} = 4.1 mg/L, Fe_{dose}/P_{ini} = 1.8 mole/mole, and time of sampling = 11 minutes after coagulant addition).

Figure 17—Effect of floc age on phosphorus removal (phosphorus solution, ferric chloride, preformed ferric hydroxides, P_{ini} = 1.0 mg/L, and Fe_{dose}/P_{ini} = 3.0 mole/mole).

phosphorus removal (within the first few minutes) will be less effective. However, this can be compensated, to a degree, by the long contact time in simultaneous precipitation, where coagulant is introduced to the activated sludge reactor, and its residence time matches that of the biological solids.

In the case of pre- or post-precipitation (dosing the coagulant before the primary or after the secondary settling tank), where the contact time is short, it is very important to ensure a high probability of phosphate ions coming in contact with ferric ions and freshly formed, positively charged ferric hydroxides. In typical wastewaters, the concentration of phosphate ions (PO_4^{3-}) is orders of magnitude lower than the concentration of HCO_3^- ions, which control ferric hydroxide [$Fe(OH)_3$] precipitation. If the coagulant is intensively mixed at the dosage point, more efficient phosphorus removal will occur.

The extent of the slow adsorption (surface complexation) reaction depends also on the residual phosphorus after the fast reaction is completed. The residual phosphorus concentration, after the first few minutes, is mainly determined by mixing, as described above, and the dosage (i.e., the Fe_{dose}/P_{ini} molar ratio). During the relatively short contact time, as a result of phase separation in pre- or post-precipitation, phosphorus removal by the slow reaction is not significant.

Influence of the Age of Flocs. The age of hydroxide flocs has a significant influence on phosphorus removal efficiency. In a jar test, hydroxide flocs were separately formed, and, after a certain aging period (denoted as ''Age of flocs'' in Figure 17), they were added to the phosphorus solution. Samples were taken at different times after adding the flocs to the phosphorus solution (denoted as ''Time of sampling'' in Figure 17). According to the results, fresh ferric hydroxides (aged 1 minute) can achieve approximately 60% phosphorus removal in 20 minutes (Figure 17). For the same initial conditions (P_{ini} = 1.0 mg/L and Fe_{dose}/P_{ini} = 3.0 mole/mole), only 30 to 35% of the original PO_4-P is removed if the ferric hydroxide floc is aged 30 minutes before it comes in contact with orthophosphate. The result is in agreement with earlier observations (Lijklema, 1980) and with qualitative changes in iron hydroxide at different ages shown in electron microscope images in the companion paper by Smith et al. (2008). If preformed flocs (i.e., chemical sludge from drinking water plants) are used for phosphorus removal in a wastewater treatment plant, the fresher the sludge and the shorter the transportation and storage time, the better the efficiency that can be expected.
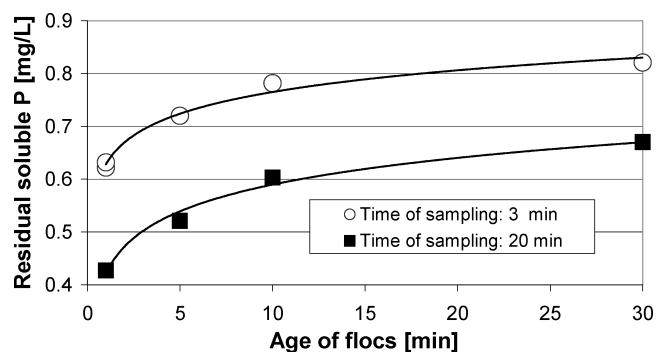
Continuous Laboratory Experiments—Methodology

System Setup. The objective of the continuous experiments was to compare phosphorus removal efficiency in short (<3 days) and long (>10 days) solids retention time (SRT) systems. Biological components (activated sludge) were not included in the system, as the aim was to examine the chemical reactions independently.

The equipment consisted of two parallel systems, including a coagulation tank (mixer), reactor (flocculator), and settling tank (Figure 18 and Table 1). Raw water (phosphorus solution) prepared from tap water and KH_2PO_4 was supplied by a peristaltic pump at a rate of 2.15 L/h. Precipitant/coagulant (concentrated ferric chloride solution) was introduced to the mixer unit (hydraulic retention time [HRT] = 2.5 minutes), where it was intensively mixed with raw water. A magnetic stirrer was used for mixing. Flocculation was carried out in a reactor, which was slowly stirred by a magnetic stirrer. The produced ferric hydroxide phosphate flocs were allowed to settle in a settling tank, with an HRT of 4.5 hours. An overwhelming part of the contact and dispersion effect for the proposed surface complexation mechanism (Smith et al., 2008) was occurring in the reactors, before the flocs were separated in the clarifier. System A was a short SRT system, in which the HRT of the reactor was 18 minutes, and no recycle was applied (SRT = HRT in this case, as there is no recycling). Chemical sludge (settled ferric hydroxide flocs) was wasted intermittently from the settling tank. In system B, all the settled sludge was recycled to the reactor (HRT = 4.7 hours). Sludge was wasted from the reactor to sustain an SRT of 5.5 days.
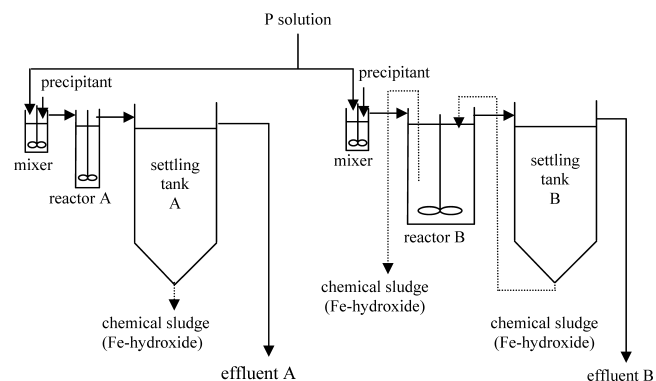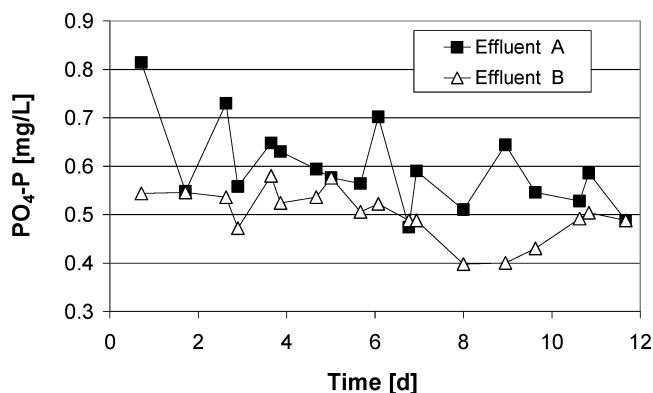

Figure 18—Flow scheme of continuous experiments.

Table 1—Operational parameters of the continuous experiments.

Parameters	System A	System B
Q (L/h)	2.15	2.15
Raw water pH	7.5	7.5
Raw water PO$_4$-P (mg/L)	4.0	4.0
Fe$_{dose}$/P$_{ini}$	1.4	1.4
HRT		
Mixer	2.5 minutes	2.5 minutes
Reactor	18 minutes	4.7 hours
Settling tank	4.5 hours	4.5 hours
Total	4.8 hours	9.3 hours
V (L)		
Mixer	0.09	0.09
Reactor	0.64	10.16
Settling tank	9.68	9.68
Total	10.41	19.93
SRT	18 minutes	5.5 days

Figure 19—Effluent PO$_4$-P concentrations in continuous experiments.

efficient phase separation in system B to promote recycling of all solids possible.

Results of Continuous Experiments

Because of recycling of the chemical sludge, the concentration of suspended solids in steady-state was 24 times higher in system B than in system A. The HRT of reactor B itself was 15 times longer than the HRT of reactor A; however, the total system HRT (including HRT of the coagulation tank, reactor, and settling tank) was only 2 times longer in system B. Based on our previous batch tests (see Figures 13 and 14), the long contact time provides opportunity for sorption reactions, causing additional phosphorus removal if the contact of ferric hydroxides and phosphate ions is ensured. This phenomenon was verified in the continuous system, in which the average soluble effluent phosphorus concentration was 15% lower in system B (with recycle). Approximately 0.47 to 0.81 mg/L residual soluble phosphorus was achieved without recycling (system A), while only 0.40 to 0.58 mg/L PO$_4$-P remained in the effluent of the long SRT system with recycle. The effluent phosphorus concentration varied less in system B, in which the standard deviation was approximately 10%. System A showed more instability, as the standard deviation of the residual PO$_4$-P was approximately 15% (Figure 19).

Based on the results of the batch tests, there are two important factors that should be considered during evaluation of the above data. First, the unusually long settling time might provide the possibility for removal of soluble phosphorus through surface

System A represents typical conditions during primary pre-cipitation (pre-precipitation), in which the coagulant is well-mixed and efficient flocculation is carried out before phase separation. However, in full-scale treatment plants, the settling time is approximately 1 to 3 hours, whereas the HRT of the laboratory sedimentation tank was 4.5 hours. The longer settling time provides better phase separation and gives a higher possibility of surface reactions, which typically does not have a high significance in typical plant operations in primary precipitation.

System B simulates systems in which the contact time between the wastewater and the metal hydroxide flocs is longer, as a result of a longer HRT and SRT. This occurs in simultaneous phosphorus removal systems, in which the chemical is dosed directly into the activated sludge reactor. The laboratory system is a representation of only one (rarely applied) configuration of such a system, in which the coagulant is fed to a coagulator (mixer) unit before the reactor. Because of this setup, a higher phosphorus removal rate is expected in the laboratory system with optimal mixing than would occur in a full-scale plant configuration, in which the coagulant is introduced to the reactor under less favorable mixing conditions (low G values). A settling tank with a relatively large volume was chosen to ensure

Table 2—Water quality parameters in the continuous experiments.[a]

Parameters	System A	System B
TSS (mg/L)	25 (17 to 30)	610 (565 to 665)
Effluent pH	6.8 (6.60 to 7.00)	7.2 (6.85 to 7.27)
Effluent PO$_4$-P (P$_{res}$) (mg/L)	0.60 (0.47 to 0.81)	0.50 (0.40 to 0.58)
Effluent PO$_4$-P (P$_{res}$) standard deviation	14.6%	10.4%
Extra removal in system B [(P$_{resA}$ − P$_{resB}$)/P$_{resA}$]		15% (0 to 38%)
Phosphorus removal rate compared with raw PO$_4$-P	85% (79 to 88%)	88% (86 to 91%)
Reactor PO$_4$-P (mg/L)	0.62 (0.51 to 0.90)	
PO$_4$-P corrected for pH 7.2 (mg/L)[b]	0.90	0.50

[a] Values shown are averages, and minimum and maximum measured values are shown in parentheses.

[b] Based on the results of batch experiments (Figures 8 and 21), it is easier to remove phosphorus (residuals are lower) at pH 6.8 compared with pH 7.2. The estimated phosphorus residual would have been 0.90 mg/L instead of 0.62 mg/L, had the pH been maintained at 7.2 (details in text).
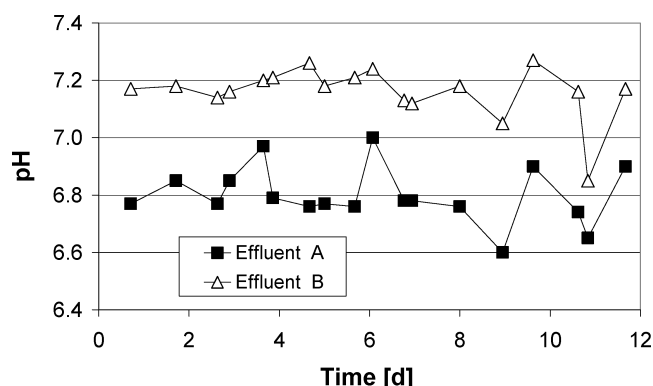
Figure 20—Effluent pH values in continuous experiment.

Figure 21—Effect of pH on the residual soluble phosphorus concentration (batch test, phosphorus solution, and P_{ini} = 4.0 mg/L).

reactions in the settling tank of system A. However, the difference in PO_4-P concentration in the reactor and in the effluent was not significant (see Table 2), indicating that phosphorus removal almost exclusively occurred in the mixing tank and the reactor (flocculator). The pH of the two systems was different because of the longer HRT in system B, resulting in a more efficient gas exchange with atmosphere (an artifact of laboratory testing) (Figure 20). Without pH control, the pH of the tap water solution increased with time, as a result of carbon dioxide loss. This was experienced in long-term batch tests also. This artificially reduced the measured benefit of solids recirculation and retention, because increased pH results in reduced phosphorus removal efficiency (Figures 7, 8, and 21).

Another question of importance to practitioners is whether the jar test results could be used to estimate continuous-flow systems in practice. The average residual phosphorus in system A was 0.60 mg/L (0.47 to 0.81 mg/L) for Fe_{dose}/P_{ini} = 1.4 mole/mole and pH 6.8. The residual phosphorus in batch jar tests for a similar Fe_{dose}/P_{ini} and the same final pH was 0.6 mg/L. This residual phosphorus was the same in the continuous and the batch systems under similar conditions, indicating that batch jar tests could effectively represent low-SRT continuous-flow systems.

The efficiency of phosphate removal is influenced by the actual pH value in the pH range occurring in the continuous experiment. The average effluent pH in system A was 6.8, and the residual phosphorus concentration averaged 0.60 mg/L. At the same time, the average pH value of effluent B was 7.2. According to batch test results with a similar coagulant dose (Fe_{dose}/P_{ini} = 1.5), the residual PO_4-P concentration was approximately 0.3 mg/L higher at pH 7.2 than at pH 6.8 (Figure 21). Thus, if a correction to account for the pH difference is applied to effluent A based on the results of batch tests shown in Figure 21, the average residual PO_4-P concentration would be approximately 0.9 mg/L in system A.

The results of the continuous experiments show that a system with a longer HRT and SRT can provide more efficient phosphorus removal than one with a short HRT and SRT, in the case of similar mixing conditions. This phenomenon is primarily the result of the longer contact time between phosphate ions and metal hydroxide particles, and it partially mitigates the effect of inefficient mixing in simultaneous phosphorus removal systems. It is important to realize that, in addition to this beneficial effect, many other aspects have to be considered when choosing between pre-, post-, or simultaneous dosing systems, such as availability of equipment, dosing configurations, sludge production, and effect on the biological system.
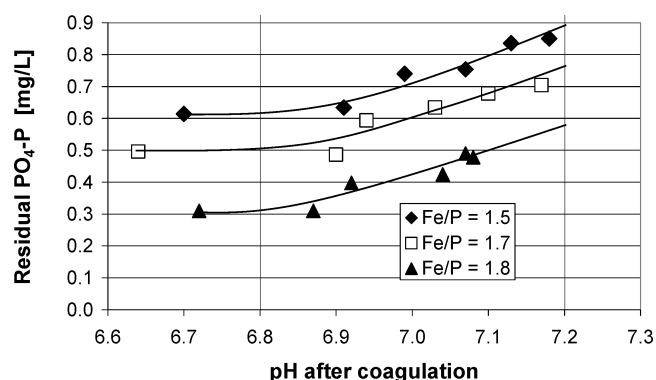
Conclusions

Batch and continuous-flow laboratory experiments were conducted using synthetic and real wastewater to quantify the effect of numerous process variables on phosphorus removal efficiency using iron and aluminum salts. The following conclusions are based on the results of the experiments:

(1) Residual soluble phosphate concentrations decrease as the molar dose of metal salt increases, although with diminishing returns.

(2) For the practical range of pH values (above approximately 5), the metal content of the precipitate can be predicted based on the metal salt dose, as essentially complete precipitation of the metal occurs.

(3) Pre-polymerized metal salt is less efficient for phosphorus removal than freshly added and formed metal hydroxide.

(4) The lowest values of soluble orthophosphate are obtained over the pH range 5 to 7 for both aluminum and iron salts, with concentrations increasing for pH values outside this range.

(5) Phosphorus removal efficiency is adversely affected by increased concentrations of alkalinity, soluble and total COD, and TSS.

(6) Phosphorus removal is characterized by an initial fast removal upon the addition of metal salt and a slower, long-term removal over time. Most of the removal occurs during the initial fast reaction, but the additional removal during the slower, long-term removal period can be significant, relative to achieving low effluent soluble orthophosphorus concentrations.

(7) Increased mixing intensity significantly improves the efficiency of the initial fast reaction.

(8) Aging of flocs adversely affects the long-term slow phosphorus removal reaction.

(9) Continuous-flow experiments verified the benefits of maintaining chemical flocs in contact with the process flow to achieve additional phosphorus removal.

These results are consistent with the surface complexation model developed in a companion paper (Smith et al., 2008).

Credits

and Adrienn Horváth, undergraduate students at the Budapest University of Technology and Economics (Budapest, Hungary), who performed some of the measurements presented here.

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