THE IMPORTANCE OF SLOW KINETIC REACTIONS IN SIMULTANEOUS CHEMICAL P REMOVAL

A. Szabó*, I. Takács**, I. Licskó***, S. Murthy****, G. Daigger*****

*Hungarian Academy of Sciences, 1051 Budapest, Roosevelt tér 9, Hungary
**EnviroSim Associates, Flamborough, ON Canada
***BME, Budapest, Hungary
****DCWASA, Washington, DC, U.S.A.
*****CH2MHill, Denver, CO, U.S.A

ABSTRACT

Laboratory and full-scale experiments were performed in order to investigate the effect of mixing, as represented by the mean velocity gradient, G-value (Grady et al, 1999), and time dynamics in chemical phosphorus removal. The results prove that the chemical reactions occurring during phosphorus removal upon addition of trivalent metal salts (Fe, Al) cannot be described with the currently applied equilibrium theory (WEF, 1998). Two reactions are postulated: a) a significant part of the phosphate, depending on the applied G, is removed instantaneously, or within the first few minutes. This fast reaction however is not a simple equilibrium precipitation, since it involves varying stoichiometry and varying residual concentrations; b) a smaller part of the total initial phosphate is removed by a slow kinetic reaction (termed adsorption). The time constant of this reaction is in the order of hours to days. Pure metal hydroxide flocs, formed without the presence of phosphate, also remove phosphorus kinetically. The role of this reaction is more expressed in plants where mixing at dosage point is inadequate, particularly during simultaneous phosphorus removal. The slow reaction has increased relevance when residual phosphate concentrations are in a very low range, below 0.1 - 0.2 mgP/L, a range that is an increasingly common permitted requirement for wastewater treatment facilities. Thus, the slow reaction can be used with advantage to achieve very low phosphorus residuals via simultaneous precipitation. Additionally, this reaction may be important for tertiary blanket clarifiers and for tertiary clarifiers with internal sludge recirculation.

KEYWORDS Chemical P removal, equilibrium, kinetic, precipitation, adsorption

SIGNIFICANCE

Chemical P removal reactions consist of fast and slow processes. The long contact time of metal hydroxide flocs in simultaneous precipitation (as opposed to the relatively short contact in primary and post-precipitation) makes an efficient use of the chemical dosed, and can counteract the effect of sub-optimal mixing conditions to provide a low residual soluble P concentration in the effluent. Furthermore, the slow reaction is efficient in sequestering residual phosphates to produce a low phosphorus effluent if necessary.

INTRODUCTION

There are three potential dosing points in chemical phosphorus removal in a wastewater treatment plant: 1) before the primary settler (primary precipitation or pre-precipitation) 2) into the aeration tank (simultaneous precipitation) or 3) in a tertiary step in the treated effluent, called post-precipitation. The contact time between the chemical flocs and the phosphate ions of the wastewater is significantly longer in simultaneous precipitation than in the other two methods. In primary and post-precipitation the chemical sludge forming after the chemical dose is separated and removed from the system within one HRT. In simultaneous precipitation the chemical sludge is captured and kept in the aeration tank for the SRT of the system. It is believed that this longer SRT is beneficial to chemical phosphorus removal. There have been recent attempts to increase the residence time in tertiary clarification by using blanket clarifiers or through internal sludge recirculation with resulting decrease in chemical dose or phosphorus residuals. This study attempts to explain these phenomena.

Many plants that practice simultaneous precipitation have an observation that while the process is resilient to perturbation, but once perturbed, it is difficult to make rapid improvements. This points to the importance of the slow kinetic rate that dominates in plants using simultaneous precipitation. Consequently, a series of laboratory experiments comprising over 1500 phosphate determinations were performed to identify the most important factors affecting instantaneous ("equilibrium") and slow (kinetic) chemical P removal. The same phenomenon was further investigated at the Kecskemét WWTP (Hungary). At this site, the role of different P removal processes in pre-precipitation was investigated.

EXPERIMENTAL BACKGROUND

Blue Plains WWTP

DCWASA's Blue Plains Advanced Wastewater Treatment Plant is designed to treat an average flow of 370 MGD (1400 MLD) domestic wastewater from the Washington D.C and surrounding areas. The plant uses a series of technologies to effectively remove a large range of pollutants from the wastewater. The most important treatment steps are:
1. Chemically enhanced primary settling
2. Short SRT secondary activated sludge for BOD removal, with addition of iron salts
3. Separate, long SRT nitrification stage including denitrification reactors using methanol as external carbon source
4. Filters

The orthophosphate (OP) concentration in the influent typically varies between 3-5 mgP/L. This is reduced to below 1 mgP/L in the primary effluent due to the iron dose into the primaries. At the effluent of the Secondary stage, soluble OP is less than 0.05 mgP/L. (It is suspected that the Nitrification stage is receiving its nutrient P in the form of chemically bound P carried over by the effluent solids from the secondary stage). Effluent TP criteria is 0.18 mgP/L and actual effluent TP in 2005 was 0.09 mgP/L, with less than half being OP.

Kecskemét WWTP

This wastewater treatment plant in Hungary receives 5 MGD (19 MLD) municipal wastewater from the town of Kecskemét and the surrounding small settlements. Treatment technology includes aerated grit chambers, primary sedimentation tanks, activated sludge bioreactors and secondary settling tanks. The sludge is stabilized in anaerobic digesters after pre-thickening. A two-week full-scale experiment was carried out at the plant dosing ferric-sulfate to the aerated grit chamber. The main objectives of the experiment at the plant are decreasing the COD load to the biological treatment units and increasing the biogas production. For a short period before and after the start of chemical dosing pH, COD, TSS, PO_4-P and TP concentrations were measured hourly in the primary effluent. The same parameters were measured in the raw wastewater every 1-4 hours.

Laboratory Experiments

Laboratory experiments to optimize chemical P removal from wastewaters are typically performed with fast mixing (mean velocity gradient, G = 300-1000 1/s), providing optimal removal efficiency in short term experiments. In wastewater treatment plants, mixing at the dosage point is usually poor (G = 20-100 1/s) and flocculation is hindered by insufficient flocculation time as well as several technological processes that disrupt floc formation: pumping, aeration, phase separation etc.

To gain a better understanding of P removal kinetics, the effect of mixing intensity (as measured by the mean velocity gradient, G) during precipitation/coagulation, and floc aging were investigated in laboratory experiments.

Coagulation-flocculation jar tests were carried out with phosphate solution prepared from tap water and KH_2PO_4 and raw wastewater. All experiments were performed in 1-litre glass cylinders with a KEMIRA flocculator device (Kemira 1990). In traditional tests, coagulants were introduced to the wastewater during intensive mixing. In order to investigate how laboratory conditions relate to typical conditions in wastewater treatment plants, reaction time and the G value applied during coagulation was varied.

In other experiments the OP removal capacity of hydrous ferric oxide flocs (HFOs) was investigated similarly to earlier experiments (Licskó, 1996). The HFOs were pre-formed in the absence of phosphate ions. This simulates the effect of dosage on plants with insufficient mixing, where these flocs are forming without coming into contact with the OP content of the wastewater. Subsequently, some of the pre-formed flocs were used immediately for phosphorus removal, while others were aged for various length of time and their residual OP removal (adsorption) capacity was tested in jar tests.

RESULTS AND DISCUSSION

Field Demonstration of Slow Reactions

Simultaneous chemical P removal at Blue Plains. Due to supply chain problems the Blue Plains AWTP was forced to skip ferric chloride addition to the raw wastewater for five days in May 2005. This resulted in higher than expected phosphates entering the simultaneous precipitation process. The effluent total soluble phosphorus (TSP) concentration downstream of simultaneous precipitation rose slowly during this period and after resuming dosing, it took another five days of increased chemical dose into the secondaries to bring TSP levels to their earlier value (Figure 1). Since the hydraulic residence time of the plant is approximately 15 hours, only a small part of these slow changes can be explained with dilution effects. The rest of the dynamics can only be explained by slow adsorption - desorption reactions on the surface of flocs already present in the two activated sludge systems. In this case, the simultaneous precipitation process was beneficial for the plant, by reducing the concentration spike in the effluent. However, the process was also slow to recover and produce low phosphate effluents. Since this experience Blue Plains is set up to substitute iron with aluminum should a similar supply chain problem occur.

Figure 1 - Primary Effluent (PE) and Secondary Effluent (SE) soluble phosphorus
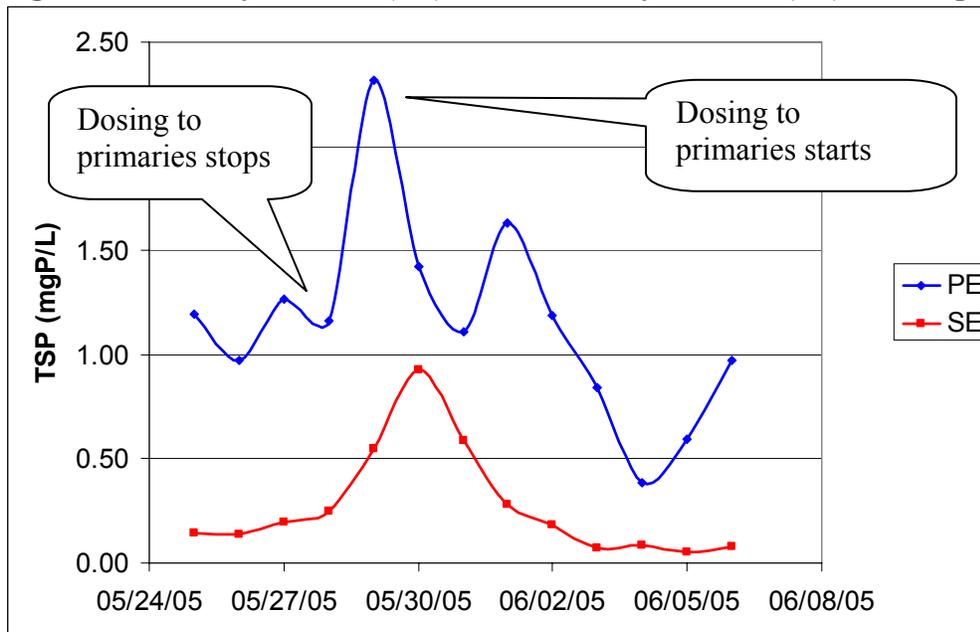
Full scale pre-precipitation experiment at Kecskemét. The startup of primary Fe dosing was tracked at the Kecskemét WWTP. 1.5-2.7 mol Fe/mol PO_4-P_{ini} was dosed to the aerated grit chamber and the residual PO_4-P concentration was measured hourly in the primary effluent. The nominal HRT of the settling tanks is about 2 h for 1100 m^3/h hydraulic load. According to a previous hydraulic flow-through experiment, due to non-ideal flow, some of the inflowing wastewater leaves the primary settling tank in less than 1 hour and some in 2.5-3.5 hours. Within 3.5-4.5 hours more than 90% of the incoming water gets through the primary treatment step. In

our experiment, however, PO$_4$-P concentration in the primary effluent continued to decrease even after 4 hours after the dosing started (Figure 2).

Figure 2 – Change of PO$_4$-P concentration in the primary effluent after the start of Fe dose (Kecskemét WWTP)
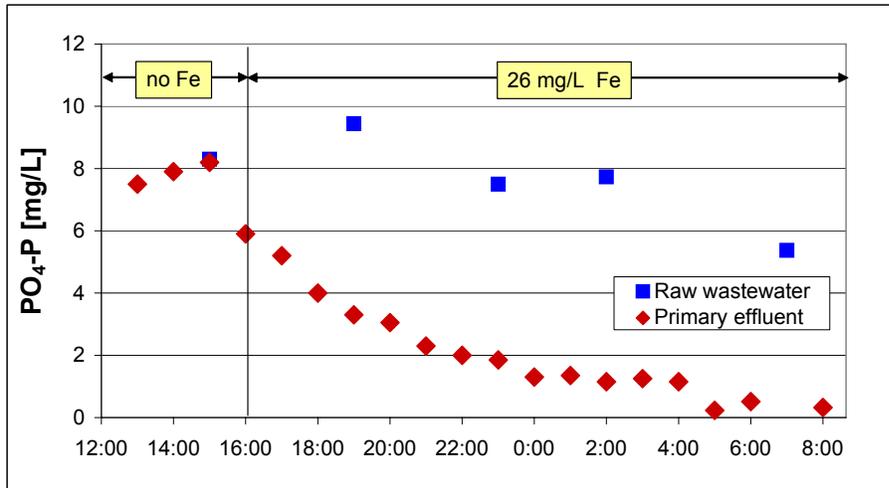
At the same time, other parameters such as pH, COD and BOD concentration have been stabilized after 2-3 hours from the starting time (Figure 3). (ONLY COD is shown?)

Figure 3 – Change of organic matter concentration in the primary effluent after the start of Fe dose (Kecskemét WWTP)
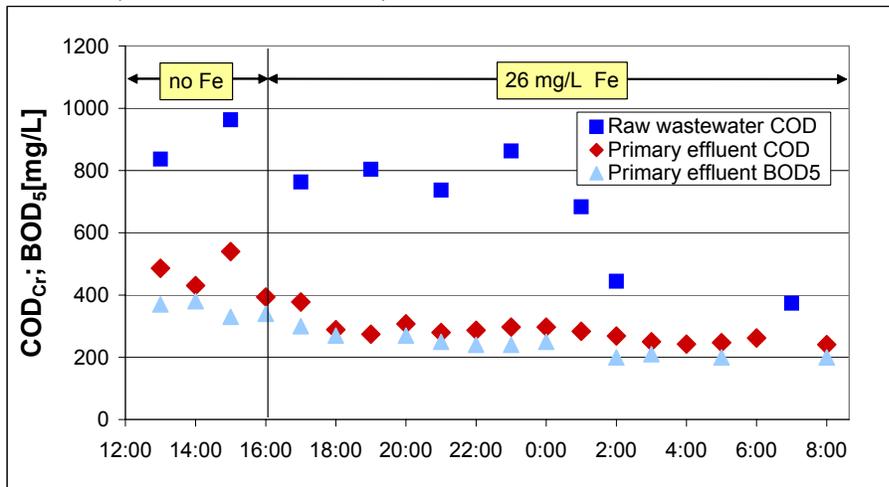

Figure 4 shows the PO$_4$-P concentration measured in the aerated grit chamber (right after the coagulant is dosed to the wastewater) and in the primary effluent (taking into account the delay caused by the 2 hour HRT) at the same plant. The fast processes reduced soluble P concentration from 8-15 mg/L to 0.2-1.5 mg/L, which was further decreased to 0.15-0.6 mg/L in the primary settling tanks within the available hydraulic residence time.

**Figure 4 – Change of PO$_4$-P removal in the primary settling tank (Kecskemét WWTP)**
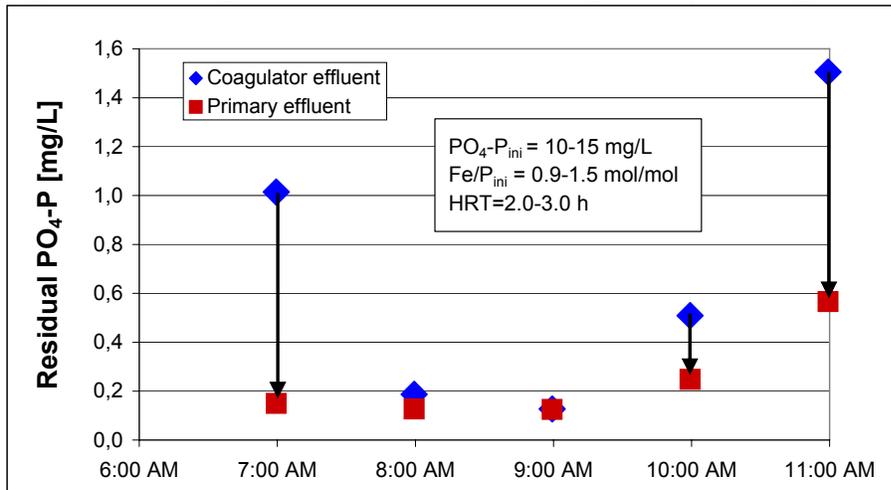
These field results demonstrate that the slow P removal process has a significant role in simultaneous precipitation. Slow P removal cannot be neglected even in pre- and post-precipitation, however, the majority of P removal occurs within a very short time if mixing at dosage point is adequate.

Laboratory results

Kinetics of phosphate removal was investigated in traditional jar tests, where the change in residual PO$_4$-P concentration was examined in time. Typical kinetics of P removal during different mixing conditions is shown in Figure 5.

Figure 5 - P removal kinetics at different G values (P$_{ini}$ = 1.0 mg/L; Fe/P = 3.0)
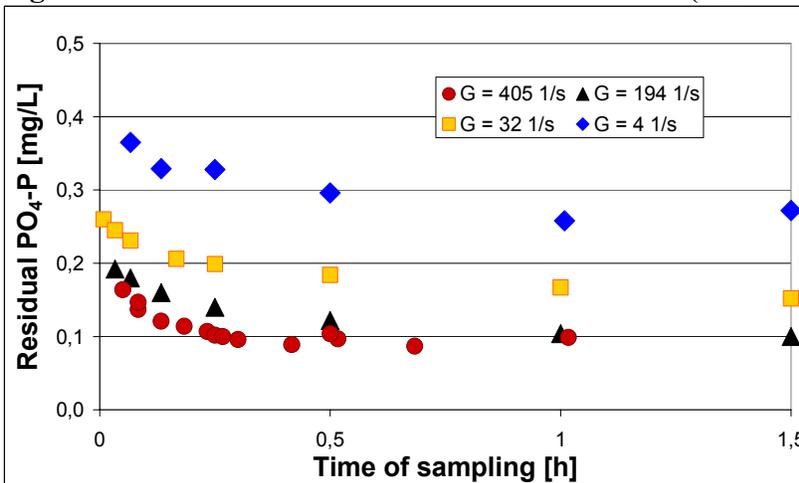
There is a significant instantaneous reduction of OP concentration under ideal mixing conditions (G = 405 1/s in this case). The majority of OP removal (close to 90%) occurs within 10-20 minutes and relatively little further removal occurs in the next few hours. When the intensity of

initial mixing is low (G = 4-32 1/s) during coagulant addition, the instantaneous removal efficiency is impaired (residual P is 0.2-0.3 mg/L after 10-20 minutes). However, P removal continues even after several hours as a slow kinetic process. In both cases, the main P removal process is very fast, however slow P removal provides further decrease ("polishing") in soluble P concentration. The extent of the two different processes depends on mixing intensity. P in a similar experimental series is shown in Figure 6 as a function of G-value.

Figure 6 - Effect of G-value on P removal (P_{ini} = 1.0 mg/L; Fe/P = 3.0)
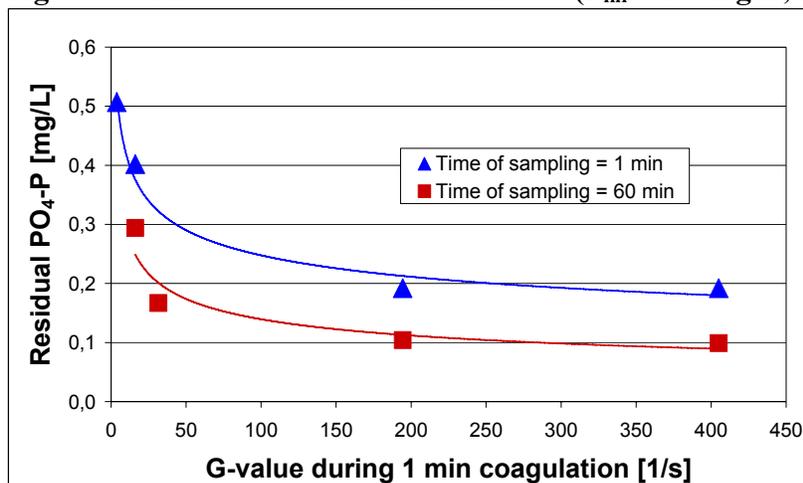

Instantaneous phosphate removal is more efficient when metal-hydroxides are being formed under high G conditions, which provides ample opportunity for contact between ferric and phosphate ions. This is the case when the metal salt is added to wastewater in pre- or post-precipitation under good mixing conditions. If pre-formed metal-hydroxide flocs come in contact with phosphate ions (because of inefficient mixing, or because pre-polymerised metal salts are used), initial P removal will be less effective. However this is compensated to a degree by the long contact time in simultaneous dosing systems.

In the case of pre- or post-precipitation, where the contact time is short, it is very important to assure a high probability of phosphate ions getting in contact with ferric ions and freshly formed, positively charged, soluble ferric-hydroxides. In typical wastewaters, the concentration of PO_4^{3-} is orders of magnitude lower than the concentration of HCO_3^- ions which controls $Fe(OH)_3$ precipitation. If the coagulant is intensively mixed at dosage, efficient P removal occurs, as the chance for frequent collision of hydrated ferric ions, $(Fe(H_2O)_6)^{3+}$ and PO_4^{3-} is higher.

The extent of the slow adsorption reaction depends also on the residual P after the fast reaction is completed. This "intermediate" residual P is mainly determined by mixing as described above, and the dosage, i.e. the Fe_{dosed}/P_{ini} molar ratio. When dosing the coagulant prior to the primary or post settling tank, contact time between the metal-hydroxide flocs and the phosphate content of the wastewater is less than 2-3 hours. During this relatively short time P removal by the slow reaction is not significant if the applied coagulant dose and mixing conditions decreased the PO_4-P concentration to low levels within a few minutes. In cases when higher PO_4-P concentration remains after the fast reaction, the slow reaction may compensate somewhat the non-ideal mixing conditions. However, the major portion of P removal still occurs instantaneously.

The age of hydroxide flocs has a significant influence on P removal efficiency. In a jar tests first hydrated ferric oxides, HFOs were formed and after a certain aging period they were added to the P solution. According to results, when HFOs are formed just before coming in contact with phosphate ions, about 60% P removal can be achieved in 20 minutes (Figure 7).

Figure 7 - Effect of floc age on P removal (lab experiments with model ww; preformed HFOs; P_{ini} = 1. 0 mg/L; Fe/P = 3.0)
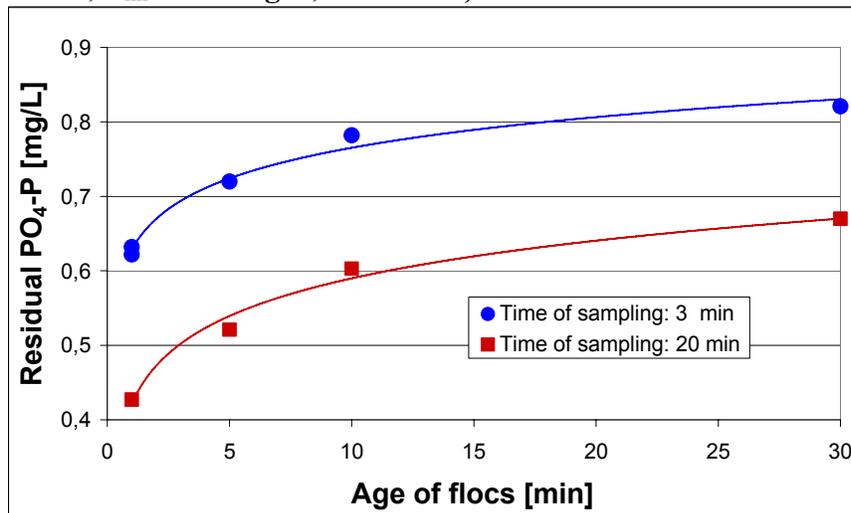
For the same initial conditions (P_{ini}=1.0 mg/L; Fe/P_{ini}=3.0), only 30-35% of the original PO_4-P is removed if the HFO floc is aged 30 minutes before it comes in contact with orthophosphate.

Based on the above experiments it is proposed that the mechanism of chemical phosphorus removal is equilibrium precipitation of HFOs, occurring simultaneously with fast co-precipitation of phosphate ions, followed by diffusion limited slow adsorption of the remaining phosphate ions. The extent of the reactions depends on initial mixing, concentration conditions and contact time.

CONCLUSIONS

If trivalent metal salt is added prior to phase separation (pre-precipitation and post-precipitation) co-precipitation is the dominant P removal process and mixing efficiency (G-value) plays an important role to ensure the required high probability of collisions between the metal and phosphate ions.

When adding metal salts into the activated sludge tank (in simultaneous precipitation), the efficiency of direct P co-precipitation is lower because of less intensive mixing. Due to the long solids residence time in aeration tanks significant adsorption (either chemisorption or physisorption) can take place unlike in the circumstances of pre- or post-precipitation. The two opposite effects (less efficient precipitation and the possibility for significant adsorption) compensate each other and efficient P removal can be achieved using simultaneous precipitation

as well. Thus simultaneous precipitation has an unrecognized advantage due to the SRT and sorption capacity of flocs. This increased contact time may advantageously be used in tertiary blanket clarifiers and through internal sludge recirculation. Further study is required to properly optimize and model this mechanism.

It was found that dosage (the Fe_{dosed}/P_{ini} molar ratio) plays a significant role in both situations. Additionally, in primary and post-precipitation the G-value (mean velocity gradient) has an important effect on P removal, while in simultaneous precipitation reaction time (equivalent to system SRT) is significant.

REFERENCES

Grady, C.P.L., Daigger, G.T. and Lim, H.C. (1999). Biological Wastewater Treatment. Marcel Dekker, New York.

KEMIRA KEMI AB Water Treatment (1990). The Handbook on Water Treatment, KEMIRA KEMI, Helsingborg, pp.: 139.

Licskó, I. (1976). Micro processes in coagulation. *Water Research*, **10**(2), 143-147.

Water Environment Federation, (1998): Biological and Chemical Systems for Nutrient Removal, Alexandria, Va. U.S.A.