

# Nutrient Research Periodical

## NEWS

Welcome to the second issue of the Nutrient Research Periodical! This biannual newsletter has been developed to inform academic, government and industrial stakeholders about activities of the Nutrient Removal and Recovery Group (NRRG). The current core of NRRG includes the research labs of **Dr. Wayne Parker** (Waterloo), **Dr. Scott Smith** (Wilfrid Laurier) and **Dr. Hyung-Sool Lee** (Waterloo).

In this issue of Nutrient Research Periodical the focus is on an update on current highly qualified personnel, past and upcoming conferences or meetings, past oral or poster

presentations focused on removal and recovery research by members of our research team. The final section will highlight research being conducted toward the advancement of nutrient removal and recovery by one of our student members.

Previous issues of the Nutrient Research Periodical can be found at [https://www.wlu.ca/page.php?grp\\_id=190&f\\_id=3&p=25139](https://www.wlu.ca/page.php?grp_id=190&f_id=3&p=25139). Any inquiries as to the features or subscription can be directed to the editor Holly Gray (contact information can be found on the last page of the newsletter).

## FUNDING

The NRRG would like to take a moment to acknowledge the funding which brought the NRRG together. In early 2013 **Wayne Parker** (PI), **Scott Smith** and **Hyung-Sool Lee** (Co-PIs) received a grant from the Canadian Water Network Canadian Municipal Water Consortium (CWN CMWP) for the project titled *"Integrated Sorption Technologies for Recovery of Nitrogen and Phosphorous from Anaerobic Membrane Bioreactor Permeates."* As suggested by the title, this grant will fund a project using sorbents to remove phosphorus and nitrogen from waste water. The nutrients will then be desorbed to produce a feed stock that is optimized for nutrient recycling.

We would like to acknowledge the various partners involved with the above mentioned grant. Our partners include: York Region, Halton Region, Region of Waterloo, Water Environment Research Foundation, GE, Ostara and Conestoga Rovers and Associates.



**Past Funding:** Members of NRRG have been involved with nutrient research in wastewater for the past several years and have received research support from the following sources:



### HIGHLY QUALIFIED PERSONNEL (HQP) AND COLLABORATORS

*There have been some changes in the last few months, including the end of another school year. The following section serves as an update on the current student members of NRRG:*

Undergraduate BSc student **Scott Robinson**, supervised by **Scott Smith**, finished his undergraduate thesis investigating the effect of mixing speed on chemical phosphorous removal. **Kai Xin** is a new undergraduate student working Smith's lab this summer to determine proton interactions with potential nutrient sorbing materials.

**Qiaosi Deng** completed her MSc thesis at the University of Waterloo supervised by **Hyung-Sool Lee**. Her research topic was ammonium nitrogen removal and recovery using natural zeolite from permeates of anaerobic membrane bioreactors.

Ph.D. student **Holly Gray**, (co-supervised by **Wayne Parker** and **Scott Smith**) is continuing her research on the use of sorbents for nutrient removal and recovery. Holly's project is a part of the CWN CMWP project titled "*Integrated Sorption Technologies for Recovery of Nitrogen and Phosphorous from Anaerobic Membrane Bioreactor Permeates.*"

**Daniela Conidi** is a Ph.D. student under the supervision of **Wayne Parker**. The focus of her research is on phosphate uptake in co-precipitation systems targeting low phosphate concentrations. This research is being conducted in collaboration with EnviroSim Associates Ltd. and Environment Canada. Daniela's work includes modeling and characterization of the kinetics of phosphate removal at ultra low concentrations. A part of Daniela's research is highlighted in the research highlight section of this issue of the Nutrient Research Periodical.

In terms of collaborator updates, recently **Jeremy Dudley** (WRc, UK) has extended Smith's original Matlab code for the Active Surface Factor-Surface Complexation Model (ASF-SCM) framework originally used for simulating chemical phosphorus removal bench tests. The application of ASF-SCM has been expanded by Jeremy to treat full plant data and improved to now include revised equilibrium parameters, calculated pH as an output, inclusion of temperature sensitivity, alkalinity effects on precipitation, COD competitive effects at surfaces as well as taking iron sulfide precipitation interferences into account. Results of this work are in preparation for publication.

### CONFERENCES

#### Past Conferences:

[Gananoque Environmental Science and Engineering Conference](#) held in Gananoque, Ontario. (February 1 – 2, 2014):

*The oral and poster presentations were presented at the above mentioned conferences by the Nutrient Removal/Recovery Group:*

Scott Robinson, Holly E. Gray and D. Scott Smith. Effect of mixing on phosphate removal in effluent wastewater. (Oral Presentation)

Holly E. Gray, D. Scott Smith and Wayne J. Parker. Nitrogen and phosphorus recycling from wastewater treatment plant effluents using commercially available sorbents. (Oral Presentation)

**The 2<sup>nd</sup> Recovery of Value-Added Products Conference** held at the University of Waterloo, Waterloo, Ontario. (February 19, 2014).

In February, the University of Waterloo was host to the 2nd Waterloo Conference "Sustainable technologies to treat organic wastes and wastewaters: the recovery of value-added products". Members of the NRRG were actively involved in the conference: **Dr. Hyung-Sool Lee** was conference chair, **Dr. Wayne Parker** and **Dr. Scott Smith** were program co-chairs.

*The following poster presentation was presented at the above-mentioned conference by the Nutrient Removal/Recovery Group:*

Holly E. Gray, D. Scott Smith and Wayne J. Parker. Nitrogen and phosphorus recycling from wastewater treatment plant effluents using commercially available sorbents. (Poster Presentation)

**4<sup>th</sup> IWA/IEF Wastewater Treatment Modeling Seminar** in Spa Belgium March 30<sup>th</sup>-April 2<sup>nd</sup> 2014

Hauduc, H., Takács, I., Smith, D.S., Szabó, A., Murthy, S., Daigger, G., and Sperandio, M. A dynamic model for physicochemical phosphorus removal: Validation and integration in asm2d. Presented at WTTmod (2014), Spa, Belgium. (In proceedings pp. 220–224). \* **Winner best poster award** \*

#### **Upcoming Conferences:**

**Water Environment Federation Technical Exhibition and Conference (WEFTEC)** to be held at New Orleans Morial Convention Center in New Orleans, Louisiana. (September 27 – October 1, 2014).

*Presentations at WEFTEC to look for ....*

Brewer, H. M.; Coombs, A. W.; Veerapaneni, S.; Puopola, J. & Smith, D. S. (2014), 'Between a Rock and a Hard Place: Microfiltration and Reverse Osmosis to Achieve Ultra-Low Total Phosphorus Concentrations', WEFTEC, [Accepted platform].

Gray, H. E.; Smith, D. S. & Parker, W. J. (2014), 'Nitrogen and Phosphorus Recycling from Wastewater Treatment Plant Effluents using Commercially Available Sorbents', WEFTEC, [Accepted alternate & poster].

## RESEARCH HIGHLIGHT



The following article highlights a sample of the research conducted by Daniela Conidi during her Ph.D. program. The research presented includes final steady state results building on preliminary steady-state results presented at WEFTEC 2011 found in the WEFTEC 2011 Conference Proceedings.

## The impact of solids residence time on low level phosphorus removal in co-precipitation systems

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### Introduction

Due to recent concern regarding effluent discharges into sensitive receiving water bodies, lower orthophosphate ( $\text{PO}_4^{3-}$ ) limits ( $<10\mu\text{g-P/L}$ ) are being targeted in a number of locations (Takács et al., 2006a). These limits can only be achieved with some level of chemical P removal through the use of metal salts. Removal with ferric chloride is the topic of this research.

Understanding and modelling the physical and chemical processes involved in attaining extremely low P concentrations with hydrous ferric oxides (HFO) has been the focus of recent research (Smith et al., 2008; Szabó et al., 2008; Newcombe et al., 2008; Weng et al., 2010; Mao et al., 2012; Hauduc et al., 2013). Addition of ferric salts to water results in the formation and rapid precipitation of HFO floc (Smith et al., 2008). When  $\text{PO}_4^{3-}$  is present it will initially co-precipitate during the rapid HFO precipitation while subsequent uptake is slower and due to adsorption/complexation reactions on the surface of the HFO floc (Smith et al., 2008; Szabó et al., 2008). These complexation reactions are a result of iron and P sharing an oxygen atom (Smith et al., 2008). The availability of reactive oxygen atoms or "surface sites" is dependent on mixing and aging. The majority of removal occurs during the initial fast reaction; however the slower long term removal is significant in achieving low effluent concentrations (Szabó et al., 2008).

Recycling solids through the wastewater treatment process provides additional solids retention time allowing for further "slow" interactions between the liquid and solid phases. Research shows that recycling solids enhances P removal and decreases metal dosing requirements (Takács et al., 2006b; Szabó et al., 2008; Newcombe et al., 2008; Takács et al., 2011; Falk et al., 2012). Szabó et al., (2008) further showed that systems with a longer hydraulic residence time (HRT) and solids residence time (SRT) provide increased  $\text{PO}_4^{3-}$  uptake.

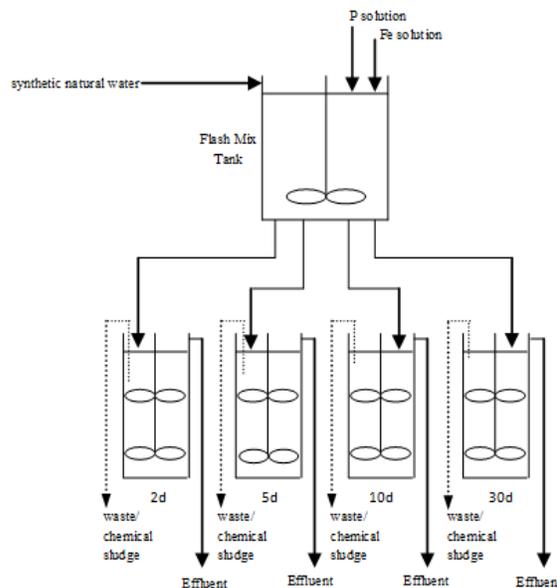
Recycling of solids leads to floc aging. The process of aging is expected to change the morphology of HFO precipitates. Smith et al. (2008) determined that the availability of surface sites decreases as a result of HFOs becoming more crystalline with age thus limiting the surface area for binding. Aging therefore affects the slow P removal reactions or adsorption mechanisms (Smith et al., 2008; Szabó et al., 2008). Reduced P removal with aged pre-polymerized HFO was found by Mao et al. (2012), Szabó et al., (2008) and Lijklema (1980). Recent work by Hauduc et al. (2013) introduces two processes of HFO aging: aging of fresh HFO to "low" HFO with a decrease in surface sites, and aging of low HFO to "old" HFO which have no reactive surface sites. This model was calibrated to the results of Szabó et al. (2008). The aging described in these studies is over shorter time frames not typical of solid residence times (SRTs)

observed in wastewater treatment processes. Therefore, a better understanding of the aging of chemical solids and the role of solids contact time and SRT on chemical use and achievable P limits is still required (Benisch et al., 2013). Ideally this will lead to relationships that quantitatively describe the influence of SRT on  $PO_4^{3-}$  sorption in continuous co-precipitation systems under conditions that are typical of wastewater treatment processes.

The objective of this work was to characterize the impact of SRT on steady state P removal. Steady state samples were obtained from lab scale continuous flow sequencing batch reactors (SBRs) using synthetic natural water dosed with phosphate.

**Materials and Methods**

Steady state experiments were conducted in four continuously operating SBRs with SRTs of 2, 5, 10 and 30 days (Figure 1). Deionized water that was dosed with known amounts of typical cations to produce an alkalinity which is typical of wastewaters was used as a feed. The water was supplied to a flash mix tank where it was dosed with  $PO_4^{3-}$  ( $3.4 \pm 0.9$  mg-P/L) and ferric chloride ( $16.1 \pm 1.8$  mg-Fe/L) under rapid mixing (HRT = 1.5minutes). The contents of the flash mix tank were then transferred into SBRs equipped with pH control, aeration, and mechanical mixing and allowed to react (flocculate), waste, settle and decant (HRT=6 hours). SRT was controlled by adjusting waste volumes based on effluent and reactor solid concentrations, and by tracking the SRT dynamically (Takács et al., 2008). The SBRs were regularly sampled for soluble P and total suspended solids (TSS) analysis once steady state was achieved with respect to SRT.



**Figure 1: Simplified Process Schematic**

**Results and Discussion**

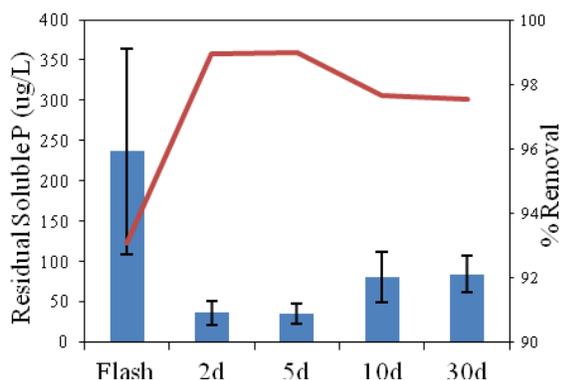
Table 1 summarizes the TSS concentrations in each SBR along with the calculated SRT. SRT was maintained close to the desired values and was found to be statistically different ( $p < 0.05$ ) between each reactor.

**Table 1: Reactor TSS and SRT. SRT was calculated using dynamic SRT (Takács et al., 2008).**

Reactor	TSS (mg/L)	SRT(d)
Flash	$31 \pm 7$	-
2d	$251 \pm 80$	$2.28 \pm 0.57$
5d	$488 \pm 172$	$4.75 \pm 0.95$
10d	$982 \pm 299$	$10.1 \pm 1.67$
30d	$1771 \pm 401$	$28.6 \pm 2.75$

Figure 2 shows the residual P concentrations observed in the flash tank and SBR effluents. The results were consistent with the observations of Szabó et al., (2008) where the majority of P removal from the aqueous phase occurred instantaneously in the flash mix tank (93%)

and further aging of solids provided additional (4.5-6%) removal. The high standard deviation in the flash mix tank was attributed to the instantaneous nature of HFO precipitation and  $\text{PO}_4^{3-}$  co-precipitation. The 2d and 5d SRT systems provided statistically lower residual P concentrations ( $p < 0.05$ ) than the 10d and 30d systems. However, differences in removal between the 2d and 5d systems and between the 10d and 30d systems were not significant ( $p > 0.05$ ).

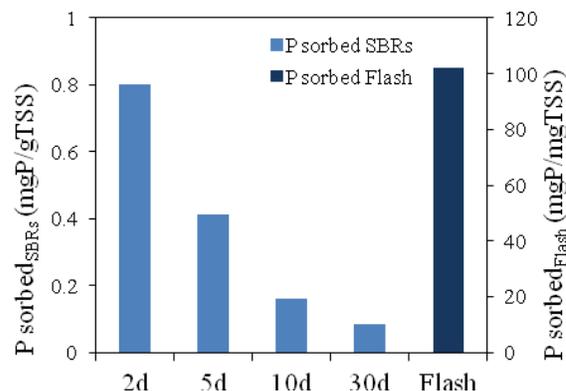


**Figure 2: Average P Removal.** Boxes correspond to average steady state residual soluble P concentrations. Black lines provide standard deviations. The red line corresponds to average % P removal.

Figure 3 compares the amount of P removed per gram of HFO solids in each reactor. P uptake was 100 times greater in the flash mix tank compared to the other reactors. The amount of sorbed P decreased with SRT. These results follow the observations of Smith et al. (2008) where decreased removals were deemed to result from reduction in the number of reactive surface sites on aged HFO.

Overall, soluble P uptake did not increase with SRTs greater than 5 days. These results contradict those of Szabó et al. (2008) where increasing HRT and SRT resulted in higher P removal. Generally, the effects of slow kinetic removal via recycling and aging (Szabó et al., 2008) contradict

the results that aging reduces active surface sites and limits P removal (Smith et al., 2008). It is hypothesized that P uptake will increase with HRT instead of SRT. The HRT provides contact time for the free soluble P that has not been co-precipitated to interact (adsorb) with the solids. However, the age of the solids will dictate the extent to which further sorption occurs.



**Figure 3: Average sorbed P concentration.** Boxes correspond to the average steady state removal observed in each reactor as a function of the solids concentration.

### Conclusions

Interactions between soluble P removal and SRT were explored. The majority of P removal (93%) occurred in the flash tank with an additional 4.5-6 percent removal in the SBRs. Soluble P uptake did not increase with SRTs greater than 5 days. The amount of sorbed P decreased with SRT providing evidence that aging changes floc morphology.

### Summary of Further Work

A summary of the major work conducted under the overall scope of this research project includes characterizations of:

- The kinetics of P removal under steady state and transient conditions,
- The impact of SRT on the rates of adsorption (isotherm and kinetic analysis), and

- The impact of SRT on floc structure (particle size analysis, microscopy evaluation)

Results will provide further enhancement of models for predicting the performance of P removal systems particularly in terms of understanding solids aging and kinetics.

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**Editor's Desk:** This newsletter is distributed by the Nutrient Removal & Recovery Group, University of Waterloo and Wilfrid Laurier University. If you know of others who would enjoy this newsletter, or if you no longer wish to receive it yourself, please contact:

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