Nutrient Removal & Recovery Group Newsletter

Nutrient Research Periodical

Welcome to the fourth issue of 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, we will be highlighting research of NRRG Master's student **Farah Ateeq** who is supervised by **Dr. Scott Smith** at Wilfrid Laurier University. Farah's research article is titled:

NEWS

"*Getting down to ultra-low P in wastewater effluents – removing organic P from wastewater using iron and oxidants*".

Previous issues of the Nutrient Research Periodical can be found on the following website: http://clearlab.synology.me/CLEARnewsletters

Any inquires as to the features or subscription to the Nutrient Research Periodical can be directed to the editor Holly Gray (contact information is located on the last page of the newsletter).   .

HIGHLY QUALIFIED PERSONNEL (HQP)

The NRRG includes a large group of students (past and present) with very diverse research projects and goals:

New to the NNRG is undergraduate BSc student **Christian Agueci**, supervised by **Dr. Scott Smith**, who is working on his undergraduate thesis comparison of the detection of total phosphorus between inductively coupled plasma optical emission spectroscopy (ICP-OES) and colorimetric analysis.

Continuing students include **Farah Ateeq** and **Captain Suyoung Choi**, both in the Masters of Chemistry program at Wilfrid Laurier University under the supervision of **Dr. Scott Smith. Captain Choi** is continuing his project on P removal and recovery using bulk and nanoparticulate TiO_2. **Farah Ateeq** (co-supervised by **Dr. Vladimir Kitaev**) continues to investigate advanced oxidation to remove organic phosphorus. Ph.D. student **Holly Gray**, (co-supervised by **Dr. Wayne Parker** and **Dr. Scott Smith**) is continuing her research on the use of sorbents for nutrient removal and recovery. **Yunxia Pan**, a visiting scholar is working with **Dr. Wayne Parker**, continuing her investigation into electrochemical techniques for nutrient recovery.

Daniela Conidi successfully defended her doctoral thesis under the supervision of **Dr. Wayne Parker** in March and graduated from University of Waterloo in June. She is currently working with EnviroSim Associates Ltd as an OCE TalentEdge Postdoctoral Fellow. EnviroSim provides simulation software solutions and consulting services for wastewater process engineers around the world. They are the developers of BioWin, PetWin and BW Controller. Daniela has been actively involved in the development of a new mechanistic model for chemical phosphorus removal which will incorporate the findings of her doctoral research. This model will be incorporated in the BioWin simulator providing the basis for improved design and optimization of municipal wastewater treatment facilities.

RECENT ACTIVITIES OF THE NRRG

Dr. Wayne Parker recently visited Wageningen University in the Netherlands to develop research collaborations. While there, he toured the Dokhaven wastewater treatment plant in Rotterdam and observed a pilot plant providing shortcut nitrogen removal for municipal wastewater.

In November, **Dr. Scott Smith** was awarded an NSERC Engage Grant "Phosphorus removal using nanosized titanium dioxide" in partnership with Purifics in London Ontario to test the potential of Purific's existing technology for phosphorus removal and recovery.

PUBLICATIONS

The following peer reviewed papers and book chapters were published by the Nutrient Removal/Recovery Group since the last newsletter:

Conidi, D. and Parker, W. J. The effect of solids residence time on phosphorus adsorption to hydrous ferric oxide floc. *Wat. Res.* **84** (2015) 323 – 332.

Smith, D. S. Phosphorus Analysis in Wastewater: Best Practices. No. NUTR1R06cc in White Paper. WERF, 2015. 60 p.

Hauduc, H., Takács, I., Smith, D. S., Szabó, A., Murthy, S., Daigger, G., and Spérandio, M. A dynamic physiochemical model for chemical phosphorus removal. Wat. Res. **73** (2015) 157-170.

Gray, H., Parker, W. and Smith, S. State of Knowledge of the Use of Sorption Technologies for Nutrient Recovery from Municipal Wastewaters, NUTR1R06x. WERF, 2015. 80 p.

Gu, A. Z., Liu, L., Onnis-Hayden, A., Smith, S., Gray, H**.**, Houweling, D., and Takács, I. Phosphorus Fractionation and Removal in Wastewater Treatment- Implications For Minimizing Effluent Phosphorus, nutr1r06l ed. White Paper. WERF, September 2014. 123 p.

Smith, D. S., and Gray, H**.** Surface Complexation Modelling and Aluminum Mediated Phosphorus Removal, nutrir06r ed. White Paper. WERF, May 2014. 22 p.

Special Mentions:

Dr. Scott Smith's research on chemical phosphorus removal was highlighted in a recent issue of *INFLUENTS* which is the official publication of the Water Environment Association of Ontario (WEAO). The two page spotlight article by Christine Hanlon titled "Scott Smith: Understanding and Maximizing Phosphorus Removal" can be found on page 8 of the fall 2015 issue (volume 10).

RESEARCH HIGHLIGHT

The following article highlights the recent research conducted by **Farah Ateeq** during her Master's program.

Getting down to ultra-low P in wastewater effluents – removing organic P from wastewater using iron and oxidants

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Introduction

Several studies have been reported in literature on the removal of phosphorus from wastewater with excellent results. These studies however often focus on the orthophosphate fractions alone, the most commonly found in wastewater. As regulations for P effluent limits are moving towards lower concentrations, the need to remove other forms of P is becoming increasingly important. One analysis revealed that removal of sRP (soluble reactive phosphorus) from wastewater can be quite effective with values from 90-100%, while removal percentages for sNRP (soluble non-reactive phosphorus, consisting of the sum of dissolved organic phosphorus and soluble acid-hydrolysable phosphorus) can vary greatly, ranging from 20% to 100%[1]. Due to their differing chemistries, various P compounds respond differently to the traditional methods of phosphate removal. The objective here was to find a method that removes essentially all sNRP forms, using technologies similar to what are already being used in the wastewater treatment industry.

Examples of compounds that make up the NRP fraction in wastewater include condensed phosphates such as adenosine triphosphate (ATP), phosphate esters, such as inositol phosphates, and phosphonates, such as 2-amino ethyl phosphonic acid. These compounds enter wastewater from various sources. ATP is generated by plants and animals[2]. Inositol phosphates are synthesized by plants and are a major component of organic P fractions in many soils, from which they can leach into water[3]. Phosphonates are used in detergents, scale-formation inhibitors, and other industrial applications from which they can be discharged into wastewater treatment plants[4]. Of these compounds, phosphonates are the most refractory due to having a C-P bond which is much more stable than O-P bonds in the other compounds.

In this study, we have hypothesized that organic P compounds (making up the NRP fraction) can be converted to inorganic forms, specifically orthophosphates (which make up the sRP fraction), and thus be made chemically reactive to already established methods for phosphate removal. To this end, we have assessed the use of oxidants including hydrogen peroxide and bleach, as well as manganese oxide and iron oxide nanoparticles as potential catalysts for the oxidation of organic P compounds. Iron chloride was then used to precipitate out inorganic P (the breakdown product of oxidation), which then becomes part of the solids. The results of various treatment

methods assessed are presented in this article.

Materials and Methods
Five different chemicals were selected to represent a mixture of phosphorus compounds in wastewater, including an orthophosphate (KH_2PO_4), tripolyphosphates (ATP and sodium triphosphate), phosphate monoester (phytic acid), and a phosphonate (2-aminoethyl phosphonate).

Up to thirteen different treatment protocols were attempted with each compound with varying types and amounts of oxidants, amount of flocculant, and pH (full details are present in Table 2 in the next section). The tests were initially done in a pure water matrix and the best result from this set was then tested in a synthetic wastewater recipe (shown in Table 1) to assess whether presence of other chemicals interferes with the P removal process.

Table 1: *Synthetic wastewater composition. Adapted from [5].*

Compound	Concentration (mg/L)
Magnesium sulfate ($MgSO_4 \cdot 7H_2O$)	24.0
Calcium chloride ($CaCl_2 \cdot 2H_2O$)	2.4
Sodium bicarbonate ($NaHCO_3$)	300.0
Sodium acetate (CH_3COONa)	820.3

Tests were done in glass vials with approximately 10 mL solutions. Stock solutions of 5 mg P/L (0.16 mM P) were prepared from each phosphorus compound. To 10 mL of these solutions, peroxide was added to get a final concentration of 0.01-0.5 M. (The exact concentration for each trial is indicated in Table 2 in Section 3.1.) In some samples bleach was

used instead of peroxide as the oxidant. Manganese(III,IV) oxide nanoparticles, prepared in-house, were then added (metal concentration of 0.4 mM). Finally, iron(III) chloride was added to get a concentration of 0.4-0.8 mM. These concentrations were chosen to allow the metal to be well in excess of the phosphorus. The samples were stirred throughout the addition of each chemical. pH was adjusted the following day using HCl or NaOH to values between 4 and 8. The samples were allowed to sit unstirred overnight, after which the solids were separated from the liquid using centrifugation. The liquid fraction was acidified using nitric acid, and then analyzed for total P using ICP-OES (Inductively Coupled Plasma – Optical Emission Spectroscopy). The %P removed from the treated samples was used as the main measurement for assessment of the treatment methods. This value was calculated as follows:

$$\% \text{ P Removed} = \frac{1 - [P] \text{ measured in supernatant (mg P/L)}}{\text{original } [P] \text{ in uncentrifuged sample (mg P/L)}} \times 100$$

Results and Discussion
3.1. Tests in pure water
The results for the %P removed for each of the five P compounds tested are summarized in Table 3, with the corresponding reaction conditions in Table 2. All the tests shown in this section were done in a pure water matrix. Each row in Table 2 corresponds to a different set of conditions tested. For example, in S. No. 1, the pH was not adjusted, the molar ratio of iron to phosphorus was 5, no manganese (as manganese oxide nanoparticles) was added to the sample, and the oxidant used was hydrogen peroxide with a concentration of 0.1 M. Table 3 shows that under these conditions, the % P removal was 6% for KH_2PO_4, 6% for ATP, 5% for sodium triphosphate (NaTP), and 5% for 2-aminoethyl phosphonate (AEP).

Phytic acid (PhyA) was not tested under these specific conditions. The uncertainties in the table represent standard deviations for the number of replicates shown.

Table 2: *Conditions used for various treatment methods done in a pure water matrix.*

S. No.	pH	Fe:P	Mn:P	[Oxidant] M
1	---	5	---	H_2O_2, 0.1
2	---	2.5	---	NaOCl, 0.1
3	4.0	5	---	H_2O_2, 0.05
4	---	2.5	2.5	NaOCl, 0.1
5	6.0	2.5	---	---
6	5.0	5	---	---
7	---	2.5	2.5	---
8	6.0	2.5	---	NaOCl, 0.1
9	5.7	2.5	2.5	H_2O_2, 0.5
10	8.0	5	---	H_2O_2, 0.05
11	---	2.5	2.5	H_2O_2, 0.1-0.5
12	5.0-7.0	2.5	---	H_2O_2, 0.05-0.5
13	5.0-7.0	5	---	H_2O_2, 0.05-0.1

It was found that when all variables were kept constant and the pH alone was changed, the %P removal remained the same for pH values between 5 and 7 (see Figure 2). For this reason, the pH values in S. Nos. 12 and 13 are shown as a range. Similarly, some of the peroxide concentrations are also shown as ranges. Initial tests were done with 0.5 M peroxide in the samples, but it was found that reducing the concentration to as low as 0.05 M did not affect the removal percentages.

The results from the testing in pure water are summarized in Figure 1 in graphical form. From this figure, it becomes obvious that S. No. 13 (pH 5-7, [Fe] 5 times the concentration of P, no Mn added, and peroxide 0.05-0.1 M) gave the best removals, close to 100%, for each of the five compounds tested. pH has a

significant effect on the results, as it influences precipitation of iron-phosphorous compounds and flocculation, and therefore determines what percentage of phosphorus can be removed from liquid into a solid form.

Table 3: *Results for %P Removal for each compound using various treatment methods, done in pure water. See Table 2 for reaction conditions used.*

S. No.	%P Removed				
	KH_2PO_4	ATP	NaTP	AEP	PhyA
1	6	6	5	5	---
2	11	9	---	4	---
3	11	23	---	---	---
4	23	18	24	3	---
5	93	89	---	14	---
6	98 ± 2 n=2	97 ± 2 n=2	99 ± 1 n=2	20 ± 5 n=2	---
7	54	41	34	86	---
8	35	48	---	15	94
9	92	82	---	---	---
10	96	84	---	---	---
11	90 ± 4 n=3	87 ± 2 n=3	85 ± 0 n=2	85 ± 3 n=2	87
12	93 ± 3 n=6	92 ± 3 n=5	89 ± 11 n=2	91 ± 4 n=6	94
13	100 ± 2 n=8	98 ± 3 n=8	101 ± 1 n=5	100 ± 2 n=6	95

Figure 2 suggests that the pH range 5-7 works best at removing phosphorus when iron(III) chloride is used as the flocculant. NaOCl was found to give poor removals in comparison to peroxide and was not tested in depth. With manganese(III, IV) oxide nanoparticles, it was expected they would act as a catalyst for the
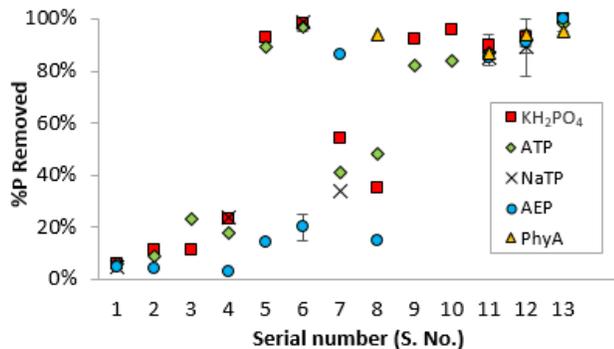
Figure 1. *%P removed for each compound under various treatment methods, done in pure water. The series number corresponds to the numbers in the first column in Table 2. ATP = adenosine triphosphate; NaTP = sodium triphosphate; AEP = 2-aminoethyl phosphonate; PhyA = phytic acid*

oxidation of organic P compounds. (The Mn^{4+} gets reduced to Mn^{3+} while the organic compound undergoes oxidation. Peroxide or bleach then restores Mn^{3+} back to Mn^{4+}.) While good removals - 85-90% - were obtained for each compound (S. No. 11), it was surprising to discover that iron alone (S. No. 12) could give even better removals. When the molar ratio of iron to phosphorus was increased from 2.5 to 5, (S. nos. 12 and 13) the %P removal was almost complete, thus giving the conditions for optimum P removal. The presence of peroxide should be noted in these experiments. Peroxide does not affect the removal for KH_2PO_4, ATP and NaTP (S. Nos. 6 and 13), however for AEP, addition of just 0.05 M peroxide increases the removal from 20% to a 100%. Thus, to achieve complete P removal, a combination of iron, peroxide and the correct pH are needed.

Figure 2 shows the %P removed for all the P compounds as pH increases from 4 to 9. The tests were done in pure water, with iron to phosphorus molar ratio of 5:1, and 0.05 M hydrogen peroxide. The symbols on the figure are experimental data points while the dashed

lines are only included as a guide to trace trends. The data suggests that the optimal pH for removal of the compounds is between 4.5 and 7 and the removal efficiency can decrease rapidly outside these ranges. This range turns out to be quite convenient as waste water is slightly basic and ends up offsetting some of the acidity of the added iron chloride to result in a pH close to 6, at which efficient removal occurs. This is consistent with previous studies performed by Szabo et. al. who studied the factors affecting phosphorus removal[6], and Smith et. al. who developed a surface complexation model for phosphate[7]. The mechanism for the removal of PO_4-P involves both adsorption and co-precipitation of phosphate onto HFO (hydrous ferric oxide, formed by neutralization of acidic ferric chloride)[7], and since it is hypothesized that the organic P compounds liberate phosphate groups on oxidation, the P removal curves of these compounds should be similar to that of orthophosphate. This is found to be true in the dataset discussed here, up to pH 7. The variations above pH 8 have not been
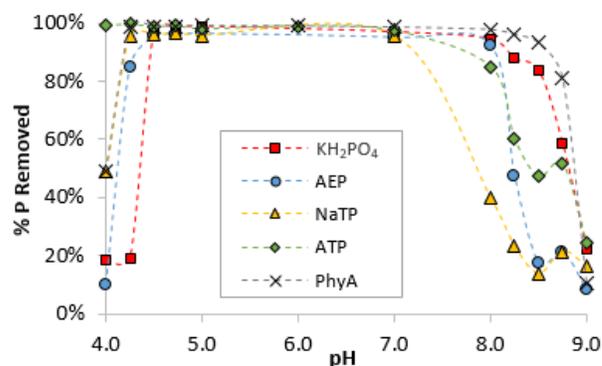

Figure 2. *Effect of pH on %P removed for various compounds. The dashed lines are included as a guide for the eye. ATP = adenosine triphosphate; NaTP = sodium triphosphate; AEP = 2-aminoethyl phosphonate; PhyA = phytic acid*

investigated yet, and are not immediately relevant due to being outside the range at which treatment plants operate.

3.2. Tests in synthetic wastewater.

The conditions that gave the best results in pure water were tested in a synthetic wastewater recipe. These conditions included adjustment of pH to 5, Fe:P = 5:1, no manganese added, and peroxide concentration 0.05 M. All of the five compounds tested gave excellent removals of 96-98% (Figure 3), indicating the treatment method works well in the presence of other chemicals found in wastewater. Testing of these conditions with a real wastewater matrix is underway.
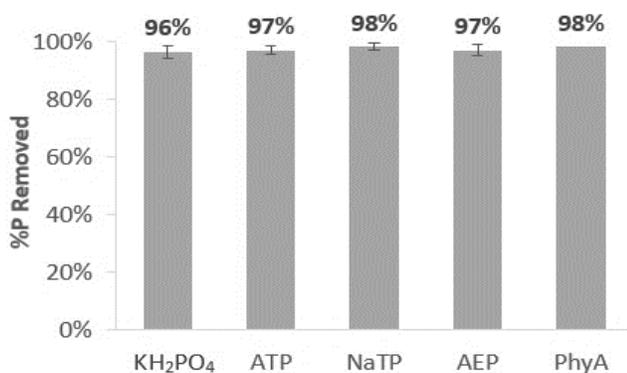
Figure 3. *%P Removed for different compounds in synthetic wastewater. The error bars represent standard deviations for n=5. ATP = adenosine triphosphate; NaTP = sodium triphosphate; AEP = 2-aminoethyl phosphonate; PhyA = phytic acid*

Conclusion

This study assessed various treatment methods to remove five different phosphorus compounds that were representative of phosphorus species in wastewater. The treatment method that was found to work best, giving almost complete removals, was a combination of the following:

- Adjustment of the wastewater pH to between 5 and 7
- Addition of iron (as ferric chloride) to 5 times the molar concentration of phosphorus
- Addition of hydrogen peroxide to get a final concentration of 0.05 M.

The first two conditions alone were able to remove most of the P compounds, but presence of hydrogen peroxide was found to be necessary to remove phosphonates in particular. Therefore, all of these conditions are required to eliminate all of the phosphorus from wastewater.

This combination was tested in a synthetic wastewater matrix and was found to give removals between 96-98%, showing great potential to work in actual wastewater.

Testing for organic P removal using the conditions studied for synthetic wastewater are underway using real wastewater matrices.

References

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[7] Smith, S., Takacs, I., Murthy, S., Daigger, G. T. & Szabo, A. *Water Environ. Res.* **80**, 428–438 (2008).