



## **INTEGRATED SORPTION TECHNOLOGIES**

FOR RECOVERY OF NITROGEN AND PHOSPHOROUS FROM ANAEROBIC MEMBRANE BIOREACTOR PERMEATES

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WAYNE PARKER, UNIVERSITY OF WATERLOO

*Research conducted 2013-2015*



Canadian  
Water  
Network

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## WHY DID WE DO THIS RESEARCH?

Municipal utilities spend considerable time, energy and chemicals to remove phosphorus and nitrogen compounds like phosphate and ammonium from municipal wastewaters, as they degrade water quality and are toxic to aquatic life. Phosphorous and nitrogen have substantial value as fertilizers or feedstock for industrial processes, and motivation for nutrient recovery from wastewaters is increasing due to limited phosphorous availability and increasing energy costs to manufacture ammonia.

Recovering these nutrients from wastewaters is currently expensive and not always commercially feasible. However, phosphorous and nitrogen found in low concentrations can still be a significant source of nutrients when flows are high. A Canadian company — Ostara, plans to concentrate dilute solutions of these compounds by adapting their struvite recovery technology. Partners like GE and GSD have expressed an interest in developing technologies that address nitrogen and phosphorous not removed in anaerobic membrane bioreactors (AnMBRs)<sup>1</sup>.

This 2013-2015 project created an effluent of specific, elevated, concentrated feedstock amenable to methods such as the Ostara process to generate fertilizer from wastewater, and developed a more economical treatment to collect ammonium nitrogen and regenerate exhausted zeolite for AnMBR permeates. The new processes developed through this project could eliminate the need for energy intensive nitrification processes and/or the need for the addition of chemicals for phosphorous removal, and will help municipalities to meet strict effluent regulations.

## WHAT WERE OUR FINDINGS?

### 1. PHOSPHOROUS AND NITROGEN RECOVERY FROM DILUTE WASTEWATER WITH COMMERCIAL SORBENTS

Fourteen commercially available sorbents were collected from a number of suppliers and tested with a synthetic wastewater solution representing typical southern Ontario wastewaters for nitrogen (N) and phosphorous (P) adsorption. Two of the fourteen sorbents were found to adsorb amounts of N that were too low for the purposes of this study, so further testing was not conducted. Seven sorbents (A to G in Table 1) were found to adsorb promising quantities of P.

The seven promising sorbents were subjected to further batch testing with synthetic wastewater.

ADSORBENT	DESCRIPTION	ADSORBED P	ADSORBED N
A	Granular ferric hydroxide based sorbent	Yes	No
B	Anion exchange resin (AER)	Yes	No
C	AER	Yes	No
D	AER	Yes	No
E	Ion-exchange resin with hydrated ferric oxide (HFO) nanoparticles	Yes	No
F	Granular activated alumina	Yes	No
G	AER	Yes	No
H	Aluminum and Titanium Oxide based sorbent	Very Low	Very Low
I	Aluminum and Titanium Oxide based sorbent	Very Low	Very Low
J	Synthetic amorphous silica hydrated	Very Low	No
K	Synthetic amorphous silica hydrated/citric acid	Very Low	No
L	Synthetic amorphous silica hydrated	No	No
M	Synthetic amorphous silica hydrated	No	No
N	TiO <sub>2</sub>	No	No

Table 1. Adsorption results for 14 commercially available sorbents

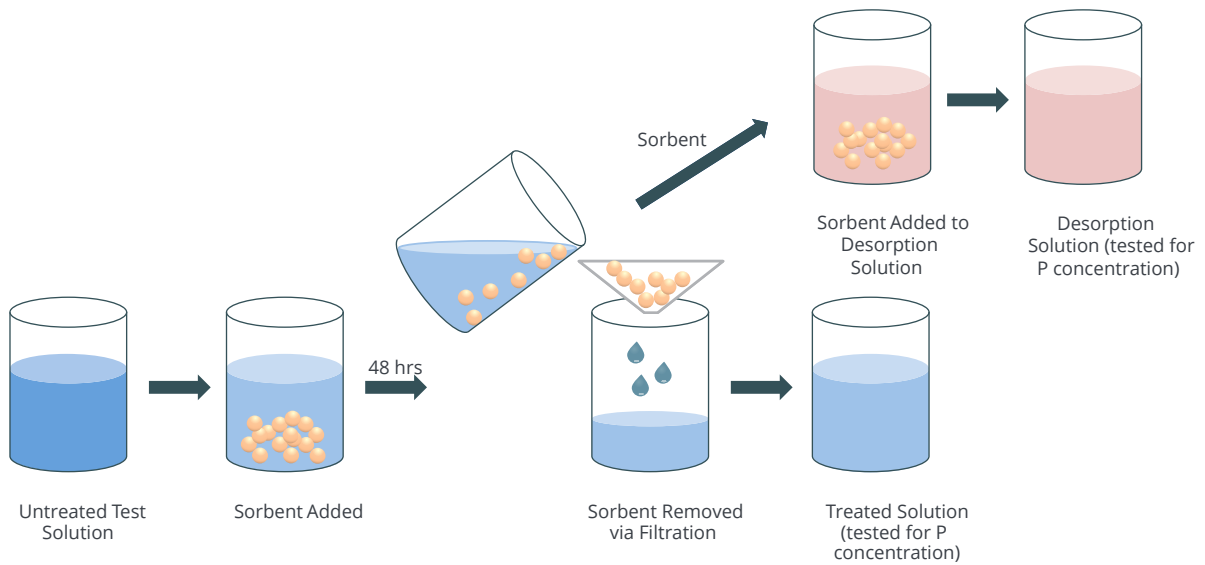


Figure 1. P recovery batch test procedure using adsorption and desorption

After 24 hours of sorption, the sorbent that was loaded with P was then added to a desorption solution for a 24-hour period. Four chemical desorption solution compositions were tested: HCl (acidic), NaOH (basic), NaCl (salt) and NaOH +NaCl (basic salt).

Overall, sorbent C — an ion exchange resin, was found to recover the largest quantity of P (23%). All other sorbents recovered less than 20% of phosphorous from the synthetic wastewater, suggesting that a mechanism to facilitate increased phosphorous recovery may be necessary (Figure 2).

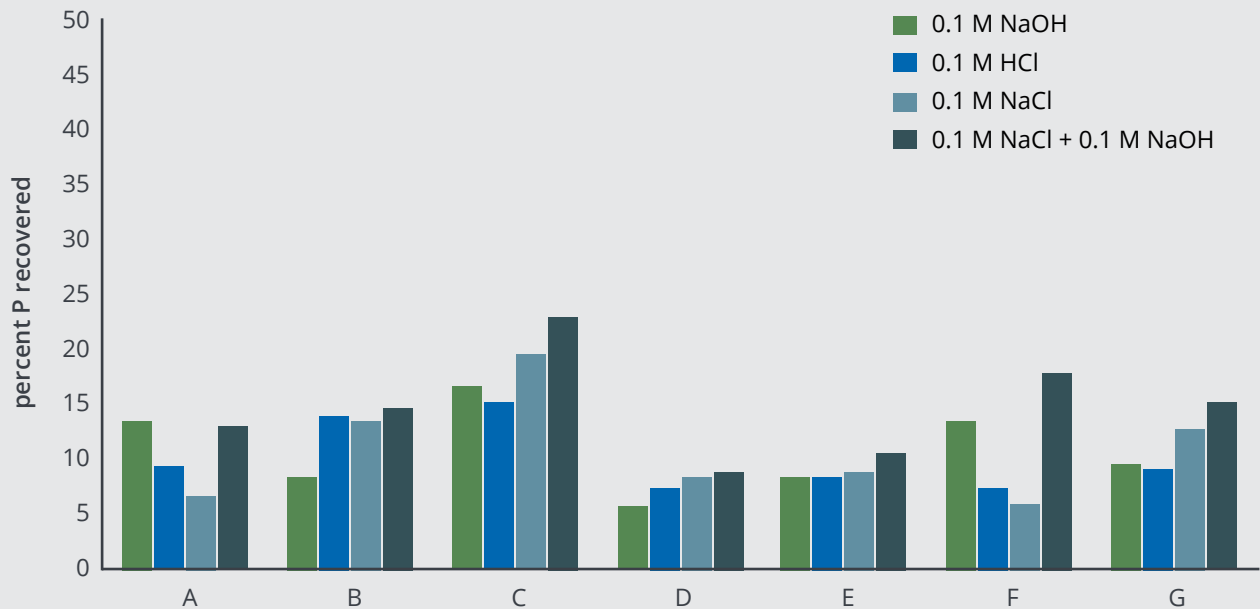


Figure 2. Percent Phosphorous Recovered

Additional desorption solutions, including sodium bicarbonate (NaHCO<sub>3</sub>) and magnesium sulfate (MgSO<sub>4</sub>), were tested on select sorbents. When NaHCO<sub>3</sub> was used as the desorbing solution, sorbent A — a granular ferric hydroxide based sorbent, increased the recovery of P from the solid phase to 62%, thus increasing the quantity of P recovered from the initial test solution from 13% to 20%. These results show that alternative desorption solutions may increase the driving force of phosphorous from the sorbent and facilitate increased phosphorous recovery.

After the initial batch screening, sorbents A, C and F were selected for continuous column testing to more closely assess how these sorbents might perform in a real wastewater treatment plant. Figure 3 shows the continuous column test setup. Three 30 cm long pipes (1.27cm dia.) were packed with 3 cm of sorbent, 6 cm of support material (glass wool and glass beads) and the rest left as void space.

Column tests with the synthetic wastewater were run until the column was saturated with P, typically 24 to 28 hours. The metal oxide based sorbents — A and F, removed 18 and 25% of P, corresponding to loadings of 5 mg P/g sorbent A and 5 mg P/g sorbent F. Sorbent C — an ion exchange resin, had a phosphorous loading of 20 mg P/g sorbent, removing 62% P from the influent.

Sorbent C, the best performing sorbent in the column sorption tests, was further subjected to phosphorous recovery testing. Acidic (HCl), basic (NaOH), salt (NaCl) and basic salt (NaOH + NaCl) solutions were used, and concentrations of desorption solutions were increased to 0.5 M to create a larger driving force for removal of P from the sorbents.

During the desorption run, desorption solutions were introduced to P saturated columns at a flow rate of 2.0 mL/min for 2.5 hours. Composite samples were collected over the entire desorption process to collect all P recovered from the sorbent. Recovery of P from sorbent C was the lowest using the acidic solution; the 0.5 M HCl solution recovered 50% of the sorbed P. Basic desorption solution increased recovery of P from the sorbent to 65% sorbed P. The salt and basic salt desorption solutions had the highest recovery of P when applied to sorbent C, both recovering 100% P. Overall, 0.5 M NaCl was determined to be the most efficient desorption solution due to its high recovery and lower cost than the basic salt mixture.

Data from time course monitoring of P desorption will be used to generate a predictive function to prepare effluent amenable to methods such as the Ostara process to generate fertilizer from wastewater. In the next phase of testing, sorbent C will be used to recover P from real wastewater effluents.

Initial results with anaerobic membrane bioreactor effluent exhibited low P adsorption, most likely due to competition with other ions in the effluent. Testing is continuing and aerobically treated wastewater effluents collected from industrial partners will also be tested.

## 2. AMMONIUM NITROGEN RECOVERY USING ZEOLITES

An innovative ammonium nitrogen recovery process was developed using a natural zeolite and an alkaline regeneration method. Five zeolites were tested using synthetic wastewater in batch experiments to determine the best natural zeolite (Figure 4). Zeobrite Lm had the best combination of ammonium exchange capacity (AEC) and regeneration efficiency and was selected for further testing.

A Zeolite Lm packed column was then fed with AnMBR permeate at flow rates of 4 and 8 Bed Volumes per hour (BV/h). These tests were repeated with a synthetic wastewater containing 30mg/L of ammonium nitrogen ( $\text{NH}_4\text{Cl}$ ). Early breakthrough times (less than 24 hours in the 8 BV/h continuous column tests) were observed due to the presence of competitive cations (mainly  $\text{K}^+$  and  $\text{Mg}^{2+}$ ) in the municipal wastewater (Figure 5). These competitive cations slightly decreased ammonium exchange capacity and imply that frequent regeneration of exhausted zeolite or its replacement with virgin zeolite would be required, which would lead to increased operating and maintenance costs for the nitrogen recovery process<sup>2</sup>.

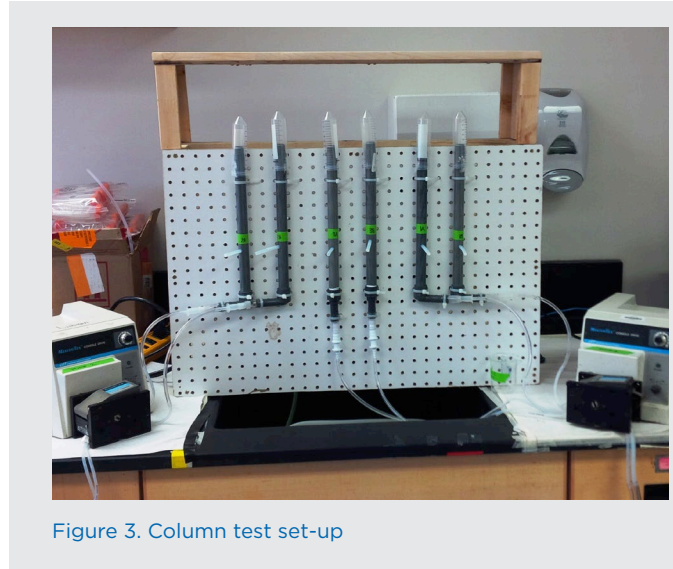


Figure 3. Column test set-up

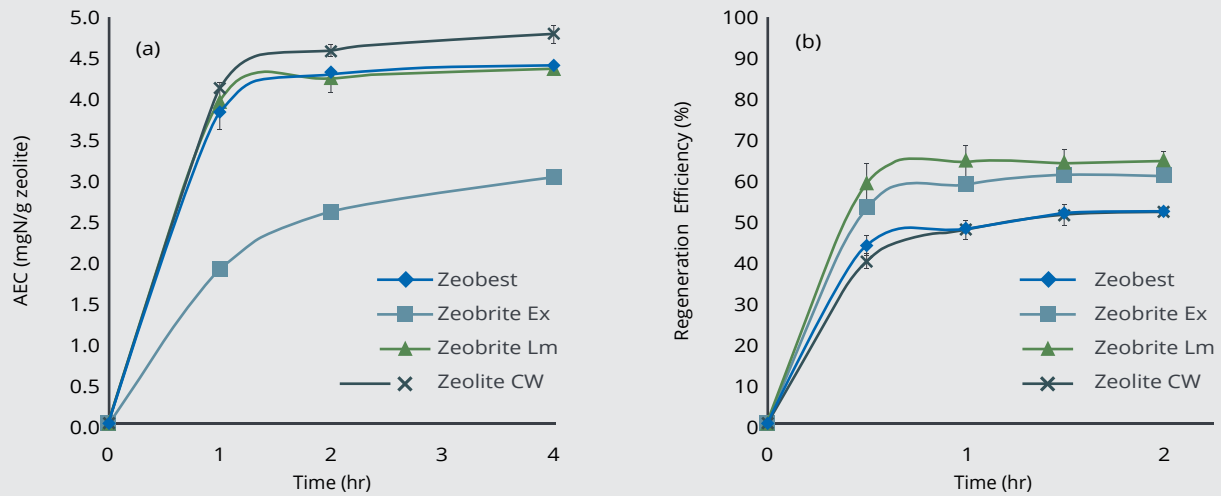


Figure 4. Comparisons of natural zeolites in exchange and regeneration tests (a) AEC for the four natural zeolites; (b) Regeneration efficiency of the four natural zeolites (NaCl 20 g/L, at pH 9)

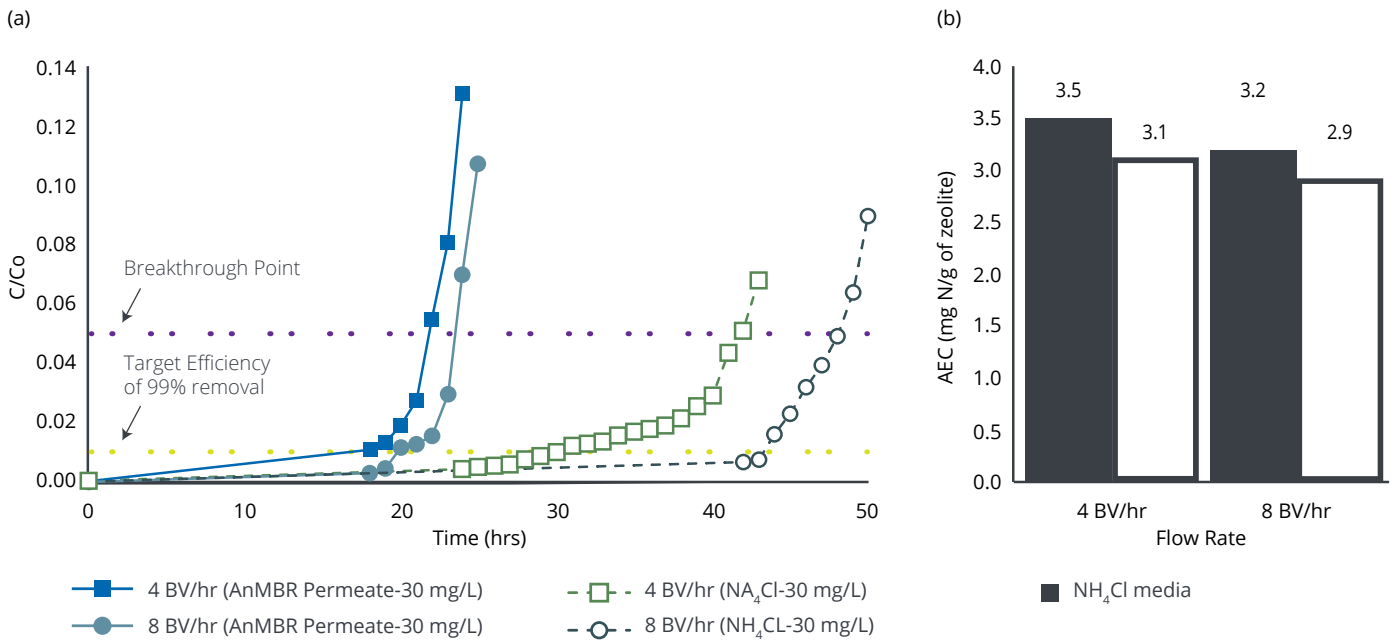


Figure 5. Continuous experiments using a zeolite Lm-packed column (a) Breakthrough curves at different flow rates using NH<sub>4</sub>Cl solution and AnMBR permeate; (b) AEC of zeolite in the column fed by NH<sub>4</sub>Cl solution and AnMBR permeate at different flow rates

Figure 6 describes the continuous zeolite-packed column for ammonium nitrogen recovery. During regeneration of exhausted zeolite, influent feeding is stopped and NaCl solution (10 g/L, pH 11-12) flows to the zeolite column. Ammonium nitrogen liberated from zeolite is immediately changed to ammonia gas driven by aeration, which is collected with acid scrubber as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. A continuous process to collect concentrated ammonium nitrogen with an alkaline regeneration method and a substantially decreased NaCl dose can reduce regeneration chemical costs to 7% of the costs in conventional regeneration systems (Figure 6); Table 2 provides more detailed information on cost analysis among conventional regeneration, alkaline regeneration, and alkaline regeneration combined with air-stripping. The performance of the packed zeolite column declined after each regeneration cycle and the time between cycles also declined. The zeolite was exhausted after 15 cycles and required replacement.

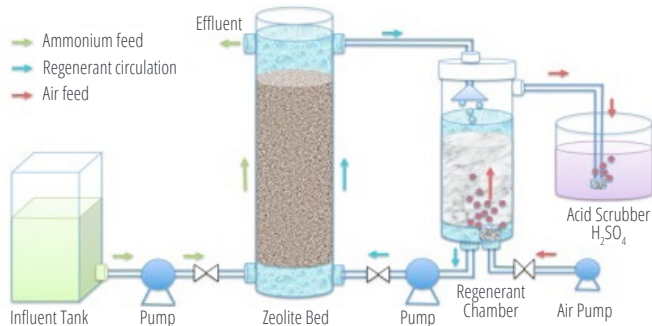


Figure 6. Schematic diagram of the continuous-flow zeolite-packed column

	Conventional regeneration	High pH regeneration (pH 12)	Integrated with Air-stripping
NaCl dosage (ton/d)	233 ton/d <sup>a</sup>	3.2 ton/d	1.6 ton/d
NaOH dosage (ton/d)	-	2 ton/d	1 ton/d
H <sub>2</sub> SO <sub>4</sub> (ton/day)	-	-	0.315 ton/day
Annual cost of chemicals (\$/year)	3,401,800	266,000	167,400
Product: (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-	-	42 ton

<sup>a</sup> Rahmani et al., 2004.; <sup>b</sup> <http://water.epa.gov>

The average flow rate of AnMBR permeate 10<sup>4</sup> m<sup>3</sup>/d; ammonium concentration in AnMBR permeate 30 mg N/L; ammonium loading rate 0.3 ton/d; NaCl price: \$40/ton, NaOH price: \$300/ton, H<sub>2</sub>SO<sub>4</sub> price: \$300/ton, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> price: \$180/ton (source: Alibaba.com)

Table 2. Economic Analysis of Chemical Costs in Regeneration

## WHAT DOES THIS MEAN FOR MUNICIPALITIES AND OTHER PARTNERS?

Although results of this study show that commercial sorbents are able to remove and recover phosphorous from wastewater, sorbent technologies will need to be improved to enhance economic viability for their use in nutrient recovery. While a variety of sorbents are commercially available, significant differences are observed between each sorbent’s ability to adsorb and recover nutrients; in this study, recovery of P from the best sorbent was shown to be substantial under optimal competitive ion desorption conditions; however, the initial quantity of P adsorbed was low. Due to this difference, there is a gap between lab-scale use of sorbents for P recovery and full scale implementation in wastewater treatment plants. Overall, the results of this study have shown that selectivity of sorbents will need to be improved to target nutrients in wastewater, eliminating competition effects during adsorption, and increasing the quantity of P recovered from the wastewater stream.

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REGION OF WATERLOO

YORK REGION

OSTARA COMPANY LTD.

HALTON REGION

GE WATER AND PROCESS TECHNOLOGIES CO. LTD.

GHD (FORMERLY CONESTOGA ROVERS & ASSOCIATES)

#### REFERENCES

A NEWSLETTER IS AVAILABLE. For more information please contact Holly Gray at [hgray@uwaterloo.ca](mailto:hgray@uwaterloo.ca).

<sup>1</sup> MCCARTY, P.L., BAE, J., KIM, J. 2011 Domestic wastewater treatment as a net energy producer – can this be achieved? *Environ. Sci. Technol.* 45, 7100–7105.

<sup>2</sup> DENG, Q., DHAR, B.R., ELBESHISHY, E., LEE, H.S. 2014 Ammonium nitrogen removal from the permeates of anaerobic membrane bioreactors: economic regeneration of exhausted zeolite. *Environ. Technol.* 35, 2008-2017.

GRAY, H., PARKER, W., AND SMITH, D. S. (2015) State of Knowledge of the use of sorption technologies for nutrient recovery from municipal wastewaters, vol. NUTR1R06x. WERF, 80 p.

BRITTON, A. KOCH, F.A., MAVINIC, D.S., ADNAN, A. OLDHAM, W.K. AND UDALA, B., (2005) Pilot-scale struvite recovery from anaerobic digester supernatant at an enhanced biological phosphorous removal wastewater treatment plant. *J. of Environ. Eng. and Sci.*, 4:265-277.

RAHMANI, A.R.; MAHVI, A.H.; MESDAGHINIA A.R.; NASSERI, S. 2004. Investigation of ammonia removal from polluted waters by Clinoptilolite zeolite. *International Journal of Environmental Science and Technology* 1, 125-133.