Evaluation of Actiflo[®] Carb Process for the Combined Removal of Trace Organic Compounds and Phosphorous during Wastewater Tertiary Treatment

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ABSTRACT

In parallel with growing concerns, the concentration of trace organic compounds (TOrCs) has increased in wastewater streams as more people rely on these products for everyday uses. In addition, as nutrient total maximum daily loads continue to be developed for receiving waters, many wastewater treatment plants are facing more stringent limits, especially for phosphorus removal. The objective of this study was therefore to evaluate the performance of sand ballasted flocculation in combination with powdered activated carbon (PAC) for the removal of both a series of TOrCs and phosphorus. A pilot unit of Actiflo[®] Carb was installed at the South Shore Water Reclamation Facility owned by Milwaukee Metropolitan Sewerage District and managed by Veolia Water North America. This study received financial support from Water Environment Research Federation and the Milwaukee Metropolitan Sewerage District.

KEYWORDS: Trace Organic Compounds, phosphorus, Actiflo[®] Carb, wastewater tertiary treatment.

INTRODUCTION

General Context

Because of concerns related to public and aquatic health, there is increasing interest in evaluating occurrence and removal of TOrCs during wastewater treatment and water reclamation. Milwaukee Metropolitan Sewerage District (MMSD) and Veolia Water Milwaukee (VWM) were also interested in such questions and partnered with University of Wisconsin-Milwaukee (UW-M) and Dr. Rebecca Klaper in 2009-2010 to assess the occurrence of a large variety of TOrCs at successive stages of the wastewater treatment and in the environment (Lake Michigan for instance), with samples collected at different times of the year (not published yet). From this assessment study, it appeared that the average final removal of all compounds across all treatment dates was 56%, with a wide variation in the removal rates across various compounds.

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The literature demonstrates that the majority of TOrCs removal is completed through the secondary treatment process (activated sludge), and this study agreed with these findings for the majority of compounds with high removal efficiencies.

At the same time, the removal of phosphorus to very low levels in wastewater treatment is a growing concern, in Wisconsin where the State regulatory agency has been considering lowering current discharge limits, and in many other States across the US as well. Indeed, phosphorus is an important parameter to be looked at since this is an essential nutrient for the plants and animals that make up the aquatic food web. Since this is the nutrient in short supply in most fresh waters, even a modest increase in phosphorus can set off a whole chain of undesirable events in a stream including accelerated plant growth, algae blooms, and low dissolved oxygen levels resulting in the death of certain fish, invertebrates, and other aquatic animals.

MMSD and VWM then engaged in discussions about testing a process that would allow the removal of various TOrCs and Actiflo[®] Carb was proposed. This technology relies on the use of powdered activated carbon (PAC) which is recirculated in the process. PAC is known for its ability to remove, with proven efficiency (Vieno et al., 2007; Stackelberg et al., 2007; Soliman et al., 2007), pesticides, taste-and-odor causing compounds, natural organic matter and many types of trace organic compounds. With the use of coagulant (metallic salts) in Actiflo[®] Carb (or Actiflo[®]), this process has the ability to perform high removal of phosphorus.

The concentration of Trace Organic Compounds (TOrCs) has increased in the wastewater stream as more people rely on these products for everyday uses. A better understanding of the removal of TOrCs in the wastewater treatment process is sought in many areas worldwide to reduce discharge into the environment and protect human health. Many TOrCs may have poor removal in traditional primary and secondary wastewater treatment processes and information is still lacking on the fate of these compounds in the environment. Numerous systems have been used to remove TOrCs from drinking water or wastewater treatment facilities, but the results vary greatly.

In Milwaukee, a series of compounds appears to be still present in significant enough concentrations in the final effluent of the wastewater treatment facility to warrant further evaluation to determine the potential for some impacts on the environment and wildlife. Since discharge of treated wastewater effluent must protect beneficial uses of receiving streams, including fishing, swimming, recreation, and municipal drinking water supply, minimizing the discharge of TOrCs is desirable.

Regarding TOrCs removal in wastewater treatment, findings from previous studies have demonstrated that sorption onto suspended solids, aerobic and anaerobic biotransformation, chemical attenuation via processes such as hydrolysis, and volatilization are the primary removal mechanisms for TOrC during conventional wastewater treatment (Clara et al., 2005; Stevens-Garmon et al., 2011). Aqueous solubility and hydrophobicity determine whether and to which extent compounds are physically removed. Physicochemical properties will influence whether a TOrC will remain in the aqueous phase (like many of the acidic, neutral, and basic hydrophilic pharmaceuticals) or interact with solid particles (such as estrogens or certain antibiotics, which

have a higher potential to be sorbed to sewage sludge). Sorption and volatilization are physical processes and their relevance for specific contaminants can be predicted using physicochemical property information, like the octanol-water partition coefficient (Kow) (Rogers, 1996). Structural properties of TOrC will also determine the likelihood for biotransformation of the parent compound. For degradable compounds, several operational factors such as sludge retention time (SRT) (Oppenheimer et al., 2007) seem to be correlated with removal, resulting in lower effluent TOrC concentrations for longer SRTs.

Different approaches may be chosen when dealing with phosphorus removal in wastewater treatment and are for the most driven by the regulatory limits for phosphorus discharge. Among these approaches, the following can be listed:

- Physical processes, filtration for particulate phosphorus or membrane technologies;
- Chemical processes, like precipitation or physical-chemical adsorption;
- Biological processes, like assimilation or enhanced biological phosphorus removal (EBPR)

The greatest interest and most recent progress has been made in EBPR, which has the potential to remove P down to very low levels at relatively lower costs. Membrane technologies are also receiving increased attention, although their use for P removal has been more limited to date.

About the physical treatment options, by considering that 2-3% of organic solids is phosphorus, an effluent total suspended solids (TSS) of 20 mg/L may then be equivalent to 0.4-0.6 mg/L of effluent phosphorus (Strom, 2006b). In plants with EBPR the P content in residuals is even higher. Thus sand filtration or other method of TSS removal (e.g., membrane, chemical precipitation) is likely necessary for plants with low effluent TP permits (Reardon, 2006).

Membrane technologies have been of growing interest for wastewater treatment in general, and most recently, for P removal in particular. In addition to particulate P, membranes also can remove dissolved P. Membrane bioreactors (MBRs, which incorporate membrane technology in a suspended growth secondary treatment process), tertiary membrane filtration (after secondary treatment), and reverse osmosis (RO) systems have all been used in full-scale plants with good results.

In regards to chemical treatment, chemical precipitation has long been used for P removal. The chemicals most often employed are compounds of calcium, aluminum, and iron (Tchobanoglous et al., 2003). Chemical addition points include prior to primary settling, during secondary treatment, or as part of a tertiary treatment process (Neethling and Gu, 2006). It is generally agreed (e.g., Hermanowicz, 2006), however, that the process is more complex than predicted by laboratory pure chemical experiments, and that formation of and sorption to carbonates or hydroxides are important factors. In fact, full-scale systems may perform better than the 0.05 mg/L limit predicted. Takács (2006) suggests the limit is probably 0.005-0.04 mg/L.

Chemical phosphorus removal is achieved by adding chemicals to the wastewater at a wellmixed location, followed by flocculation and solids removal. The commonly used chemicals are aluminum and iron based salts. Aluminum is dosed in the form of poly aluminum chloride. Iron is added as ferric or ferrous iron salt (chloride), but in some cases "pickle liquor" (from industrial iron works) that contains primarily ferric chloride, can be used.

Finally, when it comes to biological phosphorus removal, this treatment aspect from wastewater has long been achieved through biological assimilation – incorporation of the P as an essential element in biomass, particularly through growth of photosynthetic organisms (plants, algae, and some bacteria, such as cyanobacteria). Traditionally, this was achieved through treatment ponds containing planktonic or attached algae, rooted plants, or even floating plants (e.g., water hyacinths, duckweed).

Strong interest has been seen in enhanced biological phosphorus removal (EBPR). This is because of its potential to achieve low effluent P levels at modest cost and with minimal additional sludge production. Neethling et al. (2005) recently showed the performance of EBPR in full-scale plants for significant time periods, but Greenburg et al. (1955) and then Levin and Shapiro (1965) were initially the ones who demonstrated the benefits of this process at a large scale. To summarize (Strom, 2006a and 2006b), phosphate accumulating organisms (PAOs), that are able to develop under anaerobic or aerobic conditions, do store polyphosphate as an energy reserve in intracellular granules under the former conditions and release orthophosphate under anaerobic conditions, in the presence of fermentation products.

High level of performance can be achieved through chemical phosphorus removal; with the choice of Actiflo[®] technology in the case of this project, this is a particular arrangement of high rate ballasted flocculation that is considered. Actiflo[®] relies on the addition of a metal salt to achieve its performance and has already demonstrated its performance in producing very low phosphorus effluent (O'Hare and Perry, 2010).

Objectives

Based on these considerations, this project was assigned a dual objective, while using an Actiflo[®] Carb pilot unit trailer:

- Evaluate the removal of a series of Trace Organic Compounds (TOrCs) from the wastewater effluent produced by the South Shore Water Reclamation Facility, part of the MMSD's sewage system – More details are given in the Part II about the selection of compounds;
- Evaluate the removal of phosphorus by the Actiflo[®] Carb while removing TOrCs, and perform additional testing using the regular version of Actiflo[®] (coagulant use only). The phosphorus concentration considered as a target to achieve has been 0.05 mg/L.

METHODOLOGY

South Shore Water Reclamation Facility and location of the pilot unit trailer

The South Shore Water Reclamation Facility (SSWRF) is a 1.14 Mm³/day (in capacity) wastewater treatment plant which is located approximately 13 miles south of downtown Milwaukee. It is sitting on the shore of Lake Michigan (see Figure 1 for geographical location). The SSWRF is part of the MMSD facilities, which also include another wastewater treatment facility, the Jones Island Water Reclamation Facility, located close to downtown Milwaukee. These two facilities together have the ability to treat wastewaters coming from the entire 1,036 km² Milwaukee Metropolitan Sewerage District service area, which represents a population of 1.2 million inhabitants. The Actiflo[®] Carb pilot unit trailer was set up at the SSWRF (Oak Creek – Wisc.), and more specifically by the final disinfection basins (Figure 2) in order to have access to secondary effluent (after activated sludge treatment).



Figure 1. Location of the South Shore Water Reclamation Facility



Figure 2. Aerial view of the pilot unit location within SSWRF's grounds



Figure 3. View of the pilot unit trailer located by the secondary effluent channel

Description of the process: Actiflo[®] and Actiflo[®] Carb

Actiflo[®] is a compact (small area footprint) process that operates with microsand (ActisandTM) that acts as a seed for floc formation. ActisandTM provides surface area that enhances flocculation and also works as a ballast or weight to facilitate rapid settlement. Actiflo[®] is applicable to surface water clarification, industrial process water production, wastewater treatment, or storm flow water settlement.

This process is commercialized by Krüger Inc., located in Cary, North Carolina.

The process itself successively consists in (see Figure 4):

- One coagulation tank where the coagulant (mostly a metallic salt) is added to generate suspended particles destabilization;
- One flocculation tank where, via a polymer addition, the destabilized particles agglomerate to form flocs that additionally are ballasted with microsand;
- And one sedimentation tank (with lamella plate settlers), at the bottom of which the sludge is pumped, and at the top of which the clarified water overflows;
- The sludge (flocs and microsand) is then recirculated through a hydrocyclone system, where the microsand particles are separated from the actual sludge and returned to the flocculation stage.



Figure 4. General view of the Actiflo® process

The Actiflo[®] Carb process is simply a derivative from the Actiflo[®] process that includes an additional powdered activated carbon contact tank prior to the regular stages of the process. The Figure 5 presents an overview of the Actiflo[®] Carb process.

The powdered activated carbon (PAC) is composed of carbon particles that have been activated by a specific process, giving it a dramatically high surface area available per gram of material, allowing the removal of an important concentration of undesirable compounds by utilizing a minimal dose of PAC. Usually, the PAC is simply injected in the raw water to remove pesticides or taste and odor causing compounds for instance, but this is performed with a short contact time and the adsorption capacity of the carbon is therefore not fully used in this case. By combining the use of PAC and the Actiflo[®], it becomes possible to separate and recirculate the particles of activated carbon, which maximizes the full use of the adsorption capacity.



Figure 5. General view of the Actiflo[®] Carb process

The Figure 6 presents a panoramic view of the inside of the pilot trailer, and specifically of the process section. The way the trailer is set up allows for sampling at any step of the treatment and visually control the correct operation of the process.



Figure 6. Inside view of the pilot unit trailer (from the carbon contact tank on the left to the weir section on the far right end)

Testing plan

Initial batch tests have been conducted in order to determine the best powdered activated carbon for the purpose of removing the series of selected TOrCs:

- From the literature, the coconut-based activated carbons appear to be quite efficient on particular specific pollutants, provided that there are no competitive effects from the matrix as the presence of organic matter for instance. In this case, the choice of coconut should have then probably been discarded because of potential matrix interferences but this would remain an aspect to further investigate;
- Wood-based powdered activated carbons have demonstrated their efficiency, thanks to a large porosity distribution (and this type of carbon remains the reference while used with this treatment process);
- Coal-based activated carbons are known to show slightly higher efficiencies in a lot of cases, but their price is also a major factor to take into account, and they are not considered environmental-friendly because of the nature of the base.

To ensure having preliminary references regarding the performance of the activated carbon, coconut- and wood-based materials were tested through jar-testing, based on the following approach:

- The real wastewater treatment plant (South Shore Water Reclamation Facility) effluent was used, spiked with the predefined shortlist of TOrCs to be used during the pilot-scale tests;
- Two different dosages (10 and 20 mg/L) of powdered activated carbon were evaluated as well, along with two different contact times (30 and 60 minutes).

Following this step, the PAC evaluated would be used during the pilot-scale tests at the same two different PAC renewal dosages: 10 and 20 mg/L. Going above this level of dosage is allowed but would induce operating expenditures difficult to support on an industrial-scale basis.

Once the type of activated carbon to be used was validated, two pilot testing phases were conducted, the first in April 2011 and the second from mid-July to mid-August 2011. The same schedules were followed for each of these periods, while having two separate phases allowed to account for the impact of seasonality.

Each testing period lasted four weeks:

- As a matter of preparation and optimization, the first week has been dedicated to connecting the pilot unit hydraulically and electrically;
- Two weeks were dedicated to the operation of Actiflo[®] Carb;
- One week was dedicated to the operation of Actiflo[®].

Regarding sampling on the pilot unit, the Figure 7 presents the locations where phosphorus and TOrCs samples were taken.



Figure 7. General view of the Actiflo[®] Carb process, with sampling locations (1- Sample location for influent TOrCs and phosphorus, 2- Sample location for effluent TOrCs and phosphorus)

Selection of Trace Organic Compounds

Following previous research performed by Dr. Rebecca Klaper (University of Wisconsin-Milwaukee; Great Lakes WATER Institute) on the occurrence of TOrCs within the wastewater treatment line, the Table 1 presents the compounds that have been selected for monitoring regarding removal by Actiflo[®] Carb.

Compound	Туре	Typical concentration in SSWRF effluent (ng/L)	Target concentration in Actiflo [®] Carb influent (ng/L)
Carbamazepine	Anti-epileptic	200	300
Fluoxetine	Anti-depressant	100	300
Trimethoprim	Antibiotic	100	300
Sulfamethoxazole	Antibiotic	150	300
Ofloxacin	Antibiotic	150	300
Diltiazem	Anti- hypertension	100	300
Diphenhydramine	Anti-histaminic	100	300
Triclosan	Biocide	100	300
Naproxen	Anti- inflammatory	300	500
Caffeine	Tracer	1,500	2,000

Table 1. Listing of the selected trace organic compounds and their target concentrations

The real effluent coming from the SSWRF outlet prior to disinfection would be used (two days per week of Actiflo[®] Carb testing), and to simulate peak concentrations in the effluent, spiking additions of the selected compounds would be performed using standard solutions (two days per week of Actiflo[®] Carb testing). Naturally occurring concentrations of trace organic compounds in wastewater effluents may vary significantly, but it was considered important to spike the wastewater secondary effluent with significant doses of compounds to challenge the capacity of the process for the removal of these species.

In terms of sampling protocol, it was chosen to take composite samples, e.g. one sample of influent and one sample of effluent per day of TOrCs removal testing: each sample was composed of 5 200 mL fractions (total of 1 liter) taken at 1-hour intervals, which was representative considering the quick process cycle of Actiflo[®] Carb (in addition, the influent and effluent sampling times were offset based on the hydraulic retention time of the process).

Analytical methods

The methods to quantify the series of TOrCs are based upon US EPA Method 1694 protocols (modified) and consist in the following successive steps:

- 1-liter liquid samples were filtered through Whatman GF-A glass fiber filter media to retain particulate material;
- Samples were stored at -20°C;
- The filtrate was pH adjusted to 2 with concentrated sulfuric acid and 0.5 g of EDTA was added to chelate minerals for acid analytes (or pH adjusted to 10 with concentrated ammonium hydroxide for basic extraction analytes);

- Liquid samples were then spiked with a suite of mass labeled internal standard compounds and extracted with 20 mL, 1 g Waters Oasis HLB cartridges and eluted sequentially with 12 mL methanol, 6 mL methanol:acetone (50:50), and 6 mL MTBE:methanol (90:10) for acid analytes (or 6 mL of methanol followed by 9 mL methanol with 2% formic acid for basic analytes);
- The elution solvents were concentrated under nitrogen to approximately 0.2 mL and quantitatively transferred to 1.0 mL of final volume with methanol pending analysis;
- Solids Particulates on glass fiber filters or 1 g aliquots of other solids, such as soils and biosolids, were placed in 50mL polypropylene centrifuge tubes with pH 2 phosphate buffer: acetonitrile, spiked with a suite of mass labeled internal standard compounds, and extracted three times by sonication;
- The pooled acetonitrile was removed from the extract using a rotary evaporator and the aqueous extract was brought to 200 mL volume with 18 M Ω /cm water before further processing by the liquids method described above;
- 15 μL of extract was injected onto a Phenomenex Synergi MAX-RP 250x4.6 mm, 4 mm column and separated by a binary gradient employing an Agilent 1100 HPLC system. Detection was achieved with an Applied Biosystems/MDS SCIEX API 4000 MS/MS system operating with Turbo Ion Spray ionization and multiple-reaction monitoring (MRM) detection.

Monitoring phosphorus is challenging because it involves measuring very low concentrations down to 0.01 mg/L or even lower. While there are many tests for phosphorus, three of them were utilized for the purpose of the study:

- The *total orthophosphate* (Or-P) test is largely a measure of orthophosphate. Because the sample is not filtered, the procedure measures both dissolved and suspended orthophosphate. The EPA-approved method for measuring total orthophosphate is known as the ascorbic acid method;
- The *total phosphorus* (TP) test measures all the forms of phosphorus in the sample (orthophosphate, condensed phosphate, and organic phosphate). This is accomplished by first "digesting" (heating and acidifying) the sample to convert all the other forms to orthophosphate;
- The *dissolved phosphorus* (dP) test measures that fraction of the total phosphorus which is in solution in the water (as opposed to being attached to suspended particles). It is determined by first filtering the sample, then analyzing the filtered sample for total phosphorus.

TP and dP analysis were performed at the MMSD laboratory facility (the dP samples were filtered on-site by using 0.45 μ m syringe filters): the samples were analyzed using EPA Method 365.1, "Phosphorus by semi-automated Colorimetry". The samples were digested with sulfuric acid which converts the polyphosphates and some of the organic phosphorus compounds to ortho-phosphate. Ammonium molybdate and antimony potassium tartrate are then reacting with these compounds to form an antimony phospho-molybdate complex. This complex is reduced with ascorbic acid to a blue complex. The intensity of the latter is measured at 880 nm. On the other hand, Or-P samples have been performed directly on-site using equipment provided with the pilot unit trailer. These analyses were performed by using a Hach Pocket Colorimeter II, which relied on the methodology (Hach, 1992) of the reaction with ascorbic acid (a prepackaged powder reagent, consisting of sulfuric acid, potassium antimonyl tartrate, ammonium molybdate, and ascorbic acid (or comparable compounds), is added to the water sample. This colors the sample in blue in direct proportion to the amount of orthophosphate in the sample and absorbance is then measured at 880 nanometers.

The performance monitoring and potential process adjustments of Actiflo[®] Carb process were made possible through monitoring classical water quality parameters:

- pH and turbidity have been monitored thanks to Hach[®] equipment on-line devices set up on Actiflo[®] Carb piping;
- Total suspended solids (TSS) and alkalinity have been analyzed on a more point basis, in order to have information about the wastewater stream.

RESULTS AND DISCUSSION

Trace organic compounds removal (batch tests only)

The initial results from batch tests with two different PACs (coconut and wood based) pointed out that the wood-based one was the most efficient in removing the series of selected compounds, likely due to its diversity in porous distribution. This powdered activated carbon was hence chosen for the pilot testing.

The jar-tests performed with the 10 selected compounds to compare the two activated carbons showed that removal efficiency was variable depending on the molecules: some of them (fluoxitine, ofloxacin...) were better removed by wood-based PAC while others (sulfamethoxazole) were better eliminated by coconut-based PAC; but in general, the average efficiency was almost equivalent for both the activated carbons, as it appears on the Figure 8. The best removed trace organic compound was triclosan.



Figure 8. Average removal of trace organic compounds obtained during preliminary batch jar-testing

It was decided to proceed with the wood-based activated carbon because other projects in Europe also use this type of activated carbon and could therefore be used as references.

Trace organic compounds removal (using Actiflo[®] Carb)

For each testing period, the influence of several process parameters has been considered. The range of operational conditions that were tested is presented in the Table 2.

Operational parameters	Values	Units
Influent flow rate	17.1 – 21.6	m ³ /h
System HRT	27 – 34	min
Rise rate	34 - 41	m/h
Recirculation rate	0.7 to 1.0	m ³ /h
Residuals concentration	8 to 11	g/L
PAC type	Wood-based, Picahydro AFP23	-
PAC dosage	10 - 20	mg/L
PAC concentration	~ 1.5	g/L
Coagulant type	Ferric chloride	-
Coagulant dosage (as Fe)	7 to 12	mg/L
Polymer dosage	1.5 to 3.2	mg/L
Microsand effective size	82	μm
Microsand concentration	14 to 16	g/L

Table 2.	Operational	conditions	of Actifle	o® Carb
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From a general perspective:

- It immediately appears that the removal rates obtained by Actiflo[®] Carb are much higher than the ones obtained during batch tests. It relies on the fact that within the Actiflo tanks, the activated carbon is recirculated and therefore used at a higher capacity than in the case of batch tests where it is simply wasted too early;
- Higher removals were obviously obtained by using a higher PAC dose. However, a carbon dosage of 10 mg/L still enabled to obtain 68% of average removal across all TOrCs (83% in the case of 20 mg/L dosage). With the 20 mg/L PAC dosage, 8 compounds out of 10 were removed above 75%;
- The rise rate did not have any significant influence on the performance of the process;
- Spiking was used on the influent coming to the pilot unit, to ensure that significant levels of concentrations were tested. The process showed very good capability in maintaining removal performance in removing TOrCs from influent concentrations much higher than the observed annual averages;
- Overall, regarding average removal, the order of performance for all 10 compounds is the following: Diltiazem > Trimethoprim > Triclosan > Diphenhydramine > Carbamazepine > Ofloxacin > Sulfamethoxazole > Fluoxetine > Caffeine > Naproxen.

The average TOrCs removal rate across all compounds, while taking into accounts all treatment conditions, reached 75%. In more details, the Table 3 presents the listing of removal percentages for the performance of Actiflo[®] Carb versus each one of the selected molecules, while the Figure 9 presents the same results via a bar-type graphic.

With the Actiflo[®] Carb process, it is more than dramatic to ensure the minimal carryover of activated carbon to the treated water effluent. Once the targeted pollutants, the trace organic compounds in this case, have been in contact with the powdered activated carbon during the required contact time of the process, the PAC needs to be properly separated to avoid seeing it go into the treated effluent: indeed, the captured molecules may still be able to desorb from the PAC particles once in contact with a more dilute aqueous environment. That's why polymer is a key component in operating the Actiflo[®] Carb since it properly retains the particles of activated carbon.

Overall, the removal rates presented here have been calculated for each PAC dosage across all other treatment conditions, especially by merging results from regular secondary effluent and spiked secondary effluent. Given this clarification, it means that a removal rate of 50% is already very interesting and it shows that using a dosage of carbon of 10 mg/L or so may still fulfill the objectives in terms of significantly removing trace organic compounds from the wastewater effluent. But since this quality parameter is still unregulated, it is not possible to discuss performance achievement in regards to reaching a given particular concentration.

Mologulo	MDL - MQL	PAC dosage	Average
Molecule	(ng/L)	(mg/L)	removal (%)
Coffeine	21 02	10	44 %
Callellie	5.1 - 9.5	20	74 %
Carbamazanina	27 82	10	68 %
Carbanazepine	2.7-0.2	20	88 %
Diltiozom	25 104	10	89 %
Diffiazem	5.5 - 10.4	20	95 %
Dinhanhadaaniaa	2 (10.0	10	81 %
Dipnennydramine	3.0 - 10.9	20	92 %
	2.5 10.5	10	52 %
Fluoxitine	3.5 - 10.5	20	78 %
Normour	10.20	10	42 %
Naproxen	1.0 - 2.9	20	67 %
Oflowerin	20 117	10	69 %
Onoxacin	5.9 - 11.7	20	75 %
Sulfamathayazala	4 1 12 4	10	54 %
Sunametnoxazoie	4.1 - 12.4	20	75 %
Trialagen	05 16	10	90 %
Theosan	0.3 - 1.0	20	88 %
Tains other a size	2.4 10.1	10	87 %
Irimetnoprim	3.4 - 10.1	20	97 %

Table 3. Removal rates per molecule depending on the PAC dosage



Figure 9. Removal rates per molecule depending on the PAC dosage

It is nevertheless reasonable to point out that the removal performance would still be the same if the influent to be treated was containing a trace organic compounds average concentration of either 1,000 ng/L or 100 ng/L as the extent of performance in adsorbing such compounds is mainly defined by physical chemical characteristics, while these concentrations seen do not represent levels of saturation on the activated carbon.

Each molecule's removal is strongly impacted by its own physical-chemical characteristics and the octanol-water partition coefficient (Kow) may help understanding the extent of removal that is observed. For this study it appears that the removal performance of many of the selected molecules is not correlated with the Kow. However, it still can explain what is seen for some molecules, like the triclosan, which is very well removed and presents a log(Kow) of 4.76, the highest of the 10 molecules considered in this study.

Phosphorus removal

Regarding the conventional process at the plant, phosphorus is removed via addition of ferric chloride or pickle liquor. The current regulatory limit for the SSWRF is 1.0 mgP/L (reported on a monthly rolling average). During the time Actiflo[®] Carb was being tested, the SSWRF received phosphorus concentrations ranging from 0.76 to 7.50 mgP/L (average was 3.75 mgP/L), achieving final effluent P levels from 0.18 to 0.94 mgP/L (average was 0.47 mgP/L). Considering the Fe dosages used (in terms of metal), the associated average molar ratio (Fe / P) was 1.57.

Overall, regarding phosphorus removal by Actiflo[®] Carb, concentrations between 0.02 and 0.05 mgP/L have been consistently achieved in the pilot unit effluent while using coagulant (ferric chloride) dosages from 7 to 12 mg/L (expressed in metal). This meant the achievement of molar ratio (Fe concentration over P removal) between 7 and 17 have been observed for the process performance, which is expected for such low P removal achievements (in comparison to the average ratio of 1.57 for the conventional treatment).



Figure 10. Total phosphorus concentrations in pilot influent and effluent, vs. Fe / TP molar ratio, for both testing periods with Actiflo[®] Carb

The Figure 10 presents the results obtained with Actiflo[®] Carb for Total Phosphorus removal for both testing periods. Some optimization was needed for the process, especially polymer dosage: indeed, a polymer dose close to 3 mg/L was required to avoid carryover and therefore having flocs or particles, including phosphorus, going to the pilot effluent. Once this process aspect was resolved, a very low and consistent total phosphorus concentration was achieved in the effluent. Concentrations in the influent were significantly variable, which explains the large range seen in the values of Fe / TP molar ratio.

The regular Actiflo[®] process was tested for phosphorus removal as well. Similarly to the figure 10, the Figure 11 presents the results obtained with Actiflo[®] for total phosphorus (TP) removal for both testing periods. Again, a very consistent removal of TP was achieved; Actiflo[®] Carb appears to be very versatile in being able to target phosphorus removal while at the same time removing TOrCs. Indeed, the usual approach would rely on Actiflo[®] (no carbon) to perform P removal, but with the growing concern about the presence and effect of TOrCs on humans and the environment, the Actiflo[®] Carb may be an effective solution in meeting both removal targets (TP and TOrCs).



Figure 11. Total phosphorus concentrations in pilot influent and effluent, vs. Fe / TP molar ratio, for both testing periods with $Actiflo^{\$}$

To discuss the potential operating cost of an Actiflo[®] Carb process, we may consider:

- 38,000 m³/day flow to be treated, operating 24 hours a day (60,000 m³/day capacity installed);
- A polymer dosage of 3.0 mg/L (polymer is \$4,000/ton);
- A sand consumption (loss) of 2 g per m^3 of treated wastewater (sand is \$200/ton);
- A coagulant dosage of 10 mg/L (as FeCl3) (coagulant is \$340/ton);
- A fresh dosage of 15 mg/L (PAC is \$2200/ton);
- Equipments installed with 100 horsepower (and power cost of \$ 0.08/KWhr).

Based on these assumptions, the total estimated daily operating cost would be \$ 2,164, which is equivalent to an operating cost of \$57 per 1,000 m³ of treated wastewater.

What is really driving the operating costs are both the powdered activated carbon and the polymer, knowing that PAC dosage is easily adjusted depending on the need for treatment – it was presented in the section regarding TOrCs removal that a dosage of 10 mg/L was already showing good performance.

SUMMARY AND CONCLUSIONS

This project had two different objectives: evaluating the performance of Actiflo[®] Carb in removing a series of selected trace organic compounds (TOrCs), while simultaneously removing phosphorus from wastewater effluent. The pilot unit was set up two times (spring and summer time, 2011) for duration of four weeks in a row to perform extended testing of the process.

First, regarding TOrCs removal, the approach was to rely on the previous project led by Dr. Rebecca Klaper and to use the molecules that occurred in most significant levels at the end of the SSWRF wastewater treatment line. Ten TOrCs molecules were selected representing eight distinct classes of compounds in terms of therapeutic use. The average removal across all molecules and testing conditions reached 75%. Good removal was observed at the 10 mg/L PAC dosage with slightly better removal for most molecules at the 20 mg/L PAC dosage as would be expected. Overall, regarding average removal, the order of performance for all 10 compounds is the following: Diltiazem > Trimethoprim > Triclosan > Diphenhydramine > Carbamazepine > Ofloxacin > Sulfamethoxazole > Fluoxetine > Caffeine > Naproxen.

Secondly, once the process was optimized (sufficient polymer dosage), Actiflo[®] Carb was able to achieve very consistent and low phosphorus concentrations below 0.05 mgP/L in the effluent, with Fe / P molar ratios from 7 to 17, which are expected in such treatment conditions. The main beneficial results comes out from the capacity of Actiflo[®] Carb to be performing as well as Actiflo[®] in removing phosphorus from wastewater while also removing TOrCs at a high level of efficiency.

Finally, when considering a treatment unit presenting a capacity of $60,000 \text{ m}^3/\text{day}$ and treating a flow of $38,000 \text{ m}^3/\text{day}$, the operating cost could be \$57 per thousand cubic meters of treated wastewater, with the majority of the cost allocated to the activated carbon and the polymer.

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