Phosphorus adsorption on water treatment residual solids

Meaghan K. Gibbons, Md. Maruf Mortula and Graham A. Gagnon

ABSTRACT

The treatment and disposal of water treatment plant residual solids has become an increasingly important environmental priority for drinking water utilities. This study examines water treatment residual solids (WTRSs) from four North American water treatment plants to determine the role that coagulant types play in phosphate adsorption by the residual solids. In total, two alum residual solids (one solid from a plant that has a raw water with low alkalinity and one solid from a plant that has a raw water with high alkalinity), one lime residual solid and one ferric residual solid were used in batch adsorption experiments with deionized water at a pH of 6.2 ± 0.2 and secondary municipal wastewater effluent at a pH of 6.8. Langmuir isotherm modeling showed that ferric residuals had the highest adsorptive capacity for phosphate ($Q_{max} = 2,960$ mg/kg), followed by lime ($Q_{max} = 1,390$ mg/kg) and alum ($Q_{max} = 1,110$ mg/kg and 1,030 mg/kg) for adsorption experiments with P-spiked deionized water. Of the two alum residuals, the residual with a higher weight percent of metal oxides had a higher adsorptive capacity. The ferric residuals were less affected by competing species in the wastewater effluent, while the lime and alum residuals had a higher rate of phosphate removal from the deionized water compared to the wastewater effluent. Overall, ferric water treatment residuals were the best adsorbent for phosphate adsorption, followed by lime and alum residuals.

Key words | adsorption, alum sludge, Langmuir isotherm, phosphorus treatment, water treatment residual solids

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INTRODUCTION

Water treatment plant residuals are produced in the coagulation–flocculation stage of drinking water treatment, a process common among many surface water treatment plants. The common solutions for managing water treatment residuals are to direct the wet residuals to a wastewater treatment plant through a sewer connection, or to treat the wet residuals on-site to reduce the water content and subsequently direct the residual solids to a municipal landfill (Cornwell *et al.* 2000). In the latter case, transportation of the dewatered residuals to a landfill and landfill tipping fees can represent a significant cost to the utility (Walsh *et al.* 2008). The treatment and disposal of these residual solids has become an integral part in the

operation and management of water treatment facilities due to stringent local, state and federal regulations (Cornwell *et al.* 2000). Bourgeois *et al.* (2004) acknowledged that common residuals management options are not optimal solutions, and evaluated several alternative residuals management methods. As part of residual solids management, there has been a growing trend in research for possible reuse and recycle options, especially in water and wastewater treatment. In particular, alum residuals have shown to be a good adsorbent material for a variety of contaminants (Sujana *et al.* 1998; Zhao *et al.* 1998; Chu 1999, 2001; Huang & Chiswell 2000; Zhao & Bache 2002; Ippolito *et al.* 2003; Makris *et al.* 2006; Mortula & Gagnon 2007).

Galarneau & Gehr (1997) showed that adsorption is the main mechanism for phosphorus removal during coagulation with alum, and wet alum residuals had a sorption capacity for phosphorus in jar tests with municipal wastewater. Mortula *et al.* (2007) found that, out of three types of dried alum residuals (oven-dried, air-dried and freeze-dried), oven-dried residuals were the best at adsorbing phosphorus in batch adsorption studies and had the overall best fit to the Langmuir and Freundlich isotherm models. Mortula *et al.* (2007) also found that dried alum residuals were a better media for phosphorus adsorption than other waste materials, including blast furnace slag, cement kiln dust and bone char. Kim *et al.* (2003), Dayton *et al.* (2003), and Razali *et al.* (2007) showed that air-dried residuals were suitable for adsorbing phosphorus over a range of pH levels and phosphorus species. Phosphorus removal using air-dried residual solids was also investigated by Ippolito *et al.* (2003). The pH of the water treatment residuals used by Ippolito *et al.* (2003) was at 7.4 and the alum residuals contained significant amounts of calcium. Therefore, the phosphorus removal that was achieved was attributed to both phosphorus adsorption onto the residuals and also calcium phosphate precipitate, since greater phosphorus removal was achieved than had been previously reported by Galarneau & Gehr (1997).

Particle sizes have been shown to influence phosphate adsorption on WTRSs to varying degrees. Mortula (2006) found that an alum water treatment residual solid with a particle size of 250 μm yielded a higher adsorption density for phosphate adsorption at a pH of 7, compared to adsorption on WTR particles of 425 μm and 1.18 mm. Other phosphorus adsorption studies commonly used WTRSs with particle sizes of <1.25 mm to <2.00 mm (Dayton *et al.* 2003; Kim *et al.* 2003; Dayton & Basta 2005; Makris *et al.* 2005; Mortula *et al.* 2007) for adsorption on WTRSs. Additionally, Huang & Chiswell (2000) found similar phosphate removal when comparing WTRSs of a particle size of 2.8 mm and a particle size of 0.5–1.0 mm.

Phosphorus removal during land application using spent alum residuals (dried or wet) has been increasingly identified as a common residuals management option, both in the agricultural and soil science literature (Gallimore *et al.* 1999; Haustein *et al.* 2000; Elliot *et al.* 2002; Dayton *et al.* 2003). A major drawback to phosphorus removal during land application is the reduction of plant-available phosphorus in ecosystems, which has led to a reduction in plant productivity for some species (Kaggwa *et al.* 2001).

The objective of this study was to compare phosphorus adsorption onto water treatment residual solids from four surface water treatment plants, each treatment plant representing a different treatment process and different raw water quality. This study was unique in that it directly compared more than one residual type in batch adsorption experiments, and specifically compared phosphate adsorption on two alum-based residual solids to ferric- and lime-based residual solids. Phosphorus removal through adsorption on oven-dried water treatment residuals was evaluated for deionized water containing orthophosphate and a secondary municipal wastewater plant effluent.

MATERIALS AND METHODS

Water treatment residual solids

Handling and collection

Oven-dried water treatment residual solids (WTRSs) from water treatment plants were examined to determine the role that coagulant types and raw water matrix effects play in possible phosphorus adsorption by residuals. In total, two alum residual solids, one from a plant that has a raw water with low alkalinity and one from a plant that has a raw water with high alkalinity, one lime residual solid and one ferric residual solid were used in this experiment.

Residual solids were received at Dalhousie University (Halifax, Nova Scotia, Canada) as wet residuals, typically 10–30% solids. Solids were oven dried at 105°C for a period of 24 h in ceramic bowls and stored in a desiccator after cooling until use. All solids that were used in the experiment were dried within 30 d of collection to minimize the change from amorphous to crystalline structure (Duffy & vanLoon 1994), which ensured that the residuals had a maximum number of hydroxide sites available for adsorption. Before use in the experiments, the dried residual solids were gently crushed using a mortar and pestle, and separated using a series of sieves of 250 μm, 425 μm and 850 μm particle size. Two particle sizes were used in these experiments. One WTRS was very powdery and all of the particles were

$<250\,\mu$m. For the other WTRSs all of the particles that were trapped on the $425\,\mu$m sieve were used for the $425\,\mu$m particle size.

Oxide analysis of WTRSs was performed at the Minerals Engineering Center at Dalhousie University (Halifax, Nova Scotia, Canada). Dried residuals were fused with lithium metaborate and lithium tetraborate at 1,050°C and digested with nitric acid (Shapiro 1975). The resulting liquid was analyzed for oxide analysis using a flame atomic adsorption system (Varian, SpctraAA 55B).

Lake Major water treatment plant residuals

Lake Major Water Treatment Plant (LM-WTP) in Dartmouth, Nova Scotia, Canada uses alum as a coagulant. Lake Major is the source water for the plant, which has a low pH, low alkalinity and has little dissolved and particulate matter (Table 1). Lake Major has an alkalinity of less than 5 mg/L. The key treatment processes in this plant include alum coagulation, flocculation and sedimentation, followed by filtration and disinfection. LM-WTP uses lime for pH control and alum as a coagulant, and a major treatment

consideration is the removal of iron and manganese. Wet alum residuals are collected from the sedimentation tank and processed in a centrifuge to reduce the water content of the residuals. After centrifugation, the residuals are stored on site at the plant, where further drying occurs naturally due to freeze drying in the winter and air drying during the spring, summer and fall. The alum residuals used in this experiment were collected directly from the centrifuge. Water treatment residuals from LM-WTP were primarily composed of aluminum species (Table 2).

Mannheim water treatment plant residuals

Mannheim Water Treatment Plant (M-WTP) in Waterloo Region, Ontario, Canada uses alum as a coagulant. The raw water source for the M-WTP is the Grand River, which is characterized by a moderate to high alkalinity and water hardness, moderate dissolved solids, high pH, high turbidity and generally low metals concentrations (Table 1). The key treatment processes in this plant include alum coagulation, flocculation, sedimentation and filtration, followed by disinfection with chlorine, ozone and UV. Wet residuals

Table 1 | Raw water quality for LM-WTP, M-WTP and B-WTP treatment residuals

	LM-WTP[*]	M-WTP[†]	B-WTP[‡]	TB-WTP[§]
Plant influent source	Lake Major	Grand River	Assiniboine River	Hillsborough River
pH	5.4	8.18	8.08	n/a
Alkalinity (mg/L as $CaCO_3$)	<1.0	200	114	80
Hardness (mg/L as $CaCO_3$)	4.5	255	135	108
Colour (TCU)	9	20.5	<5.0	n/a
Total dissolved solids (mg/L)	22.5	370	570	169
TOC (mg/L)	2.4	5.8	6	16.4
Conductivity ($\mu\Omega^{-1}$/cm)	38	645	873	n/a
Turbidity (mg/L)	0.25	7.9–23.0	0.6	n/a
Total arsenic (μg/L)	<2	0.52	0.8	n/a
Total iron (mg/L)	0.035	0.039	<0.05	n/a
Total manganese (mg/L)	0.067	0.015	0.0013	n/a
Aluminum (mg/L)	0.185	0.019	0.05	n/a
Phosphorus (mg/L)	0.24	0.039	n/a	n/a

[*]Source: Halifax Regional Water Commission (2003).
[†]Source: Ontario Ministry of the Environment (2002).
[‡]Source: City of Brandon (2005).
[§]Source: Riess et al. (1999).
n/a = not available.

Table 2 │ Partial chemical analysis* of water treatment residual solids

	Weight percent (%)					
	Al_2O_3	CaO	MgO	Fe_2O_3	MnO	Total (%)
TB-WTP	1.27	6.66	0.39	31.27	0.11	39.70
M-WTP	35.34	3.68	0.61	1.38	0.07	41.08
LM-WTP	27.93	0.36	0.06	1.65	0.19	30.20
B-WTP	1.65	45.82	6.94	0.14	0.03	54.47

*Note: Method for dissolution adapted from Shapiro (1975).

are collected and squeezed using a filter press, creating a filter cake with a fairly low water content. The alum residuals used in this experiment were collected directly after the filter press. Water treatment residuals from M-WTP were primarily composed of aluminum species (Table 2).

Brandon water treatment plant residuals

The Brandon Water Treatment Plant (B-WTP) in Brandon, Manitoba, Canada uses alum as a coagulant and adds considerable amounts of lime during softening. The resulting residual solids contain more calcium than aluminum (Table 2). The raw water source for the B-WTP is the Assiniboine River. The Assiniboine River has a high pH and dissolved solids, moderate alkalinity and high metals concentrations (Table 1). The key treatment processes in this plant include alum coagulation, softening (lime and soda ash), flocculation, sedimentation and filtration, followed by disinfection with chlorine. Wet residuals are collected and squeezed using a filter press, creating a filter cake with a low water content. B-WTP generally ships pressed residuals to the landfill, but the lime residuals used in this experiment were collected directly after the filter press. Because of the considerable amount of lime in the Brandon residual solids, the residuals were powder-like once oven-dried and did not require crushing. Sieving of the Brandon residuals resulted in the majority of the particles passing through the 250 μm sieve, so a smaller particle size (<250 μm) was used for adsorption experiments on residual solids from B-WTP. While this particle size is not ideal from a practical standpoint (e.g. it may lead to clogging if used in a column) this particle size was all that was available for the B-WTP residual solids.

Tampa Bay water surface water treatment plant

Ferric water treatment plant residuals were obtained from the Tampa Bay Water Surface Water Treatment Plant (TB-WTP) in Brandon, Florida, USA. The primary raw water sources for the TB-WTP are the Hillsborough River, Alafia River and the Tampa Bypass Canal. The Hillsborough River has a moderate alkalinity, hardness and total dissolved solids (Table 1). The key treatment processes in this plant include coagulation with ferric sulfate, flocculation, sedimentation, disinfection with ozone, filtration and finally disinfection with chloramines before the water travels through the distribution system. Wet residuals are collected after sedimentation and backwashing. The wet residuals are dewatered, forming a residual with a low water content. Residual solids from the TB-WTP contained high amounts of iron and low amounts of aluminum (Table 2).

Challenge water

Two types of waters were used in the experiments discussed in this paper. A phosphate stock solution was created by adding 21.9 g potassium phosphate (KH_2PO_4; Fisher Chemical) to 500 mL of deionized (DI) water to create a stock solution containing 10 g/L P. The stock solution was stored in the refrigerator until use. Phosphate-spiked DI water was made by adding 0.25 mL of phosphate stock solution to 1 L of deionized water to create a phosphate concentration of 2.5 mg P/L. pH was adjusted to the appropriate level with 0.1 N hydrochloric acid or 0.1 N sodium hydroxide. Additionally, treated municipal wastewater effluent from Mill Cove Pollution Control Plant (MCPCP; Bedford, Nova Scotia, Canada) was used in the adsorption experiments. MCPCP provides secondary wastewater treatment with UV disinfection for municipal wastewater. The effluent used in the experiment was collected after UV treatment. The total phosphorus concentration in the wastewater effluent was approximately 4.2 mg P/L while the phosphate concentration in the wastewater effluent was approximately 3.95 mg P/L, meaning that 94% of the phosphorus in the wastewater effluent was phosphate. The pH level of the wastewater effluent, 6.8, was not adjusted during the experiment to model the simplest potential

treatment plant design, i.e. flow through a column to remove phosphorus, without pH adjustment.

Experimental approach and setup

A series of batch adsorption experiments were performed to evaluate the effect of water treatment residual type on phosphorus adsorption with water treatment residual solids. The first set of experiments was designed to evaluate phosphate adsorption on residual solids in the absence of potential competing species using phosphate-spiked DI water and the second set was designed to evaluate phosphate adsorption from municipal wastewater treatment plant effluent.

All batch adsorption tests were performed in 250 mL Erlenmeyer flasks (Pyrex) that had been washed with phosphate-free soap and triple-rinsed with DI water. Each experiment was conducted with at least one control containing 100 mL of water sample and no adsorbent. All other flasks contained 100 mL of wastewater sample and varying amounts of adsorbent material (0.05, 0.1, 0.5, 1 and 2 g). The pH of each flask was immediately taken after the addition of water to the flask. All experiments were performed at room temperature, approximately 22°C.

The first set of batch adsorption experiments were conducted with alum, ferric or lime WTRSs as adsorbents and using deionized water spiked with phosphate as a phosphate source. The pH level of these experiments was 6.2 ± 0.2, as previous experiments indicated that adsorption was similar between the alum and lime residual solids between a pH of 5.5 and 6.5. Additionally, results from previous studies suggest that phosphorus adsorption mechanisms with alum residual solids work best at lower pH values (Galarneau & Gehr 1997; Kim *et al.* 2003) and Shin *et al.* (2004) used a pH of 6.4 for phosphate adsorption experiments using an iron-based adsorbent.

The flasks were topped with a piece of aluminum foil to prevent debris from entering the flask, and the flasks were shielded from light for a period of 12 d, after which the phosphate concentration and pH levels were measured and recorded. The 12 d equilibrium period was chosen because the time to equilibrium in previous kinetic reaction experiments was determined to be approximately 7–9 days (Figure 1). Similarly, Dayton & Basta (2005) found
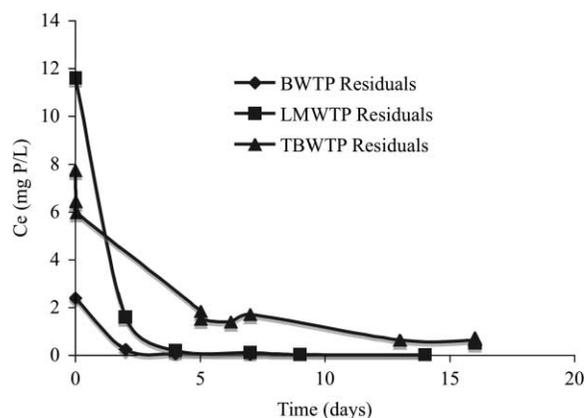

Figure 1 | Phosphorus concentration over time.

that most of the phosphorus was adsorbed within the first five days, with little change in equilibrium phosphate concentration between 12–19 d. The experimental procedure added an extra 3–5 d to account for variability in the time to equilibrium.

The second set of batch adsorption experiments was conducted with alum, ferric or lime WTRSs as adsorbents and using municipal wastewater effluent from MCPCP, containing $12\ mg\ PO_4^{3-}/L$ (4.2 mg P/L), as a phosphorus source. The pH of the wastewater effluent was not adjusted at the start of the experiment and was 6.8 ± 0.1. The flasks were topped with a piece of aluminum foil to prevent debris from entering the flask and shielded from light. The flasks were shaken on a shaker table (MaxQ2000, Barnstead International) at 200 rpm for a total of 51 h. The phosphate concentration, total phosphorus concentration and pH levels were measured and recorded after 51 h.

Analytical measurements

Analytical procedures outlined in *Standard Methods* (APHA/AWWA/WEF 1995) were followed. pH was measured using a pH probe (model 230A, Orion) that was calibrated daily before use. Phosphate results were measured using spectrophotometry (DR-4000, Hach Co., Coveland, CO) at a wavelength of 890 nm and ion chromatography (781, Metrohm-Peak LLC, Houston TX). Total phosphorus results were analyzed using spectrophotometry with potassium persulfate digestion for 30 min at 150°C (DR-4000, Hach Co., Coveland, CO) at a wavelength of 890 nm. All analyses

occurred within 24 h of sampling. All phosphate results reported in this paper are reported as phosphorus (P).

Adsorption isotherm calculations

The final and equilibrium concentrations for all batch experiments were fitted to the Langmuir adsorption isotherm equation to determine coefficients and isotherm curves for all experiments.

Langmuir equation

The Langmuir isotherm suggests that a single adsorption layer exists on the adsorbent media, which is a suitable assumption for gases and an acceptable assumption for liquids (Droste 1997). The Langmuir adsorption isotherm equation is expressed as

$$q = \frac{Q_{max}KC_e}{KC_e + 1} \tag{1}$$

where q is the adsorption density achieved in mg P/kg solid, C_e is the equilibrium concentration in mg P/L, and Q_{max} and K are unique constants for each adsorbent and adsorbate group. Q_{max} is the maximum adsorption density and K is related to the binding energy. It is common to fit the isotherm to batch adsorption experimental results using the linearized form of the Langmuir equation:

$$\frac{C_e}{q} = \frac{1}{KQ_{max}} + \frac{1}{Q_{max}} \cdot C_e \tag{2}$$

in the form $y = b + mx$, where a plot of $C_e(x)$ vs. C_e/q (y) gives the values for K and Q_{max}.

RESULTS AND DISCUSSION

Phosphate adsorption in deionized water

Phosphorus removal with all residual solids was generally high, reaching 99% removal. TB-WTP residual solids yielded an adsorption density of 1,500 mg P/kg solid when the adsorbent concentration was 4 g solid/L, which was more than three times higher than the density at 4 g/L for the other alum solids (420–440 mg P/kg) and lime solids (435 mg P/kg). Replicates of the TB-WTP experiments

yielded consistent results, with duplicate experiments within 6% of the average result.

The Langmuir isotherm model was used to describe phosphate adsorption on the alum, ferric and lime water treatment residuals. The linearized Langmuir model showed the best fit for phosphate adsorption on the alum, ferric and lime residuals from M-WTP, TB-WTP and B-WTP ($R^2 = 0.99$, 0.98 and 0.97, respectively; Table 3), and a good fit for phosphate adsorption on alum residuals from LM-WTP ($R^2 = 0.87$). Q_{max} was highest for the TB-WTP residuals at 2,960 mg P/kg solid (Table 3), followed by B-WTP (1,390 mg P/kg solid), M-WTP (1,110 mg P/kg solid) and LM-WTP (1,030 mg P/kg solid) residual solids. There was a difference in particle size between the B-WTP residuals and the M-WTP and LM-WTP residuals that may account for some of the difference in maximum adsorption density. However, given that the results for the two alum plants were very similar, it is likely that the residual type (e.g. calcium versus alum) also contributed to the higher adsorption density. Mortula *et al.* (2007) previously found a Q_{max} of 670 mg P/kg when using residuals from LM-WTP to adsorb phosphate under similar conditions. The Langmuir isotherm models showed a good fit to the experimental data for alum (Figure 2(a)), lime (Figure 3) and ferric (Figure 4) WTRSs. Specifically, the adsorption results were within a 95% level of confidence for the linearized Langmuir model.

Given the higher adsorption density, ferric residual solids appeared to be a stronger adsorbent than the alum residual solids. Comparing arsenate removal on ferric and alum coagulants, McNeill & Edwards (1997) found that

Table 3 | Langmuir isotherm* constants for phosphate-spiked DI water

	Residual types			
	LM-WTP	**M-WTP**	**B-WTP**	**TB-WTP**
Initial pH	6.0	6.04	6.0	6.4
Particle size (μm)	425	425	<250[†]	425
Initial C (mg P/L)	1.75	1.50	1.75	9.16
Q_{max} (mg P/kg solid)	1030	1110	1390	2960
k	3.98	143.2	18.2	0.91
Langmuir R^2	0.87	0.99	0.97	0.98

*Note: All experiments were performed at approximately 22°C.
[†]Smaller particles were used for the B-WTP adsorption experiments because the dried residuals were a fine powder.
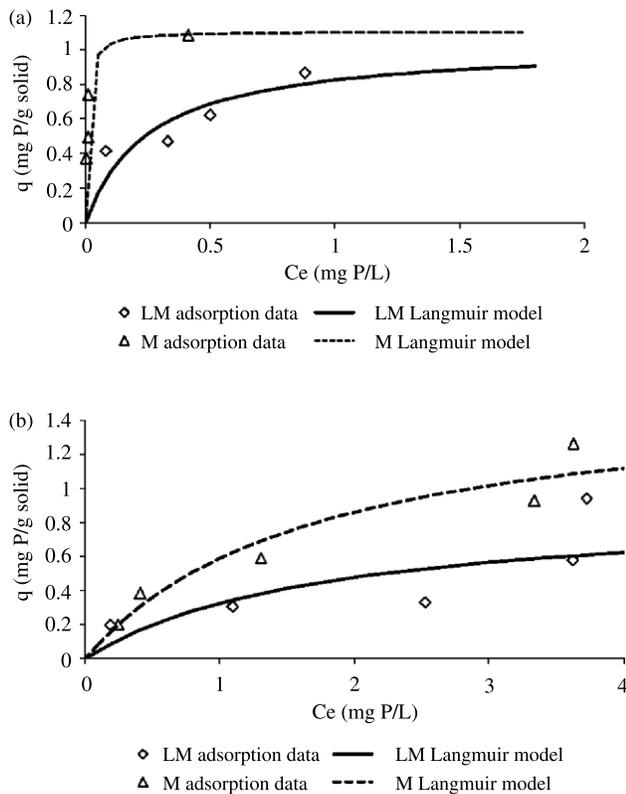
(a)

Figure 4 | Langmuir isotherms for ferric (TB-WTP) residual solids.

(b)

Figure 2 | (a) Langmuir isotherms for alum (LM-WTP and M-WTP) residual solids for P-spiked DI water as phosphate source (initial C = 1.5–1.75 mg P/L). (b) Langmuir isotherms for alum (LM-WTP and M-WTP) residual solids for municipal wastewater effluent as phosphate source (initial C = 4.2 mg P/L).

be more effective coagulants than alum for phosphate removal as well. Furthermore, ferric residual solids might be a more effective adsorbent for phosphate compared to alum residual solids. In a similar study, Genz *et al.* (2004) found that granular ferric hydroxide, an iron-based adsorbent, was a more effective adsorbent for phosphate than activated alumina, an aluminum-based adsorbent.

A comparison of recent adsorption studies of phosphate adsorption on alum WTRSs showed that similar phosphate loading rates corresponded to a similar Langmuir Q_{max} between residual types (Figure 5). Razali *et al.* (2007) summarized Langmuir Q_{max} from eight recent adsorption studies. Q_{max} ranged from 300 mg P/kg solid to over 25,000 mg P/kg solid. However, the initial phosphate concentration varied widely between these studies (14.6 mg/L P to over 1,000 mg/L P). The initial phosphate concentrations used in this study were also much lower than in previous studies. Consequently the Q_{max} found in this study appear significantly lower. Since the average P concentration in secondary municipal wastewater effluent is

ferric chloride was a more effective coagulant than alum, which Hering *et al.* (1997) attributed to incomplete precipitation of soluble aluminum hydroxide. Since the chemistry of arsenate and phosphate is similar, particularly with respect to adsorption by iron and aluminum hydroxides (Liu *et al.* 2001), ferric coagulants would likely
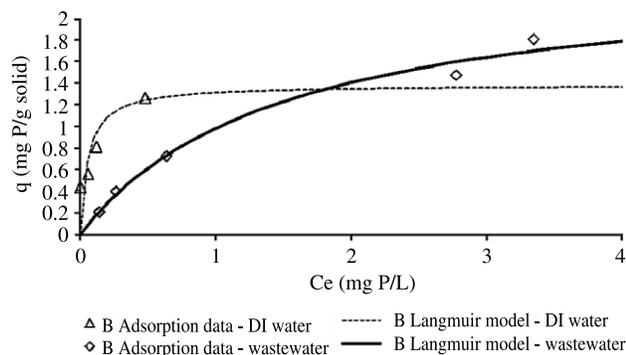

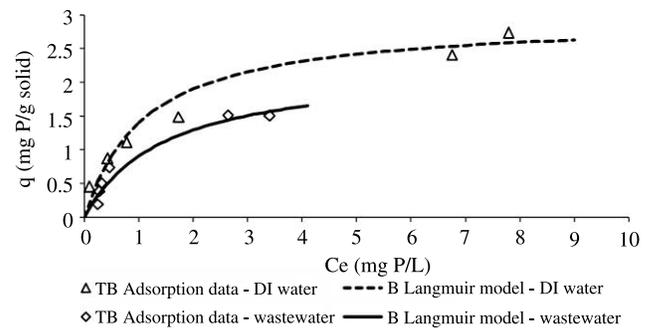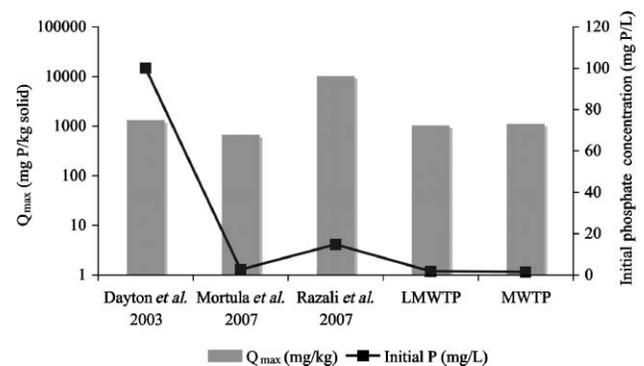**Figure 3** | Langmuir isotherms for lime (B-WTP) residual solids.

Figure 5 | Comparison of Q_{max} for phosphate adsorption on alum WTRSs.

between 2.5–3.0 mg/L (Environment Canada 2001), the initial P concentration used in this work is closer to a realistic concentration of phosphate found in wastewater effluent.

Municipal wastewater effluent

Phosphate adsorption from municipal wastewater effluent followed many of the same trends that were evident in the phosphate adsorption from phosphate-spiked DI water. All residuals achieved good levels of phosphate removal, ranging from 93.7–96.6% removal of total phosphorus. Since phosphate comprised about 95% of the phosphorus species in the wastewater, essentially all of the phosphate was removed during adsorption. Similar to the experiments with phosphate-spiked DI water, TB-WTP residual solids had the highest adsorption density at an adsorbent concentration of 5 g/L, indicating that higher rates of adsorption are achieved with less adsorbent when compared to the other residuals.

The Langmuir isotherm model was used to describe phosphate adsorption from municipal wastewater effluent on the alum, ferric and lime water treatment residuals. The linearized Langmuir model showed the best fit for phosphate adsorption on lime residuals from B-WTP ($R^2 = 0.97$; Table 4) and a good fit for phosphate adsorption on ferric residuals from TB-WTP and alum residuals from M-WTP (both $R^2 = 0.85$). The linearized Langmuir model showed a weaker fit for phosphate adsorption on the alum residuals from LM-WTP ($R^2 = 0.47$). Q_{max} was highest for the B-WTP residuals at 2470 mg P/kg solid (Table 3), followed by TB-WTP (2250 mg P/kg solid),

M-WTP (1590 mg P/kg solid) and LM-WTP (890 mg P/kg solid) residual solids. Mortula & Gagnon (2007) previously found a Q_{max} of 3,210 mg P/kg when using residuals from LM-WTP to adsorb phosphate from secondary municipal wastewater effluent (pre-activated sludge treatment). The Langmuir isotherm models and their fit to the experimental data for alum, lime and ferric WTRSs are presented in Figures 2(b), 3 and 4, respectively. The adsorption results were within a 95% level of confidence for the linearized Langmuir model.

Of the two alum residuals, M-WTP residual solids were a stronger adsorbent than LM-WTP residual solids (Figure 2(b)). For both the phosphate-spiked DI water and wastewater, the isotherm and Langmuir models for M-WTP residual solids achieved greater adsorption densities, with the LM-WTP model approximately 50% lower than the M-WTP isotherm model. Though both are alum residuals, LM-WTP residuals and M-WTP residuals differ in the total oxides present in the media, with M-WTP residuals composed of 41% (by weight) metal oxides and LM-WTP residuals composed of 30% (by weight) metal oxides (Table 2). Since the M-WTP residuals contain approximately 25% more total oxides than the LM-WTP residual solids, including 23% more aluminum oxide and 90% more calcium oxide, M-WTP residuals would be expected to adsorb more phosphate than LM-WTP residuals.

There was a difference in both the shape and general trend between the isotherms with phosphate-spiked DI water and the isotherms for the municipal wastewater effluent for the alum (Figure 2(a),(b)) and lime (Figure 3) residual solids, indicating that phosphate adsorption on these residuals was inhibited by competing species (i.e.

Table 4 | Langmuir isotherm* constants for Mill Cove treatment plant effluent (pH = 6.8; initial C = 4.2 mg P/L)

	Residual types			
	LM-WTP	**M-WTP**	**B-WTP**	**TB-WTP**
Particle size (μm)	425	425	<250[†]	425
Equilibrium C at 5 g/L adsorbent (mg P/L)	2.52	1.30	0.64	0.46
Q_{max} (mg P/kg solid)	890	1590	2470	2250
K	0.58	0.58	0.66	0.67
Langmuir R^2	0.47	0.87	0.97	0.85

*Note: All experiments were performed at approximately 22°C.
[†]Smaller particles were used for the B-WTP adsorption experiments because the dried residuals were a fine powder.

TOC) in the wastewater effluent. For adsorption on the B-WTP, LM-WTP and M-WTP residual solids, the model had a steeper slope at low concentrations, indicating higher adsorption of phosphate from the DI water. Conversely, the isotherms for ferric residual solids (Figure 4) were close in shape and appear to converge, indicating that the phosphate adsorption on the ferric residuals was not as impacted by competitive species present in the wastewater effluent. Genz *et al.* (2004) found no difference in the amount of phosphorus adsorption on granular ferric hydroxide or activated alumina when sulfate was competing for adsorption sites, compared with adsorption in the absence of competing species.

CONCLUSIONS

In general, all residual solids were capable of adsorbing phosphate from both phosphate-spiked DI water and municipal wastewater effluent. Appreciable differences in the adsorptive strength of the residual solids were apparent once the results were plotted as adsorption isotherms and Langmuir models were developed. The modeled maximum adsorption densities achieved in this study were similar to other Langmuir constants when a similar initial P concentration was used. While all residual solids were capable of adsorbing phosphorus, the maximum adsorption density was in the order of ferric (TB-WTP) > lime (B-WTP) > alum (M-WTP) > alum (LM-WTP). The results suggest that less ferric adsorbent would be required to treat phosphate-contaminated water in a fixed-bed column experiment. Furthermore, the iron-based adsorbent appears to be less influenced by competitive adsorptive species. Additionally, the alum residual solid containing a higher amount of metal oxides had a higher adsorptive capacity for phosphate than the alum residual solid containing fewer oxides. Phosphate adsorption on the lime residual solids may have been aided by the use of a smaller particle size. However, it is likely that the residual type also contributed to phosphate adsorption. A logical next step to this research should be to compare these residual solids in a column experiment to determine whether there is a difference in treated bed volumes between the ferric, alum or lime residual solids.

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