Journal of Hazardous Materials 187 (2011) 250–257

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Laboratory investigations of stormwater remediation via slag: Effects of metals on phosphorus removal

Nnaemeka C. Okochi, Dena W. McMartin*

Environmental Systems Engineering, Faculty of Engineering and Applied Science, University of Regina, Regina, Saskatchewan, Canada S4S 0A2

A R T I C L E I N F O

Article history:
Received 7 July 2010
Received in revised form
17 December 2010
Accepted 5 January 2011
Available online 12 January 2011

Keywords:
Stormwater
Slag
Adsorption
Heavy metal
Phosphorus removal

A B S T R A C T

The use of electric arc furnace (EAF) slag for the removal of phosphorus (P) from various simulated stormwater blends was investigated in the laboratory. The form of P measured was the inorganic orthophosphate (PO_4–P). The stormwater solutions used in this preliminary study were synthesized as blends of P and typical concentrations of some of the most common and abundant metals in stormwater (e.g. cadmium, copper, lead and zinc), and contacted with EAF slag to determine P removal efficiency and sorptive competition. Results showed that the presence of cadmium, lead and zinc had minimal effect on the removal process; copper was a significant inhibitor of P uptake by the EAF slag media. P removal was greatest in the metal-free and multi-metal stormwater solutions.

1. Introduction

Because rainwater had been generally considered as clean, high quality water, limited attention had been paid in the past to the impacts of stormwater discharges on receiving waters beyond quantity-related concerns, such as flooding [1,2]. During rainfall events, stormwater mobilizes and amasses suspended solids, organic matter (such as plant debris), pathogens (including bacteria and viruses), nutrients (such as inorganic nitrogen and phosphorus compounds) and toxic substances (including pesticides, heavy metals and hydrocarbons) that have accumulated on impervious urban surfaces over time. Thus, the runoff itself becomes a sort of wastewater that can create substantial degradation of water quality in receiving systems [3,4]. Even low pollutant concentrations at extremely high flows and volumes of stormwater can result in significant pollutant mass loads; today, attention is therefore expanding to consider as important not only the quantitative management of runoff in urban designs, but also its quality management and control [2].

Phosphorus (P) is most commonly present in the aqueous environment as orthophosphate (PO_4–P), which has been the target compound for several treatment technologies [5]. Excessive concentrations of P, primarily as PO_4–P, are identified as a principal source of freshwater eutrophication, defined as the over-enrichment of receiving waters with mineral nutrients [6]. A major impact of eutrophication is the significant growth of algae and cyanobacteria that reduces dissolved oxygen content leading to the loss of aquatic biodiversity, odour production, and water quality problems related to prevailing anaerobic conditions [7–9]. In addition to the potentially toxic health implications related to consumption of such water, cyanobacteria blooms may also result in significant economic losses related to decreased recreation, tourism and freshwater commercial fisheries [10–12]. Therefore, P removal currently constitutes a major challenge in both overall water quality management and wastewater treatment design. That same challenge is of significant concern in urban runoff where stormwater quality poses an increasingly significant source of pollution for aquatic ecosystems [13,14]. Most research programs for P removal have focused on wastewater treatment methods, with sparse information available relating to the removal of P in stormwater collection and retention systems. However, growing challenges with respect to water quality management, changes in the frequency and intensity of rainfall events through climate change, and identified downstream impacts on economic prosperity due to eutrophication show that stormwater merits further investigation [12,15–19]. In addition, the characteristics and composition of stormwater differ from those of municipal wastewater [20], and management of these systems may thus benefit from distinct and unique solutions.

Stormwater collection, management and treatment systems may profit from the use of media composed of natural materials, industrial by-products and artificial substrates for P removal

---

* Corresponding author. Tel.: +1 306 585 4703; fax: +1 306 585 4855.
E-mail address: dena.mcmartin@uregina.ca (D.W. McMartin).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.01.015

[21]. Of the materials investigated, industrial by-products, especially iron and steel slag materials, have garnered the most interest since these have demonstrated a significant capability to sequester P [22]. Slags are particularly attractive for use as inexpensive waste materials of reliable quantity in regions in close proximity to steel mills and recyclers [22–26]. The local availability of sizable amounts of electric arc furnace (EAF) slag in Saskatchewan and other North American locations like Iowa and Alabama through EVRAZ, a steel manufacturer, provides an opportunity for the innovative use of this by-product. Already, slag is being safely and successfully used in Saskatchewan as an aggregate in road construction and maintenance. Another potential for the use of the slag in municipalities around North America, and indeed all around the world, would be the inexpensive treatment of stormwater for the removal of nutrients, metals and other undesired constituents before its release into water bodies.

The ability of slag to remove both nutrient and metal impurities by sorptive mechanisms from wastewater has been previously proven [24–29]. P sorption experiments using raw municipal wastewater and those carried out under field conditions demonstrate considerable differences to those using artificial P solutions in the laboratory. Shilton et al. [30] noted that P sorption onto an active slag filter was significantly higher for synthetic P solutions than that observed using authentic pond effluent. Brix et al. [31] demonstrated that P sorption by a calcite substrate was ten times higher in the laboratory than under field operations. Johansson Westholm [21] and Drizo et al. [23] have related the P removal discrepancies between laboratory and field studies to the vast difference in investigative methods and materials used by researchers, which makes it difficult to compare the results. According to Pratt et al. [22], the disparity between field and laboratory results could be due to the presence of competing ions in the actual environmental samples.

The competition for slag sorption sites has been observed in the removal of heavy metals from solution [32–34]. This tendency of substrates to preferentially retain ions other than P is therefore an important consideration when developing treatment solutions [21]. In other words, the removal of P from stormwater, a complex matrix, would benefit from a better understanding of the effects of competing chemical constituents on the P removal capacity of a given adsorbent. To date, there is little to no information available about the degree to which competing ions in stormwater or wastewater affect P adsorption by slag.

A number of metals are reported to be commonly detected in stormwater. Of these, cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) are some of the most frequently studied metals that are also considered to be of greatest concern, since the concentrations of these ions in stormwater regularly exceed surface water quality guidelines by 10 times or more [1]. This present work investigates the effect of these four metals on P adsorption by EAF slag under simulated stormwater conditions. Simulated stormwater was chosen to standardize the compositions of the water samples used in these experiments, and to more accurately observe the effects of varying environmental conditions.

The outcome of this study may be useful in locations around the world where EAF slag, or materials with comparable characteristics, is generated in large enough quantities as industrial by-products, or occur naturally, and similar stormwater treatment needs for the preservation of downstream aquatic resources are identified.

2. Materials and methods

2.1. Adsorbent and characterization

EAF slag was obtained from the EVRAZ steel recycling facility in Regina, Saskatchewan, Canada. The slag was pulverized and sieved with an Endecolts Octagon 200 Test Sieve Shaker (London, England). A particle size (d_p) between 2.36 and 3.35 mm, equivalent to commercially available granular activated carbon, was used in experiments. The resulting EAF slag particles were washed with distilled water to remove residual fines, dried in a furnace at 105 °C for 24 h and stored in a desiccator until use.

Table 1
Composition of 6 synthetic stormwater solutions containing 5 mg P/L.

	Description	Composition
1	Metal-free stormwater	Cd^{2+}, Cu^{2+}, Pb^{2+}, $Zn^{2+} \approx 0$
2	Cd-dominant stormwater	Cd^{2+}: 1 mg/LCu^{2+}, Pb^{2+}, $Zn^{2+} \approx 0$
3	Cu-dominant stormwater	Cu^{2+}: 1 mg/LCd^{2+}, Pb^{2+}, $Zn^{2+} \approx 0$
4	Pb-dominant stormwater	Pb^{2+}: 1 mg/LCd^{2+}, Cu^{2+}, $Zn^{2+} \approx 0$
5	Zn-dominant stormwater	Zn^{2+}: 1 mg/LCd^{2+}, Cu^{2+}, $Pb^{2+} \approx 0$
6	Multi-metal stormwater	Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+} = 1 mg/L

The chemical oxide composition of the slag was determined by X-ray fluorescence (XRF) using a PANalytical Axios Advanced spectrometer. BET surface area was measured by N_2 adsorption using a Micromeritics ASAP 2010 instrument (Norcoss, GA, USA). Powder X-ray diffraction (XRD) was also carried out to identify the mineral species present in the slag by means of a D8 diffractometer with GADDS (Bruker AXS, USA) and equipped with a Cu source. In addition, images of scanning electron microscopy with X-ray microanalysis (SEM-EDS) of the particles were obtained for both fresh and spent slag materials using a JSM5600 (JEOL, Japan) coupled to an EDAX Genesis (EDAX, NJ, USA). Fresh and spent slag materials, as stated in this study, refer to slag obtained before and after interaction with the metal-free simulated stormwater, respectively. Spent slag characterization experiments were also repeated in a different lab and with different equipment as follows: Powder X-ray diffraction (XRD) was performed using a Panalytical X'Pert Pro Diffractometer equipped with Cu X-ray source, and the elemental composition of the slag was also studied by energy dispersive X-ray analysis (EDS) on a FEI Quanta 600F Scanning Electron Microscope coupled to a Brunker Quantax 200 Esprit 1.8.2 EDS package and a Brunker 5010 STD detector.

2.2. Batch adsorption experiment design

A series of synthetic stormwater samples was produced comprising combinations of P (5 mg/L) and one or more of the identified metal ions (Table 1). The P and metal compositions were applied within the range of relative values of P to metal concentrations observed in actual stormwater [1]. To fully elucidate the removal of P due to EAF slag sorption, control experiments containing no EAF slag were also carried out for all conditions identified in Table 1.

Stock P solution was prepared using anhydrous KH_2PO_4 (EMD Chemicals Inc., Darmstadt, Germany). Metal stocks were synthesized using $CdCl_2{\cdot}2.5H_2O$ (Acros, NJ, USA), $CuCl_2{\cdot}2H_2O$ (Fisher Scientific, NJ, USA), $Pb(NO_3)_2$ (Fisher Scientific, NJ, USA) and $ZnSO_4{\cdot}7H_2O$ (Sigma–Aldrich, MO, USA). All chemicals were analytical grade. Ultrapure laboratory water of 18.2 M Ohm-cm was used in the preparation of all stock solutions.

Adsorption studies were conducted in a temperature-regulated orbital platform shaker (Lab-line Instruments Inc., IL, USA) at 80 rpm for 120 h. At 80 rpm, no disintegration of slag was observed, and mixing remained effective. Shaking was temporarily interrupted at 24 h intervals to collect samples that were subsequently filtered through a 0.45 μm Nalgene membrane prior to analysis.

All experiments were conducted at 25 °C and initial pH of 7. Temperature was regulated by means of the platform shaker, while influent pH of the simulated stormwater blends was adjusted using 0.1 M HCl or 0.1 M NaOH, prior to interaction of the stormwater with slag.

Table 2
Chemical composition and physical characteristics of EVRAZ EAF slag.

Constituent	Composition (%)
Fe_2O_3	44.44
CaO	24.97
MgO	10.68
SiO_2	8.14
Al_2O_3	7.63
MnO	4.18
Cr_2O_3	1.54
P_2O_5	0.28
TiO_2	0.28
CuO	0.034
Na_2O	0.02
NiO	0.017
K_2O	0.01
Co_3O_4	0.006
BET SA[a] (m^2/g)	1.12
APD[b] (nm)	4.5

[a] surface area
[b] average pore diameter

2.3. *Aqueous sample analysis*

Filtered 2.40 mL samples were analyzed for P content in time-series testing using a modified colorimetric Stannous Chloride Method [35]. All analyses were completed in triplicate. Calibration curves were developed for every two to three set of samples; blanks were run for every set. Spectrophotometric analysis was completed using a Helios Alpha scanning spectrophotometer (Thermo Electron Corporation, England) set at 650 nm.

2.4. *Development of adsorption isotherms*

Adsorption isotherm studies were carried out by mixing 4 g/L of EAF slag with 250 mL P solutions of initial concentration ranging from 2.5 to 10 mg P/L. This range of P concentrations was chosen to examine the variability in P adsorption capacity values, and its dependence on the initial P concentrations [23]. 4 g/L of EAF slag was selected as an optimum for these experiments as further increase in slag mass resulted in a decrease in measured adsorption density (mg/g) values, especially at the lower range of P concentrations tested. The adsorption isotherm experiments were conducted over a 120 h period, which was found to be sufficient for equilibrium. Solution equilibrium was attained when absorbance values levelled off, and no incremental change in P concentration was detected.

2.5. *Statistical analysis*

The relative standard deviation (%) was estimated for the measurements of P adsorption density (mg/g) in all the stormwater systems. One-way analysis of variance (ANOVA) was conducted to find out if there were significant P removal differences among the various stormwater compositions. Statistical significance was set at the probability level, $\alpha = 0.05$. Scheffé's test was also applied in post hoc comparisons to determine where the differences existed between pairs of stormwater systems. Excel (Microsoft Corporation, 2007) was used to analyze the data.

3. Results and discussion

3.1. *Characterization of slag*

Chemical composition results of fresh slag analysis, reported as oxides, are shown in Table 2. In terms of metal content (%, g/g), the slag composition was as follows: Fe – 23.93, Ca – 20.71, Si – 5.83, Mn – 4.6, Al – 4.52, Cr – 1.66 and Ni – 0.023. Thus, the EVRAZ EAF slag used in these experiments consisted primarily of iron (Fe) and calcium (Ca). This observation was consistent with results obtained from previous XRF analyses of EAF slag [23,24]. For example, in Drizo et al. [23], Fe and Ca content (%, g/g) were 24.3 and 21.7, respectively, vs. 23.9 and 20.7, respectively, for this study. Also, there were noticeable differences in the concentration range of some other constituents; their EAF slag had lower levels (%, g/g) of Mn (1.01), Al (2.47) and Cr (0.22). In the case of elevated Cr levels in the present EAF slag under study, this may raise concerns for human health and the environment, due to leaching. However, studies have shown that there are no detrimental effects to human health or to the environment as a result of leaching from steel slags, and that due to the very high temperatures applied in their formation, heavy metals are bound tightly together within the slag matrix [26,36].

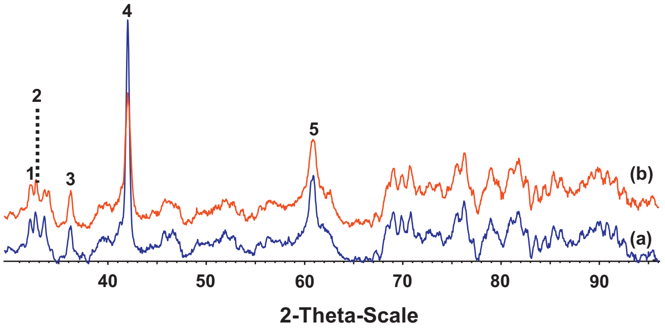

Fig. 1. XRD diagrams of the EAF slag (a) before sorption and (b) after sorption. Identified phases: A: FeO (1, 4, 5); B: Fe_2O_3 (2, 3); C: $(NiO)_{0.5}\cdot(MnO)_{0.5}$ (3,4,5).

The BET surface area of the spent slag sample from the metal-free stormwater was determined as 0.48 m^2/g. This is a decrease in surface area when compared with that of the fresh slag (1.12 m^2/g), and may likely indicate deposition of P on the slag surface. Therefore, physical adsorption could have contributed to P removal.

X-ray diffraction patterns for both fresh and spent EAF slag from the metal-free stormwater system are provided in Fig. 1. For clarity and ease of discussion, the post-sorption diffraction pattern has been stacked above that of the pre-sorption. The identified XRD peaks indicate the presence of iron oxide compounds. These iron oxide peaks were of reduced intensity in the spent slag, which suggests a depletion of Fe from the slag.

The result of the repeat XRD experiment for the spent slag sample is shown in Fig. 2.

The X-ray diffraction pattern obtained in the replicate test indicated that the major volume fraction was amorphous rather than crystalline. The analysis also uncovered the presence of the following components: Wüstite (FeO), Larnite (β-Ca_2SiO_4), Brownmillerite ($Ca_2(Al,Fe)O_5$), Lime (CaO) and Magnetite (Fe_3O_4) in the spent slag. These components are consistent with those previously identified in EAF slags by Engström et al. [37], and again confirm the occurrence of Fe and Ca as major components in the slag.

The scanning electron microscopy (SEM) micrographs for the surfaces of fresh and spent slag particles are shown in Fig. 3. A change in surface structure is noticed after the sorption process which may be as a result of deposition of P by physisorption, or the loss of Fe, or a combination of both. It may also be due to a progressive change in surface mineralogy with time, for example, as noted in the study by Bowden et al. [25]. The results of the semi-quantitative (standard less) energy-dispersive X-ray spectroscopy (EDS) scan taken at the center of a representative particle from both the fresh and spent slag samples (Fig. 4) showed a visible decrease in the relative concentration of Fe, as well as Ca. This confirmed the loss of Fe from the slag, as previously suggested from XRD analysis. The observed decrease in Ca content may be related to the loss of

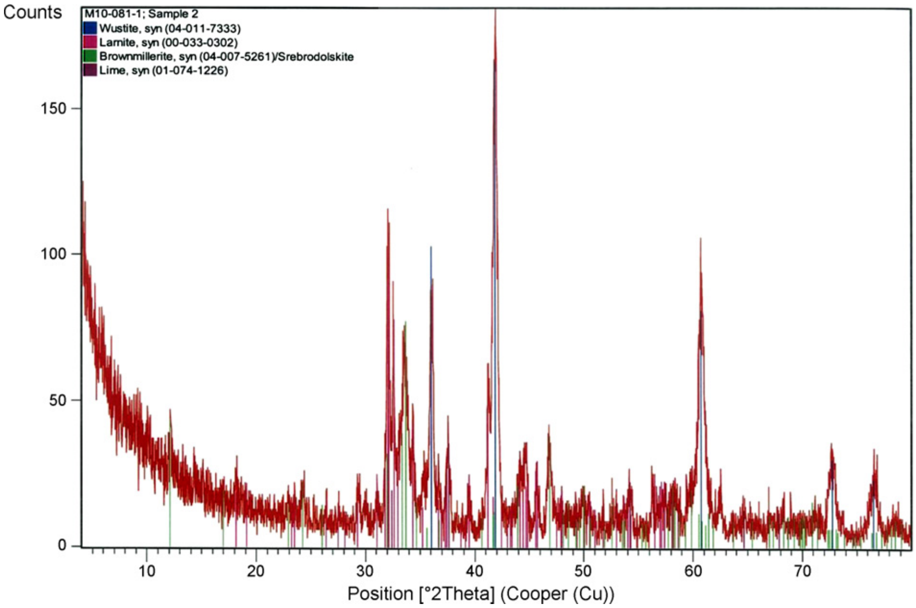

Fig. 2. X-ray diffraction pattern of spent slag from repeat experiment.

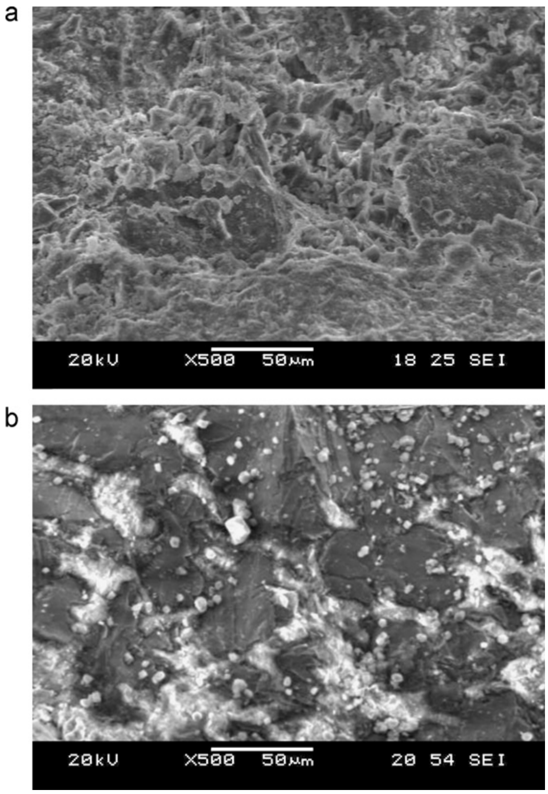

Fig. 3. SEM micrograph of the EAF slag (a) before adsorption (b) after adsorption (Initial P: 5 mg/L; metal ions: 0 mg/L; initial pH 7; T: 25 °C, rpm: 80; P removal: 95%).

free lime (CaO), which resulted in high pH [25]. In this study, the equilibrium pH of the tested stormwater solutions was ~10.2–10.5, up from an initial value of 7. Thus, for practical applications, pH control must be taken into account before downstream discharge of the treated stormwater. The formation of P was also noticed, possibly due to its deposition on the slag surface. This aligns with findings from the BET surface area tests.

The result of the replicate EDS semi-quantitative spectrum of the spent slag sample is provided in Fig. 5. The loss of Fe from the slag was evident from comparisons with previous XRF, XRD and EDS test observations. The presence of P was again noticed on the spent slag, which points to the uptake of P by the slag.

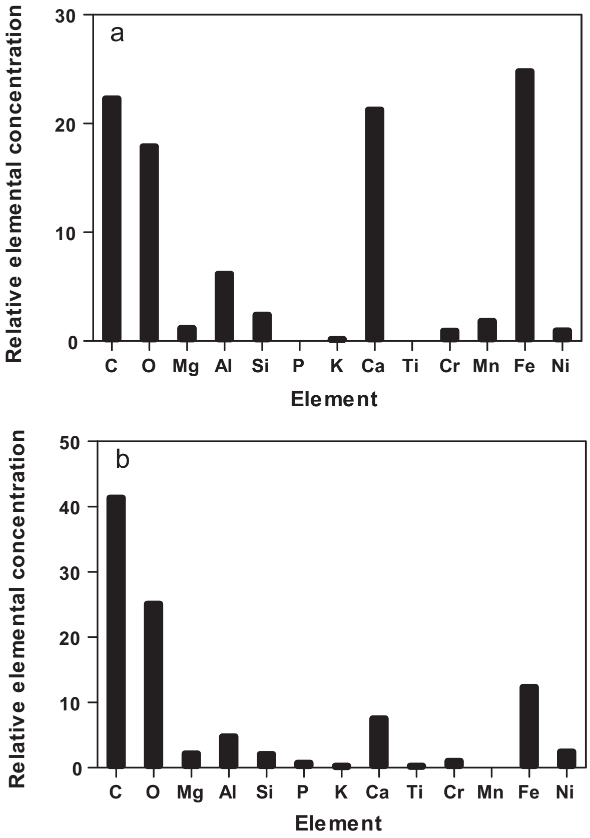

Fig. 4. EDS scan for (a) fresh and (b) spent EAF slag.

3.2. Adsorption isotherms

The sorption isotherm for uptake of P in the metal-free stormwater by the EAF slag is presented in Fig. 6. The equilibrium data for the

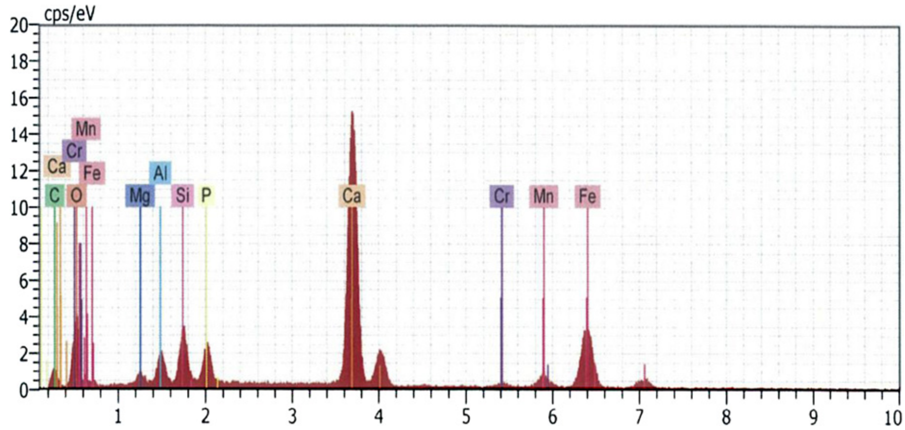

Fig. 5. Semi-quantitative EDS spectrum of spent slag from repeat experiment.

sorption process was fitted to both Langmuir (Fig. 7) and Freundlich (Fig. 8) equations.

The experimental data obtained in this work fit both the Langmuir and Freundlich linear relationships. However, the Langmuir isotherm produced a slightly better fit for modeling the data than the Freundlich equation.

It should be noted that though the Langmuir and Freundlich are the most widely used models due to their simplicity, estimation of P adsorption capacities from standard batch experiments, and from the Langmuir and Freundlich equations, result in unrealistic predictions for the long-term performance of dynamic or full-scale systems [23,26,38]. The derivation of P adsorption capacity of a material from long-term column studies could serve instead as a better indicator of the performance and longevity of full-scale systems [23].

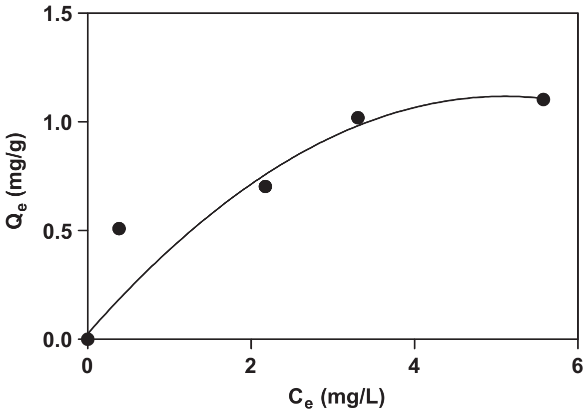

Fig. 6. Adsorption isotherm for P removal from metal-free stormwater.

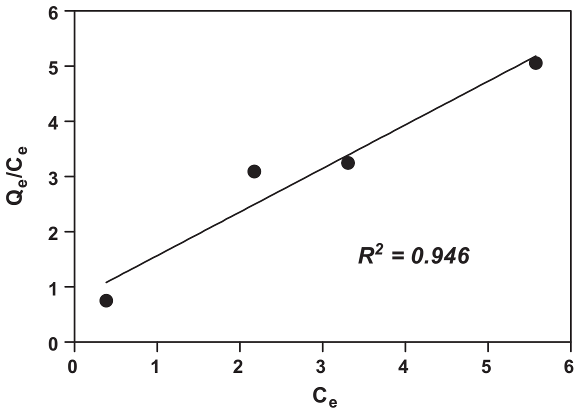

Fig. 7. Langmuir plot for P sorption onto EAF slag in metal-free stormwater.

3.3. Adsorption kinetics

P adsorption from the metal-free stormwater on to the EAF slag was analyzed by pseudo-first and pseudo-second order rate expressions as applied by Liu et al. [39]. The pseudo-first-order equation was based on the Lagergren equation [40] and given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t \tag{3}$$

where, Q_e is the amount of P adsorbed at equilibrium, Q_t is the amount of P adsorbed at time t, and k_1 is the equilibrium rate constant. k_1 can be determined by a linear plot of $\log(Q_e - Q_t)$ vs. t. This plot is shown in Fig. 9.

The pseudo-second-order equation was given by

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{t}{Q_e} \tag{4}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption and is obtained by the straight line plot of $\frac{t}{Q_t}$ vs. t.

The P adsorption from the metal-free stormwater on to the slag showed significantly better correlation with the first-order than second-order kinetics model (Table 3).

The pseudo-first order model was further tested with two sets of independent experimental data from duplicate experiments (Fig. 10). Statistical analysis was carried out on data from both the

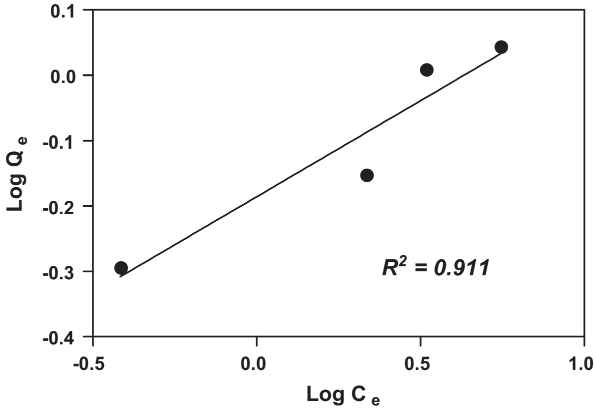

Fig. 8. Freundlich plot for P sorption onto EAF slag in metal-free stormwater.

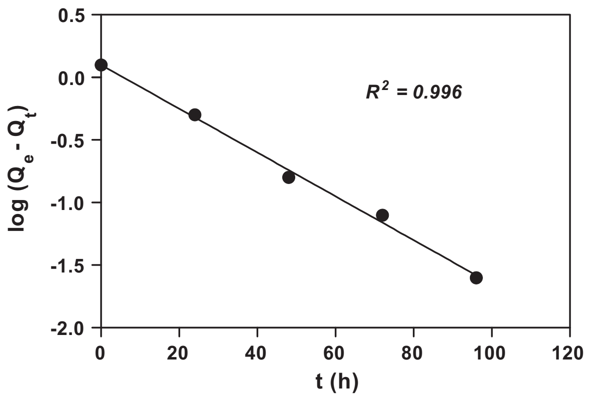

Fig. 9. Pseudo-first order equation for the adsorption of P by electric arc furnace slag.

Table 3
Values of the rate constants and correlation coefficients for the kinetic models.

Kinetic model	Rate constant	R^2
Pseudo-first order: $Q_t = 1.184 - 10^{(0.07-0.017t)}$	$k_1 = 0.04\,\mathrm{h}^{-1}$	0.996
Pseudo-second order: $Q_t = \frac{90.4t}{1.184+76.34t}$	$k_2 = 54.43\,\mathrm{g\,mg}^{-1}\,\mathrm{h}^{-1}$	0.710

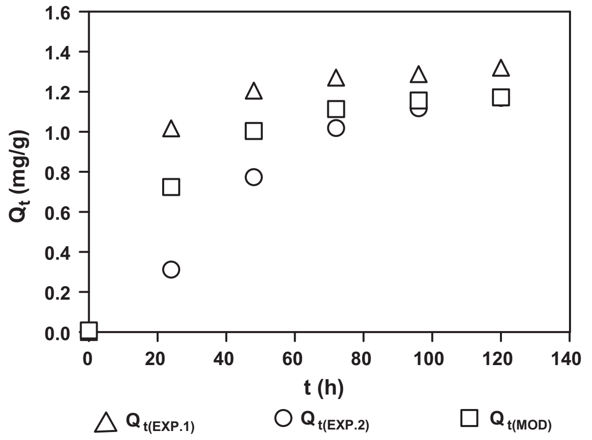

Fig. 10. Model fit for the adsorption of P by EAF slag.

repeat experiments ($Q_{t(\mathrm{EXP.1})}$ and $Q_{t(\mathrm{EXP.2})}$) and calculated model values ($Q_{t(\mathrm{MOD})}$). The model values were calculated by substituting the batch sorption time (in hours) for variable t in the pseudo first order kinetic model given in Table 3. The resulting standard deviation of Q_t from the mean with time ($Q_{t(\mathrm{MEAN})}$) proves that the model becomes more accurate in predicting the amount of P adsorbed with time, at the specified experimental conditions (Fig. 11). That is, as P adsorption on the slag approaches equilibrium the model becomes more reliable. Increase in equilibrium time thus appears to diminish some of the removal rate heterogeneity arising from the physico-chemical differences in the experimental batches.

3.4. Effect of metal contaminants on P removal

The influence of Cd^{2+} on P removal from stormwater is depicted in Fig. 12. The presence of Cd^{2+} resulted in a slight decrease in the removal of P by the slag, from about 95% (1.18 mg P/g) in the metal-free solution to 90% (1.13 mg P/g). The control experiment, i.e. in the absence of the adsorbent, shows that P removal in the Cd-dominant stormwater system is wholly attributable to the slag.

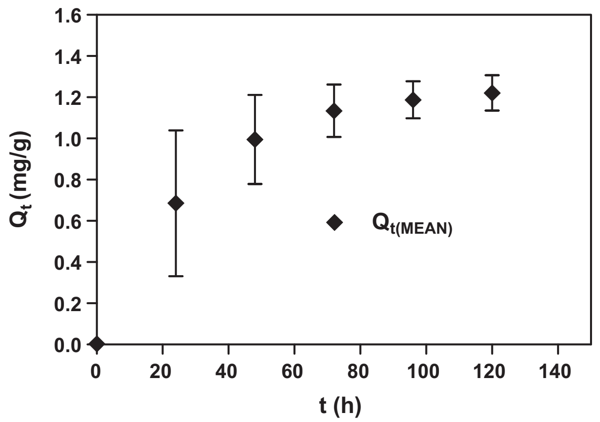

Fig. 11. Deviation of validation experiments from the pseudo-first order model.

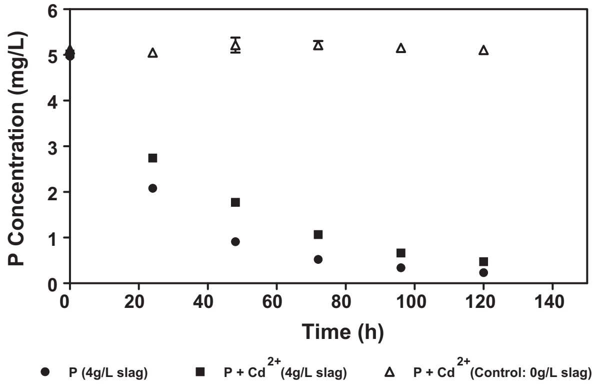

Fig. 12. Effect of Cd^{2+} on P removal under the experimental conditions identified in Table 1.

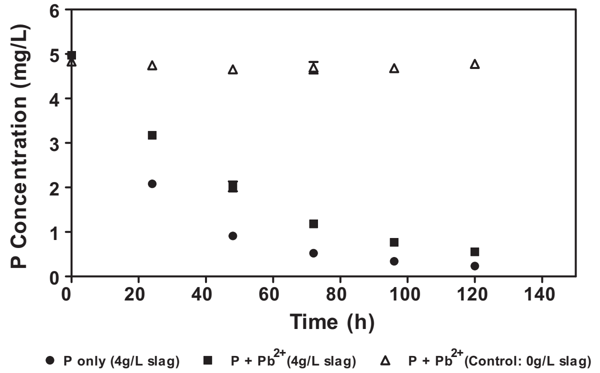

Fig. 13. Effect of Pb^{2+} on P removal under the experimental conditions identified in Table 1.

A similar pattern was also observed in the Pb- (Fig. 13) and Zn-dominant (Fig. 14) stormwater systems. In the presence of Pb^{2+} and Zn^{2+}, the removal of P was slightly reduced from that noted in the metal-free solutions. In each, approximately 90% P removal (1.10 mg P/g for Pb^{2+} and 1.12 mg P/g for Zn^{2+}) was achieved.

The initial rate of P removal in the presence of Zn^{2+} is more rapid than that observed in both the Cd- and Pb-containing systems. It appears that Zn^{2+} initially poses less competition to P uptake but becomes more competitive as adsorption sites become less available.

Of all the metal contaminants, Cu^{2+} results in the greatest decrease in the uptake of P by slag (Fig. 15). After 120 h, only about 68% of P (0.82 mg P/g) was removed from the aqueous phase in the

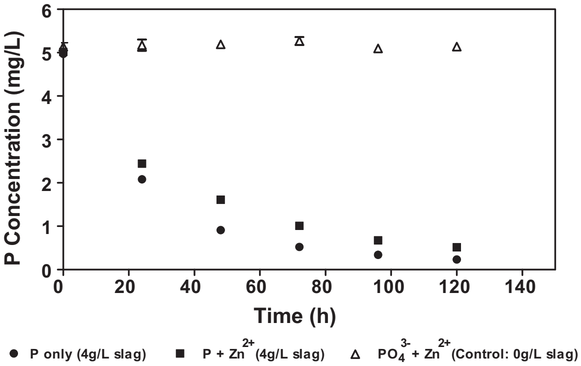

Fig. 14. Effect of Zn^{2+} on P removal under the experimental conditions identified in Table 1.

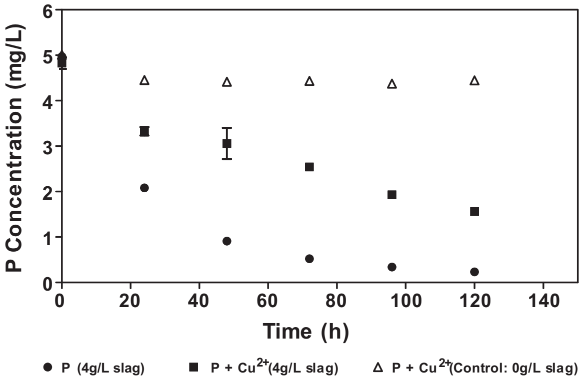

Fig. 15. Effect of Cu^{2+} on P removal under the experimental conditions identified in Table 1.

presence of Cu^{2+} as compared to 95% in the metal free stormwater solution (P only).

In the presence of Cu^{2+}, not all P removal is attributable to sorption by the EAF slag. The control experiment for the Cu-dominant stormwater matrix shows some initial P loss (about 11%) within the first 24 h, after which no further removal was measured. This observation was attributed to the precipitation of P by Cu^{2+}, represented in the simplest form by the following equation:

$$Cu^{2+}(aq) + PO_4{}^{3-}(aq) \rightarrow Cu_3(PO_4)_2(s) \downarrow \tag{5}$$

This significant reduction in the ability of the slag to remove P in the presence of Cu^{2+} may suggest that Cu^{2+} was a far more competitive adsorbate than the other metal contaminants investigated. The strong affinity of Cu^{2+} for adsorbent media has been observed in previous studies where Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} were removed from single-metal systems by adsorption onto goethite, an iron oxide mineral (α-FeO(OH)) [41] and melter slag, a Ti/Al-rich variety common in New Zealand [42]. By comparing the single-element systems in these studies, the amount of the metal ion removed from the solution by a unit mass of the adsorbent followed the sequence $Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+}$ [41] and $Cu^{2+} > Zn^{2+} \approx Cd^{2+}$ [42]. Though the solutions in those studies did not contain $PO_4{}^{3-}$, the conclusions closely mirror the observations encountered in this study.

When all four metals were present (multi-metal stormwater solution), no net effect was noticed with respect to the adsorption of P onto the slag, in comparison to the metal-free P solution (Fig. 16). The results indicated that both the presence of the selected metals as a complex mixture and the complete absence of those metals in solution produced 95% removal of the initial P concentration in those solutions. This effect has not been previously observed in other multi-element solutions containing equal quantities of Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}, where removal of these metals was attempted using various types of slag [33,42].

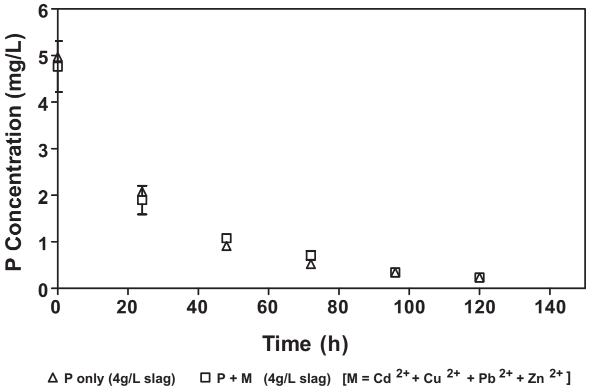

Fig. 16. Effect of mixed-metal solution on P removal under the experimental conditions identified in Table 1.

Table 4
Percent P-removal in the various synthetic stormwater systems.

	Description	P removed (%)	Adsorption density (mg P/g)
1	Metal free stormwater	95	1.18
2	Multi-metal stormwater	95	1.14
3	Cd-dominant stormwater	91	1.13
4	Zn-dominant stormwater	90	1.12
5	Pb-dominant stormwater	89	1.10
6	Cu-dominant stormwater	68	0.82

The result of this experiment (Fig. 16) indicates that the presence of P significantly weakens the competitive advantage of Cu^{2+} vis-à-vis the other metal contaminants, thus resulting in a “neutralizing” or “canceling” effect amongst the metals.

Compiled results as percent P removed from each of the synthetic stormwater systems evaluated clearly show that the phosphate removal was most significant in the metal-free and mixed-metal solutions (Table 4). However, the presence of Zn^{2+}, Cd^{2+}, and Pb^{2+} were shown to have minimal effect, while Cu^{2+} was a significant competitor for sorption sites on the EAF slag media.

3.5. Statistical analysis

The results presented were average values of the three replicates. The error bars in the graphs show the standard deviation of the measurements from their mean. The relative standard deviation was 1–12% for the measurements of equilibrium P adsorption densities. One-way ANOVA showed that the differences in P removal (mg P/g) differed significantly across the six stormwater systems ($df_B = 5$, $df_W = 12$, $F = 15.31$, $p = 7.56E-05$). An independent-samples t-test was also conducted to compare P removal in the metal-free and Cu-dominant stormwater conditions. There was a significant difference ($df = 4$, $t = 7.63$, $p = 3.06E-06$) in P removal for metal-free (Mean = 1.18, SD = 9.79E-03) and Cu-dominant (Mean = 0.82, SD = 3.70E-02) stormwater systems. Scheffé’s post-hoc comparisons between Cu-dominant and each of the remaining stormwater systems revealed a significant difference in P removal, that is, $F > F'$, where F' is the product of df_B and the critical value of F for df_B and df_W at $\alpha = 0.05$. No statistical difference ($F < F'$) was observed between metal-free and each of the remaining stormwater systems, as well as when the remaining stormwater systems were paired and compared with one another.

These results therefore suggest that the stormwater composition has an effect on P removal. Specifically, for the simulated stormwater systems under study, when the Cu-dominant system was synthesized by adding Cu^{2+} to a P only solution, P removal was significantly lower than that obtained in the P only system. However, the addition of other metals to the P only solution, individually or as a combination, made no real difference to P removal.

4. Conclusions

The results of this study support the application of EAF slag as an effective adsorbent for P removal from various stormwater compositions. Removal efficiences ranging from 0.82 mg P/g in Cu-dominant stormwater to 1.18 mg P/g in metal-free stormwater were recorded. The presence of metals in stormwater was found to influence P removal to varying degrees, with Cu^{2+} demonstrating a significant ability to decrease P removal, possibly due to a stronger affinity for the adsorbent media. It is possible that Cu^{2+} may have posed significant competition to P for sorption sites on the EAF slag. However, the affinity of Cu^{2+} to the slag is not observed in a multi-metal stormwater system containing P and the other metals tested in this work. As well, physisorption was found to be a contributing mechanism to P removal; and while the loss of Fe from the slag was confirmed, it was not certain what role this phenomenon played in the removal process. This study is currently being extended to investigate reasons behind the observed behaviour of metals in the tested stormwater systems, with a special interest on Cu^{2+} and other mixtures. On-going research also includes further examination into the fate of Fe and Ca loss from the slag, and their impact on the P removal process. As well, the influence of pH, P concentration, metal concentration, adsorbent particle size, temperature and continuous flow dynamics on the kinetics and efficiency of P removal from synthetic stormwater is being carried out.

Acknowledgments

The authors gratefully acknowledge financial support from Communities of Tomorrow and the NSERC Discovery Grant program. We are also thankful to EVRAZ and TubeCity-IMS for their kind provision and transportation of the slag to our laboratories. The constructive comments of the two anonymous reviewers who handled our manuscript were greatly appreciated and have without doubt, greatly improved the quality and outcome of this work.

References

[1] D.K. Makepeace, D.W. Smith, S.J. Stanley, Urban stormwater quality: summary of contaminant data, Crit. Rev. Environ. Sci. Technol. 25 (1995) 93–139.

[2] A. Taebi, R.L. Droste, Pollution loads in urban runoff and sanitary wastewater, Sci. Total Environ. 327 (2004) 175–184.

[3] P.A. Chambers, M. Allard, S.L. Walker, J. Marsalek, J. Lawrence, M. Servos, J. Busnarda, K.S. Munger, K. Adare, C. Jefferson, R.A. Kent, M.P. Wong, Impacts of municipal effluents on Canadian waters: a review, Water Qual. Res. J. Can. 32 (1997) 659–713.

[4] G.F. Birch, C. Matthai, M.S. Fazeli, J. Yul Suh, Efficiency of a constructed wetland in removing contaminants from stormwater, Wetlands 24 (2004) 459–466.

[5] M. Mortula, Phosphorus removal from small-scale wastewater applications using alum sludge. Ph.D. Thesis, Dalhousie University, Canada, (2006).

[6] D. Correll, The role of phosphorus on the eutrophication of receiving waters: a review, J. Environ. Qual. 27 (1998) 261–266.

[7] V.H. Smith, Eutrophication of freshwater and marine ecosystems: a global problem, Environ. Sci. Pollut. Res. Int. 10 (2003) 126–139.

[8] G.D. Cooke, R.H. Kennedy, Managing drinking water supplies, J. Lake Reservoir Manage. 17 (2001) 157–174.

[9] R.A. Corrales, J.L. Maclean, Impacts of harmful algae on seafarming in the Asia-Pacific areas, J. Appl. Phycol. 7 (1995) 151–162.

[10] S.R. Carpenter, D. Bolgrien, R.C. Lathrop, C.A. Stowe, T. Reed, M.A. Wilson, Ecological and economic analysis of lake eutrophication by nonpoint pollution, Aust. J. Ecol. 23 (1997) 68–79.

[11] C. Folke, N. Kautsky, M. Troell, The costs of eutrophication from salmon farming: implications for policy, J. Environ. Manage. 40 (1994) 173–182.

[12] J.N. Pretty, C.F. Mason, D.B. Nedwell, R.E. Hine, S. Leaf, R. Dils, Environmental costs of freshwater eutrophication in England and Wales, Environ. Sci. Technol. 37 (2003) 201–208.

[13] J.M. Pratt, R.A. Coler, P.J. Godfrey, Ecological effects of urban stormwater runoff on benthic macroinvertebrates inhabiting the Green River, Massachusetts, Hydrobiologia 83 (1981) 29–42.

[14] R. Aryal, S. Vigneswaran, J. Kandasamy, R. Naidu, Urban stormwater quality and treatment, Korean J. Chem. Eng. 27 (2010) 1343–1359.

[15] H. Bouwer, Integrated water management: emerging issues and challenges, Agric. Water Manage. 45 (2000) 217–228.

[16] O. Varis, P. Vakkilainen, China's 8 challenges to water resources management in the first quarter of the 21st century, Geomorphology 41 (2001) 93–104.

[17] Niemczynowicz Janusz, Urban hydrology and water management–present and future challenges, Urban Water 1 (1999) 1–14.

[18] N.W. Arnell, The effect of climate change on hydrological regimes in Europe: a continental perspective, Global Environ. Change 9 (1999) 5–23.

[19] M.G. Mansell, The effect of climate change on rainfall trends and flooding risk in the west of Scotland, Nord. Hydrol. 28 (1997) 37–50.

[20] Metcalf & Eddy Inc, Wastewater Engineering, Treatment and Reuse, fourth ed., McGraw-Hill, New York, 2003.

[21] L. Johansson Westholm, Substrates for phosphorus removal – Potential benefits for on-site wastewater treatment? Water Res. 40 (2006) 23–36.

[22] C. Pratt, A. Shilton, S. Pratt, R.G. Haverkamp, N.S. Bolan, Phosphorus removal mechanisms in active slag filters treating waste stabilization pond effluent, Environ. Sci. Technol. 41 (2007) 3296–3301.

[23] A. Drizo, Y. Comeau, C. Forget, R.P. Chapuis, Phosphorus potential: a parameter for estimating the longevity of constructed wetland systems, Environ. Sci. Technol. 36 (2002) 4642–4648.

[24] A. Drizo, C. Forget, R.P. Chapuis, Y. Comeau, Phosphorus removal by electric arc furnace steel slag and serpentinite, Water Res. 40 (2006) 1547–1554.

[25] L.I. Bowden, A.P. Jarvis, P.L. Younger, K.L. Johnson, Phosphorus removal from waste waters using basic oxygen steel slag, Environ. Sci. Technol. 43 (2009) 2476–2481.

[26] L. Johansson Westholm, The use of blast furnace slag for removal of phosphorus from wastewater in Sweden–A review, Water 2 (2010) 826–837.

[27] K. Sakadevan, H.J. Bavor, Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems, Water Res. 32 (1998) 393–399.

[28] N.M Agyei, C.A. Strydom, J.H. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, Cem. Concr. Res. 32 (2002) 1889–1897.

[29] E. Oguz, Thermodynamic and kinetic investigations of $PO_4{}^{3-}$ adsorption on blast furnace slag, J. Colloid Interface Sci. 281 (2005) 62–67.

[30] A.N. Shilton, I. Elmetri, A. Drizo, S. Pratt, R.G. Haverkamp, S.C. Bilby, Phosphorus removal by an 'active' slag filter-a decade of full scale experience, Water Res. 40 (2006) 113–118.

[31] H. Brix, C.A. Arias, M. Del Bubba, Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands, Water Sci. Technol. 44 (2001) 47–54.

[32] S. Dimitrova, Use of granular slag columns for lead removal, Water Res. 36 (2002) 4001–4008.

[33] Y. Xue, H. Hou, S. Zhu, Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag, J. Hazard. Mater. 162 (2009) 391–401.

[34] A. Renman, G. Renman, J. Petter Gustafsson, L. Hylander, Metal removal by bed filter materials used in domestic wastewater treatment, J. Hazard. Mater. 166 (2009) 734–739.

[35] American Water Works Association (AWWA), American Public Health Association (APHA), Water Pollution Control Federation (WPCF), Standard methods for the examination of water and wastewater, 16th ed., Washington. D.C., 1985.

[36] D.M. Proctor, E.C. Shay, K.A. Fehling, B.L. Finley, Assessment of human health and ecological risks posed by the uses of steel-industry slags in the environment, Hum. Ecol. Risk Assess. 8 (2002) 681–711.

[37] F. Engström, D. Adolfsson, Q. Yang, C. Samuelsson, B. Björkman, Crystallization behaviour of some steelmaking slags, Process Metall. 81 (2010) 362–371.

[38] S. Hwan Lee, S. Vigneswaran, H. Moon, Adsorption of phosphorus in saturated slag media columns, Sep. Purif. Technol. 12 (1997) 109–118.

[39] S.-Y. Liu, J. Gao, Y.-J. Yang, Y.-C. Yang, Z.-X. Ye, Adsorption intrinsic kinetics and isotherms of lead ions on steel slag, J. Hazard. Mater. 173 (2010) 558–562.

[40] S. Lagergren, Zur Theorie der sogenannten Adsorption gelöster Stoffe, vol. 24, Kungliga Svenska Vetenskapsakademiens: Handlingar, 1898, pp. 1–39.

[41] E.A. Forbes, A.M. Posner, J.P. Quirk, The specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite, J. Soil Sci. 27 (1976) 154–188.

[42] J. Ren, The effectiveness of steel foundry by-products in the treatment of stormwater. MASc. Thesis, Auckland University of Technology, New Zealand, (2006).