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Three novel methods for removing inorganic species from contaminated industrial stormwater at a Smelter site in London

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ABSTRACT

Stormwater represents one of the least researched forms of wastewater in environmental science. Contaminated industrial stormwater, that is stormwater generated by runoff from industrial sites such as refineries, smelters and mine sites, is even less well understood. However, contaminated industrial stormwater can have damaging environmental impacts because it generally occurs in sudden bursts of high velocity and can result in significant downstream contamination. Flows of hundreds of thousands of litres of industrial stormwater are not uncommon in heavy rain events, and even when reduced through dilution, infiltration, co-mingling and by subsequent rain events, contaminants in stormwater can pose a risk to healthy urban and industrial environments. For these reasons, more research on contaminated industrial stormwater is desirable. This study considered two laboratory-scale experiments and an on-site field trial to assess three novel approaches to the treatment of heavy-metal contaminated stormwater at a smelter site in London. The approaches included the direct addition of a reagent derived from alumina refinery residue (ARR) and two filtration applications through laboratory and on-site reactive systems, both of which contained a form of pelletised media manufactured from alumina refinery residue. These three approaches resulted in the removal of inorganic contaminants from industrial stormwater, including cadmium from 0.08 mg/L to 0.0008 mg/L and copper from 0.7 mg/L to 0.0 mg/L by direct addition and arsenic from 0.34 mg/L to below the detection limit and antimony from 9.3 mg/L to 0.3 mg/L by filtration, with all post-treatment concentrations below the allowable limits for discharge. Although preliminary in nature, this study confirms other findings associated with the reuse of modified alumina refinery residue as a viable chemical raw material in industrial wastewater and solids treatment applications throughout the world, and the use of filtration of stormwater rather than the more common direct addition approach deserves further consideration.

1. Introduction

Stormwater is one of the most under-researched subjects in environmental science and wastewater treatment studies. Perhaps this is due to the fact that stormwater is a complex topic for analysis, with a variety of technical disciplines bearing directly upon it, including chemistry, civil engineering, hydrology, hydraulics, geomorphology, ecology and hydrogeology, among other fields of specialisation, making coherent and sustained investigation challenging.

Similarly, while the potential for complex organic and inorganic chemistry makes the study of contaminated stormwater appealing, its transient, high-volume/low-contaminant character and its apparently lower environmental polluting impacts also mean that stormwater, particularly industrial stormwater, is often the "forgotten wastewater". Typically coming under the purview of municipal councils and government water agencies but generally not of great interest to academic research (Erickson, et al. 2013; Washington State Department of Transport. 2014) the profound impact of stormwater on municipal sewerage systems, means stormwater management and mitigation are often the responsibility of local councils or state governments (City of Whittlesea. 2012) making it one step removed

from being of primary industrial concern or being part of a sustained research effort.

Moreover, because stormwater is generally associated with topics such as non-point source erosion and runoff in agriculture, pesticide dispersion and contamination, and inundation and infiltration impacts on impervious urban surfaces (such as along highways and from residential and other built-up areas like shopping malls and airports), industrial stormwater (i.e., contaminated stormwater generated at hard stand industrial sites) appears to be of even less interest to industrial researchers. Despite the fact that the polluting components of industrial stormwater can not only include predictable contaminants such as inorganic nutrients, suspended solids and heavy metals, but can also incorporate more problematic organic contaminants like bacteria (including pathogens), pesticides, petroleum and polycyclic aromatic hydrocarbons (PAH), benzene, toluene, ethylbenzene and xylenes (Department of Water. 2007). Nevertheless, industrial stormwater is often completely overlooked as a potential source of significant contamination or of social concern.

For example, Muthukrishnan (2010) studied the role of ponds and wetlands in ameliorating the impacts of metal-contaminated stormwater runoff, Davies and Bavor (2000) studied the environmental

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fate of pathogens in stormwater, and Moeller (2005) showed that 40 % of U.S. water bodies are being polluted with stormwater runoff and do not meet basic water quality guidelines, however most research on stormwater such as these three representative examples centres on agriculture and urban inundation but infrequently considers industrial or industrial-scale impacts and risks.

This conclusion can be verified by surveying the published literature on industrial waste. While industrial solid waste treatment features in the vast corpus of environmental research, the majority of studies in industrial waste relate specifically to wastewater. Recent examples of comprehensive surveys of industrial wastewater include Barakat (2011), Judd (2011), and Bhandari and Ranade (2014), and the relationship of industrial wastewater to energy consumption and sustainable development has been considered (International Bank for Reconstruction and Development. 2012). However, the study of stormwater in the industrial context rarely rates a mention in relation to wastewater, necessitating studies such as the present investigation in the UK.

One overriding assumption which guides the management of industrial stormwater is the concept of the "first flush". This approach centres on a primary concern for the initial first flush of stormwater, which occurs immediately after a rain event and which it is believed will rinse most contaminants from an industrial site, with subsequent flushes of cleaner water being spontaneously discharged to receiving waterways, such as lagoons, swales, rivers and floodplains. At many sites, stormwater management systems are therefore designed to only intercept the first flush (and to treat any inherent contaminants on site before they are discharged to the sewer as "trade waste" (SA Water. 2013)) but pay little or no attention to subsequent stormwater inundation. Environmental regulators are mostly (or in some cases, only) concerned with the potential environmental impacts of the first flush, and industrial sites typically have stormwater management and mitigation plans designed to manage and treat the first flush, assuming most contaminants from sustained rain events are of no significant longer term impact to the site or the environment; such plans generally do not attempt to intercept or treat stormwater which occurs after the first flush. This approach seems justified when considering research by Wen et al. (2012) has shown that heavy metal concentrations in industrial stormwater peak shortly after the first flush but decline rapidly thereafter.

These observations in the industrial context raise questions of whether stormwater is in fact wastewater at all. For example, Reese (2012) has argued that stormwater is not wastewater. He has identified the ten primary reasons why he believes that wastewater is different to stormwater, including the observation that stormwater, unlike wastewater, has what he calls an "unlimited peak flow" and "no ultimate end-of-pipe treatment". However, his arguments are based on rain events in urban or rural circumstances (such as in urban residential and agriculture settings) but are unpersuasive in the industrial context. In fact, industrial stormwater does not have an unlimited peak flow at industrial sites (for reasons given above in relation to the first flush) and is often subject to end-of-pipe treatment, as will be discussed in the context of this research study.

Reese also maintains that stormwater (but not wastewater) is characterised by episodic discharges of non-point source pollution. But again this may be true in agriculture but is untrue at most industrial sites, including the one chosen for this study, because the point-sources of pollution are usually well defined and demarcated, often by regulatory restrictions; it would rarely be considered best practice for environmental managers at a responsible industrial site to be unclear about where contamination comes from. For the purposes of the present study, industrial stormwater at this site in London is therefore defined as a type of on-site wastewater (not simply "stormwater" in the context of Reese's framework); this conclusion becomes particularly true when both the first flush of stormwater and all in-line wastewater generated at the site are comingled and treated in a wastewater treatment plant (WTP), and are together discharged as a single point source of treated wastewater.

Of the different approaches to treating inorganic species in industrial wastewater, including heavy metals such as cadmium, copper, chromium, lead, sulphate, phosphate, and metalloids like arsenic, the direct addition of chemical agents such as calcium hydroxide ($Ca[OH]_2$), sodium hydroxide (NaOH), and magnesium oxide (MgO) features most prominently [e.g., Semerjian & Ayoub, 2003]. Where organic species are of concern, studies have focused on the direct addition of oxidising agents such as Fenton reagents,

including hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), sodium persulfate ($Na_2O_8S_2$) (Neyens & Baeyens. 2003). However, filtration is rarely cited in relation to industrial wastewater and minimal research on the relationship of filtration methods and heavy metals in industrial stormwater has been recorded in the scientific literature (with S.E. Clark et al. 2004 a rare example); very few approaches even consider filtration as a viable treatment modality, although filtration generally, including biofiltration, is somewhat more common with general stormwater treatment approaches (Hatt et al. 2011).

In addition to standard chemical reagents for treating industrial wastewater, there is also growing interest and data on the use of chemical reagents derived from alumina refinery residue, both in its powdered form for use in direct addition and in a pelletised form for use in filtration. For example, this author has conducted research on a variety of industrial wastes which have been treated by chemical reagents derived from this form of residue (Fergusson. 2014a, 2014b, 2014c) and has addressed the broader sustainability issues surrounding its widespread application (Fergusson. 2014d). Similarly, Huang, et al. [2008], have researched its use in reducing phosphate in wastewater, and Burkov et al. (2012) have studied the role of alumina refinery residue (ARR) as a coagulant and absorbent in the treatment of galvanic wastewater contaminated with heavy metals.

Alumina refinery residue (ARR) is the primary byproduct of alumina refining (i.e., extracting alumina [Al_2O_3] from bauxite). ARR has several unique physical and chemical properties of relevance to this study. For example, unlike the simple ionic binding and precipitation reactions which occur through changes in pH associated with immobilizing chemicals such as $Ca(OH)_2$ and NaOH, the metals sequestered in ARR become more tightly bound as time passes. This phenomena is due to the fact that ARR is composed of a cocktail of positively and negatively charged metals and minerals, including hematite (Fe_2O_3), beohmite (γ-AlOOH), gibbsite ($Al[OH]_3$) and sodalite ($Na_4Al_3Si_3O_{12}Cl$), anatase (TiO_2), aragonite ($CaCo_3$), brucite ($Mg[OH]_2$), diaspore (ß-Al_2O_3.H_2O), ferrihydrite ($Fe_5O_7[OH]$.$4H_2O$), gypsum ($CaSO_4$.$2H_2O$), hydrocalumite ($Ca_2Al[OH]_7$.$3H_2O$), hydrotalcite ($Mg_6Al_2CO_3[OH]_{16}$.$4H_2O$), and p-aluminohydrocalcite ($CaAl_2[CO_3]_2[OH]_4$.$3H_2O$), which together cause long-term isomorphic substitution reactions, meaning the positively charged iron-, aluminium-, magnesium- and titanium-based molecules and negatively charged hydroxides in ARR not only initially adsorb metals but also lead to the long-term "sequestration" phenomena observed with inorganic species (Fergusson 2009).

Of significance also in these formulae is the presence of the acid hydroxides and oxyhydroxides which contribute to the acid neutralizing capacity (ANC) of ARR, both of which have low solubility and hence slow reactivity with acid. At least 48 hours are required for complete "on contact" reactions, and tests involving the addition of sulfuric acid to these reagents have shown that about 40% of the ANC of ARR reagents is exhausted in five minutes, about 70 % in four hours, and about 95 % in 24 hours (McConchie et al. 2000). Thus, the ability of minerals in ARR which sequester trace metals is time dependent; moreover, while most initial acid neutralization and metal sequestration reactions are completed within the first 24 hours, research has also shown that the longer these reagents are left in-situ the more tightly sequestered metals become, indicating that long-term co-precipitation and isomorphic substitution reactions are occurring at a molecular level, making reversibility of reactions difficult. Such findings suggest longer term and more sustainable outcomes compared to reactions precipitated by adsorption alone.

These and other relevant phenomena identified with ARR-derived reagents at metaliferous mine sites around the world have been discussed elsewhere (Fergusson. 2012), and applications utilizing these and related reagents in the treatment of coal waste and radioactive elements, such as radium, and in industrial site remediation and flue gas scrubbing to sequester mercury, for example, have also been examined (Clark et al. 2004, 2011; Fergusson. 2013; Hutson and Attwood. 2008) other core technical issues associated with ARR have been the subject of specialist scientific research (Taylor et al. 2011).

In order to better understand the role of filtration and ARR in the treatment of contaminated industrial stormwater, the present study asked the following research questions: 1) does the direct addition of chemical reagents derived from alumina refinery residue remove heavy metals from contaminated industrial stormwater; and 2) does a filter system, incorporating pelletised reagents derived from alumina

refinery residue, remove heavy metals from contaminated industrial stormwater?

2. Materials and methods

This three-part research was conducted in two phases. The first two experiments were laboratory experiments conducted on industrial stormwater samples at a private laboratory in Newcastle-upon-Tyne; the third was a field trial conducted at a site in the east of London. The contaminated stormwater used in all three experiments was generated as runoff from the smelter site, which is a producer and trader of base and minor metals, particularly lead and zinc, and a manufacturer of precious and semi-precious metal products which are exported abroad to markets in Asia. Due to manufacturing processes at the site, fine particulate lead, antimony and other metals are present as airborne dust, particularly when rotary kilns are in operation. For this reason, during first flush rain events, stormwater which collects on the hard-stand parking lots, loading bays and others impervious areas around the site becomes contaminated with these metals, albeit in relatively low concentrations. However, these concentrations of metals are enough to disqualify the collected stormwater from being automatically discharged to the local river without intervention, necessitating treatment of the first flush.

Moreover, these relatively low concentrations of airborne metals which form part of the stormwater profile are complemented with contamination of other metals derived from exposed solid waste at the site. These metals leach or dissolve in water during significant rain events, and co-mingle with stormwater runoff. Fig. 1 (left) provides photographic evidence of first flush stormwater at the site, as well as examples of the solid industrial waste which has accumulated at the site and is exposed to leaching or dissolution during storm events (right).

Fig. 1. First flush stormwater collecting on hard-stand areas at the smelter site (left) and solid lead waste on the ground at the smelter site (right).

Together, these heavy metal point (i.e., from solid on-site waste) and non-point (i.e., airborne metals) sources of contamination at the site are responsible for the presence of heavy metals in the industrial stormwater at the site, and together these two sources of metals result in concentrations which are greater than the allowable discharge limits for the site, as identified and imposed by the UK's Environment Agency.

As shown in Figure 2, a first flush at the site is channelled into two concrete-bunded collection and settling bays. In this figure accumulated particulate matter can be seen in the left-hand photograph in front of the bay, with both bays representing collection points for stormwater runoff. The accumulated first flush stormwater in each collection and settling bay is then pumped to its respective

olding lagoon, with two lagoons on the site, each with a holding capacity of about 500 kL of wastewater. The collection and settling bay in Fig. 2 (left) is pumped into lagoon #1 and the bay in Fig. 2 (right) is pumped into lagoon #2. Fig. 3 shows lagoon #1 (left) and lagoon #2 (right).

Fig. 2. Stormwater collection and settling bays, for lagoon #1 (left) and for lagoon #2 (right).

As they fill up, collected stormwater from the lagoons is pumped to an on-site centralized WTP, where it is treated using standard direct addition precipitation and coagulation agents, with solids separated using a filter press; treated water is discharged to an estuary in the nearby Thames River (which is out of site in Fig. 3, but adjacent to lagoon #2), with filtered solids (i.e., filter cake) disposed to nearby regulated landfill.

Fig. 3. Lagoon #1 (left) and lagoon #2 (right).

Test 1: Two x 20 L samples of storm water were collected from lagoons #1 and #2 and transferred to the laboratory in Newcastle-upon-Tyne. On inspection, both samples were a clear liquid with dark deposits but no odour, and both had a pH of 8.3. Pre-treated samples were analysed for pH, and for cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) using anodic stripping voltammetry, an analytical technique that involves (i) pre-concentration of the metal phase onto a solid electrode surface (or into liquid mercury) at negative potentials, and (ii) selective oxidation of each metal phase species during an anodic potential sweep (Franke & De Zeeuw. 1976). Pre-treatment analysis showed the lagoon #1 sample contained concentrations of 0.08 mg/L Cd, 0.7 mg/L Cu, 0.23 mg/L Pb, and 0.54 mg/L Zn; lagoon #2 sample contained concentrations of 0.7 mg/L Cd, 0.21 mg/L Cu, 1.4 mg/L Pb, and 0.17 mg/L Zn.

As shown in Table 1, after 8.0 ml/L hydrochloric acid (HCl) was added to each sample to adjust pH, both samples had a pH of 6.5 immediately prior to treatment; 3.0 g/L of a finely powdered reagent called ElectroBind was added directly to each sample and mixed vigorously for ten minutes.

Table 1. Results of direct addition laboratory experiment on contaminated industrial stormwater.

Parameter	Lagoon #1 Before Direct Addition	Lagoon #1 After Direct Addition	Percent Reduction (%)	Lagoon #2 Before Direct Addition	Lagoon #2 After Direct Addition	Percent Reduction (%)	Allowable Discharge Limit
pH	6.5	8.3	—	6.5	8.5	—	6.0-9.0
Cd (mg/L)	0.08	0.0008	99	0.07	0	100	0.03
Cu (mg/L)	0.07	0	100	0.21	0.01	95	0.1
Pb (mg/L)	0.23	0.004	98	1.4	0	100	1.0
Zn (mg/L)	0.54	0.003	99	0.17	0.001	99	0.5
Total average change	—	—	99	—	—	98	—

ElectroBind is a chemical reagent derived mostly (about 90 %) from ARR and has the same or similar physical and chemical properties to those contained in the description above for ARR, including a pH of approximately 9.5. After ten minutes, filtered samples were analysed for the above analytes.

Test 2: Sample quantities and methods of collection for Test 2 were the same as Test 1, however in this Test 2 lagoon #1 pre-treated samples were analysed for pH, Cd, Cu, Pb, Zn as well as arsenic (As) and antimony (Sb) using anodic stripping voltammetry, while those of lagoon #2 were only analysed for pH, Cd, Cu, Pb and Zn. Pre-treatment analyses in the Test 2 showed that lagoon #1 and lagoon #2 samples contained metal concentrations consistent with Test 1, in addition to 0.64 mg/L As and 4.6 mg/L Sb for lagoon #1.

After the same HCl adjustment described in Test 1, both samples were passed through a gravity fed, trickling filter column containing a pelletised version of ElectroBind; chemical additives to the alumina refinery residue included calcium-based strengthening agents, as well as binders and so-called "blowing agents" which designed to increased pellet porosity. The volume of the column was 3.0 L or 3,000 cm^3. Each filter had a 0.25 bed volume/hour (bV/hr), i.e., a hydraulic retention time (HRT) of four hours.

Test 3: Between conducting Test 2 and Test 3, management at the smelter site determined that arsenic (As), antimony (Sb) and nickel (Ni) were also likely contaminants in on-site stormwater; these thee metals were therefore added to the suite of analytes for the field trial. Stormwater effluent from lagoon #1 was delivered to an on-site baffle weir and filter system after a first flush rain event. This pre-treated effluent was analysed for pH, As, Cd, Cu, Ni, Pb, Sb and Zn using anodic stripping voltammetry. The baffle weir consisted of a standard plastic-lined holding weir with seven baffles through which effluent flowed (see Figure 4, left); in the baffle weir, effluent was pre-treated for five minutes with 6.0 ml/L of HCL and 2.0 mg/L ferrous sulphate (pH = 3.0) to lower pH and add Fe ions to aid in the removal of As and Sb, both of which prior research had suggested were not readily amendable to cation exchange with standard chemicals or ARR. After pre-treatment in the baffle weir, effluent was pumped to the filter system via a calibrated peristaltic pump.

The filter system was composed of a 50 L (or 50,000 cm^3) column containing ElectroBind pellet media (see Figure 4, right). Effluent pH was 9.2 at the static feed-head of the filter system, which was designed to use trickling mode at 0.25 bV/hr, resulting in an HRT of approximately four hours. The filter system was run with fresh water for four hours prior to the delivery of lagoon effluent.

Due to the static feed-head, initial effluent distribution proved to be inefficient in dispersing liquid evenly across the entire filter head, and was therefore changed to a rotating arm-type filter head, as shown in Fig. 4 right. At the same time, a floating boom and gravel roughing filter were fitted at the filter head to help alleviate solids which were visibly present in the effluent. When the trial was restarted with these two modifications, pH adjustment was stopped in the weir so that inlet effluent pH to the filter column was approximately pH 9.2. The filter system during the field trial operated for one month, with approximately four significant rain events during the course of the trial.

The allowable discharge limits (or so-called "consent levels") for pH and metals to the Thames estuary from the smelter site, as determined and mandated by the UK Environment Agency, were: pH = 6.0-9.0; As ≤ 0.1 mg/L; Cd ≤ 0.03 mg/L; Cu ≤ 0.1 mg/L; Ni ≤ 0.1 mg/L; Pb ≤ 1.0 mg/L; Sb ≤ 0.5 mg/L; and Zn ≤ 0.5 mg/L.

3. Results and discussion

Test 1: Table 1 presents the results of Test 1. This table shows that Cd and Zn in lagoon #1 sample and the presence of Cd, Cu and Pb in lagoon #2 sample were above the allowable discharge limits for the site.

Table 1 also indicates that the direct addition of ElectroBind increased pH from 6.5 to 8.3 and 8.5 respectively for lagoons #1 and #2, and in all instances reduced metals significantly. In lagoon #1 sample, Cd decreased from 0.08 mg/L to 0.0008 mg/L, a 99 % reduction, Cu decreased from 0.07 mg/L to 0.0 mg/L, a 100 % reduction, Pb decreased from 0.23 mg/L to 0.004 mg/L, a 98 % reduction, and Zn decreased from 0.54 mg/L to 0.003 mg/L, a 99% reduction, for a total average reduction of 99%. In lagoon #2 sample, Cd decreased from 0.07 mg/L to 0.0 mg/L, a 100% reduction, Cu decreased from 0.21 mg/L to 0.01 mg/L, a 95% reduction, Pb

decreased from 1.4 mg/L to 0.0 mg/L, a 100% reduction, and Zn decreased from 0.17 mg/L to 0.001 mg/L, a 99% reduction, for a total average reduction of 98%. All results were within the allowable discharge limits for the site, with instrumentation detection limits of 0.005 mg/L for Zn, and 0.01 mg/L for all other metals.

Fig. 4. Baffle weir used during the field trial (left) and close up photograph of effluent inlet and roughing filter at the feed-head, rotating filter head, and pelletised filter media in the filter column (right).

The results of Test 1 indicate that pH can be adjusted and all heavy metals, including Cd and Zn which were above allowable discharge limits prior to treatment in this study, can be reduced to required levels for approved discharge to the Thames estuary when directly adding ElectroBind reagent, a product derived from alumina refinery residue, to contaminated industrial stormwater. Therefore, research question 1 is answered in the affirmative. Results indicate that heavy metals were reduced by an average of 98 % across all metals for both lagoons. This result is likely the first time that a chemical reagent of this type has been so reported for direct addition to stormwater.

Test 2: Table 2 presents the results of Test 2. As noted above for Test 1, the presence of Cd and Zn in lagoon #1 sample and the presence of As, Cd, Cu, Pb and Sb in lagoon #2 sample were above allowable discharge limits for the site.

The filtration of contaminated stormwater using a filter consisting of an ElectroBind pelletised media increased pH from 6.5 to 11.2 and 9.8 respectively for lagoons #1 and #2, both of which were outside allowable discharge limits. However, metals were significantly reduced in all cases. In lagoon #1 sample, As decreased from 0.64 mg/L to 0.1 mg/L an 85% reduction, Cd decreased from 0.08 mg/L to 0.007 mg/L, a 91 % reduction, Cu decreased from 0.07 mg/L to 0.02 mg/L, a 71 % reduction, Pb decreased from 0.23 mg/L to 0.002 mg/L, a 99 % reduction, Sb decreased from 4.6 mg/L to 0.02 mg/L, a 99 % reduction, and Zn decreased from 0.54 mg/L to 0.003 mg/L, a 99 % reduction, for a total average reduction on 91 %. In lagoon #2 sample, Cd decreased from 0.07 mg/L to 0.0009 mg/L, a 98 % reduction, Cu decreased from 0.21 mg/L to 0.01 mg/L, a 93 % reduction, Pb decreased from 1.4 mg/L to 0.01 mg/L, a 99 % reduction, and Zn decreased from 0.17 mg/L to 0.0007 mg/L, a 99 % reduction, for a total average reduction on 97 %. All results for heavy metals were at or below the allowable discharge limits for the site, with instrumentation detection limits of 0.001 mg/L for as, 0.005 mg/L for Zn, and 0.01 mg/L for all other metals.

The results of Test 2 indicate that filtering stormwater using a filter column containing ElectroBind pellets increased effluent pH to levels above allowable discharge limits for both lagoons #1 and #2. However, the results also indicate that heavy metals, including As, Cd, Cu, Pb, Sb and Zn which were above allowable discharge levels prior to treatment in this study, can be reduced to required levels for approved discharge to the Thames estuary when using ElectroBind in a filter system. Results indicate that heavy metals were reduced by an average of 94 % across all metals in both lagoons. Therefore, research question 2 is answered in the affirmative. This result is also likely the first time that a pelletised chemical reagent of this type has been so reported for treating stormwater using a trickling filter.

Test 3: Table 3 presents the average result of 30 data points obtained over one month in Test 3. Pre-treated lagoon #1 stormwater effluent had a pH of 9.2, which is marginally above the allowable discharge limit, and the presence of As, Cd, Cu, Pb, Sb and Zn in the effluent, as delivered to the filtration system, were also above the allowable discharge limits for the site.

The filtration of contaminated stormwater using a filter consisting of an ElectroBind pelletised media decreased pH from 9.2 to 7.4, which was within the allowable discharge limit, and all metals were reduced: As decreased from 0.34 mg/L to below the detection limit, a 100 % reduction, Cd decreased from 0.14 mg/L to 0.02 mg/L, an 86 % reduction, Cu decreased from 0.18 mg/L to 0.02 mg/L, an 89 % reduction, Ni decreased from 0.03 mg/L to 0.02 mg/L, a 33 % reduction, Pb decreased from 4.5 mg/L to 0.06 mg/L, a 99 % reduction, Sb decreased from 9.3 mg/L to 0.5 mg/L, a 95 % reduction, and Zn decreased from 1.5 mg/L to 0.16 mg/L, a 90 % reduction, for a total average reduction on 84 %. All results for heavy metals were at or below the allowable discharge limits for the site.

Of relevance also was the observation that for the duration of the field trial the removal efficiency of the pelletised media did not decline; in other words, the averages presented in Table 3 fairly represent removal efficiency of the filter system at the beginning and end of the field trial. This finding was surprising given that metal loadings on the media were accumulating throughout the trial, particularly when the rotary furnaces at the site were in operation during rain events.

The results of Test 3 indicate that filtering stormwater using a system containing ElectroBind pellets decreased effluent pH to levels which are within allowable discharge limits for lagoon #1. Results also indicate that heavy metals, including As, Cd, Cu, Ni, Pb, Sb and Zn, which were above allowable discharge levels prior to treatment in this study, can be reduced to required levels for approved discharge to the Thames estuary when using ElectroBind pellets in a filter system. Results indicate that heavy metals were reduced by an average of 84 % across all metals for lagoon #1. Therefore, along with Test 2, the results of Test 3 also mean research question 2 can be answered in the affirmative.

Further work needs to be conducted to determine the most effective and commercially viable way to reduce pH in contaminated industrial stormwater. The use of waste acid from the site (if available) or modifications to acid dosing levels need to be further examined. As the pelletised form of ElectroBind also contains calcium-based additives, these may need to be modified or the alumina refinery residue may need to be treated prior to use in this type of application, in order to address the issue of elevated pH in filtered water.

Table 2. Results of filtration laboratory experiment on contaminated industrial stormwater.

Parameter	Stormwater from Lagoon #1 Before Filtration	Stormwater from Lagoon #1 After Filtration	Precent Reduction (%)	Allowable Discharge Limit
pH	9.2	7.4	—	6.0-9.0
As (mg/L)	0.34	BDL	100	0.1
Cd (mg/L)	0.14	0.02	86	0.03
Cu (mg/L)	0.18	0.02	89	0.1
Ni (mg/L)	0.03	0.02	33	0.1
Pb (mg/L)	4.5	0.06	98	1.0
Sb (mg/L)	9.3	0.5	95	0.5
Zn (mg/L)	1.5	0.16	90	0.5
Total average change	—	—	84	—

Table 3. Results of filtration field trial on contaminated industrial stormwater.

Parameter	Stormwater from Lagoon #1 Before Filtration	Stormwater from Lagoon #1 After Filtration	Precent Reduction (%)	Allowable Discharge Limit
pH	9.2	7.4	—	6.0-9.0
As (mg/L)	0.34	BDL	100	0.1
Cd (mg/L)	0.14	0.02	86	0.03
Cu (mg/L)	0.18	0.02	89	0.1
Ni (mg/L)	0.03	0.02	33	0.1
Pb (mg/L)	4.5	0.06	98	1.0
Sb (mg/L)	9.3	0.5	95	0.5
Zn (mg/L)	1.5	0.16	90	0.5
Total average change	—	—	84	—

Moreover, as discussed above, the longer heavy metals are sequestered in the ElectroBind solid pellet matrix the more tightly bound they become, with the strength of ionic bonds increasing by as much as 40 % every six months after the pellets have been saturated with soluble metals (Fergusson. 2009). Thus, the "spent" ElectroBind pellets removed from the filtration system after use would likely be classified as "inert" and non-hazardous, and could therefore be disposed without difficulty. For these reasons, the class of chemical reagents of which ElectroBind is a part have been identified as a sustainable waste treatment solution; they not only address the problem of treating heavy metal-laden contaminated wastewater, in this case industrial run-off, but do not result in the production of another kind of waste. In other words, rather than merely transferring or converting one form of waste into another form of waste—solving the problem of contaminated wastewater but creating another problem of contaminated waste solids, for example—these reagents provide a practical method of addressing both the immediate and long-term

problem of industrial waste. As the pelletised media also has the potential to be used in cementitious pavers, bricks and concrete, in future research it may be worth considering its use as a pervious concrete for stormwater treatment, as discussed by Weidner et al. (2012).

4. Conclusion

Further research on a number of topics is warranted. For example, research is needed to determine filter breakthrough (i.e., the point at which the filter system no longer neutralises acid or binds metals). While breakthrough did not occur during this one-month trial but may have occurred in the second or third months, when and under what conditions it will do so need to be examined more closely. If filter breakthrough occurs too early in the filtration cycle, it may make this method for treating contaminated industrial stormwater unviable and therefore commercially and operationally unattractive. Similarly,

research on bed volumes and HRT, unit processes and life of the filter system, cost of the filter system, and other related topics will be important if this method can be justified outside laboratory and field trial conditions.

A thorough and more rigorous stormwater management and treatment system would require something more than a mere filter system to effectively counter the polluting effects of high-volume stormwater at an operating industrial site. For example, Moeller (2005) has identified the various elements of a sustainable stormwater management and mitigation program, including identifying and defining the nature and scope of the problem, identifying site characteristics and constraints, evaluating watershed constraints, evaluating water quality conditions, selecting suitable hydrologic controls and unit processes, selecting suitable chemical, biological and/or physical treatment systems, among other elements. Such an in-depth and comprehensive approach to industrial stormwater would more comprehensively approach some of the questions left unanswered by this research.

To further highlight this point, metals in urban runoff can occur as dissolved, colloidal and particulate-bound species, although most are present as dissolved ions or ions bound to particulates. Therefore, it will be important in future research to measure all forms of heavy metals in industrial stormwater, especially the particulate and filterable fractions, when determining their properties, fate and long-term effects on the environment. Moreover, principles of sustainable urban development require that industrial stormwater management plans should not be considered in isolation of other urban considerations, but should form part of an integrated water strategy which would include general water use and supply, litter management, and reuse of alternate water sources (e.g., City of Whittlesea, 2012).

However, for the purposes of this preliminary study, the focus on these three novel treatment methods, including filtration, was warranted and further research would generate a clearer understanding of the relationship between direct addition of chemical reagents and filtration, between contaminated industrial stormwater and heavy metals, and between each of these factors and the use of filtration systems using pelletised media derived from alumina refinery residue.

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