# Removal of heavy metals from urban stormwater runoff using different filter materials

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ABSTRACT

Heavy metals wash from tires, automobile exhausts, road asphalt, fuel combustion, parking dust, and recreational land into urban stormwater runoff and its subsequent discharge into surface and subsurface water sources can create public health and environmental hazards. An in-ground permeable reactive filter system is proposed to treat contaminated urban stormwater. However, the filter materials should be carefully selected. Several series of batch experiments were conducted with synthetic stormwater containing individual metal contaminants at different concentrations to determine the adsorption and removal behavior of four potential permeable inorganic filter materials (calcite, zeolite, sand, and iron filings) for six common toxic heavy metal contaminants (Cd, Cu, Pb, Ni, Cr, and Zn). The adsorbed metals, pH, oxidation–reduction potential and electrical conductivity of batch samples were determined. Isotherm modeling was performed to assess the mechanisms and quantify the adsorption of each filter material for the contaminants. The extent of adsorption and removal of metals was found to depend on the type and concentration of metal as well as the filter material. Langmuir or Freundlich isotherm proved best to describe the metal adsorption behavior. The maximum removal rates achieved for individual metals were: 95–100% Cd, Cu, Pb and Zn by calcite, zeolite and iron filings, 90% Ni by zeolite, and 100% Cr by iron filings. Sand produced low results with maximum levels of 8–58%. Based on the maximum adsorption capacity of each filter material, the typical filter size and volume of stormwater that can be treated were estimated. No single filter material was capable of removing all metals to the maximum extent; therefore, a combination of filter materials should be investigated for the simultaneous removal of multiple heavy metals.

## Introduction

Stormwater runoff washes pollutants such as nutrients, heavy metals and organic chemicals off of parking lots, parks, lawns, and other recreational centers and discharges the pollutants directly to the lakes in the Great Lakes region [1]. In particular, the major sources of heavy metals in urban-runoff are tires, automobile exhaust, road asphalt, fuel combustion, parking dust and also other pollutants left on recreational land. Such non-point contaminant sources are the main contributors of water pollution of many lakes [2]. Several research studies have found significant levels of heavy metals such as Cd, Cu, Pb, Ni, Cr, and Zn in urban stormwater, which poses harm to public health and the environment. Concentrations of heavy metals in stormwater runoff vary highly between locations. For instance, Davis et al. [3] found high levels of Pb concentrations in run-off from painted structures. Davis et al. [4] examined availability of heavy metal from various sources in

developed areas and found Cu originating from vehicle brakes, Zn from tire wear, and Pb, Cu, Cd, and Zn attributed to building siding runoff. Since heavy metals do not degrade, their removal from stormwater runoff has been a main remedial strategy in recent years.

Several best management practices (BMPs) have been developed to manage the different types of pollution found in stormwater [5–7]. Several BMPs allow the removal of pollutants and particulates [8]. Sedimentation is a well-known BMP that is used for the removal of metals and particulates [9]. In certain cases, sedimentation is quite effective especially if followed with a filtration method. Gallagher et al. [10] removed over 90% of Cu using the sedimentation method. However, they found that dissolved Cu persisted, thus making the sedimentation method inadequate. Additionally, in urban areas, it may not be possible to implement sedimentation methods simply due to the lack of adequate space that is needed for the sedimentation infrastructure. Under such situations, permeable filter systems consisting of adsorptive media have great potential to be effective and practical [11].

An in-ground permeable filter system is proposed to treat the urban stormwater runoff found near the beaches along the Lake

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Michigan in Chicago, IL [11]. The purpose of this filter system is to remove a wide range of contaminants common to urban stormwater and thereby prevent the contamination of beaches and protect the public and environment. Permeable, environmentally benign, adsorptive/reactive, easily available, less costly, and easily replaceable materials should be used in the filter systems [11].

This study investigates the four potential filter materials (calcite, zeolite, sand, and iron filings) to adsorb and remove six heavy metals (Cd, Cu, Pb, Ni, Cr, and Zn) from urban stormwater run-off. Several series of batch experiments were conducted using each filter material with synthetic stormwater containing individual metal contaminants at different concentrations. The extent of adsorption and removal of metals, and the pH, oxidation–reduction potential (ORP) and electrical conductivity (EC) of batch samples were determined. Isotherm modeling was performed to assess the mechanisms and quantify the adsorption of each filter material for the metal contaminants. The results of this study contributed to the understanding of the size and treatment capacity of the proposed in-ground permeable filter systems.

## Materials and methods

### Filter materials

Based on the published literature and preliminary column testing, four filter materials were selected for this study: calcite (limestone), zeolite, sand, and iron filings [11]. Calcite (limestone) is a sedimentary rock composed mostly of mineral calcite with varying crystal forms of calcium carbonate ($CaCO_3$) [12]. The calcite sample was acquired from DuPage Water Conditioning, West Chicago, IL. Natural zeolites are formed in basaltic lava, in specific rocks that are subjected to moderate geologic temperature and pressure [13]. The zeolite used for this study was from Bear River Zeolite Co., Inc., Preston, ID. Sand is a natural granular material with highly variable composition that depends on the local rock source and processing conditions. White Ottawa Silica sand composed of silicon dioxide ($SiO_2$) received from U.S. Silica Company, Ottawa, IL was used for this study. Iron filings are mostly a byproduct of the grinding, filing, or milling of finished iron products and this sample was obtained from Connelly-GPM, Inc., Chicago, IL.

All of the filter materials, as received from the suppliers, were air-dried and then washed with deionized water on sieve #40 to remove any very fine fraction that otherwise could increase the measure of total suspended solids in the treated stormwater. Then, filter materials were placed in the oven at 105 °C overnight to dry completely. The washed filter materials were tested to characterize the physical properties and hydraulic conductivity based on the American Society of Testing and Materials (ASTM) standard testing procedures [14]. Particle-size distribution of filter materials was determined by mechanical sieve analysis (ASTM D422). Water content and specific gravity were tested as per ASTM D2216 and D 854, respectively. A muffle furnace run at a temperature of 440 °C was used to determine the organic content of filter materials (ASTM D2974). Hydraulic conductivity of filter materials was measured using the constant-head permeability test method (ASTM D4972), and the standard method was used to determine the pH, ORP and EC of the filter materials (ASTM D1293). Scanning electron micrographs of the filter materials were also obtained to examine their structure and morphology.

### Heavy metals

Six heavy metals, specifically Zn, Cu, Pb, Cr, Ni, and Cd, were selected for this study. The concentrations of these heavy metals were based on the typical high level concentrations found in stormwater run-off. Those concentrations and the source chemicals used to prepare synthetic stormwater were: 30 mg/L Cd using $CdSO_4$; 5 mg/L Cr using $K_2CrO_4$; 5 mg/L Cu using $Cu(SO)_4$; 50 mg/L Pb using $PbCl_2$; 100 mg/L Ni using $NiCl_2$; and 50 mg/L Zn using $ZnSO_4$. All of the metals were in divalent cationic form except for chromium as it exists in anionic complex as $Cr^{6+}$. Additional tests were conducted at concentrations of one-half, five times and ten times the typical concentrations for each metal to assess the effects of concentration and the adsorption capacity of the filter materials.

### Batch experiments

Batch experiments are used to evaluate the metal removal efficiency of each of the filter materials at each concentration. The level of contaminant removal can depend on the amount of metal originally present and the length of exposure. Batch experiments were performed with different initial concentrations of metals (ranging from 15 to 300 mg/L for Cd, 2.5 to 50 mg/L for Cu, 25 to 500 mg/L for Pb, 50 to 1000 mg/L for Ni, 2.5 to 50 mg/L for Cr, and 25 to 500 mg/L for Zn), but the same exposure time of 24 h was used for all tests. The 24-h time period was found to be adequate to achieve equilibrium conditions in all of the test conditions, thus the maximum removal efficiency under different initial concentrations can be assessed [11]. Batch tests were conducted with each metal separately with the goal of identifying effective filter materials for removal of each metal. The ultimate, overreaching goal is to identify filter materials individually and in combination that can remove mixed pollutants from stormwater runoff [11].

The test procedure consisted of placing a known dry mass of filter materials ($M$) into a glass bottle containing a known volume of each metal solution ($V$) with a known initial concentration ($C_0$). The filter material and metal solution samples were mixed for 24 h in a mechanical tumbler at room temperature to reach equilibrium concentration. The supernatant was separated and the final equilibrium concentration of the metal in the solution ($C_{eq}$) was determined. The difference in the initial and final solution concentrations at equilibrium condition was used to determine the mass of the metal adsorbed per unit of the dry mass of filter material ($S$) using:

$$S = \frac{V \times (C_0 - C_{eq})}{M} \tag{1}$$

The metal removal efficiency was calculated using:

$$\text{Removal Efficiency } (\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \tag{2}$$

For each batch test, 10 grams of the selected filter material and 100 mL of the prepared metal solution were combined in a wide-mouth glass bottle. Bottles were sealed with screw caps and thoroughly mixed in a tumbler at room temperature for 24 h. After 24 h, samples were filtered through a Whatman GF/C filter and the filtrate was transferred to an empty glass bottles. The filtrate was analyzed for metal concentration, pH, ORP, and EC. All batch tests were performed in duplicate to ensure repeatability. To ensure accuracy, control batch tests were conducted on samples containing only the individual metal solution with no filter materials as well as samples containing 10 g of each filter material in deionized water with no metal contaminant.

### Analytical methods

The pH, ORP and EC of filtered samples were measured in accordance with the ASTM standard test methods D1293, D1498 and D1125, respectively [14]. The pH was measured using an Orion model 720A pH meter. The pH probe was inserted into the sample and pH value was recorded after the electrode stabilized. The ORP

**Table 1**
Properties of filter materials.

| Filter material | Effective particle size, D10 (mm) | Average particle size, D50 (mm) | Dry density (g/cm$^3$) | Organic content (%) | pH | Oxidation–reduction potential (mV) | Electrical conductivity (mS/cm) | Hydraulic conductivity $K$ (cm/s) |
|---|---|---|---|---|---|---|---|---|
| Calcite | 0.5 | 0.7 | 1.6 | 0.0 | 9.0 | −117.1 | 0.01 | 0.3 |
| Zeolite | 0.6 | 1.2 | 1.0 | 6.8 | 7.8 | −58.0 | 0.10 | 0.4 |
| Sand | 0.5 | 0.6 | 1.8 | 0.3 | 8.4 | −95.3 | 0.02 | 0.3 |
| Iron filings | 0.5 | 0.9 | 2.3 | 0.0 | 5.3 | 87.6 | 30.5 | 0.6 |

and EC of each sample were measured in the same manner using the appropriate electrodes. The metal concentrations in all of the control and filtered samples were analyzed using atomic absorption spectrophotometer (AAS) in accordance with the USEPA method 7130 for Cd, 7190 for Cr, 7210 for Cu, 7420 for Pb, 7520 for Ni, and 7950 for Zn [15]. All of the samples were analyzed in duplicate to ensure accuracy and repeatability. All of the data obtained through the batch tests were statistically treated for analysis of variance using SigmaPlot software.

## Results and discussion

### Filter materials properties

Table 1 summarizes the properties of the filter materials. The particle size distribution of filter materials is shown in Fig. 1. Particle size analysis showed that all of the materials are uniformly graded similar to typical uniform sand, with the same effective particle size of 0.5–0.6 mm and that the average particle size was the highest for zeolite (1.2 mm) and lowest for sand (0.6 mm). The particle sizes were larger in the filter material as follows: zeolite > iron filings > calcite > sand. The filter materials were washed through Sieve #200 (0.075 mm) and dried. As a result, no fine particles existed in any of the filter materials. The fines were removed so that they would not increase the total suspended solids found in the treated stormwater exiting the filter system.

Zeolite had dry density of 1 g/cm$^3$, while calcite and sand had similar dry density of 1.6–1.8 g/cm3. Iron filings had very high density of 2.3 g/cm3. Organic content as measured by loss-on-ignition was 6.8% in zeolite and 0.3% in sand and other materials were free of any organic matter. The pH of iron filing was slightly acidic (pH 5.3), zeolite and sand were slightly alkaline (pH 7.8–8.4), and calcite was highly alkaline (pH 9.0). EC values for sand, calcite, and zeolite were low (0.024–0.1 mS/cm) as a result of removal of fines and was moderate for iron filings (30.5 mS/cm). The ORP values show the existence of low redox conditions, which may

affect the electrochemical reduction of metals, especially Cr$^{+6}$. The scanning electron micrographs for the filter materials shown in Fig. 2 reveal the porous structure of the materials, which results in high porosity of these materials. As a result of high porosity, the hydraulic conductivity of the filter materials was high, ranging from 0.3 to 0.6 cm/s. The high hydraulic conductivity is a prerequisite for the filter material in order to allow the high flow rate that may exist in the filters during storm events.

### Initial chemistry of contaminant solutions and filter materials

Control batch tests were conducted using metal solutions at different concentrations without filter materials. Moreover, control tests were conducted with each filter material using deionized water alone (i.e., without metal solution). These tests allowed characterization of the initial chemistry of the contaminant solutions as well as filter materials. These tests also allowed an investigation of the accuracy of the measurements of the metal concentrations and loss of metals due to experimental methods as well as a comparison of the changes in solution chemistry in the presence of filter materials and/or the metal solutions. The pH, ORP and EC results of these control tests are shown in Table 2(a)–(f). The results showed good reproducibility and that the metal measurement errors and metal losses due to experimental methods are within acceptable limits and will not bias the batch tests that evaluate the relative effectiveness of the filter material for the removal of these heavy metals.

The pH, ORP and EC of deionized water and the individual metal contaminant solutions at different concentrations and without any filter media shown in Table 2 (labeled "None") are helpful in the assessment of the initial chemistry of the contaminant solutions (simulated stormwater with different concentrations). Table 2(a), the batch tests with Cd solutions of different concentrations without filter materials, shows that the pH ranged from 4.9 to 5.3, ORP ranged from 90.6 to 111.7 mV and EC ranged from 34.4 to 77 mS/cm. There was slight decrease in pH and increase in both
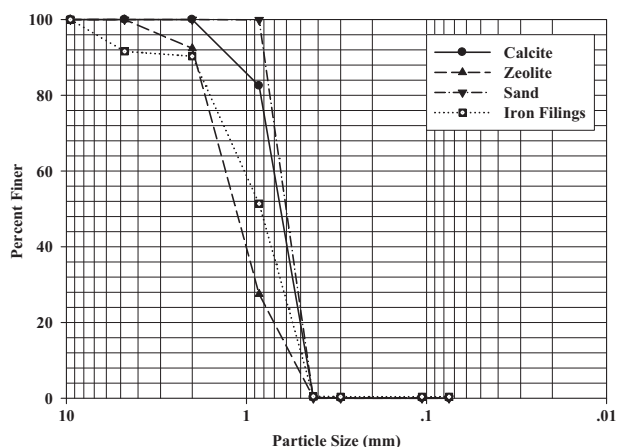


**Fig. 1.** Particle size distribution of filter materials.
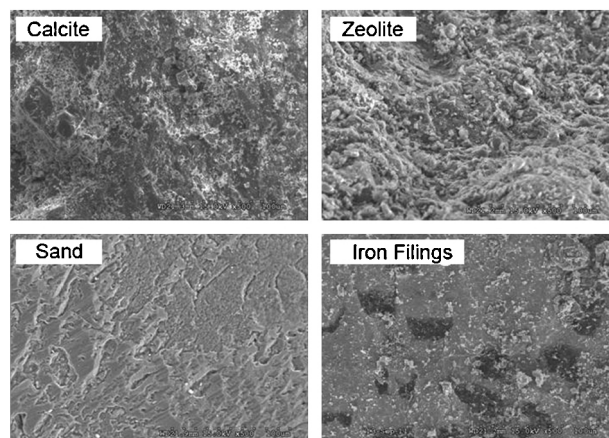


**Fig. 2.** Scanning electron micrographs of filter materials (magnification 100×).

**Table 2**
pH, ORP, and EC variation in metal batch experiments using different filter materials.

| Parameters | 0.5 × Typical conc. | | | Typical conc.[a] | | | 5 × Typical conc. | | | 10 × Typical conc. | | | Deionized water | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH | ORP (mV) | EC (mS/cm) | pH | ORP (mV) | EC (mS/cm) | pH | ORP (mV) | EC (mS/cm) | pH | ORP (mV) | EC (mS/cm) | pH | ORP (mV) | EC (mS/cm) |
| **(a) Cd** | | | | | | | | | | | | | | | |
| None[b] | 5.3 | 90.6 | 34.4 | 5.2 | 98.3 | 45.9 | 5.1 | 102.0 | 52.6 | 4.9 | 111.7 | 77.0 | 5.5 | 69.1 | 11.3 |
| Calcite | 8.5 | −96.2 | 0.1 | 7.2 | −21.2 | 0.4 | 6.4 | 25.5 | 2.7 | 6.3 | 30.3 | 3.2 | 9.3 | −152.2 | 0.003 |
| Zeolite | 7.9 | −59.8 | 0.1 | 7.5 | −38.3 | 0.2 | 7.0 | −11.0 | 0.6 | 6.7 | 6.8 | 1.3 | 7.9 | −49.2 | 0.2 |
| Sand | 6.1 | 47.1 | 6.3 | 5.9 | 53.7 | 8.1 | 5.8 | 62.4 | 11.4 | 5.5 | 77.8 | 20.7 | 7.0 | −9.1 | 0.7 |
| Iron filings | 6.2 | 37.8 | 4.2 | 5.8 | 59.3 | 10.4 | 4.8 | 123.3 | 122.0 | 4.5 | 135.0 | 190.5 | 6.8 | 2.1 | 1.1 |
| **(b) Cu** | | | | | | | | | | | | | | | |
| None[b] | 6.0 | 59.9 | 10.3 | 5.7 | 68.3 | 14.3 | 5.7 | 69.5 | 14.8 | 5.5 | 88.4 | 30.7 | | | |
| Calcite | 8.5 | −106 | 0.02 | 8.3 | −88.2 | 0.04 | 7.9 | −63.6 | 0.1 | 7.7 | −56.4 | 0.1 | | | |
| Zeolite | 8.2 | −82.9 | 0.04 | 8.1 | −75.8 | 0.1 | 7.7 | −51.7 | 0.1 | 7.4 | −31.7 | 0.3 | | | |
| Sand | 6.6 | 15.2 | 1.8 | 6.2 | 38.1 | 4.7 | 5.6 | 72.3 | 16.6 | 5.7 | 70.7 | 15.5 | | | |
| Iron filings | 7.2 | −21.0 | 0.5 | 6.1 | 34.0 | 3.9 | 5.5 | 80.8 | 34.9 | 5.0 | 113.0 | 82.4 | | | |
| **(c) Pb** | | | | | | | | | | | | | | | |
| None[b] | 5.8 | 61.3 | 11.0 | 5.7 | 68.3 | 14.1 | 5.4 | 89.2 | 31.9 | 5.4 | 91.9 | 35.6 | | | |
| Calcite | 8.2 | −80.4 | 0.2 | 7.6 | −47.5 | 0.2 | 7.7 | −52.1 | 0.1 | 7.6 | −44.3 | 0.2 | | | |
| Zeolite | 7.7 | −51.9 | 0.1 | 7.7 | −50.7 | 0.1 | 7.3 | −25.8 | 0.4 | 7.1 | −16.4 | 0.5 | | | |
| Sand | 5.9 | 58.2 | 9.5 | 5.8 | 65.1 | 12.7 | 5.5 | 81.4 | 23.9 | 5.4 | 86.0 | 29.1 | | | |
| Iron filings | 5.6 | 77.1 | 20.2 | 4.8 | 126.2 | 137.0 | 4.2 | 159.8 | 510.5 | 4.3 | 155.9 | 463 | | | |
| **(d) Ni** | | | | | | | | | | | | | | | |
| None[b] | 5.4 | 85.5 | 27.8 | 5.2 | 98.4 | 43.1 | 5.5 | 84.0 | 26.1 | 5.1 | 102.7 | 53.8 | | | |
| Calcite | 7.9 | −61.4 | 0.1 | 7.7 | −52.3 | 0.1 | 7.6 | −45.7 | 0.2 | 7.7 | −50.2 | 0.1 | | | |
| Zeolite | 7.7 | −50.6 | 0.1 | 7.4 | −36.0 | 0.2 | 7.1 | −13.7 | 0.6 | 6.9 | −6.7 | 0.8 | | | |
| Sand | 6.3 | 29.2 | 3.1 | 6.0 | 48.7 | 6.5 | 5.8 | 58.5 | 9.2 | 5.8 | 60.0 | 10.1 | | | |
| Iron filings | 4.1 | 163 | 572.5 | 4.0 | 166.0 | 635.0 | 4.2 | 157.5 | 458.0 | 4.2 | 152.7 | 381 | | | |
| **(e) Cr** | | | | | | | | | | | | | | | |
| None[b] | 6.4 | 24.7 | 2.6 | 6.6 | 13.7 | 1.7 | 7.3 | −28.1 | 0.3 | 7.6 | −47.9 | 0.2 | | | |
| Calcite | 9.5 | −162 | 0.002 | 9.6 | −163.0 | 0.002 | 9.6 | −164.2 | 0.002 | 9.6 | −164.0 | 0.002 | | | |
| Zeolite | 8.1 | −76.4 | 0.1 | 7.8 | −54.9 | 0.1 | 7.9 | −62.6 | 0.1 | 7.8 | −59.9 | 0.1 | | | |
| Sand | 6.5 | 17.9 | 2.0 | 6.8 | 5.4 | 1.2 | 7.4 | −31.8 | 0.3 | 7.7 | −52.5 | 0.1 | | | |
| Iron filings | 7.6 | −46.0 | 0.2 | 9.2 | −140.7 | 0.004 | 10.5 | −214.9 | 0.0003 | 10.1 | −189.7 | 0.001 | | | |
| **(f) Zn** | | | | | | | | | | | | | | | |
| None[b] | 6.3 | 27.4 | 2.9 | 5.9 | 54.4 | 8.3 | 5.8 | 61.0 | 10.7 | 5.9 | 60.4 | 10.5 | | | |
| Calcite | 7.9 | −3.8 | 0.1 | 7.8 | −54.7 | 0.1 | 7.1 | −16.2 | 0.5 | 6.8 | 2.3 | 1.1 | | | |
| Zeolite | 7.4 | −32.8 | 0.1 | 7.3 | −25.1 | 0.4 | 6.7 | 6.8 | 1.3 | 6.5 | 19.3 | 2.1 | | | |
| Sand | 5.8 | 58.8 | 9.8 | 5.8 | 62.9 | 12.4 | 5.7 | 67.1 | 12.8 | 6.3 | 39.5 | 4.7 | | | |
| Iron filings | 7.6 | −46.0 | 0.2 | 9.2 | −140.7 | 0.004 | 10.5 | −214.9 | 0.0 | 10.1 | −189.7 | 0.001 | | | |

[a] Typical concentrations used in this study: Cd: 30 mg/L; Cr: 5 mg/L; Cu: 5 mg/L; Pb: 50 mg/L; Ni: 100 mg/L; Zn: 50 mg/L.
[b] None = no filter material present.

ORP and EC with the increase in the concentration of Cd. The results with Pb, Cu and Zn followed the same trend as that of the Cd solution. The pH was reduced from 5.8 to 5.4, ORP increased from 61.3 to 91.9 mV and EC increased from 11 to 35.6 mS/cm for Pb solutions, while the pH ranged from 5.5 to 6, ORP ranged from 59.9 to 88.4 mV and EC ranged from 10.3 to 30.7 mS/cm for the Cu solutions. Also, the pH of the Zn solutions slightly decreased from 6.3 to 5.8 and ORP and EC increased from 27.4 to 61 mV and 2.9 to 10.7 mS/cm, respectively, with an increase in Zn concentration. For the range of Ni solutions, the results did not follow these trends as the pH did not change significantly with an increase in Ni concentration, and ORP and EC increased with an increase in concentration of Ni up to 100 mg/L and then reduced for concentrations higher than 100 mg/L. The pH, EC and ORP of Cr solutions differed from that of all the other heavy metals. Here, the pH increased from 6.4 to 7.6 and ORP and EC reduced from 24.7 to −47.9 mV and 2.6 to 0.2 mS/cm, respectively, with an increase in the Cr concentration.

Control batch tests with deionized water and the different filter material options helped to assess the chemistry of those materials. The pH, ORP and EC of deionized water were 5.5, 69.1 mV and 11.3 mS/cm, respectively. The pH ranged from 6.8 to 9.3, ORP ranged from −152.2 to 2.1 mV, and EC ranged from 0.0003 to 1.1 mS/cm depending on the filter material. High pH (alkaline)

conditions prevailed with calcite, slightly alkaline to near neutral conditions existed with zeolite and sand and slight acidic conditions occurred with iron filings. Redox potentials varied significantly, which could affect the redox sensitive contaminants such as Cr. The EC values were generally low for all cases, which indicate the low ionic strength of the solutions. Overall, these results demonstrate that the initial chemistry of filter materials can be different and that the initial chemistry of stormwater runoff can differ depending on the type and concentration of the heavy metal contaminants present in the runoff.

*Heavy metals removal*

Fig. 3 shows the percent of removal of six metals (Cd, Cu, Pb, Ni, Cr, and Zn) using different filter materials and initial concentration levels. Table 2(a)–(f) shows the final pH, ORP and EC values for different concentrations of Cd, Cu, Pb, Ni, Cr and Zn, respectively, and the various filter materials. All the batch tests were conducted for the same 24-h exposure time period, which is adequate for chemical equilibrium conditions between the filter material and metal solutions [11]. The test results shown are the average of the four values obtained based on replicate tests and duplicate analysis of samples from each test. The differences among the duplicate test results were less than 5%. Overall, these results (Fig. 3 and Table 2)
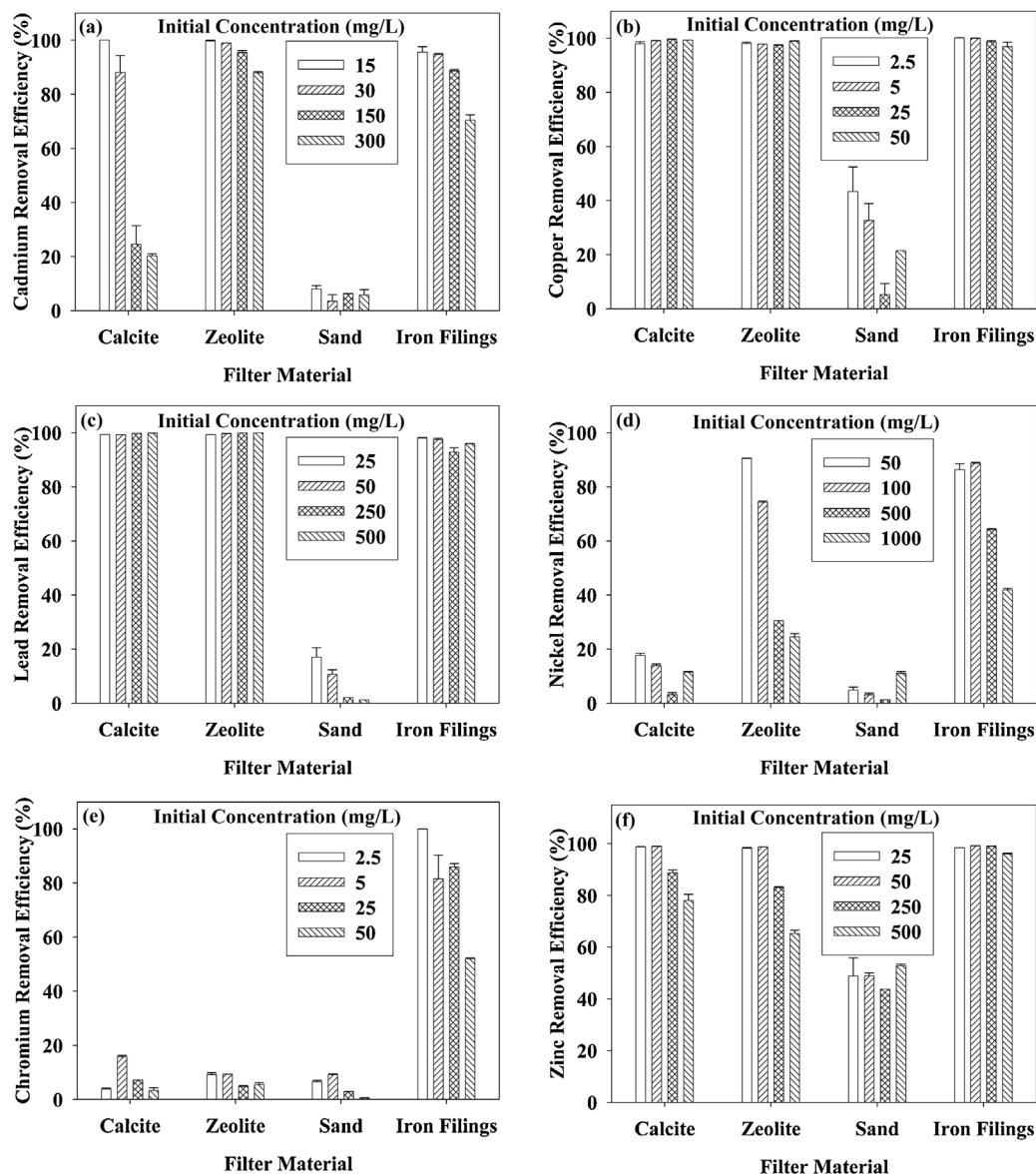
**Fig. 3.** Removal of heavy metals using different filter materials: (a) cadmium, (b) copper, (c) lead, (d) nickel, (e) chromium and (f) zinc.

show that the system chemistry and contaminant removal vary depending on the filter media and type and concentration of metal contaminant.

*Heavy metal removal with calcite*

For the batch tests with calcite, the removal ranged from 20 to 100% for Cd, 98 to 99.5% for Cu, 99.2 to 100% for Pb, 3 to 17.6% for Ni, 3.2 to 15.6% for Cr, and 78 to 98.9% for Zn (Fig. 3). The removal of Cd decreased drastically with an increase in concentration from the initial concentration, while Zn removal was slightly reduced with the increase in the concentration of Zn. The results with the Cu and Pb solution proved that calcite proved very effective for the removal of both Cu and Pb (more than 97% removal efficiency) and these levels of removal only slightly changed for different concentrations. On the other hand, calcite removal efficiency for both Ni and Cr was very low and decreased with an increase in concentration of the metals. The final conditions in these tests ranged from 6.3 to 9.6 for pH, from 0.002 to 3.2 mS/cm for EC and from 30.3 to −164 mV for ORP, respectively, (Table 2(a)–(f)). The

pH values were increased; ORP values and EC drastically reduced in the calcite batch experiments as compared to those with the control experiments with only metal solutions without filter materials. In a comparison of the batch results with the deionized water alone and with calcite solution at different concentrations, the effect of the increase in metal concentration in calcite on the final pH, ORP and EC was not significant.

The heavy metals removal in calcite may be attributed to the combination of two effects. First, the rough surface of the limestone gives solid contact, which results in the chemisorption of metal ions, and, secondly, the presence of dissolved calcium carbonate may have increased the pH of the solution, which caused the metals to precipitate as metals oxide and probably metals carbonate [12]. Also, a small quantity of metal is likely retained by the ion exchange with calcium and provides a metal carbonated compound [12]. The point of zero charge (PZC) of calcite is reported to vary from 8 to 9.5 [16,17] and the calcite batch tests had pH values ranged from 6.3 to 9.6 at which point the functional group surface sites of calcite may be neutral or slightly negatively charged, thus favoring less cationic metals adsorption.

Calcite is a carbonate mineral that consists of stable calcium carbonate ($CaCO_3$). The highest pH observed in the calcite batch tests can be attributed to the presence of the carbonates. Some amount of dissolved calcium may be present in the calcite batch tests. As a result, the high level of the removal of metals is possibly due to the formation of metal carbonate or metal hydroxide chemical precipitates. Various studies have showed that Cd and Zn cations are strongly sorbed by the calcium carbonate surface [17,18]. On the other hand, Pb is adsorbed onto the calcite surface by moving into the calcium sites [19]. In addition, Cu removal is a known result of precipitation on the surface of calcite due to the high pH values. The Ni removal may be limited by the competitive adsorption among the cationic metals. Cr in oxyanion form does not adsorb to the calcite due to high pH conditions. The results of the batch tests proved that calcite was very effective for removal of Cu and Pb and moderately effective for the removal of Cd and Zn from the synthetic storm runoff water. The removal efficiencies increased in the following order: Pb > Cu > Zn > Cd.

### Heavy metal removal with zeolite

For the zeolite batch tests, the removal efficiencies were as follows: Cd 87–99%, Cu 97.7–99%, Pb 99–100%, Ni 24–90%, Cr 5–9%, and Zn 65–98.7%. As the concentration of the metals increased, the removal efficiencies decreased except for Cu and Pb, which had very successful levels of removal (greater than 98%) for every concentration (Fig. 3). Cd, Ni, Cr, and Zn results indicate that less favorable adsorption sites become available as the metal concentrations in the aqueous solution increased. The final pH increased from 6.5 to 8.2, ORP and EC decreased from 19.3 to −82.9 mV and 2.1 to 0.04 mS/cm, respectively, when zeolite was the filter material as compared to that of metal solutions alone without zeolite (Table 2(a)–(f)). The increase in metal concentration on the final pH, ORP and EC had a negligible effect.

The processes responsible for the removal of metals in zeolite batch tests are ion exchange, precipitation and electrostatic adsorption of metals cations to negatively charged sites on the zeolite particle surfaces. The negative charge is balanced by the exchangeable cation (Na, K or Ca) and these cations are exchangeable with other cations in aqueous solution such as Pb, Cu, Cd and Zn [20–22]. The alkaline conditions also favored the precipitation of Pb, Cd and Cu [23,24]. The removal efficiencies of Ni and Zn decreased with increased initial concentrations, indicating a lower adsorption or precipitation due to the decrease in pH and/or limited surface sites available for adsorption. The removal of Cr proved to be very low due to the lower adsorption of $Cr^{+6}$ under high pH conditions.

### Heavy metal removal with sand

For the sand batch tests, the removal efficiencies for all metals were low: Cd 3.5–8%, Cu 5–43%, Pb 1.2–17%, Ni 1.2–10%, Cr 0.4–9%, and Zn 43–58% (Fig. 3). The removal was dependent on the initial concentration of metals. At higher concentrations, the metal removal was reduced for Cd, Pb, and Cr and remained almost constant for Zn. The removal of Cu and Ni first decreased with an increase in concentration and then increased for the highest concentration. The results show that sand was moderately effective for removal of Zn and Cu, but was ineffective in removal of the other heavy metals that might be found in stormwater runoff. The final pH slightly increased and ORP and EC slightly decreased with an increase Cd, Cu, and Ni concentration. However, a different trend appeared in the case of the Pb, Cr and Zn batch tests, wherein the increase in the concentration of metal caused an insignificant change in the final pH, ORP and EC. ORP values, which shows that reducing conditions prevailed. The mechanism for the removal of metals is non-specific electrostatic adsorption to negatively charged functional group sites on the sand particle surfaces or small amount of organic content present in it.

### Heavy metal removal with iron filings

Batch tests with iron filing as a filter material show that the removal of Cd ranged from 70 to 95%, Cu 96 to 100%, Pb 95 to 98%, Ni 41 to 88%, Cr 51 to 100%, and Zn 96 to 99% (Fig. 3). The increase in the initial Cd, Cu, Ni, and Cr concentration caused a reduction in the removal rate, while an increase in the initial Pb and Zn concentration did not change the removal rate significantly. According to these results, iron filings are found to be very effective for the removal of Cu, Pb and Zn and moderately effective for the removal of Cd and Ni. Cr removal highest with iron filings as it ranged from 51 to 100%.

The final pH increases significantly and ORP and EC decrease as the Cr and Zn concentrations increase. ORP values show that oxidizing conditions change into reducing conditions for higher concentrations of Cr and Zn. With increasing concentrations of Cd, Cu and Pb, the final pH decreased and, correspondingly, the final ORP and EC reading increased. Oxidizing conditions prevailed at all concentrations of Cr and Zn considered in this study. The final pH values for the Ni solution were approximately equal to 4 and did not change significantly with an increase in the concentration of Ni in the solution. Except for Cr and Zn, in all of the other metals the final pH decreased from 7.2 to 4.2, ORP and EC increased from −21 to 166 mV and 0.5 to 635 mS/cm, respectively, and provided acidic conditions due to iron filings as compared to that of metal solutions alone without iron filings (Table 2(a)–(f)). However, the opposite trend occurs in the case of the Cr and Zn batch tests, wherein the final pH increased from 7.6 to 10.5 and ORP and EC decreased from −46 to −214.9 mV and 0.2 to 0.0003 mS/cm, respectively, and provided an alkaline condition.

Several factors and processes affect the removal of metals using iron filings, which are essentially zero-valent iron in the form of iron oxides and hydroxides. Zero-valent iron removes heavy metals by several mechanisms including reductive transformation, ion exchange and adsorption/co-precipitation processes. Iron is a strong reducer and low pH environment (pH less than 4) favors higher electrochemical reduction, which explains the reduction of $Cr^{6+}$ to $Cr^{3+}$ [25]. In addition, as iron corrodes in water, the concentration of hydroxide increases (pH increases), and metals, including $Cr^{3+}$, precipitate as metal hydroxide and hydroxide complexes. It is also possible that metals are replaced with iron ions in iron oxide or hydroxide [26,27].

### Adsorption isotherms

The relationship between the amount of metal adsorbed onto the filter materials and the metal concentration in the solution at equilibrium condition is expressed as the adsorption isotherm. The equilibrium condition is reached when the rate of metal adsorption to the filter material is equal to the rate of desorption from filter material. The equilibrium concentration versus amount adsorbed for the six heavy metals in the four filter materials is shown in Fig. 4. It should be noted that these results are obtained through tests that only used individual metal solutions, thus synergistic effects of the co-existing metals on the adsorption behavior was not investigated, but is presented elsewhere by Reddy [11]. The adsorption and removal of the individual metals from the stormwater varied significantly depending on the metal and filter materials. Results in Fig. 4(a) show an increase in Cd removal with an increase in the initial Cd concentration for filter materials made of zeolite or iron filings. This implies that these two filter materials did not reach their maximum adsorption capacity and indicates
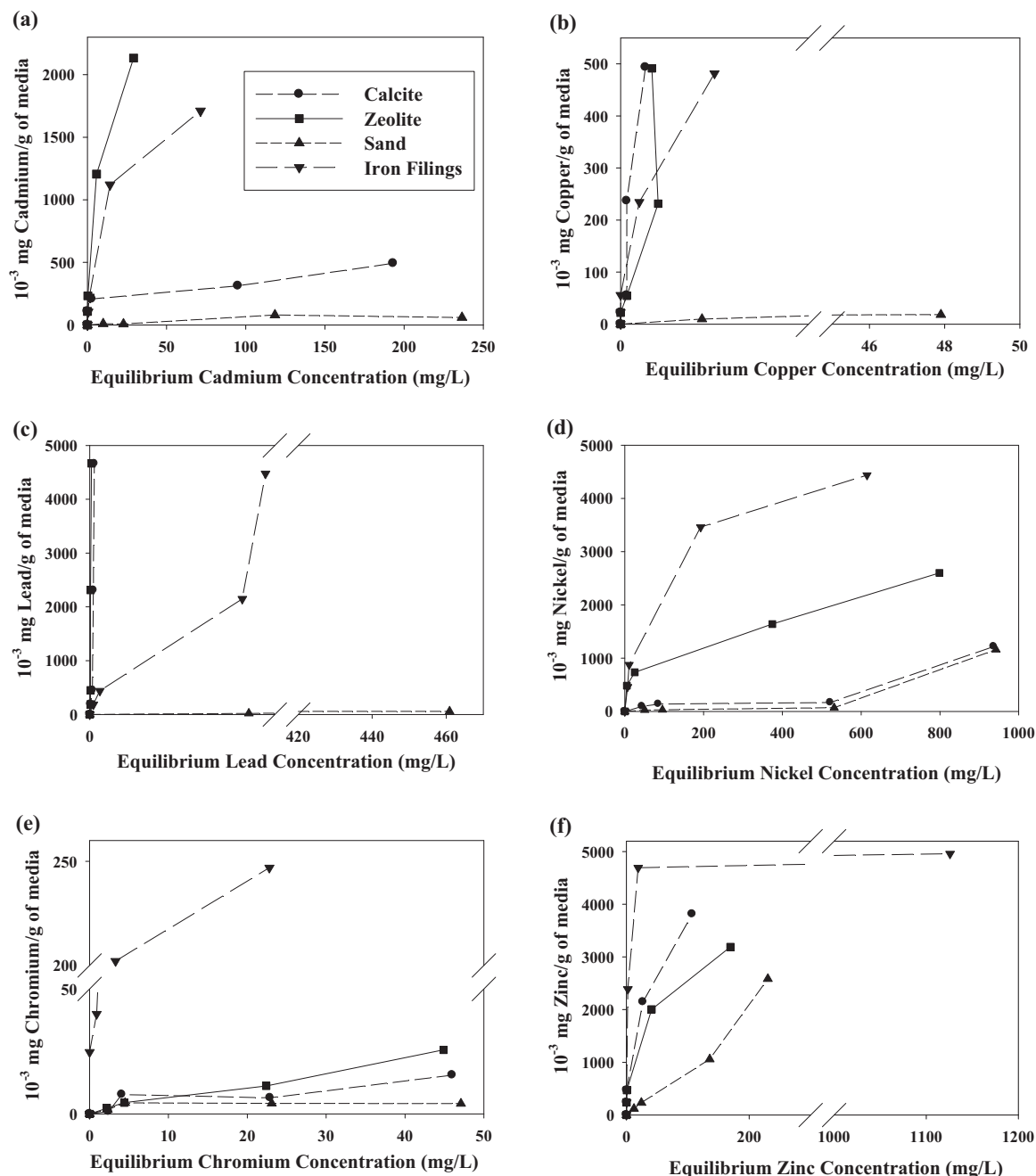
**Fig. 4.** Adsorption isotherm of heavy metals in different filter materials: (a) cadmium, (b) copper, (c) lead, (d) nickel, (e) chromium and (f) Zinc.

that they could still adsorb more Cd. On the other hand, sand and calcite reached their maximum removal capacities at the initial Cd concentration of 25 mg/L and then remained almost constant with as the concentration increased. This shows that sand and calcite active sites were occupied by Cd completely and reached the saturation condition.

Adsorption of Cu to the filter materials versus equilibrium Cu concentration for four different initial concentrations is shown in Fig. 4(b). Sand was the only filter material that reached its maximum adsorption capacity. Cu adsorption to sand increased as for the first two concentrations and reached maximum at equilibrium concentration of 22.5 mg/L; beyond that, the value of the Cu removal remained constant. In contrast, the removal of Cu by calcite, zeolite and iron filings increased with the increase in the concentration of the metal in the solution and there left more available active sites to adsorb Cu.

As seen in Fig. 4(c), calcite and zeolite worked more effectively and removed more Pb for the same concentration as compared to iron filings and sand. In this regard, it should be noted that calcite and zeolite both increased initial pH of samples (Table 2) due to the ion exchange of hydronium and decreasing protons in the solutions [28]. Therefore, it caused Pb to precipitate out. Pb removal by sand happened at a slow rate and reached its maximum adsorption capacity at its equilibrium concentration of 40 mg/L. The amount of Pb adsorbed per unit mass of iron filings was considerable, but did not reach its maximum capacity.

None of filter materials reached their maximum adsorption capacity for Ni (Fig. 4d). The highest adsorption was observed for iron filings. Ni adsorption was higher at low concentrations and it reduced at higher concentrations. Zeolite adsorbed Ni at a higher level than calcite and sand, and this increased with the increase in the concentration of Ni in the solution.

**Table 3**
Freundlich and Langmuir isotherm model constants for adsorption of heavy metals in different filter materials.

| Parameters | Freundlich isotherm | | | Langmuir isotherm | | | Freundlich isotherm | | | Langmuir isotherm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $K$ (L/kg) | $N$ | $R^2$ | $\alpha$ (L/mg) | $\beta$ ($\mu$g/g) | $R^2$ | $K$ (L/kg) | $N$ | $R^2$ | $\alpha$ (L/mg) | $\beta$ ($\mu$g/g) | $R^2$ |
| Metals | (a) Cd | | | | | | (b) Cu | | | | | |
| Calcite | 182.4 | 0.16 | 0.95 | 0.1 | 476.2 | 0.93 | 2663.8 | 1.36 | 0.85 | – | – | – |
| Zeolite | 389.0 | 0.49 | 0.94 | 0.8 | 2000.0 | 0.97 | 573.6 | 1.06 | 0.93 | – | – | – |
| Sand | 1.0 | 0.79 | 0.83 | – | – | – | – | – | 0.28 | 0.4 | 17.9 | 0.95 |
| Iron filings | 557.3 | 0.26 | 1.00 | 0.1 | 2000.0 | 1.00 | 395.6 | 0.46 | 1.00 | 10.0 | 500.0 | 0.94 |
| Metals | (c) Pb | | | | | | (d) Ni | | | | | |
| Calcite | 12,019.9 | 2.06 | 0.80 | – | – | – | 7.4 | 0.64 | 0.66 | 0.0 | 1250.0 | 0.08 |
| Zeolite | – | – | – | 7.0 | 142.9 | 0.98 | 273.5 | 0.32 | 0.98 | 0.0 | 2500.0 | 0.93 |
| Sand | – | – | – | 0.0 | 60.2 | 0.99 | 4.0 | 1.09 | 0.72 | 0.0 | – | – |
| Iron filings | 393.7 | 0.72 | 0.93 | – | – | – | 3140.5 | 0.21 | 1.00 | 0.0 | 5000.0 | 1.00 |
| Metals | (e) Cr | | | | | | (f) Zn | | | | | |
| Calcite | 1.1 | 0.68 | 0.62 | – | – | – | 507.1 | 0.44 | 0.98 | 0.1 | 5000 | 0.97 |
| Zeolite | 1.3 | 0.75 | 0.98 | – | – | – | 438.3 | 0.40 | 0.97 | 0.1 | 3333 | 0.98 |
| Sand | – | – | – | 0.6 | 4.2 | 0.99 | 29.6 | 0.67 | 0.85 | 0.0 | 2500 | 0.97 |
| Iron filings | 178.4 | 0.10 | 1.00 | 0.5 | 270.3 | 0.95 | 2621.2 | 0.10 | 0.64 | 0.3 | 5000 | 1.00 |

The Cr adsorption and removal was not effective with zeolite, calcite or sand. While the amount of Cr adsorption was low for these filter materials, iron filings proved effective for the adsorption and removal of Cr. There, the adsorption was high at low solution concentrations, but the increase in adsorption was found to be lower at higher solute concentrations.

Zeolite, calcite and sand adsorbed considerable amount of Zn and still had more available active sites to adsorb more (Fig. 4f). Adsorption of Zn by iron filings was remarkably more than that of the other filter materials. Under low solution concentrations, Zn adsorption per gram of iron filing was high; the amount of adsorption did not increase for solution concentration exceeding 50 mg/L.

*Adsorption isotherm modeling*

In order to quantify the relationship between the amount adsorbed ($S$) to the equilibrium solution concentration ($C_e$), three adsorption models, namely linear isotherm, Langmuir isotherm and Freundlich isotherm, were investigated based on the batch experimental results. Linear isotherm is the simplest adsorption isotherm model, which describes the liner relationship between $S$ and $C_e$ as:

$$S = K_d \times C_e \tag{3}$$

where $K$d is known as the distribution or partition coefficient. The linearity may be valid at low solution concentration range. However, the filter materials possesses finite surface sites for the adsorption of metals that causes a finite amount of metal adsorption, which is not accounted for in this linear adsorption model.

The Langmuir isotherm is based on the assumptions that all adsorption sites on a homogenous adsorbent surface are equivalent, the adsorption of solute is independent of the adjacent sorbed molecules and adsorption only occurs on a single monolayer. Therefore, each adsorbent site can only be occupied by one molecule of adsorbate and the saturation condition is reached when all sorbent sites are occupied with molecules of adsorbate, at which point no further sorption takes place. The Langmuir isotherm is given by:

$$S = \frac{\alpha \beta C_e}{1 + \alpha C_e} \tag{4}$$

$\alpha$ and $\beta$ can be determined by plotting $C_e$ versus $C_e/S$, which gives a straight line with an intercept of $1/\alpha\beta$ and slope of $1/\beta$ [29,30].

Langmuir isotherm may not be applicable if adsorption is dependent on the surface being heterogeneous, repulsive interaction between molecules of adsorbate or uneven adsorptive energy from site to site. In such situation, Freundlich isotherm is often used to correlate the concentration of solute in the liquid with the amount of adsorbate at the surface of solid by the following empirical equation:

$$S = KC_e^N \tag{5}$$

where $K$ and $N$ are constants and can be determined by plotting of log $C$ versus log $S$, which gives a straight line with an intercept of log $K$ and slope of $N$.

Based on the best-fits to the batch experimental results, the linear isotherm was invalid. The Langmuir or Freundlich isotherms can be used to model the observed results, and their parameters for the six metals adsorption onto calcite, zeolite, sand, and iron filings are shown in Table 3. Both isotherms can be used in modeling of filtration systems. Overall, these results show that the adsorption capacity of the filter materials varies depending on the type of filter material. The maximum adsorption capacities of the filter materials are useful in determining the life or replacement requirements of filter systems.

**Practical application**

The batch test results show that none of the four filter materials tested can remove all of the heavy metals simultaneously to the maximum levels. In urban stormwater, different metals co-exist, thus a combination of filter materials will be required [11]. According to the results, calcite was effective for removal of Cu, zeolite was effective for removal of Cd and Pb and iron filings were effective for removal of Zn, Ni, and Cr. Therefore, a combination of iron filings, zeolite and calcite should be further investigated to remove a wide range of metal contaminants found in typical urban stormwater. The specific proportion of these filter materials will depend on the concentrations of the metals present in the stormwater to be treated. The materials might be mixed together or used in layers, depending on the filter design and ease of construction.

The total volume of stormwater treated (or life time) of a filter system will depend on the quantity and types of filter materials used as well as the stormwater flow rate and volume. For example, the proposed in-ground permeable filter is 3 ft wide, 3 ft deep and 100 ft long, and the inlet and discharge concentrations of metals

**Table 4**
Heavy metals removal using 3 ft × 3 ft × 100 ft in-ground permeable filter system using different filter materials.

| Filter material | Inlet concentration, $C_i$ (mg/L) | Discharge limit, $C_f$ (mg/L) | $\Delta C = C_i - C_f$ (mg/L) | $S_{max}$ (mg/kg) | Filter material weight (kg) | Treatment capacity (gal/kg) | Treatment capacity of filter material (gal) | Amount of treated pore volume |
|---|---|---|---|---|---|---|---|---|
| **(a) Cd** | | | | | | | | |
| Calcite | 5 | 0.002 | 4.998 | 476 | 40,776 | 25 | 1,025,900 | 348 |
| | 15 | | 14.998 | | | 8 | 341,875 | 116 |
| | 30 | | 29.998 | | | 4 | 170,926 | 58 |
| Zeolite | 5 | 0.002 | 4.998 | 2000 | 25,485 | 106 | 2,694,064 | 733 |
| | 15 | | 14.998 | | | 35 | 897,782 | 244 |
| | 30 | | 29.998 | | | 18 | 448,861 | 122 |
| Sand | 5 | 0.002 | 4.998 | 79 | 45,873 | 4 | 191,548 | 84 |
| | 15 | | 14.998 | | | 1 | 63,832 | 28 |
| | 30 | | 29.998 | | | 1 | 31,914 | 14 |
| Iron filings | 5 | 0.002 | 4.998 | 2000 | 58,616 | 106 | 6,196,347 | 1399 |
| | 15 | | 14.998 | | | 35 | 2,064,898 | 466 |
| | 30 | | 29.998 | | | 18 | 1,032,380 | 233 |
| **(b) Cu** | | | | | | | | |
| Calcite | 1 | 0.018 | 0.982 | 493 | 40,776 | 133 | 5,407,912 | 1834 |
| | 5 | | 4.982 | | | 26 | 1,065,951 | 361 |
| | 10 | | 9.982 | | | 13 | 532,015 | 180 |
| Zeolite | 1 | 0.018 | 0.982 | 491 | 25,485 | 132 | 3,366,233 | 916 |
| | 5 | | 4.982 | | | 26 | 663,517 | 181 |
| | 10 | | 9.982 | | | 13 | 331,160 | 90 |
| Sand | 1 | 0.018 | 0.982 | 17.9 | 45,873 | 5 | 220,896 | 97 |
| | 5 | | 4.982 | | | 1 | 43,541 | 19 |
| | 10 | | 9.982 | | | 0 | 21,731 | 10 |
| Iron filings | 1 | 0.018 | 0.982 | 481 | 58,616 | 129 | 7,584,651 | 1712 |
| | 5 | | 4.982 | | | 26 | 1,495,007 | 337 |
| | 10 | | 9.982 | | | 13 | 746,156 | 168 |
| **(c) Pb** | | | | | | | | |
| Calcite | 5 | 0.05 | 4.95 | 4661 | 40,776 | 249 | 10,143,038 | 3440 |
| | 20 | | 19.95 | | | 62 | 2,516,694 | 853 |
| | 50 | | 49.95 | | | 25 | 1,005,166 | 341 |
| Zeolite | 5 | 0.05 | 4.95 | 143 | 25,485 | 8 | 194,357 | 53 |
| | 20 | | 19.95 | | | 2 | 48,224 | 13 |
| | 50 | | 49.95 | | | 1 | 19,261 | 5 |
| Sand | 5 | 0.05 | 4.95 | 60 | 45,873 | 3 | 147,380 | 65 |
| | 20 | | 19.95 | | | 1 | 36,568 | 16 |
| | 50 | | 49.95 | | | 0 | 14,605 | 6 |
| Iron filings | 5 | 0.05 | 4.95 | 4476 | 58,616 | 239 | 14,001,898 | 3161 |
| | 20 | | 19.95 | | | 59 | 3,474,155 | 784 |
| | 50 | | 49.95 | | | 24 | 1,387,575 | 313 |
| **(d) Ni** | | | | | | | | |
| Calcite | 30 | 0.47 | 29.53 | 1217 | 40,776 | 11 | 443,937 | 151 |
| | 60 | | 59.53 | | | 5 | 220,216 | 75 |
| | 100 | | 99.53 | | | 3 | 131,714 | 45 |
| Zeolite | 30 | 0.47 | 29.53 | 2600 | 25,485 | 23 | 592,767 | 161 |
| | 60 | | 59.53 | | | 12 | 294,044 | 80 |
| | 100 | | 99.53 | | | 7 | 175,871 | 48 |
| Sand | 30 | 0.47 | 29.53 | 1161 | 45,873 | 10 | 476,448 | 209 |
| | 60 | | 59.53 | | | 5 | 236,343 | 104 |
| | 100 | | 99.53 | | | 3 | 141,359 | 62 |
| Iron filings | 30 | 0.47 | 29.53 | 4436 | 58,616 | 40 | 2,326,109 | 525 |
| | 60 | | 59.53 | | | 20 | 1,153,872 | 260 |
| | 100 | | 99.53 | | | 12 | 690,144 | 156 |
| **(e) Cr** | | | | | | | | |
| Calcite | 1 | 0.000316 | 0.9997 | 15.5 | 40,776 | 4 | 167,018 | 57 |
| | 3 | | 2.9997 | | | 1 | 55,661 | 19 |
| | 5 | | 4.9997 | | | 1 | 33,395 | 11 |
| Zeolite | 1 | 0.000316 | 0.9997 | 26 | 25,485 | 7 | 172,406 | 47 |
| | 3 | | 2.9997 | | | 2 | 57,456 | 16 |
| | 5 | | 4.9997 | | | 1 | 34,472 | 9 |
| Sand | 1 | 0.000316 | 0.9997 | 4 | 45,873 | 1 | 50,914 | 22 |
| | 3 | | 2.9997 | | | 0 | 16,968 | 7 |
| | 5 | | 4.9997 | | | 0 | 10,180 | 4 |

**Table 4** (*Continued*)

| Filter material | Inlet concentration, $C_i$ (mg/L) | Discharge limit, $C_f$ (mg/L) | $\Delta C = C_i - C_f$ (mg/L) | $S_{max}$ (mg/kg) | Filter material weight (kg) | Treatment capacity (gal/kg) | Treatment capacity of filter material (gal) | Amount of treated pore volume |
|---|---|---|---|---|---|---|---|---|
| Iron filings | 1 | 0.000316 | 0.9997 | 270.3 | 58,616 | 71 | 4,186,830 | 945 |
| | 3 | | 2.9997 | | | 24 | 1,395,316 | 315 |
| | 5 | | 4.9997 | | | 14 | 837,154 | 189 |
| **(f) Zn** | | | | | | | | |
| Calcite | 10 | 0.12 | 9.88 | 5000 | 40,776 | 134 | 5,451,390 | 1849 |
| | 20 | | 19.88 | | | 66 | 2,709,242 | 919 |
| | 50 | | 49.88 | | | 26 | 1,079,786 | 366 |
| Zeolite | 10 | 0.12 | 9.88 | 3333 | 25,485 | 89 | 2,271,185 | 618 |
| | 20 | | 19.88 | | | 44 | 1,128,738 | 307 |
| | 50 | | 49.88 | | | 18 | 449,866 | 122 |
| Sand | 10 | 0.12 | 9.88 | 2500 | 45,873 | 67 | 3,066,407 | 1344 |
| | 20 | | 19.88 | | | 33 | 1,523,949 | 668 |
| | 50 | | 49.88 | | | 13 | 607,380 | 266 |
| Iron filings | 10 | 0.12 | 9.88 | 5000 | 58,616 | 134 | 7,836,373 | 1769 |
| | 20 | | 19.88 | | | 66 | 3,894,535 | 879 |
| | 50 | | 49.88 | | | 26 | 1,552,192 | 350 |

are known. Based on the adsorption capacity of each filter materials for individual metal contaminant, the total stormwater volume that can be treated can be estimated for each of the different metals, as summarized in Table 4(a)–(f). If the stormwater volume and inlet metal concentrations are known, the life of the filter can be determined.

## Conclusions

This study quantified the extent of adsorption and removal of six metals (Cd, Cu, Pb, Ni, Cr, and Zn) from stormwater using four filter materials (calcite, zeolite, sand, and iron filings). Batch experiments were conducted with synthetic stormwater solutions with individual metals at different concentrations. The extent of metal adsorption and removal and changes in pH, redox potential and electrical conductivity of the filtrates were measured. The following conclusions are drawn from this study:

- The extent of adsorption and removal of heavy metal contaminants depends on the type and concentration of metal as well as the selected filter material.
- The maximum removal of individual heavy metals found were: 95–100% Cd, Cu, Pb, and Zn by calcite, zeolite and iron filings, 90% Ni by zeolite and 100% Cr by iron filings. The metal removal with sand was low with maximum removals of 8–58% depending on the metal. No single filter material was capable of removing all metals to the maximum extent. Hence, a combination of the filter materials may be investigated for the simultaneous removal of multiple contaminants.
- For some combinations of metal and filter material, adsorption reached maximum adsorption capacity; however, for some other cases filter materials had much higher adsorptive capacity remaining.
- Removal of all metals, except Cr, was attributed to surface adsorption to negatively charged surfaces of the filter materials. Precipitation, ion exchange, chemisorption, or combinations of these processes were also responsible for the removal of heavy metals. Iron filings electrochemically reduced $Cr^{6+}$ that was initially present to $Cr^{3+}$ and then $Cr^{3+}$ was removed by adsorption and precipitation similar to other metals.
- The adsorption of metals onto filter material can be described by the Langmuir or Freundlich isotherm models. Based on the maximum adsorption capacity, the filter size and volume of stormwater that can be treated may be estimated.

## Acknowledgements

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