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

Krishna R. Reddy *, Tao Xie, Sara Dastgheibi

University of Illinois at Chicago, Department of Civil and Materials Engineering, 842 West Taylor Street, Chicago, IL 60607 USA

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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

* Corresponding author. Tel.: +1 312 996 4755; fax: +1 312 996 2426.
E-mail address: kreddy@uic.edu (K.R. Reddy).

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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:

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

The metal removal efficiency was calculated using:

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

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