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Heavy Metal Adsorbents for Storm Water Pollution Prevention

U.S. DEPARTMENT OF THE NAVY
CARDEROCK DIVISION,
NAVAL SURFACE WARFARE CENTER

in cooperation with
National Steel and Shipbuilding Company
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FINAL REPORT

**HEAVY METAL ADSORBENTS FOR STORM WATER
POLLUTION PREVENTION**

Prepared by

William D. Burgos, Ph.D.

Department of Civil and Environmental Engineering
The Pennsylvania State University

For

National Steel and Shipbuilding Company

Harbor Drive and 28th Street
Post Office Box 85278
San Diego, CA 92186-5278

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	1
Project Objectives.....	1
II STORM WATER COLLECTION SYSTEMS.....	2
A. Principal Components.....	2
B. Stormceptor™ Sedimentation Basin.....	3
III. STORM WATER CONTAMINANT SOURCES.....	3
IV. STORM WATER BEST MANAGEMENT PRACTICES.....	5
V. REGULATORY BACKGROUND.....	6
A. Water Quality Regulations.....	7
B. Storm Water Regulations.....	7
C. Shipbuilding and Repair Industry Regulations.....	7
VI. HEAVY METAL ADSORBENTS.....	9
A. Adsorption Mechanisms and Models.....	9
B. Adsorbent Materials.....	10
VII. PRELIMINARY LABORATORY TESTING.....	11
A. Methods and Materials.....	11
B. Experimental Results.....	12
VIII. CONCLUSIONS.....	16
IX. REFERENCES.....	17

I. INTRODUCTION

Common shipyard activities such as metal cutting, welding, surface preparation and painting are potential sources of heavy metal pollution. Even with the most sophisticated and rigorous best management practices (BMPs), some heavy metals are invariably transported into storm water collection systems. Storm water discharges into adjacent receiving waters are facing increasing regulatory compliance requirements which include not only additional BMPs, but chemical monitoring programs. Heavy metals such as copper, lead, nickel and zinc may become problematic in maintaining compliance with new Storm Water National Pollution Discharge Elimination System (NPDES) permits.

A potentially effective storm water pollution prevention strategy would be to strategically place porous heavy metal adsorbents *within* storm water collection systems. Conceptually, these adsorbents would function as a heavy metal “sponge,” effectively removing these contaminants as storm water passes through the porous matrix. Selection of the adsorbent material would depend on the capacity and kinetics of heavy metal uptake under typical and high flow conditions, and the porosity and head loss characteristics of the matrix. In addition to material selection, placement of the porous adsorbent within the storm water system must be given careful consideration.

Project Objectives

This report was prepared as the final deliverable for a feasibility study under the National Shipbuilding Research Program (NSRP) N1-96-04 Subtask 27, “Environmental Studies and Testing.” This limited study is not intended to provide a complete evaluation of the use of porous adsorbents for the removal of dissolved heavy metals from storm water, but to determine if commercially available products could be adapted for this task. As defined in the project proposal, the objectives of the project were to (1) evaluate the potential use of a number of adsorbents for the removal of heavy metals from storm water, and (2) determine the feasibility of placing a porous adsorbent within a storm water system as a BMP.

To prepare this report, Dr. William D. Burgos, Assistant Professor of Environmental Engineering, Department of Civil and Environmental Engineering, The Pennsylvania State University (Penn State), was assisted by U.S. Navy Lieutenants Gordon E. Clark, Jr. and John A. Kliem, enrolled as M.S. graduate students in the Environmental Engineering at Penn State. We reviewed a considerable amount of technical and commercial product information, and NPDES permits for commercial and Naval shipyards to initiate this project. After identifying the most promising component of a conventional storm water collection system for the placement of a *replaceable reusable porous adsorbent cartridge for the removal of dissolved heavy metals*, we focused on identifying effective, commercially available adsorbent materials and testing them for this application.

II. STORM WATER COLLECTION SYSTEMS

A. Principal Components

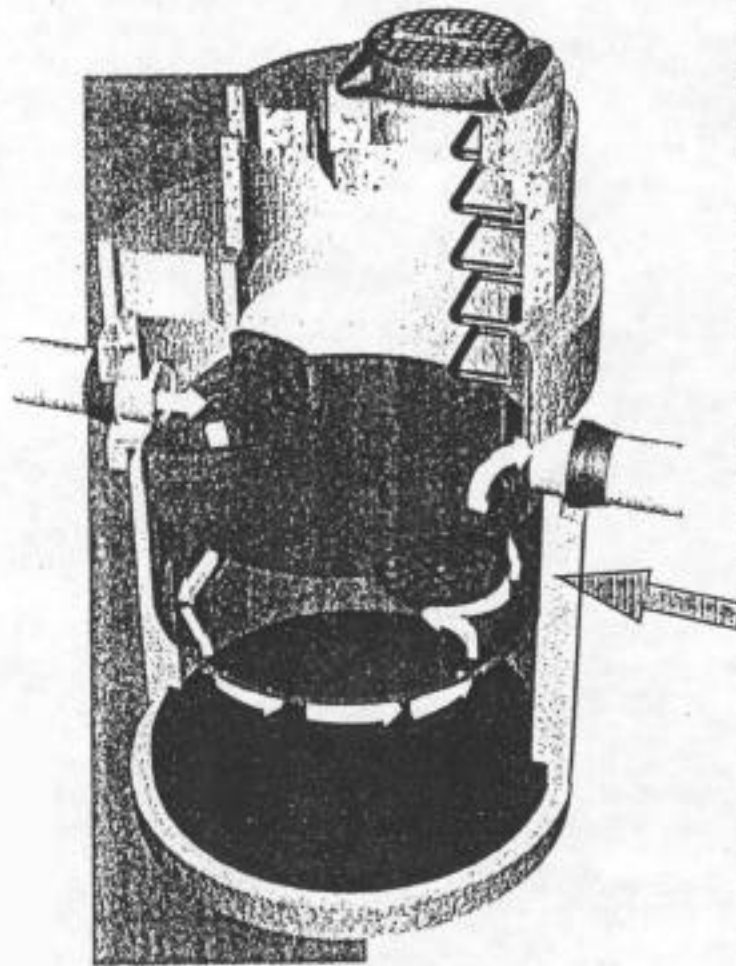
A combined sewer carries both wastewater and storm water. Although new combined sewer systems are no longer being built in the United States, they are an extensive part of the existing infrastructure in many locations, particularly in older urban areas. A sanitary sewer carries primarily domestic and industrial wastewater. The engineering literature provides no details on the specific configurations of storm water collection systems typically encountered at a large commercial or Naval shipyard, however, a mix of combined sewers, sanitary sewers and separate storm water sewers would be expected. The primary components of these sewer systems include (1) the contributing drainage area (and wastewater sources in the case of combined and sanitary sewers), (2) the sewer pipe network, (3) the regulator and diversion structures, and (4) the sewer outlets.

Many shipyards were constructed when it was acceptable practice to discharge process wastewater and sanitary wastes directly into adjacent receiving waters. As environmental regulations have eliminated or restricted these practices, shipyards have altered and cross-connected the sewer pipe network to redirect wastes to dedicated sanitary sewers. These reconnections have created a complex maze of sometimes old, corroded and broken underground pipes (Gauthier *et al.*, 1995). Thorough knowledge of a storm water sewer's drainage area and pipe network will greatly improve the effectiveness of any storm water BMP.

B. Stormceptor™ Sedimentation Basin

Flow regulators and diversion structures would be the most logical location(s) to place the proposed porous cartridge adsorber. A typical manhole or weir would not be adequate for the placement of a cartridge adsorber because the direct opposing flow may foul the adsorber with debris or possibly dislodge the whole cartridge. However, the baffled sedimentation basin produced by Stormceptor Canada Inc. could be (easily) retrofitted with a porous cartridge adsorber (Figure 1). The Stormceptor™ unit is an improved sedimentation basin which has been demonstrated to be effective in removing both settleable solids and floatable oils. Stormceptor has a patented baffled flow design which eliminates scour and the possible resuspension of the segregated contaminant sources. All Stormceptor units have a 24-inch diameter outlet riser pipe of variable length (18 to 44 inches) which could be equipped with a replaceable reusable porous adsorber cartridge for dissolved contaminant removal.

**Commercially
Available
Baffled
Stormwater
Sedimentation
Basin Insert**



**Simple
Modification:
Porous
Adsorber
Placed within
Outlet
Down Pipe
Removes
Heavy Metals**

Figure 1. Conceptual design for the modification of a Stormceptor™ unit to hold a porous adsorber for the removal of dissolved heavy metals from storm water.

III. STORM WATER CONTAMINANT SOURCES

Shipyards are heavily industrialized areas where abrasive grit blasting, painting, metal cutting, hull defouling, and machinery component replacement operations may be conducted. Because of the size of commercial and Naval vessels, many of these activities must be conducted outdoors in floating dry docks, graving docks or ways. Abrasive grit blasting, metal cutting and overspray from antifoulant paints results in fine particles of metal and paint deposited on the dry dock floor (Host, 1996). The heavy metals of concern at commercial and Naval shipyards are primarily chromium, copper, lead, mercury, nickel, silver and zinc. To remove microorganisms and animals from a ship's hull, chemical sprays used for defouling produce a similar waste stream. Machinery component replacement generates spent solvents and waste oils with metal leachate (Manning, 1995). Boiler rehabilitation is a source of soluble metals, and bilge cleaning is a source of both soluble and particulate metals.

While all of these activities or materials are potential contaminant sources, a pathway must exist for these surface deposited contaminants to be transported into the storm water collection system. Most shipyard BMPs (discussed below) focus on minimizing contact between storm water and contaminant source material to prevent pollution and reduce the pollutant's pathway into the receiving water. However, storm water discharges can also be affected by groundwater and seawater infiltration. For example, at the San Diego Naval Station storm water sewers discharge at intertidal elevations which allows seawater to periodically enter the storm sewer pipe network (Gadbois, 1997). Puget Sound Naval Shipyard and Portsmouth Naval Shipyard also experience tidal flushing of their storm sewer pipe networks (Key *et al.*, 1995). These conditions result in additional discharge volume and the periodic reduction of hydraulic head required to discharge storm water.

Groundwater infiltration into the storm sewer pipe network can also be a significant problem. In most cases groundwater infiltration will only increase the volume of storm water discharges, and can dilute the concentration of specific contaminants. If storm water treatment is still required, the additional infiltration flow will represent a significant environmental compliance cost. If the infiltration flow is itself contaminated, the purpose of the shipyard BMPs will be undermined. For example, dissolved nutrients and free-phase and dissolved oil seep into the storm water sewer at Pearl Harbor Naval Shipyard, contaminate the storm water discharge and require additional treatment (Key *et al.*, 1995).

IV. STORM WATER BEST MANAGEMENT PRACTICES

Review of the literature on current shipyard practices for storm water management, and NPDES permits for commercial and Naval shipyards provided considerable insight into the design of BMPs. BMPs are planned to help minimize pollution discharges in those cases for which numerical limits are not practical (EPA, 1991). BMPs are guidelines that are to be followed by the shipyard during its day-to-day operations (Ross, 1993). The most common

(and common sense) aspect of BMPs is to minimize the contact of storm water with contaminant sources. Whenever possible, processes which generate a significant amount of contaminants are enclosed, shrouded and/or separated from other activities. EPA's major concern with shipyards are associated with spent paint and abrasive blasting material.

The details of BMPs which address abrasive grit blasting and antifoulant painting are very similar. Storm water should not contact these materials during storage, and the cleanup of these materials should occur shortly after use to prevent their entry into drainage systems (e.g., manual sweeps of the dry dock between shifts). BMPs for managing storm water that contacts spent blasting materials include modifications to the dry dock floor to allow for the segregation or collection of the "first flush" of storm water. The segregation of process wastewaters, sanitary wastes, and gate and hydrostatic leakage within dry docks are also very common BMPs. These contaminated segregated waste streams are often treated on-site before discharge to a municipal wastewater treatment facility. Costs associated with this treatment and disposal are significant.

V. REGULATORY BACKGROUND

A. Water Quality Regulations

The Federal Water Pollution Control Act of 1972 (FWPCA) made the EPA responsible for promulgating national effluent standards for each industrial category. The EPA was required to set these standards based on pollution control technologies and on the economic achievability of compliance with the standards. More stringent discharge standards could be imposed if technology-based effluent standards did not protect receiving water quality. The Water Quality Act of 1987 (WQA) strengthened the control on specific toxic pollutants by implementing toxics-oriented water quality criteria.

The FWPCA also established the NPDES program to regulate discharges from municipal and industrial facilities. Under the NPDES program a permit would be issued to a facility specifying effluent limits, actions to be taken to meet the limits, and monitoring and self reporting requirements for those limits. States were allowed to take over the administration of the NPDES program provided their standards were as stringent as the Federal standards. Once a permit has been issued with numerical limits and monitoring requirements, the "anti-backsliding" provision in the WQA makes it difficult to relax any permit condition. The anti-backsliding provision states that a permit may not be renewed, reissued, or modified to contain effluent limits which are less stringent than the comparable limits in the previous permit.

The Clean Water Act (CWA) in force today is a combination of the FWPCA and WQA (Arbuckle, 1993). The objective of the CWA is to restore and maintain the physical, chemical, and biological integrity of the Nation's waters. To fulfill this objective, the EPA recommends that state regulatory agencies integrate the Whole Effluent Toxicity (WET) test, chemical-specific water quality criteria (WQC), and bioassessment approaches into NPDES permit writing. The

EPA also advises that no single approach be considered superior to another, and that all three approaches be applied equally in order to most accurately determine the impact of a discharge on its receiving water (EPA, 1991).

B. Storm Water Regulations

Storm water discharges from areas of industrial activity can be a significant source of pollution and must be issued a NPDES permit under the WQA (EPA, 1993). Three types of permit applications are used for NPDES storm water discharges: general permits; group permits; and, individual outfall permits. Most states and EPA regional offices issue a general permit for one facility to cover all individual outfalls. These general permit requirements are likely to be less stringent than requirements under individual outfall storm water permits (Dodson, 1995). Group permits would allow “representative discharge monitoring” of a single outfall to be used for all similar outfalls at a particular facility to reduce monitoring costs.

C. Shipbuilding and Repair Industry Regulations

The EPA published draft effluent guidelines for the Shipbuilding and Repair Industry to provide guidance for writing NPDES permits for shipyards (EPA, 1979). However, the EPA found that the imposition of national industry-wide numerical limits was impractical due to the wide variety of industrial activities and pollutant sources present at shipyards. Instead, the document described BMPs and associated monitoring plans to be applied to shipyards on a case-by-case basis. Although BMPs are common elements of shipyard NPDES permits, numerical contaminant limits are also regularly applied.

Because no national effluent standards exist for the Shipbuilding and Repair Industry, numerical permit limits are based upon Best Professional Judgment (BPJ) and Best Engineering Judgment (BEJ) (Arbuckle, 1993). Individual regulators write a NPDES permit for a shipyard based on *their own* BPJ and BEJ, facility-specific industrial practices, and site-specific environmental conditions. For example, a shipyard which uses abrasive grit blasting for paint removal would have BMPs to prevent the contact of blasting material with storm water. These activity-specific BMPs may also contain numerical limits for contaminants present in the paint or blasting material. The numerical limits would be based upon BPJ/BEJ which would consider WQC and characteristics of the receiving water.

The shipyard NPDES permits that we reviewed did not specify effluent limits for storm water discharges, only common BMPs. However, storm water does contribute to dry dock drainage discharges that are regulated. The metal permit effluent levels for dry dock drainage are summarized in Table 1 (Gauthier *et al.*, 1995; Won, 1997). Surprisingly, only two commercial shipyards (Electric Boat and NASSCO) have specific effluent requirements for metals in their dry dock discharges. Environmental compliance requirements associated with dry dock discharges are much more stringent for Naval shipyards compared to commercial shipyards.

Table 1. NPDES discharge limits for the dry dock drainage for select commercial and Naval shipyards¹.

Shipyard	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Atlantic Marine	NA	NA	NA	NA	NA	NA	NA
Avondale	NA	NA	NA	NA	NA	NA	NA
Bath Iron Works	NA	NA	NA	NA	NA	NA	NA
Electric Boat Corporation	NA	NA	0.49	NA	NA	0.335	NA
Ingalls	NA	NA	NA	NA	NA	NA	NA
NASSCO	NA	0.2	NA	NA	NA	NA	1.0
Newport News Shipbuilding	NA	NA	NA	NA	NA	NA	NA
Norfolk Naval Shipyard	0.1	0.1	0.335	0.002	NA	0.1	0.765
Pearl Harbor Naval Shipyard	NA	1.1	NA	0.0021	NA	0.14	0.094
Puget Sound Naval Shipyard	NA	NA	0.033	NA	NA	NA	NA

¹All **concentrations** reported in mg/L.

NA - effluent limit not applicable for NPDES permit.

VI. HEAVY METAL ADSORBENTS

The final sections of this report focus on the evaluation and testing of adsorbent materials for the removal of heavy metals from a synthetic saline storm water. Carbonaceous based adsorbent materials were selected over ion-exchange resins because of the anticipated high salinity of the storm water found in a shipyard's storm sewer network. High saline waters can promote the desorption of metals attracted to ion-exchange resins.

A. Adsorption Mechanisms and Models

The chemical reaction for the adsorption of a metal onto a solid substance is described by:



where M is the metal sorbate, S is the solid sorbent and MS is the metal-solid sorbent complex. Sorbate molecules are held on the surface of the sorbent primarily by two mechanisms, chemisorption and physisorption. Chemisorption is usually described as a covalent bond between the sorbate and sorbent. Physisorption is usually described as a weak, reversible attraction between the sorbate and sorbent. For the sorption of metals to the carbonaceous adsorbents we tested, physical entrapment of the metal into internal pores was probably the dominant sorption mechanism (i.e., physisorption).

The amount of sorbate that a sorbent can accumulate is a key parameter for process engineering design. This capacity is determined by generating an equilibrium sorption isotherm, which is a plot of the equilibrium aqueous concentration (C_{eq} - mass sorbate/volume of solution) versus the corresponding sorbed concentration (C_{sorb} - mass sorbate/mass sorbent). There are numerous isotherm models used in industry but the most common are the Linear and Freundlich adsorption models.

The Linear adsorption model is used when there is a linear relationship between C_{eq} and C_{sorb} . The sorbent distribution coefficient (K_d) is described by:

$$C_{sorb} = K_d \times C_{eq} \quad (2)$$

where the units of K_d are determined by the units of C_{eq} and C_{sorb} . For example, if C_{eq} is reported in mg/L and C_{sorb} is reported in mg/g, then K_d will have units of L/g. Larger K_d values represent a greater sorbent capacity.

The Freundlich adsorption isotherm model is an empirical model described by:

$$C_{sorb} = F \times C_{eq}^n \quad (3)$$

where F is the Freundlich coefficient and n is the nonlinearity constant. The units of F are dependent on the units of C_{eq} and C_{sorb} and the value of n (dimensionless). In a general sense, the sorbent capacity is described by F , while the strength of the sorbate-sorbent interaction is described by n . Larger F values (like K_d) represent a greater sorbent capacity, while smaller n values represent a stronger interaction.

B. Comparison of Available Materials

Brown *et al.* (1992) compared the performance of 17 carbon based adsorbents for the removal of dissolved copper from water. Twelve of the adsorbents studied were peats of different types, geographic origin, and processing history. The remaining adsorbents were lignite, lignite char, bone char, and two activated carbons. The capacity (i.e., $C_{sorb,MAX}$) of each sorbent was determined from batch tests and the results showed a wide range of performance. The most effective sorbent was bone char, with a capacity of approximately 100 mg copper per gram of bone char. An adsorbent with a capacity of 40 mg copper per gram was considered “good” by Brown *et al.* (1992).

New adsorbent materials are being developed for the removal of metals from water. Two of the more promising types of material are mesoporous silica and microporous carbon. Mesoporous silica are effective because of their large surface area and well defined pore size and shape. The specific removal efficiency for a target metal can be dramatically improved by adding functionalized organic monolayers onto the silica surface (Feng *et al.*, 1997). These modified sorbents have been described as heavy metal “super soakers.” Experiments conducted for the removal of mercury from wastewater revealed that surface-modified mesoporous silica had a capacity of approximately 210 mg mercury per gram of silica. These sorbents have a high metal loading capacity (i.e., large K_d) and a high selectivity for the target heavy metal against background cations (e.g., Ca^{2+}). For shipyard storm water discharges which may contain a variety of heavy metals, high selectivity may not be advantageous. Compared to modified mesoporous silica, microporous carbons do not have as high of a metal loading capacity but may be able to remove a wider range of heavy metals.

VII. PRELIMINARY LABORATORY TESTING

A. Methods and Materials

Experiments were performed to measure the adsorbent capacity, sorption kinetics and contaminant breakthrough characteristics of copper (Cu^{2+}) and nickel (Ni^{2+}) using two commercially available adsorbents, Supelcarb™ and Carboxen-1011™ (Supelco Inc., Bellefonte, PA). These microporous carbonaceous adsorbents have nearly identical physical characteristics (e.g., particle size, pore size distribution and surface area) except for their pore configuration, which controls metals sorption. Supelcarb has funnel-shaped “dead-end” pores, while Carboxen has hourglass-shaped “flow-through” pores. Experimental variables included the influent

contaminant concentration (2.5 to 10 mg/L), the solution flow rate (100 to 300 mL/min), and the ionic strength of the synthetic storm water (10 to 200 mM NaCl). Batch adsorption isotherms were determined for Cu^{2+} with both adsorbents in a synthetic storm water solution of 100 mM NaCl adjusted to pH 6.3 ± 0.2 with 100 mM $\text{Na}(\text{HCO}_3)_2$. For flow-through experiments, synthetic storm water solutions (representative of saline waters anticipated in shipyard storm water collection systems) containing the contaminant(s) of concern were pumped through adsorbent cartridges at bed velocities expected within a collection system, and effluent concentrations were measured by atomic absorption spectrometry (AAS) on a semi-continuous basis. For an individual flow-through test, a peristaltic pump was used to convey the synthetic storm water through a one-inch diameter, twelve-inch long stainless steel column filled with a constant mass of adsorbent, and column effluent Cu^{2+} concentrations were measured by AAS. All experiments were performed in triplicate. Experiments measuring the competitive adsorption of Cu^{2+} and Ni^{2+} are currently being conducted.

B. Experimental Results

Linear adsorption isotherm coefficients (i.e., K_d) were determined in batch experiments for Cu^{2+} with Supelcarb and Carboxen-1011 and were 0.40 and 0.38 L/g, respectively (Figure 2). The adsorption capacities (i.e., $C_{\text{sorb,MAX}}$) for Cu^{2+} with Supelcarb and Carboxen-1011 were 14 and 13 mg/g, respectively. Compared to the reported $C_{\text{sorb,MAX}}$ value for bone char (100 mg Cu^{2+} /g) (Brown *et al.*, 1992), these materials have a moderate capacity for the removal of Cu^{2+} from water. However, our tests were performed at much higher ionic strengths than those reported by Brown *et al.*(1992). Also, at initial Cu^{2+} concentrations of ≤ 10 mg/L, these adsorbents were able to reduce the Cu^{2+} to well below 1 mg/L. In most cases the Cu^{2+} was reduced to below the detection limit of the AAS (ca. 10 ng/l), and this occurred after only the 10 minute equilibration period used in the batch tests.

“Breakthrough” curves collected for Supelcarb and Carboxen-1011 revealed how these adsorbents will perform under actual operating conditions. For our experiments breakthrough was defined when the column effluent concentration reached 10% of the influent feed concentration. As shown in Figure 3, a linear increase in the influent Cu^{2+} concentration (at a constant flow rate) produced a nearly linear decrease in the time required for contaminant breakthrough to occur. Similarly, a linear increase in the influent flow rate (at a constant Cu^{2+} concentration) produced a nearly linear decrease in the time required for contaminant breakthrough to occur (Figure 4). These results are important because future tests can be conducted at only one set condition, yet the results can be linearly scaled to any other operating condition.

Flow-through experiments revealed that for any given test condition, Carboxen-1011 took approximately 30% to 50% longer than Supelcarb before Cu^{2+} breakthrough occurred. After breakthrough had occurred, we switched to pumping a Cu^{2+} -free storm water solution through the adsorber to measure any Cu^{2+} “wash out.” Carboxen-1011 released a low concentration of Cu^{2+} , while Supelcarb did not release any Cu^{2+} . The “dead end” pores of Supelcarb are apparently more effective at retaining the adsorbed Cu^{2+} .

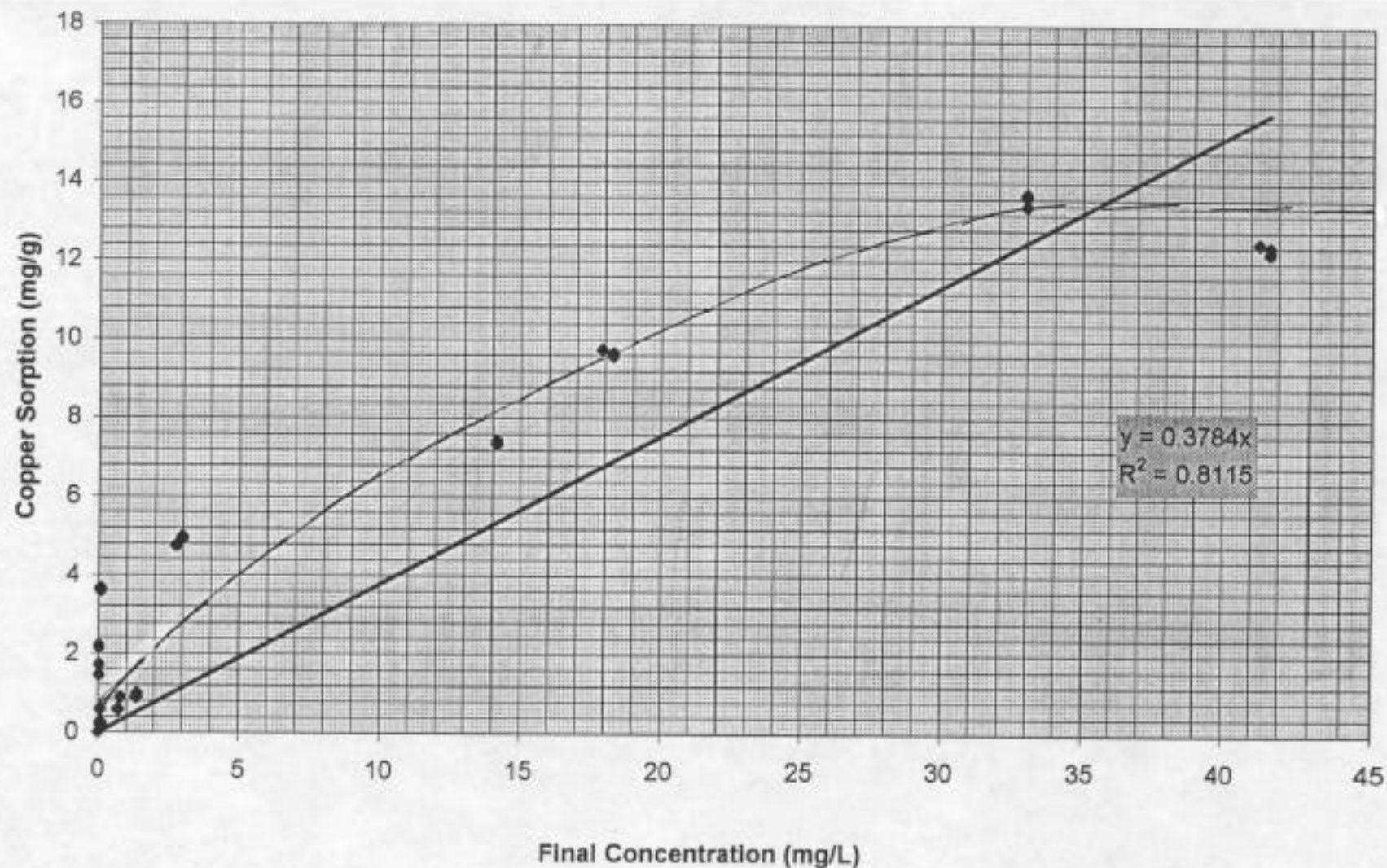
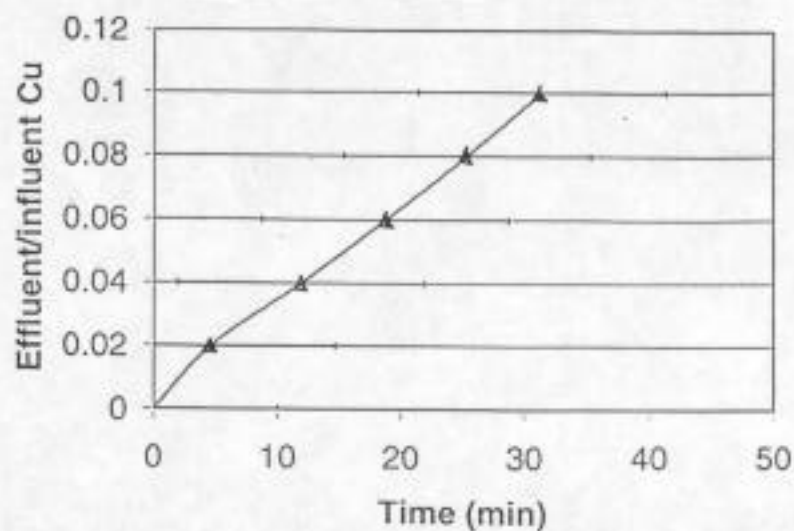
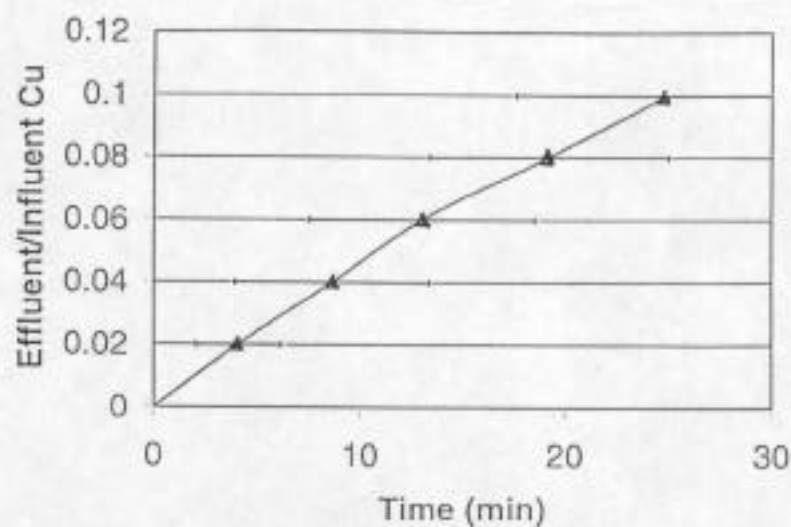


Figure 2. Experimental results for the batch equilibration of Carboxen-1011 with synthetic stormwater solutions of Cu^{2+} . All systems were prepared in 100 mM NaCl buffered with 100 mM NaHCO_3 and 100 mM HCl or 100 mM NaOH to achieve a final pH of 6.0 ± 0.5 , and were prepared in triplicate.

(a) $\text{Cu}^{2+} = 2.5 \text{ mg/L}$



(b) $\text{Cu}^{2+} = 5 \text{ mg/L}$



(c) $\text{Cu}^{2+} = 10 \text{ mg/L}$

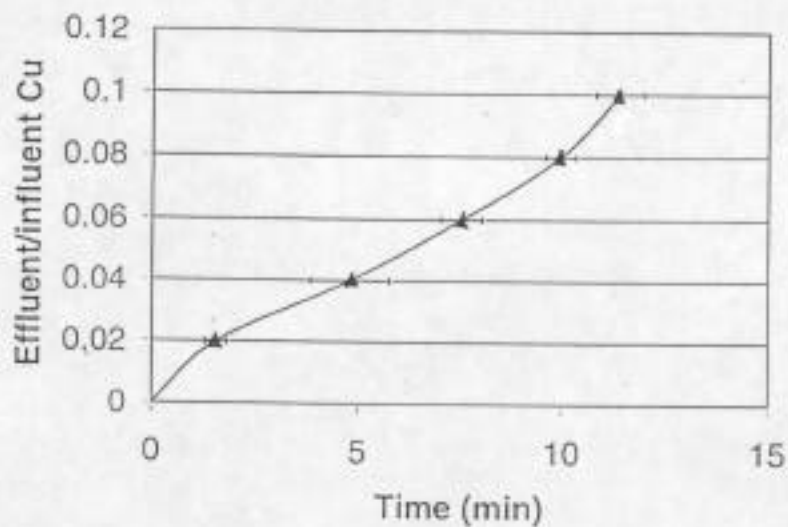
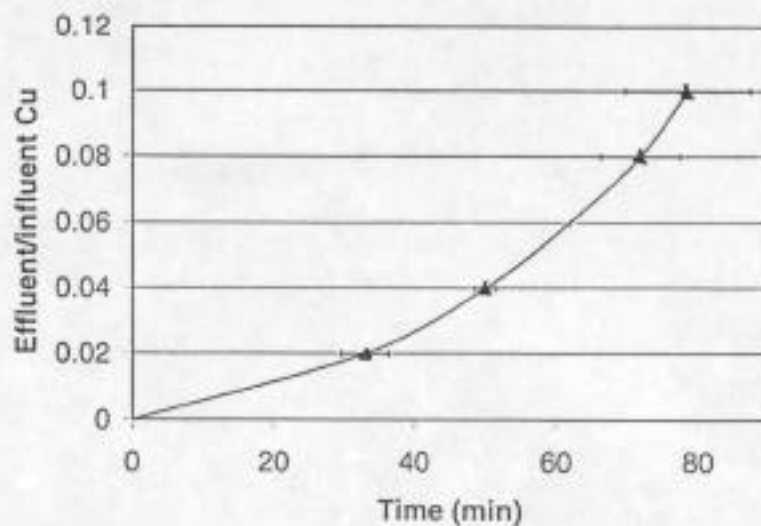
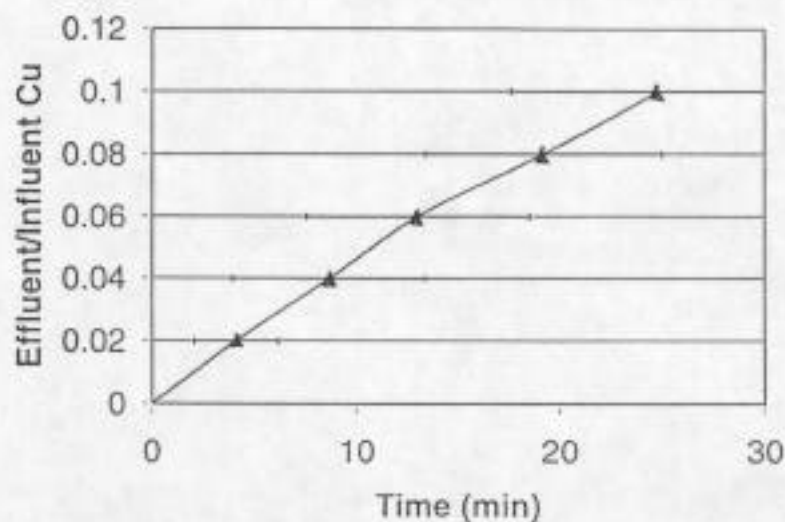


Figure 3. Experimental results for the breakthrough of Cu^{2+} with Carboxen-1011. All systems were conducted at a constant flow rate of 100 mL/min and a varied influent Cu^{2+} concentration. Error bars represent the ± 1 standard deviation for triplicate measurements.

(a) $\text{Cu}^{2+} = 100 \text{ mL/min}$



(b) $\text{Cu}_2^{+} = 200 \text{ mL/min}$



(c) $\text{Cu}_2^{+} = 300 \text{ mL/min}$

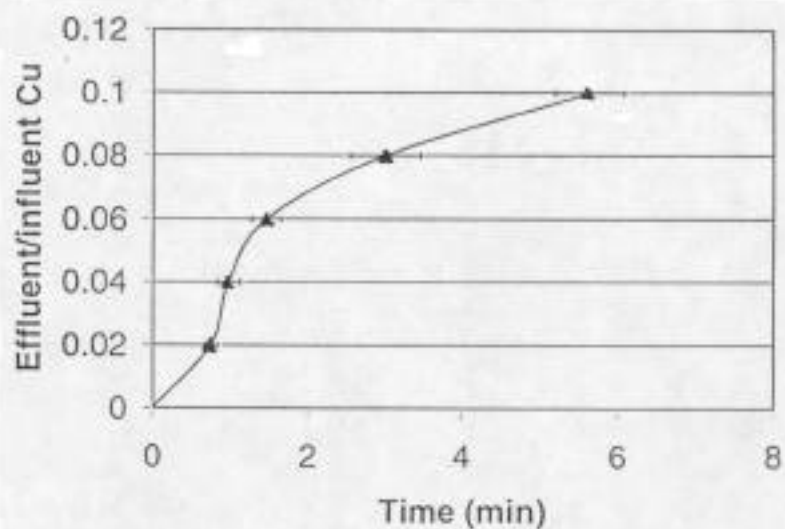


Figure 4. Experimental results for the breakthrough of Cu^{2+} with Carboxen-1011. All systems were conducted at a constant influent Cu^{2+} concentration of 5 mg/L and a varied flow rate. Error bars represent the ± 1 standard deviation for triplicate measurements.

VIII. CONCLUSIONS

This feasibility study revealed that commercially available storm water collection system components (e.g., Stormceptor™ sedimentation basin) can be adapted to contain a porous adsorber for the removal of dissolved heavy metals from storm water. The selection of an adequate adsorbent material will require additional research. Ideally, the adsorbent material will have a high capacity for heavy metals, exhibit non-specificity for heavy metals but not be affected by background salts (e.g., Ca^{2+}), be reusable and relatively inexpensive. In addition, the headloss developed across the porous adsorber must be kept to a minimum to allow storm water to pass through for treatment. The development of such a pollution prevention BMP should aid in maintaining environmental compliance with the anticipated more stringent future storm water requirements.

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