EVALUATION OF WASTE SLAG TO REMOVE TARGET METALS FROM INDUSTRIAL STORMWATER RUNOFF

by

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To Ammu and Baba.

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Abstract

Contaminated industrial stormwater runoff can contribute elevated high organic and inorganic pollution mass loads to receiving surface water bodies. Metals, such as cadmium (Cd), iron (Fe), manganese (Mn) and zinc (Zn) are non-biodegradable and can accumulate in living tissue. The objective of this study was to evaluate two waste slag: (1) Air-Cooled Blast Furnace Slag (ACBFS), (2) Open-Hearth Slag (OHS) produced during iron and steel production in removing target metals (Cd, Fe, Mn, Zn) from industrial stormwater runoff. These slags are evaluated based on their metal removal and adsorption capacity. Bench-scale batch adsorption experiments were conducted using a shaker table with actual industrial stormwater runoff obtained from a Biomass Power Generation facility in Nova Scotia, Canada and synthetic water simulated closely to the actual stormwater runoff. The results indicate that 90% of Cd, Fe, Mn and Zn were removed when OHS and ACBFS were used. This study also investigated the effect of natural organic matter (NOM) presence in stormwater runoff in terms of adsorption capacity and final total concentration of metals.

List of Abbreviations and Symbols Used

ACBFS	Air-Cooled Blast Furnace Slag
Al2O3	Aluminum Oxide
ASTM	ASTM International
BFS	Basic Furnace Slag
BOFS	Basic Oxygen Furnace Slag
CaO	Calcium Oxide
CCME	Canadian Council for the Ministers of the Environment
Cd	Cadmium
EAFS	Electric Arc Furnace Slag
Fe	Iron
Fe2O3	Ferric Oxide
g/cm3	grams per centimeter cube
g/L	grams per litre
GAC	Granulated Activated Carbon
LOI	loss on ignition at 1000 degree Celsius
mg/L	milligrams per litre
MgO	Magnesium Oxide
Mn	Manganese
NSA	National Slag Association
NSEQS	Nova Scotia Environmental Quality Standards
OHS	Open-Hearth Slag

rpm	revolutions per minute
SEM	Scanning Electron Microscope
SiO2	Silicon Dioxide
USEPA	United States Environmental Protection Agency
Zn	Zinc

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Chapter 1: Introduction

1.1. Background

Slag is an alkaline material that is a by-product of iron and steel production. When iron ore, coke and limestone is heated at a temperature of about 1000ºC in a blast furnace, molten iron is produced. This molten iron is heated even at a higher temperature of about 1500ºC in a furnace to produce steel. During these processes, different kinds of slags are produced which are categorized mainly into two categories: (1) iron slag and (2) steel slag. (National Slag Association, n.d.). Figures 1.1 and 1.2 illustrate the iron and steel slag production.

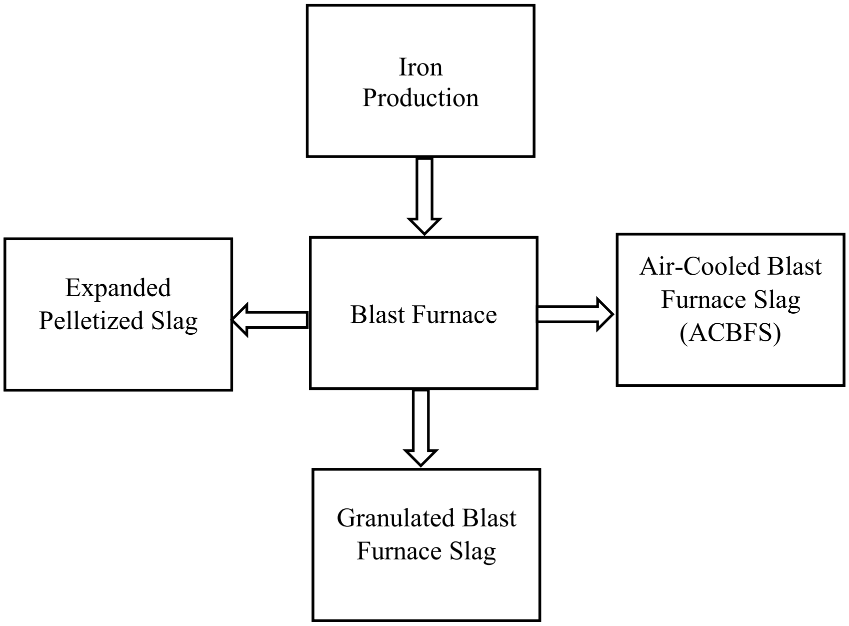

Figure 0.1: Production of different types of iron slags in blast furnace

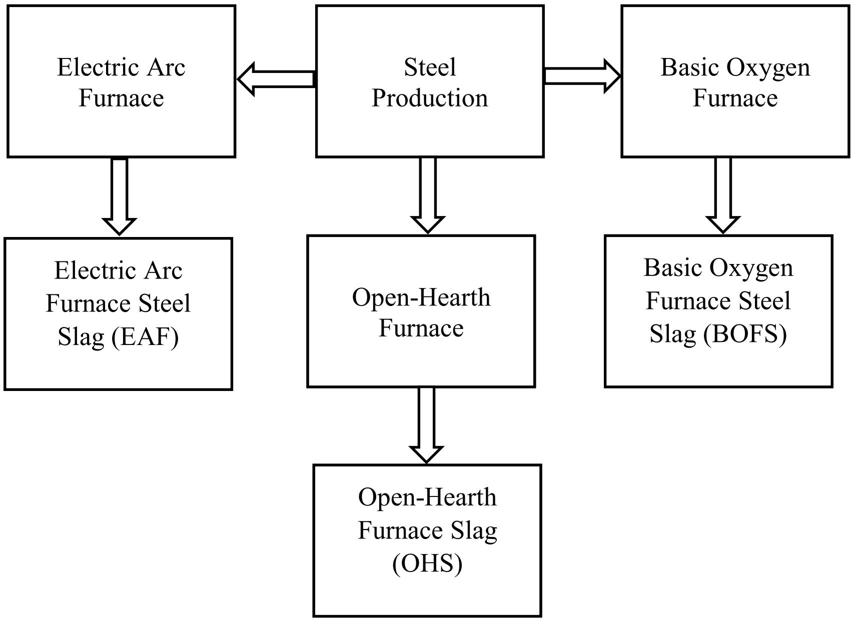

Figure 0.2: Production of various steel slags in different furnaces

Iron slag, specifically, air-cooled blast furnace slag (ACBFS) is used for subbase construction and in concrete pavement. ASTM D 694 and D 1241 standard requirements are met by ACBFS; hence it is widely used in local highway departments for macadam and crushed aggregate bases in the United States (US) (National Slag Association, n.d.). Steel slag contains free lime (CaO), that gives it an expansive nature that can cause differential movement when used as a base in road construction. Hence, steel slag does not meet the ASTM D 694 and D1241 standard requirements and is not used in highway construction without proper aging and testing (National Slag Association, n.d.). To divert these materials from onsite storage and landfill, there is a need to find alternative uses for these waste materials.

Stormwater runoff from industrial sites is identified as one of the main sources of pollutants in urban runoff. Industrial land use contributed to substantially higher pollutant loads in stormwater when compared to other types of land use (Cross & Duke, 2008). Little is known about non-point sources that contribute to the fraction of pollutant loading to local waterways due to stormwater runoff. Investigations have concluded that stormwater runoff is a major source of pollutants to receiving waters. Elevated levels of heavy metals are identified as the major concern in stormwater and have gained more significance than other aquatic pollutants due to their persistence, biomagnification and the fact that metals cannot be chemically transformed or destroyed (Davis et al., 2001 & Kadirvelu et al., 2001).

Activated carbon has been one of the most popular and widely used adsorbents in removing metals from water. Wood, lignite and coal are some of the materials that are high in organic content and typically used to make granulated activated carbon (Environmental Protection Agency (EPA), n.d.). While GAC treatment can achieve metals and heavy metals removal from water, it's cost remains high and finding an alternative material that can remove metals from water is essential for municipalities and industries (Babel & Kurniawan, 2003). Finding alternative adsorbent materials can provide cheaper avenue and more sustainable approach that would be associated with using waste by-products for environmental remediation projects.

The experiments and analyses performed as part of this research study were founded on the hypothesis that iron slag, specifically air-cooled blast furnace slag (ACBFS), and steel slag, specifically open-hearth slag (OHS), can be used to effectively to remove metals from industrial stormwater runoff.

1.2. Objective

The main hypothesis of this research was tested using the following sub-objectives:

- To evaluate physical and chemical characteristics of OHS and ACBFS
- To investigate slag particle size effect on the removal of target metals
- To evaluate adsorption capacity of OHS and ACBFS compared to a commercially available granulated activated carbon (GAC).

The sub-objectives were performed through bench-scale study on stormwater runoff collected from a biomass generation plant located in Liverpool, Nova Scotia, Canada.

1.3. Thesis Organization

This thesis constitutes seven chapters. Chapter 2 focuses on relevant literature review on iron and steel slag, stormwater generated in biomass power generating industry, adsorption process and metal solubility pH. Chapter 3 outlines the common materials and methods used in this study. Chapter 4 presents stormwater and slag characterization study results. Chapter 5 presents the batch adsorption study results on metal removal from an actual biomass power generating plant stormwater using OHS, ACBFS and GAC. Chapter 6 focuses on the impact of natural organic matter on adsorption. Chapter 7 summarizes the results of the study and presents recommendations for future research.

1.4. Originality of Research

Previous studies have evaluated blast furnace slag (granulated, ungranulated, air-cooled) and GAC to remove various metal-ions from synthetic solutions in batch adsorption studies (Lu & Bai, 2008; Nehrenheim & Gustafsson, 2008; Oguz, 2004; Dimitrova & Mehangiev, 1998). Most of these previous studies focused on evaluating the removal of individual metal ions from water. The current study uses real stormwater and mixed metal ions synthetic water that closely simulate actual stormwater generated in a biomass power plant site. The current study also attempted to evaluate a steel slag, OHS, which has not been investigated in previous studies to determine its efficacy in removing metals from water. This study also investigated the impact of humic-acid derived organic concentrations on metal adsorption capacity.

This research is valuable in evaluating a possible cost-effective treatment of stormwater to remove metals (Cadmium, Iron, Manganese and Zinc). The use of ACBFS and OHS, waste by-products from the iron and steel manufacturing industry, to remove metals from stormwater would reduce the need to use expensive GAC for industries and municipalities. It would also ensure that a circular economy is maintained in which waste of a process is used in a different application to divert waste from landfills or piling up on sites. The results of this research may also be applicable for other environmental remediation projects and applications, where elevated metal concentration is present in wastewater.

Chapter 2: Literature Review

A thorough literature review was conducted to gather background information on the production, physical and chemical properties of ACBFS and OHS. Literature review on stormwater generated in a biomass power generating plant was also conducted. Relevant regulations on stormwater discharge in United States and Canada are also summarized. A summary of relevant studies concerning metal removal with blast furnace slag and steel slag is also presented.

2.1. Slag

During the production of iron and steel, slag is produced as a waste material. The National Slag Association (NSA) categorizes slag in two main types: blast furnace slag and steel furnace slag. Actual data of slag production in the US and Canada are unavailable. However, it is estimated that about 16 to 22 million tons of slag were produced in 2015 in the US alone. It is also estimated that from 2011 to 2015, slag production increased about 2 million tons. Slag sales in 2015 were about 17 million tons at a value of $330 million (US) (U.S. Geological Survey, Mineral Commodity Summaries, 2016). The province of Ontario produces about 80% of the steel manufactured in Canada. The Canadian Slag Association estimates that about 1.5 million and 1.2 million tons of blast furnace slag and steel slag is produced, respectively, in Canada (Canadian National Slag Association, 2009).

2.1.1. Production and Characteristics of Air-Cooled Blast Furnace Slag

Blast furnace slag is produced during the iron production. Iron ore, flux stone (limestone and/or dolomite) and coke are added to charge the blast furnace. Molten iron and slag are the two products that are obtained from the furnace. The molten iron comes out of the furnace at about 1500° C as a liquid, which resembles molten lava. The condition that these waste slags are processed or stored gives rise to different types of slag, as outlined in Figure 2.1.

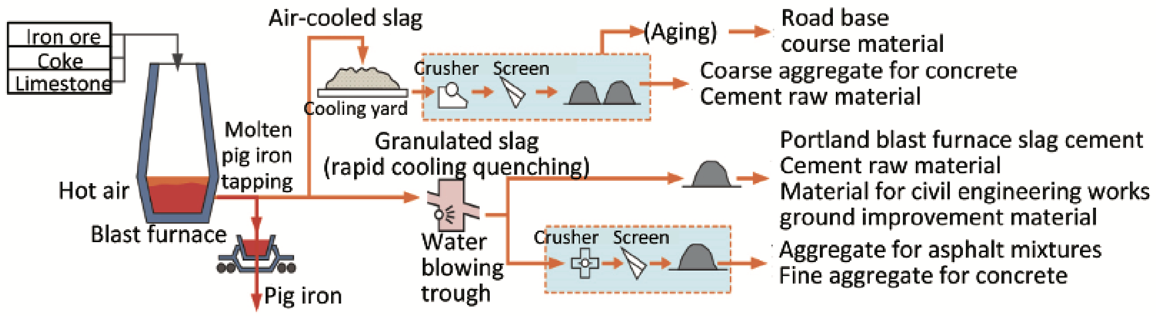

Figure 0.1: Different types of blast furnace slags (Missing: Expanded Pelletized Blast Furnace Slag). (Miyamoto et al., 2015)

During the production of iron the raw materials used include limestone which gives the waste slag an alkaline pH. All blast furnace slag contains oxides silica, alumina, lime and magnesia. These constituents make up approximately 95% percent of slag produced in iron production. Air cooled blast furnace slag (ACBFS) is formed when slag is left to cool in open pits or yards (Miyamoto et. al., 2015). ACBFS primarily consists of silicates and alumino-silicates of lime. It is a crushed product that has angular, roughly cubical particles with pitted, vesicular surfaces. The primary waste-to-resource use of ACBFS is in the construction industry where it is used as a base material for pavements, concrete, backfill and slope protection (NSA, n.d.).

Mostafa et al. (2001) reported that ACBFS contains approximately 50 to 70% by mass of crystalline phases. ACBFS is inorganic in nature and contains silica (30 to 35%), calcium oxide (28 to 35%), magnesium oxide (1 to 6%), aluminum oxide (18-20%) and iron(II) oxide (5-10%) (Das et al., 2007). Another study conducted by Johansson (1999) stated that there are traces of manganese oxide, sulphur, vanadium oxide and titanium oxide in ACBFS. The same study found that the pH of slag was between 10.2 to 10.6. Density was reported between 1.4-1.6 g/cm^3 and porosity 40-55%. Both studies reported the components of ACBFS, however, they are not similar. This is due to the condition of iron making and depending on slag cooling condition-temperature, humidity (NSA, n.d.).

2.1.2. Open-Hearth Slag Formation and Characteristics

Open-hearth slag (OHS) is a by-product of steel making. OHS used to be produced in open-hearth furnace where pig iron was heated at a temperature of 2000° C to burn excess carbon and other impurities to produce steel (Crawford, 1969). US and Canada discontinued the use of open-hearth furnace to produce steel in the early 1990s. It was replaced with basic oxygen furnace and electric arc furnace. Currently, steel is predominantly made in electric arc furnace which produces electric arc furnace slag (NSA, n.d.). All steel slags have some limitations when used in structural fills and bases. Due to high free lime content present in steel slag, it is expansive and may cause differential movement when used as a base. Proper selection, processing and aging is required for steel slags to be used in construction. Figure 2.2 shows OHS formation in open-hearth furnace.

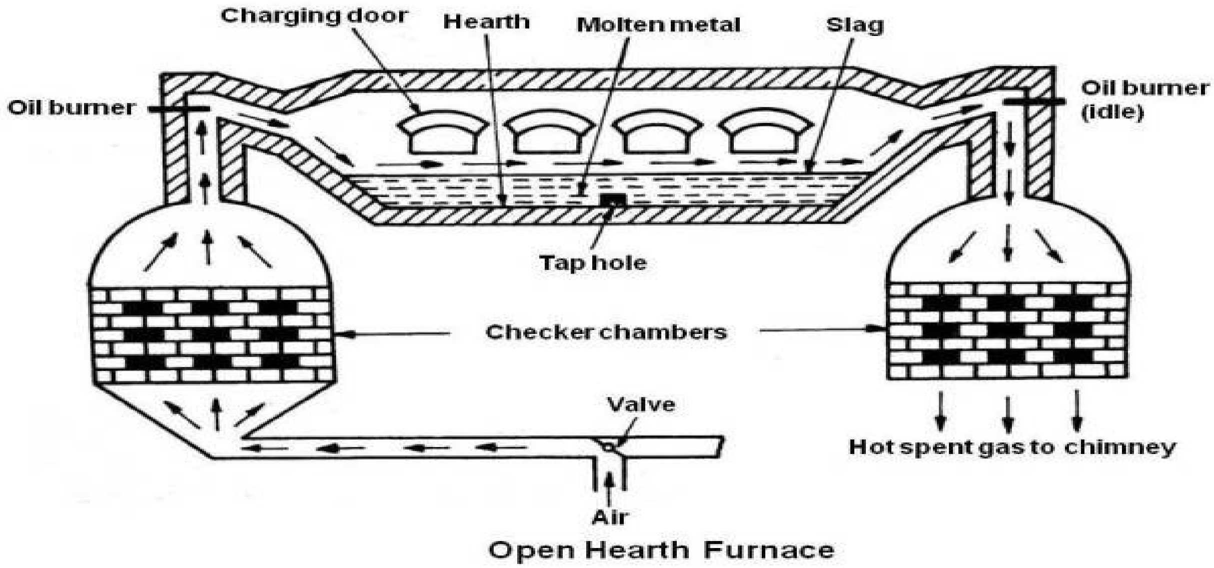

Figure 0.2: Open Hearth Furnace showing OHS production (K.P. Shah, n.d.)

Unlike blast furnace slag, OHS is not a popular choice of material in the construction industry (Gnaedinger 1987). This is due to the requirements of further processing and aging that is required before it is suitable for use in construction applications. Hence, finding an alternative waste-to-resource uses for this material is important to management strategies for current stock piles of OHS.

Information on the chemical composition of OHS in literature is very limited. However, several studies have reported that electric arc furnace slag's chemical composition is almost like basic oxygen furnace slag (Shen, et al., 2004; Schoenberger, 2001; Juckes, 2003). If the processes of producing steel are compared, open-hearth furnace and blast oxygen furnace have the same raw feed and operate almost at the same temperature. Electric arc furnace is fed recycled steel to produce new steel (Shen et al., 2004).

The primary chemical constituents of basic oxygen furnace slag and electric arc furnace slag are ferrous oxide (FeO), calcium oxide (CaO), and silicon dioxide (SiO_2). Other chemical constituents that are present in BOFS and EAFS are magnesium oxide (MgO), Alumina (Al_2O_3), manganese oxide (MnO), sodium oxide (Na_2O), potassium oxide (K_2O), phosphorus pentoxide (P_2O_5), titanium dioxide (TiO_2), and sulfur trioxide (SO_3). Table 2.1 summarizes the chemical composition of basic oxygen furnace slag and electric arc furnace slag reported in several studies.

Table 0.1: Summary of BOFS and EAF reported in literature (1Xue, et al., 2009; 2Mahieux, et al., 2009; 3Drizo, et al., 2006; 4Manso, et al., 2004)

Slag	SiO_2	CaO	Fe_2O_3	MgO	Al_2O_3	MnO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3
BOFS[1]	13.7	45.4	17.8	7.3	6.8	-	-	-	-	-	-
BOFS[2]	11.8	47.5	22.6	6.3	2.0	1.9	0.2	0.1	2.7	0.5	0.2
EAF[3]	13.7	30.4	34.7	13.1	4.67	1.30	-	-	0.32	-	-
EAF[4]	11	25	25	5	5	4	-	-	-	-	-

2.2. Stormwater

An important non-point source for the dispersion of variety of pollutants is stormwater runoff (Jartun, et al., 2008; Park & Roesner, 2012; Lee, et al., 2007; Brezonik & Stadelmann, 2002). The different potential sources of stormwater are municipal, industrial and commercial sites. In urban areas, stormwater runoff may result in deterioration of receiving water quality (Donigian & Huber, 1991; House, et al., 1993; Eriksson, et al., 2007; Beenen, et al., 2011; Langeveld, et al., 2012). Several studies have reported on the associated risks and potential impacts on the environment and human health due to stormwater runoff (Hoffman et al., 1984; Walker, McNutt, & Maslanka, 1999; Lundy, Ellis, & Revitt, 2012).

2.2.1. Stormwater Generation and Characteristics from Biomass Power Plants

Stormwater runoff generated at commercial and industrial sites may contribute significantly high pollution loads to receiving waters. This is due to the characteristics of the materials stored and processes taking place on-site (Brezonik & Staddelman, 2002; Beenen et al.,2011). In recent years, biomass-fired combined heat and power plants have gained great popularity in the energy sector, as biomass represents an important renewable energy conversion system. Biomass power plants generally use outdoor storage facilities of biomass fuels (Viana, et al., 2010; McIIveen-Wright, et al., 2013). The on-site storage of biomass fuel can result in various physical, chemical and biological transformations of the neat fuel as it sits exposed to the elements (Eriksson, 2011).

A study conducted by Larsson et al. (2016) reports that runoff water quantity in a biomass power plant is dependent not only on the precipitation patterns, but also on the amount of biomass stored on-site. That study also demonstrated that the amount of biomass stored on-site can significantly reduce the amount of runoff from a plant site, due to the ability of biomass to absorb water.

Biomass can leach heavy metals into the water phase. Zinc, lead, mercury, nickel, cadmium, silver, copper and chromium are some of the major heavy metals that can have been measured in stormwater run-off generated at biomass power plant facilities. The concentrations of metals that have been measured in stormwater runoff generated at biomass power plants have been shown to be linked to the type of biomass used and precipitation intensity measured at different sites (Eriksson, 2011).

Larsson et al. (2016) also stated that in the simulated experiment, zinc concentrations decreased as precipitation intensity increased. Cadmium was found to have very low solubility and concentration did not change with variable precipitation. The pH of the stormwater runoff can also change seasonally. In the span of a year, pH in stormwater runoff samples collected in Stockholm, Sweden were found to range from 6.7 to 7.7 (Larsson, et al., 2016). However, precipitation did not have a significant effect on the pH of stormwater. The study also concluded that biomass also contains organic compounds that can leach out from on-site stored biomass (wood) locations (Larsson, et al.,2016).

2.2.2. Stormwater Treatment Options

Clark and Pitt (2012) outline that proper stormwater design to prevent excess runoff quantities and pollutant generation by source control is not enough to eliminate discharge of contaminated runoff. Particle size of contaminants in stormwater affects the treatment. Some pollutants also interact with solids, and treatability is controlled by the removal of associated solids (House, et al., 1993 and Li, et al., 2005). Morquecho et al. (2005) conducted a study on stormwater runoff to identify the percent pollutant reductions achieved after removing all particulates greater than sizes- 20 µm, 5 µm, 1 µm and 0.45 µm. Total phosphorus, zinc, lead and suspended solids were significantly removed after 0.45 µm filtration. However, nitrate, cadmium and copper resulted in lower observed reductions due to the solubility of these metals present in the stormwater samples.

Clark and Pitt (2012) concluded that stormwater treatment should be based on pollutant size and type. That study determined that for solids with diameter greater than 5 to 10 µm, sedimentation processes can achieve significant reductions in pollutant loads. Solids with diameter 1 to 5 µm, physical removal of solids from the water phase can be achieved with filtration. For organic compounds and metals, both ion-exchange and chemically active media filtration have been shown to be useful (Clark & Pitt, 2012). Copper, zinc and cadmium can attach to very small particles depending on organic content, pH and oxidation-reduction conditions. It is also reported that these metals form complexes with a variety of organic compounds and inorganic ligands, and to remove these complexes, adsorbents such as GAC and peat have been shown to be useful.

2.2.3. Industrial Stormwater Discharge Regulations

In Canada, there are no specific regulations for stormwater quality. The guidelines produced by the Canadian Council of Ministers of the Environment (CCME) called "*Canadian Environmental Quality Guidelines (CEQG)*" is generally followed for stormwater management. This guideline contains the *Canadian Water Quality Guidelines for the Protection of Aquatic Life* that sets the maximum concentration limits for metals and other substances that can be discharged into freshwater and marine water. The guideline is not enforceable unless adopted by the provincial/territorial government (CCME, 2015). The Canadian provinces have regulations set up for industrial waste discharges. In NS, the "Contaminated Sites Regulations" is administered by the Nova Scotia Environment (NSE). The NSE has developed a *Numerical Environmental Quality Standards (EQS)* for NS contaminated sites. Currently, two standards are in place- Tier 1 EQS and Tier 2 EQS. These standards are developed to protect human health and ecology (Nova Scotia Environment, 2014)

Tier 1 EQS require minimal site information and are simple tabular values. This regulation was developed in a conservative manner to protect sites that are prone to be contaminated. Some EQS are pH specific and Ca, Mg hardness dependent, (i.e. depending on water quality EQS may change in this regulation). Tier 2 Pathway Specific Standards (PSS) can only be used if site concentrations exceed the Tier 1 EQS. Table 2.2, outlines the surface water (fresh water) metal discharge regulations as mentioned in Tier 1, 2 EQS and the CCME guidelines.

Table 0.2: Tier 1 and 2 NSEQS; CCME guideline on surface water discharge to protect human and aquatic life

	Concentration (µg/L)			
	Tier 1	Tier 2	CCME	
			Short Term	Long Term
Aluminum	5	5	No Data	Variable
Antimony	20	20	*	*
Arsenic	5	5	No Data	5
Barium	1000	1000	*	*
Beryllium	5.3	5.3	No Data	No Data
Boron	1200	1200	29,000	1500
Cadmium	0.01	0.01	1.0	0.09
Chromium (hexavalent)	1.0	1	No Data	1
Cobalt	10	10	*	*
Copper	2	2	No Data	No Data
Cyanide	5	5	*	*
Iron	300	300	No Data	300
Lead	1	1	No Data	Equation
Manganese	820	820	*	*
Mercury (total)	0.026	0.026	No Data	0.026
Methlymercury	0.004	0.004	*	*
Molybdenum	73	73	No Data	73
Nickel	25	25	No Data	Equation
Selenium	1.0	1	No Data	1
Silver	0.1	0.1	NRG	0.25
Strontium	21,000	21,000	*	*
Thallium	0.8	0.8	No Data	0.8
Uranium	300	300	33	15
Vanadium	6	6	*	*
Zinc	30	30	No Data	30

- *= No guideline in CCME
- NRG = No regulation guidelines

2.3. Waste Slag for the Removal of Metals from Water

Dimitrova (1996) studied the removal of copper, nickel and zinc ions from water using ungranulated blast furnace slag and described the sorption data using Freundlich's parabolic equation. Particle used in that study ranged between 0.041-0.25 mm. That study mentioned alkaline characteristic of the slag favored metal ion sorption. The results of that study found that BFS is an effective sorbent for copper, zinc and nickel ions. Due to the alkalizing ability of slag, the metal ions sorption mainly take place in the form of hydrooxocomplexes.

Gupta et al. (1997) conducted batch adsorption studies to evaluate blast furnace slag (BFS) in the removal of zinc and cadmium from water. The BFS used in the study had an average particle size of 0.089 nm, and optimum pH for Cd^{2+} and Zn^{2+} removal was determined to be 5.0 and 6.0, respectively. The results of that study showed that 90% removal of zinc and concentration was achieved when low concentration metal ions was present, whereas 55% removal was achieved at high concentration of metal ions. Freundlich and Langmuir constants (qm, K_F, n and b) were obtained- and showed that the slag treatment demonstrated less adsorption capacity for zinc than cadmium-slag system for both the models.

Dimitrova and Mehandgiev (1998) studied the removal lead using granulated blast-furnace slag from aqueous solution. Lead nitrate solution was used at a concentration of 1g/L. The researchers used 300 mL conical flask and added 125 mL of lead nitrate solution; using a rotary shaker at a speed of 100 rpm for 330 min. Freundlich isotherm was used to describe the sorption of lead. Maximum adsorption capacity of 35mg/g was obtained when lowest particle size was used. The results concluded that as the slag dose increased the sorption of lead and pH increased.

Babel and Kurniawan (2003), in a review of adsorbents that can uptake heavy metals, mentioned that BFS's adsorption capacity to remove lead and chromium was 40 and 7.5 mg/g. Kim et al. (2007) conducted a study to describe the removal process of copper using steel-making slag obtained from steel plants of Republic of Korea. The researchers report that major removal mechanisms of metal removal using slag are precipitation and adsorption. At pH above 3.0, the removal of copper depended on precipitation and adsorption. When the pH was at 1, it showed 100% sorption and no precipitation removal of copper. The results concluded that as pH increased precipitation had a significant effect on copper removal. Hence, the study suggested principle mechanism for removing copper using slag is not adsorption on slag surface but precipitation due to hydroxide dissolved from slag.

Nehrenheim and Gustafsson (2008) modelled kinetic sorption of copper, nickel, zinc, lead and chromium ions to blast furnace slag in a batch adsorption study. Volume of the solution used was not mentioned. The time for agitation ranged between 1 to 1000 seconds. The researchers concluded that low concentration and increased agitation time resulted in better metal sorption.

Figure 2.3, presents the metal hydrolysis of different metals. The figure explains specific pH of minimum solubility of different metals. For example, at pH 8.5, Fe^{3+} has a minimum pH solubility, whereas Zn at pH 10 and Cd at pH 11. At the pH of minimum solubility, the metals in dissolved form comes out of the water as it precipitates maximum at these pH values. This shows the significant effect on treatment that pH can have on metals removal by precipitation.

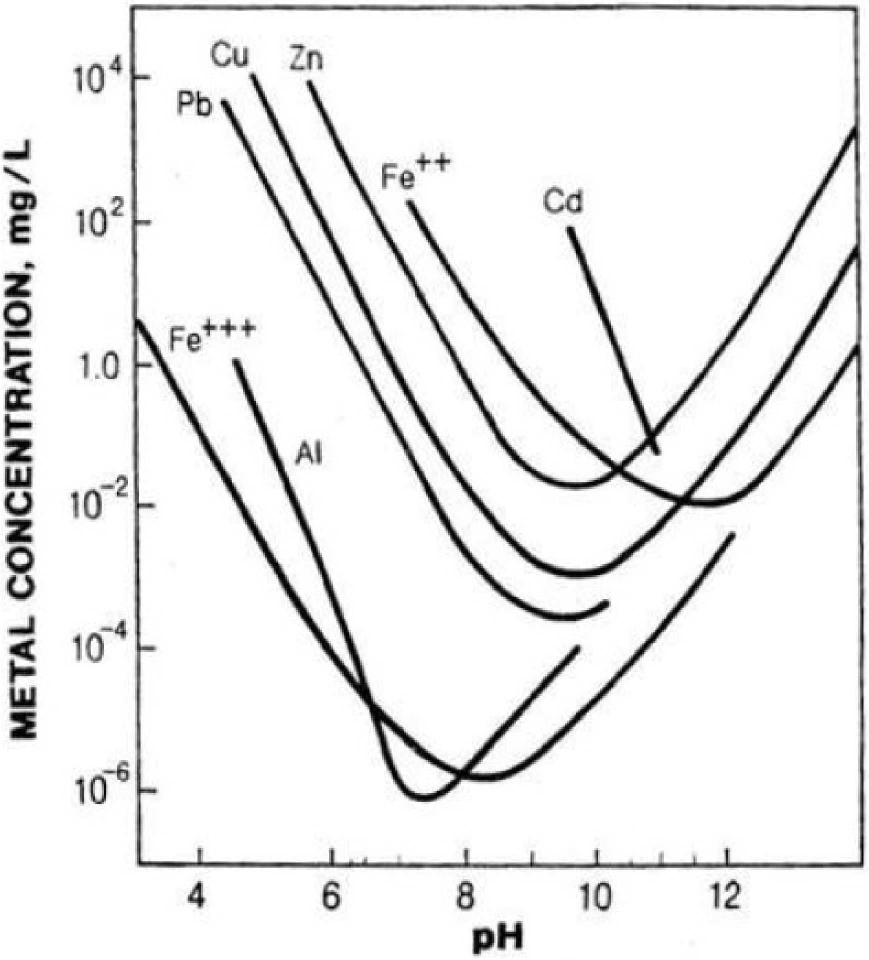

Figure 0.3: Minimum pH solubility of several metals (Aube and Zinck, 2003)

Chapter 3: Materials and Methods

Common materials and methods used throughout this study are outlined in this chapter. Bench-scale equipment, analytical and data analysis methods are also outlined. However, materials and methods specific to individual studies/sets of experiments are presented within their respective chapter.

3.1. Source Water Collection

All stormwater run-off samples were collected from a biomass power generating plant located in Liverpool, Nova Scotia, Canada. The stormwater run-off water samples (n = 3) were collected between December 2016 and June 2017. The samples were stored at 4° C for a month while being used for experiments.

Currently, the runoff flows into a sump and then enters a vault where it gets treated using a commercial absorbent. Samples were collected at the inlet and outlet in HDPE bottles. Figure 3.1, shows a sketch of the current treatment set up and collection point for this study.

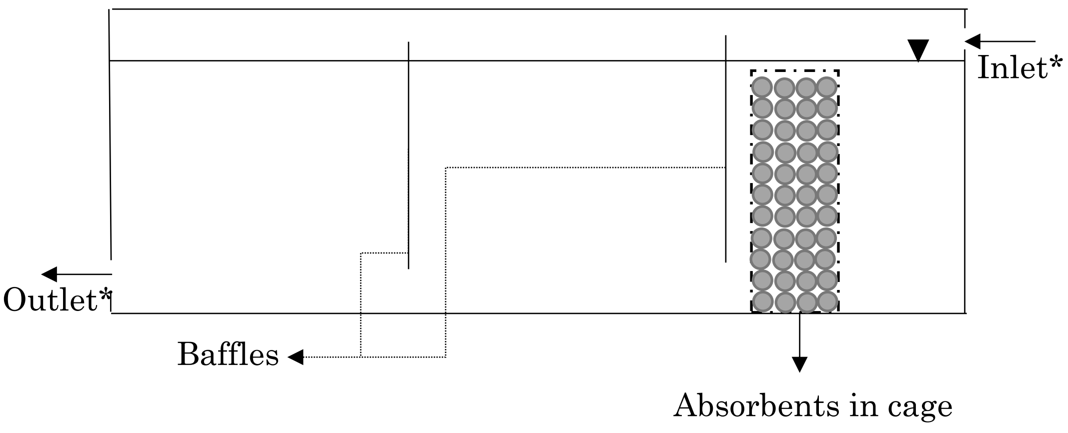

Figure 3.1: Current Treatment Setup and Collection Point (*)

3.2. Synthetic Stormwater

Synthetic stormwater was prepared according to the average concentrations (n = 3) present in the actual stormwater collected from biomass power generating plant. Two types of stormwater were prepared: (1) without natural organic matter (2) with natural organic matter. Certified ACS grade reagents were used to prepare stock solutions of the metal ions by dissolving 1 gram of cadmium chloride ($CdCl_2$), zinc chloride ($ZnCl_2$), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) and manganese sulfate monohydrate ($MnSO_4. H_2O$) in 1L of de-ionized water. These solutions were used in both types of water. The synthetic stormwater with organics was spiked with natural organic matter using stock solution which was prepared using 1L of humic acid sodium salt and then later adding it in required amount. Initial concentration of Cd, Fe, Mn, Zn and DOC were 0.05 mg/L, 10 mg/L, 5 mg/L, 0.05 mg/L and 40 mg/L, respectively.

3.3. Slag and GAC Preparation

ACBFS and OHS samples were obtained from Portside Aggregates Ltd., Sydney, Nova Scotia, Canada. These slags were formed during the iron and steel production at the Sydney Steel plant which operated for about 100 years (1899-1990). These slags are mined, processed and stored on-site in Cape Breton under natural weather conditions. ACBFS and OHS were shipped in 20 L buckets and stored in the laboratory at room conditions (20° C).

The slag samples were prepared for adsorption experiments based on methodology outlined by Gupta et. al. (1997). Sieve analysis was done to determine particle size distribution of both the slag samples. After obtaining 1.18 mm and 0.25 mm particle sizes, the slag samples were placed in 1 L jars and washed using de-ionized water from Milli-Q purification system (Barnstead Pacific Pro, ThermoFisher Scientific) to remove any impurities. The slag samples were dried at 105 ± 5° C for 24 hours in an oven (ThermoFisher Scientific) before activating in a muffle furnace (ThermoFisher Scientific) at 600° C for an hour. After cooling down, slags were transferred to a desiccator for storage before further use. A schematic diagram in Figure 3.2 shows the slag preparation process used in this research.

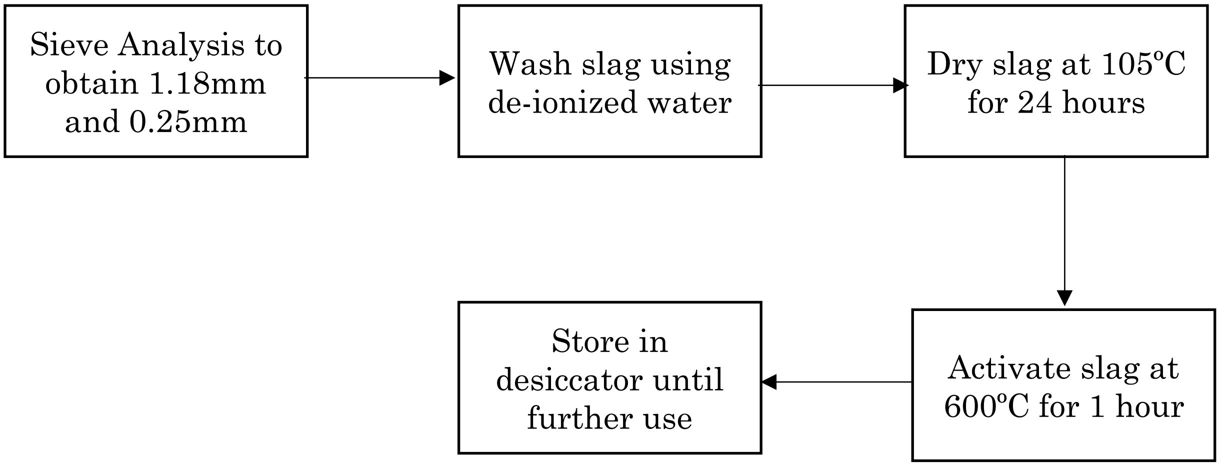

Figure 3.2: Slag preparation Process

Granular activated carbon (GAC) samples were obtained from General Carbon Corporation, Paterson, New Jersey. A virgin activated carbon, in granular form made from coconut shell was used in this study. The average GAC particle size was 1 mm and with a surface area of 1,100 m^2/g.

3.4. Bench-Scale Methods

A standard shaker table (MAXQ-2000, Barnstead International, Iowa, US) with 15 slots was used in all the batch-adsorption experiments in Chapters 5 and 6. The shaker table was operated at 250 rpm under room temperature conditions (i.e., 20 ± 1°C). Adsorbents were added in 250 mL Erlenmeyer flasks, containing 200 mL stormwater or synthetic water. The slag and GAC experiments evaluated doses of each media at 10, 15, 20, 25, 30, 35 g/L. After adding the adsorbent, a plastic film was applied to the opening of the Erlenmeyer flask to prevent any contamination or spill during shaking period. In Chapter 5, two slag sizes (1.18mm and 0.25mm) were evaluated and in chapter 6, only 0.25mm slag size was evaluated. After shaking for 24 hours, the flasks were removed from the shaker table and left to settle for 30 minutes. A schematic diagram of the batch-adsorption experiment is shown in Figure 3.3. pH adjustment was not done in any batch-adsorption experiments instead natural pH of real stormwater and synthetic water was used.

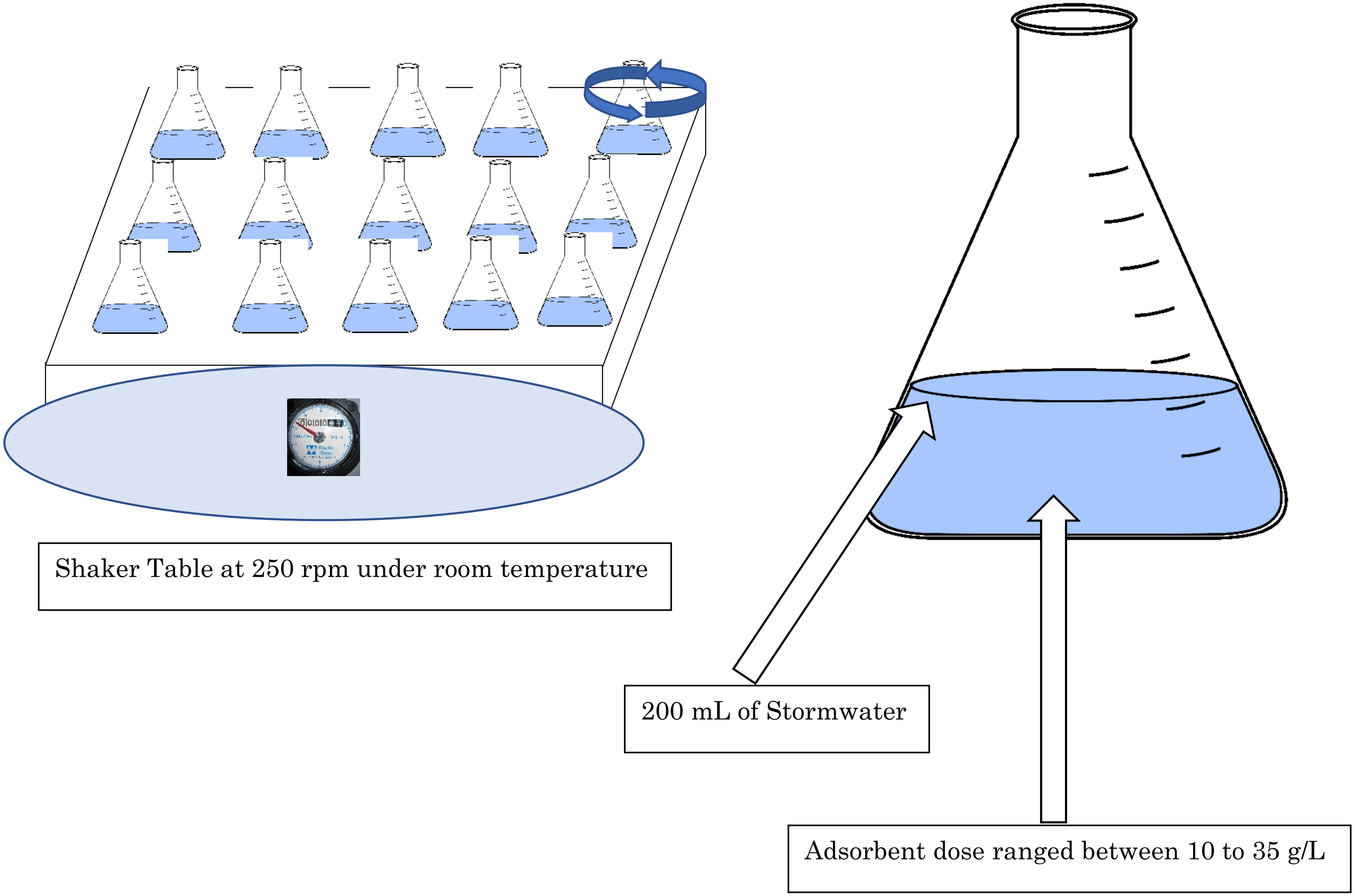

Figure 3.3: Batch-Adsorption Experiment Setup

3.5. Analytical Methods

Common water quality parameters that were measured throughout this study include pH, dissolved organic carbon (DOC), iron, manganese, cadmium and zinc.

3.5.1. General Water Quality Parameters

For all chemical stock preparations and cleaning procedures reverse osmosis (RO) water from a Milli-Q purification system was used. All Erlenmeyer flasks, jars used throughout this study was washed in 10% nitric acid bath for a day and then rinsed with RO water. pH was measured using an Accumet XL50 meter (Fisher Scientific), calibrated each day before use.

3.5.2. Organic Matter

Using a 0.45 μm polysulfone filter membrane (GE Water and Process Technologies) that was pre-rinsed with 100 mL Milli-Q water to avoid leaching of organics from filter papers, raw stormwater and treated stormwater samples were filtered for DOC analysis. 40 mL pre-cleaned glass vials were used, and DOC samples were preserved with concentrated phosphoric acid to pH < 2. A TOC-V CPH analyzer with a Shimadzu ASI0-V autosampler (Shimadzu Corporation, Kyoto, Japan) that have a 0.25mg/L method detection limit, was used for DOC measurements.

3.5.3. Metal Concentrations

Total and dissolved metal concentrations were measured for iron, manganese, cadmium and zinc using an inductively couple plasma mass spectrometry (ICP-MS) (XSERIES 2, Thermo-Fisher Scientific). Dissolved metal water samples were prepared by filtering water through a 0.45 μm polysulfone filter membrane that was pre-rinsed with 100 mL Milli-Q water to avoid leaching of any metals from filter papers. Due to metal concentration variability, serial dilution was carried out to 100-fold. Concentrated nitric acid was added to preserve the samples to pH <2.

3.6. Data Analysis

All experiments were carried out in triplicates and error bars on graphs represent one standard deviation. 2-way ANOVA tests were used to determine the significance of each parameter (adsorbent dose, adsorbent type, adsorbent size) in Chapter 5 using Minitab 17 (Minitab Incorporation). Langmuir and Freundlich isotherm models were plotted using Origin Pro 2017 (OriginPro Corporation) in chapter 6. Paired t-tests were used to determine if treated samples with natural organic matter were significantly different than the ones with no natural organic matter.

Chapter 4: Slag and Stormwater Characterization Study

4.1. Introduction

Slag is an alkaline material that is formed during the production of iron and steel. The blast furnace, where iron is produced, is charged with iron ore, limestone and coke for fuel. Two products are formed during this process: molten iron and slag. The slag consists mainly of silica, alumina, magnesium and calcium oxides. Slag comes out of the furnace at a temperature of about 1500°C in liquid form. The condition in which this liquid slag cools down and solidifies results in three different types of slag- air-cooled blast furnace slag (ACBFS), expanded pelletized and granulated blast furnace slag (NSA, n.d.). Molten pig iron is mixed with scrap and lime and heated in different kinds of furnace such as, open-hearth furnace, electric arc furnace and basic oxygen furnace, to produce different grade steels. Depending on which furnace was used to produce the steel results in different types of slag. Open-hearth furnace produces open-hearth slag (OHS). (NSA, n.d.).

There are several reuse options for ACBFS, mainly in the construction industry. ACBFS is widely used in road sub-base, concrete mix, pavement and backfill. While ACBFS has been widely used, OHS is not due to its nature of expanding. Several researchers have reported OHS's expanding behaviour and it can only be used if proper aging and processing is done before being used in construction industry (Crawford, 1969)

Excessive amounts of metals, including heavy metals are being released into the environment due to industrialization, and stormwater runoff which can be detrimental to human and aquatic life. Due to their persistence, bio-magnification, and toxicity, heavy metals have gained more significance than other aquatic pollution. Metals, such as cadmium (Cd), zinc (Zn), iron (Fe) and manganese (Mn) can accumulate in living tissue, and unlike organic wastes metals are non-biodegradable. Treating stormwater that has elevated metal concentrations above regulatory water quality limits before discharging it in the water body is important to protect aquatic and human life.

This study was undertaken to characterize and compare two different types of slag (1) air-cooled blast furnace slag (ACBFS) and (2) open-hearth slag (OHS). In addition, stormwater collected from a biomass power generating plant was characterized. The objectives of this study were as follows:

- Determine chemical characteristics of waste slags (ACBFS & OHS) in terms of major oxides and X-Ray diffraction.
- Investigate physical characteristics of waste slags (ACBFS & OHS) using scanning electron microscope (SEM).
- Determine run-off stormwater water quality characteristics from a Biomass Power Generating Facility

4.2. Materials and Methods

Slag and real stormwater runoff collection and preparation is explained in detail in Chapter 3.

SEM images of slag samples were obtained using a Hitachi S-4700 FEG Scanning Electron Microscope. X-ray diffraction (XRD) of slag samples were measured using a Philips XRG3100 X-Ray diffractometer. Major oxides were measured using with inductively coupled plasma-optical emission spectrometry or ICP-OES (Vista-PRO Radial, Varian).

pH of stormwater was measured using Accumet XL50 meter (Fisher Scientific), calibrated each day before use. DOC was measured using A TOC-V CPH analyzer with a Shimadzu ASI0-V autosampler (Shimadzu Corporation, Kyoto, Japan) that has a 0.08mg/L method detection limit after passing it through 0.45 µm polysulfone membrane. All metal concentrations (total and dissolved) were measured using an inductively couple plasma mass spectrometer (ICP-MS) (XSERIES 2, Thermo-Fisher Scientific). A 0.45 µm polysulfone filter membrane which was pre-rinsed with 100 mL of Milli-Q water to avoid leaching of any metals from filter paper was used to filter before analyzing for dissolved metals. To preserve the samples to $pH < 2$ concentrated nitric acid was added.

4.3. Slag Physiochemical Characterization Results

This section contains the physical and chemical characterization results of ACBFS and OHS. Samples used in this study were all dry. Physiochemical characterisitcs of ACBFS and OHS are compared to each other.

4.3.1. Sieve Analysis

Sieve analysis was conducted on the slag samples obtained after the slags were cleaned and dried as mentioned in Chapter 3. The results of sieve analysis are shown in Figure 4.1.

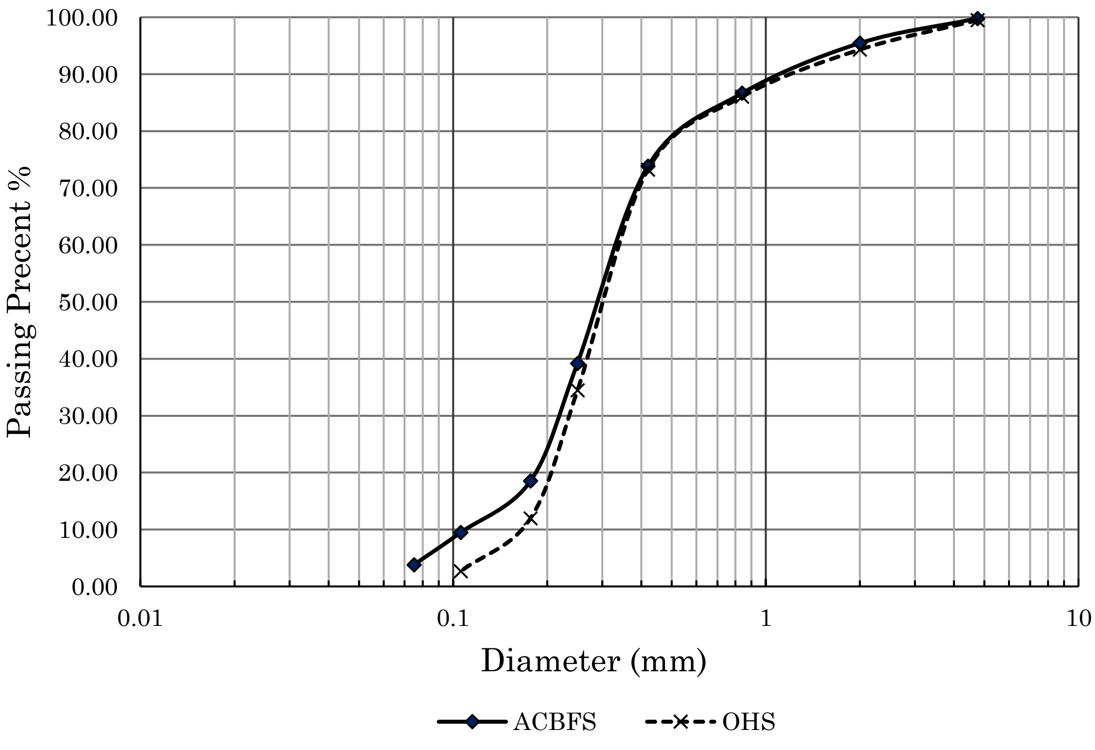

Figure 4.1: Sieve analysis results on ACBFS and OHS

The sieve analysis indicate that the particle size distribution was quite similar in both types of slag. This also depends on how it was sampled from the slag site.

4.3.2. Major Oxides

Table 4.1 presents the results of the major oxides analysis of ACBFS and OHS. This table also includes the total CaO available lime content of ACBFS and OHS.

Table 4.1: Major Oxides of ACBFS and OHS

Parameter	ACBFS (wt. %)	OHS (wt. %)
Al_2O_3	10.95	4.78
BaO	0.05	0.03
CaO	40.33	15.97
Cr_2O_3	<0.01	0.24
Fe_2O_3	3.95	37.67
K_2O	0.77	0.82
MgO	3.18	4.76
MnO	0.41	1.93
Na_2O	0.3	0.24
P_2O_5	0.21	0.61
SiO_2	29.55	20.89
S (As SO_3)	4.02	0.66
SrO	0.06	0.02
TiO_2	0.57	0.42
V_2O_5	0.02	0.05
ZrO_2	0.03	0.01
LOI 1000 °C	5.57	10.8
Total	99.98	99.9

ACBFS samples were shown to contain higher aluminum oxide (Al_2O_3), calcium oxide (CaO) and silicon dioxide (SiO_2) levels than the OHS samples. Iron (III) oxide was found to be significantly higher in OHS (37.67 Wt.%) compared to ACBFS (3.95 Wt.%).

Several studies have previously reported that Fe_2O_3 content is lower in ACBFS. In a study conducted by Demoulian et al. (1980) found Fe_2O_3 in ACBFS at a minimum of 0.30 wt.% to a maximum of 9.30 wt.%. The same study reported similar values found in this study of other major oxides in their slag- SiO_2 (32.0-37.3 wt%), CaO (37.9-44.4 wt.%), Al_2O_3 (10.3-16.0 wt.%), MgO (3.60-8.70 wt.%), MnO (0.34-1.31 wt.%), TiO_2 (0.49-0.65 wt.%), Na_2O (0.25-0.50 wt.%), K_2O (0.44-0.98 wt.%). Another study conducted by Das et. al. (2006) agrees with the values of major oxides found in this study – SiO_2 (37.14 wt.%), CaO (37.40 wt.%), Al_2O_3 (9.15 wt.%), Fe_2O_3 (1.05 wt. %), MgO (11.70 wt.%).

Since the process of OHS production is quite similar to that of EAFS and BOFS, the results of major oxides of OHS are compared with them. The major oxides of OHS, summarized in Table 4.1, in this study show almost similar results of Fe_2O_3 (34.7 wt.%) and Al_2O_3 (4.67 wt. %) as reported in a study conducted by Drizo et. al., (2006) on EAFS. The results obtained for OHS also shows that CaO is present at a significantly lower amount compared to EAFS and BOFS.

The major oxides result of ACBFS and OHS shows that these two materials are different and have different characteristics. While CaO in ACBFS is about 40 wt.%, OHS has only about 16 wt.%. Fe_2O_3 and $Al2O_3$ results show another significant difference in these two materials' chemical characteristic.

4.3.3. X-Ray Diffraction

ACBFS's mineralogical composition is shown in Figure 4.2. XRD reveals that the main mineral in ACBFS is gehlenite ($Ca_2Al_2SiO_7$). This observation agrees with another study conducted by Mostafa et. al., (2001), where their ACBFS showed gehlenite as the main mineral with an intensity scale factor of 0.86. There are other non-pronounced peaks of calcium carbonate ($CaCO_3$) (0.52) and potassium thiocyanate (KSCN) (0.14).

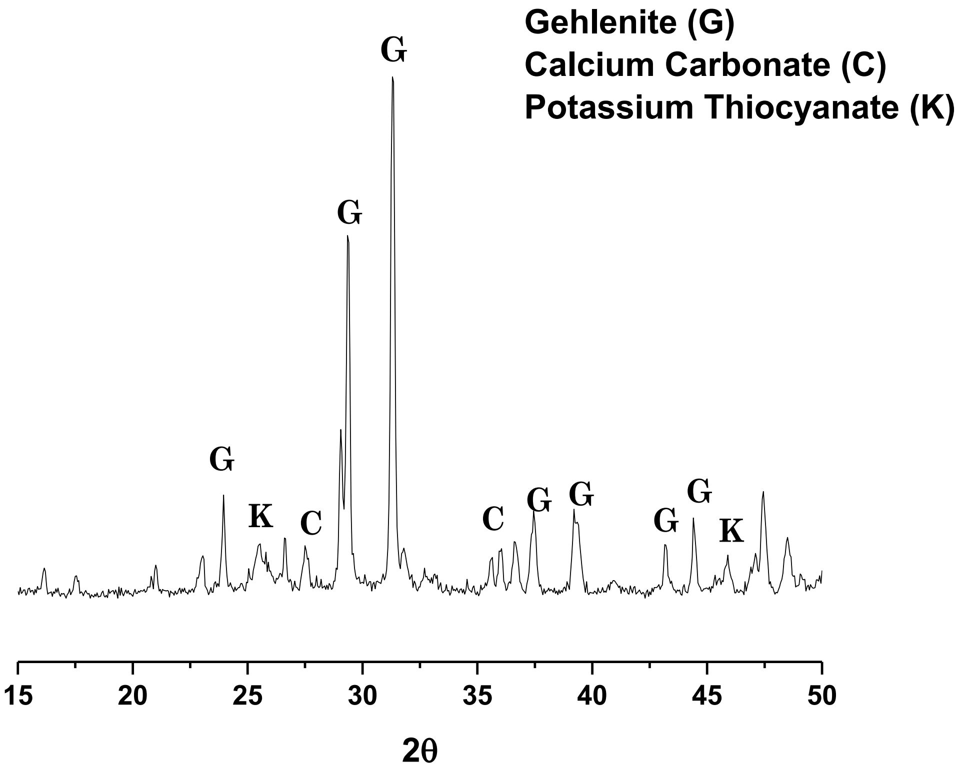

Figure 4.2: XRD pattern of ACBFS

OHS's mineralogical composition is shown in Figure 4.3. The main mineral in OHS was found to be quartz (SiO_2) with an intensity scale factor of 0.99. The other peaks which are not as pronounced as quartz are calcium carbonate ($CaCO_3$) (0.29), magnetite (Fe_3O_4) (0.22) and Akermanite-Gehlenite ($(Ca_2\ (Mg0_{.5}Al_{0.5})\ (Si_{1.5}Al_{0.5}O_7)$ (0.23). Literature published on EAFS and BOFS do not show similar XRD results, this may be due to the condition OHS was produced or stored.

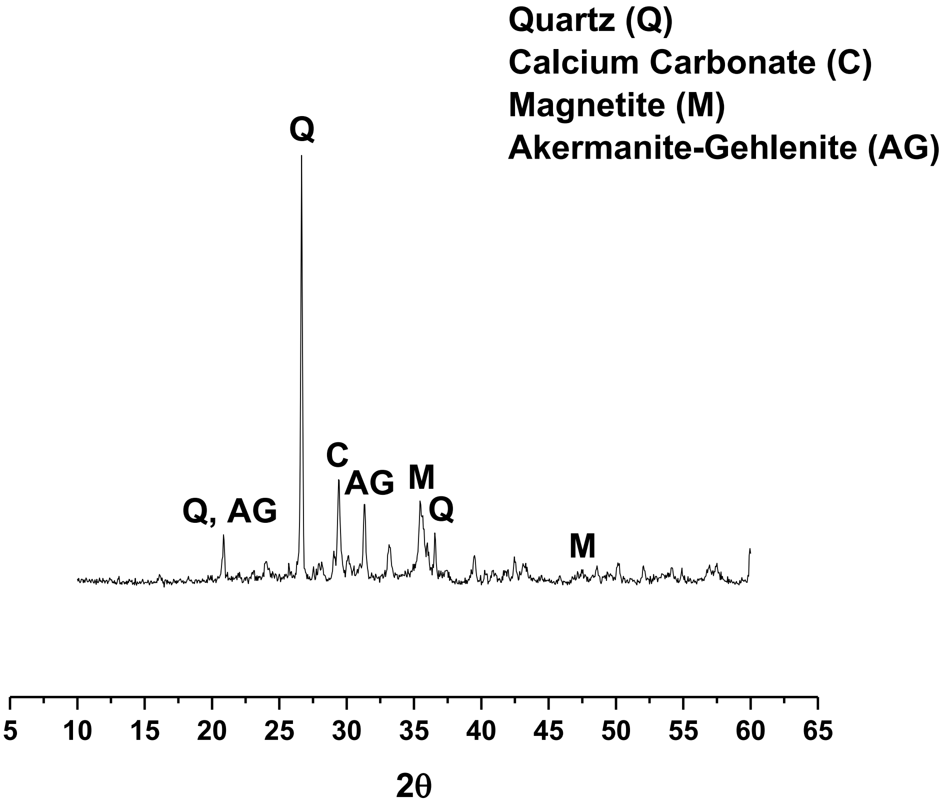

Figure 4.3: XRD pattern of OHS

The mineralogical composition analysis confirms that ACBFS and OHS have different phases. However, gehlenite is present in a different form in OHS. This characteristic difference may show different behaviour when used in application for the same purpose.

4.3.4. SEM Analysis

The SEM images that were taken for OHS and ACBFS are shown in Figure 4.4.

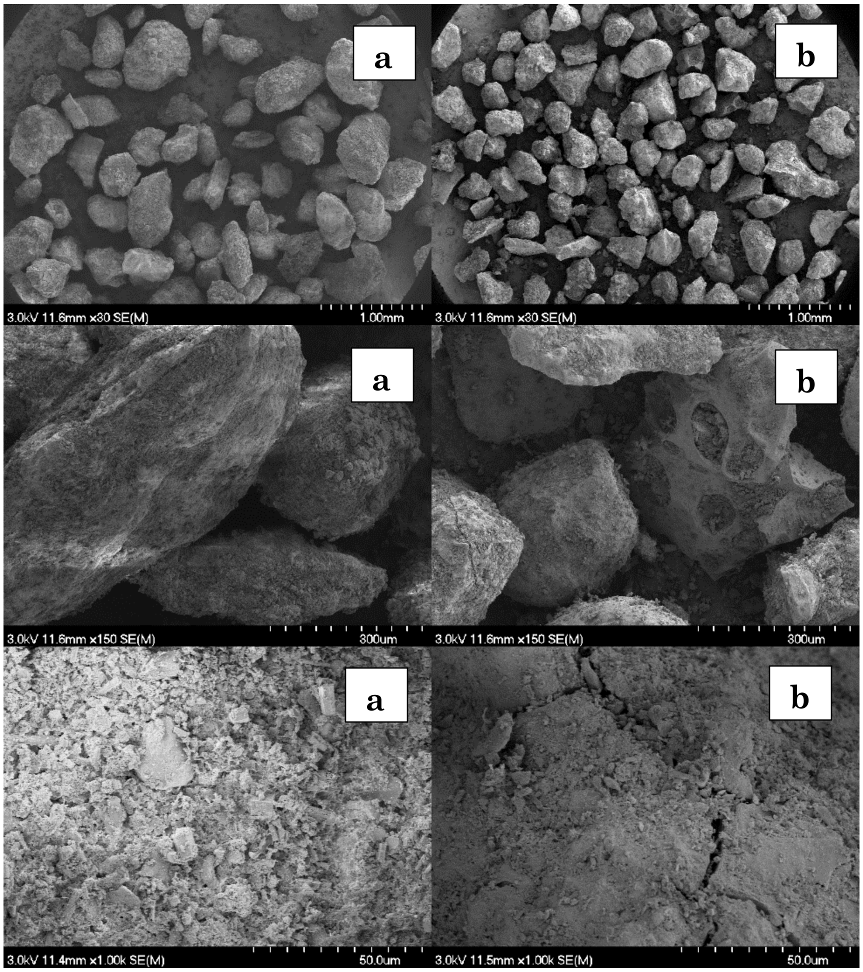

Figure 4.4: SEM images of (a) ACBFS-0.25 mm and (b) OHS-0.25 mm

The images confirm that ACBFS and OHS both have irregular particle shapes even after sieving. ACBFS has larger particles compared to OHS. Smoother surface is also observed on ACBFS than OHS. Large variability in composition and particle shape is observed in these images.

4.4. Stormwater Run-Off Characterization

Three separate stormwater run-off samples (20-L) were obtained from a biomass power generating plant as outlined in Chapter 3. pH and dissolved organic carbon (DOC) were found to be 7.4 ± 0.4 and 40 ± 5 mg/L. Total metal concentrations are shown in Table 4.2.

Table 4.2: Total Metal Concentration in Stormwater from biomass power generating plant site (n=3)

Metal	Concentration (μg/L)	Metal	Concentration (μg/L)
Aluminum (Al)	634 ± 348	Manganese (Mn)	5400 ± 1435
Antimony (Sb)	<1.0	Molybdenum (Mo)	<2.0
Arsenic (As)	7.88 ± 1.60	Nickel (Ni)	4.4 ± 0.75
Barium (Ba)	54 ± 14	Phosphorus (P)	770.25 ± 219.78
Beryllium (Be)	<1.0	Potassium (K)	41675 ± 5437
Bismuth (Bi)	<2.0	Selenium (Se)	<1.0
Boron (B)	151 ± 24	Silver (Ag)	<0.10
Cadmium (Cd)	55 ± 15	Sodium (Na)	14900 ± 1628
Calcium (Ca)	45600 ± 5226	Strontium (Sr)	214.25 ± 28
Chromium (Cr)	7.35 ± 3.71	Thallium (Tl)	<0.10
Cobalt (Co)	6.91 ± 3.28	Tin (Sn)	<2.0
Copper (Cu)	9.85 ± 2.58	Titanium (Ti)	15.43 ± 6.63
Iron (Fe)	10500 ± 4543	Uranium (U)	<0.10
Lead (Pb)	2.5 ± 0.6	Vanadium (V)	8.05 ± 1.47
Magnesium (Mg)	12275 ± 1375	Zinc (Zn)	24.26 ± 5.71

The total metal concentrations in stormwater show elevated concentrations of cadmium (Cd), iron (Fe), manganese (Mn) and zinc (Zn), that are above the NSEQS Tier 1 regulation and CCME guidelines.

Chapter 5: Removal of Target Metals from Stormwater Runoff Using Slag and GAC

5.1. Introduction

A major environmental pollution source from industrial sites is heavy metals (Kim et al., 2007). Extremely toxic and non-biodegradable gives rise to a unique character to heavy metals. Through the food chain, the human body can accumulate these metals that can cause harmful side effects (Ortiz et. al., 2001). Chemical precipitation, cementation, ion exchange, electrodeposition are conventional water treatment methods, that are costly.

Renewable energy popularity has increased in the recent years. This has given rise to the popularity of using biomass power plants to generate electricity. Often biomass power plants store biomass fuels onsite in open pits. Storing biomass fuel in outdoor storage can result in physical, chemical and biological transformation of the stored biomass material. Stormwater from these outdoor storage sites may increase pollutant load in stormwater runoff. This can be a major concern for the environment since stormwater may be directly discharged into fresh water bodies (Larsson et al., 2016). Environmental impacts of stormwater runoff from biomass facilities have been reviewed in a study conducted by Hedmark and Scholz (2008). The researchers concluded that biomass storage resulted in elevated metal concentrations in stormwater. Due to the characteristics of the materials stored and processes taking place on site, commercial and industrial sites such as biomass power plants can contribute to significantly higher metal concentrations in receiving waters through stormwater runoff.

Dimitrova (1996) conducted an adsorption study of heavy metals using blast furnace slag. The study indicated that blast-furnace slag is an effective sorbent for heavy metals and its efficiency depend on contact time, ions concentration and pH setpoints. In another study carried out by Gupta et al. (1997), zinc and cadmium were removed from wastewater using slag. The researchers used Langmuir and Freundlich isotherm model to fit the experimental results. That study concluded that blast furnace slag removed zinc and cadmium efficiently, and suggested use of blast furnace slag in environmental remediation where heavy metals need to be removed. The aim of this study was to evaluate the removal capacity of heavy metals, particularly cadmium, zinc, iron and manganese, from actual stormwater using ACBFS and OHS and a commercially available adsorbent, GAC. The specific objectives of this study were:

- To investigate the effect of two particle sizes of slags (1.18mm and 0.25mm) on metal removal
- Investigate high and low dose of adsorbents on metal removal
- Compare ACBFS and OHS to GAC’s metal removal capacity
- Evaluate the effect of final pH on metal removal

5.2. Materials and Methods

5.2.1. Source Water

Industrial site stormwater was obtained from a biomass power generating plant located in Liverpool, Nova Scotia, Canada. Stormwater samples (n=3) used for this study was sampled on August 16th, 2017 and were stored at 4 °C. The raw water sample used in this study is characterized and summarized in Table 5.1. Elevated metal concentrations above NSEQS Tier I regulation and high natural organic matter content were observed in the stormwater generated from the biomass power plant. Natural organic matter was quantified as dissolved organic carbon (DOC) in this study.

Table 5.1. Industrial Site Stormwater Characteristics for samples obtained on August 16th, 2017 (n=3)

Analyte	Average
pH	7.10 ± 0.10
Dissolved organic carbon (mg/L)	43.5 ± 3.7 mg/L
Total cadmium (µg/L)	0.4 ± 0.014 µg/L
Total iron (µg/L)	6250 ± 25 µg/L
Total manganese (µg/L)	1890 ± 19.5 µg/L
Total zinc (µg/L)	25 ± 3.5 µg/L

5.2.2. Slag and Activated Carbon

Two kinds of slag (ACBFS and OHS), each with two different sizes (1.18 and 0.25 mm) were evaluated in this study. Material preparation is described in detail in Chapter 3. For comparison purposes, GAC was also evaluated to remove target metals- iron, manganese, cadmium and zinc from real stormwater. Particle size of GAC was 1.00 mm, details of GAC is provided in Chapter 3.

5.2.3. Statistical Analysis

A 2-way ANOVA was conducted on results of each target metal. Three variables with 2 factors were analyzed to find the significant variable for removing each metal. All statistical analysis excludes GAC and only compare ACBFS and OHS in this chapter.

5.3. Removal of Target Metals from Stormwater

The target metals evaluated in this study were iron, manganese, cadmium and zinc. Removal results, Langmuir and Freundlich isotherm, statistical analysis of each metal are shown in the following sub-sections. Also, pH effect in metal removal is also included.

5.3.1. Cadmium (Cd) Removal

The initial total concentration of cadmium in the stormwater samples was 0.4 ± 0.014 μg/L. NSEQS Tier 1 regulation set a limit of 0.01 μg/L in surface water discharge. Figure 5.1 shows the total change in cadmium concentrations as the adsorbent dose was increased for two particle sizes of ACBFS and OHS compared to GAC.

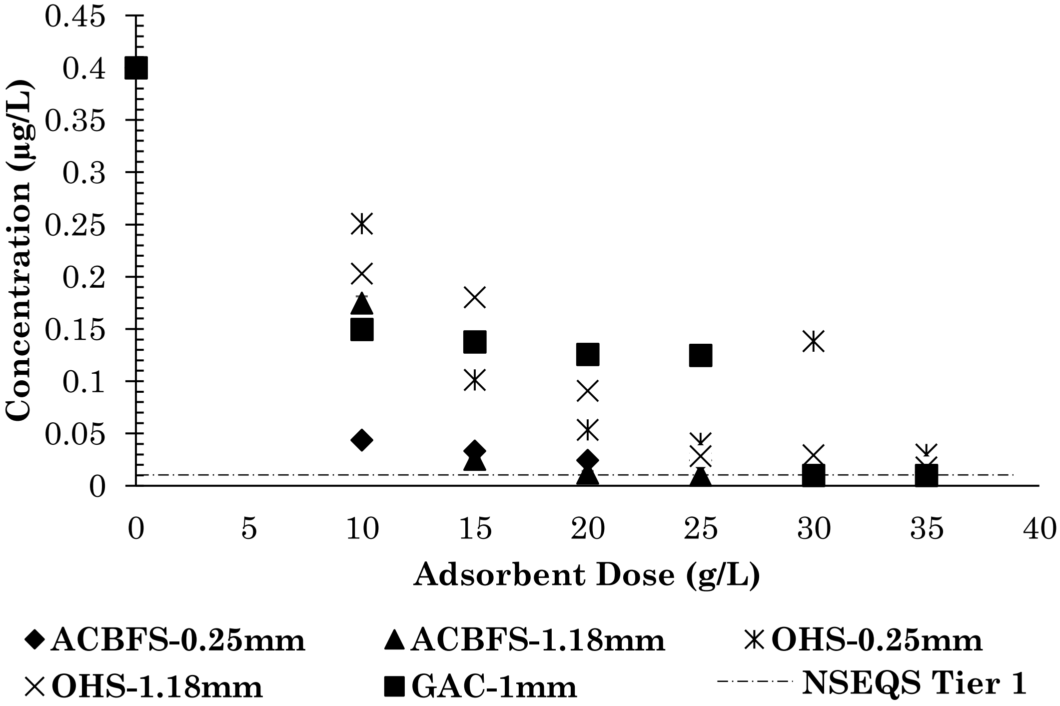

Figure 5.1: Total cadmium concentration vs. adsorbent dose

As the dose of the adsorbents increased, the cadmium concentration decreased. ACBFS-0.25 mm particle size at the lowest dose of 10 g/L resulted in the lowest concentration of cadmium compared to other adsorbents and sizes at a 10 g/L dose. At 30 g/L adsorbent dose, treatment with both particle sizes of ACBFS resulted in cadmium concentrations that would meet NSEQS Tier 1 regulations. GAC at doses between 10 to 25 g/L, resulted in a plateau concentration of Cd (0.14 mg/L). At 35 g/L, treatment of the stormwater samples with all of the adsorbents resulted in treated water that met the NSEQS Tier 1 regulation. Figure 5.2, shows metal removal efficiency of Cd at low (10 g/L) and high (35 g/L) doses for different adsorbents.

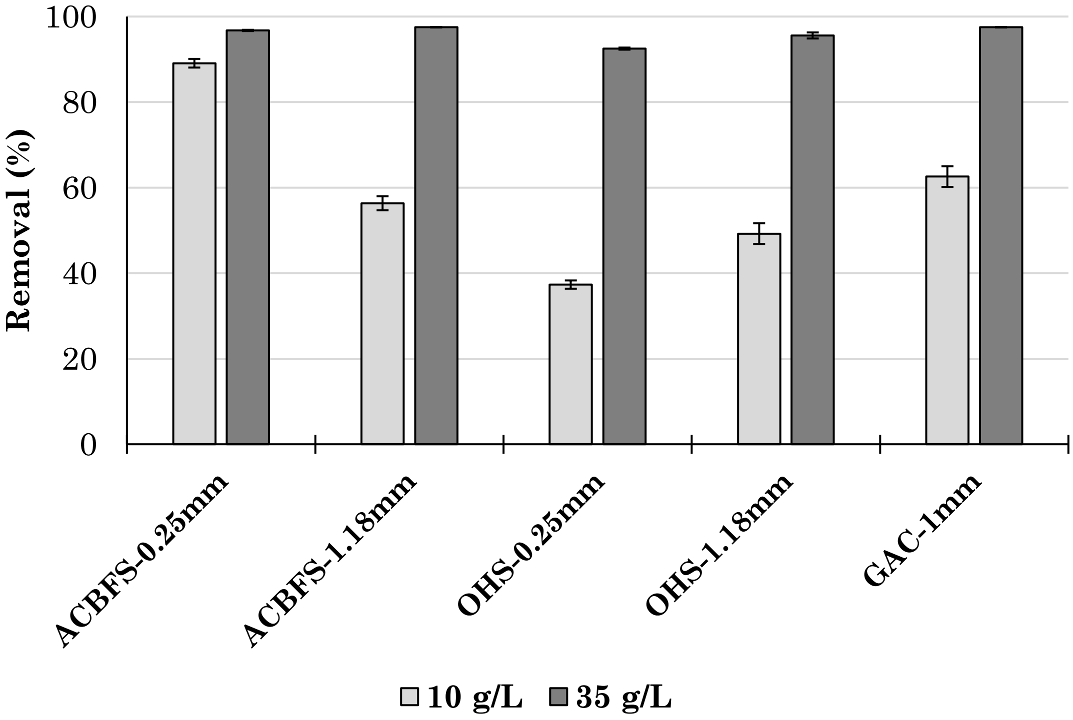

Figure 5.2: Removal percent of cadmium using different slags and GAC

Higher dose resulted in more than 90% removal of Cd from stormwater regardless of the particle size of ACBFS and OHS. GAC removed 90% of Cd at higher dose whereas only 60% when lower dose is used. OHS-0.25 mm removed the least amount of Cd at smaller dose which is less than 40%. A 2-way ANOVA confirmed that the slag's type and size did not have a significant effect on the final concentration of cadmium in stormwater. The significant effect was found to be the dose of the slag ($p < 0.05$). Appendix A contains the ANOVA analysis results conducted on cadmium concentration.

5.3.2. Iron (Fe) Removal

The initial total concentration of iron in stormwater was 6250 ± 25 µg/L. NSEQS Tier 1 regulation set a limit of 300 µg/L of Fe in surface water discharge. Figure 5.3 shows the total change in iron concentrations as the adsorbent dose was increased for two particle sizes of ACBFS and OHS.

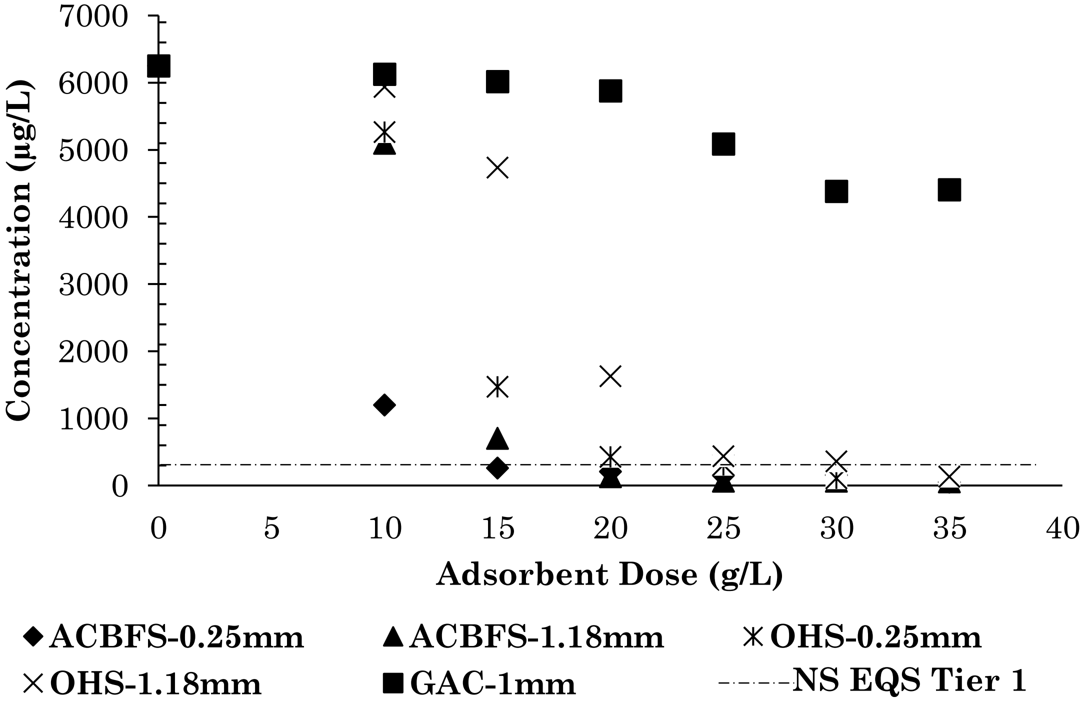

Figure 5.3: Concentration of iron vs. adsorbent dose

From the above figure, treatment of the stormwater with both slags decreased the concentration of iron as the slag dose was increased. At higher doses, treatment with these slags was shown to produce water that would meet the NS EQS Tier 1 regulation. However, treatment of the stormwater with GAC was not found to result in sufficient removal of iron to meet the NS EQS regulation. Figure 5.4, shows the iron removal efficiency at low (10g/L) and high (35g/L) doses of the different adsorbents.

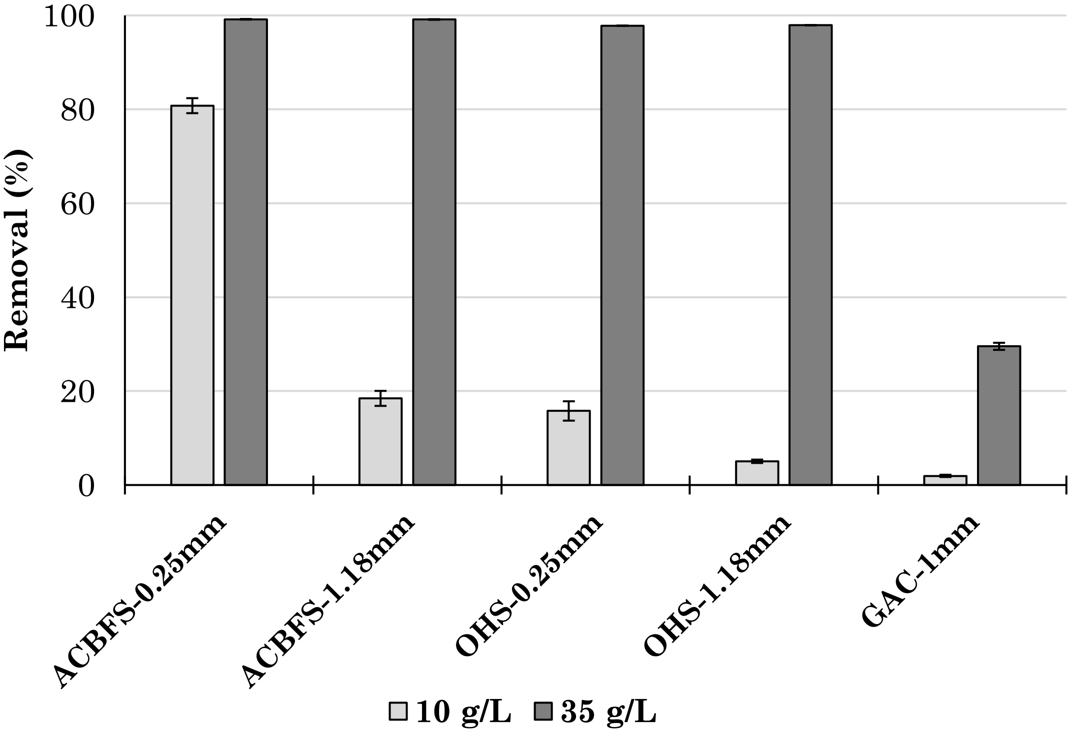

Figure 5.4: Removal percent of iron using different slags and GAC

Smaller particle sizes aided in better iron removal compared to larger particle sizes. ACBFS with smaller particle size at low dose removed more than 80% of iron from stormwater, whereas OHS with smaller particle size removed only up to 18%. At higher dose regardless of the particle size ACBFS and OHS, both slags removed more than 95% of iron. At higher dose, GAC removed about 30% of iron, however, smaller dose did not remove more than 5% of iron from stormwater. A 2-way ANOVA confirmed that the slag's type and size did not have a significant effect on the final concentration of iron in stormwater. The significant effect was found to be slag's dose at p-value <0.05. Appendix A contains the ANOVA analysis results conducted on iron concentration.

5.3.3. Manganese (Mn) Removal

The total initial concentration of Mn in stormwater was 1890 ± 19.5 µg/L which was higher than the NSEQS Tier 1 regulation. The maximum limit permitted, according to NSEQS Tier 1, is 820 µg/L in surface water discharge to protect aquatic and human life. Figure 5.5 shows the total change in manganese concentrations as the adsorbent dose was increased for two particle sizes of ACBFS and OHS.

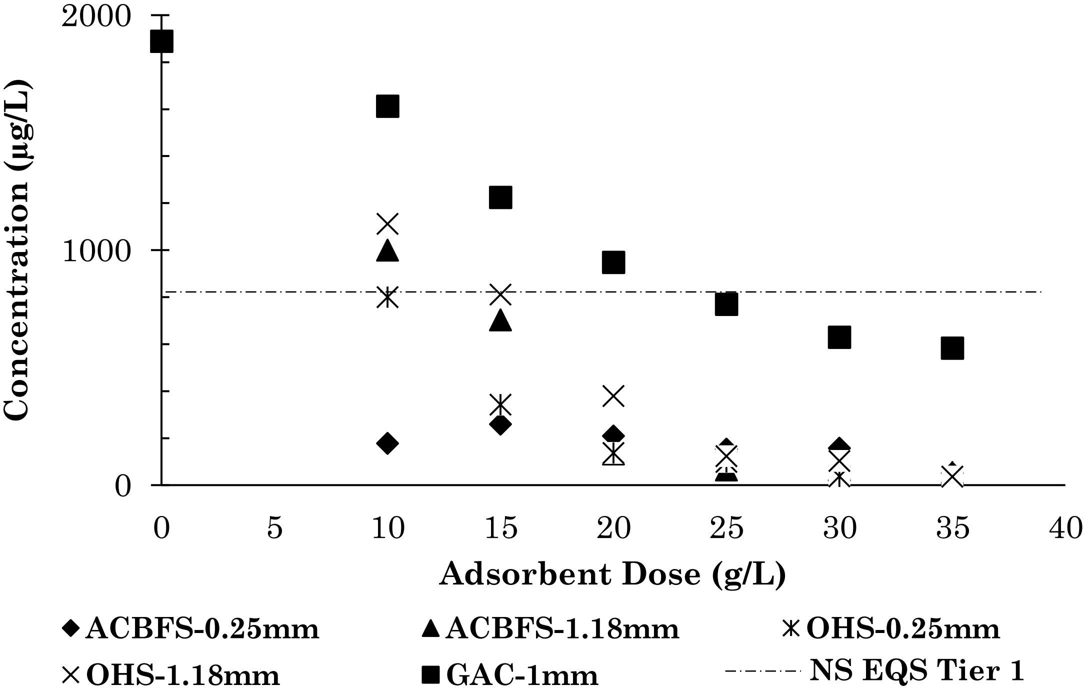

Figure 5.5: concentration of manganese vs. adsorbent dose

As the dose of the adsorbents increased the Mn concentration in stormwater decreased. At higher doses, treatment with these slags was shown to produce water that would meet the NS EQS Tier 1 regulation. ACBFS-0.25 mm showed that even at lower dose, it can remove Mn from stormwater that meet the NSEQS Tier 1 regulation. However, this is not the case for other adsorbents. GAC requires almost more than double the amount of dose to meet this regulation. OHS smaller and larger particle size also removed Mn at smaller doses compared to GAC. Figure 5.6, shows the Mn removal efficiency of adsorbents at high and low dose.

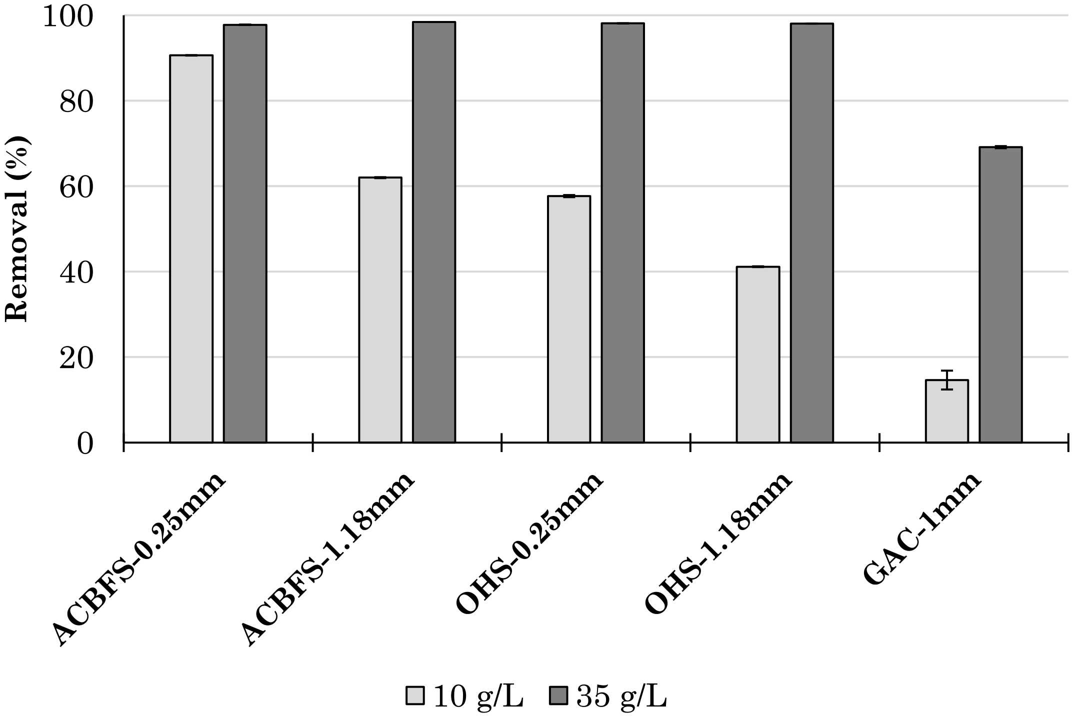

Figure 5.6: Removal percent of Mn at low and high dose of slags and GAC

More than 90% of Mn was removed at high dose when ACBFS and OHS was used. However, GAC removed only up to 65% of Mn from stormwater runoff. ACBFS-0.25 mm removed about 90% at low dose which was not achieved by OHS or GAC. OHS-0.25 mm removed less than 60% when lower dose was used and OHS-1.18 mm removed even lower percent of Mn at lower dose. A 2-way ANOVA confirms that slag's type and size did not have a significant effect on the final concentration of manganese in stormwater. The significant effect was found to be slag's dose at p-value <0.05. Appendix A contains the ANOVA analysis results conducted on manganese concentration.

5.3.4. Zinc (Zn) Removal

The total initial concentration of Zn was 25 ± 3.5 µg/L which is below the NSEQS Tier 1 regulation. However, due to the other samples (sampled in 2014 and 2016) obtained having higher concentration of Zn present in stormwater, the metal removal was still evaluated using slag and GAC. Figure 5.7, shows the change in concentration of Zn when adsorbent doses are increased.

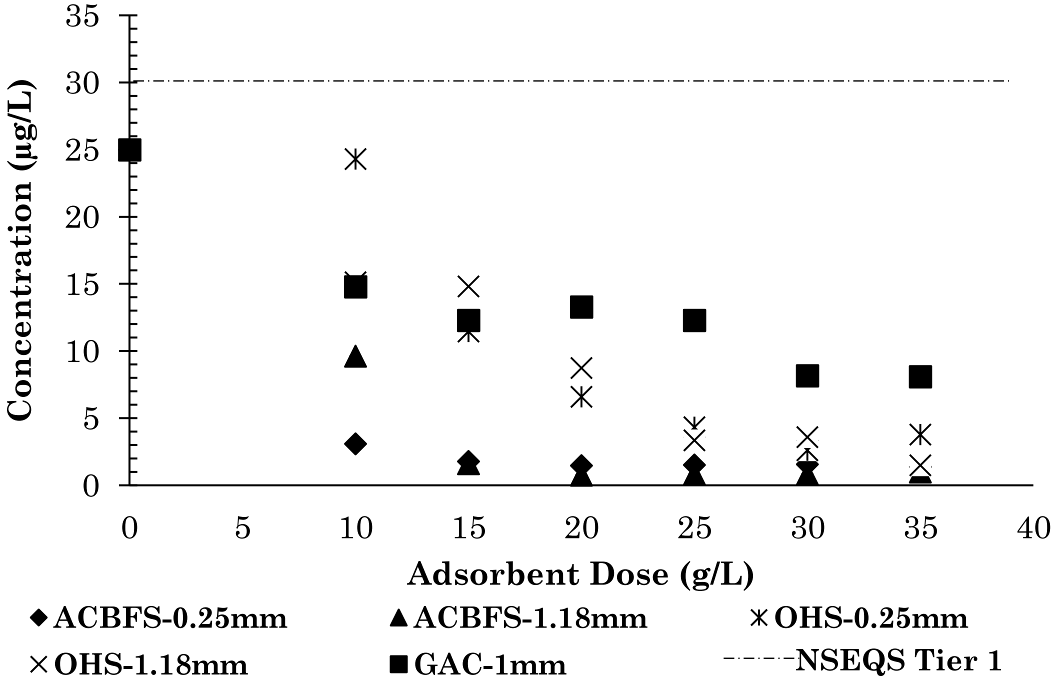

Figure 5.7: Zn concentration vs. adsorbent dose

Zn concentration decreased in the stormwater runoff as the adsorbent dose increased. ACBFS-0.25 mm decreased Zn concentration at lower dose and continued to be at a plateau concentration (2 µg/L) even when more of ACBFS-0.25mm was added to the water. Both particle sizes of OHS removed Zn but not at a same concentration as ACBFS. GAC did not decrease Zn concentration even when adsorbent dose was increased. Figure 5.8, shows the removal percent of Zn when slags and GAC are used.

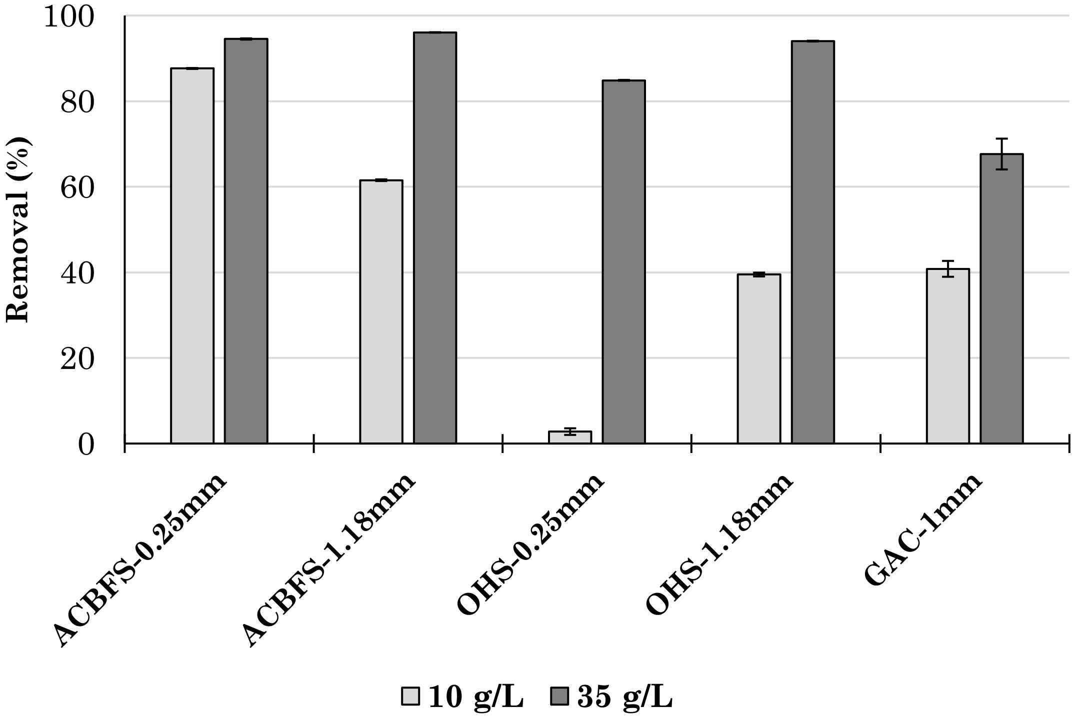

Figure 5.8: Percent removal of Zn at low and high dose of slags and GAC

ACBFS and OHS at high dose removed more than 85% of Zn from stormwater. However, OHS-0.25 mm showed very small removal of Zn at low dose. Zn removal GAC was at maximum of about 70% when high dose was used. A 2-way ANOVA confirms that slag's type, size and dose did not have a significant effect on the final concentration of zinc in stormwater. Appendix A contains the ANOVA analysis results conducted on zinc concentration.

5.4. pH Effect

The final settled water pH of all the treatments are shown in Figure 5.9.

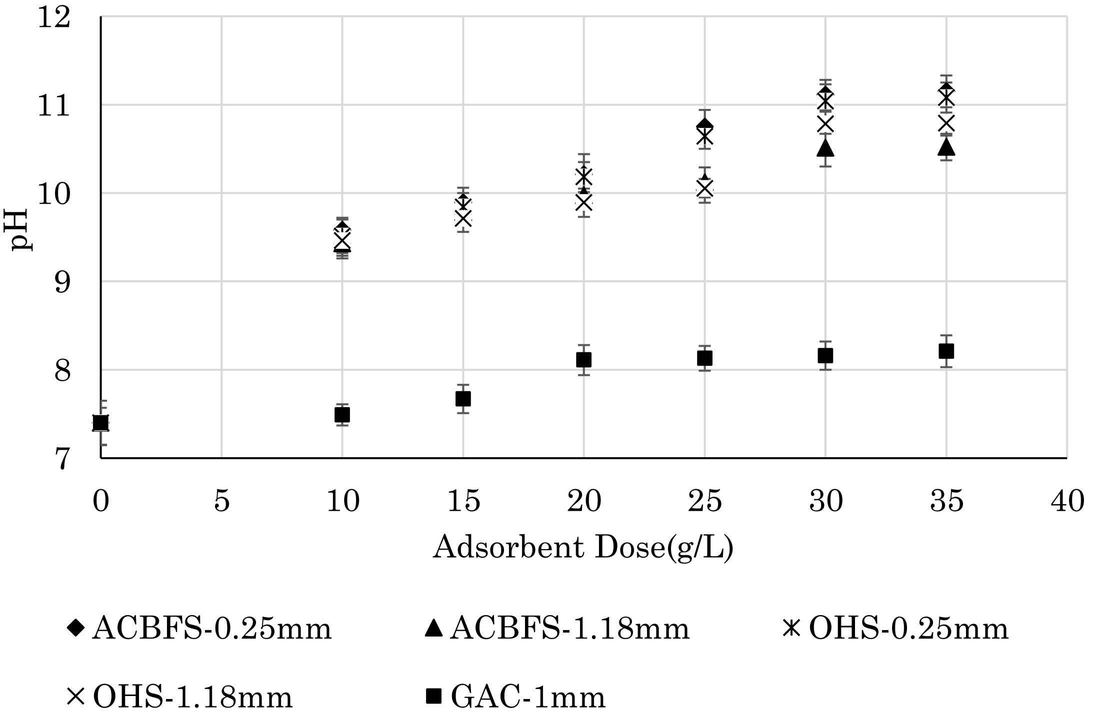

Figure 5.9: Final pH of settled water

Addition of ACBFS and OHS resulted in significantly higher settled water pH compared to GAC addition. The metal removal was likely dependent on the pH of the water as the final pH of settled water when ACBFS and OHS was used resulted in pH levels greater than 10. As outlined earlier, the minimum pH of solubility for Cd, Fe, Mn, Zn are 10, 8.5, 10.5 and 11, respectively. The final settled water pH with ACBFS and OHS addition ranged from 9.5 to 11.2. Therefore, it is likely that the 90% metal removal achieved with treatment of the water with the slags may have been due to precipitation of the metals and removal from the water phase by settling at the end of the shaker table experiments. Further study would be required to determine exact removal mechanism of the metals either due to adsorption or precipitation/sedimentation processes.

Chapter 6: Impact of Natural Organic Matter (NOM) on Slags and GAC: An Adsorption Study to Determine Effect of NOM in Target Metal Removal

The previous chapter summarized the results of the two particle sizes of ACBFS and OHS in terms of metal removal. In addition, it was also demonstrated that the GAC evaluated in this study was unable to remove metals effectively, likely due to its inability to increase pH and target pH of minimum solubility of metals. This chapter presents the results of batch adsorption studies in the presence and absence of natural organic matter (NOM) to evaluate if NOM has a significant effect on removal metal concentration in adsorption systems.

6.1. Introduction

NOM influences adsorption capacity and strength of adsorbents. Different fractions of NOM interact in different ways with adsorbents (Hyung and Kim, 2008). Due to their high toxicity, heavy metals are ecologically important and need to be removed before being discharged into surface water. There are several ways to remove metals from water- ion exchange, biodegradation, oxidation, and solvent extraction. Adsorption is a process that has been widely used to remove metals from water produced due to industrial activities (Dada et al., 2012). Adsorption capacity is measured using two isotherm models- Langmuir and Freundlich isotherm models.

Langmuir isotherm assumes that adsorption happens in monolayer and at specific homogenous sites whereas Freundlich isotherm is not restricted to the monolayer adsorption. Freundlich isotherm is used in heterogenous systems and due to its empirical nature, multilayer adsorption can also be modelled (Shahbeig, et al., 2013)

The aim of this study was to investigate the impact of NOM on target metal removal using ACBFS and OHS with their smaller particle size (0.25mm) on synthetic stormwater runoff. The sub-objectives are listed below:

- Compare ACBFS, OHS and GAC in terms of maximum adsorption capacity using two isotherm models.
- Evaluate the effect of NOM present in water on metal removal and adsorption.
- Conduct Energy-Dispersive X-Ray Spectroscopy (EDS) analysis on slags and GAC to investigate their surface.

6.2. Materials and Methods

6.2.1. Synthetic Stormwater

Metal concentrations measured in actual stormwater was used to prepare synthetic stormwater for this set of experiments. Preparation of synthetic stormwater is outlined in Chapter 3. Table 6.1, shows the concentration of metals, DOC and pH of synthetic stormwater used for this study.

Table 6.1: Synthetic stormwater quality (n=3)

Analyte	**Average**
pH	5.14 ± 0.19
Dissolved organic carbon (mg/L)	40 ± 5 mg/L
Total cadmium (µg/L)	0.05 ± 0.01 mg/L

Total iron (μg/L)	10 ± 0.7 mg/L
Total manganese (μg/L)	5 ± 0.6 mg/L
Total zinc (μg/L)	0.05 ± 0.01 mg/L

6.2.2. Slag and Activated Carbon

ACBFS and OHS at particles size of 0.25 mm were evaluated in this study. Material preparation is described in detail in Chapter 3. For comparison purposes, GAC was also evaluated to remove target metals- iron, manganese, cadmium and zinc from synthetic stormwater. Particle size of GAC was 1.00 mm, details of GAC is provided in Chapter 3.

6.2.3. Data Analysis

The equilibrium adsorption capacity, Q_e (mg/g), was calculated using Equation 1.

$$\mathrm{Qe} = \frac{\mathrm{V}(C_o - C_e)}{\mathrm{m}} \quad (1)$$

where V is the volume of the solution (L), C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of target metals, respectively, and m is the mass of the adsorbent (g). For fitting the experimental data non-linear Langmuir and Freundlich isotherm models were used. Equation 2 and 3, shows the Langmuir and Freundlich isotherm models.

$$\mathrm{Qe} = \frac{\mathrm{Qm} * K_L * C_e}{1 + K_L * C_e} \quad (2)$$

where Q_e is the amount of solute adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_m is the maximum adsorption capacity (mg/g) and K_L is the constant related to the free energy of adsorption (L/mg).

$$Qe = K_f * Ce^{1/n} \text{ (3)}$$

where Q_e is the amount of solute adsorbed per gram of the adsorbent at equilibrium (mg/g), K_f is a constant that indicates the relative adsorption capacity of the adsorbent ($mg^{1-(1/n)}L^{1/n}g^{-1}$) and n is a constant that represents intensity of adsorption.

A 1-way ANOVA was also conducted to investigate if NOM presence impacted the concentration of target metals after treatment with ACBFS, OHS and GAC. This analysis was done on each adsorbent material separately to understand NOM's effect on final concentration of target metals after treatment in stormwater.

6.2.4. Energy-Dispersive X-Ray Spectroscopy (EDS)

EDS was carried out using a Hitachi S-4700 FEG Scanning Electron Microscope. This was done to analyze the surface of the slags and GAC to confirm the target metals are adsorbed on to the surface. Slags and GAC were dried after use and then powdered before analyzing. Samples with high NOM and high dose were analyzed with EDS.

6.3. Adsorption Isotherm Model Results

6.3.1. Cadmium (Cd)

The batch adsorption data of Cd was fit to the Langmuir and Freundlich isotherm models and the results are shown in Table 6.2.

Table 6.2: Langmuir and Freundlich isotherm constants for the adsorption of Cd onto slags and GAC

Adsorbent	**Langmuir**				**Freundlich**			
	DOC = 0 mg/L		**DOC = 40 mg/L**		**DOC = 0 mg/L**		**DOC = 40 mg/L**	
	Q_m (mg/g)	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**
ACBFS	0.041	0.979	0.008	0.911	0.223	0.981	0.040	0.890
OHS	0.018	0.985	0.003	0.759	0.131	0.981	0.004	0.774
GAC	0.016	0.141	2.70E-4	0.499	0.0016	0.141	2.70E-4	0.499

Batch adsorption experiments with the ACBFS and OHS fit the Langmuir ($R^2 > 0.97$) and Freundlich isotherm ($R^2 >0.98$) models well when there was no NOM present in test water. These fits are similar to that mentioned in the study conducted by Gupta et al. (1997). In presence of NOM, the adsorption data fit less in Langmuir ($0.75 < R^2 < 0.91$) and Freundlich ($0.77 < R^2 < 0.89$) isotherm models. Cd adsorption onto GAC data did not show a good fit with either the Langmuir or Freundlich isotherm models. Maximum adsorption capacity also showed that the GAC does not adsorb Cd effectively onto its surface compared to ACBFS and OHS. In addition, the maximum adsorption capacity was showed to increase in the absence of NOM in the test water. Gupta et al. (1997) mentions a maximum adsorption capacity of $1.87 * 10^9$ mg/g using Langmuir isotherm model. Figure 6.1, 6.2, 6.3 show the experimental data fitted to the Langmuir and Freundlich isotherm model for Cd.

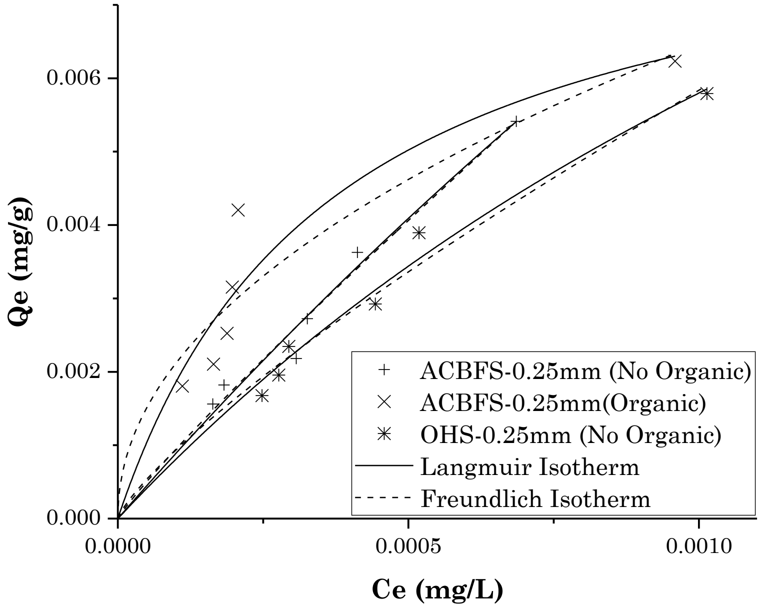

Figure 6.1: Langmuir and Freundlich Isotherm Fit of Cd on ACBFS and OHS (No Organic)

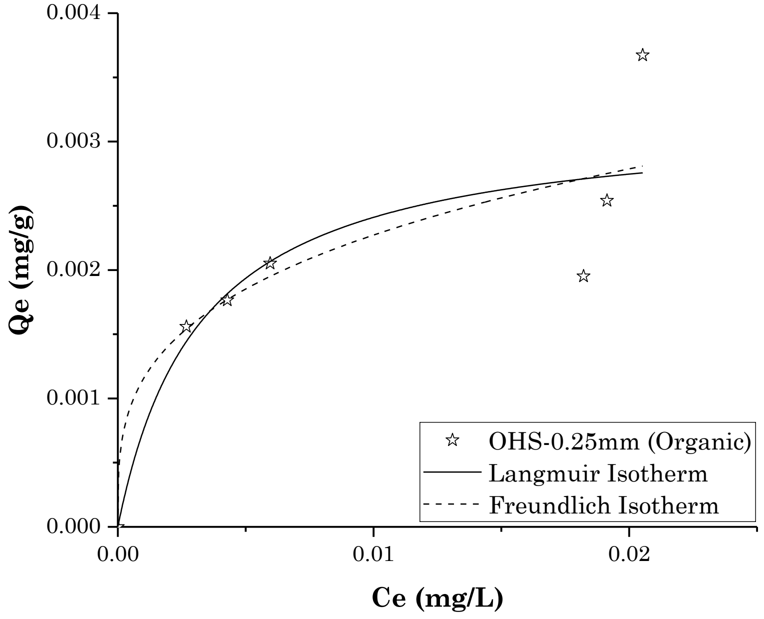

Figure 6.2: Langmuir and Freundlich Isotherm Fit of Cd on OHS (Organic)

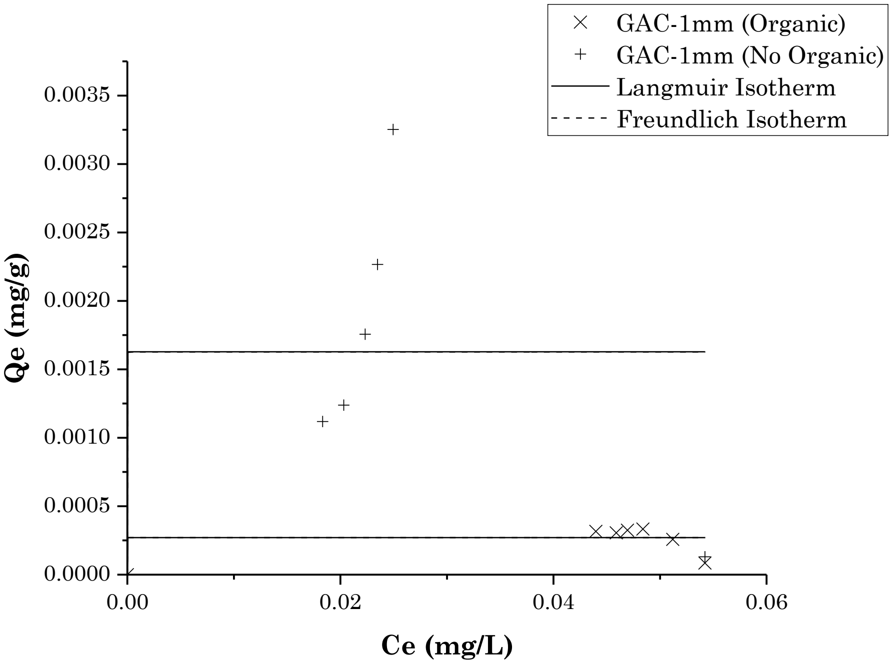

Figure 6.3: Langmuir and Freundlich Isotherm fit of Cd on GAC (Same fit obtained for both models)

6.3.2. Iron (Fe)

The batch adsorption data of Fe was fit to the Langmuir and Freundlich isotherm models and the results are shown in Table 6.3.

Table 6.3: Langmuir and Freundlich isotherm constants for the adsorption of Fe onto Slags and GAC

	Langmuir				**Freundlich**			
Adsorbent	**DOC = 0 mg/L**		**DOC = 40 mg/L**		**DOC = 0 mg/L**		**DOC = 40 mg/L**	
	Q_m (mg/g)	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**
ACBFS	0.969	0.928	0.651	0.847	1.721	0.946	1.527	0.967
OHS	0.593	0.291	0.158	0.688	0.838	0.295	0.161	0.778
GAC	0.191	0.189	0.143	0.975	0.191	0.189	0.143	0.975

Batch adsorption experiments with ACBFS-0.25mm fit the Langmuir ($R^2 >$ 0.92) and Freundlich (R^2 >94.6) isotherm models fit better when there was no NOM present in test water compared to NOM present in water. In presence of NOM, the adsorption data fit less in Langmuir ($0.68 < R^2 < 0.84$) and Freundlich ($0.77 < R^2 < 0.96$) isotherm models. Fe adsorption onto GAC data did show a good fit for Freundlich isotherm model but show poor fit for Langmuir isotherm model. OHS shows relatively better adsorption capacity compared to GAC, adsorbing almost five times more than GAC. However, ACBFS shows higher adsorption capacity compared to OHS. Figure 6.4, 6.5 and 6.6 show, the experimental data fitted to the Langmuir and Freundlich isotherm model for Fe.

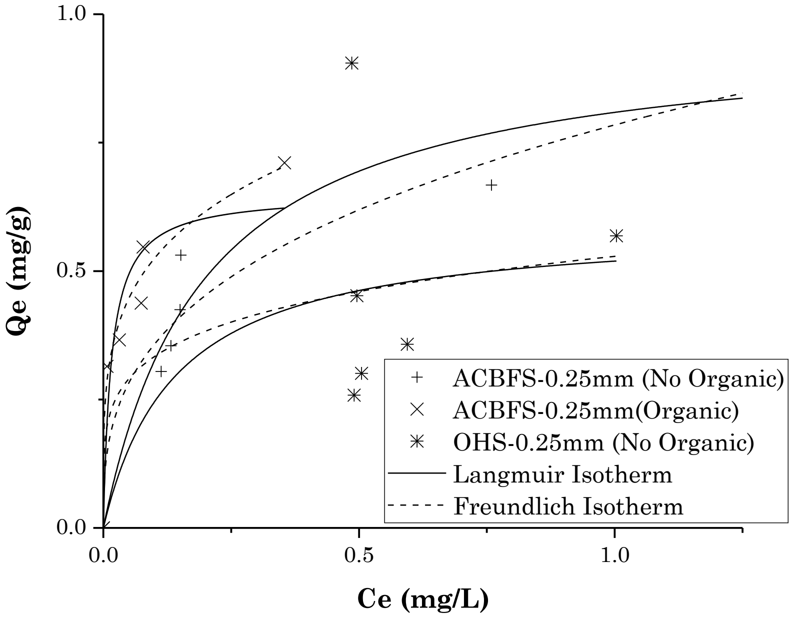

Figure 6.4: Langmuir and Freundlich Isotherm Fit of Fe on ACBFS and OHS (No Organic)

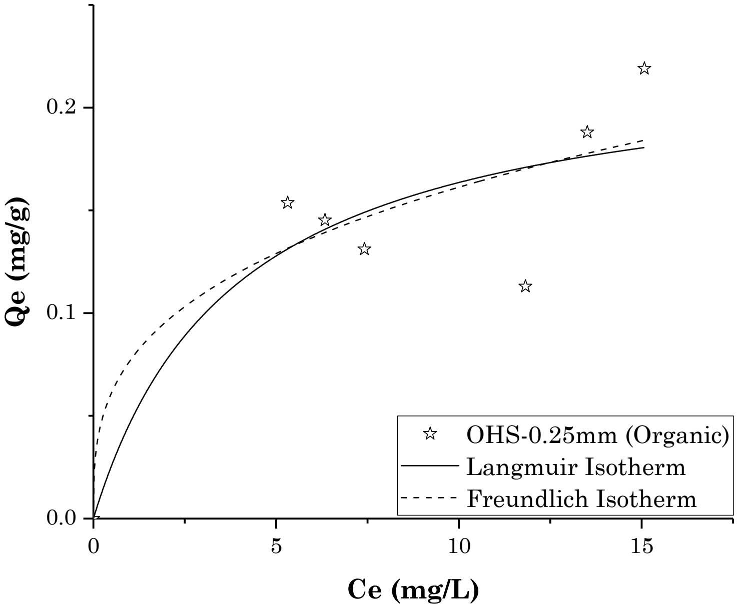

Figure 6.5: Langmuir and Freundlich Isotherm Fit of Fe on OHS (Organic)

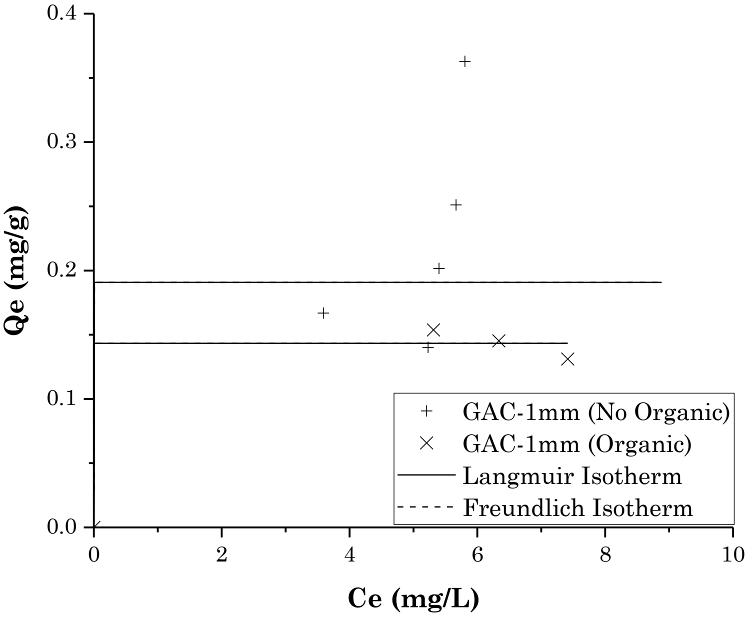

Figure 6.6: Langmuir and Freundlich Isotherm Fit of Fe on GAC (Same fit obtained for both models)

6.3.3. Manganese (Mn)

The batch adsorption data of Fe was fit to the Langmuir and Freundlich isotherm models and the results are shown in Table 6.4.

Table 6.4: Langmuir and Freundlich isotherm constants for the adsorption of Mn onto slags and GAC. (*Fit did not converge)

Adsorbent	**Langmuir**				**Freundlich**			
	DOC = 0 mg/L		**DOC = 40 mg/L**		**DOC = 0 mg/L**		**DOC = 40 mg/L**	
	Q_m (mg/g)	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**	**Q_m (mg/g)**	**R^2**
ACBFS	0.501	0.899	1146*	*	1.801	0.915	87.4*	*
OHS	0.413	0.615	0.263	0.323	0.527	0.596	0.101	0.305
GAC	0.147	0.218	0.101	0.195	0.147	0.218	0.101	0.195

Highest adsorption capacity and good fit (0.501 mg/g, $0.89 < R^2 < 0.91$) was exhibited by ACBFS in absence of NOM, however, data set involving NOM did not converge and generated a high standard error. This indicates that Langmuir and Freundlich isotherm model do not show a reliable model for Mn adsorption on ACBFS when NOM is present in test water. OHS shows better maximum adsorption capacity than GAC in both type of test water conditions with a better fit than GAC. Presence of organics decreased the adsorption capacity and data fit (R^2) of Mn on all kinds of adsorbents. Figure 6.7, 6.8 and 6.9 show, the experimental data fitted to the Langmuir and Freundlich isotherm model for Mn.

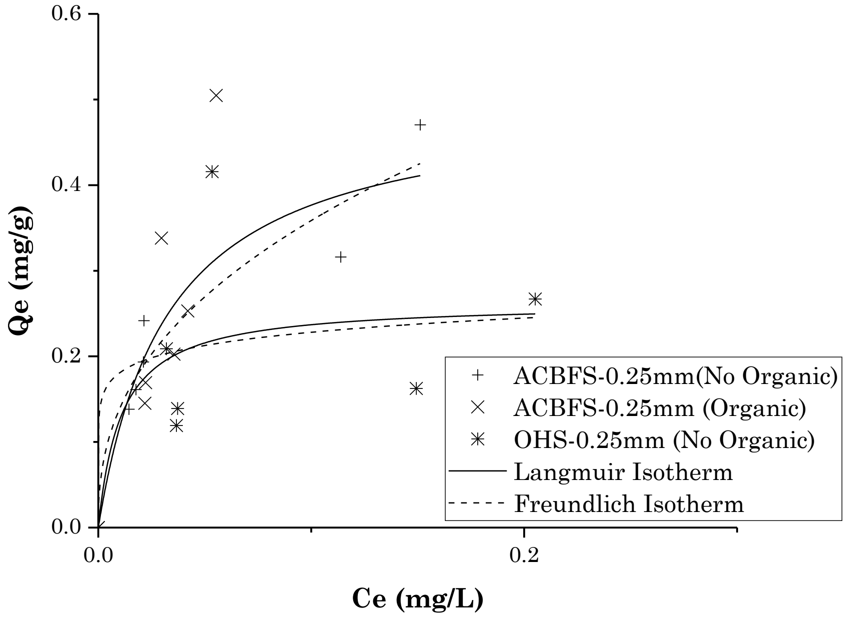

Figure 6.7: Langmuir and Freundlich Isotherm Fit of Mn on ACBFS and OHS (No Organic). (ACBFS-0.25mm (Organic)'s isotherm lines are excluded due to non-convergence)

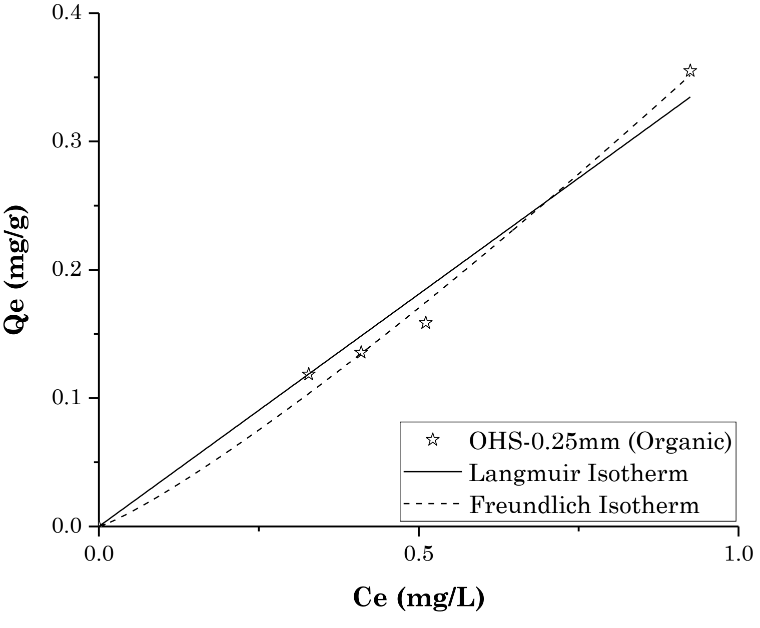

Figure 6.8: Langmuir and Freundlich Isotherm Fit of Mn on OHS (Organic)

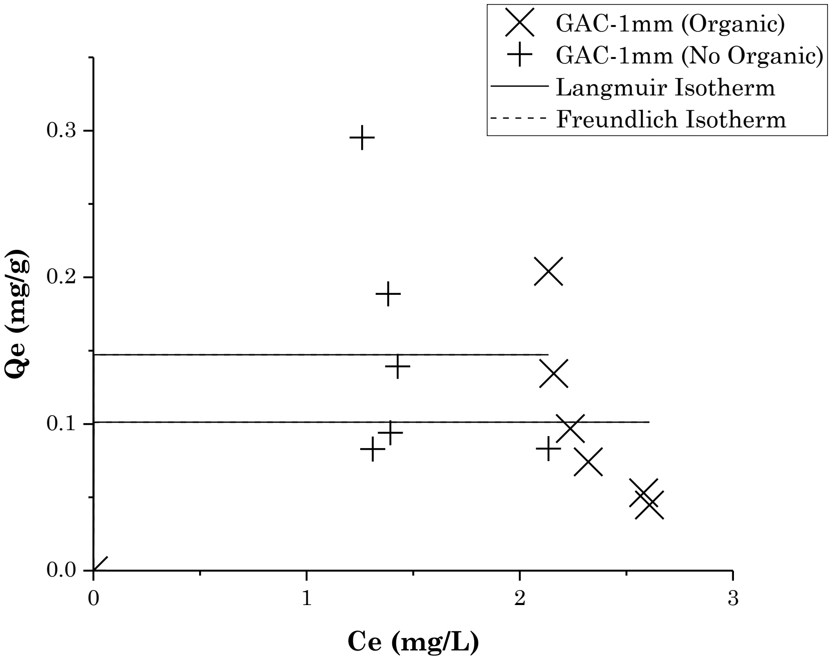

Figure 6.9: Langmuir and Freundlich Isotherm Fit of Mn on GAC (Same fit obtained for both models)

6.3.4. Zinc (Zn)

The batch adsorption data of Zn was fit to the Langmuir and Freundlich isotherm models and the results are shown in Table 6.5.

Table 6.5: Langmuir and Freundlich isotherm constants for the adsorption of Zn onto slags and GAC

Adsorbent	Langmuir				Freundlich			
	DOC = 0 mg/L		DOC = 40 mg/L		DOC = 0 mg/L		DOC = 40 mg/L	
	Q_m (mg/g)	R^2	Q_m (mg/g)	R^2	Q_m (mg/g)	R^2	Q_m (mg/g)	R^2
ACBFS	0.007	0.987	0.005	0.935	0.012	0.984	0.007	0.935
OHS	0.015	0.846	3.90E-4	0.693	0.008	0.841	0.0004	0.693
GAC	0.001	0.576	3.90E-4	0.693	0.001	0.576	0.0004	0.693

Test water with NOM showed significantly less Zn adsorption onto slags and GAC compared to NOM presence in test water. ACBFS exhibited high data fit (R^2 >

0.93) compared to OHS ($R^2 > 0.69$). Gupta et al. (1997) observed better fit ($R^2 > 0.98$) compared to the one obtained in this study. GAC showed very similar fit in both Langmuir and Freundlich model for both types of test water. GAC, for both types of test water showed low adsorption capacity compared to ACBFS and OHS. ACBFS showed highest adsorption capacity of about 0.012 mg/g (Freundlich model) in absence of NOM and 0.007 mg/g (Freundlich model) in presence of NOM. Gupta et al. (1997) reported the adsorption capacity was about 1.77 * 10^9 mg/g. Figure 6.10, 6.11 and 6.12 show, the experimental data fitted to the Langmuir and Freundlich isotherm model for Zn.

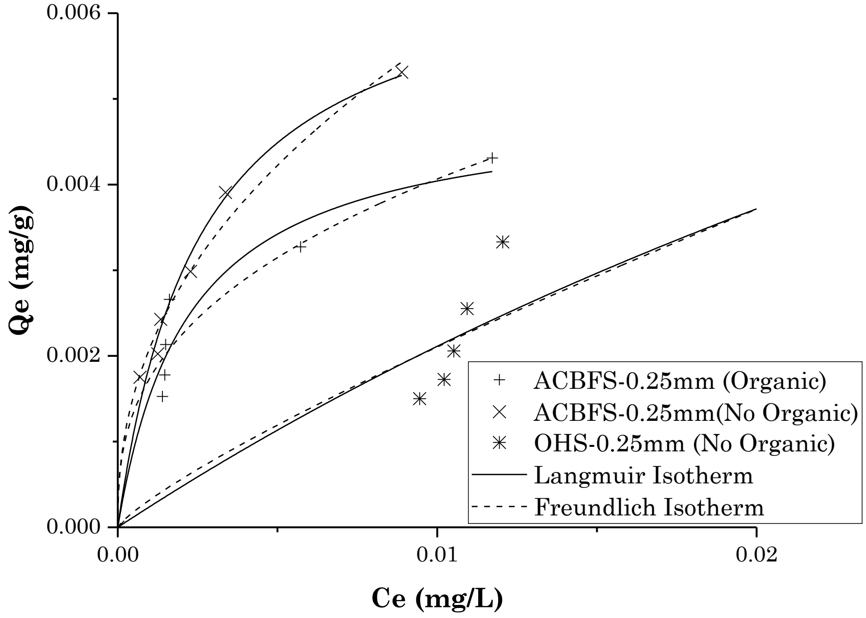

Figure 6.10: Langmuir and Freundlich Isotherm Fit of Zn on ACBFS and OHS (No Organic)

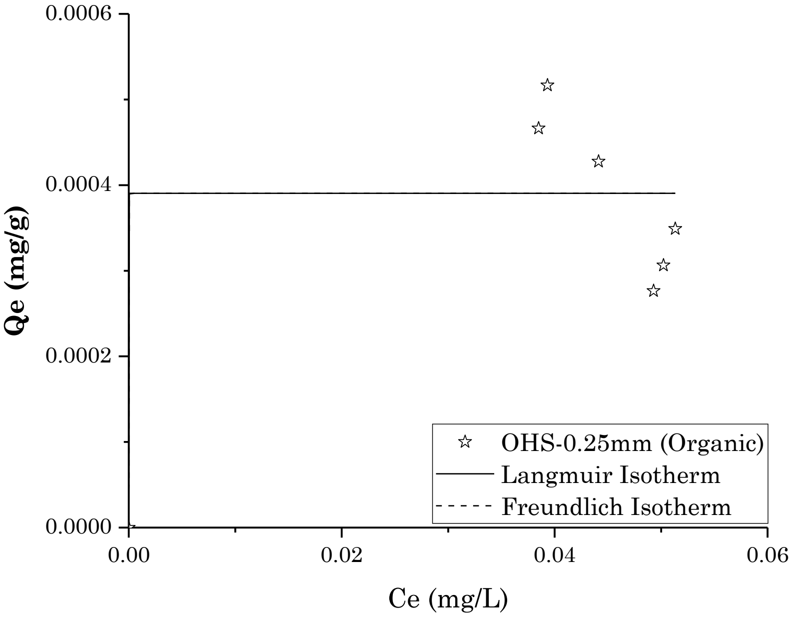

Figure 6.11: Langmuir and Freundlich Isotherm Fit of Zn on OHS (Organic)

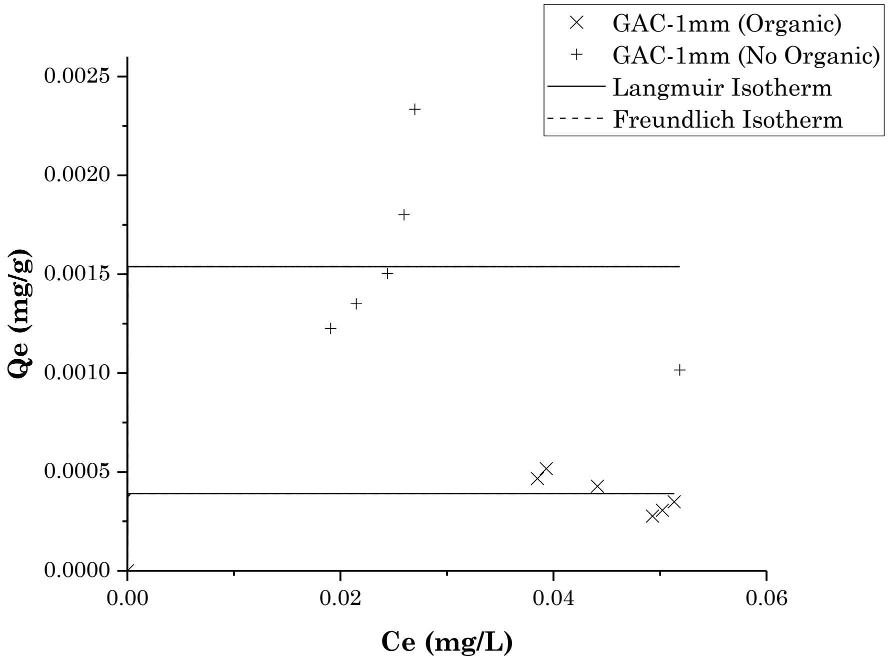

Figure 6.12: Langmuir and Freundlich Isotherm Fit of Zn on GAC (Same fit obtained for both models)

6.4. Effect of NOM on final concentration of target metals

Dissolved organic carbon (DOC) concentration was measured on high and low treatments with slags and GAC. The initial concentration was at 40 ± 5 mg/L. Figure 6.13 shows the concentration of DOC after the treatment.

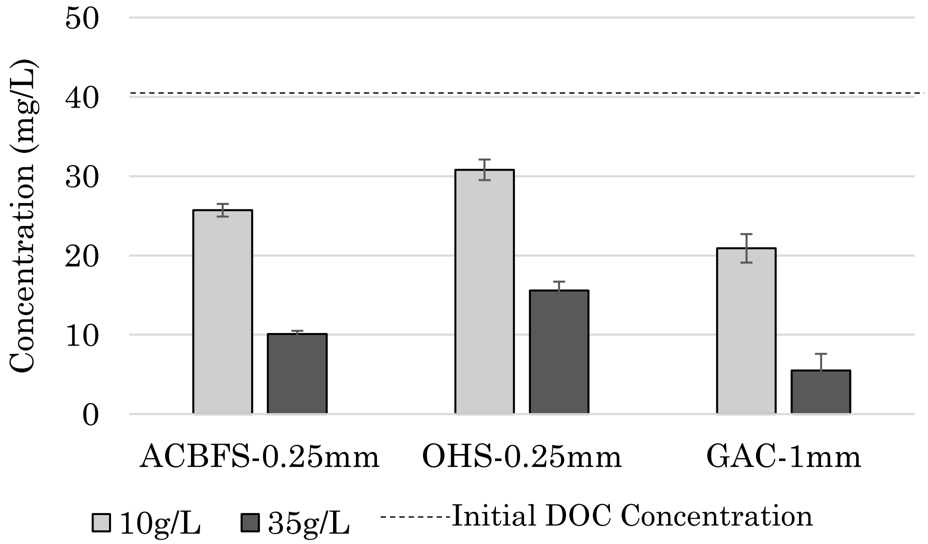

Figure 6.13: DOC concentration after treatment with high and low doses of adsorbents

Results indicated that GAC treatment had the lowest concentration at both low (10 g/L) and high (35 g/L) of dose. ACBFS and OHS also decreased the DOC concentration in settled water with OHS decreasing more DOC concentration compared to ACBFS. In all types of adsorbent treatments, high dose resulted in the lowest DOC concentration.

A 1-way ANOVA was conducted on the final concentration on each target metal for the different adsorbents and doses (10 g/L and 35 g/L). This analysis enables to understand if the mean concentration of stormwater treatment was significantly different when there were high levels of NOM present in test water. Results are summarized in Table 6.6. ANOVA results indicate that NOM did not have a significant impact on the final concentration of any target metals when ACBFS used. However, NOM presence had a significant effect on the final metal concentration when OHS and GAC were used.

Table 6.6: Summary of Effect of NOM in test water

	Effect of NOM Significant?			
Adsorbent	**Cd**	**Fe**	**Mn**	**Zn**
ACBFS	×	×	×	×
OHS	✓	✓	✓	✓
GAC	✓	✓	✓	✓

6.5. SEM and EDS results

Figure 6.14 shows the SEM images. Comparing figure 6.14 to 4.4, after the treatment there was an accumulation of precipitates on the surface of the slag particles. EDS analysis is a qualitative analysis and shows a particular part of the adsorbent where elements of interest are present. EDS results indicated that Mn and Fe were present on the surface of ACBFS and OHS. However, GAC did not show any target metal trace on its surface. This could be, perhaps there was adsorption but too small for EDS to capture that in this analysis. Tables 6.7 shows the EDS results of these SEM images and the numbers do not correspond to total amount adsorbed from test water.

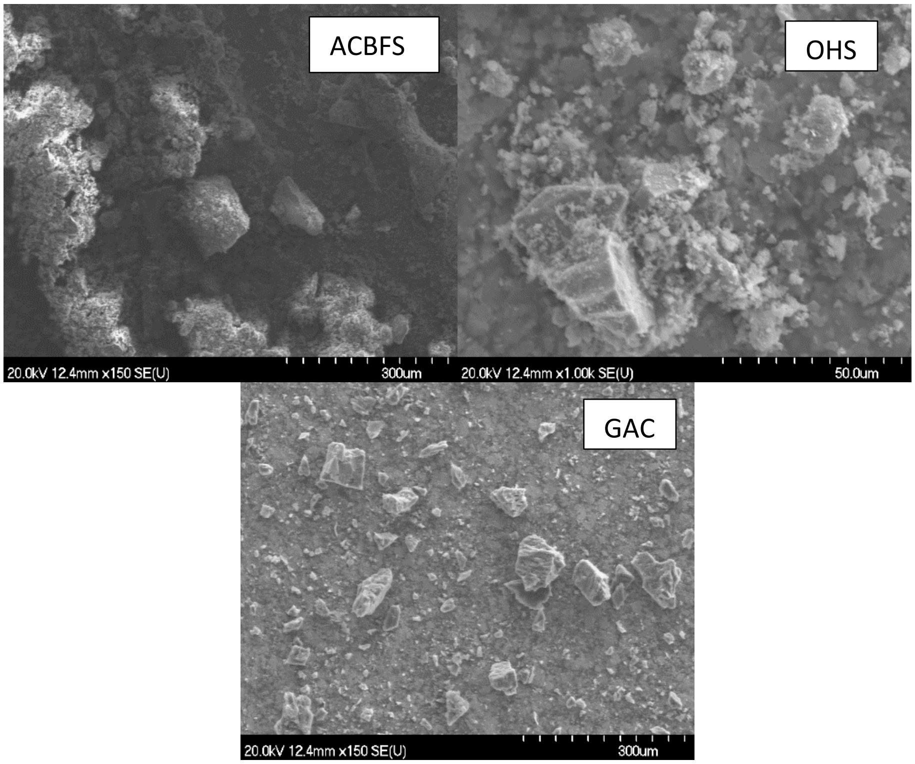

Figure 6.14: SEM images of used ACBFS, OHS and GAC

Table 6.7: Results of EDS showing elements captured in particular parts of ACBFS, OHS and GAC ([1]Used adsorbent and [2]Unused adsorbent)

	Element								
Adsorbent	**C**	**O**	**Mg**	**Al**	**Si**	**Ca**	**Ti**	**Mn**	**Fe**
ACBFS[1]	-	60.28	1.32	3.67	10.51	22.40	0.28	0.24	1.30
OHS[1]	11.07	29.07	0.43	4.10	0.68	0.66	8.95	6.56	36.75
GAC[1]	99.49	-	-	-	0.14	-	-	-	-
ACBFS[2]	-	61.12	1.41	4.12	11.91	24.30	-	-	-
OHS[2]	12.87	31.72	0.37	5.13	0.91	0.71	7.64	-	29.71
GAC[1]	98.12	-	-	-	1.59	-	-	-	-

Chapter 7: Conclusion and Recommendation

7.1. Conclusions

Waste slag & biomass stormwater characterization study:

- ACBFS and OHS showed the presence of CaO, Al_2O_3, SiO_2 and Fe_2O_3 as the main oxides.
- The amount of these oxides varied significantly from ACBFS to OHS as the iron and steel production process is different. ACBFS had more CaO and OHS had more Fe_2O_3.
- Industrial stormwater runoff collected from a biomass power generation facility showed elevated metal concentrations of Cd, Fe, Mn, Zn.
- The main phase of ACBFS was found to be gehlenite and some smaller peaks of calcium carbonate and potassium thiocyanate. OHS's XRD pattern was not like ACBFS; OHS showed main phase as quartz and other peaks of calcium carbonate, magnetite and akermanite-gehlenite. The difference of these patterns occur may be due to the production condition and how it was stored.
- SEM images confirm that particle shapes of both slags are irregular. OHS shows smaller particle size compared to ACBFS. Some cracks on the surface were observed in OHS, however, ACBFS showed smoother surface.

Target metal removal using slag and GAC:

- Results indicated that ACBFS and OHS both remove target metals (Cd, Fe, Mn, Zn) from stormwater runoff with a high efficiency (90% removal with 35 g/L of slag dose).
- The results also indicate that slag size or type did not have a statistically significant effect on final concentration of metals.
- The statistically significant term was slag dose that influenced final concentration of metals.
- Final pH of water had a significant impact on the target metal removal. GAC did not raise the pH of the water at a pH that corresponds to Cd, Fe, Mn and Zn's minimum pH solubility. However, ACBFS and OHS raised pH more than these target metals minimum pH solubility, hence, removing 90% of target metals from stormwater runoff. This indicates that precipitation is likely the main removal mechanism when using slag to remove metals.

Batch-Adsorption study on synthetic stormwater runoff:

- ACBFS has the highest adsorption capacity when compared to OHS and GAC. The isotherm models also indicate that OHS may have adsorbed better than GAC. Generally, the fits of the isotherm were good. However, some data set either did not converge or showed poor fit.

- Statistical analysis confirm that NOM did not have any effect on final concentration when ACBFS was used. However, OHS and GAC's metal removal capacity was negatively impacted by the presence of NOM in test water.
- EDS analysis confirmed that ACBFS and OHS both adsorbed Fe and Mn onto their surfaces in presence of organics but did not show any Cd and Zn. This could be due to the particular point that these slags were analyzed. GAC did not show any sign of adsorption, perhaps it did adsorb but at a very small amount which was not captured in EDS analysis.

7.2. Recommendations

To determine the practicality of using slag in removing target metals from stormwater testing at pilot or full-scale is recommended. Batch-adsorption study with smaller contact time (3h , 6h, and 12h) could be done to investigate if pH increases with contact time or not. Column studies should also be performed with variable contact time and bed volume to investigate if pH is the main reason why metals are being removed. Also, a thorough study on adsorption and precipitation must be conducted to understand which process dominantly removes metal from stormwater runoff. Other types of slags such as BOFS and EAFS should also be tested further to compare their results to that of ACBFS and OHS. Desorption of these target metals is another parameter that should be studied before implementing this results in pilot or full-scale.

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Appendix A: 2- Way ANOVA Results

Cadmium

General Linear Model: Concentration versus Adsorbent Type, Adsorbent Dose, Adsorbent Size

```
Method

Factor coding  (-1, 0, +1)


Factor Information

Factor          Type   Levels  Values
Adsorbent Type  Fixed       2  ACBFS, OHS
Adsorbent Dose  Fixed       2  10, 35
Adsorbent Size  Fixed       2  0.25, 1.18


Analysis of Variance

Source            DF    Adj SS    Adj MS  F-Value  P-Value
  Adsorbent Type   1  0.007407  0.007407     1.99    0.231
  Adsorbent Dose   1  0.051642  0.051642    13.90    0.020
  Adsorbent Size   1  0.001497  0.001497     0.40    0.560
Error              4  0.014858  0.003715
Total              7  0.075404


Model Summary

        S    R-sq  R-sq(adj)  R-sq(pred)
0.0609470  80.30%     65.52%      21.18%


Coefficients

Term               Coef  SE Coef  T-Value  P-Value   VIF
Constant         0.0877   0.0215     4.07    0.015
Adsorbent Type
  ACBFS         -0.0304   0.0215    -1.41    0.231  1.00
Adsorbent Dose
  10             0.0803   0.0215     3.73    0.020  1.00
Adsorbent Size
  0.25          -0.0137   0.0215    -0.63    0.560  1.00


Regression Equation

Concentration = 0.0877 - 0.0304 Adsorbent Type_ACBFS + 0.0304 Adsorbent Type_OHS
                + 0.0803 Adsorbent Dose_10 - 0.0803 Adsorbent Dose_35
                - 0.0137 Adsorbent Size_0.25 + 0.0137 Adsorbent Size_1.18
```

Iron

General Linear Model: Concentration versus Adsorbent Type, Adsorbent Dose, Adsorbent Size

```
Method

Factor coding  (-1, 0, +1)


Factor Information

Factor          Type   Levels  Values
Adsorbent Type  Fixed       2  ACBFS, OHS
Adsorbent Dose  Fixed       2  10, 35
Adsorbent Size  Fixed       2  0.25, 1.18


Analysis of Variance

Source            DF    Adj SS    Adj MS  F-Value  P-Value
  Adsorbent Type   1   3201842   3201842     1.60    0.275
  Adsorbent Dose   1  36653494  36653494    18.28    0.013
  Adsorbent Size   1   2602347   2602347     1.30    0.318
Error              4   8019240   2004810
Total              7  50476923


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
1415.91  84.11%     72.20%      36.45%


Coefficients

Term            Coef  SE Coef  T-Value  P-Value   VIF
Constant        2234      501     4.46    0.011
Adsorbent Type
  ACBFS         -633      501    -1.26    0.275  1.00
Adsorbent Dose
  10            2140      501     4.28    0.013  1.00
Adsorbent Size
  0.25          -570      501    -1.14    0.318  1.00


Regression Equation

Concentration = 2234 - 633 Adsorbent Type_ACBFS + 633 Adsorbent Type_OHS
                + 2140 Adsorbent Dose_10 - 2140 Adsorbent Dose_35
- 570 Adsorbent Size_0.25
                + 570 Adsorbent Size_1.18
```

Manganese

General Linear Model: Concentration versus Adsorbent Type, Adsorbent Dose, Adsorbent Size

```
Method

Factor coding  (-1, 0, +1)


Factor Information

Factor          Type   Levels  Values
Adsorbent Type  Fixed       2  ACBFS, OHS
Adsorbent Dose  Fixed       2  10, 35
Adsorbent Size  Fixed       2  0.25, 1.18


Analysis of Variance

Source            DF   Adj SS   Adj MS  F-Value  P-Value
  Adsorbent Type   1   273530   273530     1.42    0.300
  Adsorbent Dose   1  1700786  1700786     8.81    0.041
  Adsorbent Size   1   459241   459241     2.38    0.198
Error              4   771998   192999
Total              7  3205555


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
439.317  75.92%     57.85%       3.67%


Coefficients

Term            Coef  SE Coef  T-Value  P-Value   VIF
Constant         506      155     3.26    0.031
Adsorbent Type
  ACBFS         -185      155    -1.19    0.300  1.00
Adsorbent Dose
  10             461      155     2.97    0.041  1.00
Adsorbent Size
  0.25          -240      155    -1.54    0.198  1.00


Regression Equation

Concentration = 506 - 185 Adsorbent Type_ACBFS + 185 Adsorbent Type_OHS
                + 461 Adsorbent Dose_10 - 461 Adsorbent Dose_35
- 240 Adsorbent Size_0.25
                + 240 Adsorbent Size_1.18
```

Zinc

General Linear Model: Concentration versus Adsorbent Type, Adsorbent Dose, Adsorbent Size

```
Method

Factor coding  (-1, 0, +1)


Factor Information

Factor          Type   Levels  Values
Adsorbent Type  Fixed       2  ACBFS, OHS
Adsorbent Dose  Fixed       2  10, 35
Adsorbent Size  Fixed       2  0.25, 1.18


Analysis of Variance

Source            DF   Adj SS   Adj MS  F-Value  P-Value
  Adsorbent Type   1  109.811  109.811     3.29    0.144
  Adsorbent Dose   1  247.561  247.561     7.42    0.049
  Adsorbent Size   1    3.544    3.544     0.11    0.761
Error              4  133.367   33.342
Total              7  494.284


Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
5.77424  73.02%     52.78%       0.00%


Coefficients

Term             Coef  SE Coef  T-Value  P-Value   VIF
Constant         7.47     2.04     3.66    0.022
Adsorbent Type
  ACBFS         -3.70     2.04    -1.81    0.144  1.00
Adsorbent Dose
  10             5.56     2.04     2.72    0.049  1.00
Adsorbent Size
  0.25           0.67     2.04     0.33    0.761  1.00


Regression Equation

Concentration = 7.47 - 3.70 Adsorbent Type_ACBFS + 3.70 Adsorbent Type_OHS
                + 5.56 Adsorbent Dose_10 - 5.56 Adsorbent Dose_35
+ 0.67 Adsorbent Size_0.25
                - 0.67 Adsorbent Size_1.18
```

Appendix B: Isotherm Model Data Set

Cadmium

GAC-1mm/Organic

Dose (g)	V (L)	C (mg/L)	Qe
		0.05506	
2	0.2	0.05422	8.46667E-05
3	0.2	0.05119	0.000258222
4	0.2	0.04839	0.000333667
5	0.2	0.04695	0.000324667
6	0.2	0.04589	0.000305667
7	0.2	0.04398	0.000316667
0	0.2	0	0

GAC-1mm/No Organic

Dose (g)	V (L)	C (mg/L)	Qe
		0.05747	
2	0.2	0.02495	0.003252
3	0.2	0.02348	0.002266
4	0.2	0.02233	0.001757167
5	0.2	0.05422	0.000130133
6	0.2	0.02031	0.001238556
7	0.2	0.01833	0.001118286
0	0.2	0	0

OHS-0.25mm/Organic

Dose (g)	V (L)	C (mg/L)	Qe
		0.05725	
2	0.2	0.02053	0.003672333
3	0.2	0.01913	0.002541111
4	0.2	0.01822	0.001951667
5	0.2	0.00596	0.002051653
6	0.2	0.00428	0.001765511
7	0.2	0.00268	0.001559038
0	0.2	0	0

OHS-0.25mm/No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		0.05894	
2	0.2	0.00101	0.0057923
3	0.2	0.00052	0.003894556
4	0.2	0.00044	0.002924683
5	0.2	0.00029	0.002345693
6	0.2	0.00028	0.001955322
7	0.2	0.00025	0.001676819
0	0.2	0	0

ACBFS-0.25mm/ Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		0.05482	
2	0.2	0.00069	0.005413767
3	0.2	0.00041	0.0036274
4	0.2	0.00033	0.002724867
5	0.2	0.00031	0.002180653
6	0.2	0.00018	0.001821356
7	0.2	0.00016	0.001561714
0	0.2	0	0

ACBFS-0.25mm/ No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		0.06328	
2	0.2	0.00096	0.006232433
3	0.2	0.00021	0.004205089
4	0.2	0.0002	0.003154317
5	0.2	0.00019	0.002523813
6	0.2	0.00016	0.002103956
7	0.2	0.00011	0.001804924
0	0.2	0	0

Iron

GAC-1mm/Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		10.664	
2	0.2	8.8833333	0.17807
3	0.2	8.1293333	0.16898
4	0.2	7.9363333	0.13638
5	0.2	7.906	0.11032
6	0.2	7.425	0.10797
7	0.2	6.5536667	0.11744
0	0.2	0	0
GAC-1mm/No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		9.433	
2	0.2	5.8046667	0.36283
3	0.2	5.667	0.25107
4	0.2	5.3996667	0.20167
5	0.2	8.8833333	0.02199
6	0.2	5.2286667	0.14014
7	0.2	3.5906667	0.16692
0	0.2	0	0
OHS-0.25mm/Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		12	
2	0.2	11.823333	0.113
3	0.2	13.513333	0.188
4	0.2	15.076667	0.219
5	0.2	7.4146667	0.18341
6	0.2	6.3366667	0.18878
7	0.2	5.313	0.19106
0	0.2	0	0
OHS-0.25mm/No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		9.5346667	

2	0.2	0.4857667	0.90489
3	0.2	1.0032333	0.56876
4	0.2	0.4957667	0.45195
5	0.2	0.5942667	0.35762
6	0.2	0.5049	0.30099
7	0.2	0.4905667	0.2584
0	0.2	0	0
ACBFS-0.25mm/ Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		10.77	
2	0.2	1.5166667	0.92533
3	0.2	0.7589333	0.6674
4	0.2	0.1514	0.53093
5	0.2	0.1499667	0.4248
6	0.2	0.1321667	0.35459
7	0.2	0.1131	0.30448
0	0.2	0	0
ACBFS-0.25mm/ No Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		11.013333	
2	0.2	7.7713333	0.3242
3	0.2	0.3543	0.7106
4	0.2	0.0777833	0.54678
5	0.2	0.0740967	0.43757
6	0.2	0.0312933	0.36607
7	0.2	0.007	0.31447
0	0.2	0	0

Manganese

GAC-1mm/Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		4.1753	
2	0.2	2.1343	0.2041
3	0.2	2.1593	0.1344
4	0.2	2.237	0.096916667
5	0.2	2.321	0.074173333
6	0.2	2.5813	0.053133333
7	0.2	2.608	0.044780952
0	0.2	0	0
GAC-1mm/No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		4.2137	
2	0.2	1.2607	0.2953
3	0.2	1.383	0.188711111
4	0.2	1.427	0.139333333
5	0.2	2.1343	0.083173333
6	0.2	1.393	0.094022222
7	0.2	1.31	0.082961905
0	0.2	0	0
OHS-0.25mm/Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		4.4753	
2	0.2	0.9246	0.355073333
3	0.2	1.0263	0.229933333
4	0.2	1.1167	0.167933333
5	0.2	0.511	0.158573333
6	0.2	0.4102	0.135504444
7	0.2	0.3281	0.118493333
0	0.2	0	0
OHS-0.25mm/No Organic			
Dose	V	C	Qe
(g)	(L)	(mg/L)	
		4.211	

2	0.2	0.0535	0.415754333
3	0.2	0.2052	0.267053333
4	0.2	0.032	0.208951167
5	0.2	0.1493	0.162466667
6	0.2	0.0373	0.139125
7	0.2	0.0367	0.119266286
0	0.2	0	0
ACBFS-0.25mm/ Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		5.1027	
2	0.2	0.0554	0.504728
3	0.2	0.0297	0.338199778
4	0.2	0.042	0.253032833
5	0.2	0.0355	0.202685467
6	0.2	0.0222	0.169347667
7	0.2	0.0219	0.14516619
0	0.2	0	0
ACBFS-0.25mm/ No Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		4.855	
2	0.2	0.1512	0.47038
3	0.2	0.1139	0.316073333
4	0.2	0.0214	0.2416785
5	0.2	0.0212	0.193352
6	0.2	0.0177	0.161244111
7	0.2	0.0144	0.138302381
0	0.2	0	0

Zinc

GAC-1mm/Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		0.054823333	
2	0.2	0.051333333	0.000349
3	0.2	0.050226667	0.000306444
4	0.2	0.049293333	0.0002765
5	0.2	0.044133333	0.0004276
6	0.2	0.039323333	0.000516667
7	0.2	0.0385	0.000466381
0	0.2	0	0
GAC-1mm/No Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		0.062	
2	0.2	0.051846667	0.001015333
3	0.2	0.026983333	0.002334444
4	0.2	0.02598	0.001801
5	0.2	0.02441	0.0015036
6	0.2	0.02149	0.001350333
7	0.2	0.01909	0.001226
0	0.2	0	0
OHS-0.25mm/Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		0.054823333	
2	0.2	0.051333333	0.000349
3	0.2	0.050226667	0.000306444
4	0.2	0.049293333	0.0002765
5	0.2	0.044133333	0.0004276
6	0.2	0.039323333	0.000516667
7	0.2	0.0385	0.000466381
0	0.2	0	0
OHS-0.25mm/No Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	

		0.062	
2	0.2	0.022526667	0.003947333
3	0.2	0.012053333	0.003329778
4	0.2	0.010936667	0.002553167
5	0.2	0.010523333	0.002059067
6	0.2	0.010216667	0.001726111
7	0.2	0.009452	0.001501371
0	0.2	0	0
ACBFS-0.25mm/ Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		0.054823333	
2	0.2	0.011723333	0.00431
3	0.2	0.005723	0.003273356
4	0.2	0.001617	0.002660317
5	0.2	0.0015	0.002132933
6	0.2	0.001472	0.001778378
7	0.2	0.001399667	0.00152639
0	0.2	0	0
ACBFS-0.25mm/ No Organic			
Dose	**V**	**C**	**Qe**
(g)	**(L)**	**(mg/L)**	
		0.062	
2	0.2	0.008888333	0.005311167
3	0.2	0.003371667	0.003908556
4	0.2	0.002278	0.0029861
5	0.2	0.001342667	0.002426293
6	0.2	0.001253667	0.002024878
7	0.2	0.000696	0.001751543
0	0.2	0	0