IMPACT OF NATURAL ORGANIC MATTER (NOM) ON ADSORPTION OF TARGET METALS FROM INDUSTRIAL STORMWATER RUNOFF

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Abstract: Contaminated stormwater runoff from industrial sites can contribute significantly high organic and inorganic pollution mass loads to receiving surface water bodies. Metals, such as cadmium(Cd), iron(Fe), manganese(Mn) and zinc(Zn) can accumulate in living tissue, and unlike organic wastes, metals are non-biodegradable. The objective of this study was to evaluate the impact of natural organic matter (NOM) on the adsorption of target metals from industrial stormwater runoff. Two waste-by-products from the iron and steel manufacturing sector were evaluated in terms of their adsorption capacity for metal removal from the test water in this study: (1) Open-Hearth Slag(OHS) and (2) Air Cooled-Blast Furnace Slag (ACBFS). Bench-scale batch adsorption experiments were conducted using a shaker table and synthetic stormwater runoff simulated according to a sampled stormwater runoff from a Biomass Power Generation facility in Nova Scotia, Canada. 200mL of the synthetic runoff water spiked with humic acid TOC= 40 mg/L) and control with no humic acid (TOC= 0 mg/L) were dosed at low (10 g/L) and high (35 g/L) OHS and ACBFS concentrations. Batch adsorption experiments were also conducted with Granulated Activated Carbon (GAC) of 1 mm particle size at doses of 10 and 35 g/L for comparison with the OHS and ACBFS material. After shaking for a 24-hour period at room temperature, each flask was removed, and the water was settled for 30 minutes. Results of this study showed that more than 90% of Cd, Fe, Mn, and Zn was removed from the water phase with ACBFS and OHS addition at the higher dose. Adsorption capacity of OHS and ACBFS was found to be higher in control experiments (TOC = 0 mg /L) compared to experiments conducted with the test water at higher TOC concentrations (40 mg/L). Comparatively, GAC did not perform as well as OHS and ACBFS for the removal of the metals evaluated in this study.

1 INTRODUCTION

Industrial stormwater runoff is defined as any water that is discharged from an industrial site. One of the major causes of the deterioration of the quality of receiving waters is nonpoint pollution resulting from stormwater runoff (Lee and Bang 2000). Industrial and commercial sites may contribute significantly high pollution loads to receiving waters with stormwater runoff because of the characteristics of the materials stored and processes taking place on-site (Brezonik and Stadelmann 2002, Beenen et al. 2011). Biomass power generating plants are gaining popularity in the recent years due to its renewable energy conversion system. These power plants have outdoor on-site storage of biomass fuels that contribute significant pollutant loadings in the stormwater runoff. (Viana et al. 2010, McIiveen-Wright et al. 2013). Zinc, lead, mercury, nickel, cadmium, silver, copper and chromium are some of the heavy metals that can leach off the biomass material stored on-site.

During the production of iron and steel, slag is produced as a waste material. The National Slag Association (NSA) categorizes slag into two main types: blast furnace slag and steel furnace slag. Actual data of slag

production in 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 was about 17 million tons at a value of US$330 million (U.S. Geological Survey, Mineral Commodity Summaries 2016). The province of Ontario produces about 80% of the steel produced 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). There are several reuse options for ACBFS, mainly in the construction industry as a road sub-base, concrete mix, pavement and backfill material. In contrast, there are limited reuse options for waste OHS due to its swelling nature. 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.

Dimitrova (1996) conducted 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 in the experimental results. The 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 overall objective of this study was to evaluate ACBFS's and OHS as adsorbents to remove metals (Cd, Fe, Mn, Zn) from industrial stormwater run-off. The impact of NOM concentrations on adsorption capacity of the test adsorbents was also evaluated. The sub-objectives are listed below:

- Compare ACBFS to OHS in terms of metal removal capacity

- Compare both slags to GAC in terms of metal removal capacity

- Compare ACBFS and OHS in terms of maximum adsorption capacity using two isotherm models

- Evaluate effect of NOM on metal removal and adsorption capacity

2 MATERIALS AND METHODS

2.1 Stormwater Collection and Preparation

Synthetic stormwater was prepared to simulate actual stormwater collected from biomass power generating plant. Synthetic stormwater runoff without organics was prepared in the lab using Certified ACS grade reagents. Stock solutions of the metal ions were prepared 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. A 1-L stock NOM solution was generated by adding 1g of humic acid sodium salt in 1 L of de-ionized water. The NOM stock solution was added to the test waters to 40 mg /L DOC concentrations. Initial concentration of Cd, Fe, Mn, Zn and DOC were 0.05mg/L, 10 mg/L, 5 mg/L and 0.05 mg/L respectively.

2.2 Slag and GAC Preparation

ACBFS and OHS samples were obtained from Portside Aggregates Ltd., Sydney, Nova Scotia, Canada. These slags are stored on-site in Cape Breton under natural weather conditions. ACBFS and OHS were shipped in 40L buckets and stored in laboratory at room conditions (20 ± 1º C). Sieve analysis was done to determine particle size distribution of both the slag samples. After obtaining 0.25mm particle size, the slag samples were placed in 1L jars and washed using de-ionized water from Milli-Q purification system (EMD Millipore Corporation, Germany) to remove any impurities. The slag samples were dried at 105 ± 5º C for 24 hours in an oven (ThermoFisher Scientific) before activating in a muffle furnace (ThermoFisher Scientific) at 600 ± 1º C for an hour. After cooling down, slags were transferred to a desiccator (ThermoFIsher Scientific) for storage before further use. A virgin activated carbon (General Carbon

Corporation, Paterson, New Jersey, USA), in granular form made from coconut shell was used in this study. The average GAC particle size was 1mm.

2.3 Bench-Scale Methods

A standard shaker table (MAXQ-2000, Barnstead International, Iowa, USA) with 15 slots was used in all of the batch-adsorption experiments. The shaker table was operated at 250 rpm under room conditions, (i.e. 20 ± 1º C). Adsorbents were added in 250 mL Erlenmeyer flasks, containing 200mL of synthetic stormwater. The slag and GAC experiments evaluated doses of each media at 10, 15, 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. After shaking for 24 hours, the flasks were removed from the shaker table and left to settle for 30 minutes.

2.4 Analytical Methods

Total metal concentration of cadmium, iron, manganese and zinc were measured using an Inductively Couple Plasma Mass Spectrometry (ICP-MS) (XSERIES 2, Thermo-Fisher Scientific). Concentrated nitic acid was added to preserve the samples to pH <2.

2.5 Data Analysis

The equilibrium adsorption capacity, q_e (mg/g), was calculated using Equation 1:

[1] $Qe = \frac{V(C_o - C_e)}{m}$

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. Equations 2 and 3, show the Langmuir and Freundlich isotherm models:

[2] $Qe = \frac{Qm * K_L * C_e}{1 + K_L * C_e}$

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).

[3] $Qe = K_f * Ce^{1/n}$

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.

All experiments were conducted in triplicate and error bars on graphs represent one standard deviation. Analysis was done using Microsoft Excel (Microsoft Corporation, USA) and OriginPro 2017 (OriginPro Corporation, USA).

3 RESULTS AND DISCUSSION

3.1 Adsorption Capacity

The batch adsorption data of Cd, Fe, Mn and Zn were fit to the Langmuir and Freundlich isotherm models and the results are shown in Table 1.

Table 1. Langmuir and Freundlich isotherm constants for the adsorption of target metals onto slags and GAC.

Cadmium

Adsorbent	Langmuir				Freundlich			
	TOC = 0 mg/L		TOC = 40 mg/L		TOC = 0 mg/L		TOC = 40 mg/L	
	Q_m (mg/g)	R^2	Qm (mg/g)	R^2	Qm (mg/g)	R^2	Qm (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

Iron

Adsorbent	Langmuir				Freundlich			
	TOC = 0 mg/L		TOC = 40 mg/L		TOC = 0 mg/L		TOC = 40mg/L	
	Q_m (mg/g)	R^2	Qm (mg/g)	R^2	Qm (mg/g)	R^2	Qm (mg/g)	R^2
ACBFS	0.041	0.979	0.008	0.911	0.223	0.981	0.04	0.89
OHS	0.018	0.985	0.003	0.759	0.131	0.981	0.004	0.774
GAC	0.016	0.141	2E-4	0.499	0.0016	0.141	2E-4	0.499

Manganese

Adsorbent	Langmuir				Freundlich			
	TOC = 0 mg/L		TOC = 40 mg/L		TOC = 0 mg/L		TOC = 40mg/L	
	Q_m (mg/g)	R^2	Qm (mg/g)	R^2	Qm (mg/g)	R^2	Qm (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

Zinc

Adsorbent	Langmuir				Freundlich			
	TOC = 0 mg/L		TOC = 40 mg/L		TOC = 0 mg/L		TOC = 40mg/L	
	Q_m (mg/g)	R^2	Qm (mg/g)	R^2	Qm (mg/g)	R^2	Qm (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	3E-4	0.693	0.008	0.841	0.0004	0.693
GAC	0.001	0.576	3E-4	0.693	0.001	0.576	0.0004	0.693

*Fit did not converge

For cadmium, ACBFS and OHS fit the Langmuir ($R^2 > 0.97$) and Freundlich isotherm ($R^2 > 0.98$) model well when there was no organics (control) present in test water. In presence of organics, adsorption data did not fit as well 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 fit well either in Langmuir and Freundlich isotherm models. Maximum adsorption capacity also showed that GAC did not adsorb Cd effectively on to its surface compared to ACBFS and OHS. In addition, the maximum adsorption capacity of GAC increased in the control test waters but remained lower than ACBFS and OHS.

Iron adsorption onto ACBFS showed the highest Q_m, indicating that ACBFS had the best capability to remove iron from test water. Adsorption data fit well for both types (control and TOC spiked) of test water within Langmuir and Freundlich when ACBFS was used. OHS showed relatively better adsorption capacity compared to GAC, adsorbing almost five times more of the metals than the GAC media.

The batch adsorption data of Mn was fit to the Langmuir and Freundlich isotherm models. Highest adsorption capacity was exhibited by ACBFS, however, experiments conducted with NOM addition in the test water did not converge and generated a high standard error. This indicates that Langmuir and Freundlich do not show a reliable model for Mn adsorption on ACBFS when organics are present in test

water. OHS shows better maximum adsorption capacity than GAC in both type of test water conditions. Presence of organics decreased the adsorption capacity and data fit (R^2) of Mn for all of the adsorbents evaluated in this study.

Similarly, the experiments with TOC spiked into the synthetic water showed significantly less Zn adsorption on the slags and GAC. ACBFS exhibited high data fit (R2 > 0.93) compared to OHS (0.69 < R2 < 0.93). However, GAC showed very poor fit (R2) in both Langmuir and Freundlich models. Overall, GAC, for both types of test water showed low adsorption capacity compared to ACBFS and OHS.

3.2   Metal Removal Capacity

ACBFS at low (10 g/L) and high (35 g/L) doses effectively removed more than 90% of Cd from both types of test water. At high dose OHS removed more than 90% of Cd in both types of water. However, in presence of organics in test water, low dose of OHS? removed less than 60% of Cd. GAC, in presence of organics, removed the least amount of Cd. When there was no organic present, GAC removed up to 70% of Cd at high dose.

In presence of organics, ACBFS at low (10 g/L) dose removed around 30% of Fe. However, at higher (35 g/L) dose of the slag Fe was removed more than 95%. OHS removed more than 90% Fe from test water when there was no organic present but in presence of organics, even at high dose OHS removed about 50% of Fe. GAC did not remove Fe effectively and removed only about 30% in presence of organics. When there was no organics present, at high dose GAC removed about 60% of Fe.

ACBFS removed more than 95% of Mn in both types of test water. OHS, in presence of organics removed less Mn compared to when there was no organics. GAC removed about 70% of Mn when there was no organics present. In presence of organics, GAC removed about 50% Mn at both low and high doses.

At high (35 g/L) and low (10 g/L) dose, ACBFS removed almost the same percentage of Zn in both types of water. More than 90% of Zn was removed when ACBFS was used at high dose. OHS was not effective in removing Zn when there was organic present in test water. About 80% Zn was removed at high dose of OHS when there was no organic present in water. GAC removed a maximum of 70% of Zn when there was no organic present in water. At high dose, in presence of organics GAC removed only up to 30% of Zn.

4   CONCLUSIONS

The overall objective of this study was to evaluate ACBFS's and OHS as adsorbents to remove metals (Cd, Fe, Mn, Zn) from industrial stormwater run-off. The impact of NOM concentrations on adsorption capacity of the test adsorbents was also evaluated. The sub-objectives are listed below:

The results of this study are summarized below:

- ACBFS was found to able to achieve greater reductions in target metal concentrations compared to OHS. Treatment with ACBFS achieved greater than 90% removal of target metals in both the control and NOM spiked test waters, indicating that this adsorbent material was not impacted by the presence of humic acids in the test waters.

- Both the waste slages ACBFS and OHS were shown to achieve greater removal of target metals compared to GAC. Although GAC is a commercially available adsorbent, the results in this study indicate the performance in removing the four target metals (Cd, Fe, Mn, Zn) was poor.

- Among three materials, ACBFS demonstrated the best adsorption capacity in adsorbing metals. However, the presence of organic compounds was found to impact the adsorption capacity of ACBFS. OHS was found to have better adsorption capacity than GAC, but both of these materials exhibit poor adsorption capacity in presence of organics, in general.

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