Metal Adsorption and Desorption Studies with Paint Waste Generated during Bridge Rehabilitation in New York State

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ABSTRACT

METAL ADSORPTION AND DESORPTION STUDIES WITH PAINT WASTE GENERATED DURING BRIDGE REHABILITATION IN NEW YORK STATE

by
Xuanming Zhang

Adsorption and desorption behavior for Resource Conservation and Recovery Act (RCRA) metals as well as Zn in paint waste is investigated in this study. New York State Department of Transportation (NYSDOT) uses steel grit as a blasting abrasive in the rehabilitation of bridge structures where paint coatings are applied to prevent corrosion. Although magnetic separation is used to remove the steel grit, a large fraction of the particles remain with the paint waste. As a result, hydrous ferric oxide (HFO) forms on the steel grit surfaces. The cross-section of the steel grit particles is examined with field emission scanning electron microscope (FE-SEM) to assess the average coating thickness on the steel grit surface. The total concentration of metals in the paint waste is analyzed using field portable X-ray fluorescence (FP-XRF) in soil mode and mining mode. Subsequently, macroscopic experiments are conducted in the pH range from 3 to 10 at room temperature and an ionic strength of 0.01 M. The Langmuir adsorption isotherm is found to describe the entire adsorption and desorption process within the pH interval of 4 to 6. Other processes are considered, namely precipitation, but adsorption is found to be the dominant process.
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GENERATED DURING BRIDGE REHABILITATION IN NEW YORK STATE

by

Xuanming Zhang

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirement for the Degree of
Master of Science in Environmental Engineering

Department of Civil and Environmental Engineering

May 2014
METAL ADSORPTION AND DESORPTION STUDIES WITH PAINT WASTE GENERATED DURING BRIDGE REHABILITATION IN NEW YORK STATE

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PERSONAL DEDICATION

The author dedicates this thesis to every people provided their help throughout this process.

Appreciate my parents for their support, encouragement, and selfless love during this period.

Appreciate NJIT which provided me the opportunity of research and further education to U.S.A.

Especially appreciate my advisor Dr. Lisa B. Axe for her selfless and wholehearted instruction.
ACKNOWLEDGEMENT

The author wishes to especially express his gratitude to his advisor, Professor Lisa B. Axe, for her guidance throughout this research for three semesters, and sacrificed lot of her personal time. Same gratitude is also expressed to committee members, Dr. Michel Boufadel and Dr. Wen Zhang.

Thanks are extended to the director, members, and colleagues of the New Jersey Institute of Technology metal laboratory for their help, assistance, and encouragement throughout this research.
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LIST OF ABBREVIATIONS

As: Arsenic
Ag: Silver
Ba: Barium
Cd: Cadmium
Cr: Chromium
Fe: Iron
FE-SEM: Field Emission Scanning Electron Microscopy
HDPE: High-Density Polyethylene
HFO: Hydrous Ferric Oxide
Hg: Mercury
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
MCLG: Maximum Contaminant Level Goal
Pb: Lead
QA/QC: Quality Assessment/Quality Control
RCRA: Resource Conservation and Recovery Act
Se: Selenium
TCLP: Toxicity Characteristic Leaching Procedure
Zn: Zinc
As anthropogenic activities increase, trace metals, especially Resource Conservation and Recovery Act (RCRA) metal contaminants in soil and water have become a serious environmental problem because of their toxicity and risk posed by exposure to human health. Paint wastes have made a considerable contribution to trace metal contamination due to the wide application and relatively high trace metal concentrations. Between 1950 and 1980, paint containing trace metals was applied on bridges to protect them from corrosion, and involved a number of metals including lead and chromium (Shu et al., 2013). Paint wear from New York State Department of Transportation (NYSDOT) bridges may impact the surrounding environment including vicinity surface waters. Steel grit has been applied as a blasting abrasive in NYSDOT (Hansel, 2000). Although the waste undergoes magnetic separation, a fraction of the steel grit remains. As a result a surface coating of iron oxide coating forms. From earlier studies (Shu et al., 2013), hydrous ferric oxide (HFO) was observed as the dominant oxide on steel grit surfaces. Based on previous studies (Wilkie and Hering, 1995) on trace metal adsorption and desorption, HFO has proved to be an excellent adsorbent for aqueous trace metal contaminant removal, including RCRA metals. In this research, metal contaminants including arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), zinc (Zn), silver (Ag) and selenium (Se) in paint waste samples from bridges undergoing rehabilitation in New York were studied for desorption as a function of pH and then further through isotherms.

Desorption from the paint waste was investigated after 24 hours of equilibration, and
therefore reflects the mobility and potentially bio-availability of aqueous metal contaminants. Desorption has traditionally not been considered in most studies, although desorption of trace metals potentially impacts human health through a number of pathways including ingestion of contaminated drinking water and dermal contact. Thus, it is important to study trace metal desorption under environmentally relevant factors including pH, ionic strength, complexing ligands, temperature, and time.

The objective of this thesis was to understand the trace metal removal mechanisms and desorption potential from paint waste with steel grit. The percentage of desorbed RCRA metals (i.e., As, Ba, Cr, Hg, Pb, Ag, Se, and Cd) and Zn as a function of pH was investigated. Additionally, adsorption-desorption isotherms were conducted to evaluate the affect of concentration, which resulted in modeling of the adsorption-desorption process.

This study includes a review of adsorption edges and isotherm studies with trace metals. Subsequently, hypotheses for this study are stated and followed by methods used to test them. The results for the desorption edges and isotherm studies are then presented and discussed. Finally, conclusions for this research are drawn.
CHAPTER 2
LITERATURE REVIEW

In this chapter, a review of literature is presented on paint waste and its characteristics. Because steel grit is used as an abrasive to remove paint waste from bridges undergoing rehabilitation in New York State through the NYSDOT, steel grit makes up to as much as 80% of the waste generated. As a result, trace metal adsorption and desorption to HFO is an important process. Adsorption/desorption edges as well as isotherm studies are two types of work used to evaluate sorption behavior. Recently, X-ray fluorescence (XRF) analysis for evaluating metal concentrations in a solid phase including paint waste has been demonstrated to be a viable and reproducible method. This chapter concludes with a summary of key points and questions raised based on the literature.

2.1 Paint Waste

In the past, paint waste has contributed to the significant affect of metal contamination in the environment (Hyatt et al., 2014). Singh and Turner (2009) collected soil samples contaminated by antifouling paint with approximately 1% by weight paint waste, Zn and Cu concentrations were an order of magnitude greater than “background” concentrations. There are a number of sources of paint waste including boat hull cleaning, flaking off structures, and abandoned vessels (Turner et al., 2009). During bridge paint removal, closed systems are used to collect paint fragments to prevent environmental contamination (British Marine Federation, 2005). However, despite of these methods, paint waste may result in considerable environmental impact due to the corrosion and short-term wear (Singh and Turner, 2009).
Therefore, RCRA metals are no longer used in paint formulations and waste characterization will continue to be required.

One important tool that has been demonstrated to be more than a screening tool (Zegeye et al., 2013) is X-Ray fluorescence (XRF). As a field portable tool, it has been used to characterize soil contaminated with paint waste (He et al., 2013) as well as in other studies of Larks and Scheib (2013) and Al-Eshaikh and Kadachi (2011). For example, Zegeye et al. (2013) applied XRF to analyze trace metal concentrations in paint containing kaolin slurries. Furthermore, United States Environmental Protection Agency (U.S. EPA) Method 6200 for field portable XRF (FP-XRF) is specific for quantifying elements in soil and sediment samples. Each element has a characteristic excitation energy. The intensity of X-rays at a specific energy is related to the concentration of the element in the sample. FP-XRF can be applied for analysis of all eight RCRA trace metals and is a viable method for analyzing trace metals in many solid wastes.

2.2 Adsorption/Desorption Edges: Metal Adsorption/Desorption as a Function of pH

The focus of this literature review is on sorption behavior with hydrous ferric oxide (HFO) as this surface is an important and dominant interface in the paint waste, which includes steel grit particles (Shu et al., 2013). Adsorption behavior of polyvalent metal ions onto oxides and hydrous oxides makes them promising candidates for application in trace metal contaminant removal (Ajouyed et al., 2010; Luo et al., 2010). Oxides of iron are expected to play an important role in attenuating and controlling trace metal mobility because they are ubiquitous in the environment, exhibit a high affinity for trace metals, have a large sorption capacity, and
are selective for certain ions (Payne and Abdel-Fattah, 2005; Dong et al., 2002). One of the most significant factors is pH, which affects trace metal adsorption onto iron oxides through its surface charge and impacts the solubility of metal hydroxides, carbonates, and phosphates (Appel and Ma, 2002; Bruemmer et al., 1986; McBride, 1994; Sauve et al., 1988). Thus, studies of trace metal adsorption/desorption onto iron oxide are presented in this section.

Contamination of soils and sediments has been studied and evaluated using adsorption and desorption edges (as a function of pH) (Akgul et al., 2006; Appel and Ma, 2002; Barnes and Davis, 1996; Davranche and Bollinger, 2000; Goldberg and Johnston, 2000; Igwe and Abia,, 2007; Kendall, 2003; Ndiba and Axe, 2010; Pandey, 2010; Rout, 2009; Shahmohammadi-Kalalagh, 2011; Tack et al., 1995; and Zaman et al., 2009). The pH point of zero charge (PZC) results in an oxide sorbent exhibiting a net surface charge as a function of pH, and reflects the surface properties of hydroxides. The PZC is the pH value at which the net surface charge is zero. In acidic conditions (pH<pH_{PZC}), the surface exhibits a net positive charge. In basic conditions (pH>pH_{PZC}), the net surface charge is negative (Ajouyed et al., 2010). The PZC of hydrous ferric oxide (HFO), lying in the near neutral pH range (Tewari and McLean, 1972) also makes it a model adsorbent in the study of adsorption of ion species on negatively and positively charged surfaces (Mishra and Tiwary, 1999). As the pH of the aqueous solution increases, the positively charged species interact favorably with the negatively charged surface sites and their retention to sorbent surfaces via adsorption increases (McBride, 1994; Sparks, 1995; Ajaelu et al., 2011). With an increasingly negative net surface charge, cation sorption increases and results in decreases in aqueous trace metal concentrations (Mishra and Tiwary, 1999). Alkaline conditions result in a negatively charged
surface; increasing the uptake of metal cations such as Ba$^{2+}$ and Zn$^{2+}$. Researchers (e.g., Chukwu and Iyagba, 2012) have hypothesized that a negatively charged sorbent surface may promote cation precipitation when sorption exceeds the surface site capacity. For cations, adsorption is a minimum in the acidic regions (Mishra and Tiwary, 1999), while adsorption increases as pH increases (Gao et al., 2003). Luo et al. (2010) studied Cr (VI) removal: increasing pH reduces anion adsorption. On the other hand, at pH conditions less than the pH PZC, the oxide surface is positively charged through a protonated surface and thus exhibits a greater affinity for anions, as electrostatic repulsion reduces cation attraction for the positively charged surface.

Generally, adsorption and desorption edges are studied within a specific range of pH. The effect of pH on Cd adsorption to bio-adsorbents was not studied beyond pH 7.0 because of the precipitation of cadmium hydroxide (Ajaelu et al., 2011). Uptake of cadmium ions onto Fe$_3$O$_4$ nanoadsorbents increased as pH increased from 2.5 to 6.0, and for a pH greater than 6 distinguishing between adsorption and precipitation requires further analyses (Nassar, 2012). Silver (I) adsorption by zeolites as a function of pH was studied by Akgul et al. (2006); they found that when pH was lower than 4, the adsorption capacity was low due to the competition from protons for the adsorbent exchange sites. However, for pH greater than 4, adsorption showed no significant increase (Akgul et al., 2006).

The results of adsorption and desorption edges are related to site capacity of the sorbent. In adsorption edge studies, the effect of pH addressed through modeling has been considered (Ghaemi et al., 2011; Chukwu and Iyagba, 2012). The site capacity of adsorbents may also be examined through isotherm studies, where adsorption capacity ($q_m$) is one of the
parameters of the Langmuir isotherm model (Petrova et al., 2011). Maximum adsorption helps to resolve site capacity, which is a function of adsorbent and pH when invoking the Langmuir isotherm.

Trace metal speciation affects the affinity of an ion for a surface, the degree to which it will be sorbed, and the surface complexes that form. Goldberg (2000) studied sorption (mmol/g) as a function of pH for arsenate and arsenite. Arsenic (V) sorption showed a decrease as pH increased, which demonstrates arsenate is effectively removed under more acidic conditions; however, adsorption of As (III) showed an increase as pH increased. Thus, thermodynamic modeling of trace metal speciation is needed when evaluating data and interpreting results.

In addition to pH, other factors affect adsorption edges. The presence of mono and divalent co-ions along with the studied ions suppresses their removal appreciably due to the competition affects (Mishra and Tiwary, 1999). Adsorption is also dependent on the sorbent properties. For example, zeolites with high adsorption capacity due to the high surface area have been applied to mitigate groundwater contaminated by arsenic as a point-of-use sorbent material (Payne and Abdel-Fattah, 2005). Ionic radius of the adsorbate also contributes to sorption. For example, metal ions with larger ionic radii have smaller hydrated radii and consequently lower hydration energy. The ions with smaller hydrated radii bind with greater energies than those with larger radii (Nassar, 2012). Because Cd (II) has the largest ionic radius of 109 pm (Esalah and Husein, 2008) among Cd(II), Co(II), and Ni(II), it is expected to have the greatest affinity for a surface (Nassar, 2012).

With an understanding of sorption behavior as function of pH, ionic strength,
competing ions, and temperature, adsorption can be modeled through isotherms that depict adsorption as a function of concentration at equilibrium.

2.3 Isotherm Studies

Adsorption isotherms provide a relationship between concentration of trace metal ions in the bulk aqueous phase and the concentration adsorbed at equilibrium. The adsorption isotherm can be used to predict whether adsorption is favorable or unfavorable both in fixed-bed systems as well as in batch processes (Ghaemi et al., 2011). Petrova et al. (2011) studied the adsorption of trace metal ions Co (II), Cr (VI), Cr (III), and Se (VI). The Langmuir isotherm model was used to fit the adsorption data. This model proved to describe adsorption well with the parameters of $q_m$ (monolayer capacity) and $K_L$ (Langmuir constant represents the sorption affinity the adsorbate has to the adsorbents) for As, Ba and Sr. The linearized Langmuir equation is the following:

$$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}$$

Where $q_e$ is the adsorbed metal ion concentration and $C_e$ is the equilibrium aqueous metal concentration (Ghaemi et al., 2011, Payne and Abdel-Fattah, 2005).

Selection of an isotherm model is dependent on the sorbent and its properties. Both Langmuir (1918) and Freundlich (1926) models have been applied in studying adsorption and trace metal affinity for adsorbents under constant temperature, pH, and ionic strength. Correlation coefficients ($R^2$) are used to select the best-fit isotherm model (Payne and Abdel-Fattah, 2005). In the study of Mishra and Tiwary (1999), concentration dependent data were best fit with the Langmuir isotherm for Ba and Sr adsorption over the entire range of
concentrations studied. The experimental results of Ghaemi et al. (2011) indicated a non-linear relationship between Ba (II) ions adsorbed per unit mass (g) of dolomite and the concentration of Ba (II) remaining in the aqueous phase (mg/L). This system was modeled with the Langmuir isotherm. The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interactions between adsorbed molecules. This theory assumes that all surface sites have the same adsorption energy. In some studies of environmental systems (Luo et al., 2010), the Freundlich isotherm model has shown better fits than the Langmuir isotherm.

The parameters for the adsorption isotherm are critical factors for predicting adsorbent performance. Evaluating affinity of trace metals for an adsorbent is one of the important targets of an isotherm study. Iron oxides have a high affinity for As (III) and As (V) as demonstrated by the Langmuir constant (Petrova et al., 2011). Adsorption of As (III) and As (V) to iron oxide loaded slag increased linearly with an increase in aqueous arsenic concentration; however, the adsorption capacity for As (V) (48.65 g/kg on average) was greater than that of As (III) (15.5 g/kg on average) (Zhang and Itoh, 2005). In the study of Appel and Ma (2002), Pb adsorption was greater than or roughly equal to Cd. The greater affinity of Pb for most functional groups in organic matter, which are hard Lewis bases—carboxylic and phenolic groups, as well as its higher electronegativity, make it a better candidate than Cd for electrostatic and inner-sphere surface complexation reactions (Huheey, 1983; McBride, 1994). Furthermore, Appel and Ma found that organic matter had a more significant impact on Pb adsorption, while inorganic ligands were more critical to Cd and Zn adsorption.
2.4 Summary

Trace metal adsorption is generally a rapid process. Typical equilibration involves short periods of times, as low as 4 hours, to reach an equilibrium or pseudo-equilibrium condition with sorbent surfaces (Bhaumik et al., 2011). Others (Payne and Abdel-Fattah, 2005; Mishra and Tiwary, 1999; Pandey et al., 2010) have employed up to 24 hours for equilibration. Based on a number of studies (Akgul, 2006; Appel, 2002; Barnes, 1996; Davranche, 2000; Ndiba and Axe, 2010; Goldberg, 2000; Kendall, 2003; Rout, 2009; Zaman, 2009), metal desorption increased as pH decreases for cations. Thus, pH is a crucial factor for trace metal adsorption; all studies need to be conducted over a relevant pH range.

The Langmuir isotherm has been widely applied for trace metal adsorption isotherm studies (Igwe, 2007; Shahmohammadi-Kalalagh, 2011; Akgul, 2006). Additionally, the Langmuir isotherm parameters are important in considering affinities and adsorption capacities of sorbents for trace metals. Based on the Langmuir isotherm parameters, the performance of HFO is highly pH-dependent; thus, isotherm studies at relevant and constant pH are needed when studying a system.

In the next chapter, hypotheses for this research are presented. Methods to test the hypotheses are then reviewed and the results of conducting the studies follow.
Hypothesis 1: Desorption Of Trace Metals Is A Function of Affinity for the Adsorbent, Properties of Paint Waste, And Metal Solubility.

Trace metal desorption increases as affinity for the surface decreases (Petrova et al., 2011). Desorption is also a function of the mixture of trace metals present and their competition for the sorbent surfaces in the paint waste. The low or non-detectable concentrations of aqueous trace metals may be due to the high affinity for the sorbent, the low concentrations in the paint waste, or the sparingly low solubility of the precipitates under neutral to high pH conditions.

Hypothesis 2: Metal Adsorption to HFO Can Be Modeled with One Type of Adsorption Site.

In an adsorption isotherm study of arsenic where the Langmuir model was invoked (Zeng, 2004), As(III) showed a good fit for the two pH condition considered. This observation suggests that the Langmuir model may be an appropriate model for other metals at multiple pH conditions. As reviewed in the previous chapter, the Langmuir model is developed based on one type of adsorption site. Other metals observed in the paint waste will be evaluated with this model.

Hypothesis 3: The Adsorption Capacity And Affinity of HFO Is Affected by pH.

Because the surface charge is affected by pH for HFO, then the adsorption capacity and
adsorbent affinity for trace metal ions is a function of pH and reflected in two parameters of the Langmuir isotherm model, $q_m$ and $K_L$. 
CHAPTER 4
EXPERIMENTAL METHODS

4.1 Quality Assurance and Quality Control (QA/QC)
All Quality Assessment/Quality Control (QA/QC) procedures followed standard methods (Eaton et al., 2005). High-Density Polyethylene (HDPE) containers and glass ware were cleaned with a metal-free nonionic detergent solution, rinsed with deionized water, soaked in 10% nitric acid (trace metal grade) for 24 hours (48 hours for glass ware), and then rinsed with metal-free deionized water (ASTM, 1990; Eaton et al., 2005). Orion Star™ and Star Plus Meter with Thermo Scientific Orion Ross Ultra, Ross and PerpHecT Ross electrodes were used in pH measurements. The electrode was cleaned with 0.1 M nitric acid solution, refilled with ROSS fill solution, then soaked in standard pH electrode storage solution. The pH meter was calibrated at pH 4, 7, and 10 in buffer solutions at the beginning of each day and experiment (Thermo Fisher Scientific Inc., 2008).

4.2 Materials
For bridges repainted after 1989 in the 10 New York State regions, 24 bridges were selected for the study (Shu, 2013); the paint waste samples were collected from five random locations/drums for each bridge under rehabilitation. Specifically, paint samples were obtained by using trowels where the sampled material was stored in HDPE containers that preserved the integrity of the sample. All sample bottles were listed with the region number, bridge, and location/drum ID (e.g., Bridge 11-1a). Samples were sealed and stored at 4 °C in NJIT Metals Lab. Preserved samples was stored up to 6 months prior to analysis in a
refrigerator at 4°C (U.S. EPA, 2007; Shu, 2013).

Steel grit is used as blasting abrasive in removing the paint from bridges under rehabilitation. Although the contractor used magnetic separation to remove these iron particles from the waste, a significant fraction remained. The oxide coated steel grit was found to be dominated by hydrous ferric oxide (HFO) coating using X-ray diffraction (Shu, 2013). HFO or ferrihydrite exhibits a high affinity for trace metal ions. In this research, to address the thickness and morphology of the oxide coating on the steel grit particles, scanning electron micrographs of the iron oxide sorbents were obtained using LEO 435 VP field emission scanning electron microscope (FE-SEM).

4.3 FP-XRF Analysis

All paint samples were analyzed by field portable X-ray fluorescence (FP-XRF) before desorption experiments to measure the concentration of trace metals in paint by mass (mg/kg paint) (U.S. EPA Method 6200). The XRF analyzer was calibrated for two modes, mining (%) and soil (ppm). In this study, Pb, Zn, and Fe in paint waste were analyzed in mining mode due to the relatively high concentrations; on the other hand, As, Ba, Cd, Cr, Ag and Se were analyzed in soil mode. In XRF, the energy source is cadmium-109 (88.0 keV), a radioactive source in the instrument. The 88.0 keV gamma-rays excite K-shell electrons from trace metal atoms (Bohr model), which result in fluorescence. This approach is used for analyzing RCRA trace metal measurements in paint (U.S. EPA Method 6200). For metal samples, the minimum limit of detection (LOD) ranged from 4 to 75 ppm (Furl et al., 2012).

Two bridges from Regions 10 and 11 (Bridge 10-5b and Bridge 11-2a) out of the 24
sampled bridges as part of the NYSDOT project were investigated in the desorption edge study. Eight bridges from Region 10 (Bridge 10-1c to Bridge 10-8d) were investigated for the isotherm study. A number of studies have shown that characteristic subsamples can be used to represent entire populations (Barnes, 1996; Appel, 2002). In this study, the mean Pb concentration from Regions 10 and 11 was greater than that observed from the other five regions; furthermore, the variance of Pb concentrations from samples collected in Regions 10 and 11 is less than or equal to the total variance over the 24 bridges. The bridges were selected to represent the 24 bridges (Table 4.1). The total concentration for each metal contaminant (mg/kg paint) in paint waste was measured with FP-XRF; however, Hg as one of the RCRA trace metals was not detected in the paint waste from Regions 10 and 11.

**4.4 Desorption and Isotherm Procedures**

To examine the effect of pH on desorption, 10 grams of paint waste were applied in 250 ml high density polyethylene (HDPE) bottles with 200 ml of extraction solution, resulting in 50 g/L. This concentration is also used in the U.S. EPA toxicity characteristic leaching procedure (TCLP) (U.S. EPA, 1996). An ionic strength of 0.01 was prepared with NaNO₃ and de-ionized water open to the atmosphere; this ionic strength is within the range of 0.001 to 0.02 typical for surface water and groundwater (Table 4.2). In a similar experiment conducted by Appel et al. (2002), a 0.01 ionic strength was applied to investigate the adsorption of chromium and lead.

Studies were conducted at 23 ± 0.1°C (room temperature), open to the atmosphere, and under turbulent conditions (Re of 1.0×10⁴) using a C-1 Platform Shaker during the experiment to eliminate resistance due to external mass transfer and simulate hydrodynamic conditions of a
Table 4.1 Mean Concentration (% by mass) and Variance of Lead in Different Regions

<table>
<thead>
<tr>
<th>Region</th>
<th>Mean Concentration % by mass as Pb</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.98</td>
<td>1.26</td>
</tr>
<tr>
<td>2</td>
<td>0.55</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>2.37</td>
<td>1.50</td>
</tr>
<tr>
<td>5</td>
<td>0.44</td>
<td>0.10</td>
</tr>
<tr>
<td>7</td>
<td>6.20</td>
<td>15.7</td>
</tr>
<tr>
<td>10</td>
<td>7.51</td>
<td>0.83</td>
</tr>
<tr>
<td>11</td>
<td>6.99</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Average mean or variance over 24 bridges from seven regions: 4.5, 11.49

natural surface water environment. Samples were equilibrated for 24 hours (Barnes, 1996).

The pH of the solution was monitored and controlled by adding either 0.1 M HNO₃ or 0.1 M NaOH (Appel, 2002).

After this period, 30 ml samples were withdrawn with a syringe and filtered through a 0.22 μm cellulose filter. The filtrate was acidified to a pH less than 2 with 0.1 N HNO₃ and stored in closed Nalgene® bottles under refrigeration at 4 °C until analyzed with inductively coupled plasma mass spectrometry (ICP-MS) (Talbot and Weiss, 1994). ICP-MS calibration with standards preceded sample analysis (Eaton et al., 2005). The aqueous metal concentration is defined as that desorbed, as adsorption-desorption was assumed as the dominant trace metal process in this study. Adsorption was calculated based on the total metal
### Table 4.2 Typical Ionic Strength in Nature Water

<table>
<thead>
<tr>
<th></th>
<th>Ionic Strength (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface water</td>
<td>0.001–0.005</td>
</tr>
<tr>
<td>Potable water/ groundwater</td>
<td>0.001–0.02</td>
</tr>
<tr>
<td>Seawater</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Source: [http://www.aqion.de/site/69](http://www.aqion.de/site/69), accessed on June 6th, 2013

concentration and desorbed concentration examined by FP-XRF and ICP-MS, respectively. However, Se and Ag are two of the RCRA trace metals that were not detected in the solution, even though both were present at considerable concentrations in the paint waste samples based on FP-XRF. In the experiments, 10% replicates and 10% duplicates were collected (Reed, 2002).

The pH affects the oxide surface charge and therefore the degree to which a trace metals sorb. Similar studies have focused in the range of 2 to 10 (Barnes and Davis, 1996; Appel and Ma, 2002; Kendall, 2003; Zaman et al., 2008; Martinez and Motto, 2000). A pH range of 3 to 10 was applied in this study given the nature of the waste and the potential for dissolution at lower pH conditions. Moreover, isotherm studies were conducted to evaluate the adsorption capacity and relative affinity the metal ions have for the surface. This work involved eight bridges from Region 10 (Bridge 10-1 to 10-8). The pH range for the isotherm studies was 4 to 6 similar with other studies (Nassar, 2012; Shahmohammadi-Kalalagh, 2011) that have demonstrated through the adsorption-desorption edge significant changes in sorption. The isotherm studies were conducted at the same ionic strength, temperature, and
equilibration period as the desorption edges.
CHAPTER 5
RESULTS AND DISCUSSION

In this section, results from studying the iron oxide dimensions associated with the steel grit are discussed based on FE-SEM. Additionally, results from FP-XRF analysis addressing trace metal concentrations in the paint waste are also reviewed. Subsequently, trace metal desorption edges and isotherm studies are presented. Best-fit isotherm parameters based on the Langmuir model are shown for the metals studied and as a function of pH conditions.

5.1 FE-SEM Analysis for Iron Oxide Coated Steel Grit

Hydrous ferric oxide is an ideal adsorbent for aqueous trace metal removal (Ajouyed et al., 2010; Luo et al., 2010). Shu (2013) showed that HFO is the dominant iron oxide mineral on the steel grit surface in the paint waste. Therefore, the thickness of oxide coating on steel grit surface was evaluated using FE-SEM.

The cross-section of samples was prepared by embedding steel grit in resins, followed by grinding and polishing (Mak et al., 2011). The components of steel grit could be generally considered as two parts: iron and iron oxides (Shu, 2013). Based on the elemental data of steel grit oxide coating assessed with energy dispersive X-ray analysis (EDX) (Figure 5.1 and 5.2), O makes up 8.28% by atomicity and Fe 5.61% by atomicity. The oxide is consistent with elemental
Figure 5.1  Electron micrograph of the iron oxide coating on the steel grit surface at 3.0 keV using a LEO 1530VP Field Emission Scanning Electron Microscope with an Oxford EDS Detector (FESEM-EDS) / Zyvex Nanomanipulator System.

<table>
<thead>
<tr>
<th>Element</th>
<th>% by weight</th>
<th>% by atomicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>8.95</td>
<td>8.28</td>
</tr>
<tr>
<td>Fe</td>
<td>21.17</td>
<td>5.61</td>
</tr>
</tbody>
</table>

Iron oxide/Total Steel grit = 0.008% by weight

Figure 5.2  Electron micrograph of a cross sectional area of the steel grit studied at 3.0 keV using a LEO 1530VP Field Emission Scanning Electron Microscope with an Oxford EDS Detector (FESEM-EDS) / Zyvex Nanomanipulator System.

<table>
<thead>
<tr>
<th>Element</th>
<th>% by weight</th>
<th>% by atomicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2.52</td>
<td>3.69</td>
</tr>
<tr>
<td>Fe</td>
<td>60.96</td>
<td>25.58</td>
</tr>
</tbody>
</table>
mapping (Figure 5.2) reveals the iron oxide coating makes up a small contribution of the steel grit particle (0.008% by weight); however, the high surface area of the coating results in it playing a dominant role in surface interactions with metal ion species.

As presented by the cross-sectional figure (Figure 5.1), the white edge which represents oxide coating stretches throughout the whole surface of steel grit, although the steel grit presents irregular morphology (Figure 5.2). The relatively significant surface area of the oxide coating on the steel grit could greatly optimize the performance of the sorbent, providing a large site capacity typical of HFO (Reynolds, 1983).

5.2 FP-XRF Analysis for Paint Waste Samples

Total concentrations of trace metals in paint waste from nine bridges in Region 10 (Bridge 10-1 to 10-8) and 11 (Bridge 11-2) reveal that steel grit in the paint waste comprises on average 20.52% by weight of the sample. FP-XRF data reveal that Pb, Zn, and Fe are present at elevated concentrations with Pb ranging from 64 to 152 mg/g paint, Zn from 7 to 60 mg/g paint, and Fe from 76 to 252 mg/g paint (Figure 5.3).

Concentrations were elevated as well to As from 3.5 to 4 mg/g paint, Ba from 0.5 to 19 mg/g paint, and Cr from 1.8 to 12 mg/g paint, respectively. For
Figure 5.3 Total metal concentrations of Pb, Zn, and Fe in paint waste analyzed using the NITON XL3t-600 series FP-XRF. Mining mode was used for samples with metal concentrations greater than 2% by weight, while soil mode was applied for samples with metal concentrations less than 2% by wt. The sample ID represents the region and bridge sampled.

The paint waste samples of the nine studied bridges in Region 10 and 11, Pb and Zn have relatively greater concentrations than other trace metals such as As and Cr.

Concentrations of other metals evaluated included Cd at 0.05 to 2.6 mg/ g paint, Ag at 0.01 to 2.15 mg/ g paint, and Se at 0.003 to 3.3 mg/ g paint. Pb and Zn were widely used as pigments in paint. Other metals were used as pigments and preservatives as well. In New York State, steel grit is typically applied as an abrasive material to remove paint during bridge rehabilitation. Although magnetic separation is applied to collect and reuse the steel grit, the fraction remaining in the paint waste ranges from 5 to 80% by weight (Shu, 2013). Based on the previous studies (Shu, 2013), iron oxide formed on the steel grit surface providing an
important sorbent surface for metal ions. In this study, Fe concentrations in the samples ranged from 65.35 to 229.18 mg/ g paint, which reflects both the iron and the oxide coating present. The concentration of Pb in paint wastes was generally consistent in Region 10; however, paint waste from Region 11 revealed greater Pb concentrations than those observed from Region 10, which suggests the potential for increased leaching. By contrast, the concentrations of Zn, As, Ba, and Cr show little difference between the two studied regions (Figures 5.3 and 5.4). The concentration of Ba ranged from 4.17 to 18.68 mg/ g paint and was similar to the range of concentrations found for As of 3.6 to 19.19 mg/ g paint; however, the concentration of Cr was lower than As and Ba ranging from 0.7 to 11.82 mg/ g paint. Interestingly, the concentrations of Ba, Cd, Se, and Ag in the paint waste from Bridge 10-1 are much greater than that of other bridges (Figure 5.4 and 5.5); however, Bridge 10-1 still had the lowest concentration of Cr (Figure 5.4). In conclusion, the sample from Bridge 10-1c presented the greatest concentration of trace metals, Cd, Ag, Ba, and Se, while Bridge 11-2a revealed the greatest As, Cr, and Pb concentrations. All of the studied bridges showed that Zn concentrations ranged from 9 to 52 mg/ g paint. Again, elevated Fe concentrations were introduced through the abrasive blasting during NYSDOT rehabilitation projects. To investigate adsorption/desorption behavior for the trace metals desorption edges and
Figure 5.4  Total metal concentrations of As, Ba, and Cr in paint waste analyzed using NITON XL3t-600 series FP-XRF. Mining mode was used for samples with metal concentrations greater than 2% by weight, while soil Mode was applied for samples with metal concentrations less than 2% by weight. Bridge ID represents the region number and bridge sampled in this region.

Figure 5.5  Total metal concentrations of Cd, Ag, and Se in paint were analyzed using NITON XL3t-600 series FP-XRF. Mining mode was used for samples with metal concentrations greater than 2% by weight; while soil mode was applied for samples with metal concentrations less than 2% by weight. Bridge ID represents the region number and bridge sampled in this region.
isotherm studies were applied.

5.3 Desorption as a Function of pH

In an effort to better understand metal behavior in the paint waste, studies were conducted to investigate metal desorption (%) from the dominant adsorbent (HFO) as a function of pH. Based on FP-XRF, the fraction of metal remaining after 24 hours equilibration is shown as the percent adsorbed; this representation can be compared to other work on adsorption edges with HFO. This type of study is routinely conducted to evaluate the mobility of adsorbed trace metals based on short-term equilibration periods (Goldberg, 2000; Alain Manceau and Laurent Charlet, 1991; Douglas Kendall, 2003; Muhammad Zaman et al., 2009; Tack et al., 1995). Edges provide information on the affect of pH on the adsorbed concentration (Murat Akgul et al., 2006; Axe and Anderson, 1996; Rout et al., 2009; Pandey et al., 2010). While metals are bound in the paint waste and associated steel grit, the dominant surface assumed and considered in this work is the HFO coating on the steel grit surface. As a result, desorption as a function of pH can be examined. Similar pH conditions have been applied in other studies (Appel and Ma, 2002; Zaman et al. 2008; Martinez and Motto, 2000; Barns and Davis, 1996; Kendall, 2003).

In this section, \( q_e \) (mg/kg paint) is the trace metal concentration associated with the solid phase at equilibrium and assumed as adsorbed in this work. The concentrations were calculated based on the equation:

\[
q_e = C_T - \frac{C_e}{0.05 \text{ kg paint}/L}
\]

Equation (1)
In this expression, $C_T$ is the total concentration of the trace metal in the paint waste initially (based on FP-XRF analysis, mg/kg paint); and, $C_e$ is the desorbed metal concentration (mg/L) in the aqueous phase determined by ICP-MS analysis. Therefore, percent adsorbed and desorbed are simply $q_e/C_T$ and $C_e/(C_T \times 0.05 \text{ kg paint/L})$, respectively.

Desorption of arsenic was observed as 0.0024% at pH 3 for Bridge 11-2, then decreased to approximately 0.001% for a pH greater than or equal to 4 (Figure 5.6). A similar trend was observed for Bridge 10-5. Dzombak and Morel (1989) compiled studies with HFO, arsenate adsorption decreases as pH increases from 3 to 10, while arsenite adsorption increases from pH 3 to 5 and then plateaus from pH 5 to 9. Based on results in this research, the dominant form for As appears to be arsenite (Figure 5.6). Moreover, oxidation of arsenite is expected to be negligible in the aqueous system that is open to atmosphere as oxidation of As (III) by atmospheric oxygen is very slow (Clara and Magalhaes, 2002). Based on modeling (Schecher and McAvoy, 1998) (Appendix A), the dominant As (III) form is $\text{H}_3\text{AsO}_3$ from pH 3 to 9.3 and $\text{H}_2\text{AsO}_3^-$ from pH 9.3 to 10. The adsorption edge is consistent with arsenite (Goldberg and Johnston, 2001) where maximum adsorption plateaus at pH 6. The relatively high aqueous concentration at low pH is due to the protonated ions.

Similarly with other cations, desorption of the Ba cation decreased as pH
Figure 5.6  Desorption (a) and adsorption (b) edges for arsenic in paint waste from Bridge 10-5b and Bridge 11-2a are shown after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C.
increased from 3 to 10 for Bridges 10-5 and 11-2 (Figure 5.7). The trend in this study is consistent with that reported in the review of Dzombak and Morel (1989). Mishra and Tiwary (2012) also evaluated adsorption of Ba (II) on hydrous ferric oxide as a function of pH and found an increasing trend from pH 4 to 12. Moreover, the dominant aqueous Ba (II) in this study is Ba$^{2+}$ from pH 3 to 9.5 and BaCO$_3$ (aq) from pH 9.5 to 10 (Appendix A) based on thermodynamic modeling (Schecher and McAvoy, 1998). While HFO adsorption appears to be the dominant process, other adsorbents may not be negligible, such as adsorption to organics present in the paint waste. Chukwu and Iyagba (2012) reported that activated palm kernel shell and husk are effective sorbents for Ba$^{2+}$ under neutral or basic conditions; however, adsorption decreased under acidic conditions.

Desorption of Cd decreased as pH increased from 3 to 10 both for Bridges 10-5 and 11-2 (Figure 5.7). Dzombak and Morel (1989) also observed that Cd adsorption increased as pH increased from 4.5 to 8.0. Ndiba and Axe (2010) studied Cd leaching as a function of pH from treated and untreated sediments, which showed a similar trend to Figure 5.6. Moreover, in the study of Zaman et al. (2009), adsorption of Cd on manganese dioxide as a function of pH also showed a similar trend. The dominant form of Cd (II) is Cd$^{2+}$ from pH 3 to 8.6, and CdOH$^+$ from pH 8.6 to 9 (Schecher and McAvoy, 1998) (Appendix A). It is important to note that while the HFO surface is a dominant sorbent in the
5.7 Desorption (a) and adsorption (b) edges for barium and cadmium in paint waste from Bridge 10-5b and Bridge 11-2a are shown after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO$_3$, and 25 ± 1.2 °C.
paint waste, Cd is likely bound in other complexes given the nature of the paint and the form in which Cd is initially added. Dong et al. (2002) suggested that organic material associated with nature metal oxide exhibits a high affinity for both Cd and Pb.

Desorption of Cr showed the same trend as pH increased from 3 to 10 for both Bridges 10-5 and Bridge 11-2 (Figure 5.8), with adsorption peaking at pH 5. Dzombak and Morel (1989) showed adsorption of Cr (VI) as chromate (CrO$_4^{2-}$) decreases as pH increases from 5 to 9; however, adsorption of Cr (III) increases as pH increases from 3 to 6. Therefore, results in this study are more consistent with Cr(III) (Figure 5.8b). The dominant Cr(III) species is Cr$^{3+}$ from pH 3 to 3.8, Cr(OH)$^{2+}$ from pH 3.8 to 6, Cr(OH)$_2^+$ from pH 6 to 8.6, Cr(OH)$_3$ from pH 8.6 to 9.4, and CrO$_2^-$ from pH 9.4 to 10 (Appendix A) (Schecher and McAvoy, 1998).

Similarly, desorption of Pb decreased as pH increased from 3 to 10 (Figure 5.8). The adsorption edge for Pb is consistent with other studies (Dzombak and Morel, 1989). Based on the thermodynamic modeling (Appendix A), the dominant form of aqueous lead is Pb$^{2+}$ from pH 3 to 7.5, PbOH$^+$ from pH 7.5 to 9 (Schecher and McAvoy, 1998). Adsorption of Pb on natural sediments (Gao et al., 2003) showed a very similar trend to this study (Figure 5.8b). Pb adsorption to HFO shows greater pH dependence than other RCRA metals, especially over acidic conditions (Figure 5.8b). This observation indicates that although HFO exhibits a high affinity for Pb and a significant adsorption capacity, Pb dissolution in paint may further increase concentrations.
Figure 5.8  Desorption and adsorption edges for chromium and lead in paint waste from Bridge 10-5b and Bridge 11-2a are shown after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C.
Figure 5.9  Desorption (a) and adsorption (b) edges for zinc in paint waste from Bridge 10-5b and Bridge 11-2a are shown after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C.
Adsorption of Zn increased as pH increased from 3 to 10 (Figure 5.9 b). Dzombak and Morel (1989) reviewed similar results with adsorption increasing as pH increased from 4 to 8 (Figure 5.9). The dominant form of aqueous Zn (II) is Zn$^{2+}$ from pH 3 to 8.5, and ZnCO$_3$ from pH 8.5 to 10 (Schecher and McAvoy, 1998) (Appendix A). Ndiba and Axe (2010) and Kendell (2003) also showed similar results with Zn adsorption edges.

In this research, given the dominant sorption process is consistent with adsorption to HFO, isotherms were conducted to further evaluate surface interactions.

5.4 Desorption Isotherm Study

Isotherm models are important for characterizing trace metal behavior. The affinity and adsorption capacity of the adsorbent can be addressed in isotherm parameters. Thus, adsorption-desorption isotherm studies were carried out.

Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1926) isotherms are frequently applied to model the adsorption process of aqueous contaminants onto iron oxide surfaces. These models are useful in characterizing adsorption capacity and efficiency (Mohan and Pittan, 2007). The Langmuir isotherm is applied in this study because the HFO adsorbent is dominant with respect to concentration in the paint waste and because the interactions observed in desorption edge experiments are consistent with HFO edges. The ability to use one type of site to describe adsorption is evaluated in this study (Chávez 2010; Pandey 2010). Langmuir parameters adsorption capacity ($q_m$) and Langmuir constant ($K_L$) were determined from modeling.

The theoretical adsorption capacity of HFO for trace metals can be calculated by an
adsorption isotherm (Payne et al., 2005). The Langmuir isotherm model can be linearized and applied as \( \frac{C_e}{q_e} \) as a function of the equilibrium aqueous metal concentration \( C_e \) as mg/L (Ghaemi, 2011). The main advantage of Langmuir modeling is to observe the adsorption capacity \( q_m \) and Langmuir constant \( K_L \) based on linear regression. The Langmuir equation could be written as the Linear form as:

\[
\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{C_e}{q_m}
\]

Equation (2)

Where

- \( q_e \) (mg/ kg paint) sorbed concentration at equilibrium.
- \( q_m \) (mg/ kg) adsorption capacity (maximum mg adsorbed trace metal/ paint).
- \( K_L \) (L/ mg) Langmuir adsorption constant related to adsorption energy.

The fit of the Langmuir isotherm is reflected in the coefficient of determination, \( R^2 \), of the Langmuir linear functions (Table 5.1). Based on the isotherm study parameters (Table 5.1), \( R^2 \) values of fourteen Langmuir isotherms out of fifteen are greater than 0.75, which suggests the model could capture the adsorption process applying one average site. The parameters \( q_m \) and \( K_L \) are significant factors in evaluating the effectiveness of a sorbent. As demonstrated by the Langmuir isotherm studies and best-fit parameters at pH 4, 5, and 6 (Table 5.1), the trace metal adsorption capacity of HFO is 1.2108
### Table 5.1  Isotherm parameters for the Langmuir model

<table>
<thead>
<tr>
<th>pH</th>
<th>( q_m ) (mg/kg)</th>
<th>( q_m ) (mole/kg)</th>
<th>( K_L ) (L/mg)</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>4</td>
<td>3\times10^3</td>
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<tr>
<td>Ba</td>
<td>4</td>
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<td>7\times10^{-2}</td>
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<tr>
<td></td>
<td>5</td>
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<tr>
<td>Cd</td>
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<td>5\times10^4</td>
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<td>4\times10^{-2}</td>
</tr>
</tbody>
</table>

| Total | 4 | 1.2108 |
|       | 5 | 1.5708 |
|       | 6 | 1.3709 |
mole/kg paint at pH 4, 1.5708 mole/kg paint at pH 5, and 1.3709 mole/kg paint at pH 6. The Langmuir constant ($K_L$) represents the degree of sorption affinity of the adsorbed ions to the adsorbent. As the isotherm study results suggest, the parameters varied for trace metals. Moreover, changes in these isotherm parameters as a function of pH were observed.

The best-fit model is shown in the isotherm figures as well. In addition, the confidence interval (CI) was also plotted along with the best-fit model based on confidence level of 95% (Table 5.1). The errors in the Langmuir isotherm parameters were determined using least squares analysis (Ross, 2009).

For adsorption isotherm studies of arsenic, the lower $R^2$ (0.5617) observed in this study (Figure 5.10a) is likely due to the heterogeneous nature of the paint waste. The relative degree of the sorption affinity ($K_L$) at pH 4 was 2,000 L/mg, which was much greater than that of other trace metals (Table 5.1. Moreover, desorption of arsenic was less than the detection limit of 0.001 ppm. This result suggests that iron oxide has a significant affinity for arsenic. Interestingly, the adsorption capacity of HFO in this study was 3 mg/g paint at pH 4, while a capacity of 41.49 mg/g was observed for a polyacrylamide hybrid material at a pH less than 5 (Mandal et al., 2013). This result indicates that HFO has lower adsorption capacity than this modified sorbent.

The Langmuir adsorption isotherm results for Ba (Figure 5.11) reveal strong fits for the three pH conditions. Similar results were also obtained in other isotherm studies of Mishra and Tiwary (1999), Kurbatov (1946), Ghaemi et al. (2011).
Figure 5.10  Langmuir adsorption isotherm for arsenic (a) and data along with model with 95% confidence intervals (CI) (b) at pH 4 after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Figure 5.11  Langmuir adsorption isotherm for barium (a) and data long with model with 95% confidence intervals (CI) at pH 4 (b), 5 (c) and 6 (d) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Ghaemi et al. (2011) found that Ba had an adsorption capacity of 3.96 mg/g dolomite powder. The increased adsorption capacity of Ba for HFO (10 mg/g paint) suggests that HFO is a more effective adsorbent for barium. $K_L$ values for Ba increased from 0.9 to 2 L/mg as pH increased from 4 to 6, indicating increased adsorption as pH increases. However, relatively, this alkaline earth metal has a smaller affinity for HFO compared to the trace metals studied 9 (Table 5.1).

For Cd (Figure 5.12), the Langmuir isotherm resulted in strong coefficients of determination (Table 5.1). Similar Cd isotherms were obtained in the study of Ajaelu et al. (2011) and Nassar (2012). The adsorption capacity of HFO demonstrated that cadmium ranged from 90 to 100 mg/ kg paint (Table 5.1). Interestingly, the Langmuir constant did not change from pH 4 to 5 (500 L/ mg), but changes drastically at pH 6 (20,000 L/ mg). This observation suggests that neutral and alkaline aqueous conditions will greatly improve the adsorption efficiency of HFO to Cd. In the study of Nassar (2012), cadmium had an adsorption capacity of 0.019 mg/ kg and affinity of 21,520 L/ mg to iron oxide nano adsorbents at pH 5.5 and 298 K.

Adsorption isotherms for Cr are consistent with others (e.g., Ai et al., 2008; Ajouyed et al., 2010; Bhaumik et al., 2011; Wei et al., 2009; Zhao et al., 2010). Detectable aqueous concentrations of Cr were observed for pH conditions 4 and 5. The Langmuir isotherms revealed good fits for pH 5 ($R^2 0.955$) and pH 4 ($R^2 0.9465$) (Figure 5.13) (Table 5.1). Similar fits were found in the isotherm
Figure 5.12  Langmuir adsorption isotherm for cadmium (a) and data long with model with 95\% confidence intervals (CI) at pH 4 (b), 5 (c) and 6 (d) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Figure 5.13  Langmuir adsorption isotherm for chromium and data long with model with 95% confidence intervals (CI) at pH 4 (a) (b) and 5 (c) (d) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
study of Bhaumik et al. (2011). The Langmuir parameters (Table 5.1), revealed that affinity ($K_L$) increased from 10 to 200 L/mg as pH increased from 4 to 5. Moreover, the adsorption capacity for Cr on HFO increased from 5 to 10 mg/g paint as pH increased from 4 to 5. In the isotherm study of Bhaumik et al. (2011), adsorption of aqueous chromium on the Fe$_3$O$_4$ magnetic nanocomposite demonstrated an adsorption capacity of 169.49 mg/g and chromium affinity of 0.33 L/mg at 25°C. This result indicates that HFO has a much significant affinity for Cr.

The Langmuir isotherm for Pb (Figure 5.14 and 5.15) showed strong coefficients of determination as a function of pH (Table 5.1). Similar adsorption isotherm trends for Pb were obtained in the studies of Fan et al. (2005), Dong et al. (2002), and Boonfueng et al. (2006) for HFO and similar trace metal adsorbents of metal oxide. Nevertheless, Pb showed lower affinities for HFO (0.2 L/mg at pH 4 and 0.15 L/mg at pH 5) compared to the other metals studied, although $K_L$ increased to 2 L/mg at pH 6. On the other hand, Pb exhibited the greatest adsorption capacity of 100 mg/g paint among the studied metals; moreover, the adsorption capacity of Pb is constant between pH 4 and 6. In the isotherm study conducted by Ejikeme et al. (2011), Pb was observed with an adsorption capacity of 18.52 mg/g and affinity of 0.044 L/mg to a modified activated carbon.

The Langmuir adsorption isotherm for Zn (Figure 5.16) revealed, again, strong coefficients of determination for the pH range of 4 to 6 (Table 5.1).
Figure 5.14  Langmuir adsorption isotherm for lead at pH 4 (a), 5 (b) and 6 (c) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Figure 5.15  Langmuir adsorption isotherm data and model for lead along with 95% confidence intervals (CI) at pH 4 (a), 5 (b) and 6 (c) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO$_3$, and 25 ± 1.2 °C. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Figure 5.16  Langmuir adsorption isotherm for zinc (a) and data long with model with 95% confidence intervals (CI) at pH 4 (b), 5 (c) and 6 (d) after 24 hours of equilibration with 50 g/L paint waste, 0.01 M NaNO₃, and 25 ± 1.2 ºC. Samples were collected from Bridges 10-1c, 10-2e, 10-3e, 10-4c, 10-5b, 10-6a, 10-7a, and 10-8 d.
Dada et al. (2012) showed an $R^2$ of 0.99 for Zn(II) adsorption to Zn at pH 6.5. The Langmuir isotherm is an effective model for Zn. Boonfueng et al. (2006) had a similar adsorption isotherm trend of Zn on Mn oxide coated adsorbents. However, similar to Pb, Zn showed the lowest Langmuir constant ($K_L$) for HFO among the studied metals (0.01 L/mg at pH 4 and 5, while 0.04 L/mg at pH 6). The affinity for HFO did not change at lower pH conditions (pH less than 5). Moreover, the adsorption capacity for Zn was 30 mg/g paint at pH 4, while 50 mg/g paint at pH 5 and 6 (Table 5.1). This observation indicates that HFO has high adsorption potential for Zn, especially as pH increases. In the isotherm study of Dada et al. (2012), adsorption of Zn (II) revealed 101.01 mg/g capacity and 0.065 L/mg affinity for a phosphoric acid modified organic sorbent at pH 6.5, which is similar to the Langmuir parameters found in this study. In conclusion, HFO has a significant adsorption capacity and affinity for trace metal ions.
CHAPTER 6
CONCLUSIONS

In this research, paint waste samples with steel grit were studied. Desorption edge experiments and isotherms were conducted with an equilibration period of 24 hours. The presence of steel grit from bridge rehabilitation work resulted in iron oxide coatings. These coatings may impart an environmental advantage in reducing contaminant mobility. The desorption experiments reflect the potential for trace metal mobility. Adsorption-desorption is a short-term process that was studied over 24 hours in this research.

The paint waste samples from Region 10 and Region 11 showed elevated trace metal concentrations based on FP-XRF analysis with peak concentrations of As 19.19 mg/g paint, Ba 18.68 mg/g paint, Cd 2.55 mg/g paint, Cr 11.82 mg/g paint, Pb 152.44 mg/g paint, Se 3.25 mg/g paint, Ag 2.09 mg/g paint, and Zn 60.39 mg/g paint. Nevertheless, the greatest aqueous concentrations observed in desorption edge studies included As 0.022 mg/L, Ba 0.965 mg/L, Cd 0.048 mg/L, Cr 4.116 mg/L, Pb 325.136 mg/L, Zn 375.3 mg/L, Se less than 0.01 mg/L (limit of detection), and Ag less than 0.1 mg/L (limit of detection). However, the EPA Toxicity Characteristic Levels (TCL) for trace metals are As 5 mg/L, Ba 100 mg/L, Cd 1 mg/L, Cr 5 mg/L, Pb 5 mg/L, Se 1 mg/L, and Ag 5 mg/L, while for Zn 5 mg/L is the EPA Secondary Drinking Water Standard, Maximum Contamination Level Goal (MCLG). Desorption edges revealed trace metals were less than the U.S. EPA TCL under all pH conditions studied with the exception of Pb which was greater than TCL. Steel grit coated with HFO exhibits significant affinity for the trace metals studied. The research further demonstrated that the dominant sorbent in the system was the HFO coating formed on the
steel grit surface. The Langmuir isotherm model was found to successfully describe the isotherm data. Furthermore, based on the Langmuir isotherm parameters, the adsorption capacity for Ba, Cd, and Pb is relatively constant over the pH range of 4 to 6; however, for Cr and Zn, adsorption capacity increased as pH increased. Metal affinities for HFO increased as pH increased as well. Additionally, HFO showed a greater affinity for Cd and As as compared to other metals. Overall, HFO demonstrated a significant adsorption capacity and affinity for the studied trace metals.
Appendix A

MINEQL+4.5 Trace Metal Speciation Results

For the sake of explaining desorption behavior of trace metal, speciation by MINEQL+ software is necessary to verify the main existence form of metal ions under different oxidizing state and pH. The dominant forms of As (III), As (V), Ba (II), Cd (II), Cr (III), Cr (VI), Pb (II) and Zn (II) are listed in Table A.1.

Table A.1 Speciation of studied trace metal ions from pH=3 to 10

<table>
<thead>
<tr>
<th>Metal</th>
<th>Dominant speciation</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (III)</td>
<td>H$_3$AsO$_3$ (pH=3 to 9.3), H$_2$AsO$_3^-$ (pH=9.3 to 10)</td>
</tr>
<tr>
<td>Ba (II)</td>
<td>Ba$^{2+}$ (pH=3 to 9.5), BaCO$_3$ (pH=9.5 to 10)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>Cd$^{2+}$ (pH=3 to 8.6), CdOH$^+$ (pH=8.6 to 9)</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>Cr$^{3+}$ (pH=3 to 3.8), Cr(OH)$^{2+}$ (pH=3.8 to 6), Cr(OH)$_2^-$ (pH=6 to 9), Cr(OH)$_3^-$ (pH=8.6 to 9.4), CrO$_2^-$ (pH=9.4 to 10)</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>Pb$^{2+}$ (pH=3 to 7.5), PbOH$^+$ (pH=7.5 to 9)</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>Zn$^{2+}$ (pH=3 to 8.5), ZnCO$_3$ (pH=8.5 to 10)</td>
</tr>
</tbody>
</table>
Figure A.1  Speciation of As (III) in paint samples with $2.93 \times 10^{-7}$ M total arsenic, 0.01 M NaNO$_3$, open to atmosphere, and under 25°C.

Figure A.2  Speciation of Ba (II) in paint samples with $7.04 \times 10^{-6}$M total barium, 0.01 M NaNO$_3$, open to atmosphere, and under 25°C.
Figure A.3  Speciation of Cd (II) in paint samples with $4.29 \times 10^{-7}$ M total cadmium, 0.01 M NaNO$_3$, open to atmosphere, and 25°C.

Figure A.4  Speciation of Cr (III) in paint samples with $7.92 \times 10^{-5}$ M total chromium, 0.01 M NaNO$_3$, open to atmosphere, and 25°C.
A.5 Speciation of Pb (II) in paint samples with $1.57 \times 10^{-3}$ M total lead, 0.01 M NaNO$_3$, open to atmosphere, and 25°C.

Figure A.6 Speciation of Zn (II) in paint samples with $5.77 \times 10^{-3}$ M total zinc, 0.01 M NaNO$_3$, open to atmosphere, and 25°C.
Appendix B

Error Report

Error 1: Experiment error-quantitative error
Several steps especially the quantitative steps of the experiment bring error to the final analyzing results. Based on log book of the experiment, errors of different steps in the experiment are:

1. Error from NaNO3 weighing: 0.07%.
2. Error from paint waste weighing: 0.02%.
3. Error from volume measurement: 0.05%.
4. Error from pH calibration: 1.32%.

Above all, the quantitative error in this experiment is:

\[0.07\% + 0.02\% + 0.05\% + 1.32\% = 1.46\%\] 

Error 2: Experiment error-operational error
There are 5 duplicates data in the 47 samples of this experiment. The duplicates stand for “operational error” from manual operation process in the experiment.

The operational error from the 5 duplicates is:

\[(20.3\% + 2.67\% + 4.73\% + 9.25\% + 6.91\%)/5 = 8.77\%\]

Error 3: Analytical error
There are 4 replicates data in the 47 samples of this experiment. The replicates stand for “analytical error” from ICP-MS analysis.
The analytical error from the 4 replicates is:

\[(1.04\% + 0.53\% + 8.36\% + 2.79\%)/4 = 3.18\%\].

**General error**: 1.46\% + 8.77\% + 3.18\% = 13.41\%. 
### Appendix C

**Adsorption Unit and Isotherm Model Selection**

1. **Reason for selecting Adsorption (mg)/ paint (kg) as the presenting method rather than Adsorption (mg)/ total Fe (mg).**

For example, isotherm for arsenic:

![Graph showing Adsorption isotherm comparison between Adsorption (mg)/ paint (kg) and Adsorption (mg)/ total Fe (mg) as a function of equilibrium As concentration (mg/L).](image)

**Figure C.1** Adsorption isotherm comparison between Adsorption (mg)/ paint (kg) and Adsorption (mg)/ total Fe (mg) as a function of equilibrium As concentration (mg/L).

Adsorption isotherm of Adsorption (mg)/ total Fe (mg) as a function of equilibrium As
concentration (mg/L) showed an obvious decreasing trend which is opposite with most study results ever found (Figure C.1).

2. **Reason for selecting Langmuir isotherm rather than Freundlich isotherm.**

Both of the two isotherm models are frequently utilized in trace metal adsorption capacity study. However, for our study, Langmuir isotherm is obviously more suitable than Freundlich. For example of arsenic isotherm model comparison: Freundlich isotherm of As in this study showed and decreasing trend, which is also opposite with actual adsorption trend; however, Langmuir isotherm showed an more reasonable model result (Figure C.2 a and b).
Figure C.2 Langmuir (a) and Freundlich (b) isotherm for As adsorption
Appendix D

U.S. EPA Drinking Water Maximum Contamination Level Goal (MCLG) and Toxicity Characteristic Levels (TCL) for Trace Metals

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>MCL and/or MCLG limits (mg/L)</th>
<th>TCL limits (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic (As)</td>
<td>0.01 (MCL)</td>
<td>5</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>2 (MCL &amp; MCLG)</td>
<td>100</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.005 (MCL &amp; MCLG)</td>
<td>1</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.1 (MCL &amp; MCLG)</td>
<td>5</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>0.015 (MCL action level)</td>
<td>5</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>5 (MCLG secondary standard)</td>
<td>———</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.05 (MCL)</td>
<td>1</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>0.1 (MCL secondary standard)</td>
<td>5</td>
</tr>
</tbody>
</table>

(U.S. EPA, September; 2005 and 2009)
REFERENCES


37: 5566-5573.


