A Preliminary Investigation of Treating Metal Pollutants in Water by Slow-Release Hydrogen Peroxide

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A Preliminary Investigation of Treating Metal Pollutants in Water by Slow-Release Hydrogen Peroxide

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ABSTRACT

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A Preliminary Investigation of Treating Metal Pollutants in Water by Slow-Release Hydrogen Peroxide

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Urban runoff can come into contact with a range of pollutants. Metal pollutants can pose an especially significant threat to water quality. This study focused on metals: Cd, Zn, Cu, Pb, Fe and Mn. These metals were chosen after previous studies reported finding them in first flush stormwater collected throughout the Midwestern US. This study tested the effectiveness of SR-HP forms to remove metals from DI water with standard solutions of metals added. Two sizes of SR-HP forms were constructed from sodium percarbonate ($Na_2CO_3 \bullet 1.5H_2O_2$) salts and resin and release rates were quantified. The smaller size released hydrogen peroxide (H_2O_2) at a steady average rate of 0.063 mg/min after 6.2 hours. One proof-of-concept treatment test was conducted utilizing smaller SR-HP forms and DI water containing dissolved metals. During the treatment test, SR-HP released H_2O_2 and alkalinity at the rates ranging from 1.35 mM to 0.135 mM and 0.90 mM to 0.09 mM, respectively. The pH of metal loaded deionized water was raised from 1.74 to 1.87 indicating slight neutralization by added carbonate. This resulted in removal efficacies ranging from 4.17% - 0.65%, 4.52% - +0.76%, 8.59% - 2.92%, 7.44% – 0.29%, 0.52% - +2.24% for Cd, Cu, Fe, Pb and Zn respectively. No consistent treatment was evident for all metals except for iron, which saw a modest removal of 8.6%. This 8.6 removal was most likely due to Fe^{2+} being used during Fenton's reaction.

This result indicates effective removal by SR-HP could be feasible, especially if the pH is more alkaline. Further investigation of SR-HP form performance in a wide range of pHs could be possible.

DEDICATION

To Lily and our parents.

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TABLE OF CONTENTS

LIST OF TABLES

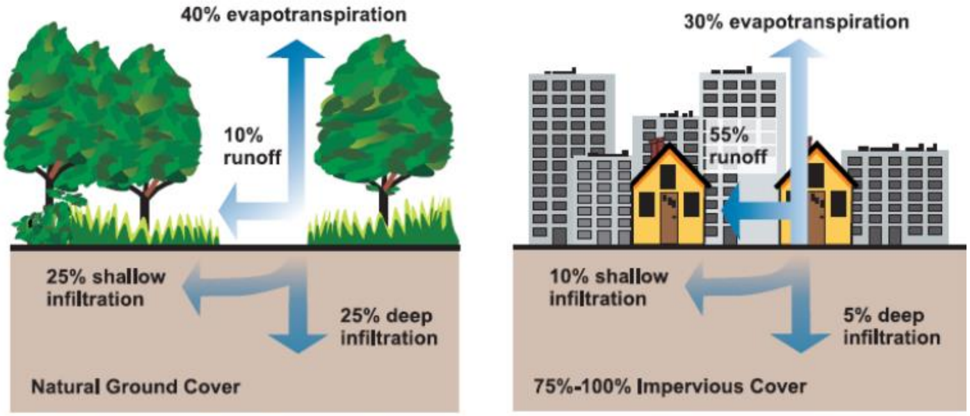
LIST OF FIGURES

CHAPTER 1: INTRODUCTION

Storm water is simply water introduced to the environment during a rain event. In undeveloped areas or areas with natural pervious landscapes, the majority of stormwater will infiltrate the soil and lead to recharge of the underlying aquifer. The remaining percentage of stormwater runoff travels to surface water bodies or returns to the atmosphere by evapotranspiration.

Population growth and the movement of people to city centers have drastically altered this natural system. Urban sprawl and larger, farer reaching infrastructure to support larger urban populations has increased not only the volume of stormwater that comes in contact with pollutants found in urban settings but also increased the concentrations of pollutants found in urban runoff.

In developed or urban areas, a majority of the surface area is covered by impervious materials. These impervious materials make up necessary structures such as roadways, roofs, parking lots, but they impair the ability of water to infiltrate into the ground. “An area the size of one typical city block generates more than five times more runoff than a woodland area of the same size” (USEPA, 2003). In an urban area with 75% - 100% impervious cover (Figure 1-1), only 15% of storm water can infiltrate, leaving 55% to runoff and the rest goes to the atmosphere via evapotranspiration (USEPA, 2003). This 55% is referred to as urban runoff.



Relationship between impervious cover and surface runoff. Impervious cover in a watershed results in increased surface ruunoff. As little as 10 percent impervious cover in a watershed can result in stream degradation.

Figure 1-1: Illustration showing the effect impervious surfaces have on the distribution of rainwater. Increasing impervious surfaces increases urban runoff (USEPA ,2003).

Urban runoff generates contamination problems for the surrounding area because of its ability to transport nonpoint source pollution (NPS). In urban areas, the most common causes of NPS pollution are gasoline spills, vehicle exhaust, factory emissions and toxic organics from asphalt sealcoats (Eyerdom, 2014) . Pollutants can pool and accumulate on impervious surfaces like parking lots or roads during dry periods. The next precipitation flushes the accumulation of pollutants off the impervious areas and they enter the nearest waterway with urban runoff. This process is referred to as the first flush, which refers to the first 50% or less of volume from a storm period (CDOT, 2005).

Urban runoff transports many different kinds of pollutants from impervious surfaces to local water ways. Runoff can become contaminated with sediment, oil and chemicals from vehicles, pesticides, bacteria from pet waste, heavy metals and road salts. All of these pollutants are harmful to water quality and aquatic life (USEPA, 2003).

Previous studies (Eyerdom, 2014), have focused on organic pollutant removal, this present study will focus on heavy metal removal.

1.1 Hypothesis and Objectives

The hypothesis to be tested: SR- HP forms are able to effectively and quickly treat some metals found in urban runoff. Specific objectives are as follows: (i) Characterize slow- release hydrogen peroxide (SR-HP) using column tests (ii) Identify key metal pollutants in urban runoff and their general concentrations (iii) perform 1 proof-of-concept treatment test with SR-HP forms using a long cylinder as the treatment system, standard metal solutions as polluted water.

CHAPTER 2: BACKGROUND

2.1 Slow Release Technologies

Slow release technology was the mode of dispersal for this study. This technology allows the release of a chemical to be staggered and is readily utilized in pharmaceuticals and in pollution remediation. (Eyerdom, 2014). By choosing slow release as a mode of treatment the possibility of over or undertreating an area is eliminated because diffusion is the vehicle for dispersion of treatment. In remediation, a slow release system can release chemicals to water as it comes in contact with the SR form. This allows treatment to occur as water is flowing through the forms by releasing chemicals. The release of chemicals causes a concentration gradient and allows the target chemical to disperse and react with any contaminants present in the system. Ideally, a diffusion based release will occur because the chemical would stay within the SR form until water is present and flows through it (Lee et al., 2008; Eyerdom, 2014).

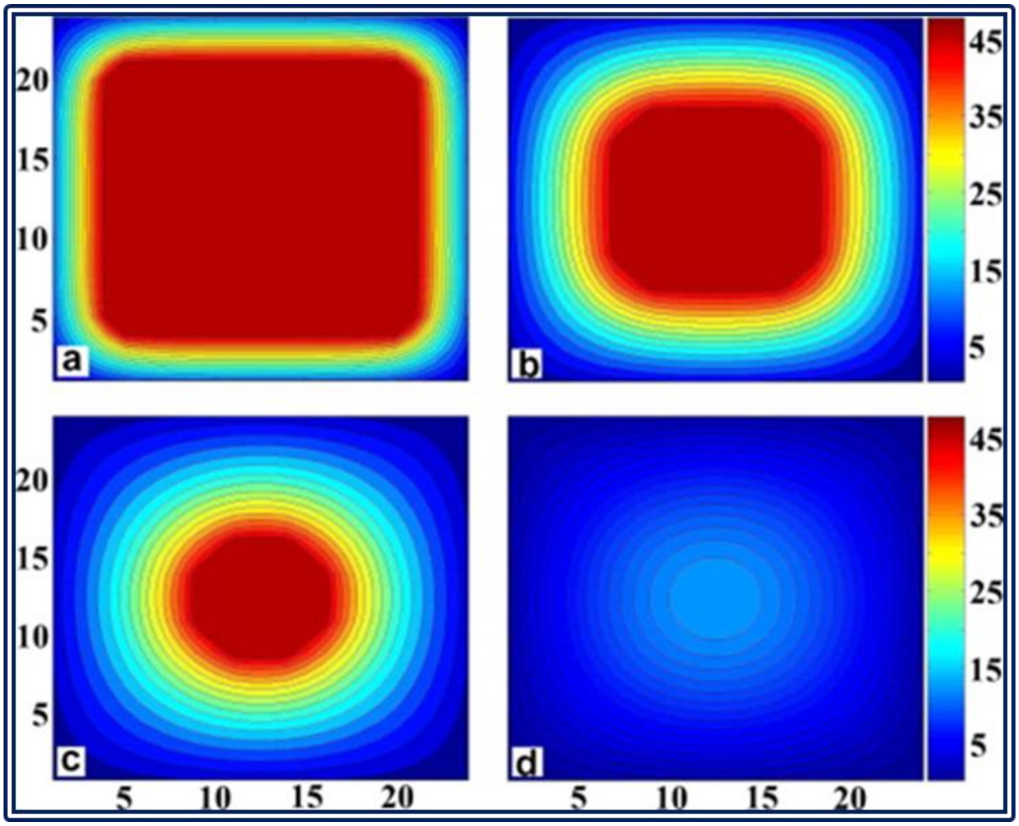
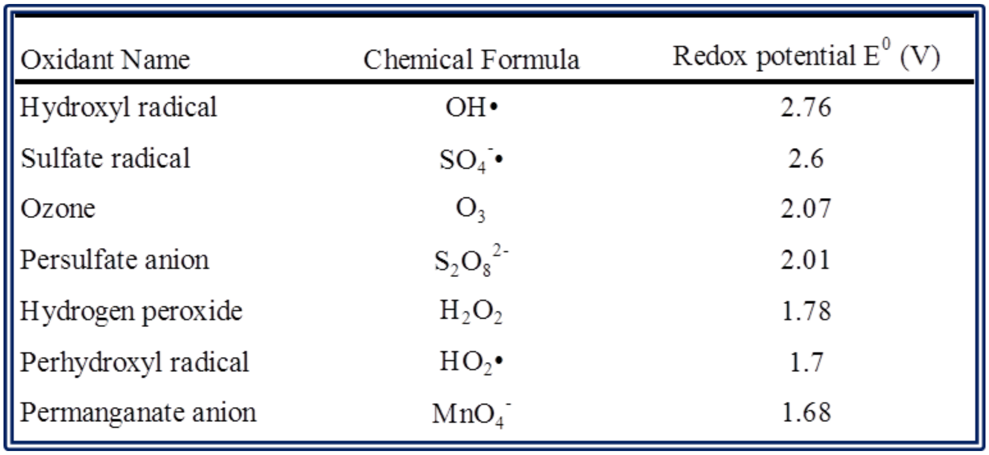


Figure 2-1: Simulated data in cross sectional view of slow release diffusion detailing expected change of concentration as time increases from [a] – [d]. Concentrations in µg mm-3 (Lee et al., 2008;Eyerdom, 2014;Holmes,2016)

2.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are a type of oxidation process often employed in water treatment to oxidize contaminants. AOPs work well for treating contaminants because they produce extremely reactive radical species like SO4-• and HO• (Crittenden et al., 2012 ; Holmes, 2016). Catalysts are used to activate each oxidant which spurs the production of free radicals. These radicals are expressed by the addition of a dot because it indicates the unpaired electron in the outer electron orbital of the species. These electrophilic compounds are driven to fill their outer valence shell and do so by taking electrons from hazardous organic compounds to produce CO_2, H_2O, and minerals (Crittenden et al., 2012). AOPs are also specifically suitable for use as in situ contaminant treatment because they preform without requiring an elevation of pressure or temperature. Instead, production of the radical species can be accomplished through activation by metals or base (Furman et al., 2010).

Some species can be more efficient as oxidants in AOPs than others. A species' usefulness as an oxidant is tied to its redox potential (E^0). The redox potential measures a chemical's affinity for gaining electrons. Strong oxidants have high will have high E^0 values.



Oxidant Name	Chemical Formula	Redox potential E^0 (V)
Hydroxyl radical	$OH\bullet$	2.76
Sulfate radical	$SO_4^{-}\bullet$	2.6
Ozone	O_3	2.07
Persulfate anion	$S_2O_8^{2-}$	2.01
Hydrogen peroxide	H_2O_2	1.78
Perhydroxyl radical	$HO_2\bullet$	1.7
Permanganate anion	MnO_4^{-}	1.68

Figure 2-2: Various oxidants listed (some are radicals) with Redox Potential. This project will utilize 3 (Hydroxyl, Perhydroxyl and Hydrogen Peroxide) (adapted from Huang et al., 2002; Eyerdom, 2014; Tong, 2013).

2.3 Advanced Oxidation Processes in Slow Release Forms

Recent studies have incorporated the use of AOPs into SRS with promising results (Tong, 2013; Eyerdom, 2014; Miller 2015). Hydrogen peroxide is the chosen oxidant for this study due to it being odorless, colorless, easy to obtain and ability to provide high redox potentials.

2.3.1 Success Using AOPs in Slow Release Treatment

Previous studies have had moderate success in treating organic pollutants by integrating AOPs into three different slow release forms. Eyerdom et al., (2014) explored the use forms with three oxidants: hydrogen peroxide, hydroxide and base activated persulfate. Sodium Persulfate ($Na_2S_2O_8$) is very soluble and served as the source of persulfate in the SR-PS forms.

Base activation produces the hydroperoxide species (HO_{2-}) which reacts with a persulfate ion ($S_2O_8^{2-}$). Sodium Persulfate produces a persulfate ion when activated and it has an E^0 of 2.01 V. After this initial reaction a sulfate radical is produced that produces a hydroxyl radical. The hydroxyl radical has a substantial E^0 of 2.76 (V) which makes it an effective oxidant. The production of radicals using base-activation of $S_2O_8^{2-}$ is shown in Eqs (5-10) (Furman et al., 2010).

$$S_2O_8^{2-} + H_2O \xrightarrow{OH^-} SO_5^{2-} + SO_4^{2-} + 2H^+ \quad \text{(Eq. 5)}$$

$$SO_5^{2-} + H_2O \xrightarrow{OH^-} + HO_2^- + SO_4^{2-} + H^+ \quad \text{(Eq. 6)}$$

$$S_2O_8^{2-} + H_2O \xrightarrow{OH^-} HO_2^- + 2SO_4^{2-} + 3H^+ \quad \text{(Eq. 7)}$$

$$S_2O_8^{2-} + HO_2^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ + O_2^{\bullet-} \quad \text{(Eq. 8)}$$

$$2S_2O_8^{2-} + 2H_2O \longrightarrow 3SO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-} + 4H^+ \quad \text{(Eq. 9)}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + OH^\bullet \quad \text{(Eq.10)}$$

To maximize effectiveness and SO_{4-}• formation Eyerdom, (2014) used SR-HP with SR-PS and SR-OH forms simultaneously. After the introduction of a base, hydrogen peroxide decomposes to HO_{2-} illustrated in equation 10 (Payne et al., 1961).

$$H_2O_2 + OH^- \rightarrow H_2O + HO_2^- \quad \text{(Eq. 11)}$$

After incorporating AOPs into three different SR forms Eyerdom et al., (2014) had success in removal of contaminants from both dionized water and stormwater. All of the PAHs tested showed at least an 80% decrease in dionized water. Storm water samples exhibited removal of 40-70% (Figure 2-3).

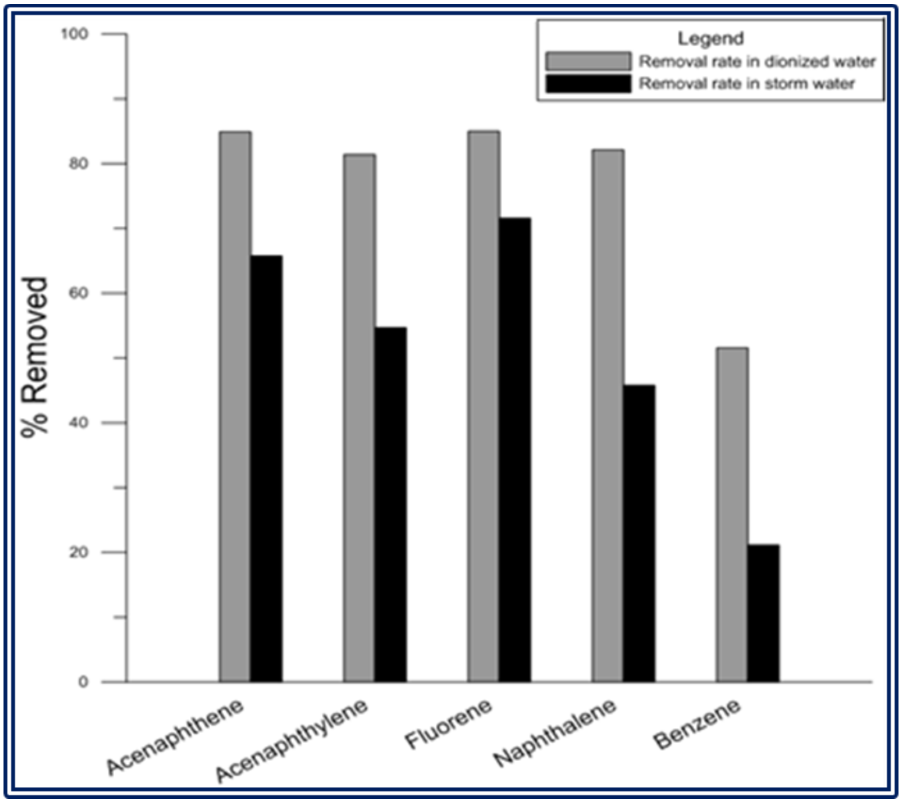


Figure 2-3: Data of removal efficiencies by all 3 forms in the DI water and in storm water compared to the baseline control. Four of the priority PAHs tested and Benzene all had promising results. (Eyerdom. 2014).

2.4 Complications of AOPs in Real Life Environments

Some factors will govern the success of AOPs such as the composition and parameters of the water, the abundance of ions like carbonate and bicarbonate, and the amount of natural organic matter (NOM). These factors can drastically decrease the effectiveness of AOPs by scavenging HO• radicals that would otherwise be used to destroy and treat pollutants in runoff. AOPs utilized in the field usually generate a HO• concentration between 10^{-11} and 10^{-9} mol/L (Gaze et al., 1987; Glaze and Kang 1988 Crittenden et al., 2012). These substances are classified as radical scavengers.

The second order hydroxyl rate constant is an indicator of the speed of an AOP reaction. AOP reactions are usually very quick, with rate constants of 10^{8} to 10^{10} l/mol-s which makes them well suited for treating water with lower residence times, like conditions found in stormwater pipes (Crittenden et al., 2012). Reaction rate constants and half-life values for a sampling of radical scavengers are listed below (Figure 2-4) from Crittenden et al. (2012). Higher rate constants are related to shorter half-lives because it means the reaction is occurring faster.

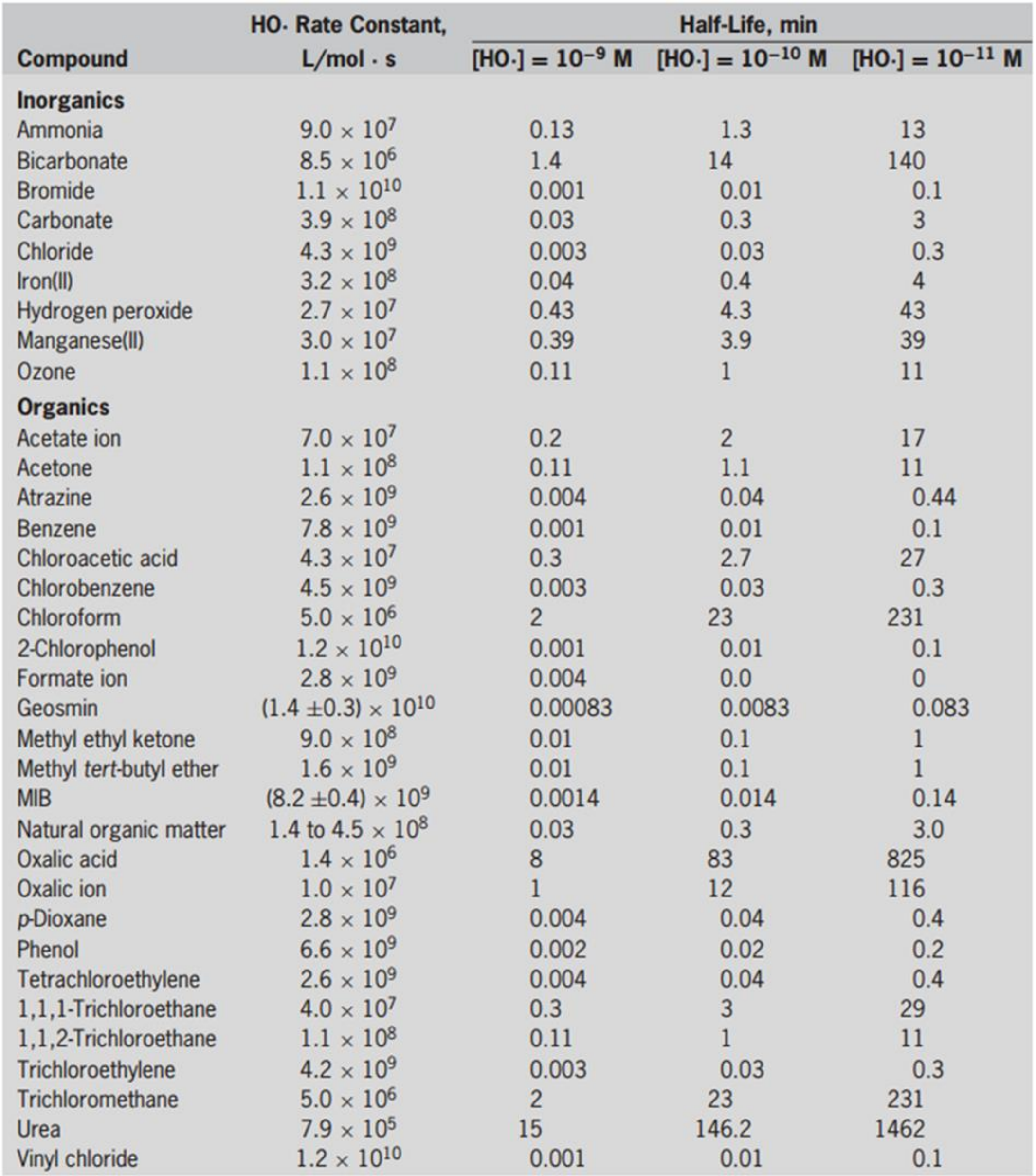
Radical scavengers are capable of halting or quenching the reaction utilized for treatment by AOPs by taking radical hydroxyl, thus interfering with the degradation of the target pollution. Quenching equations can be used to estimate the amount of interference inflicted (Crittenden et al., 2012; Holmes, 2016). NOM has a relatively high rate constant and is present in most waters; its quenching equation is given in Crittenden (2012 originally adapted from Westerhoff et al. 2007) as:

$$Q_R = \frac{k_R C_R}{k_{NOM} C_{DOC} + k_R C_R} \qquad \text{(Eq.12)}$$

Where 1/ Q_R is the reduction in reaction of the target pollutant (R) and an oxidant due to the NOM interference (dimensionless); k_R is the second-order rate constant for degradation of R with the oxidant (M^{-1} s^{-1}); C_R is the concentration of R (M); k_{NOM} is the second-order hydroxyl radical rate constants with NOM; and C_{DOC} is the concentration of NOM (M).

Bicarbonate and carbonate ions also quench the oxidation reaction due to scavenging. Even though their rate constants are much smaller than that of NOM or other ions the extent of interference is still a problem due to carbonate species sheer abundance in water from both geologic and anthropogenic sources. The effect bicarbonate and carbonate ions have on AOPs can be calculated using the below equation. (Crittenden et al, 2012). The term $k_{\mathrm{CO3}}{}^{2-}$ is the second-order hydroxyl radical rate constants for carbonate and $C_{\mathrm{CO3}}{}^{2-}$ is the concentration of carbonate in mol/L (Crittenden et al., 2012). The term $k_{\mathrm{HCO3}}{}^{2-}$ is the second-order hydroxyl radical rate constants for bicarbonate and $C_{\mathrm{HCO3}}{}^{2-}$ is the concentration of bicarbonate in mol/L (Crittenden et al., 2012).

$$Q_R = \frac{k_R C_R}{k_R C_R + k_{HCO_3} - C_{HCO_3} - + k_{{CO_3}^{2-}} C_{{CO_3}^{2-}}} \qquad \text{(Eq. 13)}$$



Compound	HO· Rate Constant, L/mol · s	Half-Life, min $[HO\cdot] = 10^{-9}$ M	$[HO\cdot] = 10^{-10}$ M	$[HO\cdot] = 10^{-11}$ M
Inorganics				
Ammonia	9.0×10^{7}	0.13	1.3	13
Bicarbonate	8.5×10^{6}	1.4	14	140
Bromide	1.1×10^{10}	0.001	0.01	0.1
Carbonate	3.9×10^{8}	0.03	0.3	3
Chloride	4.3×10^{9}	0.003	0.03	0.3
Iron(II)	3.2×10^{8}	0.04	0.4	4
Hydrogen peroxide	2.7×10^{7}	0.43	4.3	43
Manganese(II)	3.0×10^{7}	0.39	3.9	39
Ozone	1.1×10^{8}	0.11	1	11
Organics				
Acetate ion	7.0×10^{7}	0.2	2	17
Acetone	1.1×10^{8}	0.11	1.1	11
Atrazine	2.6×10^{9}	0.004	0.04	0.44
Benzene	7.8×10^{9}	0.001	0.01	0.1
Chloroacetic acid	4.3×10^{7}	0.3	2.7	27
Chlorobenzene	4.5×10^{9}	0.003	0.03	0.3
Chloroform	5.0×10^{6}	2	23	231
2-Chlorophenol	1.2×10^{10}	0.001	0.01	0.1
Formate ion	2.8×10^{9}	0.004	0.0	0
Geosmin	$(1.4 \pm 0.3) \times 10^{10}$	0.00083	0.0083	0.083
Methyl ethyl ketone	9.0×10^{8}	0.01	0.1	1
Methyl *tert*-butyl ether	1.6×10^{9}	0.01	0.1	1
MIB	$(8.2 \pm 0.4) \times 10^{9}$	0.0014	0.014	0.14
Natural organic matter	1.4 to 4.5×10^{8}	0.03	0.3	3.0
Oxalic acid	1.4×10^{6}	8	83	825
Oxalic ion	1.0×10^{7}	1	12	116
p-Dioxane	2.8×10^{9}	0.004	0.04	0.4
Phenol	6.6×10^{9}	0.002	0.02	0.2
Tetrachloroethylene	2.6×10^{9}	0.004	0.04	0.4
1,1,1-Trichloroethane	4.0×10^{7}	0.3	3	29
1,1,2-Trichloroethane	1.1×10^{8}	0.11	1	11
Trichloroethylene	4.2×10^{9}	0.003	0.03	0.3
Trichloromethane	5.0×10^{6}	2	23	231
Urea	7.9×10^{5}	15	146.2	1462
Vinyl chloride	1.2×10^{10}	0.001	0.01	0.1

Figure 2-4: Reaction rate constants and half-life values for a sampling of radical scavengers are listed below in a table from (Crittenden et al., 2012; Holmes, 2016;) original data values from Buxton and Greenstock, (1988), Lal et al., (1988), and Mao et al., (1991)).

2.5 Hydrogen Peroxide and Fenton's Reaction

Three powerful oxidants are produced by using SR-HP forms in the presence of iron, the hydroxyl radical, the perhydroxl radical and hydrogen peroxide (Figure 2-2).

The hydroxyl radical has a very high oxidation potential (2.76 E^0 (v)) , perhydroxyl can also be used as an oxidant (1.7 E^0 (v))and hydrogen peroxide itself has a high oxidation potential (1.78 E^0 (v)) (Figure 2-2). Hydrogen peroxide is released by the SR- HP forms when the sodium carbonate comes in contact with water and begins to dissolve (Eq.14). The radical can be produced by ferrous iron activating hydrogen peroxide in solution (Eyerdom, 2014). This reaction is called Fenton's reagent (Eq.15). Subsequent reactions can occur from other ions in solution. Perhydroxyl is formed by either a reaction between hydrogen peroxide and ferric iron (Eq. 16) or a reaction between hydrogen peroxide and the produced hydroxide radical (Eq. 17) (De Laat et al., 1999; Eyerdom, 2014).

$$Na_2CO_3 \cdot 1.5H_2O_2 \rightarrow Na_2CO_3 + 1.5\ H_2O_2 \qquad \text{(Eq. 14)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \qquad k= 63x10^1\ M^{-1}s^{-1} \qquad \text{(Eq.15)}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \qquad k= 3.1x10^{-3}\ M^{-1}s^{-1} \qquad \text{(Eq. 16)}$$

$$\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad k= 3.3x10^7\ M^{-1}s^{-1} \qquad \text{(Eq. 17)}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe(III)(OH)_2^{2+} \qquad k=1.2x10^6\ M^{-1}s^{-1} \qquad \text{(Eq. 18)}$$

2.6 Metals Targeted

Values found in studies of first flush chemistry were used to select target pollutants for this study. Cadmium, iron, zinc, copper, manganese, and lead were noted as prevalent metal pollutants in urban runoff by Sansalone et al., (1997). These metals were chosen for this study. Some are expected to be removed by oxidation, while others may hydrolyze for removal. Manganese and iron were hypothesized to undergo treatment by oxidation by the SR-HP system and then precipitate out of solution. In order for this to take place, iron and manganese need to undergo oxidation until they reach an oxidation state which allows them to form insoluble complexes (NESC, WVU 1998).

2.7 Metal Oxidation

2.7.1 Manganese Oxidation

Wekesa et al., (2011) proposed the following mechanism involving Mn^{2+}, Mn^{3+} and H_2O_2 under alkaline conditions (Eqs. 19-20). Many Mn^{2+} compounds are found to occur in water like manganese (II) sulfate, and manganese (II) chloride (Wekesa, 2011). The Mn^{3+} oxidation state can occur in compounds like manganese (III) acetate. The form of manganese supplied in this present study is Mn^{2+}. In conditions with a pH below 10, manganese can form colloidal oxo-briged complexes in the presence of H_2O_2 (Eq.20-22). These complexes could involve Mn^{2+} or Mn^{3+} (Wekesa 2011; Ramo 2000; Messaoudi 2011). The following reaction scheme describes the reactions between Mn^{2+} or Mn^{3+} and H_2O_2 (Colodette 1988; Wekesa 2011).

$$Mn^{2+} + H_2O_2 \rightarrow 2Mn^{3+} + 2\ OH^- \qquad \text{(Eq. 19)}$$

$$2Mn^{3+} + H_2O_2 + 2OH^- \rightarrow 4Mn^{3+} + 4OH^- \qquad \text{(Eq. 20)}$$

If a pH of less than 10 is reached Wekesa (2011) proposes the above reactions.

$$Mn^{4+} + H_2O_2 \rightarrow Mn^{3+} + 2H^+ + O_{2-} \qquad \text{(Eq. 21)}$$

$$Mn^{3+} + H_2O_2 \rightarrow Mn^{2+} + 2H^+ + O_{2-} \qquad \text{(Eq. 22)}$$

2.7.2 Iron Oxidation

As illustrated in equations 15 – 18, Fe^{2+} can oxidize in the presence of H_2O_2 and the hydroxyl radical. A simplified version of Fenton's reaction is found in equation 23 (Walling, 1975). The implication of H^+ being neccesary to the breakdown of H_2O_2

indicates the neccesaity of an acidic pH for manimum Fenton's reaction efficency. A pH close to 3 has been suggested as optimal for hydroxyl radical formation (Neyens and Baeyens, 2003; Miller, 2015).

$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$ (Eq. 23)

2.8 Metal Hydrolysis

All other metals present in this study (Cd, Zn, Cu, Pb) were hypothesized to undergo removal by hydrolysis then precipitation. A metal ion, M^{z+} is hydrated by water and is present as the hydrated ion $M(H_2O)^{Z+}$ where z is the charge of the metal ion and n is its coordination number in an aqueous solution (Brown et al., 2016). The water bound to the metal can also hydrolyze, thus producing a proton and a metal hydroxide complex (Eqs.24 -27 from Brown et al., 2016).

$M(H_2O)^{Z+}{}_n \leftrightharpoons MOH(H_2O)^{(z-1)}{}_{n-1} + H +$ (Eq. 24)

The pH where the metal ion can hydrolyze is controlled by the metal's ionic charge (z) and the ionic radius (r) (Brown et al., 2016). Usually the higher the charge and smaller the radius the lower the pH can be and still be conductive to hydrolysis (Brown et al., 2016). As pH increases multiple hydrolysis steps are possible.

$M(H_2O)_n{}^{z+} \leftrightharpoons M(OH)_q (H_2O)^{(z-q)}{}_{(n-q)} + {}_qH^+$ (Eq. 25)

P and q are stoichiometric coefficients of the hydrolysis species produced, Brown et al., (2016) lists all of the coefficients in appendixes for reference.

The general hydrolysis reaction that involves another ligand is given below in Eq.26 by Brown et al., (2016). In Eq.26 M is the metal cation, L is the anionic ligand of charge, n and p, and q and r are the stoichiometric coefficients relating to the metal M, water, and the ligand L, respectively (Brown et al., 2016).

$pM^{z+} + qH_2O + rL^{n-} \leftrightharpoons M_pL_r(OH)_q^{(pz\text{-}rn\text{-}q)} + qH^+$ (Eq. 26)

A simplified hydrolysis reaction is described by Brown et al.,(2016), below in Eq. 27.

$pM^{z+} + qH_2O \leftrightharpoons M_p(OH)_q^{(pz\text{-}q)} + qH^+$ (Eq. 27)

Hydrolysis species for some of the metals in this study, (lead, copper and zinc) are reported in Brown et al., 2016. Lead (II) can form several polymeric species, such as $Pb_3(OH)_4^2+$, $Pb_4(OH)_4\ ^{4+}$, $Pb_3(OH)_5^+$ and $Pb_6(OH)_8^{4+}$. Copper (II) has 2 hydrolysis species $CuOH_{(aq)}$ and $Cu(OH)_2^{-2}$. Zinc was reported as forming monomeric hydrolysis species from $ZnOH^+$ to $Zn(OH)_4^{2-}$(Brown et al., 2016).

2.9 Carbonate Buffering

A carbonate species is produced by the dissolution of sodium percarbonate in the SR-HP forms at a ratio of 1 mole CO_3^{-2} for every 2 moles of Na^+. The production of a carbonate species allows the forms to have some control over the pH. The carbonate could neutralize the acidity content present in the runoff and raise the pH. Due to carbonate's ability to buffer pH previous studies by Miller (2015) have explored SR-AOP's ability to both oxidize metals and neutralize acidity in acid mine drainage with some success.

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

In order to produce SR forms and conduct column tests various materials were needed. Following similar methods found in Eyerdom (2014) and Holmes (2016), reagent grade sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$, 99.5%) was purchased from Fisher Scientific. For use as a binding agent and structural matrix of SR forms, Castin'Craft clear liquid plastic casting resin and its necessary catalyst was obtained. In order to determine the concentration of H_2O_2, pure solution of Cupric sulfate (1%), Neocuproine and ethanol were purchased from Fisher Scientific and Acros Organics. A counter-mounted Milli-Q system produced by Millipore will be used to yield ultrapure deionized water for dilutions and as a general laboratory water source.

For the flow-through treatment test, reagent grade standard solutions of 100 mL for each metal at a concentration at 1000 mg/L were purchased from Fisher Scientific. A carboy with a large capacity of ~40 L was used to store the solution of DI and metals. Twenty-five feet of reinforced PVC braided tubing, manufactured by Watts was purchased from Lowe's Home Improvement. For release test sampling, disposable 3.5 ml cuvettes manufactured by BRAND GMBH + CO were used in the spectrophotometer. For sample collection during the flow-through treatment test, 30 mL wide mouth Nalgene sample bottles purchased from Fisher Scientific were used. Two 30 gallon Rubbermaid trashcans with lids purchased from Wal-Mart were used to serve as a larger receptacle of inflow and outflow during the longer term release rate tests.

3.2 Construction of Slow Release Forms

Twelve SR-HP forms were produced by combining sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) and resin. A 3:1 ratio was found to be most successful in releasing H_2O_2 in Eyerdom (2014) and Miller (2015). Miller (2015) found that a higher oxidant to resin ratio would lead to less density and cause forms to float. Eyerdom (2014) found the 3:1 SR-HP forms to still release oxidant. These findings influenced the ratio of the SR-HP in this study to be 3:1. If 30 g of $2Na2CO_3 \cdot 3H_2O_2$ is combined with 10 g of resin, there is 9 g of releasable hydrogen peroxide available. (Eyerdom 2014) Using this ratio, H_2O_2 will account for 24% of the form's total mass. Resin was chosen over the paraffin wax, because it aids in supporting the matrix and overall durability of the forms (Eyerdom, 2014).

Castin'Craft clear liquid plastic casting resin was mixed with its corresponding Castin'Craft catalyst and $2Na_2CO_3 \cdot 3H_2O_2$ in appropriate masses to reach the necessary 3:1 ratio. The combination was immediately stirred using an electric handheld mixer to reach homogeneity. The mixture was then rapidly poured into a disposable cylindrical mold made from plastic transparency paper, compressed on both ends and left to cool. To help the resin and salt to remain homogenous the forms were rolled and rotated routinely while they cooled. Before they were removed from the molds for testing, the forms were left for several days to harden and fully cure. Weight, height and diameter of the forms made were measured and recorded before being used in release or treatment tests.

3.3 Estimating Release Rate: Column Leaching Tests

Release rates of H_2O_2 for each type of form were estimated using a series of column tests. A form was placed in a glass column (15 cm x 4.8 cm) that was filled with DI water. Masterflex peristaltic tubing pumps were used to control the inflow and outflow of each column. DI water was pumped into the bottom and pumped out of the top of each column to maintain perfect sink condition (Lee and Schwartz, 2008; Eyerdom, 2014). The optimal flow rate to reach and maintain optimal testing conditions was found to be 7 mL/min in a recent study by Eyerdom (2014). The Masterflex was set at a constant rate of 7mL/ min and the flow rate was measured each time a sample was taken by timing how long the outflow took to fill an 8 mL sample vial. Two sizes of forms were used in release rate tests. Each test was performed in pairs and followed a strict sampling schedule utilizing the on-site spectrophotometer. Sampling occurred very often the first few days of testing in order to catch the release rate stabilizing, then sampling became daily.

Figure 3-1: Larger size of form used in release rate test in columns connected to Masterflex set at 7ml/min.

Figure 3-2: Smaller size of HP SR forms used in release rate test. These two were part of a suite of 12. The flow-through test utilizes the other 10.

3.3.1 Sampling Schedule of Column Tests

During the first five hours, samples were collected from each column every 10 minutes. For the following 2 hours, samples were collected every 30 minutes. Next, outflow was sampled every 60 minutes for the next 2 hours,. After the initial 5 hours, 1 sample was collected after 2 more hours and 1 sample 4 hours after that sample. This accounts for 11 hours of initial sampling. After the initial 11 hours another sample was collected after an additional 8 hours, then another one after an additional 12 hours. Following these, all following samples were collected daily.

3.3.2 Determination of H_2O_2 Concentration

The concentration of H_2O_2 was measured using the Copper-DMP method outlined in Baga et al., (1988) and Eyerdom (2014). In this method a Copper (I) – DMP complex is formed by Copper (II) being reduced by hydrogen peroxide in the presence of DMP (2,9 dimethyl-1, 10-phenanthroline). The formation of copper (I)- DMP complex is illustrated below. (Eq 16)

$$2\mathrm{Cu}^{2+} + 2\mathrm{DMP} + \mathrm{H_2O_2} \rightarrow 2\mathrm{Cu(DMP)}^{2+} + \mathrm{O_2} + 2\mathrm{H}^{+} \qquad \text{(Eq.16)}$$

An ethanolic DMP solution was prepared by adding 1g of neocuprione to 100 mL of ethanol. 0.5 mL of 0.1 M copper (II) sulfate and 0.5 mL of the ethanolic DMP solution will be added to 4mL of sample. This solution was vigorously mixed then analyzed by spectrophotometer at a wavelength of 454 nm.

3.4 Characterizing Metal Pollutants in Urban Runoff

Key metal pollutants found in urban runoff and their usual concentrations were identified through literature research of sampled first flush waters and its chemistry. A site in Cincinnati was used by Sansalone et al., (1997) to characterize first flush constituents. Cadmium, iron, zinc, copper, manganese, lead were noted as prevalent metal pollutants and were chosen to use as the metal pollutants for this study.

3.5 Flow-Through Treatment Test

In an effort to simulate the flow condition in storm sewers, an experimental setup using a PVC tubing and a carboy was used (Figure 3-3). A large Nalgene carboy with a spigot and cap was filled with 30 L of a mix containing 29.820 L DI and 30 mL of each 1,000 mg/L standard solution of all 6 target metals from Fisher Scientific. The goal concentration was 1 mg/L for each of the 6 target metals (Cd, Mn, Zn, Fe, Cu, Pb). Below the spigot 25 feet of PVC tubing with an inside diameter of 1-1/2 in was attached with the spigot slightly open releasing water at a rate 0.475 L/min.

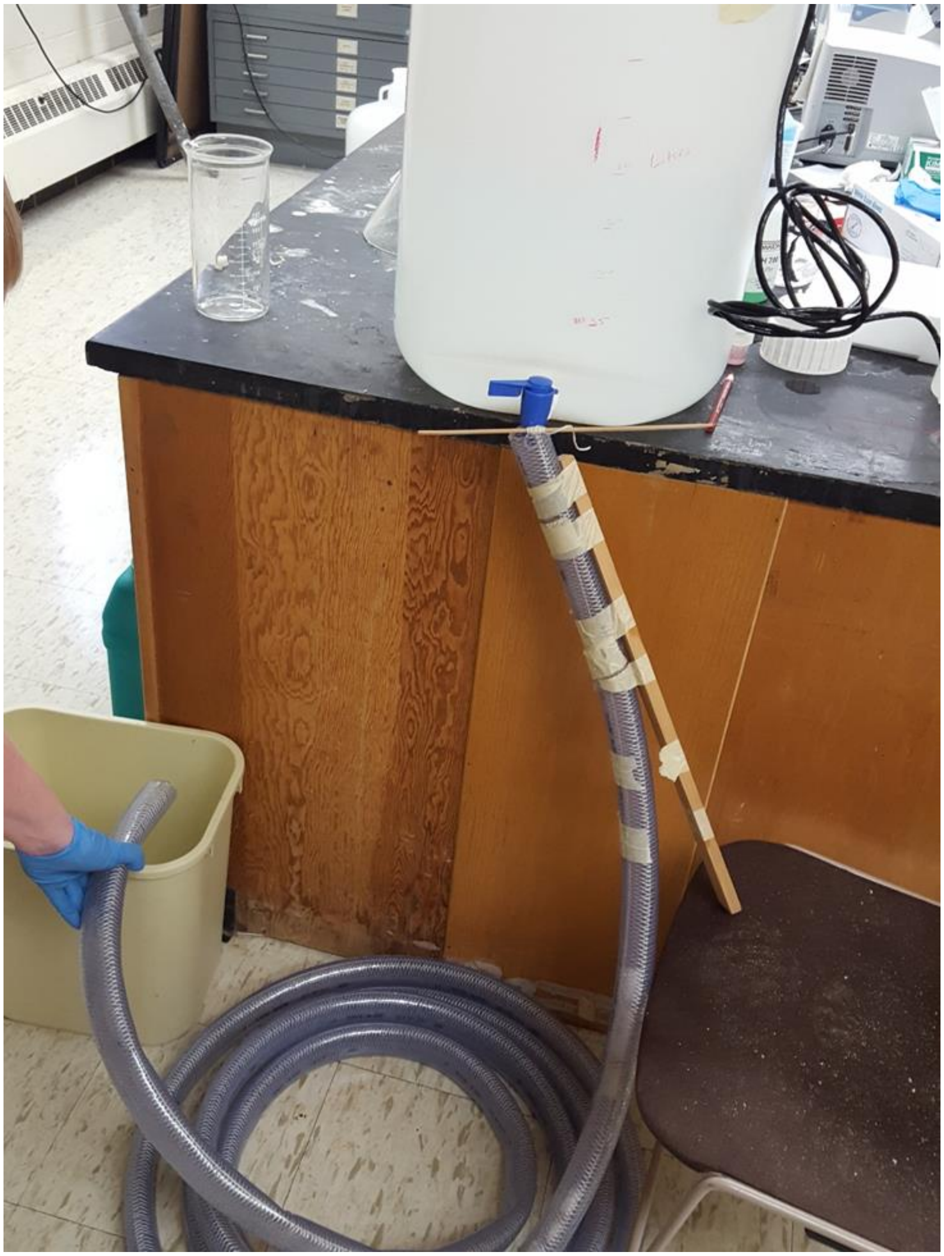


Figure 3-3: Flow through test setup during test with forms in place and tied to wooden skewer. Enough twine was left at the top of the string of ten forms, so that once in place, the forms would sit below the head of the outflow.

Figure 3-4: Flow through test set up. PVC tubing loaded with ten forms.

Three dry to outflow tests and a dye test were conducted to find an optimal flow rate for a residence time of approximately 15 minutes (Figure 3-5). The valve was marked where 0.475 L/min could be achieved and a dye test was conducted. At the marked flow rate, the tubing went from dry to outflow in 16.12 minutes. Once the tube was full and producing outflow, red dye was added to the inflow and the plume of dye did not reach the outflow until 30.04 minutes, demonstrating a residence time of ~14 minutes.

Figure 3-5: Dye test conducted using red food coloring. Dry to outflow test was conducted first. Once outflow began dye was added.

Ten SR- HP forms were tied together using cotton twine then all were attached to a bamboo skewer (Figure 3-6). The forms were submerged in a bucket with ~ 18L) of DI water for 6 hours previous to the start of the treatment test. The string of forms was loaded into the PVC tubing and the bamboo skewer was placed horizontally across the opening of the tubing to keep the forms in place. The string was made long enough so the forms were below the head of the outflow container (Figures 3-4, 3-6, 3-7), thus, allowing maximum contact with the water initially entering and allowing the forms to remain fully covered. The YSI 60 pH meter was calibrated using three standard solutions with pHs of 4, 7 and 10. The meter was then suspended in the carboy allowing continuous and consistent pH readings to be measured during the experiment. The pH meter was also used to measure the pH and temperature of the outflow collected twice at the conclusion of the treatment test. (Figure 3-8).

Figure 3-6: String of the ten SR-HP forms tied together with cotton twine used in flow-through test.

Figure 3-7: The 10 SR-HP forms loaded into the PVC tubing.

A total of 10 samples were collected and sent to the Institute for Sustainable Energy and the Environment, a part of The Russ College of Engineering and Technology at Ohio University, for analysis by ICP-OES. Concentration of the 6 target metals are analyzed as well as sodium content. Sodium content was recorded because it allows the concentration of H_2O_2 and CO_3 released to be calculated using stoichiometry. Three initial samples were taken of the inflow and 7 samples were taken of outflow after being in contact with the 10 SR-HP forms. The first outflow sample was taken when the first outflow reached the end of the tubing (19.22 minutes) and the following 6 outflow samples were taken every 4 minutes. The goal was to sample long enough to collect water that had been in contact with the forms for an entire turnover volume of water, 2 x 19. Samples were collected at19 minutes into test (first outflow), 23 minutes, 27 minutes, 31 minutes, 35 minutes, 39 minutes, and 43 minutes. Each sample was collected in new 30 ml Nalgene bottles and preserved with nitric acid. They stored in a refrigerator for approximately 12 days before they were analyzed for dissolved metals and sodium.

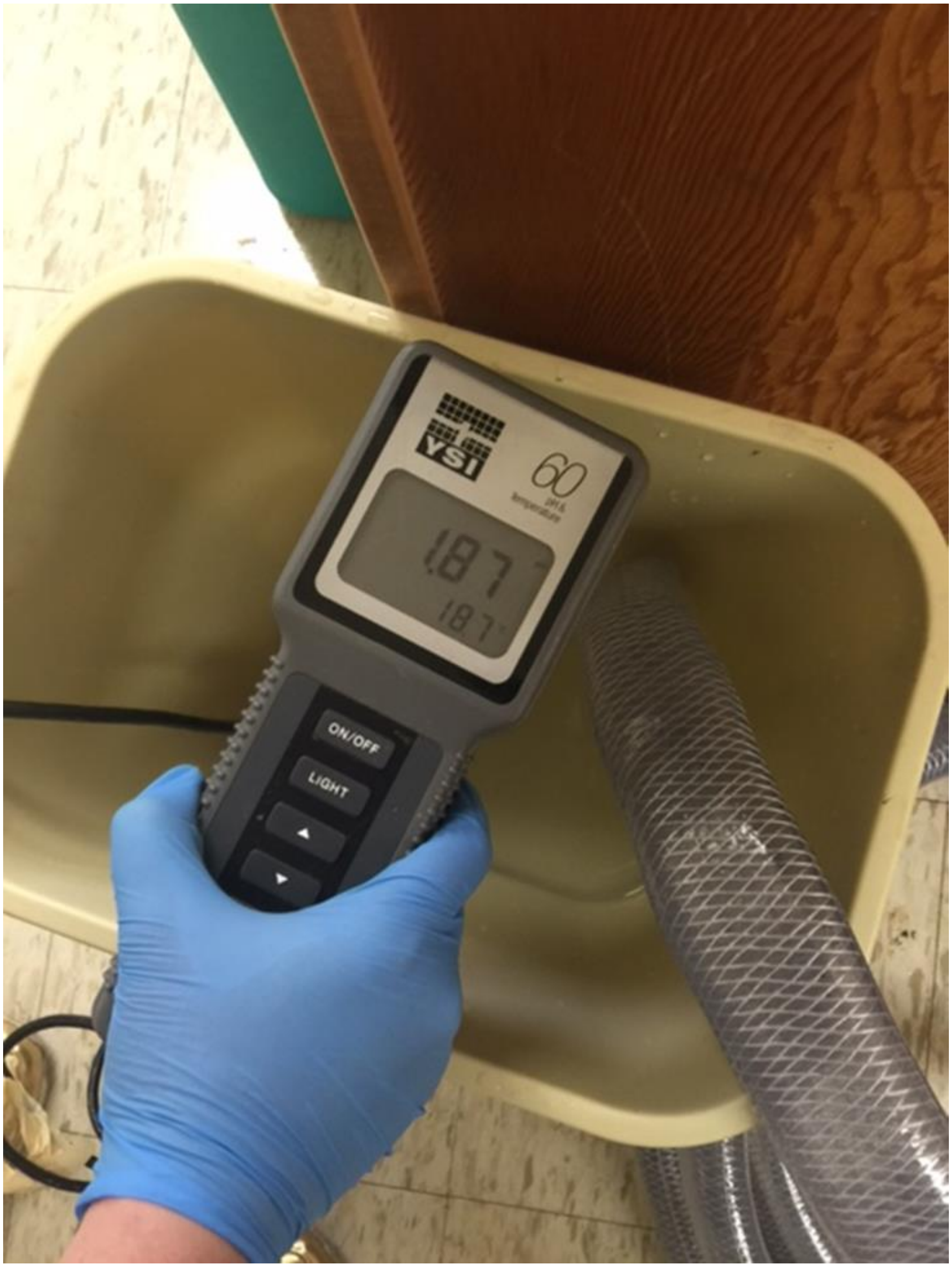
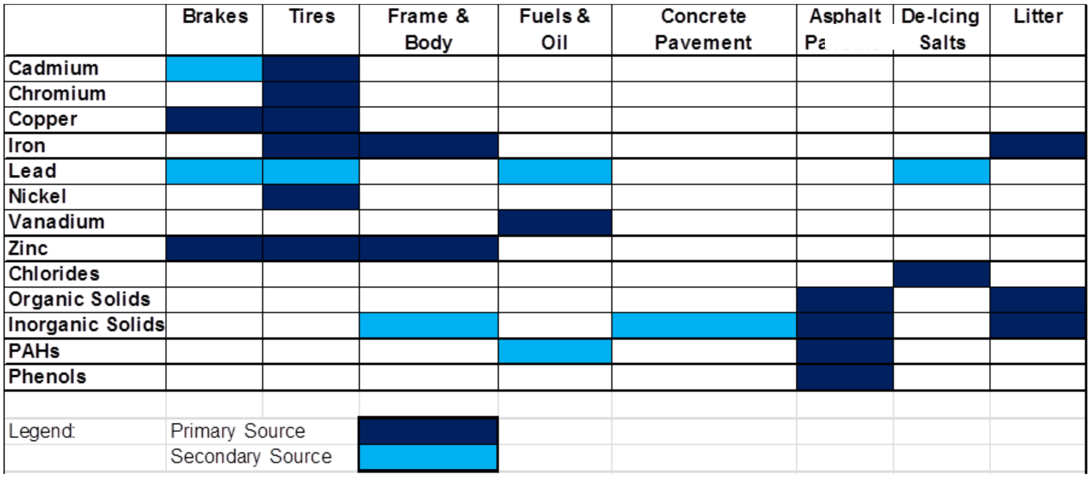


Figure 3-8: The YSI-60 pH meter measuring pH in the outflow receptacle.

CHAPTER 4: RESULTS AND DISCUSSION

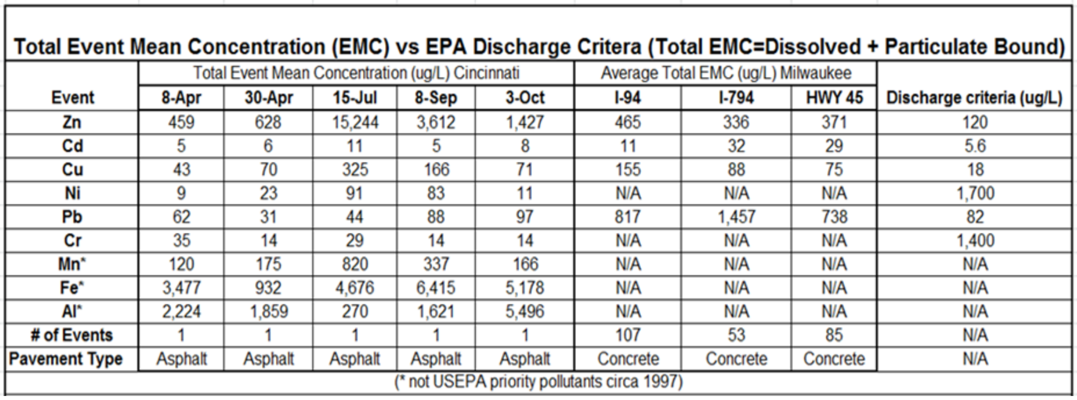
4.1 Key Metal Pollutants Identified in Urban Runoff

Values found in studies of first flush chemistry were used to select target pollutants for this study. Cadmium, iron, zinc, copper, manganese, and lead were noted as prevalent metal pollutants in urban runoff. Sansalone et al., (1997) characterized the pollutant load of first flush runoff in two locations, Cincinnati, Ohio and Milwaukee, Wisconsin. The values published by Sansalone et al., (1997) influenced the selection and concentration of metal pollutants to be tested in this current study.



	Brakes	Tires	Frame & Body	Fuels & Oil	Concrete Pavement	Asphalt Pa	De-Icing Salts	Litter
Cadmium	🟦	■						
Chromium		■						
Copper	■	■						
Iron		■	■					■
Lead	🟦	🟦		🟦			🟦	
Nickel		■						
Vanadium				■				
Zinc	■	■	■					
Chlorides							■	
Organic Solids						■		■
Inorganic Solids			🟦		🟦	■		■
PAHs				🟦		■		
Phenols						■		
Legend:	Primary Source	■						
	Secondary Source	🟦						

Figure 4-1: Pollutants and sources found in urban runoff at both sites reported in Sansalone et al. 1997. Data adapted from Sansalone et al., (1997).

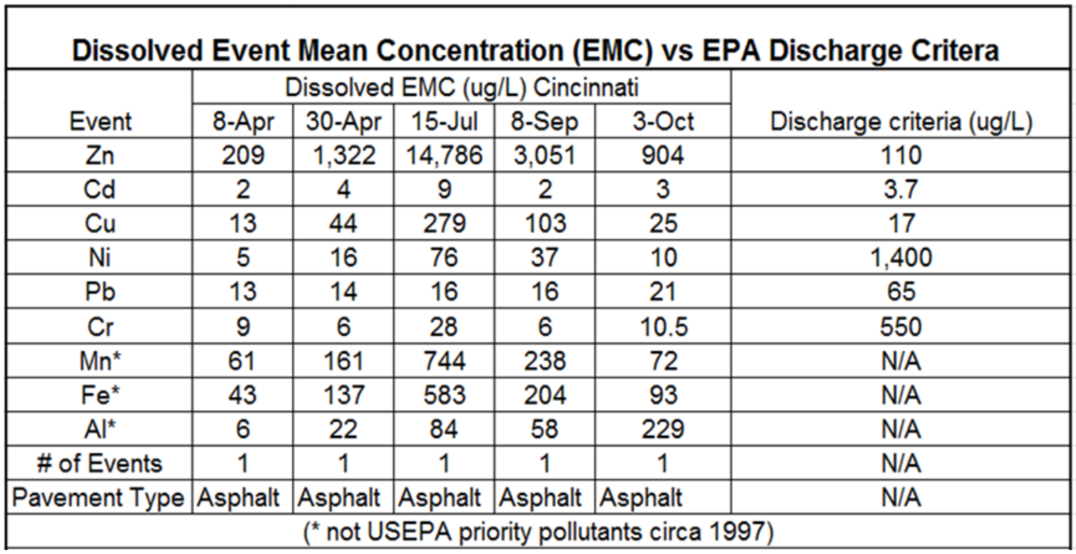


Total Event Mean Concentration (EMC) vs EPA Discharge Critera (Total EMC=Dissolved + Particulate Bound)

	Total Event Mean Concentration (ug/L) Cincinnati					Average Total EMC (ug/L) Milwaukee			
Event	8-Apr	30-Apr	15-Jul	8-Sep	3-Oct	I-94	I-794	HWY 45	Discharge criteria (ug/L)
Zn	459	628	15,244	3,612	1,427	465	336	371	120
Cd	5	6	11	5	8	11	32	29	5.6
Cu	43	70	325	166	71	155	88	75	18
Ni	9	23	91	83	11	N/A	N/A	N/A	1,700
Pb	62	31	44	88	97	817	1,457	738	82
Cr	35	14	29	14	14	N/A	N/A	N/A	1,400
Mn*	120	175	820	337	166	N/A	N/A	N/A	N/A
Fe*	3,477	932	4,676	6,415	5,178	N/A	N/A	N/A	N/A
Al*	2,224	1,859	270	1,621	5,496	N/A	N/A	N/A	N/A
# of Events	1	1	1	1	1	107	53	85	N/A
Pavement Type	Asphalt	Asphalt	Asphalt	Asphalt	Asphalt	Concrete	Concrete	Concrete	N/A

(* not USEPA priority pollutants circa 1997)

Figure 4-2: Data from Sansalone et al., (1997). Displays the total event mean concentration measured in several from outflow collected in Cincinnati and Milwaukee. These sites are compared to the EPA criteria for surface water.



Dissolved Event Mean Concentration (EMC) vs EPA Discharge Critera

	Dissolved EMC (ug/L) Cincinnati					
Event	8-Apr	30-Apr	15-Jul	8-Sep	3-Oct	Discharge criteria (ug/L)
Zn	209	1,322	14,786	3,051	904	110
Cd	2	4	9	2	3	3.7
Cu	13	44	279	103	25	17
Ni	5	16	76	37	10	1,400
Pb	13	14	16	16	21	65
Cr	9	6	28	6	10.5	550
Mn*	61	161	744	238	72	N/A
Fe*	43	137	583	204	93	N/A
Al*	6	22	84	58	229	N/A
# of Events	1	1	1	1	1	N/A
Pavement Type	Asphalt	Asphalt	Asphalt	Asphalt	Asphalt	N/A

(* not USEPA priority pollutants circa 1997)

Figure 4-3: Data adapted from Sansalone et al., (1997). Displays the mean dissolved event mean concentration measured from outflow in Cincinnati and Milwaukee. These sites are compared to the EPA criteria for surface water.

A higher zinc concentration in Milwaukee is attributed to sampling occurring much earlier than at the Cincinnati sites. The Cincinnati sites were sampled in 1995 and Milwaukee sites were collected in the late 1970's and early 1980s before galvanized and corrosion resistant automobile parts act as sources of zinc were as common. Rainfall pH and average pavement residence time were also found to have significant influence on whether the metal was dissolved or particulate bound (Sansalone et al., 1997). The days sampled where rainfall pH was lowest (3.8) and the average pavement residence time was relatively long (5.6 minutes) produced the highest fractions of metal element dissolved (Sansalone et al., 1997).

How the metals appear in runoff depend on a few factors, the pH of surrounding water, the redox potential, and the chemistry of the runoff. The metals found in runoff can occur in particulate bound forms or dissolved forms (Shaver, 2007; BMP Database, 2011). The dissolved or aqueous forms of each metal usually appear as cations and complexes (BMP Database, 2011). Complexes can be formed between the metals and common ligands like carbonate (CO_3^{2-}), chloride (Cl^-), hydroxide (OH^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}) and dissolved organic matter (DOM) (WERF, 2005; BMP Database, 2011).

4.1.1 Cadmium

Smelting of non-ferrous metal ores and leaching from landfills are estimated to be the largest anthropogenic sources of cadmium to water (USGS,1982;2016). The volume of traffic can indicate the level of some metals and pollutants in general in runoff from the area. Cadmium, zinc and lead concentrations in runoff show a direct correlation to how the amount of traffic on surrounding roadways (WDNR, 1997). Other anthropogenic sources of cadmium are the production and use of some paints and plated metals, and some wood products treated for outdoor use (WDNR, 1997). A small portion of cadmium in water is introduced from natural rock weathering processes (BMP Database, 2011).. Cadmium has some adverse health effects if ingested. It can replace zinc in the body and lead to high blood pressure, damage to the kidneys, liver, testicular tissue and anemia (USGS,1982;2016). The BMP Database (2011) lists common forms of cadmium in surface waters as CdDOM, $CdCO_3$, $CdSO_4$ and dissolved as free ion Cd^{2+}. The dominate forms of Cd in urban runoff are complexes with organics and Cd^{2+} with cadmium appearing dominantly in its dissolved state (BMP Database, 2011).

4.1.2 Iron

Iron is introduced to urban runoff by both natural and anthropogenic sources. Naturally, iron is released to surrounding water by sediments and rock weathering. Anthropogenic sources of iron include mining, industrial wastes, and corrosion of metal products (USGS,1982;2016). Iron can cause an unappealing taste in water and cause an orange-brown coloration (USGS,1982;2016). Locally, Appalachia especially has problems with iron in surface waters due to acid mine drainage (AMD). According to the BMP Database (2011), iron is usually present as ferrous (Fe^{2+}) and ferric (Fe^{3+}) oxidation states with Fe^{3+} being most likely to appear in the oxidized conditions present in most urban runoff. Ferric iron has the ability to form stable complexes with many ligands and insoluble complexes then settle out of solution (BMP Database, 2011).

4.1.3 Zinc

Zinc is commonly found in the earth’s crust and is released to the environment from the weathering of rocks (BMP Database, 2011). Mining operations and wastes can release zinc to surrounding water (BMP Database, 2011). Building materials and automobiles were reported to be the largest anthropogenic sources of zinc. ATSDR attributes as much as 95% of zinc in urban runoff to automobile usage (ATSDR, 2005).

The dominant species of zinc in urban runoff are complexes with organics (ZnDOM) and the divalent Zn^{2+} (BMP Database, 2011).

4.1.4 Copper

Copper is introduced to water by mining, mining wastes, mineral leaching and metal plating. The largest anthropogenic source is copper smelting operations and ore processing facilities (ATSDR, 2004). Copper is an essential trace element but could cause damage to the intestines, stomach, liver and kidney (USGS,1982;2016). Aquatic plants and algae can also be harmed by copper. The BMP Database (2011) found copper can appear as complexes in five chemical groups: organics as CuDOM, carbonate as $CuCO_3$, hydroxide as $CuOH^+$, sulfates as $CuSO_4$ and rarely chlorides as CuCl. Complexes with organics and carbon are most often found in urban runoff (BMP Database, 2011).

4.1.5 Manganese

The USEPA does not consider manganese to be a risk to human health. Runoff can come in contact with manganese by natural sources like the weathering of sediments or rocks. Anthropogenic sources like mining and industrial wastes also contribute to the manganese concentration (USGS,1982;2016). While manganese may not be toxic to humans, it can cause aesthetic issues for water quality like poor taste and brown stains on plumbing fixtures (USGS,1982;2016).

4.1.6 Lead

Lead poses one of the greatest threats to water quality. The previous use of leaded gasoline introduced lead to the water and soil, especially in the areas around heavily trafficked roadways (WDOT,2007). Lead also used to be included as an additive in paints. Other anthropogenic sources of lead include fossil fuel combustion, mining and some industrial wastes (WDOT, 2007). Lead can cause significant harm to humans, especially young children. Children exposed to lead face delays in both physical and mental development (USGS,1982;2016). Lead has also been linked to deficiencies in both learning and hearing in children (USGS,1982;2016). Adults can exhibit abnormal red blood chemistry as well as a slight increase in blood pressure. The USGS Water Division also lists lead as a "probable carcinogen". Lead behaves similarly to copper as its common species in runoff are complexes with organics (PbDOM), carbonate ($PbCO_3$) and more rarely hydroxide ($PbOH^+$) (BMP Database 2011). Less commonly in water lead is found as Pb^{2+} (BMP Database, 2011).

4.2 Release Test Results

Two column release tests were conducted using SR-HP forms. The first was a pair of large forms both weighing approximately 150 g before testing and 75 and 95 g after testing. Column B began first, samples were collected August 5th 2016 until August 10th 2016. The form was then dried and stored until testing resumed September 6th with daily collections. Column A began a release test on September 8th. Daily sampling of both columns continued until October 11th but due to ineffective storage practices samples after September 10th (when storage began) revealed no H_2O_2 concertation present. It was assumed H_2O_2 present decayed due to caps on the sample vials not being air-tight. Overall, viable data for column A (Figure 4-4) ranges from September 8th to September 10th, after this daily samples were stored ineffectively due to supply shortages and did not show H_2O_2 concentration. Column B had viable data (Figure 4-5) 5th through 10th of

August 2016. During the initial hours of testing H_2O_2 release varies, in the large B column 0.4mg/min to 1.2 mg/min in the first 33 hours (Figure 4-5).

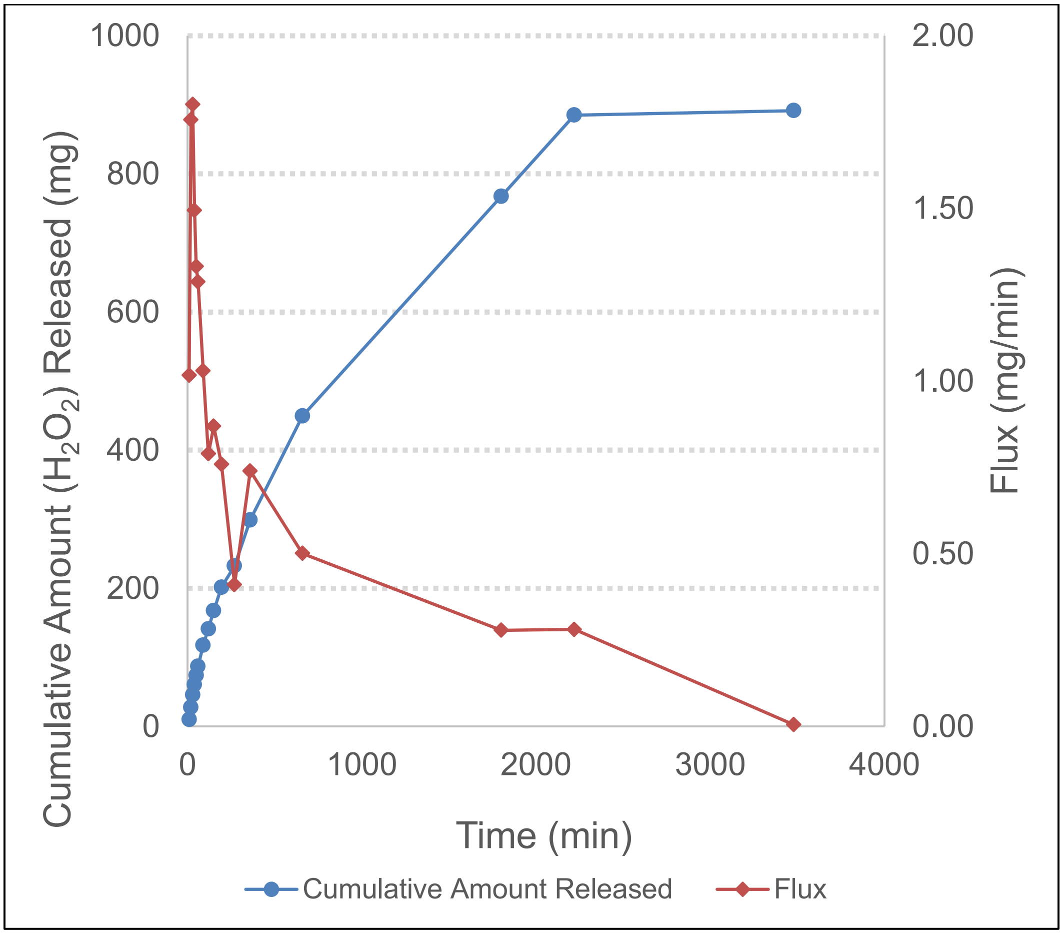


Figure 4-4: Release graph for large column A with data from the 8th ,9th and 10th of September 2016. Cumulative amount of H_2O_2 released and flux of H_2O_2.

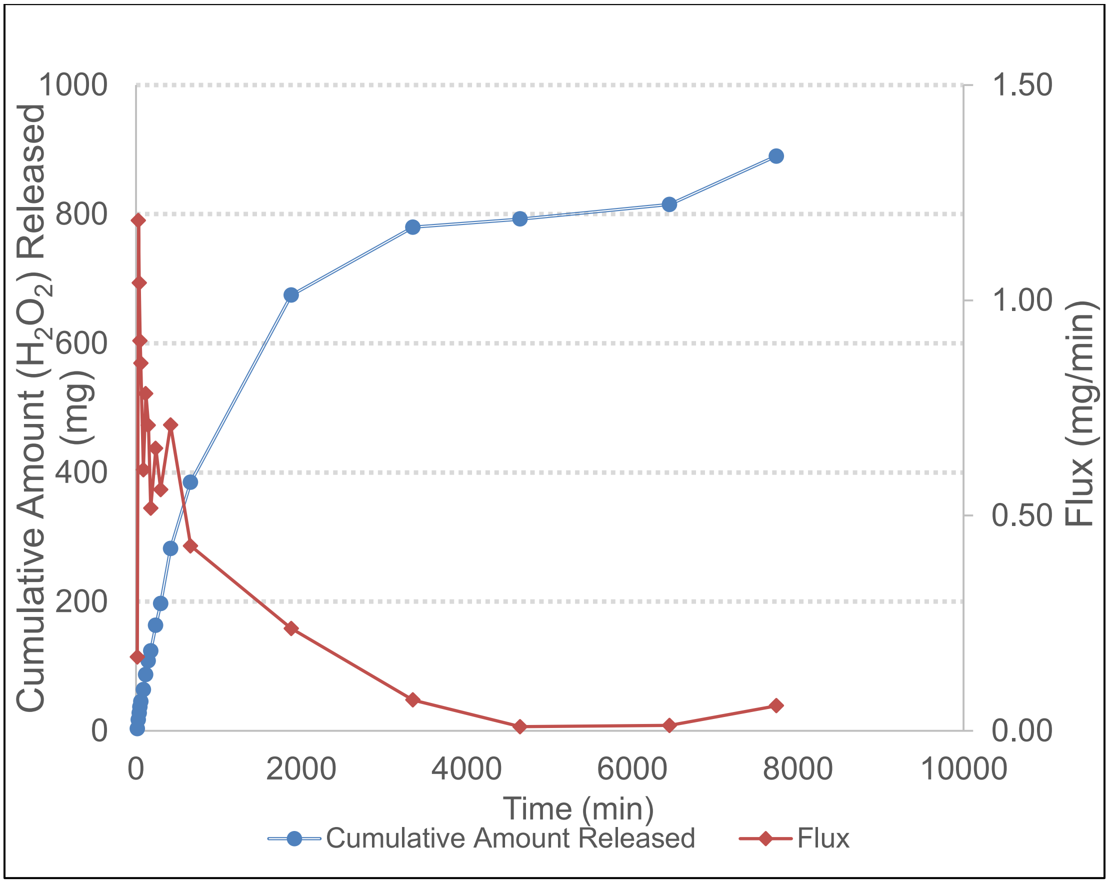


Figure 4-5: Release graph for large column B with data from the 5th through 10th of August 2016. Cumulative amount of H_2O_2 released and flux of H_2O_2.

A generation of 12 much smaller forms weighing ~19.5 g a piece were produced because the larger forms were too large to fit in the tubing for the treatment test. The height of the larger form A was 3 ¾ in and B was 4 in. Both the larger forms had a diameter of 1.5 in and the tubing had an inside diameter of exactly 1.5 in. The smaller size form had a diameter of 3/4th of an inch and a height of 2 ½ in. Two were used for release rate tests.

The smaller forms showed less variance, form A showed oscillations varying from 0.12 to 0.06 mg/min. Previous studies in Eyerdom (2014) also saw variation in the beginning of release testing. This could be attributed to the forms not being completely homogenous. These smaller forms both showed steadier release rates from 372 minutes (6.2 hours) from the beginning of sampling and onward. (Figure 4-6 & 4-7). After 6 hours, small column A averaged a release of 0.063 mg/min for the remainder of the test. By this trend, it was decided to submerge the forms used in the treatment test for 6 hours prior to the beginning of sampling. It was assumed that the other 10 forms manufactured from the same batch of resin/agent mixture should yield similar release kinetics, so after being submerged in DI water for 6 hours these forms would also perform with a steady release rate at 0.063 mg/min.

Small column A was used to calculate average flux in mg/min as well as milligrams per 30 minutes. The average flux of 3 selected points after 6 hours was 0.063 mg/min. If this average flux remained constant for 30 minutes, which was the assumed duration of the treatment test, the amount of H_2O_2 released was ~1.9 mg per 30 minutes. These measurements were scaled up by 10 to estimate the release of $H_2O_2$by the other 10 forms from its generation. For all 10 forms the estimated release is 0.628 mg/min and ~19 mg in 30 minutes. These approximations were used to calculate the molar ratios of H_2O_2 released to each metal with the goal molar ratio being at least 2:1 mM H_2O_2/min to millimoles of each metal per minute but the optimal ratio was set at 3:1 mM H_2O_2/min to millimoles of each metal per minute. Hydrogen peroxide's molar weight is 34.01 g/mol or 34010 mg/mol. The estimated release of 10 forms per minute at a rate of 0.63 mg/min was divided by the molar mass of H_2O_2 in milligrams, 34010mg, to yield $1.85E^{-05}$ moles of H_2O_2 per minute released. This was converted to mmol/min by multiplying it by 1000 yielding 0.018 mmol of H_2O_2 per min with 10 forms. To estimate the mmol of H_2O_2

released in 30 minutes by 10 forms this was multiplied by 30 yielding 0.554 mmol H_2O_2 per 30 min. The mmol of H_2O_2 per min with 10 forms (0.018) was divided by 475 for the flow rate of 475 ml/min then multiplied by 1000 to yield 0.039 mmol of H_2O_2 per liter.

Similar calculations were made for lead, zinc, iron, manganese, cadmium and copper. For a goal concentration of each metal being 1 mg/L, the molar weight in milligrams was divided by 0.475 mg/min (to account for the flow rate of .475L/min X 1 mg per L concentration) to yield moles per min. This was then multiplied by 1,000 to calculate mmol of metal per minute. Each metal's estimated value of mmol per minute was divided by the approximate mmols per minute produced by the ten forms. This gave a ratio of hydrogen peroxide to metal. The goal was 3:1 following the results obtained by Miller (2015) as optimal molar ratio between H_2O_2 and Fe^{2+} but a ratio of 2:1 was deemed acceptable due to lower steady release rate than expected.

Lead was estimated to have a mmol ratio of 8.055:1 mM of H_2O_2 per min to each 1 mM of lead per minute. Zinc was estimated to have a mmol ratio of 2.54:1 mM of H_2O_2 per min to each 1 mM of zinc per minute. Iron was estimated to have a mM ratio of 2.17:1 mM of H_2O_2 per min to each 1 mM of iron per min. Manganese was estimated to have a mM ratio of 2.13:1 mM of H_2O_2 per min to each 1 mM of manganese per min. Cadmium was estimated to have a mM ratio of 4.37:1 mM of H_2O_2 per min to each 1 mM of cadmium per min. Copper was estimated to have a mM ratio of 2.47:1 mM of H_2O_2 per min to each 1 mM of copper per min.

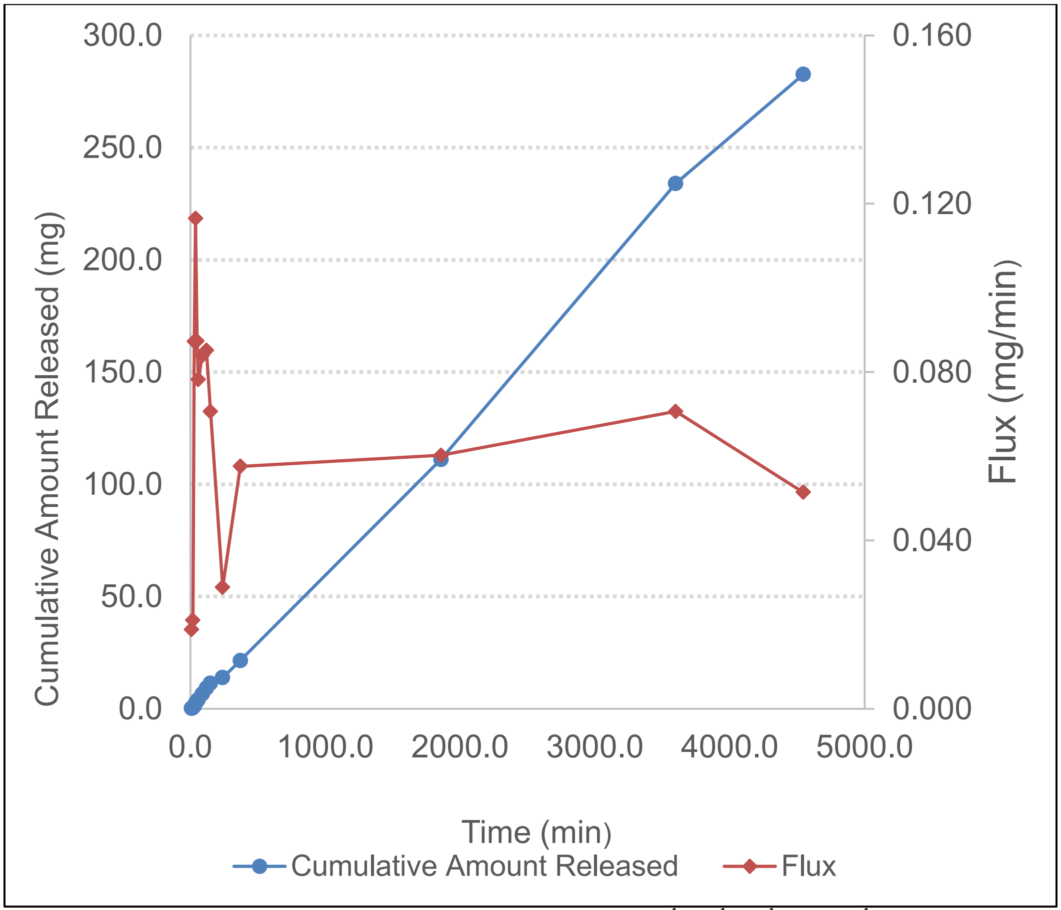


Figure 4-6: Release graph of small form A for the 6th, 7th, 8th and 9th of December 2016. Cumulative amount of H_2O_2 released and flux of H_2O_2.

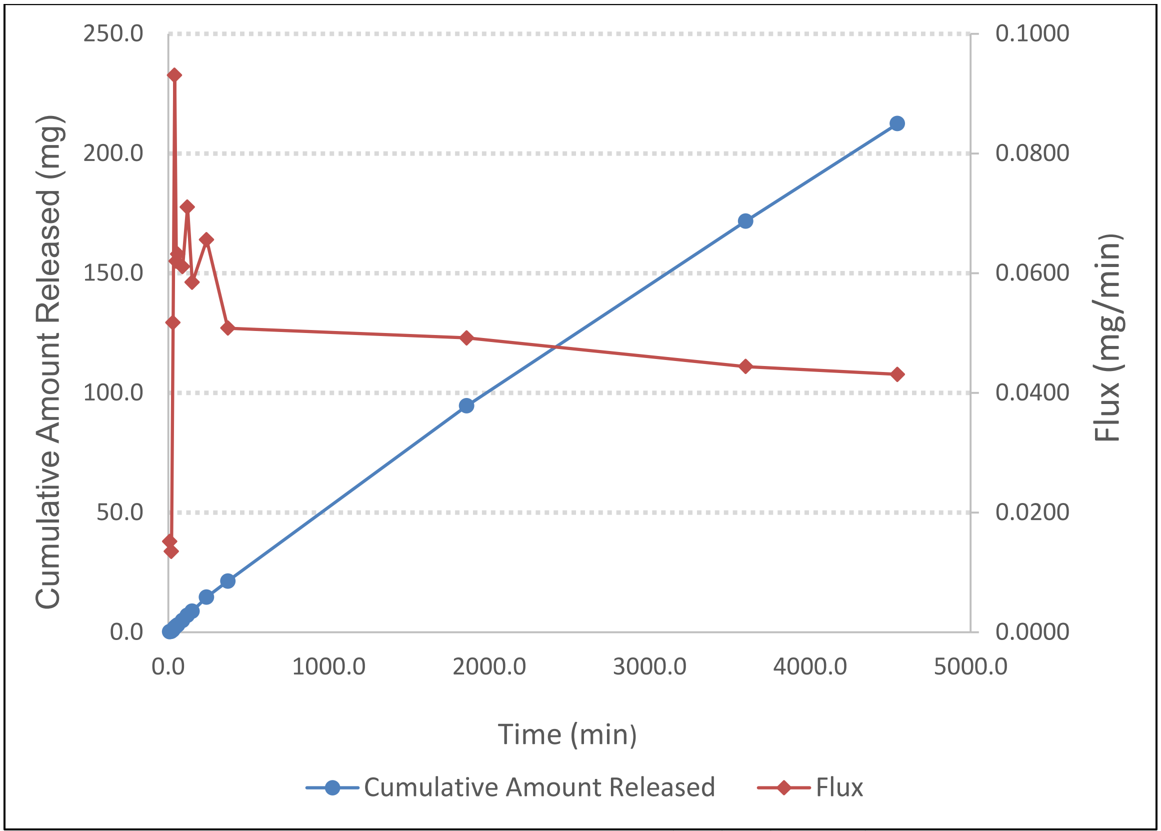


Figure 4-7: Release graph of small form B for the 6th, 7th, 8th and 9th of December 2016. Cumulative amount of H_2O_2 released and flux of H_2O_2.

4.3 Metal Removal and pH-Eh Conditions

The results of the ICP analyses are shown in Table 1. An average baseline very close to the target of 1.00 mg/L for each metal was achieved. Copper had the lowest baseline concentration with a concentration of 0.976. And zinc had the highest average baseline concentration with a concentration of 1.1 mg/L.

At equilibrium, the pH and Eh of solution constrain dominant metal species in a solution. The redox diagrams of each metal are shown in Figures 4-8 – 4-11(Drever, 1997; Wei 2009). The redox potential (pE, Eh) was not measured during the course of the treatment test. The pH was continually measured in the inflow and measured twice in the outflow of the treatment test. The inflow of the DI and metal solution was measured at 1.74. This is outside the lowest calibration point of 4, so the 1.74 is not as accurate but instead an estimation. Due to the very acidic pH of the inflow, 1.74, it is estimated all metals occurred as dissolved ions. An increase in pH due to carbonate release from the dissolution of the SR-HP forms was small but evident by an increase in pH to 1.87.

Sansalone et al. (1997) recorded the pH of the initial 10 L of urban runoff sampled as 5.6-6.4. The rainfall pH was 3.8-4.5. Wei et al., (2005) found that at equilibrium most iron to precipitate at a pH of above 4 while manganese required a much higher pH of ~ 8.5 or higher (Figure 4-9). Iron and Manganese precipitating and leaving solution under these higher pH (above 4 and 8.5 respectively) are due to the metals reaching equilibrium with their solid forms and leaving solution, not treatment by oxidation. At a pH of 6 or higher the majority of metals present in this study would not appear as dissolved metals in water and thus would not need to be treated to be removed from solution.

At a pH of 4 and an Eh of 0 (v) PbS will probably be the dominate lead species if sulfur is available in water. If the pH stays at 4 but the Eh increases to 0.5 (v), Pb^{2+} may be the dominate species. At a pH of 6 lead could appear as $PbCO_3$ at an Eh of both 0 and 0.5 (v) (Figure 4-8).

At a pH of 4 copper could appear as Cu-metal at an Eh of 0 (v) or Cu^{2+} at an Eh of 0.5 (v). If the pH is 6, Cu_2O could be present at an Eh of 0 (v). At a pH of 6 and an Eh of 0.5(v) 2 copper species could occur $Cu_2(OH)_2CO_3$ or CuO (Figure 4-8).

In Figure 4-9, Wei et al., (2009) found manganese did not precipitate until alkaline conditions were reached. A slight decrease in concentration was documented around a pH of 7 and the optimal removal pH by equilibrium was around 8.5 when oxidation was not considered. Iron was also examined by Wei et al., (2005). Iron concentrations decreased significantly at a pH of 4 without oxidation suggesting that this pH provides more optimal condition for iron precipitation. When oxidation is considered, however, oxidation of iron from Fe^{2+} to Fe^{3+} and aid precipitation can occur in acidic condition with pH value of as low as 2. Therefore if oxidant is added to raise the Eh to a certain value, $Fe(OH)_3$ precipitation can be expected to occur at these low pH conditions (Figure 4-10).

Zinc and cadmium would still both occur as dissolved Zn^{2+} and Cd^{2+} at pHs of 4 and 6 with Ehs of both 0 (v) and 0.5 (v) (Figure 4-11). Wei et al., (2005) found zinc precipitated out of solution once the pH reached 7 and above by equilibrium (Figure 4-12).

Badmus et al., (2007) studied the treatment of wastewater polluted by heavy metals with H_2O_2-aided hydrolysis and a bed of activated clay. Displayed in Figure 4-13 is the amount of metals removed versus the amount of H_2O_2 supplied to the system. The optimal concentration of H_2O_2 found by Badmus et al., (2007) was 1.5%. Badmus et al. (2007) also found pH to play a large effect on how much metals were removed. The optimal pH for maximum removal found by Badmus et al .,(2007) was 7.6. A 7.6 pH yielded 77.98%, 81.27%, and 76.70% removed for $Pb^{2+,}$ Zn^{2+} and Cu^{2+} respectively (Badmus et al., 2007).

Table 1

ICP Results From Treatment Test – concentration in mg/L – accurate to 0.005

Sample	Cd	Cu	Fe	Mn	Pb	Zn
Shaw Initial "A"	1.074	0.970	1.009	0.996	1.004	1.078
Shaw Initial "B"	1.074	0.9715	0.997	1.009	0.996	1.086
Shaw Initial "C"	1.086	0.986	0.996	0.999	1.005	1.102
Avg of Baseline	**1.078**	**0.976**	**1.001**	**1.002**	**1.002**	**1.089**
1 - 19 min	1.033	0.932	0.930	1.026	0.927	1.083
2 - 23 min	1.045	0.948	0.944	1.024	0.957	1.093
3 - 27 min	1.054	0.959	0.941	1.033	0.963	1.108
4 - 31 min	1.04	0.938	0.915	1.023	0.932	1.088
5 - 35 min	1.06	0.965	0.937	1.039	0.974	1.107
6 - 39 min	1.058	0.964	0.956	1.032	0.987	1.099
7 - 43 min	1.071	0.983	0.972	1.03	0.999	1.113

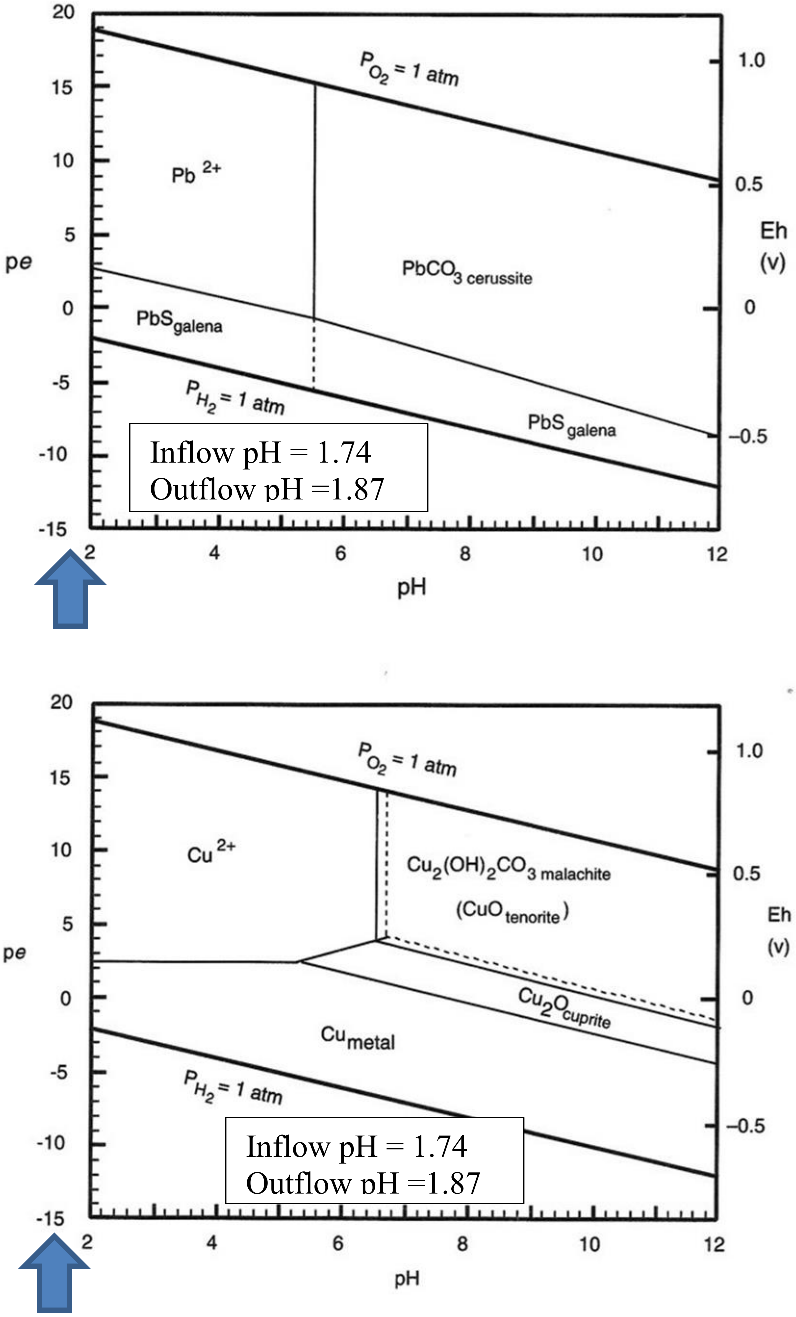


Figure 4-8: Redox potential vs pH diagram for lead (above) and copper (below) at standard conditions (25 C 1 atm) The pH for this present study ranged from approximately 1.74 -1.87(adapted from Drever, 1997).

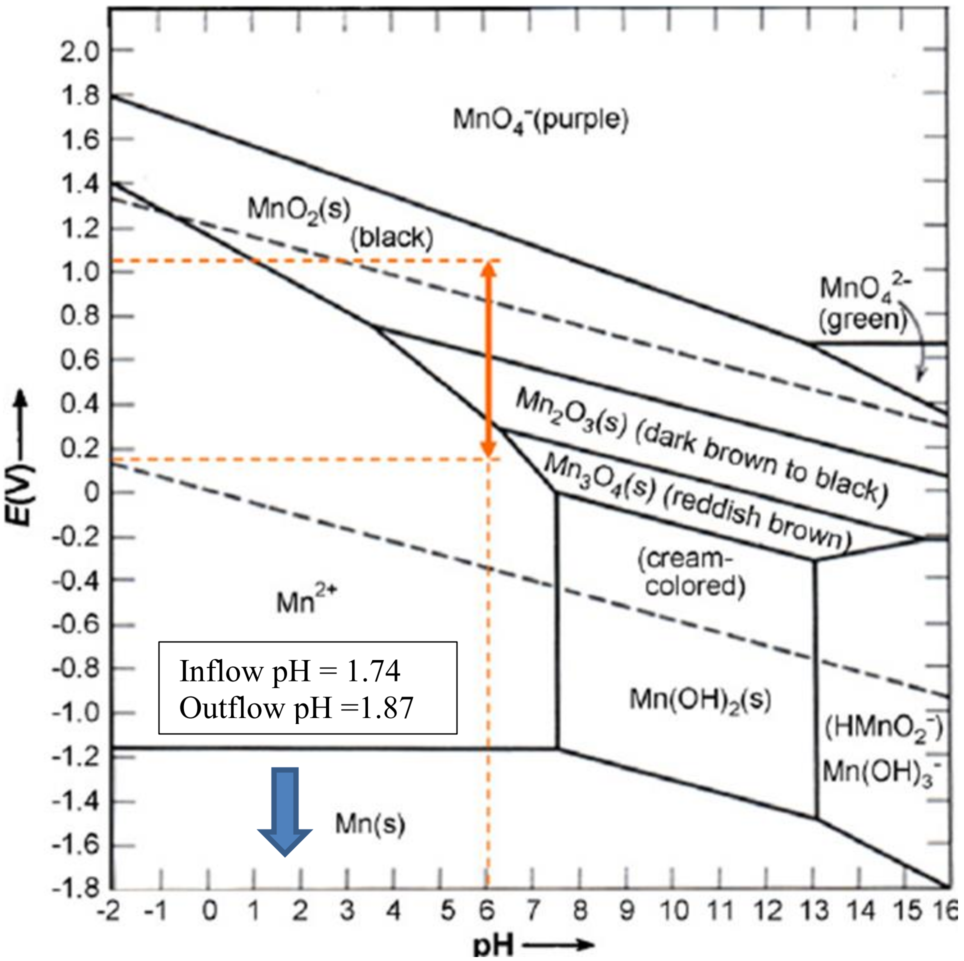


Figure 4-9: Redox potential vs pH diagram for manganese at standard conditions (25 C 1 atm) The pH for this present study ranged from approximately 1.74 -1.87 (Wei et al., 2009).

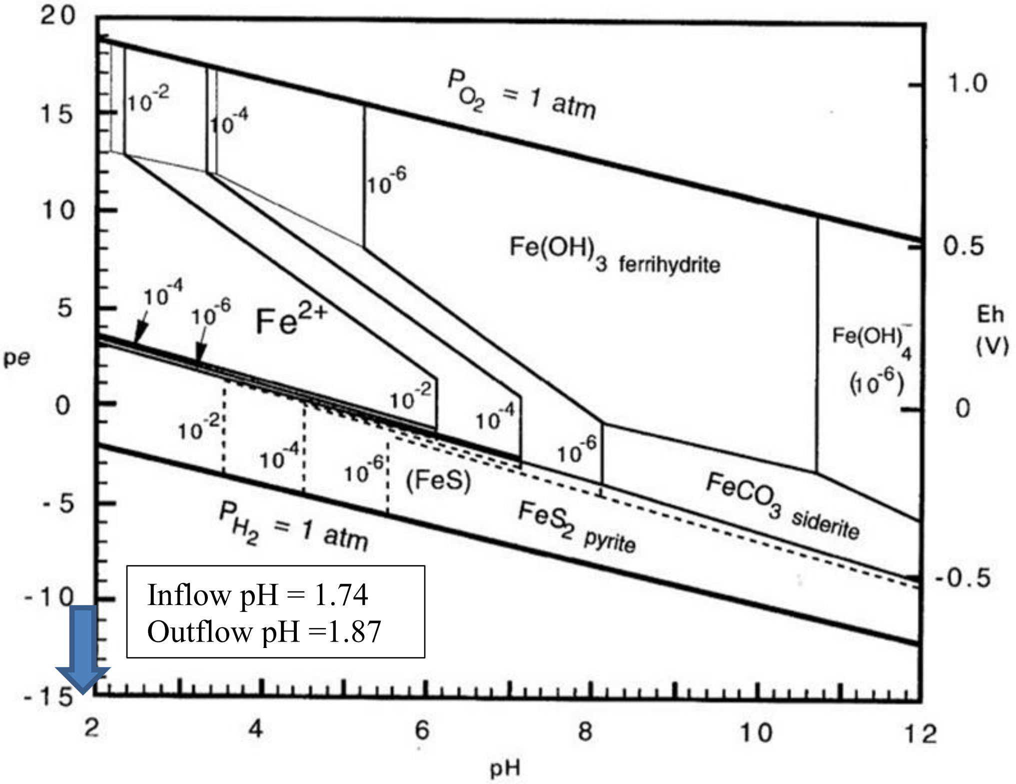


Figure 4-10: Redox potential vs pH diagram for iron at standard conditions (25 C 1 atm) The pH for this present study ranged from approximately 1.74 -1.87 (adapted from Drever, 1997).

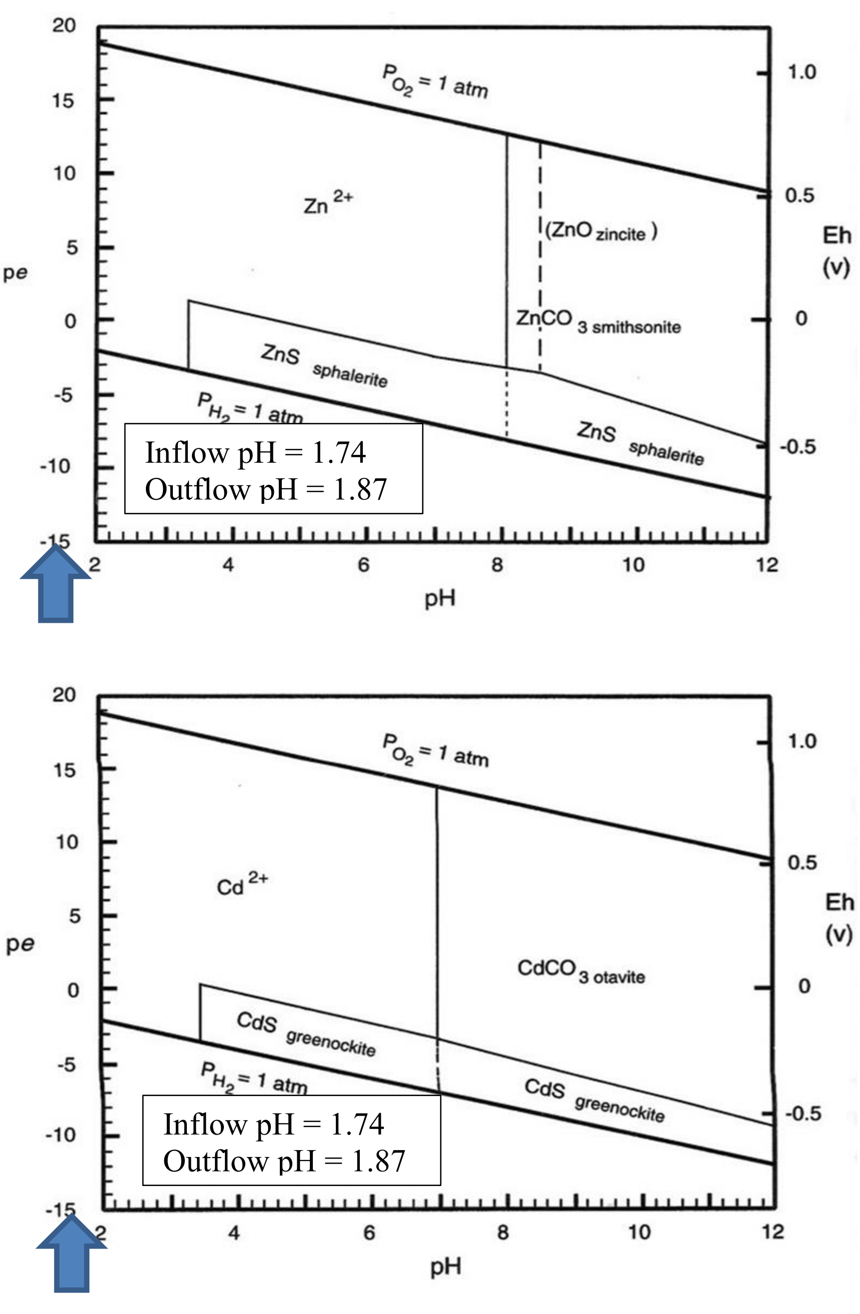


Figure 4-11: Redox potential vs pH diagrams at standard conditions (25 C 1 atm) for zinc (above) and cadmium (bottom) The pH for this present study ranged from approximately 1.74 -1.87 (adapted from Drever, 1997).

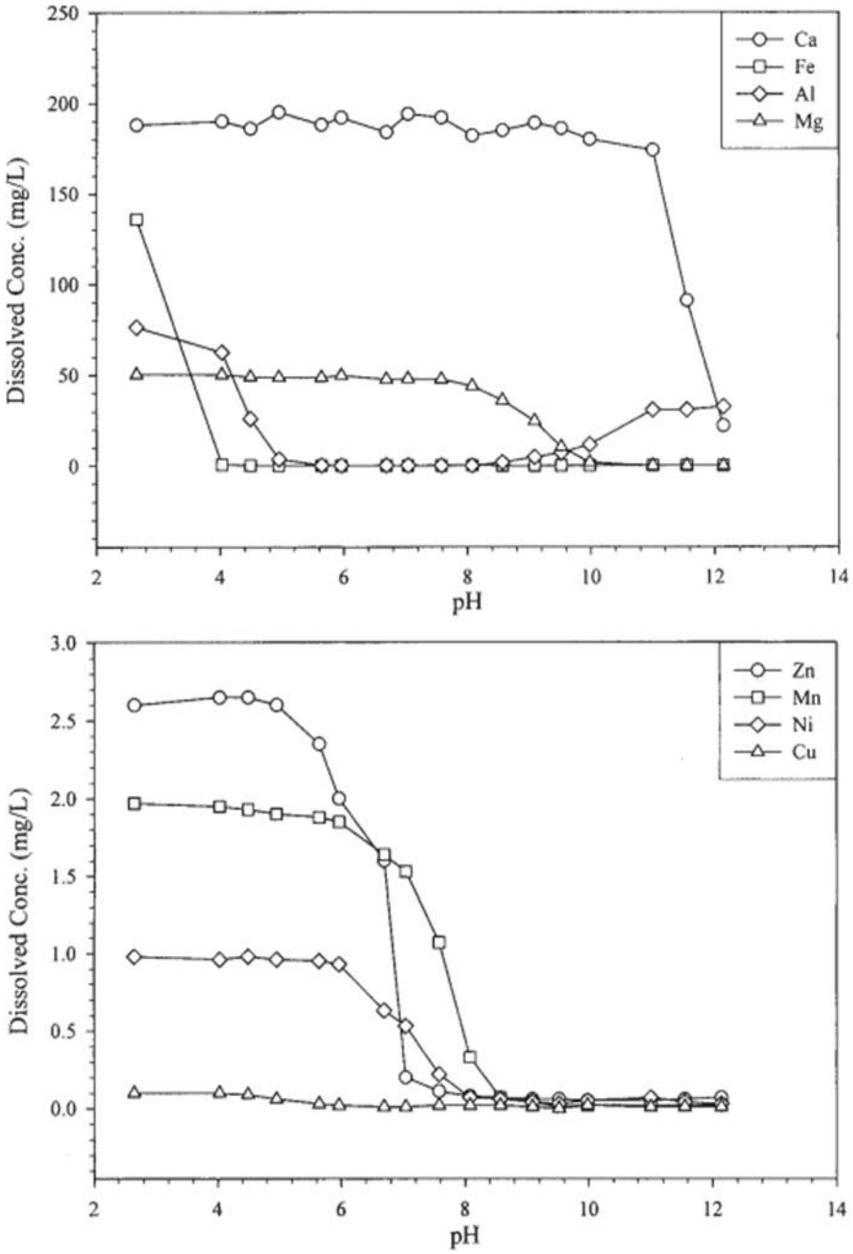


Figure 4-12: Metals found in acid mine drainage and the pHs they were found to precipitate by pH control. The pH for this present study ranged from approximately 1.74 - 1.87 From Wei et al., (2005); Miller (2015).

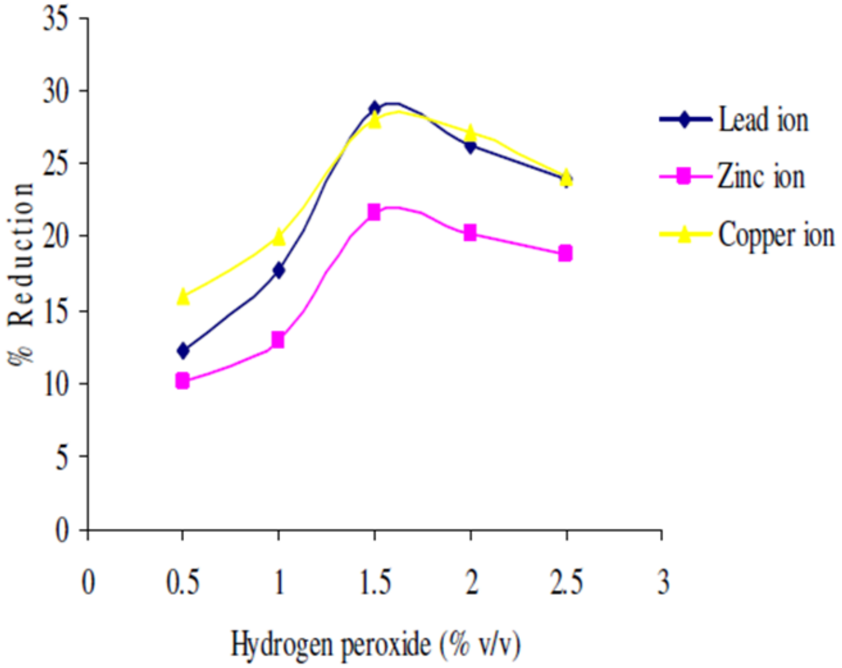


Figure 4-13: Removal of lead, zinc and copper relative to the amount of hydrogen peroxide introduced. The pH for this present study ranged from approximately 1.74 -1.87 (Badmus et al., 2007).

4.4 Results of Treatment Test

Very low to no removal of metals was documented during the treatment test. The concentration of metals found in each sampling and baseline measurements are found in Table 1. The average baseline of each metal was compared to the minimum concentration recorded during the flow through test and the last measurement collected during the treatment test (Table 2). Maximum removal rates for Cd, Cu, Fe, Mn, Pb, and Zn were: 4.17% , 4.52% , 8.59% ,-2.14% , 7.44%, and 0.52%, respectively. There was a slight increase in manganese; this is suggested to be from the mix of standard solutions not being completely homogenous or from analytical error. The maximum 8.6% removal of

Fe is most likely due to Fe $^{2+}$ being used up for Fenton's reaction. The concentrations of each metal throughout the treatment test are displayed in figure 4-14.

The overall little to no removal of metals could be attributed to the pH being exceptionally low. If the pH and/or Eh had been higher more removal could have been achieved. A molar ratio of 2:1 H_2O_2 to metals was assessed to be adequate for treatment and a molar ratio of 3:1 being optimal according to the results found from the previous study for iron oxidation by Fenton's reaction (Miller, 2015). In a laboratory setting Miller (2015) saw rapid removal by oxidizing the majority of Fe^{2+} within a minute. Many ratios of Fe^{2+} / H_2O_2 were examined during that study, but ratios < 2 ($H_2O_2/Fe^{2+} > 0.5$) were found most effective for Fe^{2+} removal, removing around 90% (Figure 4-15). Due to the results achieved in Miller (2015) an initial goal ratio of 3:1 H_2O_2/metal was suggested to ensure as much H_2O_2 as possible is available to treat the metals. However based on the release rates measured from the column test, 2:1 was considered an achievable maximum ratio. Because individual tests were not performed for other metals, information about optimal ratios for other metals was not available for this study. The expected molar ratios (Table 3) were calculated using the small form release rates and were found to all be above 2:1 for each of the 6 metals. The H_2O_2 ratios calculated for each sample during the treatment test were all found to be well above 2:1 some even reaching 300:1. More H_2O_2 than expected was released during the test. The additional oxidant load could be due to some forms having more $2Na_2CO_3 \cdot 3H_2O_2$ in the outside resin layer or an overall heterogeneity of the forms. It could also be due to the flow rate during the treatment test not exactly matching the 0.475 L/min flow rate of the practice runs.

The amount of carbonate (CO_3) released from the forms did raise the pH as expected, but not enough to raise it above 2 neutralizing the acid in the standard solutions. Miller et al., (2015) had success in removing Fe^{2+} using SR-HP forms. The initial pH in Miller (2015) was around 2, after 10 minutes of treatment the pH raised to 2.35 – 3.22 due to addition of alkalinity by carbonate release. The forms used in Miller (2015) had additional surface area due to a hole drilled in the center of each form, this additional surface area could account for more H_2O_2 released during some tests.

Sodium concentrations of each sample allowed the approximate carbonate and H_2O_2 concentrations to be calculated though stoichiometry. As Eq. 14 states, from the dissolution of the SR-HP forms, Na^+, $CO_{3,}$ and H_2O_2 are produced at a 2 : 1 : 1.5 ratio. The concentrations of Na^+ were reported in mg/L they were then taken to mmol/L by dividing by 22.99 mg/mmol. Once in mmol/L the concentration could be manipulated using the molar ratios to produced $CO_{3,}$ and H_2O_2 concentratrions (Table 4). The expected release rate of H_2O_2 was 0.063 mg/min per each form based on concentrations observed during column tests. The average per form release of H_2O_2 was 1.03mg/min during the treatment test (Table 5). The presense of much more H_2O_2 than expected could also be due to how the forms were submereged before the treatment test. The forms were submereged in a bucket of DI to simulate the 6.2 hours until stablized release rate observed in the column tests. But, there was no flow thoughtout the bucket. The no flow conditons could have not allowed the usual peak realase in the first several hours due to the concentration gradient not being as severe due to no influx of new water.

Table 2

ICP treatment results-removal percentages– concentration in mg/L

Sample `	Cd	Cu	Fe	Mn	Pb	Zn
Average Baseline	1.08	0.98	1.00	1.00	1.00	1.09
Minimum Concentration	1.03	0.93	0.91	1.02	0.93	1.08
Difference from Baseline to Min	0.05	0.04	0.09	-0.02	0.07	0.01
Ending Concentration	1.07	0.98	0.97	1.03	1.00	1.11
Difference from Baseline to End	**0.01**	**-0.01**	**0.03**	**-0.03**	**0.00**	**-0.02**
Change from Baseline to Min (%)	4.17	4.52	8.59	-2.14	7.44	0.52
Change from Baseline to End (%)	0.65	-0.76	2.92	-2.84	0.29	-2.24
Average Concentration	**1.05**	**0.96**	**0.94**	**1.03**	**0.96**	**1.10**
Change from Baseline to Avg	-0.03	-0.02	-0.06	0.03	-0.04	0.01
Change from Baseline to Avg (%)	-2.64	-2.02	-5.88	2.80	-3.90	1.00

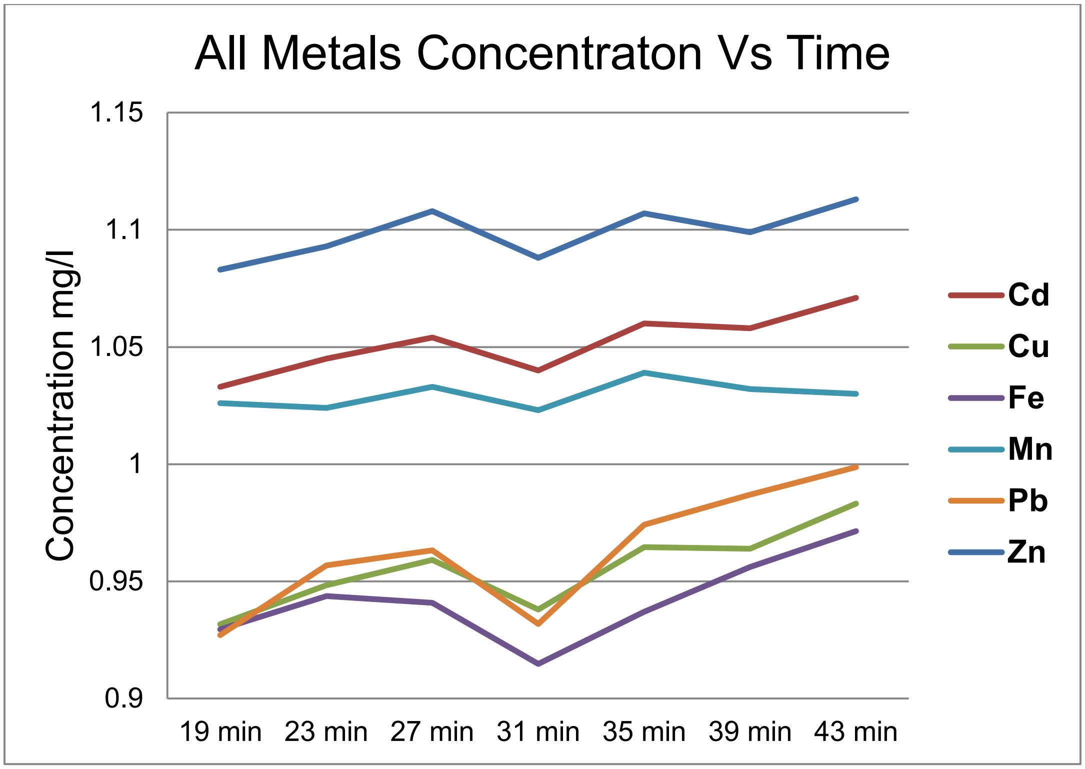


Figure 4-14: The 6 metals and their respective concentrations throughout the treatment test.

Table 3

Molar ratios of H_2O_2 to each metal

Sample	Cd	Cu	Fe	Mn	Pb	Zn
1 - 19 min	146.52	91.83	80.89	72.09	300.91	81.28
2 - 23 min	79.46	49.49	43.71	39.63	159.96	44.18
3 - 27 min	61.56	38.24	34.26	30.70	124.14	34.06
4 - 31 min	80.72	50.59	45.59	40.11	166.06	44.88
5 - 35 min	58.68	36.45	32.98	29.26	117.69	32.68
6 - 39 min	40.39	25.06	22.20	20.24	79.80	22.61
7 - 43 min	14.12	8.70	7.74	7.18	27.92	7.90
Expected molar ratio:	4.37	2.47	2.17	2.14	8.06	2.54

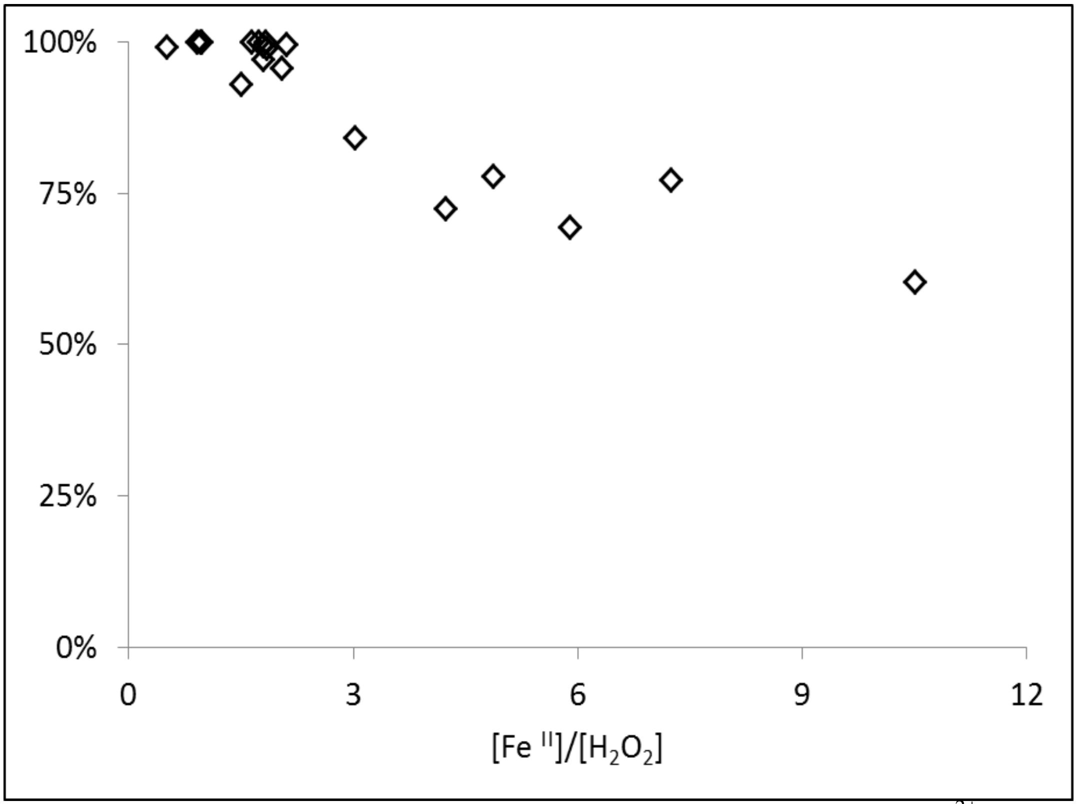


Figure 4-15: Removal efficacies ferrous iron in 10 minutes by different Fe^{2+}/H_2O_2 ratios (Adapted from Miller 2015).

Table 4

H_2O_2 and Na+ measured by ICP. CO_3, H_2O_2 found by stoichiometry

Sample	Na in mg/L	corrected Na mg/L	mM Na	mM CO_3	mM H_2O_2
19 min	42.36	41.272	1.795	0.898	1.346
23 min	23.73	22.642	0.985	0.492	0.739
27 min	18.78	17.692	0.770	0.385	0.577
31 min	23.98	22.892	0.996	0.498	0.747
35 min	18.05	16.962	0.738	0.369	0.553
39 min	12.74	11.652	0.507	0.253	0.380
43 min	5.213	4.125	0.179	0.090	0.135

Table 5

H_2O_2 released during the treatment test. Estimated by molar relationships

Sample	mmol/L of H_2O_2	mg/L H_2O_2	mg/min H_2O_2	Per form mg/min
1 - 19 min	1.35	45.80	21.75	2.18
2 - 23 min	0.74	25.12	11.93	1.19
3 - 27 min	0.58	19.63	9.33	0.93
4 - 31 min	0.75	25.40	12.07	1.21
5 - 35 min	0.55	18.82	8.94	0.89
6 - 39 min	0.38	12.93	6.14	0.61
7 - 43 min	0.13	4.58	2.17	0.22
Max Release Rate	1.35	45.80	21.75	2.18
Min Release Rate	0.13	4.58	2.17	0.22
Avg Release Rate	**0.64**	**21.76**	**10.33**	**1.03**
Expected Release			**0.631**	**0.063**

CHAPTER 5: CONCLUSION

The objectives of this study were as follows: (i) Characterize slow- release hydrogen peroxide (SR-HP) using column tests (ii) Identify key metal pollutants in urban runoff and their general concentrations (iii) perform 1 proof-of-concept treatment test with SR-HP forms using a long cylinder as the treatment system, standard metal solutions as polluted water.

Column release data suggest that the H_2O_2 release from the SR-HP forms stabilize after ~6 hours at an average rate of 0.063 mg/ min. Literature review of relevant studies, cadmium, iron, zinc, copper, lead and manganese were identified as key metal pollutants in urban runoff with approximate total concentrations of 5 ug/L, 3,477 ug/L, 459 ug/L, 43 ug/L, 62 ug/L and 120 ug/L respectively. An experimental concentration of 1 mg/L was chosen for each metal.

One proof-of-concept treatment test was conducted with SR-HP forms and DI water with dissolved metals. During the treatment test, SR-HP released H_2O_2 and alkalinity at the rates ranging from 1.35 mmol/L to 0.135 mmol/L and 0.90 mmol /L to 0.09 mmol/L, respectively. The pH of metal loaded deionized water was raised from 1.74 to 1.87 indicating slight neutralization by added carbonate. At that pH, no treatment was evident for all metals except for iron, which saw a modest removal of 8.6%. This 8.6 removal was probably due to Fe^{2+} being used during Fenton's reaction. Theoretical investigations suggest that at pH of 4 and 6, more Fe and Mn can be removed from water as $Fe(OH)_3$ and MnO_2, respectively, under the given Eh condition achieved by Fenton's reaction within the tube. Other metals will not be removed regardless of low or high (up to 6) pH, due to their non-oxidizable nature. These results suggest that of the common metals in urban runoff, Fe and Mn could be most susceptible to treatment by SR-HP. Multiple tests with natural runoff samples and with varying pH conditions are warranted to further evaluate the treatment efficiencies of SR-HP for oxidizable metals in urban runoff.

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