

Reduction of the Organic Load of Industrial Wood Preserving Wastewater via Chemical  
Oxidation

by

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## **Abstract**

The efficacy of chemical oxidation as a wastewater treatment method for Stella Jones Inc. (Atlantic Canada) was evaluated using 3 chemical oxidants; Fenton's Reagent, Modified Fenton's and potassium permanganate. Reduction of the organic load and toxic compounds in the wastewater to increase the longevity of carbon filters was the end goal. Effectiveness was primarily based on the reduction of chemical oxygen demand (COD), and reduction of toxic and recalcitrant compounds including 18 polycyclic aromatic hydrocarbons (PAHs) and pentachlorophenol (PCP). Fenton's Reagent resulted in the greatest COD reduction of 86%. Modified Fenton's and potassium permanganate resulted in improved reduction of PAHs with notable reductions seen in the larger ringed PAHs (4-6 rings). Low confidence in PCP results were noted. As PAHs were found in low concentrations in the wastewater, Fenton's Reagent was chosen as the best treatment oxidant due to the overall reduction of the organic load of the wastewater.

## **List of Abbreviations Used**

AOP	Advanced oxidative process
ANOVA	Analysis of Variance
°C	Degrees Celsius
CaO <sub>2</sub>	Calcium Peroxide
CCA	Chromated copper arsenate
COC	Contaminant of concern
COD	Chemical oxygen demand (mg O <sub>2</sub> consumed per litre of water)
DNAPL	Dense non-Aqueous phase liquid
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
ISCO	In-situ chemical oxidation
KMnO <sub>4</sub>	Potassium permanganate
LNAPL	Light non-Aqueous phase liquid
mL	millilitre (10 <sup>-3</sup> L)
PAH	Polycyclic aromatic hydrocarbon
PCP	Pentachlorophenol
ROS	Reactive oxygen species
SCO	Simple chemical oxidation
Tukey's HSD	Tukey's Honestly Significant Difference
USEPA	United States Environmental Protection Agency

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## **Chapter 1 Introduction**

Wood protection is a process in which chemicals (often toxic) are applied to wood products as a mean to protect the product from attack by insect and fungal decay (USEPA 2008a; USEPA 2008b). Wood preservatives that are applied in accepted concentrations and that have achieved sufficient penetration into the wood, results in a product that has a greatly increased lifespan. The cost of replacement for an installed utility pole averages 2500\$ CAN, providing an economic incentive to maximize the lifespan of the pole (UTS 2010). As the lifespan of a pole increases, the need for harvesting more wood and lumber decreases thus reducing impact on our forest resources. Stella Jones Inc. is one of the largest Canada-based marketers and producers of pressure treated wood. Stella Jones Inc. supplies North American telecommunication and electrical utility companies with utility poles, railroad operators with railway ties and retailers/wholesalers with residential lumber. Industrial products such as wood for bridges, construction timbers and marine and foundation piling are also made (Stella Jones 2012).

In Canada there are a total of 10 commercial and residential wood preservatives registered with the Pest Management Regulatory Agency of Health Canada and are divided into two categories; oil-borne and water-borne preservatives (WPC 2013, WPC 2014). The 8 registered water-borne preservatives include alkaline copper quaternary (ACQ), copper azole (CA), micronized copper azole (MCA), didecyl dimethyl ammonium carbonate (DDAC), disodium octaborate tetrahydrate (DOT), ammoniacal copper zinc arsenate (ACZA) and chromated copper asenate (CCA). The 2 registered oil-borne preservatives include pentachlorophenol (PCP) and creosote. The wastewater produced from water-borne preservatives is often able to be reused in new preservative mixtures and therefore is not as problematic as oil-borne generated wastewater. Oil-borne preservative wastewater however, has no immediate use and must be treated prior to

discharge or reuse (in other water applications) to reduce the high concentration of organic compounds, some of which are toxic and recalcitrant.

PCP and creosote are two of the most frequently used oil-borne compounds in wood preservative industries and are used as fungicides, insecticides, miticides and sporicides to protect wood (USEPA 2008a; USEPA 2008b). Historically, PCP was used extensively as an insecticide/herbicide in agriculture but currently the only remaining industrial use is as a wood preservative (Li et al. 2011). PCP is classified by the US Environmental Protection Agency (USEPA) as a Restricted Use Product and a priority toxic pollutant primarily used to treat utility poles (USEPA 2008b; Shih et al. 2011). Environment and Climate Change Canada (2014a) classifies PCP as an anthropogenic compound. Historically creosote was used as a wood preservative for transmission poles, railway ties, crib timbers and large size lumber. Currently the use of creosote to treat poles and lumber is being phased out (in favour of PCP) however the majority of railway ties are still being treated with creosote (USEPA 2008a). Characterisation of USEPA's 16 priority PAHs and PCP are presented in Table 1-1 along with regulatory guidelines set forth by Environment and Climate Change Canada (ECCC 2014a; ECCC 2014b). Of the 16 priority pollutants, 7 are considered probable human carcinogens. These compounds generally have higher molecular weight, greater number of aromatic rings and lower solubility in water.

Wood preservative plants that use creosote and PCP preservatives have to deal with chlorinated phenols and PAHs in their wastewater systems. Highly polluted wastewater with known environmental contaminants is problematic as the toxicity of the contaminants can effect aquatic ecosystems if not treated before discharged to bodies of water (Bayo et al. 2009). Activated carbon is Stella Jones' primary treatment option for removing organic contaminants from their wastewater due its high surface area and charge that facilitates adsorption (Laird 2008; Xiao et al.

**Table 1-1:** Physical properties of pentachlorophenol and selected 18 priority pollutant compounds (Bojas & Pope 2007; Yang et al. 2014; ECCC 2014a; ECCC 2014b)

PAHs	# of Rings	Molecular Weight Category	Aqueous Solubility 25°C (mg/L)	Guideline Value (ug/L)
Naphthalene	2	LMW	31.6	1.1
1/2-Methylnaphthalene	2	LMW	25	NRG
Acenaphthene	3	LMW	3.9	5.8
Acenaphthylene	3	LMW	3.93	NRG
Anthracene	3	LMW	0.043	0.012
Phenanthrene	3	LMW	1.3	0.4
Fluorene	3	LMW	1.9	3.0
Fluoranthene	4	HMW	0.26	0.04
Benzo(a)anthracene <sup>a</sup>	4	HMW	0.0090	0.018
Chrysene <sup>a</sup>	4	HMW	0.0018	NRG
Pyrene	4	HMW	0.13	0.025
Benzo(a)pyrene <sup>a</sup>	5	HMW	0.0038	0.015
Benzo(b)fluoranthene <sup>a</sup>	5	HMW	0.0015	NRG
Benzo(k)fluoranthene <sup>a</sup>	5	HMW	0.00080	NRG
Dibenzo(a,h)anthracene <sup>a</sup>	6	HMW	0.00050	NRG
Benzo(ghi)perylene	6	HMW	0.00026	NRG
Indeno(1,2,3 cd)pyrene <sup>a</sup>	6	HMW	0.060	NRG
Pentachlorophenol	N/A	HMW	20	0.5

<sup>a</sup> - Classified as probable human carcinogens by USEPA

NRG - No Regulatory Guidelines

LMW - Low Molecular Weight

HMW - High Molecular Weight

2015; Abdel-Ghani et al. 2016). Although the use of activated carbon can remove these contaminants from treatment water it is often expensive and the compounds that are accumulated on the active charcoal matrix must be disposed of, adding to the overall cost. An alternate or complementary approach is the use of remedial techniques to degrade contaminants of concern (COCs) in wastewater to either less harmful compounds or to completely mineralize them to carbon dioxide and water (Forsey 2004; Huling & Pivetz 2006; Petri et al. 2011a). These remedial techniques include biological or chemical techniques as discussed further in Chapter 2. The

advantage of these approaches is that the COCs are transformed and/or degraded and not simply transferred to a different matrix which then must be disposed of.

Chemical oxidants are of interest as a wastewater treatment option due to their ease of handling, potential lower costs and effectiveness over a wide selection of contaminants (Prasse et al. 2015). Chemical oxidation followed by an activated carbon polishing step, as a means of reducing the organic load on the activated carbon sorbent, is a potential option that Stella Jones (Atlantic Canada) wishes to evaluate. Although there are many chemical oxidants that can be used (discussed in Chapter 2), Stella Jones Inc. had specific interests in Fenton's Reagent, Modified Fenton's and potassium permanganate, as these oxidants are the most applicable to use in their current wastewater treatment schemes, as further explained in Chapter 2.

### **1.1 Research Objectives**

The overall goal of this research was to evaluate three chemical oxidation treatments to reduce chemical oxygen demand of wood treatment wastewaters as a result of the oxidation of organic contaminants (PAH/PCP) present in the wastewater. These reductions would increase the lifespan of current organic filters (sand and activated carbon), reducing the associated replacement and disposal costs.

Over the course of this research 5 objectives were evaluated:

*Objective 1* – Determine the optimum loading concentration of each oxidant (Fenton's Reagent, Modified Fenton's and permanganate) required to reduce chemical oxygen demand (COD) levels from wastewater collected from a Stella Jones wood treatment facility.

*Objective 2* – Determine the most effective iron catalyst and iron catalyst concentration for Fenton's and Modified Fenton's. Iron catalysts included ferrous sulfate and ferrous

chloride. Effectiveness was based on the extent to which COD levels were reduced from wastewater.

*Objective 3* - Evaluate the change in pH, temperature and flocculent production that occurred after treatment with each oxidant.

*Objective 4* - Evaluate the effectiveness of each oxidant to reduce the concentration of PAHs/PCP in the industrial wastewater.

*Objective 5* - Select the optimum reaction holding time of the most effective oxidant based on COD reduction.



## **Chapter 2 Literature Review**

### **2.1 Wood Preserving**

The general process of pressure treating wood involves the application of heat, pressure and chemicals to permeate the wood providing long term resistance to wood decay from bacteria, insects, fungi and the environment (USEPA 1999a; Environment Canada 2013; Hiziroglu 2013). Temperature, pressure and holding time varies depending on preservatives being used and species of wood being treated (Environment Canada 2013). By extending the life of treated lumber the wood preserving industry reduces the need for the constant harvest of forests, ensures safe and reliable structural integrity, and reduces the operating and repair costs in industries such as the railway and utility sectors. The two general classes of wood preservatives used are oil-borne preservatives and water-borne preservatives (Environment Canada 2013). The type of preservative used depends on the intended purpose for the wood.

Wood is often conditioned prior to treatment by decreasing the moisture content. Freshly cut wood contains a significant amount of free water that can impede the penetration of the preservative into the wood (USEPA 1999a; Hiziroglu 2013). Moisture reduction can be achieved through air-drying or artificial conditioning. Air-drying is often preferred for poles as it is a cheaper drying method. Air drying is accomplished by stacking wood outside until the moisture content comes into equilibrium with the relative humidity. This can be problematic however, because some wood species rot before this equilibrium is reached (USEPA 1999a). Artificial conditioning can be achieved by 3 different methods: 1) kiln drying, 2) steaming and vacuum, 3) boiling under vacuum. Kiln drying is the process of “oven” drying wood by introducing it into large heating chambers. In the steaming and vacuum method the wood charge is heated with live steam within the treating cylinder, turning water in the poles to steam and a vacuum is drawn at the end of the

process to remove any excess moisture. Boiling under vacuum also occurs in the treatment cylinders where heated preservative is pumped in to heat the wood for anywhere between 1 to 24 hours after which a vacuum is drawn and the preservative reclaimed (USEPA 1999a; Hiziroglu 2013). The latter methods can produce wastewater.

Pressure treatment of wood occurs in steel cylinders that range from 2 to 3 meters in width and can be 50 meters or more in length. The wood is loaded onto specially designed tram cars that are used to transport the wood into the cylinders where either a full-cell or empty-cell treating process is implemented (USEPA 1999a; Environment Canada 2013). A full-cell treating process is often used when the highest retention of preservative is desired. It typically involves treatment with water-borne preservatives and occurs by filling the cells in the wood with preservative. The full-cell treating process involves applying a vacuum (minimum -77kPa) to the treating cylinder to remove as much air and residual water as possible from the wood. Without breaking the vacuum, preservative is introduced into the cylinder until filled and then pressurized (maximum 1040kPa) allowing the preservative to be driven into the empty cells and held until the desired amount of preservative has been retained in the wood. The pressure inside the cylinder is then released, the preservative is pumped out and a final vacuum (minimum -77kPa) is used to remove excess preservative that can drip from wood (USEPA 1999a; Environment Canada 2013). An empty-cell treating process is often more economical, and typically involves treatment with oil-borne preservatives and occurs by utilizing trapped air within wood cells to coat the interior of the cells with preservative rather than filling the entire cell. The empty-cell treating process involves applying an initial pressure (typically 240-275kPa) to the treating cylinder causing air and water in the wood cells to become compressed. The preservative is then introduced, the cylinder is filled and pressure (typically 950-1000kPa) is further increased until the desired amount of preservative

has been retained in the wood. The pressure in the cylinder is then released, allowing the air and any water within the wood cells to expand pushing out the preservative leaving a coating within the cell. A final vacuum (minimum -77kPa) is applied to remove excess preservative that may remain. A final conditioning step is often employed in which steam is applied to treatment cylinders to ensure that any excess oil is driven off the pole after treatment as well as to clean the surface of the pole. Other than residual water that may be present in wood prior to treating, steam application is a major source of wastewater for empty-cell oil-borne wood preservative treatment processes (USEPA 1999a; Environment Canada 2013).

## **2.2 Remedial Options**

Conventional physical methods of removing recalcitrant compounds involve removal or isolation and can include oil separators, the removal of contaminated water into holding ponds or incineration of the matrix to destroy contaminants (Petri et al. 2011a; Petri et al. 2011b; Prasse et al. 2015). These practices are often labour intensive, expensive and involve transferring the contaminant from one medium to another. Approaches that can transform compounds into less harmful/non harmful compounds are being developed (Haritash & Kaushik 2009; Prasse et al. 2015). These approaches include microbial degradation and chemical oxidation.

### **2.2.1 Microbial Degradation**

PAHs are known to undergo chemical degradation, volatilization, and photolysis, however, microbial degradation is the major natural degradation process (Yuan et al. 2001; Haritash & Kaushik 2009). Microbes capable of degrading PAHs include algae, fungi and bacteria. Degradation involves the transformation of these compounds into less complex metabolites and, in some cases, complete mineralization producing inorganic minerals such as carbon dioxide and water under aerobic conditions and methane under anaerobic conditions (Dua et al. 2002). There

are a variety of factors that influence the microbial degradation of recalcitrant organics including temperature, oxygen, pH, accessibility to nutrients, and chemical structure of the compound (Dua et al. 2002; Haritash & Kaushik 2009; Bosso & Cristinzio 2014). The bacteria and fungi most effective at degrading recalcitrant organics are often found in soils contaminated with organics and can be isolated from these systems and cultured. Romero et al. (1998) noted that microbes isolated from a phenanthrene contaminated stream were able to almost completely mineralize phenanthrene when placed in a basal medium for 1 month. The same strain of bacteria, when introduced into a PAH contaminated soil, was able to remove 98% of the total PAH content of the soil (Dhamodharan & Jayapriya 2015). Noticeably, the 5 to 7 ringed PAHs (which have the greatest carcinogenicity) were decreased to 3% of their original value (Dhamodharan & Jayapriya 2015). Verrihiest et al. (2002) demonstrated that microbial communities isolated from natural freshwater uncontaminated sediment were able to reduce smaller ringed PAHs by 94-97%, whereas larger PAHs (ie. benzo(k)fluoranthene) remained unchanged over the month long study.

Microbial degradation occurs for PCP under both aerobic and anaerobic conditions. This degradation process is often completed through oxygenolysis, hydroxylation or reductive dehalogenation (Huang et al. 2013; Bosso & Cristinzio 2014). Oxygenolysis is an enzyme (monooxygenase) mediated process that catalyzes oxidative carbon-carbon bond cleavage of aromatic compounds through the use of molecular oxygen (Field & Alvarez 2008). Hydroxylation is another enzymatic (hydroxylase) mediated process where oxidative displacement of chlorine occurs incorporating a hydroxyl group into PCP, often making intermediate products more susceptible to future chemical + microbial degradation (Xun et al. 2010). Under anaerobic conditions bacteria can transform PCP via reductive dehalogenation where hydrogen atoms sequentially replace chlorine atoms followed by ring cleavage (Bosso & Cristinzio 2014). The

most desirable microbes for PCP degradation are those that are able to completely mineralize PCP to  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Microbes from PCP contaminated tannery effluent were isolated and found to degrade 56% of the PCP with increased microbial activity reported as PCP concentrations decreased. It was concluded that the microbes were using PCP as a substrate for their source of energy (Tripathi et al. 2011). Chandra et al. (2009) used a mixture of isolated bacteria and added nutrients on paper mill effluent and observed 100% PCP degradation.

### **2.2.2 Chemical Oxidation**

Chemicals that have the ability to oxidize other chemical species are considered oxidizing agents. They have the ability to “take” electrons (oxidize) from other chemical species and are themselves reduced (Rivas 2006). Chemical oxidation is often employed due to its simplicity and reliability in comparison to biological methods. In chemical oxidation the chemicals added are responsible for degrading COCs and optimum growth rates/survivability of microorganisms do not have to be factored in. These chemical oxidants can usually be classified as simple chemical oxidation (SCO) processes, advanced oxidative processes (AOP) or can be used as one or the other (SCO/AOP) depending on if an activator is used. A list of the most commonly used industrial and remedial chemical oxidants are presented in Table 1-2.

SCO's are oxidants that do not specifically require an activation method to oxidize contaminants. Hydrogen peroxide, persulfate, ozone and permanganate are examples of SCO's that oxidize through either the production of oxygen and radicals (hydrogen peroxide/ozone/persulfate) or direct electron transfers between ions (permanganate/persulfate). Although SCO's have been shown to degrade contaminants, they are being substituted by AOP's which have quicker reactions times and wider degradation spectrums (Petri et al 2011a;

**Table 2-1:** Chemical oxidants commonly used for chemical oxidation of wastewater/groundwater (Northup & Cassidy 2008; Petri et al. 2011a; Petri et al. 2011b).

Oxidant	Chemical Species	Type of Oxidation	Activator	Reactive Species
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	SCO/AOP	None, Fe <sup>2+</sup> , Fe <sup>3+</sup>	OH•, O <sub>2</sub> • <sup>-</sup> , HO <sub>2</sub> •, HO <sub>2</sub> <sup>-</sup>
Calcium Peroxide	CaO <sub>2</sub>	SCO/AOP	None, Fe <sup>2+</sup> , Fe <sup>3+</sup>	H <sub>2</sub> O <sub>2</sub> , OH•, O <sub>2</sub> • <sup>-</sup> , HO <sub>2</sub> •, HO <sub>2</sub> <sup>-</sup>
Permanganate	KMnO <sub>4</sub> or NaMnO <sub>4</sub>	SCO	None	MnO <sub>4</sub> <sup>-</sup>
Persulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	SCO/AOP	None, Fe <sup>2+</sup> , Fe <sup>3+</sup> , heat, H <sub>2</sub> O <sub>2</sub> , high pH	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> , SO <sub>4</sub> • <sup>-</sup>
Ozone	O <sub>3</sub>	SCO/AOP	None	O <sub>3</sub> , OH•

*SCO* – Simple chemical oxidant

*AOP* – Advanced oxidative process

Rubio-Clemente et al. 2014; Ribeiro et al. 2015). AOP's are often used when conventional SCO's cannot oxidize recalcitrant contaminants. They involve the generation of reactive oxygen species (ROS), such as hydroxyl radicals that are known to degrade a wide variety of organic contaminants (Rubio-Clemente 2014 et al.; Ribeiro et al. 2015). The use of AOP's or SCO's does not always lead to complete mineralization and oxidized compounds may have increased biodegradability and/or reduced toxicity to parent compound (Petri et al. 2011a; Ammar et al. 2015). Alternatively,

the reactions may also produce more toxic and less biodegradable chemicals (Rodriguez et al. 2011; Yang et al. 2015).

Although the oxidants in Table 1-2 represent the different chemical oxidants historically used in wastewater remediation and/or in-situ chemical oxidation (ISCO), the following sections more closely examine hydrogen peroxide, calcium peroxide and permanganate based oxidants which were examined in this study. The oxidants not chosen were due to operational issues relating to their longer reaction time (persulfate) or inadequacy to fit into current wastewater treatment schemes at Stella Jones Inc. (gaseous ozone).

### **2.3 Fenton's Reagent (Iron Catalyzed Hydrogen Peroxide)**

Hydrogen peroxide is a strong oxidant that can be used with or without a catalyst. Hydrogen peroxide alone has a high reduction potential ( $E_h=1.8V$ ) indicating an ability to have direct electron transfers with organic compounds. These direct reactions however, are thought to have little importance in the degradation of organic compounds as the reactions rates are thought to be too slow (Watts & Teel 2005; Petri et al. 2011a). Hydrogen peroxide does have a high degree of direct electron reactivity with inorganic minerals that are often present in soil and water media which catalyzes the production of ROS. As such it is often difficult to differentiate between the direct electron transfer oxidation of organic compounds and hydroxyl radical oxidation. As hydroxyl radicals possess extremely high reduction potential ( $E_h=2.7V$ ) it is often desired to include a catalyst with hydrogen peroxide. One frequently used combination is hydrogen peroxide with an iron catalyst and is commonly referred to as Fenton's Reagent.

#### **2.3.1 Reaction**

Fenton's Reagent is considered an AOP made by the combination of hydrogen peroxide and an iron catalyst and can be used to oxidize contaminants in wastewaters (Petri et al. 2011a). A

general sequence of Fenton's reaction is shown in the reactions [1] to [5] below (Petri et al. 2011a; Rosas et al. 2013; Bagal & Gogate 2014) and produces 3 key ROS. There is an initial reaction between the peroxide and the ferrous iron ( $\text{Fe}^{2+}$ ) [1].



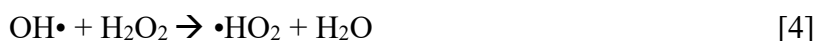
This reaction yields hydroxyl radicals ( $\text{OH}\cdot$ ), hydroxyl ions ( $\text{OH}^-$ ) and ferric iron ( $\text{Fe}^{3+}$ ). The  $\text{Fe}^{3+}$  produced in the reaction is subsequently reduced by hydrogen peroxide back to  $\text{Fe}^{2+}$  [2].



A superoxide ion radical ( $\text{O}_2^{\cdot-}$ ) is also produced from this reaction and is considered the reaction rate-limiting step due to very slow rate constants (Pignatello et al. 2006; Bagal & Gogate, 2014; Ribeiro et al. 2015). The superoxide ion radical produced is also responsible for reducing more  $\text{Fe}^{3+}$  back to  $\text{Fe}^{2+}$  [3].



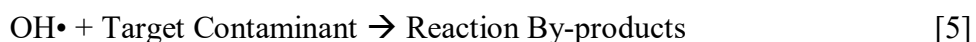
Reactions [1-3] occur until the hydrogen peroxide within the Fenton's Reagent is completely consumed. The hydroxyl radicals also react with the peroxide in Fenton's Reagent to produce protonated superoxide's (hydroperoxyl radicals;  $\cdot\text{HO}_2$ ) that have the potential to react with other compounds [4].



The hydroxyl radicals produced are highly reactive and are deemed nonspecific oxidants which react with a variety of organic contaminants represented in reaction [5]. This is attributed to the extremely high reduction potential ( $E_h=2.7\text{V}$ ) which enables the radicals to acquire electrons readily (Huling & Pivetz 2006; Prasse et al. 2015) and has the highest reduction potentials in comparison to other conventional oxidants used in wastewater. Due to the non-specific nature of



hydroxyl radicals, radical scavenging can occur where radicals react with each other rather than the desired contaminants, reducing the efficiency of Fenton's Reagent.



Hydroxyl radicals are known to degrade contaminants by three processes; (i) radical addition, (ii) radical abstraction and (iii) electron transfer (Hepponiemi & Lassi 2012; Petri et al. 2011a; Stratton 2014). Radical addition is where a radical is added to organic compounds and can improve the ability of it to be oxidized by ferrous iron/oxygen. Radical abstraction is where the hydroxyl radical is used to remove a hydrogen atom from organic compounds, thus producing an organic radical which is then able to react with other organic compounds. Electron transfer occurs when organic compounds transfer an electron to a hydroxyl radical producing ions of higher valence states (hydroxide anion). These ions can be oxidized to form free radicals again or atoms. For ringed compounds (chlorinated phenols/PAHs) these reactions facilitate ring cleavage and subsequent degradation (Lundstedt et al. 2006; Rubio-Clemente et al. 2014).

The pH of a Fenton driven system plays a significant role in its effectiveness as an oxidant. The optimum pH of Fenton's chemistry ranges from 2.5 to 4 (Benitez et al. 2001; Gogate & Pandit 2004; Pignatello et al. 2006; Rubio-Clemente et al. 2014; Hayat et al. 2015). At pHs greater than 4,  $\text{Fe}^{3+}$  has been reported to complex with hydroxide ions, producing insoluble iron hydroxide. This inhibits  $\text{Fe}^{2+}$  regeneration and the production of more hydroxyl radicals (Pignatello et al. 2006). Optimum  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratios have been found to vary, however a 5:1 (w/w) ratio has been reported most consistently (Lee & Carberry 1992; Wang & Xu 2012, Bagal & Gogate 2014).

### **2.3.2 Oxidation Capacity**

The use of Fenton's Reagent for treatment of municipal (Ksibi 2006), industrial (Chakinala et al. 2009), sawmill (Munoz et al. 2014) and textile wastewaters (Hayat et al. 2015; Zou et al.

2015) has been examined with up to a 50% or more reduction in COD levels (or target contaminants). All research supports the practicality of using Fenton's Reagent in treating real wastewater by COD (and target contaminant) reduction. Depending on the method of hydrogen peroxide addition, Fenton's Reagent generally has rapid reaction times, ranging from minutes to a few hours. For the previous stated wastewater studies, reaction times varied from 30 min to 2.5 h

Engwall et al. (1999) examined the use of Fenton's chemistry to simultaneously oxidize PCP and creosote in water using a photo-assisted approach. They placed PCP and creosote in water for 10 days (saturating it) examining the effect that Photo-Fenton's Reagent had at reducing 37 PAHs and PCP. It was found that all compounds had a 90% transformation within the first 5 min, except for 4- and 5-ringed PAHs where further transformations occurred at the end of the 180 min reaction time. Detection was completed by a modified EPA method 625 and later results demonstrated that any by-products formed were not toxic by using a standard fathead minnow toxicity study. Zimbron & Reardon (2011) examined the effect of Fenton's Reagent with prepared aqueous solutions of PCP and found that, although no mineralization was detected, the majority (99%) of PCP had been degraded into by-products. Alternatively Mandonado, et al. (2007) used greater concentrations of hydrogen peroxide coupled with a photo-catalysis approach and demonstrated total PCP degradation (disappearance of the parent PCP compound), complete dechlorination (chloride ion quantification), and a reduction of total organic carbon (TOC) resulting in 65% mineralization in 25 minutes.

### **2.3.3 Degradation Pathways for PCP**

Chlorophenols including PCP have been shown to be very susceptible to degradation by Fenton's Reagent (Petri et al. 2011a). Chlorinated phenols are degraded by hydroxyl radicals to form intermediate organic radicals (ie. chloro-hydroxy-cyclohexadienyl•). Being reactive

themselves, these organic radicals react with other compounds in the water (other chlorophenols, hydroxyl radicals etc.) and subsequently form benzene-diols and phenols. Hydrolysis reactions follow, leading to cleavage of the benzene/phenol rings. This results in relatively low weight molecular carboxylic acids which include fully dechlorinated formic and oxalic acids (Pera-Titus et al. 2004; Pignatello et al. 2006; Petri et al. 2011a). Carboxylic acid compounds are not nearly as susceptible to hydroxyl radical attacks and therefore tend to accumulate in oxidative water. In natural systems however, these compounds are readily used as substrates by microorganisms (Petri et al. 2011a).

Lee & Carberry (1992) postulated that in the presence of PCP, hydroxyl radicals break down the compound through breaking of C-Cl bonds rather than C-C bonds within the aromatic ring or C-OH bond. Chlorinated phenol kinetics may vary from one isomer to another, depending on the position of the chloro- functional groups on the phenol ring. These functional groups affect degradation pathways by directing hydroxyl radicals to attack the ring at positions either para- or ortho- to these groups (Tang & Huang 1995; Peng et al. 2016). For this reason degradation rates vary among chlorophenols with some having higher susceptibility to hydroxyl radical attacks. Generally speaking, susceptibility differences are smaller between isomers of the same compound (ie. 2,4-dichlorophenol vs. 3,4-dichlorophenol) than when comparing to two different compounds (ie. dichlorophenol vs. trichlorophenol). Organic by-products from the reaction can sometimes support ferrous iron catalyst regeneration. Benzene-diols for example, have reducing agent properties and may regenerate ferrous iron from ferric iron allowing ferrous iron to immediately be available for the production of more hydroxyl radicals (Petri et al. 2011a; Peng et al. 2016).

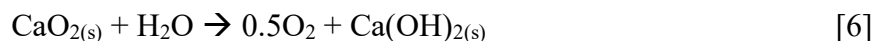
### **2.3.4 Degradation Pathways for PAHs**

PAHs are degraded by hydroxyl radicals by either abstracting hydrogen or the addition to double bonds (Ukiew et al. 2013). PAH degradation can be relatively complex, and theoretically it would take multiple oxidation reactions to completely degrade PAHs that have 3 or more benzene rings (Ferrarese et al 2008; Rubio-Clemente et al. 2014). Treating PAHs to the point of complete mineralization can prove difficult, due to the large structure of PAHs as well as the radical scavenging inefficiencies of Fenton's Reagent. This difficulty was noted by Watts et al. (2003), in which the 5 membered ring benzo(a)pyrene was mineralized using a Fenton's Reagent slurry. It was found that the stoichiometric ratio of hydrogen peroxide needed to mineralize 85% of the benzo(a)pyrene was 1000:1 to 10,000:1 which resulted in a significant amount of oxidant being used. Jonsson et al. (2007) further found that degradation efficiency was higher for 2 and 3 ringed PAHs (59-89%), whereas 4 and 5 ringed PAHs had lower degradation efficiency (0-38%). Both authors stated their results were likely attributed to the angular structures of larger PAHs, as well as increased electron delocalization. Unless these compounds are broken down entirely, it has been shown that intermediates could be formed which include phenols, aldehydes, ketones, quinones and carboxylic acids (Kanel et al. 2003; Lundstedt et al. 2006; Ukiew et al. 2013; Rubio-Clemente et al. 2014).

### **2.4 Modified Fenton's (Iron Catalyzed Calcium Peroxide)**

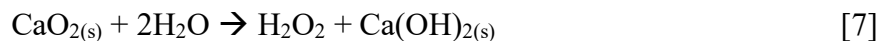
Calcium peroxide is considered one of the safest and most multipurpose solid peroxy compounds, as well as a solid form of hydrogen peroxide (Ma et al. 2007; Zhang et al. 2015a). The use of calcium peroxide alone has been used as an oxygen generating compound for bioremediation due to low solubility, which allows for a slow release of oxygen over a prolonged period of time. Calcium peroxide also has the ability to be a bleaching, deodorizing and

disinfecting agent and thus has been used in medical, agricultural and aquaculture fields (Ma et al. 2007; Zhang et al 2015b). When placed into neutral/alkaline water, calcium peroxide undergoes decomposition yielding oxygen and calcium hydroxide [6]. The generation of oxygen is considered beneficial as it facilitates natural aerobic bioremediation of contaminants (Kao et al. 2003; Liu et al. 2006; Qian et al. 2015).



#### 2.4.1 Reaction

Calcium peroxide can also produce hydrogen peroxide which in turn forms ROS such as hydroxyl, superoxide ion and hydroperoxyl radicals. When placed into acidic water, calcium peroxide dissolves to form hydrogen peroxide (Qian et al. 2015) observed in reaction [7].



The efficiency of calcium peroxide as an oxidant is the result of hydrogen peroxide production (Northup & Cassidy 2008; Goi et al. 2011). The maximum amount of hydrogen peroxide that can be produced by this reaction is 0.47g of  $\text{H}_2\text{O}_2/\text{g}$  of  $\text{CaO}_2$  (Northup & Cassidy 2008; Qian et al. 2015). Northup & Cassidy (2008) observed that decreasing the pH of the solution from 9 to 6 increased the rate of calcium peroxide dissolution, as well as increased hydrogen peroxide formation (from 47% to 82%) showing the benefit of acidic pH adjustment. The ROS are formed by hydrogen peroxide obtaining a single electron from the suspended calcium peroxide which produces a hydroxyl radical (Ma et al. 2007). The difficulty of hydrogen peroxide to obtain electrons directly from calcium peroxide reduces reaction times (Ma et al. 2007; Zhang et al. 2015a; Zhang et al. 2015b). Adding a ferrous iron compound as an electron donor to the formed hydrogen peroxide is much more efficient and results in a solution referred to as Modified Fenton's

Reagent. The reaction kinetics for the hydrogen peroxide produced in Modified Fenton's follow classic Fenton's Reagent kinetics and is shown in reactions [1] to [5] outlined in Section 2.3.1.

#### **2.4.2 Oxidation Capacity**

Although Fenton's Reagent (hydrogen peroxide) is the classic oxidant used in chemical oxidation, the use of Modified Fenton's (calcium peroxide) has recently been used for the remediation of groundwater and wastewater (Ma et al. 2007; Zhang et al. 2015a). Ye et al. (2009) and Zhai & Jiang (2014) observed that calcium peroxide reduced the presence of target compounds in swine manure and glyphosphate wastewaters, respectively. Several malodour compounds were examined in swine wastewater with a 30-90% reduction and glyphosphate wastes had an overall COD reduction of 62%. Lu et al. (2014) was able to decrease COD using a Modified Fenton's approach by 81.8% while treating textile wastewater. Zhang et al. (2015a) examined using calcium peroxide as an oxidant to remove endocrine disruptors from waste activated sludge. At optimum calcium peroxide concentrations all of the endocrine disruptors examined had a 50% removal efficiency. Iron, copper and zinc metals were found to have positive effects on endocrine disruptor removal attributed to the Fenton's Chemistry that occurs from hydrogen peroxide production. It was found that the most important ROS produced were hydroxyl radicals. Calcium peroxide has been deemed a more efficient source of hydrogen peroxide for processes such as in-situ chemical oxidation due to the slow and controlled release (Ndjou'ou & Cassidy 2006; Ma et al. 2007). This reduces the radical scavenging observed in classical Fenton's Reagent.

The majority of work with calcium peroxide has been used as an oxygen adding species in bioremediation work. The use of Modified Fenton's to degrade PAHs/chlorophenols in wastewater through chemical oxidation has received limited attention while the use of Modified Fenton's for PCP removal has not been investigated. Bogan et al. (2003) demonstrated that substituting calcium

peroxide for hydrogen peroxide in a soil slurry pretreated with vegetable oil increased removal efficiency (notably for 4-5 ring PAHs) from 5% to 44%. Gryzenia et al. (2009) demonstrated that the Modified Fenton's approach in soils resulted in greater PAH removal (92.3%) than conventional Fenton's Reagent with improved 4-5 ring PAH removal. Qian et al. (2015) examined the combined approach of using both calcium peroxide and persulfate in reducing the concentration of  $\alpha$ -methylnaphthalene in an aqueous solution. The combination of both oxidants completely removed  $\alpha$ -methylnaphthalene after 72 h. Using calcium peroxide alone was only able to reduce the concentration of  $\alpha$ -methylnaphthalene by 33.94%. Goi et al. (2011) observed 80% degradation of chlorophenol in soil using a Modified Fenton's reagent. The use of Modified Fenton's to remove PAHs or PCP from wastewater has yet to be examined.

#### **2.4.3 Degradation Pathways for PAH/PCP**

The oxidation capacity of calcium peroxide depends solely on the production of hydrogen peroxide which in turns produces hydroxyl radicals and other ROS. Calcium peroxide alone has not yet been demonstrated to directly produce ROS (Northup & Cassidy 2008; Khodaveisi et al. 2011). For this reason, the degradation pathways for PAHs and PCP are assumed to be similar to those outlined in Section 2.3.3 and 2.4.4.

### **2.5 Permanganate**

#### **2.5.1 Reaction**

Permanganate ( $\text{MnO}_4^-$ ) is one of the best understood and used oxidants for degrading organic contaminants (Dash et al. 2009; Petri et al. 2011b). The permanganate ion is chemically stable resulting in long contact time with organic contaminants. This stability promotes the delivery of permanganate through both diffusive and dispersive processes in wastewater treatment application (Guan et al. 2010).

The permanganate ion is tetrahedral in nature with extensive  $\pi$ -bonding and as such, often reacts with double bonds by donating oxygen, extracting hydride ions, hydrogen atoms or electrons (Guan et al. 2010). The ion is a transitional metal at low pH and has a high reductive potential ( $E_h=1.7V$ ) that enables it to readily accept electrons (Munter 2001; Huling & Pivetz 2006; Rauscher et al. 2012). The oxidizing potential of the permanganate ion is derived from manganese being in a heptavalent form which will accept electrons from any available organic or inorganic substance (Urynowicz et al. 2008). The non-specific and high reductive potential nature of permanganate allows it to be an extremely effective oxidizing agent.

The mechanism involved in permanganate oxidation chemistry occurs from direct electron transfer reactions rather than ROS production seen in Fenton's Reagent or Modified Fenton's. The pH of the permanganate solution determines which chemical mechanism occurs and the number of electrons transferred (USEPA 1999b; Petri et al. 2011b; Haynes 2014). In acidic conditions the half-reactions can proceed as:



Although the reduction potential of permanganate ions are not as great as hydroxyl radicals, they have been seen to oxidize compounds over a wider pH range (Beattie et al. 1994; Hood et al. 2000; Ghausul-Hossain & McLaughlan 2012). Under alkaline conditions however the reduction potential of the ion is significantly reduced [10]:



For wastewater oxidation purposes, the pH can be decreased in order to increase the efficiency of permanganate by favouring reaction mechanism [8]. In this reaction the



permanganate ion is reduced to manganese dioxide which then precipitates out of solution (Waldemer & Tratynek 2006; Liang et al. 2009; Liang et al. 2015).

### **2.5.2 Oxidation Capacity**

The use permanganate has been reported for the treatment of olive mill (Abassi 2009), steroid hormone (Fayad et al. 2013), cyanobacterial contaminated (Fan et al. 2014) and hair dyeing (Yin and Hu 2014) wastewaters. It was found that the use of permanganate for the removal of COD was 90% effective for olive mill wastewater, 50-97% effective for steroid hormones wastewater, 90% effective for hair dye wastewater and 90% effective for the removal of cyanobacteria (by cell membrane rupturing) contaminated wastewater.

Many PAH degradation studies are conducted in soil experiments due to PAHs affinity to soil particles. Ferrarese et al. (2008), Souza et al. (2009) and Chen et al. (2015) represent recent studies using potassium permanganate slurry solutions to degrade PAHs in soil matrices. These studies demonstrated a 50% or greater reduction in target PAHs ranging from 2-6 rings. These studies demonstrate the ability of permanganate to degrade PAHs. Due to permanganates high stability, current research involving PAH degradation has generally been employed in ISCO applications. Thompson et al. (2008) demonstrated the degradation of 16 priority PAHs via an ISCO study using permanganate on a creosote plume in the subsurface. It was seen that the PAHs examined were on average 47% lower in the water discharge post treatment when compared to pre-treatment. This decrease was attributed to the degradation of selected PAHs by flushing the plume with a potassium permanganate solution. Thompson et al. (2008) concluded that although the treatment with permanganate may degrade PAHs to some extent (and as such significantly reduce the mass of creosote), the remaining non aqueous phase liquid (NAPL) would be enriched with resistant PAHs. Complete mineralization of the PAH compounds examined could not be

demonstrated. Examining PAHs specifically in water (urban runoff), Rauscher et al. (2012) demonstrated that the use of slow release permanganate candles were able to reduce the concentrations of anthracene, pyrene, benzo(a)anthracene, benzo(k)fluoranthrene and benzo(a)pyrene to below detectable levels within 2 to 4 h although no mineralization was recorded.

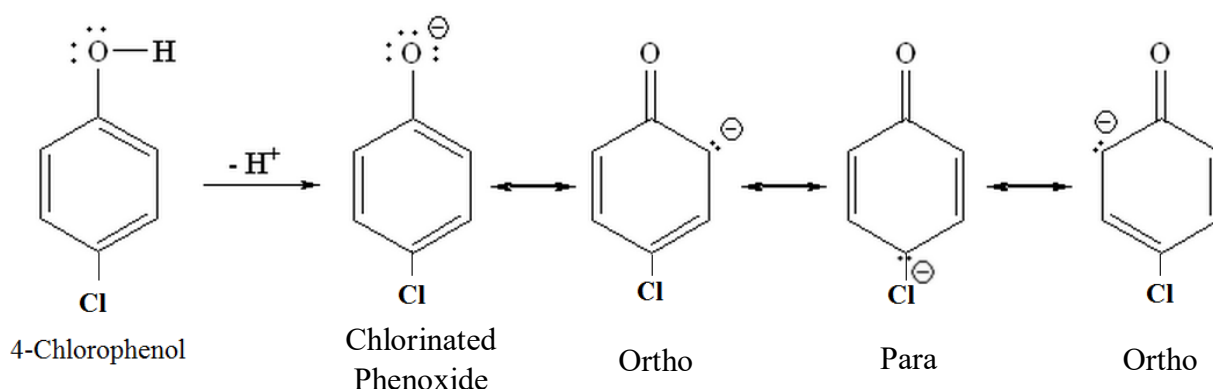
Beattie et al. (1994) looked at the ability of permanganate to degrade PCP under basic conditions. It was found that using permanganate in stoichiometric excess resulted in a quick and almost complete oxidation (2 hours with 80% reduction). Frasco et al. (2006) examined the use of spiked PCP in deionized water and the application of permanganate to oxidize it. Fast reaction kinetics with the formation of chlorinated intermediates were identified, including tetrachloro-1,4 benzoquinone and tetrachlorophenol. Mineralization was eventually confirmed to chloride, water and carbon dioxide. Ghausul-Hossain & McLaughlan (2012) examined the oxidation of 2-chlorophenol (2-CP), 3-chlorophenol (3-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4 DCP) and 2,6-dichlorophenol (2,6-DCP) in the presence of potassium permanganate. They found that the reaction rates were relatively rapid (20 minutes) with 80-90% removal at a pH of 5.3. Reactivity followed the sequence 2-CP > 2,6-DCP > 4-CP > 2,4 DCP > 3-CP. All chlorophenol contaminants demonstrated degradation to some extent in the presence of the permanganate ions. It was concluded that the position of chlorine substitution on the phenolic ring had an effect on degradation.

### **2.5.3 Degradation Pathways for PCP**

Chlorine substitution on aromatic rings has been shown to affect the oxidation rates of permanganate (Zhang et al. 2003; Guan et al. 2010; Ghausul-Hossain & McLaughlan 2012). Zhang et al. (2003) demonstrated that chlorophenol oxidation was reduced as chlorine substitution on the aromatic ring increases. Ortho-substituted chlorophenol isomers demonstrated lesser oxidation

rates when compared to meta or para-substituted isomers. It was concluded that the substituted chlorine atoms are much greater in size than hydrogen atoms present on un-substituted phenols so the steric hindrance effect was attributed to sterically inhibiting the permanganate ion from abstracting electrons from chlorine atoms on the phenol ring. Permanganate initially reacts with the chlorinated phenolate anion (Aromatic ring-O<sup>-</sup>) which is produced at higher pHs (>7). Electrons are abstracted resulting in the formation of phenoxy radicals or other by-products.

Greater phenolate anion formation occurs with more stable compounds, therefore substitutions on the anion that make the compound more stable would increase oxidation (Zhang et al. 2003; Ghausul-Hossain & McLaughlan 2012). Due to chlorine's greater electronegativity, the presence of substituted chlorines tends to result in less stable structures due to their  $\sigma$ -bond withdrawing effect, essentially attempting to pull electrons outside of the stable resonance structure (Figure 2-1). This actually makes the compound less susceptible to oxidation as electrons are less equally shared. At the same time, the  $\pi$ -bond donating effect of the aromatic structure supersedes the  $\sigma$ -bond withdrawing effect (Zhang et al. 2003; Guan et al. 2010).



**Figure 2-1:** Availability of electrons for permanganate on the compound 4-chlorophenol (Modified From Zhang et al. 2003).

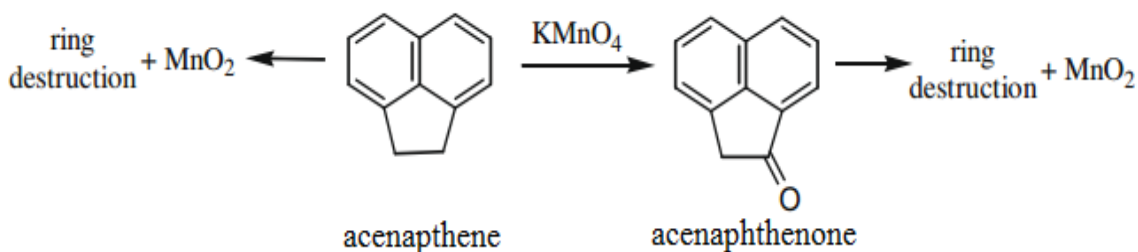
In the para and ortho positions of aromatic compounds (seen in Fig. 2-1) the  $\pi$ -bond donating effect can be seen and as such results in the ability for electrons to be more easily extracted from these positions by the permanganate ion. When the ortho position is chlorinated, the steric hindrance effect comes into play and although there is a possibility for electron extraction, they are more easily extracted from the para position.

#### **2.5.4 Degradation Pathways for PAHs**

Forsey et al. (2004) examined the intermediates formed and the kinetics of permanganate degradation of a variety of PAHs that occurred in dense non aqueous phase liquid (DNAPL) creosote. Of the variety of PAHs considered, those that were most easily oxidized included anthracene, phenanthrene, acenaphthene, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, fluoranthene, pyrene fluorene, and chrysene. The degradation of naphthalene led to the intermediate phthalic acid. Forsey et al. (2004) also identified some carbonyl group substitution onto the original PAH, converting fluorene to 9-fluorenone and acenaphthene to acenaphthenone (an unstable by-product). It was noted that these intermediates were later oxidized by permanganate as the experiment progressed, however the oxidation of anthracene yielded 9,10-anthraquinone, a very stable compound in oxidizing environments. It is apparent that the oxidation of some PAHs can in fact lead to the formation of stable organic by-products.

The permanganate ion is able to oxidize PAHs to form 3 types of products including aromatic quinones, aromatic ketones and aliphatic/aromatic acids (Forsey et al. 2004; Forsey et al. 2010; Liao et al. 2014). Certain oxy-PAHs are known to be toxic and their formation as by-products is of concern. The formation of polar functional groups which are often (but not always) unstable increases the susceptibility of the compound to hydrolysis reactions and ring cleavage (Forsey et al. 2010). Further degradation via permanganate oxidation has also been reported.

Forsey et al. (2010) reported the formation and disappearance of oxy-PAHs in water. Figure 2-2 represents the oxidation of acenaphthene via two mechanisms – direct oxidation of the ring system, or initial side chain oxidation of acenaphthene to acenaphthenone, followed by ring destruction. Rapid destruction of acenaphthenone was reported as it is an unstable compound (Forsey et al. 2010). The oxidation of fluorene was reported to occur similarly with significant side chain oxidation resulting in the production of the intermediate 9-fluorenone. This was further oxidized to below detection limits, however due to the stability of the compound, it took 4 days.



**Figure 2-2:** Two mechanism permanganate oxidation of acenaphthene (Forsey et al. 2010).

Zang et al. (2007) used permanganate as a pre-treatment for benzo(a)pyrene prior to fungal degradation. They reported that the oxidation of benzo(a)pyrene by permanganate was an effective pre-treatment, as it resulted in oxygenation of the parent compound and so reduced toxicity. This allowed for the fungus being examined to provide increased removal of the compound.

Although PAH reactivity to permanganate oxidation varies substantially, some general trends can be explained by electron distribution throughout individual PAHs. Brown et al. (2003) concluded this after his experiments looked at the structure relationships of PAHs that were sorbed

to soils. It was found that the amount of degradation declined in order of benzo(a)pyrene > pyrene > phenanthrene > anthracene > fluorine > chrysene. Brown et al. (2003) found that although complete mineralization could not be achieved, reaction by-products had greater solubility thus increasing their availability for microbial mineralization.

## **2.6 Summary**

Fenton's Reagent, Modified Fenton's and potassium permanganate are promising or currently established oxidants used for industrial water/wastewater treatment as well as PAH and PCP oxidation (Prasse et al. 2015), and therefore practical oxidants for this experiment. Their application in liquid/solid media is suitable for the current wastewater system of Stella Jones Inc. (Atlantic Canada) and their reaction times are sufficiently rapid. Fenton's Reagent and permanganate have high solubility's allowing for concentrated solutions to be used while Modified Fenton's provides a controlled release of hydrogen peroxide.

Initial oxidant loading concentration, the oxidant:Fe<sup>2+</sup> ratio (for Fenton's Reagent and Modified Fenton's), reaction holding time and characteristics of the wastewater can all impact the extent of degradation of the target compound (Petri et al. 2011a; Petri et al. 2011b; Prasse et al. 2015) requiring situation specific operating conditions to be investigated. These three oxidants have been shown to degrade PAHs and PCP in either/all wastewaters, soils, ground water and spiked samples. These oxidants have also previously been used to treat a variety of different wastewaters unrelated to PAH/PCP oxidation. These systems have shown that they are effective at reducing CODs or other specific contaminants present. The effectiveness of these three oxidants has not been examined in wastewater produced from wood preserving industries. The knowledge that these oxidants have the ability to degrade many organic contaminants in water and their use with other types of wastewater systems warrants their evaluation for the treatment of wood

preservative wastewater. The results obtained will allow assessment of their suitability as treatment options for Stella Jones Inc. (Atlantic Canada) to treat wood preservative wastewater.

## **Chapter 3 Methodology**

### **3.1 Chemicals Used**

This section defines the chemical terminology used throughout the thesis. The hydrogen peroxide used was a 30% solution in H<sub>2</sub>O (ACS Reagent from Sigma-Aldrich). The calcium peroxide solutions were prepared from 75% pure - 200mesh (ACS Reagent from Sigma Aldrich). Potassium permanganate was an ACS Reagent Grade  $\geq 99.0\%$  pure chemical from Sigma Aldrich. Ferrous sulfate solutions were prepared using ferrous sulfate heptahydrate (ACS Reagent  $\geq 99.5\%$  pure chemical from Fischer Scientific). Ferrous chloride solutions were prepared using ferrous chloride tetrahydrate (ACS Reagent  $\geq 99.0\%$  pure chemical from Sigma Aldrich). The sulfuric acid used was 98% pure (ACS Reagent from Fischer Scientific). The sodium hydroxide used was 50% pure (ACS Reagent from Fischer Scientific). The sodium sulfite used was  $\geq 98\%$  pure (ACS Reagent from Sigma Aldrich).

### **3.2 Site Description**

Currently at Stella Jones wood preserving plant in Eastern Canada there are two separate oil-borne wood preserving cylinders; one is used for pentachlorophenol (PCP) and the other for creosote. Wastewater is produced during treatment with PCP, however many of the same pipes are used to transport both PCP and creosote preservative solutions and wastes. Contaminants from both systems are expected in the wastewater. Wastewater is produced from steam that is applied to treatment cylinders as a wood conditioning step to ensure that any excess oil is driven off the pole after treatment as well as to clean the surface of the pole. Once the treatment process is complete, a vacuum is applied to the PCP cylinder to remove excess preservative and the steam condensate. The liquid is collected in a sump and pumped through a stainless steel filter (to remove any large wood scraps) into settling tanks where liquid phases are allowed to separate and settle



out for 2-3 days. These phases include (i) any dense non-aqueous phase liquid (DNAPL) creosote that may have come from residual creosote in the piping, (ii) a light non-aqueous phase liquid (LNAPL) containing PCP and (iii) an aqueous wastewater phase. The DNAPL and LNAPL are reclaimed while the aqueous phase is transferred to a flocculation tank and an Ultrion® 8186 coagulant (10-30% aluminum chloride hydroxide by Nalco Inc.) is added to promote flocculation. Calcium peroxide is also added primarily to adjust the pH to approximately 6-7, but it also promotes some chemical oxidation of the wastewater. The flocculent sludge is removed and dewatered. Finally, the flocced aqueous solution is filtered and pumped through sand and activated carbon filter towers to remove any remaining organic particles, such as PCP and PAHs. This relatively clean water is reused within the plant to dilute Stella Jones' water based wood preservative, chromated copper arsenate (CCA).

### **3.3 Wastewater Collection**

The aqueous phase wastewater used in these experiments was obtained before any flocculation and calcium peroxide pre-treatment steps. It was collected from the sump previously described in Section 3.2 and transferred to standard 55 gallon steel drums and allowed to settle for 3 days to separate out the aqueous phase. The aqueous phase was separated from the oil phase using a vacuum pump and a modified pipette (Figure 3-1). This aqueous layer was used throughout the rest of the experimentation and is referred to here as wastewater. An initial characterisation of wastewater collected from 2 different Red Pine batches was performed via a private laboratory (AGAT Laboratories 5385 Coopers Ave. Mississauga ON) and shown in Table A-1.

### **3.4 Measurement of COD**

Initial oxidant loading concentrations for all experimental sections (3.6-3.8) were calculated based on an initial determination of the chemical oxygen demand (COD) of the aqueous



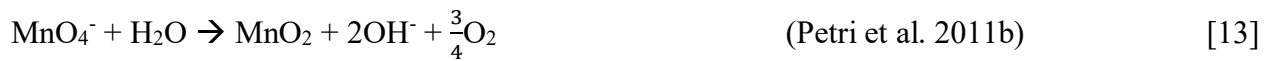
**Figure 3-1:** Wastewater collection method using a vacuum pump, vacuum flask and modified pipette.

phase collected from the settled wastewater (described above in Section 3.3). COD is often used to estimate the amount of oxidant required to oxidize wastewater (Lucas & Perez 2009; Munoz et al. 2014). Determination of the initial COD was done using standard operating procedure (SOP) #8000 from the HACH Company (2014) using the 200-15,000 mg/L colorimetric method. This SOP includes a kit containing pre-measured and pre-mixed test tubes containing sulfuric acid, potassium dichromate (oxidizing agent) and mercuric sulfate. The principle of this method is that 0.2 mL of sample is added to the pre-made COD test tubes and heated in a digester oven block at 150°C for 2 h. Oxidizable organic compounds react, reducing the dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) to a green chromic ion ( $\text{Cr}^{3+}$ ). The amount of green chromic ion produced was then measured using a

DR2000 spectrophotometer programmed for SOP #8000. Deionized water was used as a blank. The results (in mg/L) are defined as milligrams of O<sub>2</sub> consumed per liter of sample. The COD test is an indirect measure of the load of organic contaminants present in the water (USEPA 1999b).

### **3.5 Determination of the Initial Oxidant Loading Concentrations**

The calculation that was used to estimate the desired initial loading concentrations for each oxidant used in these experiments was based on the theoretical stoichiometric weight ratio (R) between the oxidant and COD, assuming the complete oxidation of the COD where 1g COD=1g O<sub>2</sub> used (Lucas & Peres 2009). The amount of O<sub>2</sub> required to completely oxidize 1g of COD by hydrogen peroxide, calcium peroxide and potassium permanganate was calculated as follows.



$$1\text{g COD} = 1\text{g O}_2 = (0.03125\text{mol O}_2)$$

For H<sub>2</sub>O<sub>2</sub> to produce enough O<sub>2</sub> [11]: multiply by 2 =(0.0625mol) H<sub>2</sub>O<sub>2</sub> = 2.125g H<sub>2</sub>O<sub>2</sub>

For CaO<sub>2</sub> to produce enough O<sub>2</sub> [12]: multiply by 2 =(0.0625mol) CaO<sub>2</sub> = 4.505g CaO<sub>2</sub>

For MnO<sub>4</sub><sup>-</sup> to produce enough O<sub>2</sub> [13]: multiply by 1.33 =(0.0417mol) MnO<sub>4</sub><sup>-</sup> = 6.590g KMnO<sub>4</sub>

Therefore theoretical weight ratios for each oxidant are: R<sub>H<sub>2</sub>O<sub>2</sub>/COD</sub> = 2.125, R<sub>CaO<sub>2</sub>/COD</sub>=4.505, and

$$R_{\text{KMnO}_4/\text{COD}}=6.590$$

The oxidant dosages chosen for study were expressed as a % of the stoichiometric weight ratio (R) of the oxidant necessary to completely oxidize the COD load.

### **3.6 Screening Trial**

The screening trial addressed research objectives 1 to 3, which were (i) to determine the optimum loading concentration for each oxidant (hydrogen peroxide, calcium peroxide and

potassium permanganate), (ii) the optimum oxidant:Fe<sup>2+</sup> ratios (for hydrogen and calcium peroxide), and (iii) monitor flocculent production and pH/temperature change associated with varying treatments. For the screening experiments the variable being measured was COD. Although a reduction in COD does not directly demonstrate a reduction in PAH and PCP compounds, COD values are based on the complete oxidation of any organic compounds in a sample (USEPA 2005). For this reason it was assumed that a COD reduction was indicative of a corresponding reduction in PAHs and/or PCP.

### 3.6.1 Experimental Design

End-point experiments (sampling at the beginning and end of the oxidation process) were performed using 150 mL of wastewater per experimental unit. The wastewater was initially added to 250 mL Erlenmeyer flasks and placed on a two speed (high and low) Eberbach table shaker (Figure 3-2). For oxidant treatments requiring ferrous iron catalysts (ie. Fenton's Reagent and Modified Fenton's), pre-measured amounts of ferrous iron were added and then mixing was begun. The oxidant was then added signifying the reaction start time and allowed to react for 3 h. The first 15 min of mixing were rapid (high shaker setting) in order to promote coagulation, while for the remaining time the sample was mixed more slowly (low shaker setting) in order to promote flocculation (Tony et al. 2012). All experimental controls were wastewater samples with no additions and mixed for the 3 h reaction period. Temperature and pH were taken for each sample at 0, 30, 90 and 180 min using a standard pH probe (Fisher Scientific™) and thermometer. At the end of the allotted mixing period the 150 mL samples were filtered using Whatman Filter paper (Qualitative #5) with a particle filtration of 2.5 µm in a vacuum flask in order to remove any flocculent that may have been produced from the reaction of the oxidants and any iron catalysts.



**Figure 3-2:** Bench shaker mixer (Eberbach Corporation) used in screening trials.

The flocculent collected on the filter paper was dried in an oven at 80°C for 2 days and then weighed. The filtered treated wastewater was then sampled for COD (as outlined in Sec. 3.4).

A randomized block design (RBD) experiment was constructed for each separate oxidant, blocking by wastewater batch. A total of 4 batches of wastewater were used for each oxidant stated in the following section (3.6.2) as the bench shaker could not hold all samples at once. Wood species associated with each batch was based on availability at Stella Jones at the time of experimentation. A single treatment was performed per wastewater batch. Blocking by wastewater batch accounted for variability between batches. As the COD of each batch was different the initial oxidant loading concentration was adjusted for each batch using the calculation described in Sec. 3.5. As variability among batches is expected, the response variable was based on normalized  $COD_F/COD_o$  where  $COD_F$  was the final COD of the sample at the end of the reaction period ( $t=3$  h) and  $COD_o$  was the COD of the wastewater solution before oxidants were added ( $t=0$ ). An

analysis of variance (ANOVA) was performed with a significance level set at  $\alpha=0.05$ . The data were tested for normality and constant variance. Independence of COD results was assumed through randomization of treatments on the bench shaker. A Tukey's Honestly Significant Difference (HSD) multiple means comparison test was performed to determine means that were significantly different from one another. A Tukey's HSD was chosen because it is not as conservative as other tests, therefore significant differences are more likely to be detected if they exist (Montgomery 2009; Marusteri & Bacarea 2010).

### **3.6.2 Oxidant Concentration and Oxidant:iron Ratio Optimization**

#### **3.6.2.1 Fenton's Reagent (Hydrogen Peroxide + $Fe^{2+}$ )**

The iron catalyst compounds used to make Fenton's Reagent were ferrous sulfate and ferrous chloride. The three initial oxidant loading concentrations (calculated from Sec. 3.5) were hydrogen peroxide additions at a rate sufficient to consume 50%, 100% and 150% of the COD on a stoichiometric weight ratio basis. Optimum  $H_2O_2:Fe^{2+}$  ratios have been found to be 5:1 (w/w) (Lee & Carberry 1992; Wang & Xu 2012; Bagal & Gogate 2014), however the manager of the wood treatment plant reported iron concentrations in the wastewater to be higher than average water and so this information was used, in combination with literature values, to choose the 3  $H_2O_2:Fe^{2+}$  ratios used which were 5:1, 15:1 and 25:1 (w/w). The three oxidant loading concentrations were also tested with no iron addition. A total of 3 hydrogen peroxide initial loading concentrations (50%, 100% and 150%; Table A-2), each at 3  $H_2O_2:Fe^{2+}$  ratios (5:1, 15:1 and 25:1 w/w; Table A-3), and each with 2 iron catalysts (ferrous sulfate and ferrous chloride; Table A-3) as well as the 3 no-iron additions were examined to give a total of 21 treatment samples per wastewater batch ( $3 \times 3 \times 2 + 3$ ).

For hydrogen peroxide, multiple oxidant additions were used by adding a 50% stoichiometric weight ratio every 10 min until the desired loading concentrations were reached (one addition for the 50% weight ratios, two additions for the 100% weight ratios and 3 additions for the 150% weight ratios). This periodic addition was done to prevent the violent reactions that were observed at the higher rates of loading.

The hydrogen peroxide samples followed a slightly different flocculent quantification procedure than outlined in Section 3.6.2 above. After filtering and testing for COD it was noted that the treated wastewater samples had a very red tinge (Figure 3-3), which was assumed to be left over iron, therefore the sample pH was adjusted to  $7 \pm 0.1$  using concentrated sodium hydroxide and filtered again (Figure 3-4). Each filtered wastewater sample was then dried in an oven at  $80^\circ\text{C}$  over a 2 day period to quantify remaining flocculent (Figure 3-5). All flocculent quantities were added together (post reaction filtering, pH adjusted filtering and dried down) to determine the total flocculent produced from Fenton's Reagent.

### ***3.6.2.2 Modified Fenton's (Calcium Peroxide + $\text{Fe}^{2+}$ )***

The iron catalyst compounds used were ferrous sulfate and ferrous chloride. The three initial oxidant loading concentrations (calculated from Sec. 3.5) were calcium peroxide additions at a rate sufficient to consume 50%, 100% and 150% of the COD on a stoichiometric weight ratio basis. The 3  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratios added to the wastewater were 5:1, 15:1, 25:1 (w/w). These ratios were calculated based on  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  assuming that 0.47g  $\text{H}_2\text{O}_2$  are produced/g  $\text{CaO}_2$  (Northup & Cassidy 2008). The three oxidant loading concentrations were also tested with no iron addition. A total of 3 calcium peroxide initial loading concentrations (50%, 100% and 150%; Table A-2), each at 3  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratios (5:1, 15:1 and 25:1 w/w; Table A-4), and each with 2 iron catalysts



**Figure 3-3:** Filtered Fenton's Reagent samples with remaining reddish tinge.

(ferrous sulfate and ferrous chloride; Table A-4) as well as the 3 no-iron additions (Table A-2) were examined to give a total of 21 treatment samples per batch wastewater ( $3 \times 3 \times 2 + 3$ ).

### 3.6.2.3 Permanganate

Potassium permanganate required no iron catalyst and was examined initially in a preliminary study to determine its residual effect on COD before the full scale screening trial. Due to solubility issues, loading concentrations chosen had to be less than that of Fenton's Reagent and Modified Fenton's. The experiment was conducted using 150 mL of deionized water and loading





**Figure 3-4:** Fenton's Reagent samples after neutral pH adjustment.



**Figure 3-5:** A dried down sample of Fenton's Reagent.

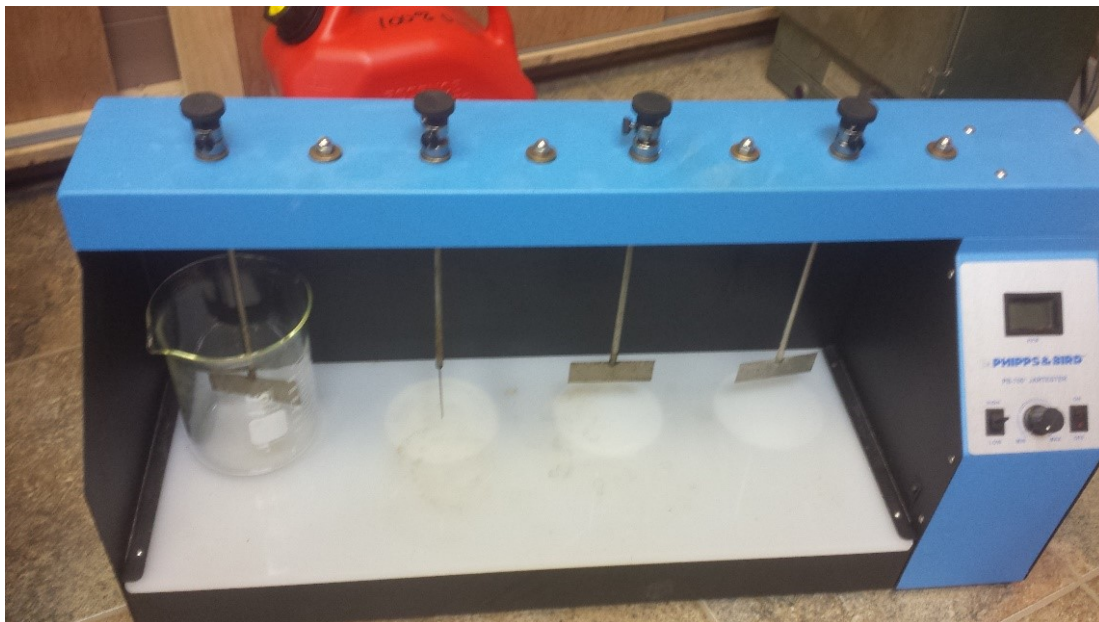
concentrations chosen (calculated from Sec. 3.5) included potassium permanganate additions at a rate sufficient to consume 7.5%, 14.4%, 21.7%, 28.9%, 36.1% and 43.3% (Table A-5) of the COD on a stoichiometric weight ratio basis. These were completed in quadruple replication as a completely randomized design (CRD) and shaken for 3 h. A COD value of 14000 mg/L was chosen to base the permanganate loading concentrations on and results were presented as final COD values. This COD value was chosen as it fell within the range of CODs observed in batches of wastewater used in the Fenton's Reagent and Modified Fenton's studies (Sec. 3.6.2.1 and 3.6.2.2). After the 3 h reaction time the COD of the samples were tested and the effect of residual permanganate on the response of COD was analyzed in Minitab. The significance level was 0.05. Normality and constant variance were examined.

Following the preliminary examination the full scale RBD experiment screening trial was performed (outlined in Sec. 3.6.1) in order to determine the effect permanganate had at lowering COD. Temperature was not recorded. The experiment was conducted using permanganate at the same 6 stoichiometric weight ratio loading concentrations used above (7.5%, 14.4%, 21.7%, 28.9%, 36.1% and 43.3%; Table A-6) to give a total of 6 treatments per wastewater batch.

### **3.7 Polycyclic Aromatic Hydrocarbon and Pentachlorophenol Reduction Study**

The PAH/PCP reduction study addressed objective 4 to assess the effectiveness of three oxidants (Fenton's Reagent, Modified Fenton's and potassium permanganate) to reduce concentrations of these compounds in the aqueous phase. Experiments noted in Section 3.6 determined the optimum loading concentration for each of the three examined oxidants. These concentrations included: (i) a hydrogen peroxide addition at a rate sufficient to consume 100% (Table A-7) of the COD on a stoichiometric weight ratio basis with a 25:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  w/w; Table A-8) ratio of  $\text{H}_2\text{O}_2$  to ferrous chloride catalyst ( $\text{FR}_{100\%}^{25:1}$ ), (ii) calcium peroxide addition at a rate

sufficient to consume 50% (Table A-7) of the COD on a stoichiometric weight ratio basis with a 5:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  w/w; Table A-8) ratio of  $\text{H}_2\text{O}_2$  to ferrous chloride catalyst ( $\text{MF}_{50\%}^{5:1}$ ) and (iii) potassium permanganate addition at a rate sufficient to consume 7.5% (Table A-7) of the COD on a stoichiometric weight ratio basis ( $\text{KMnO}_4_{7.5\%}$ ). Reaction holding time (3 h), pH adjustment ( $3.5 \pm 0.01$ ) and the RBD design remained the same as Sec. 3.6 however pH, temperature and flocculent production were not recorded. All tests were conducted using automated mixers (Phipps & Bird PB-700) at an 80 rpm stirring setting, which held up to four beakers at one time (Figure 3-6) and 1.5 L of wastewater was used per experimental unit.



**Figure 3-6:** Phipps & Bird automated beaker mixer used in PAH/PCP reduction study.

At the end of the 3 h mixing period all samples were centrifuged at 7000 rpm for 5 min to remove any flocculent. The samples were then immediately centrifuged and analyzed for COD (as

outlined in Section 3.4) and quenched with sodium sulfite at 1.25x the maximum stoichiometric concentrations required to consume the oxidant (Lucas & Peres 2009). This was done to prevent any possible degradation that could have occurred to organic compounds/surrogates from any residual oxidant. Solutions were made up to a final volume of 1L prior to extraction. Samples were diluted to fall within analytical laboratory specifications. A 10x dilution for all oxidized wastewater and 100x dilution for all controls was performed. A 100x dilution was also performed on the t=0 h wastewater, which was used as a reference point for the original PAH and PCP concentrations. Each diluted sample was then spiked with 10 µg/L of 2,4,6-tribromophenol and chrysene-d<sub>12</sub> surrogates to validate sample extraction efficiencies. The samples were then extracted and concentrated based on a modified procedure from USEPA's (1996) method 3510C: "Separatory Funnel Liquid-Liquid Extraction". The 1L of diluted sample was serially extracted with dichloromethane initially at a pH >11 and again at pH <2 using a separatory funnel. The extract was dried with anhydrous sodium sulfate and concentrated using a Kuderna-Danish Apparatus to a volume of ~5mL and further evaporated to 1 mL using a nitrogen blowdown technique. Modifications to the procedure referred to the method calling for the use of a Kuderna-Danish evaporation flask and concentrator tube, however a 500 mL round bottom flask was used. The 1 mL extracts were placed into GC-vials and immediately refrigerated (~2°C). Once all replications were complete, the extracted samples were sent to AGAT Laboratories (5385 Coopers Ave. Mississauga ON) where they underwent GC-MS analysis based on USEPA's (2007) method 8270D: "Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)". The analysis quantified the following organic compounds present in the sample: Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)Pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, Fluoranthene,

Fluorene, Indeno(123- cd)pyrene, 1-methylnaphthalene, 2- methylnaphthalene, Naphthalene, Pentachlorophenol, Phenanthrene, Pyrene, 2,4,6-trichlorophenol. Four blind replicated standard samples were included in order to assess accuracy and reproducibility. A stock solution of known concentrations of PAHs were made from a certified standard purchased from AccuStandard® Inc. while PCP and surrogates were prepared and sent by AGAT respectively. Concentrations of the standards are shown in Table 4-9 of the results. All samples and hidden standards were randomly assigned numbers via Minitab to allow for randomization of the blind analysis.

Prior to running the PAH/PCP reduction study, a validation experiment was done in order to determine whether the results obtained by this analyst were accurate and/or precise when implementing USEPA's (1996) method 3510C. Deionized water was spiked with PCP, 18 PAHs and surrogate compounds and then extracted in quadruplicate and concentrated; spiking concentrations shown are in Table 4-8 in the results.

The PAH reduction study was done as a RBD and the blocking factor was wastewater batches. All tests were conducted on 4 wastewater batches, with a single treatment performed per wastewater batch. To ensure consistency between wastewater batches all batches were obtained from the treatment of Red Pine poles. As variability among batches is expected, the response variable was based on normalized  $C_F/C_o$  where  $C_F$  was the final compound concentration of the sample at the end of the reaction period ( $t=3$  h) and  $C_o$  was the compound concentration of the wastewater solution before oxidants were added ( $t=0$ ). An ANOVA was performed with a significance level set to  $\alpha=0.05$  and the data were tested for normality and constant variance. Independence of the PAH/PCP results was assumed through randomization of the treatments on the automated beaker mixer. A Tukey's HSD multiple means comparison test was performed to determine means that were significantly different from one another.

### **3.8 Reaction Holding Time Optimization**

The optimization study addressed research objective 5 which was to determine the optimum reaction holding time for the most effective oxidant. The combined results from experiments outlined in Sec. 3.6 and Sec. 3.7 were used to determine the most effective oxidant for treating wastewater produced by Stella Jones Inc. The oxidant FR<sub>100%</sub><sup>25:1</sup> treatment of Fenton's Reagent was selected for the remainder of this section. A quadruple replicated experiment was performed by taking aliquots of the reaction over a 3 h period.

Values from the wastewater batches observed throughout sections 3.6-3.7 demonstrated COD variation, and to account for this the batches in this section were chosen to be similar to the lowest (~7000mg/L; Table A-9) and highest (~14000mg/L; Table A-10) COD batches observed in Sections 3.6-3.7. This allowed for determining if reactions stopped at different times with varying initial CODs (high vs. low).

The effect on COD over time was examined as 2 different CRD's. Reaction holding time (3 h), pH adjustment ( $3.5 \pm 0.01$ ) and the use of the automated beaker mixer remained the same as Section 3.7, however centrifuging was not necessary. A COD analysis of the samples was done at 0, 10, 30, 60, 120 and 180 min intervals. At each sampling time, 100 mL of the aqueous phase was extracted and immediately analyzed for COD (as outlined in Sec. 3.4).

A PROC Mix repeated measures version of ANOVA was performed in SAS to determine significant differences in this time series experiment. Fisher's least significant difference comparison was done in order to determine which time interval means were significantly different. There are several covariance structures when using a PROC Mix and they must all be run to determine which one is suitable. The covariance structure that resulted in the smallest Akaike's Information Criterion (AIC) absolute value was deemed the most appropriate structure

(Montgomery 2009). The autoregressive order 1 covariance structure was omitted as this structure is only appropriate for equally spaced time points. The analyses allowed for determining whether COD levels were changing or remaining constant for each time interval, indicating when the reaction had stopped lowering the COD.

## **Chapter 4 Results**

### **4.1 Screening Trials**

The first step in evaluating each of the three oxidants (Fenton's Reagent, Modified Fenton's and potassium permanganate) was to determine the optimal operational parameters. The operational parameters considered included varying the oxidant loading concentration and, for oxidants requiring iron catalysts (Fenton's Reagent and Modified Fenton's), varying the iron catalysts and iron ratios. Since there was variability in the wastewater, four separate batches were used to block in statistical analyses (Sec. 3.6). The ratio of COD at the end of the reaction period to that present initially ( $COD_F/COD_o$ ) was used as the benchmark response variable for determining oxidant effectiveness. The lowest  $COD_F/COD_o$  values signify the greatest amount of COD reduction in the wastewater samples.  $COD_F$  values for Fenton's Reagent, Modified Fenton's and potassium permanganate are represented in Table A-11, Table A-12 and Table A-13 respectively of the Appendix. Flocculent production, pH and temperature change were all noted but were secondary considerations in the selection of favourable operating parameters.

#### **4.1.1 Fenton's Reagent**

Characteristics of each of the 4 wastewater batches obtained from Stella Jones Inc. and used as a blocking factor in the Fenton's Reagent screening trial are shown in Table 4-1.

##### ***4.1.1.1 Reduction in Chemical Oxygen Demand (COD)***

To satisfy the assumptions of normality and constant variance the  $COD_F/COD_o$  data were transformed using a cubed root transformation. Statistics were done on the transformed data but untransformed data are presented in Table 4-2. Treatments are listed in order of their  $COD_F/COD_o$ .



Following an ANOVA a significant difference between treatment means and blocks were identified ( $p < 0.05$ ; Table A-15). A Tukey's HSD was performed and letter groupings are outlined in Table 4-2 below.

**Table 4-1:** Characteristics of wood preservative treatment wastewater batches (blocking factor) used for assessment of the ability of Fenton's Reagent to reduce chemical oxygen demand.

Batch	COD <sub>o</sub> (mg/L)	Pole Species	pH	Temperature (°C)
1	10960	Red Pine	4.91	22.6
2	6230	Red Pine	4.62	23.1
3	13040	Red Pine	4.08	22.4
4	14160	Southern Yellow	4.25	22.5

It can be seen from Table 4-2 that the highest COD<sub>F</sub>/COD<sub>o</sub> values tend to occur in treatments that used the lowest amount of oxidant (50% stoichiometric weight ratios) while the lowest COD<sub>F</sub>/COD<sub>o</sub> values tend to occur in treatments using greater amounts of oxidant (150/100% stoichiometric weight ratios). There are 10 treatments that have the lowest COD<sub>F</sub>/COD<sub>o</sub> values (sharing the letter grouping 'H'). Among these 10 treatments are both ferrous sulfate (6 treatments) and ferrous chloride (4 treatments) iron catalysts. All treatments having hydrogen peroxide additions without an iron catalyst were found to have increased COD<sub>F</sub>/COD<sub>o</sub> values ranging from 1.15-1.50. A reduction in COD<sub>F</sub>/COD<sub>o</sub> was observed by the control that had no oxidants added but which underwent the same mixing method as the other samples. It is worth noting that all true Fenton's Reagent combinations (containing hydrogen peroxide and iron

**Table 4-2:** Effect of amount of hydrogen peroxide added, form of ferrous iron catalyst and iron ratio on reduction in chemical oxygen demand ( $COD_F/COD_o$ ) in the screening trial for 3 hours. Means followed by different letters are significantly different at  $p \leq 0.05$ .

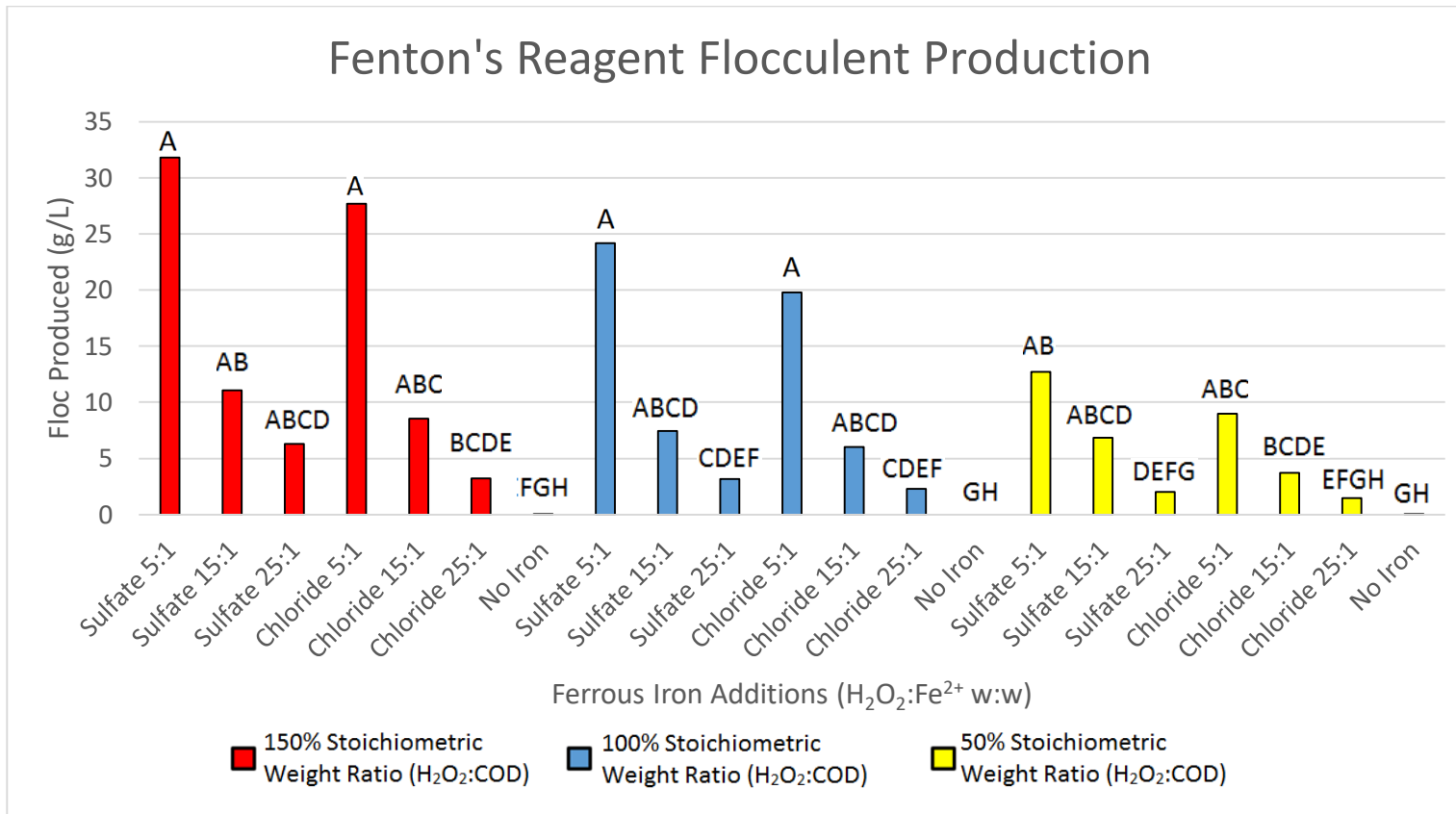
H <sub>2</sub> O <sub>2</sub> :COD Stoichiometric Weight Ratio (%)	Ferrous Catalyst	Iron Ratio (H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> )	N	Mean $COD_F/COD_o$	Standard Deviation	Tukey's Letter Grouping
150	None	None	4	1.50	0.46	A
100	None	None	4	1.38	0.25	A B
50	None	None	4	1.15	0.12	A B
0 (Control)	None	None	4	0.89	0.069	B
50	Sulfate	25:1	4	0.48	0.25	C
50	Sulfate	15:1	4	0.39	0.18	C D
50	Chloride	5:1	4	0.38	0.029	C D
50	Sulfate	5:1	4	0.35	0.064	C D
50	Chloride	25:1	4	0.33	0.083	C D
50	Chloride	15:1	4	0.31	0.056	C D E
100	Chloride	5:1	4	0.27	0.022	C D E F
150	Chloride	5:1	4	0.24	0.033	D E F G
100	Chloride	15:1	4	0.16	0.028	E F G H
100	Sulfate	5:1	4	0.15	0.022	E F G H
100	Chloride	25:1	4	0.15	0.026	E F G H
150	Chloride	15:1	4	0.13	0.036	F G H
150	Chloride	25:1	4	0.11	0.037	G H
100	Sulfate	15:1	4	0.10	0.039	H
100	Sulfate	25:1	4	0.10	0.047	H
150	Sulfate	5:1	4	0.07	0.032	H
150	Sulfate	25:1	4	0.07	0.038	H
150	Sulfate	15:1	4	0.06	0.039	H

catalysts) were found to have significantly reduced  $COD_F/COD_o$  values compared to the control.

Values were <0.48 which is a >52% reduction in the COD of the wastewater.

#### 4.1.1.2 Flocculent Production

To satisfy the assumptions of normality and constant variance the flocculent data were transformed using a  $1/x$  transformation. Statistics were done on the transformed data but untransformed data are presented in Figure 4-1. Following an ANOVA a significant difference



**Figure 4-1:** Average cumulative flocculent production for the reduction in chemical oxygen demand as a result of the addition of Fenton's Reagent using different amounts of hydrogen peroxide, different iron catalysts and different iron ratios. Means with different letters are significantly different at  $p \leq 0.05$ .

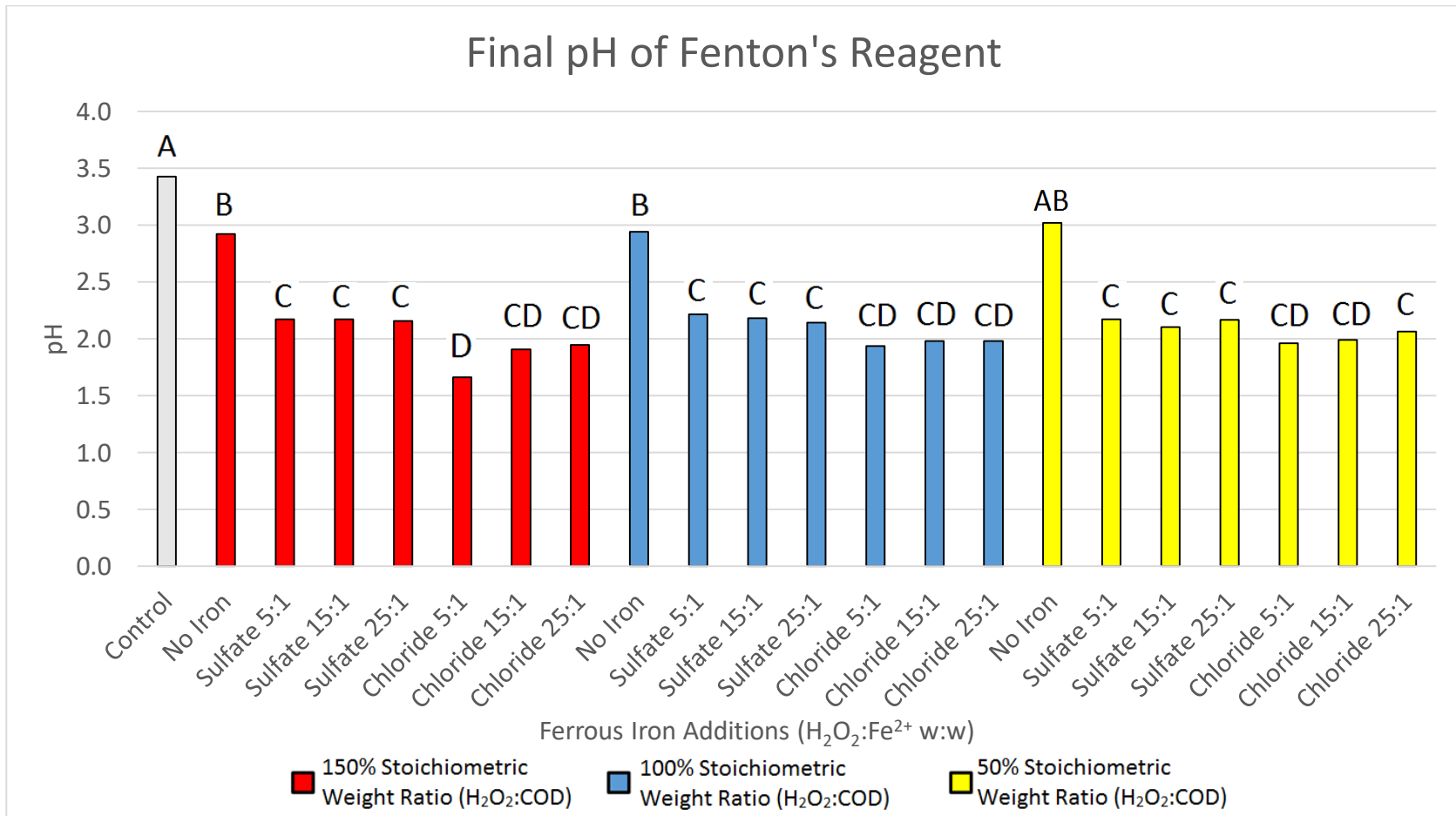
between treatment means was identified ( $p < 0.05$ ). The cumulative amount of flocculent that was produced from filtering directly after the 3 h reaction period, filtering after adjusting the pH to 7 and after drying down of the samples is presented in Figure 4-1 with Tukey's HSD letter groupings. Flocculent production results were highly variable due to variations in  $\text{COD}_o$  of the wastewater batches (refer to Table 4-1). All results had the control (no  $\text{H}_2\text{O}_2$  added) subtracted from each sample in order to determine flocculent production attributed to oxidant addition. The ANOVA was performed on data after the control was subtracted.

Many treatments indicated no significant difference in flocculent production. The general trend noted was a decrease in flocculent production as oxidant weight ratios were decreased from 150% to 50%. A decrease in flocculent production was noted as iron ratios were decreased from 5:1 to 25:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ). Less flocculent production was observed by ferrous chloride treatments when compared to that of ferrous sulfate although this was not significantly different. Little to no flocculent production was observed for all treatments with hydrogen peroxide but no iron addition.

#### ***4.1.1.3 pH Change***

The pH change over time was recorded for qualitative purposes to observe trends and as such an ANOVA was only performed on the final pH taken after the 3 h reaction period. The trend noted was a decrease of pH over the first 30 min and little change occurred following the remainder of the 3 h reaction. No transformation was required to satisfy the assumptions of normality and constant variance of the final pH data. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ). Final pH treatments are labeled with their Tukey's HSD letter groupings (Figure 4-2).

Across all stoichiometric treatments containing true Fenton's chemistry (combination of peroxide and iron) a drop in final pH by 1 unit or greater can be seen in comparison to the control.



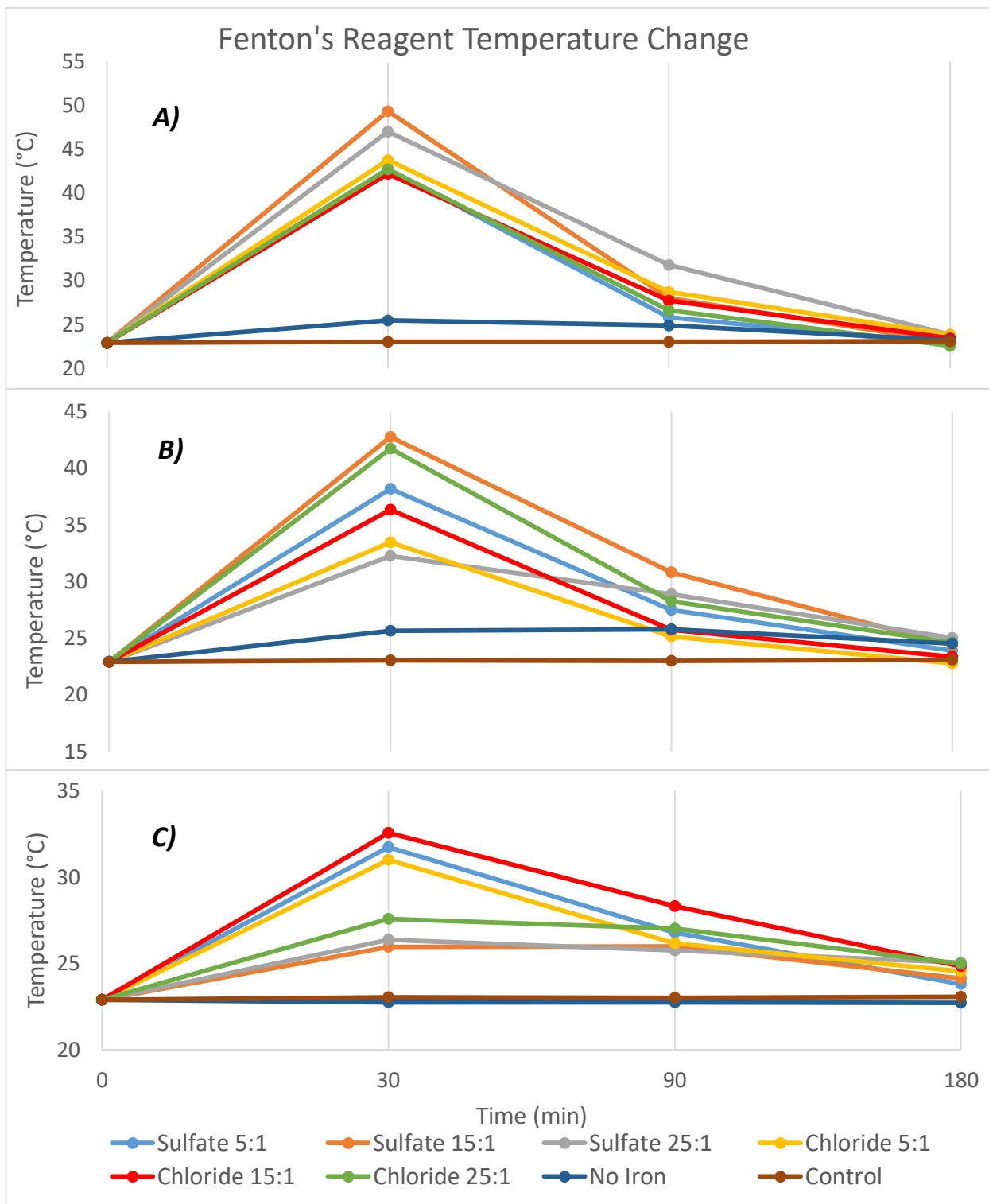
**Figure 4-2:** Final pH of wastewater after a 3 h reaction period following Fenton's Reagent using different amounts of hydrogen peroxide, different iron catalysts and different iron ratios. Means with different letters are significantly different at  $p \leq 0.05$ .

The true Fenton chemistry combinations demonstrated no significant differences for varying stoichiometric weight ratios (150%, 100% and 50%) except for the 150% hydrogen peroxide 5:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  w/w) ferrous chloride treatment. An approximate pH drop of 0.5 was observed by hydrogen peroxide with no iron additions compared to the control and were not significantly different from one another, indicating that a change in the sample chemistry had occurred.

#### ***4.1.1.4 Temperature Change***

The temperature change over time was recorded for qualitative purposes to observe trends and examine spikes in temperature that may be of concern if Fenton's Reagent is to be implemented at full scale at Stella Jones Inc. (Atlantic Canada). An ANOVA was not performed on these data. Temperature changes over time is presented below (Figure 4-3): note differences in the Y-axis temperatures.

Across all stoichiometric treatments containing true Fenton's chemistry (peroxide and iron) sharp increases in temperature of the treated samples (+10 to 33°C) was observed with eventual cooling occurring. For the majority of these treatments the increase was within the first 30 min with the temperature decreasing after 90 min. Greater concentrations of hydrogen peroxide in Fenton's Reagent resulted in greater temperature increases. Reduced temperature increases were observed by hydrogen peroxide addition without iron catalysts, and only at higher concentrations (Figure 4-3A & 4-3B). No change in temperature was observed by the 50% hydrogen peroxide loading concentration with no iron (Figure 4-3C) relative to the control treatment (no oxidant). By 180 min the data for all treatments demonstrated decreasing temperatures with many returning back close to room temperature.



**Figure 4-3:** Temperature change of wastewater after a 3 h reaction period following Fenton's Reagent using A) 150%, B) 100% and C) 50% stoichiometric weight ratio concentrations ( $H_2O_2:COD$ ) with different iron catalysts and different iron ratios.

### 4.1.2 Modified Fenton's Reagent

Characteristics of each of the 4 wastewater batches obtained from Stella Jones Inc. and used as a blocking factor in the Modified Fenton's screening trial are shown in Table 4-3.

**Table 4-3:** Characteristics of wood preservative treatment wastewater batches (blocking factor) used for assessment of the ability of Modified Fenton's to reduce chemical oxygen demand.

Batch	COD <sub>o</sub> (mg/L)	Pole Species	pH	Temperature (°C)
1	11820	Douglas Fir	3.98	22.3
2	12855	Douglas Fir	4.25	21.5
3	12765	Douglas Fir	3.79	21.9
4	10770	Douglas Fir	4.61	22.1

#### 4.1.2.1 Reduction in Chemical Oxygen Demand (COD)

To satisfy the assumptions of normality and constant variance the COD<sub>F</sub>/COD<sub>o</sub> data were transformed using a 1/x<sup>2</sup> transformation. Statistics were done on the transformed data but untransformed data are presented in Table 4-4. Treatments are listed in order of their COD<sub>F</sub>/COD<sub>o</sub>. Following an ANOVA a significant difference between treatment means and blocks were identified (p<0.05; Table A-15). A Tukey's HSD was performed and letter groupings are outlined in Table 4-4 below.

It can be seen from Table 4-4 that the highest COD<sub>F</sub>/COD<sub>o</sub> tend to occur in treatments that use the lowest amount of oxidant (50% stoichiometric weight ratios) while the lowest COD<sub>F</sub>/COD<sub>o</sub> values tend to occur in treatments using greater amounts of oxidant (150/100% stoichiometric weight ratios). There are 14 different treatments that have lowest COD<sub>F</sub>/COD<sub>o</sub> values (sharing the letter grouping 'E'). Among these 14 are both ferrous sulfate (7 treatments) and ferrous chloride



**Table 4-4:** Effect of amount of Modified Fenton's added, form of ferrous iron catalyst and iron ratio on reduction in chemical oxygen demand ( $COD_F/COD_o$ ) in the screening trial for 3 hours. Means followed by different letters are significantly different at  $p \leq 0.05$ .

CaO <sub>2</sub> :COD Stoichiometric Weight Ratio (%)	Ferrous Catalyst	Iron Ratio (H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> )	N	Mean COD <sub>F</sub> /COD <sub>o</sub>	Standard Deviation	Tukey's Letter Grouping
0 (Control)	None	None	4	0.88	0.110	A
50	None	None	4	0.66	0.066	B
100	None	None	4	0.65	0.061	B
50	Sulfate	25:1	4	0.64	0.055	B C
50	Sulfate	15:1	4	0.64	0.073	B C
50	Chloride	25:1	4	0.63	0.055	B C
150	None	None	4	0.62	0.054	B C
50	Chloride	15:1	4	0.62	0.045	B C D
50	Sulfate	5:1	4	0.61	0.066	B C D E
50	Chloride	5:1	4	0.60	0.063	B C D E
100	Sulfate	15:1	4	0.59	0.072	B C D E
100	Chloride	25:1	4	0.59	0.071	B C D E
150	Chloride	25:1	4	0.57	0.076	B C D E
150	Sulfate	15:1	4	0.57	0.070	B C D E
150	Sulfate	25:1	4	0.57	0.066	B C D E
100	Chloride	15:1	4	0.57	0.070	B C D E
100	Sulfate	25:1	4	0.57	0.075	B C D E
100	Sulfate	5:1	4	0.55	0.069	C D E
150	Chloride	5:1	4	0.53	0.080	D E
150	Chloride	15:1	4	0.53	0.070	E
150	Sulfate	5:1	4	0.53	0.058	E
100	Chloride	5:1	4	0.53	0.080	E

(7 treatments) iron catalysts. All treatments that have calcium peroxide additions without iron catalysts were observed to have decreased  $COD_F/COD_o$  values. The control itself had a reduction in  $COD_F/COD_o$  having no oxidants added and undergoing the same mixing method as the other samples. All treatments were found to have significantly reduced  $COD_F/COD_o$  compared to the control with values  $< 0.66$  which is a  $> 34\%$  reduction in the COD of the wastewater.

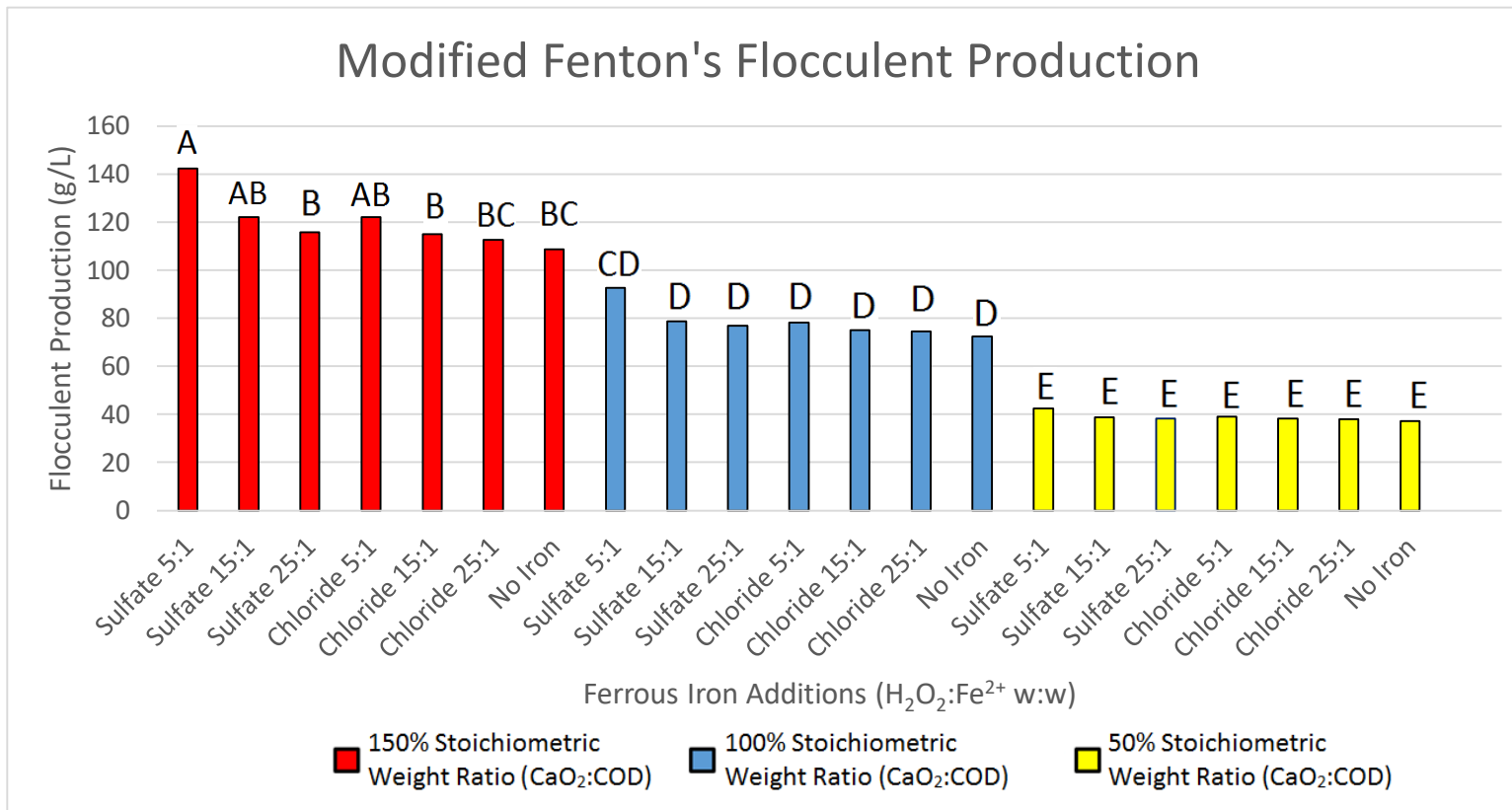
#### **4.1.2.2 Flocculent Production**

No transformation was required to satisfy the assumptions of normality and constant variance of the flocculent data. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ). A Tukey's HSD was performed and letter groupings are included in flocculent production outlined in Figure 4-4 below.

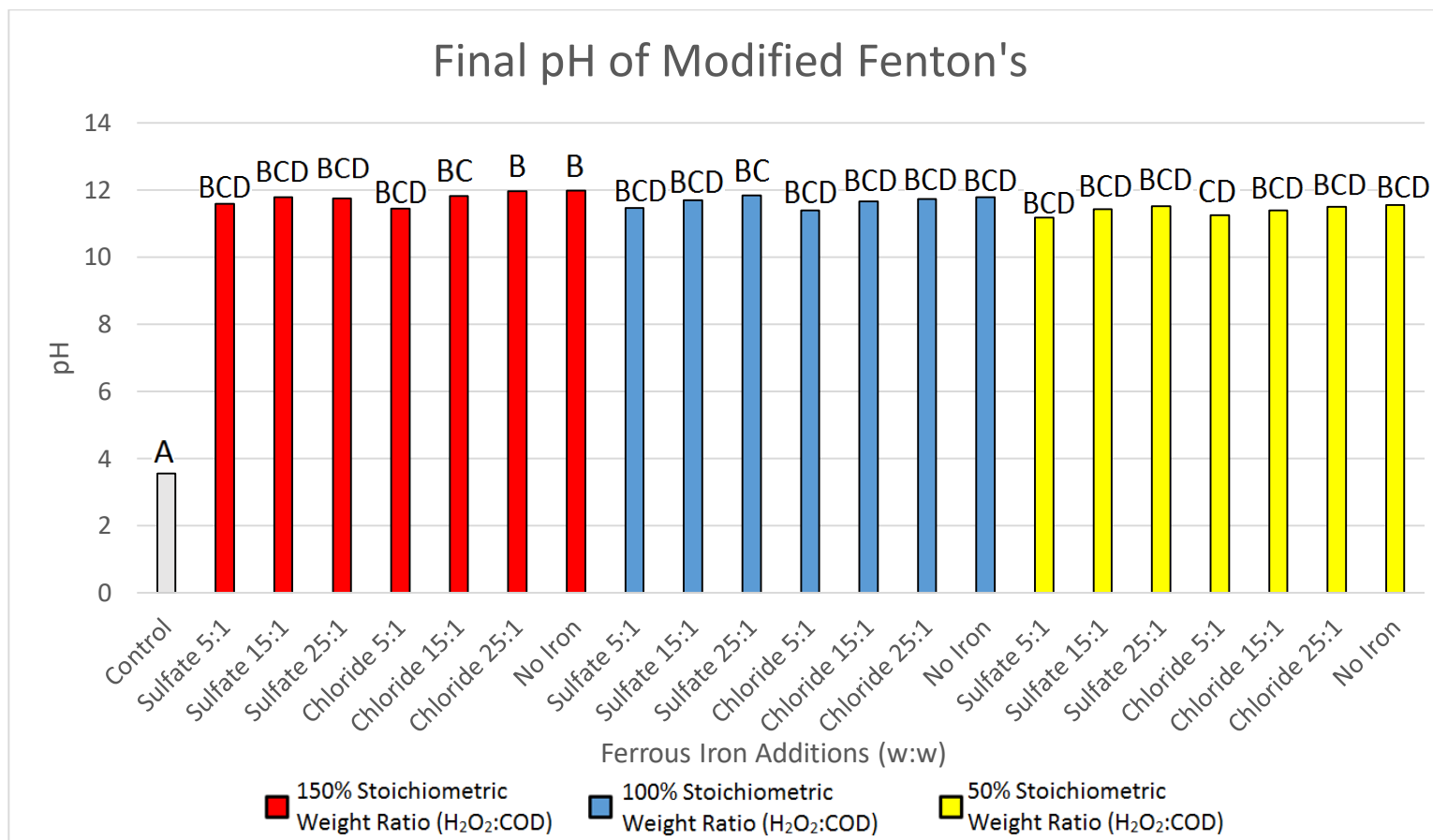
As calcium peroxide additions were increased in Modified Fenton's, significantly increased flocculent production was also observed. For the 150% stoichiometric weight ratio treatments, only the 5:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ ) ferrous sulfate treatment shows a significant difference. The 100/50% stoichiometric weight ratio treatments do not show any significant differences among varying iron catalysts or ratios. All treatments having calcium peroxide additions without an iron catalyst have no significant difference in flocculent production when compared to those containing iron catalysts of the same stoichiometric weight ratio treatments (excluding 150%, 5:1 ferrous sulfate).

#### **4.1.2.3 pH Change**

The pH change over time was recorded for qualitative purposes to observe trends and as such an ANOVA was only performed on the final pH taken after the 3 h reaction period. A sharp increase in pH over the first 30 min of the reaction, with a  $< 0.5$  unit increase in pH was observed following the remainder of the reaction. To satisfy the assumptions of normality and constant variance of the final pH data a cubed root transformation was required. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ). Final pH treatments are labeled with their Tukey's HSD letter groupings (Figure 4-5).



**Figure 4-4:** Average flocculent production for the reduction in chemical oxygen demand as a result of the addition of Modified Fenton's using different amounts of calcium peroxide, different iron catalysts and different iron ratios. Means followed by different letters are significantly different at  $p \leq 0.05$ .



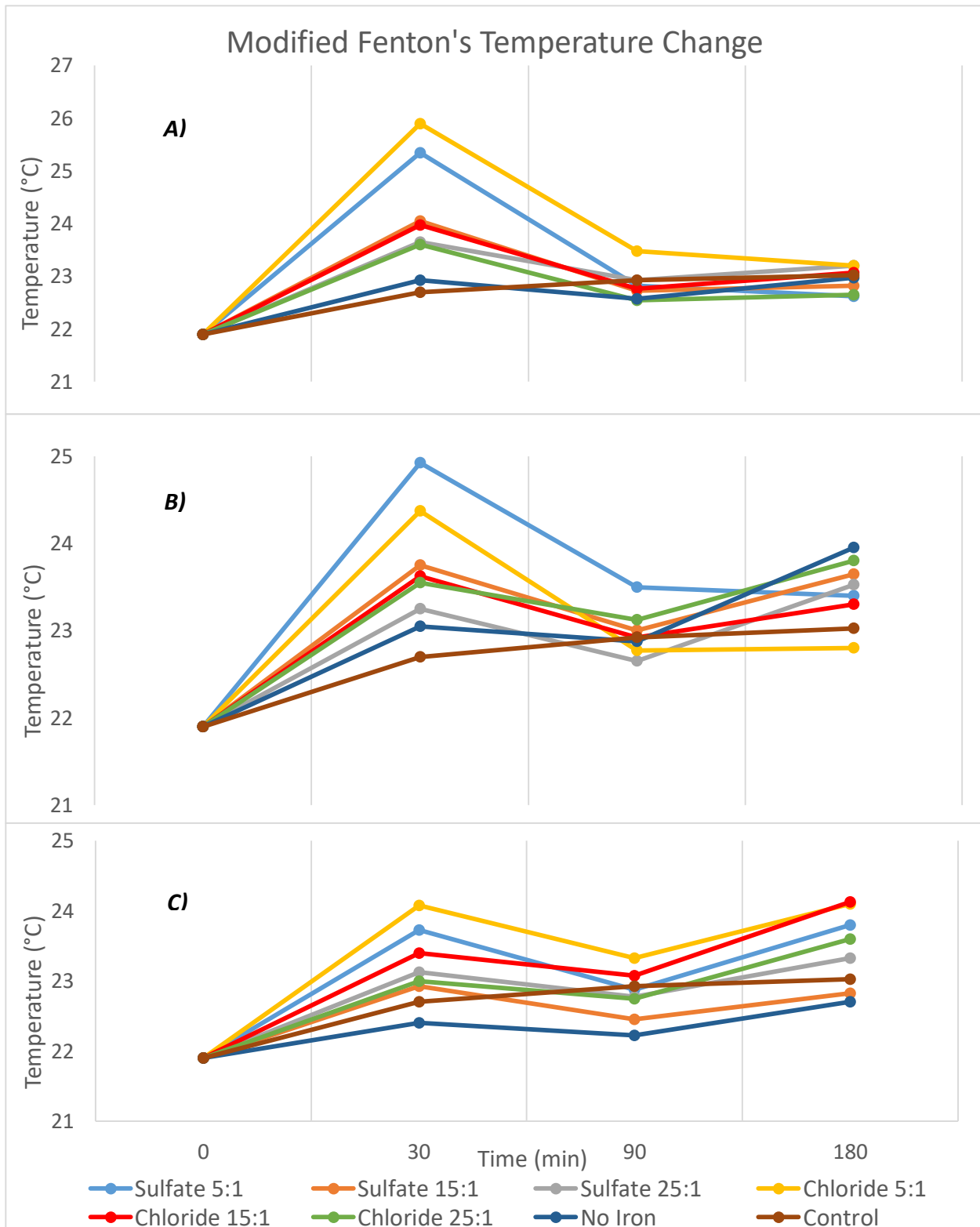
**Figure 4-5:** Final pH of wastewater after a 3 h reaction period following Modified Fenton's using different amounts of calcium peroxide, different iron catalysts and different iron ratios. Means with different letters are significantly different at  $p \leq 0.05$ .

All calcium peroxide stoichiometric weight ratio treatments (50-150%) resulted in a pH increase of ~11 or greater. No significant differences were observed between calcium peroxide with no iron additions and true Modified Fenton's combinations (calcium peroxide and iron). When examining the 150% weight ratios a maximum pH of ~12 was reached while at the 50% weight ratios maximum pH reached was ~11.6 however almost no significant differences were found for final pH values when increasing calcium peroxide stoichiometric weight ratios. The 150% weight ratio with 25:1 ferrous chloride and no iron addition were the exceptions, having significantly increased pH than the 50% weight ratio with 5:1 ferrous sulfate and ferrous chloride.

#### **4.1.2.4 Temperature Change**

The temperature change over time was recorded for qualitative purposes to observe trends and examine spikes in temperature that may be of concern if Modified Fenton's is to be implemented at full scale at Stella Jones. An ANOVA was not needed for these reasons. Temperature changes over time are presented below (Figure 4-6): note the slight differences in the Y-axis temperature.

Across all stoichiometric treatments an increase in temperature over the first 30 min was observed, followed by a decrease at 90 min, and a final increase at the 180 min mark. Higher concentrations of calcium peroxide in Modified Fenton's resulted in greater temperature increases. A high of 26°C in the 150% weight ratios (Fig. 4-6A) was seen compared to a low of 24°C in the 50% weight ratios (Fig. 4-6C). The greatest temperature increases were observed when 5:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  w/w) iron ratio treatments were used.



**Figure 4-6:** Temperature change of wastewater after a 3 h reaction period following Modified Fenton's using A) 150%, B) 100% and C) 50% stoichiometric weight ratio concentrations (CaO<sub>2</sub>:COD) with different iron catalysts and different iron ratios.

### 4.1.3 Permanganate

#### 4.1.3.1 Preliminary Work

The preliminary experiment was to address the residual purple colour of the potassium permanganate ion in oxidized samples. The presence of this ion may affect COD readings through chemical reactions or absorbance issues and was consequently investigated as a CRD outlined in Section 3.6.2.3 of the methods. The response variable for the preliminary work was final COD ( $COD_F$ ) of the water.

No transformation was required to satisfy the assumptions of normality and constant variance of the  $COD_F$  data. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ; Table A-15). A Tukey's HSD was performed and letter groupings are outlined in Table 4-5 below.

**Table 4-5:** Effect of amount of potassium permanganate added to deionized water and mixed for 3 hours on change in chemical oxygen demand. Means followed by different letters are significantly different at  $p \leq 0.05$ .

<b>KMnO<sub>4</sub>:COD Stoichiometric Weight Ratio (%)</b>	<b>N</b>	<b>Mean COD<sub>F</sub> (mg/L)</b>	<b>Standard Deviation (mg/L)</b>	<b>Tukey's Letter Grouping</b>	<b>Residual Purple Colour?</b>
<b>43.3</b>	4	12064	168	A	Yes
<b>36.1</b>	4	10128	160	B	Yes
<b>28.9</b>	4	8165	203	C	Yes
<b>21.7</b>	4	6163	150	D	Yes
<b>14.4</b>	4	4113	131	E	Yes
<b>7.5</b>	4	1950	159	F	Yes
<b>0 (control)</b>	4	8	10	G	N/A

Results from a Tukey’s HSD test confirms that in fact all means were significantly different from one another. Trends show that as the amount of permanganate added increased, a greater COD<sub>F</sub> was also observed. All permanganate treatment additions were found to have residual permanganate identified by the purple colour change of the solution.

#### **4.1.3.2 Screening Trial**

##### **4.1.3.2.1 Reduction in Chemical Oxygen Demand (COD)**

Following the preliminary investigation the full scale screening trial of the evaluation of permanganate’s COD reduction on wastewater batches was performed. Characteristics of each of the 4 wastewater batches obtained from Stella Jones Inc. and used as a blocking factor are shown in Table 4-6 below.

**Table 4-6:** Characteristics of wood preservative treatment wastewater batches (blocking factor) used for assessment of the ability of potassium permanganate to reduce chemical oxygen demand.

<b>Batch</b>	<b>COD<sub>o</sub> (mg/L)</b>	<b>Pole Species</b>	<b>pH</b>	<b>Temperature (°C)</b>
<b>1</b>	14080	Southern Yellow	3.81	23.2
<b>2</b>	14095	Southern Yellow	4.26	22.5
<b>3</b>	15490	Douglas Fir	4.45	22.5
<b>4</b>	14530	Douglas Fir	4.13	22.5

No transformation was required to satisfy the assumptions of normality and constant variance of the COD<sub>F</sub>/COD<sub>o</sub> data. Following an ANOVA a significant difference between treatment means and blocks were identified ( $p < 0.05$ ; Table A-15). A Tukey’s HSD was performed and letter groupings are outlined in Table 4-7 below.



**Table 4-7:** Effect of amount of potassium permanganate on reduction in chemical oxygen demand ( $COD_F/COD_o$ ) for 3 hours in the screening trial.

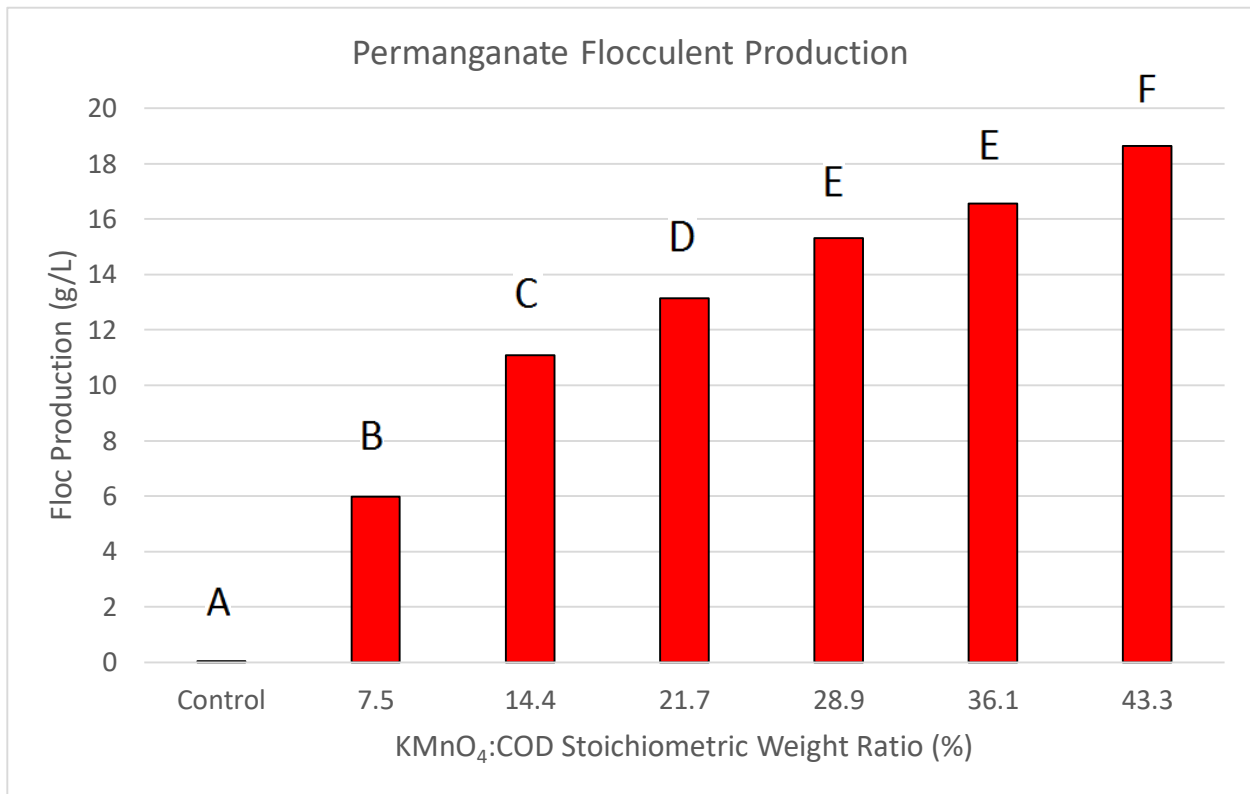
<b>KMnO<sub>4</sub>:COD Stoichiometric Weight Ratio (%)</b>	<b>N</b>	<b>Mean COD<sub>F</sub>/COD<sub>o</sub></b>	<b>Standard Deviation</b>	<b>Tukey's Letter Grouping</b>	<b>Residual Purple Colour?</b>
<b>0 (control)</b>	4	0.97	0.036	A	N/A
<b>7.5</b>	4	0.73	0.082	B	No
<b>14.4</b>	4	0.71	0.048	B	No
<b>43.3</b>	4	0.70	0.028	B	Yes
<b>28.9</b>	4	0.70	0.037	B	Yes
<b>36.1</b>	4	0.69	0.036	B	Yes
<b>21.7</b>	4	0.69	0.039	B	Yes

The amount of reduction in  $COD_F/COD_o$  values varied from 0.73-0.69 (or 27-31%). These values however were not significantly different from one another, other than the control. Residual purple permanganate was observed for all treatments except for the 7.5% and 14.4% weight ratio treatments.

#### 4.1.3.2.2 Flocculent Production

Due to experimental error, pH was not recorded over time and temperature was also not recorded. The pH was recorded only at the end of the 3 hour mixing period. Flocculent production was also recorded.

No transformation was required to satisfy the assumptions of normality and constant variance of the flocculent data. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ). A Tukey's HSD was performed and letter groupings are included in flocculent production outlined in Figure 4-7 below.



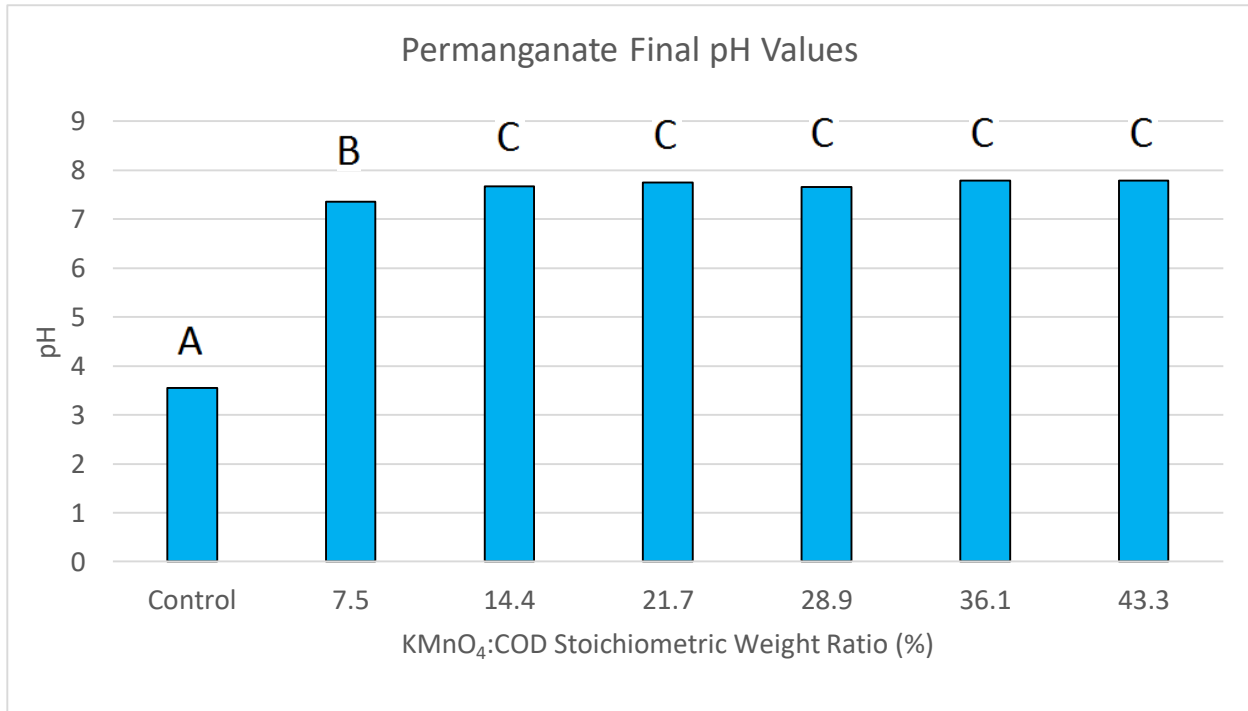
**Figure 4-7:** Flocculent production for the reduction in chemical oxygen demand as a result of the addition of potassium permanganate at varying stoichiometric weight ratio concentrations (KMnO<sub>4</sub>:COD).

The amount of flocculent ranged from ~6 g/L to ~18 g/L for 7.5% and 43.3% weight ratios respectively. Increased amounts of potassium permanganate resulted in greater flocculent production. With each increase in weight ratio addition, significant increases in flocculent production were observed for all treatments except between the 28.9% and 36.1% weight ratios.

#### 4.1.3.2.3 pH Change

To satisfy the assumptions of normality and constant variance of the final pH data a square root transformation was required. Statistics were done on the transformed data but untransformed

data are presented in Figure 4-8. Following an ANOVA a significant difference between treatment means was identified ( $p < 0.05$ ). A Tukey's HSD was performed and letter groupings are included in flocculent production outlined in Figure 4-8 below.



**Figure 4-8:** Final pH of wastewater after 3 h following the addition of potassium permanganate at varying stoichiometric weight ratio concentrations (KMnO<sub>4</sub>:COD).

All permanganate treatments resulted in an increase in pH and were approximately within the neutral range (~7). Of these treatments only the 7.5% stoichiometric weight ratio demonstrated a significantly lower pH than other treatments.

## **4.2 Reduction of Polycyclic Aromatic Hydrocarbons and Pentachlorophenol**

### **4.2.1 Extraction Validation**

Deionized water was spiked with known concentrations of 18 PAHs and PCP to determine the effectiveness of USEPA's extraction and concentration method 3510C "Separatory Funnel Liquid-Liquid Extraction". Results are shown in Table 4-8.

When averaged across all compounds, there was a 77% recovery. The lowest % recovery was shown by naphthalene (51.9%) while the highest was shown by benzo(k)fluoranthene (95%). Variability among the samples was relatively low (C.V.<10%), indicating reproducible results. Exceptions include naphthalene, 1/2-methylnaphthalene, 2,4,6-tribromophenol and PCP with a relatively high C.V. PCP was notably the compound with the lowest accuracy and precision with a % recovery of 64% and a C.V. 34% calling into question both the accuracy and precision of this measurement. Even including the compounds having high C.V., the average C.V. for the compounds examined was only 11%. Higher variations were found for PAHs that had lower molecular weight.

### **4.2.2 Laboratory Validation**

Four hidden standards were prepared and sent with the experimental samples in order to address the accuracy and reproducibility of AGAT Laboratories. Results are shown below in Table 4-9.

**Table 4-8:** Validation of EPA method 3510C. Means, standard deviations (S.D.), coefficients of variation and % recoveries are included.

Compound	RDL (mg/L)	Spike Concentration (mg/L)	Reported Mean (mg/L)	S.D. (±mg/L)	C.V. (%)	% Recovery
Naphthalene	0.30	50.1	26.0	4.1	16	52
1-Methylnaphthalene	0.50	49.8	43.3	6.4	15	87
2-Methylnaphthalene	0.50	49.4	43.3	6.4	15	88
Acenaphthylene	0.31	99.3	66.2	6.8	10	67
Acenaphthene	0.30	49.7	30.2	3.5	12	61
Fluorene	0.31	10.1	8.1	0.6	7	80
Phenanthrene	0.32	5.0	4.2	0.2	5	83
Anthracene	0.30	5.0	3.4	0.2	6	68
Fluoranthene	0.27	10.1	8.8	0.5	6	87
Pyrene	0.20	5.0	4.3	0.2	5	86
Benzo(a)anthracene	0.20	5.1	4.0	0.2	5	79
Chrysene	0.27	5.1	4.3	0.3	7	84
Benzo(b)fluoranthene	0.20	10.1	8.2	1.1	13	81
Benzo(k)fluoranthene	0.20	5.1	4.8	0.6	13	95
Benzo(a)pyrene	0.09	5.0	3.3	0.2	6	67
Indeno(1,2,3- cd)pyrene	0.27	5.0	4.2	0.5	12	84
Dibenz(a,h)anthracene	0.20	10.0	7.1	1.0	14	70
Benzo(g,h,i)perylene	0.20	9.9	7.2	0.9	12	75
Pentachlorophenol	0.50	50.0	30.2	10.2	34	64
2,4,6-tribromophenol <sup>s</sup>	N/A	10.00	8.9	1.5	17	89
Chrysene-d12 <sup>s</sup>	N/A	10.00	8.3	0.5	6	82
				Average	11	77

Contaminants extracted from deionized water using dichloromethane and were quantified using a Gas-Chromatograph Mass-Spectrophotometer.

RDL – Reported Detection Limits

<sup>s</sup> – Surrogate Compound

**Table 4-9:** Analyses of hidden standards for the validation of AGAT Laboratories for precision and accuracy. Means, standard deviations, coefficients of variation and % recoveries are included.

Compound	RDL (mg/L)	Hidden Std. Conc. (mg/L)	Measured Conc.(mg/L)	S.D. (±mg/L)	C.V. (%)	% Recovery
Naphthalene	0.02	4.00	4.15	0.31	7	101
1-Methylnaphthalene	0.50	3.98	3.85	0.31	8	97
2-Methylnaphthalene	0.50	3.95	4.33	0.33	8	109
Acenaphthylene	0.02	7.94	6.38	0.33	5	80
Acenaphthene	0.02	3.97	3.43	0.10	3	86
Fluorene	0.02	0.81	0.58	0.08	14	71
Phenanthrene	0.01	0.40	0.39	0.02	5	98
Anthracene	0.01	0.40	0.40	0.04	10	99
Fluoranthene	0.02	0.80	0.67	0.04	6	84
Pyrene	0.02	0.40	0.32	0.02	6	80
Benzo(a)anthracene	0.02	0.41	0.18	0.04	22	43
Chrysene	0.01	0.41	0.28	0.02	10	68
Benzo(b)fluoranthene	0.01	0.81	0.65	0.07	11	80
Benzo(k)fluoranthene	0.01	0.40	0.75	0.16	21	185
Benzo(a)pyrene	0.01	0.40	0.33	0.05	15	82
Indeno(1,2,3-cd)pyrene	0.02	0.40	0.29	0.01	3	72
Dibenz(a,h)anthracene	0.02	0.80	0.49	0.03	6	61
Benzo(g,h,i)perylene	0.02	0.79	0.50	0.03	6	63
Pentachlorophenol	0.50	10.00	5.75	2.7	47	58
2,4,6-tribromophenol <sup>S</sup>	N/A	10.00	9.9	2.5	25	99
Chrysene-d12 <sup>S</sup>	N/A	10.00	7.1	0.6	8	71

RDL – Reported Detection Limits

<sup>S</sup> – Surrogate Compound

Good accuracy (with >80% recoveries) and reasonable precision (with C.V. < 10%) were noted for the majority of compounds. Fluorene, benzo(a)anthracene, chrysene and pentachlorophenol demonstrated both poor accuracy (<75% recoveries) and precision (C.V. >10%). Compounds reported to have greater concentrations in the hidden standard than the quantified concentrations included naphthalene, 1-methylnaphthalene and benzo(k)fluoranthene.

The greatest deviation from known concentration and greatest C.V. of all compounds in the hidden standards was again shown to be PCP, further calling into question the accuracy and precision of this measurement.

#### 4.2.3 PAH Reduction Results

The effectiveness of FR<sub>100%</sub><sup>25:1</sup>, MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4</sub> 7.5% to reduce the concentration of PAHs was evaluated. Similarly to COD<sub>F</sub>/COD<sub>o</sub>, the response variable for the compounds being examined was based on C<sub>F</sub>/C<sub>o</sub>. COD<sub>F</sub>/COD<sub>o</sub> results were also recorded to examine comparable reproducibility results obtained from Section 4.1, while PCP was reported for observational purposes. COD<sub>F</sub> and C<sub>F</sub> values for FR<sub>100%</sub><sup>25:1</sup>, MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4</sub> 7.5% are represented in Table A-14 of the Appendix. Characteristics of each of the 4 wastewater batches obtained from Stella Jones Inc. and used in the reduction study are shown in Table 4-10 below.

**Table 4-10:** Characteristics of wood preservative treatment wastewater batches (blocking factor) used for assessment of the ability of Fenton’s Reagent, Modified Fenton’s and potassium permanganate to reduce PAHs/PCP.

Batch	COD <sub>o</sub> (mg/L)	Pole Species	pH	Temperature (°C)
1	10715	Red Pine	5.03	22.6
2	12930	Red Pine	4.11	23.7
3	10695	Red Pine	4.52	23.2
4	9815	Red Pine	4.22	22.9

The reduction in chemical oxygen demand (COD<sub>F</sub>/COD<sub>o</sub>) and the reduction of levels of examined contaminants (C<sub>F</sub>/C<sub>o</sub>) for all but 4 were found to have normality and constant variance and no data transformation was needed. The 4 examined contaminants that did not exhibit

normality and constant variance included; benz(k)fluorene, indeno(1 2 3-cd)pyrene, dibenzo(a h)anthracene and benzo(g h i)perylene. A square root transformation was performed on each and the resulting transformed data were found to exhibit normality and constant variance. Untransformed data are reported in Table 4-11.

A significant ( $p \leq 0.05$ ) effect of choice of oxidant on reductions in  $COD_F/COD_o$  and  $C_F/C_o$  (for 15/19 of the compounds) was observed (Table A-16).  $C_F/C_o$  values for PCP, indeno(123-cd)pyrene, dibenzo(ah)anthracene and benzo(ghi)perylene were found to not be significantly changed as a result of the addition of an oxidant or the choice of oxidant. Only  $COD_F/COD_o$  displayed a significant blocking effect (Table A-16). In order to determine whether there was a significant influence of choice of oxidant addition on the reduction in wastewater composition, a Tukey's HSD test was performed comparing means for each compound (Table 4-11).

$FR_{100\%}^{25:1}$ ,  $MF_{50\%}^{5:1}$  and  $KMnO_4$  7.5% had  $COD_F/COD_o$  values of 0.14, 0.54 and 0.59 respectively. These values were significantly different from one another indicating that oxidant effectiveness at reducing COD decreased in the order of Fenton's Reagent > Modified Fenton's > permanganate > no oxidant.

The three oxidants demonstrated similar capacity to reduce the concentration of PAHs in wastewater samples and were not statistically different from one another for 2-ringed PAHs to 4-ringed PAHs (Refer to Table 1-1 to for ring structures). These compounds had  $C_F/C_o$  values of <0.22 which is equivalent to a 78% or greater reduction. This trend continues up until benzo(a)anthracene and other 5-6 ringed PAHs in which  $FR_{100\%}^{25:1}$  shows less reduction. No difference was observed for  $FR_{100\%}^{25:1}$  from the control for the majority of 5-6 ringed PAHs, indicating an inability of  $FR_{100\%}^{25:1}$  to reduce these PAHs to the extent of  $MF_{50\%}^{5:1}$  and  $KMnO_4$  7.5%. The inability of the  $FR_{100\%}^{25:1}$  to lower  $C_F/C_o$  values for larger ringed PAHs is also



**Table 4-11:** Concentration reduction ( $COD_F/COD_o$  or  $C_F/C_o$ ) as a result of treatment with Fenton's Reagent, Modified Fenton's and permanganate for 3 hours. Means  $\pm$  standard deviation. Means followed by different letters are significantly different at  $p \leq 0.05$  with each row considered separately.

Compound	FR <sub>100%</sub> <sup>25:1</sup>	MF <sub>50%</sub> <sup>5:1</sup>	KMnO <sub>4</sub> 7.5%	Control
<b>COD</b>	0.14 $\pm$ 0.05 D	0.54 $\pm$ 0.04 C	0.59 $\pm$ 0.04 B	0.92 $\pm$ 0.02 A
<b>Naphthalene</b>	0.01 $\pm$ 0.01 B	0.24 $\pm$ 0.11 B	0.14 $\pm$ 0.04 B	1.12 $\pm$ 0.30 A
<b>1-Methylnaphthalene</b>	0.00 $\pm$ 0.00 B	0.07 $\pm$ 0.03 B	0.05 $\pm$ 0.02 B	0.80 $\pm$ 0.19 A
<b>2-Methylnaphthalene</b>	0.01 $\pm$ 0.02 B	0.07 $\pm$ 0.02 B	0.05 $\pm$ 0.01 B	0.85 $\pm$ 0.17 A
<b>Acenaphthylene</b>	0.01 $\pm$ 0.02 B	0.07 $\pm$ 0.02 B	0.02 $\pm$ 0.02 B	0.83 $\pm$ 0.28 A
<b>Acenaphthene</b>	0.02 $\pm$ 0.02 B	0.06 $\pm$ 0.02 B	0.03 $\pm$ 0.01 B	1.05 $\pm$ 0.04 A
<b>Fluorene</b>	0.13 $\pm$ 0.11 B	0.05 $\pm$ 0.02 B	0.02 $\pm$ 0.01 B	1.03 $\pm$ 0.09 A
<b>Phenanthrene</b>	0.22 $\pm$ 0.21 B	0.04 $\pm$ 0.02 B	0.01 $\pm$ 0.01 B	1.07 $\pm$ 0.10 A
<b>Anthracene</b>	0.07 $\pm$ 0.05 B	0.04 $\pm$ 0.02 B	0.01 $\pm$ 0.02 B	1.03 $\pm$ 0.06 A
<b>Fluoranthene</b>	0.21 $\pm$ 0.29 B	0.03 $\pm$ 0.02 B	0.01 $\pm$ 0.02 B	0.97 $\pm$ 0.13 A
<b>Pyrene</b>	0.39 $\pm$ 0.33 B	0.03 $\pm$ 0.02 B	0.01 $\pm$ 0.01 B	0.96 $\pm$ 0.15 A
<b>Benzo(a)anthracene</b>	0.59 $\pm$ 0.56 AB	0.03 $\pm$ 0.02 B	0.00 $\pm$ 0.01 B	0.89 $\pm$ 0.26 A
<b>Chrysene</b>	0.61 $\pm$ 0.50 A	0.03 $\pm$ 0.02 B	0.00 $\pm$ 0.01 B	0.82 $\pm$ 0.19 A
<b>Benzo(b)fluoranthene</b>	0.68 $\pm$ 0.66 AB	0.03 $\pm$ 0.02 B	0.01 $\pm$ 0.01 B	0.87 $\pm$ 0.27 A
<b>Benz(k) fluoranthene</b>	0.68 $\pm$ 0.65 AB	0.02 $\pm$ 0.01 B	0.00 $\pm$ 0.01 B	0.85 $\pm$ 0.11 A
<b>Benzo(a)pyrene</b>	0.54 $\pm$ 0.49 AB	0.02 $\pm$ 0.02 B	0.00 $\pm$ 0.01 B	0.86 $\pm$ 0.33 A
<b>Indeno(123-cd)pyrene<sup>1</sup></b>	0.43 $\pm$ 0.11 A	0.00 $\pm$ 0.00 A	0.00 $\pm$ 0.00 A	0.55 $\pm$ 0.78 A
<b>Dibenzo(ah)anthracene<sup>1</sup></b>	0.19 $\pm$ 0.27 A	0.00 $\pm$ 0.00 A	0.00 $\pm$ 0.00 A	0.00 $\pm$ 0.00 A
<b>Benz(ghi)perylene<sup>1</sup></b>	0.38 $\pm$ 0.15 A	0.00 $\pm$ 0.00 A	0.00 $\pm$ 0.00 A	0.53 $\pm$ 0.75 A
<b>Pentachlorophenol</b>	1.00 $\pm$ 1.23 A	3.67 $\pm$ 2.85 A	0.22 $\pm$ 0.36 A	2.22 $\pm$ 2.71 A

<sup>1</sup> N=2, compounds only present in 2/4 wastewater batches

reflected in the greater variability between blocked samples (S.D.>0.5). With the exception of dibenzo(ah)anthracene, FR<sub>100%</sub><sup>25:1</sup> resulted in reduction rates of 32-62% for the 4, 5 and 6-ringed PAH structures while both MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4</sub> 7.5% resulted in reduction rates of 97-100% over the same range of PAHs while also showing lower variability (Table 4-11).

There were no significant differences in  $C_F/C_o$  values for PCP as a result of the addition of oxidants. KMnO<sub>4</sub> 7.5% had the numerically lowest mean value and variability among samples. For both FR<sub>100%</sub><sup>25:1</sup>, MF<sub>50%</sub><sup>5:1</sup> and the control,  $C_F/C_o > 1$  values were obtained indicating an apparent

increase in PCP concentrations.  $FR_{100\%}^{25:1}$ ,  $MF_{50\%}^{5:1}$  and the control also had extremely high variability with a S.D. of 1.23 or greater. These results call into question the PCP data and may indicate methodological or analytical issues with the measurement of this compound.

### **4.3 Reaction Holding Time Optimization**

From Section 4.1, 4.2 it was determined that  $FR_{100\%}^{25:1}$  was the most effective oxidant to be used as a treatment option for wastewater produced from Stella Jones Inc. Optimization experiments were then used to determine how quickly the reaction came to completion.

#### **4.3.1 Low COD**

“Low” COD was defined as wastewater possessing a COD similar to the lowest COD observed in previous experimental sections (Section 4.1 and 4.2). The 3 h oxidation reactions were replicated 4 times on a single batch of Red Pine wastewater obtained from Stella Jones Inc. that was characterized by low COD. The characteristics of each replicate used are shown in Table 4-12 below.

**Table 4-12:** Characteristics of Red Pine treatment wastewater replicates used for assessment Fenton’s Reagent reaction optimization for low COD wastewater.

<b>Replicate</b>	<b>COD<sub>o</sub> (mg/L)</b>	<b>Pole Species</b>	<b>pH<sub>o</sub></b>	<b>Temperature (°C)</b>
<b>1</b>	7700	Red Pine	4.07	23.1
<b>2</b>	7630	Red Pine	4.10	23.1
<b>3</b>	7600	Red Pine	4.08	23.1
<b>4</b>	7670	Red Pine	4.08	23.1

After running several covariance structures for data obtained from low COD wastewater in a PROC Mix repeated measures version of ANOVA, the autoregressive heterogeneous structure

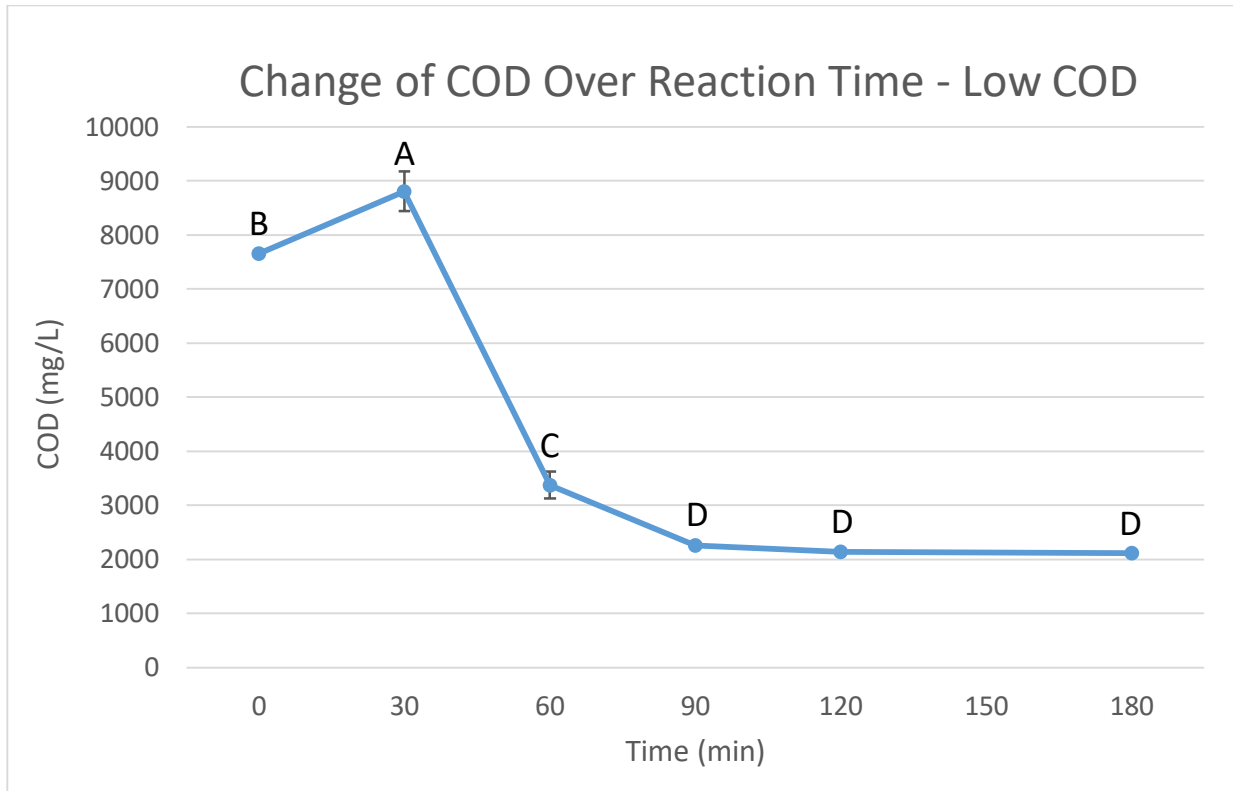
was used as this obtained the lowest AIC value. No transformation of the COD data were required to satisfy the assumptions of normality and constant variance. A repeated measures version of ANOVA identified a significant difference between time intervals ( $p < 0.05$ ). A Fisher's LSD was performed and letter groupings for each time interval is outlined below in Figure 4-9.

An initial increase in COD of the wastewater was observed over the first 30 min, followed by a sharp decrease in COD with the reduction leveling off at 90 min. After 90 min there was no significant reductions in COD which was noted by time intervals sharing the letter grouping D. The only notable variability (noted by standard deviation bars) was observed between replicates at the 30 and 60 min time intervals.

#### **4.3.2 High COD**

“High” COD was defined as wastewater possessing a COD similar to the highest COD observed in previous experimental sections (Section 4.1 and 4.2). The 3 h oxidation reactions were replicated 4 times on a single batch of Douglas Fir wastewater obtained from Stella Jones Inc. that was characterized by high COD. The characteristics of each replicate used are shown in Table 4-13.

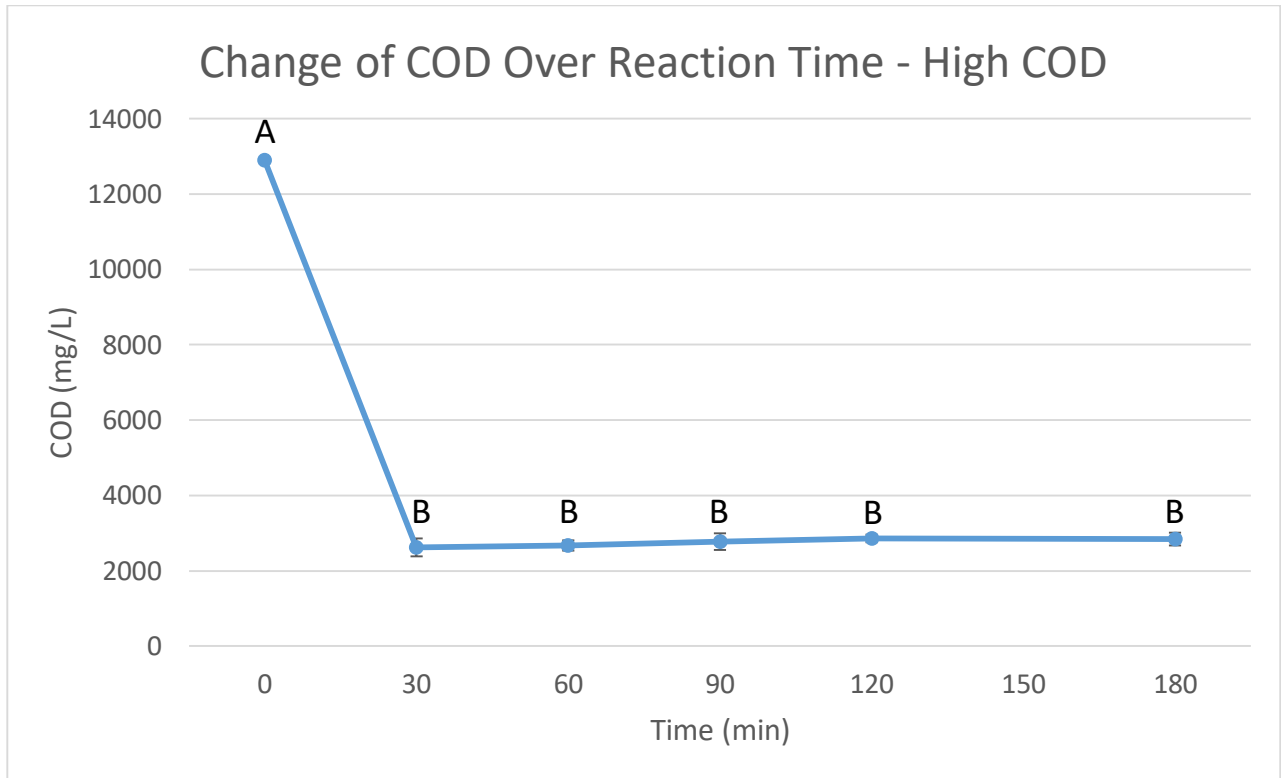
After running several covariance structures for data obtained from high COD wastewater in a PROC Mix repeated measures version of ANOVA, the autoregressive heterogeneous structure was used as this obtained the lowest AIC value. No transformation of the COD data were required to satisfy the assumptions of normality and constant variance. A repeated measures version of ANOVA identified significant difference between time intervals ( $p < 0.05$ ). A Fisher's LSD was performed and letter groupings for each time interval is outlined below (Figure 4-10).



**Figure 4-9:** Fenton's Reagent change of COD over a 3 h reaction period for low COD wastewater to optimize reaction holding time. Standard deviation bars are included. Means with different letters are significantly different at  $p \leq 0.05$ .

**Table 4-13:** Characteristics of Red Pine treatment wastewater replicates used for assessment Fenton's Reagent reaction optimization for high COD wastewater.

Replicate	COD <sub>0</sub> (mg/L)	Pole Species	pH <sub>0</sub>	Temperature (°C)
1	12930	Douglas Fir	4.37	22.8
2	12930	Douglas Fir	4.35	22.8
3	12900	Douglas Fir	4.35	22.8
4	12880	Douglas Fir	4.37	22.8



**Figure 4-10:** Fenton's Reagent change of COD over a 3 h reaction period for high COD wastewater to optimize reaction holding time. Standard deviation bars are included. Means with different letters are significantly different at  $p \leq 0.05$ .

The only time interval that was significantly different from the rest was found to be the original COD of the wastewater ( $t=0$ ). All COD reduction was observed in the first 30 min of the reaction with no significant differences occurring from 30 min to the 3 h reaction end time. Variability among samples in each time interval were relatively low.

## **Chapter 5 Discussion**

### **5.1 Screening Trials**

#### **5.1.1 Fenton's Reagent**

The  $COD_F/COD_o$  values greater than 1 observed by the 3 hydrogen peroxide additions without iron catalysts show a potential for peroxide interference in the COD measurement. The effect of hydrogen peroxide on COD has been reported to range from 8.5 mg COD/mmol  $H_2O_2$  to 20 mg COD/mmol  $H_2O_2$  (Wu & Wang 2012; Wang & Xu 2012). As an iron catalyst was not used for these 3 treatments, hydrogen peroxide catalyses was assumed to be minimal with a great deal of hydrogen peroxide remaining in the samples resulting in an apparent increase in COD. These values indicate a potential for all treatments containing (Fenton's Reagent) or generating hydrogen peroxide (Modified Fenton's) that does not get consumed through catalysis reactions to be a positive interference in COD sampling. For the catalyzed treatments however, this potential is assumed to be low due to Fenton Reaction's [1] to [3] outlined in Section 2.3.1 which proceeds until the complete consumption of hydrogen peroxide has been achieved.

Of the 21 treatments considered, ten treatments of varying hydrogen peroxide loading concentrations, iron catalysts and ratios of  $H_2O_2$  to iron catalyst resulted in the greatest reduction in COD ( $COD_F/COD_o$ ). The  $COD_F/COD_o$  values ranged from 0.06 to 0.16, but were not significantly different (Table 4-2). For this reason all ten were deemed acceptable for use in the PAH/PCP reduction study. Of these ten, the treatment chosen to represent "Fenton's Reagent" was a hydrogen peroxide addition at a rate sufficient to consume 100% of the COD on a stoichiometric weight ratio basis with a 25:1 ( $H_2O_2:Fe^{2+}$  w/w) ratio of  $H_2O_2$  to ferrous chloride catalyst ( $FR_{100\%}^{25:1}$ ). This treatment was chosen for a number of reasons. Firstly, lesser amounts of hydrogen peroxide and iron catalyst were required, and this treatment produced one of the lowest amounts

of flocculent (Figure 4-1), thus reducing the operating and disposal costs. A ferrous chloride iron catalyst was chosen over a ferrous sulfate catalyst due to operational concerns as wastewater can sit in holding tanks at Stella Jones Inc. for days, facilitating anaerobic reducing conditions (Sharma et al. 2014; Karstens et al. 2016). Microbial reduction of sulfate to hydrogen sulfide (Sharma et al. 2014) results in several workplace safety concerns including odors, corrosion, and toxicity (Pomeroy & Parkhurst 1972; USEPA 1974; Lindermann et al. 2010).

The pH and temperature resulting from the addition of the oxidant were also considered when choosing the Fenton's Reagent formulation for further study. The pH of the oxidized wastewater must be neutralized before it can be filtered and discharged to holding ponds or be reused in other wood preserving processes (i.e. water-borne CCA). Also, pH adjustment flocculates soluble iron (from iron catalyst in treatments) which must then be removed prior to activated carbon filtration, preventing iron from building up on the carbon filter. All 10 treatments made the pH acidic (pH ~ 2) and were not significantly different from one another (Figure 4-2). A substantial addition of base will be required by Stella Jones in full scale applications to neutralize these solutions. The oxidation of the organic contaminant is an exothermic reaction (Petri et al. 2011a; Chen et al. 2015; Ribeiro et al. 2015) resulting in a sharp temperature increase over the first 30 min with all treatments in these trials (Figure 4-3). For safety reasons, exothermic reactions must be watched closely by treatment plant operators at Stella Jones Inc. Wastewater treatment with FR<sub>100%</sub><sup>25:1</sup> had a limited temperature increase of only 18.8°C, representing one of the least hazardous treatments. Although there were 2 other treatments having lower temperature increase ( $\leq 5^\circ\text{C}$ ), these required greater chemical inputs. It is important to confirm these lab-scale temperature observations at larger scales.

The 85% reduction in COD of wastewater treated with  $FR_{100\%}^{25:1}$  is comparable to the literature values found. Zou et al. (2015) and Hayat et al. (2015) who both demonstrated 97.6% and 87% reduction in dye wastewater respectively, while Ksibi (2006) demonstrated a similar reduction of 86% in municipal wastewater using similar beaker scale methods. The majority of literature for Fenton's Reagent examines low COD wastewater ( $<2000\text{mg/L}$ ) and it can be seen that high COD wastewater ( $7000>\text{mg/L}$ ) used in this study was shown to have comparable reduction levels. Klauson et al. (2015) is an example of work in which high COD landfill leachate ( $8000\text{-}15000\text{mg/L}$ ) was able to be reduced by 90% through treatment with Fenton's Reagent.

### **5.1.3 Modified Fenton's**

Of the 21 treatments considered, fourteen treatments of varying calcium peroxide loading concentrations, iron catalysts and ratios of  $\text{H}_2\text{O}_2$  to iron catalyst resulted in the greatest reduction in COD ( $\text{COD}_F/\text{COD}_0$ ). The  $\text{COD}_F/\text{COD}_0$  values ranged from 0.53 to 0.61, but were not significantly different (Table 4-4). For this reason all fourteen were deemed acceptable for use in the PAH/PCP reduction study. Of these fourteen, the treatment chosen for Modified Fenton's was a calcium peroxide addition at a rate sufficient to consume 50% of the COD on a stoichiometric weight ratio basis with a 5:1 ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  w/w) ratio of  $\text{H}_2\text{O}_2$  to ferrous chloride catalyst ( $\text{MF}_{50\%}^{5:1}$ ). This treatment was chosen for a number of reasons. Firstly, lesser amounts of calcium peroxide and iron catalyst were required, and this treatment produced one of the lowest amounts of flocculent (Figure 4-4), thus reducing the operating and disposal costs. As previously stated (Section 5.1.1), a ferrous chloride iron catalyst was preferred over a ferrous sulfate catalyst due to operational concerns to ensure toxic and corrosive hydrogen sulfide gas is not produced from wastewater left in anaerobic conditions (Sharma et al. 2014).



The final pH and changes in temperature were also considered when choosing the Modified Fenton's formulation for further study. Treatment with Modified Fenton's resulted in an alkaline product (to ~12) for all 14 treatments (Figure 4-5). This will result in a substantial amount of acid being required to achieve the neutral pH range required by Stella Jones in full scale applications. The least pH increase was determined to be MF<sub>50%</sub><sup>5:1</sup> treatment, however it was not significantly different than 12 of the other 13 acceptable treatments. The slight temperature increases noted over the first 30 min for all treatments in these trials (Figure 4-6) indicates an exothermic reaction. Wastewater oxidized with MF<sub>50%</sub><sup>5:1</sup> had only a 2°C increase and so was found to be less hazardous than other treatments that had greater temperature increases. A safety consideration may not be warranted in larger scales (in comparison to Fenton's Reagent) however this should be confirmed.

The 40% reduction in COD of wastewater treated with MF<sub>50%</sub><sup>5:1</sup> was slightly lower when compared to other Modified Fenton's work in wastewater application. A key difference is the majority of controlled studies use buffers in order to compensate for pH increases associated with calcium peroxide (Ye et al 2009; Lu et al. 2014; Zhai & Jiang 2014), but from operational perspective this is too costly. Lu et al. (2014) were able to obtain an 81.8% reduction in COD for textile wastewater using Modified Fenton's which was an improvement (>35%) when compared to using calcium peroxide alone. For this study only a significant improvement of ~9% was observed between calcium peroxide+iron catalyst and calcium peroxide alone. While examining the use of Modified Fenton's in pre-treating glyphosate wastewater prior to microbial oxidation, Zhai & Jiang (2014) were able to observe a 62.1% COD reduction indicating a benefit for using it as a pre-treatment step.

### 5.1.3 Permanganate

#### 5.1.3.1 Preliminary Experiments

It was observed that unreacted permanganate dissolved in deionized water increased COD readings (refer to Section 4.13.1). This “apparent” increase in COD was deemed the result of the oxidant remaining. This influence may result from the reaction of the permanganate ion with compounds in the closed reflux COD test, or by spectrophotometer absorbance interference when reading colorimetric change.

The absorbance interference in the permanganate system is shown in Figure 5-1 below. The potassium dichromate in the COD test tubes oxidizes samples producing green chromic ions ( $\text{Cr}^{3+}$ ) as seen by the raw wastewater (Figure 5-1B). Figure 5-1C and D show samples having residual permanganate present causing the solution to change colour. 620 nm is the wavelength required for the absorbance of  $\text{Cr}^{3+}$  by method #8000 from the HACH Company (Section 3.4). The peak absorbance for the permanganate ion is 545 nm, while only slightly absorbing at 620 nm (Mancott & Tietjen 1970) meaning there should be little interference from permanganate in the final colorimetric results. The “apparent” increase in COD observed in the preliminary experiment may therefore be contributed by permanganate reactions in the closed reflux COD tubes, or transmittance interference that occurred over all wavelengths due to the dark colour of the solution.



**Figure 5-1:** Comparing colour changes in closed reflux chemical oxygen demand (COD) test tubes between the blank (A), raw wastewater (B), 100% permanganate:COD (C) and 50% permanganate:COD (D).

### **5.1.3.2 Screening Trial**

All 6 treatments of varying permanganate loading concentrations resulted in the same amount of reductions in COD ( $COD_F/COD_o$ ). The  $COD_F/COD_o$  values ranged from 0.73-0.69, but were not significantly different (Table 4-7). Thus all 6 were deemed equally acceptable for use in the PAH reduction study. Of these 6, the treatment chosen for reduction study was the addition of permanganate at a rate sufficient to consume 7.5% of the COD on a stoichiometric weight ratio basis ( $KMnO_4$  7.5%). This was chosen for a number of reasons. Firstly, lesser amounts of permanganate were required, and this treatment produced the significantly lowest amounts of flocculent (Figure 4-7), thus reducing the operating and disposal costs. Incomplete oxidation and

the colour of residual permanganate were identified as issues. Residual permanganate, indicated by the purple colour of the solution, are either over saturated with the permanganate ion, or the oxidation has not yet come to an end (Noreen et al. 2013). Only the 7.5% and 14.4% permanganate stoichiometric weight ratio loading concentrations demonstrated the lack of residual purple colour (Table 4-7). Other than the increase in COD of residual permanganate noted in the preliminary experiments (Table 4-5) permanganate is known to have long lasting effects on aquatic life and should not be released at high concentrations (Hobbs et al. 2006; Petri et al. 2011b). For the purpose of treating wood preservative wastewater at Stella Jones Inc., the complete consumption of the permanganate ion is favoured to save on chemical costs and reduce environmental impact.

Both pH and temperature were considered when choosing the most adequate permanganate treatment for further study. Wastewater treated with  $\text{KMnO}_4$  7.5% resulted in a pH of 7.3 (Figure 4.8) which was significantly closer to the Stella Jones' required discharge limits of 7 than other treatments. This is very beneficial as a final pH adjustment would not be needed, reducing costs for the company. As permanganate reactions are not sufficiently exothermic (Wiberg et al. 2006) temperature was not taken into consideration in the selection of the permanganate formulations

A 27% reduction in COD of wastewater treated with  $\text{KMnO}_4$  7.5% was observed however, previous works seem to differ in results for various wastewater streams. Abassi (2009) examined olive mill wastewater with an extremely high COD (+80,000mg/L) and was able to reduce overall COD by 90% over only a 30 min reaction time. Olive mill wastewater is often rich in organic matter and suspended solids, with aromatics and aliphatic compounds constituting the majority of pollutants. Conversely Misra et al. (2009) examined industrial landfill leachate with a high COD (~19,000mg/L) and found that the greatest reduction observed was 12.3% over a 1 h reaction time. Landfill leachate is often characterized by chlorides, ammonium and reduced nitrogen and high

dissolved solids (Misra et al. 2009). The landfill leachate had 15x the dissolved solids than the olive mill wastewater presented by Abassi (2009). Noreen et al. (2013) demonstrated similarly reduction results when treating permanganate textile dye wastewater with a very low COD (75 mg/L) with only a 12% reduction in COD over a 90 min reaction period. High total organic carbon, salt contents, extremes in pH and carcinogenic compounds such as naphthalene, benzidine and other aromatic compounds are often indicative of textile wastewater. This difference in wastewater sources indicates that the chemical makeup of the wastewater plays a significant role in permanganate's oxidation effectiveness.

## **5.2 Reduction of Polycyclic Aromatic Hydrocarbons and Pentachlorophenol**

### **5.2.1 Extraction Validation**

The accuracy and precision of the extraction and quantification of 18 PAHs and PCP under consideration was first determined to ensure that confidence could be placed in these results. The compounds being examined were the 18 PAHs and PCP, as outlined in Section 3.7. For 8 of the 18 PAHs, a high degree of precision (coefficient of variation C.V. < 10%) was observed while an acceptable degree of precision (C.V. <15%; Table 4.8) was observed for 7 more. For 10 of the 15 precise PAHs, a high degree of accuracy (recovery > 75 %) was observed, with 5 PAHs having low accuracy (Table 4.8). As this study was attempting to assess the reduction ( $C_F/C_o$ ) of PAHs and PCP as a result of various oxidation treatments, the precision of the method was more significant than the accuracy. Average C.V. of 9% and percent recovery of 78% was reported for these 15 PAHs. A high coefficient of variation (C.V  $\geq$ 15%) was demonstrated by naphthalene and 1/2-methylnaphthalene which are the compounds with the highest vapour pressure (Mollea et al. 2005; Bojas & Pope 2007). Volatilization may have contributed to this, calling into question the reliability of the quantification of these compounds. Naphthalene also had the lowest recovery

(51.9%) of any compound. The quantification of PCP demonstrated low percent recovery (64%) and a high C.V. (34%) (Table 4-8) calling into question the extraction efficiency of this compound.

### **5.2.2 Accuracy and Precision of Laboratory**

Hidden standards were included in the samples submitted for analysis to provide quality assurance and control. The results obtained for 13 of the 18 PAH hidden standards examined demonstrated low variability (C.V.  $\leq 10\%$ ) as well as high recovery ( $>75\%$ ; Table 4-9). An average C.V. of 7% and percent recovery of 86% was reported for these 13 PAHs indicating confidence in the laboratory's analytical equipment. A low recovery ( $<75\%$ ) and high C.V. ( $>10\%$ ) were observed for fluorene, benzo(a)anthracene and chrysene, indicating a low degree of confidence for the quantification of these compounds. Benzo(a)pyrene and benzo(k)fluoranthene were noted to have variability greater than acceptable (C.V.  $>15\%$ ) and so the possibility of laboratory error should also be noted for those compounds. A 185% recovery was observed for benzo(k)fluoranthene and could be explained by the analytical equipment or, less likely, an improper concentration of the certified standard solution.

In the hidden standards, PCP had the highest C.V. (47%) and lowest percent recovery (58%) of the compounds examined. These results are similar to those obtained for the recoveries of known concentrations in the extraction validation experiments (Section 4.2.1). As a result a high degree of confidence cannot be placed on the PCP results reported in Section 4.2.3 and as such it was decided that a reduction in PCP would not be considered when selecting the most effective oxidant, its optimization or in evaluating the extent of oxidation.

### **5.2.3 PAH Reduction Discussion**

The extent of COD reduction was again examined along with the reduction of PAHs to compare reductions due to the change in mixing apparatus used in this study (refer to Section 3.7).

Oxidant COD reduction results for this study were similar when comparing them to the oxidant screening trial (Section 4.1) for the two peroxide-based oxidants (FR<sub>100%</sub><sup>25:1</sup> and MF<sub>50%</sub><sup>5:1</sup>), however permanganate (KMnO<sub>4 7.5%</sub>) was found to differ. At optimal loading concentrations, a COD<sub>F</sub>/COD<sub>o</sub> value of 0.15 (85% reduction; Table 4-2) was obtained by FR<sub>100%</sub><sup>25:1</sup> during the screening trial, while a similar value of 0.14 (86% reduction; Table 4-11) for COD<sub>F</sub>/COD<sub>o</sub> was obtained in the PAH reduction experiment. Similarly, a COD<sub>F</sub>/COD<sub>o</sub> value of 0.60 (40% reduction Table 4-4) was obtained for MF<sub>50%</sub><sup>5:1</sup> in the screening trial, while a similar value of 0.54 (or 46% reduction Table 4-11) was obtained in the PAH reduction experiment. KMnO<sub>4 7.5%</sub> however resulted in a COD<sub>F</sub>/COD<sub>o</sub> value of 0.73 (27% reduction; Table 4-7) in the screening trial, while a value of 0.59 (41% reduction; Table 4-11) was obtained in the PAH reduction experiment. This meant that the COD reduction improved by 14% in the PAH reduction experiment than the screening trial. This could be explained by a change of mixing that occurred between the two experiments. In the screening trial mixing occurred via a bench shaker (Figure 3-2), whereas in the PAH reduction study an automated beaker mixer was used (Figure 3-6).

MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4 7.5%</sub> had improved overall PAH reductions in comparison to FR<sub>100%</sub><sup>25:1</sup>, with the most notable reductions occurring in PAHs possessing >4 rings in their structure (Table 4-11). This indicated favourable treatments for these compounds in wastewater produced from Stella Jones (Table 4-11). Chen et al. (2015) found a 72.8% reduction in overall PAHs when applying permanganate for sediment remediation, compared to Fenton's Reagent which had a 30.9% reduction. Again in soil, improved PAH removal was observed by Bogan et al. (2003) when supplementing hydrogen peroxide in Fenton's Reagent with calcium peroxide (Modified Fenton's). The use of Modified Fenton's resulted in a 47% reduction in total PAHs with the greatest improvements occurring in higher molecular weight PAHs (>4 ring structure)

compared to Fenton's Reagent, which resulted in only a 20% reduction. Improved removal efficiency was attributed to the slow formation of hydrogen peroxide via the decomposition of calcium peroxide (Bogan et al. 2003).

There were two compounds that were not observed in some of the original wastewater blocks but were identified after treatment. 2,4,6-Trichlorophenol (TCP) was a compound identified in 1 block of FR<sub>100%</sub><sup>25:1</sup> and 3 blocks of MF<sub>50%</sub><sup>5:1</sup>. The partial degradation of PCP would explain the appearance of 2,4,6-TCP due to oxidation that was occurring in the wastewater (Lee & Carberry 1992; Petri et al. 2011a). Hydroxyl radical degradation of PCP both in aqueous and soil slurry solutions have been well documented with 2,4,6-TCP being identified as a formed intermediate (Oturán et al. 2001; Zimbron & Reardon 2011). Although the extent of degradation of PCP was analytically unreliable, the appearance of 2,4,6-TCP post oxidation shows degradation occurring.

In 1 block of FR<sub>100%</sub><sup>25:1</sup> the apparent formation of the three 6 member ringed PAHs (refer to Table 1-1) were observed. This was not observed for the other two oxidants. Although nowhere reported in Fenton's Reagent literature, this phenomenon has been reported elsewhere through the process of pyrosynthesis. Lower molecular weight PAHs have been reported to attribute to the formation of larger molecular weight PAHs through synthesis of free radicals containing one or more carbon as a result of an initiation of heat (Rajput & Lakhani 2009; De Pieri et al. 2014). Fenton's Reagent treatments were the only oxidant to have a large jump in temperature during its reaction (~25°C). This increase in temperature, coupled with low molecular weight free radicals, could explain the formation of the larger PAHs. These formations would have a negative impact on the wastewater by possibly increasing toxic large ringed PAHs, thus demonstrating the continued need for an activated carbon filter as a final polishing step.



Theoretically, COD levels of wastewater contaminated with PAHs and PCP would be high as they are large compounds requiring more oxygen to break down (Sponza & Gok 2011). As an example, the 5-ring structure of benzo(a)pyrene would require 23 moles of oxygen in order to oxidize 1 mole of benzo(a)pyrene to carbon dioxide and water ( $C_{20}H_{12} + 23O_2 \rightarrow 6H_2O + 20CO_2$ ; Sponza & Gok 2011). As  $MF_{50\%}^{5:1}$  and  $KMnO_4 7.5\%$  resulted in greater reduction of PAHs, a greater reduction in COD would be expected due to these compound's theoretical contribution to COD, but this was not observed. This could be explained by the generally low concentration of PAHs/PCP observed in samples. These compound's theoretical contribution to COD can be estimated by the oxygen required to mineralize each PAH/PCP compound (Kim et al. 2000; Sponza & Gok 2011). Theoretical COD contribution for the PAHs considered and PCP are given in Table 5-1 based on theoretical mole ratios of oxygen required to completely mineralize the compounds to  $H_2O$  and  $CO_2$ .

Lower molecular weight PAHs were present at higher concentrations within the wastewater, thus contributing more to the theoretical estimation of COD. The contribution of large ringed PAHs to the theoretical COD was much less in view of their low concentrations in the wastewater samples, possibly associated with lesser aqueous solubility (Bojas & Pope 2007) or the original PAH concentrations of the parent creosote material. The total contribution of the theoretical COD by the PAHs and PCP examined was 244 mg/L, with naphthalene being the greatest contributor (118.6 mg/L). Considering the wastewater examined in this reduction study had COD values ranging from 10,000-13,000 mg/L, the theoretical COD from all contaminants was less than 2.5%. This indicates the presence of other compounds within the wastewater that were contributing to the COD.

**Table 5-1: Theoretical chemical oxygen demand attributed by each contaminant of concern. Average experimental concentrations ( $C_o$ ) and standard deviations (S.D.) are included.**

Compound	Formula	Experimental Concentration (mg/L)	S.D. (mg/L)	Theoretical COD (mg/L)
Naphthalene	$C_{10}H_8 + 12O_2 \rightarrow 4H_2O + 10CO_2$	39.6	38.2	118.6
1-Methylnaphthalene	$C_{11}H_{10} + 13.5O_2 \rightarrow 5H_2O + 11CO_2$	5.2	5.1	15.8
2-Methylnaphthalene	$C_{11}H_{10} + 13.5O_2 \rightarrow 5H_2O + 11CO_2$	10.5	9.8	31.9
Acenaphthylene	$C_{12}H_8 + 13O_2 \rightarrow 4H_2O + 12CO_2$	0.2	0.1	0.6
Acenaphthene	$C_{12}H_{10} + 14.5O_2 \rightarrow 5H_2O + 12CO_2$	6.1	4.5	18.4
Fluorene	$C_{13}H_{10} + 15.5O_2 \rightarrow 5H_2O + 13CO_2$	3.5	2.6	10.5
Phenanthrene	$C_{14}H_{10} + 16.5O_2 \rightarrow 5H_2O + 14CO_2$	5.6	4.0	16.0
Anthracene	$C_{14}H_{10} + 16.5O_2 \rightarrow 5H_2O + 14CO_2$	1.2	0.9	0.4
Fluoranthene	$C_{16}H_{10} + 18.5O_2 \rightarrow 5H_2O + 16CO_2$	1.3	1.0	3.8
Pyrene	$C_{16}H_{10} + 18.5O_2 \rightarrow 5H_2O + 16CO_2$	1.7	1.2	5.0
Benzo(a)anthracene	$C_{18}H_{12} + 21O_2 \rightarrow 6H_2O + 18CO_2$	0.4	0.3	5.0
Chrysene	$C_{18}H_{12} + 21O_2 \rightarrow 6H_2O + 18CO_2$	0.5	0.3	1.5
Benzo(b)fluoranthene	$C_{20}H_{12} + 23O_2 \rightarrow 6H_2O + 20CO_2$	0.5	0.3	1.5
Benzo(k)fluoranthene	$C_{20}H_{12} + 23O_2 \rightarrow 6H_2O + 20CO_2$	0.2	0.2	0.6
Benzo(a)pyrene	$C_{20}H_{12} + 23O_2 \rightarrow 6H_2O + 20CO_2$	0.3	0.2	1.5
Indeno(1,2,3 cd)pyrene	$C_{22}H_{12} + 25O_2 \rightarrow 6H_2O + 22CO_2$	0.1	0.0	0.3
Dibenzo(a,h)anthracene	$C_{22}H_{14} + 25.5O_2 \rightarrow 7H_2O + 22CO_2$	0.1	0.0	0.3
Benzo(ghi)perylene	$C_{22}H_{12} + 25O_2 \rightarrow 6H_2O + 22CO_2$	0.1	0.0	0.3
PCP	$2C_6HCl_5O + 12O_2 \rightarrow H_2O + 12CO_2 + 10Cl^-$	16.6	24.9	12.0
			<b>Total:</b>	<b>244</b>

Although FR<sub>100%</sub><sup>25:1</sup> was unable to reduce recalcitrant PAHs to the extent of MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4</sub><sub>7.5%</sub>, its ability to decrease the COD was found to be more effective. Although a reduction in probable known human carcinogens is important it is apparent that these compounds play a small role in COD values and there is a significant amount of other compounds that contribute to the high oxygen demand of the wastewater. In consultation with Stella Jones, it was determined that the significant decrease in COD attributed by FR<sub>100%</sub><sup>25:1</sup> cannot be overlooked as the goal of this experimentation was not to completely oxidize all compounds in their wastewater streams, but to reduce the organic load on the carbon filters. As well as alleviating the organic load on the activated carbon filters, these filters do have the ability to filter out the contaminants examined in this thesis, thus reducing toxicity. These reductions help the company get closer to a COD goal of <600 mg/L set for discharge limits (CMCC 2015). As Fenton's Reagent, and specifically the FR<sub>100%</sub><sup>25:1</sup> treatment has shown to greatly reduce the COD content of wastewater compared to the other 2 oxidants, as well as partially reduce PAHs, it is the recommended oxidant to be implemented at a larger scale at the Stella Jones facility located in Atlantic Canada in order to reduce the organic load on activated carbon filters.

### **5.3 Reaction Holding Time Optimization**

The reaction of FR<sub>100%</sub><sup>25:1</sup> was determined to be complete when the COD of the wastewater remained unchanged over time. The COD reductions observed varied depending on whether the wastewater originally had low or high COD (Figure 4-9 and 4-10). Application of FR<sub>100%</sub><sup>25:1</sup> to high COD wastewater resulted in the fastest reduction rates with COD reducing drastically over the first 30 min and remaining unchanged thereafter (Figure 4-10). The decrease in pH (Figure 4.2) and increase in temperature (Figure 4-3) over the first 30 min of reaction that was observed in the screening trial for FR<sub>100%</sub><sup>25:1</sup>, also emphasises the quick reaction rates of Fenton's Reagent

leading to quick reduction in COD. Low COD wastewater was observed to take longer to reduce COD as it took up until 90 min for COD to remain unchanged (Figure 4.9). The difference between the 2 reduction rates can be explained with the second order reaction kinetic characteristics of Fenton's Reagent (Petri et al. 2011a; Ribeiro et al. 2015). As more hydrogen peroxide and ferrous chloride were required for the high COD wastewater, reaction kinetics increased. Similar observations were seen in the screening trial, where greater loading concentrations of Fenton's Reagent resulted in greater temperature increases (Figure 4-3a vs 4-3b) indicative of an exothermic reaction. The difference in reduction end points between high and low COD wastewater is important when deciding when a certain batch of FR<sub>100%</sub><sup>25:1</sup> treated wastewater is complete at an industrial scale.

The increase in COD observed from 0 to 30 min in the low COD wastewater (Figure 4-9) can be explained by residual or unreacted hydrogen peroxide adding to the COD of the wastewater samples. In acidic conditions hydrogen peroxide does not decompose into water and oxygen as it normally would in basic conditions (Petri et al. 2011a). Therefore any unreacted hydrogen peroxide is assumed to remain in solution which is known to add to theoretical COD (Wu & Wang 2012; Wang & Xu 2012). Increases in COD were noted in the Fenton's Reagent screening trial treatments that used only hydrogen peroxide with no iron catalyst (Table 4-2), underlying the importance of complete oxidant consumption.

The quick reaction times of FR<sub>100%</sub><sup>25:1</sup> observed in this study follows similar trends in the literature. Extremely high COD pharmaceutical wastewater (362000 mg/L) was examined by Martinez et al. (2003) where it was concluded that 90% of the total COD reduction occurred in the first 10 min of reaction. Manufacturing wastewater with a COD of 14160 mg/L was able to be reduced to 76% of the original COD, also within 10 min of the reaction time (Li et al. 2014). Low

COD olive mill wastewater (~2000mg/L) was examined by Lucas & Peres (2009) using hydrogen peroxide at a concentration to consume 82% of the COD on a stoichiometric weight ratio basis. Principal reductions (~60%) in COD were observed within the first 20 min and interestingly noted, a further 10% reduction occurred over the following 60 min of reaction indicating extended reaction times occurring in low COD wastewater. Increased COD and staggered oxidant addition used in this experiment in comparison to Lucas & Peres (2009) could explain why the low COD wastewater took 90 min to come to completion.

The optimization experiment demonstrated that when using  $FR_{100\%}^{25:1}$ , the allotted 3 h reaction time far exceeds the time required for COD reductions to come to a stop. Low COD wastewater was observed to finish reacting in 90 min while higher COD wastewater finished in 30 min. Although only high and low COD wastewaters were examined it is assumed that for wastewater with COD values that fall within the high and low range (~7000-14000 mg/L; Section 3.8), reaction times would end anywhere from 30-90 min. If a universal Fenton's Reagent treatment design is to be implemented for the wastewater produced by Stella Jones Inc. it is recommended that a reaction holding time of 120 min be chosen. The additional 30 min of allotted reaction time would ensure no reactions are being missed.

## **Chapter 6 Conclusion & Recommendations**

### **6.1 Conclusion**

The goal of this research was to determine the most effective chemical oxidant to reduce the organic load of wood preservative wastewater from Stella Jones Inc. (Atlantic Canada). Effectiveness was based on a variety of difference factors and included reduction in COD, flocculent production, change in pH and temperature, and reduction of toxic and recalcitrant PAHs/PCP compounds. The three oxidants examined included Fenton's Reagent, Modified Fenton's and potassium permanganate. Based on results from these works several conclusions were made.

In the screening trial, favourable operating conditions for each oxidant were able to be chosen based on COD reduction, with minor considerations made for flocculent production and pH and temperature change. The FR<sub>100%</sub><sup>25:1</sup> treatment was found to be the most effective for Fenton's Reagent resulting in an initial COD decrease of 86%. The MF<sub>50%</sub><sup>5:1</sup> treatment was found to be the most effective for Modified Fenton's resulting in an initial COD decrease of 46%. The KMnO<sub>4</sub> 7.5% treatment found to be the most effective for potassium permanganate resulting in an initial COD decrease of 27%. With a change in mixing that occurred this was improved to 41%.

Although FR<sub>100%</sub><sup>25:1</sup> was not the most effective oxidant at reducing PAHs in comparison to MF<sub>50%</sub><sup>5:1</sup> and KMnO<sub>4</sub> 7.5%, it was more effective at reducing the overall organic content of the wastewater (COD). COD reductions represents the oxidation of many unknown compounds present in the wastewater and alleviates the contaminant loading on activated carbon and sand filters. FR<sub>100%</sub><sup>25:1</sup> did demonstrated the ability to reduce the majority of 2-4 ringed PAHs as well as partial reduction of remaining 4-6 ringed PAHs. Carbon/sand filter have the ability to remove these PAHs that did not get reduced while longevity of these towers is still expected due to the

overall organic reduction demonstrated by FR<sub>100%</sub><sup>25:1</sup>. In addition to the overall organic reduction, FR<sub>100%</sub><sup>25:1</sup> produced the least amount of flocculent production as well as reduced pH enabling a possibility for a two-stage oxidation approach described in Section 6.2. Upon the optimization completion of FR<sub>100%</sub><sup>25:1</sup>, it is recommended a universal reaction holding time of 2 h be implemented as the COD reductions for both high and low COD wastewaters ceased.

## **6.2 Recommendations**

As the contribution of recalcitrant PAHs and PCP to the total organic content of the wastewater was shown to be low, other compounds must attribute to the high COD. These compounds are suspected to be derivatives of the wood itself (lignin, celluloses and hemicelluloses) as well as soluble organics attributed by treatment chemicals. Further characterisation of the wastewater is warranted to get a more complete understanding of which compounds are actually being degraded to achieve the high COD reductions observed.

Beyond the scope of lab scale success seen in this thesis, the use of the Fenton's Reagent FR<sub>100%</sub><sup>25:1</sup> treatment should be increased to semi-industrial/industrial scale in order to determine the feasibility as a treatment option for Stella Jones Inc. (Atlantic Canada). Careful attention should be given to the exothermic heat production when up scaling to industrial practices to ensure all equipment is compatible with the change of temperature that can be expected. The production of iron hydroxide should also be taken into account. This analyst's work involved filtering/centrifuging the flocculent produced however settling may be another option with dewatering of the sludge and so further investigation is warranted. Finally, an economical analysis should be undertaken in order to determine the cost effectiveness of using Fenton's Reagent as a wastewater treatment option.

The acidic final pH (~2) of Fenton's Reagent treated wastewater should be taken into account to ensure the compatibility of the mixing equipment and holding tanks. Calcium peroxide is used for a basic pH adjustment currently at Stella Jones Inc. Further research is recommended for a two stage oxidation process, first with Fenton's Reagent and further with calcium peroxide to adjust pH but also create oxidation through Modified Fenton's chemistry. This combined effort could further increase oxidation and thus the degradation of organic compounds.



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## Appendix

### Initial Wastewater Characterisation

*Table A-1: Initial characterisation of two separate Red Pine wastewater batches obtained from Stella Jones Inc. (Atlantic Canada) including chemical oxygen demand (COD), 18 PAHS and PCP.*

Parameter	Batch Characterisation #1	Batch Characterisation #2
COD	6630 mg/L	9650 mg/L
pH	3.94	4.32
Chloride	245 mg/L	87 mg/L
Compounds (µg/L)		
Naphthalene	560	1900
1-Methylnaphthalene	160	610
2-Methylnaphthalene	160	610
Acenaphthylene	<RDL	<RDL
Acenaphthene	140	510
Fluorene	98	300
Phenanthrene	<RDL	530
Anthracene	<RDL	130
Fluoranthene	<RDL	<RDL
Pyrene	<RDL	130
Benzo(a)anthracene	17	43
Chrysene	17	47
Benzo(b)fluoranthene	9.4	<RDL
Benz(k) fluoranthene	3.3	<RDL
Benzo(a)pyrene	4.8	<RDL
Indeno(123-cd)pyrene	<RDL	<RDL
Dibenzo(ah)anthracene	<RDL	<RDL
Benz(ghi)perylene	<RDL	<RDL
Pentachlorophenol	20000	19000

### Oxidant Loading Concentrations

All iron calculations for Fenton's and Modified Fenton's were based off of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratios. For Modified Fenton's (Calcium peroxide) the calculations was based off of 0.47g  $\text{H}_2\text{O}_2$  produced per gram of  $\text{CaO}_2$ .

### Screening Trial

All Screening trial calculations were based on 150mL (0.15L) of wastewater.

**Table A-2:** Mass of hydrogen peroxide and calcium peroxide used for each wastewater batch in the RBD optimization screening trial.

Hydrogen Peroxide & Calcium Peroxide Loading Concentration								
Wastewater		$\text{H}_2\text{O}_2:\text{COD}$ Stoichiometric Weight Ratio			$\text{CaO}_2:\text{COD}$ Stoichiometric Weight Ratio			
Batch	$\text{COD}_o$ (mg/L)	50% (g)	100% (g)	150% (g)	$\text{COD}_o$ (mg/L)	50% (g)	100% (g)	150% (g)
1	10960	1.75	3.49	5.24	11820	3.99	7.99	11.98
2	6230	0.99	1.99	2.98	12855	4.34	8.69	13.03
3	13040	2.08	4.16	6.23	12765	4.31	8.63	12.94
4	14160	2.26	4.51	6.77	10770	3.64	7.28	10.92

**Table A-3:** Mass of iron catalysts (ferrous sulfate and ferrous chloride) and H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratios for Fenton's Reagent (hydrogen peroxide) used for each wastewater batch in the RBD optimization screening trial.

<b>Hydrogen Peroxide Iron Catalysts and H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Loading Concentrations</b>												
	<b>50% H<sub>2</sub>O<sub>2</sub>:COD Stoichiometric Weight Ratio</b>						<b>100% H<sub>2</sub>O<sub>2</sub>:COD Stoichiometric Weight Ratio</b>					
	<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>		
<b>Batch</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>
<b>1</b>	1.74	0.58	0.35	1.24	0.41	0.25	3.48	1.16	0.70	2.49	0.83	0.50
<b>2</b>	0.99	0.33	0.20	0.71	0.24	0.14	1.98	0.66	0.40	1.41	0.47	0.28
<b>3</b>	2.07	0.69	0.41	1.48	0.49	0.30	4.14	1.38	0.83	2.96	0.99	0.59
<b>4</b>	2.25	0.75	0.45	1.61	0.54	0.32	4.49	1.50	0.90	3.20	1.07	0.64
	<b>150% H<sub>2</sub>O<sub>2</sub>:COD Stoichiometric Weight Ratio</b>											
	<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>								
<b>Batch</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>						
<b>1</b>	5.22	1.74	1.04	3.73	1.24	0.75						
<b>2</b>	2.97	0.99	0.59	2.12	0.71	0.42						
<b>3</b>	6.21	2.07	1.24	4.44	1.48	0.89						
<b>4</b>	6.72	2.24	1.34	4.80	1.60	0.96						

**Table A-4:** Mass of iron catalysts (ferrous sulfate and ferrous chloride) and H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratios for Modified Fenton's (calcium peroxide) used for each wastewater batch in the RBD optimization screening trial.

<b>Calcium Hydroxide Iron Catalysts and H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Loading Concentrations</b>												
	<b>50% CaO<sub>2</sub>:COD Stoichiometric Weight Ratio</b>						<b>100% CaO<sub>2</sub>:COD Stoichiometric Weight Ratio</b>					
	<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>		
<b>Batch</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>
<b>1</b>	1.87	0.62	0.37	1.34	0.45	0.27	3.74	1.25	0.75	2.67	0.89	0.53
<b>2</b>	2.03	0.68	0.41	1.45	0.48	0.29	4.06	1.35	0.81	2.91	0.97	0.58
<b>3</b>	2.02	0.67	0.40	1.44	0.48	0.29	4.05	1.35	0.81	2.90	0.97	0.58
<b>4</b>	1.70	0.57	0.34	1.22	0.41	0.24	3.41	1.14	0.68	2.44	0.81	0.49
	<b>150% CaO<sub>2</sub>:COD Stoichiometric Weight Ratio</b>											
	<b>Ferrous Sulfate Heptahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>			<b>Ferrous Chloride Tetrahydrate H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> Ratio (g)</b>								
<b>Batch</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>	<b>5:1</b>	<b>15:1</b>	<b>25:1</b>						
<b>1</b>	5.61	1.87	1.12	4.01	1.34	0.80						
<b>2</b>	6.10	2.03	1.22	4.36	1.45	0.87						
<b>3</b>	6.05	2.02	1.21	4.33	1.44	0.87						
<b>4</b>	5.11	1.70	1.02	3.65	1.22	0.73						

**Table A-5:** Mass of potassium permanganate used for varying  $KMnO_4$ :COD Stoichiometric Weight Ratio (%) in the CRD preliminary work addressing residual permanganate interference on the COD results.

Wastewater		$KMnO_4$ :COD Stoichiometric Weight Ratio					
Replicate	COD <sub>o</sub> (mg/L)	7.5% (g)	14.4% (g)	21.7% (g)	28.9% (g)	36.1% (g)	43.3% (g)
1	14050	6.94	13.33	20.09	26.76	33.42	40.09
2	14110	6.97	13.39	20.18	26.87	33.57	40.26
3	14090	6.96	13.37	20.15	26.83	33.52	40.21
4	14090	6.96	13.37	20.15	26.83	33.52	40.21

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**Table A-6:** Mass of potassium permanganate used for varying  $KMnO_4$ :COD Stoichiometric Weight Ratio (%) for each wastewater batch in the RBD optimization screening trial.

Wastewater		$KMnO_4$ :COD Stoichiometric Weight Ratio					
Batch	COD <sub>o</sub> (mg/L)	7.5% (g)	14.4% (g)	21.7% (g)	28.9% (g)	36.1% (g)	43.3% (g)
1	14080	1.04	2.00	3.02	4.02	5.02	6.03
2	14095	1.04	2.01	3.02	4.03	5.03	6.03
3	15490	1.15	2.20	3.32	4.43	5.53	6.63
4	14530	1.08	2.07	3.12	4.15	5.19	6.22



## PAH/PCP Reduction Study

All PAH/PCP reduction study calculations were based on 1000mL (1L) of wastewater.

**Table A-7:** Mass of hydrogen peroxide, calcium peroxide and potassium permanganate used for each wastewater batch in the RBD PAH/PCP reduction study.

Wastewater		Oxidant:COD Stoichiometric Weight Ratio		
Batch	COD (mg/L)	100% H <sub>2</sub> O <sub>2</sub> (g)	50% CaO <sub>2</sub> (g)	7.5% KMnO <sub>4</sub> (g)
1	10715	22.77	24.14	5.30
2	12930	27.48	29.12	6.39
3	10695	22.73	24.09	5.29
4	9815	20.86	22.11	4.85

**Table A-8:** Mass of iron catalyst (ferrous chloride) and H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratios for Fenton's Reagent (hydrogen peroxide) and Modified Fenton's (calcium peroxide) used for each wastewater batch in the RBD optimization screening trial.

Wastewater Batch		Ferrous Chloride Tetrahydrate Additions (H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> ) (g)	
Batch	COD (mg/L)	H <sub>2</sub> O <sub>2</sub> (25:1)	CaO <sub>2</sub> (5:1)
1	10715	3.24	8.08
2	12930	3.91	9.75
3	10695	3.24	8.06
4	9815	2.97	7.40

## Reaction Holding Time

All screening calculations were based on 1000mL (1L) of wastewater.

**Table A-9:** Mass of hydrogen peroxide and ferrous chloride used for each wastewater batch in the “low” wastewater batch optimization experiment.

Wastewater Batch		Hydrogen Peroxide	Ferrous Chloride Tetrahydrate ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ )
Replicate	COD (mg/L)	100% $\text{H}_2\text{O}_2$ :COD Weight Ratio (g)	25:1 (g)
1	7700	16.36	2.33
2	7630	16.21	2.31
3	7600	16.15	2.30
4	7670	16.30	2.32

**Table A-10:** Mass of hydrogen peroxide and ferrous chloride used for each wastewater batch in the “high” wastewater batch optimization experiment.

Wastewater Batch		Hydrogen Peroxide	Ferrous Chloride Tetrahydrate ( $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ )
Replicate	COD (mg/L)	100% $\text{H}_2\text{O}_2$ :COD Weight Ratio (g)	25:1 (g)
1	12930	27.48	3.91
2	12920	27.46	3.91
3	12870	27.35	3.89
4	12890	27.39	3.90

## Organic Loading Final Values

### Screening Trial

**Table A-11:** *Effect of amount of hydrogen peroxide added, form of ferrous iron catalyst and iron ratio on final chemical oxygen demand (COD<sub>F</sub>) in the screening trial.*

H <sub>2</sub> O <sub>2</sub> :COD Stoichiometric Weight Ratio (%)	Ferrous Catalyst	Iron Ratio (H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> )	N	Mean COD <sub>F</sub> (mg/L)	Standard Deviation (mg/L)
150	Sulfate	5:1	4	737.5	143.0
150	Sulfate	15:1	4	677.5	163.2
150	Sulfate	25:1	4	692.5	144.1
150	Chloride	5:1	4	2646.3	747.5
150	Chloride	15:1	4	1406.3	445.1
150	Chloride	25:1	4	1226.3	298.6
150	None	None	4	15780.0	1440.0
100	Sulfate	5:1	4	1650.0	538.1
100	Sulfate	15:1	4	1107.5	260.4
100	Sulfate	25:1	4	1026.3	231.0
100	Chloride	5:1	4	2956.3	847.0
100	Chloride	15:1	4	1701.3	441.1
100	Chloride	25:1	4	1586.3	335.8
100	None	None	4	14720.0	2674.1
50	Sulfate	5:1	4	3908.6	1357.3
50	Sulfate	15:1	4	4850.0	3264.8
50	Sulfate	25:1	4	6192.5	4419.2
50	Chloride	5:1	4	4236.3	1578.1
50	Chloride	15:1	4	3476.3	1386.6
50	Chloride	25:1	4	3595.0	922.2
50	None	None	4	12805.0	4302.0
Control	None	None	4	9933.8	3270.9

**Table A-12:** Effect of amount of calcium peroxide added, form of ferrous iron catalyst and iron ratio on final chemical oxygen demand (COD<sub>F</sub>) in the screening trial.

CaO <sub>2</sub> :COD Stoichiometric Weight Ratio (%)	Ferrous Catalyst	Iron Ratio (H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> )	N	Mean COD <sub>F</sub> (mg/L)	Standard Deviation (mg/L)
150	Sulfate	5:1	4	6485.0	770.1
150	Sulfate	15:1	4	6950.0	959.3
150	Sulfate	25:1	4	6942.5	906.4
150	Chloride	5:1	4	6602.5	1199.8
150	Chloride	15:1	4	6510.0	901.6
150	Chloride	25:1	4	6920.0	673.3
150	None	None	4	7540.0	803.6
100	Sulfate	5:1	4	6775.0	848.3
100	Sulfate	15:1	4	7142.5	904.8
100	Sulfate	25:1	4	6997.5	901.3
100	Chloride	5:1	4	6487.5	1040.4
100	Chloride	15:1	4	6952.5	818.4
100	Chloride	25:1	4	7157.5	809.7
100	None	None	4	7947.5	730.8
50	Sulfate	5:1	4	7410.0	956.1
50	Sulfate	15:1	4	7842.5	877.7
50	Sulfate	25:1	4	7775.0	820.7
50	Chloride	5:1	4	7230.0	387.4
50	Chloride	15:1	4	7477.5	552.2
50	Chloride	25:1	4	7602.5	747.7
50	None	None	4	8005.0	779.2
Control	None	None	4	11452.5	634.0

**Table A-13:** Effect of amount of potassium permanganate on reduction in chemical oxygen demand (COD<sub>F</sub>) for 3 hours in the screening trial.

KMnO <sub>4</sub> :COD Stoichiometric Weight Ratio (%)	N	Mean COD <sub>F</sub> (mg/L)	Standard Deviation (mg/L)
7.5	4	10588.8	807.8
14.4	4	10371.3	267.8
21.7	4	9980.0	308.5
28.9	4	10090.0	154.3
36.1	4	10060.0	357.5
43.3	4	10150.0	374.4
Control	4	13655.0	715.8

## PAH/PCP Reduction Study

**Table A-14:** Effect of amount of the addition of Fenton's Reagent, Modified Fenton's and potassium permanganate on final chemical oxygen demand (COD<sub>F</sub>), 18 PAHs and PCP compounds (C<sub>F</sub>) in the reduction study.

	Final Loading Concentrations (C <sub>F</sub> ) for Compounds (µg/L)				
	N	FR <sub>100%</sub> <sup>25:1</sup>	MF <sub>50%</sub> <sup>5:1</sup>	KMnO <sub>4</sub> 7.5%	Control
Parameter (mg/L)					
COD	4	1493	5933	6459	10109
Compounds (µg/L)					
Naphthalene	4	92	10345	6585	49250
1-Methylnaphthalene	4	29	369	304	3743
2-Methylnaphthalene	4	80	774	473	8275
Acenaphthylene	4	3	12	3	151
Acenaphthene	4	79	407	185	6250
Fluorene	4	310	193	56	3483
Phenanthrene	4	808	271	71	5700
Anthracene	4	62	51	15	1208
Fluoranthene	4	146	49	16	1385
Pyrene	4	445	69	14	1498
Benzo(a)anthracene	4	165	15	2	358
Chrysene	4	201	16	3	368
Benzo(b)fluoranthene	4	177	14	3	343
Benz(k) fluoranthene	4	89	5	1	182
Benzo(a)pyrene	4	85	7	1	178
Indeno(123-cd)pyrene	2	18	0	0	20
Dibenzo(ah)anthracene	2	3	0	0	0
Benz(ghi)perylene	2	17	0	0	20
Pentachlorophenol	4	36773	27750	6459	13300

## ANOVA Tables

**Table A-15:** Analysis of variance (ANOVA) results for COD<sub>F</sub>/COD<sub>o</sub> versus treatments and batch (block) in the screening trial

<b>Fenton's Reagent</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	21	4.33400	0.206381	63.25	0.000
Batch (Block)	3	0.05393	0.017978	5.51	0.002
Error	63	0.20555	0.003263		
Total	87	4.59349			
<b>Modified Fenton's</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	21	23.757	1.1313	9.69	0.000
Batch (Block)	3	19.415	6.4718	55.45	0.000
Error	63	7.353	0.1167		
Total	87	50.524			
<b>Potassium Permanganate (CRD)</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	6	457787821	762979770	3936.02	0.000
Error	21	407075	19385		
Total	27	458194896			
<b>Potassium Permanganate (RBD)</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	6	0.20987	0.03492	44.03	0.000
Batch (Block)	3	0.0299	0.0010	12.55	0.000
Error	18	0.0143	0.0008		
Total	27	0.2541			

**Table A-16:** Analysis of variance (ANOVA) results for PAHs, PCP and COD<sub>F</sub>/COD<sub>o</sub> versus treatments and batch (block) in the reduction study

<b>COD</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	3	1.2285	0.4094	1001.71	0.000
Batch (Block)	3	0.0121	0.0041	9.90	0.003
Error	9	0.0037	0.0004		
Total	15	1.2443			
<b>Naphthalene</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value
Treatment	3	3.0410	1.0137	44.48	0.000
Batch (Block)	3	0.1026	0.0342	1.50	0.280
Error	9	0.2051	0.0228		
Total	15	3.3487			
<b>1-Methylnaphthalene</b>					
Source	DF	Adj SS	Adj MS	F-Value	P-Value

Treatment	3	1.7281	0.5760	58.78	0.000
Batch (Block)	3	0.0249	0.0083	0.85	0.503
Error	9	0.0882	0.0098		
Total	15	1.8412			
<b>2-Methylnaphthalene</b>					
<b>COD</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Source	3	1.9806	0.6602	87.79	0.000
Treatment	3	0.0260	0.0087	1.15	0.379
Batch (Block)	9	0.0677	0.0075		
Error	15	2.0743			
<b>Acenaphthylene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	1.9132	0.6377	36.43	0.000
Batch (Block)	3	0.0729	0.0243	1.39	0.309
Error	9	0.1576	0.0175		
Total	15	2.1436			
<b>Acenaphthene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	3.0640	1.0213	1404.98	0.000
Batch (Block)	3	0.0012	0.0004	0.54	0.669
Error	9	0.0065	0.0007		
Total	15	3.0717			
<b>Fluorene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.8296	0.9432	224.86	0.000
Batch (Block)	3	0.0238	0.0079	1.89	0.202
Error	9	0.0378	0.0042		
Total	15	2.8911			
<b>Phenanthrene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.9826	0.9942	75.21	0.000
Batch (Block)	3	0.0464	0.0155	1.17	0.374
Error	9	0.1190	0.0132		
Total	15	3.1480			
<b>Anthracene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.9347	0.9782	630.34	0.000
Batch (Block)	3	0.0068	0.0022	1.45	0.292
Error	9	0.0140	0.0016		
Total	15	2.9554			
<b>Fluoranthene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.4561	0.8187	28.90	0.000
Batch (Block)	3	0.0432	0.0144	0.51	0.687
Error	9	0.2550	0.0283		

<b>Total</b>	15	2.7542			
<b>Pyrene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.3589	0.7863	27.98	0.000
Batch (Block)	3	0.1423	0.0475	1.69	0.238
Error	9	0.2530	0.0281		
<b>Total</b>	15	2.7542			
<b>Benzo(a)anthracene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.2866	0.7622	9.26	0.004
Batch (Block)	3	0.4101	0.1367	1.66	0.244
Error	9	0.7410	0.0823		
<b>Total</b>	15	3.4377			
<b>Chrysene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.0205	0.6735	9.78	0.003
Batch (Block)	3	0.2506	0.0836	1.21	0.360
Error	9	0.6199	0.0689		
<b>Total</b>	15	2.8910			
<b>Benzo(b)Fluoranthene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.3665	0.7888	7.32	0.009
Batch (Block)	3	0.5460	0.1820	1.69	0.238
Error	9	0.9701	0.1078		
<b>Total</b>	15	3.8826			
<b>Benzo(k)Fluoranthene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.3345	0.7782	7.67	0.008
Batch (Block)	3	0.3782	0.1261	1.24	0.351
Error	9	0.9132	0.1015		
<b>Total</b>	15	3.6259			
<b>Benzo(a)pyrene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	2.1490	0.7163	10.00	0.003
Batch (Block)	3	0.4007	0.1336	1.87	0.206
Error	9	0.6444	0.0716		
<b>Total</b>	15	3.1941			
<b>Indeno(123-cd)pyrene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Treatment	3	0.4930	0.1643	1.18	0.448
Batch (Block)	1	0.1968	0.1968	1.41	0.321
Error	3	0.4188	0.1396		
<b>Total</b>	7	1.1086			
<b>Dibenzo(a,h)anthracene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>



<b>Treatment</b>	3	0.05539	0.0185	1.00	0.500
<b>Batch (Block)</b>	1	0.0184	0.0185	1.00	0.391
<b>Error</b>	3	0.0554	0.0185		
<b>Total</b>	7	0.1292			
<b>Benzo(g,h,i)perylene</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
<b>Treatment</b>	3	0.4388	0.1463	1.15	0.456
<b>Batch (Block)</b>	1	0.2021	0.2021	1.59	0.297
<b>Error</b>	3	0.3817	0.1272		
<b>Total</b>	7	1.0227			
<b>Pentachlorophenol</b>					
<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
<b>Treatment</b>	3	27.35	9.116	2.35	0.141
<b>Batch (Block)</b>	3	16.37	5.455	1.41	0.304
<b>Error</b>	9	34.94	3.882		
<b>Total</b>	15	78.66			