Removing Chemical Oxygen Demand (COD) Assay Interference from Landfill Leachate Treated with Fenton’s Reagents

by
Matthew Palmer

A THESIS

submitted to
Oregon State University
Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

Presented June 1, 2016
Commencement June 2016
AN ABSTRACT OF THE THESIS OF

Matthew Palmer for the degree of Honors Baccalaureate of Science in Chemical Engineering presented on June 1, 2016. Title: Removing Chemical Oxygen Demand (COD) Assay Interference from Landfill Leachate Treated with Fenton’s Reagents.

Abstract approved: ________________________________________________________

Tyler Radniecki

Incompatibility between Fenton’s Reagents and a potassium dichromate COD test provides interference that prevent accurate measurements of the concentration of organics from oxidized samples. Several treatment options were tested to remove this interference. Oxidation of reagents was eliminated as a potential method for removal of interference due to sample contamination. Potassium iodide was used to remove the interference of hydrogen peroxide from samples through catalysis of its decomposition. pH adjustment was capable of eliminating the interference of ferrous iron through precipitation at the expense of removing the target analyte from solution.

Key Words: Fenton’s Process, hydrogen peroxide, ferrous iron, COD assay, assay interference
Corresponding e-mail address: palmerm@oregonstate.edu
Removing Chemical Oxygen Demand (COD) Assay Interference from Landfill Leachate Treated with Fenton’s Reagents

by
Matthew Palmer

A THESIS

submitted to
Oregon State University
Honors College

in partial fulfillment of
the requirements for the
degree of

Honors Baccalaureate of Science in Chemical Engineering
(Honors Scholar)

Presented June 1, 2016
Commencement June 2016
Honors Baccalaureate of Science in Chemical Engineering project of Matthew Palmer presented on June 1, 2016.

APPROVED:

_____________________________________________________________________
Tyler Radniecki, Mentor, representing Department of Environmental Engineering

_____________________________________________________________________
Lewis Semprini, Committee Member, representing Department of Environmental Engineering

_____________________________________________________________________
Gavin Bushee, Committee Member, representing Department of Environmental Engineering

_____________________________________________________________________
Toni Doolen, Dean, Oregon State University Honors College

I understand that my project will become part of the permanent collection of Oregon State University, Honors College. My signature below authorizes release of my project to any reader upon request.

_____________________________________________________________________
Matthew Palmer, Author
1. Introduction:

Landfills are one of the most common destinations for municipal waste, with the US compiling over 250 million tonnes per year from direct disposal of waste or the dumping of waste byproducts, i.e. sludge (Powell et al. 2016). A major concern for the operation of a landfill is the water introduced through rain or through water originally contained in the waste. This water is capable of dissolving the waste and forming a concentrated waste known as leachate (Calace et al. 2001). The specific composition of landfill leachate changes based on the different wastes disposed into the landfill and with landfill age (Renou et al. 2008). Landfill leachate typically will contain large amounts of organic pollutants due to the generation of fatty acids and humic-like substances (Kjeldsen et al. 2002)

Some of these organics can be readily degraded and removed by the aerobic activity of certain microbes. The organics removed by this activity are represented by the Biochemical Oxygen Demand (BOD) of the landfill leachate (Sawyer et al. 2003). However, the total amount of organics in a system, both readily degradable and those recalcitrant to degradation, is measured using the Chemical Oxygen Demand (COD) (Raposa 2008), as seen by Equation 1. Thus, the COD of a system will always be equal to or greater than the BOD of a system. Both BOD and COD are reported in terms of mg/L of oxygen, which represents the equivalent amount of oxygen required to oxidize a sample.

\[
\text{C}_n\text{H}_a\text{O}_b\text{N}_c + d\text{Cr}_2\text{O}_7^{2-} + (8d+c)\text{H}^+ \rightarrow n\text{CO}_2 + \frac{a+8d-3c}{2}\text{H}_2\text{O} + c\text{NH}_4^+ + 2d\text{Cr}^{3+}
\]

(Equation 1)

The ratio of COD to BOD is affected by various factors, but most notably by the age of the landfill (Renou et al. 2008). Younger landfills tend to contain a larger amount of readily degradable material that is easy for microorganisms to breakdown, resulting in BOD: COD ratios between 0.4 and 0.7. Landfills in use for 25 years or more will tend to result in BOD: COD ratios between 0.04 and 0.4 as more of the readily degradable organics have already been removed from the system in the form of methane gas and carbon dioxide. COD concentrations can range from 100 ppm to 70,000 ppm (Renou et al. 2008).

The remainder of the COD not composed of BOD, which is the recalcitrant group of organics that cannot be easily biodegraded, can be removed chemically through advanced oxidation process (AOP) (Renou et al. 2008). AOP’s uses powerful oxidizing agents to oxidize and mineralize organic contaminants (Andreozzi et al. 1999). Fenton’s Reagent, also known as the Fenton Process, is an AOP which produces powerful oxidizing reagents, such as the hydroxyl radical (·OH) and the hydroperoxyl radical (HO₂·), which are capable of mineralizing recalcitrant COD to water and carbon dioxide.

The Fenton Reagent is one of many different methods that use the hydroxyl radical as an oxidizing agent (Zhang et al. 2005). Hydroxyl radicals can be generated through several different processes, particularly through the use of hydrogen peroxide as one of the reagents (Andreozzi et al. 1999). The Fenton Process utilizes an iron catalyst in combination with hydrogen peroxide (Equations 2 and 3) to achieve this. The iron, in its ferrous form, is oxidized by the hydrogen peroxide, resulting in the production of a hydroxide ion and a hydroxyl radical, which is then free to oxidize any reducible contaminants that are present. The iron, now
in its oxidized ferric state, is recycled back to ferrous iron by being reduced by more hydrogen peroxide, resulting in the production of a hydrogen ion and a hydroperoxyl radical. This radical is effective at oxidizing material, though not to the same extent as a hydroxyl radical, which is among the most powerful oxidizing compounds (Andreozzi et al. 1999).

\[
\begin{align*}
    \text{Fe(II)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(III)} + \cdot \text{OH} + \text{OH}^- \quad (2) \\
    \text{Fe(III)} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe(II)} + \text{HO}_2^\cdot /\text{O}_2^- + \text{H}^+ \quad (3)
\end{align*}
\]

Previous literature has indicated that the effectiveness of the Fenton Process is influenced by multiple factors. The Fenton Process is most effective within the pH range of 2.5 to 3.5, as the iron requires an acidic environment to remain in solution (Georgi et al 2007). Also, the process is temperature dependent, and occurs at faster rates as temperature increases past room temperature (Aygun et al. 2012). Lastly, it is established that the initial COD will affect the amount of COD that can be removed, as hydrogen peroxide can quench the hydroxyl radicals produced if there is more hydrogen peroxide available in solution than available organics (Equation 4) (Mashal et al. 2012). To ensure that the radicals are used to oxidize organics instead of peroxide, the hydrogen peroxide is often added in incremental steps to maintain a low concentration (Zhang et al. 2005).

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^\cdot /\text{O}_2^- + \text{H}_2\text{O} \quad (4)
\]

The oxidation of the iron occurs at a rate faster than the reduction of iron, making the reduction of ferrous iron the rate limiting step in the Fenton Process, as seen in Table 1 (Duesterberg and Waite 2006). Furthermore, it is the oxidation of the iron catalyst that produces the desired hydroxyl radical, not the reduction. Therefore, it is advantageous to add the iron catalyst as ferrous iron, so it can readily be oxidized, delaying the iron’s introduction to the process’s rate limiting step and resulting in a faster production of hydroxyl radicals.

Table 1: Rate constants for all processes involved in the Fenton Reaction. Rate constants in terms of L/mol*s

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant at pH 3</th>
<th>Rate Constant at pH 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \cdot \text{OH} + \text{OH}^-</td>
<td>41.7</td>
<td>41.7</td>
</tr>
<tr>
<td>\text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \text{HO}_2^\cdot /\text{O}_2^- + \text{H}^+</td>
<td>2.00 \times 10^{-3}</td>
<td>2.50 \times 10^{-3}</td>
</tr>
<tr>
<td>\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{HO}_2^\cdot /\text{O}_2^- + \text{H}_2\text{O}</td>
<td>3.30 \times 10^{7}</td>
<td>3.30 \times 10^{7}</td>
</tr>
<tr>
<td>\text{Fe(III)} + \text{HO}_2^\cdot /\text{O}_2^- \rightarrow \text{Fe(II)} + \text{O}_2 + \text{H}^+</td>
<td>7.82 \times 10^{5}</td>
<td>6.84 \times 10^{6}</td>
</tr>
<tr>
<td>\text{Fe(II)} + \cdot \text{OH} \rightarrow \text{Fe(III)} + \text{OH}^-</td>
<td>3.20 \times 10^{8}</td>
<td>3.20 \times 10^{8}</td>
</tr>
<tr>
<td>\text{Fe(II)} + \text{HO}_2^\cdot /\text{O}_2^- \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2</td>
<td>1.34 \times 10^{6}</td>
<td>2.40 \times 10^{6}</td>
</tr>
</tbody>
</table>
There is dissenting opinion as to what is the optimum molar ratios of hydrogen peroxide to iron. Because the iron is recycled in solution, it operates as a catalyst and can be added in smaller amounts than the hydrogen peroxide counterpart, which will be the limiting reagent. Different literature sources report different molar ratios, though the consensus lies between a 1.5:1 and 10:1 molar ratio of hydrogen peroxide to iron (Martinez et al. 2003, Zhang et al. 2005a, 2006b, Benatti et al. 2009). Another concern is that hydrogen peroxide undergoes violently exothermic reaction above 5 M, and therefore must be maintained at low concentrations (Martinez et al. 2003).

While COD is used as a surrogate for the amount of organic compounds that can be oxidized in a sample, it actually measures the oxygen required to completely oxidize the entire sample, both organic and non-organic. This means that any compound that can be oxidized in the sample, such as hydrogen peroxide (Kang et al. 1999) will be included in the COD of a system, allowing COD to overestimate the actual amount of organic contaminants in the system. This is a concern for the Fenton Process, as both the hydrogen peroxide and ferrous iron can both be oxidized (Equations 5 and 6). Therefore, any unreacted reagent will contribute to the sample’s COD and overestimate the amount of organics remaining in solution and underestimate the effectiveness of Fenton’s Reagent. Methods need to be developed and implemented in order to remove or account for any excess reagent inside the samples to determine the actual removal rate of a system being oxidized by the treatment.

\[
\text{Cr}_2\text{O}_7^{2-} + 6 \text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6 \text{Fe}^{3+} + 7\text{H}_2\text{O} \quad (5)
\]

\[
\text{H}_2\text{O}_2 + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 5\text{H}_2\text{O} + 2\text{O}_2 \quad (6)
\]

This work developed methods to eliminate any potential interference from excess Fenton’s Reagent when determining the extent to which the Fenton Process can reduce the COD of a mixture of 50% wastewater/50% landfill leachate, and to determine the most effective method for treatment of the mixture. This will be done through the manipulation of iron and hydrogen peroxide additions to determine the optimal amount of reagents to add to reduce organic content in leachate samples, and by testing potential precipitating and oxidizing agents to remove interfering agents.

2. Methods:

2.1 Materials:

Landfill leachate samples were collected from the Coffin-Butte Landfill, Benton Country, Oregon. Wastewater samples were collected from the Adair Village Wastewater Treatment Plant, Adair Village, Oregon. Leachate will have a higher organic composition, which will make wastewater’s organic
composition relatively negligible. Samples were composed of 50% landfill leachate and 50% wastewater to reflect operating condition for Adair Village’s newly proposed wastewater treatment plant.

The hydrogen peroxide, ferrous iron heptahydrate, and potassium iodide, and potassium dichromate COD tests were all acquired from Thermo Fisher Scientific. The COD assays measured COD in the range of 0-1500 ppm, and were conducted following the manufacturer’s instructions.

2.2 Oxidation of Landfill Leachate

25 mL of wastewater and 25 mL of landfill leachate were combined into a 200 mL beaker at the same time, and were mixed via a magnetic stir bar. 0 to 8.34 g of powdered ferrous iron heptahydrate was added to the mixture to form solutions with iron concentrations between 0 and 0.5 M. Nitric acid was used to adjust the pH of the solution to 3 +/- 0.1 after addition of iron to enhance the dissolution of iron and enhance the kinetics of the Fenton’s Process. It should be noted that hydrochloric acid was not used as the manufacturer states that chloride ions are known to interfere with COD measurement with potassium dichromate. 10 mL of a 1.5 M hydrogen peroxide solution was then added to the mixture, now a 60 mL sample with 0.25 M hydrogen peroxide, to initiate the Fenton process. All experiments were performed in triplicate.

After the solution mixed for 30 minutes, samples were immediately stored at 4 °C to effectively end the reaction until COD measurements could be taken for multiple samples. Samples were preserved for 2 to 26 hours before testing. When all samples were ready for analysis, 30 mL of each sample were centrifuged at 9000 rpm for 15 minutes to remove precipitated iron. 1 mL of the supernatant was extracted and measured following manufacturer’s instructions.

2.3 Interference Removal Experiments

To determine their potential to interfere with COD assays, potassium iodide (6 to 60 mM), ferrous iron (100 to 400 mM), and hydrogen peroxide (20 to 90 mM) were added to COD test vials, which were incubated and analyzed following the manufacturer’s instruction. The samples were not centrifuged, as this would potentially remove the reagent being tested.

2.3.1 Iron Removal Experiments

Ferrous iron was precipitated by elevating the pH to 10 with sodium hydroxide. The solutions were then centrifuged, added to a COD vials, incubated, and measured with a spectrophotometer according to manufacturer’s instructions. This was then repeated in a sample of 50/50 landfill leachate/ wastewater samples to determine if comparable results could be attained in sample.

2.3.2 Hydrogen Peroxide Removal Experiments

Potassium permanganate (9.5 to 25.3 mM) and potassium iodide (6 to 60 mM) were used to remove 90 mM hydrogen peroxide solution. The samples were mixed for 60 minutes before the COD vial was measured according to the manufacturer’s instructions. This process was then repeated for 0.32 mM to 6.3 mM
potassium permanganate in a sample of 50/50 landfill leachate/wastewater samples to determine if comparable results could be attained in sample.

2.3.3 Potassium Iodide Removal Experiments

Oxidation experiments were performed by exposing 60 mM potassium iodide solution to 37 to 185 mM potassium persulfate for 30 minutes before the COD was measured according to the manufacturer’s instructions. Precipitation experiments were performed by exposing 60 mM potassium iodide solution to 30 to 75 mM lead nitrate or to 44 to 200 mM copper (II) sulfate pentahydrate for 30 minutes before the COD was measured according to the manufacturer’s instructions.

3. Results and Discussion:

3.1 Proof of Reagent Interference

Initial experiments did not account for any interference from added Fentonn’s Reagent, and assumed that all reported COD was from the organic content of the landfill leachate. Between 0 and 8.34 g of iron (II) sulfate heptahydrate was added to a constant concentration of 250 mM hydrogen peroxide to determine the optimal molar ratio of peroxide to iron in the Fenton Process (Figure 1). Two control were prepared at pH 7 and 3 respectively to see if decreasing the pH substantially affect the COD assay, which it did not. Most experiments resulted in drastic changes in color. This is due to the oxidation and removal of the organics that give leachate its dark color, allowing the solution to turn orange due to the amounts of ferric iron and iron hydroxides that form from in solution. Samples were observed to form a foam-like sludge in samples containing larger amounts of iron. Analysis of this foam was not performed, but it is suspected that it was due to the large amount of oxygen generated by side reactions involving hydrogen peroxide, and iron increasing the surface tension of the solution to allow the formation of bubbles.

![Figure 1: (A) The measured COD of samples with 250 mM hydrogen peroxide and 0 to 500 mM iron. A neutral and acidic control (1 and 2 respectively) were also tested. 90% confidence intervals are displayed. (B) The percent COD removed from samples with various H₂O₂:Fe ratios. Samples that exhibited an increase in COD were excluded. 90% confidence intervals are displayed.](image-url)
Samples with higher hydrogen peroxide to iron ratios had greater removal of organics, with the optimal ratio of 30:1 removing 63% of the COD compared to a control of 50/50 landfill leachate/wastewater with no Fenton Reagent. Samples containing either large or negligible amounts of ferrous iron (0.5:1 and no iron) were seen to have COD values that exceeded the control. This suggests that unreacted reagents, ferrous iron in the case of the 0.5:1 ratio and hydrogen peroxide in the case of the no iron sample, may constitute COD, thus causing the dichromate COD tests to underestimate the Fenton Reagent's removal of organic content.

### 3.2 Hydrogen Peroxide

#### 3.2.1 Calibration of Hydrogen Peroxide Interference

To quantify the potential interference caused by excess hydrogen peroxide, a calibration was performed for hydrogen peroxide. Figures 2 shows that increasing the concentration of hydrogen peroxide causes a measurable increase in COD which must be accounted for. If 250 mM hydrogen peroxide were added to sample with no iron, such as the sample in Figure 1, the sample would encounter an interference of almost 4000 ppm COD, which agrees with the previous literature values (Kang et al. 1999) and proves a need for a method to remove excess hydrogen peroxide.

![Figure 2: A calibration curve relating the COD measured to the concentration of hydrogen peroxide in a sample. 90% confidence intervals are displayed.](image)

Unreacted hydrogen peroxide remaining in solution will constitute COD, as seen in Figure 2. To chemically remove hydrogen peroxide from solution, samples containing 120 mM hydrogen peroxide were exposed to varying amounts of potassium permanganate, which is capable of oxidizing the hydrogen peroxide due to its higher reduction potential, removing it from solution. Removal percentages of hydrogen peroxide as high as 90% were achieved with 1.5 g/L (Figure 3). There was a detectable increase in COD as permanganate concentrations increased, which is evidence of interference that would need to be accounted for. This also means that the reading for 1.5 g/L may be influenced by interference and the actual removal of hydrogen peroxide may be more than 90% of hydrogen peroxide.

#### 3.2.2 Permanganate Oxidation

Unreacted hydrogen peroxide remaining in solution will constitute COD, as seen in Figure 2. To chemically remove hydrogen peroxide from solution, samples containing 120 mM hydrogen peroxide were exposed to varying amounts of potassium permanganate, which is capable of oxidizing the hydrogen peroxide due to its higher reduction potential, removing it from solution. Removal percentages of hydrogen peroxide as high as 90% were achieved with 1.5 g/L (Figure 3). There was a detectable increase in COD as permanganate concentrations increased, which is evidence of interference that would need to be accounted for. This also means that the reading for 1.5 g/L may be influenced by interference and the actual removal of hydrogen peroxide may be more than 90% of hydrogen peroxide.
Another issue with permanganate is that it can be used to oxidize wastewater during wastewater treatment (Nyer and Suthersan 1993). This suggests that testing is required to determine if permanganate oxidized the leachate-wastewater samples as well, which would result in an overestimation of the effectiveness of the Fenton Process. Figure 4 shows that even low concentration of permanganate can substantially oxidize the leachate-wastewater samples, making oxidation of hydrogen peroxide a non-viable option for increasing the accuracy of the COD test.

3.2.2.2 Iodide-Catalyzed Decomposition

A catalyst for the decomposition of hydrogen peroxide was tested to see if hydrogen peroxide could be converted to oxygen and water. This would remove hydrogen peroxide without the risk of reacting with the sample so long as the catalyst is inert to the sample. Potassium iodide is a known catalyst for this process (Conklin and Kessinger 1996). Figure 5 shows that potassium iodide also constitutes COD. However, if the concentration of potassium iodide in the solution is known, this calibration could account for the interference that iodide would constitute given that iodide is not reactive with leachate. This interference could then be subtracted from the reported COD to attain the actual COD.
Figure 5: Above is the calibration comparing the amount of COD interference to the concentration of potassium iodide. This calibration can be used to correct COD readings to account for oxidation of potassium iodide. 90% confidence intervals are displayed.

An experiment to decompose hydrogen peroxide, shown in Figure 6, initially did not suggest that iodide would be a satisfactory agent for removal of hydrogen peroxide due to a large amount of COD interference. However, if Figure 5 is used to account for the amount of COD attributed by the known concentration of potassium iodide in the solution, the actual COD is revealed to be considerably lower, with potassium iodide capable of removing up to 99% of interfering hydrogen peroxide.

Figure 6: The measured COD of samples containing 90 mM hydrogen peroxide exposed to potassium iodide. The interference is the COD attributed to oxidation of potassium iodide, and the true COD is attributed to hydrogen peroxide. 90% confidence intervals are displayed for all samples except 10 g/L, which was done in singlet.

3.2.3 Iodide Removal

Potassium persulfate, cupric sulfate, and lead nitrate were tested to determine if they could remove potassium iodide from solution in the event that there was an unknown amount of potassium iodide in the solution, which would occur if a landfill contained potassium iodide that entered its leachate. This would prevent the use of a calibration curve to correct COD readings.

3.2.3.1 Iodide Oxidation
Potassium persulfate not only oxidizes iodide to inert iodine (Rawling and Glasset 1924) but it is also capable of oxidizing any remaining hydrogen peroxide due to its higher oxidation potential (Kronholm et al. 2000). The persulfate was incapable of exceeding 70% removal of potassium iodide (Figure 7). This suggests oxidation cannot be used for removal of iodide, as an oxidizing compound strong enough to remove enough iodide runs the risk of oxidizing the sample as seen with permanganate.

![Figure 7: The amount of COD measured in samples of 60 mM potassium iodide and various concentrations of potassium persulfate. All samples were at pH 3. Samples were not performed in replicates.](image)

### 3.2.3.2 Iodide Precipitation

The other two compounds tested for removal of iodide were cupric sulfate and lead nitrate for the purpose of precipitating iodide. Cupric sulfate binds to iodide to form copper (II) iodide, which then degrades to form copper (I) iodide (Wiberg et al. 2000), which is insoluble (Weast 1988-1989). Lead nitrate forms lead iodide (Clever 1980).

Cuprous sulfate was incapable of exceeding a 25% removal of potassium iodide, while lead nitrate was capable of removing 90% of the potassium iodide from solution (Figure 8). However lead could not exceed this threshold, which means that 10% of potassium iodide would remain in solution. Based on Figure 6, approximately 15 mM of potassium iodide would need to be added to solution to remove excess hydrogen peroxide. If 10% of this remained in solution, that would constitute 70 ppm interference, which would serious obscure results. As a general rule, lead nitrate would need to be able to remove at least 97% of potassium iodide, which suggests potassium iodide cannot be effectively removed from solution via precipitation.
3.2 Ferrous Iron

3.2.1 Calibration of Ferrous Iron Interference

To quantify the potential interference caused by excess iron, a calibration was performed for ferrous iron. Figure 9 shows that increasing the concentration of iron causes a measurable increase in COD which must be accounted for.

3.2.1 Iron Removal

Iron only causes significant amounts of interference at high concentration. The optimal ratio of 30:1 required the use of 8.33 mM ferrous iron total, which would constitute approximately 70 ppm interference if it was all in its ferrous form based on Figure 2. However, while iron does act as a catalyst, it typically remains in its completely oxidized ferric form due to the difference in kinetic rates, as shown by Table 1. This means that so long as a higher ratio of hydrogen peroxide to iron is used during the Fenton Process, there would be negligible ferrous iron remaining in solution to generate interference with results.

While iron doesn’t interfere at low concentrations, a method for removing iron from solution must be developed if the COD of samples that naturally contain higher iron concentrations of iron are to be measured.
The solubility of iron decreases as a solution becomes more basic. While ferric iron hydroxide becomes insoluble when above a pH of 3, the ferrous form of iron doesn’t become insoluble until the pH rises above pH 7 (Whitman et al. 1925). Therefore, iron could be precipitated from solution after the Fenton Process but before the COD measurement occurs. Thus, the pH was raised to 10 to precipitate iron out of solution as ferrous hydroxide (Figure 10).

![Figure 10](image)

**Figure 10:** Above is the measured COD of samples containing iron before and after pH increases. 90% confidence intervals are displayed. Over 98% percent removal was encountered in all trials.

This method removed over 98% of iron (Figure 10). While this is effective enough to be used in analysis techniques, the process of precipitating iron is the mechanism used in flocculation to precipitate contaminants from wastewater (Howe et al. 2012). Thus, if the formation of iron hydroxide precipitates organics out of solution along with the interfering iron, the COD test will overestimate the actual removal of organics.

To determine if iron hydroxide precipitation removed COD from the leachate-wastewater mixture the pH was raised to 10 and changes in COD were measured (Figure 11). The increase in pH in the presence of iron did remove approximately 25% of organics from solution when 100 mM iron was added to solution. Furthermore, the sample containing no iron observed a 10% decrease in COD, most likely due to the precipitation of the already present concentration of metals in the samples, confirming that precipitation is not a viable option. Because precipitation cannot be used to correct samples with lower hydrogen peroxide to iron ratios, it is recommended that researchers stay in a region of higher ratios to avoid the need to precipitate iron from solution.
Figure 11: Above is the measured COD of leachate/wastewater samples whose pH was increased to 10, forming insoluble ferric hydroxide. Samples are sorted by added concentration of iron. 90% confidence intervals are displayed.

4. Conclusion:

The ferrous iron in the Fenton Process will cause interference in samples with low hydrogen peroxide to iron molar ratios. Methods to remove iron from solution risk removal of organics due to precipitation, which would overestimate removal efficiencies. Hydrogen peroxide cannot be removed by oxidation due to their oxidation of the samples, overestimating removal efficiencies. They also introduce new sources of electrons for potassium dichromate, which may constitute interference that also must be accounted for. Hydrogen peroxide can be removed through decomposition to water and oxygen, which can be enhanced by catalysts. These catalysts may also provide accountable interference in systems that are inert to the catalyst. If there are no compatible catalysts and high concentrations of iron are present, another test, such as TOC (Total Organic Carbon), should be used. Oxidizing agents should be avoided for the same reason that hydrogen peroxide can’t be oxidized.

Acknowledgments:

I would like to thank Dr. Tyler Radniecki for his guidance and mentorship. I would also like to thank the City of Adair Village, Civil West Engineering, and Coffin butte Landfill for their funding of the project and donations of wastewater and leachate, and Gavin Bushee and Dr. Mohammed Azizian for their expertise with leachate management and lab maintenance.
References:


