

# Use of Fe(VI) for Removal of Total Organic Carbons (TOC) and Heavy metals from Coproduced Water in Wyoming

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Final Report

*Submitted to*

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## Abstract

The objective of the research is to develop a new, simple, and environmentally friendly method for the simultaneous removal of heavy metals and total organic carbon (TOC) in coproduced water (CW) from the energy production industry. Ferrate anions ( $\text{FeO}_4^{2-}$ ) or Fe(VI) oxidation ability is very strong over the whole pH scale. Fe(VI) has been considered one of the future-generation water quality improvement agents. The oxidation of CWs TOC into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be done via Fe(VI). The result of the reduction of Fe(VI) is Fe(III) which is an excellent adsorbent for removal of heavy metals in CWs. Once the heavy metals and TOC have been removed from the CWs it is much easier to then remove the total dissolved solid (TDS) from the CWs. Water supply around the world is becoming insufficient for the growing populations and sources for additional water supplies must be established. Treated CWs can potentially be used to partly mitigate the tight water supply dilemmas in states such as Wyoming.

## 1. Description of Proposed Research

Wyoming is widely considered to be in a semi-arid hydro-climatic region. A vast majority of the time, rivers and streams throughout the state have little flow, granted during rare events, these rivers and streams can swell to very large levels. Wyoming has limited sustainable surface water available for use in general. Furthermore natural disasters such as droughts and tornadoes can suddenly scourge some regions of Wyoming by undermining agricultural and industrial productivity as well as the well-being and social fabric of communities. Point and nonpoint pollution is a manmade disaster that has been a long-standing concern that may further weaken Wyoming's capability to reach its water requirements. It is vital that Wyoming will not be threatened indefinitely due to a lack of water resources. In response to the water crisis, Wyoming statute Title 35, Chapter 11, Article 3 (35-11-309) declares "water is one of the Wyoming's most important natural resources, and the protection, development and management of Wyoming's water resources is essential for the long-term public health, safety, general welfare and economic security of Wyoming and its citizens." Wyoming mining and energy production companies have generated a great deal of water known as coproduced water (CW). These CWs regularly contain difficult to remove inorganic heavy metals and organic compounds whose disposal will not only cause serious environmental problems, but also waste the precious water resources that are desperately required in Wyoming. Consequently, treatment of CWs for use in Wyoming is a win-win approach.

CWs from various energy production industries [1] have been considered as important new water resources. Nonetheless some of the CWs need to be treated due to quality issues including heavy metals, total dissolved solids (TDS), and high total organic carbon (TOC) associated with fossil fuels [2-3], natural gas and coal. Removal of heavy metals and TOC can greatly help facilitate TDS reduction and removal. Presently there are two separate steps and two different technologies to remove heavy metals and TOC. The first step is to remove the TOC. TOC can be degraded through biological processes that are environmentally friendly, but slow [4]. TOC can also be destroyed using UV photolytic [5] and electrochemical [6] methods, but they are expensive and difficult to control. Most recently a combination of the methods has been studied [7-10] to achieve high removal efficiencies of TOC with some progress being made, however these processes are complex. To overcome these downfalls of a multistep method efforts have been put into using a simple multifunctional technology for simultaneous removal of the organic compounds and heavy metals to improve the overall CW quality of Wyoming. Specifically, a proprietary green method to produce a multifunctional  $K_2FeO_4$  (simply called Fe(VI) henceforth) and propose to use it for the simultaneous removal of total organic carbons (TOC) and heavy metals in numerous CWs preceding their further treatments for total dissolved solids (TDS) removal with other technologies such as reverse osmosis. Success in this project will benefit water resource conservation, environmental quality protection, and agricultural and energy development. These benefits will be accomplished with the following results. Firstly, the optimal Fe(VI) quality for removal of TOC and heavy metals in CWs will be established. Second, the operation conditions for the proposed CW contaminant removal technology will be obtained from laboratory bench-scale data collection. A TOC analyzer will be used to find the concentrations of TOC before and after treatment to determine the effectiveness of Fe(VI) on removing TOC from the CWs. The concentrations of heavy metals will be measured before and after treatment with an inductively coupled plasma mass spectrometer (ICP-MS) to determine the

performance of Fe(VI) in removing the heavy metals. Lastly, to demonstrate the applicability of the proposed technology, a pilot-scale test set-up will be designed and built based upon test results from the laboratory bench-scale setup. The results from the pilot-scale set-up are expected to reveal the operation conditions needed for use of the proposed technology in industry for future use. Studies in the use of Fe(VI) have not been done for its application in CW treatment, but it has for other water treatments. Success in the proposed project will advance the application of Fe(VI) in the energy industry as well as other industries working with organic compounds and heavy metals.

Ferrate anions ( $\text{FeO}_4^{2-}$ ) or Fe(VI) oxidation ability is very strong over the whole pH scale. Fe(VI) has been considered one of the future-generation water quality improvement agents. The oxidation of CWs TOC into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be done via Fe(VI). The result of the reduction of Fe(VI) is Fe(III) which is an excellent adsorbent for removal of heavy metals in CWs.

## 2. Tasks

Task 1 includes building the laboratory setups seen in Figure 1 and Figure 2. The first step for treatment of CW will be to add 1 L of collected CW to the vessel followed by turning on and setting the stirrer to the desired speed. The temperature control unit will then be turned on to control the operating temperature (5, 10, 15, 20, or 25 °C) depending on the test. Next a chosen amount of Fe(VI) will be added once the CW reaches the desired temperature. The reaction will be conducted for a predetermined amount of time with samples being taken periodically to monitor TOC and heavy metal concentrations during the reaction.

Task 2 includes analyzing the samples from the as-received CWs as well as the CWs treated with Fe(VI) under varying conditions. A TOC analyzer will be used to measure the concentrations of TOC and an ICP-OES will be used to measure the concentrations of heavy metals. Other water quality parameters such as suspended solids (SS), total dissolved solids (TDS), electrical conductivity (EC), and pH values of CWs will also be monitored using corresponding instruments available on UW campus. Also, the concentrations of Fe(VI) solution used to treat the CWs will be determined using UV spectroscopy.

Task 3 is the performance evaluation of Fe(VI) on the removal of TOC and heavy metals from CWs on the bench-scale set-up under different conditions. These tests will be used to investigate the TOC and heavy metal removing efficiencies of Fe(VI) under different CW conditions including TOC and heavy metal concentration levels, SS, pH, TDS, temperature, stirring speed and Fe(VI) dosage. The major organic compounds (major TOC contributors) in the CWs will be identified, as well as the kinetics associated with reactions between major organic compounds and Fe(VI).

Task 4 will be to test if the sludge resulting from treatment of CW with Fe(VI) is stable when landfilled. The TOC is expected to be completely decomposed into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when the optimal treatment conditions and dosage of Fe(VI) are used. So, this task is designed to evaluate the stability of heavy metals in the sludge using EPA SW-846 Method 1311 (Toxicity Characteristic Leaching Procedure (TCLP)). The optimal CW treatment conditions for achieving the greatest heavy metal stabilities in sludge will be investigated.

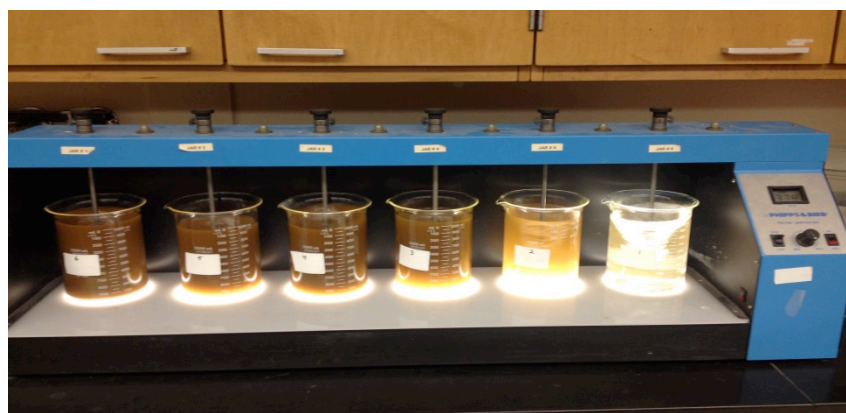
Task 5 is to perform industrial/commercial-scale demonstration of the proposed CWs management technology based on the results achieved with bench-scale tests. The volume of the batch vessel will be scaled to up to 1,000-2,000 L. The on-site industrial/commercial-scale demonstrations will be done in one of oil or natural gas production companies. The specific

location of the project will be determined by discussing with the associated landowner and oil/gas companies. Less than 0.5 acre of land will be used for pilot-scale and industrial/commercial-scale demonstrations of the proposed technology. The quality parameters (including TOC and heavy metal concentrations, pH, SS and TDS) of the as-received CW from the chosen company will be characterized. The data obtained from bench-scale tests will be used as the references of the industrial/commercial-scale tests. Factorial tests will be done to assess the performance of Fe(VI) on CWs treatment at industrial/commercial-scale.

### 3. Methods

#### 3.1 Jar tester

A photo (Figure 1) shows the PB-700 jar tester that is being used for water sample mixing. It is equipped with six stainless steel 1" x 3" paddles which are spaced six inches apart and are adjustable to a maximum depth of nine inches. An electronic motor control system offers regulated variable speeds of all paddles simultaneously, from 1-300 rpm, with the exact speed clearly displayed on a digital readout. A fluorescent lamp illuminator is built into the jar tester base to provide soft, diffused lighting of samples being tested. This setup is used in the first part of this project and the final analysis of water samples are analyzed via Total Organic Carbon (TOC) analyzer.

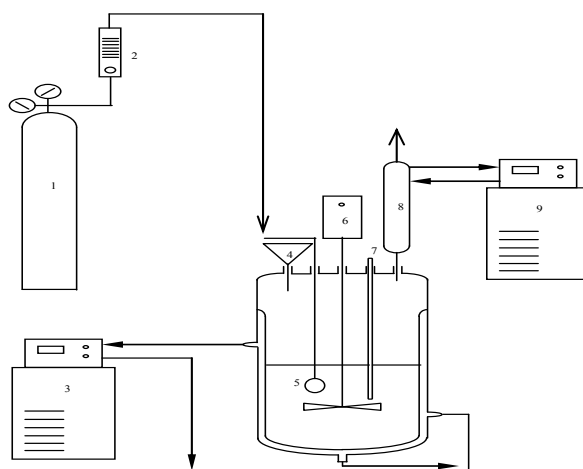


**Fig. 1** Photo of the jar tester setup

#### 3.2 Glass reactor

A comparative laboratory scale set-up that will be used to remove TOC and heavy metals from CWs with Fe(VI) is schematically illustrated in Figure 2. Each of the experiments will be executed in a 1 L stirred glass vessel (5). The glass vessel will have five inlets through its lid. In the center inlet of the glass lid a Teflon shaft with a propeller will be inserted (6). The next inlet will be used to introduce CWs and Fe(VI) into the vessel (4). A thermometer will be inserted into another one of the five inlets (7) to monitor the temperature that will be controlled by a separate temperature control unit (3). The fourth inlet will be used to introduce nitrogen when needed to increase the efficiency of mixing in the vessel, which will be controlled by a rotameter (2). A condenser (8) will be connected to the last inlet to condense any vapor released from the reaction mixture and return it to the vessel. The condenser regulating unit (9) will be used to

control the condenser temperature. A sampling port will be fitted at the bottom of the vessel as can be seen in Figure 2.

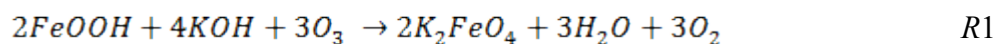


**Fig. 2** Experimental setup for removal of TOC and heavy metals from CWs with Fe(VI) [(1) nitrogen tank (2) rotameter (3) temperature control unit (4) funnel (5) vessel (6) stirrer motor (7) thermometer (8) condenser (9) condenser regulating unit]

## 4. Progress

### 4.1 Fe(VI) Synthesis

In accordance to task 1 the first set-up as seen in Figure 1 is currently running and being used for experiments. Original results have shown that TOC was not being removed effectively. To determine the source of this problem the Fe(VI) that had been used was tested using Mössbauer spectroscopy. The results from this have shown that our original Fe(VI) samples were less than two percent of the Fe(VI) oxidation state, with the rest being Fe(III). To overcome this difficulty we had decided to produce our own Fe(VI) samples. To complete this we have developed a process of oxidizing Fe(III) into Fe(VI) using ozone. The solid preparation method has been realized through the reaction seen in R1.



Fe(VI) preparation consists of two principal steps. First the loading of KOH onto the surface and pores of FeOOH through adsorption is completed to prepare the reactants. Next, oxidation of the reactant complex by ozone is done to produce potassium ferrate. The setup for preparation of Fe(VI) can be seen in Figure 3. The first step consists of measuring a quantity of FeOOH and introducing it into a KOH solution. Next this mixture was slightly heated to about 60 °C and simultaneously stirred for one minute. The resulting solution is then placed into an oven at 90 °C to evaporate the water from the solution. Once dried the complex (FeOOH+KOH) was then

placed in the fluidized bed reactor. Step two consists of the following stages. Ozone is produced from oxygen by an ozone generator and streamed into a humidifier containing distilled water. The humidified ozone is then fed to fluidized bed reactor to oxidize the KOH FeOOH complex. Glass wool is used to retain the reactants in the reactor. The reaction product is a dark purple powder containing a proportion of potassium ferrate and unreacted reactant.

## 4.2 Fe(VI) Analysis

### 4.2.1 Spectrometry

At the end of the reaction the solid product purity is measured using a UV/vis spectrophotometer. The solid product is filtered with a large quantity of deionized water. This filtrate is what is measured using the UV/vis spectrophotometer at 510 nm. Molar absorptivity at 510nm had been determined previously as  $1150 \text{ M}^{-1} \text{ cm}^{-1}$  by Bielski and Thomas (1987), based on the Beer-Lambert law as shown in the equation  $A=\epsilon bc$ , in which “A” is absorbance (no units, since  $A = \log_{10} P_0 / P$ ); “ $\epsilon$ ” is molar absorptivity, with units of  $\text{L mol}^{-1} \text{ cm}^{-1}$ ; “b” is the path length of the sample (i.e., the path length of the cuvette in which the sample is contained, expressed in centimeters); and “c” the concentration of the compound in solution, expressed in  $\text{mol L}^{-1}$ . The determination of the molar absorptivity of the ferrate and the immediate measurement of the filtrate with the spectrophotometer gives the absorbance of light by Fe(VI). This value can then be used to calculate the concentration of Fe(VI) in the product through the equation E1.

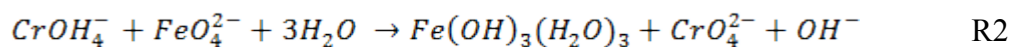
$$\text{Conversion} = \frac{\left( \frac{\text{Abs}}{1150 \times 1} \right) \times 56 \times \text{Vol}(\text{filtrate})}{\text{Iron}(\text{content}) \times \text{FeOOH}(\text{weight})} \quad \text{E1}$$

Abs is the value from the spectrophotometer, Vol(filtrate) is the volume of deionized water used in the filtration, expressed in L. Iron(content) is the proportion of iron contained in the FeOOH used for the reaction, FeOOH(weight) is the weight of FeOOH used for the reaction in grams, and last the 1=1cm for the path length of the cuvette used in the spectrophotometer. 10% conversion is the current maximum we have achieved with the current set-up. Optimization will be completed.

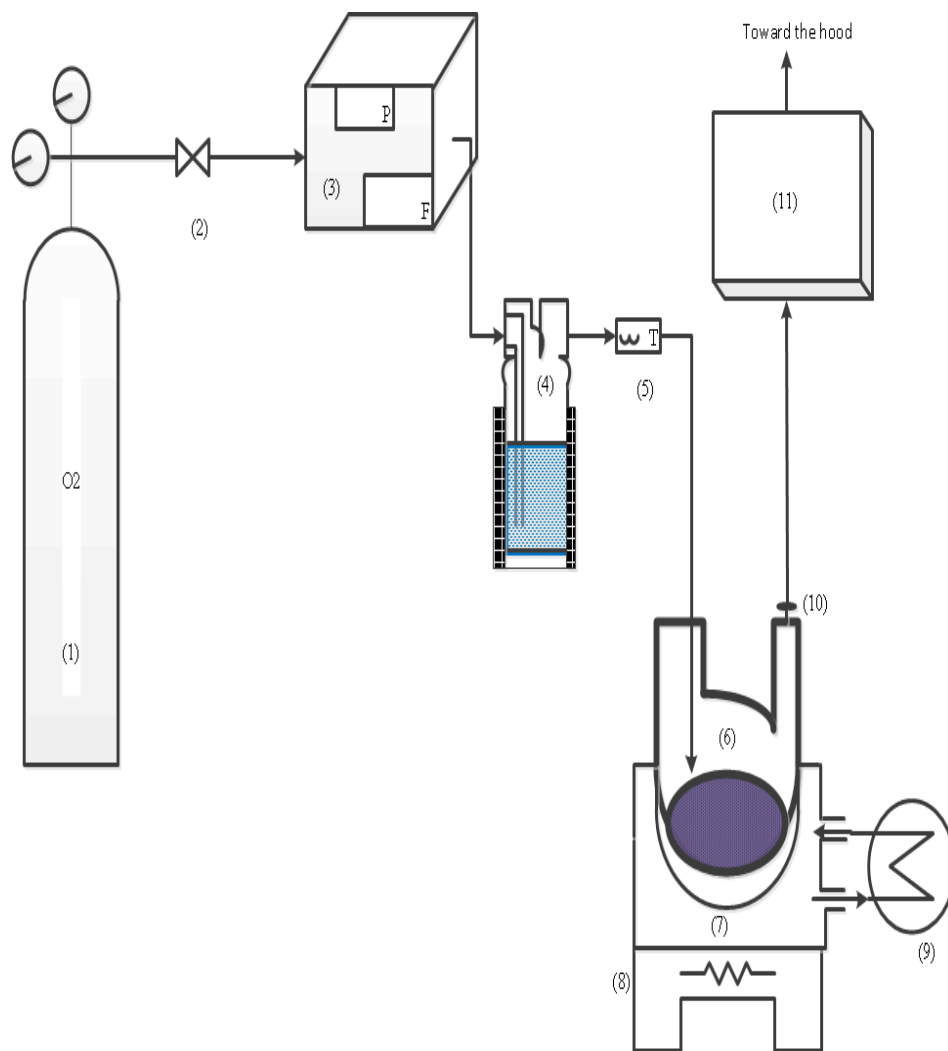
Fe(VI) has been purchased as well to make sure ferrate properties are constant throughout the study of organic removal. This potassium ferrate has been analyzed using UV/vis in conjunction with Beer-Lamberts law to give a concentration of 30% ferrate w/w.

### 4.2.2 Titration

The previous analysis of Fe(VI) purity in potassium ferrate only works for samples that were made in the lab.  $\text{K}_2\text{FeO}_4$  has also been bought from a chemical company. To determine the purity of this Fe(VI) another method is needed. A method from J.M. Schreyer of the University of Kentucky [12] will be used. This method is based on the oxidation of chromite in strongly alkaline solution with the ferrate(VI) ion as shown in reaction 2.



This method is applicable to the analysis of solutions containing low concentrations of the ferrate(VI) ion. The procedure is as follows. First saturated sodium hydroxide is added to a chromic chloride solution.



**Fig. 3** Diagram of Fe(VI) preparation setup (1) Oxygen cylinder; (2) Valve; (3) Ozone generator; (4) Humidifier containing distilled water and heat tape; (5) Set of thermometers for wet and dry temperatures; (6) Fixed bed reactor containing FeOOH+KOH particle to be oxidized; (7) Jacket heat exchanger; (8) Magnetic stirring machine; (9) Temperature controller for heat exchanger; (10) Particle filter; (11) Ozone analyzer.

To this the sample to be analyzed is added and stirred until dissolution of the potassium ferrate is complete. Dilution is then done with distilled water followed by addition of sulfuric and phosphoric acids. Titration is then completed with a standard ferrous solution and a sodium diphenylamine sulfonate indicator. The end point is marked by a change from purple to light green. From the known amount used of the ferrous solution titrant the percent potassium ferrate can be calculated as seen in equation 2.

$$\text{Percent } K_2FeO_4 = \frac{(\text{ml of } Fe^{2+} * N Fe^{2+}) * K_2FeO_4 \text{ MW}}{3000 * m} \quad E2$$

Where  $Fe^{2+}$  is the titrant solution used, N is normal, MW is molecular weight, and m is the weight of sample used in the analysis.

Due to the inherent properties of this method only low concentrations of ferrate can be measured accurately. For our study we want to analyze much larger concentrations therefore this is not practical unless solutions are diluted. Dilutions will be performed and analysis will be done to compare the values from different analysis methods.

#### 4.3 Total Organic Carbon (TOC) Removal

Studies by the United States Geological Survey have found that many organics are present in produced water from shale and coal bed methane (CBM) wells across the United States, including Wyoming. This is due waters interaction with coal during the natural gas production process. The total organic carbon varies across the wells, but on average it was found that there is 1.18-4.5 ppm TOC in produced water from CBM wells and 8.12-346 ppm TOC in produced water from shale gas wells. The values for Wyoming only included CBM wells with an average of 4.5 ppm TOC. A large variation of organic components make up the TOC in produced waters; for Wyoming these were categorized as polycyclic aromatic hydrocarbons (PAH), heterocyclic compounds, phenols, aromatic amines, other aromatics, and non-aromatic compounds [13]. Of these categories PAH's, phenols, and heterocyclic compounds were the most prolific. In this study components have been chosen from these categories for further research. So far compounds from the phenol group and the heterocyclic group have been chosen including phenol, and benzothiazole respectively.

Reactions studied include variation of Fe(VI) dosage, pH, and reaction times to find the optimal conditions at which Fe(VI) oxidizes the most efficiently. Later studies will also be done at varying initial organic concentrations, varying temperatures, and varying volumes.

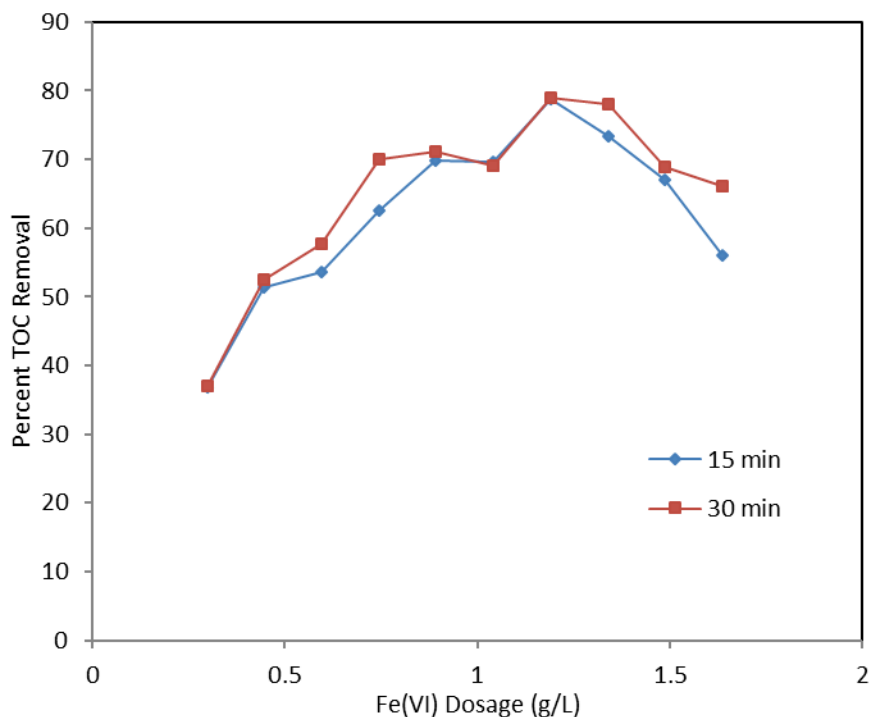
##### 4.3.1 Phenol removal

Phenol removal tests at varying initial Fe(VI) concentrations were completed. The reactions for the variation of Fe(VI) concentrations was done at a pH=4 for 15 min., an initial TOC concentration of 20 ppm, and a stirring rate of 250 RPM. It has been found that after adding more than 1.2 g/L of Fe(VI) the percent of TOC removal plateaued, meaning the extra Fe(VI) did not oxidize anymore organics giving an optimal Fe(VI) concentration of 1.2 g/L as seen in Figure 4. This concentration of Fe(VI) was then used to measure the removal efficiencies at varying pH's. This data can be seen in Figure 10. An optimal pH of 4 has been found to be the condition where phenols oxidation occurs most efficiently by Fe(VI). Reactions were also run at longer times to see if any oxidation occurs later then 30 min. Studies show that after 30 min no reaction is occurring and the TOC concentrations stay constant, as seen in Figure 5.

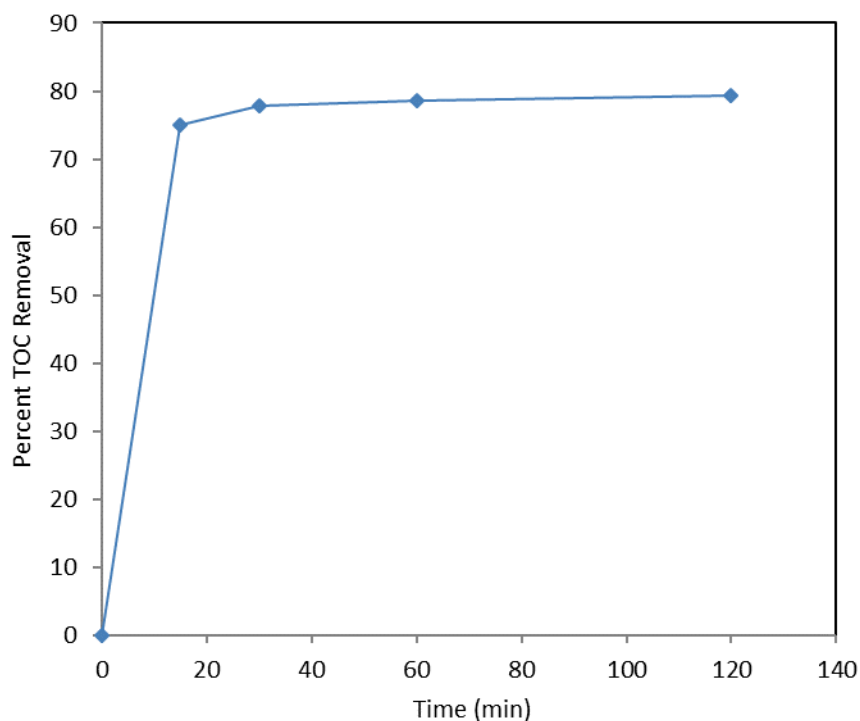
A high performance liquid chromatograph (HPLC) was recently purchased for use in Dr. Fan's research group. Using this it has been found that all the phenol is being oxidized in the reaction. Figure 6 shows the 20 ppm phenol peak that appears at a resonance time of 1.784 min. An



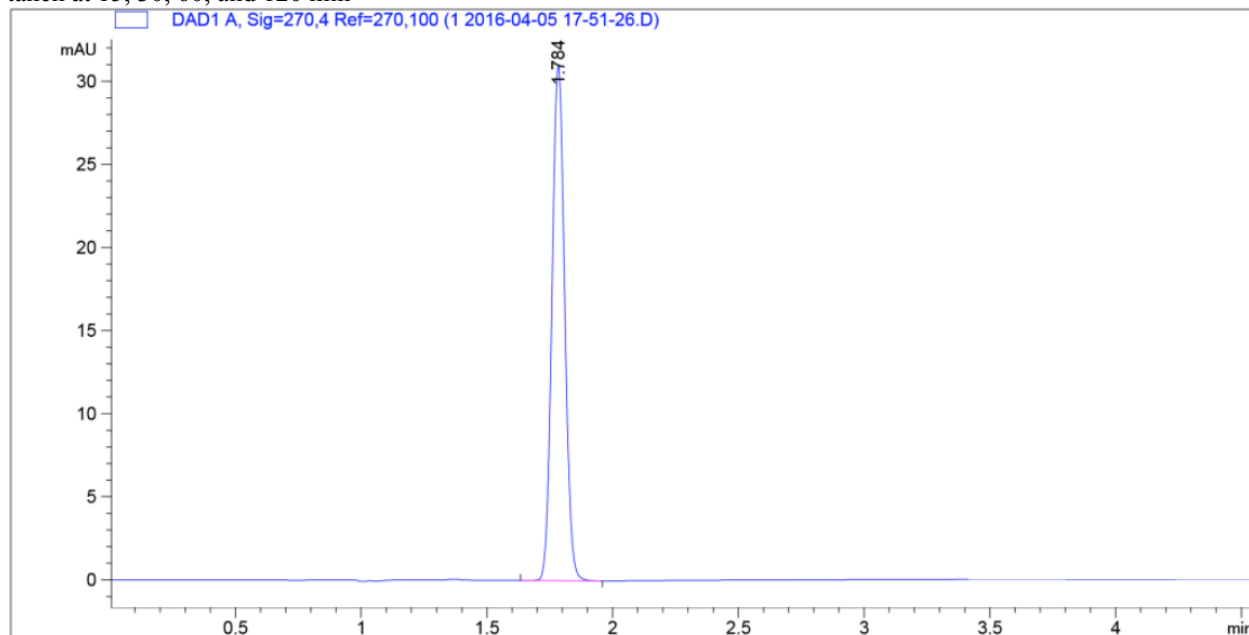
analysis of the water after oxidation shows that this peak completely disappears at 1.784 min. as seen in Figure 7. A negative peak shows up in the water after oxidation suggesting that



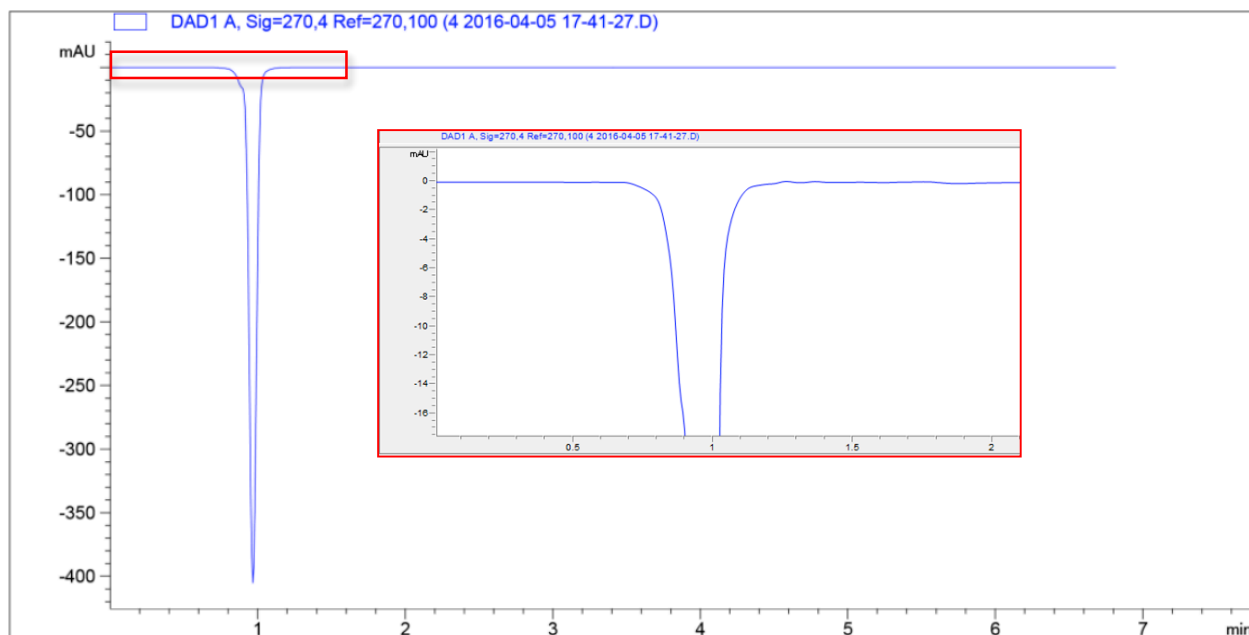
**Fig. 4** Percent TOC removal at varying Fe(VI) concentrations. The initial concentration of TOC as phenol was 20 ppm with pH value of 4. The reaction was run for 30 min. at a stirring speed of 250 RPM with samples taken at the end of reaction and in the middle of the reaction.



**Fig. 5** Percent TOC removal at varying times. The initial concentration of TOC as phenol was 20 ppm with an initial dosage of 1.2 g/L Fe(VI). The reaction was run for 120 min. at a stirring speed of 250 RPM with samples taken at 15, 30, 60, and 120 min



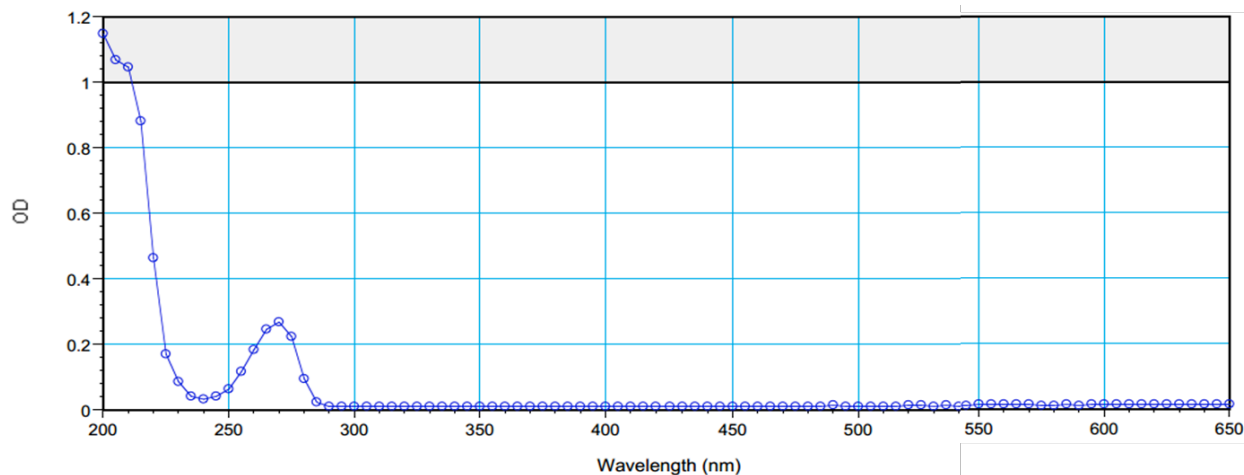
**Fig. 6** HPLC chromatogram for initial 20 ppm phenol sample before Fe(VI) oxidation reaction



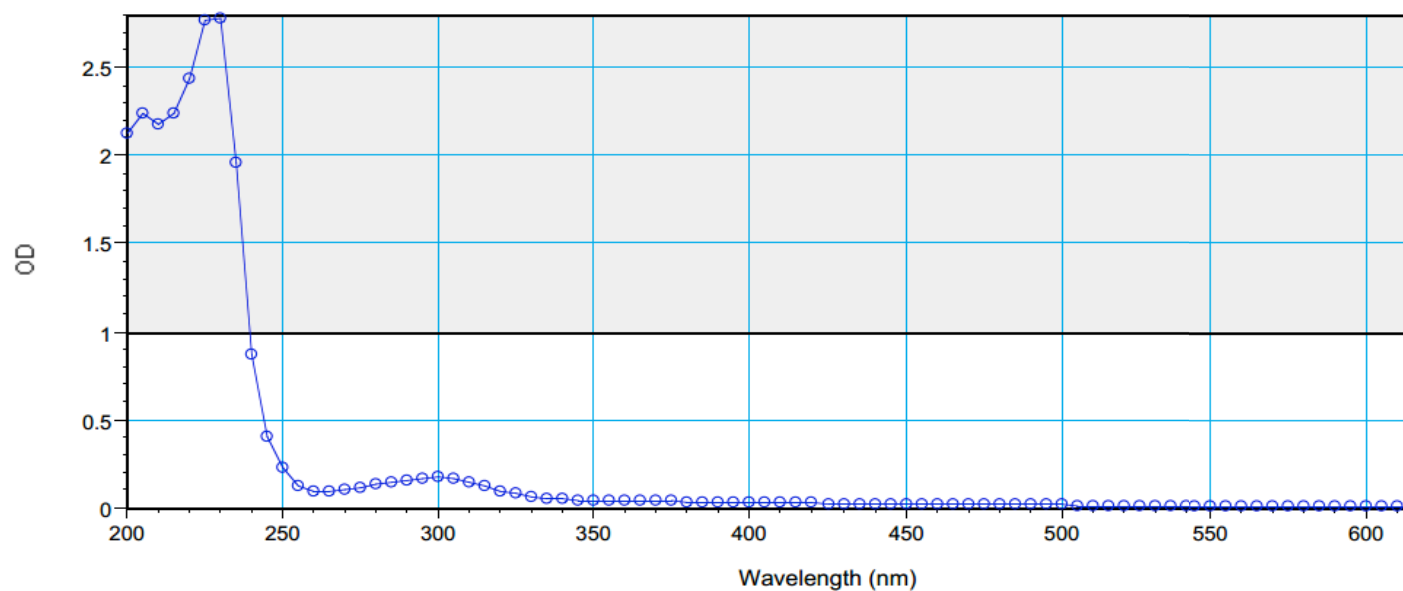
**Fig. 7** HPLC chromatogram for Phenol removal after 15 min reaction with initial dosage of 1.2 g/L Fe(VI) and phenol initial concentration of 20 ppm at a pH of 4

phenol is being oxidized into other organics that remain in the water, and the peak being negative because the absorbance of the component is lower than that of the HPLC carrier compounds. A UV/Vis spectrum analysis was then completed as seen in Figures 8 and 9. Here it can be seen that the phenol peak at 270 nm is gone and new peaks have formed at 300 nm and below 250

nm. These unknown organic compounds will be identified using nuclear magnetic resonance (NMR) as well as liquid chromatography mass spectrometry (LC-MS).



**Fig. 8** UV/Vis spectrum for initial 20 ppm phenol sample before Fe(VI) oxidation reaction



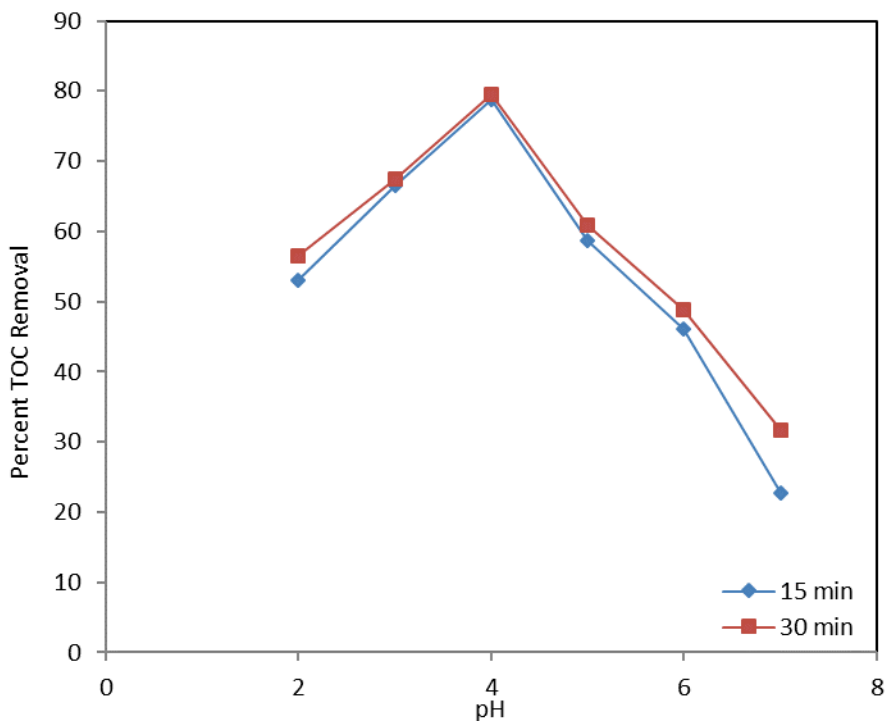
**Fig. 9** UV/Vis spectrum for Phenol removal after 15 min reaction with initial dosage of 1.2 g/L Fe(VI) and a phenol initial concentration of 20 ppm at a pH of 4

Chemical oxygen demand (COD) analysis was also completed on the samples obtained from experiments. The same trend exists in COD removal as in TOC removal. The optimal pH of three and four can be seen in Figure 6 where 100% COD removal occurred. The pH of one was not able to be completed due to the reagents used in the COD analysis not being compatible to such a low pH value.

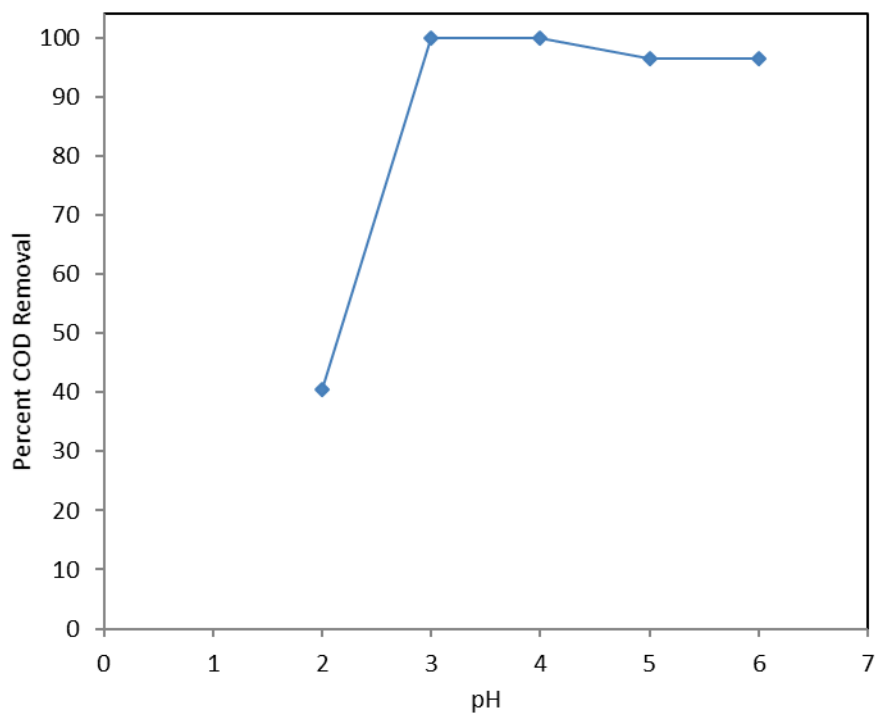
#### 4.3.2 Benzothiazole Removal

Benzothiazole removal has also been studied. The same variation of conditions as seen in phenol removal has also been done. This includes variation of pH and Fe(VI) concentrations. It can be

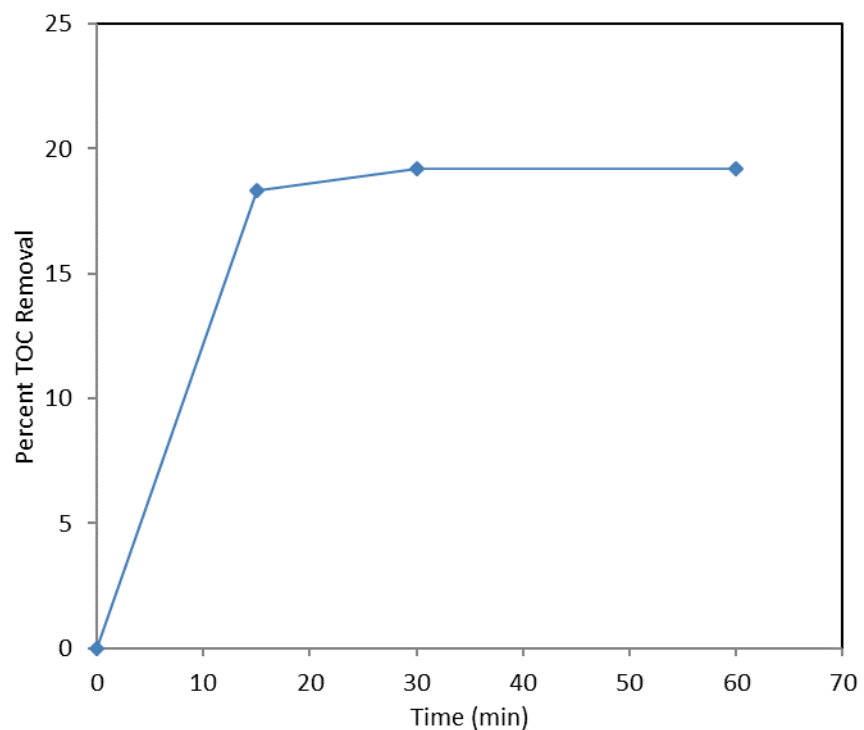
seen in Figure 13 that the optimal Fe(VI) concentration still has yet to be found as the removal efficiency is still increasing. Samples were taken at 15 and 30 minutes. There is no notable difference at Fe(VI) concentrations below 1.35 g/L, meaning the reaction has finished. Although above this concentration more removal is done at the 30 minute sampling time. This means with the higher Fe(VI) concentrations the reaction takes longer to finish, but more benzothiazole removal is achieved.



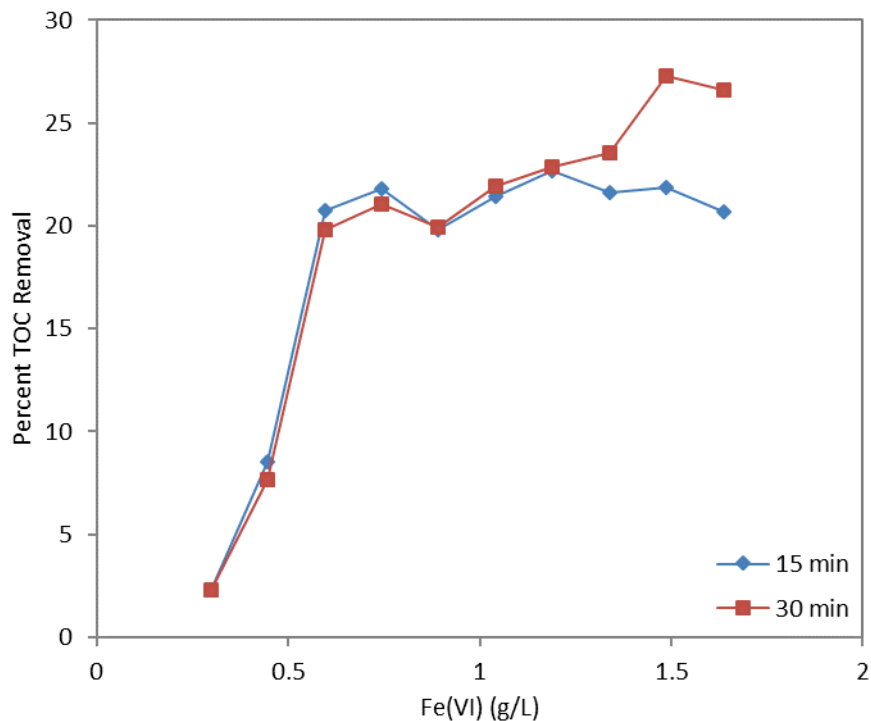
**Fig. 10** Percent TOC removal at varying pH levels. The initial concentration of TOC as phenol was 20 ppm with an initial dosage of 1.2 g/L Fe(VI). The reaction was run for 30 min. at a stirring speed of 250 RPM with samples taken at the beginning, end, and middle of the reaction.



**Fig. 11** Percent COD removal at varying pH levels. The initial concentration of TOC as phenol was 20 ppm with an initial dosage of 0.4 g/L of Fe(VI). The reaction was run for 15 min. at a stirring speed of 250 RPM.

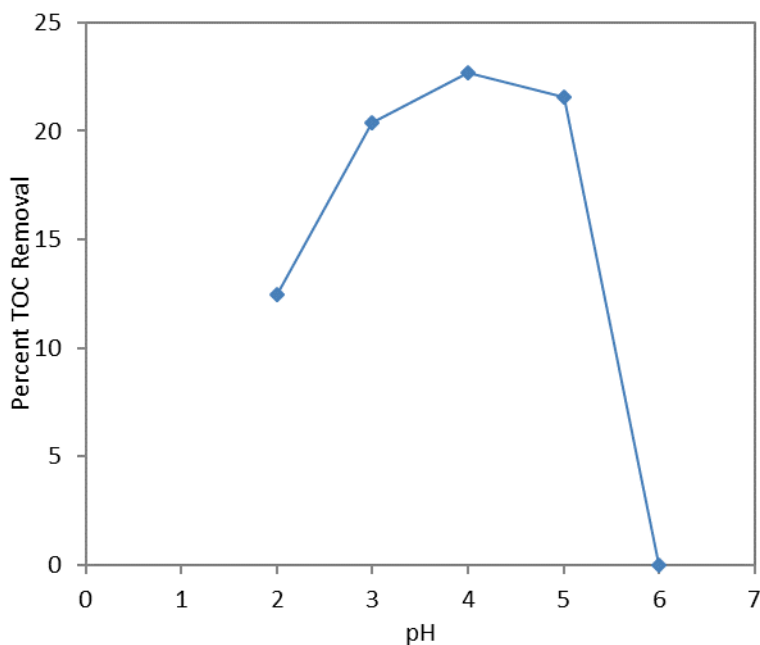


**Fig. 12** Percent TOC removal at varying time. The initial concentration of TOC as benzothiazole was 20 ppm with an initial dosage of 1.05g/L Fe(VI). The reaction was run for 60 min. at a stirring speed of 250 RPM with samples taken at 15, 30, and 60 min

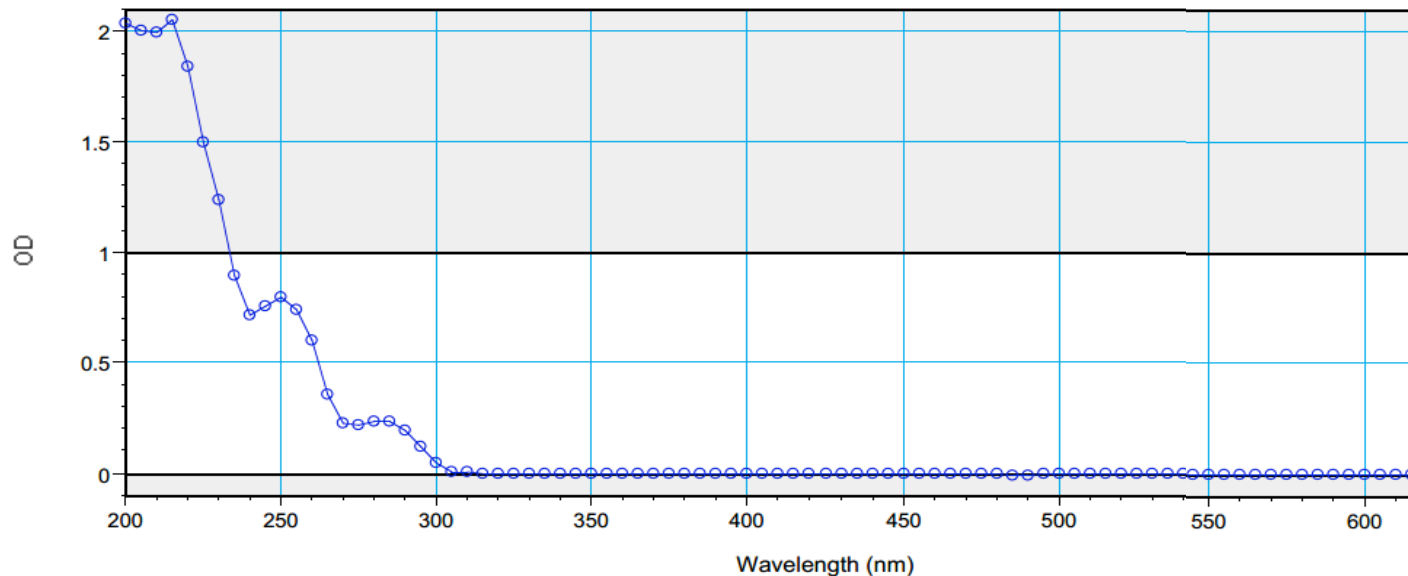


**Fig. 13** Percent TOC removal at varying Fe(VI) concentrations. The initial concentration of TOC as benzothiazole was 15 ppm at a pH of 4.0. The reaction was run for 30 min at 250 RPM with sampling taken at the end and the middle of the reaction.

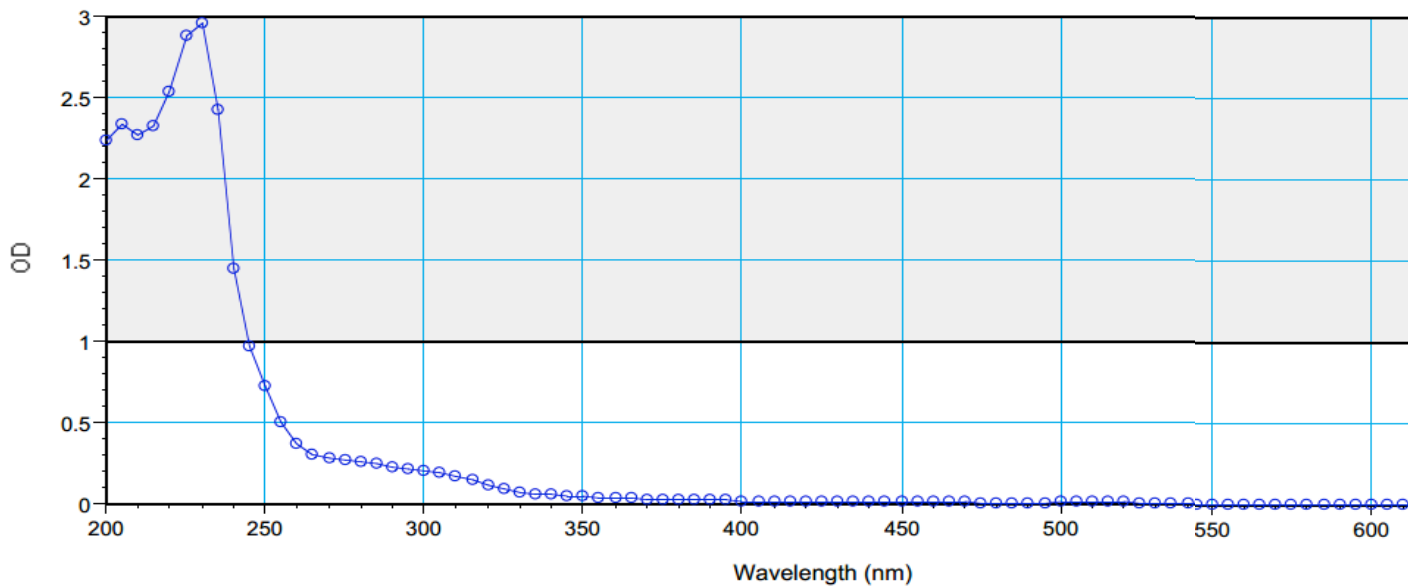
Variation of pH on benzothiazole removal after 15 min. can be seen in Figure 14. For pH values of 2, 3, and 4 the samples that were taken at 30 minutes had no notable difference to the 15 minute samples. For the rest of the pH values the 30 minute TOC values actually increased instead of decreasing. The reason behind this is unknown and will be figured out in future work.



**Fig. 14** Percent TOC removal at varying pH values. The initial concentration of TOC as benzothiazole was 15 ppm at a Fe(VI) concentration of 4 g/L. The reaction was run for 15 min at 250 RPM with sampling taken at the end of the reaction.



**Fig. 15** UV/Vis spectrum for initial 20 ppm benzothiazole sample before Fe(VI) oxidation reaction



**Fig. 16** UV/Vis spectrum for benzothiazole removal after 15 min reaction with initial dosage of 0.72 g/L Fe(VI) and benzothiazole initial concentration of 20 ppm at a pH of 4

UV/Vis analysis has also been done for benzothiazole removal. Figure 15 shows 20 ppm benzothiazole in water before any oxidation has taken place. Peaks at 250 nm and 285 nm can be seen, as well as a peak around 220 nm. Since only benzothiazole is present these peaks are characteristic of benzothiazole. Figure 16 shows the UV/vis spectrum of the benzothiazole removal solution after the reaction has taken place. The characteristic peaks of 250 nm and 285 nm seem to have gone away, however they may be too small to see. HPLC analysis will be done on this to see if all the benzothiazole is removed. Peaks at 205 nm, 230 nm, and 300 nm have appeared though. These are the products of the reaction and need to be analyzed using NMR/LC-MS to be identified. The peaks are in the same location as the phenol removal peaks seen in Figure 9. This leads to a belief that the phenol and benzothiazole oxidation products are the same compounds. This hypothesis will be decided valid through the use of analysis techniques such as NMR and LC-MS to identify these compounds.

### *4.3 Analysis Methods*

#### *4.3.1 TOC Analyzer*

TOC analysis requires that 20 mL samples of the treated water be introduced to a glass vial. These glass vials are then placed into the ASI-V Shimadzu auto sampler. A calibration curve is then set-up for the TOC analysis. Air zero is used as the supply gas for the TOC-V<sub>CSN</sub> Shimadzu total organic carbon analyzer.

#### *4.3.2 COD Analyzer*

Small portions of the treated water samples were taken out for Chemical Oxygen Demand (COD) measurements via a colorimetric technique. Prior to the colorimetric determination of COD, specified amount of the samples were added into reagent vials containing dichromate solutions provided by Hach Co., followed by vigorous mixing and then placed in a pre-heated COD reactor for two hours at 150°C. The vials were then cooled down to room temperature, removed from the reactor and then analyzed colorimetrically via Hach DR/4000 instrument at a wavelength of 620 nm.

#### *4.3.3 High Performance Liquid Chromatography*

An Agilent Technologies 1260 infinity high performance liquid chromatograph system was used. For phenol analysis a ratio of 60/40 water to methanol was used as they carrier. The HPLC is equipped with a diode array detector and phenol was analyzed at a wavelength of 270 nm.

### *4.4 Parties Involved*

The completion of this project has been assumed by Abdulwahab M. Ali Tuwati, a post doc with a PhD in chemistry, Andrew Thomas Jacobson, a Masters candidate in chemical engineering at the University of Wyoming, and Mohammad Tarabzoni an undergraduate student in chemical engineering at the University of Wyoming; all under the supervision of Professor Maohong Fan. The ideas behind the project have also been introduced to students through the GK-12 Environmental and Energy Nanotechnology NSF Fellowship through Andrew Jacobson. As a fellow, travel has been done to Chugwater, WY to introduce science topics including this ongoing research. Students from around Wyoming have also been given lab tours explaining the ideas behind the setups of this research and what the goal of this research is.



## 5. Future Work

Future work will contain a number of duties. First and foremost other molecules besides phenol and benzothiazole need to be investigated. Since phenols and benzothiazole fall into two main groups that have been found in Wyoming produced water (heterocyclic compounds and phenols) the next component to be studied will be a polyaromatic hydrocarbon (PAH) due to their abundance in produced water across the US including Wyoming. Also removal of a combination of these compounds will be completed to find the selectivity of the Fe(VI) ion for oxidation on the simultaneous removal of multiple contaminants. More analyses will be completed using high performance liquid chromatography (HPLC) with a mass spectrometer along with NMR to identify the products from the oxidation reactions with Fe(VI). The method in synthesizing potassium ferrate from KOH and FeOOH will be optimized by varying initial conditions to give rise to higher Fe(VI) conversion. This higher conversion will be beneficial in that less Fe(VI) powder will need to be used in oxidation reactions. Once the Fe(VI) has been oxidized to Fe(III) for the removal of TOC there is still potential for the removal of heavy metals such as arsenic and selenium. This work will be completed once optimal conditions for the removal of TOC have been studied. Once the method has been validated for removal of multiple organic carbon types and inorganic molecules it will be applied to real water samples from various places in Wyoming.

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