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# Decolorization of Reactive Blue 4 Dye by Fenton Process Using Heterogeneous Fe/SBA-15 Catalyst

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**Decolorization of Reactive Blue 4 Dye by Fenton Process Using Heterogeneous Fe/SBA-15**

**Catalyst**

A Thesis

Submitted to the Faculty

of

Rose-Hulman Institute of Technology

by

John Christopher Overton

In Partial Fulfillment of the Requirements for the Degree

of

Master of Science in Chemical Engineering

11/12/2018

# DEFENSE REPORT

**ROSE-HULMAN INSTITUTE OF TECHNOLOGY**

**Final Examination Report**

John Overton

Name

Chemical Engineering

Graduate Major

Thesis Title  Decolorization of Reactive Blue 4 Dye by Fenton Process Using Heterogeneous Fe/SBA-15

Catalyst

**DATE OF EXAM:**    October 9, 2018

**EXAMINATION COMMITTEE:**

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PASSED ___X___          FAILED _____

# ABSTRACT

Overton, John Christopher

M.S.Ch.E.

Rose-Hulman Institute of Technology

10/27/2018

Decolorization of Reactive Blue 4 Dye by Fenton Process Using Heterogeneous Fe/SBA-15 Catalyst

Thesis Advisor: Dr. Gregory Neumann

Remediation of textile wastewater, particularly concerning dyes, has been a longstanding concern. With the rise of more stringent regulations, the study of advanced methods of waste treatment is becoming necessary. The objective of this study was to synthesize and observe the use of a heterogeneous catalyst in a Fenton reaction by doping an SBA-15 catalyst support with iron. The catalyst was successfully synthesized, was easily filterable, exhibited resistance to acidic environments, and showed thermal stability. When used in a Fenton's Reagent reaction setup, the single trial use of the catalyst achieved a final dye conversion of 86.8% at the optimal conditions of 2 g/L catalyst to volume ratio, 0.15 wt% Fe catalyst, 20 mM of $H_2O_2$, and temperature of 30 ºC. Reusability was a concern, as iron was observed to be leaching from the catalyst, and suggestions for preventing leaching and enhancing reusability were presented.

# ACKNOWLEDGEMENTS

First, I would like to thank my thesis advisor, Dr. Gregory Neumann, for all of his assistance throughout the course of the project. I couldn't have completed this work without having his ear to run ideas by. Whenever I became stuck in my research, he made sure to throw out plenty of suggestions to help get me started back on my feet. I would also like to thank my other committee advisors, Dr. Michael Robinson and Dr. Stephanie Poland. I had the idea of looking into wastewater treatment for my thesis due to a class I took with Dr. Robinson, and his friendliness and vast knowledge of wastewater treatment was invaluable to my project. Dr. Poland helped me flesh out some ideas with my project in the early stages, and helped make the chemistry department an inviting and familiar place. I would also like to thank Dr. Daniel Morris for help with some analytical methods employed in my thesis. Even though I approached him with a couple of challenging tasks, he was still happy to take the time to assist me. I would like to give a special thanks to Frank Cunning, Lou Johnson, and Michelle Sharp for providing me with all of the equipment and supplies I needed throughout the duration of my experimentation. Frank was especially helpful and supportive, and he was always making sure us master's students were doing alright. Lastly, I'd like to thank my other master's peers, Rachel Weber, Jenn Mobley, and Ryan Beere, for the insight, laughs, and support throughout the whole process.

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# LIST OF ABBREVIATIONS

AOP    Advanced Oxidation Process

BOD    Biological Oxygen Demand

COD    Chemical Oxygen Demand

DI    Deionized

RB4    Reactive Blue 4

SBA    Santa Barbara Amorphous

TEOS    Tetraethylorthosilicate

TOC    Total Organic Carbon

UV-Vis    Ultra-Violet Visible

XRD    X-Ray Diffraction

# LIST OF SYMBOLS

| | | |
|---|---|---|
| X | Dye Conversion | *unitless* |
| $C_{Ao}$ | Initial Dye Concentration | *ppm* |
| $C_A$ | Dye Concentration at Time t | *ppm* |
| t | Time | *hr* |

# LIST OF EQUATIONS

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^{+} \tag{2}$$

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \tag{3}$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{4}$$

$$Fe^{2+} + OOH^{\cdot} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \tag{5}$$

$$Fe^{3+} + OOH^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+} \tag{6}$$

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \tag{7}$$

$$R^{\cdot} + H_2O_2 \rightarrow ROH + OH^{\cdot} \tag{8}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \tag{9}$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{10}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{11}$$

$$R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR \tag{12}$$

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROOR + O_2 \tag{13}$$

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \tag{14}$$
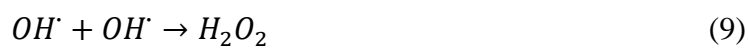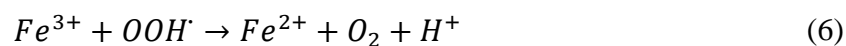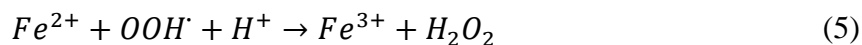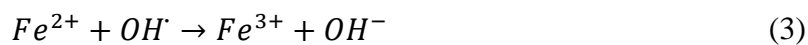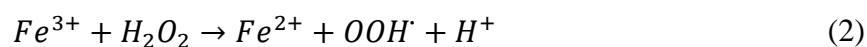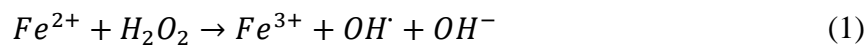
$$A = \epsilon l c \tag{15}$$

$$\% \; conversion \; (X) = \frac{C_{Ao} - C_A}{C_{Ao}} \times 100\% \tag{16}$$

$$\ln\left(\frac{[C_A]}{[C_{Ao}]}\right) = -kt \tag{15}$$

$$\ln(1 - X) = -kt \tag{16}$$

$$\frac{dC_A}{dt} = -k[C_A]^2 \tag{17}$$

$$\frac{1}{[C_{Ao}]} - \frac{1}{[C_A]} = -kt \tag{18}$$

$$k = Ae^{\left(-\frac{E_A}{RT}\right)} \tag{19}$$

# 1. INTRODUCTION

## 1.1 General Background

The remediation of textile wastewater is a long-standing and still prevalent battle. In many developing countries, the textile industry serves as one of the greatest sources of untrained, paid labor[1]. Due to the size and output of the industry, an increasingly large amount of waste is being generated, as it takes around 200 L of water to produce one kg of textile[2]. Textile wastewater is also difficult to efficiently and environmentally consciously remediate[1]. The contents of textile wastewater vary between industries, but typically include suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), various chemicals, colors, and odors[1]. BOD and COD are measurements of the amount of dissolved oxygen required for biological and chemical decomposition of organic molecules in solution, respectively. When effluent from a textile plant enters a body of water, both the suspended solids and coloration reduce the ability of light to penetrate the water, inhibiting photosynthesis[1]. Dyes and suspended solids also interfere with the natural reoxygenation of the water, making it difficult for aquatic life to flourish[1].

Dyes are of particular concern as they are not typically capable of degradation by conventional means. One issue is that dyes can be synthetic in nature, which limits the feasibility of decomposition by microorganisms[3]. Often times, the dyes are toxic or carcinogenic to living organisms, further posing a problem for biological decomposition[3]. Standard methods of oxidation tend to prove ineffective as well, as dye molecules are complex, often containing at

least one aromatic ring. The standard wastewater treatment processes of filtration, sedimentation, and flocculation are typically ineffective. Filtration, while it can be effective, only removes dye from solution instead of degrading it. Dye molecules are resistant to forming sediment or effective flocs, which is when large clumps of molecules settle out of solution, pulling other molecules out of solution as they settle[1]. In order to effectively degrade dyes in wastewater, alternative, advanced methods need to be used.

1.2 Background on Dyes

Before discussing textile wastewater treatment, it is helpful to understand some basic characteristics of dyes. Dyes are a type of colorant, the other main colorant being pigments[4]. The main difference between pigments and dyes is that dyes are soluble in at least one solvent, while pigments are not. Roughly 75% of dyes are organic, yet over $7x10^5$ tons of synthetic dyes are produced annually[4]. In the textile industry, dyes are classified by the process in which the dye is imparted to a material. Some common types of dyes are acidic, basic, reactive, and direct dyes[5].

Each dye varies in its ability to bond with a material, known as its affinity. For instance, reactive dyes are better suited for wool and cotton, while direct dyes are useful in dying linens[1]. The strength of a dye's affinity to a particular material varies as well. Some dyes, such as reactive dyes, form strong bonds with certain materials[4], but have a low affinity for these materials[6]. A large amount of dye remains in solution after the dying process, and therefore, a significant amount of spent dye is sent off as waste.

The component of dyes that gives them their color is known as the chromogen[4]. The chromogen is composed of two parts: chromophore and auxochrome. The chromophore is the

portion primarily responsible for the color produced by the dye, and is capable of yielding color on its own. The auxochrome interacts with the chromophore to alter the dye color, but cannot produce color on its own. Dyes can alternatively be classified by their chromophores, with some common types being azo, nitro, methine, and anthraquinone dyes[4]. Following is a figure of the dye solvent yellow 7 with the different components highlighted. The chromophore is an azo group, with an alcohol auxochrome. The entire molecule serves as the chromogen in this instance.
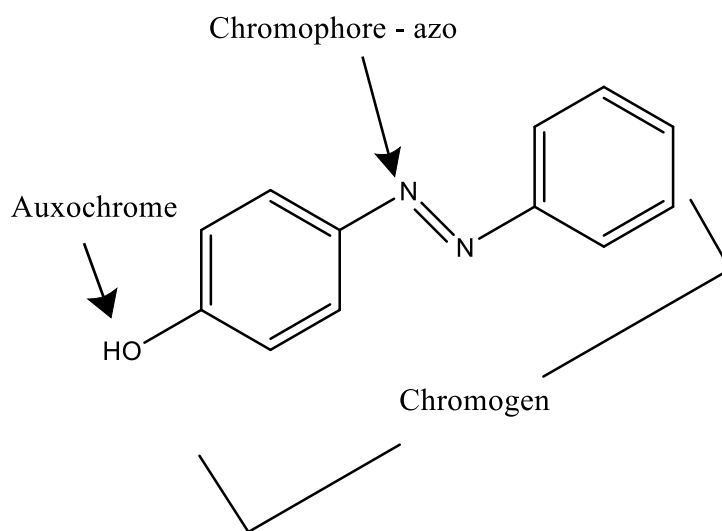


Figure 1.1: Solvent yellow 7, an azo dye. MW of 198.23 g/mol.

Although solvent yellow 7 is simple and small, dyes can vary immensely in size and complexity. Dyes can contain several chromophores and auxochromes, yielding larger molecules such as Reactive Blue 4 and Reactive Red 120.
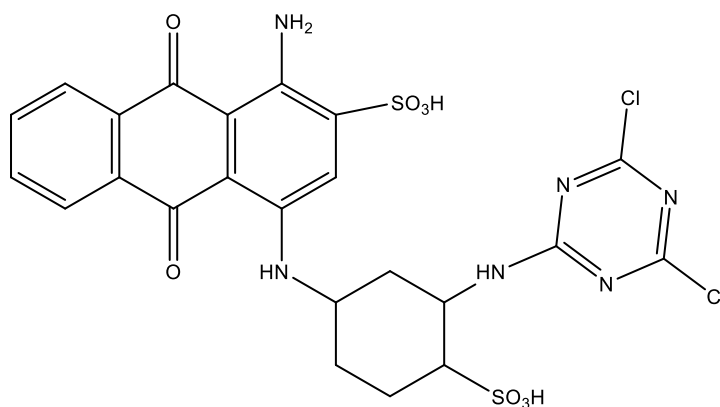
Figure 1.2: Reactive Blue 4, an anthraquinone dye. MW of 637.43 g/mol.
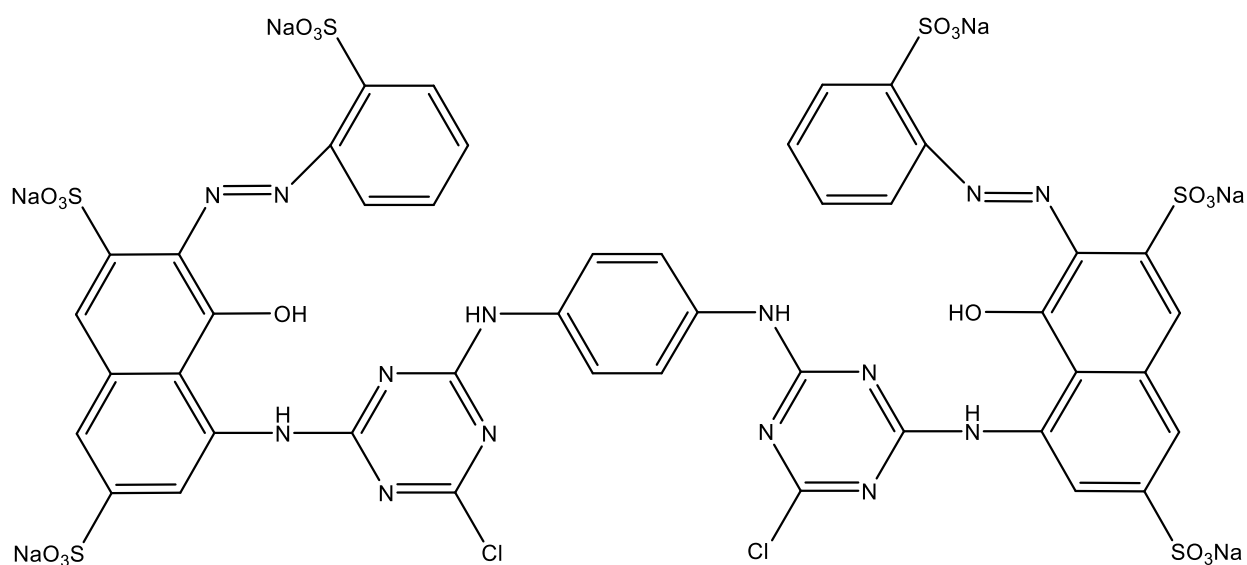


Figure 1.3: Reactive Red 120, an azo dye. MW of 1469.98 g/mol.

It was decided that Reactive Blue 4 would be used in this study, as reactive dyes pose an issue of low affinity to materials and are fairly commonplace in the textile industry[6]. Reactive Blue 4 (RB4) is a decently sized molecule (MW: 637.43 g/mol) with a complex anthraquinone chromophore, so degradation by standard methods could prove challenging. There exist several studies exploring different methods of degradation with RB4 as well, which assists with analysis and experimental design.

There are three primary potential methods for treating textile wastewater: chemical treatments (particularly advanced oxidation processes), physical treatments, or biological means[3]. Advanced oxidation processes (AOP's) are more complex methods that generally rely on the production of hydroxyl radicals, OH•, as the main oxidizing reagent to fully degrade compounds. Physical treatments include processes such as adsorption, filtration, irradiation, and electrokinetic coagulation. Biological treatments can be difficult to control, but some strains of bacteria and microbial organisms have been utilized to effectively remediate textile wastewater[3],[7]. Chemical processes have proven to be promising in lab-scale experiments, and they also have the added benefit of degrading compounds instead of simply removing them.

1.3 Chemical Processes

Chemical means of textile wastewater remediation consists of a large variety of possible treatment processes. Prevalent options include Fenton's Reagent reactions, ozonation, photochemical oxidation, and electrochemical oxidation/destruction[3]. Of these options, ozonation is the only method that does not involve the use of hydroxyl radicals, as ozone is the primary oxidizing agent.

One of the simpler and more documented methods is known as Fenton's reagent reaction, which involves using $Fe^{2+}$ and $H_2O_2$. The iron in solution acts as a catalyst for breaking apart $H_2O_2$ molecules into hydroxyl radicals, which in turn oxidize organic chains and molecules. The interaction between iron and hydrogen peroxide is as follows[8]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^{+} \tag{2}$$

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \qquad (3)$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (4)$$

$$Fe^{2+} + OOH^{\cdot} + H^{+} \rightarrow Fe^{3+} + H_2O_2 \qquad (5)$$

$$Fe^{3+} + OOH^{\cdot} \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (6)$$
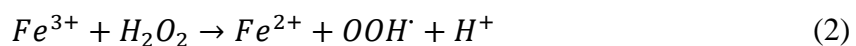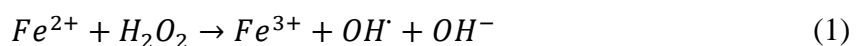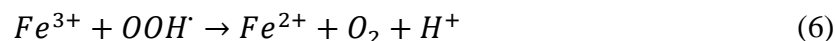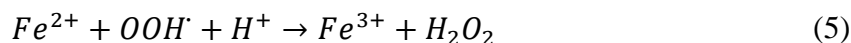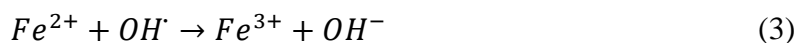
As seen in equation 1, the iron(II) in solution is oxidized by hydrogen peroxide, yielding a hydroxyl radical and a hydroxyl group. Then, by the pathways of either reaction 2 or 6, the iron(III) can revert to iron(II). Although the exact reaction pathway for oxidation of organics is difficult to determine, an approximate pathway is as follows:

$$OH^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \qquad (7)$$

$$R^{\cdot} + H_2O_2 \rightarrow ROH + OH^{\cdot} \qquad (8)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad (9)$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \qquad (10)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (11)$$

$$R^{\cdot} + RO_2^{\cdot} \rightarrow ROOR \qquad (12)$$

$$RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROOR + O_2 \qquad (13)$$
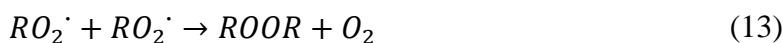
where R represents an organic molecule or chain[9]. Equations 7 and 8 illustrate the process in which the hydroxyl radicals oxidize organics. Equations 9 through 12 are termination steps, where radicals combine and end the chain reaction. The reaction steps for oxidation of organics by the Fenton reaction differ between molecules, and the reaction pathways are complex[10].

However, as long as hydrogen peroxide is present in solution, the reaction can theoretically continue until all organics are broken down to $H_2O$ and $CO_2$, known as mineralization[10].

The simplicity of the Fenton reaction has benefits and drawbacks. First, the Fenton's Reagent method is one of the most inexpensive AOP's presented. In a review by Holkar et al[11], out of the cost analyses that have been conducted on AOP processes, Fenton and Fenton-like wastewater treatment processes ranked as the most inexpensive arrangements. Table 1.1 below was adapted and simplified from their review, and it compares the price of the Fenton reaction to a couple of processes that will be discussed later. The relative inexpensive price of the Fenton reaction is likely due to the moderate cost of iron salts and hydrogen peroxide as the only reagents[12]. However, the values presented in the review did not take into account one major drawback of the Fenton process: sludge generation. Iron(III) is capable of precipitating in the presence of hydroxide molecules into iron hydroxide sludge, as well as flocculating with the dye molecules[11]. The sludge can be filtered off and disposed of, but it is not the most environmentally sound option.

Table 1.1: Simplified summary of treatment prices for various textile wastewater treatment methods. Adapted from a review by Holkar et al[11].

| Process for treatment of textile wastewater | Treatment cost ($/m$^3$) (the sludge disposal cost and labor cost are excluded) | References |
|---|---|---|
| Color removal by Fenton's process followed by COD removal by activated sludge | 0.4 USD per m$^3$ | [13] |
| Ozonation for the color and COD removal from biologically pretreated textile wastewater(Textile factory in Turkey) | 4.94 USD per m$^3$ | [14] |
| Fenton's process followed by coagulation (polyaluminium chloride) followed by ion exchange process applied to textile wastewater | 3.5 USD per m$^3$ | [15] |

Photochemical oxidation operates similarly to the Fenton's Reagent reaction, except that it utilizes UV irradiation to break hydrogen peroxide into hydroxyl radicals. The reaction is as follows[16]:

$$H_2O_2 + hv \rightarrow 2OH^{\cdot} \tag{14}$$

The hydroxyl radicals generated then react with organics in solution in a manner similar to the Fenton process. One major benefit to using photochemical oxidation is that it generates a high concentration of hydroxyl radicals, as it creates two for every hydrogen peroxide molecule. With more hydroxyl radicals present, degradation of molecules in solution proceeds fairly rapidly. A higher concentration of hydroxyl radicals also increases the likelihood that organics will be mineralized[3],[16]. UV irradiation should also generate little to no sludge, and the treatment acts as a disinfectant[1]. However, the use of UV could become an issue when used at a large scale. A industrial-scale cost analysis has yet to be performed, but it is expected that the cost of photochemical oxidation operation may be expensive to maintain[3]. Depending on the length of treatment, it would be difficult to prevent the formation of by-products as well, such as inorganic acids, halides, and organic aldehydes[3]. The figure below is an example of a small scale lab setup using a photochemical treatment process. The feed solution is pH adjusted, $H_2O_2$ is added, and the solution is passed through a reactor with a UV lamp.
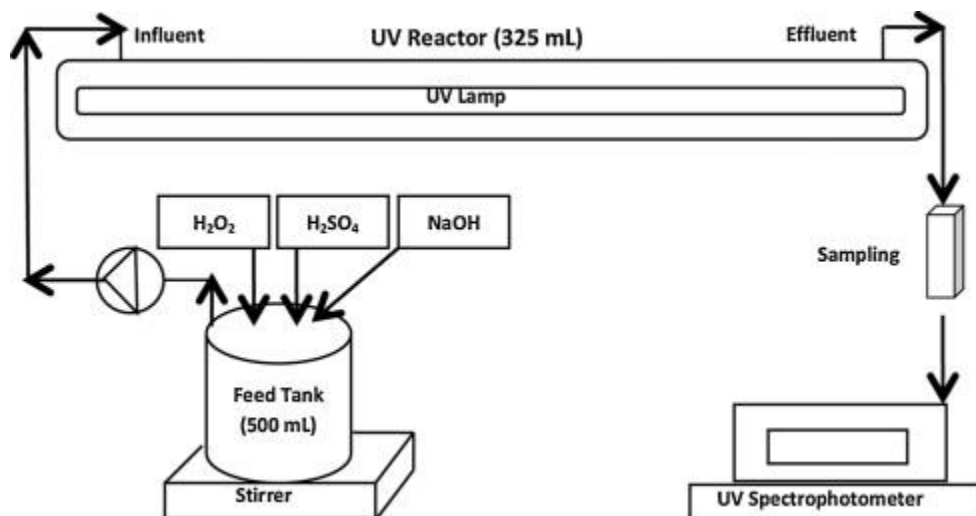
Figure 1.4: Example setup for a photochemical process[16].

The electrochemical process utilizes $TiO_2$ and $H_2O_2$ to generate hydroxyl radicals, often

with the help of UV light. When UV light makes contact with a $TiO_2$ semiconductor, it excites

an electron from the valance band to the conducting band[17]. This creates a positively charged

hole, which acts as a strong oxidizing agent. The hole can then either react with water molecules

to form hydroxyl radicals, or with organic molecules directly. In addition, the UV light works

similarly to the photochemical process, yielding more hydroxyl radicals. Therefore, with a

photoelectrochemical process, there are two sources of strong oxidizing potential: the valence

band holes and hydroxyl radicals. The combination of these two oxidizers yields substantial

results, as one study reported that they were able to achieve complete color removal for several

dyes[17]. Similar to the UV process, the photoelectrochemical process is limited by the cost

needed to operate both the UV source and electricity for the semiconductor. The price of

electricity in the electrochemical process alone is comparable to the price of chemicals used in

other processes, such as the Fenton reaction[3]. However, the photoelectrochemical process is

effective at mineralization and it is less likely to form by-products than the photochemical

process alone[3],[17]. Below is an example of a small-scale reactor designed for a photoelectrochemical process.
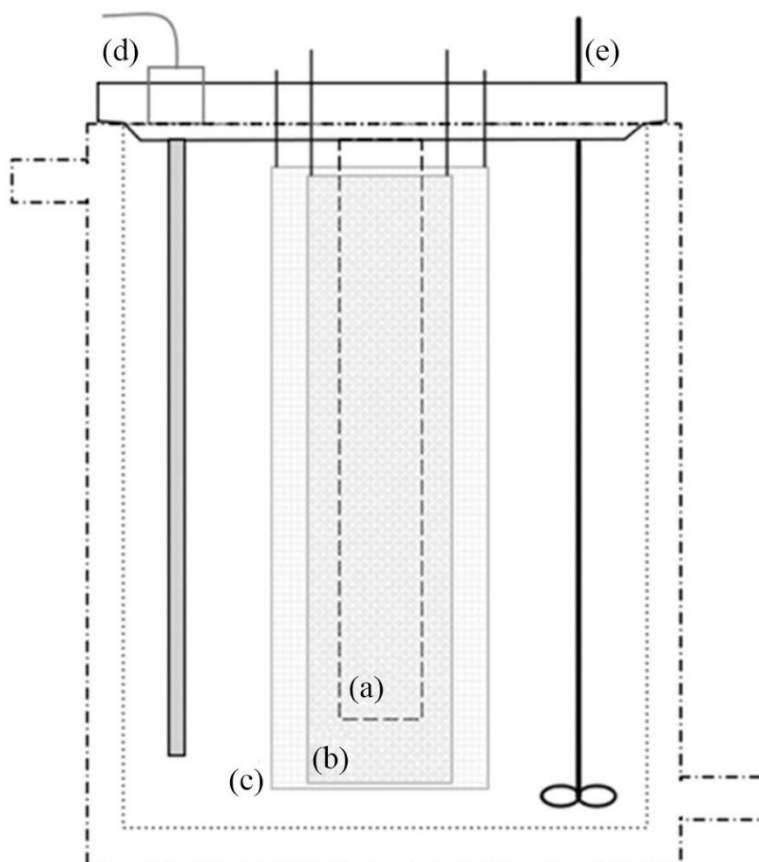


Figure 1.5: Example photoelectrochemical reactor setup[17]. (a) UV mercury lamp; (b) TiO$_2$ anode; (c) titanium mesh cathode; (d) reference electrode; (e) mechanical stirrer

On its own, ozone holds some of the greatest potential for degrading dyes in wastewater. Ozone has greater oxidation potential than hydrogen peroxide, 2.07 V to 1.78 V, which is due to the greater instability of the ozone molecule[3]. However, it does have a lower oxidation potential than hydroxyl radicals, 2.33 V, meaning that it is slightly less efficient than the products of breaking apart hydrogen peroxide[1]. Ozone provides many benefits when used as an oxidant for textile wastewater, as it does not form hazardous sludge and it is utilized in its gaseous state, which does not increase the total volume of wastewater[7]. However, properly using ozone is

complicated, as ozone has a half-life of approximately 20 minutes, which can become costly when continuous ozonation is required (see Table 1.1)[3].

1.4 Physical Treatments

Physical treatment of textile wastewater generally relies on removing products from solution instead of breaking them down. There are several possibilities with how the separation can be achieved, but some of the more popular options are: adsorption, filtration, ion exchange, and electrokinetic coagulation.

Adsorption encompasses a wide range of methods and materials that remove components from wastewater by adsorbing them onto the surface of the material. The list of possible materials is extensive, but includes activated carbon, silica gel, peat, wood chips, and fly ash[3],[18]. Activated carbon offers an advantage in that the solid can be reactivated once it has been used at the cost of efficiency[11]. However, activated carbon is expensive, as it costs about $1.5 US per kg of material[18]. Therefore, inexpensive, more natural options have been researched such as peat and wood chips that cost less than $0.1 US per kg[18]. Although not generally reusable, these natural options can be incinerated once used for energy generation[3].

Advanced filtration methods, including ultrafiltration, nanofiltration, and reverse osmosis, are capable of yielding high-quality effluent that can be reused in the textile process[11]. The reuse of water limits the output of waste effluent from the operation, essentially lowering the environmental impact of the process. There have even been studies that utilize filtration methods to reuse spent dye in the effluent[19]. Some dyes, in particular reactive dyes, have a low affinity to materials, meaning that dye in solution is more likely to remain in solution than it is to attach to fabric[6]. Being able to reuse spent dye would decrease the amount of total dye introduced to the

process, reducing the overall environmental impact. However, membranes used for filtration have a possibility of fouling, and the selection of membranes is particular to the type of dye and conditions of the textile wastewater[11]. Figure 1.6 below is an example small-scale setup for a nanofiltration process. The inlet fluid is passed over a membrane at high pressure, allowing for water to diffuse through while preventing the flow of contaminants. The highly concentrated solution that did not diffuse through the membrane, the retentate, was recycled back into the feed tank.
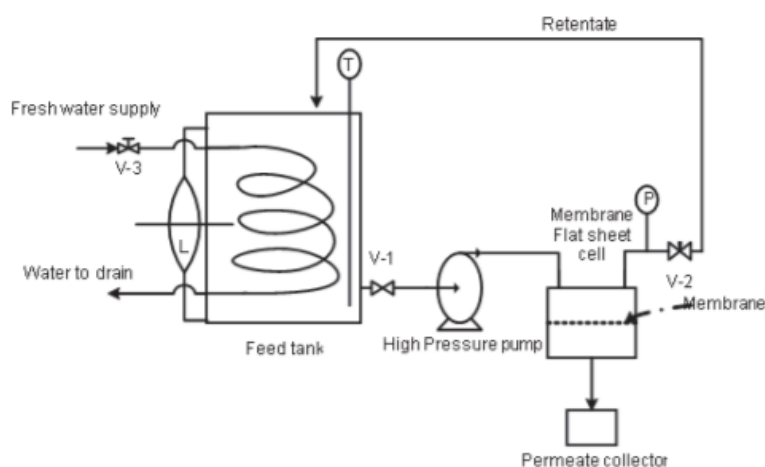


Figure 1.6: Example setup for nanofiltration[19].

Ion exchange and electrokinetic coagulation methods both rely on the charged nature of some dyes in order to adsorb dyes onto a surface and coagulate dyes, respectively. Each method is effective at removing soluble dyes, with ion exchange being capable of removing both positively and negatively charged ions, and electrokinetic coagulation specializing in removing direct dyes[3]. However, neither of the two methods are particularly useful when it comes to non-ionic or insoluble dyes. Ion exchange is also expensive to maintain, while electrokinetic coagulation produces a large amount of sludge that requires disposal[3].

1.5 Biological methods

Despite the complex and varying nature of dyes, there have been certain organisms that have proven effective at remediating textile wastewater. One particular group of microorganisms are fungi, as there are a few strains that are capable of degrading dyes. White rot fungi has shown great promise, where one study reports that the fungus *P. sanguineus* MUCL 51321 completely decolorized water containing dyes Reactive Blue 4 and Orange G[7]. The reason white rot fungi are particularly effective is that they produce enzymes that degrade lignin, some of which utilize hydrogen peroxide[3].

Using biological means to remediate wastewater has payoffs and drawbacks. Effective use of microorganisms is an environmentally safe option, as they generally require a low energy investment and do not produce toxic products that may result from AOPs[7]. In addition, biological processes are widely used in standard wastewater treatment plants, so there is a possibility of incorporating new strains into existing treatment plants[1]. However, not all dyes are capable of degradation by microorganisms. The conditions of wastewater streams also affect the efficiency of microorganisms, as not all will flourish or survive in the same environments[6].

Table 1.2 below summarizes the information presented thus far. It details a quick outline of the benefits and drawbacks of each method.

Table 1.2: Summary of remediation methods discussed in this study.

| Process | Benefits | Drawbacks |
|---|---|---|
| **Chemical** | | |
| Fenton's Reagent | Inexpensive, simple setup | Sludge generation |
| Photochemical | High levels of degradation, no sludge generation | Expensive |
| Photoelectrochemical | Complete reduction to $H_2O$ and $CO_2$, multiple sources of oxidation | Expensive |
| Ozonation | No increase in liquid volume, standalone reactant | Short half-life, ozone must be produced on site |
| **Physical** | | |
| Adsorption | Some inexpensive and natural alternatives | Activated carbon is expensive, disposal required of adsorbents |
| Advanced Filtration | Filtered effluent and dye can be reused | Fouling, expensive startup, specific to waste stream conditions |
| Ion Exchange | Effective at removing cationic and anionic dyes | Expensive |
| Electrokinetic Coagulation | Effective at charged dyes, particularly direct dyes | Expensive, sludge generation |
| **Biological** | | |
| White Rot Fungi | Low energy investment, no toxic by-products | Specific dyes only, susceptible to variation in conditions |

1.6 Catalysis and Applicability to This Study

Of the methods discussed, the Fenton's Reagent reaction seemed the most attractive due to its simplicity and accessibility. It could be a relatively easy option for textile wastewater treatment plants to implement to reduce effluent color while using relatively inexpensive reactants. However, the drawbacks of the method, especially sludge generation and lack of reusability, bring into question the overall environmental impact.

To better understand the issues presented, a review of catalysis was necessary. A catalyst is a substance added to a reaction solution that promotes reactions, but is not consumed[20]. It achieves this effect by lowering the activation energy needed for a reaction to occur, so that the products may be formed with a lower energy investment. Another benefit of catalysts is that they selectively promote reactions[20]. Catalysts do not lower the activation energy of all reactions in the medium, only the reactions they are selective to.

There are two main types of catalysis: homogeneous and heterogeneous catalysis. In homogeneous catalysis, the catalyst is in the same phase as the reactants[21]. Homogeneous catalysts are primarily employed in liquid phase reactions. Heterogeneous catalysts exist in a different phase than the reactants, with the most prominent combinations being gas/solid or liquid/solid[21]. Both types of catalysis have benefits and drawbacks. Heterogeneous catalysts are easier to filter out and are capable of operating in a wider range of conditions, but diffusion limitations can inhibit reaction rates[21]. Homogeneous catalysts are able to interact directly with reactants and the reactions are more easily observable with spectroscopy methods. However, homogeneous catalysts are more difficult, if not impossible, to filter out of solution[21].

In the Fenton's Reagent reaction, $Fe^{2+}$ typically acts as a homogeneous catalyst to create hydroxyl radicals. However, it also forms undesirable solids and sludge when it bonds with compounds in solution. Heterogeneous catalysis could avoid this issue, as bonding the $Fe^{2+}$ particles to a solid support could prevent the iron atoms from existing in solution. If the iron remains attached to the support, it cannot precipitate to form sludge, and the catalyst can then be filtered and reused. In theory, this solution could remove one of the more prominent drawbacks of the Fenton reaction while making it reasonable to recycle catalyst used in the reaction.

In order to synthesize a heterogeneous catalyst, an appropriate catalyst support must be selected. The main concerns considered when picking a catalyst support was the variety of dye sizes and the stability of the support in varying environments. Dyes can vary immensely in size, so being able to utilize a support with a tunable pore volume could help adjust the support for the difference between dyes. The other issue, resistance to conditions of the medium, comes mainly from the necessity of running Fenton reactions at a lower pH, usually around 3-5[12],[6],[22]. The support needs to be resistant to acidic environments and oxidation from the hydrogen peroxide and hydroxyl radicals. An inorganic, acidic type catalyst support would be suitable for these conditions.

The catalyst support utilized in this study was SBA-15 (Santa Barbara Amorphous). It is a mesoporous, silica-based support that is acidic in nature, inert, and non-toxic[23]. The pores in SBA-15 are consistent in size and are tunable depending on the amount of time spent heating the solid during synthesis, with average pore diameters of around 4-30 nm[24]. The pores of SBA-15 are interconnected, giving it a large surface area for reactions[24]. In addition, SBA-15 has high thermal stability, and can be synthesized using an inexpensive source of silica making it economically viable[25]. In its ordered arrangement, SBA-15 takes on a hexagonal structure[25],

but it is easily usable in its amorphous, powder form to make a slurry-like mixture with

wastewater. SBA-15 exhibits many useful qualities as a heterogeneous catalyst support, and

should fit the position well for an iron support in a Fenton's Reagent reaction. Following is a

microscopic image of SBA-15's hexagonal structure.
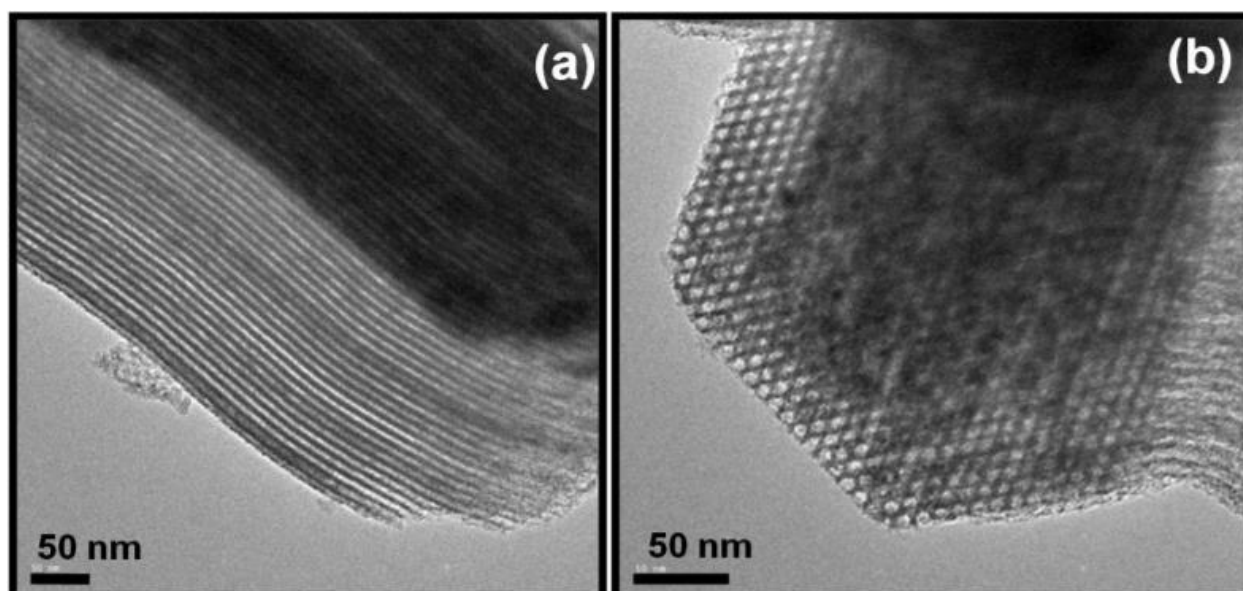


Figure 1.7: High-resolution transmission electron microscopy image of the hexagonal pore structure of SBA-15[24].

## 2. EXPERIMENTAL PROCEDURE

There were three main goals with experimentation: successfully synthesize an Fe/SBA-15 catalyst, measure the capability of the catalyst to degrade RB4 dye, and determine the reusability of the catalyst. Calibration curves for RB4 and Fe were generated to assist with dye concentration measurements and iron-leaching determination, respectively. Experimentation was performed in the Analytical Laboratory at the Rose-Hulman Institute of Technology. The primary instrument utilized was the Thermo Scientific NanoDrop 2000 spectrophotometer.

Tetraethylorthosilicate (TEOS), 12 M hydrochloric acid, EO-PO-EO block copolymer (pluronic-123), and 35% Reactive Blue 4 dye were obtained from Sigma Aldrich. Iron(III) nitrate nonahydrate was obtained from Alfa Aesar. The 3% $H_2O_2$ was obtained from a local, accessible shopping location. The following materials were obtained from the Rose-Hulman Chemistry Stockroom: 6 ppm $Fe(NH_4)_2(SO_4)_2$, hydroxylamine hydrochloride, 0.1% 1,10-phenanthroline, 0.2 M potassium biphthalate, 15% ammonium hydroxide.

<u>2.1 Synthesis of SBA-15</u>

SBA-15 was synthesized according to previous literature methods[26]. The values listed are from the first batch of SBA-15. Subsequent batches used amounts similar to the values presented. To a 1 L Erlenmeyer flask, 561.18 g of ultra-pure $H_2O$, 18.51 g of EO-PO-EO block copolymer, and 99.1 g of 12 M HCl were added and stirred overnight at room temperature. The next day, 39.77 g of TEOS was slowly added to the solution. The solution was again allowed to stir overnight at room temperature. The white solid formed in the solution was then filtered and

rinsed with approximately 2 L of deionized (DI) H$_2$O. After rinsing, the solid was calcined with the following conditions: 1.5 ºC/min ramp up to 550 ºC, then dwell at 550 ºC for 4 hours. The SBA-15 was then stored in closed containers until further use. About 14 g of SBA-15 was synthesized from this method.
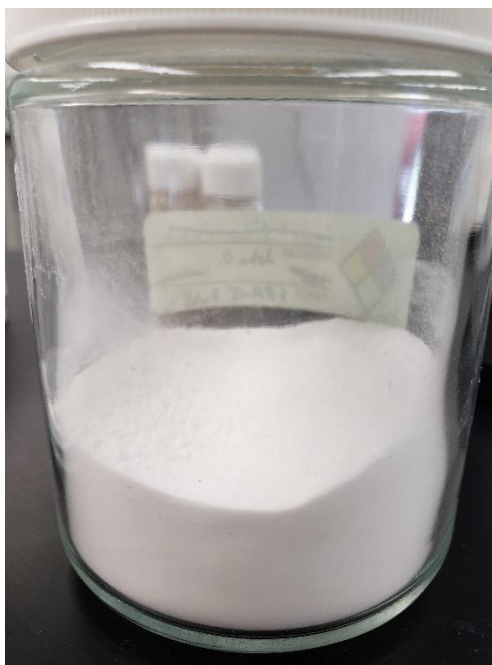


Figure 2.1: Fresh SBA-15

2.2 Addition of Iron to SBA-15

Iron addition to the synthesized SBA-15 catalyst support was performed using the incipient wetness method[27]. The desired amount of SBA-15 was measured out and bone-dried in an oven. Using an average pore volume of 1 cm$^3$/g, an amount of ultra-pure H$_2$O was obtained equal to the total pore volume of the measured amount of SBA-15. $Fe\,(NO_3)_3 \cdot 9H_2O$ was measured out to obtain the desired weight percent of iron for the catalyst support (0.05, 0.1, 0.15, or 0.20 wt%). The iron nitrate was dissolved in the water, then added dropwise to the bone-dry

SBA-15. The wet Fe SBA-15 was then calcined at 500 °C in the same method as described

before, and the resulting catalyst was stored in vials until use.

2.3 Degradation Trials of Reactive Blue 4 (RB4)

To a 200 mL volumetric flask, the desired amount of 3% $H_2O_2$ and 100 µL of 12 M HCl

were added, then diluted to the mark with ultra-pure $H_2O$. To a 200 mL Erlenmeyer flask,

approximately 40 mg of RB4 was added, followed by the solution in the 200 mL volumetric

flask. The new mixture was allowed to stir in a water bath until the desired temperature was

achieved. At this point, Fe SBA-15 was added to the solution. The reaction was allowed to take

place over a four hour period. After the reaction time had finished, the contents of the flask were

disposed of appropriately.



Figure 2.2: Setup for degradation trial. Reaction flask is submerged in a temperature controlled
bath, with stirring rods in the bath and flask.

In order to determine the degradation of the dye, absorbance values for the solution were obtained using a Thermo Scientific NanoDrop 2000 spectrophotometer. Samples in the size of five microliters were pipetted onto the measuring surface. Absorbance readings were collected before adding the heterogeneous catalyst to the solution, and then every hour proceeding the addition of the catalyst. For two trials, about six mL of the final solution was centrifuged in order to separate the solid catalyst from the pipetted sample. This was performed to determine if the solid had an effect on the value and variation of the absorbance readings.

2.4 Calibration Curve Generation for Reactive Blue 4

In order to determine the RB4 concentration in solution, a calibration curve was generated to convert between concentration and absorbance. This correlation is given through Beer's Law:

$$A = \epsilon l c \tag{15}$$

where $A$ is the absorbance (unitless), $\epsilon$ is the extinction coefficient or molar absorptivity (L mol$^{-1}$ cm$^{-1}$), $l$ is the path length (mm), and $c$ is the concentration of solute (g/L). The path length is given in the instrument specifications, which for the NanoDrop 2000 is 1 mm. The extinction coefficient is provided by literature and estimated to be over 4000 L mol$^{-1}$ cm$^{-1}$. Therefore, there is a direct, linear relationship between absorbance and concentration.

To create the calibration curve, 0.0212 g of RB4 was added to 100 mL of water, yielding an initial concentration of 0.212 g/L of RB4. The absorbance was recorded from the maximum peak value at 595 nm wavelength. The initial sample was half-diluted five times, yielding a calibration curve with six points.
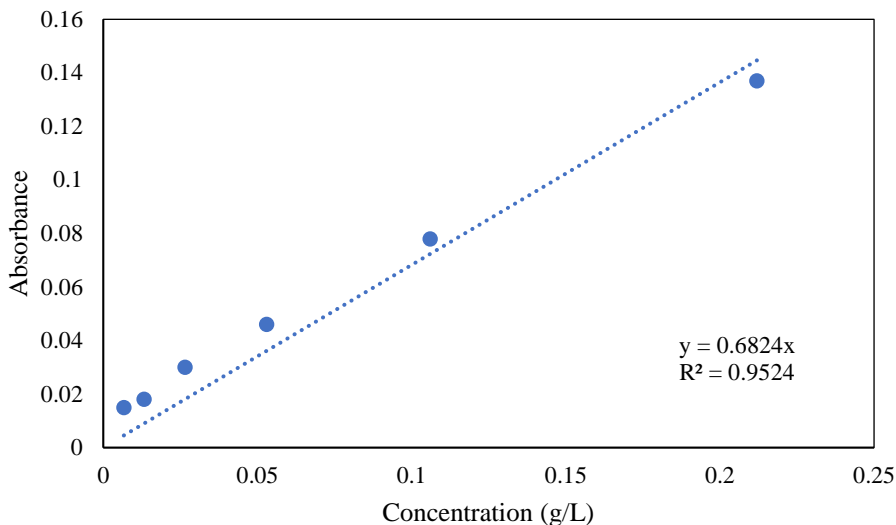
Figure 2.3: Calibration curve for dye Reactive Blue 4 for the peak at 595 nm.

The extinction coefficient obtained from the calibration curve was 4350 L mol$^{-1}$ cm$^{-1}$, which aligns with the literature value of greater than 4000 L mol$^{-1}$ cm$^{-1}$.

2.5 Calibration Curve Generation for Iron

Similarly to RB4, a calibration curve for iron can be generated by causing the iron in solution to form an iron complex, which produces an orange color. The absorbance values obtained for a known concentration of iron will allow for the determination of unknown iron concentrations. A separate UV-vis instrument, a NanoDrop One$^c$ by Thermo Scientific, was utilized for the iron calibration curve, as the 1 cm pathlength using cuvettes was required.

To five 100 mL volumetric flasks the following was added: 1 mL of hydroxylamine hydrochloride, 5 mL of 0.1% 1,10-phenanthroline, 20 mL of potassium biphthalate, and the necessary amount of 6 ppm iron(II) stock solution to achieve iron(II) concentrations of 3, 1.5, 0.6, 0.3, and 0.15 ppm. The flasks were diluted to 100 mL with ultra-pure H$_2$O. A blank solution was created using the same method listed above, but omitting the iron(II) stock solution and

replacing it with $H_2O$. The absorbance values at a peak wavelength of 508 nm were collected for each of the standard solutions. Plotting the concentration against the absorbance values yields the calibration curve.
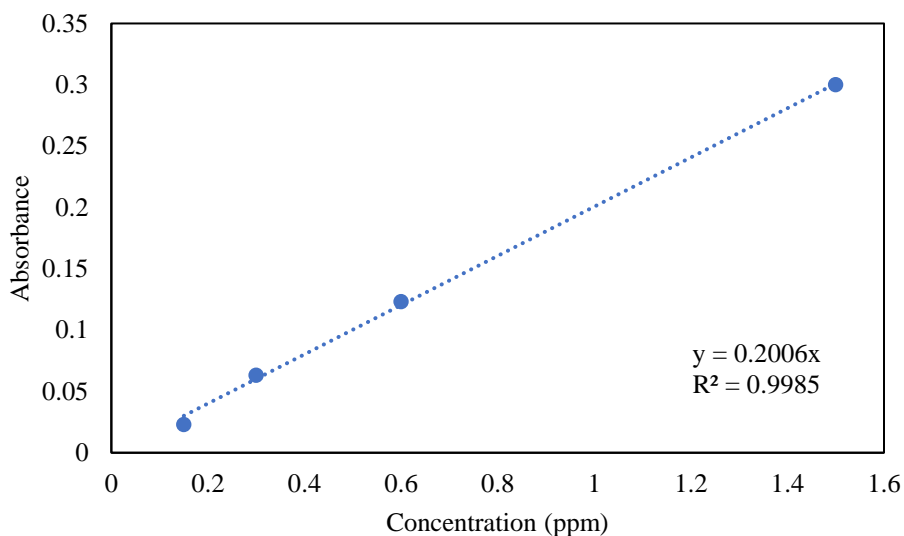


Figure 2.4: Calibration curve for $Fe^{2+}$ for the peak at 508 nm.

To test reaction solutions for iron(II) content, the solution was first filtered to remove the solid catalyst. The solution was then diluted to 250 mL with ultra-pure $H_2O$. A 100 mL flask was prepared in the same method as described above, but substituting the iron(II) stock solution with 50 mL of unknown sample solution. The absorbance of the sample could then be obtained, and using the calibration curve equation, the concentration of iron(II) in solution could be determined.

2.6 Intra-matrix Fe SBA-15

The purpose for synthesis of intra-matrix Fe/SBA-15 is discussed in the Recommendations and Future Work section at the end of this thesis (page 42). Formation of the intra-matrix Fe/SBA-15 follows a similar setup as standard SBA-15 synthesis. First, 2.093 g of

Pluronic P-123 was dissolved in 60 mL of 2 M HCl, which was obtained from dilution of 12 M

HCl. After the copolymer had dissolved, 4.5 mL of TEOS was added to the solution and stirred

at 38 ⁰C for 30 minutes. During this time period, 0.4928 g of iron(III) nitrate nonahydrate was

dissolved in 10 mL of de-ionized water. At the 30 minute mark of stirring, the iron nitrate

solution was added to the cloudy white mixture, turning the solid in the mixture yellow. The pH

of the solution was adjusted to approximately 7 aqueous ammonia, and then left to stir overnight.

The solid-liquid mixture was then placed in an autoclave at 85 ⁰C. A yellow solid was observed

at this point, which dulled to a light brown color after several days of drying. Figure 2.5 below

shows the final product.



Figure 2.5: Intra-matrix Fe/SBA-15

## 3. RESULTS AND DISCUSSION

The parameters of catalyst to volume ratio, iron loading, hydrogen peroxide concentration, and temperature were each varied independently while holding the other parameters constant. The percentage of dye removal over the length of a trial was measured as percent conversion of dye, using the calculation as follows:

$$\% \ conversion \ (X) = \frac{C_{Ao} - C_A}{C_{Ao}} \times 100\% \tag{16}$$

Where $C_{Ao}$ is the initial concentration of dye and $C_A$ is the dye concentration at any time, t.

3.1 Control Trial

In order to determine if unmodified SBA-15 interacted with Reactive Blue 4, a control trial was conducted. For the trial, the conditions of 2 g/L of fresh SBA-15 and an RB4 concentration of 200 ppm was utilized at a constant temperature of 30 ⁰C. Figure 3.1 below illustrates the results. Although the points fluctuate around the starting conversion, there is not a definite change in conversion by the final hour value.
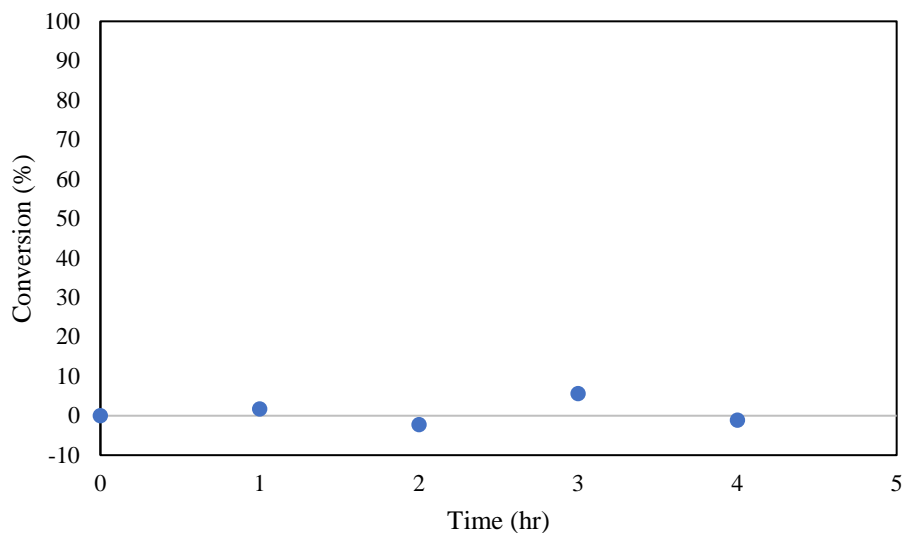
Figure 3.1: Control trial to determine if RB4 adsorbs onto SBA-15. Despite some fluctuation, there does not appear to be a clear change in conversion over the length of the trial.

Since there does not appear to be a clear change in absorbance over the four-hour length of the trial, it seemed reasonable to conclude that RB4 does not adsorb onto SBA-15. Next, an additional control trial was conducted to determine if $H_2O_2$ in the presence of plain SBA-15 was capable of degrading dye molecules. For the trial, the following conditions were utilized: 2 g/L catalyst, 20 mM $H_2O_2$, 100 μL of 12 M HCl, and a temperature of 30 ⁰C.
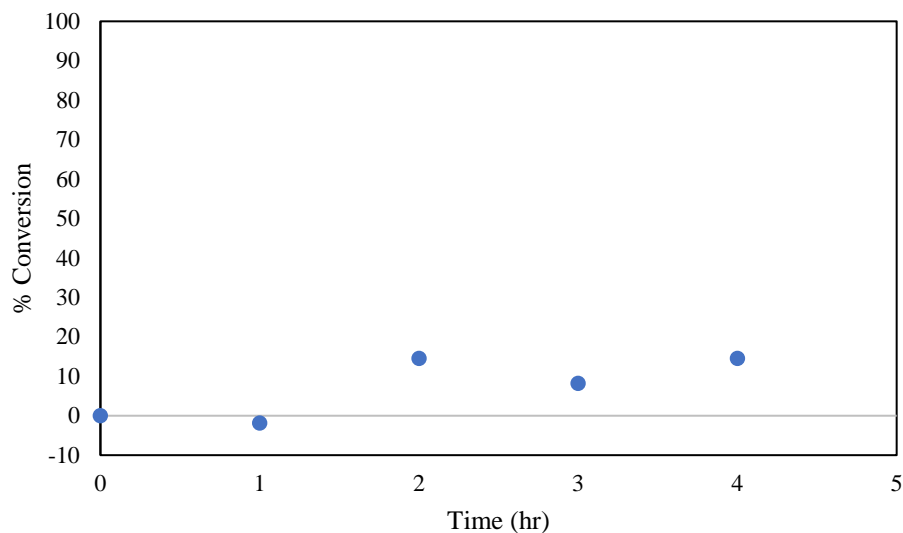
Figure 3.2: Conversion vs. time for the control trial. Variation is noted, but it appears that $H_2O_2$ in the presence of fresh SBA-15 has a small effect on absorbance, decreasing the initial absorbance by about 15%.

According to Figure 3.2, $H_2O_2$ in the presence of plain SBA-15 does have a minor effect on the concentration of Reactive Blue 4 in solution. At the four-hour mark, a decrease in absorbance of about 15% was noted. However, it is difficult to say if 15% is an accurate estimation of the total effect, as there is variation in the data over the four hour period. Notably, between the start of the trial and the first hour, the absorbance value increased by about 2% of the initial value, and then decreased by about 15% over the next hour. It was assumed at this point that the variation was due to random variation or interference by the catalyst support particles. Based on the data presented, the change in absorbance was assumed to be low enough that the effect of $H_2O_2$ and SBA-15 without iron would not have a significant effect on the following trials.

3.2 Variation of Catalyst to Volume Ratio

The catalyst to volume ratio was tested for 1, 2, 3, and 4 g of catalyst per liter. The remaining conditions were left constant at 40 mM $H_2O_2$, 0.20 wt% Fe catalyst, and a temperature of 30 ⁰C. The results are presented in Figure 3.3. Table 3.1 (page 36) documents the conversion values over time for these and all other trials.
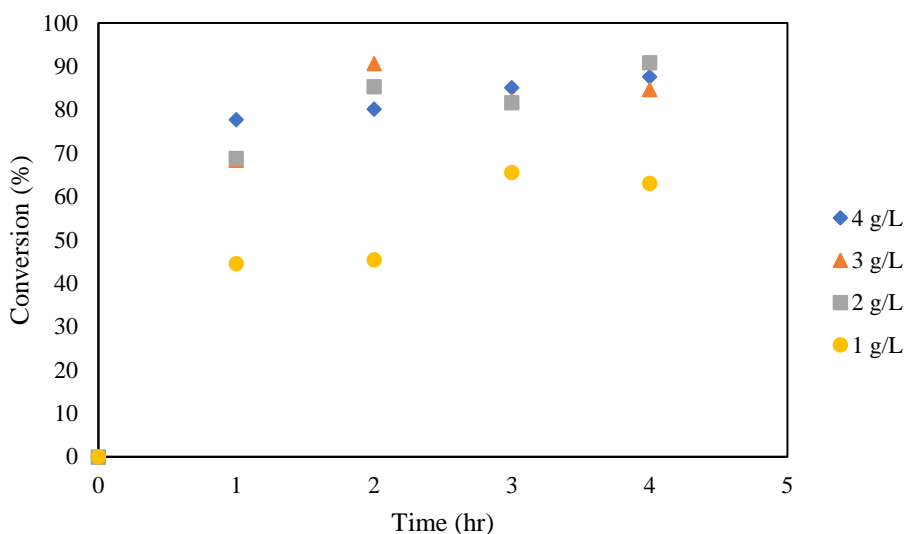


Figure 3.3: Conversion vs. time for trials varying catalyst/volume ratio. Ratios of 2, 3, and 4 yielded fairly similar results, with variation at the time being attributed to interference by catalyst particles/random variation.

According to the figure, the catalyst ratios of 2, 3, and 4 g/L yielded similar results, with 2 g/L yielding the highest conversion of 90.8%. It is likely that not enough surface area and iron were present in the 1 g/L trial, leading to a significantly lower overall conversion of 63.0%.

Before further pursuing the experiment, it became necessary to address the variation in values, as they became noticeably significant, especially between hours two and three for the 2 and 3 g/L trials. It is uncertain what exactly could be causing this variation, but it could be attributed to several factors, including interference by catalyst particles, difficulty with the

instrument measuring lower values of absorbance, and pathlength being too short. Figure 3.4

below provides a graphical representation of the deviation seen in the control trial with $H_2O_2$ and

SBA-15. Each point is an average of collected data points, and the error bars displayed are three

standard deviations from the average point. Even with multiple data points being collected at

each hour, there appears to be a decent amount of variation. The one hour mark is especially

notable, with the error bars encompassing almost 0.05 absorbance units when the average

absorbance for the hour is 0.112.
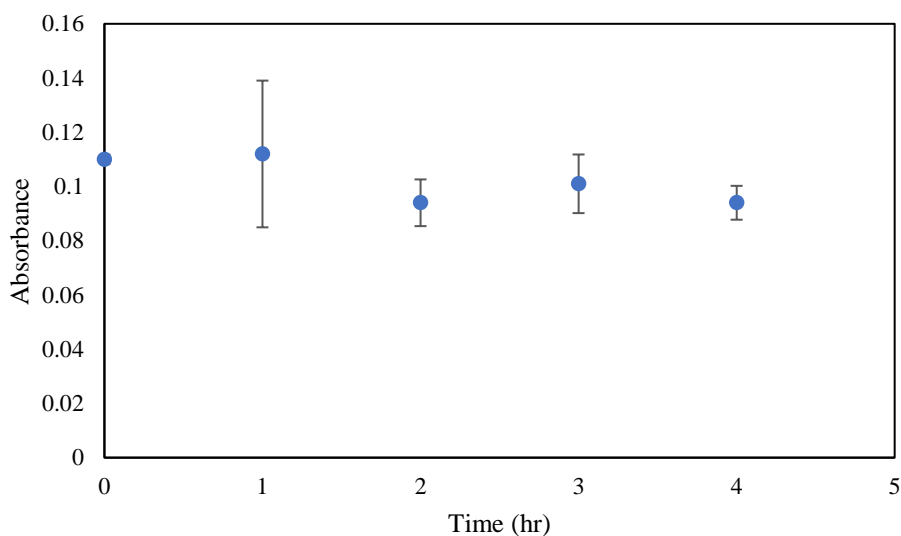


Figure 3.4: Absorbance values for the control trial of $H_2O_2$ in the presence of SBA-15. Error bars show three standard deviations from the average data point.

One interesting observation is that the initial point had little variation, to where its error

bars are nearly hidden behind the average point. This observation seemed to suggest that

interference by catalyst particles or other suspended solids may be resulting in greater variation.

To determine if interference by catalyst particles was an issue, another trial for the 2 g/L

condition was conducted, and a 15 mL sample of the solution at the four-hour mark was

centrifuged. The absorbance values obtained from the centrifuged sample yielded results similar to the base test results, so interference by catalyst particles did not appear to be a clear problem.

Low pathlengths for measuring absorbance can be an issue when the molecules producing color have a low molar absorptivity. This was noticed when attempting to read peaks for the iron calibration curve on the NanoDrop 2000. With a pathlength of 1 mm, no peaks in the visible range appeared. Utilizing a NanoDrop One[c] instrument, which used 1 cm pathlength cuvettes, yielded peaks at the expected wavelength of about 508 nm. It is uncertain whether utilizing a longer pathlength would help better define consistent peaks for Reactive Blue 4, as it has a high molar absorptivity and registered peaks consistently on the NanoDrop 2000.

Since the source of variation was uncertain, consistency between trials was practiced diligently to eliminate any source of variation by human error. The solutions were well-mixed to ensure homogeneity, and a clean pipet tip was used for each sample. Further conclusions in the study incorporate the possibility of random error as best possible.

Being mindful of variation, the final conversion values for 2, 3, and 4 g/L seemed close enough to say that they all approximately yielded the same results. Therefore, using a catalyst to volume ratio of 2 g/L would give the best results while utilizing the least amount of catalyst. Less catalyst used would lead to greater affordability at a larger scale, as less would then need to be synthesized, filtered, and calcined for reuse. For the rest of the study, 2 g/L catalyst to volume was used as the optimum ratio.

3.3 Variation of Iron Loading

Iron was deposited onto SBA-15 to yield four different weight percentages: 0.05, 0.10, 0.15, and 0.20 wt% iron. Each type was tested with 2 g/L catalyst to volume ratio, 40 mM of $H_2O_2$, and temperature of 30 ºC. The results are presented in Figure 3.5.
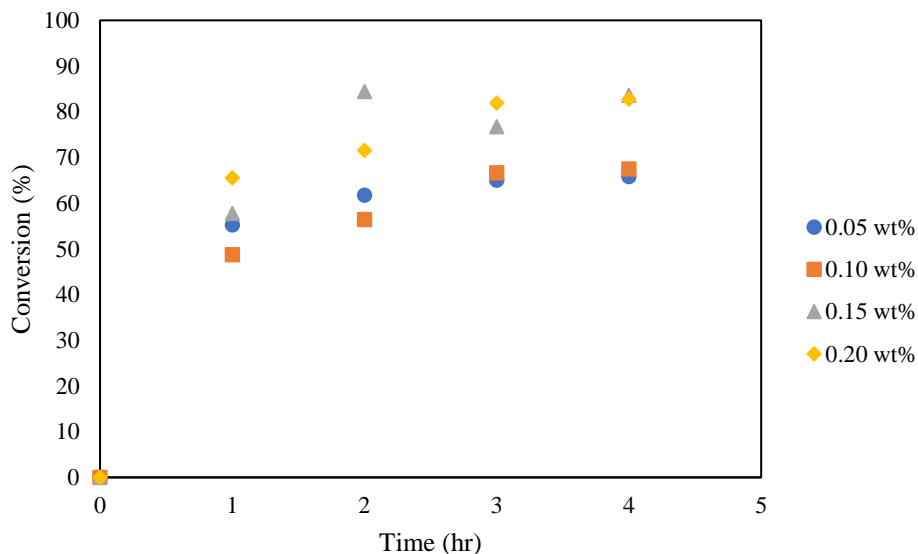


Figure 3.5: Conversion vs. time for trials varying iron loading. Weight percentages of 0.15 and 0.20 yielded the best results, with overall conversions of about 83%.

According to the results, the trials using 0.15 and 0.20 wt% iron yielded approximately the same result, with a total conversion of about 83%. Trials using iron loadings of 0.05 and 0.10 wt% also yielded similar results to each other, with a final conversion of about 66-67%. Since both 0.15 and 0.20 wt% iron catalyst yielded approximately the same results in the end, it would be advantageous and economical to use 0.15 wt% as the optimum value.

3.4 Varying $H_2O_2$ Concentration

Hydrogen peroxide trials were conducted using volumes of 3% $H_2O_2$ to yield concentrations of 4, 8, 12, 16, 20, and 40 mM. The reason the values picked were all less than

the concentration used up to this point of 40 mM is that 40 mM is considered to be in excess of

the expected optimum concentration (8 mM) based on a similar study of heterogeneous catalysis

with iron for the Fenton's Reagent reaction[22]. Excess had been used to ensure that there was

enough $H_2O_2$ for the reaction to occur. Condensed results for the trials are presented in Figure

3.6, with the full results available in Appendix A, Figure A.1.
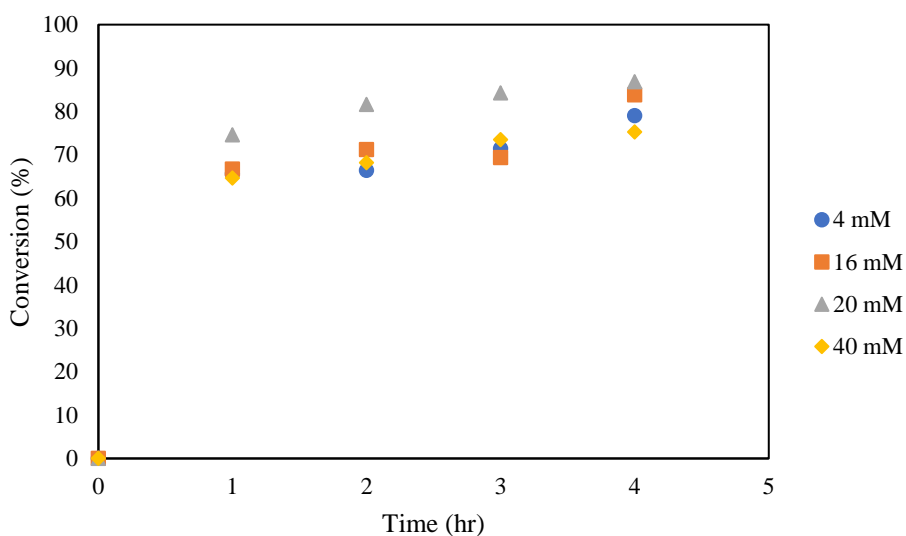


Figure 3.6: Conversion vs. time for trials varying concentration of $H_2O_2$. The trials of 8 and 12 mM were excluded, having results similar to 16 and 40 mM, respectively. A concentration of 20 mM yielded the best results, with a final conversion of about 87%.

Several trials yielded results that were fairly close, notably 20 mM at a final conversion

of about 87% followed by 8 and 16 mM at 84%. With a difference of 3%, however, it appears

that 20 mM is the more optimized point. It should be worth noting that random variation did

have an effect of this set of trials. The 40 mM trial was run under identical conditions to the iron

loading trials; despite this, it achieved a final conversion of about 75% in this set of trials as

opposed to the 83% in the previous set. The 12 mM trial produced the same conversion as the 40

mM trial as well, despite the values around it, 8 and 16 mM, yielding final conversions 9% higher.

Total conversion of the dye in solution is expected to decrease once the optimum concentration of $H_2O_2$ is exceeded, as the scavenging of excess hydroxyl radicals reduces their availability for reactions[22]. However, with the 40 mM conversion being lower than the previous trial (75% vs. 83%), it was assumed that random variation had an effect in this set of trials. Additional trials could have been conducted for repeatability measurements, but time was constrained to complete the research. Therefore, 20 mM of $H_2O_2$ was selected as the optimal concentration.

To determine if the optimal conditions found were reasonable, the results were compared to a similar study[22]. The comparison study utilized a kaolin catalyst support instead of SBA-15, but otherwise the reaction setup was similar. Variation of iron loading, catalyst to volume ratio, $H_2O_2$ concentration, and pH were documented at 30 °C. The optimal conditions obtained in the study were an iron loading of 0.080 wt%, 4.0 g/L catalyst to volume ratio, 8.0 mM of $H_2O_2$, and a pH of 3.0. With these conditions, a dye conversion of 98.46% was achieved. The optimal conditions from this study were 0.15 wt% Fe, 2.0 g/L catalyst to volume ratio, 20 mM $H_2O_2$, and pH of about 2.5, with a maximum conversion of 86.8%. The values can also be found in Table 3.1 below.

Table 3.1: Comparison table of optimal values between this study and reference study[22].

| Condition | Optimal value from this study at 30 °C | Optimal value from comparison study as 30 °C |
|---|---|---|
| Iron loading (wt% Fe) | 0.15 | 0.08 |
| Catalyst to volume ratio (g/L) | 2 | 4 |
| $H_2O_2$ Concentration (mM) | 20 | 8 |
| pH | 2.5 | 3 |
| % Dye conversion | 86.8 | 98.46 |

The comparison study was able to yield a much higher conversion with more conservative values in each category except for catalyst to volume ratio. It is interesting to note that in our study, despite using only half as much catalyst in a reaction, about twice as much iron loading was required for the optimal condition. This indicates that similar amounts of iron were available for both studies, but the comparison study required twice as much catalyst. It would be interesting to see if more repetitions of the experiment would yield different results that are more consistent with those found in the comparison study. Random variation may have caused the difference in optimum values, but the difference could also be contributed to the use of another catalyst support. Although the final conversions are off by over 10%, the optimal values for each study are relatively close, indicating that the values obtained in this study are reasonable.

3.5 Variation of Temperature

Temperature is known to have a significant effect on the kinetics of the Fenton's Reagent reaction, and textile wastewater can vary in temperature depending on the process[7]. Therefore, the effect of temperature was studied in this experiment with a range of 30-40 ⁰C at 2 ⁰C intervals. The optimum conditions of 2 g/L catalyst to volume ratio, 0.15 wt% Fe, and 20 mM of $H_2O_2$ were used for each trial. The condensed results are presented in Figure 3.7, with the full results found in Appendix A, Figure A.2.
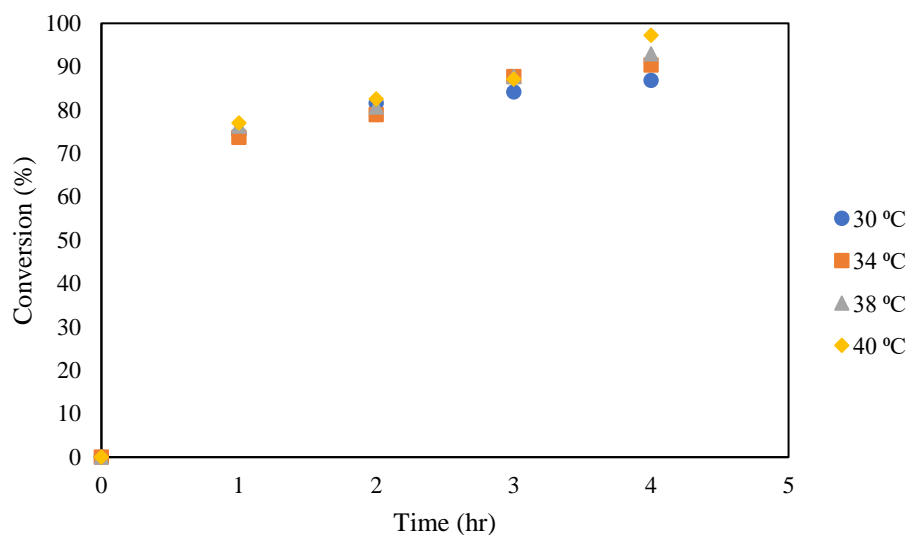
Figure 3.7: Conversion vs. time for trials varying temperature. Trials of 32 and 36 °C were excluded to create a clearer graph. Temperature has a fairly clear positive effect on conversion, with conversion increasing from 86.8% at 30 °C to 97.2% at 40 °C.

It can be difficult to tell due to the tight clumping of the points, but there is a positive relationship between temperature and conversion. The final conversion increases with each temperature increase except from 36 °C to 38 °C, which could be due to random variation. The 40 °C trial did yield the highest conversion, however, with a 97.2% removal of dye, nearly 11% higher than the 86.8% conversion at 30 °C. As mentioned earlier, textile wastewater can vary in temperature, and if a textile facility had excess heat from the total process, it could be applied to increase the conversion of dye in the wastewater treatment step. However, it can become expensive to control higher temperatures for larger volumes of water when the spare heat and cooling water are not available. In this situation, a cost-benefit analysis would need to be conducted.

For ease of comparison, Table 3.2 below lists the conversion values over the 4-hour trial period for all of the trials conducted. The trial utilizing all of the optimal conditions is highlighted for reference.

Table 3.2: Conversion data over time for each trial. The highlighted row is the trial that yielded the highest conversion.

| Catalyst to Volume Ratio (g/L) | Iron Loading (wt% Fe) | $H_2O_2$ Concentration (mM) | Temperature (°C) | % Dye Conversion | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | Initial | 1 hr | 2 hr | 3 hr | Final |
| 1 | 0.20 | 40 | 30 | 0 | 44.5 | 45.4 | 65.5 | 63.0 |
| 2 | 0.20 | 40 | 30 | 0 | 68.8 | 85.3 | 81.7 | 90.8 |
| 3 | 0.20 | 40 | 30 | 0 | 68.4 | 90.6 | 82.1 | 84.6 |
| 4 | 0.20 | 40 | 30 | 0 | 77.7 | 80.2 | 85.1 | 87.6 |
| 2 | 0.05 | 40 | 30 | 0 | 55.3 | 61.8 | 65.0 | 65.9 |
| 2 | 0.10 | 40 | 30 | 0 | 48.7 | 56.4 | 66.7 | 67.5 |
| 2 | 0.15 | 40 | 30 | 0 | 57.8 | 84.5 | 76.7 | 83.6 |
| 2 | 0.20 | 40 | 30 | 0 | 65.5 | 71.6 | 81.9 | 82.8 |
| 2 | 0.20 | 4 | 30 | 0 | 65.5 | 66.4 | 71.4 | 79.0 |
| 2 | 0.20 | 8 | 30 | 0 | 65.0 | 78.6 | 77.8 | 83.8 |
| 2 | 0.20 | 12 | 30 | 0 | 58.7 | 71.9 | 78.5 | 75.2 |
| 2 | 0.20 | 16 | 30 | 0 | 66.7 | 71.2 | 69.4 | 83.8 |
| 2 | 0.20 | 20 | 30 | 0 | 74.6 | 81.6 | 84.2 | 86.8 |
| 2 | 0.20 | 40 | 30 | 0 | 64.6 | 68.1 | 73.5 | 75.2 |
| 2 | 0.20 | 20 | 32 | 0 | 72.1 | 73.0 | 84.7 | 89.2 |
| 2 | 0.20 | 20 | 34 | 0 | 73.7 | 78.9 | 87.7 | 90.4 |
| 2 | 0.20 | 20 | 36 | 0 | 75.2 | 84.4 | 92.7 | 95.4 |
| 2 | 0.20 | 20 | 38 | 0 | 76.3 | 80.7 | 87.7 | 93.0 |
| 2 | 0.20 | 20 | 40 | 0 | 77.1 | 82.6 | 87.2 | 97.2 |

3.6 Reusability Study

Reusability of the catalyst was performed by utilizing the optimum conditions determined so far in the study aside from temperature, which at 30 °C. After each trial, the catalyst was filtered from solution, dried, and calcined before it was used in the next trial. Samples from each trial after filtration were used to determine the amount of iron that had leached from the catalyst

into solution. The reaction was performed a total of three times. Results are summarized in Table 3.3.

Table 3.3. Summary of results from reusability study. Optimal conditions from the study at 30 °C were used for the each trial, with the catalyst being filtered and reused between trials.

| Trial | Final Conversion (%) | Concentration of $Fe^{2+}$ (ppm) |
|---|---|---|
| 1 | 85.0 | 0.80 |
| 2 | 55.0 | Undetermined |
| 3 | 46.6 | Undetermined |

As evidenced by the data, the catalyst was not capable of yielding the same results between trials. The total conversion from the first trial was as expected, but the conversion decreased drastically for the second, and slightly more for the third. This is likely attributed to the fact that a large amount of iron had leached from the catalyst into solution in the first trial. The concentration of iron detected in solution from the first trial was 0.8 ppm. With a reactor volume of 200 mL, the mass of iron in solution was about 0.16 mg. For the trial, 0.4 g of 0.15 wt% catalyst was used, meaning there was a total of about 0.6 mg of iron deposited on the catalyst support. With over a quarter of the iron from the catalyst found in solution, it brings into question whether the majority of the dye conversion was being performed by the iron in solution or the iron on the catalyst support surface. Figure 3.8 below illustrates a reaction volume with a high amount of iron leaching.
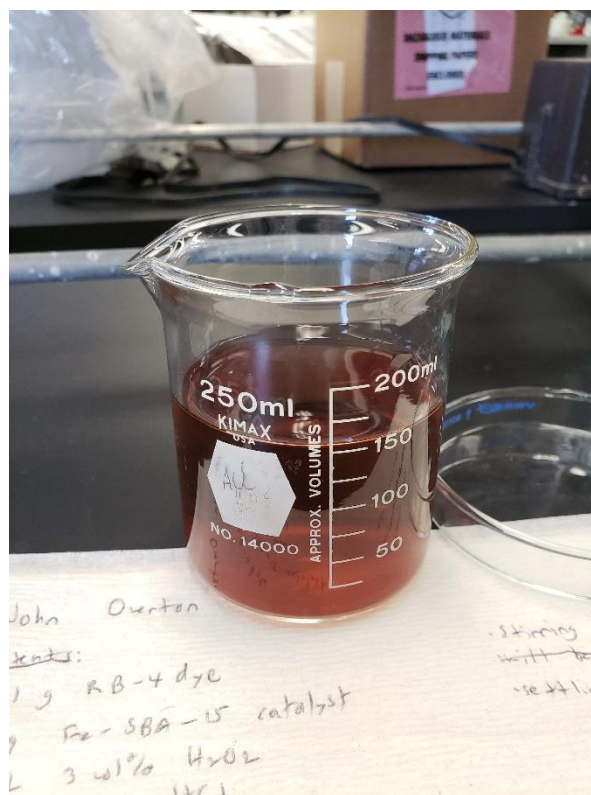
Figure 3.8: Post-reaction mixture with high amount of iron leaching. The reaction pictured was from earlier trials with 10 wt% Fe/SBA-15 that was not utilized in the study.

Since the loss of iron in the first trial reduced the amount of iron available for use in the following trials, the total dye conversion suffered. Therefore, the color of the solution remained a fairly deep blue after the trial length. Unfortunately, this made sampling the iron concentrations in the second and third trial difficult, as the peak for RB4 at 595 nm was too close to the peak for the iron complex at 508 nm. The RB4 peak overshadowed the presence of the iron peak, so determining the amount of iron that leached in that last two trials was not possible with the method used in this study. However, observing that the conversion between the second and third trials decreased even further, it is likely that iron continued to leach from the catalyst in the later trials.

Iron leaching from a solid catalyst support employed in a Fenton reaction has been observed in other reports. The comparison study mentioned in the $H_2O_2$ variation section conducted an analysis on reusability as well[22]. The researchers noticed a significant decrease in conversion after the second trial, dropping from 92.78% conversion from the second trial to 35.66% with the third. The study was inconclusive as to the exact cause of the decrease in conversion, but it provided several plausible reasons. One explanation could simply be loss of catalyst between trials. The study claims that other researchers believe it might be poisoning of the catalyst from active organic species, possibly from intermediates of the Fenton reaction. Regardless, the study conducted an experiment to determine the amount of iron leaching in each trial, similar to the one done in this study. A significant amount of iron was detected in each solution post-reaction, indicating that leaching may have been one of the major causes of conversion loss.

A likely explanation for the leaching of iron into solution is that strong oxidants, the $H_2O_2$ molecules, are forcing iron to dissociate from the catalyst support surface. One such reaction path results when $H_2O_2$ particles bond to free sites on the catalyst support surface, form complexes with the iron attached to the surface, and then dissociate as iron-hydrogen peroxide complexes[28]. Since hydrogen peroxide is required for Fenton's Reagent processes, it would be difficult to prevent this situation from occurring.

One possible option to circumvent iron leaching would be to investigate the use of an intra-matrix iron catalyst. Instead of simply depositing the iron on the catalyst support surface, the iron would be embedded into the catalyst support matrix. This would likely prevent $H_2O_2$ from forming complexes with iron, as the bonds of the matrix would hold it in position. It has been shown that synthesis of intra-matrix iron with SBA-15 has been successfully achieved[25],

so further research using the synthesis method provided could help determine if intra-matrix iron

SBA-15 is viable for the Fenton's Reagent reaction.

## 4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

The remediation of textile wastewater in an environmentally friendly and accessible way remains a prominent issue for the textile industry, but increased study in advanced remediation methods is aiming to improve the situation. The aim of this study was to attempt to synthesize a reusable, inexpensive heterogeneous catalyst that could be employed in Fenton's Reagent type reactions. The synthesis of the catalyst was successful, and it proved to be filterable and resistant to acidity.

The Fenton's Reagent reaction method using a heterogeneous iron catalyst proved to be effective at decoloring a solution containing Reactive Blue 4. It was shown that the catalyst to volume ratio, amount of iron loading on the catalyst support, $H_2O_2$ concentration, and temperature all had a significant effect on the remediation of dye. At the optimal conditions determined in this study at a temperature of 30 ⁰C, a total dye conversion of 86.8% was achieved. Increasing the temperature yielded even higher conversions, with the maximum temperature tested of 40 ⁰C yielding a conversion of 97.2%.

The Fe/SBA-15 synthesized in the study proved ineffective at yielding consistent results when reused. The conversion of dye decreased after every use, with a decrease of 30% after the first trial using optimum conditions at 30 ⁰C. This occurrence is likely due to iron leaching from the catalyst into solution, with around 25% of the iron available on the catalyst leaching in the first trial. The existence of strong oxidizers required for the Fenton reaction are most likely the

reason for iron leaching, and it is unsure whether the majority of the decolorization is due to the iron deposited on the catalyst or the iron in solution.

4.2 Recommendations and Future Work

There are a few recommendations and improvements that would help further develop the study. One of the greatest improvements that could be pursued is a more reliable method/instrument for data collection. The NanoDrop 2000 used in the study was helpful in that it used only small amount of liquid for sampling and gave quick results, but it may have been a major source of error. Most times, when measuring the same sample multiple times, the instrument would report different absorbances, making consistent data collection difficult. Using an instrument with a longer pathlength, such as the NanoDrop One[c], may yield more consistent results, but the use of more reaction solution for absorbance measurements would need to be accounted for.

Another recommendation would be to measure the total organic carbon (TOC) in solution. TOC is a measure of the concentration of organic carbon atoms in solution, and is often used as an approximation of organic contaminants in solution. Since the final products of complete reactions with AOP's are $H_2O$ and $CO_2$, and $CO_2$ is an inorganic carbon molecule, TOC can reveal how successful the Fenton process employed in this study is at completely breaking down contaminants. TOC does not quantify the level of decolorization, however, so a combination of TOC and absorbance could provide a better understanding of how effective the remediation process employed is at removing contaminants and color.

Further research into the use of an intra-matrix Fe/SBA-15 catalyst could help to solve the issue of iron-leaching. A sample batch of such catalyst was synthesized before the end of the

experimentation period, and the RHIT Chemical Engineering Department is working on

processing and testing to see if the synthesis process was successful. It would be important to

characterize both the intra-matrix Fe/SBA-15 and the catalyst that was used throughout the study

as well. Characterization would involve the use of methods such as X-ray diffraction (XRD) to

determine if the crystalline structure is consistent with SBA-15, and $N_2$ adsorption/desorption to

determine the volume and diameter of pores as well as the available surface area[23].

One parameter that could additionally be studied for the reaction is pH. As mentioned

earlier in the paper, the Fenton reaction is dependent on pH, and typically requires an acidic

environment to function well. Performing the reaction at a wide range of pH, such as 2-5, could

help find an optimal pH that might increase total dye conversion. In addition, the pH used in this

study was measured to be about 2.5 before an experiment was initiated, but this value may

change over the length of the experiment due to the creation of hydroxyl ions ($OH^-$) in the

Fenton process. Measuring the pH before and after the length of the trial could indicate if the pH

was affected, and if so, it would be interesting to study the effect of pH control on the process.

Lastly, there was a lack of repeatability measurements for the trials performed in the

study. However, future repetitions of the experiments performed could help reduce the effects of

random error and could further validate or disprove the conclusions made in this study. Being

able to run multiple reactions simultaneously would improve the efficiency of the testing

process, as the four hour trial time limits the number of reactions that can performed in a day.

Despite the list of recommendations and possible improvements, the study that was

conducted showed potential for a solution to several of the issues present with remediation of

textile wastewaters. Future students who wish to continue this research now have a useful

starting point. With a bit more time, experimentation, and thought, they will be able to reach

even more conclusions beyond those presented in this thesis.

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**APPENDIX A: EXTRA FIGURES**
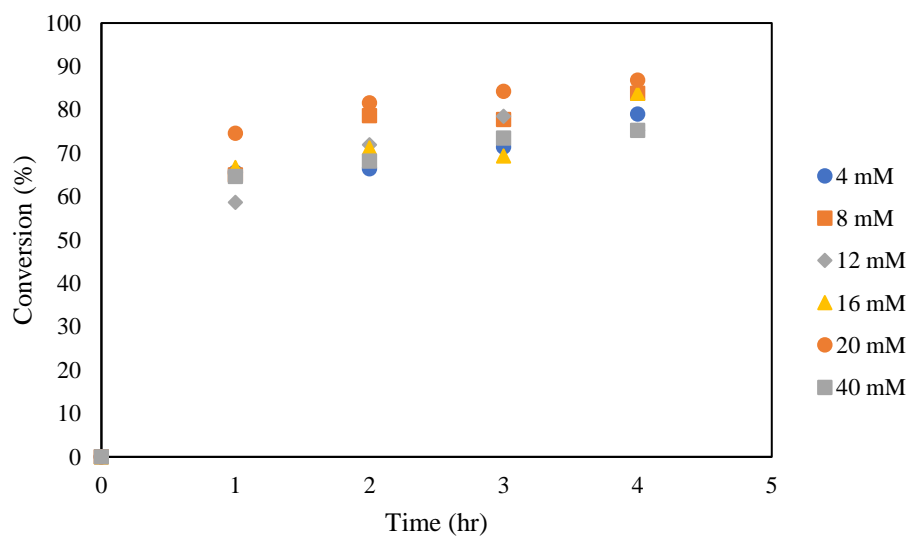


Figure A.1: Full graph of data from H$_2$O$_2$ trials.
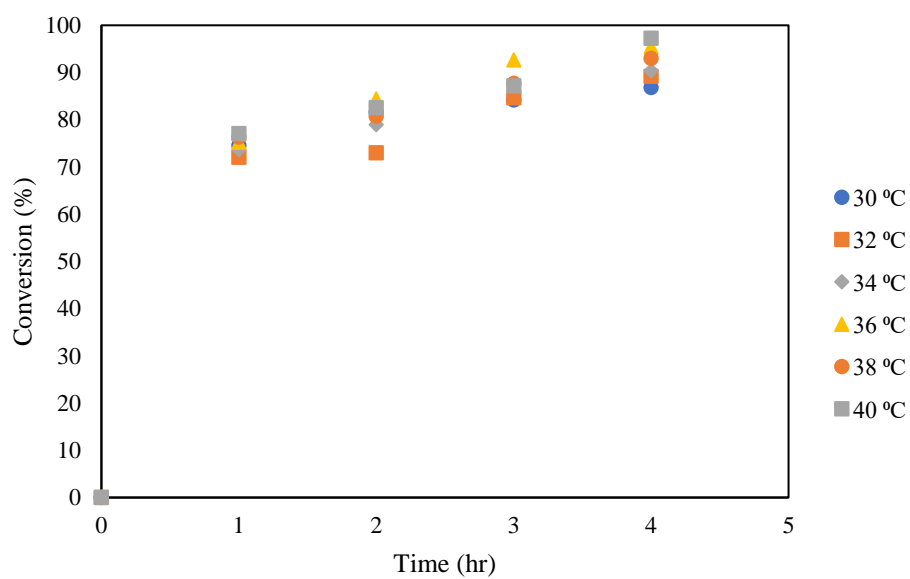


Figure A.2: Full graph of data from temperature trials.
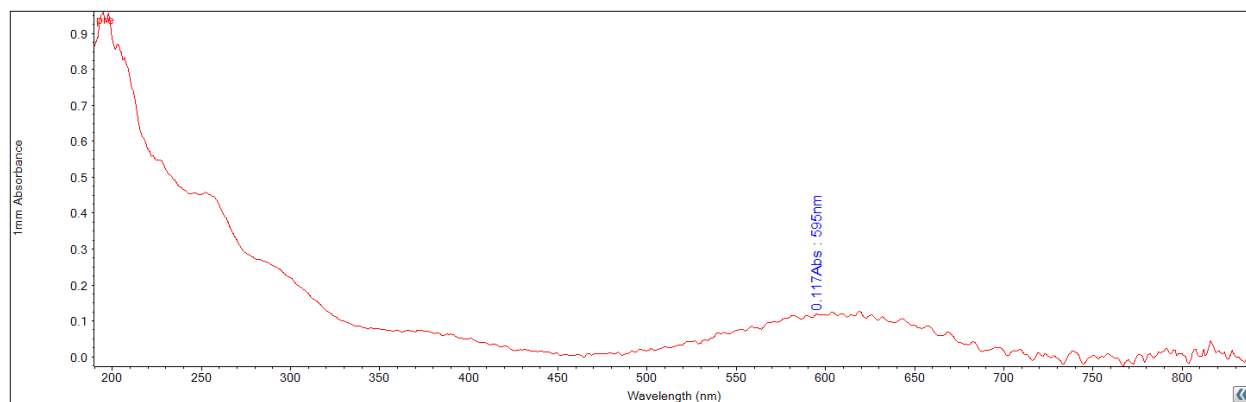
Figure A.3: Sample absorbance spectrum of approximately 200 ppm RB4. The peak at 595 nm is displayed. The wavelength of 595 nm was chosen due to literature claiming it to be the maximum peak wavelength.

# APPENDIX B: DATA TABLES

Table B.1: List of data from trials

| Trial and Notes | Time (hr) | Value 1 | Value 2 | Value 3 | Value 4 | Average | Std. Dev. |
|---|---|---|---|---|---|---|---|
| 1 | pre | 0.117 | | | | 0.117 | |
| | 1 | 0.117 | | | | 0.117 | |
| This trial was not used, as the pH was only adjusted to 3 and the reaction was limited. | 2 | 0.097 | 0.098 | | | 0.098 | 0.001 |
| | 3 | 0.121 | 0.110 | | | 0.116 | 0.008 |
| | 4 | 0.082 | 0.080 | | | 0.081 | 0.001 |
| 2 | pre | 0.121 | | | | 0.121 | |
| 4 g/L catalyst | 1 | 0.027 | | | | 0.027 | |
| | 2 | 0.024 | | | | 0.024 | |
| | 3 | 0.018 | | | | 0.018 | |
| | 4 | 0.015 | | | | 0.015 | |
| 3 | pre | 0.117 | | | | 0.117 | |
| 3 g/L catalyst | 1 | 0.037 | | | | 0.037 | |
| | 2 | 0.011 | | | | 0.011 | |
| | 3 | 0.021 | | | | 0.021 | |
| | 4 | 0.018 | | | | 0.018 | |
| 4 | pre | 0.109 | | | | 0.109 | |
| 2 g/L catalyst | 1 | 0.034 | | | | 0.034 | |
| | 2 | 0.016 | | | | 0.016 | |
| | 3 | 0.020 | | | | 0.020 | |
| | 4 | 0.010 | | | | 0.010 | |
| 5 | pre | 0.119 | | | | 0.119 | |
| 1 g/L catalyst | 1 | 0.066 | | | | 0.066 | |
| | 2 | 0.065 | | | | 0.065 | |
| | 3 | 0.041 | | | | 0.041 | |
| | 4 | 0.044 | | | | 0.044 | |
| 6 | pre | 0.123 | | | | 0.123 | |
| 0.05 wt% Fe | 1 | 0.055 | | | | 0.055 | |
| | 2 | 0.047 | | | | 0.047 | |
| | 3 | 0.043 | | | | 0.043 | |
| | 4 | 0.042 | | | | 0.042 | |
| 7 | pre | 0.117 | | | | 0.117 | |
| 0.10 wt% Fe | 1 | 0.060 | | | | 0.060 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 2 | 0.051 | | | | 0.051 | |
| | 3 | 0.039 | | | | 0.039 | |
| | 4 | 0.038 | | | | 0.038 | |
| **8** | pre | 0.116 | | | | 0.116 | |
| 0.15 wt% Fe | 1 | 0.049 | | | | 0.049 | |
| | 2 | 0.018 | | | | 0.018 | |
| | 3 | 0.027 | | | | 0.027 | |
| | 4 | 0.019 | | | | 0.019 | |
| **9** | pre | 0.116 | | | | 0.116 | |
| 0.20 wt% Fe | 1 | 0.040 | | | | 0.040 | |
| | 2 | 0.033 | | | | 0.033 | |
| | 3 | 0.021 | | | | 0.021 | |
| | 4 | 0.020 | | | | 0.020 | |
| **10** | pre | 0.114 | | | | 0.114 | |
| 20 mM $H_2O_2$ | 1 | 0.029 | | | | 0.029 | |
| | 2 | 0.021 | | | | 0.021 | |
| | 3 | 0.018 | | | | 0.018 | |
| | 4 | 0.015 | | | | 0.015 | |
| **11** | pre | 0.119 | | | | 0.119 | |
| 4 mM $H_2O_2$ | 1 | 0.041 | | | | 0.041 | |
| | 2 | 0.040 | | | | 0.040 | |
| | 3 | 0.034 | | | | 0.034 | |
| | 4 | 0.025 | | | | 0.025 | |
| **12** | pre | 0.121 | | | | 0.121 | |
| 12 mM $H_2O_2$ | 1 | 0.050 | | | | 0.050 | |
| | 2 | 0.034 | | | | 0.034 | |
| | 3 | 0.026 | | | | 0.026 | |
| | 4 | 0.030 | | | | 0.030 | |
| **13** | pre | 0.113 | | | | 0.113 | |
| 40 mM $H_2O_2$ | 1 | 0.040 | 0.040 | | | 0.040 | 0.000 |
| | 2 | 0.037 | 0.036 | | | 0.037 | 0.001 |
| | 3 | 0.031 | 0.029 | | | 0.030 | 0.001 |
| | 4 | 0.028 | 0.029 | | | 0.029 | 0.001 |
| **14** | pre | 0.117 | | | | 0.117 | |
| 8 mM $H_2O_2$ | 1 | 0.041 | | | | 0.041 | |
| | 2 | 0.025 | | | | 0.025 | |
| | 3 | 0.026 | | | | 0.026 | |
| | 4 | 0.019 | | | | 0.019 | |
| **15** | pre | 0.111 | | | | 0.111 | |
| 16 mM $H_2O_2$ | 1 | 0.037 | | | | 0.037 | |
| | 2 | 0.032 | | | | 0.032 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 3 | 0.034 | | | | 0.034 | |
| | 4 | 0.019 | 0.017 | | | 0.018 | 0.001 |
| **16** | pre | 0.117 | | | | 0.117 | |
| Repeat of trial 3, with centrifugation of the end results | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.014 | 0.020 | 0.017 | | 0.017 | 0.003 |
| **17** | pre | 0.114 | | | | 0.114 | |
| Repeat of trial 5, with centrifugation of the end results | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.036 | 0.049 | 0.045 | 0.041 | 0.043 | 0.006 |
| **18** | pre | 0.115 | | | | 0.115 | |
| Repeat of trial 4. Temp probe misplaced, end temp of 44 ºC. | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | -0.003 | -0.004 | | | -0.004 | 0.001 |
| **19** | pre | 0.110 | 0.117 | 0.111 | | 0.113 | 0.004 |
| Repeat of trial 4, with centrifugation of the end results | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.013 | 0.015 | 0.014 | | 0.014 | 0.001 |
| **20** | pre | 0.111 | 0.108 | 0.114 | | 0.111 | 0.003 |
| T=32 ºC | 1 | 0.028 | 0.034 | 0.031 | | 0.031 | 0.003 |
| | 2 | 0.025 | 0.035 | 0.030 | | 0.030 | 0.005 |
| | 3 | 0.020 | 0.012 | 0.018 | | 0.017 | 0.004 |
| | 4 | 0.014 | 0.011 | 0.009 | 0.014 | 0.012 | 0.002 |
| **21** | pre | 0.115 | 0.113 | | | 0.114 | 0.001 |
| T=34 ºC | 1 | 0.031 | 0.027 | 0.033 | | 0.030 | 0.003 |
| | 2 | 0.026 | 0.022 | 0.023 | | 0.024 | 0.002 |
| | 3 | 0.013 | 0.017 | 0.012 | | 0.014 | 0.003 |
| | 4 | 0.011 | 0.014 | 0.012 | 0.008 | 0.011 | 0.003 |
| **22** | pre | 0.106 | 0.110 | 0.111 | | 0.109 | 0.003 |
| T=36 ºC | 1 | 0.030 | 0.029 | 0.023 | | 0.027 | 0.004 |
| | 2 | 0.012 | 0.014 | 0.019 | 0.022 | 0.017 | 0.005 |
| | 3 | 0.008 | 0.009 | 0.008 | | 0.008 | 0.001 |
| | 4 | 0.006 | 0.006 | 0.002 | | 0.005 | 0.002 |
| **23** | pre | 0.108 | 0.116 | 0.117 | | 0.114 | 0.005 |
| T=38 ºC | 1 | 0.028 | 0.024 | 0.028 | | 0.027 | 0.002 |
| | 2 | 0.027 | 0.020 | 0.019 | | 0.022 | 0.004 |
| | 3 | 0.011 | 0.013 | 0.019 | | 0.014 | 0.004 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 4 | 0.007 | 0.006 | 0.010 | | 0.008 | 0.002 |
| **24** | pre | 0.105 | 0.112 | 0.111 | | 0.109 | 0.004 |
| T=40 ºC | 1 | 0.023 | 0.023 | 0.020 | 0.033 | 0.025 | 0.006 |
| | 2 | 0.019 | 0.023 | 0.015 | | 0.019 | 0.004 |
| | 3 | 0.018 | 0.015 | 0.016 | 0.007 | 0.014 | 0.005 |
| | 4 | 0.004 | 0.003 | 0.002 | | 0.003 | 0.001 |
| **25** | pre | 0.111 | 0.113 | 0.116 | | 0.113 | 0.003 |
| Reusability attempt 1, trial 1 (not used, reusability study was reperformed) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.019 | 0.018 | 0.014 | | 0.017 | 0.003 |
| **26** | pre | 0.108 | 0.110 | 0.109 | | 0.109 | 0.001 |
| Reusability attempt 1, trial 2 (not used, reusability study was reperformed) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.046 | 0.057 | 0.050 | 0.043 | 0.049 | 0.006 |
| **27** | pre | 0.114 | 0.117 | 0.117 | | 0.116 | 0.002 |
| Reusability attempt 1, trial 3 (not used, reusability study was reperformed) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.060 | 0.061 | 0.064 | | 0.062 | 0.002 |
| **28** | pre | 0.114 | 0.114 | 0.116 | | 0.115 | 0.001 |
| Reusability attempt 2, part 1a (data used for reusability study) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.029 | 0.034 | 0.028 | | 0.030 | 0.003 |
| **29** | pre | 0.122 | 0.123 | 0.118 | | 0.121 | 0.003 |
| Reusability attempt 2, part 1b (side trial run to supplement catalyst from 1a for 2) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.031 | 0.024 | 0.036 | | 0.030 | 0.006 |
| **30** | pre | 0.105 | 0.114 | 0.110 | | 0.110 | 0.005 |
| Reusability attempt 2, part 2 (catalyst from 1a and supplemented from 1b to make 2 g/L) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.049 | 0.047 | 0.052 | | 0.049 | 0.003 |
| **31** | pre | 0.108 | 0.115 | 0.108 | | 0.110 | 0.004 |
| Reusability attempt 2, part 3 (catalyst from trial 30) | 1 | | | | | | |
| | 2 | | | | | | |
| | 3 | | | | | | |
| | 4 | 0.066 | 0.064 | 0.068 | | 0.066 | 0.002 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **32** | pre | 0.110 | 0.109 | 0.110 | | 0.110 | 0.001 |
| Control of SBA-15 and H$_2$O$_2$ | 1 | 0.116 | 0.126 | 0.108 | | 0.117 | 0.009 |
| | 2 | 0.097 | 0.090 | 0.094 | 0.094 | 0.094 | 0.003 |
| | 3 | 0.100 | 0.105 | 0.098 | | 0.101 | 0.004 |
| | 4 | 0.096 | 0.092 | 0.093 | | 0.094 | 0.002 |
| **33** | pre | 0.178 | | | | 0.178 | |
| Control of SBA-15 only | 1 | 0.175 | | | | 0.175 | |
| | 2 | 0.182 | | | | 0.182 | |
| | 3 | 0.168 | | | | 0.168 | |
| | 4 | 0.180 | | | | 0.180 | |

Table B.2: Data for RB4 calibration curve

| Concentration (g/L) | Absorbance at 595 nm |
|---|---|
| 0.212 | 0.137 |
| 0.106 | 0.078 |
| 0.053 | 0.046 |
| 0.0265 | 0.03 |
| 0.01325 | 0.018 |
| 0.00663 | 0.015 |

Table B.3: Data for iron(II) calibration curve

| Concentration (ppm) | Absorbance at 508 nm |
|---|---|
| 3 | 0.408 |
| 1.5 | 0.3 |
| 0.6 | 0.123 |
| 0.3 | 0.063 |
| 0.15 | 0.023 |