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Degradation of Orange G Through Persulfate Activated Nanoscale Zerovalent Iron Composites and Boron-Doped Diamond Electrodes

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Abstract: Properly treated wastewater is necessary for water reuse and to avoid unnecessary impacts on the environment. The poultry industry utilizes large amounts of water for poultry processing. The need for innovative ways to treat organic contaminants in the poultry wastewater industry is especially necessary due to increased poultry consumption. The U.S. Department of Agriculture projected Americans would consume approximately 92 pounds of chicken per person in 2017.[1] Dissolved air flotation (DAF) is currently used in poultry wastewater treatment, but DAF does not remove organic contaminants efficiently per effluent standards. Implementation of processes that degrade contaminants directly would benefit the poultry industry economically. Potential organic treatment options are nanoscale zerovalent iron (nZVI) composites that activate persulfate to degrade contaminants by sulfate radical generation and boron-doped diamond electrode (BDDE) electrochemical oxidation processes that mineralize organic content through hydroxyl radical electro-generation. These processes have shown potential in decolorization of Orange G (OG) dye contaminant through UV/Vis spectroscopy and decreasing oxygen necessary for oxidation of OG through Chemical Oxygen Demand (COD) testing. Standard and lyophilized 1:5 mass ratio nZVI/biochar composites showed decolorization and COD concentration decreases for 30-mintute experimental runs. 30-minute and 120-minute BDDE experiments utilizing a current density of 2-mA/cm^2 and varying OG starting concentrations indicated potential for OG decolorization through azo bond breaking and decreased COD readings by OH radical oxidation of organic content. Ultimately, industrial poultry wastewater will be used to test organic contaminant degradation through both nZVI/biochar composites and BDDE.

Section 1:

1.1. *Introduction*

Recently, interest has risen in recycling the waste created by modern society, including industrial wastewaters, but water quality is threatened by the presence of new and increasing concentrations of contaminants.[2] As a result of increasing needs for water treatment and recycling, the amount of sewage sludge requiring treatment and disposal is expected to increase in the future.[3] One of the industries that uses a large amount of water for its processing steps is the poultry industry. The United States poultry industry produced 8.54 billion chickens and 238 million turkeys in 2014.[4] With a typical processing facility estimated to utilize 9 gallons of water per chicken and roughly 30 gallons per turkey, the wastewater for 2014 alone amounts to 76.9 billion and 7.14 billion gallons of wastewater for chickens and turkeys, respectively.[5] To remove contaminants from wastewater and satisfy the regulations of the Clean Water Act, poultry processors employ wastewater treatment processes. However, biological and organic contaminant levels can vary depending on the facility and the efficiency of the treatment processes used, influencing the amount of contaminants released into the environment.

New York City, New York had a population of approximately 8 million people in 2012. An average person uses 102 gallons of water per day, so roughly 298 billion gallons of water were used that year in New York. Approximately 84 billion gallons of water were used for processing chickens and turkeys in 2014. The amount of water used for poultry

processing amounts to roughly 28% of the water used by the most populated city in America for a year.

1.2. *Background*

Meat processing facilities produce wastewater with large amounts of fats, oils, grease, and solids. For poultry processing plants, wastewater is heavily contaminated with organic materials that contribute to elevated total suspended solids, fats, oils, grease, and chemical oxygen demand, which are regulated water quality parameters.[6] Chemical oxygen demand, which is a standard chemical oxidation analysis that is related to the total oxidizable organic content of a water sample, would necessarily include any dissolved organics. Before the water can be sent from a processing facility, water treatment is required to remove organic contaminants.[7] Preliminary treatment is used to separate suspended solids and large particles from liquids with screens, filters, or strainers.[8, 9] The effluent from preliminary treatment is then further treated using primary and secondary treatments. One of the most commonly used methods for primary treatment is dissolved air flotation (DAF), which is used to reduce the amount of fat and other suspended solids present in the effluent.[9] For DAF, air bubbles are injected at the bottom of a flotation tank, and the air bubbles transport light solids and other material such as fat and grease to the surface where the accumulated scum is consistently skimmed off.[9] DAF separates small particles faster and more completely compared to other methods such as gravity settling.[9] Common disadvantages and limitations of DAF include occasional malfunctioning, poor total suspended solid elimination, and moderate nutrient removal.[8] Preliminary and primary processes typically do not treat wastewater to regulation standards. Secondary treatment is used to remove remaining soluble organic compounds from primary treatment. Secondary treatment uses biological processes such as lagoons with anaerobic, aerobic, or microorganisms and bioreactors for organic and nutrient removal.[8] There are also tertiary treatments that remove nitrogen, phosphorus, or suspended solids combinations in the wastewater treatment process.[9]

Degradation of organic contaminants within wastewater, including poultry processing wastewater, has received interest in order to break down harsh contaminants into less harsh products. Implementing a process that degrades organic contaminants in wastewater onsite would be economically beneficial for the poultry industry as DAF often falls short in terms of efficiently removing the organic contaminant load to meet effluent standards.

Advanced oxidation processes (AOPs) are complementary treatment options for primary or secondary treatment of wastewater that are able to degrade organic wastewater contaminants through oxidation reactions.[8] AOPs are diverse and include gamma radiation, ozonation, ultrasound technology, UV/H_2O_2, UV/O_3, photocatalysis, etc. for the oxidation and degradation of organic matter.[8]

Two of the most common AOPs include UV/H2O2 and ozone. UV/H2O2 is an advanced oxidation process, and UV/H2O2 oxidation appears to be sufficient to degrade pollutants.[10] AOPs make use of hydroxyl radicals (*OH) that react non-selectively with

organic molecules.[10] Among many AOPs, UV/H2O2 process has become a standard advanced oxidation process for the reduction of many organic contaminants and naturally occurring organic matter by formation of *OH.[10] Ozone efficiently degrades many trace organic contaminants in wastewater and is increasingly being used to remove compounds from municipal and industrial wastewater effluent.[11]

1.3. *Nanoscale Zerovalent Iron-Biochar/Persulfate Activated Systems*

Nanoscale zerovalent iron composites that activate persulfate are potential alternative organic treatment options. Supported nanoscale zerovalent iron (nZVI) composites activated by persulfate have shown promise in degrading organic contaminants in wastewater.[12] Biochar (BC), a porous structure that possesses large surface area and a significant density of oxygen-containing functional groups, has shown potential as both a dispersion medium and activator.[3] Biochar has been used as an adsorbent for removal of organic contaminants and heavy metals and has been utilized for dispersion and stabilization of nanoparticles to enhance performance.[3] Previous articles have shown that certain organic contaminant degradation efficiencies are consistently higher with nZVI/BC composites compared to the use of only nZVI systems.[3] Because of the large surface area of the composite components and the reactivity of nZVI, nZVI composites are ideal for activation of persulfate due to increased generation of sulfate radicals.[12] Sulfate radicals have high redox potentials that are capable of oxidizing most organics in water and are necessary to enhance and accelerate the degradation of organic contaminants.[12, 13]

1.4. *Electrochemical Oxidation: Boron-Doped Diamond Electrodes (BDDE)*

Electrochemical oxidation (EO) processes have become some of the most promising techniques for treatment of wastewaters containing organic compounds since the processes efficiently mineralize and oxidize organic contaminants in an environmentally friendly way.[14] BDDE have been an attractive anode material for the past ten years for environmental applications.[15] BDDE employ EO, an advanced oxidation process for water treatment to mineralize organic contaminants, and have demonstrated degradation for a range of emerging pollutants in water.[16] In EO, heterogeneous hydroxyl radicals (*OH) are electro-generated.[16] OH radicals are powerful oxidants that non-selectively react with organic pollutants until complete mineralization to CO_2, H_2O, and inorganic ions is achieved.[16] Because OH radicals have weak interactions with the BDDE, the radicals are highly reactive toward organic contaminants.[15] BDDE are promising anodes for EO water treatment applications compared to conventional catalytically active anode materials such as Pt, PbO_2, or SnO_2 since BDDE possess higher overpotentials for water splitting and thus greater oxidation power in terms of the potential window where water contaminant oxidation can occur.[16]

1.5. *Orange G (OG) Model Water Contaminant*

Dyes are considered one of the largest sources of water pollution.[17] The largest class of dyes used in textile processing is azo dyes, which are largely constituted by aromatics

functional groups linked by azo bonding (–N=N–).[17, 18] Azo dyes are very resistant to biodegradation.[17] Azo dyes are released in textile industry wastewaters in developed and underdeveloped countries worldwide, so the dyes are highly persistent in different areas of the environment.[17, 18]

Orange G (OG) is a common synthetic azo dye with the chemical formula $C_{16}H_{10}N_2Na_2O_7S_2$, which can be seen in Figure 1. OG contains organic carbon within the structural aromatic rings and is resistant to biodegradation due to azo bonding. Since OG is considered less toxic compared to other chemicals, OG is considered a good choice for a model water contaminant for experimental analysis.

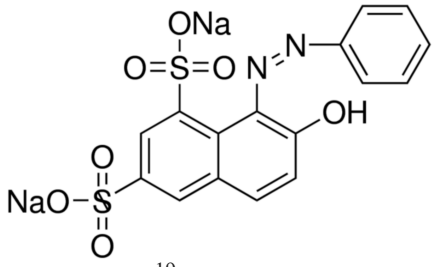

Figure 1: Orange G molecular structure.[19]

1.6. *Experimental Testing Mechanisms: Chemical Oxygen Demand (COD) and UV/Vis Spectrophotometry*

For testing the concentration of organic, carbon-based compounds in water, common tests include Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Organic Carbon (TOC), and Oil and Grease (O&G), and these tests aim to establish the relative strength of organics in wastewater.[20] COD is one of the more popular options for establishing the concentration of organic matter in wastewater samples. COD describes the amount of oxygen needed to consume the organic materials in a sample and is a measurement of the amount of material that can be oxidized into carbon dioxide and water in the presence of a strong chemical oxidizing agent, such as potassium dichromate.[21] Activated sludge effluent has a normal COD range of 30 to 70 mg/L.[21] Some advantages of COD tests are relatively fast and reproducible results, and a disadvantage of COD is that COD does not differentiate between biologically available and inert organic content.[21] Instead, COD measures all the organic contaminants that can be oxidized. Using OG as a model contaminant, treatment processes should lower the COD observed for samples taken at intervaled experimental times. A starting sample with a high COD means that there is a high concentration of oxidizable content present in the sample, and a lowered COD shows that there is decreased oxidizable material within the sample. A lowered COD for OG would imply the oxidation of OG molecules and a decrease in the organic content of an experimental sample.

Another analytical tool used to observe OG is UV/Vis Spectrophotometry. A chromophore is a covalently unsaturated functional group responsible for absorption in the UV or visible region.[22] Examples of chromophores include C=C, C≡C, C=O, C≡N, N=N, and NO_2.[22] If a compound absorbs light in the visible region between 400 and 800

nm, then the compound appears colored.[22] OG contains the −N=N− chromophore.[17] For OG, a spectral scan reveals that the −N=N− azo bond in OG is observed at roughly 480 nm.[17] Experimentation should show decolorization of OG throughout the test at intervaled times, and lowered absorbance values through spectroscopy should confirm the breaking of the OG azo bonds at a wavelength of 480 nm.

While COD is used to show the concentration of organic, carbon-based material in a sample, spectrophotometry can be used to illustrate the breaking of chromophores, such as nitrogen bonds, and implications in decolorization of a compound, such as OG.

Section 2: nZVI/BC Nanoparticles

In this study, work in developing persulfate activated nZVI composites is discussed. In particular, the role of 1:5 nZVI/BC mass ratio nanoparticles used for persulfate activation through batch reactor experiments is examined. Chemical oxygen demand (COD) analysis and UV/Vis spectrophotometry are used to assess the degradation of contaminants by the synthesized composites.

2.1. *Methods*

2.1.1. *Materials*

For nanoparticle synthesis, Millipore water, Alfa Asear iron (III) sulfate heptahydrate ($FeSO_4 \bullet 7H_2O$, 98%), and Millipore sodium borohydride ($NaBH_4$) were used. Aminotris(methylenephosphonic acid) (ATMP) stabilizer, biochar, and argon were obtained from commercial grade sources. For testing, CHEMetrics chemical oxygen demand (COD, 0-1500 ppm (HR)) kits and COD calibration standards (10,000 ppm), Sigma Aldrich sodium persulfate ($Na_2O_8S_2$, 98%), and Ameresco Orange G sodium salt (OG, high purity grade) were purchased.

2.1.2. *Synthesis of Nanoparticles with Biochar*

For nanoparticle testing, a 10 g/L iron concentration in 20 mL of water and biochar (BC) as the carbon support was used. Lyophilized nanoparticles with 10 g/L Fe concentration in 20 mL of water were also tested. A 1:5 mass ratio of nZVI to BC was chosen to start preliminary testing of the effect of both standard and lyophilized nanoparticles on the degradation of organic contaminants. To synthesize the standard nanoparticles, water, ATMP stabilizer, iron, and biochar were added into a 3-neck borosilicate flask. The solution was allowed to bubble with argon gas while rotating at 100 rpm for 15 minutes open to the ambient atmosphere and on an orbital shaker. Sodium borohydride ($NaBH_4$) was used as a reducing agent and was added drop-wise to the continuously stirred solution. nZVI particles are synthesized by $FeSO_4 \bullet 7H_2O$ reduction using $NaBH_4$, which is a reducing agent since the compound donates an electron to the iron cation during synthesis. $NaBH_4$ reduces the ferrous iron present, allowing the iron atoms to nucleate and form nanoparticles. The ATMP stabilizer controls this nucleation and particle growth process and controls nanoparticle size. These nanoparticles are deposited on the surface

of the biochar through the stirring and drop-wise addition of $NaBH_4$.The solution was then rotated at 100 rpm for 15 more minutes while under vacuum. The nanoparticle solution was added to a centrifuge tube and placed in an Eppendorf 5430 R centrifuge. The excess water was decanted. 20 mL of purified water was added back to the nanoparticles to create the 10 g/L desired concentration. The lyophilized nanoparticles were synthesized in the same way as the standard nanoparticles but went through additional steps. To obtain the lyophilized nanoparticles, standard nanoparticles were allowed to freeze completely at -80 degrees Celsius for 3 days. Once frozen, the nanoparticles were placed in a vacuum-sealed tube and connected to a lyophilizer set to approximately -75 to -85 degrees Celsius for a few days. 20 mL of water were added back to allow testing of the lyophilized nanoparticles.

2.1.3. *Experimental Set-Up*

A 40 mL testing volume was utilized for all experiments. For testing, 1.9 mL of sodium persulfate from a 100 g/L stock and 6 mL of OG from a 5 g/L stock were added to 24.1 mL of water. The OG and persulfate concentrations were consistently kept at 0.75 g/L and 4.75 g/L, respectively, for the duration of testing. 8 mL of either the standard or lyophilized 1:5 nZVI/BC mass ratio 10 g/L Fe nanoparticles were also added to the testing solution. The solution in a centrifuge tube was continually mixed using an automated rotator once the nanoparticles were added. For sampling, a syringe filter was used for each sample taken to filter out nanoparticles and lessen nanoparticle interaction with persulfate; however, samples would need to be quenched immediately to completely stop the reaction. The duration of the experiment was 30 minutes total. Before the nanoparticle addition, a sample was taken for t=0 minutes, and samples were also taken at t=10, 20, and 30 minutes.

2.1.4. *Chemical Oxygen Demand Standard Curves*

Chemical Oxygen Demand (COD) is a measure of the oxidizable organic matter content of a sample and is especially useful in wastewater research.[23] Since the ultimate goal of the nanoparticle-OG tests is to transition to nanoparticle-chicken wastewater testing, COD was utilized as a tool for OG model organic contaminant experiments. For COD, a 2 mL sample is added and reacted in a COD vial containing an acidic solution of potassium dichromate and a silver catalyst, which is then digested for 2 hours at 150°C.[23] During digestion, oxidizable organic compounds reduce dichromate ions to chromic ions, and the amount of chromic ion produced is measured.[23] The COD test results are expressed in units of micrograms of oxygen consumed per mL of sample (μg O_2/mL).[23]

For COD testing, two separate digestion blocks were used: HACH DRB 200 and HACH 45600 COD Reactor. Once sample vials went through digestion and had time to cool, a Beckman DU 800 UV/Vis Spectrophotometer was used to analyze the COD readings of each testing sample.

Since the COD vials contain sulfuric acid, silver sulfate, and potassium dichromate before a testing sample is added, there was a safety concern in transferring the contents of the reacted solution into a plate reader spectrophotometer, and the cell cuvette holder for

the instrument was not capable of testing the circular COD vials. Therefore, a 3D model was created in Autodesk Inventor Pro for an adapter to fit the vials in the spectrophotometer. The 3D model and printed model of the adapter can be seen in Figure 2. The adapter allowed the vial to be tested directly in the spectrophotometer without disturbing the contents. Testing was done using the adapter, and a 5% error in reading was observed when vials were placed one way in the adapter versus when the vials were rotated 180°.

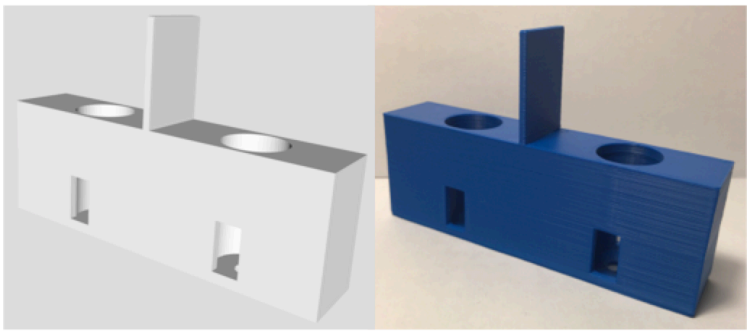

Figure 2: 3D model and printed model adapter for DU800 UV/Vis Spectrophotometer.

A COD standard curve was created before testing and sampling with nanoparticles and OG started. Potassium hydrogen phthalate (KHP) is used as the standard for COD.[24] KHP has a theoretical COD of 1.176 mg O_2/mg, and a solution of 425 mg of KHP dissolved in 1000 mL of water has a theoretical COD of 500 µg O_2/mL.[24] Based on the theoretical CODs, the standard curve was made with 1500 to 10 µg O_2/mL dilutions of KHP. A 2 mL sample of each KHP dilution was added to COD vials, allowed to digest for 2 hours and cool off, and was tested using the spectrophotometer. A wavelength scan was used on 1500 µg O_2/mL, the highest concentration sample of KHP, from 350 to 700 nm. The peak absorbance of the wavelength scan was used as the fixed absorbance for the standard curve. The peak absorbance was seen at 602 nm.

The average standard curve used for experimental comparison included two separate dilution tests to confirm the accuracy of each curve. The average COD standard curve was used to gather unknown concentration data for experimental samples of known absorbance at 602 nm. The average standard curve can be viewed in Figure 3.

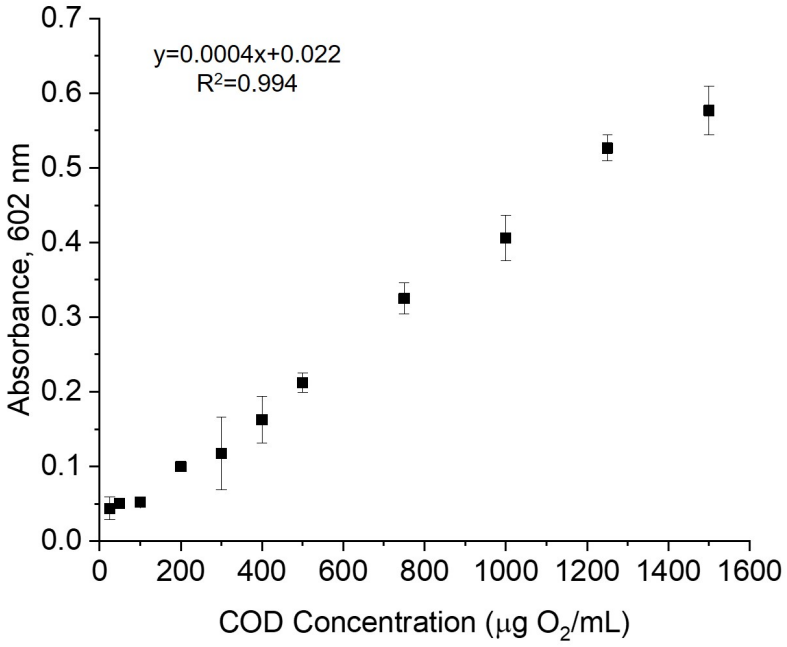

Figure 3: Average COD standard curve at 602 nm.

2.1.5. *UV/Vis Orange G Standard Curves*

An Orange G standard curve was prepared for testing the model contaminant decolorization through experiments. Two separate sets of dilutions were created to confirm the accuracy of the standard curve, and an average standard curve was used to evaluate experimental data concentrations. Water was used as the blank, and OG dilutions ranging from 0.2 to 1 g/L were made. The blank and dilutions were added to a cell culture plate in separate wells. The dilutions were tested at a fixed wavelength of 530 nm, which was based on previous lab work on OG. A BioTek Epoch 2 Microplate Spectrophotometer was used to obtain absorbance values of the known OG concentrations. The absorbance versus concentration data was plotted and used as a tool to determine unknown concentrations of samples with known absorbance values at 530 nm. The plot of the average standard curve can be seen in Figure 4.

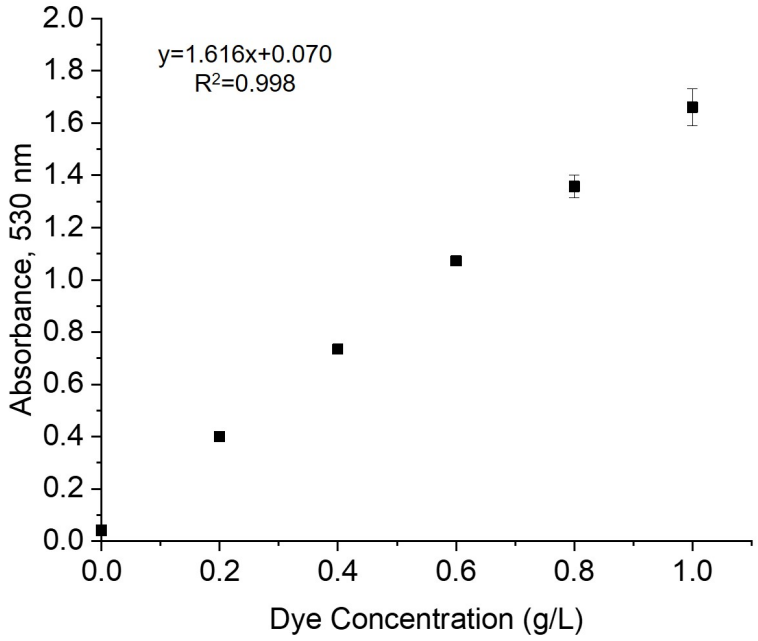

Figure 4: Average Orange G standard curve at 530 nm.

2.2. *Results and Discussion*

Testing started with 1:5 nZVI/BC mass ratio of 10 g/L Fe nanoparticles and OG and persulfate concentrations of 0.75 g/L and 4.75 g/L, respectively, for the duration of a 30-minute test. Figure 5 shows the experimental run. At t=0 minutes, the COD starting concentration for 0.75 g/L OG was 1373.70 μg O_2/mL. Once 8 mL of nanoparticles were added to the testing solution, 10 minutes passed before another sample was taken. At t=10 minutes, the COD concentration decreased to 1114.78 μg O_2/mL. The COD readings were 996.86 μg O_2/mL and 989.09 μg O_2/mL for t=20 minutes and t=30 minutes, respectively. Between t=0 and t=30 minutes, a 28% in COD readings was observed. The COD concentration decrease implies that some OG was oxidized due to the persulfate-activated nanoparticles and that less oxygen is required to oxidize the organic contaminants present in the sample as time progressed.

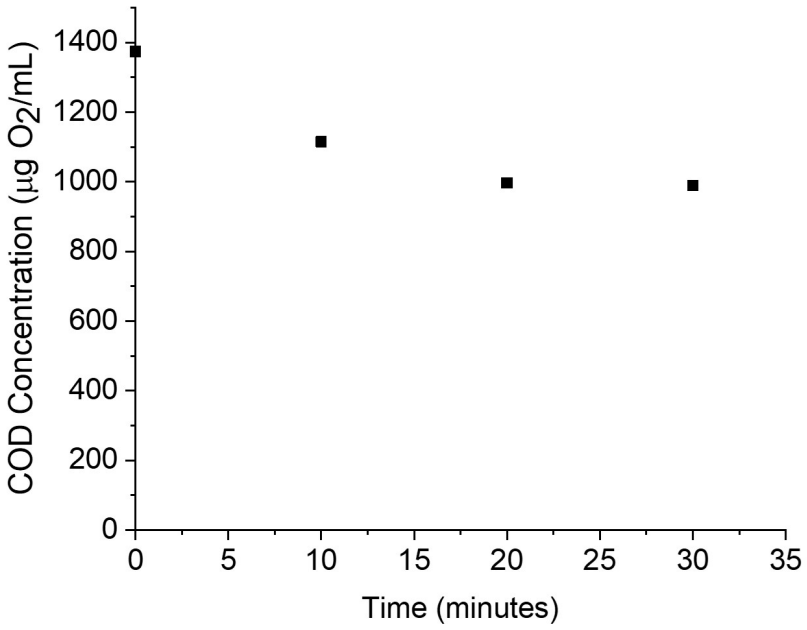

Figure 5: Fe-biochar nanoparticles tested for COD degradation over 30 minutes.

Two lyophilized 1:5 nZVI/BC mass ratios of 10 g/L Fe nanoparticles were tested with OG and persulfate concentrations of 0.75 g/L and 4.75 g/L, respectively. These experiments were 30-minute tests. The average COD and OG plots for the runs can be seen in Figure 6. Though the OG concentration should have started at 0.75 g/L, the actual OG starting concentration at t=0 minutes was an average of 0.86 g/L. This discrepancy could be due to experimental error when the OG stock solution was created. At t=10 minutes, the OG concentration decreased to 0.24 g/L. From t=0 minutes to t=10 minutes, there was a 72% decolorization in OG. The OG concentrations for t=20 minutes and t=30 minutes was roughly 0.22 g/L for both times. There was very little decolorization of OG between 10 minutes and the full 30-minute duration. This implies that more azo bonds for OG were broken during the first 10 minutes of the experimental run due to the lyophilized nanoparticles and persulfate compared to the last 20 minutes. Overall, there was a 75% decolorization of OG for the full 30-minute duration of the experiment. The COD starting concentration for an observed 0.86 g/L OG starting concentration was 1408.04 μg O_2/mL. The COD readings were 1799.91, 1632.61, and 1503.16 μg O_2/mL for t=10, 20, and 30 minutes. This data illustrates that there was more oxidizable material present as the duration of the experiment progressed. During experimentation, sampling was difficult since the nanoparticle-biochar mix affixed to the bottom of the reactor container. When the test volume was better mixed, the nanoparticle-biochar was better dispersed throughout the volume. The COD readings could have increased from t=0 minutes to t=20 minutes due to more biochar present in the sample taken, which increases the carbon and oxidizable content; however, the true source for the increase COD reading is still unclear. Additional experiments would need to be performed to better understand the COD readings. The decreased OG concentration for the experiment implies that the SO_4 radicals generated by the persulfate and nanoparticles were able to break azo bonds

to decolorize OG, but the increased COD readings illustrate that there is more oxygen necessary to consume the organic materials present in the samples.

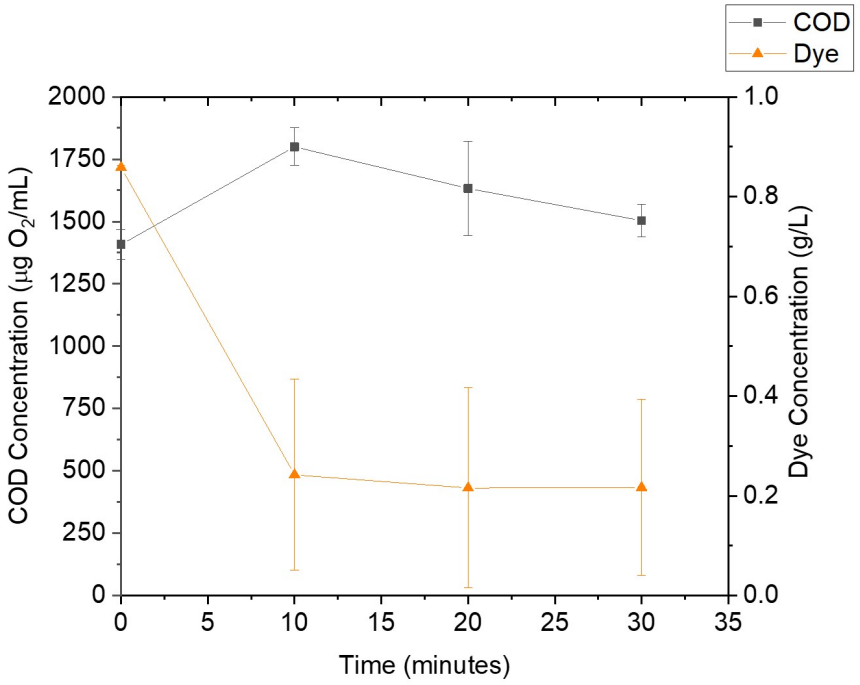

Figure 6: Two-run average for lyophilized Fe-biochar nanoparticles tested for Orange G decolorization and COD degradation over 30 minutes.

2.3. *Conclusions*

Based on the current experimental runs, there is not a clear conclusion to make between standard and lyophilized nanoparticles on the decolorization and COD readings associated with OG. However, the experiments showed promise in both decolorization and decreased COD readings for OG. Repeats of the experiments would indicate better relationships and conclusions.

Section 3: Boron-Doped Diamond Electrodes

Work in using boron-doped diamond electrodes (BDDE) for electrochemical oxidation is discussed. Particularly, the role of BDDE to electro-generate hydroxyl radicals to degrade organic contaminants through batch reactor experiments is examined. Chemical oxygen demand (COD) analysis and UV/Vis spectrophotometry are used to assess the degradation of contaminants by OH radical oxidation.

3.1. *Methods*

3.1.1. *Materials*

BDH sodium chloride (NaCl), Ameresco Orange G sodium salt (OG, high purity grade), and Standard NeoCoat boron doped diamond electrodes (100 ppm B doping level) were purchased. An American Elements stainless steel metal disc (25 mm diameter, 0.5 mm thickness) and commercial grade graphite were used as counter electrodes. Ag/AgCl was used as the reference electrode.

3.1.2. *Experimental Set-Up*

For the BDD electrode experimental set-up, a 43 mL total volume was used, which consisted of a solution of varying concentrations of OG as the model contaminant and NaCl as the electrolyte. Target starting concentrations of interest for OG included 0.5 g/L, 0.75 g/L, and 5 g/L and either 0.02 M or 0.1 M starting NaCl concentration was used. Three electrodes were placed into the solution once mixed. A silver/silver chloride reference electrode was consistently utilized. For the counter electrode, a stainless steel disk was predominantly employed, but graphite was also tested as the counter electrode. The working electrode was the boron-doped diamond electrode. A beaker with test solution was placed on a stir plate along with a stir bar for continuous mixing. A 2-mA/cm^2 current density was applied during all testing. The surface area of the BDD electrode was consistently kept at 4.5 cm^2 for the duration of testing with the exception of one 12.5 cm^2 BDD electrode surface area test. Based on the surface area of the working electrode, the current was either 0.009 A or 0.025 A, where 0.009 A was utilized most often. Once the electrodes were set-up in the testing solution, a constant current was applied with a Gamry Reference 3000 Potentiostat. Samples of the test solution were taken at time (t)= 0, 10, 20, and 30 minutes for both COD and OG decolorization testing. Some experiments focused on the effect of the BDD electrode on degradation through extended run times, so t=120 minutes samples were also taken.

3.1.3. *Standard Curves*

The same average COD and Orange G standard curves were used for BDD experiments as for nanoparticle experiments. See sections 2.1.4 *Chemical Oxygen Demand Standard Curves* and 2.1.5 *UV/Vis Orange G Standard Curves* for details.

3.2. *Results and Discussion*

BDDE testing started with three runs of 0.5 g/L OG and 0.1 M NaCl solutions while using stainless steel as the counter electrode. For these experimental runs, the surface area of the BDDE was 4.5 cm^2, and a 2-mA/cm^2 current density was used for both. A 0.009 A current was applied to the solutions for a 30-minute duration. Figure 7 shows the average COD and OG decolorization plots for these experiments. At t=0 minutes, the OG starting concentration was 0.51 g/L. The OG concentration dropped to 0.42 g/L at t=10 minutes. During the first 10 minutes of the experimental runs, the decolorization of OG was roughly 17%. The OG concentrations for t=20 minutes and t=30 minutes were 0.29 g/L and 0.20 g/L, respectively. The OG decolorization plot shows proportional decolorization between each time interval. OG decolorized by 62% for the full 30-minute duration of the experiment. The decolorization in OG indicates that the OH radicals

electro-generated during the electrochemical oxidation process broke azo bonds present in OG. The COD starting concentration for an observed 0.51 g/L OG starting concentration was 3701.51 µg O_2/mL. Since a 0.86 g/L OG concentration for nanoparticle experiments indicated a COD reading of roughly 1500 µg O_2/mL, a higher COD reading of 3701.51 µg O_2/mL for 0.51 g/L OG indicates a likely error in COD measurement, but results are still reported to demonstrate the usefulness of the BDDE approach for COD removal. The average COD readings were 3554.04, 3472.66, and 3534.43 µg O_2/mL for t=10, 20, and 30 minutes. From t=0 minutes to t=10 minutes, the COD reading decreased by 4%. The COD also dropped for the t=10 minutes to t=20 minutes time interval. The COD reading decreased by 6% for the first 20 minutes of the experiment. However, from t=20 minutes to t=30 minutes, the COD reading increased. This COD data illustrates that there was more oxidizable material present for this time interval. Overall, the COD reading for the full 30-minute experiment decreased by 4%. The small decrease in COD readings for the duration of the experiment indicates that only a small amount of organic contaminants were oxidized using the BDDE since the oxygen demand remains roughly constant for each sample time.

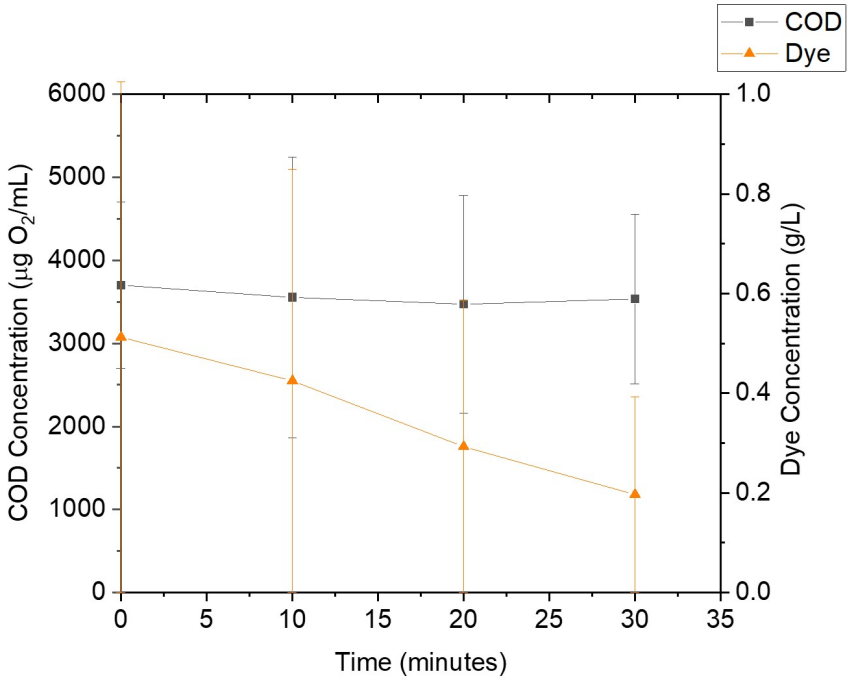

Figure 7: Three-run average for decolorization of Orange G with a starting concentration of 0.5g/L and degradation of COD using boron doped diamond electrode in 0.1 M NaCl at a current density of 2-mA/cm^2 for 30 minutes.

Figure 8 below shows the decolorization of Run #2 for an OG starting concentration of 0.5 g/L for 30 minutes. The run used BDDE with a current density of 2-mA/cm^2. The OG coloring visibly decreases from left to right for each of the 10-minute interval samples taken.

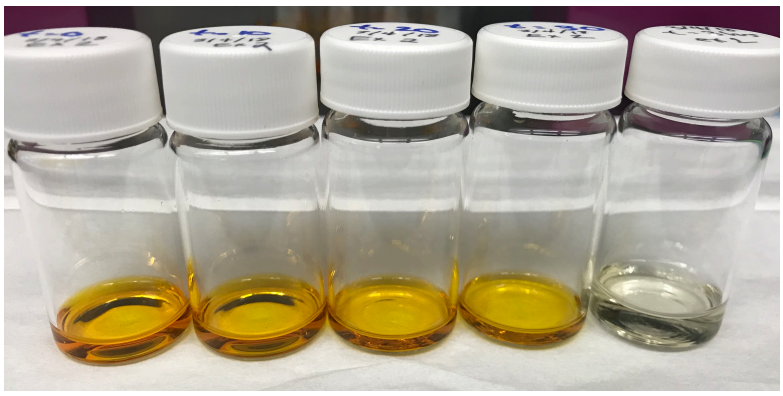

Figure 8: Visual Orange G decolorization for Run #2 over 30 minutes.

Two 5 g/L OG and 0.1 M NaCl solutions with graphite as the counter electrode were tested with BDDE. For these experimental runs, the surface area of the BDDE was either 4.5 cm^2 or 12.5 cm^2, and a 2-mA/cm^2 current density was used for both. For a set 2-mA/cm^2 current density, a 0.009 A or 0.025 A current was applied to the solutions, depending on which BDDE surface area was used. Currents were applied to the solutions for a total of 120 minutes. The average COD and OG decolorization plots for these experiments are shown in Figure 9. The starting OG concentration observed at t=0 minutes was 5.14 g/L. For t=10, 20, and 30 minutes, the OG concentrations were 5.19, 4.97, and 4.67 g/L. Though the OG concentration slightly increased from t=0 minutes to t=30 minutes, the overall trend for the 30-minute run was a decrease in the OG concentration. There was a 9% decolorization of OG observed for the 30-minute experiment. These experiments consisted of extended run times, so sampling occurred at t=120 minutes. The OG concentration decreased to 2.34 g/L at t=120 minutes. Overall, there was a 54% decolorization of OG for the full 120-minute duration of the experiment, and a roughly linear OG decolorization trend was observed for samples taken. This trend shows promise for continual azo bond breaking by OH radicals for extended time experiments. The COD concentration for the observed 5.14 g/L OG was 5177.33 µg O_2/mL. For t=10, 20, and 30 minutes, the COD concentrations were 4898.46, 5056.94, and 4556.86 µg O_2/mL. A 12% decrease in COD concentration occurred for the 30-minute experiment duration. The extended run at t=120 minutes decreased the COD concentration to 3682.67 µg O_2/mL. A 29% COD concentration decrease was observed for the full 120-minute run. The COD trend was also approximately linear for the full experimental duration. Since both the UV/Vis signal and COD readings lessened for the experiment, both decolorization and contaminant oxidation is implied for OG. The UV/Vis reading indicates that the OH radicals are breaking down the azo bonds of OG, which cause decolorization in samples that are taken. Decreased COD readings imply that less oxygen is needed to oxidize the contaminants present in the water due to OH radicals oxidizing organic content over time.

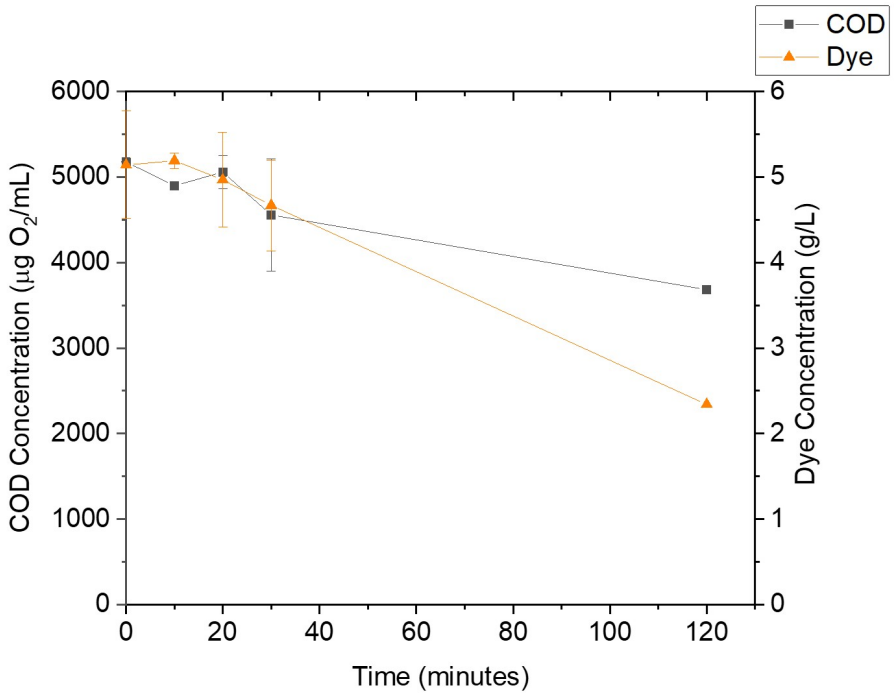

Figure 9: Two-run average for decolorization of Orange G with a starting concentration of 5g/L and degradation of COD using boron doped diamond electrode in 0.1 M NaCl at a current density of 2 mA/cm^2 for 2 hours.

Since elevated COD readings were observed for previous experiments, a control experiment was performed to test if the BDDE had any effects on COD concentrations. A 0.75 g/L OG and 0.02 M NaCl solution with stainless steel used as the counter electrode was tested with BDDE. The surface area of the BDDE was 4.5 cm^2, and a 2-mA/cm^2 current density was used. A 0.009 A current was applied to the solution for a total of 30 minutes. A sample of the solution without any electrodes was taken, which was the control. The BDDE and other electrodes were placed in the solution, and no current was applied for 10 minutes. After the 10 minutes, another sample was taken, which was labeled as the sample for t=0 minutes. From there, current was applied and regular samples were taken at 10-minute intervals. The COD and OG decolorization plots for this experiment are shown in Figure 10. The starting OG concentration observed for the control was 0.78 g/L. For t=0, 10, 20, and 30 minutes, the OG concentrations were 0.77, 0.74, 0.65, and 0.58 g/L. For the control and t=0 minutes, the OG concentration was roughly the same, which indicates that BDDE with no applied current have almost no effect on the breaking of azo bonds and decolorization of OG. When the current was applied, decolorization of OG was observed. The OG was decolorized by 25% for the 30-minute run. The COD concentrations for the control and t=0, 10, 20, and 30 minutes were 3722.07, 4161.11, 4204.13, 4218.90, and 3863.06 µg O_2/mL. The control and t=0 minutes concentrations show that there could be a correlation to elevated COD readings due to BDDE placed in the solution with no applied current. Carbon from the BDDE could increase COD concentrations since more oxygen would be required to oxidize organic content, which would include the carbon from the electrode. Between the control and t=0 minutes, a 12% increase in COD concentration was observed. COD continued to

increase until t=30 minutes. Between t=20 and 30 minutes, the COD reading decreased, but the reading was still slightly above the control reading. A 4% COD increase was observed for the full 30-minute experiment. This indicates that the BDDE could release carbon into the solution for a limited period of time until a stopping point is reached. However, more control experiments would need to be performed to better understand how BDDE influences COD readings. There was also a discrepancy between nanoparticle and BDDE COD readings. Though COD concentrations for nanoparticle testing at OG starting concentrations of 0.75 g/L were roughly 1500 μg O_2/mL, the COD reading for BDDE with 0.75 g/L starting OG was approximately 3700 μg O_2/mL. The inconsistent COD readings between nanoparticle and BDDE experiments with the same starting OG concentration need to be examined further as well.

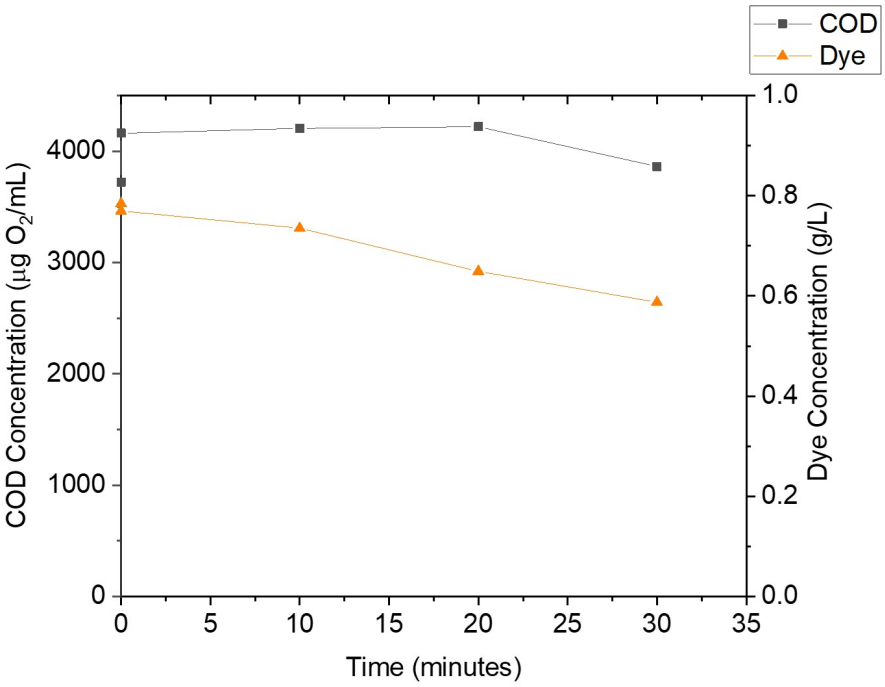

Figure 10: Decolorization of Orange G with a starting concentration of 0.75g/L and degradation of COD using boron doped diamond electrode in 0.02 M NaCl at a current density of 2-mA/cm^2 for 30 minutes.

3.3. *Conclusions*

Experiments showed promise for OG in both decolorization through azo bond breaking and decreased COD readings by OH radical oxidation of contaminants using BDDE. BDDE is shown to be useful in both decolorization of OG and decreasing oxygen required to oxidize contaminants using COD. Through repeated experimental runs, better relationships between OG concentration, current density, and the use of BDDE for oxidation of organic content could be established.

Section 4: Future Work

One approach for testing degradation efficiency of nanoparticles is conducting experiments with double and triple nanoparticle mass ratios of 1:5. Loading more nanoparticles on a set BC mass could allow higher nanoparticle surface area to enhance the activation site of persulfate for sulfate radical generation. For nZVI/BC composites, the dispersion of particles between layers of BC surface has helped BC sheet aggregation, which in turn has shown promise in degradation of contaminants.[25] Varying mass ratios, such as 1:1, 1:3, and 1:7, should be tested to better identify the correlation between particle dispersion and BC aggregation. In previous articles, an observation between contaminant removal efficiency and nZVI to BC ratios has been shown.[25] An optimum mass ratio is needed since an excessive amount of BC could block reactive sites of iron particles, which would decrease contaminant degradation. Longer duration testing for nanoparticle experiments should also be examined. For BDDE, longer test times indicated further decolorization and decreased COD reading for OG, which could also be true for nanoparticles. Further experimental work would need to be done to show this relationship.

For BDDE, further research and analysis should be done to understand the discrepancy between nanoparticle and BDDE COD readings for the same starting OG concentration. Repeat experiments of 0.75 g/L OG should be performed once the COD discrepancy is better understood. With varying experimental conditions, different correlations between electrochemical oxidation processes and mineralization current efficiency could be observed.[16] For this reason, a range of current densities should be tested with BDDE to find the optimum one.

Ultimately, wastewater from a poultry facility will be tested. Some known COD concentration ranges are 500-700 μg O_2/mL and 1000-1500 μg O_2/mL; however, COD readings for poultry wastewater could vary since the amount of organic content present could change depending on the poultry process. Testing varying starting OG concentrations is recommended for this reason. Poultry wastewater contaminants could also act differently compared to the OG model contaminant, so adjustments and further testing of experimental conditions would most likely be necessary.

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