

Florida Student is Stockholm Junior Water Prize Finalist

For the second straight year, a Florida student has been selected as one of the four finalists in the U.S. competition for the Stockholm Junior Water Prize. Kathleen Schwarz of Tallahassee joined more than 30 other students from across the country at the national competition May 30-June 2 in Dallas. She was chosen to represent Florida after her project won the grand prize in physical science at one of the state's regional science fairs.

Kathleen is a senior in the International Baccalaureate Program at Tallahassee's James S. Rickards High School. She has earned honors at regional and state science fairs since 1998. This year she also earned the INTEL Environment Award at the regional fair and placed third in environmental science at the state level. A varsity athlete in cross country, she participated in Florida State University's 2001 Young Scholars Program, a six-week research program for outstanding high-school students.

The Stockholm Junior Water Prize is the most prestigious international youth award



In addition to her success at the Stockholm Junior Water Prize competition in Dallas, Kathleen Schwarz also advanced to the International Science and Engineering Fair in Louisville, Kentucky. There she had the opportunity to meet Willie Rose, one of the "Rocket Boys" of West Virginia, whose teenage exploits designing and building homemade rockets were chronicled in the motion picture *October Sky*.

for a water-science research project. Its purpose is to increase students' interest in water-related issues and research, and to sensitize them—as future leaders—to global water challenges. In Florida, the Public Education Committee of the Florida Water Environment Association (FWEA) selects the state representative from regional science fair winners. Reviewing the projects and selecting this year's representative were committee chairman Tom Jones, Tommy Tyson, Tim Madhanagopal, Frank Wyche, and Doug Cochran.

The prize is administered internationally by the Stockholm International Water Institute. ITT Industries is the international and U.S. co-sponsor, and the Water Environment Federation and its member associations co-sponsor and facilitate the competition in the United States. The FWEA co-sponsors the Florida winner's participation at the national competition.

The *Florida Water Resources Journal* is proud to publish Kathleen Schwarz's award-winning entry on the following pages.

4-Chlorophenol Pollution: Is Fenton's Reaction the Answer?

Kathleen Schwarz

Fenton's reaction was used to chemically remediate water containing 4-chlorophenol. The study was designed to determine the feasibility of using Fenton's reaction in-situ. It investigated using chloride concentration measurement as a marker for decreased toxicity.

4-chlorophenol was degraded using substoichiometric amounts of Fenton's reagent, which consists of hydrogen peroxide and a ferrous iron salt. The kinetics were studied using ion chromatography to observe the release of chloride. The final chloride concentration was measured to determine which of two possibilities would occur. If Fenton's reagent completely degraded a small amount of 4-chlorophenol, a low chloride concentration would be produced and the solution's toxicity would be reduced. If Fenton's reagent partially degraded a large amount by releasing the chlorine but not necessarily breaking the phenol ring, a high chloride concentration would be produced and the toxicity of the solution would depend on the toxicity and concentrations of the intermediates.

The final solutions contained high chloride concentrations, indicating that the reaction did not completely degrade the 4-chlorophenol. The resulting solutions emitted a strong odor and changed color from clear to orange, suggesting the presence of various organic molecules that are potentially more toxic than the original 4-chlorophenol. The LD50 toxicity tests on *Ceriodaphnia dubia* support this, and the solution with the most chloride was also the most toxic; therefore, chloride concentration can not be used to indicate reduced toxicity, and substoichiometric amounts of hydrogen peroxide can actually reduce the water quality instead of improving it.

Kathleen Schwarz, a Tallahassee high-school student, is a national finalist for the 2002 Stockholm Junior Water Prize. She wrote this paper on the research project that she entered in the competition (see details above).

Problem

This project addresses the question, "Is Fenton's reaction a feasible alternative to other forms of water remediation?" Two laboratory tests were performed to test the effectiveness of substoichiometric amounts of Fenton's reagent on 4-chlorophenol and the toxicity of the resulting solutions. Degradation was determined by measuring chloride concentration, and acute toxicity was estimated using *Ceriodaphnia dubia*.

Hypothesis

Fenton's reaction, when prepared with a substoichiometric amount of hydrogen peroxide, should cause one of two results: the complete decomposition of a small amount of 4-chlorophenol, resulting in a low chloride concentration, or the partial decomposition of a large amount of 4-chlorophenol, resulting in a high chloride concentration proportional to the original 4-chlorophenol and hydrogen peroxide concentrations.

The phenol ring structure is stable and the chlorine on the ring is considerably less stable, so partial decomposition of the 4-chlorophenol should occur.

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Dechlorination to some degree should occur, so the resulting products should be less toxic regardless of which reaction mechanism occurs; however, if the solutions have a low level of chloride, there is a lesser likelihood that the solutions will be more toxic because the solutions would contain only a chloride salt, water, carbon dioxide, and low levels of 4-chlorophenol. Solutions containing a high chloride concentration should also be less toxic, but these solutions include intermediates that might increase the solution's toxicity.

Independent Variable

The concentration of hydrogen peroxide is an independent variable, influencing the rate of reaction and determining to what extent the 4-chlorophenol degrades. Iron is the reaction's catalyst, so the iron concentration influences the rate of the degradation but does not affect the ultimate chloride concentration.

For the second part of the experiment, the varying amounts of Fenton's reagent is the independent variable because the amount of degradation of the pollutant determines the mortality of the test organisms.

Dependent Variable

The chloride concentrations in the solutions are the dependent variable for the first part of the experiment. The mortality of the *Ceriodaphnia dubia* is the dependent variable in the second part.

Extraneous Variables

The pH and temperature were not monitored throughout the first part of the experiment. The pH was measured at the end of the first part, and the temperature remained at room temperature. In the second part of the experiment, temperature, pH, dissolved oxygen, and conductivity were monitored and controlled.

Introduction

Chlorinated aromatics are notorious water pollutants. Many methods of water remediation have been tried, but the procedures are often costly or ineffective. One possible method of removing chlorinated aromatics is chemical oxidation. One form of chemical oxidation, Fenton's reaction, is generally less expensive than most other oxidation methods (Pérez et al., 2002). Under certain conditions, it has been shown to completely degrade organic molecules in the laboratory, releasing only harmless end-products: water, chloride salts, and carbon dioxide. Though Fenton's reaction seems appealing because of its apparent advantages, research has demonstrated that more investigation is still needed for the safe in-situ clean-up of waste sites.

4-Chlorophenol (also known as 4-CP, C_6H_5ClO , and p-Chlorophenol) is one of the many chlorinated organic compounds produced industrially in wood preservatives, fungicides, pesticides, and bleaching products. It is an inadvertent byproduct of chlorination of polluted waters and is an intermediate in the degradation of compounds including higher chlorophenols and 2,4 dichlorophenoxyacid (Healy et al., 2001; Kao et al., 2000). Some research (Grimvall et al., 1995) suggests that chlorophenol is also produced naturally by sponges and marine animals.

4-Chlorophenol has contaminated drinking water as well as the water and soil around saw mills. It remains in the water cycle for a long time period because its halogenation makes it a stable and toxic molecule, resisting biological and chemical degradation (Tang et al. 1995). 4-Chlorophenol is known to be mutagenic to animals; it produces reproductive effects, and in high concentrations, it causes methemoglobinemia, liver and kidney damage, and skin and gastrointestinal irritation (Fisher MSDS). Because of its toxicity, longevity, and the possibility that it is a carcinogen, 4-chlorophenol is undesirable in the water supply.

Scientists have studied multiple ways of removing chlorophenols,

notably Fenton's reaction, photo-Fenton's reaction, pulsed corona systems, ozonation, and bioremediation. One advantage of Fenton's reaction is that it can be carried out under many different water conditions, whereas bioremediation only works under conditions favorable to the survival of the bacterial culture and the bacteria's dependence on chlorophenol (Healy et al., 2001).

Fenton's reagent consists of hydrogen peroxide and an iron catalyst (Chamarro et al., 2001). Ferrous iron from ferrous ammonium sulfate were used in this experiment. Fenton's reaction consists of a series of complex steps involving the creation of hydroxyl radicals and the oxidation and reduction of ferrous and ferric iron (Grymonpre et al., 2000). The precise kinetics and mechanisms of the reaction have been studied since its discovery in 1894, but are still not completely understood ("Reference library peroxide applications").

Two major drawbacks of the laboratory experiments using Fenton's reaction were noted in the literature (Hirvonen et al., 2000). Some scientists maintain that testing Fenton's reaction using high chlorophenol concentrations is relatively useless from an environmental standpoint. They contend that high concentrations of 4-chlorophenol are rarely encountered in polluted waters with the exception of areas surrounding sawmills.

Other scientists (Hirvonen et al., 2000) criticize researchers' reliance solely on dechlorination when evaluating degradation. The use of chloride concentration for evaluation is a problem because the removal of the chlorine atom does not necessarily mean that the remaining products are less toxic and more biodegradable. In fact, one of the important intermediates of the oxidation of 4-chlorophenol is catechol, which is cited as "approximately 1.1 to 2.2 times more toxic than phenol, depending on the route of exposure" (CDC, 1989).

Fenton's reaction was reported to be successful in cleaning some waste sites, (Levin et al., 2000), but major shortcomings were reported in the field experiments. The most-noted shortcoming was the decrease, then rebound, of the concentrations of the chlorinated organic pollutants. One study (Roberts et al., 2000) cited heterogeneous soil conditions as the cause: The injection wells created preferential flow paths of the hydrogen peroxide, then continued to create new paths, which led to the exposure of more pollutant, which then flowed to the test wells where the measurements were taken.

Another report cited DNAPL's (Dense non aqueous phase liquid) as the cause of the rebound, though this study was involved in TCE (trichloroethylene) degradation, and probably is not applicable to chemicals such as 4-chlorophenol that are more water soluble. A recent study (Tarr et al., 2000), concluded that dissolved natural organic matter inhibited degradation of aromatic pollutants more than the researchers' models predicted. This is important because if researchers do not add enough peroxide to completely degrade the pollutants, they will produce intermediates that might be just as dangerous, if not more so, than the original pollutants.

Intermediates could be produced using high concentrations of chlorophenol (400 ppm) and comparatively low levels of hydrogen peroxide and iron (II). These conditions were used in this experiment to determine which of two possibilities would occur. If Fenton's reagent completely degraded a small amount of 4-chlorophenol, a low chloride concentration would be produced, and the solution's toxicity would be reduced. If Fenton's reagent partially degraded a large amount by releasing the chlorine but not necessarily breaking the phenol ring, a high chloride concentration would be produced, and the toxicity of the solution would depend on the toxicity and concentrations of the intermediates. This situation might occur if there is dissolved natural organic matter which might react with the peroxide, thus requiring more peroxide for complete degradation.

Chloride concentration was measured as a function of time to study the kinetics of the reaction and to reveal if the dechlorination of the molecules could decrease their toxicity. If simple dechloriniza-

tion was sufficient, complete oxidation would not be required to decrease the severity of pollution; however, the results indicate that almost complete dechlorination actually increased the toxicity of the solutions. This indicates that Fenton's reaction should not be used to clean waste sites until these significant problems can be resolved.

Materials for Part One:

4-Chlorophenol Oxidation and Observation

- Dionex Ion Chromatograph AS4A Output range 30 μ S
- 400 ppm 4-chlorophenol (aq)
- 14 clear clean Teflon bottles with caps
- Spex standard (Spex is a solution containing 1053 μ M Fluoride, 1613 μ M Nitrate, 1561 μ M Sulfate, 1563 μ M Phosphate, and 846 μ M Chloride.)
- 17.9 mM $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (aq)
- 30% H_2O_2 (aq)
- Stop watch
- E-Lab software, computer, and printer
- Ultrapure water (Barnstead Nano pure deionized water system)
- Mechanical pipettes and disposable pipette tips
- Kim wipes
- Syringe
- 50 mL Volumetric Flask
- permanent marker
- refrigerator

Procedure: Part One

Prepare standards containing the five anions detectable by the AS4A column using various dilutions of Spex standards. Make 1/10, 1/20, 1/50, 1/100, and 1/200 dilutions using ultrapure water. Measure the Spex Solution and the water using mechanical pipettes with disposable pipette tips. Store each solution in a Teflon bottle and place in a refrigerator away from heat and light to prevent bacterial growth, which would result in lower nitrate levels.

Run the standards using the Dionex Ion Chromatograph AS4A with an output range of 30 μ S and flow speed of 2.6 mL per minute, and use E-Lab software to calibrate the Chromatograph. Check the plots of peak height or area versus actual molarity to make sure that the five points form a straight line and that the regression line produces a reasonable correlation. This assures that the standards were all made correctly.

Run a deionized water blank.

Prepare solutions of 4-chlorophenol (4-CP), $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, and H_2O_2 separately in deionized water, and run the samples to detect impurities in the solutions. (4-CP solution: 400 ppm aqueous 4-CP) ($\text{Fe}(\text{II})$ solution: 25 mL water, 21.5 μ L 17.9 mM ferrous ammonium sulfate) (hydrogen peroxide solution: add 20 μ L 3% H_2O_2 to 25 mL water).

Prepare Solution 1, the reaction expected to take the most time to complete. Pipette 25 mL 4-CP into a Teflon bottle, then add 11 μ L 17.9 mM iron solution and 22 μ L 3% H_2O_2 solution. Start the stopwatch and shake the bottle to mix. Measure this solution's chloride levels periodically, but dilute the solution before running it to prevent the organic compounds from hurting the column. To dilute, pipette out 1 mL Solution 1 into a clean Teflon bottle, add 9 mL deionized water, shake to mix, then run the 1/10 dilution. Record the time when the solution was diluted because the dilution almost stops the reaction and the chloride reading corresponds with the time of dilution.

Prepare Solutions 3 and 4. Solution 3: pipette 5.5 μ L iron solution, 220 μ L H_2O_2 , and 25 mL 4-CP into a Teflon bottle. Solution 4: pipette 21.5 μ L iron solution, 22 μ L H_2O_2 , and 25 mL 4-CP into a Teflon bottle. Record the time the solution was made. Run a 1/10 dilution of the solution, and record the time it was diluted.

For the next four hours, run 1/10 dilutions of one solution after the other. Periodically run standards so that by the end of the experiment, at least four of the five standards have run.

Prepare Solution 2 by pipetting 11 μ L iron solution, 220 μ L H_2O_2 , and 25 mL 4-CP into a Teflon bottle. Record the time the solution is created. Run a 1/10 dilution of the solution, and record the time diluted.

For the next 3.5 hours, run all of the solutions and run any remaining standards. Place any bottles containing reacting solutions in the fume hood. After one week, remove the samples from the fume hood and run them and the standards again. Once the toxicity testing is complete, run the samples for the last time.

Materials for Part Two:

Culturing of *Ceriodaphnia dubia* and Toxicity Testing

- Teflon bottles of solutions from Procedure: Part One
- Two additional Teflon bottles: one with 25 mL 400 ppm 4-chlorophenol; and one with 25 mL 400 ppm 4-chlorophenol and 11 μ L 17.9 mM ferrous ammonium sulfate
- 138 *Ceriodaphnia dubia* neonates
- 100 mL graduated cylinder
- 10 mL Scienceware Fast-Release Pipette Pump II Filler/Dispenser used with Pyrex Disposable Glass Serological Pipettes
- 48 Fisherbrand Polystyrene Sample Vials
- All other materials listed in SOP (Standard Operating Procedure) #TA-04.01

Procedure: Part Two

Keep the solutions for four months in their Teflon bottles within a plastic bag under the fume hood, away from sunlight and heat. Begin the test culture of *Ceriodaphnia dubia* on a Monday. Select 138 neonates culture them for one week by following the Florida Department of Environmental Protection's SOP #TA-04.01, under "Chronic-Bioassay Cultures." This procedure is the same for chronic and acute tests.

On the following Monday, follow SOP #TA-05.01 for the "Production of *Ceriodaphnia dubia* Young for Acute Toxicity Testing." Also begin culturing a second "Chronic-Bioassay Culture," SOP #TA-04.01.

On the Tuesday of Week Two, begin the first round of toxicity testing. Immediately feed the test culture. The culture must be fed two to 24 hours before the test to assure that the *Ceriodaphnia* are not stressed. The culture started the day before will not be used in the tests, so it should not be fed. In the two hours before the toxicity tests are performed, prepare the test vials for the *Ceriodaphnia*.

Place 48 sample vials in a plastic tray. Twenty-four vials will be used for the 4-CP solution, and the other 24 will be used for the 4-CP and iron solution. Label the plastic tray and arrange the cups for both solutions so that the tray appears as follows: four vials in a row under a 'control' heading, four under a '56 ppm' heading, four under a '28 ppm' heading, four under a '14 ppm' heading, four under a '7 ppm' heading, and four under a '3.5 ppm' heading. Pour 15 mL of DMW (Dissolved Mineral Water) into four vials in the 4-CP 'control' solution group, and 4 vials in the 4-CP and iron 'control' solution group. Create the control solutions first to avoid cross-contamination.

Using a Pyrex pipette and a Scienceware pipette pump, pipette 16.8 mL of the 4-CP solution into a clean, empty graduated cylinder. Fill the graduated cylinder with DMW so that there is a total of 120 mL of liquid, and pour this solution into a clean beaker. Remove 60 mL of the solution, and pour 15 mL into each of the 4-CP '56 ppm' test vials.

Use the graduated cylinder to measure out 60 mL of DMW and add it to the remaining 60 mL of solution. Remove 60 mL of the new solution and pour 15 mL into each of the 4-CP '28 ppm' test vials. Continue this dilution series until all vials contain 15 mL of solution. Using different glassware, follow this same dilution series for the 4-CP and iron solution group.

Locate and mark the cups containing the organisms in the test culture that have produced six offspring or more. Following SOP's

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#TA-06.03 through #TA-06.06, measure and record the dissolved oxygen, temperature, conductivity, and pH of the solution. Take these parameters on only one cup per dilution group for each toxicant.

Once two hours have passed since the *Ceriodaphnia* were fed, load the organisms into the test vials. To do this, select the first marked cup and capture one neonate. Release it into a control cup. Release the next one into a '3.5 ppm' cup, and continue up the dilution series until each cup in the row has one neonate from the parent in the selected marked cup. Repeat this process multiple times with different marked cups until each of the cups has six organisms.

Place a thermometer diagonally over the center of the tray, and place the Plexiglas sheet over the top. Place the tray under the fume hood because the chemicals are volatile and might damage the other organisms in the incubator. Mix Solutions 1 and 4 (from Part One; Fenton's reaction) together to create Product 1. Mix Solutions 2 and 3 (from Part One; Fenton's reaction) together to create Product 2.

On Wednesday of Week Two, change the water and feed the new culture, following the same procedure followed on the Wednesday of Week One. The test culture must also be examined. Remove the test culture from the fume hood and examine each vial. Count and record the number alive in each vial. Record parameters for every vial. Dispose of the vials and their contents in the proper manner.

On Friday of Week Two and Monday of Week Three, continue following SOP #TA-04.01.

On Tuesday of Week Three, perform the toxicity tests exactly as they were performed on Tuesday of Week Two, except for two changes: Test "Product 1" and "Product 2" instead of the 4-CP solution and the 4-CP solution with iron.

Using the Trimmed Spearman-Kärber method, analyze the data and extrapolate the LC50.

Solution concentrations, ratios, initial and final colors, and odors

SOLUTION 1

<u>Ratios</u>	<u>Concentrations</u>	<u>Initial and Final colors and odors</u>
1	25 mL 4-chlorophenol (400 ppm)	Solution 1 began clear and
.0025	11 $\mu\text{L Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (17.9 mM)	with a slight odor, ended faintly
.25	22 $\mu\text{L H}_2\text{O}_2$ (aq) (3%)	orange and with a strong odor.

SOLUTION 2

<u>Ratios</u>	<u>Concentrations</u>	<u>Initial and Final colors and odors</u>
1	25 mL 4-chlorophenol (400 ppm)	Solution 2 began clear and
.0025	11 $\mu\text{L Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (17.9 mM)	with a slight odor, ended bright
2.5	220 $\mu\text{L H}_2\text{O}_2$ (aq) (3%)	orange with a dark precipitate and with a strong odor.

SOLUTION 3

<u>Ratios</u>	<u>Concentrations</u>	<u>Initial and Final colors and odors</u>
1	25 mL 4-chlorophenol (400 ppm)	Solution 3 began clear and
.00125	5.5 $\mu\text{L Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (17.9 mM)	with a slight odor, ended bright
2.5	220 $\mu\text{L H}_2\text{O}_2$ (aq) (3%)	orange with a dark precipitate and with a strong odor.

SOLUTION 4

<u>Ratios</u>	<u>Concentrations</u>	<u>Initial and Final colors and odors</u>
1	25 mL 4-chlorophenol (400 ppm)	Solution 4 began clear and
.005	21.5 $\mu\text{L Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (17.9 mM)	with a slight odor, ended faintly
.25	22 $\mu\text{L H}_2\text{O}_2$ (aq) (3%)	colored orange and with a strong odor.

Results of Toxicity Tests:

Test 1: 4-chlorophenol LC50 estimate: 6.74 ppm. 95% confidence interval (5.43, 8.35)

Test 2: 4-chlorophenol and iron salt LC50 estimate: 5.77 ppm. 95% confidence interval (5.04, 6.61)

Test 3: Product 1 LC50 estimate: 3.97 ppm. 95% confidence unreliable (concentrations of solutions are too high to determine LC50)

Test 4: Product 2 No LC50 estimate: killed all organisms in smallest solution concentration, 3.5 ppm.

Discussion

The purpose of this project was to determine the feasibility of using Fenton's reaction to remediate water polluted by chlorinated aromatic hydrocarbons. A two-part experiment was designed to study various aspects of the reaction as they relate to field studies. This integrated approach provided the benefits of applying multiple analytical techniques to evaluate environmental processes. Part One was developed to study the reaction kinetics, and Part Two was designed to examine the products of the reaction in relation to an aquatic environment. In Part One, Fenton's reaction successfully removed the majority of the chlorine in two of the solutions, but the data from part two indicated that the partially oxidized solutions were more toxic than the original 4-chlorophenol solutions.

Discussion for Part One

The objective of the first experiment was to evaluate the kinetics of 4-chlorophenol degradation in order to better understand Fenton's reaction, as well as to produce solutions that could be used later for toxicity testing.

The results of the experiment indicate that the kinetics of the reaction in terms of chloride concentration are not pseudo-first order. When the log of the total concentration of chloride minus the measured concentration is plotted against time, the resulting regression lines indicate that the points are not linear, even when the activation period is not included in the regression lines.

The results also indicate that the reaction is not second order, because when the inverse of the remaining chloride concentration is plotted against time, the regression line indicates that the points are not linear. Solution 2 was not included on the graphs because the reaction had not progressed far enough to determine a pattern. The baseline for Solution 2 is almost all that can be observed because the concentrations were so close to the machine's detection point, around .6 to 1.2 μM .

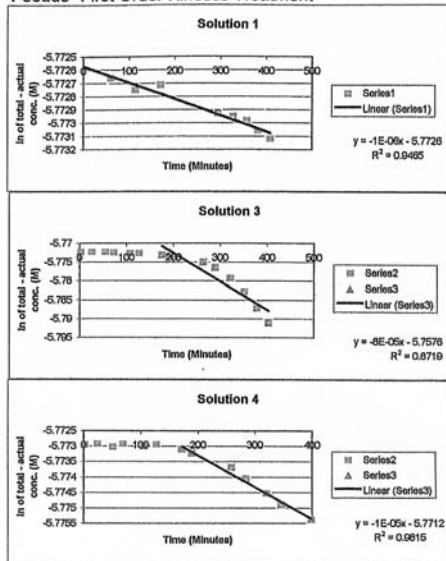
The fact that the kinetics are not first or second order is not surprising, because the rate is obviously determined by the amount of remaining 4-chlorophenol, the concentration of iron, and the concentration of hydrogen peroxide. Although this experiment did not demonstrate the rate determination by 4-chlorophenol concentration, the literature supports this assertion.

The effect of the other two factors, hydrogen peroxide and iron, can be observed in the graphs. When Solutions 3 and 4 are graphed on the same graph, Solution 4 appears to occur more slowly. Solution 4 has more iron but less hydrogen peroxide, which indicates that the lower levels of hydrogen peroxide cause the reaction to occur more slowly.

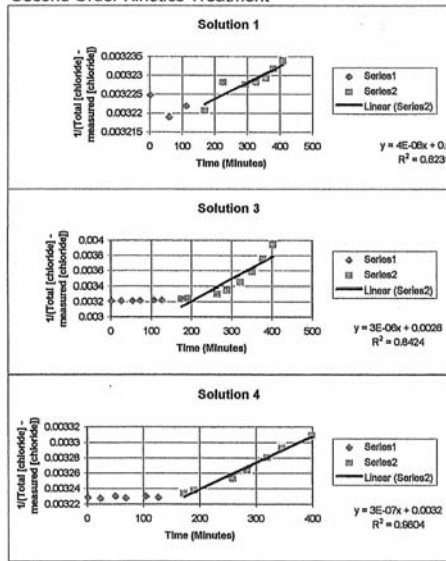
The iron effect can be seen in Solutions 1 and 4. Solution 4 has more iron and reaches about 9 μM , whereas Solution 1 has less iron and the same amount of hydrogen peroxide but only reaches 2 μM . The only effect not explained by any of the reagents' concentrations is the activation period evident from the graphs. This might represent the rate determining step.

The high final chloride concentrations at the end of the experiment agree with the hypothesis that chlorines will be removed from

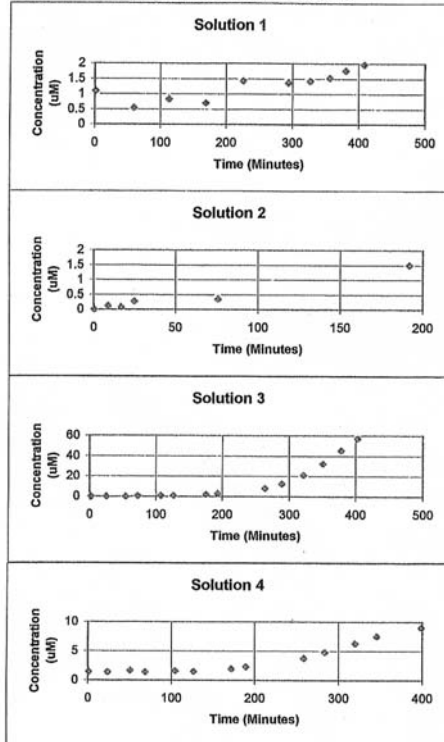
Pseudo- First Order Kinetics Treatment



Second Order Kinetics Treatment



Chloride Concentration as a function of time



the phenol ring before the hydrogen peroxide attacks the ring because the ring is more stable than the chlorine at the ring's edge. Because there was less hydrogen peroxide present than the amount required to decompose the entire 4-chlorophenol, the reaction produced intermediates in the degradation of the 4-chlorophenol. The solutions changed from clear to orange and emitted a strong odor, providing evidence of the presence of intermediates.

Some of the organic intermediates were insoluble, although originally the precipitation observed in Solutions 2 and 3 was thought to result from iron insolubility. Iron precipitation can occur at the final pH's of the solutions, which were 2.5 and 2.6 respectively, but for precipitation to occur at these pH's, the negative log of the iron concentration must be less than 4.5 (Stumm 248). The highest amount of iron used in both solutions is Solution 2's 11 μL of 17.9 mM $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. This converts into a solution concentration of 7.87×10^{-6} M, and the negative log of this concentration is 5.1, well above the negative log of the concentration required to make the iron precipitate. Furthermore, Solutions 2 and 3 had smaller iron concentrations than Solution 4, which did not show any signs of precipitation. It is also of interest that the precipitates went back into solution after many months.

Systematic error or measurement error could have affected the results; however, a number of measures were taken to avoid this problem. There were four experimental solutions, with differing amounts of either hydrogen peroxide or iron salt, therefore any effect caused by hydrogen peroxide or iron could be observed by examining two experiments. If a solution was made improperly, it would be obvious because either the final chloride concentration would not be congruent with the amounts of 4-chlorophenol and hydrogen peroxide, or the reaction would have occurred too rapidly if the iron salt concentration was wrong. The experiments progressed as expected and the results agree with the literature, so the solutions were probably mixed in the correct proportions.

The other possible source of error lies in the measurement. The fact that the chloride concentration was monitored throughout the experiment means that incorrect measurements would be outliers in the pattern of increasing chloride concentration. The standards run throughout the experiment produced the correct concentration readings (+1 to 2 μM , depending on concentration distance from detection level), indicating that the equipment did not malfunction. The final chloride concentrations were measured a number of times, revealing that they probably reflect the actual chloride concentration.

The results imply that substoichiometric amounts of Fenton's reagent successfully dechlorinated 4-chlorophenol.

Discussion for Part Two

The objective of the second experiment was to determine the toxicity of the solutions produced by the first experiment, in relation to 4-chlorophenol. By the time that the LC50 test was run, little solution remained in the Teflon bottles; therefore, the solutions were mixed together to produce sufficient material for one test. Because Solutions 1 and 4 received the same amount of peroxide and had about the same amount of chloride in solution, they were mixed together and labeled "Product 1." For the same reason, Solutions 2 and 3 were combined to make "Product 2."

The results are surprising in that they reveal increased toxicity in the products. When the experiment was planned, 4-chlorophenol's toxicity was slightly underestimated; however, the ranges were unchanged for the second group of toxicity tests because the toxicity was expected to be lower for the products. When the toxicity was discovered to be higher, there was no remaining solution with which to retest and determine the actual value. This is why there is no LC50 estimate for Product 2. This value is not important because it is much lower than the 4-chlorophenol and the 4-chlorophenol and iron tests, and its toxicity falls outside of the 95-percent confidence intervals of both of the tests.

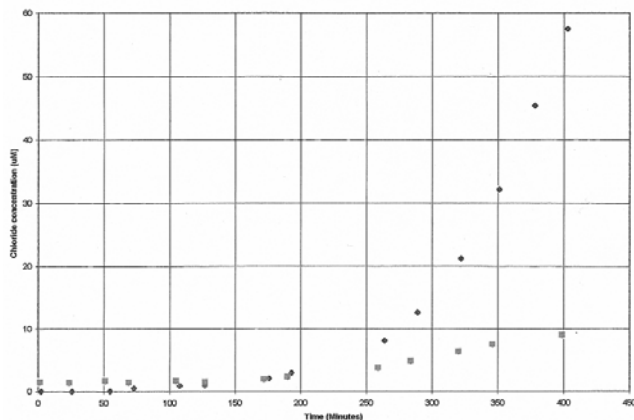
Errors and bias could have influenced the results. The 4-chlorophenol test was conducted before the product tests because there was enough 4-chlorophenol to perform the tests a second time if the range had been incorrect, or if the procedure did not work. Unfortunately, this meant that the products were tested on the same day and the 4-chlorophenol was tested on a separate day.

Another concern was the fact that the ferrous ammonium sulfate might have increased the toxicity of the solutions. This was controlled by testing the 4-chlorophenol and the iron salt. The results revealed a higher toxicity estimate for the 4-chlorophenol and iron salt, but this does not appear to be significant, again because it falls within the 95-percent confidence interval of the 4-chlorophenol's LC50 estimate.

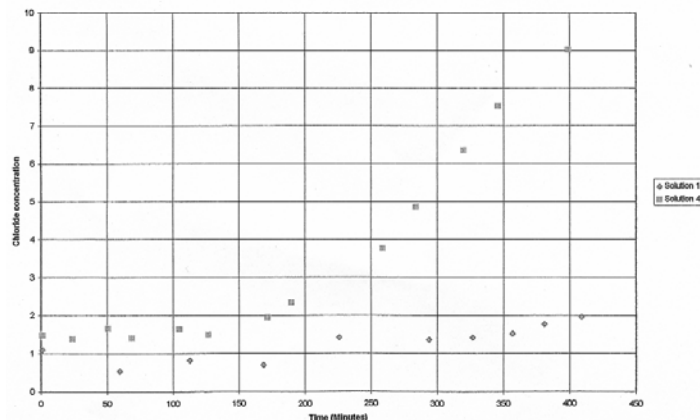
The toxicity of the products may be attributed to many chemi-

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Solutions 3 and 4



Solutions 1 and 4



Continued from page 31

icals, but catechol is the most likely cause. Catechol is a phenol with an additional -OH group on the fourth carbon. It is twice as toxic as phenol. Other compounds which might have influenced the toxicity include long chain carboxylic acids, and aldehydes or ketones.

Regardless of the products, the increased toxicity raises an important question of whether Fenton's reaction experiments should be permitted to occur at waste clean-up sites. The obvious answer is no: Scientists might ultimately spread the pollution, increase the toxicity of the pollutants, and expose keystone water organisms to toxic pollutants. Scientists should not experiment with Fenton's reaction in the field until further laboratory tests have been completed. Unfortunately, these risks do not appear to play a large role in this decision, as field tests have already taken place, and not all have been successful.

Conclusion

The results of the experiment indicate that Fenton's reaction should not be used in the field until further laboratory experiments have taken place. The first part of the hypothesis appears correct in that each 4-chlorophenol is partially degraded by the hydrogen peroxide, as opposed to the complete degradation of a small amount of 4-chlorophenol. The second part of the hypothesis appears incorrect: Substoichiometric amounts of Fenton's reagent increase the toxicity of the solutions, as opposed to decreasing or not changing the toxicity. These conclusions are particularly significant because they indicate that small amounts of oxidizing agents do not necessarily enhance the quality of the water they are meant to improve.

Acknowledgments

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