

Kinetic studies of Fenton oxidation reaction by UV-VIS spectroscopy

SUPPORTING INFORMATION

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The information contained in this document is outlined as follows:

- 1. List of chemical and reagents**
- 2. Experiment procedure**
- 3. Data treatment**
- 4. Exercise implementation and evaluation**
- 5. Work Plan Guidelines**
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- 8. Experimental introduction**

1. List of chemicals

Table S1. List of chemicals

Compounds	CAS number	Molecular Mass(g/mol)	Concentration/Purity	Supplier
Naphtol blue black (NBB)	1064-48-8	616.49	BioReagent	Sigma
Iron(II) sulfate heptahydrate	7782-63-0	278.01	99%	Sigma
Hydrogen peroxide (H₂O₂)	7722-84-1	34.01	30% in water	Sigma
Sodium hydroxide	1310-73-2	40	98%	Sigma
Sulfuric acid	7664-93-9	98.08	95%	Sigma-fluka

Deionized-water was produced in-house and used to prepare 0.5 M solution of NaOH and H₂SO₄ to control the pH of the reaction solution. Two magnetic hotplate stirrers (IKA® RCT basic) were purchased from Fisher Scientific, Norway. One pH meter (S220 SevenCompact™ pH/Ion meter) was purchased from METTLER TOLEDO. UV/VIS absorbance system was purchased from Avantes with an AvaLight-DH-S deuterium-halogen light source and an AvaSpec-2048 fiber optic spectrometer.

2. Experiment procedure

The reaction was carried out in a ‘black box’, an Erlenmeyer flask wrapped in aluminum foil, to avoid contamination with the light from external sources. The reaction vessel is equipped with the UV-VIS transmission dip probe and a pH meter with an integrated thermocouple and is immersed into a thermostatic water bath (as shown in **Figure S1**) in order to maintain a set temperature.

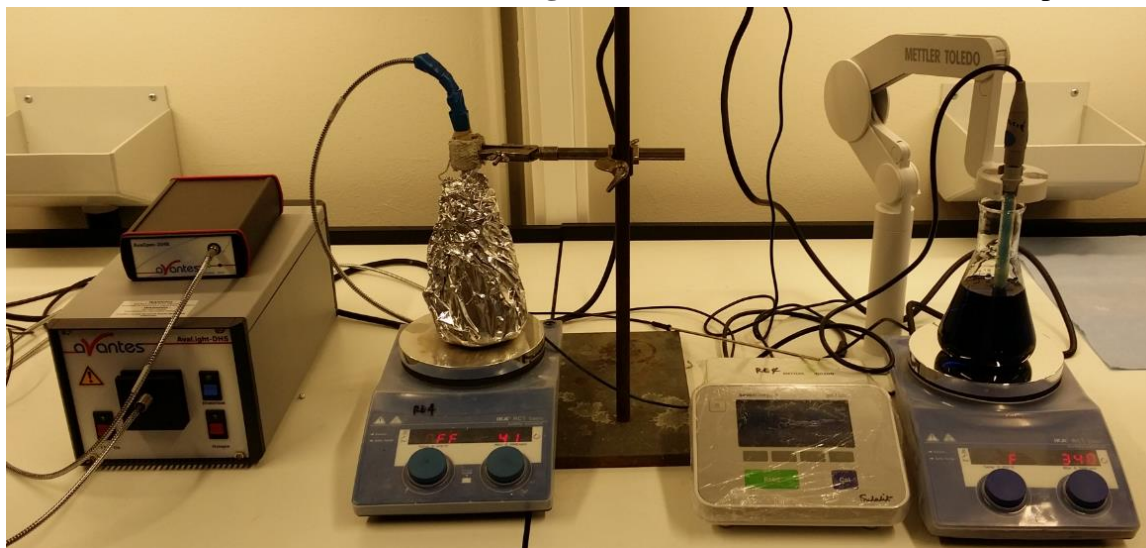


Figure S1. Experiment setup. From left to right: UV-light source and UV-light detector (small black box on top), magnetic stirrer with reactor. The reactor was protected by aluminum foil to avoid light pollution from atmosphere. The UV-VIS transmission probe is dipped into the solution. pH meter with pH sensor in the reaction solution, which is placed on a second magnetic stirrer on the right side.

The arrangement allows for three types of experiments, namely the effects of the concentrations of H_2O_2 , FeSO_4 , and/or that of the pH of the solution. The tables below show typical sets of conditions for which the overall reaction constant k_{app} can be estimated.

Table S2. Experimental conditions for each version*

Version 1---changing H_2O_2						Volume		
	T(°C)	$[\text{H}_2\text{O}_2]$, M	pH	[NBB], M	$[\text{FeSO}_4]$, M	H_2O_2	[NBB]	$[\text{FeSO}_4]$
Run 1	21	1.97×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 2	21	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 3	21	4.41×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 4	30	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 5	40	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			

Version 2--- changing pH						Volume		
	T(°C)	H_2O_2	pH	$[\text{FeSO}_4]$	$[\text{FeSO}_4]$, M	H_2O_2	[NBB]	$[\text{FeSO}_4]$
Run 1	21	2.94×10^{-4}	2	1.62×10^{-5}	1.32×10^{-4}			
Run 2	21	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 3	21	2.94×10^{-4}	4	1.62×10^{-5}	1.32×10^{-4}			
Run 4	30	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			

Run 5	40	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Version 3 --- changing FeSO₄						Volume		
	T(°C)	[H ₂ O ₂],M	pH	[NBB], M	[FeSO ₄], M	H ₂ O ₂	[NBB]	[FeSO ₄]
Run 1	21	2.94×10^{-4}	3	1.62×10^{-5}	0.66×10^{-4}			
Run 2	21	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 3	21	2.94×10^{-4}	3	1.62×10^{-5}	2.64×10^{-4}			
Run 4	30	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			
Run 5	40	2.94×10^{-4}	3	1.62×10^{-5}	1.32×10^{-4}			

*H₂O₂ solution (0.5 mg/ml) was prepared by diluting 0.1ml of 30 wt. % H₂O₂ to be 60ml with DI water. NBB solution (10 mg/L) was prepared by solving 20 mg NBB in 2 L water. FeSO₄ solution (5 mg/ml) was prepared by dissolving 0.5 g FeSO₄ in 100 mL DI water. H₂SO₄ solution (0.5 mol/L) was prepared by diluting 6.68 ml H₂SO₄ (95% wt) to 250 ml with DI water. NaOH (0.5 mol/L) solution was prepared by diluting 125 ml of 1 mol/L NaOH solution to 250 ml.

In all cases, NBB and FeSO₄·7H₂O are mixed in the reactor first, and then H₂SO₄ and NaOH solutions are added drop by drop until desired pH value is reached. A water bath is used to adjust the temperature of the mixture. H₂O₂ is added when the desired temperature is reached. The time started to add H₂O₂ in the solution is referred as T₀ and considered as the starting point of the reaction.

3. Data treatment

3.1 Reaction constant

A series of plots were made with the data collected by the UV-VIS instrument. $\ln (A_{RH0}/A_{RH})$ for the different conditions were plotted against time t . Commonly used plot software such as Microsoft Excel, Sigmaplot and Origin can be used to plot the graphs. A linear fitting was made on the graphs to determine if a pseudo-first order was a reasonable assumption for the reaction. The reaction rate constant, k_{app} , which is the slope of the linear relation, was then found by fitting equation (14) to the data.

The rate of decolourization (618 nm) and the rate of aromatic content removal (320 nm) were compared by plotting absorbance of NBB at 680 nm and 320 nm against time to compare the changes. When finding the trend lines to the plotted points, the values for the correlation coefficient R^2 was also taken into consideration. The values for R^2 give an indication of how well the trend line fits the plotted points. If the trend line to the plotted points corresponds to a completely linear graph, then $R^2 = 1$.

3.2 Activation energy calculation

The activation energy E_a can be estimated by fitting the data to the function in Equation (15). The reaction constants k_{app} obtained from different temperatures were plotted against $-1/T$. The slope of the line equals to E_a/R , thus E_a can be determined by dividing the slope by the gas constant R .

4. Exercise implementation and evaluation

In the past three years, there were normally around 12 to 14 groups of students (2 students per group) taking this exercise every year, and it takes 2.5 hour to 3 hour to finish this exercise, depending on how well the students prepared for the exercise. For each group, one work plan and one report are required to be delivered before and after the exercise. The performances of the groups were assessed according to the work plan (20%), the final reports (60%) as well as the completion of the objectives (20%).

According to the written work plans and reports from the students in the past 3 years, most of the students had no problem with capturing and understanding the main process from reading the exercise instruction, and they can carry out the experiment with minimal aid from the teaching assistant. Only one demonstration was needed for most of the students to use these two apparatuses.

Their final reports after the exercise were collected and analyzed. The students had two weeks to prepare the final reports. Regarding the analysis and discussion of the results, most of the students were able to process the data they collected and extract the kinetic constants, k_{app} and E_a . However, only a few students discuss in-depth the variations and the apparent non-linear behavior. For example, some students observed a non-linear behavior at a high H_2O_2 , high $FeSO_4$ content, or high temperature in the reaction solution, conditions where the pseudo-first-order reaction no longer represents an appropriate model. Most of the students would execute the linear fitting as instructed without further questioning the reaction order. It is where teaching assistants can provide more guidance to the students for them to discover more by exploring their experiment results further. Also, as mention before, the students have only one experiment for each set of operating conditions, the experiment error itself may be so large that it leads them to draw wrong conclusions. For example, many students reported the highest reaction constant at a pH of 2 instead of 3, which can be attributed to the experimental error and having only on experimental point. When confronted, most students can identify potential error and suggest ways to avoid or reduce them.

To evaluate the pedagogical effectiveness of the exercise, the students were asked to give their opinions on this exercise. Some questions were sent to the students by the end of the exercise. The feedback from students was very positive. Most of them agreed that UV-VIS spectroscopy was quite easy and simple to operate. Majority of the students agreed that this exercise was quite useful to their study program. They confirmed that this exercise provided an experience of determining chemical reaction constant in real state reaction.

5. Work Plan Guidelines

The work plan is a brief document that clearly describes specific goals and objectives of the project and how these goals and objectives will be accomplished. The work plan must describe the necessary tasks to be carried out, such as calibrations, specific data to be collected during the experimental work, a brief description of how the data are to be analyzed. Furthermore, a detailed experimental design should be included in the work plan. This overall description should explain to the reader why you are doing the research project as you have planned.

The work plan should also give indication that all the tasks will be carried out in a timely manner and that all the deadlines of the assignment will be met. The work plan must be addressed to the laboratory instructor in the form of a memorandum, which should be approximately one to two pages of text plus attachments, if necessary, such as figures, tables, charts, sample calculations, etc. Chemical cards and apparatus card must be included in the attachments.

Specially, the following questions should be addressed in the work plan:

- (1) What industrial applications can use Fenton oxidation?
- (2) What kind of instruments can be used to determine reaction kinetics?
- (3) What is Lambert-Beer's law?
- (4) What is pseudo-first order approximation and how to get it?

6. Report Guidelines

Title Page

Title, author(s) name(s), supervisor, course number, date

Introduction

Describe in about 200-500 words briefly the project, the objectives and goals.

Theory

Give a brief summary of the applicable theory and the characteristics of the plant usually in the form of a mathematical model, the specification of the operating conditions and the background of the instrumentation, if applicable. Provide the details on the data processing being employed.

Experimental Procedures

Outline both the experimental work performed. Provide the details of the operating conditions and a description of details a third person would require to repeat the experiment.

Results and Discussion

Results should be presented in tables and graphs, as appropriate. A clear explanation should accompany both such that the reader has no trouble to understand the meaning and how the information has been obtained. Contents, spreadsheets and other extensive listing of original laboratory data and calculations should be relegated to the appendices. The analysis should include a statistical data analysis. It is essential to determine on how much confidence one can have in the experimental results. The discussion should be short and to the point. Problems that were met during the experiment or the data analysis are to be reported carefully any suggestions for improvements. The text should not exceed one page.

Summary and Conclusions

Summarize the work done and draw your conclusions.

References

Provide the complete information including author(s), title, journal or if book the editor, volume, number, page numbers xy and year of publication, for example:

Perry, R.H., and Chilton, C.H., eds., Chemical Engineers' Handbook, 6th. ed., McGrawHill, New York (1984).

Appendices

Measurements, if applicable. Sample calculations. Instrument calibrations. Copy of laboratory notebook pages.

7. Grading criteria

Work plan (20%):

- Is the work plan properly described before the experiments?
- Is the experimental design well done?

Report (60%):

Introduction (5%):

- Is the objective clearly outlined?
- Is the necessary theoretic background briefly described?

Experimental section (10%):

- Is the experimental procedure clearly described, from which one can repeat his experiments?
- Is the key equation stated for generate main results?

Results and discussions (30%):

- Are the experimental results presented clearly and correctly?
- Are the measured values in the range?
- Are the final results calculated correctly and related to the appendix?
- Is a brief discussion made including error sources, validation of the assumption in calculation?

Appendixes (10%)

- Are the necessary experimental observations included?
- Are the examples of calculation included?

Readability (5%)

- How clear is the writing? Is it easy to follow? Does it seem that the report has been proofread?
- Does the report clearly lay out the process, results and conclusions or is it disjointed?
- Are equations mentioned and then not used? Are equations not mentioned and then used in calculations?
- Are references sited properly?
- Is nomenclature used properly?

20% Completion of objectives

- Has the work plan been followed properly?

- Have the experiments been performed properly?
- Have the HMS rules been followed properly?
- Have all the experimental observations been recorded in lab journal?
- To what extent have the objectives been completed?
- Is a good grasp of the objectives obvious from the report?
- Have proper data collection and analysis been conducted for the objectives?
- Have substantial results and conclusions been derived from performing the objectives?
- How valid are the conclusions that have been drawn?
- Was the report delivered in time?

Note:

- One working day delay in delivering report will cost 20% of the grades for completion of objectives (4 points). Delay longer than five days is not acceptable.
- Plagiarism is not acceptable. The group will receive zero point if any one copies from fellow groups or reports of earlier students.

8. Experimental introduction

Kinetic studies using UV-VIS spectroscopy Fenton reaction

Abstract

The goal of this exercise is to demonstrate the possibility of using a modern in situ spectroscopic method (UV-VIS spectroscopy) to investigate the reaction kinetics. The method is based on the continuous measuring of changes in a pollutant concentration by the on-line determination of its absorbance. The reaction mechanism is rather complicated and simple reaction rate expression can be applied only under very specific limiting conditions. Your task would be to study the influence of various parameters (temperature, pH, H₂O₂/Fe(II) ratio) on the degradation efficiency and to discuss whether describing the reaction by the means of the pseudo-first order kinetic model is convenient. The calculation of kinetic parameters would be an integral part of the report.

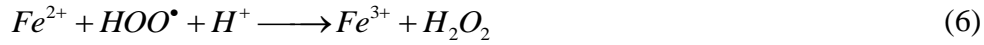
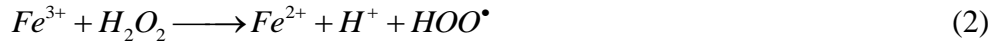
Introduction

Chemical reactions vary greatly in the speed at which they occur. Some are essentially instantaneous, while others may take years to reach equilibrium. Chemical reaction kinetics is the measurement of how quickly reactions occur, it is critical for discovering the mechanism of many reactions. In the past years, different methods have been applied to demonstrate chemical kinetics as laboratory exercise in the lab, such as stopped-flow methods, chemical relaxation methods and spectrophotometry methods. Among these methods, detecting chemical reaction kinetics in diluted aqueous solution using spectrophotometry is most commonly used due to its simplicity and safety. This exercise is going to use UV-VIS spectroscopy to monitor the concentration changes of the reactants and study the kinetics of the reaction accordingly.

Fenton oxidation

Fenton oxidation, a mixture of an iron catalyst and hydrogen peroxide in water, is an example of advanced oxidation processes (AOPs) used in the waste water treatment ¹. These processes are based on the generation of highly reactive hydroxyl radicals, which are very effective oxidative species (standard reduction potential of $HO^{\bullet} + H^+ + e^- \rightarrow H_2O$ is 2.8 V) ². In waste water treatment, biodegradation is a predominant process. However, many pollutants are of a non-biodegradable nature. Azo dyes, used in textiles, cosmetics, printing and pharmaceutical industries, represent an important type of contaminants that are not biodegradable, but can be eliminated by the Fenton oxidation process.

The formation of the hydroxyl radicals during Fenton process is the result of hydrogen peroxide reacting with ferrous ions (reaction 1). Ferric ions can further react with H_2O_2 to give Fe^{2+} and hydroperoxyl radicals (reaction 2), by which the redox cycle $Fe^{2+}-Fe^{3+}$ is accomplished. The concentration of the hydroxyl radicals in the reaction mixture can also be lowered by scavengers (reactions 3, 4 and 8). Reaction is usually carried out at low pH in order to avoid formation of ferric oxohydroxide precipitates, which is favored at higher pH levels. The main reactions taking place in Fenton process are listed in (1) - (8) ³:



Kinetics of degradation

The oxidation of organic pollutants by the HO^\bullet radicals can be described by several reaction mechanisms: HO^\bullet radicals react with the organic pollutant by abstracting H from $C-H$, $N-H$, or $O-H$ bonds, or by adding to $C-C$ bonds or conjugate aromatic rings. In any case, the large number of involved steps leads to a very complex kinetic model. A general rate law for the reactions with the key organic molecule can be written as follows:

$$r = -\frac{dc_{RH}}{dt} = k_{OH}c_{HO^\bullet}c_{RH} + \sum_i k_{ox_i}c_{ox_i}c_{RH} \quad (9)$$

The term ox_i represents other oxidants that are present besides the HO^\bullet , such as ferryl $[Fe(IV)O]^{2+}$ or HOO^\bullet . In order to simplify the model, only the hydroxyl radical is considered to be the active oxidant. The concentration of HO^\bullet cannot be measured directly. It is considered to be large and constant under certain reaction conditions, leading to the pseudo-first reaction order where HO^\bullet concentration is a part of the apparent rate constant k_{app} (10,11).

$$r = -\frac{dc_{RH}}{dt} = k_{app} c_{RH} \quad (10)$$

$$\ln c_{RH} = \ln c_{RH_0} - k_{app} t \quad (11)$$

Activation energy is normally defined as the minimum energy required to start a chemical reaction. It indicates the sensitivity of the reaction rate to temperature. For the Fenton oxidation reaction, the reaction rate is normally assumed to be exponentially dependent on the temperature (known as the Arrhenius equation, equation (12)). The two parameters, namely activation energy (E_a) and pre-exponential factor (A), are specific for each reaction and are assumed to remain constant over the validity range of the model.

$$k_{app} = A e^{-\frac{E_a}{RT}} \quad (12)$$

Where A is the pre-exponential factor, E_a is the activation energy, T and R is the temperature and gas constant, respectively.

The use of UV-VIS spectroscopy for kinetic measurement

Spectrophotometry is a commonly used method to experimentally determine the reaction rates⁴⁻⁵. The UV-VIS spectroscopy can measure the change of the concentrations of reactants or products over time. In this study, the UV-VIS spectroscopy was used to monitor the concentration of NBB (chemical structure shown in **Figure 1**) due to the absorption of the aromatic rings and azo group. Naphthol blue black (NBB) is an important acidic diazo dye in industrial applications, which has been widely used in the textile industry for dyeing wool, nylon, silk and textile printing. On the other hand, NBB also presents a high toxicity to the environment because of the presence of phenolic, anilino, naphthalene and sulfonated groups (as shown in **Figure 1**). In addition, it has high photo- and thermal-stability. Therefore, removing NBB from wastewater of textile industry is of great importance.

The main absorption peak at 618 nm is due to the azo group, whereas the peak at 320 nm is from the absorption of the aromatic rings.

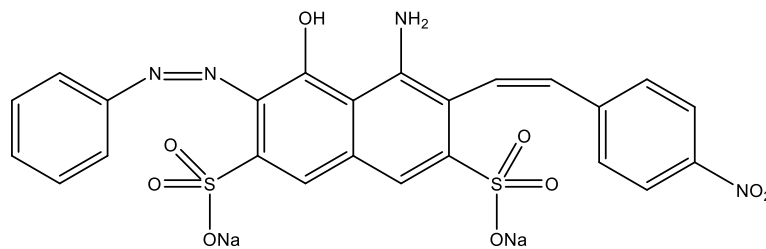


Figure 1. Chemical structure of Naphthol blue black

The magnitude of the absorbance is proportional to its concentration and follows the Beer-Lambert equation.

In case of NBB, the absorbance at 100% conversion (A_∞) approaches the absorbance of the reference sample (A_{ref}), which is water for our case ($A_\infty = A_{ref} = 0$), thus the rate constant can be estimated using linear regression by fitting $\ln(A_{RH0}/A_{RH})$ versus the time t .

$$\ln\left(\frac{A_{RH0}}{A_{RH}}\right) = k_{app} \cdot t \quad (13)$$

Where the A_{RH0} is the absorbance at time zero, while A_{RH} is the absorbance at time t .

In case of activation energy, equation (13) can be rewritten as:

$$\ln(k_{app}) = \ln(A) - \frac{E_a}{RT} \quad (14)$$

Thus the activation energy E_a can be found by fitting $\ln(k_{app})$ versus $-1/T$ via linear regression. A plot of $\ln(k)$ versus $-1/T$ yields a straight line with a slope of E_a/R and y-intercept $\ln(A)$, the natural logarithm of the Arrhenius constant.

Experimental

The reaction would be carried out in the black box (to avoid interference with the light from external sources) equipped with the UV-VIS transmission dip probe and pH meter with an integrated thermocouple. Since the experiment should be done under isothermal condition, the reactor would be sunk in the thermostatic water bath. The description how to operate the UV-VIS device would be provided by the supervisor of the lab-exercise.

Preparation of samples

You should do some calculation before the exercise. Design all the equations you need to prepare solutions of concentration given in table S2.

Kinetic tests

Mix all the compounds but H_2O_2 in the reactor and wait until the temperature stabilizes (you will be told all the reaction conditions and how to operate the UV-VIS device on the day of your experimental work). After that, add H_2O_2 at once by automatic micropipete. This time will be considered as the start of the reaction.

Preparation for the lab exercise

- Read and learn about the chemicals used in the experiment (especially on its hazards) and fill out the apparatus card;
- Read the HSE book, sign it to confirm that you are familiar with its content and bring it to the supervisor;
- Prepare the work plan (up to 2 pages) that contains:
 - Short theoretical introduction to the reaction system
 - Plan on how the experiments would be organized
 - Explain how the measured values would be used to calculate kinetic parameters

The main tasks of the exercise

Version 1 (pH)

1. Study the influence of pH on the decolourization of Naphtol blue black by comparing the degradation efficiency (conversion) at the specific reaction time (at least 3 different pH values in the range 2-5). Discuss the reaction order is the reaction of pseudo-first order in the entire pH range? Are there any deviations?
2. Design the experiment to calculate the activation energy of decolourization at pH 3. (at least 3 different experiments) Finding literature value of the activation energy for Fenton oxidation and compare with your data.

Version 2 (H₂O₂ concentration)

1. Study the influence of H₂O₂ concentration on the decolourization of Naphtol blueblack (pH 3) by comparing the degradation efficiency (conversion) at the specific reaction time (at least 3 different H₂O₂ concentrations). Discuss the reaction order is the reaction of pseudo-first order in the entire concentration range? Are there any deviations?
2. Design the experiment to calculate the activation energy of decolourization at pH 3 (at least 3 different experiments). Finding literature value of the activation energy for Fenton oxidation and compare with your data.

Version 3 (Fe(II) concentration)

1. Study the influence of Fe(II) concentration on the decolourization of Naphtol blue black (pH 3) by comparing the degradation efficiency (conversion) at the specific reaction time (at least 3 different pH values in the range 2-5). Discuss the reaction order is the reaction of pseudo-first order in the entire pH range? Are there any deviations?
2. Design the experiment to calculate the activation energy of decolourization at pH 3 (at least 3 different experiments). Finding literature value of the activation energy for Fenton oxidation and compare with your data.

References

1. Neyens, E.; Baeyens, J., A review of classic Fenton's peroxidation as an advanced oxidation technique. *J Hazard Mater* **2003**, *98* (1-3), 33-50.
2. Nalliah, R. E., Oxone/Fe²⁺ Degradation of Food Dyes: Demonstration of Catalyst-Like Behavior and Kinetic Separation of Color. *Journal of Chemical Education* **2015**, *92* (10), 1681-1683.
3. Bokare, A. D.; Choi, W., Review of iron-free Fenton-like systems for activating H₂O₂ in advanced oxidation processes. *J Hazard Mater* **2014**, *275*, 121-135.
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5. Via, G.; Williams, C.; Dudek, R.; Dudek, J., Decay Kinetics of UV-Sensitive Materials: An Introductory Chemistry Experiment. *Journal of Chemical Education* **2015**, *92* (4), 747-751.