Exploring the Electro-Fenton Reaction in Chemistry Class

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Abstract

The removal of pollutants from wastewater is a task that is tackled by many different processes in wastewater treatment plants. If conventional mechanical and biological treatment processes are not sufficient to break down persistent organic pollutants such as the drug diclophenac, for example, other methods such as oxidative degradation using ozone and ultraviolet radiation are used [1,2]. Another degradation option is the Fenton reaction or its modification: the electro-Fenton reaction, which describes the catalytic decomposition of in-situ generated hydrogen peroxide to highly reactive radicals, capable of subsequently decomposing organic molecules [3,4].

In addition to a brief explanation of the electro-Fenton reaction itself, a series of experiments are presented to integrate this interesting and topical phenomenon into chemistry class [4]. This proposed inquiry-based lesson is designed in a way to allow the students to investigate the individual steps of the electro-Fenton reaction as independently as possible. After each experiment, they should develop interpretations and experimentally verifiable hypotheses based on the observations made to design the following experiment.

In order to determine the extent to which the students develop these conclusions independently and where help from the instructor is necessary, the series of experiments was carried out with a group of students in the XLAB student laboratory while documenting the classroom discussions. During this structured lesson observation, particular attention was paid to the interpretation of the observations with regard to the investigation of individual steps of the electro-Fenton reaction. The resulting findings are supplemented by a short questionnaire, which was employed at the end of the teaching unit and aimed at measuring the acquired subject knowledge and the general opinion about the interest and the difficulty in the experiments.

Keywords: *electrosynthesis, electro-Fenton reaction, inquiry-based teaching*

1. Introduction

Humankind is responsible for emitting a wide range of pollutants into the environment. One particular type of pollutant is pharmaceuticals, which are released into different bodies of water via private households, industrial animal farming and other routes. An example of this is diclophenac, which is used as a painkiller for animals and humans and can cause kidney failure in various bird and fish species at high concentrations in the environment. Diclophenac can also not be decomposed in a reasonable timeframe by natural means and therefore accumulates in the environment; due to these two properties, diclophenac and similar substances are also known as persistent organic pollutants. The removal of such pollutants from wastewater is a task that is tackled by many different processes in wastewater treatment plants. If conventional mechanical and biological treatment processes are not sufficient to break down persistent organic pollutants, other methods such as oxidative degradation using ozone and ultraviolet radiation are used [1,2]. Another degradation option is the Fenton reaction, which describes the generation of highly reactive hydroxyl radicals through the reaction of hydrogen peroxide and iron(II) ions and has been known as a reaction since the 19th century [3]. The radicals formed in this way can then oxidatively degrade even highly persistent molecules

However, as the storage and transportation of large quantities of hydrogen peroxide is associated with safety risks, a modification of this “old” reaction is garnering the interest of the scientific community: the electro-Fenton reaction, in which the required hydrogen peroxide is produced *in-situ* by electrolytic means [4]. In addition to the safety aspects, this reaction also has the potential to be more sustainable than conventional hydrogen peroxide production methods considering the use of renewable electricity. The aims of current research on this topic include optimizing the electrodes and heterogeneous catalysts used and generating the required electrical energy using microbial fuel cells [5,6].

2. The Electro-Fenton Reaction

2.1 Chemical Fundamentals

The electro-Fenton reaction consists of two parts: The electrochemical generation of hydrogen peroxide and the formation of highly reactive radicals through the reaction of this peroxide and iron ions (the actual Fenton reaction).
Hydrogen peroxide synthesis in an aqueous solution can take place in both oxidative and reductive ways. On the one hand, the electrolytic oxidation of water at the anode is possible:

$$2\ H_2O \rightarrow H_2O_2 + 2\ H^+ + 2\ e^-$$

On the other hand, under atmospheric conditions and thus in the presence of dissolved atmospheric oxygen, the latter can be reduced to hydrogen peroxide at the cathode:

$$O_2 + 2\ H^+ + 2\ e^- \rightarrow H_2O_2$$

The actual occurrence of the reactions is determined by the reaction conditions. In our case, the series of experiments shows that it is mainly the reduction of dissolved oxygen that takes place.
The hydrogen peroxide formed in this way can then react with the iron(II) ions present to generate highly reactive hydroxyl radicals:

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

This leads to an oxidation of the iron(II) to iron(III). In a subsequent step, this can react with additional hydrogen peroxide to form further radicals (in this case hydroperoxyl radicals):

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

The iron ions therefore act as a catalyst to continuously convert electrolytically formed hydrogen peroxide into reactive radicals that can oxidatively degrade even inert organic molecules.
The model dye Brilliant Blue FCF is used in the experiments presented. This is known as a food colorant, which already presupposes a certain chemical stability. At the same time, brilliant blue FCF also has several structural properties that suggest poor biodegradability [7]. For these reasons, the dye is suitable as a model substance for persistent organic pollutants.

2.2 Series of Experiments

The experiments and their observations are presented chronologically with observations and resulting conclusions (see Figure 1). The necessary hypotheses for follow-up experiments are also outlined. Detailed experimental instructions are not included in this publication and can instead be found in Lanfermann et al. [4].

The lesson begins with experiment 1 which shows the decomposition of the organic dye brilliant blue FCF by electrolysis of an acidic sodium sulphate solution to which dye and iron(II) sulphate have been added. In addition to this “complete” solution, a dye solution without iron(II) sulphate is also electrolyzed, which does not lead to any decoloration. Subsequent addition of iron(II) sulphate to this electrolyzed solution, on the other hand, again leads to decoloration. The observations allow two basic interpretations: Firstly, both the electrolysis and the iron(II) ions are required to decompose the dye. Secondly, a stable intermediate product is formed during electrolysis which reacts with the iron(II) in a further step to finally decompose the dye. Based on the chemicals present in the solution, the students can then formulate assumptions as to which intermediate product this could be. In addition to correctly suspecting the formation of hydrogen peroxide from the oxidation of water or the reduction of oxygen, they can also discuss side reactions that take place, such as the electrolysis of water or reactions that do not take place, like the reduction of sodium ions.
After formulating the hypothesis (hydrogen peroxide is formed during electrolysis), this can be tested in experiment 2. For this purpose an acidic sodium sulphate solution without dye and iron(II) sulphate is electrolyzed and then titanyl sulphate is added. In the presence of hydrogen peroxide, this leads to a yellowish discoloration due to the formation of a titanium-peroxo complex, which is the case here. A negative and positive sample is also carried out for comparability. The hypothesis of hydrogen

peroxide formation is confirmed by this evidence. The next question that arises is to what extent this reacts with the iron(II) ions to decompose the dye. This question should be explored in the classroom discussion, whereby the conversation should be directed as gently as possible towards the formation of radicals. The fact that the dye is a relatively stable substance and therefore a particularly reactive species must form to decompose the dye can be mentioned as helpful information. The aim of the discussion should be to formulate the hypothesis that highly reactive hydroxyl radicals are formed during the reaction of hydrogen peroxide and iron(II) ions.
This hypothesis is then tested in the third experiment by adding coumarin to an acidic sodium sulphate solution containing iron(II) and electrolyzing it. Coumarin reacts with hydroxyl radicals to form 7-hydroxycoumarin, which exhibits a characteristic blue-green fluorescence when exposed to UV light. The experiment confirms that hydroxyl radicals are formed, meaning that a large part of the electro-Fenton reaction has already been experimentally clarified by experiments 1-3: Electrolytically produced hydrogen peroxide reacts with iron(II) ions present to form highly reactive hydroxyl radicals, which can decompose the organic dye.

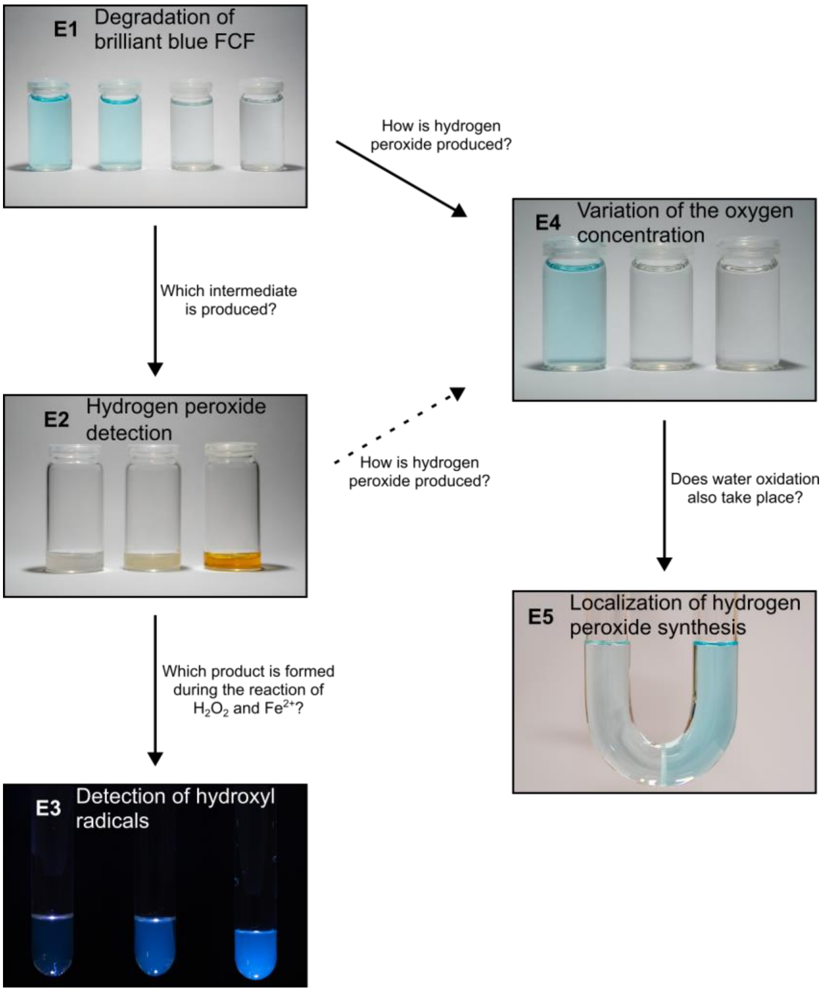

Fig. 1. Summary of the proposed lesson with images of the observations made and the central questions that lead to the following experiments (adapted from Lanfermann et al. [4]).

The question of which of the two possible reactions (water oxidation and oxygen reduction) act as the source of hydrogen peroxide or whether both reactions take place has not yet been clarified. The experiment to investigate this should be designed by the students themselves, and if necessary, it should be pointed out that the concentration of the substances involved can be varied experimentally. A comparison of the two reaction equations reveals that varying the oxygen concentration is a good way to check the importance of oxygen for the generation of hydrogen peroxide. This can then be carried out in experiment 4 by first boiling the reaction solution to remove as many physically dissolved gases as possible. The solution can then be electrolyzed as in experiment 1, with the difference that air or oxygen is additionally introduced in a separate setup. The experiment shows that the solution is

only decolored when this is done. It can therefore be concluded that oxygen reduction plays an important role in the formation of hydrogen peroxide under the given reaction conditions.
In order to substantiate this hypothesis and to investigate whether water oxidation also plays a role, the electrolysis can then be carried out in the fifth experiment with separate anode and cathode compartments. This shows that it is mainly the solution around the cathode that decolors, while the solution on the anode side retains its blue color. This eliminates water oxidation as a relevant reaction for the formation of hydrogen peroxide.
With these five experiments, the electro-Fenton reaction was able to be clarified inquiry-based: Hydrogen peroxide is produced electrolytically via the reduction of physically dissolved atmospheric oxygen, which then reacts with iron ions present to form highly reactive radicals that decompose the model dye.

3. Evaluation

3.1 Structured Lesson Observation

Due to its inquiry-based nature, the lesson outlined above contains several conclusions and experimental approaches that should be developed by the students as independently as possible. The most important of these are shown in table 1.

Table 1. Important conclusions and experimental ideas regarding the inquiry-based exploration of the electro-Fenton reaction.

Chronological placement in the lesson	Important conclusions and experimental ideas
After Experiment 1	I. Both iron ions and electric current are needed to break down the dye. II. The electrolysis produces an intermediate, which then reacts further with the ion ions. III. Hypothesis: Hydrogen peroxide is produced as an intermediate by the electrolysis of the aqueous solution. IV. Hydrogen peroxide can be produced either by the oxidation of water or the reduction of dissolved oxygen.
After Experiment 2	V. The dye is degraded by radicals, which are formed by the reaction of hydrogen peroxide and ion ions.
Before experiment 4	VI. To investigate which hydrogen peroxide generation reaction occurs, it is advisable to vary the oxygen concentration experimentally.

The lesson was carried out in the XLAB student laboratory with 10 students with a relatively high knowledge level from the upper secondary school level in order to assess the extent to which students can draw these conclusions themselves and what support and assistance is required. The lesson structure always consisted of an experiment and a subsequent plenary discussion in which the observations were interpreted and conclusions as well as questions for further experiments were developed together. The instructor paid particular attention to allowing students to formulate their own hypotheses first and only intervening if necessary. The actual course of the lesson was recorded in writing by an independent person using the method of a structured classroom observation, with a specific focus regarding the discussions about the conclusions from table 1. The discussions that are relevant to these conclusions are summarized and presented below with the intention of highlighting any difficulties in understanding that the students may have with the lesson.

I: After the first experiment, the students immediately stated without any further guidance that the presence of iron ions is crucial for the decomposition of the dye. After briefly requesting further possible interpretations (“What else can be concluded from the observations?”), it was also correctly stated that electrolysis is also a necessary condition for dye degradation.

II: Immediately following the previous discussion related to conclusion I, the instructor drew attention to a specific part of the observations (“As said, iron ions and electrolysis are important for dye decomposition, what else can be concluded from the observation that the solution also decolors due to the later addition of iron ions following the electrolysis?”). This observation was correctly interpreted by the students to indicate that the iron ions do not play a role in the electrolysis itself but react in a following step. Accordingly, a substance must be produced during electrolysis that subsequently reacts further with the iron ions and thus causes the discoloration.

III: To investigate the exact nature of the electrolysis taking place, the instructor posed the question of which substances are present in the reaction solution. The students initially only named the substances that they had added themselves (Na^+, SO_4^{2-}, H^+, H_2O, dye). After a further hint ("We are not in a vacuum, we are working in an atmosphere."), the students also named oxygen and nitrogen. They then formed assumptions about possible reactions. Nitrogen was ruled out due to its low reactivity; instead, the hypothesis was proposed that water is electrolyzed. After establishing the redox equation for water electrolysis, the students discussed the products as possible reasons for dye decoloration. As oxygen is already present in the solution, this was ruled out by the students. The instructor was also able to rule out hydrogen by means of experimental proof. The students then mentioned the possible reduction to elemental sodium and the oxidation of sulphate ions, both of which were ruled out after a discussion with the instructor. The autoprotolysis of water, the formation of sulphuric acid and the binding of sodium ions to the dye were also discussed and rejected as possible reasons for the decoloration. To initiate the deduction of hydrogen peroxide, the instructor asked the students about reactive compounds they already knew and pointed out that many of the components of the electrolyte solution such as sodium ions and sulphate ions had already been excluded in the discussion. In response to this hint, the students correctly named hydrogen peroxide as a possible resulting substance.

IV: Following this conclusion, the instructor asked which possible redox reactions contain hydrogen peroxide as a product. The students immediately named water oxidation and were also able to correctly represent the formula for this reaction with some help. On further inquiry and assistance ("We have found an oxidation, is there also a possible reduction reaction?"), the students were also able to formulate the corresponding oxygen oxidation.

V: The hydrogen peroxide detection in experiment 2 and the observations from experiment 1 show that although hydrogen peroxide is formed by electrolysis, it cannot be solely responsible for the degradation of the dye. Based on this, the students put forward the hypothesis that hydrogen peroxide reacts with existing iron ions, which initiates the degradation of the dye. The students then expressed theories such as the formation of iron oxides or "iron peroxide". Here the instructor intervened by adding that metal ions often act as a catalyst. The instructor also asked which particularly reactive groups of substances the students were familiar with. Following this information, the students named radicals as possible products. The formation of hydroxyl radicals at formula level was then developed together in a classroom discussion.

VI: After the evaluation of the third experiment, the instructor asked the students what unanswered questions they still had regarding the reactions discussed so far. The students were also asked to look at the blackboard, which showed the two possible hydrogen peroxide generation reactions, among other things like experimental details and setup instructions. Students were then asked which of the two reactions took place. The instructor then tasked them with designing a suitable experiment to investigate this question. First, the students mentioned measuring the water content, as water was consumed during water oxidation. They also suggested measuring the pH value, as H^+ ions are formed or consumed in both reactions. During a subsequent discussion, however, these two ideas were rejected, as both factors are difficult to measure on a student laboratory scale (water content of an aqueous solution, small changes of H^+ ion concentration in an acidic solution already at pH 2). After a short time, it was suggested to change concentrations in order to influence the occurrence of the reactions. After reviewing the reaction equations again, the students correctly named oxygen as an easy concentration to change.

Overall, it can be concluded that the proposed lesson (with the help of the instructor) was of appropriate difficulty for the students. Conclusions I and II were achieved by the students without help, conclusions IV and VI were also able to be developed with little help from the instructor. Only conclusions III and V proved to be relatively difficult, although here too a result was achieved in the class discussion after deliberate questioning and with gentle guidance.

3.2 Questionnaire

In addition to the structured lesson observation, a short questionnaire was issued after completion of the series of experiments. One part consisted of three opinion questions, which were to be answered using a five-point Likert scale, with answers ranging from "strongly disagree" to "strongly agree" (see table 2).

Table 2. Opinion questions and results (N=10). The scale ranges from 0 (“strongly disagree”) to 4 (“strongly agree”). Answers between two possible choices were considered to be the worse answer in each case.

Question	Responses (0/1/2/3/4) and resulting mean
I found the topic of “Electro-Fenton” interesting.	0/0/0/8/2 and 3.2 ± 0.4
I enjoyed the experiments.	0/0/1/4/5 and 3.4 ± 1.1
Overall, I had the feeling that I understood the explanations.	0/0/3/7/0 and 2.7 ± 0.5

As can be seen in Table 2, the questions relating to interest and motivation turned out positively with mean values of 3.2 and 3.4 respectively. The self-assessment of understanding of the theory was slightly worse, with a mean value of only 2.7.

The second part of the questionnaire was comprised of two free-text questions that covered aspects related to the Electro-Fenton reaction which were presented during the course. Firstly, students were asked to describe in their own words and/or with reaction equations which reactions occur during the electrolysis of the acidic sodium sulfate solution. The answer was scored as correct if the students described the correct reaction of hydrogen peroxide generation or formulated the correct reaction equations. It was scored as partially correct if at least hydrogen peroxide was named as the product.
The second question asked which substance formed is ultimately responsible for the decoloration of the dye and how it is formed. The answer was scored as correct if the students described the correct reaction of radical generation or formulated the correct reaction equations. It was scored as partially correct if at least radicals were named as the responsible substance (see table 3).

Table 3. Free-text questions and the response profile of the students.

Question	Answers (incorrect/partially correct/ correct)
Which reaction occurs during the electrolysis of the acidic sodium sulfate solution?	0/3/7
Which substance is responsible for the discoloration and how is it formed?	3/1/6

Overall, the response profile of this learning group shows that the electrolytic synthesis of hydrogen peroxide was either fully or at least partially understood by the students. With regard to the formation of radicals, the target group was split into correct and incorrect answers. This could lead to the conclusion that more attention should be paid to this part of the topic when conducting the lesson, as it may be particularly difficult for the students to grasp.

REFERENCES

[1] Rodríguez, A. et al. (2008). Ozone-Based Technologies in Water and Wastewater Treatment. In: Barceló, D., Petrovic, M. (eds) Emerging Contaminants from Industrial and Municipal Waste. The Handbook of Environmental Chemistry, vol 5. Springer, Berlin, Heidelberg.
[2] Iervolino, G., Zammit, I., Vaiano, V., Rizzo, L. (2020). Limitations and Prospects for Wastewater Treatment by UV and Visible-Light-Active Heterogeneous Photocatalysis: A Critical Review. In: Muñoz-Batista, M., Navarrete Muñoz, A., Luque, R. (eds) Heterogeneous Photocatalysis. Topics in Current Chemistry Collections. Springer, Cham.
[3] Barbusinski, K. (2009). Henry John Horstman Fenton: Short Biography and Brief History of Fenton Reagent Discovery. Metrologia, 14(1-2), 101-105.
[4] Lanfermann, P., Weidmann, C., Waitz, T. (2024). The Electro-Fenton Reaction in Chemistry Class. CHEMKON, 31(6), 226-231.
[5] Guo, J. et al. (2023). Transition Metal Catalysts in the Heterogeneous Electro-Fenton Process for Organic Wastewater Treatment: a Review. Environ. Sci.: Water Res. Technol. 9, 2429.
[6] Li, S. etal. (2020). Bio-electro-Fenton Systems for Sustainable Wastewater Treatment: Mechanisms, Novel Configurations, Recent Advances, LCA and Challenges. An Updated Review. J. Chem. Technol. Biotechnol., 95, 2083–2097.
[7] Hiromatsu, K. et al. (2000). Prediction for Biodegradability of Chemicals by an Empirical Flowchart. Chemosphere 41, 1749–1754.