NTNU

NORWEGIAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

FELLESLAB 2021

RE4 – Kinetic Studies Using UV-VIS Spectroscopy

Fenton Reaction

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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 specific limiting conditions. Your task would be to study the influence of various parameters (temperature, pH, H_2O_2/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.

Theory
I. Fenton oxidation

Fenton oxidation is an example of Advanced Oxidation Processes (AOPs) used in the waste water treatment. These processes are based on the generation of highly reactive hydroxyl radicals which are very effective oxidative species (standard reduction potential of $\cdot OH + H^+ + e^- = H_2O$ is 2.8 V). In the waste water treatment, the biodegradation is a predominant process, however, many pollutants are of a non- biodegradable nature. Among them, azo dyes (originating from the textile, cosmetic, printing and pharmaceutical industries) represent important contaminants that could be eliminated by the Fenton process.

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

$$
\begin{array}{lll}
Fe(II) + H_2O_2 & \rightarrow \quad Fe(III) + OH^- + HO\cdot & (1) \\
Fe(III) + H_2O_2 & \rightarrow \quad Fe(II) + HOO\cdot + H^+ & (2) \\
HO\cdot + H_2O_2 & \rightarrow \quad HOO\cdot + H_2O & (3) \\
HO\cdot + Fe(II) & \rightarrow \quad Fe(III) + OH^- & (4) \\
Fe(III) + HOO\cdot & \rightarrow \quad Fe(II) + O_2H+ & (5) \\
Fe(II) + HOO\cdot + H+ & \rightarrow \quad Fe(III) + H_2O_2 & (6) \\
2\ HOO\cdot & \rightarrow \quad H_2O_2 + O_2 & (7) \\
HO\cdot + H+ + e- & \rightarrow \quad H_2O & (8)
\end{array}
$$

II. The kinetics of degradation

The oxidation of organic pollutants by the OH radicals can be provided by several reaction mechanisms. Hydroxyl radical react with the organic pollutant by abstracting H from C-H, N-H, or O-H bonds, by adding to C-C bonds, or adding to conjugate aromatic rings. The large number of involved steps leads to a very complex kinetics. General rate law of the key organic molecule can be written as follows:

$$r = -\frac{dc_{RH}}{dt} = k_{OH}c_{OH}c_{RH} + \sum_i k_{ox_i}c_{ox_i}k_{RH_i} \tag{9}$$

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

$$r = -\frac{dc_{RH}}{dt} = k_{app}c_{RH} \tag{10}$$

$$\ln c_{RH} = \ln c_{RH_0} - k_{app}t \tag{11}$$

$$\ln \left(\frac{c_{RH_0}}{c_{RH}}\right) = k_{app}t \tag{12}$$

The reaction rate is normally exponentially dependent on temperature (following the Arrhenius equation). The activation energy and pre-exponential factor are specific for each reaction and remain constant over certain temperature range. These constants can be determined either by linear regression analysis (from the plot of logarithmic dependence of the rate constant on the reciprocal temperature) or by non-linear regression analysis (which can be applied directly to the dataset).

From Arrhenius equation:

$$k_A(T) = Ae^{-\frac{E}{RT}} \tag{13}$$

where A is the frequency factor; E is the activation energy; R is the gas constant; T is the absolute temperature. By taking the natural logarithm:

$$\ln c_{RH} = \ln A + \frac{E}{R}\left(-\frac{1}{T}\right) \tag{14}$$

III. The use of UV-VIS spectroscopy for kinetic measurement

Organic azo-dyes absorb light in both UV and visible region. In this exercise, the concentration of naphtol blue black (Figure 1) will be monitored. The main peak of azogroup responsible for its color is at 618 nm, whereas peak at 320 nm corresponds to the presence of aromatic rings.
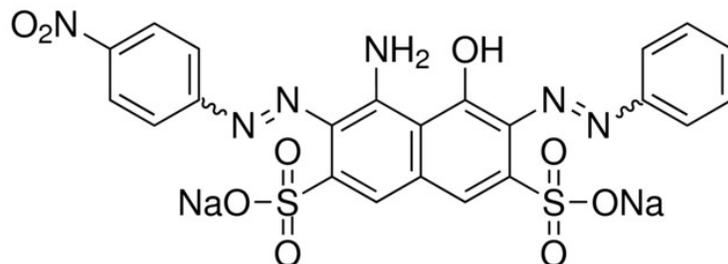
Figure 1. Chemical structure of Naphtol blue black

The absorbance of detected compound is proportional to its concentration according to the Lambert-Beer equation (15) and as such the absorbance can be used in the rate expression instead of concentration (16):

$$A = \varepsilon_{RH} c_{RH} l \tag{15}$$

(A is the absorbance; ε states molar absorption coefficient; l represents the length of the lightpath through the sample)

$$\ln(A_{RH} - A_\infty) = \ln(A_{RH_0} - A_\infty) - k_{app}t \tag{16}$$

(A_{RH} is the absorbance at time t, A_{RH_0} represents the absorbance at the beginning of reaction, A_∞ states the absorbance at 100% conversion).

In case of naphtol blue black you can consider absorbance at 100% conversion A_∞ to be of the same value as the absorbance of the reference sample ($A_\infty = A_{ref} = 0$). Thus, the equation 16 can be rewritten as follows:

$$\ln \left(\frac{A_{RH_0}}{A_{RH}} \right) = k_{app}t \tag{17}$$

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 the Table 1.

Table 1: Concentration of compounds

Compound	Volume	Concentration
Naphtol Blue Black	200 ml	10 mg/l
$FeSO_4 \cdot 7H_2O$	5 ml	1 mg/ml
H_2SO_4	drops	0.5 mol/l
NaOH	drops	0.5 mol/l
H_2O_2	1-3 ml	0.5 mg/ml

Kinetic tests

Mix all the compounds except H_2O_2 in the reactor and wait until the temperature stabilized (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 micropipette. This time will be considered as the start of the reaction.

To be done before the lab exercise:

- Read and learn about the chemicals used in the experiment.
- 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:
    1. Short theoretical introduction to the reaction system.
    2. Plan about how the experiments would be organized.
    3. Explain how the measured values would be used to calculate kinetic parameters.
    4. Name the possible risks for this experiment and explain how to avoid/reduce risks.

The tasks of the exercise - Report

Version 1. Changing 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 3 different pH values in the range 2-4) at the room temperature. Discuss the reaction order is the reaction of pseudo-first order in the entire pH range? Are there any deviations? Compare the rate of decolourization (618 nm) to the rate of aromatic content removal (320 nm) at one pH value of your own choice.

2. Design the experiment to calculate the activation energy of decolourization at two additional reaction temperature (keep pH constant at 3).

Version 2. Changing H_2O_2

1. Study the influence of H_2O_2 concentration on the decolourization of Naphtol blue black by comparing the degradation efficiency (conversion) at the specific reaction time (at 3 different H_2O_2 volume in the range of 1-3 ml) at pH=3 and room temperature. Discuss the reaction order is the reaction of pseudo-first order in the entire concentration range? Are there any deviations? Compare the rate of decolorization (618 nm) to the aromatic content removal (320 nm) at one H_2O_2 of your own choice.

2. Design the experiment to calculate the activation energy of decolourization at two additional reaction temperature at pH 3 (keep H_2O_2 volume constant at 2 ml).