Master's Thesis Engineering Technology 2021-2022

Kinetic study of the degradation of sulfamethoxazole by UV light combined with H_2O_2 and photo-Fenton treatment

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1 Introduction

More **pharmaceutical products** find their way **into the environment** because of increased use and increase in population and population aging. The pharmaceutical and personal care products (PCCPs) are mostly **disposed** through **excretion and household waste**. **Incomplete removal** of PCCPs in **wastewater treatment** can cause **health risks**, but these long-term health risks remain **poorly understood**. Der Beek et al. find evidence of **30 to 200 different pharmaceuticals** in surface water, groundwater or tap/drinking water (der Beek et al., 2015) in most countries of Western Europe. One of the compounds under **scrutiny** is **sulfamethoxazole**.

2 Sulfamethoxazole

Background and objective

Sulfamethoxazole (figure 1) is among the most used **sulphanilamide antibiotics**. Due to its polarity and **antibacterial nature**, it **cannot easily be degraded** with biological treatment. Sulfamethoxazole can be **present in surface water** in the range of **nanogram per litre to microgram per litre** (Gao et al., 2016; J. Wang & Wang, 2016). **More information is needed** on the degradation of sulfamethoxazole to **estimate its effect on the aquatic environment**. This paper studies the **degradation** of sulfamethoxazole with **UV/H_2O_2** and **photo-Fenton oxidation**. A **kinetic study** of the change in **sulfamethoxazole concentration**, **colour (absorbance at 455 nm), aromaticity (absorbance at 254 nm) and turbidity** during the reaction is done. The results are linked to existing literature about the degradation of sulfamethoxazole.

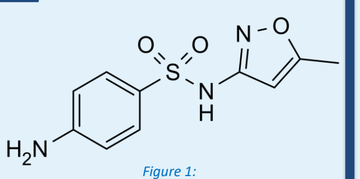

Figure 1: sulfamethoxazole

Goals

Reaction kinetics	Degradation analysis	Link the results
1. Perform reactions 2. Measure turbidity, aromaticity and colour 3. Fit a model	1. Perform HPLC analysis of the samples 2. Determine reaction intermediates and sulfamethoxazole degradation	1. Support degradation pathway with colour, turbidity and aromaticity kinetics 2. Validate analysis methods

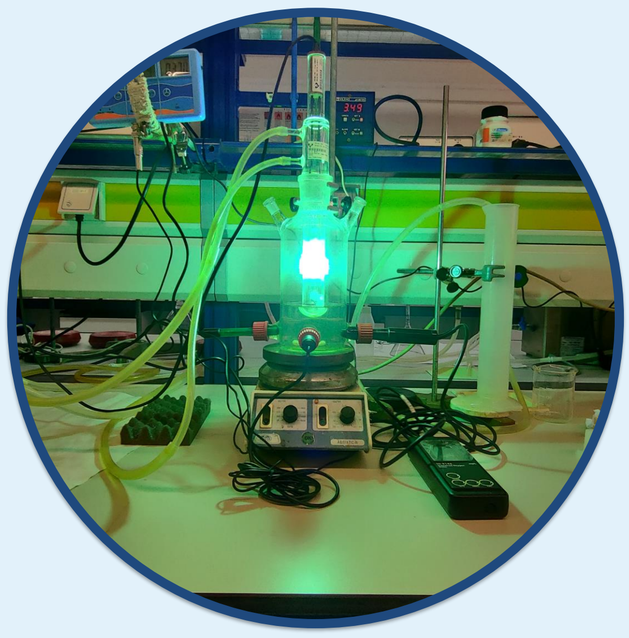

Figure 6: Photocatalytic reactor

3 Materials and methods

Reaction system

-pH
-Dissolved oxygen
-Temperature

The tests were conducted by oxidizing aqueous solutions of **50.0 mg L^{-1} sulfamethoxazole** of 1.0 L in a **photocatalytic reactor** that used a **150W UV mercury lamp** (figure 5). The temperature was maintained around **25°C** (figure 4). The pH was monitored (figure 2) and kept constant during the treatment by adding diluted NaOH and HCl. A dissolved oxygen meter was also added to the reactor (figure 3).

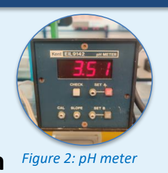

Figure 2: pH meter

Figure 3: Dissolved oxygen meter

Figure 4: Cooling system

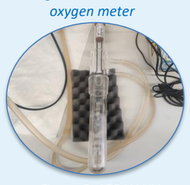

Figure 5: 150 W UV mercury lamp

Sample analysis

Samples were taken from the reactor **every 5 minutes**. Immediately **the turbidity, absorbance at 254 nm and absorbance at 455 nm** was analyzed. **IC analysis** was also performed on the steady-state samples.

Performed reactions

UV/H_2O_2
-[H_2O_2] = 100 mM
-pH = varied (2.0 – 12.0)

UV/H_2O_2/Fe^{2+} = photo-Fenton
-[H_2O_2] = varied (5 mM – 100 mM)
-pH = 3.0
-Fe^{2+} = 2 ppm

-[H_2O_2] = 10 mM
-pH = 3.0
-Fe^{2+} = varied (0.5 ppm – 5 ppm)

4 Degradation pathway

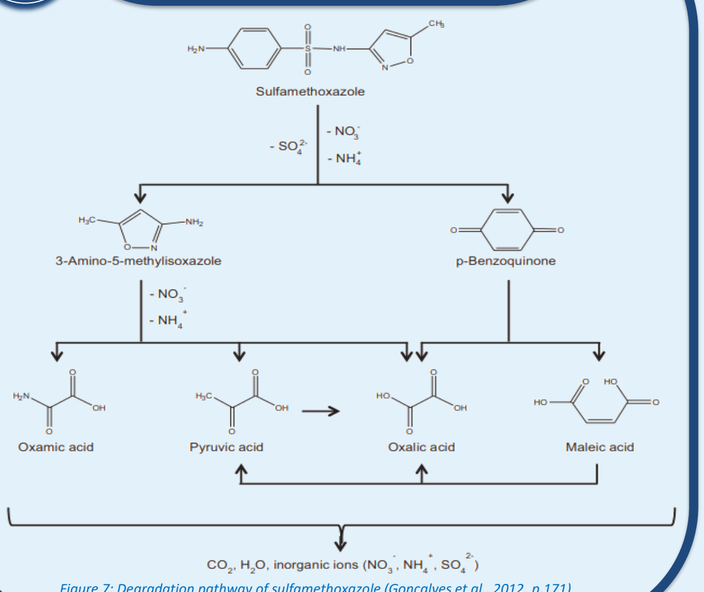

Figure 7: Degradation pathway of sulfamethoxazole (Gonçalves et al., 2012, p.171)

5 Kinetic models

UV/H_2O_2 – pseudo first-order

$$[SMX] = [SMX]_0 * \exp(-k_{SMX} * t) \quad (1)$$

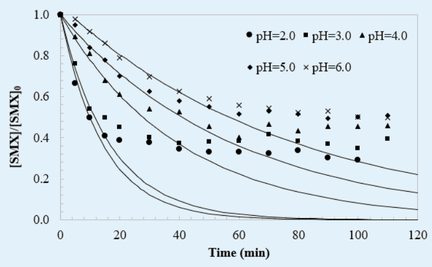

Figure 8: Absorbance at 260 nm during the UV/H_2O_2 degradation of sulfamethoxazole at varying pH

Figure 8 shows the measured values of **absorbance at 260 nm** and a **fitted model**. A **pseudo first-order** model is proposed, for the reactions at **varying pH**. A **great error** occurs when the **reaction stops**, as the model does not take into account the **effect of the hydroxyl radical concentration**.

Photo-Fenton – second-order

$$[SMX] = \frac{1}{-k_{SMX} * t + \frac{1}{[SMX]_0}} \quad (2)$$

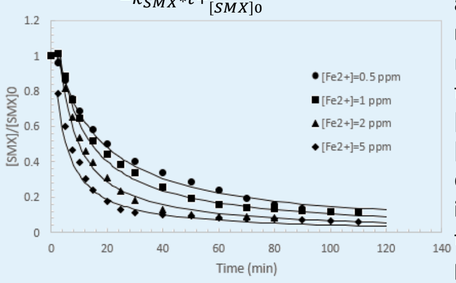

Figure 9: Absorbance at 260 nm during the photo-Fenton degradation of sulfamethoxazole at varying [Fe^{2+}]

Figure 9 shows the measured of **absorbance at 260 nm** and a **fitted model**. A **second-order** model is proposed, for the reactions at **varying [Fe^{2+}] and varying [H_2O_2].** The reaction is completed due to the **increased efficiency** of the **photo-Fenton process**. For this reason, the **model is more correct.**

6 Conclusion

Discussion

The **effect of pH** on SMX degradation was attributed to the **ionization of SMX**, as it has two ionizable amino groups. It is believed that **turbidity** was caused by **p-Benzoquinone** and **oxamic acid dimers**. For **UV/H_2O_2 reactions** a **pseudo first-order kinetic model** was used to describe the observed changes in the measured parameters, while for the **photo-Fenton reactions** a **second-order model** was proposed. The **photo-Fenton** reactions had a clear effect of formed intermediates due to the more complete degradation of SMX.

Future look

Further research can be done regarding the degradation of **sulfamethoxazole** under **different conditions**. This lab scale research can be used to **determine the decomposition** of sulfamethoxazole **in natural waters** and **determine** whether it has a **negative effect** on the environment. This research could start with **identifying and quantifying** intermediates such as **p-Benzoquinone** and **oxamic acid**.

Supervisors / Co-supervisors / Advisors

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