# Photosensitizer Using Visible Light: An Undergraduate Laboratory Experiment Utilizing an Affordable Photocatalytic Reactor

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## Abstract

*In this experiment, the visible light reactive photosensitizer (PS) derived from chlorophyllin sodium copper salt has been synthesized via a simple synthetic route. The enhanced photocatalytic activity for the decomposition of the pharmaceutical compound Diclofenac Potassium available as Voltfast sachets under visible light irradiation was demonstrated by comparing the photocatalytic decomposition of Diclofenac Potassium in the presence and absence of the new synthesized visible light photosensitizer under the same photocatalytic conditions. Based on the experimental results, higher activity was achieved for the sample composed of the new synthesized visible light photosensitizer. The photosensitized sample using the new derivative of chlorophyllin sodium copper salt exhibited approximately 21 times higher rate when compared with that of Chlorophyllin sodium copper salt sample. This photocatalytic activity can be attributed to the enhanced visible light harvesting of the new derivative of Chlorophyllin sodium copper salt.*

**Keywords:** Diclofenac Potassium; visible light; photosensitizer (PS); Chlorophyllin sodium copper salt

## 1. Introduction

Over the past few decades, photocatalysis has received much attention due to the ability of photocatalysts to generate hydrogen from water splitting[1] and the elimination of hazardous pollutants.[2,3] To date, $TiO_2$ and $TiO_2$-based catalysts have been the most extensively studied photocatalysts.[4,5] $TiO_2$ is only active under UV light irradiation due to its wide bandgap of ~3.20 eV. [6] Ultraviolet (UV) light occupies only ~ 4% of the entire solar spectrum, whereas visible light occupies ~ 45% of the solar energy. Therefore, the development of visible-light responsive photocatalysts is necessary requirement to tune the band gap and enhance the photocatalytic activity of the such photocatalysts. Aside from $TiO_2$, many other single-phase multicomponent oxides were introduced, and were found to be active for degradation of organic pollutants and water splitting under visible light irradiation.[7]

Solar energy is free, most abundant among all renewable energy sources. Energy from the sun reaches the earth surface at a rate of $1.2 \times 10^5$ TW by far, exceeding the current world energy consumption of 17 TW ($1TW = 10^{12}$ J/s).[8] In plants, chlorophyll, a highly abundant tetrapyrrolic compound, plays an important role in harvesting light energy and conserve it as ATP and NADPH through photosynthesis.[9,10]

There have been a few reports on the utilization of chlorophyll as a photosensitizer as an alternative for different photocatalytic materials i.e. chlorophyll-modified Pt/KTa(Zr)$O_3$ and chlorophyll-Cu modified $ZrO_2$ have been shown to enhance water splitting over pure semiconductor counterpart.[11,12] Moreover, chlorophyll modified MCM-41 and ZnO have been shown to accelerate dye degradations under UV–vis irradiation.[13,14]

Chlorophyllin sodium copper salt ($C_{34}H_{31}CuN_4Na_3O_6$; Figure 1), a water-soluble bright green color pigment derived from chlorophyll has been found to have antimutagenic activity as well an antioxidative properties which attributed to its highly delocalized electron system with the ability to act as a radical scavenger.[15-17] Moreover, the photochemical behaviour of chlorophyllin sodium copper salt have been studied using organic photovoltaics and optical spectroscopy.[18-22] Nonetheless, the utilization of SCC as a photosensitizer in organic reactions has yet to be investigated thoroughly.[23,24]

A drawback of using chlorophyll as photosensitizer is its instability under thermally or photochemically conditions. There are many reports that show the thermal and photochemical instability of chlorophylls and isolation/characterization of their degradation pathways/products.[25-29] The structural similarity of chlorophyllin sodium copper salt to chlorophyll makes its vulnerable when subject to either thermal or photochemical conditions. Furthermore, photobleaching of chlorophyllin was investigated[30] as well as that of chlorophyllin sodium copper salt which was found to be temperature dependent.[31]

The purpose of this experiment is to use derivative of chlorophyllin sodium copper salt photosensitizer[32] shown in Figure 2 as a thermally and photochemical stable substitute of commercially available chlorophyllin sodium copper salt for the decomposition of diclofenac potassium as a model pharmaceutical contaminant present in water.

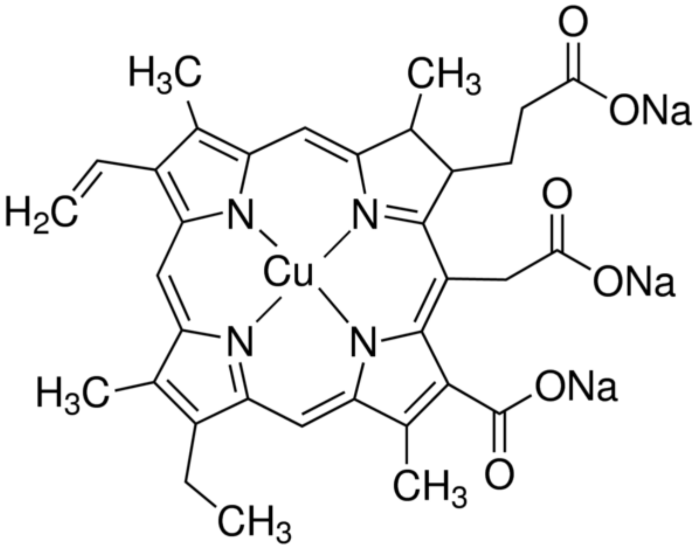

Figure 1. Chlorophyllin sodium copper salt

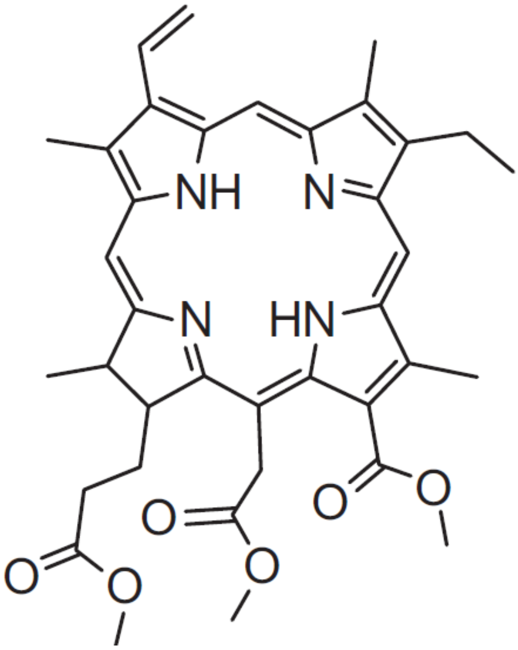

Figure 2. Derivative of copper-chlorophyllin as photosensitizers

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from Sigma Aldrich and were used as received without any further purification. Diclofenac Potassium commercially known as Voltfast was purchased from local drug store. Aqueous solutions were prepared using doubly distilled water passed through a Milli-Q apparatus.

### 2.2. Preparation of the photosensitizer

1 g of chlorophyllin sodium copper salt was dissolved in a 100mL solution of 37% HCl and absolute methanol (50% each v/v). The mixture allowed to stir for 4 hours at room temperature. To monitor the progress of the reaction, thin-layer chromatography was performed to identify the new photosensitizer product formed. The mixture then was purified by column chromatography using silica gel and eluted with Dichloromethane (DCM)/Methanol (MeOH) = 10:1 (v/v). Eluted solution was then removed using rotary evaporator.[32]

### 2.3. Photocatalytic activities

The photocatalytic activity was evaluated by measuring the rate of decomposition of Diclofenac Potassium (commercially available as Voltfast sachet) as a model pharmaceutical compound from aqueous solution at neutral pH. The photocatalytic experiments were carried out using 200 mL ($0.8 \times 10^{-4}$ M) solution placed in a 500 mL round bottom flask irradiated from the side (10 cm from the radiation source) with visible light using 500 W Halogen lamp (OSRAM HALOLINE) with wavelength range 380-780 nm. The round-bottom flask was attached to condenser open from the top to the atmosphere. In all experiments, an optimized amount of 25 mg/100 mL of the photocatalyst dispersed in 300 mL of DI water. The irradiation was performed under magnetic stirring at room temperature. Sample aliquots (3 ml) were taken at the desired time and then filtered to separate the solid photocatalyst. The experimental setup is shown in Figure 3. The decomposition efficiency of the samples was defined in terms of the $C/C_0$ ratio, where $C_0$ and C represent the initial and final concentrations of the Diclofenac Potassium at $t_0$ and t respectively. Moreover, solution of chlorophyllin sodium copper salt ($5 \times 10^{-5}$ M) was also prepared, tested with and without adding Diclofenac Potassium in order to compare the efficiency of chlorophyllin sodium copper salt with the new synthesized photosensitizer derivative of chlorophyllin sodium copper salt.

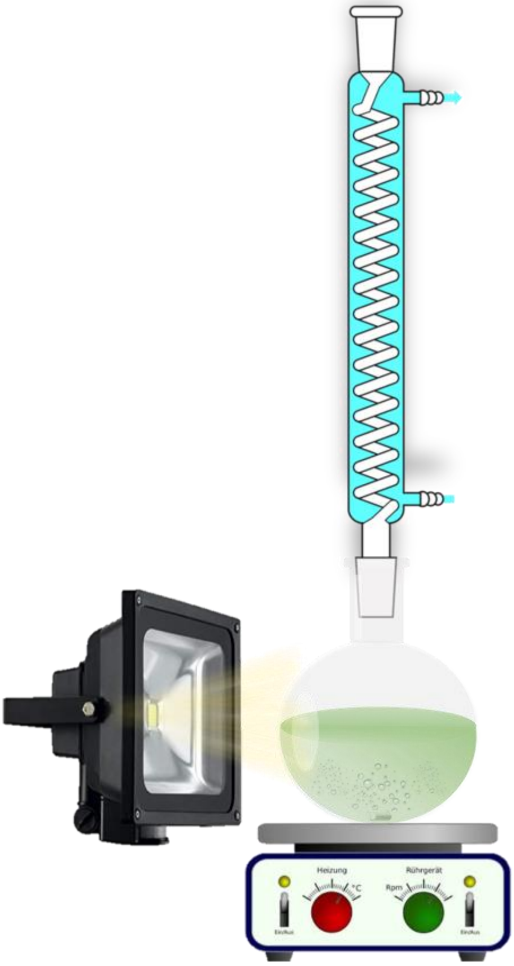

Figure 3. Photoreactor setup

## 3. Results and discussion

Photocatalytic instability of chlorophyllin sodium copper salt was studied by analyzing its decomposition rate under UV-Visible irradiation in aqueous medium. Figure 4 shows the UV-Vis absorption spectra for decomposition of chlorophyllin sodium copper salt. As shown, results indicate that chlorophyllin sodium copper salt decomposes rapidly over time. For a period of 3 hours, the Q band appeared around 360 nm of chlorophyllin sodium copper salt is almost completely decomposed with calculated rate of $4.9 \times 10^{-3}$ $min^{-1}$ as shown in Figure 11. Therefore, light harvesting capability of chlorophyllin sodium copper salt under photochemical or thermal condition is limited. Although, we attempt to test the decomposition of Diclofenac Potassium in presence of chlorophyllin sodium copper salt solution, results are shown in Figure

6 demonstrating a lower observed rate when compared to the new synthesized chlorophyllin sodium copper salt derivative photosensitizer i.e. 0.002 $min^{-1}$ relative to 0.0042 $min^{-1}$. Furthermore, as a control experiment, Diclofenac Potassium decomposition rate (Figure 5) was analyzed in the absence of the new synthesized photosensitizer, the decomposition rate constant found to be 0.0017 $min^{-1}$. In contrast, decomposition of Diclofenac Potassium in presence of the new chlorophyllin sodium copper salt derivative photosensitizer exhibits higher photocatalytic activities (Figure 7) compared to that of chlorophyllin sodium copper salt with a rate constant of $4.2x10^{-3}$ $min^{-1}$. Figures 8 and 9 present the graph of $C/C_0$ vs. time by which the variation of the concentration of observed for the different photosensitizers as well as control

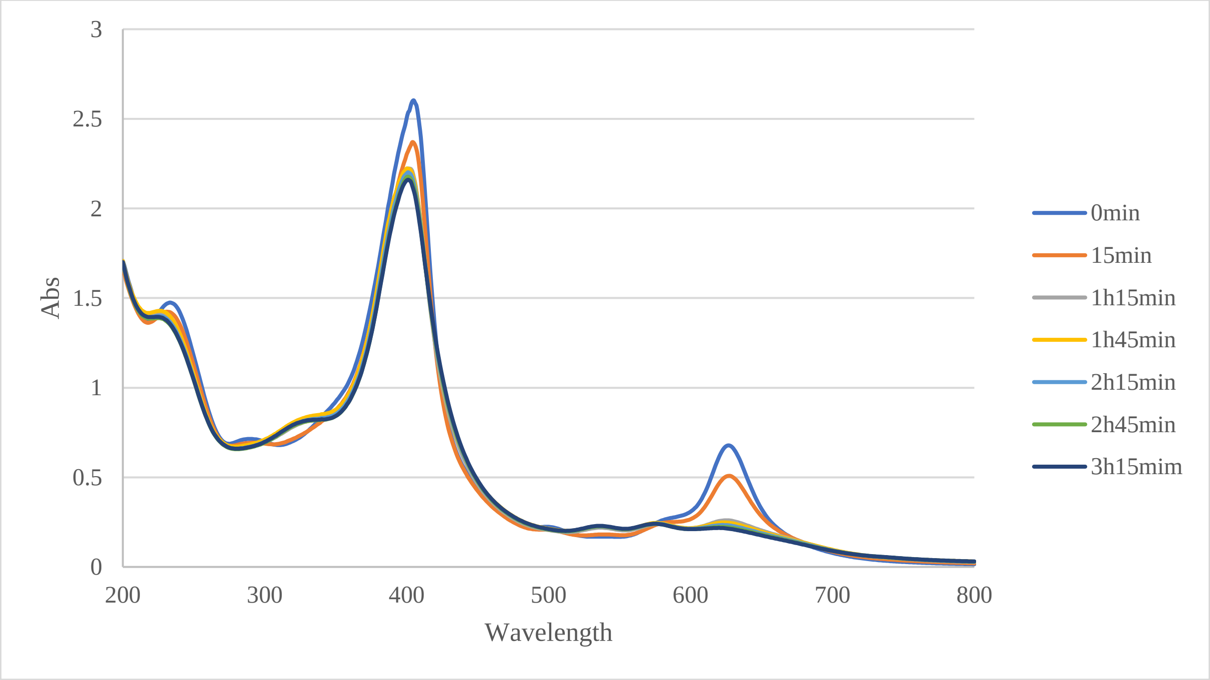

Figure 4. Decomposition of chlorophyllin sodium copper complex under visible light irradiation

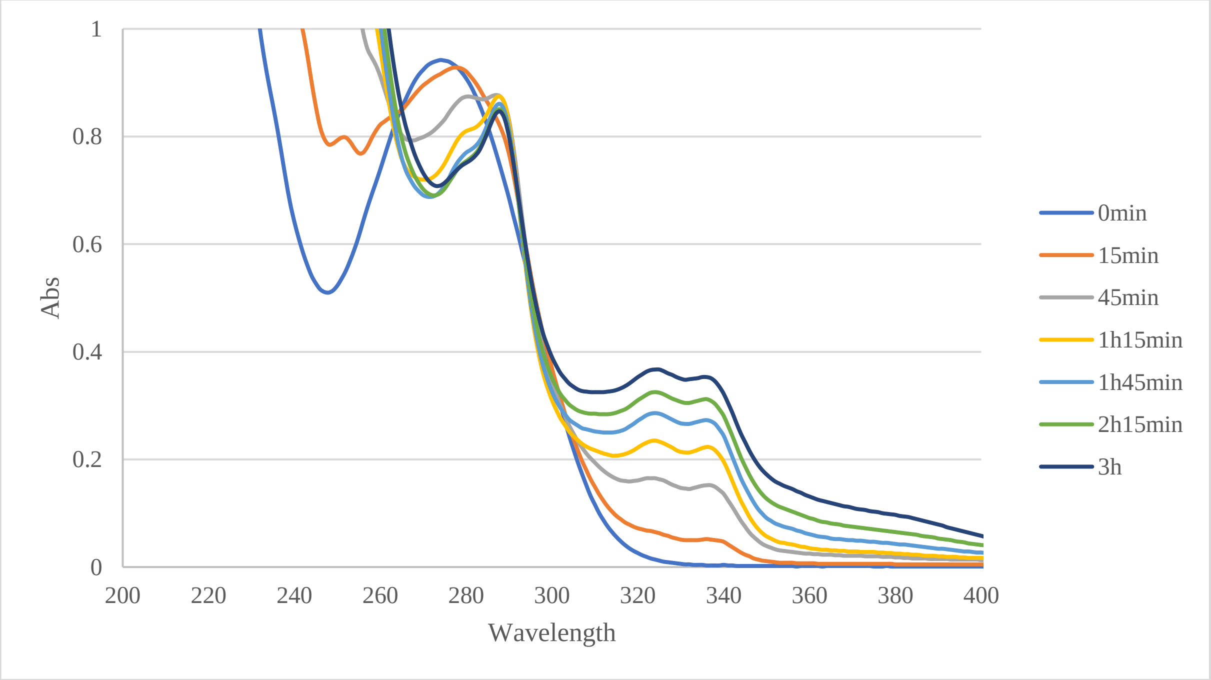

Figure 5. Decomposition of diclofenac under visible light irradiation

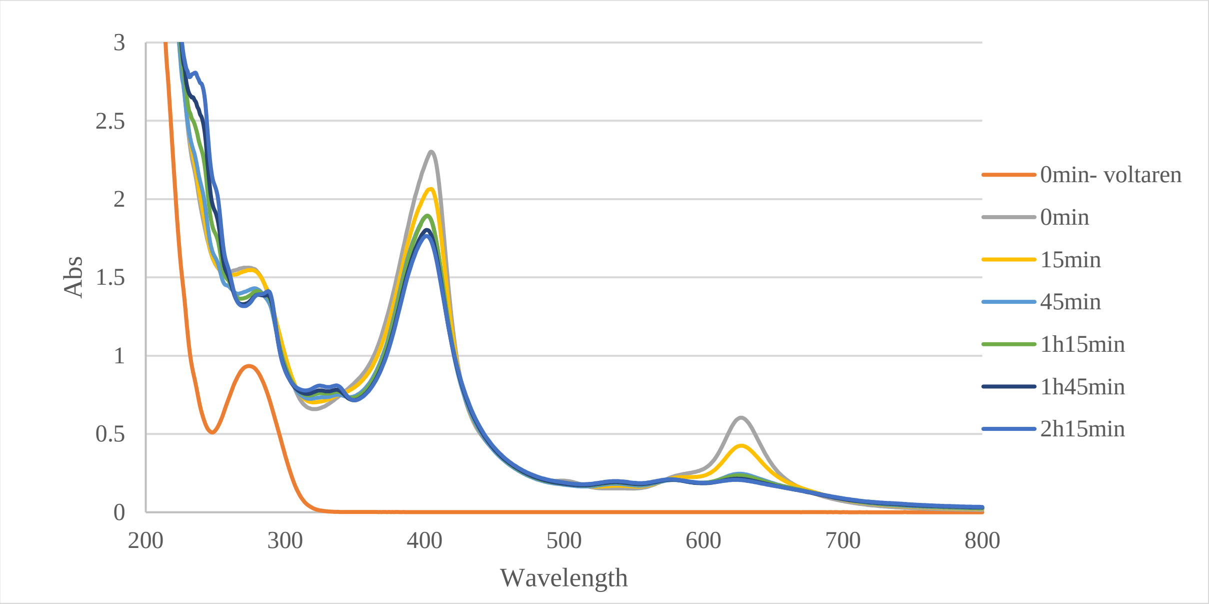

Figure 6. Decomposition of diclofenac in chlorophyllin sodium copper solution under visible light irradiation

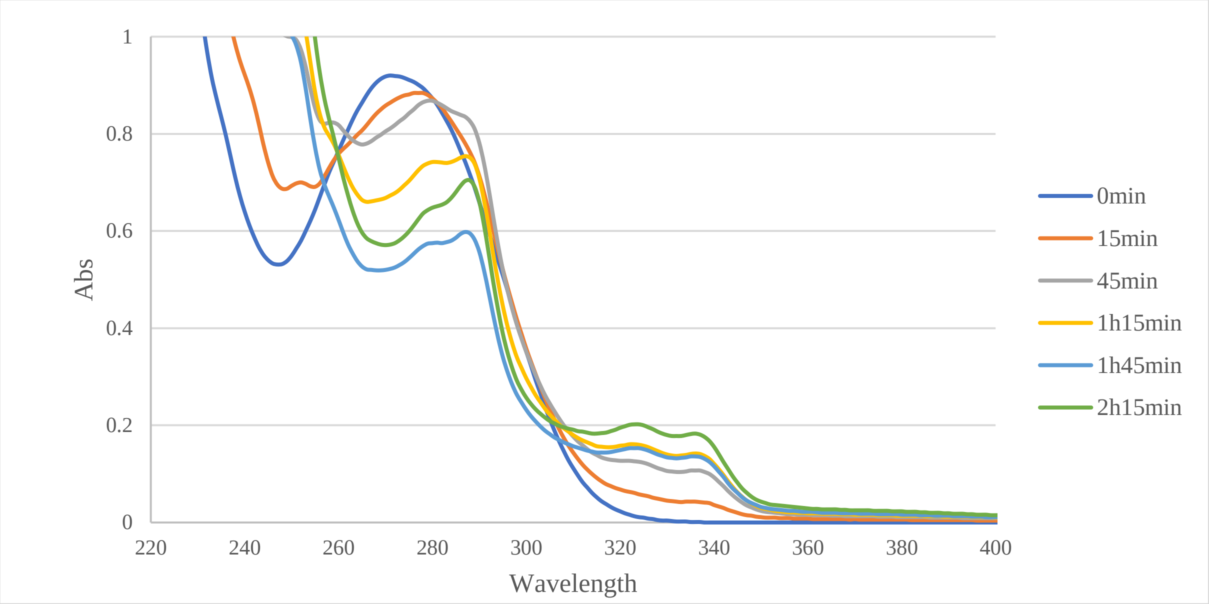

Figure 7. Decomposition of diclofenac under visible light irradiation in the presence of copper-chlorophyllin derivative.

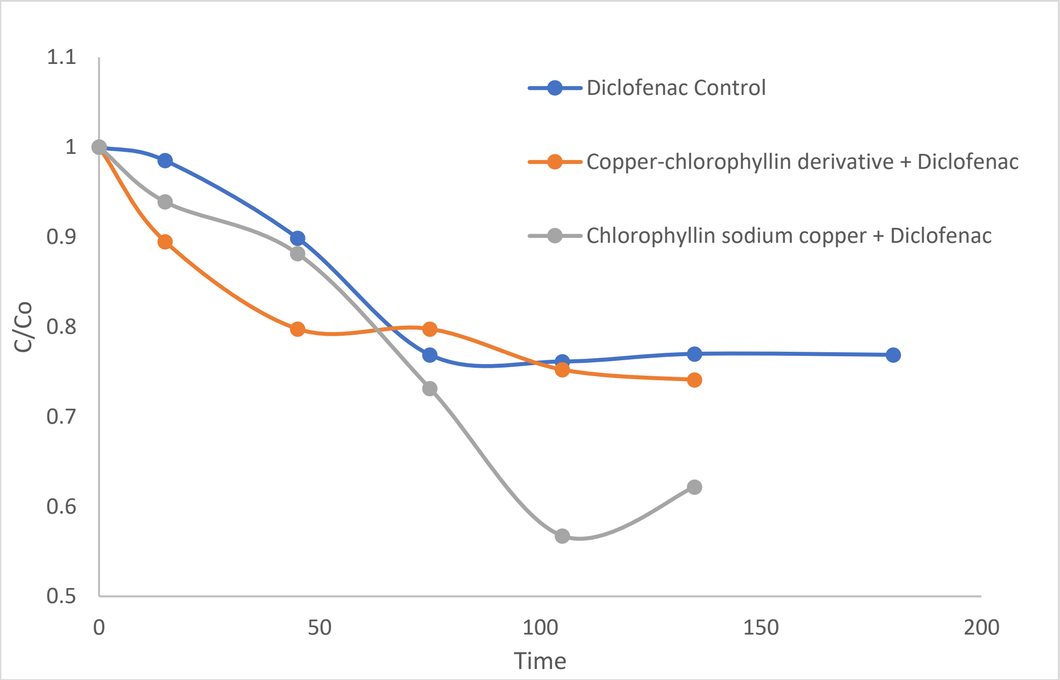

Figure 8. Variation of concentration of diclofenac over time under visible irradiation

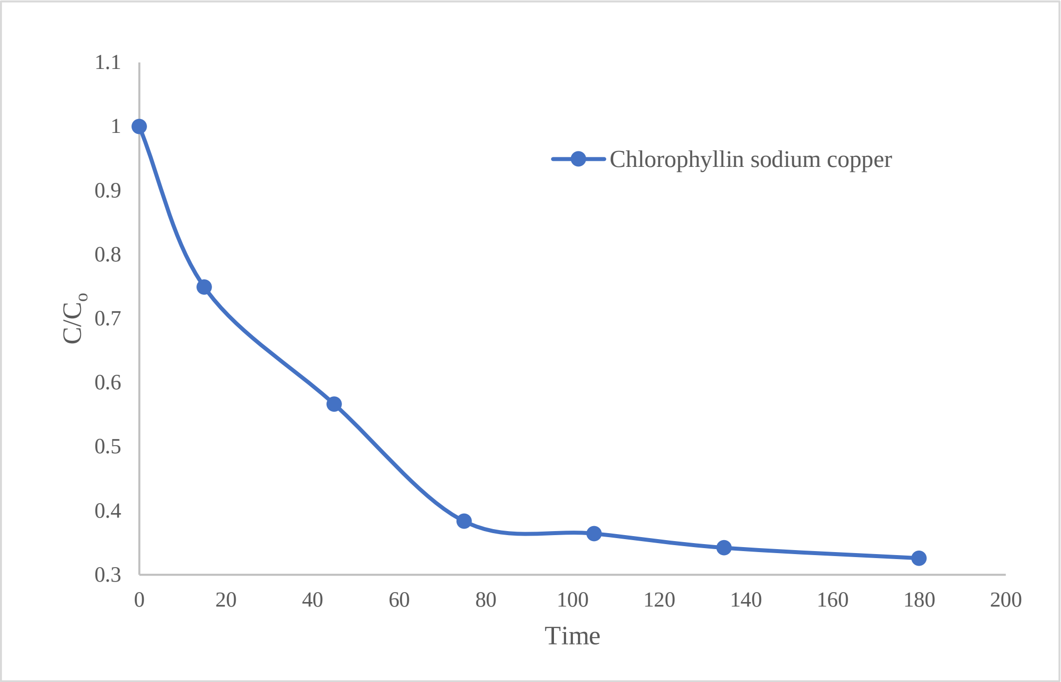

Figure 9. Variation of concentration of chlorophyllin sodium copper complex over time under Vis irradiation

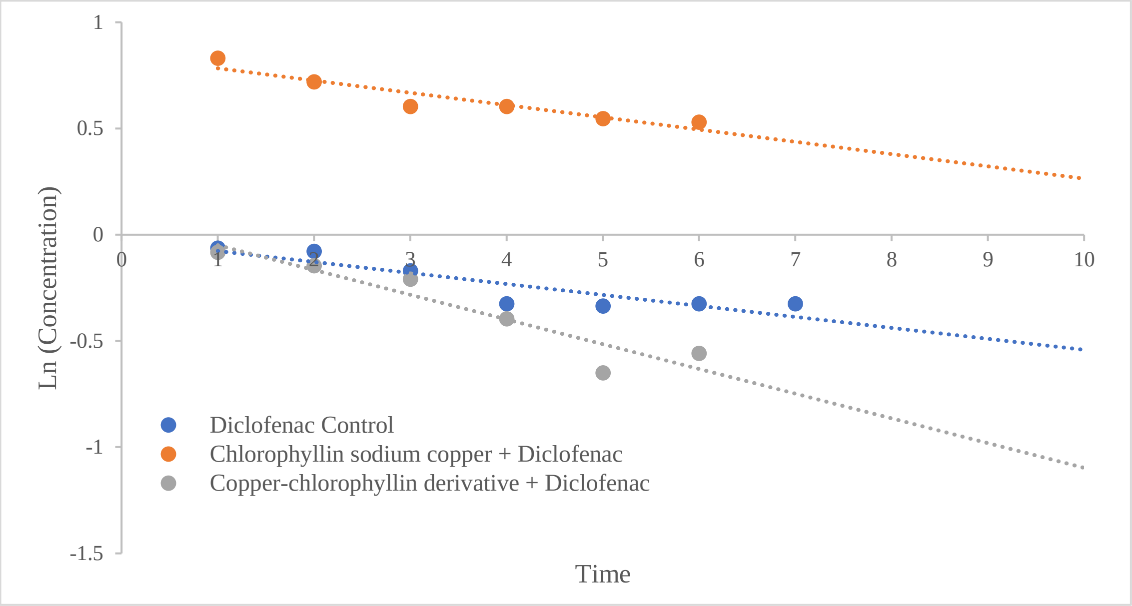

Figure 10. Kinetic plot of (Ln (Concentration)) over time for the disappearance of diclofenac.

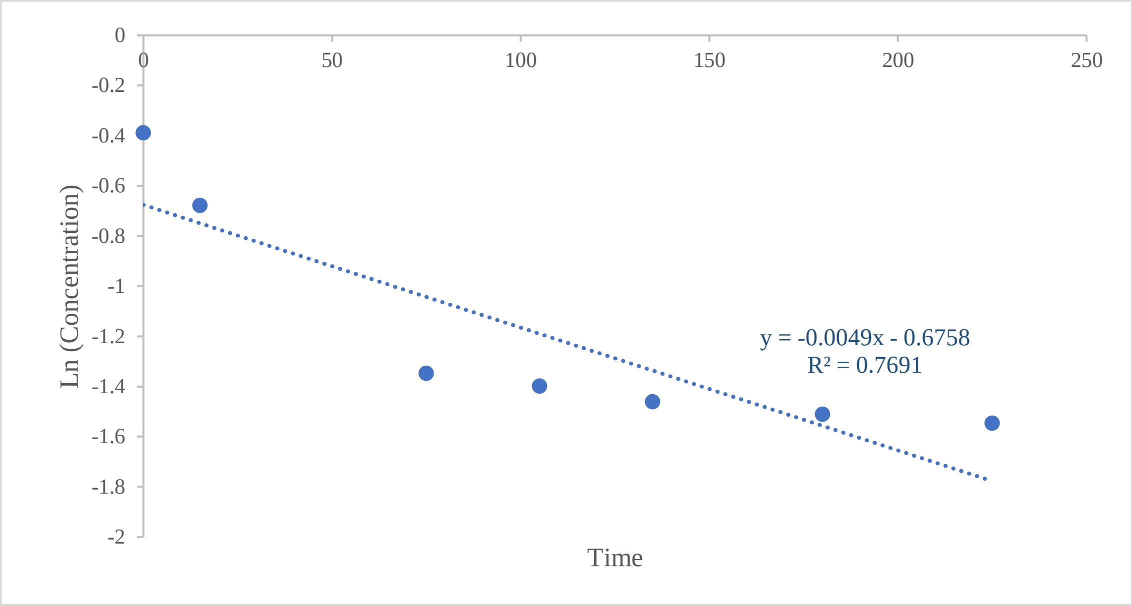

Figure 11. Kinetic plot of (Ln (Concentration)) over time for the decomposition of chlorophyllin sodium copper complex under visible irradiation.

experiments under visible light irradiation with time up to almost 3 hours. The variation in -ln ($C_o/C$) as a function of irradiation time was reported in Figures 10 and 11 by which the rate constants were calculated. The observed photocatalytic activity follows the order depicted in Figure 12.

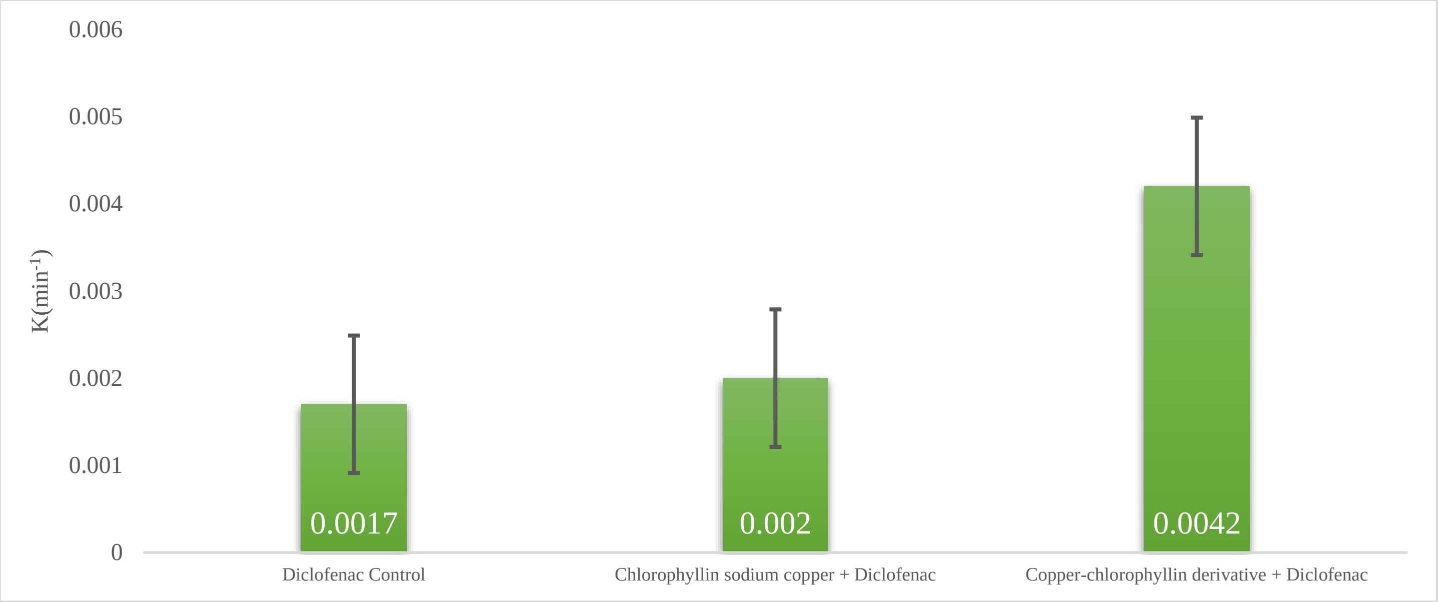

Figure 12. Rate constant for kinetic study

## Conclusion

New chlorophyllin copper complex derivative photosensitizer was synthesized using affordable commercially available copper-chlorophyllin as a starting material and a simple chemical method. The activity of the new photosensitizer was measured using model pharmaceutical Diclofenac Potassium in aqueous medium. The enhanced photocatalytic activity of the new synthesized photosensitizer is attributed to its stability under photochemical conditions when compared to chlorophyllin copper complex. The newly developed photosensitizer can be used as light harvesting in combination with photocatalyst which can be applied in photocatalytic energy relevant processes such as water splitting and carbon dioxide reduction.

## Acknowledgments

This research project was financially supported by the United Arab Emirates University research start-up fund, Ahmed Alzamly (grant no. 31S304).

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