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Original scientific article

REMOVAL OF XENOBIOTICS FROM WASTEWATERS USING PHOTOLYSIS UNDER SUN-LIGHT IRRADIATION: EXPERIMENTAL APPROACH AND PROCESS DESIGN

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Abstract

Conventional wastewater treatment processes are increasingly difficult to fulfill strict standards of achieving the required quality. Therefore, it is necessary to apply processes that in an efficient and economically justified way reach the necessary limits in order to discharge wastewater into the recipient. The process of photolysis represents the degradation of the starting pollutant practically to water and carbon dioxide. The whole process takes place under the action of a UV lamp that imitated solar irradiation. The process is environmentally justified since, unlike some other advanced oxidation processes - AOPs, there is no use of additional, hazardous, chemicals which possibly results in the precipitates formation that are leading to further treatment. In this paper, photolytic degradation of pesticide thiophanate methyl was performed in doubled wall quartz reactor equipped with a thermoregulation system. Reaction was forced under Osram ULTRA VITALUX UV lamp (300W). Kinetics of photodecomposition process was followed by pseudo-first order. In certain time periods, specimens were sampled, filtered and monitored by UV spectrophotometer Shimadzu 1800 with an aim to determine the concentration of xenobiotic. Complete degradation of present xenobiotics was obtained after 240 min. With an aim to enhance the degradation process, hydrogen peroxide was added as a boosting agent which cause a shortening in demanded time (150 min) for complete degradation. Verification of the success of decomposition was confirmed by the obtained values of chemical oxygen demand (COD), which reveal that the established system has a basis for real application in industrial or municipal wastewater.

Keywords: wastewater treatment, pesticide degradation, photolysis, AOPs, COD.

Introduction

Due to the excessive or improper use of pesticides, the rising demand for food production worldwide has not only produced a major decline in food quality and severe environmental effects (Abhilash & Singh, 2009). Various pesticides used in agricultural techniques to assure crop quality and food safety might cause the release of these compounds into non-target environmental matrices, such as freshwater bodies (Bustos et al, 2019). This is a serious issue because pesticides are typically recognized to have harmful qualities that can make exposure to these chemicals potentially lethal. In terms of human health, pesticide exposure has been linked to an increase in the occurrence of some forms of cancer and birth abnormalities, among other disorders (Kaur & Kaur, 2018). Furthermore, it is generally understood that these substances might pose a health danger to other living species (Damalas & Eleftherohorinos, 2011). A fungicide called thiophanate methyl was frequently applied

to crops to prevent fungal infections (Correia et al., 2016). It is not particularly persistent in soil or water systems, has a low aqueous solubility, and is not particularly volatile. Although it is not poisonous to mammals, it can irritate, cause skin sensitivity, and even be mutagenic (Jia et al., 2020). Most aquatic species and earthworms are poisonous to it, while birds and bees are less susceptible. Due to high water pollution with different organic compounds, many researchers are trying their best to develop techniques for the removal and degradation of them. Wastewaters from industrial factories and agricultural fields present a tremendous problem for modern society, in the area of health care and sustainability (Ungureanu et al., 2020). Therefore, oxidative process like photolysis is increasingly used in smaller wastewater treatment plants (Liu et al., 2011; Anisuzzaman et al., 2022). This process provides the degradation of many classes of organic compounds and biological pollutants. Photolysis is a process of degradation of various pollutants under the action of UV irradiation, where the parent molecule is converted into smaller ones.

The goal of this study was to thoroughly investigate the degradation of thiophanate methyl (TPM) under simulated sunlight in order to develop an appropriate technique for its removal from water. Measurement of chemical oxygen demand (COD) will help in further explanations of process efficiency. The effects of hydrogen peroxide addition and the distance of the UV lamp on degradation were examined. The reaction kinetics was further investigated using UV-VIS.

Materials and Methods

All used chemicals are analytically pure and without the need for further purification. Pesticide thiophanate methyl was obtained from Sigma Aldrich (European Commission, 2022). Hydrogen peroxide was also acquired from Sigma Aldrich. Photolytic experiments were performed in a doubled-wall quartz glass reactor (Figure 1). For irradiation of pesticide solutions, Osram Ultra Vitalux UV lamp nominal wattage of 300 W (UVA : UVB = 13.6 : 3) was used. During irradiation, the reactor is consistently cooled down by coolant water in the reactor jacket to avoid uncontrolled heating of the treated solutions. Photolytic tests in this study were carried out with starting TPM concentrations of 5 and 10 mg dm⁻³. For initial experiments, in the reactor 150 dm⁻³ of the abovementioned fungicide solutions were added. In certain periods, 3.0 dm⁻³ of the solution was taken and recorded via UV spectrophotometry. All measurements were taken in triplicate. In photolytic experiments, the concentration of TPM was measured using UV-VIS Spectrophotometer 1800, Shimadzu, Japan. COD was measured by EPA 410.4: 1993 standard.

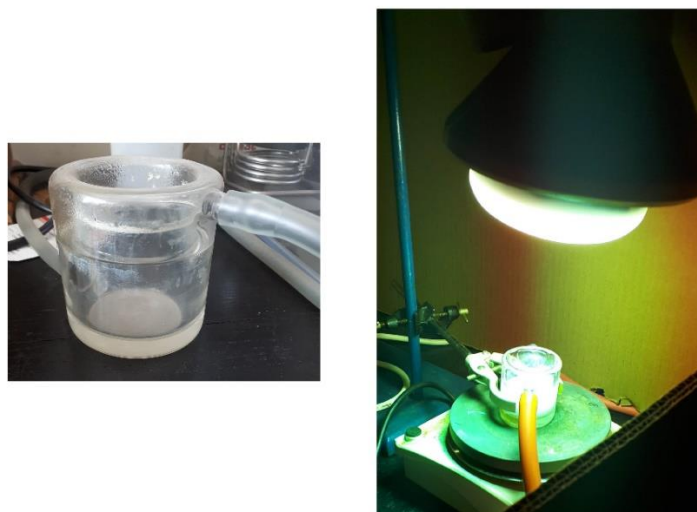


Figure 1. The reactor used for photolytic experiments

Results and discussion

At low concentrations of the organic pollutant, a pseudo-first order equation can be used to estimate the kinetics of photolytic reactions (Yusuff et al., 2020). In the Figure 2 are shown obtained curves with different symbols for all tests. They are representing the degradation of the present pollutant by sun-imitated irradiation and by sun-imitated irradiation with an addition 5% solution of H₂O₂.

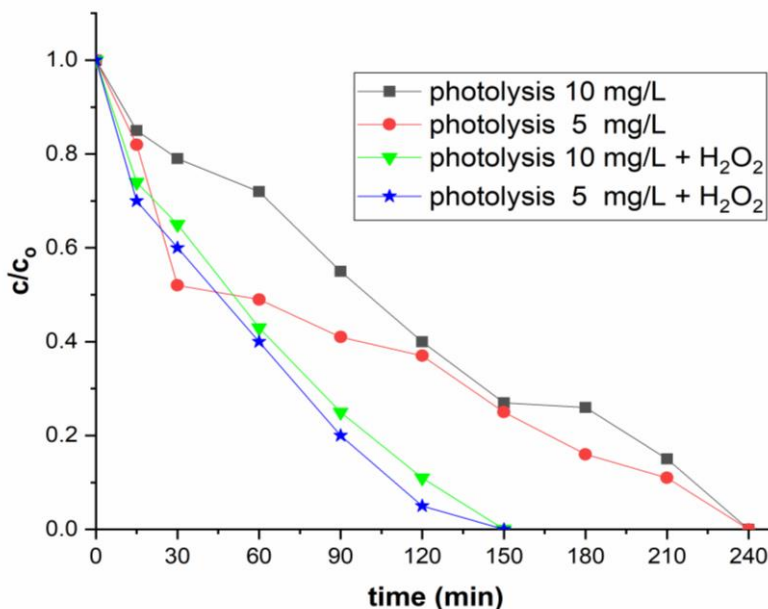


Figure 2. Degradation of TPM under different conditions

Photolytic tests reveal the relatively average degradation of TPM, which indicates the stability of this pesticide (which is in agreement with literature from Introduction). Results show that for both TPM concentrations, 5 and 10 mg dm⁻³, the needed time for complete decomposition was 240 min.

This is the reason for advancing photolytic reaction with the addition of H₂O₂ in order to fasten degradation of presented organic. The formation of peroxide radicals reduces the duration of the process due to accelerated oxidation of the pollution, which drives the degradation reaction and justify the necessity for an advanced process. Therefore, acquired results prove usage of this combination - 150 min as the required time for total decomposition of TPM (Figure 2).

By varying the distance of the lamp from reactor (from 100 to 400 mm), it was concluded that a distance of 200 mm has the best impact on degradation reactions. When the distance was the higher then 200 nm, photolytic degradation was lower by approximately 15% for 300 mm and approximately 25% for 400 mm. This can be explained by dissipation of emitted light. Contrastingly, when the gap between the rector and UV lamp was smaller, solution of TPM started to evaporate because of inability of the system to cool the working solution.

Measurement of COD values are shown in Figure 3.

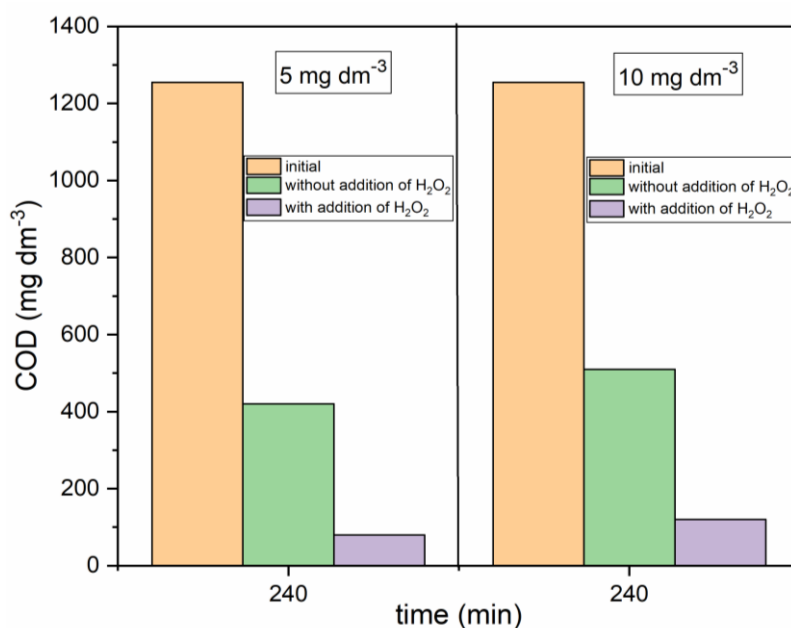


Figure 3. Monitoring of COD values prior and after the degradation of TPM

Determined initial value of COD for TPM solution was 1255 mg dm^{-3} . Following the 240 min of photolytic reactions, obtained values were 510 and 420 for 10 and 5 mg dm^{-3} , respectively. After the addition of 5% solution of H_2O_2 , values of COD were decreased, 120 and 80 for 10 and 5 mg dm^{-3} , respectively. This shows that the used system showed significant improvements.

Conclusion

Typical wastewater treatment systems are becoming increasingly difficult to meet stringent quality standards. As a result, in order to discharge wastewater into the recipient, processes that are efficient and economically justified must be used. Therefore, entire procedure is carried out under the influence of a UV light that simulates sun irradiation. The kinetics of the photodecomposition process was followed by pseudo-first order. Complete degradation of the present TPM was obtained after 240 min. With an aim to enhance the degradation process, hydrogen peroxide was added as a boosting agent which cause a shortening in demanded time (150 min) for complete degradation. Also, it was concluded that the optimal reactor-to-lamp distance was 200 mm. The estimated chemical oxygen demand (COD) values were used to evaluate the decomposition's success: 80 mg dm^{-3} for the concentration of TPM of 5 mg dm^{-3} , which reveal that the established system has a basis for real application in industrial or municipal wastewater.

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