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VISIBLE-LIGHT PHOTOCATALYTIC DEGRADATION OF TARTRAZINE USING ZnO NANOPARTICLES: PRELIMINARY PHYTOTOXICITY INVESTIGATIONS ON TREATED SOLUTIONS

BY

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Abstract. Effluents containing synthetic dyes are often discharged untreated, contributing to widespread contamination and disrupting aquatic ecosystems. Advanced oxidation processes (AOPs), particularly photocatalysis, offer promising alternative solutions to address this issue. This study investigates the photocatalytic degradation of tartrazine (TZ) using elaborated zinc oxide. The toxicity of the transformation products generated during this process was also examined. Preliminary phytotoxicity tests using *Lepidium sativum* L. seeds revealed significant growth of vegetative organs in untreated solutions. Similar values to the control sample were observed in photocatalytically treated solutions, possibly due to the conversion of toxic intermediates into less harmful by-products. The successful elimination of TZ under visible-light irradiation

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conditions confirms the potential of ZnO-based photocatalysis as a viable solution for mitigating water pollution caused by food dye contaminants.

Keywords: degradation, food dyes, *Lepidium sativum*, photocatalysis, phytotoxicity.

1. Introduction

The discharge of pollutants in water effluents, particularly residual colors from various industries such as paper and pulp, textile, dye, pharmaceutical, cosmetics, rubber, paints, and printing industries, poses a significant environmental threat globally (Ali *et al*., 2018). Beyond compromising the aesthetic quality of water, these pollutants also pose a threat to marine flora and fauna (Alcantara-Cobos *et al*., 2020).

Food colors play a significant role in influencing food choices by impacting taste, sweetness, and overall pleasantness. Synthetic food dyes, in particular, are preferred due to their stability, cost-effectiveness, and their pivotal role in the food industry (Spence, 2015). Among the commonly used artificial food colors are azo dyes, specifically aromatic azo compounds such as tartrazine (TZ). For the present research, tartrazine is selected as a model pollutant representative of such dyes. This dye, identified as an orange-colored, water-soluble substance, known also as Acid Yellow 23, E102 or FD & C Yellow 5 or C.I. 19140), is widely employed (Soufi *et al*., 2022).

Some studies have highlighted the potential hazards associated with tartrazine, including food allergies, mutagenicity, carcinogenicity, and phototoxicity (Aoudjit *et al*., 2018; Chekir *et al*., 2017; Gupta *et al.*, 2011). Additionally, its chemical composition and reactivity pose challenges for its elimination through conventional treatments, as well as biological and physicochemical processes, leading to difficulties in achieving effective removal (Masunga *et al*., 2022).

In this particular context, the demand arises for advanced and effective treatment methods aimed at eliminating resilient organic pollutants. This ensures their proper removal and adherence to environmental regulations. Two key approaches for this purpose are adsorption (Wang *et al*., 2019; Harja *et al*., 2016) and advanced oxidative processes (AOP) (Hama Aziz, 2019; Hien *et al*., 2019; Favier *et al*., 2019). Advanced oxidative processes (AOPs) have proven effective in treating dye wastewater due to their capacity to generate highly reactive free radicals, particularly the hydroxyl radical (•OH) (Zhang *et al*., 2021; Lutic *et al*., 2022). These radicals exhibit a significant capability to engage in redox reactions, facilitating the degradation of organic pollutants. Among the various AOPs, heterogeneous photocatalysis stands out for its unique characteristic of inducing redox reactions under irradiation, whether from UV or visible light, utilizing different catalysts (Silva *et al.*, 2022). This method showcases its efficiency in the breakdown of organic pollutants through photochemical reactions.

Considering the available information, the primary objective of this study was to examine the effectiveness of photocatalytic treatment in eliminating the tartrazine dye. Following this, the viability of the photocatalytic process was evaluated concerning the elimination of toxicity, determined through ecotoxicity tests utilizing a higher plant species. The study provides relevant details regarding the efficacy of the visible-light/ZnO system in removing organic pollutants such as TZ, from aqueous matrices and suggests the implementation of environmentally safe techniques for water purification.

2. Materials and methods

2.1. Chemicals

The photocatalyst used in this study was zinc oxide (ZnO) obtained by the low super-saturation coprecipitation method, using a NaOH solution as (co)precipitation agent, at a constant pH of 10, following the method proposed by Lutic *et al*., 2012. The anionic dye tartrazine (TZ) ($C_{16}H_9N_4Na_3O_9S_2$, 534.3 g/mol, purity ≥85%) was purchased from Sigma Aldrich, its chemical structure is given below (Fig. 1).

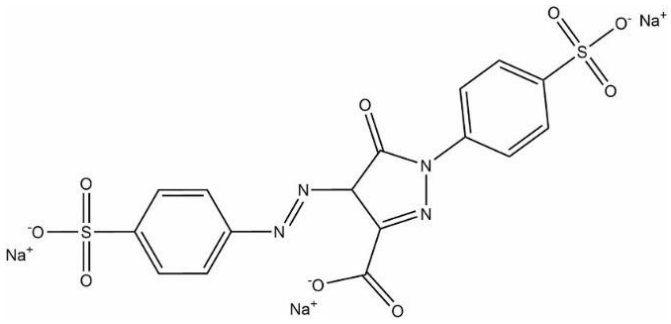

Fig. 1 – Chemical structure of tartrazine.

2.2. Photocatalytic tests

Photocatalytic experiments were conducted within a discontinuous glass reactor with a total capacity of 600 mL, isolated from light and maintained at room temperature. A volume of 300 mL of TZ working solution was introduced into the reactor, followed by the addition of a known quantity of catalyst.

The solution was agitated at 450 rpm throughout the experiment. The visible light lamp was preheated for 30 minutes before utilization, ensuring its maximum illumination power. In order to monitor the progression of the photocatalytic reaction, samples were extracted at various time intervals. The kinetics of the experiments were investigated through absorbance spectroscopy.

The photocatalytic reactions were carried out over an irradiation period of 330 minutes.

The degradation percentage of TZ was calculated using Eq. (1):

$$(\%)Degradation = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where:
C_0 = Concentration of dye solution, measured at time zero (mg/L);
C_t = Concentration of the dye solution over time (mg/L).

2.3. Phytotoxicity tests on the species "*Lepidium sativum* L."

Lepidium sativum L. (water cress) seeds were used in the current study. The tests performed involved the analysis of the initial pollutant solution and the final dye photo-treated solution, using the procedure followed by Vrinceanu *et al*. (2019). The seeds were not pretreated. Ten selected and undeteriorated seeds of nearly identical size were placed on filter paper (Whatman No. 1) in a 90 mm Petri dish and 3 mL of solution was added. The seeds were placed evenly on the surface of the filter paper on the bottom of the Petri dish. As a control sample, Petri dishes were prepared in which only distilled water was added. To avoid water loss and seed fungal contamination, the Petri dishes were sealed with parafilm and further on, placed in a growth chamber at 23 ± 2°C, under a photoperiod of 16 h light/8 h dark. The number of germinated seeds was then counted and root elongation was measured after 72 hours. All the experiments were carried out in duplicate and the data were expressed as ± standard error of the mean.

The Seedlings Vigor Index (*SVI*, %) was evaluated based on the germination percentage, considering both radicle and hypocotyl length (Garrido *et al*., 2023). Equation (2) was used to determine the value of *SVI*.

$$SVI = \frac{L_r + L_h}{G} \times 100 \quad (2)$$

where:
L_r – average radicle length and L_h – average hypocotyl length in the polluted sample (test solution) (mm);
G – seed germination degree (%).

2.4. Tartrazine analysis

Samples were taken out at regular intervals, and the supernatants were used to test the absorbance of the solution using a UV-visible double beam

spectrometer (SHIMADZU UV -1280) set to λ_{max} = 440.5 nm to determine the residual dye concentration.

3. Results and discussion

Preliminary experiments were conducted to assess the effectiveness of photocatalysis. Our analysis involved testing three primary removal methods to evaluate the degradation efficiency of TZ in contaminated water. To optimize the experimental conditions, we assessed the impact of photocatalysis, photolysis and adsorption on a 20 mg/L TZ solution, monitoring the process for 330 minutes through absorption spectrophotometry. Photolysis, conducted without the introduction of a catalyst, aimed to elucidate tartrazine photosensitivity and its potential degradation under visible light exposure. The adsorption experiment involved the addition of 0.4 g/L ZnO, isolating the system from light. This step determined the minimum adsorption time required for effective experimentation. The selected 60-minute adsorption time was found to be ideal for achieving full saturation of the photocatalyst before initiating photocatalysis, ensuring consistent pollutant adsorption and degradation rates. Consequently, this time was selected for further experiments.

The results (Fig. 2) indicate that both adsorption and photolysis exhibit limited effectiveness in tartrazine removal, as evidenced by the sustained low degradation rates ranging from 1.4% to 2.9%. This contrasts significantly with the degradation rate achieved through the application of the photocatalysis process, which reached 26%.

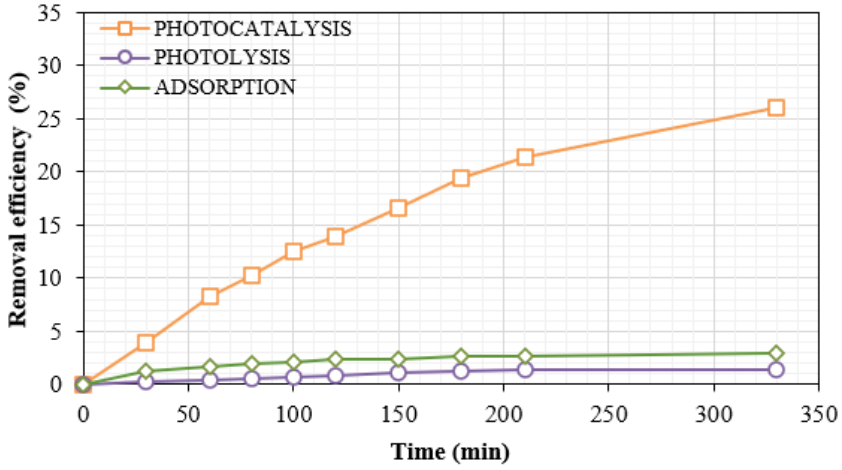

Fig. 2 – Influence of photocatalysis, photolysis and adsorption on tartrazine dye degradation (initial TZ concentration of 20 mg/L, catalyst loading of 0.4 g/L, visible-light irradiation, pH of natural solution, ambient temperature).

The initial concentration of the pollutant in water is a critical parameter required thorough analysis, given its potential impact on the treatment process efficiency. Consequently, the experiment was conducted with variations in the initial concentration of TZ, ranging from 5 mg/L to 20 mg/L.

The degradation process was carried out under the following controlled conditions: a constant catalyst loading of 800 mg/L, irradiation with visible light, natural solution at pH 7.4, and at room temperature. Analysing Fig. 3, the results obtained on the degradation process show that a low concentration (5 mg/L) leads to 100% degradation in 330 minutes, indicating high efficiency of the process. At higher concentrations, such as 10 mg/L, the efficiency decreases to 66%, while at 20 mg/L, we obtained a 55% degradation. This is the result of a restricted quantity of active catalyst sites, which limited the production of oxidants while increasing the quantity of pollutant. Several researchers have also reported a similar phenomenon (Bouarroudj *et al*., 2021; Cao *et al*., 2022; Dou *et al*., 2020).

Thus, we can conclude that the initial TZ concentration has a significant impact on the efficiency of the degradation process. The lower the initial concentration, the faster and more efficient will be the degradation process.

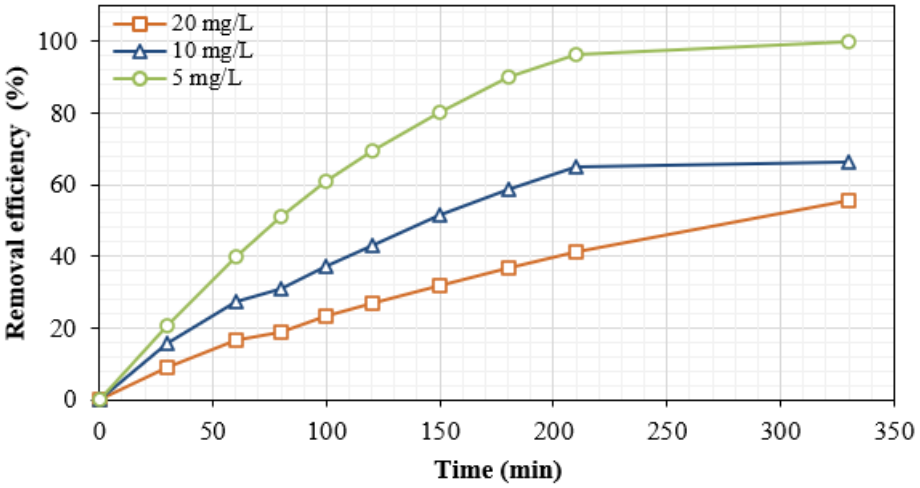

Fig. 3 – Influence of initial tartrazine concentration on the degradation process (pollutant concentration [TZ] = 5, 10 and 20 mg/L, catalyst loading = 0.8 g/L, visible-light irradiation, pH of natural solution, ambient temperature).

Moreover, time-dependent UV-vis spectra is reported for the photocatalytic degradation of TZ dye (Fig. 4). The absorption peak at 440.5 nm showed a gradual decrease with no shift or alteration of the spectrum at this wavelength for the investigated pollutant. A decrease in absorbance can be observed as the photocatalytic reaction time is longer indicating dye degradation.

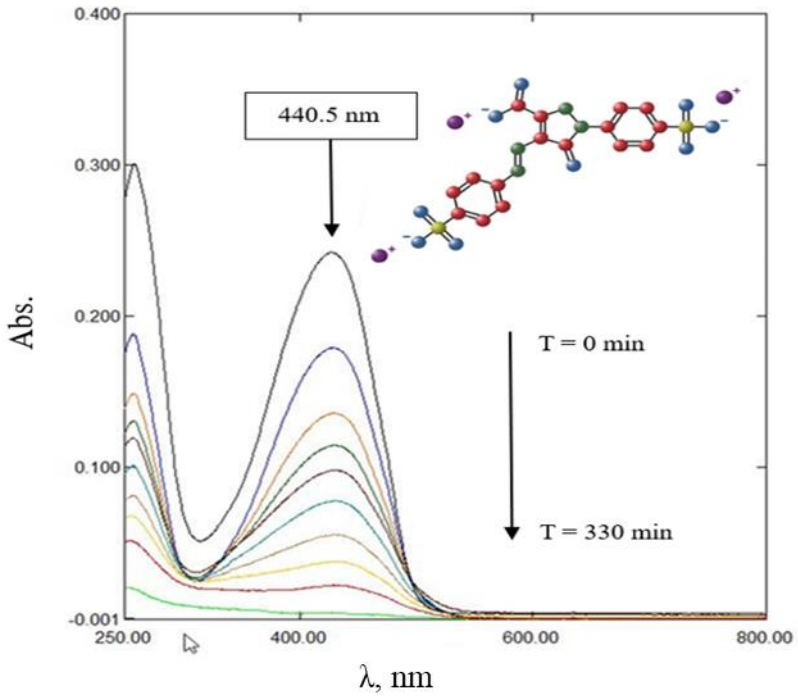

Fig. 4 – Absorption UV-vis spectra of samples taken at specific time intervals during the photocatalytic degradation process of TZ (20 mg/L, 0.8 g/L ZnO catalyst, visible-light irradiation, pH of natural solution, ambient temperature).

In order to determine the feasibility and effectiveness of the visible light/ZnO system photocatalytic degradation process, phytotoxicity tests were carried out. The purpose of these tests was to determine how much toxicity is eliminated during the oxidation of an organic contaminant. The pollutant molecules undergo a variety of chemical breakdown processes during this phase, such as oxidation, reduction, and addition. By-products from these modifications are probably going to be more dangerous than the initial material. In this work, we evaluated the toxicity of TZ samples derived from photocatalytic treatment using a higher plant species, *Lepidium sativum* L. In this study, initial phytotoxicity experiments were carried out using an untreated solution with a starting dye concentration of 20 mg/L and a sample taken at the final reaction time of 330 min, in the presence of 0.8 g/L catalyst.

Figure 5 provides an overview of the results, presenting the mean values for radicle, hypocotyl, and leaves lengths for the plant species under investigation. It was noted that the untreated solution led to a significant increase in the components of *L. sativum* L. plants, possibly attributable to a hormesis effect. Hormesis is a dose-response relationship characterized by inhibition at high doses and growth stimulation at low doses of the pollutant (Małkowski *et al*., 2020).

Similarly, Alcantara-Cobos *et al*. (2020) reported a 20% stimulation in root and stem growth at an initial concentration of 10 mg/L TZ. This phenomenon has been observed previously in plants exposed to other organic compounds, such as antibiotics at concentrations of 0.01 mg/L (Pan and Chou, 2016).

Following our results, we can notice that more pronounced hormetic effect was observed in the radicles compared to the hypocotyl and leaves. Subsequently, at the final reaction time, the results approached those of the control sample, indicating the efficiency of the photocatalytic degradation process for the target compound and other potential by-products generated during the process.

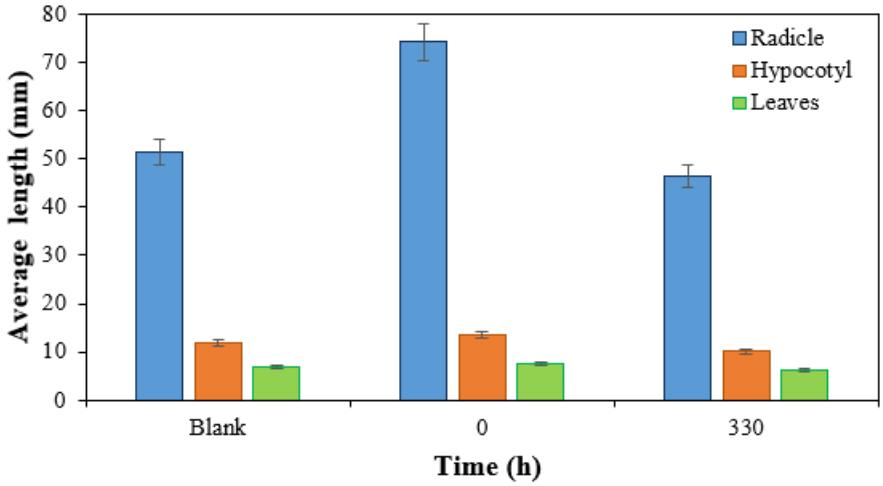

Fig. 5 – Average radicle, hypocotyl, and leaves length for *Lepidium sativum* L. determined for control (blank sample), initial and phototreated solution (20 mg/L initial TZ concentration, 0.8 g/L catalyst load).

Regarding the values obtained for the *SVI*, the results are presented in Fig. 6. We considered to investigate this toxicity parameter in order to assess germination performance. The results acquired demonstrated a similar pattern in the case of the initial dye solution, indicating the manifestation of the hormesis effect. Baderna *et al*. (2015) states that this biostimulation, which was found at low doses, may be the first adaptive reaction to low concentrations of one or more toxicants. The first stimulation may then develop into strong toxicity at higher concentrations of toxicants or at longer exposure times. Subsequently, at the end of the treatment, minor difference of only 6.77% was observed in relation to the control sample.

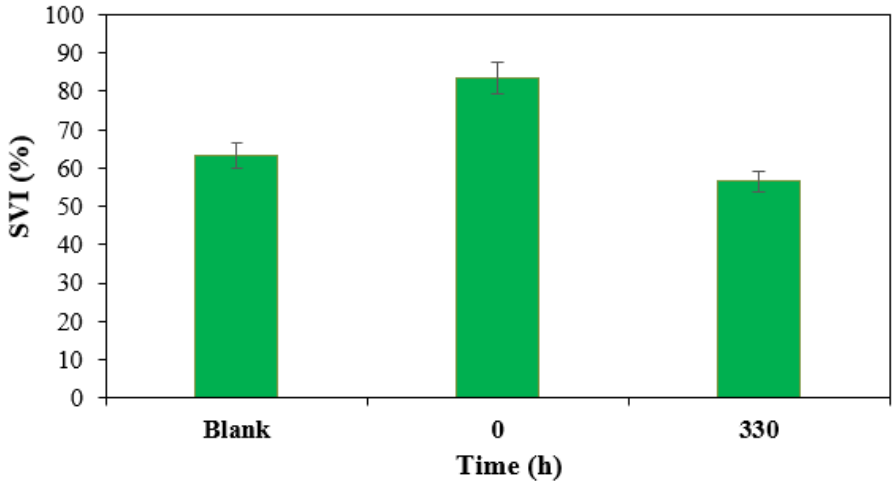

Fig. 6 – *SVI* (%) of *Lepidium sativum* L. determined at time zero and 330 min of reaction (initial TZ concentration, 0.8 g/L catalyst load).

4. Conclusions

The findings presented in this study validate the potential of the advanced oxidation method employing the ZnO/visible-light system as a promising option for eliminating the TZ dye. This dye is recognized for its notable stability and solubility within the aqueous environment.

At a concentration of 5 mg/L, 100% degradation was achieved in 330 minutes according to the results of the degradation procedure, suggesting high efficiency.

Additionally, ecotoxicity data obtained in this research revealed a 23% increase in the case of radicle, as well as for the other vegetative organs, for the initial solution, most likely due to the phenomenon of hormesis. This aspect should be kept in mind for conducting more detailed research in the near future.

It has been demonstrated that the values of samples collected after 330 minutes of irradiation exhibit profiles similar to those of the uncontaminated control sample, supporting the idea of the effectiveness of the degradation process in reducing toxicity and the occurrence of reaction by-products that may have a more toxic nature than the initial compound.

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DEGRADAREA FOTOCATALITICĂ ÎN LUMINĂ VIZIBILĂ A TARTRAZINEI FOLOSIND NANOPARTICULE DE ZnO: CERCETĂRI PRELIMINARE PRIVIND FITOTOXICITATEA SOLUȚIILOR TRATATE

(Rezumat)

Efluenții care conțin coloranți sintetici sunt adesea deversați netratați și contribuie la contaminarea generalizată, provocând perturbări în ecosistemele acvatice. Procesele de oxidare avansată (AOP), în special fotocataliza, au fost evidențiate ca alternative promițătoare pentru a rezolva această problemă. În acest cadru, lucrarea prezentă explorează degradarea fotocatalitică a Tartrazinei (TZ) în prezența unui oxid de zinc prelucrat. Toxicitatea produselor de transformare generate în timpul acestui proces a fost, de asemenea, studiată și discutată. Testele preliminare de fitotoxicitate folosind semințe de *Lepidium sativum* L. dezvăluie o creștere semnificativă a organelor vegetative ale plantelor în soluția netratată. Valori similare cu cele ale probei de control au fost observate și în cazul soluțiilor tratate fotocatalitic, posibil datorită conversiei intermediarilor toxici în subprodușI mai puțin dăunători. Conform rezultatelor colectate, eliminarea cu succes a TZ în condițiile de iradiere cu lumină vizibilă este confirmată, evidențiind potențialul fotocatalizei pe bază de ZnO ca soluție viabilă pentru atenuarea poluării apei cauzată de coloranți alimentari.