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Solar Light-Driven Degradation of Isoprinosine – Efficiency of the Processes and Kinetic Calculations

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ABSTRACT

The photocatalytic degradation of the antiviral drug Isoprinosine (inosine pranobex, IPN) by TiO_2-P25, ZnO and SnO_2 was investigated in two different aquatic matrices, i.e. milli-Q-water (MQ) and tap water (TW) under solar irradiation of 500 W/m^2. The changes in concentration of IPN during all experiments were monitored using HPLC at a wavelength of 260 nm, and the photocatalytic degradation of IPN followed pseudo-first-order kinetics. The highest value of the pseudo-first-order rate constant of IPN photodegradation (k) was obtained by the presence of 20 mg/l TiO_2-P25, (k = 0.0483 min^{-1}) in MQ water with the value of the coefficient of determination (R^2) equal to 0.9268. The study also assessed the impact of photocatalyst doses and initial IPN concentrations on the efficacy of IPN photodegradation. The results showed that IPN was resistant to degradation under only sunlight (without any photocatalysts addition), with a degradation rate of 9% after 2 hours in milli-Q water and 16% after 2 hours in tap water. However, the addition of selected photocatalysts resulted in the breakdown of the IPN molecule. TiO_2-P25 was particularly promising among the tested photocatalysts. The research also discovered that IPN partially adsorbed to TiO_2 particles (33% after 2 hours), ZnO particles (26% after 2 hours), and SnO_2 (4% after 2 hours). Based on the findings, solar-light-driven photocatalysis could be a promising technique for the degradation of certain antiviral drugs in water matrices after optimizing the process.

Keywords: isoprinosine, photocatalysts, solar light degradation, water pollution.

INTRODUCTION

Anthropogenic micropollutants are a broad and chemically heterogeneous group of environmental pollutants, in which residues of various types of pharmaceuticals play a particular role. Their common feature is that they occur in the environment in low concentrations ranging from the level of ng/L to µg/L (Wang et al., 2023), but even at such concentrations they have biological activity and pose a potential threat to living organisms. There are several routes for drugs and their metabolites to infiltrate the aquatic environment, but wastewater treatment plants are often recognized as the principal focal source (Kumar et al., 2020). Pharmaceuticals are found in rivers and streams in significantly lower concentrations than the authorized doses; yet there is concern that long-term exposure to some substances may cause serious health issues and that specific chemicals can interact with one another to harm the body (Ahmed et al., 2023). Antiviral drugs occupy a very special place among anthropogenic micropollutants. Antivirals are frequently excreted primarily in the bioactive condition of their parent dosage. The metabolism of antiviral medications in the human body has a significant impact on how much of them is released into the environment (Jain et al., 2013). Isoprinosine (IPN), for example, which is used for the treatment of various viral infections (e.g. caused by herpes viruses (HSV), measles and some respiratory viruses), and has also been tested as an adjunct to COVID-19 treatment, was excreted in substantial amounts by patients during the pandemic and reached the WWTPs (waste water treatment plant) in biologically active forms (Gwenzi et al., 2022). Isoprinosine is regarded as an emerging pollutant because of its increased use

and consequent environmental discharge during the COVID-19 pandemic. At present, there is no data reported on the toxicity of IPN in water environment. However, about 7 ng/L and <0.08 µg/L of azithromycin and ivermectin respectively were found in water. Dexamethasone was detected with 0.73 ng/L in surface water, and an average of 50-60 ng/L of favipiravir (Efrain Merma Chacca et al., 2022). The presence of antiviral drugs in natural waterways is heavily influenced by epidemic cycle, antiviral drug intake, and environmental conditions (Dharmaraj et al., 2021; Nippes et al., 2021). Thus, seasonality alters antiviral fate and transit in the aquatic environment.

Isoprinosine, known also as Inosine pranobex, is an antiviral and immunostimulant medication. Although this drug is not an officially approved drug in the treatment of COVID-19, some physicians have recommended this drug for the treatment of COVID-19 in an outpatient setting, and additionally, some publications show the potential of this drug in the therapy of COVID-19 (Beran et al., 2021). In many countries, inosine pranobex-based medications are only accessible on prescription; however, in Poland, these preparations are available over the counter (OTC). As a result of it, the consumption of isoprinosine has increased significantly during the past few years. In the treatment of more severe cases, inosine pranobex was also used, although in combination with other medications. Like other antivirals, it is expected that the residues of IPN that are not metabolized can end up in the environment, which could lead to anthropogenic contamination (Nannou et al., 2020).

It is necessary to apply various treatment technologies to purify effluents containing pharmaceutical compounds. Among the available techniques, advanced oxidation processes (AOPs) are more efficient than other methods (Garrido-Cardenas et al., 2020). For example, activated carbon adsorption (Guillossou et al., 2019), air stripping (Nanda & Berruti, 2021), and reverse osmosis (Trishitman et al., 2020), these techniques only move the pollutants from one phase to another without their degradation. The efficiency of biological processes depends on the degradability of compounds. Unfortunately, drug residues often remain undecomposed due to their resistance to biodegradation. (Saleh et al., 2020). As a solution, new approaches are investigated for the ultimate sewage treatment following the biological process. Among these alternatives, photocatalysis is particularly promising, especially if it can be activated by sunlight, which lowers the overall expenses of the treatment. Photocatalysis is an advanced oxidation process, emerging as a promising technology in wastewater treatment. One of the main advantages of the process is that there are no mass transfer limitations, and it can operate under ambient conditions (Dong et al., 2022). In addition, the catalyst used in photocatalysis is such as TiO_2 are inexpensive, commercially available, non-toxic, and photochemically stable. However, there are currently more photocatalysts being searched for that have the aforementioned characteristics.

Photocatalytic processes are highly effective in breaking down various organic pollutants, including carboxylic acids (Chen et al., 2020), chloroanilines (Iazdani & Nezamzadeh-Ejhieh, 2021), chlorophenols (Zhen et al., 2020), dyes (Rafiq et al., 2021), pesticides (Zeshan et al., 2022), volatile organic compounds (Kutluay, 2021; Yadav & Ahmaruzzaman, 2023), and pharmaceuticals (El Mouchtari et al., 2020). In particular, studies have shown that TiO_2 photocatalysis can successfully degrade lincomycin (Khamani et al., 2021), sulfamethoxazole (Zhu et al., 2019), and antivirals (Prakash et al., 2022). However, no study on degradation of isoprinosine (IPN) in water matrices using photocatalysis has been reported.

The aim of this research is to assess the susceptibility to degradation of isoprinosine, an antiviral drug, that has been recommended by some physicians as an alternative therapy for outpatient treatment of COVID-19, in the broadly understood aquatic environment, using processes initiated by (artificial) sunlight by using photocatalysts i.e., TiO_2-P25, ZnO and SnO_2, and to determine the impact of selected matrix parameters on the efficiency of degradation of this drug.

MATERIALS AND METHODS

Chemicals

Analytical standard of Isoprinosine (IPN) was purchased in highest available purity (≥ 98%) CAS number 36703-88-5 from Cayman Chemical, Poland. Acetonitrile Chromoscan® for HPLC analysis was purchased from POCH S.A. (Poland). Titanium (IV) oxide degussa P25 (CAS number 13463-67-7), zinc oxide (CAS number 1314-13-2; purity 99.9%), and Tin

(IV) oxide (CAS number 18282-10-5; purity 99.9%). All photocatalysts were purchased from Sigma-Aldrich.

Artificial solar light setup

The research focused on the degradation of isoprinosine using artificial solar light and was carried out in the Solar-box 1500e System, manufactured by Co.fo.me.gra in Italy. This advanced system comprises a 1500 W polychromatic Xenon lamp that releases electromagnetic radiation. The radiation passes through a long-lasting soda-lime glass filter, providing natural outdoor exposure conditions. The filtered xenon light's spectral power distribution is closest to the sun, providing a similar environment to conduct research. The radiant heat emitted by the Xenon Lamp is continuously controlled and monitored by a built-in B.S.T. (Black Standard Thermometer). The internal temperature of the system was maintained at 35±2 °C. In this study, the behavior of the investigated drug with two different water matrices, such as milli-Q (MQ) and tap water (TW), at irradiance 500 W/m² (reported as the average insolation for the 52nd parallel north is precisely measured at midday in September, tracing across several countries including Aleutian Islands, Germany, Netherlands, England, Canada, and the US.), as well as the impact of selected photocatalysts such as TiO_2, ZnO, and SnO_2 doses on IPN, and photodegradation efficiency were studied using artificial solar light. All experiments were performed at two different concentrations: 10 mg/L, and 20 mg/L of each selected photocatalyst. For photolysis, about 200 mL of an aqueous solution of IPN was filled into a glass beaker and then placed on a magnetic stirrer inside the Solarbox system for 120 minutes. In the case of photocatalysis, the studies were carried out with a specific dose of each photocatalyst. All of the experiments were done in duplicate.

Dark probe studies

In order to determine the adsorption isotherms of the investigated substance with each selected photocatalyst, the experiments were performed with the stock solution of 500 mg/L of IPN, diluted to 200 mg/L with each water matrix in different beakers, tightly covered with aluminum foil to minimize the potential exposure of the samples to sunlight, and then placed on a magnetic stirrer inside the Solar-Box system for 120 minutes. All of the experiments were carried out in duplicate.

HPLC-UV analysis

IPN was quantified using high-performance liquid chromatography with a variable wavelength detector (UltiMate 3000 system, Dionex Corp., Sunnyvale, CA). All samples were filtered using MCEMF-Millipore® Membrane Filters with 0.22 µm pore size from Merck, Germany. For chromatographic separation, a C18 Hypersil™ Gold column (250×4.6 mm; pore size: 5 mm) from Thermo Scientific, Polygen, Poland was used. The mobile phase consisted of a 40:60 (v/v) volumetric ratio of acetonitrile. An isocratic flow rate of 1.0 mL/min was utilized during the analysis, resulting in a retention time (RT) of IPN at 5.0 ± 0.1 min under the specified conditions. The limit of quantification for IPN was established as 0.1 mg/L, which is the first lowest calibration point of the calibration curve (linear regression, $R^2 > 0.99$). The calculated signal-to-noise ratio (S/N) was found to be greater than 10, indicating high sensitivity of the method used. The limit of detection (LOD) for IPN was determined as 0.03 mg/L, based on an S/N ratio of 3. The wavelength used for the analysis was 260 nm, and the data was evaluated using Dionex Chromeleon™ 6.8 software.

Kinetics studies

To examine the kinetic mechanisms of photolysis and photocatalytic removal of IPN using specific semiconductors, the pseudo-first-order kinetics method is used with all the experimental data. This method relies on the concentration of the reactant in a chemical reaction. The linear form of the pseudo-first-order equation is given below:

$$C_{IPN}/Co_{,\mathrm{IPN}} = exp^{-kt \cdot t} \quad (1)$$

where: C_{IPN} and $Co_{,IPN}$ – drug amount adsorbed at equilibrium and at time t, respectively (mg/g), k_t – a rate constant (min^{-1}), obtained from the slope of the graph C/C₀ vs time (min).

The half-life of the reaction is determined by the following equation:

$$½t = ln2/k_t \quad (2)$$

Half-life of the reaction is the time needed to achieve 50% photolytic or photocatalytic removal of selected pollutant (½t, min). All pseudo

first order calculation is calculated by using SAP Interactive Excel.lnk.

RESULTS AND DISCUSSION

Photolytic removal of isoprinosine

As illustrated in Figure 1, the photolysis of isoprinosine, a complex of acetaminobenzoic acid, dimethylaminoisopropanol, and inosine in a 3:3:1 ratio ($C_{10}H_{12}N_4O_5$: $3C_9H_9NO_3$: $3C_5H_{13}NO$, 1115.23 g/mol) in two different water matrices was observed. The finding shows that after 90 mins of exposure of light irradiance 500W/m^2, IPN was only degraded by 9%, in MQ water. However, in the case of environmental matrices (TW), the removal rate of isoprinosine was 14% after 120 mins, indicating that in environmental conditions, IPN will not undergo further changes. According to predicted environmental concentration (PEC), IPN should be remove with the efficiency of >80% (Tobólska et al., 2018). However, the limited experimental data does not provide sufficient evidence to support this claim. The degradation kinetics of photolysis of IPN (Table 1) followed the pseudo-first-order kinetics. The degradation rate constant of isoprinosine was 0.0006 and 0.0013 min^{-1} in MQ and TW respectively. The photolysis time necessary for the half-life of isoprinosine was 1155 and 533 min in MQ water and environmental water matrices, respectively. According to the study findings, the photodegradation rate constant for IPN removal from tap water is higher than that of Milli-Q water and the slight decomposition of isoprinosine under solar light indicates that it will not undergo further changes in environmental conditions. It was observed that the total organic carbon (TOC) content did not decrease during photolysis, which suggests that the IPN did not break down into minerals. Instead, the reason for the IPN's removal from MQ water when exposed to sunlight was due to the conversion of its compounds into byproducts. In contrast, the concentration of TOC was reduced in TW, but this could be due to the presence of other organic matter in TW that underwent mineralization.

Selection of photocatalysts

The advance oxidation (solar-light driven) process using semiconductors has been promising process in degrading the organic pollutants in water environment as it does not require additional chemicals and generates harmless compounds, such as carbon dioxide (CO_2), water (H_2O), and mineral acids. This process involved two steps:

1. Photoexcitation of the semiconductor, which generates the electrons (e^-) and holes (h^+) as charge carriers.
2. The migration/recombination of charge carriers with the emission of light.

According to reported studies, various semiconductors are used as photocatalysts. For example, tungsten (VI) oxide (WO_3) (Guo et al., 2023), zinc sulfide (ZnS) (Domyati, 2023), iron (III) oxide (Fe_2O_3) (Adekunle et al., 2021), gallium arsenide (GaAs) (Xu et al., 2022), and cadmium sulfide (CdS) (Iqbal et al., 2019). (Wang W.L. et al., 2015) demonstrated the effectiveness

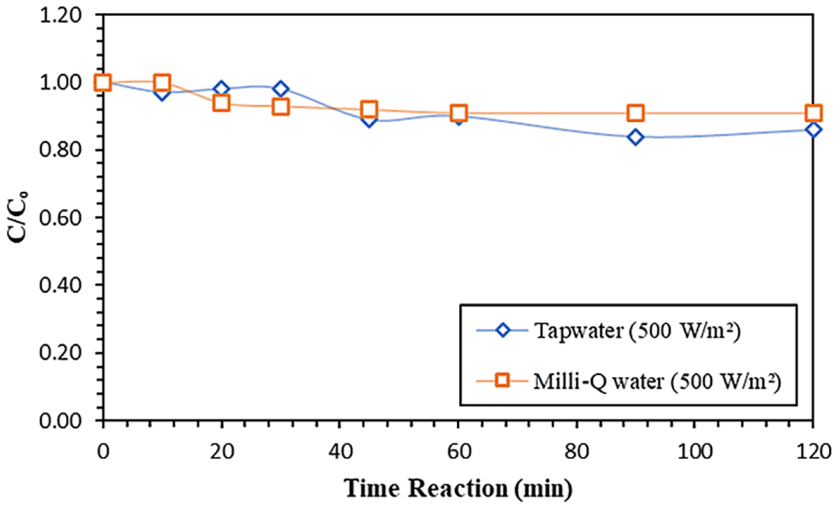

Figure 1. Solar light driven photolysis of IPN (10.0 mg/L) at irradiance of 500 W/m^2

of TiO_2-P25 for the photocatalytic removal of the antiviral drug Tamiflu (oseltamivir phosphate). The kinetic rate constant value was 0.040 min^{-1}, followed by pseudo-first-order kinetics with an R^2 value greater than 98.0%. The results showed that 95% of the drug (21 μM) was eliminated after 80 min of UV-A irradiation using 100 $mg \cdot L^{-1}$ of TiO_2-P25. In another reported work, ZnO proved to be a highly efficient photocatalyst in the photodegradation of three pharmaceutical contaminants progesterone (PGS), ibuprofen (IBU), and naproxen (NAP) in water. After 120 minutes of UVA irradiation, PSG, IBU, and NAP were degraded up to 92.3%, 94.5%, and 98.7%, respectively, when ZnO was present in concentrations of 100 and 200 $mg \cdot L^{-1}$ (Sabouni & Gomaa, 2019). Another study reported the photocatalytic degradation of naproxen by using SnO_2/Activated carbon nanocomposite (SnO_2/AC). The results indicated that within 2 hours, 94% of naproxen had degraded. The photodegradation rate constant (k) was found to be $2.5 \cdot 10^{-2}$ min^{-1}, consistent with a pseudo-first-order reaction (Begum & Ahmaruzzaman, 2018).

In this study, titanium dioxide (TiO_2-P25), zinc oxide (ZnO), and tin (IV) dioxide (SnO_2) have been chosen for solar light degradation of targeted compound at very low doses such as 5.0, 10.0 and 20.0 mg/L which are considered as safe . Also, the selected photocatalyst are promising material that has been widely used in photocatalytic processes due to their properties, such as excellent optical and electronic properties, high photocatalytic activity, high chemical stability, low cost, non-toxicity, and environmental friendliness.

Photocatalytic removal of isoprinosine

Removal of isoprinosine by using TiO_2-P25

The removal efficiency of the investigated compound in the presence of artificial solar light was dependent on the exposure time and water matrices, as mentioned in "Photolytic removal of Isoprinosine" chapter. The study has shown that IPN is not susceptible to degradation by artificial solar light with an irradiance of 500 W/m^2. In order to compare, the experiment was conducted in the presence of selected photocatalyst. At the beginning of the experiment, a kinetic study in the absence of light on the selected photocatalyst (TiO_2-P25) was performed. The degradation kinetics of IPN in dark probe experiments is pseudo first order. It has been shown that under dark probe studies, the removal efficiency of targeted compound is 33% after 120 min. It means that IPN is partially adsorbed on TiO_2-P25 particles.

The photocatalytic experiment was performed on the IPN under the exposure of 500 W/m^2 artificial light irradiance, with the doses of TiO_2-P25: 5.0 mg/L, 10.0 mg/L, and 20.0 mg/L in both water matrices. After 30 min of the process, the concentration of IPN in MQ at doses of 5.0 and 10.0 mg/L was below its <LOD: 100% (Fig. 2). However, in the case of the TW, with the doses of 10.0 and 20.0 mg/L of TiO_2-P25, the <LOQ: 15% and <LOQ: 88% were observed with the passage of 120 min of reaction time, respectively. The increase in the reaction rate of IPN photodegradation in the presence of TiO_2 in both water matrices obtained in direct photolysis, was confirmed by the estimation of the kinetic parameters of these

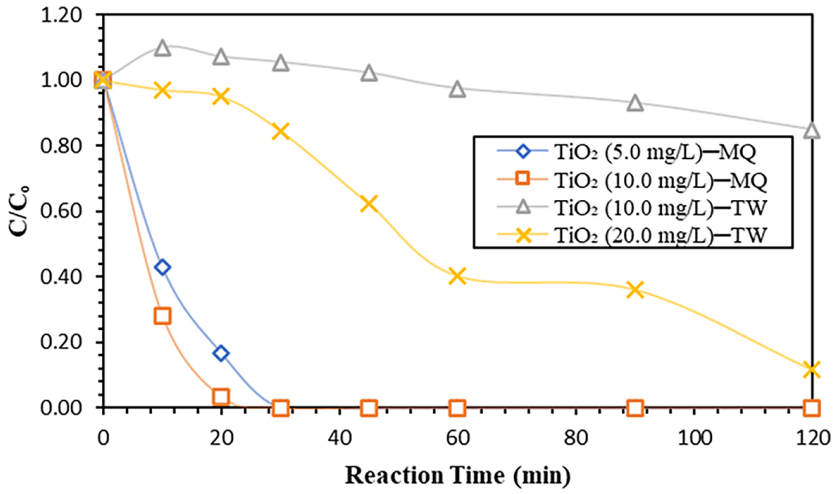

Figure 2. Solar light degradation of IPN using TiO_2-P25

reactions. Direct photolysis usually described by a first-order equation. The kinetic parameters of the above findings are listed in (Table 1). The kinetic rate constant of IPN based on the results obtained by UV-TiO_2-P25 is higher in TW with a catalytic dose of 20.0 mg/L. The coefficient of determination (R^2) shows that the experimental data of this study obtained fits the regression model. The results suggest that increasing the dose of the selected photocatalyst can eliminate the IPN in environmental water matrices.

Removal of isoprinosine by using ZnO

In order to check the photocatalytic removal efficiency with ZnO in both water matrices, the dark probe study has been performed initially. It has been shown that under the absence of solar irradiance, only 26% of IPN was degraded with the reaction time of 90 min. which indicates that the removal efficiency of IPN by sorption to the surface of ZnO under dark conditions is lower than TiO_2P-25. In addition, experiments in the presence of solar light irradiance (500 W/m^2) with the selected doses of ZnO; 5.0 mg/L, 10.0 mg/L, and 20.0 mg/L in both water matrices have also been studied. After 120 min to the exposure of irradiance combined with the doses of ZnO 5.0 and 10.0 mg/L, the degradation of IPN in MQ was found to be <LOQ: 88% and 98% respectively. The k_t values determined for IPN by ZnO show that the study followed pseudo first order reaction kinetics (Table 1). In contrast, degradation of IPN in TW, 36% and 93% removal of IPN was observed with the catalysts dose of 10.0 and 20.0 mg/L respectively (Fig. 3). Among all selected concentrations of catalytic doses, 20.0 mg/L (in MQ) showed the highest pseudo kinetic rate constant $k_t = 0.0101$ min^{-1} with the R^2 of 0.9178.

Removal of isoprinosine by using SnO_2

The kinetics of photocatalytic degradation of the targeted compound were studied by experimenting with SnO_2 without solar light. The results showed that only 4% of IPN degraded after 120 min in the dark probe experiment, which is considered negligible for kinetic analysis. Figure 4. illustrates that the photocatalytic degradation of IPN followed pseudo-first-order kinetics with an irradiance of 500 W/m^2. The degradation of IPN had slightly high-rate constant (0.0025 min^{-1}) in TW, compared to the degradation constant in MQ water (0.0023 min^{-1}), with a catalyst dose of 20.0 mg/L. Table 1 shows the coefficient of determination (R^2) and the half-life of the process. The <LOQ: 28% and <LOQ: 32% were observed with the passage of 120 min of reaction time in MQ and TW, respectively.

Various investigations have been reported on photocatalytic activity of SnO_2 in environmental research and energy. For example, SnO_2 NPs was able to degrade organic pollutant from aqueous solution with the efficiency of 91.7% at 298 K within 190 min (Ebrahimian et al., 2020). However, in current study, SnO_2 was unable to degrade

Table 1. Kinetic parameters–first-order pseudo constants of isoprinosine degradation

Process	Conc. mg/L[a]	Water Matrices	Kt [b], min^{-1}	½ t^c, min^{-1}	R^2
Photolysis	10.0	MQ	0.0006	1155.2	0.6576
		TW	0.0013	533.2	0.813
UV-TiO_2 P–25	5.0	MQ	0.0326	21.3	0.9252
	10.0		0.0483	14.3	0.9268
	10.0	TW	0.0018	385.1	0.7832
	20.0		0.0079	8.77	0.9497
UV-ZnO	5.0	MQ	0.0076	91.2	0.9101
	10.0		0.0088	78.8	0.8081
	10.0	TW	0.0032	216.6	0.8419
	20.0		0.0101	68.63	0.9178
UV-SnO_2	10.0	MQ	0.001	69.3	0.9402
	20.0		0.0023	301.4	0.9914
	10.0	TW	0.001	693.1	0.7377
	20.0		0.0025	277.3	0.9588

Note: [a] Concentration of photocatalysts,[b] pseudo first order reaction constant, [c] half-life of the reaction.

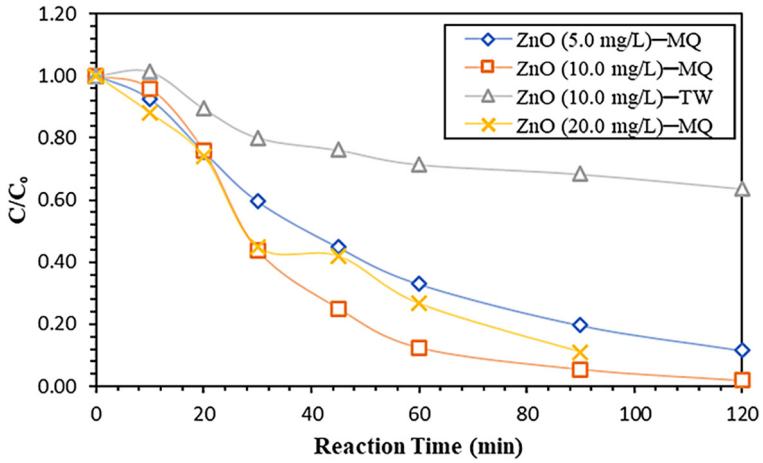

Figure 3. Solar light degradation of IPN using ZnO

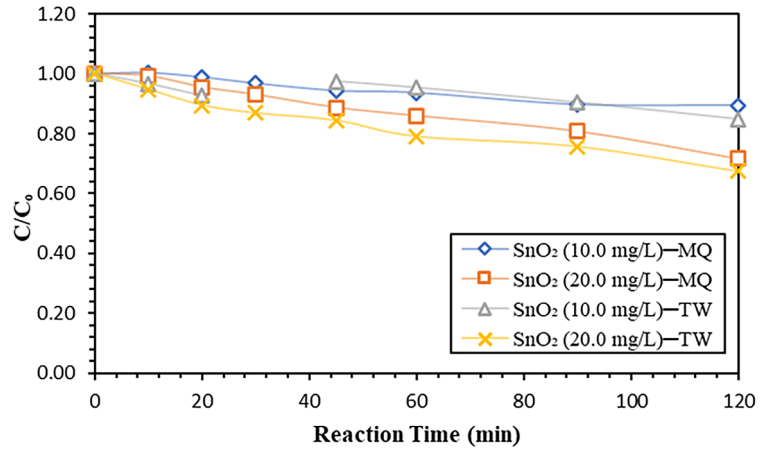

Figure 4. Solar light degradation of IPN using SnO_2

the targeted pollutant effectively. According to reported studies, the practical application of traditional SnO_2 in photocatalysis falls short due to its inherent physical features. Its wide bandgap of approximately 3.6 eV restricts the absorption of ultraviolet light, resulting in low sunlight utilization (Sun et al., 2022). Additionally, there is a significant recombination of photogenerated electrons and holes. Therefore, it is imperative to adjust the SnO_2 band to significantly increase charge, optimize carrier separation to improve transmission, and undertake surface modification to ensure a highly efficient redox reaction, which further enhances its photocatalytic activity.

CONCLUSION

The study examined the effectiveness of three different photocatalysts, i.e., TiO_2-P25, ZnO, and SnO_2, in degrading Isoprinosine in two types of water under artificial solar irradiation. The results indicated that SnO_2 (10 mg/L) was not successful in decomposition the pollutant in either type of aquatic matrices. On the other hand, TiO_2-P25 (5.0 and 1.0 mg/L) was the most effective in MQ water, achieving a degradation rate of 100% after 30 minutes of exposure. The photocatalytic reactions followed pseudo-first order kinetics rate constants in all experiments, and the highest kinetic rate constant was observed in TiO_2-P25 (0.0483 min^{-1}) in MQ water. The rate constant was 0.0079 min^{-1} in TW for TiO_2-P25 and ZnO with a catalysts dose of 20.0 mg/L each. However, the physical properties of SnO_2 limited its efficiency in breaking down the pollutant. Thus, future research should focus on enhancing its photocatalytic activity by improving its physical characteristics through surface modification, band gap adjustment, and carrier separation optimization.

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