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Comparison of photocatalytic performance of $Sr_{0.9}La_{0.1}TiO_3$ and $Sr_{0.25}Ca_{0.25}Na_{0.25}Pr_{0.25}TiO_3$ toward metoprolol and pindolol photodegradation

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ABSTRACT

The photocatalytic performance of Sr0.9La0.1TiO3 and Sr0.25Ca0.25Na0.25Pr0.25TiO3 perovskite-based catalysts was studied under different radiation types (simulated solar, LED, and UV radiation) for the removal of metoprolol and pindolol. The results showed that both materials effectively removed metoprolol and pindolol, with the highest degradation efficiency observed under UV radiation. The degradation efficiency of metoprolol went up to 30% using Sr0.9La0.1TiO3 and Sr0.25Ca0.25Na0.25Pr0.25TiO3 with all the radiation types mentioned. Pindolol was degraded more efficiently, using Sr0.9La0.1TiO3, 68%, 94%, and 100% of pindolol was degraded after 240 min under SSI, UV-LED, and UV irradiation. Using Sr0.25Ca0.25Na0.25Pr0.25TiO3, degradation efficiency was 65%, 84%, and 93%, under SSI, UV-LED, and UV irradiation, respectively. The chemical oxygen demand showed that these materials were highly efficient in mineralizing metoprolol and pindolol as well as their intermediates. The mechanisms behind the degradation of metoprolol using perovskite catalysts are complex. Still, ongoing research has indicated that the degradation mechanism occurs through hydroxylation of the aromatic ring or side chains. A similar degradation pathway is suggested for the degradation of pindolol, including opening an indole ring at the nitrogen atom site.

Keywords: Beta-blockers, Perovskite-type Catalysts, UFLC, COD.

1. Introduction

The need for sustainable water treatment technologies has grown recently due to insufficiently effective conventional methods for removing emerging pollutants from wastewater (Galvis et al. 2014). Advanced Oxidation Processes (AOPs) are effective and eco-friendly methods for purifying contaminated water and air by generating highly reactive species, e.g., hydroxyl radicals, which convert pollutants into less harmful substances. AOPs are a promising solution due to their high oxidation power and universality in removing contaminants such as organic and inorganic substances, pathogens, and novel pollutants (Hasan and Jhung 2015; Armaković, Savanović, and Armaković 2023). Beta-blockers, commonly prescribed pharmaceuticals, have become an emerging concern as contaminants in water sources. Currently, regulations and monitoring of these substances vary across countries. Studying these pharmaceuticals in aquatic systems is essential because they can harm aquatic organisms through their slow accumulation. Their harmful effects can beirreversible once they reach dangerous levels. Beta-blockers can be excreted unchanged or undergo changes after digestion and interact with other substances in the water environment (Cleland et al. 2018). Pindolol (PIN) (1-(1H-indol-4-yloxy)-3-isopropylaminopropan-2-ol) and metoprolol (MET) (1-[4-(2-methoxyethyl)phenoxy]-3-(propan-2-ylamino)propan-2-ol) are beta-blockers used for various medical purposes. Metoprolol is mainly used for treating high blood pressure and heart conditions and works by slowing down the heart rate and reducing the amount of blood pumped out by the heart. Pindolol is used for hypertension, angina, and glaucoma and works by blocking the effects of hormones that increase heart rate and blood pressure. MET and PIN are detected in an aqueous environment in a mixture with other antibiotics, antidepressants, etc. (James et al. 2014; Kim et al. 2014; Bilić et al., 2023; Marković and Čapelja 2023). Armaković et al. have suggested AOPs that can effectively remove up to 90% of beta-blockers. Photocatalytic degradation using nanomaterials was shown to be most effective (Armaković et al. 2018).

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Perovskite-type catalysts are materials with a unique crystal structure that exhibit exceptional catalytic properties. These catalysts have a high surface area, good chemical stability, and unique electronic properties that make them well-suited for catalyzing a wide range of chemical reactions. The crystal structure of perovskite-type catalysts is defined by a particular arrangement of atoms in a three-dimensional lattice, which creates a unique set of physical and chemical properties. The structure of a perovskite-type catalyst typically consists of a metal cation (such as cobalt, iron, or nickel) surrounded by oxygen anions, forming a metallic oxide (ABO_3). A high tolerance factor facilitates co-doping and co-substituting at the A and B sites while preserving the crystal structure. This feature allows for optimizing the materials' various characteristics and performances (Sun, Alonso, and Bian 2021). Photocatalytic reactions facilitated by perovskite-based materials are highly efficient. They use light energy to drive the chemical reaction, forming electrons and holes that can oxidize pollutants. Hence, perovskite-type photocatalysts have been widely studied and employed for environmental applications, such as air and water purification (Ismael and Wark 2019).

The photocatalytic performance of synthesized $Sr_{0.9}La_{0.1}TiO_3$ and $Sr_{0.25}Ca_{0.25}Na_{0.25}Pr_{0.25}TiO_3$ was studied through the degradation of MET and PIN under different radiation types (simulated solar irradiation (SSI), UV-LED, and UV irradiation). Chemical oxygen demand (COD) measured the amount of oxygen needed to oxidize organic matter in treated samples after 240 minutes. Results showed that these materials were highly effective in removing MET and PIN as well as intermediates formed during degradation.

2. Experimental details

2.1. Chemicals and Solutions

All chemicals were used in their as-received form without further purification: MET ($(C_{15}H_{25}NO_3)_2 \cdot C_4H_6O_6$, M = 684.81 g/mol, ≥99% purity, Sigma-Aldrich, Taufkirchen Germany) and PIN ($C_{14}H_{20}N_2O_2$, M = 248.32 g/mol, ≥98% purity, Sigma-Aldrich, Taufkirchen Germany). All solutions were made using ultrapure water. Other used chemicals were 85% H_3PO_4 (Lachema, Neratovice Czech Republic), acetonitrile (J.T. Baker, Germany), $K_2Cr_2O_7$ (Sigma-Aldrich, Taufkirchen Germany), H_2SO_4 (95–97%, Pharma Hemija, Šabac Serbia), $HgSO_4$ (≥99.5%, Sigma-Aldrich, Taufkirchen Germany), Ag_2SO_4 (≥99.9, Sigma-Aldrich, Taufkirchen Germany), and $HOOCC_6H_4COOK$ (≥ 99.5%, Merck, Taufkirchen Germany).

2.2. Photocatalytic Activity

The synthesis of $Sr_{0.9}La_{0.1}TiO_3$ ($SrLaTiO_3$) and $Sr_{0.25}Ca_{0.25}Na_{0.25}P_{r0.25}TiO_3$ ($SrCaNaPrTiO_3$) was described previously by Jovanoski Kostić et al. (Jovanoski Kostić et al. 2022). The photocatalytic activities of the powders were evaluated by the degradation of aqueous solutions of MET and PIN. Photodegradation experiments were performed using 20 cm³ of 0.05 mmol/dm³ solutions of MET and PIN containing 1.0 mg/cm³ catalyst. This mass concentration of catalyst was chosen based on previous research (Armaković et al. 2018; Uzelac et al. 2022; Jovanoski Kostić et al. 2022). Selvam and Swaminathan (2017) found that the reduction in the degradation rate of pollutants and aggregation of catalyst particles occurs at higher catalyst concentrations. Also, in the presence of higher catalyst concentrations, the process is not economical, and there are difficulties when removing the catalyst from the suspension (Selvam and Swaminathan 2017). The suspension was placed in an ultrasonic bath for 10 min to keep the catalyst particle size uniform and achieve adsorption/desorption equilibrium. The vessel containing the suspension was placed on a magnetic stirrer and maintained at 25 ± 0.5 °C with stirring in a stream of O_2 for 5 min before irradiation. In each case, during irradiation, the solution was continuously stirred on a magnetic stirrer, and a flow of O_2 (3.0 cm³/min.) was continued, thus achieving its constant concentration.

A halogen lamp (Philips, 12V, 50 W, Mr16) was used as a source of SSI. The photon flux for the halogen lamp was 0.1 W/cm² in the visible region and $2.2 \cdot 10^{-4}$ W/cm² in the UVA region. As a source of UV-LED radiation, a 5W UV-LED Lamp was used (Enjoydeal, China, type: MR16 AC 85-265V/ 12) with photon flux $7.4 \cdot 10^{-2}$ W/cm² in the visible region and $4.0 \cdot 10^{-2}$ W/cm² in the UVA region. A high-pressure mercury lamp (Philips, HPL-N, 125 W, with emission bands in the area of UVA radiation) was used as a source of artificial UV radiation (304, 314, 335, and 366 nm with emission maximum at 366 nm), with a suitable concave mirror with energy flux of $2.6 \cdot 10^{-3}$ W/cm² in the visible region and $7.5 \cdot 10^{-2}$ W/cm² in the UVA region.

2.3. Analytical Procedures

The kinetics of PIN and MET degradation were monitored using ultra-fast liquid chromatography with diode array detection (UFLC-DAD, Shimadzu) equipped with an Eclipse XDB-C18 column (150 mm × 4.6 mm i.d., particle size 5 µm, 30 °C). The UV/Vis DAD detector was set at 223 nm for MET and 217 nm for PIN (wavelength of maximum absorption of MET and PIN). Samples of 0.30 cm³ were taken from the reaction mixture at the beginning of the experiment and at regular time intervals, causing a maximum volume variation of approximately 10%. After irradiation, the samples were passed through membrane filters (Millex-GV, 0.22 µm) to separate the catalyst particles. The mobile phase (flow rate 0.8 cm³/min) was a mixture of ACN and 0.1% H_3PO_4, with the following gradient: 15% ACN at 0 min, which was increased to 30% ACN in 5 min after which 30% ACN was constant for 5 min post time was 2 min.

The COD was determined according to the United States Environmental Protection Agency standard method 410.4. The COD concentration was determined spectrophotometrically by measuring the absorbance of the formed Cr^{3+} at 600 nm according to the calibration curve (Fig. 1). Aliquots of 2.5 cm³ samples were taken, and the COD measurements were performed according to the manual method.

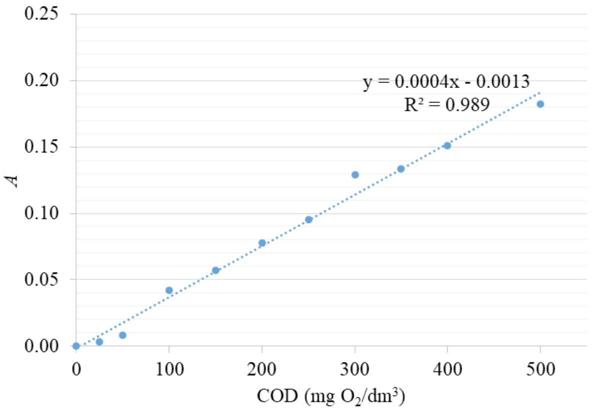

Fig 1. Calibration curve for COD determination

The radiation energy fluxes were measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer, which was fitted with the LP 471 UV (spectral range 315-400 nm) and LP 471 RAD (spectral range 400-1050 nm) sensors. For spectrophotometric measurements, a double-beam T80+ UV/Vis Spectrometer (UK) with a fixed slit width (2 nm), using a quartz cell (1 cm optical length), and computer-loaded UV Win 5 data software were used.

3. Results and discussion

3.1. *Evaluation of Photodegradation and COD for MET*

SrLaTiO3 and SrCaNaPrTiO3 were first examined in MET photodegradation (Figs. 2 and 3) and mineralization. Using SrLaTiO3 and SrCaNaPrTiO3 the degradation efficiency of MET was 17% and 20% after 240 min under SSI, respectively. Under UV-LED irradiation, the degradation efficiency of MET was somewhat higher, at 20% using SrLaTiO3 and 26% using SrCaNaPrTiO3. UV irradiation improved the efficiency of MET photodegradation by up to 30% for both photocatalysts. COD measurements showed that these materials are highly effective in mineralizing MET and its intermediates, as shown by a comparison of results from UFLC and COD (Fig. 4). Fig. 4 shows that degradation and mineralization efficiencies were similar, especially using SrLaTiO3. Namely, 30% of MET was degraded using UV irradiation, while even 27% was mineralized. In the case of SrCaNaPrTiO3, mineralization efficiency was somewhat lower. Still, 30% of MET was degraded using UV irradiation, while 19% was mineralized.

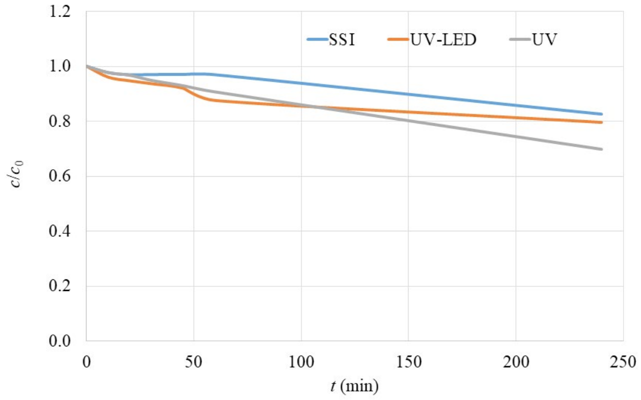

Fig. 2. Photocatalytic degradation of MET using $SrLaTiO_3$

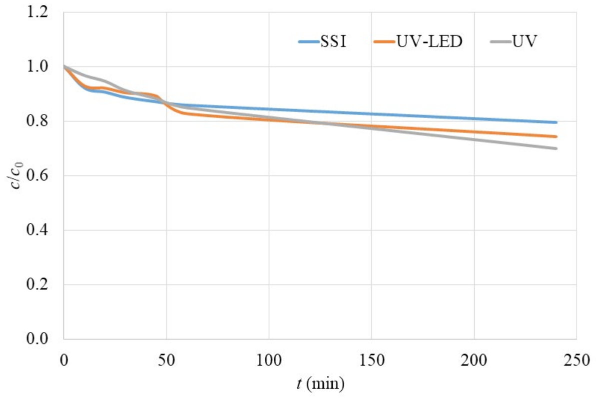

Fig. 3. Photocatalytic degradation of MET using $SrCaNaPrTiO_3$

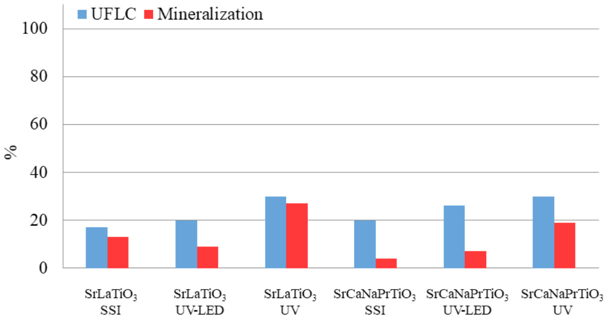

Fig. 4. Comparison of UFLC and COD results for MET photodegradation after 240 min

The highest degradation efficiency of MET was observed using a catalyst in conjunction with UV radiation. This result was anticipated due to the absorption maximum of MET at 223 nm, and improved results were observed when using shorter wavelength radiation such as UV-LED and UV. Despite ongoing research efforts, the mechanisms behind MET degradation using perovskite catalysts are not yet fully understood. However, the significance of this topic is emphasized by the some research on this topic (Romero et al. 2011; Yang et al. 2010). Romero et al. conducted a study wherein the intermediate photocatalytic degradation products of beta-blockers MET, and propranolol were identified. The results indicated that the primary route of photocatalytic degradation was hydroxylation of the aromatic ring or side chains. Furthermore, a shortening of the aliphatic parts of the molecule was also observed (Romero et al. 2011). Yang et al. studied the kinetics and proposed a generalized mechanism for the photocatalytic degradation of three beta-blockers (atenolol, MET, and propranolol). The reaction with hydroxyl radicals ($^{\cdot}OH$) was found to play a crucial role in the degradation of the targeted pharmaceuticals (Yang et al. 2010). Armaković et al. reported that the interaction of MET and $^{\cdot}OH$ radicals lead to the formation of a new bond, wherein $^{\cdot}OH$ radical was bonded to the aromatic ring (Armaković et al. 2023). MET degradation is expected to occur on the surface of the $SrLaTiO_3$ and the $SrCaNaPrTiO_3$, as they are TiO_2-like materials (López et al. 2021). Pinedo et al. proposed a mechanism for MET degradation. First, the aryl ether's C-O bond is broken, forming 4-(2-methoxyethyl) phenol, which is further hydroxylated to form 2-(4-hydroxyphenyl) ethanol. After its oxidation to 4-hydroxybenzaldehyde, it is transformed into hydroquinone (Pinedo et al. 2016). Hydroquinone may then be oxidized to form 1,2,4-benzene-triol, producing low molecular weight organic acids before complete mineralization (Moctezuma et al. 2007). The results of the COD analysis demonstrate substantial mineralization of MET. The most noteworthy efficiency was achieved using $SrLaTiO_3$ and UV radiation. A comparison of results highlights the better mineralization capabilities of the $SrLaTiO_3$ catalyst. Yang et al. noted that the mineralization of MET resulted in the predominant formation of CO_2, H_2O, and nitrogen in the form of NH_3/NH_4^+ as end products (Yang et al. 2010). Comparing the results of experiments with perovskite catalysts to the López et al. work shows that commercial TiO_2 is more effective. However, further research is necessary about perovskite catalysts (Armaković et al. 2023).

3.2. *Evaluation of photodegradation and COD for PIN*

The photocatalytic activity of the SrLaTiO3 and the SrCaNaPrTiO3 was also examined on the PIN molecule in the presence of SSI, UV-LED, and UV irradiation. The SrLaTiO3 and the SrCaNaPrTiO3 degraded approximately the same amount of PIN, but slightly higher photocatalytic activity was obtained for the SrLaTiO3. Namely, 68%, 94%, and 100% of PIN were degraded after 240 min under SSI, UV-LED, and UV irradiation (Fig. 5). Using SrCaNaPrTiO3 the degradation efficiencies were 65%, 84%, and 93%, respectively (Fig. 6). It is evident that UV irradiation increased the photocatalytic activity of two photocatalysts so that in the case of the SrLaTiO3 PIN was removed entirely, and in case of the SrCaNaPrTiO3, removal was almost completely removed. High mineralization of above 70% for both photocatalysts, obtained by COD measurements, showed that these two photocatalysts are very efficient in the degradation of PIN and intermediates formed during the degradation process, especially when exposed to UV irradiation. Fig. 7 shows the COD and UFLC results for the PIN obtained after 240 min. As in the case of MET, SrLaTiO3 showed high mineralization efficiency, and in the case of PIN, UV irradiation degraded 100% of PIN, while 80% was mineralized. Under UV light, the degradation efficiency of SrCaNaPrTiO3 was 93%, while the mineralization efficiency was 73%.

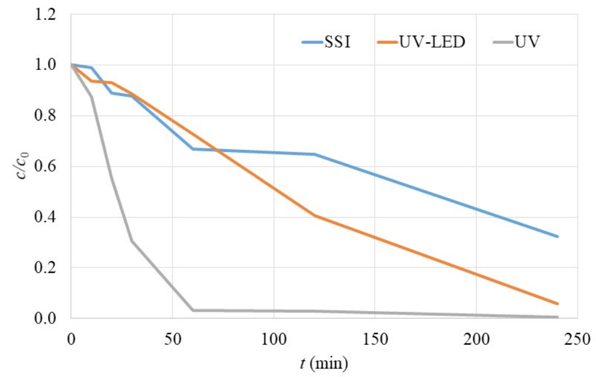

Fig. 5. Photocatalytic degradation of PIN using $SrLaTiO_3$

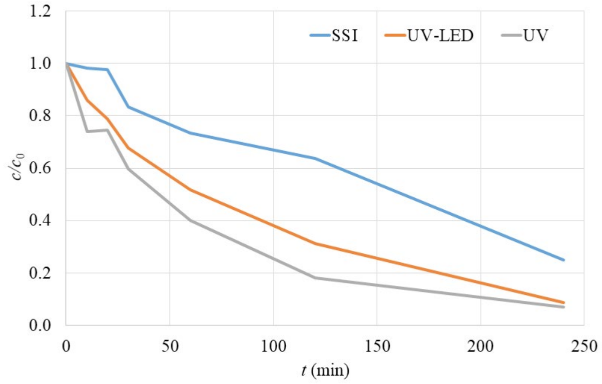

Fig. 6. Photocatalytic degradation of PIN using $SrCaNaPrTiO_3$

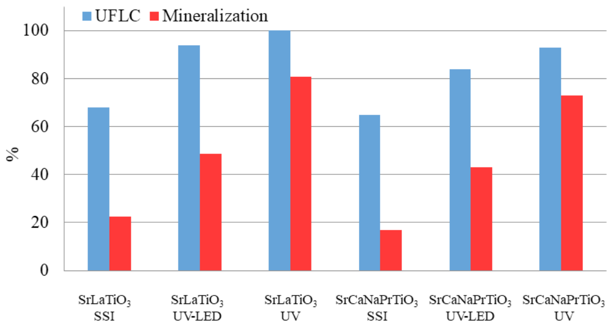

Fig. 7. Comparison of UFLC and COD results for PIN photodegradation after 240 min

Both photocatalysts showed high photocatalytic activity toward PIN, with efficiencies ranging from 60% to 100%, for all irradiation types. The $SrLaTiO_3$ showed slightly higher efficiency, completely removing PIN after 60 min under UV irradiation. Consequently, UV irradiation was identified as the most efficient irradiation source, which was expected considering the absorption maximum of PIN at 217 nm. In our previous work, Jovanoski Kostić et al. have proven that oxidative reactive species are responsible for PIN degradation under the described conditions (Jovanoski Kostić et al. 2022). The final photooxidation products of PIN were found to be salicylaldehyde, amino salicylaldehyde, and *o*-substituted derivates (Criado et al. 2003). Langlois et al. reported that N-formyl kynurenine and L-kynurenine formation occur after breaking the indolic group of tryptophan in reaction with molecular oxygen (Langlois, Ali, and Van Lier 1993). Since the mineralization was above 70% for both photocatalysis and degradation of PIN was higher than 90%, this indicates that PIN and formed intermediates were efficiently degraded from the suspensions. While CO_2 and H_2O are the main products expected to be obtained by photocatalytic degradation, heteroatoms transform into inorganic ions and probably remain in solutions. Armaković et al. proposed the degradation mechanism of PIN by opening the ring with nitrogen, hydroxylating the aromatic ring, and separating the lateral chain. They also identified nine intermediates, including: 3-(propane-2-ylamino)propane-1,2-diol and 1-({6-[(2-aminoethenyl]cyclohexa-1,3-dien-1-yl}oxy)-3-(propan-2-ylamino)propan-2-ol (Armaković et al. 2020).

3.3. *Comparison of MET and PIN photodegradation*

Compared with MET, PIN was degraded more than three times as efficiently, comparing both catalysts and all three irradiation types. MET and PIN have similar structures. They have an entirely identical side chain on the benzene ring. The major differences between the two are PIN's indole structure, which is not present in MET's structure, and the 2-methoxyethyl group attached to MET's aromatic ring. The prominent MET and PIN degradation pathways are aromatic ring hydroxylation and lateral chain separation. PIN also has a third way for degradation: opening the nitrogen ring from the indole group. As described above, ${}^{\bullet}OH$ generated species are responsible for the photocatalytic degradation of both MET and PIN (Pinedo et al. 2016). Two aromatic rings in the PIN structure may be one of the reasons for its more efficient degradation. Another photocatalytic study showed PIN as more reactive than MET (Armaković et al. 2023).

3.4. *Conclusion*

Due to the high production of hydroxyl radicals in AOPs, which are efficient in pharmaceutical degradation, wastewater treatment plants should include these processes to mineralize such organic compounds completely. These processes lead to the complete mineralization of pharmaceuticals, forming products such as CO_2 and H_2O. Perovskite-type catalysts are widely investigated and proven very efficient in AOPs, especially when doped with metals, enhancing their photocatalytic abilities. Also, the radiation source is significant in these processes.

Two perovskite-type photocatalysts, $Sr_{0.9}La_{0.1}TiO_3$ ($SrLaTiO_3$) and $Sr_{0.25}Ca_{0.25}Na_{0.25}Pr_{0.25}TiO_3$ ($SrCaNaPrTiO_3$) were investigated in MET and PIN degradation. The $SrLaTiO_3$ efficiently degraded 17%, 20%, and 30% of MET and 68%, 94%, and 100% of PIN under SSI, UV-LED, and UV irradiation, respectively. The $SrCaNaPrTiO_3$ led to the degradation of 20%, 26%, and 30% of MET and 65%, 84%, and 93% of PIN under SSI, UV-LED, and UV irradiation, respectively. In this study, UV irradiation was the most efficient in the degradation and mineralization of MET and PIN. The $SrLaTiO_3$ and $SrCaNaPrTiO_3$ showed very similar photocatalytic activities toward MET and PIN. However, $SrLaTiO_3$ showed slightly higher efficiency in the degradation and mineralization of parent compounds. Also, PIN degradation was more than three times more efficient than the degradation of MET. The mineralization rate was high for both compounds, indicating that the degradation of intermediates was also efficient. Species that were responsible for the degradation of MET and PIN are ${}^{\bullet}OH$. It is assumed that the main degradation pathway for MET and PIN is by hydroxylation the side chain and aromatic ring of these compounds, including the opening of the nitrogen ring in the PIN's structure.

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Conflicts of Interest

The authors declare no conflict of interest.

Author Contributions

Milana Kudus – Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft; Aleksandra Jovanoski Kostić - Data curation, Formal analysis, Investigation, Validation, Visualization, Writing – original draft; Maria M. Savanović – Data curation, Investigation, Validation, Methodology, Writing – review & editing; Sanja J. Armaković – Conceptualization, Data curation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – review & editing.

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