



ORIGINAL ARTICLE

Oxone activated TiO₂ in presence of UV-LED light for the degradation of moxifloxacin: A mechanistic study



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Received 14 May 2022; accepted 16 June 2022

Available online 21 June 2022

KEYWORDS

Moxifloxacin;
Photocatalytic degradation;
UV-LED;
Advanced Oxidation Process

Abstract This work provides new insight into the development of the TiO₂/Oxone/UV-LED process for organic contaminant degradation as well as hospital waste management. The Moxifloxacin (MOX) degradation using Oxone activated TiO₂ under UV-LED was studied. The TiO₂/Oxone/UV LED process was carried out by the addition of Oxone (0.025, 0.05, 0.1 and 0.2 mM) activated by TiO₂ different concentrations 0.0125, 0.025, 0.05, 0.1 and 0.5 g/L. The degradation efficiency was studied by HPLC having UV/Vis detector, C18 column (5μ, 4.6 × 250 mm²). The complete removal of 10 ppm of MOX occurred at 0.1 g/L TiO₂ and 0.1 mM Oxone with UV-LED exposure time of 12 min. The TOC analysis was performed and 55% TOC reduction was observed at described procedure. The parameters such as drug initial concentration, Oxone, TiO₂ dosages and pH were optimized and their effects on degradation were noted. The pseudo-first order reaction kinetics was observed for MOX degradation. It was revealed from the mechanism of activation that SO₄⁻ and OH⁻ have played a key role in the degradation. The effect of pH (3.6–11) was observed to evaluate the degradation rate of Moxifloxacin. The pH 9.4 achieved the maximum degradation. The

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Peer review under responsibility of King Saud University.



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UPLC-ESI-MS analysis was performed to identify the intermediates and degraded end-products.

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1. Introduction

The Moxifloxacin is a Fluoroquinolone (FQ) and is a broad-spectrum antibiotic and has been frequently utilized to cure infection (Sayed et al., 2015a; Sayed et al., 2015b; Kümmerer, 2009; Speltini et al., 2010). The minute amount of this antibiotic affects the aquatic bodies badly when get mixed in any water body (Robinson et al., 2005; Celiz et al., 2009; Jjemba, 2006; Petrovic et al., 2003). The pharmaceutical based wastewater requires treatment prior to its discharge. The routine treatment methods have been applied to treat, but these exhibited a less performance for the removal of the pollutants (Adu et al., 2020; Jamil et al., 2020; Sohail et al., 2020). The methods such as filtration, coagulation, chlorination, etc are technologically deficit to meet the complete degradation and transfer pollutants from one phase to other rather elimination (Nebot et al., 2015; Muneer, 2020; Kanjal et al., 2020; Alsager et al., 2018; Saeed et al., 2018; Basfer et al., 2018). The advanced oxidation processes (AOPs) are efficient and innovative for the treatment of antibiotics as well as other toxic compounds (Liu et al., 2014; Iqbal and Bhatti, 2015; Kanjal et al., 2020). These include $O_3/UV/H_2O_2$, γ/H_2O_2 , UV/H_2O_2 , $UV/Fe^{2+}/H_2O_2$, and UV/TiO_2 etc. are effective methods to degrade the organic matter present in the aquatic environment (Van Doorslaer et al., 2015, 2012, 2011; Paul et al., 2007; Muneer et al., 2020; Saeed et al., 2015; Muneer et al., 2012). Among AOPs, the TiO_2 assisted photo-catalysis is an efficient option due to production of h^+ , OH^* , e^- and *O_2 when exposed to UV light as shown in equation (1) (Yahya et al., 2017; Marugan et al., 2010; Izumi et al., 1981).



While, e^- and h^+ represent the electron and hole generated during photo-catalysis respectively (Jaeger and Bard, 1979; Kessler, 2013). The UV-LED lamps are eco-friendly than conventional UV lamps (Yoshihiko et al., 2014; Ibrahim et al., 2014; Crawford et al., 2005). However, the e^- and h^+ recombine and decrease the photo-catalysis efficiency. To fill this gap, the electron acceptors species such as hydrogen peroxide, persulfate, and Oxone were used during photocatalytic process (Liu et al., 2014). The use of Oxone as an electron acceptor is a better option in order to degrade the organic compounds via reactive radicals generation as shown in equation (2) (Moradi et al., 2014; Oh et al., 2016).



The Oxone activation by UV-LED can be achieved by transition metals or photo-catalysts such as TiO_2 (Chen et al., 2012). In the established literature, a few studies were reported about the TiO_2 /Oxone/UV-LED process for the drug degradation. In the present study, the TiO_2 /Oxone/UV-LED was used to degrade the Moxifloxacin antibiotic. The degradation study and intermediate/end-product analysis was carried out by using the UPLC-ESI-MS.

2. Material and methods

2.1. Chemicals

The physicochemical properties of Moxifloxacin are shown in Table 1. The titanium dioxide (TiO_2) was used as a catalyst and purchased from Degussa Company, Germany. The Acetonitrile and formic acid were used as mobile phases. While

Table 1 Physicochemical properties of Moxifloxacin (MOX).

Name of drug	Molecular formula	Molecular weight	λ_{max}
Moxifloxacin	$C_{21}H_{24}FN_3O_4$	401.438 g/mol	

methanol (CH_3OH), sodium thiosulfate ($Na_2S_2O_3$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) were procured from Sigma-Aldrich, USA.

2.2. Experimental setup

The MOX solutions having concentrations 10 to 40 mg/L were prepared using ultra-pure water; photodegradation was performed in photo-reactor as described in Fig. 1. The UV-LED lamp having 100 W intensity, emitting 365 nm light with self-cooled chamber with agitation. A catalyst (TiO_2) was mixed with 100 mL of drug (10 mg/L) solution and was placed in dark. The Oxone (oxidant) was then added and after predetermined time interval solution was utilized for further analysis. The UV-LED lamp was fixed vertically 8 cm above the solution.

2.3. Analytical procedures

The decrease in MOX concentrations was monitored by HPLC, C18 column with UV/Vis detector. A mixture of Acetonitrile, water and phosphoric acid (20%, 80% and 0.1% respectively) was used as a mobile phase with flow rate of 1 mL/min while degassing was done prior to run. The Shimadzu TOC-L analyzer was used for TOC analysis. The intermediate were identified using UPLC-ESI-MS detector. The Tribid Mass Spectrometer Orbitrap Fusion Lumos (Thermo

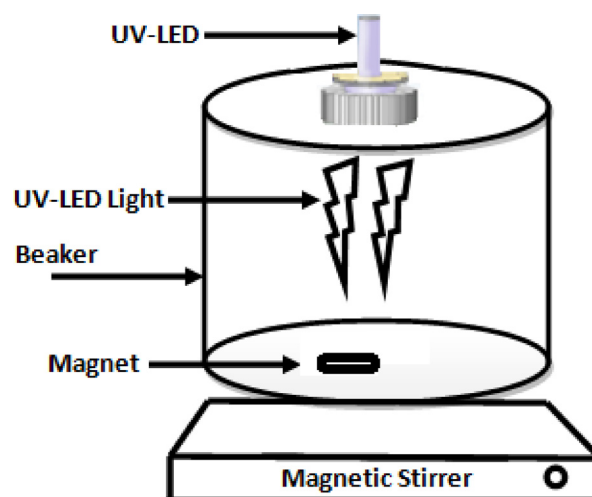


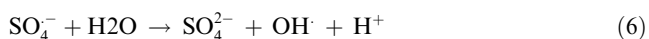
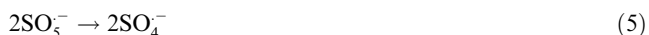
Fig. 1 Experimental setup of UV chamber.

Fisher Scientific, USA) and the UPLC Waters Acquity (Waters, USA) comprised with Acquity BEH C18 column (1.7 μm , 2.1 mm \times 50 mm) was employed. The mobile phase used for intermediates detection was a mixture of acetonitrile and formic acid (100% and 0.1% respectively) with the flow rate of 0.3 mL/min.

3. Results and discussion

3.1. Degradation of MOX using UV-LED/TiO₂/PMS

The performance of different processes such as TiO₂/dark, Oxone/dark, TiO₂/Oxone/dark, UV-LED, Oxone/UV-LED, TiO₂/UV-LED and TiO₂/Oxone/UV-LED was examined and then the MOX degradation efficiency was compared (Fig. 2). The obtained data showed 4% and 10% degradation for 10 ppm solution using the adsorption (TiO₂/dark) and photolysis (UV-LED) respectively. The degradation was noted as 20% and 56% after Oxone/UV-LED and TiO₂/UV-LED treatments respectively. The complete degradation was achieved after TiO₂/Oxone along with UV-LED for 12 min exposure time. The degradation of MOX suggests the seminal role of Oxone (HSO₅⁻) in capturing the generated h⁺ and may cause to produce excess sulfate and hydroxyl radicals as shown in Eqs. 3–6 (Zhang et al., 2015; Chen et al., 2007).



The pseudo-first order kinetics was observed for data (Eq. (7)).

$$dC/dt = -kt \quad (7)$$

Where k and C indicate the reaction rate constant and concentrations of MOX at time t respectively. The slope of ln(C/C₀) versus t gives the value of k and C₀ represents the initial concentration of the drug.

$$\ln[C/C_0] = kt \quad (8)$$

3.2. Initial concentration influence on MOX degradation

The TiO₂/Oxone/UV-LED process was used to check the effect of the initial MOX concentration on the photodegradation efficiency (Fig. 3) having concentrations 10–40 mg/L of drug. The degradation efficiency was reduced as the MOX concentration increased. This can be rationalized by the increase the number of targeted molecules, compete with a limited number of reactive species (*OH and SO₄⁻) and may decrease the rate of drug degradation due to competition among the molecules. Furthermore, the active sites of the catalyst become over occupied can render the production of *OH and O₂⁻ (Tokode et al., 2012). The results are in accordance to the.

findings of Van Doorslaer and his co-workers performed in the degradation of MOX by UV/TiO₂ process (Van Doorslaer et al., 2011).

3.3. pH influence on MOX degradation

The pH of the media affects the photocatalytic activity (Hermann, 1999) and may alter the catalyst's surface property

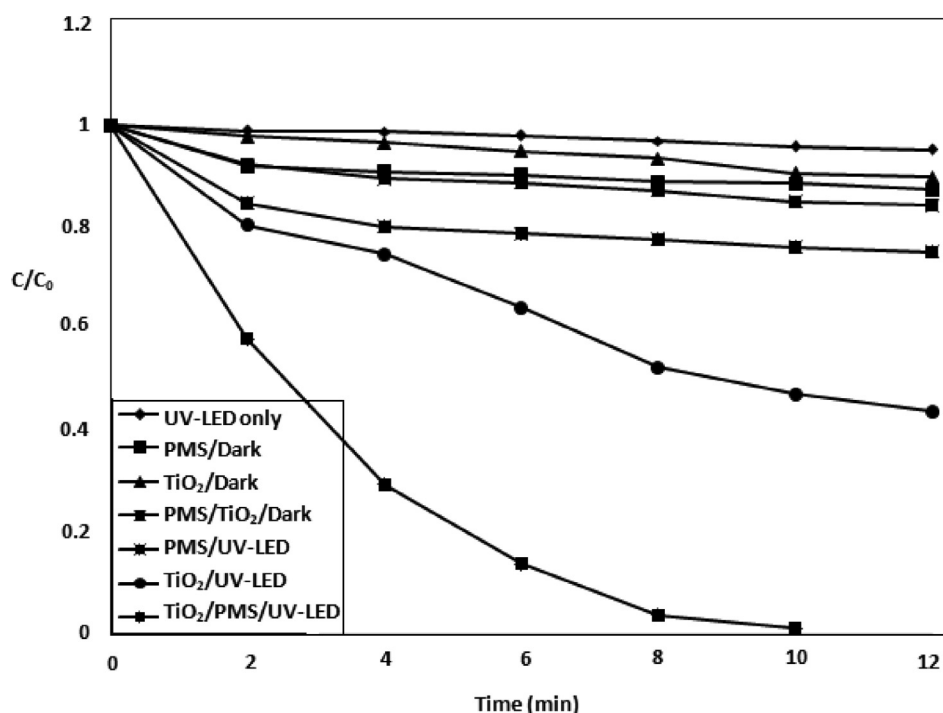


Fig. 2 Degradation kinetics of MOX by using the oxidant along with catalyst.

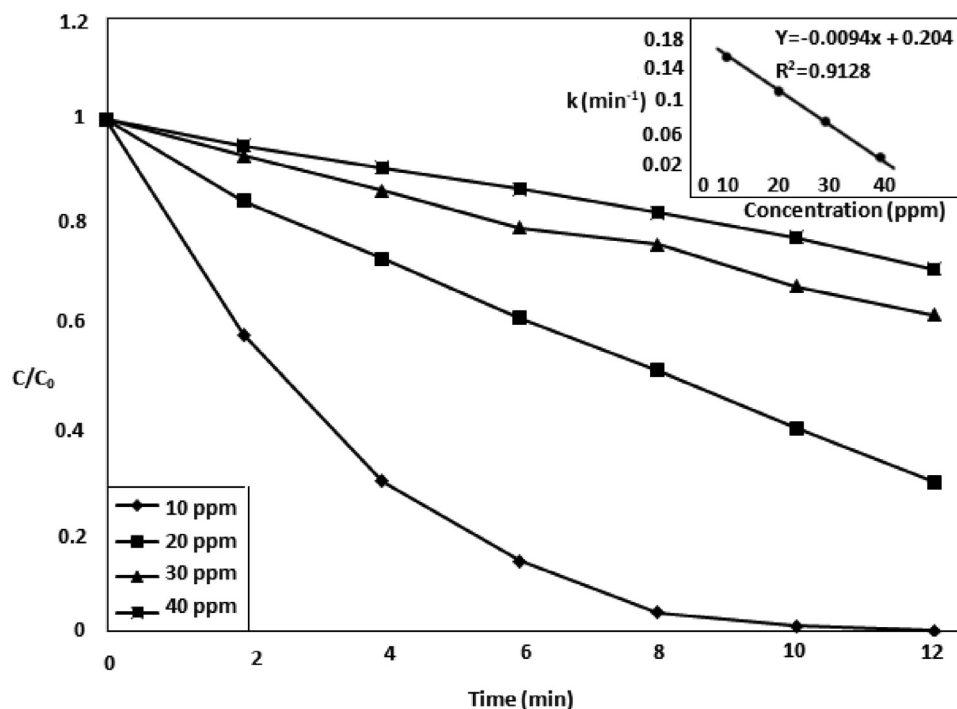


Fig. 3 Effect of drug concentration in presence of oxidant and catalyst.

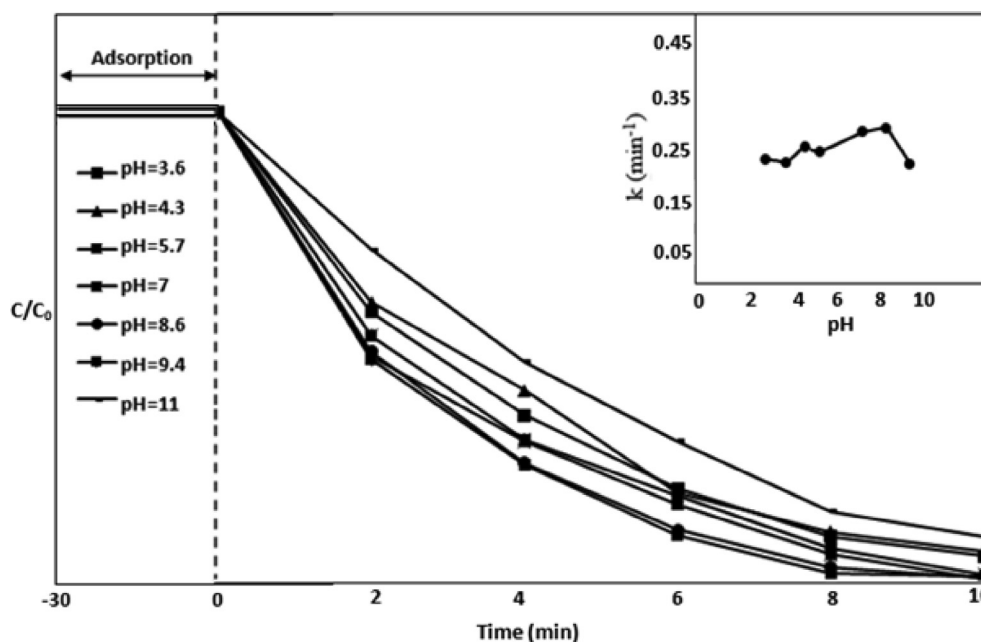
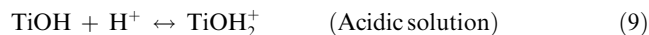


Fig. 4 The effect of pH on MOX along with oxidant and catalyst.

and may influence the adsorption nature of the pollutant (Abdelhaleem and Chu, 2017; Hsiung et al., 2016; Natarajan et al., 2011; Ahn et al., 2016). The effect of change in pH from 3.6 to 11 using 0.1 mM Oxone and 0.1 g/L TiO₂ using UV-LED light was examined (Fig. 4). The complete degradation at pH 9.4 while 80% and 90% in case of acidic and neutral media was observed respectively. In acidic and alkaline media, the TiO₂ is positively and negatively charged respectively as shown in eqs. (9) & (10) (Langlois et al., 2005).



In acidic condition, the H-bonding between hydrogen ion and O-O group in HSO₅⁻ reduces the positive charge on HSO₅⁻ and decreases the photodegradation by hindering the interaction of HSO₅⁻ with surface of catalyst (Liu et al., 2015; Guan et al., 2011). Furthermore, H⁺ can scavenge

sulfate and hydroxyl radicals at low pH (pH 3 or below) based on equations 11–13 (Sun et al., 2012; Jaafarzadeh et al., 2017). The complete degradation was achieved in alkaline condition (at pH 9.4) which is due to increase in OH⁻ formed due to adsorption of OH⁻ on the surface of catalyst (Guan et al.,

2011). This is also the optimum pH. Further increase in pH may reduce the process efficiency due to less adhesion of drug molecules on the surface of catalyst as a result of repulsion between TiO₂ and MOX (Muruganandham and Swaminathan, 2004).

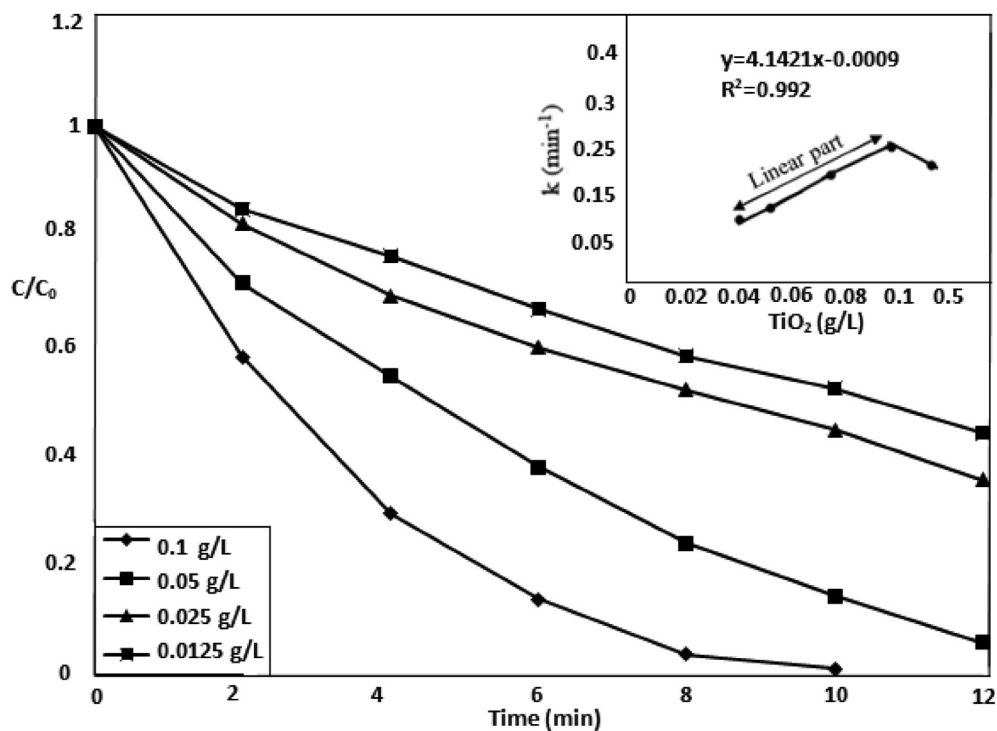


Fig. 5 Effect of TiO₂ dosage on the degradation of MOX.

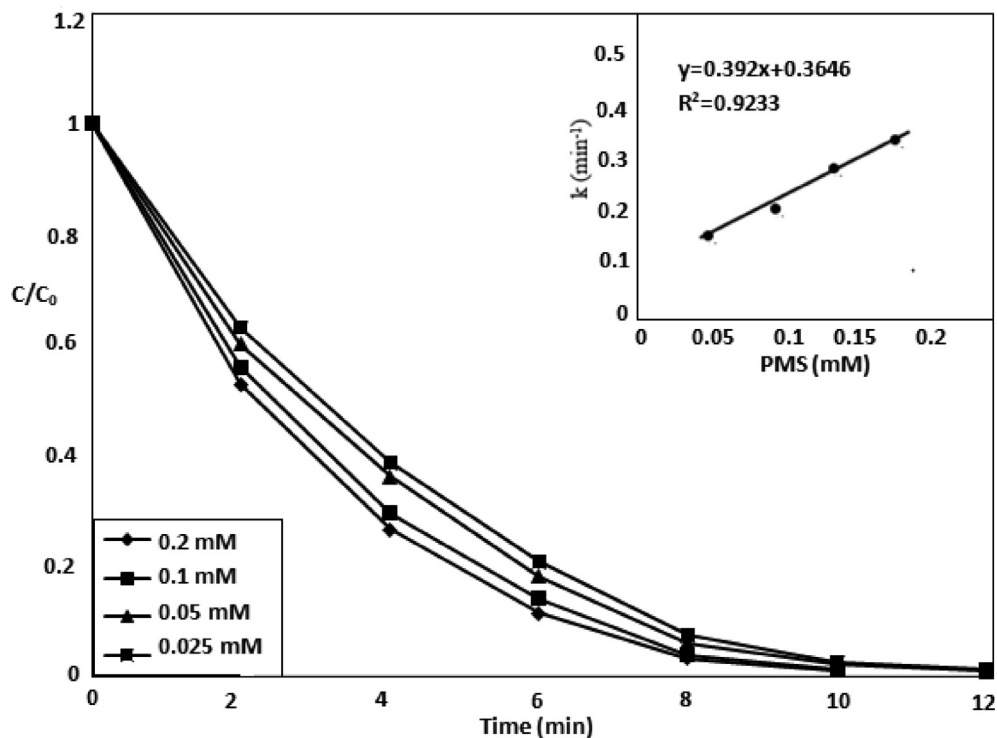


Fig. 6 Effect of Oxone on degradation efficiency along with catalyst.

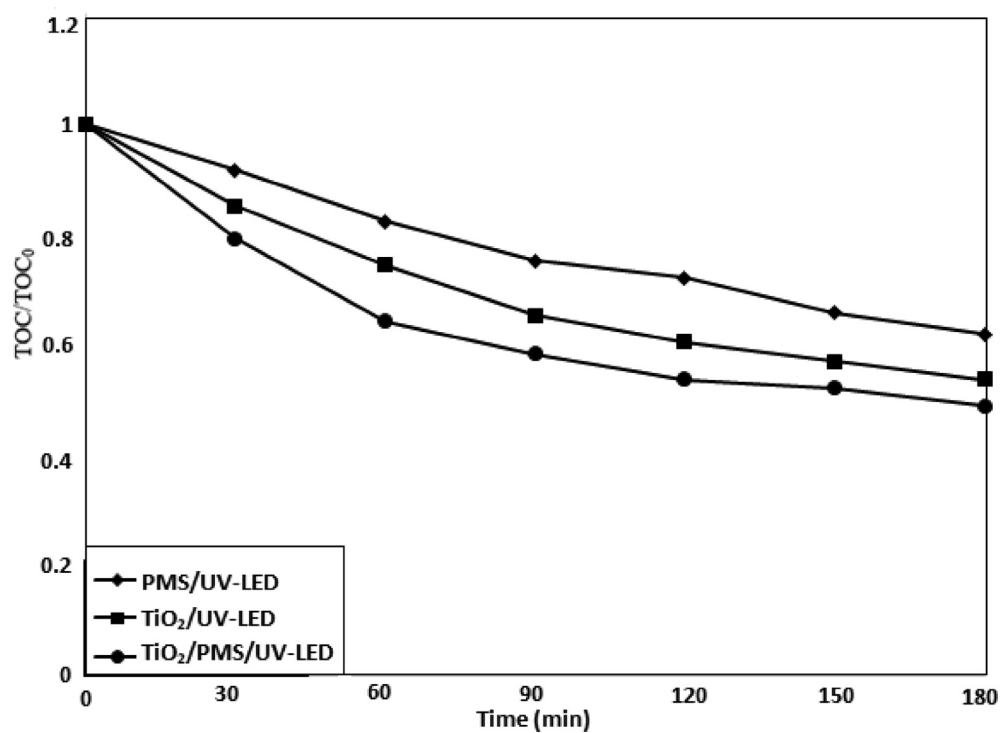
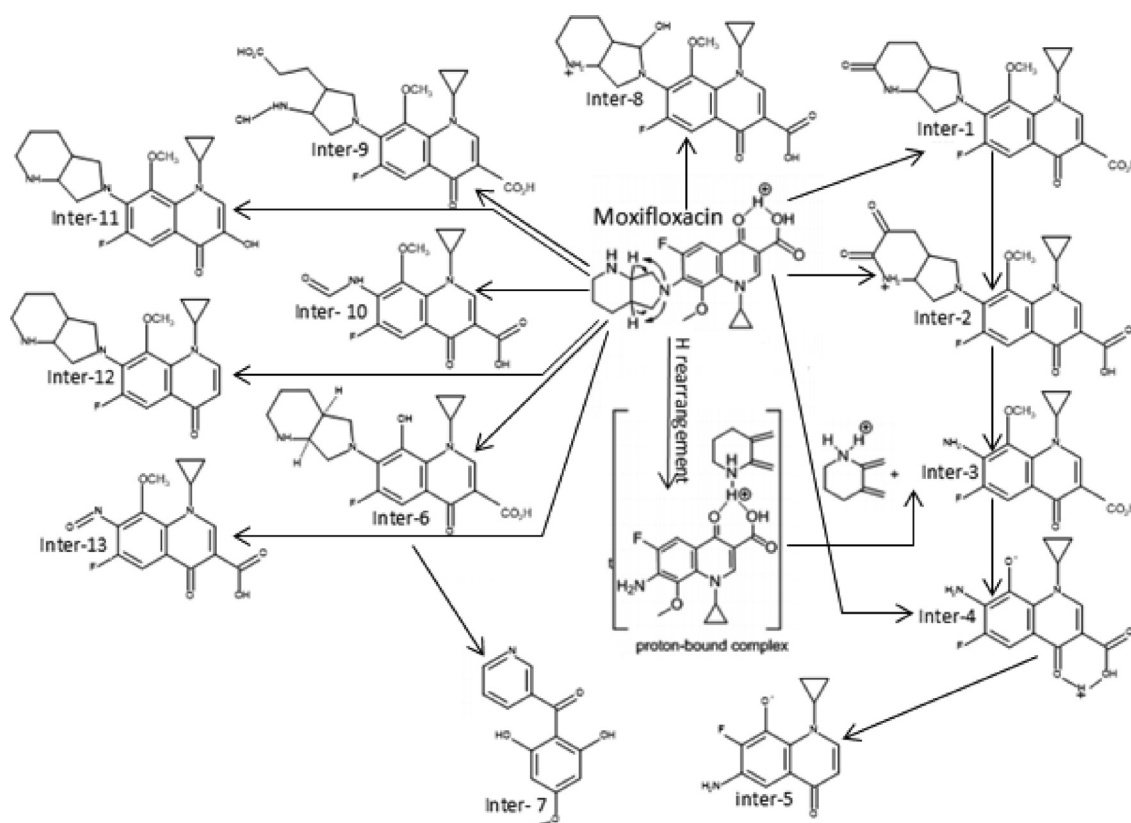
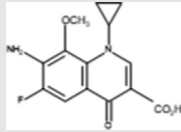
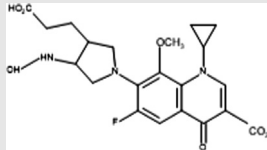
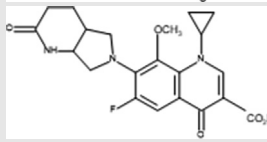
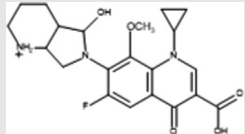
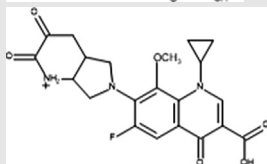
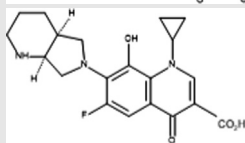
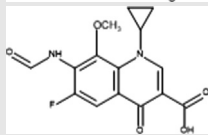
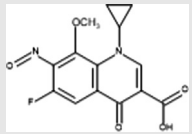
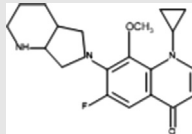
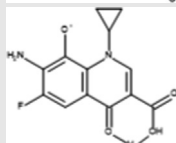
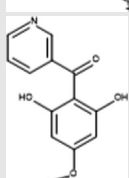
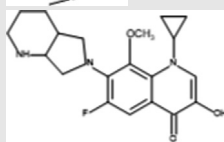


Fig. 7 TOC measurements in UV-LED/TiO₂/Oxone process.



Scheme 1 Proposed pathways of Moxifloxacin using UV-LED/TiO₂/Oxone process.

Table 2 The information of the intermediates.

Product ID	Molecular Ion [M + H ⁺]	Proposed Structure
Inter-1	293	
Inter-2	434	
Inter-3	416	
Inter-4	418	
Inter-5	430	
Inter-6	387	
Inter-7	321	
Inter-8	306	
Inter-9	358	
Inter-10	279	
Inter-11	246	
Inter-12	374	

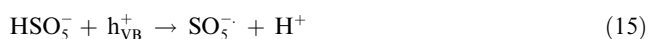
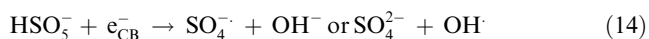


3.4. Catalyst dose influence on MOX degradation

The Fig. 5 shows the effect of catalyst dosage (0.0125–0.5 g/L) on the degradation efficiency of MOX. The complete degradation was achieved for 10 ppm drug aqueous solution by using UV-LED light in combination of oxidant and catalyst at UV-LED exposure time of 12 min. The availability of more active sites due to increased amount of catalyst enhanced the drug degradation. The degradation reduced suddenly when TiO_2 was overdosed (0.5 g/L) due to the reduction in the penetration of light at higher catalyst dosages (Chu and Wong, 2004).

3.5. Oxidant influence on MOX degradation

During the photocatalysis, electrons and the holes may recombine, which result limited degradation. Electron acceptor such as oxone is added to the reaction system in order to overcome the recombination. The TiO_2 /UV-LED process have shown 55% degradation, which enhanced to 100% along with Oxone (0.2 mM) as shown in Fig. 6. The increase in MOX degradation efficiency can be justified by the production of reactive radicals through the Oxone decomposition by the photocatalyst (Madhavan et al., 2006) as shown by the equations 14–16 (Dhanalakshmi et al., 2008).



3.6. Mineralization efficiency

The organic compounds could be more harmful to the environment as compared to parent compounds when degraded to smaller molecules via oxidation process. The mineralization was carried out by using total organic carbon (TOC) analysis (Zazouli et al., 2007). Fig. 7 shows the mineralization results of Moxifloxacin at different experimental conditions. During TiO_2 /Oxone/UV-LED process, about 55% of TOC reduction was observed while only 18% TOC removal was observed in case of Oxone/UV-LED process. The mineralization took place in the following order TiO_2 /Oxone/UV-LED > UV-LED/ TiO_2 > UV-LED/Oxone. The TOC reduction in the TiO_2 /Oxone/UV-LED process reveals that the process could be effective technique for the removal of the intermediates resulting from the photodegradation of Moxifloxacin.

3.7. Byproducts distribution

The proposed mechanism of MOX photocatalytic degradation by TiO_2 /Oxone/UV-LED process is shown in scheme 1. The ion $[\text{M} + \text{H}^+]$ where M is the molecular mass of the respective analyte generated because of a proton in order to get positively

charged molecular ion in all analytes while Table 2 summarizes the intermediates' information with structure. The MS spectra of MOX (m/z 402) yields ions at m/z 374 and 358 as a result of CO and CO_2 loss, respectively. Whereas, the intermediate specie at m/z 321 identified with the loss of HF at m/z 341 (Chai et al., 2011). The proton-bound complex resulted complementary products at m/z 293 and 110 (Zhang et al., 2012) formed by the rearrangement of hydrogen (Hudson and McAdoo, 2007). Due to loss of CH_3 and H_2O , the ion with m/z 293 produced an ion at m/z 279 (Kingston et al., 1975). The fragment pathways for protonated moxifloxacin have shown conflict with the fragment pathways reported by (Raju et al., 2012). However, the elimination of neutral species such as CO, H_2O and CO_2 took place via same fragment pattern in both studies, while, a significant variation in relative abundance of the ions was observed.

4. Conclusions

In this study, the performance of MOX degradation was assessed by using UV-LED/ TiO_2 /Oxone process. The obtained data revealed that TiO_2 had a catalytic activity for Oxone activation under the UV-LED light. A complete degradation of Moxifloxacin and 55% mineralization revealed the outstanding performance of TiO_2 /Oxone/UV-LED combined process for the removal of the intermediates. The TiO_2 /Oxone/UV-LED process could be implemented through the activation of Oxone as a sustainable and environmentally friendly approach to degrade of organic matter in aquatic environment.

Funding

This research was funded by Princess Nourah bint Abdulrahman University Researchers Supporting Project (Grant No. PNURSP2022R11), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors express their gratitude to Princess Nourah bint Abdulrahman University Researchers Supporting Project (Grant No. PNURSP2022R11), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia.

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