Photocatalytic Degradation of Ciprofloxacin HCl using Visible Active BiOS Photocatalyst and Artificial radiation

G. Patil [2,1], N. Bodawar [1,1], G. Khotari [1], P. Mulay [3], P.Khurpade [2], S. Kamble [1]*

1*. Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411 008, India
2. Dr Vishwanath Karad, Maharashtra Institute of Technology, World Peace University, Paud Road Pune – 411038
3 Rutgers University, Piscataway, New Jersey, United States
*Email: sp.kamble@ncl.res.in

Abstract

Ciprofloxacin, a potent biologically active substance, has caused significant environmental issues when present in natural waters. The current study aimed to investigate the visible light-induced degradation of ciprofloxacin HCl (CFX) using bismuth oxysulfide (BiOS) as a photocatalyst. A new photocatalyst BiOS has been developed and tested for the photocatalytic degradation (PCD) of pharmaceutical pollutants in wastewater using artificial radiation. Specifically, this novel material was examined for its ability to degrade ciprofloxacin HCl (CFX). A nanocomposite of BiOS photocatalyst has been synthesized utilizing the sol-gel method and subsequently characterized using UV-DRS, SEM, and EDAX techniques. A tungsten lamp was utilized to simulate artificial radiation during the PCD of CFX. Based on studies on the ideal operating conditions for the BiOS photocatalyst, the maximum rate of photocatalytic degradation (PCD) was reached at a neutral pH of 7. When compared to a salt-free environment, the rate of PCD was observed to be increased by anionic salts (NaCl, Na_2CO_3, and $(NH_4)_2SO_4$). The Cl^- and CO^{3-} ions have notably increased the rate of PCD than SO^{4-} ions. According to Langmuir-Hinshelwood kinetic modeling, the PCD of CFX exhibits a pseudo-first-order reaction behavior. Therefore, it can be said that BiOS is a suitable photocatalyst for treating wastewater from pharmaceutical plants.

Keywords: ciprofloxacin, bismuth oxysulfide, photocatalytic degradation, pharmaceutical pollutants

1. Introduction

Pollution of water by pharmaceuticals is a persistent issue that affects regions around the globe. Many of these substances are difficult to break down. About 1% of India's GDP comes from the pharmaceutical sector, which is the third-largest in the world in terms of manufacturing volume. The industry's continued growth is driven by international demand. Pharmaceutical products from India are exported to over 65 countries, with earnings from these exports accounting for over 50% of the company's total sales. The country's cost advantages make it an attractive location for manufacturing. In 2007, India exported $1.4 billion worth of pharmaceutical products to the United States alone[1]. The discharge of substantial quantities of hospital wastewater containing antibiotics into the environment via wastewater systems is becoming increasingly prevalent because of the growing utilization of these antibiotics[2]. Broad-spectrum antibiotics like fluoroquinolones (FQs) are frequently prescribed for use in both human and veterinary medicine. The function of these antibiotics is to impede the activity of critical bacterial enzymes that are necessary for DNA replication and transcription, such as DNA gyrase and topoisomerase IV[3]. Second-generation fluoroquinolone (FQ) antibiotics like ciprofloxacin, or CFX, are often given and can be detected at nanogram levels in wastewater. The development of bacterial resistance may result from this. CFX is useful in treating typhoid, legionnaire's disease, and anthrax because it works against both gram-positive and gram-negative bacteria.

It is categorized as a strong FQ that has been linked to major side effects such tendon ruptures and seizures-related brain damage[4]. Most pharmaceutical substances are not readily biodegradable, which makes their removal by traditional wastewater treatment facilities ineffective[5]. To ensure compliance with regulations, it is necessary to lower the concentration of CFX in the wastewater before it is released into the drainage system. In recent times, several promising methods for treating wastewater to remove CFX have been applied, such as ozonation[6-8], photo Fenton[9], sonolysis[10], photolysis[11] and titanium dioxide (TiO_2) photocatalytic degradation[12,13]. These methods have been used to remediate FQs. Due to their capacity to function under natural sun radiation, photocatalysts—cheap, safe semiconductors that serve as photo-oxidants—offer an appealing solution in the context of green chemistry[13]. TiO_2 has been used extensively to remove contaminants. However, TiO_2 has a number of disadvantages, such as low surface area (55 m^2/g for Degussa P-25 TiO_2) and low porosity. Moreover, it is specifically activated by particular ultraviolet light wavelengths, with rutile and anatase having broad band gap energies of 3.0 eV and 3.2 eV, respectively. This

corresponds to approximately 4-8% of the solar radiation that reaches the surface of the Earth. Consequently, it is essential to design photocatalysts that are sensitive to visible light [14].

In the present article, a novel BiOS visible active photocatalyst has been developed and tested for photocatalytic remediation of Ciprofloxacin from wastewater using artificial radiation. The sol-gel approach has been used to synthesis a composite of BiOS. The developed BiOS photocatalyst has been characterized with UV-DRS, SEM and EDAX techniques. The optimum operating conditions for the BiOS photocatalyst synthesized were determined through examination of numerous factors such as initial CFX concentration, solution pH and occurrence of co-existing ions.

2. Experimental Section

2.1 Reagents

Bismuth (III) oxide (Bi_2O_3, 99.99% purity) was purchased from Sigma-Aldrich. Absolute ethanol (EtOH, 99.9% purity, ACS spectrophotometric grade) and sulfuric acid (H_2SO_4, 98% purity, ACS reagent) were obtained from Merck. Acetonitrile (C_2H_3N, 99% purity, gradient grade) was sourced from Sigma-Aldrich. Sodium carbonate (Na_2CO_3, 99% purity, ISO grade), sodium chloride (NaCl, 99% purity, ISO grade), and ammonium sulfate (($NH_4)_2SO_4$, 99% purity, ISO grade) were acquired from Merck India Pvt. Ltd., Mumbai, India. A Ciprofloxacin HCl (CFX) sample Purity >99% was procured from Granules India Pvt. Ltd., Hyderabad.

2.2 Preparation of Photocatalyst

The method for the preparation of Photocatalyst has been mentioned in our previously published patent. Kindly refer to the patent number US 9,409,791 B2 published in August 2016 [15].

2.3 Photocatalytic Reactor

The description of the experimental setup as shown in Figure 1 has been given in our previously published patent. Kindly refer to the patent number US 9,409,791 B2 published in August 2016[15].

2.4 Analytical Procedure

The details of the analytical procedure used to analyze the concentration of CFX in aqueous solution have been reported in our previously published patent. Kindly refer to the patent number US 9,409,791 B2 published in August 2016[15].

2.5. Characterization of BiOS photocatalyst

The details of the characterization techniques used to analyze the BiOS photocatalyst have been reported in our previously published patent. Kindly refer to the patent number US 9,409,791 B2 published in August 2016[15].

3. Results and Discussion

3.1 Characterization of BiOS photocatalyst

The results of the characterization of the BiOS photocatalyst have been reported in our previously published patent. Kindly refer to the patent number US 9,409,791 B2 published in August 2016[15].

3.2 Effect of initial concentration of CFX

At Initial concentrations of 50, 100, and 200 mg/L, photocatalytic degradation (PCD) of CFX was carried out utilizing a fixed photocatalyst loading of 2 g/L, a 4-hour reaction period and a 400 W lamp rating. Figure 2 illustrates how the initial CFX concentration affects the PCD rate. It was discovered that CFX may entirely disintegrate in two hours at concentrations up to 100 mg/L under artificial radiation. The concentration of CFX greatly influences the degradation rate of CFX. Additionally, Figure 2 shows that as the initial CFX concentration increases, so does the amount of time needed for complete degradation. For a specific BiOS photocatalyst loading, the number of active centers is limited, so the PCD rate was faster for lower initial concentrations of CFX. However, as the CFX concentration increased, the PCD rate decreased because the number of molecules of CFX exceeded the number of active centers on the photocatalyst[16].

3.3 Effect of pH

When treating wastewater, the pH level is a crucial aspect to take into account because it influences the photocatalyst's photocatalytic activity and, in turn, the rate of PCD. The pH level of the CFX solution has an impact on the adsorption behaviour of the organic substrate and the surface charge characteristics of the photocatalyst, which in turn affects the PCD of

CFX as well as the BiOS concentration[13]. This study investigated the effects of pH at pH 3, 5, 7 and 9 on the degradation of CFX in BiOS aqueous solution. As Figure 3 illustrates, at different pH values, CFX degraded at different rates. The CFX solution was mixed with 0.1 N HCl and 0.1 N NaOH aqueous solutions to achieve the required pH values while keeping the catalyst loading at 2 gm/L and the CFX content at 100 mg/L. When CFX was subjected to somewhat acidic pH 5 circumstances as opposed to severely acidic pH 3 and alkaline pH 9, the highest degradation of CFX was found. This study shows that the pH of the reaction solution is a significant parameter that influences the rate of CFX degradation. In acidic media (pH < 5) and alkaline media (pH > 7), the BiOS surface maintains its positive charge[17]. Since CFX and the BiOS surface are positively charged in extremely acidic environments (pH 3), so there is repulsion between them. Conversely, both BiOS and CFX are negatively charged in basic environments (pH 9), resulting them to repel one another and a lower rate of reaction. Therefore, it can be concluded that mild acidic conditions favor PCD of CFX.

3.4 Effect of presence of co-existing ions

The impact of specific inorganic ions on the photocatalytic degradation of pollutants is significant. The degradation of CFX was investigated in relation to the effects of inorganic ions from sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and ammonium sulfate ((NH_4)$_2SO_4$). The photocatalyst loading was maintained at 2 g/L, the reaction duration was set at 2 hours, and the lamp rating (400 W) was kept constant. A CFX solution at an initial concentration of 100 mg/L, and 500 mg/L of sodium carbonate, sodium chloride, as well as ammonium sulfate ions were added individually. The rate of CFX photocatalytic degradation in the presence of these ions is shown in Figure IV. In the presence of these ions, complete CFX degradation was achieved in 45 minutes. Conversely, in the absence of ions, the degradation time extended to 120 minutes.

The prevalence of chloride ions improves the adsorption of CFX on the surface of BiOS [13,18]. Furthermore, the equilibrium pH of the CFX solution rises to 6.56 and 5.9, respectively, as a result of the presence of these ions, specifically carbonate and chloride. The highest PCD value for CFX is observed at near neutral pH, as previously discussed in Section 4.2. Consequently, the presence of these ions resulted in a higher PCD rate for CFX compared to their absence.

4. Mechanism of photocatalytic degradation of CFX

Owing to the formation of unknown intermediates during the photocatalytic degradation of aromatic compounds, it is imperative to comprehend the mechanism of pollutant degradation. These intermediates may pose greater risks of toxicity than their parent compounds. Organic molecules can be photo catalytically degraded through the interaction of OH● (hydroxyl radical) with the substrate[13,14].

LC-MS/MS was used to determine the intermediates that were produced when CFX was photo oxidized. The molecular masses of these intermediates as well as their retention times and mass spectra, are presented in Table 1. In the first half hour of the process, the concentration of these intermediates rose rapidly, then over time, it declined. Although their exact concentration could not be determined due to the unavailability of commercial standard compounds. Previous researchers have also observed similar intermediates during the photochemical degradation of CFX[19,20]. Three possible pathways for the degradation of CFX have been suggested based on these studies: electron cleavage of nitrogen atoms, hydroxyl radical breakdown of aromatic ring double bonds and degradation of fluorine atoms. Eventually, the molecules may be entirely mineralized through these pathways.

5. Kinetic modeling of photocatalytic oxidation of CFX

For heterogeneous photocatalytic degradation, the Langmuir-Hinshelwood (L-H) model can provide an explanation for the reaction rate. The relationship between the initial concentration of the organic substrate and the initial degradation rate can be determined using this model. The initial CFX concentration has been raised from 50 to 200 mg/L using the BiOS photocatalyst to investigate the kinetics of the photocatalytic degradation reaction. A pseudo-first-order kinetics is shown by the linearity between the ln (C_0/C) and t plot (Fig. Ⅵ), where C_0 is the initial concentration of CFX (mg/L) and C is the concentration of CFX (mg/L) at treatment time t (min). Table Ⅱ lists the kinetic parameters, such as the half-lives and rate constants. The calculated rate constants, k (min^{-1}) (slopes of the lines), decreased from 0.0177 min-1 (for 50 mg/L) to 0.0116 min^{-1} (for 200 mg/L) (Table Ⅱ). This reduction was able to attributed to the decrease in the interaction between photons and active sites. The half-lives were calculated to be about 60 min for initial CFX concentrations of 50-100 mg/L, while the 200 mg/L CFX concentration provided a half-life of 105 min. The Langmuir-Hinshelwood model was also confirmed by utilizing the model equation's rearranged version (Eq. 1). [21]

$$1/_R = \frac{1}{k_r\ K\ C_0} + \frac{1}{k_r} \tag{1}$$

The adsorption coefficient of CFX onto the catalyst surface (K, L/mg) and the reaction rate constant (kr, mg/L min) both affect the rate of degradation, represented by R. The linear relationship seen in the plot of the reciprocal of rates ($1/R$) versus the reciprocal of initial CFX concentrations ($1/C_0$) (Figure Ⅴ). The values of K and kr were determined to be 0.0956 L/mg and 4.28 mg/L min, respectively.

The efficiency of the BiOS photocatalyst was assessed through recycling experiments (Figure 5). The photocatalyst was filtered, washed and dried at 100°C for two hours while the other reaction parameters remained unchanged for every new experiment. Following the initial trial, there was a about 8.5% drop in CFX degradation from 85% to 76% indicating that BiOS's photocatalytic activity is still stable. This finding suggests that the photocatalyst does not break down into its component parts or release sulphur or bismuth into the treated water and that the chemical structure of BiOS, which is responsible for its photocatalytic activity remains intact. To fully restore the activity and repeatability of the BiOS photocatalyst, more research is necessary. By-product generation and its aggregation on the catalyst's active surface sites may be the cause of the small decrease in catalyst activity seen in the repeated studies. Catalyst activity decline can also result from photocatalyst loss during catalyst recovery and work-up procedures.

6. Conclusions

In this study, a novel active photocatalyst with visible light was synthesized using the sol-gel method. The synthesized photocatalyst exhibited significant photocatalytic activity for PCD of CFX. The influence of various operational parameters on PCD was investigated, and it was determined that the optimal PCD rate was achieved at neutral pH 7. The rate of degradation was also substantially affected by the initial concentration of CFX, with higher degradation rates observed at lower initial concentrations (below 100 mg/L). The investigation further revealed that carbonate, chloride, and sulfate ions enhanced the rate of PCD, with chloride and carbonate ions demonstrating a more pronounced increase compared to sulfate ions. It was established that a catalytic loading of 2 g/L was optimal. Moreover, throughout regeneration and reuse cycles, the chemical structure of BiOS remained unaltered, and the photocatalyst did not release sulfur or bismuth into the treated water.
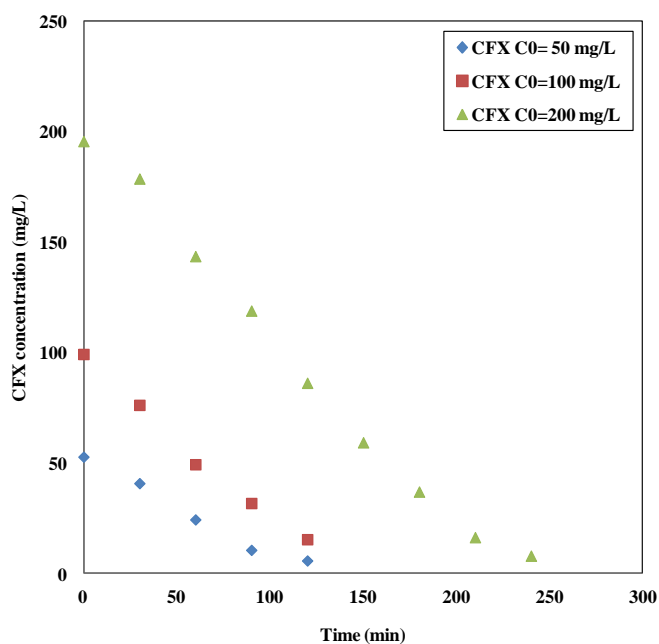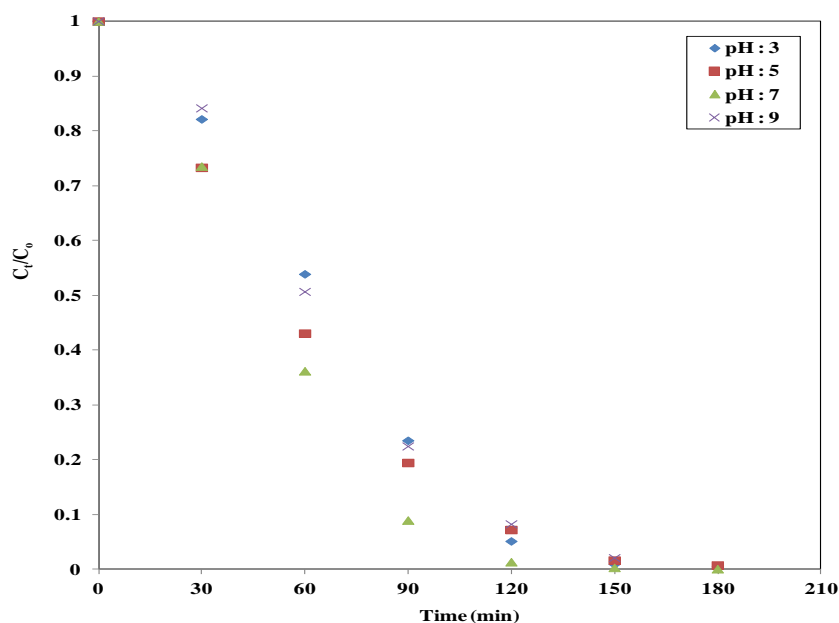
Figures:
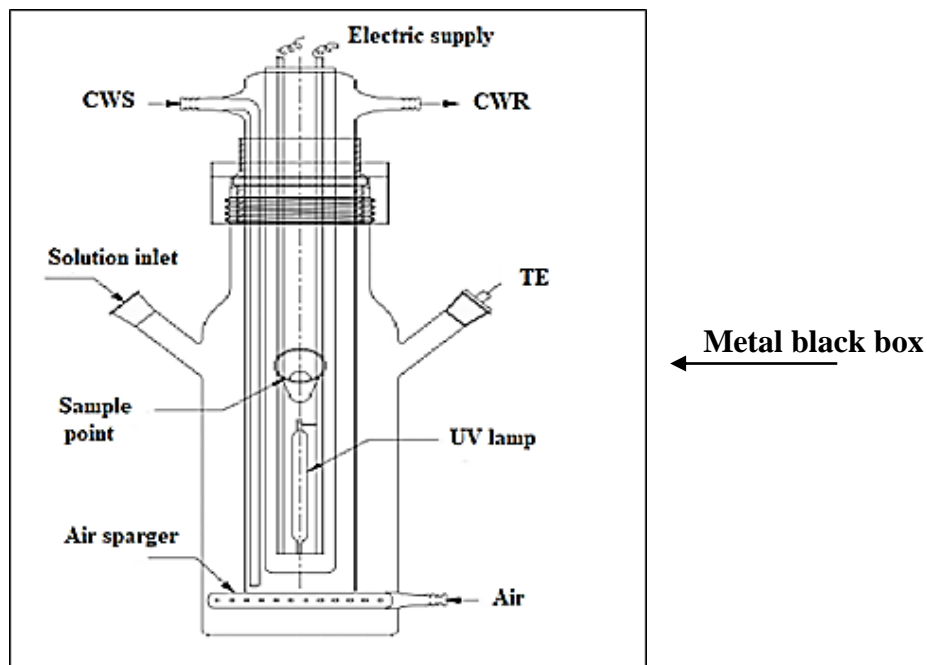
**Fig. 1** Schematic diagram for the photocatalytic reactor system

Fig. 2 Effect of initial CFX concentrations on PCD with artificial radiation and BiOS photocatalyst (2 g/L catalyst loading and 400 W lamp rating)

Fig. 3 Effect of pH on artificial radiation [(C/C$_t$=0) vs. time] and BiOS photocatalyst on the photocatalytic degradation of CFX (CFX initial concentration: 100 mg/L; catalyst loading: 2 g/L and lamp rating: 400 W).
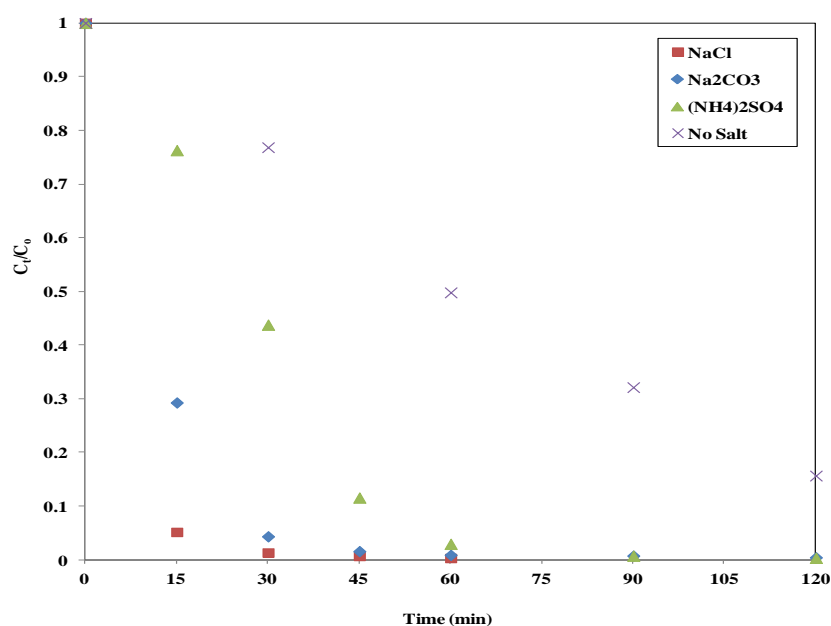
Fig. 4 Utilizing artificial radiation and BiOS catalyst, PCD of CFX in the presence of coexisting ions (CFX initial concentration: 100 mg/L; catalyst loading: 2 g/L; lamp rating: 400 W).
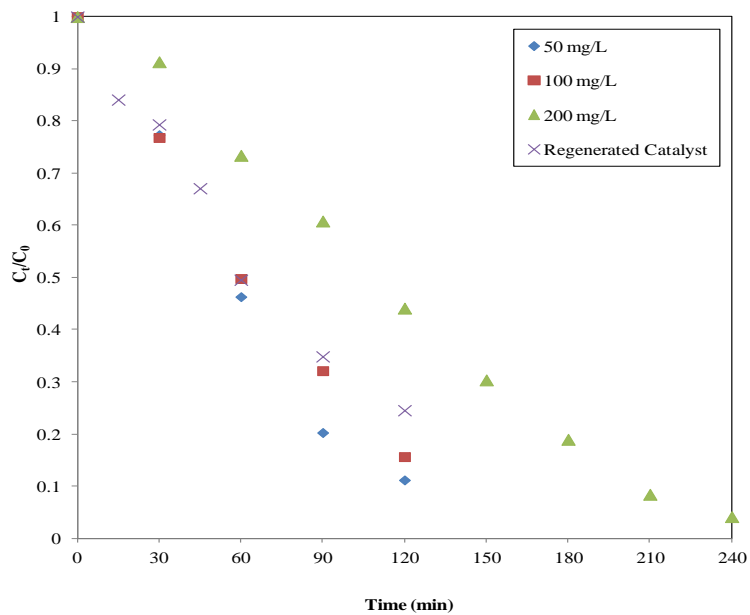
Fig. 5 Kinetics of PCD of CFX using BiOS photocatalyst and artificial radiation (catalyst loading: 2 g/L and lamp rating: 400 W)
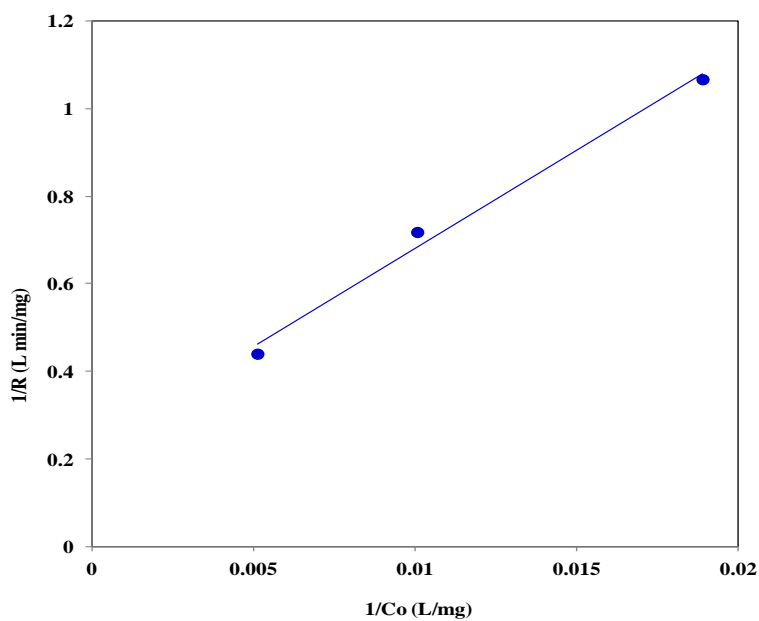
Fig. 6 Langmuir-Hinshelwood kinetic model (1/R vs. $1/C_0$) application for BiOS photocatalyst

Table 1 Intermediates discovered by LC-MS/MS during the PCD of CFX

Sr.	RT (min)	[M+H]$^+$ and Chemical Formula	Structure
1.	3.24 5.15	378, 334 $C_{17}H_{17}O_6N_3F$	
2.	3.67 5.24	362 $C_{17}H_{17}O_5N_3F$	
3.	5.94	306.12 $C_{15}H_{17}O_3N_3F$	
4.	6.34	330.1 $C_{17}H_{17}O_3N_3F$	
5.	8.35	348.1 $C_{17}H_{19}O_4N_3F$	
6.	8.35	348.1 $C_{17}H_{19}O_3N_3F$	

Table 2 Kinetic parameters at different initial concentrations of CFX in the presence of BiOS photocatalyst

Initial concentration CFX (mg/L)	R^2	K_{app} min^{-1}	$t_{1/2}$ (min)
50	0.976	0.0177	60
100	0.9635	0.0140	60
200	0.9392	0.0116	105
100 (reused photocatalyst)	0.9824	0.0114	60

References

1. P. J. Chakraborty, Health Manag.22, 424, 2020.

2. D. G. J. Larsson, C. de Pedro and N. Paxeus, J. Hazard. Mater., 148, 751, 2007.

3. A. A. Robinson, J. B. Belden and M. J. Lydy, ET&C, 24, 423, 2005.

4. R. Mellisa, M. Weller, S. Wentzell, J. Bergendahl and R. Thompson, Worcester Polytechnic Institute, 2011.

5. W. Gebhardt and H. Fr. Schröder, J. Chromatogr. A, 1160, 34, 2007.

6. B. De Witte, H. Van Langenhove, K. Demeestere, K. Saerens, P. De Wispelaere and J. Dewulf, Chemosphere, 78, 1142, 2010.

7. T. G. Vasconcelos, K. Kümmerer, D. M. Henriques, and A. F. Martins, J. Hazard. Mater., 169, 1154, 2009.

8. S. P. Sun, H.Q. Guo, Q. Ke, J. H. Sun, S. H. Shi, M. L. Zhang and Q. Zhou, Environ. Eng. Sci., 26, 753, 2009.

9. E. De Bel, J. Dewulf, B. De Witte, H. Van Langenhove and C. Janssen, Chemosphere, 77, 291, 2009.

10. X. Van Doorslaer, K. Demeestere, P. M. Heynderickx, H. Van Langenhove and Dewulf, Appl. Catal., B, 101, 540, 2011.

11. T. A. Gad-Allah, M. E. M. Ali and M. I. Badawy, J. Hazard. Mater., 186, 751, 2011.

12. D. S. Bhatkhande, V. G. Pangarkar and A. A. C. M. Beenackers, JCTB, 77, 102, 2002.

13. P. Mangrulkar, M. V. Joshi, S. P. Kamble, N. K. Labhsetwar and S. Rayalu, Int. J. Photoenergy, 35, 10859, 2011.

14. S. P. Kamble. US 9,409,791 B2, 2016.

15. M. F. Hanafi, and N. Sapawe, Mater. Today. Proc., 31, 320, 2020.

16. M. Qamar, and M. Muneer, Desalination, 249, 535, 2009.

17. F. Chen, H. Liu, S. Bagwasi, X. Shen, and J. Zhang, J. Photochem. Photobiol. A, 215, 76, 2010.

18. U. Hubicka, P. Żmudzki, P. Talik, B. Żuromska-Witek, and J. Krzek, Chem. Cent. J. 7, 133, 2013.

19. A.S. Maia, A. R. Ribeiro, C. L. Amorim, J. C. Barreiro, Q. B. Cass, P. M. L. Castro and M. E. Tiritan, J. Chromatogr. A, 1333, 87, 2014.

20. K. Hayat, M. A. Gondal, M. M. Khaled, S. Ahmed and A. M. Shemsi, Appl. Catal. A. Gen., 393, 122, 2011.