



UV-C/NaOH based degradation of ciprofloxacin antibiotic in aqueous medium: A negative emission water treatment technology

Priyanshu Verma^{a,b} and Sujoy Kumar Samanta^a

^aDepartment of Chemical and Biochemical Engineering, Indian Institute of Technology Patna, Bihta, Patna-801 106, Bihar, India

^bDepartment of Biotechnology, Bansal Institute of Engineering and Technology, Lucknow-226 021, Uttar Pradesh, India

E-mail: priyanshuvermamickey@gmail.com, sksamanta@iitp.ac.in

Manuscript received online 17 November 2019, revised and accepted 07 January 2020

The presence of pharmaceutical compounds in open water streams has become an alarming concern over the couple of years due to their adverse effect on the environment, especially the emergence of multidrug resistance. Hence, their removal is quite essential from the open water streams. In this regard, the present work reports a novel approach that involves UV-C irradiation for the degradation of ciprofloxacin antibiotic present in a highly alkaline environment. It is observed that the UV-C/NaOH based degradation of ciprofloxacin follows almost zero-order reaction kinetics. Here, the process degradation efficiency is about 83% for an initial concentration of $C_0 = 10$ ppm, NaOH = 0.15 M, UV-C fluence rate = 1.03 mW/cm², irradiation time = 6 h, reaction volume = 25 ml. Moreover, this process has also shown a remarkable characteristic of negative CO₂ emission technologies. Therefore, not similar to other AOPs, this UV-C/NaOH based pollutant degradation approach has strong potential for the treatment of diverse alkaline cum industrial wastewater streams with simultaneous CO₂ sequestration.

Keywords: Advanced oxidation processes (AOPs), alkaline treatment, UV-C irradiation, wastewater treatment, negative emission technology, CO₂ capture.

Introduction

The emergence of micro-pollutants in natural water bodies has become a global concern due to the non-stop industrialization and growth of several manufacturing units (including textiles, pharmaceuticals, foods, fertilizers, pesticides, tanneries, petrochemicals, etc.)¹⁻⁶. Notably, the pharmaceutical compounds have been emerged as major pollutants in wastewater streams⁷⁻¹², especially antibiotics due to their overuse and successive contribution to the emergence of antimicrobial resistance^{10,13,14}. Consequently, several endeavours have been made regarding the removal of pharmaceutical compounds from the open water streams^{4,8,15-17}. In the last few years, several water treatment techniques, especially advanced oxidation processes (AOPs), have been studied and improvised for effective and efficient degradation of water pollutants¹⁻⁶. Conventionally, AOPs offer inevitable feasibility to reduce the organic pollutants' level from

ppm to ppb¹⁸. However, the degradation of pollutants present in real wastewater matrices containing various other constituents such as natural organic matters, inorganic salts, fatty compounds, surfactants, and many other substances generally used to be quite challenging and difficult in comparison to the treatment of bare water matrices. That processing would be more difficult in case of heterogeneous photocatalysis based water treatments^{6,19-27}. As per the existing literature, this difficulty is primarily due to limited penetration of photons through other ions and organic entities present in aqueous matrices that used to pre-absorb photons and results in an inadequate activation of photocatalysts^{21,24,25,28}. In addition, poor dispersion or enhanced aggregation of solid photocatalyst in complex water matrices^{23,29}; and shielding/hindering of solid photocatalyst by inorganic salts, proteinous and/or fatty compounds^{19,30} may also cause substantial reduction in the degradation effi-

ciency of heterogeneous photocatalysts. Since, there are conjugate pros and cons of established AOPs, the sustainable advancement of existing AOPs and the evolution of new AOPs have become an indispensable necessity. These developments may provide additional option to choose and opt for a better and subject effective AOP. Besides this, it should be consider that most of the established AOPs are effective in acidic or neutral pH environment only for example Fenton related AOPs are effective in acidic environment only^{31–34}. By the way, the industrial wastewater streams used to have a basic pH environment^{33,34}. Therefore, it is very essential to establish an alternative way for the treatment of alkaline wastewater streams without any prior pH correction.

In this regard, we studied the effectiveness of UV-C/NaOH based degradation of ciprofloxacin antibiotic present in aqueous medium. In addition, the degradation kinetics of the same has also been studied with 4 different initial concentrations of ciprofloxacin antibiotics. More notably, this process has also shown the characteristic of CO₂ sequestration processes that makes it more advantageous over other existing AOPs. Overall, this comprehensive study exploring the applicability of UV-C/NaOH based novel AOP (that requires a highly alkaline environment and continuous UV-C irradiation for its activity) will add a great value to the existing literature, and benefit a wide spectrum of researchers around the globe working in similar directions.

Experimental

The experiments were performed in a simple batch photocatalytic reaction system equipped with an inverted bell-shaped quartz vessel (with matrix volume of 25 ml) and two parallel UV-C irradiation rods (Philips TUV-11W-G11 T5, cylindrical low pressure Hg lamp) placed above 15 cm of the reaction vessel's base, at ambient temperature (25±2°C). The UV-C fluence rate was found to be about 4.778 mW/cm² (just at the irradiation source) and 1.03 mW/cm² (on the base of the reaction vessel). It was measured with the help of EIT UV Power Puck® II Profiler. The schematic of the whole reaction system has also been shown in Fig. 1. Here the reaction conditions were fixed at NaOH = 0.15 M, UV-C fluence rate = 1.03 mW/cm², irradiation time = 0 to 6 h, reaction volume = 25 ml.

The details of materials used in this work have been given in Table 1. All the reaction matrices were prepared in double distilled water. The pH of the studied matrix was measured

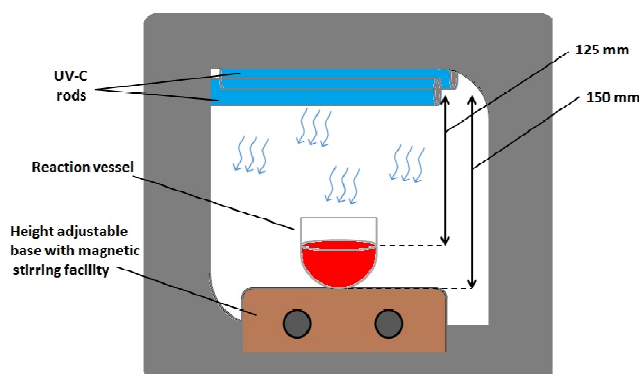


Fig. 1. Schematic of the modified batch photocatalytic reactor used in this study.

with the help of BIOBASE PH-900 multiparameter water quality meter (±0.005 pH). The primary degradation of pollutant species was observed and analyzed using UV-Visible spectrophotometer (Shimadzu UV-2600). Here, the absorbance at λ_{\max} of specific pollutant was calibrated as the concentration of the respective pollutant species in the studied matrix. Herein, the individual λ_{\max} under highly alkaline medium for ciprofloxacin had been identified and calibrated at 271 nm. Subsequently, the degradation efficiency or percentage degradation of ciprofloxacin was calculated by the formula $[(1 - C/C_0) \times 100]$, where C_0 and C were the initial ($t = 0$) and final ($t = t$) concentrations of the studied pollutant species, respectively.

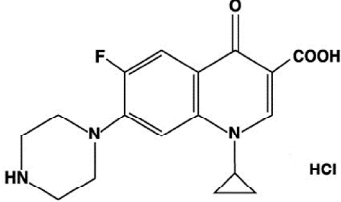
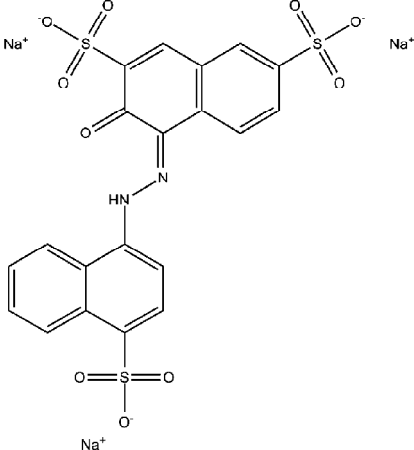
Moreover, the antimicrobial activity of UV-C/NaOH treated and UV-C photolyzed ciprofloxacin matrices was also studied with the help of disk diffusion based antimicrobial assay. The detailed disk diffusion assay protocol has been described in our earlier publication⁴. Besides this, to check the carbon absorption and mineralization level of this process, total organic carbon (TOC) and total inorganic carbon (TIC) analyses were performed through a total carbon analyzer (OI Analytical Aurora 1030W).

Results and discussion

Assessment of UV-C/NaOH based degradation of ciprofloxacin antibiotic:

Initially, 0.15 M NaOH solution (pH ≈ 13.0) with 10 ppm of ciprofloxacin (CIP) antibiotic has been continuously irradiated with UV-C lamp up to 6 h that has caused about 82.8% primary decomposition of CIP (Fig. 2). In addition, the same has also been studied for various other initial CIP concentra-

Table 1. List of chemical compounds and media used in this study

Name	Molecular formula/Structure	Brand/Supplier	Purity	CAS No.
Ciprofloxacin HCl (CIP)	$C_{17}H_{21}ClFN_3O_4$ 	TM MEDIA	>98%	86393-32-0
Amaranth (Ama)	$C_{20}H_{11}N_2Na_3O_{10}S_3$ 	Sigma-Aldrich	85–95%	915-67-3
Sodium hydroxide	NaOH	Merck	≥ 97%	1310-73-2
Mueller Hinton Agar	–	TM Media	–	–

tions (5, 15 and 50 ppm). The obtained UV-C/NaOH based degradation profile of CIP present in the distilled water matrix has been shown in Fig. 2 and also fitted with suitable kinetic models. From Table 2, it has been observed that there are notable differences between the theoretically calculated (through the optimal fitting of experimental data) half-life values for different initial CIP concentrations and their respective experimental half-life values. Hence, to cover the broad range of CIP concentrations, degradation kinetics has been determined through the n-th order kinetic model using the half-life method for this UV-C/NaOH based degradation of CIP. For the same, a graph has been plotted between the experimental $\ln(C_0)$ vs $\ln(t_{1/2})$. The obtained data points has been fitted with a straight line having a slope of $(1-n)$, as per the n-th order kinetic model (Fig. 3). This fitting has given the overall order of UV-C/NaOH based degradation of CIP

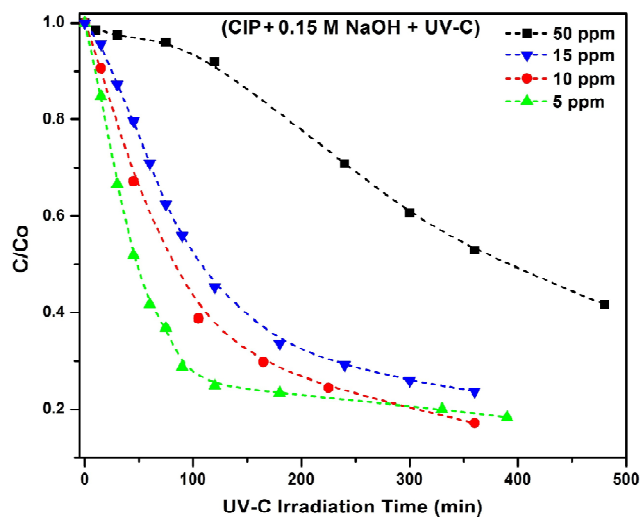


Fig. 2. UV-C/NaOH based degradation profile of CIP present in distilled water matrix with different initial concentrations.

Table 2. The kinetic parameters for UV-C/NaOH based degradation of different CIP concentrations

Initial CIP concentration (ppm)	Best suited kinetics	Coefficient of determination (R^2)	Rate constant (k)	Theoretical half-life ($t_{1/2}$, min)	Experimental half-life ($t_{1/2}$, min)
50	Zero-order	0.998	0.06 ppm min ⁻¹	417	390
15	First-order	0.968	0.00474 min ⁻¹	146	107
10	First-order	0.952	0.00575 min ⁻¹	121	84
5	Second-order	0.946	0.00274 ppm ⁻¹ min ⁻¹	73	47

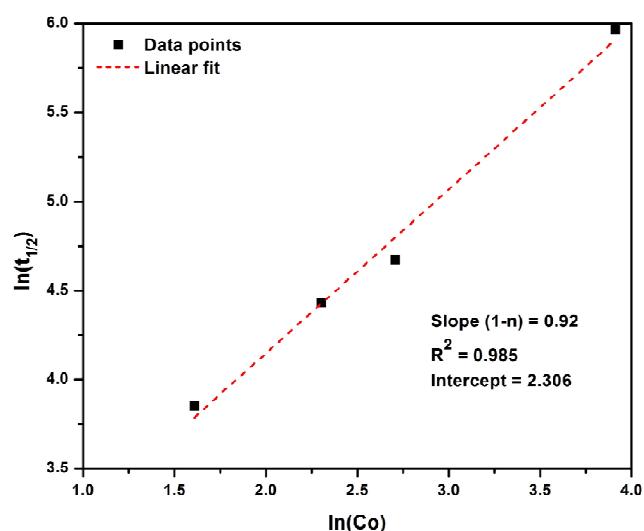


Fig. 3. The n-th-order kinetic model fitting of the CIP degradation profile using the half-life method.

ca. 0.08, which is quite close to zero-order. Furthermore, the rate constant has been reckoned about 0.051 ppm^{0.92} min⁻¹. It may be noted that the UV-C/NaOH based CIP degradation is following zero-order kinetics at higher CIP concentration, whereas at lower CIP concentrations, it is clearly showing a considerable shift in degradation kinetics (from lower order to higher order). On the other hand, it should be noted that the UV-C irradiation alone had also shown some degradation of CIP (at $C_0 = 10$ ppm, the degradation $\approx 37\%$ in 6 h of continuous UV-C irradiation) that was quite insignificant in comparison to that with UV-C/NaOH based degradation of the CIP that was around 82.8%. Hence, the synergy between UV-C irradiation based photolysis and UV-C/NaOH based AOP could be a prime reason for shifting of degradation order from lower order to higher order in lower concentration ranges of CIP. Besides this, the disk diffusion assay of various combinations has shown a complete loss of bacterial susceptibility in UV-C/NaOH treated CIP matrices as no zone

of inhibition has been observed in UV-C/NaOH treated matrices (Fig. 4). Moreover, it also indicates that the minimum inhibitory concentration of CIP matrix is below 10 ppm, as the CIP matrix with $C_0 = 10$ ppm (after 6 h of UV-C irradiation) has shown no perceptible zone of inhibition.

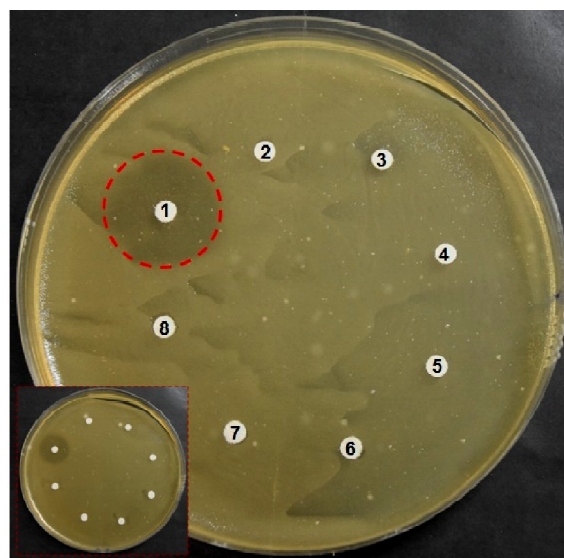


Fig. 4. Antimicrobial activity test of UV-C/NaOH treated CIP samples using the disk diffusion assay (Test microorganism = *E. coli* DH5 α ; Growth media = Mueller-Hinton Agar): (1) CIP-50 ppm after 36 h UV-C irradiation, (2) CIP-50 ppm + 0.15 M NaOH after 36 h UV-C irradiation, (3) CIP-10 ppm after 6 h UV-C irradiation, (4) CIP-10 ppm + 0.15 M NaOH after 6 h UV-C irradiation, (5) CIP-5 ppm + 0.15 M NaOH after 6 h UV-C irradiation, (6) CIP-15 ppm + 0.15 M NaOH after 6 h UV-C irradiation, (7) 0.15 M NaOH, and (8) Distilled water. The inset is a replicate of the same test.

Simultaneous CO₂ sequestration during UV-C/NaOH based degradation:

CO₂ is one of the highly emitted greenhouse gases in the environment that offers an extreme impact on global

warming³⁵. As a result, there are various carbon capture and storage techniques that have been evolved in the last few decades³⁶. However, in the context of this study, there are some reported studies that have established the application of NaOH based aqueous solution for CO₂ capture or sequestration^{35,37–39}. Hence, in this study, the treatment matrix for different combinations and conditions has also been analyzed for TIC and TOC contents (where TOC has been measured through the subtraction of TIC from total carbon content). Here, a substantial increment in the TIC has been observed in all cases with open air treatment up to 1 h which implies a CO₂ absorption behavior of UV-C/NaOH based treatment matrix that capture CO₂ from open environment as well as from the degraded pollutant species during the treatment process (Fig. 5A). However, to confirm these observations, one more experiment has been conducted for blank or pollutant free UV-C/NaOH based treatment matrix (0.15 M NaOH) with increased open air contact area, in the presence and absence of UV-C irradiation for 1 h. The obtained results have ascertained that UV-C and visible irradiations have negligible influence on the CO₂ absorption capability of treatment matrix (Fig. 5B). Conceivably, the CO₂ absorption capability of treatment matrix is found to be relatively increased with an increase in exposure or open air contact area of the treatment matrix that could be further increased by means of aeration or use of spargers. Besides this, the mineralization level of UV-C/NaOH based degradation of Ama dye is found to be about 47%.

Plausible mechanisms of ROS formation, pollutant degradation, and CO₂ sequestration in UV-C/NaOH based AOP:

The mechanism of UV-C/NaOH based AOP for degradation of pollutants present in an aqueous matrix involves multiple steps, and the feasibility of these steps has been supported by the suitable references. The steps are as follows: Step 1: The first step of UV-C/NaOH based AOP is the dissociation of NaOH into hydroxyl anions (OH⁻) and its respective cations (Na⁺)⁴⁰; Step 2: Next, the UV-C irradiation causes the photoionization of OH⁻ ions and convert them into OH• radicals by generating equivalent aqueous electrons^{41,42}; Step 3: After that, the aqueous or solvated electron (e⁻_{aq}) reacts with the dissolved oxygen molecule (O₂) and produces O₂•⁻ radical^{41,43}; Step 4: Finally, all the available free radicals attack the pollutant species either separately or combined, and readily oxidize the organic pollutant compounds

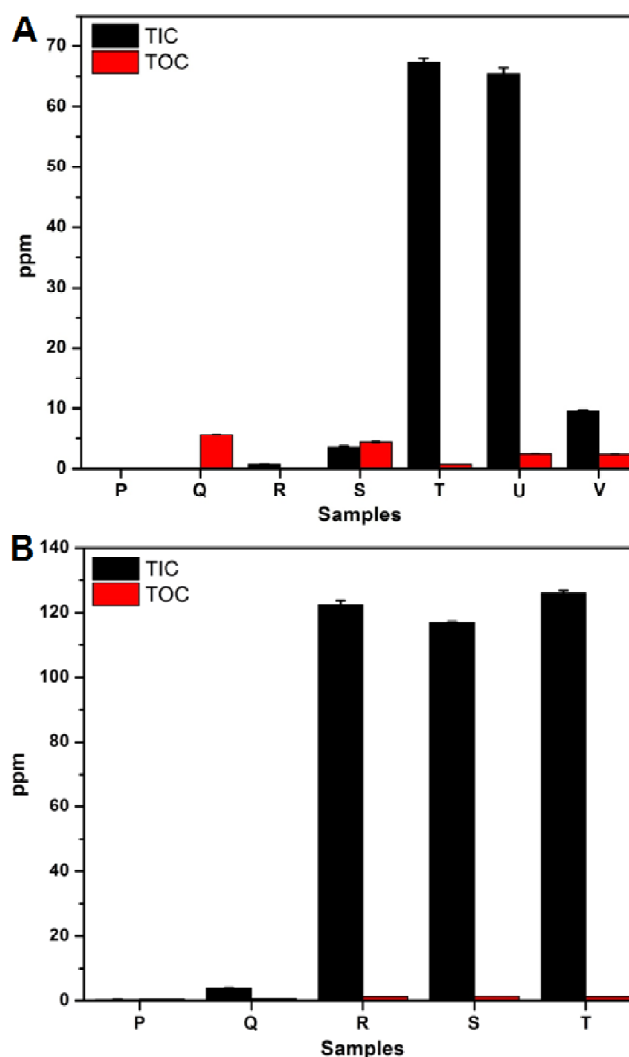
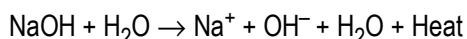


Fig. 5. Total organic carbon (TOC) and total inorganic carbon (TIC) content of different combinations. (A) For double distilled water matrix (P), matrix with 10 ppm Ama dye (Q), matrix with 0.15 M NaOH (R), and matrix with 10 ppm Ama dye + 0.15 M NaOH (S) in closed vessels; for double distilled water matrix with 0.15 M NaOH alone (T) and in the presence of 10 ppm Ama dye + 0.15 M NaOH (U) under 1 h UV-C irradiation in open vessels; for 10 ppm Ama dye + 0.15 M NaOH under 1 h UV-C irradiation in close lid vessel (V). (B) For double distilled water matrix (P) and matrix with 0.15 M NaOH stored in an airtight vessel (Q); Matrix with 0.15 M NaOH under UV-C irradiation (R), under dark condition (S) and under visible light exposure (T) for 1 h in open vessels. Note: Ama dye was used here as direct visual indicator of degradation process; Error bars are standard error of mean.

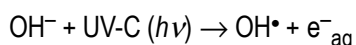
into some intermediates, and/or go through the complete mineralization (that produces CO₂, H₂O and inorganic salts)^{4,5}; Step 5: It's a simultaneous step that involves absorption of

CO₂ from the open air as well as capturing of CO₂ evolved from the mineralization of pollutant species, and finally fixing it into carbonates and bicarbonates³⁵.

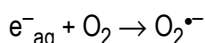
Step 1: Dissociation of NaOH



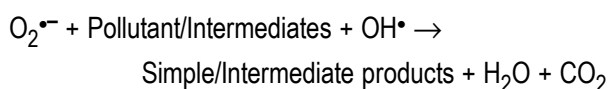
Step 2: Photoionization of OH⁻ ion



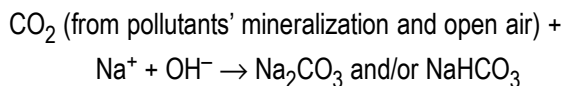
Step 3: Scavenging of solvated electrons



Step 4: Degradation or mineralization of pollutants



Step 5: CO₂ absorption in the form of carbonates and bicarbonates



Conclusions

In brief, this study reports a novel AOP for the degradation of organic pollutant species; namely ciprofloxacin, a pharmaceutical compound present in an aqueous medium. In addition, unlike other AOPs, this UV-C/NaOH based AOP used to follow almost zero-order reaction kinetics for the degradation of ciprofloxacin antibiotic. Furthermore, the plausible mechanisms of ROS formation followed by pollutant degradation and CO₂ sequestration via this UV-C/NaOH based AOP have also been proposed. The observations of this study are very useful to the scientific community dealing with the limitations of other AOPs, and global CO₂ emission issues. Overall, this UV-C/NaOH based AOP seems to be very promising for the oxidation cum degradation of various organic pollutant species. It could be quite advantageous for the treatment of versatile aqueous matrices over other existing AOPs (especially for the alkaline pollutant streams).

Acknowledgements

The authors would like to acknowledge the support and facilities provided by the Indian Institute of Technology Patna to conduct this research work.

References

1. S. K. Khetan and T. J. Collins, *Chem. Rev.*, 2007, **107**, 2319.
2. M. Muruganandham, R. P. Suri, S. Jafari, M. Sillanpää, G. J.

3. Lee, J. J. Wu and M. Swaminathan, *Int. J. Photoenergy*, 2014, **2014**, 821674.
4. L. L. S. Silva, C. G. Moreira, B. A. Curzio and F. V. da Fonseca, *J. Water Resource Prot.*, 2017, **9**, 411.
5. P. Verma and S. K. Samanta, *Res. Chem. Intermed.*, 2017, **43**, 6317.
6. P. Verma and S. K. Samanta, *Res. Chem. Intermed.*, 2018, **44**, 1963.
7. P. Verma and S. K. Samanta, *Environ. Chem. Lett.*, 2018, **16**, 969.
8. S. Singh, S. Singh, S. L. Lo and N. Kumar, *J. Taiwan Inst. Chem. Eng.*, 2016, **67**, 385.
9. S. Klementova, D. Kahoun, L. Doubkova, K. Frejlichova, M. Dusakova and M. Zlamal, *Photochem. Photobiol. Sci.*, 2017, **16**, 67.
10. L. Rimoldi, D. Meroni, E. Falletta, V. Pifferi, L. Falciola, G. Cappelletti and S. Arizzzone, *Photochem. Photobiol. Sci.*, 2017, **16**, 60.
11. C. Cui, Q. Han, L. Jiang, L. Ma, L. Jin, D. Zhang, K. Lin and T. Zhang, *Environ. Sci. Pollut. Res.*, 2018, **25**, 19393.
12. J. Hu, J. Zhou, S. Zhou, P. Wu and Y. F. Tsang, *Process Saf. Environ. Prot.*, 2018, **113**, 483.
13. Q. Li, Z. Guan, D. Wu, X. Zhao, S. Bao, B. Tian and J. Zhang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 6958.
14. P. Verma and S. K. Samanta, *Comp. Clin. Pathol.*, 2016, **25**, 1163.
15. M. Laquaz, C. Dagot, C. Bazin, T. Bastide, M. Gaschet, M. C. Ploy and Y. Perrodin, *Environ. Sci. Pollut. Res.*, 2018, **25**, 9243.
16. D. Wu, J. Li, J. Guan, C. Liu, X. Zhao, Z. Zhu, C. Ma, P. Huo, C. Li and Y. Yan, *J. Ind. Eng. Chem.*, 2018, **64**, 206.
17. X. Yan, K. Gan, B. Tian, J. Zhang, L. Wang and D. Lu, *Res. Chem. Intermed.*, 2018, **44**, 1.
18. S. Bao, J. Wan, B. Tian and J. Zhang, *Res. Chem. Intermed.*, 2018, **44**, 6137.
19. R. Munter, *Proc. Estonian. Acad. Sci. Chem.*, 2001, **50**, 59.
20. C. Guillard, E. Puzenat, H. Lachheb, A. Houas and J. M. Herrmann, *Int. J. Photoenergy*, 2005, **7**, 1.
21. W. Zhang, Y. Li, Y. Su, K. Mao and Q. Wang, *J. Hazard. Mater.*, 2012, **215**, 252.
22. J. Brame, M. Long, Q. Li and P. Alvarez, *Water Res.*, 2015, **84**, 362.
23. H. Dong, G. Zeng, L. Tang, C. Fan, C. Zhang, X. He and Y. He, *Water Res.*, 2015, **79**, 128.
24. J. F. Budarz, A. Turolla, A. F. Piasecki, J. Y. Bottero, M. Antonelli and M. R. Wiesner, *Langmuir*, 2017, **33**, 2770.
25. C. S. Uyguner-Demirel, N. C. Birben and M. Bekbolet, *Catal. Today*, 2017, **284**, 202.
26. L. Furatian and M. Mohseni, *Chemosphere*, 2018, **201**, 503.

Verma *et al.*: UV-C/NaOH based degradation of ciprofloxacin antibiotic in aqueous medium *etc.*

26. M. Ren, M. Drosos and F. H. Frimmel, *Chem. Eng. J.*, 2018, **334**, 968.
27. F. Sieland, N. A. Duong, J. Schneider and D. W. Bahnemann, *J. Photochem. Photobiol. A: Chem.*, 2018, **366**, 142.
28. C. Duca, G. Imoberdorf and M. Mohseni, *J. Environ. Sci. Health A: Tox. Hazard. Subst. Environ. Eng.*, 2017, **52**, 524.
29. D. Jassby, J. Farner Budarz and M. Wiesner, *Environ. Sci. Technol.*, 2012, **46**, 6934.
30. K. N. Clayton, J. W. Salameh, S. T. Wereley and T. L. Kinzer-Ursem, *Biomicrofluidics*, 2016, **10**, 054107.
31. A. Babuponnusami and K. Muthukumar, *J. Environ. Chem. Eng.*, 2014, **2**, 557.
32. N. Wang, T. Zheng, G. Zhang and P. Wang, *J. Environ. Chem. Eng.*, 2016, **4**, 762.
33. G. Boczkaj and A. Fernandes, *Chem. Eng. J.*, 2017, **320**, 608.
34. G. Boczkaj, A. Fernandes and P. Makosi, *Ind. Eng. Chem. Res.*, 2017, **56**, 8806.
35. M. Yoo, S. J. Han and J. H. Wee, *J. Environ. Manage.*, 2013, **114**, 512.
36. D. Y. Leung, G. Caramanna and M. M. Maroto-Valer, *Renew. Sust. Energ. Rev.*, 2014, **39**, 426.
37. P. C. Chen, C. F. Huang, H. W. Chen, M. W. Yang and C. M. Tsao, *Energy Procedia*, 2014, **61**, 1660.
38. J. K. Stolaroff, D. W. Keith and G. V. Lowry, *Environ. Sci. Technol.*, 2008, **42**, 2728.
39. N. Zhenqi, G. Yincheng and L. Wenyi, in: "Energy and Environment Technology", International Conference on Energy and Environment Technology, 2009, pp. 52-55 (IEEE). <https://doi.org/10.1109/ICEET.2009.479>.
40. C. D. Wick and L. X. Dang, *J. Chem. Phys.*, 2010, **133**, 024705.
41. M. C. Gonzalez and D. O. Mártire, *J. Chem. Research (S)*, 1997, 54.
42. P. Attri, Y. H. Kim, D. H. Park *et al.*, *Sci. Rep.*, 2015, **5**, 9332.
43. J. A. Rosso, M. C. Gonzalez and D. O. Mártire, *Int. J. Chem. Kinet.*, 2000, **32**, 111.