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Degradation of antibiotic norfloxacin in aqueous solution using advanced oxidation processes (AOPs)—A comparative study

G. Shankaraiah[a], Saritha Poodari[b], D. Bhagawan[a], Vurimindi Himabindu[a,*], S. Vidyavathi[c]

[a]*Centre for Environment, Institute of Science and Technology, Jawaharlal Nehru Technological University, Hyderabad 500 085, India, Tel. +91 9912297832; email: shankar_cool2008@yahoo.com (G. Shankaraiah), Tel. +91 9441184024; email: bhagawanist@gmail.com (D. Bhagawan), Tel. +91 9849693828; email: drvhimabindu@gmail.com (V. Himabindu)*
[b]*Civil Department, Malla Reddy Engineering College, Hyderabad 500 085, India, Tel. +91 9849332474; email: poodarisaritha@gmail.com*
[c]*Department of Civil Engineering, JNTUH College of Engineering Hyderabad, Jawaharlal Nehru Technological University, Hyderabad 500 085, India, Tel. +91 9392493533; email: vidyasom@yahoo.co.in*

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ABSTRACT

The consumption of antibiotics in today's world has increased tremendously and as such they are frequently found in effluents, sewage treatment plants, hospital waste water and surface water like lakes and rivers. The aquatic organisms are severely affected due to the presence of these antibiotics. Moreover, as these antibiotics are mostly recalcitrant, biological treatment methods are not feasible. Hence, the present study is focused on the treatment of one such antibiotic called norfloxacin using advanced oxidation processes (AOPs). The parameters considered in this study include the effect of UV, initial pH of the recalcitrant solution, UV/H_2O_2, Fenton, photo-Fenton process, UV/TiO_2 and UV/TiO_2 immobilization with glass beads. Among all the processes studied, photo-Fenton process has found to be effective and removed 96% of the norfloxacin. The optimum conditions obtained for the maximum degradation with photo-Fenton process are: pH 3, H_2O_2 concentration of 200 mg/L and iron concentration of 30 mg/L, for an initial drug concentration of 150 ppm.

Keywords: Antibiotics; Pharmaceuticals; Norfloxacin; Photocatalysis; Non-biodegradable; TiO_2 immobilization glass beads

1. Introduction

Several pharmaceuticals have been detected in aquatic environment such as treated drinking water, surface water, groundwater, wastewater treatment plants (WWTPs) effluents and sludge [1]. Release of these chemicals in the environment can be of high concern for public health, and may have undesirable health effects on humans, animals and ecosystem. Antibiotics are such materials that can reach the environment via different routes like: human or animal excretions, pharmaceutical manufacturing plants effluents, medical wastes, municipal WWTPs and hospital wastewater [2]. Antibiotics in the environment has been reported worldwide, such as in rivers of Europe [3,4], surface water of America [5,6], rivers of Australia [7] and seas and rivers of Asia [8,9].

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*Corresponding author.

The presence of antibiotics in environmentally relevant levels has been associated with chronic toxicity to some non-target organisms and evolution of antibiotic-resistant bacteria [10]. Thus, the antibiotics in wastewater are of particular concern, as they can induce bacterial resistance, even at low concentrations [11].

The fluoroquinolone group (ciprofloxacin, norfloxacin and enrofloxacin) is one of the most important pharmaceuticals used worldwide for humans and veterinary purposes. Norfloxacin is a synthetic antibacterial agent occasionally used to treat common as well as complicated urinary tract infections. The presence of such broad-spectrum antibiotics in aquatic environments may pose serious threat to the ecosystem and human health by inducing proliferation of bacterial drug resistance [12]. To avoid the dangerous accumulation of antibiotics in the aquatic environment, research efforts are underway to develop powerful treatment**.** Although different physical, biological and chemical methods are available for the treatment of waste water and as since antibiotics are non-biodegradable, physical and biological treatment methods are not applicable for degradation of antibiotics. Hence, advanced oxidation processes (AOPs) technique is chosen in the present study. AOPs are based on the generation of hydroxyl radical (OH) as oxidant. AOPs are very efficient methods for destruction and mineralization of recalcitrant organic compounds in pharmaceutical effluents.

Recent studies show that AOP can be successfully applied for the treatment of drug wastewater [13,14]. Degradation of amoxicillin by ozonation and photo-Fenton has also been reported [15,16]. UV/H_2O_2 process also could degrade carbamazepine very effectively [17]. UV/TiO_2 immobilization glass beads process is used effectively for decolourization of an Azo Dye C.I. Direct Red 23 [18]. Photoreactors used for liquid-phase oxidation are typically based on the slurry system, in which TiO_2 particles are suspended in an aqueous solution. The immobilized TiO_2 glass beads under UV light are configured more effective towards the treatment of recalcitrant organic pollutants. Moreover, release of TiO_2 particles into the environment leads to potential adverse effects on human and ecological health. Interactions of TiO_2 particles with exposed cells and organic pollutants disrupt cellular energy metabolism and increase intra-cellular oxidative stress, DNA double-strand breaks and chromosomal damage, although nano-TiO_2 alone shows no significant cytotoxicity or genotoxicity [19,20]. Norfloxacin was selected as the model pollutant in this paper since it had been widely detected in aqueous environment and it is known to cause severe pollution problems to the aquatic environments. The different UV combination methods such as UV/H_2O_2, Fenton process, photo-Fenton, UV/ TiO_2 and UV/ IGBT were applied for the degradation of norfloxacin.

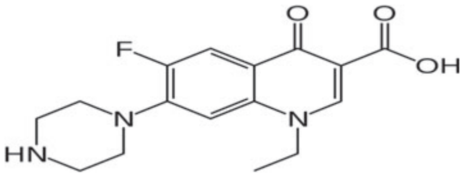
2. Materials and methods

2.1. Chemicals and reagents

Norfloxacin is procured from one of the reputed pharma laboratory with purity of 99%. Degussa P_{25} titanium dioxide is obtained from Degussa Corporation, Pune, India. H_2O_2 solution (30%, reagent grade) is procured from Lobacheme. $FeSO_4·7H_2O$ (ferrous sulphate) as the source of Fe(II), H_2SO_4 (sulphuric acid) and NaOH (sodium hydroxide) are purchased from Merck. All the chemicals used in the present study are of analytical grade. Distilled water is used for the entire study. Chemical structure of norfloxacin is shown in Fig. 1.

2.2. Reactor set-up

All the experiments are performed in a cylindrical photoreactor (Fig. 2) with a total volume of 1.0 L (diameter 12 cm and height 13.3 cm). The UV lamp is encased in a quartz tube to protect it from direct contact with an aqueous solution flowing through an annulus between the inner surface of the vessel and the outer surface of the quartz tube, located at the axis of the vessel. The reactor is provided with inlets for feeding reactants, and ports for measuring temperature and withdrawing samples. The reactor is open to air with Teflon coating. A magnetic stirrer is placed at the bottom for homogenization. The UV irradiation sources is 250-W low-pressure mercury vapour lamp (maximum emission at 365 nm) encased in the quartz tube. The lamp was axially centred and immersed in the solution containing the respective norfloxacin. A gas tight syringe is used to collect the sample at regular intervals from the sample-port of the reactor.



1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1H-quinoline-3-carboxylic acid

Fig. 1. Structure of norfloxacin.

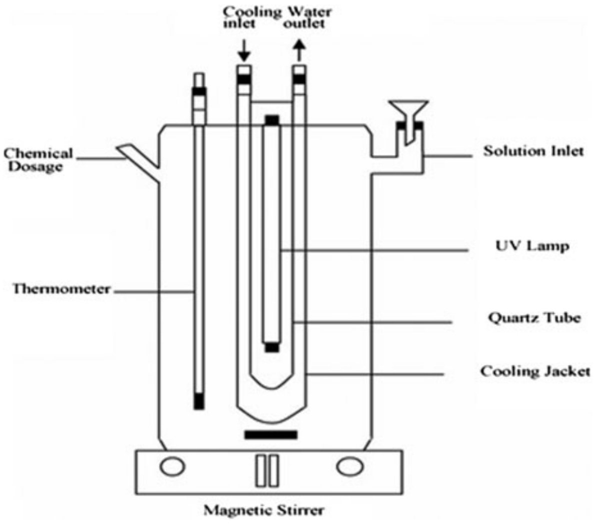


Fig. 2. The schematic of the laboratory-scale photochemical reactor.

2.3. Experimental set-up

Desired quantities of substituted norfloxacin is weighed and dissolved in distilled water to prepare 1,000 ppm stock solution. The shelf life of the stock solutions was maintained for 1 week. Further dilutions are made from stock solution. All the stock solutions, standards and pure compounds are stored in dark below room temperature. The samples are brought to room temperature before experimentation. Control samples are run for every experiment to validate the degradation and also check for any loss on volatilization. Norfloxacin solutions are treated at different pH values. The adjustment of pH is made with 0.1 N/1.0 N solution of H_2SO_4 or 0.1 N/1.0 N NaOH.

Experiments are carried out in batch mode. Different concentrations of H_2O_2 and Fe^{2+} in the ratio of 10:1 are used in photo-Fenton experiments. In case of UV/H_2O_2, different concentrations of hydrogen peroxide (50, 100, 150, 200 and 250 ppm) are used to observe norfloxacin degradation. Initial concentration of norfloxacin is 150 mg/L. In Photocatalytic experiments with TiO_2, the dosage of TiO_2 is varied from 0.1 to 0.5 g. The reaction mixture is homogenized by magnetic agitation for 15 min before introducing into the photoreactor. Samples are withdrawn at regular intervals and centrifuged, followed by filtration through 0.25-μm membrane disc filters (MDI, India type SY25NN). The filtrate is stored at 4˚C and further analysed for compound degradation and COD reduction. The samples containing H_2O_2 are treated with MnO_2 powder to decompose the residual H_2O_2 since it interferes with the COD and absorbance measurements [21]. In order to arrest oxidation after treatment time, the filtered samples are quenched by adding 10% Na_2SO_3 aqueous solution [22].

2.4. Preparation of Immobilization of TiO_2 on Glass Beads

TiO_2 is supported on glass beads by heat attachment method as follows. Glass beads are etched with dilute hydrofluoric acid (5% v/v) for 24 h and washed thoroughly with distilled water, making a rough surface for better contact of TiO_2 on the glass beads surface. TiO_2 slurry is prepared with a known amount of TiO_2 (2 g) in 200 mL distilled water and continuously mixed for 24 h. The glass beads are immersed in the slurry of TiO_2 and were thoroughly mixed for 20 min. It is then removed from the suspension and placed in an oven for 1.5 h at 150˚C. It is subsequently placed in the furnace for 2 h at 500˚C. The samples are thoroughly washed with doubly distilled water for the removal of free TiO_2 particles [23–26].

2.5. Analytical procedure

Norfloxacin concentration is measured by Shimadzu-2450 UV–vis Spectrophotometer at a wave length of 272 nm and TOC measured by Shimadzu TOC-L CPH E 200. COD analysed as per the standard method No. 5220 C, from STANDARD METHODS for the examination of Water and Wastewater 20th addition 1998, APHA.

The norfloxacin removal percentage (%) is calculated as follows:

$$\text{Removal of the norfloxacin}\,(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i is the initial pollutant concentration (mg/L) and C_f is the final pollutant concentration (mg/L).

3. Results and discussion

3.1. UV Photolysis

3.1.1. Effect of pH on the degradation of norfloxacin

To study the effect of pH on norfloxacin degradation, a series of experiments are carried at different pH values ranging from 3 to 11 with initial concentration of norfloxacin 150 mg/L, and COD reduction, the results of which are illustrated in Figs. 3 and 4. It has been observed that the photodegradation of norfloxacin is influenced by the pH value, and the maximum compound degradation % and COD reduction of norfloxacin (49 and 46%) is achieved at pH 7 after 180-min irradiation. The compound degradation

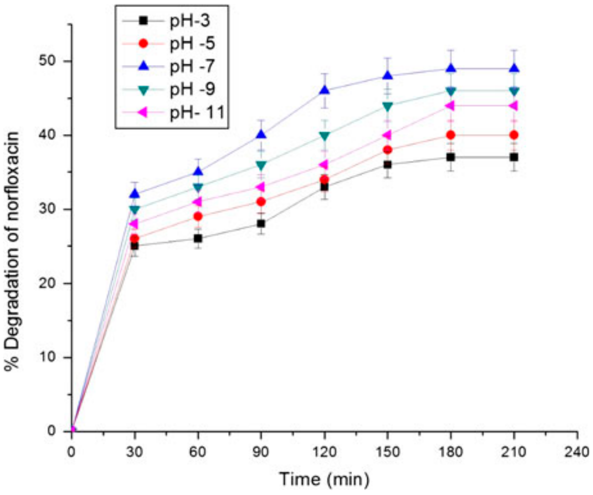


Fig. 3. Variation in initial pH on the degradation of norfloxacin and initial drug concentration of 150 ppm.

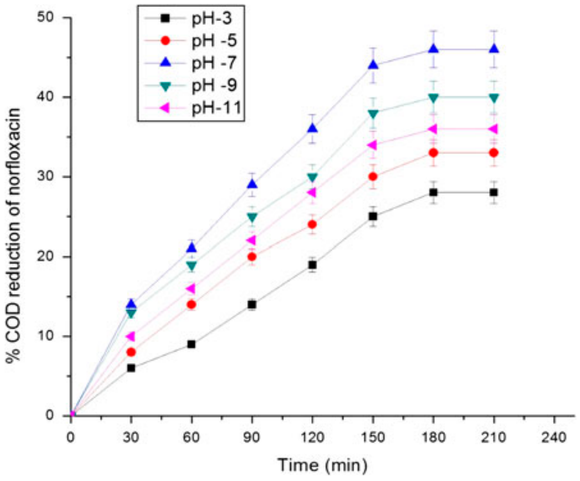


Fig. 4. Variation in initial pH on the COD reduction of norfloxacin and initial drug concentration of 150 ppm.

decreased from 49 to 37% with increasing pH from 7 to 11. This is in agreement with the observation of Stefan et al. [27] that direct photolysis contributions decreased when the pH is increased from 3 to 7. pH may affect the formation of active substance in the generation of hydroxyl radical. Effect of pH on the photodegradation of norfloxacin demonstrates that pH plays an important role in the photochemical degradation of norfloxacin in aqueous solution.

3.2. *Effect of Initial concentration on the degradation of norfloxacin*

Optimization experiments on direct photolysis of norfloxacin are first carried out by irradiating the aqueous solution to determine the effect of initial concentration with 250-W UV lamp. Photolysis is a common method for generating free radicals through sigma bond cleavage. These radicals are most often the precursors that generate other free radicals [28]. The first step in a photochemical reaction is the excitation of a molecule through absorption of one photon. The excited molecule leads to a chemical reaction. Thus, the organic substrate is progressively degraded. In order to choose the effective concentration of norfloxacin, studies are conducted in the range of 50–250 ppm of norfloxacin at pH 7 (Figs. 5 and 6). From the concentration screening experiments, it has been observed that 150 mg/L of the norfloxacin compound concentration is efficiently degraded with maximum COD % reduction (45 and 40%). And above 150 mg/L, the degradability diminished and COD reduction diminished. For all further experiments, 150 ppm of the norfloxacin is considered as optimum concentration.

3.3. *Peroxide with UV process*

The effect of initial H_2O_2 concentration on the degradation of norfloxacin and COD reduction is illustrated in Figs. 7 and 8. Hydrogen peroxide doses are varied from 50 to 250 ppm. In the presence of UV/H_2O_2 process, the norfloxacin photodegradation increased when compared to direct photolysis even at low initial H_2O_2 concentrations. The efficiency increased with increasing H_2O_2 concentration. However, increasing the initial hydrogen peroxide concentration enhanced the oxidation up to a certain level. On further increase in concentration, hydrogen peroxide inhibition on the photolytic degradation of the drug is observed. From these experiments, it has been observed that the optimum H_2O_2 concentration is 200 ppm at which 72% compound removal and 66% COD reduction has achieved. Further addition of H_2O_2 did not improve the degradation rate due to self-decomposition of H_2O_2. Moreover, at higher concentrations, hydrogen peroxide acted as a free-radical scavenger itself, thereby decreasing the hydroxyl radical concentration and reducing compound elimination efficiency [29–32]. From all these experiments, it is concluded that the optimum H_2O_2 concentration is 200 ppm at which 72% of norfloxacin degradation is absorbed from the suspension at pH 7 after 180-min irradiation.

The following reactions are observed in peroxide-mediated photo-oxidation. The photolysis of hydrogen peroxide leads to the formation of $^{\cdot}OH$ radicals [33].

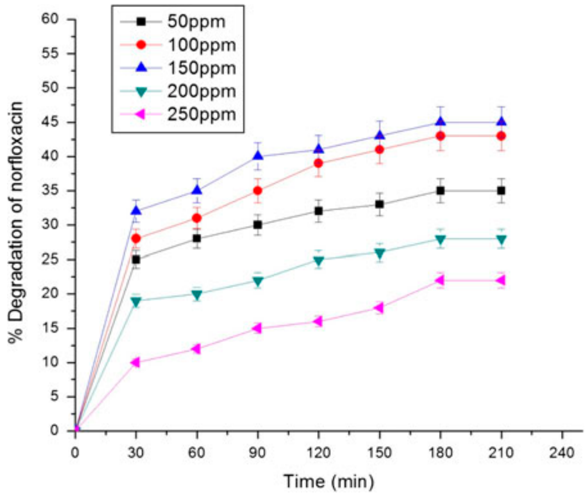


Fig. 5. Variation in initial norfloxacin concentration.

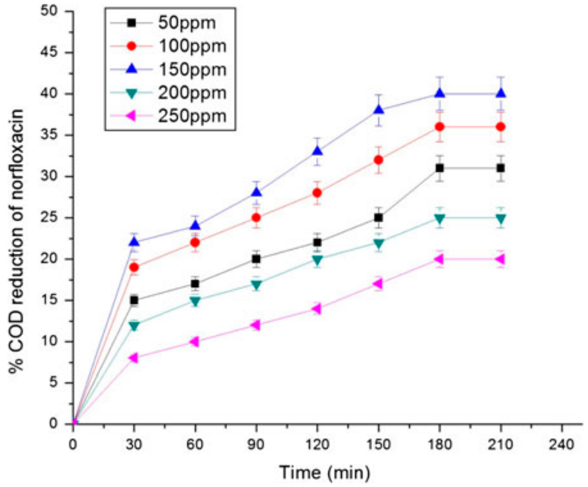


Fig. 6. Variation in initial norfloxacin concentration of the COD reduction.

$$H_2O_2 + hv \longrightarrow 2HO^{\cdot} \quad (2)$$

Also, HO_2^-, which is in acid and base equilibrium with H_2O_2, absorbs the UV radiation of the wavelength at 365 nm and releases ${}^{\cdot}OH$ radicals which are responsible for the oxidation of norfloxacin.

$$H_2O_2 \rightleftarrows HO_2^- + H^+ \quad (3)$$

$$HO_2^- + hv \longrightarrow {}^{\cdot}OH + O^{\cdot -} \quad (4)$$

3.4. Fenton and photo-Fenton oxidation

Results reported in the relevant literature clearly indicate that the operation pH determines the degree of oxidation reached in the treatment, with pH 3.0 being the most effective value [34] (Kang et al.). The efficiency of the treatment experiencing strong reductions as the pH is set out of this interval [35,36]. At higher pH levels, iron precipitates as hydroxide, and at lower levels, self-decomposition of hydrogen peroxide is promoted [37]. Hence, in the present study, the Fenton and photo-Fenton experiments are performed at an acidic pH of 3.0 ± 0.1 with an initial H_2O_2 concentration of 200 ppm.

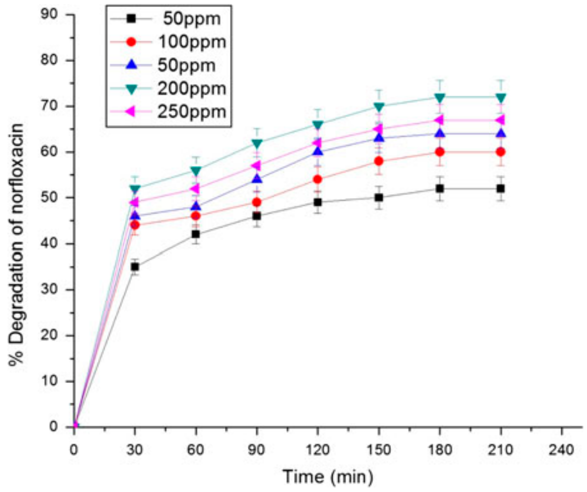


Fig. 7. Effect of initial H_2O_2 concentration on the degradation of 150 ppm of norfloxacin in peroxide with UV at pH 7.

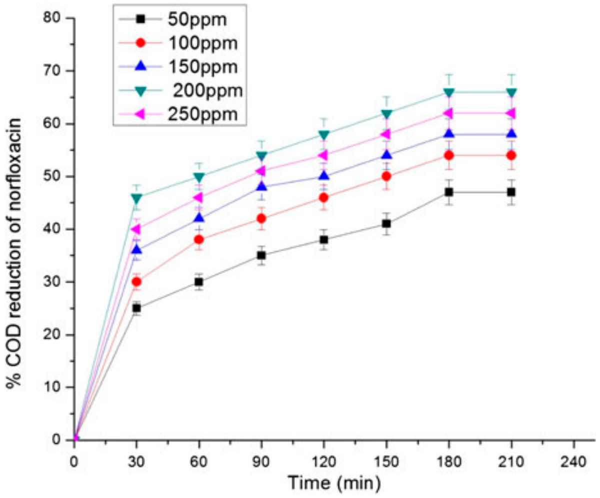


Fig. 8. Effect of initial H_2O_2 concentration on the COD reduction of 150 ppm of norfloxacin in peroxide with UV at pH 7.

3.4.1. Effect of initial Fe^{2+} concentrations on the degradation of norfloxacin

The effect of initial Fe^{2+} concentrations on the degradation of the drug in Fenton and photo-Fenton processes is presented in Figs. 9–12 by varying Fe^{2+} concentration from 10 to 50 ppm. The degradation rate of the drug increased with an increase in iron concentration. With Fenton reagent (Fe^{2+}), only 38 and 36% of compound degradation and COD reduction has been achieved. While with photo-Fenton (Fe^{2+} concentration 30 ppm), the maximum compound and COD% reduction observed to be 96 and 93%, respectively. Further increase in iron concentration did not show any change in the degradation rate [38]. This is due to the fact that at a Fe(II) concentration higher than the optimum, most of the hydroxyl radicals are consumed by the side reactions before they could be utilized effectively for the removal of the compound [39]. Moreover, it resulted in brown turbidity that hindered the absorption of the UV light required for photolysis and caused the recombination of OH radicals [40]. The following reactions occur in photo-Fenton process when Fe^{3+} ions are added to the H_2O_2/UV.

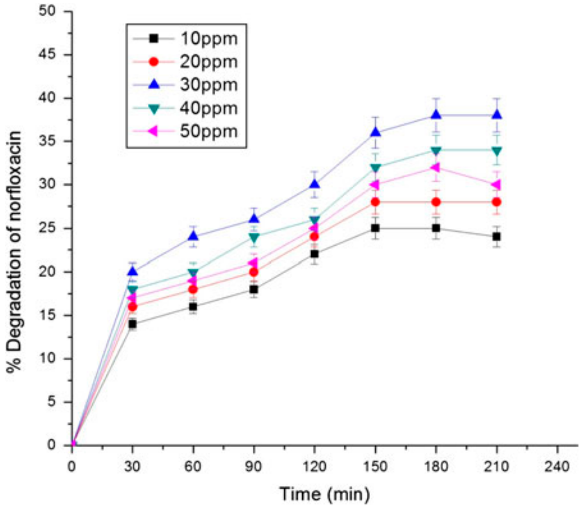


Fig. 9. Effect of initial Fe^{2+} concentrations on the degradation of 150 ppm norfloxacin in Fenton process.

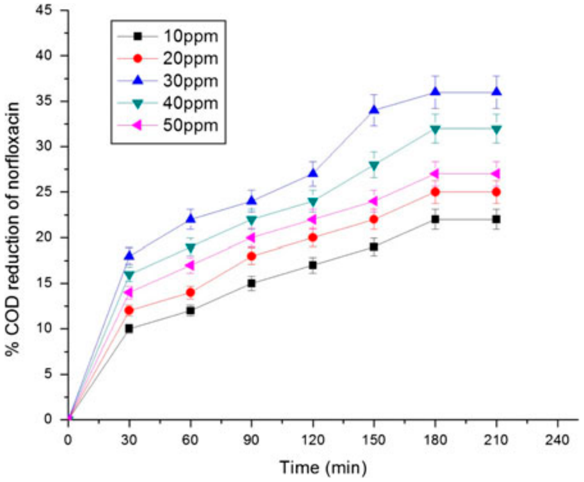


Fig. 10. Effect of initial Fe^{2+} concentrations on the COD reduction of 150 ppm norfloxacin in Fenton process.

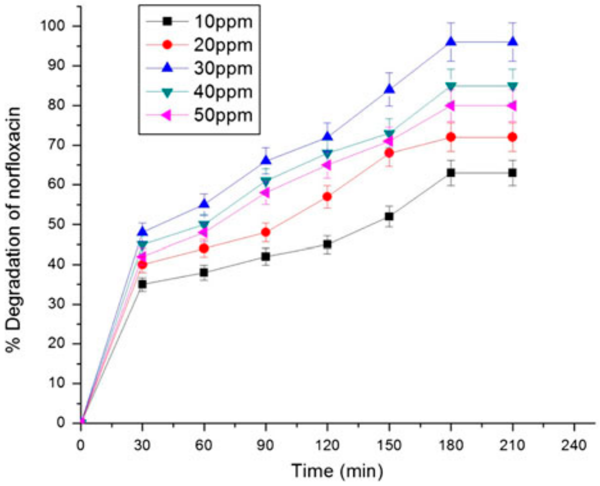


Fig. 11. Effect of initial Fe^{2+} concentrations on the degradation of 150 ppm norfloxacin in photo-Fenton process.

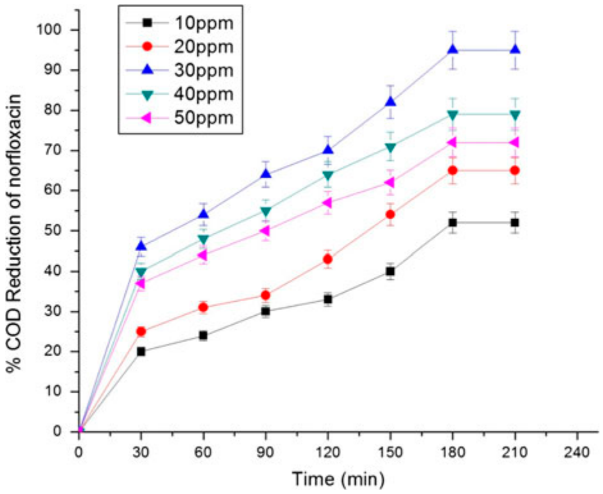


Fig. 12. Effect of initial Fe^{2+} concentrations on the COD reduction of 150 ppm norfloxacin in photo-Fenton process.

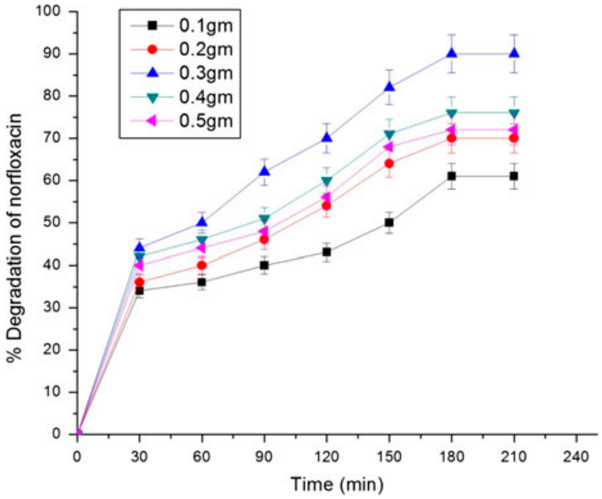


Fig. 13. Effect of TiO_2 dosage on the degradation of 150 ppm norfloxacin at pH 7.

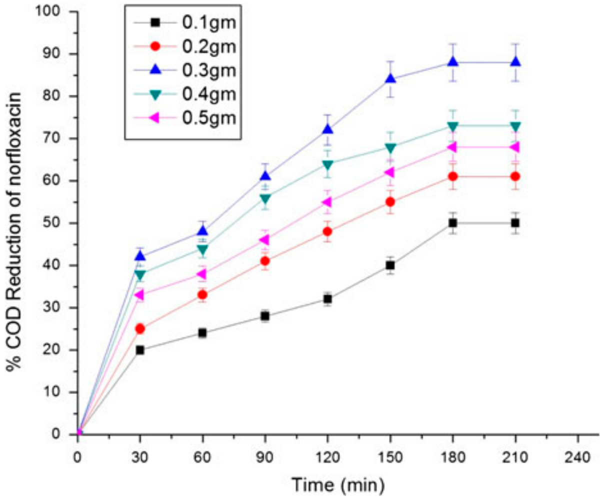


Fig. 14. Effect of TiO_2 dosage on the COD reduction of 150 ppm norfloxacin at pH 7.

$$Fe^{3+} + H_2O \longrightarrow Fe(OH)^{2+} + H^+ \tag{5}$$

$$Fe(OH)^{2+} \rightleftarrows Fe^{3+} + OH^- \tag{6}$$

In reaction (7), $Fe(OH)^{2+}$ complex is formed at pH 3 which when exposed to UV irradiation, the complex is further subjected to decomposition and will produce $^{\cdot}OH$ and Fe^{2+} ions:

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + {}^{\cdot}OH \tag{7}$$

3.5. TiO_2-mediated photooxidation (UV/TiO_2)

The effect of different TiO_2 dosages on the degradation COD reduction of norfloxacin is illustrated in Figs. 13 and 14 by varying the dosages from 0.1 to 0.5 g. UV/TiO_2 results observed that the degradation of norfloxacin is influenced by the pH 7 [41]. Therefore, the surface of the TiO_2 is positively charged under acidic conditions and negatively charged under alkaline conditions. The maximum oxidizing capacity of the TiO_2 is at lower pH; however, the reaction rate is known to decrease at low pH due to excess H^+ [42]. In the presence of TiO_2 process, the efficiency increased with increasing TiO_2 dosage. However, increased initial TiO_2 dosage enhanced the oxidation only up to a certain level. On further increase in the dosage of the catalyst, TiO_2 inhibition on the photolytic degradation of the norfloxacin is observed. Figs. 13 and 14 show 61, 70, 90, 76 and 72% of compound degradation and 50, 61, 88, 73 and 68% of COD reduction at 0.1, 0.2, 0.3, 0.4 and 0.5 g dosage of TiO_2, respectively. From these experiments, it is concluded that the optimum TiO_2 dosage is 0.3 g at which 90 and 88% compound removal and COD reduction is achieved after 180-min irradiation.

The basis of photocatalysis is the photo-excitation of a semiconductor that is solid as a result of the absorption of electromagnetic radiation, often, but not exclusively, in the near-UV spectrum. Under near-UV irradiation, a suitable semiconductor material may be excited by photons possessing energies of sufficient magnitude to produce conduction band electrons and valence band holes [40]. These charge carriers are able to induce reduction or oxidation, respectively. At the surface of the TiO_2 particle, these may react with absorbed species.

$$e^- + O_2 \longrightarrow {}^{\cdot}O_2^- \tag{8}$$

$$H^+ + A^- \longrightarrow {}^{\cdot}A \tag{9}$$

$$H^+ + OH^- \longrightarrow {}^{\cdot}OH \tag{10}$$

$${}^{\cdot}OH + RH \longrightarrow {}^{\cdot}RHOH \tag{11}$$

$${}^{\cdot}OH + RH \longrightarrow {}^{\cdot}R + H_2O \tag{12}$$

$$H^+ + RH \longrightarrow {}^{\cdot}RH^+ \tag{13}$$

Holes possess an extremely positive oxidation potential and should thus be able to oxidize almost all chemicals. Even the one-electron oxidation of water resulting in the formation of hydroxyl radicals should be energetically feasible.

$$H_2O + H^+ \longrightarrow {}^{\bullet}OH + H^+ \qquad (14)$$

3.6. UV/TiO$_2$-immobilized glass beads

The effect of TiO$_2$-immobilized glass beads (IGBT) on the degradation of norfloxacin and COD reduction has been illustrated in Figs. 15 and 16. The TiO$_2$ IGBT dosage varied from 2 to 12 g [41]. In the presence of TiO$_2$ process, the efficiency increased with increasing IGBT. From the results (Figs. 15 and 16), it has been observed that 45, 56, 63, 67, 78 and 70% norfloxacin degradation and 42, 48, 57, 62, 74 and 68% of COD reduction % at 2, 4, 6, 8, 10 and 12 g of IGBT, respectively. However, increased initial IGBT enhanced the oxidation only up to a certain level (10 g) and further increase in the IGBT dose, TiO$_2$ inhibition on the photolytic degradation and COD reduction of the norfloxacin is observed. From these experiments, it is concluded that the optimum IGBT is 10 g at which 78 and 74% of norfloxacin degradation and COD reduction has been observed at 180-min irradiation, respectively.

3.7. Comparison of various AOPs

3.7.1. COD and TOC reduction

A comparison of UV, UV/H$_2$O$_2$, Fenton processes, photo-Fenton, UV/TiO$_2$ and UV/IGBT in terms of COD and TOC reduction is determined to find the efficacy of the treatment systems. Initial COD and TOC of the norfloxacin are 610 and 495 mg/L, respectively. Percentage reduction of COD and TOC with different AOPs is shown in Figs. 17 and 18. UV alone, Fenton process, UV/H$_2$O$_2$, UV/TiO$_2$ and UV/IGBT could not totally remove COD and TOC in Table 1. Hence, it is observed that the photo-Fenton process is increased; reduction in COD and TOC is found to be 95 and 93%, respectively (Figs. 19 and 20).

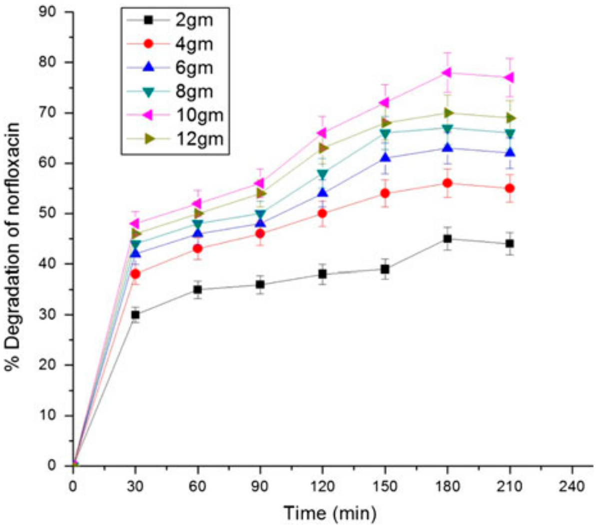


Fig. 15. Effect of TiO$_2$ IGBT on the degradation of 150 ppm norfloxacin at pH 7.

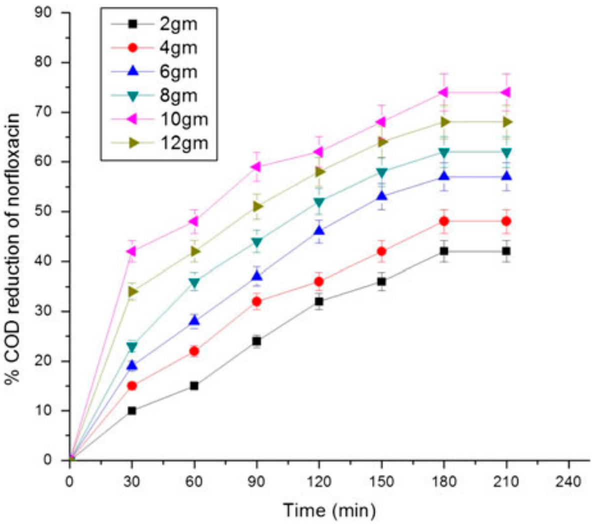


Fig. 16. Effect of TiO$_2$ IGBT on the COD reduction of 150 ppm norfloxacin at pH 7.

3.8. Cost estimation

Cost evaluation is one of the important aspects in the treatment of waste. Cost estimates are developed to allow direct comparison among the various AOPs studied. The costs for AOPs are highly dependent on the quality of the source water to be treated and effluent treatment goals.

Hence, in the present section, an attempt is made on the estimation of operating costs for the treatment processes used considering norfloxacin as the model compound. The cost of reagents is given in Table 2.

Cost evaluation for UV processes was based on electrical energy per order (EE/O) [43] using the following formula:

$$\mathrm{EE/O}\,(\mathrm{kWh/m^3}) = \frac{Pt \times 1000}{V \times 60\,\log(C_{\mathrm{in}}/C_{\mathrm{fin}})}$$

where P is the rated power (kW), V is the volume (in litres) of water treated, t is the time (min), C_{ini} and C_{fin}

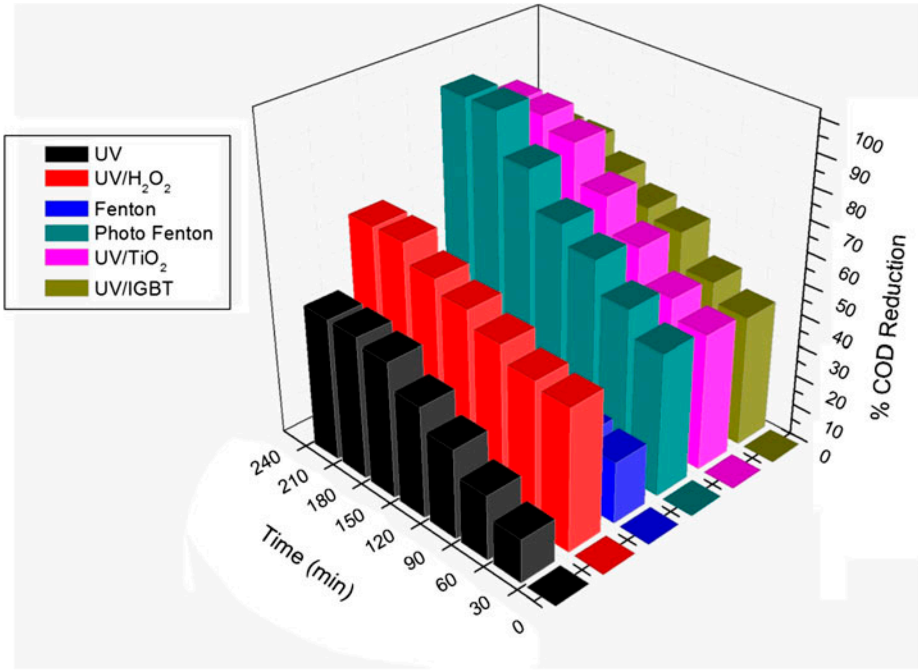


Fig. 17. COD reduction in norfloxacin using various (AOPs).

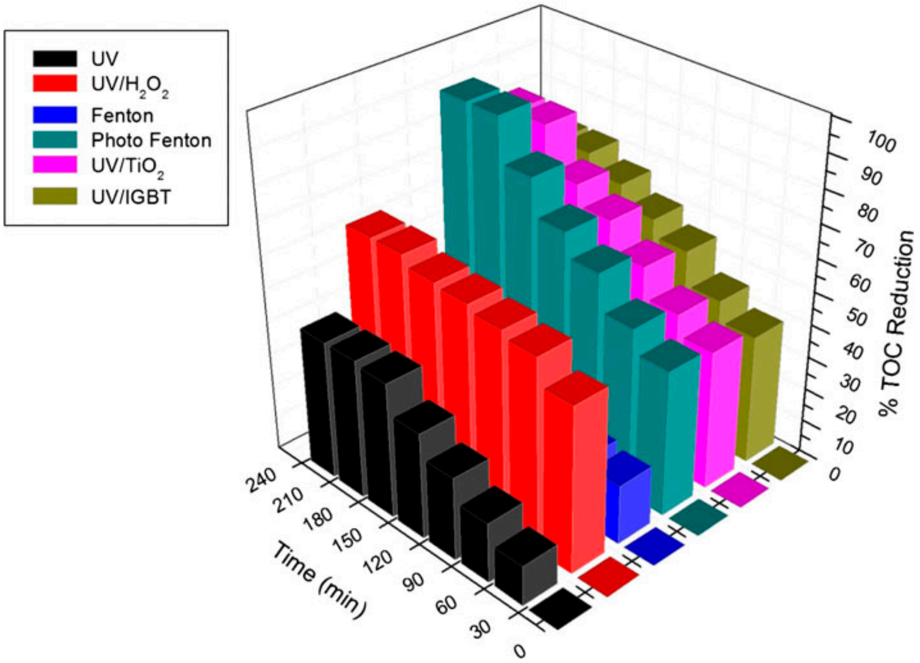


Fig. 18. TOC reduction in norfloxacin using various (AOPs).

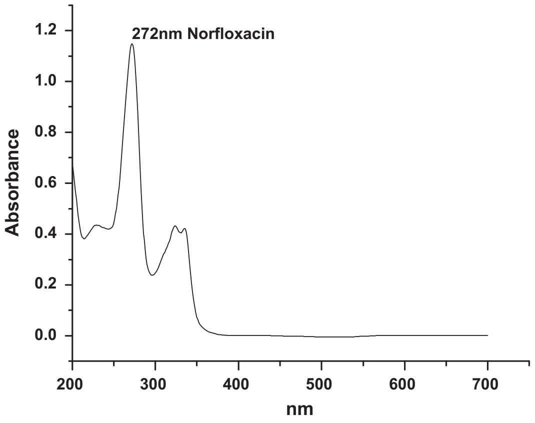


Fig. 19. Initial norfloxacin UV–vis spectrum.

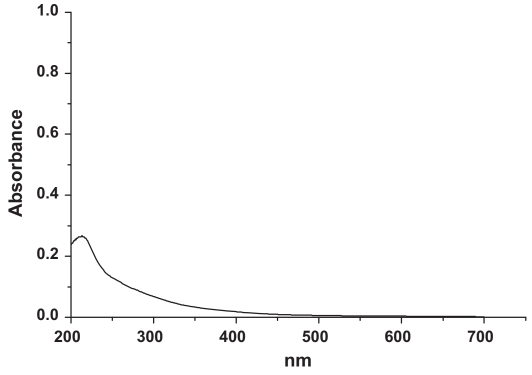


Fig. 20. Final spectrum of norfloxacin After treating with US/Fenton.

are the initial and final concentrations of the compound to be treated. The operating costs of the treatment processes used in the degradation of norfloxacin are given in Table 3.

Table 1
Several AOPs for norfloxacin degradation expressed % and mg/L (Initial concentration of norfloxacin 150 mg/L)

S. no.	Different AOPs	Norfloxacin degradation (%)	Norfloxacin degradation (mg/L)
1	UV	45	67.5
2	UV/H_2O_2	72	108
3	Fenton processes	38	57
4	Photo-Fenton	96	144
5	UV/TiO_2	90	135
6	UV/IGBT	78	117

Table 2
Cost of the reagents

S. no.	Reagent	Basis	Cost ($)
1	H_2O_2	kg	6.17
2	$FeSO_4{\cdot}7H_2O$	kg	4.76
3	TiO_2	kg	33.98
4	HF	kg	10.58
4	Glass beads	kg	17.95
5	Electricity	KW h	0.088

Table 3
Operating costs of the treatment methods used in the degradation of norfloxacin

S. no.	Process	Treatment cost ($/m^3)	Norfloxacin degradation (%)
1	UV	2.94	45
2	UV/H_2O_2	9.98	72
3	Fenton	8.82	38
4	UV/Fenton	18.35	96
5	UV/TiO_2	21.80	90
6	UV/IGBT	6.99	78

4. Conclusions

(1) The results of this study showed that the degradation of norfloxacin is strongly accelerated by the oxidation process.
(2) pH 7 is found to be considerable for the degradation of norfloxacin in UV irradiation.
(3) The rate of degradation of norfloxacin by photo-Fenton process is greater than that which can be achieved by either UV alone, Fenton process, photo-Fenton, UV/H_2O_2, UV/TiO_2 and UV/IGBT or in combination with any other chemical or reagent used in the present study.
(4) The optimum conditions obtained for the best degradation with photo-Fenton process were pH 3, iron concentration of 30 ppm and 200 mg/L H_2O_2 for an initial antibiotic concentration of 150 mg/L.
(5) It was found that the TiO_2 suspension had better degradation than that of IGBT.

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