International Journal of Environmental Science and Technology (2019) 16:4275–4284
https://doi.org/10.1007/s13762-018-1836-2

ORIGINAL PAPER

Photocatalytic degradation of metronidazole from aquatic solution by TiO_2-doped Fe^{3+} nano-photocatalyst

M. Malakootian[1] · N. Olama[2] · M. Malakootian[3,2] · A. Nasiri[3]

Received: 24 March 2016 / Revised: 25 June 2017 / Accepted: 30 May 2018 / Published online: 8 June 2018

Abstract

Indiscriminate consumption of antibiotics, their discharge into the environment, and the development of resistant genes in a natural ecosystem are ever-increasing global threats. Metronidazole is applied to treat infection diseases caused by anaerobic bacteria and protozoa. In this research, TiO_2/Fe^{+3} was used as a heterogeneous nano-photocatalyst for the degradation of metronidazole with UV-C radiation as the energy source. Parameters tested in the removal process were pH = 3, 7, and 11; antibiotic concentration of 80 mg/L; contact times of 30, 60, 90, and 120 min; and nano-photocatalyst of TiO_2/Fe^{+3} with concentrations of 30, 60, 90, 250, 500, 750, and 1000 mg/L. The photocatalytic degradation kinetics of metronidazole was studied. Optimal conditions were achieved on synthetic solutions; then, all experiments were performed on wastewater from the pharmaceutical industry. Antibiotic concentrations were measured using an HPLC device. All tests were replicated three times according to the standard methods of water and wastewater experiments, the 20th edition. Data were analyzed using SPSS 19 and the statistical test ANOVA. The optimal conditions for removing metronidazole from synthetic solution included, 500 mg/L for nano-photocatalyst concentration, pH = 11 and 120 min contact time. Removal efficiency of antibiotic under optimal conditions was 97% from synthetic solutions and 69.85% from pharmaceutical wastewater. Finally, Fe^{+3}–TiO_2/UV-C were identified as a promising technique for the removal of metronidazole with high efficiency from aqueous solutions.

Keywords Antibiotic · Advanced oxidation · Wastewater · Water

Introduction

Antibiotics are important pharmaceutical compounds commonly used by humans and animals are fed antibiotics in concentrated animal feeding operations (CAFOs) (Peterson et al. 2012). Following digestion and metabolism in the body, their residuals and metabolites enter the environment through human urine and stool deposits (Zhang et al. 2008). The most significant problem caused by antibiotics is the development of antibacterial resistance (Elmolla and Chaudhuri 2010a). The development of resistant genes in a natural ecosystem challenges the dynamics and physiology of a microbial population. Resistant genes can remain and develop in an environment even without the presence of antibiotics (Martinez 2009; Hu et al. 2007). Antibiotics enter the environment through various other means as well, such as pharmaceutical industry wastewater, hospitals, and human and animal waste deposits (Elmolla and Chaudhuri 2011).

A variety of methods are available for the removal of pharmaceutical compounds from aqueous solutions, including absorption by active carbon, reverse osmosis, air stripping, and biological methods. However, contaminants are not entirely removed by these methods; rather, they are just transferred from one phase to another (Daghrir et al. 2012; Elmolla and Chaudhuri 2010a). Advanced oxidation methods (AOPs) such as UV/ZnO, UV/TiO_2, and UV/H_2O_2 are useful because hydroxyl radicals are used for the oxidation of resistant compounds, and they are converted to harmless products such as H_2O and CO_2 (Klavarioti et al. 2009). These radicals are able to oxidize most organic compounds,

Editorial responsibility: Abhishek RoyChowdhury.

✉ M. Malakootian
m.malakootian@yahoo.com

[1] Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, CA, USA

[2] Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran

[3] Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran

and this process can be conducted using a photocatalytic system (Gad-Allah et al. 2011; Hapeshi et al. 2010).

Heterogeneous photocatalysis is one of the AOPs and is based on the direct or indirect absorption of photons from ultraviolet (UV) or visible light by a semiconductor that possesses the appropriate energy gap. The semiconductor for photocatalysis should be chemical or biological, inert, stable, inexpensive, easy to synthesis, and produced without human or environmental risks. Photocatalytic reactions using TiO_2/UV can convert non-biodegradable organic compounds into biodegradable species. Considering characteristics of the AOP, it can be used as pre- or post-treatment process in wastewater treatment because of its ease of installation in conventional wastewater treatment facilities (Elmolla and Chaudhuri 2010b). TiO_2 is among the most effective of these methods as it has high-level photocatalytic activity, nontoxicity, stability in aquatic solutions, and a relatively low cost (Haque and Muneer 2007). Metronidazole is an important derivative of nitroimidazole (Cheng et al. 2013). It is one of the most commonly applied antibiotics in the world, possessing both antibacterial and anti-inflammatory properties. It also has clinical applications and is commonly used to treat infectious diseases caused by anaerobic bacteria and protozoa such as *Giardia lamblia* and *Trichomonas vaginalis*. In addition to consumption by humans, it is also used as an additive in cattle feed, for poultry, and to remove fish parasites (Bendesky et al. 2002; Carrales-Alvarado et al. 2014). The survival of this compound has diverse effects on humans; it has carcinogenic potential and the potential for mutagenicity as it can damage DNA in lymphocytes (Bendesky et al. 2002).

Metronidazole has low degradability and high solubility in water, so it cannot be removed from water by conventional treatment methods. Accumulation of this medication in aquatic environments has an adverse effect on humans and the environment (Fang et al. 2011). Various methods have been proposed for metronidazole removal from aquatic environments, including gamma ray, photo-Fenton processes, photocatalysis by TiO_2 photolysis of UV, UV/H_2O_2 (Gonçalves et al. 2012), and absorption by nanoscale zerovalent iron (Mao et al. 2009).

Malakootian et al. studied the removal of pharmaceutical compounds and organic and inorganic pollutants from aqueous solutions by adsorption processes and photocatalytic methods (Malakootian and Mansuri 2015; Malakootian et al. 2014; Malakootian et al. 2016a, b, c ; Malakootian et al. 2017).Giraldo et al. (2010) in Colombia used a photocatalytic system with TiO_2 to remove the antibiotic oxolinic acid, and desirable results were achieved (Giraldo et al. 2010). Dimitrakopoulou et al. (2012) reported acceptable results in their investigation of the effects of TiO_2/UV-A on amoxicillin (Dimitrakopoulou et al. 2012). Numerous studies have been done on the removal of antibiotics by advanced oxidation, but so far, no study has been done on the application of Fe^{+3}–TiO_2/UV-C for the removal of metronidazole.

This research aimed to evaluate the application of titanium dioxide-doped particles (Fe^{+3}–TiO_2) using the sol–gel method together with UV-C irradiation for the removal of metronidazole from aquatic solutions. Furthermore, this study aimed to determine the optimal conditions for maximum removal efficiency and to apply these optimal conditions to a real pharmaceutical wastewater sample.

Materials and methods

This experimental research was conducted in 2015 at the Environmental Health Engineering Research Center of Kerman University of Medical Sciences. Tests on the metronidazole removal process using the Fe^{+3}–TiO_2/UV-C nano-photocatalytic system were done to measure the effects of pH, Fe^{+3}–TiO_2 nano-photocatalyst concentration, and reaction time on the extent of antibiotic removal from aquatic environments. Samples were determined based on the number of parameters that were tested. Their range was specified by the one-factor-at-a-time method of change. The sum of levels was considered for the variables of interest, and 72 samples were tested with a control and three replications.

Metronidazole with a purity of 99.82% was purchased from Pars Daru Co. and used to fabricate the synthetic sample. The physicochemical properties of metronidazole are shown in Fig. 1 (Farzadkia et al. 2015).

Compounds used in the tests were supplied by Merck Co., Germany. The UV-C Lamp for radiation was purchased from ARDA Co., France. It had an intensity of 125 W/m^2 and wavelength of 247 nm. The utilized devices included a centrifuge 3K30 (Sigma, Germany) for the separation of nano-photocatalyst particles from the solution and balance at an accuracy of 4 decimals (AND HR 200, Japan), and the pH-meter (Metrohm 744, Switzerland). Scanning electron microscopy (SEM) (EM3200, KYKY Co. China) was employed to determine the mean diameter

Molecular formula	$C_6H_9N_3O_3$
Molecular weight (g/mol)	171.2
Water solubility (g/L)	9.5
pK_a	2.55
Melting point (°C)	159-163
K_H (mol/dm3.atm)	5.92×10^7
V_p (Pa)	4.07×10^{-7}

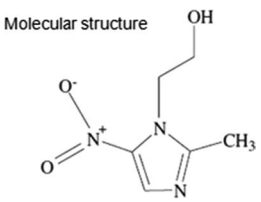

Fig. 1 Chemical structure of metronidazole (Farzadkia et al. 2015)

of the nano-photocatalyst particles and their appearance. An HPLC device (YL 9100 Waters, USA) was utilized to identify and measure metronidazole. The structure of the catalyst's crystal was determined using a D8 Advanced Ray Diffractometer (XRD) (Bruker AXS, Germany).

The sol–gel method was used to prepare the Fe^{+3}–TiO_2 nano-photocatalyst powder. The first step, ferrous nitrate was dissolved in half of propanol (121.77 mL) and completely mixed. After 15 min, 121.77 mL of propanol was mixed with 62.77 mL of titanium tetraisopropoxide (TTIP), and then, the mixture was added very slowly to the former solution over 75 min to form the sol. Meanwhile, deionized distilled water (8.33 mL) was added to the solution as well. Thirty minutes after the addition of propanol to TTIP, the pH was adjusted to 3 by nitric acid. All the processes were carried out in mixing mode using a homogenizer. Then, the resulting solution was placed on the magnetic mixer for 24 h to form jelly. This was put in the oven at 80 °C for 10 h to evaporate the alcohol. To activate the catalyst, the jelly was placed in oven at 500 ± 50 °C for 2 h. The activated catalyst was put in a desiccator until it was cool. Finally, the catalyst was powdered (Nasseri et al. 2011). The mean diameter of the nano-photocatalyst particles and their appearance were determined by scanning electron microscopy (SEM). XRD for the catalyst was determined.

A photocatalytic reactor of 2L volume was constructed to evaluate the effects of different parameters on the process of Fe^{+3}–TiO_2/UV-C of metronidazole solution at 80 mg/L. The initial antibiotic concentration was considered constant across all test samples (Hashemi et al. 2015; Farzadkia et al. 2015).

To determine the optimal pH for photocatalytic removal, tests were done at three pH levels: acidic (3), neutral (7), and alkaline (11). Ammonium hydroxide 1 N and HCl1 N were used to adjust the pH in the samples. The samples were placed inside the reactor following pH adjustment. The Fe^{+3}–TiO_2 nano-photocatalyst was added to the antibiotic solution in powder form and constantly exposed to ultraviolet radiation. An adjustable stirrer was used on the reactor for better mixing. The nano-photocatalyst was investigated at concentrations of 30, 60, 90, 250, 500, 750, and 1000 mg/L to determine the optimal amount of nano-photocatalyst in the Fe^{+3}–TiO_2/UV-C process. To specify optimal time, samples were taken from the reactor at intervals of 30, 60, 90, and 120 min. at the end of each test and placed under centrifuge of 10,000 rpm for 10 min to separate the nano-photocatalyst particles from the metronidazole solution. Samples were then passed through a 0.22 µm-syringe filter. The remaining amounts of antibiotic were measured using an HPLC device. All tests were done in three replications and a control (Dimitrakopoulou et al. 2012; Dehghani et al. 2014).

A real wastewater sample was obtained from the Dana pharmaceutical factory. Determinations were made for quality and amount of antibiotic in the sample. No trace of metronidazole was observed; therefore, to investigate the effect of optimal conditions for removal in real wastewater; 80 mg/L metronidazole was added to the pharmaceutical wastewater, its removal efficiency was calculated, and then compared with that determined from the synthetic solution. SPSS 19 and ANOVA were used for data analysis.

The metronidazole removal efficiency was calculated by (Eq. 1):

$$E\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C represent the metronidazole concentration before and after the titanium catalyst doped with iron (Fe^{+3}–TiO_2) process, respectively, and E represents the efficiency.

Specifications of the photochemical reactor are indicated in Fig. 2.

The research was conducted in a glass batch reactor (volume: 2L) with an internal stirrer. The source of radiation was a UV-C lamp, 125 W and 247 nm, protected by a quartz tube 30 cm long and 5 cm in diameter. The entire reactor was protected by aluminum foil to prevent reflection.

Standard metronidazole with a purity of 99% was used to adjust and run the device. Acetonitrile and deionized water were also used as mobile phases with volume ratios of 30:70. The utilized column was C_{18} with 5-µm particles, length of 250 mm, and internal diameter of 4.6 mm. Metronidazole was identified by a UV absorbance detector within the wavelength of 348 nm with an injection volume of 20 µL and flow rate of 1 mL/min.

Results and Discussion

Structural and morphological characterization

Results of injection of metronidazole by the HPLC device are shown in Fig. 3 in the form of a chromatogram peak.

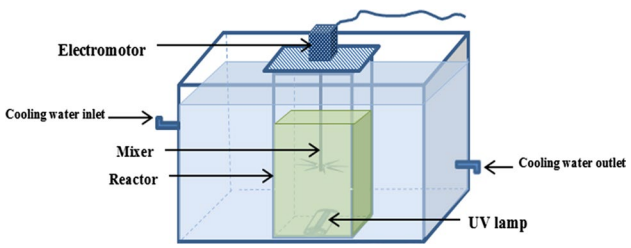

Fig. 2 The photochemical reactor

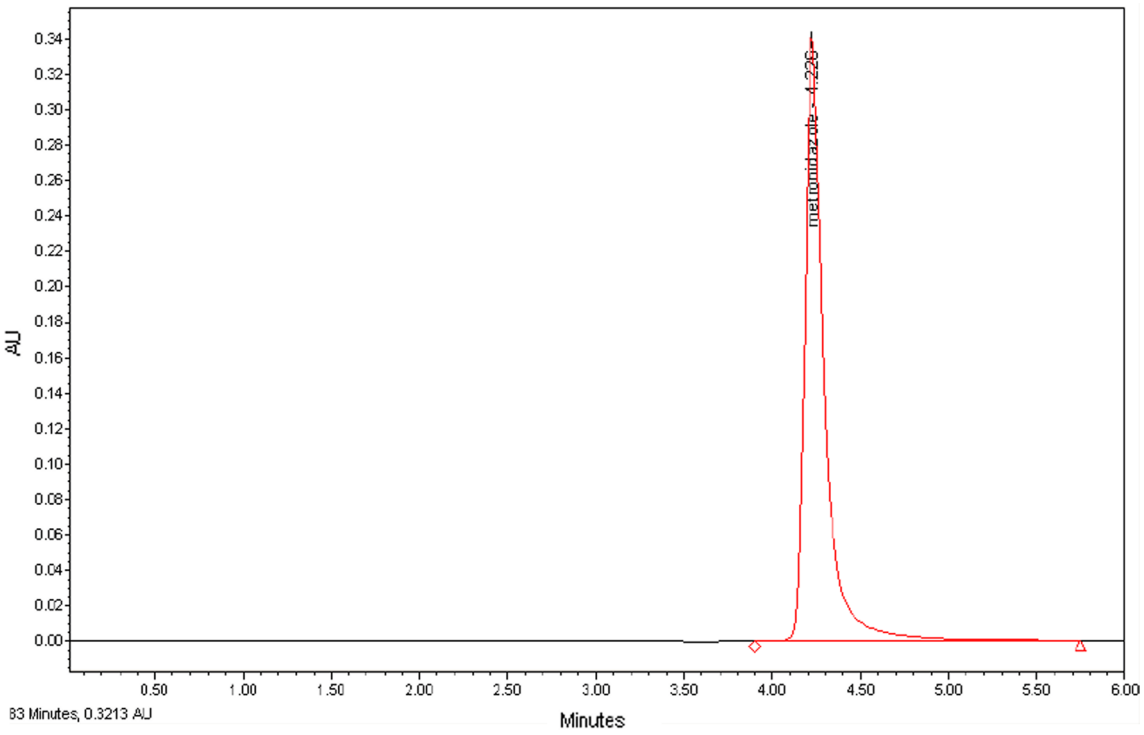

Fig. 3 Chromatogram of metronidazole obtained by HPLC

SEM was used to characterize the size, shape, and morphology of the nano-photocatalyst. Figure 4 shows electron microscopy images of the nano-photocatalyst particles (Fe^{+3}–TiO_2).

The XRD patterns of pure TiO_2 and Fe^{3+}–TiO_2 are illustrated in Fig. 5.

The red lines show anatase structure and the blue lines are rutile structure. Anatase had a greater intensity before the synthesis of TiO_2, but rutile had a greater intensity after the doping of TiO_2 with iron trivalent. Peaks of the iron ions in the crystalline structure of titanium dioxide were observed.

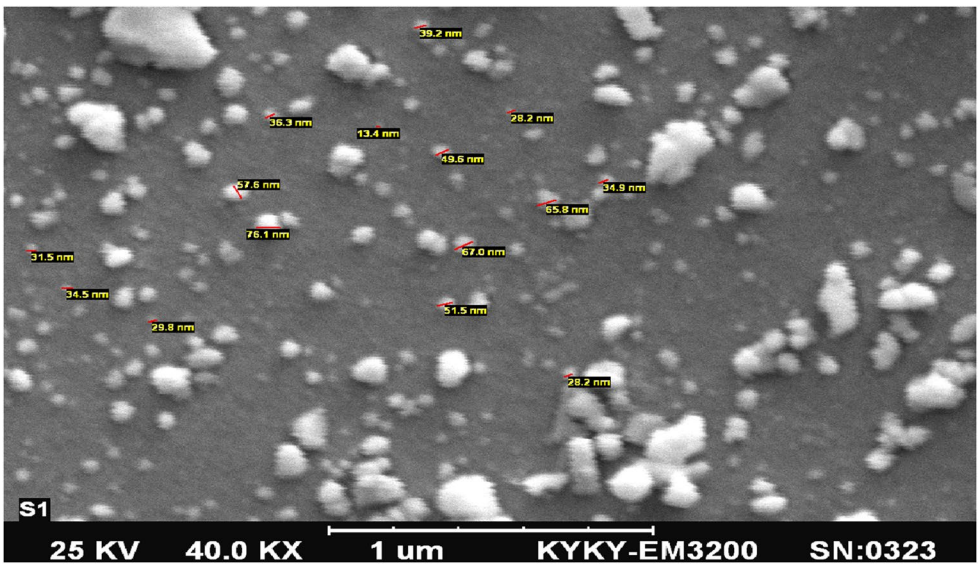

Fig. 4 The image obtained from SEM considering the size of the Fe^{+3}–TiO_2 nano-catalyst particles

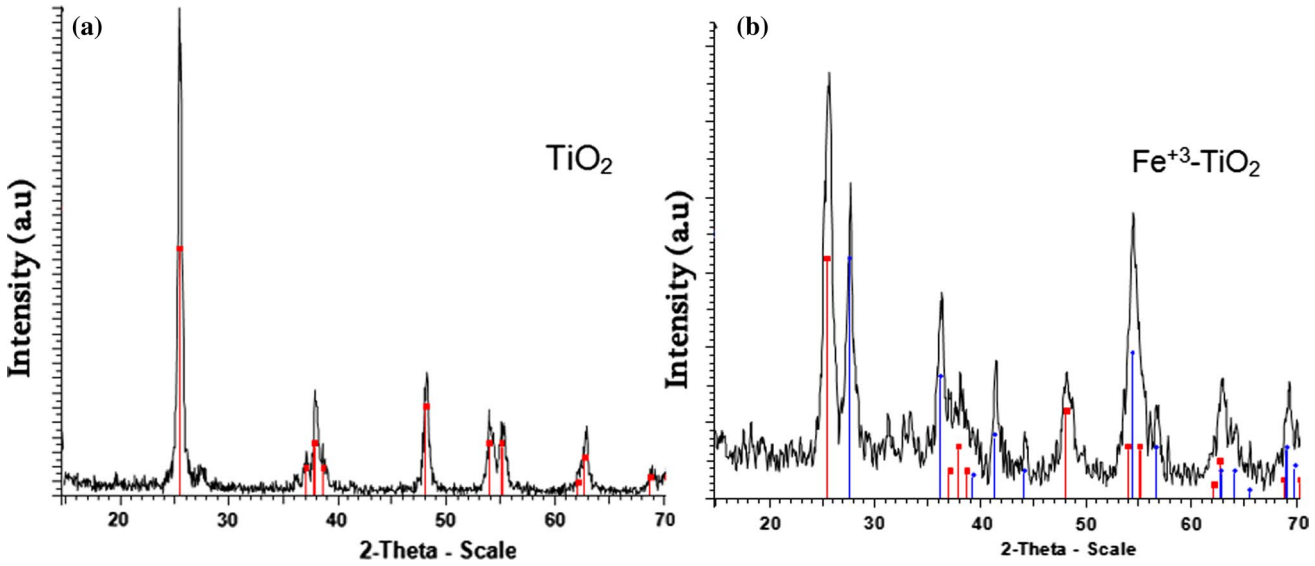

Fig. 5 XRD pattern of pure TiO_2(a) and Fe^{3+}-TiO_2(b)

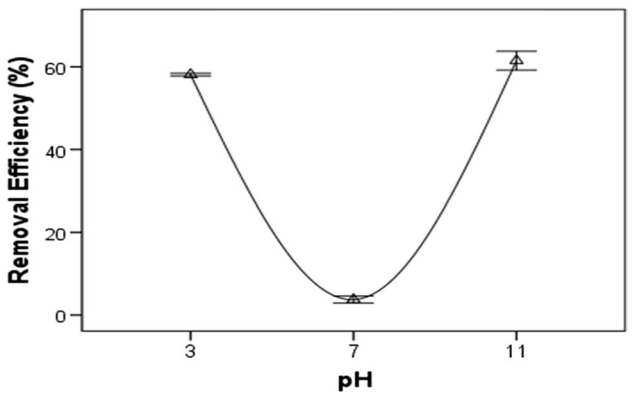

Fig. 6 The effect of pH on photocatalytic removal of metronidazole under the following conditions: t=30 min, Fe^{+3}–TiO_2=500 mg/L, C_0=80 mg/L

Influence of pH on removal of metronidazole

Results from the investigation of the effects of pH on the extent of metronidazole removal by the Fe^{+3}–TiO_2/UV-C process are shown in Fig. 6.

Removal efficiency rates at pH levels of 11, 7, and 3 were 61.51, 3.74, and 58.1%, respectively.

As known, pH is an important factor affecting the removal efficiency of many chemical and biological reactions (Dehghani et al. 2014). Results of the current study indicate that the most effective removal took place at pH = 11 due to the high concentration of hydroxyl radical in the solution ($p < 0.05$)(Nasseri et al. 2011).

Radicals play an important role in the oxidation of organic contaminants (Konstantinou and Albanis 2002). Advanced oxidation processes are also based on hydroxyl radicals, causing the oxidation and removal of contaminants (Dehghani et al. 2014; Nasseri et al. 2011). Moreover, pH has an important impact on contaminant molecules, the surface charge of nano-photocatalyst, and the mechanism that determines the degree of hydroxyl radical production (Saien and Shahrezaei 2012).The reactions are schematically shown in Fig. 7.The reactions are schematically shown from (Eqs. 2–14) (Sood et al. 2015):

$$(Fe^{+3} - TiO_2) + h\nu \rightarrow e^- + h^+ \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

$$Fe^{3+} + h^+ \rightarrow Fe^{4+} \quad (4)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \quad (5)$$

$$Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+} \quad (6)$$

$$Fe^{4+} + OH^- \rightarrow Fe^{3+} + {}^{\cdot}OH \quad (7)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (8)$$

$$Fe^{2+} + h^+ \rightarrow Fe^{3+} \quad (9)$$

$$Ti^{3+} + O_2 \rightarrow Ti^{4+} + O_2^- \quad (10)$$

$$O_2^- + h^+ \rightarrow O^- \quad (11)$$

$$O^- + h^+ \rightarrow O^{\cdot} \quad (12)$$

$$O^- + H_2O \rightarrow {}^{\cdot}OH + OH^- \quad (13)$$

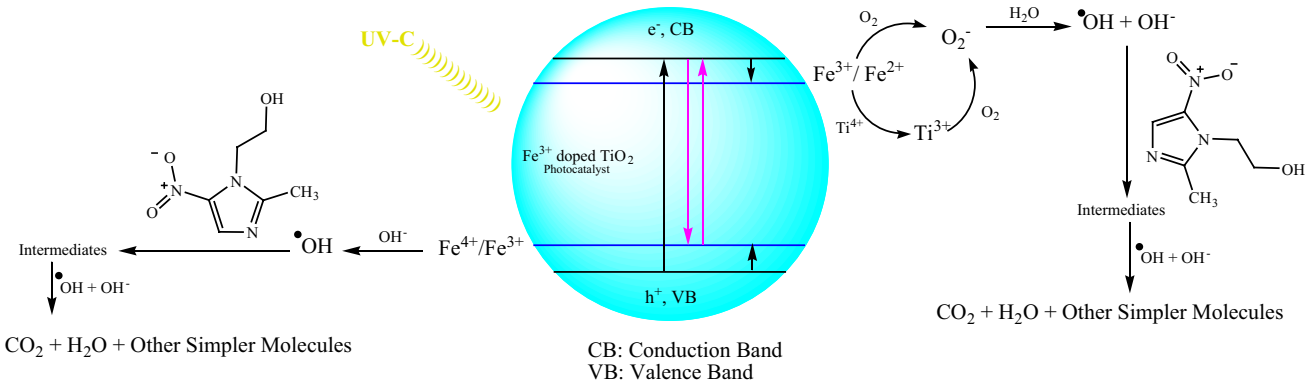

Fig. 7 Schematic diagram of mechanism of photocatalytic reaction taking place on the surface of Fe^{3+} doped TiO_2 nanoparticles

$$\text{Metronidazole} + {}^{\cdot}\text{OH} \rightarrow \text{Intermediates} + {}^{\cdot}\text{OH}\,/\text{OH}^{-}/\text{O}_2^{-} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{other simpler molecules} \quad (14)$$

Results reported by Méndez-Arriaga et al. (2011) in their study conducted in Spain on UV/TiO_2, UV/O_3, TiO_2/H_2O_2/O_3, and TiO_2 processes on the removal of fluoxetine indicate that the photolysis of fluoxetine was only justifiable in an alkaline environment. The reason for this was that an increased pH level resulted in the increased absorption of fluoxetine on TiO_2 (Méndez-Arriaga et al. 2011), congruent with the results of this research. Elmolla et al. (2010) studied the photocatalytic removal of the antibiotics amoxicillin, ampicillin, and cloxacillin from aquatic environments in Iran.

The most effective removal was obtained at pH = 11. It has been reported that more hydroxyl ions become available to the catalyst in an alkaline pH, thereby producing more hydroxyl radicals that participate in the oxidation of the antibiotic (Elmolla and Chaudhuri 2010b). This is consistent with the results of the current research. Dehghani et al. (2014) and Nasseri et al. (2011) reported on the use of the Fe^{+3}–TiO_2/UV-A process for removing penicillin-G and phenol in Iran. The most effective removal took place at acidic pH. Results reported by these studies are not in accordance with the results of the current research. This may be attributable to the presence of H^+ ions in an acidic environment that cause the formation of ${}^{\cdot}\text{H}$ and ${}^{\cdot}\text{HO}_2$ radicals through dissolved oxygen. Eventually, they changed into hydroxyl radicals (Nasseri et al. 2011; Dehghani et al. 2014).

Influence of nano-photocatalyst concentrations on removal of metronidazole

Results of the investigation of the impact of loading the Fe^{+3}–TiO_2 nano-photocatalyst on the photocatalytic removal of metronidazole are presented in Fig. 8.

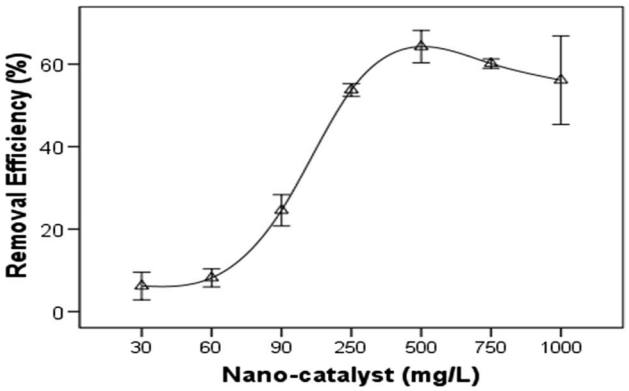

Fig. 8 The effect of the concentration of Fe^{+3}–TiO_2 on the photocatalytic removal metronidazole under the following conditions: t=30 min, C_0=80 mg/L, Fe^{+3}–TiO_2=500 mg/L, pH=11

Removal efficiency shown by the investigation of amounts of nano-photocatalyst at concentrations of 30, 60, and 90 mg/L was 6.24, 8.21, and 24.6%, respectively. Considering the very low efficiency of antibiotic removal, nano-photocatalyst amounts of 250, 500, 750, and 1000 mg/L were tested (Farzadkia et al. 2015; Hashemi et al. 2015). At concentrations of 250, 500, 750, and 1000 mg/L, removal efficiency evaluations were 53.72, 64.22, 60.14, and 55.98%, respectively.

The mechanism of the photocatalytic removal method is based on the production of active radicals such as •OH; contaminants are then removed through these radicals. Titanium dioxide, due to its chemical stability, lack of toxicity, low cost, electronic and optical properties, and high photo activity, has become the main semiconductor nano-photocatalyst for removing contaminants from water and air. This compound, however, has some drawbacks, including the less effective use of photons in comparison with samples doped by other elements, relatively high velocity of recombination of electrons, and pores developed by light, together with activity within the wavelength

range below 400 nm. To improve the photocatalytic efficiency of TiO_2, to develop its effective absorption light on a visible light range, and to prevent recombination of electrons-pores, some modifications have been made using various operations. These include TiO_2 doping by metal and nonmetal ions. Due to semi-full electron arrangements and because they have an ion radius close to the ion radius of Ti^{4+}, metal ions are easily replaced throughout the TiO_2 network, causing increased photocatalytic activity within the visible light range. Fe^{3+} ions in the TiO_2 network develop a surface trap for electrons and pores created from radiation. By decreasing the recombination of electrons and pore development, quantum efficiency and photocatalytic efficiency were enhanced.

Based on results of the current study, at nano-photocatalyst concentrations of 30, 60, and 90 mg/L, efficiency evaluations were 6.24, 8.21, and 24.6%, respectively; thus, removal rates were determined to be not acceptable. As recommended in the literature, nano-photocatalyst values of 250, 500, 750, and 1000 mg/L were considered (Farzadkia et al. 2015; Hashemi et al. 2015). The most effective removal efficiency of metronidazole was 97% for 500 mg/L of the nano-photocatalyst ($p < 0.05$). With an increase in nano-photocatalyst concentration, there was an increase in absorbed photons resulting in the enumeration of active sites across the nano-photocatalyst (Zhou et al. 2005). Under increased nano-photocatalyst concentrations, the extent of contaminant removal grew to some extent; however, removal efficiency declined at the concentration range of 500–1000 mg/L. Increasing the nano-photocatalyst concentration up to 500 mg/L increased removal efficiency (Yang et al. 2008; Mahvi et al. 2009; Hoseini et al. 2013).

A further increase in the nano-photocatalyst concentration resulted in the accumulation of TiO_2 nanoparticles and a decrease in the number of active superficial sites of the nano-photocatalyst (Thakur et al. 2010). Nasseri et al. (2011) in Iran determined that the removal efficiency of phenol increased when concentrations of the nano-photocatalyst were increased. The photocatalytic removal efficiency of phenol grew with increases in nano-photocatalyst concentration up to 0.5 g/L; with further increases up to 1 g/L, there was no significant change due to the decreased number of active sites on the nano-catalyst in response to the accumulation of TiO_2 particles (Nasseri et al. 2011). Results of the mentioned research are in line with those of the current study. The study by Dehghani et al. (2014) in Iran on the photocatalytic removal of penicillin-G revealed that removal efficiency increased under increased concentrations of Fe^{+3}–TiO_2. This was attributable to the increased number of absorbed photons and elevated number of active sites on the nano-photocatalyst, leading to an increased number of hydroxyl radicals (Dehghani et al. 2014); these results are congruent with the results of the current research.

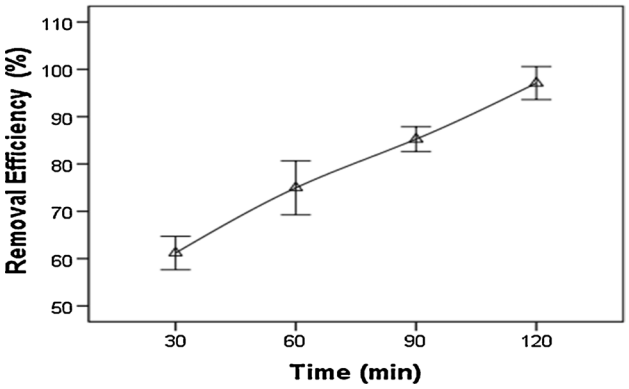

Fig. 9 The effect of time on the photocatalytic removal at pH=11, C_0=80 mg/L, and Fe^{+3}–TiO_2=500 mg/L

Influence of time on metronidazole removal

Results of investigations into the effect of time on the removal efficiency of metronidazole in the Fe^{3+}–TiO_2/UV-C process are illustrated in Fig. 9.

Removal efficiency evaluations for 60, 30, 90, and 120 min for the catalyst of 500 mg/L were 61.21, 74.80, 85.19, and 97%, respectively.

Contact time is an important parameter in chemical reactions that needs to be optimized (Dehghani et al. 2014; Dehghani et al. 2013). These results demonstrate increased removal efficiency under a longer duration of reaction. Its maximum removal efficiency took place at 120 min ($p < 0.05$). This can be attributed to the fact that the contaminant was further exposed to UV-C rays, with the oxidation process growing in the presence of hydroxyl radicals. The extent of removal after 120 min reached an almost constant value. Dehghani et al. (2013) and Baghapour et al. (2016) reported maximum removal efficiency after 120 min for the removal of penicillin-G and the photocatalytic removal of atrazine in Iran. This result was attributed to the further contact with UV-C ray and increased number of active sites on the nano-photocatalyst in response to ultraviolet radiation; these results are in accordance with the results of the current research (Dehghani et al. 2013; Baghapour et al. 2016). Salaices et al. (2001) reported in the US that the efficiency of phenol removal and TOC by the photocatalytic process of titanium dioxide and UV radiation rose with the residence time; at 180 min, TOC removal efficiency with an initial concentration of 50 mg/L reached around 100%. This result was attributed to increased oxidation by the hydroxyl radical in response to further contact with the catalyst and UV (Dehghanifard et al. 2012); these results are in line with those of the current study.

Kinetics study of metronidazole removal

The removal of metronidazole by nano-photocatalyst (Fe^{3+}-TiO_2/UV-C) was observed to the pseudo-first-order kinetics (Eq. 15):

$$\mathrm{Ln}\left(C_0/C_t\right) = kt \tag{15}$$

where k is the rate constant of the reaction, and C_t and C_0 are the metronidazole concentration (mg/L) after exposure time t and the initial concentration of metronidazole (mg/L), respectively; t is the exposure time (min). The pseudo-second-order kinetics is (Eq. 16):

$$1/\left(C_t\right) - 1/\left(C_0\right) = Kt \tag{16}$$

The pseudo-first-order degradation curves are depicted in Fig. 10. A plot of $\mathrm{Ln}(C_0/C_t)$ shows a linear relationship with the irradiation time where the slope equals the rate constant (k=0.0274) and R^2=0.8972.

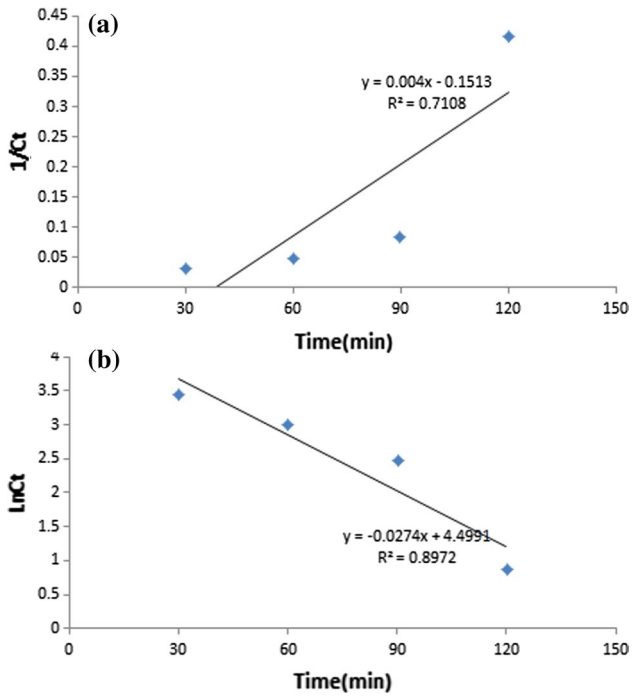

Fig. 10 Comparison of the second-order kinetic (**a**) and first-order kinetic (**b**) model for the photocatalytic degradation of metronidazole at C_0=80 mg/L, Fe^{+3}–TiO_2=500 mg/L, pH=11

Influence of nano-photocatalyst on pharmaceutical wastewater

Results of investigation into the physiochemical quality of wastewater of the Dana pharmaceutical factory are provided in Table 1.

COD and BOD evaluations of the real wastewater sample with an addition of 80 mg/L metronidazole were 616, and 483 mg/L, respectively. Metronidazole removal efficiency under the application of optimal conditions from the real wastewater sample was 69.85%, a lower value compared with that from synthetic solutions. Amounts of remaining antibiotic, COD, and BOD were 24.12, 430, and 340 mg/L.

Results indicated that the removal efficiency of metronidazole at 80 mg/L was 69.85% in the Fe^{3+}-TiO_2/UV-C process. Removal efficiency in the real sample of industrial wastewater was lower than that determined from synthetic samples. Interfering factors such as organic and cyclic compounds as well as turbidity inside the wastewater resulted in diminished removal efficiency compared to synthetic samples. This lower removal efficiency was due to the fact that, under considerably increased concentrations of the contaminant, the larger area of nano-photocatalyst is occupied by it. In addition, the destruction of interfering factors leads to the occupation of the nano-photocatalyst surface, resulting in adverse effects in the application of hydroxyl radicals with positive pores in the capacity band of the nano-photocatalyst surface. Furthermore, an increase in the concentration of contaminant causes further absorption of UV light by its molecules and the occurrence of an internal filtration effect which, in turn, causes decreased reception of photons by the nano-photocatalyst surface (Farzadkia et al. 2015).

Conclusion

In this work, a sol–gel method was used to prepare the Fe^{+3}–TiO_2 nano-photocatalyst. This method shows higher photocatalytic performance for the removal of metronidazole under UV-C radiation as the energy source. The influences of different factors (pH, concentration of nano-photocatalyst, and contact time) on the degradation were studied. Under optimal conditions of pH = 11, catalyst concentration = 500 mg/L, and reaction time = 120 min, removal efficiency rates of 97 and 69.85% were achieved for synthetic

Table 1 The physiochemical quality of the wastewater of Dana pharmaceutical factory

COD (mg/L)	BOD (mg/L)	TDS (mg/L)	TSS (mg/L)	pH	Turbidity (NTU)	Chloride (mg/L)	Sulfate (mg/L)	EC (µs/cm)
609	480	132	21	6	0.39	395	3	1535

EC electrical conductivity, *TSS* total suspended solids, *COD* chemical oxygen demand, *BOD* biological oxygen demand, *TDS* total dissolved solids

samples and pharmaceutical wastewater, respectively. These results suggest that Fe^{+3}–TiO_2 nano-photocatalyst in the presence of UV-C radiation may be used as a promising technique for the removal of metronidazole from aqueous solutions for the treatment of pharmaceutical wastewaters.

Acknowledgements This research was conducted at the Environmental Health Engineering Research Center and was sponsored by the Vice Chancellor for Research and Technology of Kerman University of Medical Sciences. The authors' appreciation is expressed here to the Vice Chancellor and to all university staff who provided assistance to make this study possible. The authors also wish to acknowledge the cooperation of Shiraz University of Medical Sciences—Health and Nutrition Faculty, the assistance of Dr. Mohammad Reza Kazemi, Head of the Statistics Sector and Financial Deputy of Fasa University, Pars Daru Pharmaceutical Company, and Dana Pharmaceutical Company which greatly facilitated this research.

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