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Removal of metformin from aqueous solution using Fe^{3+} doped TiO_2 nanoparticles under UV irradiation

Seyede Zahra Nematolahi[a], Mansooreh Dehghani[b,*], Saeed Yousefinejad[b], Hassan Hashemi[c], Mohammad Golaki[c], Amin Mohammadpour[c], Seyyed Hossein Abdollahi[d]

[a]*Department of Environmental Health Engineering, School of Health, Student Research Committee, Shiraz University of Medical Sciences, Shiraz, Iran, email: zahranemati339@gmail.com*
[b]*Research Center for Health Sciences, Department of Environmental Health, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran, emails: mandehghani@yahoo.com (M. Dehghani), yousefisa@sums.ac.ir (S. Yousefinejad)*
[c]*Department of Environmental Health Engineering, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran, email: h_hashemi@sums.ac.ir (H. Hashemi), m_golaki@yahoo.com (M. Golaki), aminmohammadpour7777@gmail.com (A. Mohammadpour)*
[d]*Department of Chemistry, College of Sciences, Shiraz University, Shiraz, Iran, email: seyyedhosseinabdollahi94@gmail.com*

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ABSTRACT

In this work, a photocatalytic process was used for removing metformin as a widely prescribed drug to reduce blood sugar in type 2 diabetes. Photocatalytic processes are one of the most common oxidation processes in degrading organic compounds. This study aimed to investigate the efficiency of Fe^{3+} doped TiO_2 nanoparticles in degrading metformin in synthetic wastewater. Therefore, in the first step, Fe^{3+} doped TiO_2 nanoparticles were synthesized by the sol–gel method and characterized using X-ray diffraction, energy-dispersive X-ray spectrometry, scanning electron microscopy, and $pH_{(PZC)}$ techniques. Then, the effects of parameters, such as the initial concentration of metformin (10–45 mg/L), catalyst dose (25–75 mg/L), pH (3–11), and time (30–150 min), were studied on the photocatalytic degradation of metformin. Results showed that by increasing the experimental parameters, including pH, catalyst dose, and contact time, the nanoparticle removal efficiency increased. Overall, these findings indicated that under optimum conditions, including pH = 11, nanoparticle dose of 75 mg/L, and contact time of 150 min, photocatalytic degradation can remove 93.8% of metformin with an initial concentration of 35 mg/L. Moreover, Fe^{3+} doped TiO_2 nanoparticles with UV light (as a photocatalytic treatment system) have good efficiency in degrading metformin.

Keywords: Degradation; Kinetics; Metformin; Photocatalytic process

1. Introduction

Pharmaceutical compounds are one of the emerging contaminants that have shown negative consequences on humans, animals, and the environment [1–4]. Metformin is one of the most widely used drugs to reduce blood sugar in type 2 diabetic patients [5–7]. About 30%–90% of pharmaceutical compounds, such as metformin, are not totally metabolized in the body and thus, can be excreted into the sewerage system through urine and feces. The entry of these compounds into our environment via discharged sewage from numerous sources, including laboratories, hospitals, and pharmaceutical factories, is one of the most challenging problems.

Thus, because of their small molecular size and extreme resistance to bacterial biodegradation, they may be released

* Corresponding author.

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through the effluents of wastewater treatment plants. In addition, the concentration of pharmaceutical compounds in wastewater is very low (μg–ng/L). Traditional technologies of removal treatment cannot remove these compounds at low concentrations and eventually discharge them into the ground, surface water, and oceans. Therefore, the development of new wastewater treatment technologies to degrade these compounds is essential before discharging them into the environment [8–10].

In recent years, there has been an increasing interest in the advanced oxidation processes (AOP_S) as the main and effective techniques for removing numerous organic pollutants [11–16]. As a result of oxidation reactions, the remediation technology comprises decomposing hard and non-biodegradable organic substances using active free radicals. As an AOP, the photocatalytic process has been effectively used for eliminating organic matters, such as pharmaceutical materials, for example, antibiotics.

In general, the photocatalytic process results in free radicals. This process using an irradiation source, that is, UV, sunlight, or simulated sunlight, employs a semiconductor material as a catalyst, for example, TiO_2 and ZnO nanoparticles. Further, the collision of photons with the catalyst surface leads to the excitation of electrons, as well as their transfer from the bandgap to the conduction band, which, simultaneously, leads to the creation of cavities (hole+) at the catalyst surface. Eventually, the reaction of these holes with water molecules or OH^- ions results in the formation of $OH^•$ [13,17–20]. Nonetheless, high-energy consumption, safety, and wastewater turbidity issues are the main disadvantages of photocatalytic processes in a practical system [21].

TiO_2 nanoparticles are one of the most practical nanocatalysts used in the photocatalytic process for degrading organic matters. Non-toxicity, high chemical stability in a wide range of pH, high performance in electron conduction as a semiconductor are the advantages of these nanoparticles [22,23].

Doping TiO_2 using different metal or non-metal ions has been applied as a helpful tool to upgrade the photocatalytic properties. Among a variety of transition metals, Fe has been suggested to be a suitable option due to the similarity of the Fe^{3+} radius to Ti^{4+}, which allows Fe to easily penetrate the TiO_2 crystal lattice [24]. Previous studies have shown that by increasing the Fe weight percentage, which forms Fe^{3+} ions, the bandgap of TiO_2 nanoparticles decreases. On the other hand, to increase the photocatalytic efficiency and UV light utilization in TiO_2, Fe^{3+} as a dopant was doped in these particles [25].

Furthermore, several research studies have investigated the photocatalytic degradation of organic contaminants in aqueous solutions by the UV/Fe^{3+} doped TiO_2 process [25–31]. Various methods, including adsorption, biodegradation, phytoremediation, and photodegradation, can eliminate metformin [26]. Numerous studies have been performed on the removal of metformin by AOPs [20,33], but no study has investigated the performance of the UV/Fe^{3+} doped TiO_2 process to remove metformin from aqueous solutions.

In this regard, this paper aimed to synthesize and analyze the characterization of Fe^{3+} doped TiO_2 magnetic nanoparticles, as well as the practical application of this synthesized catalyst for the degradation of metformin using a pilot-scale photocatalytic reactor with simultaneous UV radiation.

2. Materials and methods

2.1. Materials

Metformin (chemical formula: $C_4H_{11}N_5$; purity >96%; solubility: insoluble in water; molecular weight: 129.16 g/mol; and pK_{a1} value: 12.4) with analytical grade was purchased from Sigma-Aldrich (Germany). The spatial formula and chemical structure of metformin are illustrated in Fig. 1. Using opaque glass containers, all the working solutions and stocks were prepared by dilution. All solutions, before the use, were stored in a refrigerator at <4°C and utilized in experimental work for a maximum period of 1 week. Other analytical grade chemicals and reagents, such as titanium isopropoxide, iron(III) nitrate, propanol, and nitric acid, were obtained from Merck Company (Germany). Also, during the experimental time, the pH values were controlled by adding 0.1 M HCl and 0.1 N NaOH.

2.2. Synthesis of the Fe^{3+} doped TiO_2 nanocatalyst

To prepare Fe^{3+} doped TiO_2 nanocatalyst via the sol-gel method, first, iron(III) nitrate was dissolved in 121.775 mL of propanol and then thoroughly mixed. Next, 121 mL of propanol was mixed with 62 mL of titanium isopropoxide and then added to the previous supernatant within 75 min. At the same time, 33 mL of distilled water was added drop by drop to the suspension until the formation of the solution. After 30 min, a few drops of nitric acid were added to reach a sample pH of 3.

Then, the obtained mixture was stirred on a magnetic stirrer for 24 h. Thereupon, the sample was placed in an oven at 80°C for 10 h. Finally, the sample was placed in an oven at 500°C ± 50°C for 2 h [27,34].

2.3. Characterization analysis

The characterization analysis of the synthesized nanoparticles was conducted via various techniques. The surfaces, average diameter, appearance, and morphology of the used catalyst were assessed using high-resolution images, which were captured at different magnifications by field emission scanning electron microscopy analysis (FE-SEM; Mira 3-XMU, SMAX Company, Germany). X-ray diffractometer (D8 ADVANCE, USA) was utilized to detect the crystalline structure, which was equipped with a generator of high-power CuKα radiation and maintained at a scan rate of 2°/min. A Zeiss-SIGMA (VP-500, Germany) energy-dispersive

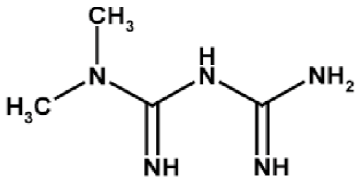

Fig. 1. The structural and spatial formula of metformin.

X-ray spectroscope (EDXS) was utilized to identify the elemental distribution of Fe^{3+} doped TiO_2 nanoparticles.

2.4. Analytical methods

To measure the amount of metformin, we used a high-performance liquid chromatography (HPLC) device with a C_{18} column and mobile phase containing 40% water: 60% acetonitrile, and a flow rate of 1.3 mL/min. The remaining metformin in the photocatalytic process was detected by a UV absorbance detector at 227 nm and a total run time of 10 min, in which metformin appeared at the retention time of 5.8 min (Fig. 2). The chromatograms before and after the photocatalytic process of a sample with an initial concentration of 30 mg/L are shown in Fig. 2, which shows the process efficiency well.

2.5. Photocatalytic degradation experiments

The metformin degradation by Fe^{3+} doped TiO_2 nanoparticles (as a catalyst) was assessed using a photochemical reactor. A UV lamp (1020 μW/cm^2) was employed as a source of irradiation to prepare the needed photons in the photocatalytic reactions. All the photocatalytic experiments were performed at room temperature (20°C ± 5°C), and the mixing was performed by magnetically stirring at 300 rpm (rotation/min).

To investigate the photocatalytic activity of metformin degradation (using Fe^{3+} doped TiO_2 nanoparticles in the presence of UV light), the effect of pH (3, 7, and 11), a dose of catalyst (25, 35, and 75 mg/L), and initial concentration of metformin (10, 30, and 50 mg/L) at contact times of 30, 90, and 150 min were examined. The prepared solutions were placed in darkness (30 min) before UV irradiation for the study of adsorption and desorption. The residual concentration of metformin was determined using HPLC; Eq. (1) was considered to evaluate the efficiency of the process.

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100(\%) \tag{1}$$

In this equation, the values of C_0, C_t, and R are the initial concentration of metformin, the concentration of metformin after degradation, and the efficiency of the process, respectively.

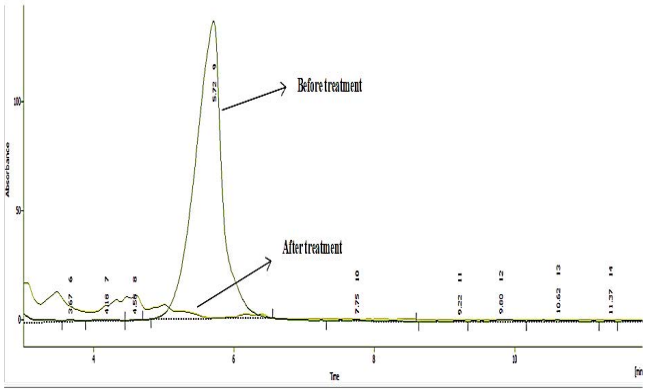

Fig. 2. HPLC chromatograms of metformin hydrochloride before and after the removal process.

2.6. Kinetics of metformin degradation

Understanding the kinetic mechanism of photocatalytic processes is required to evaluate the degradation resulting from the catalyst applied to remove organic contaminants. In the present study, the evolution curves resulting from the investigation of the reaction time at various initial metformin levels during the degradation process were employed for the kinetic study.

Furthermore, to accurately design the treatment system, the kinetic data should be modeled and fitted with the applied kinetic models. The Langmuir–Hinshelwood model is one of the most popular kinetic models used in the modeling of organic contaminant degradation data. The Langmuir–Hinshelwood formula can be written as a first-order expression for very low pollutant concentration, Eq. (2).

$$\ln\left(\frac{C_t}{C_0}\right) = -k_a \tau \tag{2}$$

where k_a stands for the reaction rate of the first-order expression (min^{-1}), is the initial concentration of metformin (mg/L), and C_t represents the metformin concentration (mg/L) measured in photocatalytic time (t, min).

The accuracy of the fitting between the experimental data and the applied kinetic models was assessed based on the resulting values of the regression coefficient (R^2) [2,20,22].

3. Results and discussion

3.1. Fe^{3+} doped TiO_2 characterization

3.1.1. X-ray diffraction spectra

To identify the crystallographic structures and to estimate the particle size of the Fe^{3+} doped TiO_2 nanoparticles, X-ray diffraction (XRD) patterns were graphed as depicted in Fig. 3. The 2θ peaks were observed at 25.60°, 30.00°, 48.56°, 54.76°, 55.68°, 62.76°, 67.60°, 70.04°, and 75.28° in the XRD pattern of TiO_2 nano-powders, which are consistent with anatase (1 0 1), (2 2 0), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (1 1 6), (2 2 0), and (1 0 7) lattice planes. The diffraction peaks corresponding to the rutile phase also appeared at 27.16°, 36.00°, and 41.72° corresponding to (1 2 1), (1 0 1), and (1 1 1) planes [30–32].

Nanoparticles' crystalline size was assessed by the Debye–Scherrer formula; Eq. (3) shows its mathematical relation. In this equation, D represents crystalline size; β is full width at half maximum of the peak corresponding to the plane; λ stands for the wavelength of XRD radiation; θ represents the angle obtained from 2θ value corresponding to the XRD pattern [26,35,36].

$$D = \frac{0.98\lambda}{\beta \cos\theta} \tag{3}$$

The mean crystallite size of Fe^{3+} doped TiO_2 nanoparticles was calculated using this formula and obtained, which was about 70 nm.

3.1.2. EDXS technique

EDXS analysis was performed for Fe^{3+} doped TiO_2 nanoparticles to determine the abundance of particular elements. The EDXS method relies on the interaction between the X-ray source and the samples and can be utilized to understand the material chemical composition up to a few microns in size [30].

The result of EDXS analysis of Fe^{3+} doped TiO_2 nanoparticles is shown in Fig. 4. Based on this analysis, peaks with taller heights demonstrate a higher concentration of the corresponding element in the material structure. According to Fig. 4, Ti, O, and Fe are present in the structure of nanoparticles with a mass percentage of 27.34, 63.45, and 3.07, respectively. Also, the highest percentage belongs to the Ti element.

3.1.3. FE-SEM images

FE-SEM was used to evaluate the size and structure of the synthesized material, and the result is shown in Fig. 5. Based on the SEM image, the surface of synthesized material is clearly visible and indicates that the surface of the synthesized nanomaterials is a mass with a mild protrusion, and also, the particles have an almost spherical shape. On the other hand, it was also found that the particles of the synthesized material have less than 70 nm.

3.2. Degradation of metformin under different experimental parameters

3.2.1. pH impact

The pH of the solution can influence the treatment efficiency, which is one of the most vital experimental factors in the photocatalytic process. The pH of the solution can also affect the performance of photocatalytic activities. Further, pH can impact the surface charge of the employed catalyst, dissolution property of contamination molecules, mechanism of radical manufacturing, and kinetics of photocatalytic activities. Thus, before conducting the tests, the pH(pzc) of the nanoparticles was determined, which was 7 ± 0.5.

In the present study, the impacts of pH values (3, 5, 7, 9, and 11) were tested on the performance of photocatalytic activities in metformin degradation in the presence of other conditions (catalyst dose = 35 mg/L, metformin concentration = 20 mg/L, reaction time 90 min, and irradiation from UV; Fig. 6).

Based on the results, in acidic pH, the photocatalytic activity showed poor performance; this could be because nanoparticles have a strong tendency to clump under acidic conditions, reduce the surface area, and diminish the destructive ability in photocatalytic reactions. Also, in this condition, the surface of the photocatalyst has a positive charge, and metformin exists in proton forms; thus, the electrostatic repulsion between them reduces the reaction of attraction+ ions with holes+. This finding is consistent with the results of some studies [19,37].

As shown in Fig. 6, the highest removal rate of metformin is at pH 11. This may be due to better conditions

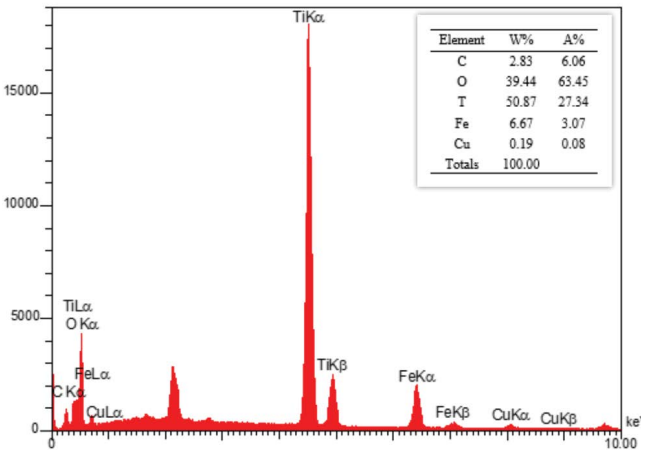

Fig. 4. EDXS spectrum of the Fe^{3+} doped TiO_2 nanoparticles.

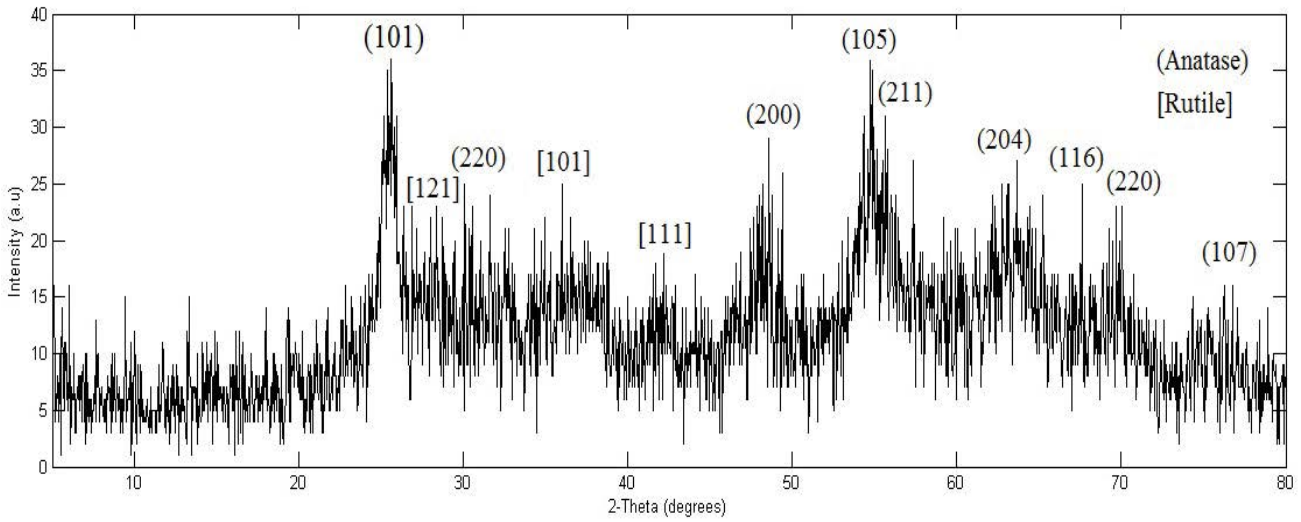

Fig. 3. XRD pattern of the Fe^{3+} doped TiO_2 nanoparticles.

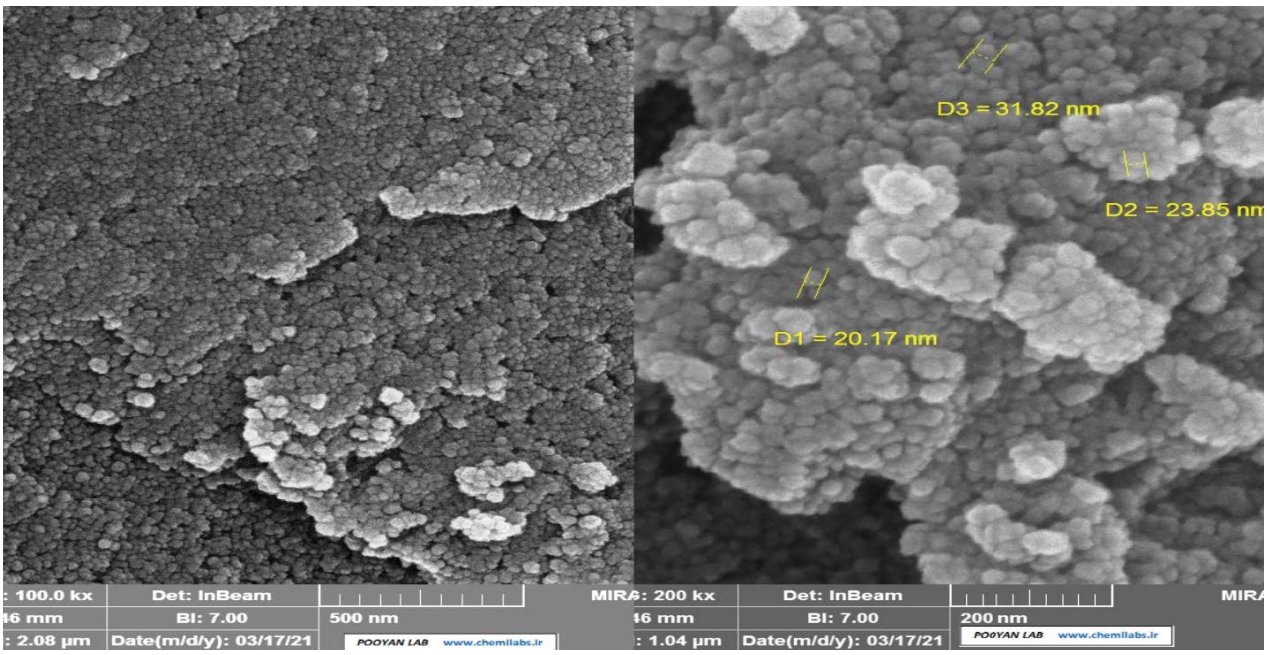

Fig. 5. SEM image of the Fe^{3+} doped TiO_2 nanoparticles.

for the formation of hydroxyl radical in higher pH, and the electrostatic adsorption between nanoparticles and metformin is higher due to the negative charge on the nanoparticle surface under high-pH conditions [36]. Examination of the pH range shows that the metformin removal efficiency in the range of pH 3 to 11 was higher than 85%, so it seems that Fe^{3+} doped TiO_2 nanoparticles can be used in a wide range of pH.

3.2.2. Catalyst dosage effect

Catalyst dosage is another important parameter, which affects the efficiency of photocatalytic processes [37]. To determine the optimal dosage of Fe^{3+} doped TiO_2, the effect of dosage in values (25, 35, 55, and 75 mg/L) on the efficiency of metformin photocatalytic degradation was investigated; the result is shown in Fig. 7.

Based on the results, by increasing the catalyst dose from 25 to 75 mg/L, the process efficiency increased from 87.38% to 92.4%; the reason is that increasing in catalyst dosage leads to the increase in the number of available uptake sites and consequently the adsorption capacity of UV (higher adsorption of photons), in which the production of hydroxyl radical increases. Increasing the catalyst dose from 35 to 75 mg/L only led to a 1.3% increase in efficiency, which shows that increasing the catalyst dose from 35 mg/L had little effect on the removal efficiency of metformin.

This result can be due to the maximum production capacity of hydroxyl radicals by nanoparticles and the

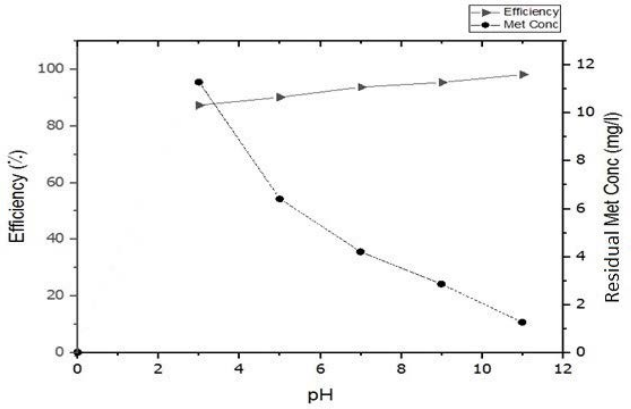

Fig. 6. Effect of pH on the removal of metformin by the photocatalytic activity of the Fe^{3+} doped TiO_2 nanoparticles under UV irradiation (initial concentration = 20 mg/L, catalyst dosage = 35 mg/L, and time = 90 min).

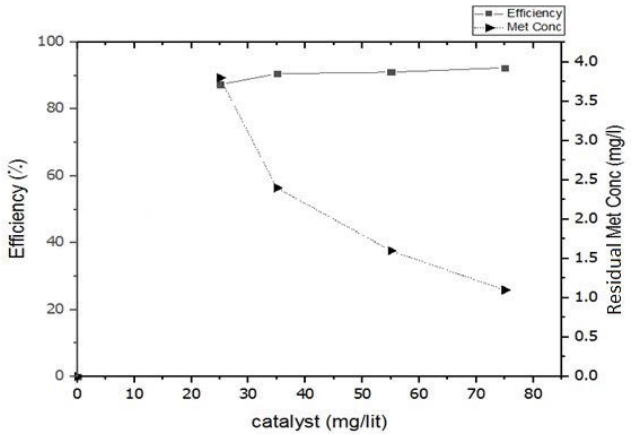

Fig. 7. Effect of catalyst dose on the removal of metformin by the photocatalytic activity of the Fe^{3+} doped TiO_2 nanoparticles under UV irradiation (initial concentration = 20 mg/L, pH = 11, and time = 30 min).

power of the corresponding lamp. The results are consistent with photocatalytic studies conducted by other researchers [6,20,37].

3.2.3. Impact of initial metformin concentration

The effect of initial metformin concentrations (10, 25, 35, and 45 mg/L) on its degradation rates by the UV/Fe^{3+} doped TiO_2 process is shown in Fig. 8. Other experimental factors, including catalyst dose and pH, were optimized in previous experiments. Based on the result, increasing the concentration of metformin from 10 to 45 mg/L led to the reduction of process efficiency from 91.85% to 80.15%. This can be related to the fact that more surface is available on the nanocatalyst, which adsorbs more metformin in lower concentrations.

Also, in the high concentration of metformin, the repulsive forces between the molecules of metformin (adsorbed onto the surface of the catalyst) increased. Additionally, the concentration of radicals produced in the solution is constant; thus, the rate of degradation is higher in the solution with a low concentration of metformin. In similar research studies, parallel results were obtained [20,40].

Another reason for the decrease in metformin removal efficiency could be due to the increased turbidity of synthetic wastewater (as a result of increasing metformin concentration), which reduces UV radiation to the surface of Fe^{3+} doped TiO_2 nanoparticles and thus results in fewer hydroxyl radicals [39].

3.2.4. Reaction time effect

Some experiments with varied reaction times were conducted to determine the optimum reaction time. For this purpose, values of reaction time in the range of 30–150 min were investigated; the result is illustrated in Fig. 9. Based on Fig. 9, process efficiency is improved by increasing the contact time. However, increasing efficiency was more significant in the first 30 min. It can be justified by this fact that the concentration of metformin at the first 30 min is high, and, at the same time, there is an abundance of free hydroxyl radicals, which makes higher removal efficiencies. On the other hand, in the higher reaction times, the degradation process was slower because the concentration of metformin is low and so can decrease the possibility of contact of nanoparticles and as well [40].

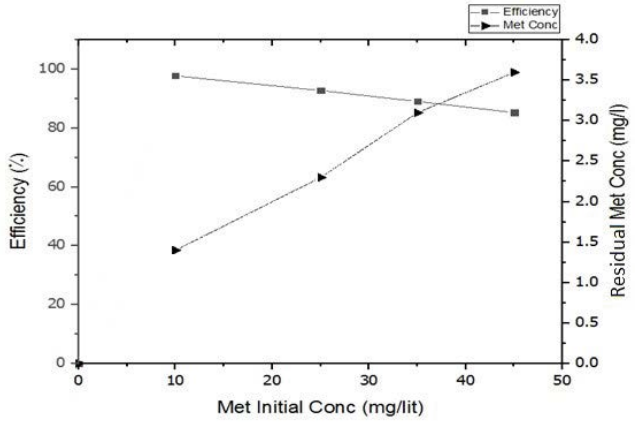

Fig. 8. Effect of initial metformin concentration on the elimination of metformin by the photocatalytic activity of the Fe^{3+} doped TiO_2 nanoparticles under UV irradiation (pH = 11, catalyst dosage = 75 mg/L, and time = 30 min).

3.2.5. Kinetics of photocatalytic activity

Computing the reaction kinetics is essential to assess the organic pollutants' degradation rate. The Langmuir–Hinshelwood model is utilized to explain the kinetics of

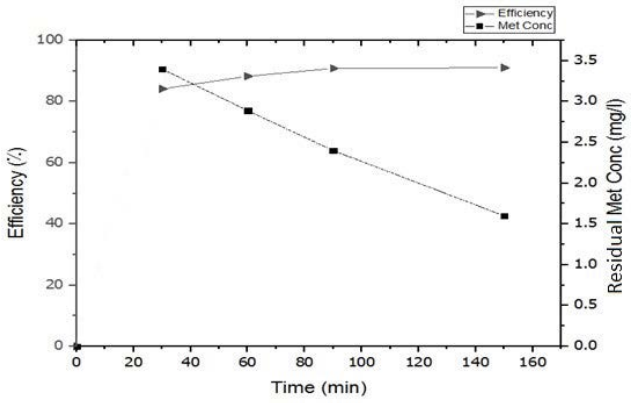

Fig. 9. Effect of contact time on the removal of metformin by the photocatalytic activity of the Fe^{3+} doped TiO_2 nanoparticles under UV irradiation (initial concentration = 35 mg/L, pH = 11, and catalyst dosage = 75 mg/L).

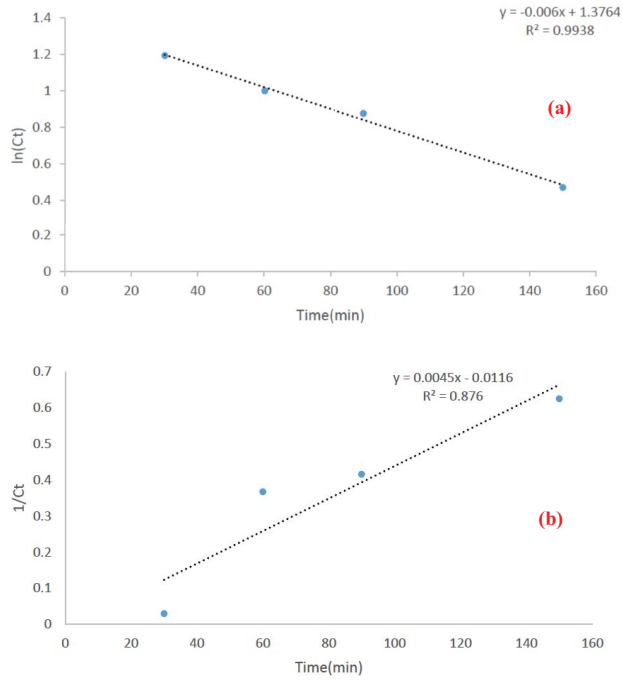

Fig. 10. Pseudo-first-order (a) and pseudo-second-order (b) kinetics model of metformin degradation.

photocatalytic reactions of organic pollutants in a chemical process. In this work, this model was used to study the pseudo-first-order and pseudo-second-order kinetics of metformin degradation. The results of the reaction kinetics' study to describe the UV/Fe^{3+} doped TiO_2 process are shown in Fig. 10.

Regarding the value of correlation coefficient (R^2), the comparison of graphs A and B indicates that the linear correlation between the data in the pseudo-first-order kinetic (R^2 = 0.99) is higher than in the pseudo-second-order kinetic (R^2 = 0.876). Thus, it can be noticed that the data follow the pseudo-first-order kinetic.

4. Conclusion

In the current study, first, Fe^{3+} doped TiO_2 nanoparticles were synthesized and applied as a catalyst for the degradation of metformin in a photochemical reactor under UV irradiation. The available peaks on the XRD pattern of the Fe^{3+} doped TiO_2 nanoparticles showed that this nanoparticle was contained the crystalline structure of TiO_2 and Fe^{3+}. According to the morphological analysis and characterization of synthesized nanoparticles, it was found that the particles have an almost spherical shape with a size between 60–75 nm. Furthermore, based on the EDXS technique, Ti, O, and Fe are present in the structure of nanoparticles, and the crystal size of the nanoparticles was found at about 70 nm.

The results of the photocatalytic process showed that under optimal conditions (pH = 11, nanoparticle dose of 75 mg/L, and reaction time of 90 min), the degradation process was able to remove about 93.8% of the metformin with an initial concentration of 35 mg/L. On the other hand, the removal efficiency of metformin in the range of pH 3 to 11 was higher than 85%, so it seems that Fe^{3+} doped TiO_2 nanoparticles can be used in a wide range of pH.

Furthermore, the kinetic analysis indicated that the experimental data of metformin degradation could be modeled via the Langmuir–Hinshelwood equation (pseudo-first-model), which revealed a high regression coefficient value (R^2 = 0.99). Based on our findings, it can be concluded that the Fe^{3+} doped TiO_2 nanoparticle under UV irradiation is an efficient method for the degradation of metformin in aqueous solutions.

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