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Feasibility study of metformin removal from synthetic wastewater using doped-TiO_2 as catalyst and UVA-LED

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ABSTRACT

The feasibility of using titanium dioxide (TiO_2) and ultraviolet-light-emitting diode in a batch reactor to remove metformin from synthetic wastewater was studied. The primary tests were using TiO_2 and light-emitting diode (LED) lamps, and complimentary steps continued using modified (m-TiO_2, FeFNS-TiO_2). Variation of different factors such as pH, the concentration of TiO_2, radiation intensity, the concentration of metformin in a solution and duration of experiments were tested. Results indicated that in the normal pH range, removal of metformin by m-TiO_2 increased up to 60% in comparison with using an unmodified catalyst. Although the highest efficiency was represented in basic (alkaline) pH range, contaminated waters usually are in a range of neutral pH. Therefore, changing pH before or after the process is not justified economically. The concentration of catalyst was another factor that was studied in the range of 0.1 to 1 g L^{-1}. Results indicated that the increasing catalyst concentration up to 0.8 leads in augmentation of removal efficiency of metformin and in higher concentrations, the efficiency, reduced, which may be as a result of preventing crossing radioactive radiation due to solution turbidity. Furthermore, an increase in metformin concentration, reduced efficiency. Removal of metformin in the concentration of 2mg L^{-1} was equal to 98% and in a concentration of 10 mg L^{-1} was equal to 72% using modified TiO_2. Also, the increase of reaction process time increased the removal efficiency, but the optimum process time was selected 30 min according to the results and economic interests. Adding anions and scavengers to the synthetic wastewater in the batch reactor also reduced the efficiency. The reason for this reduction may be decreasing free active spaces on the catalyst surface by sulfate, ultraviolet ray absorption by nitrate and using hydroxyl radicals by carbonate, bicarbonate, chloride, methanol and salicylic acid scavengers. Similar results were also observed while using tap water instead of distilled water in producing synthetic wastewater and the efficiency of metformin removal decreased in comparison with using distilled water. Evaluation of the results similarly indicated conformity of the results to a Lagergren's first-order model semi first-order kinetics.

Keywords: Metformin; TiO_2; UV-LED; Scavenger

1. Introduction

Metformin is the most widely used and proven drug in the world for the treatment of diabetes type 2, which is used to treat diabetes for non-insulin dependent diabetes. It is the first line of treatment for diabetes type 2 [1,2]. Metformin is also prescribed in carbohydrate metabolism disorders (helping to reduce obesity), the treatment of polycystic ovary syndrome [1], and even control of blood cholesterol.

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The growth of prescription of metformin in recent years is also significant. In the United States, it was administered with a steady increase from 49.2 million in 2007 to 76.9 million in 2014, indicating an increase of over 56% over 8 years. In New Zealand, in 2014, it has been ranked as the 16th most widely prescribed drug with 5,000,000 prescriptions and is ranked as the 9th drug with the highest volume of consumption [2]. In Australia, the annual prescribed rate is 5.1 million [2]. Scheurer et al. [3] explained the occurrence of vast consumed pharmaceutical metformin in Germany surface water and stated that the high concentrations correlated with consumption data.

Due to the 100% renal excretion from human body and non-metabolises of this drug and its high solubility in aqueous environments at 300 mg/ml in the range of 1.2 to 6.8 of pH and intense polarization of its molecule (pKa: 2.8, 11.5, log KOW (The logarithm of the molecular 1-octanol-water partition coefficient (log P) of compounds, which is a measure of hydrophobicity, is widely used in numerous quantitative structure-activity relationship models for predicting the pharmaceutical properties of molecules): water = –2.6) [1,4,5], the environment is exposed to significant concentrations and is expected to be found in aqueous environments [2].

Due to the potential of endocrine disorders (ED) and the toxicity of metformin and its biological degradation products, special attention is required in this regard, although a comprehensive standard of these drugs has not yet been developed in the United States, Canada, and the European Union. However, the German Environment Agency estimates that the maximum permissible concentration of non-genotoxic substances for long-term use in drinking water is less than 3 μg L^{-1} [2].

The chemical name of metformin is (7) N,N-dimethylimidodicarbonimidic diamide hydrochloride and its molecular formula is $C_{14}H_{11}N_5$. The molar mass is 129.16 $gmol^{-1}$ and it is melting point is 224.5°C. Fig. 1 indicates the chemical structure of metformin [6].

The potential of dysfunction on reproduction, brain and neuron system and the immune system is mentioned in the literature. By definition, an endocrine-disrupting chemical is a material or an external mixture that changes the function of the endocrine system and then may affect an organism or its next generation. Some of the other bad effects are a reduction of sperms, congenital defects, cancers, retarded growth, retarded neurobehavioral, obesity, diabetes and heart diseases.

In a study that evaluated the degree of decomposition of pharmaceuticals and personal care products (PPCPs) in the activated sludge process, the treatment of 57 types of PPCP was investigated; the concentration of metformin at the effluent was about half of its concentration in the influent, so that the absorbed concentration remained almost constant about 10 mg L^{-1}. The concentration of metformin at the influent was about 129,000 ng L^{-1} and the removal efficiency was about 41%–98% [5]. Margot et al. concluded that 50 organic micropollutants out of 70 dissolved organic micropollutants which are detected in untreated wastewater, treated on average less than 50% due to the conventional treatments. They also obtained that both ozonation and sand filtration or using activated carbon and ultrafiltration decreased the concentration of removing compound on average more than

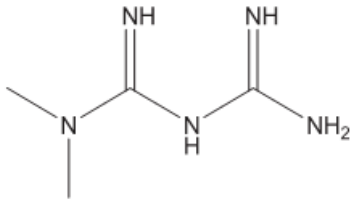

Fig. 1. Metformin chemical structure [5].

70% while using 5.65O_3 L^{-1} or 13 mg L^{-1} of powder of activated carbon [7]. Kim et al. [8] studied 91 PPCPs in influent and final effluent of a membrane bioreactor (MBR) wastewater treatment plant and found the final effluent of metformin and a few other medicines greater than 500 ng L^{-1}. They stated that removal efficiencies of PPCPs by MBR wastewater treatment plant were varied from 34 to greater than 99% [8].

In general, it may be stated that the removal efficiency of drug compounds during the activated sludge process is low (35%–90%). Therefore, the drug compounds exist in the effluent of wastewater treatment and there is a risk of their entry into drinking water [2]. The results of researches in Germany on drinking water in a laboratory scale and also on the water treatment plant indicated that sand filtration, as well as flocculation with ferric chloride, did not play an important role in the removal of drug compounds [2]. Another study also presented that the efficiency of aluminum sulfate and ferric chloride coagulants or lime softening in removing emerging contaminants was less than 25% [8]. However, filtration with activated carbon in treatment plants had a very good efficiency in the removal of pharmaceutical compounds (other than chloroferric acid) [9]. Macerak et al. [10] conducted a study for the removal of metformin using UV/H_2O_2 photocatalyst. Their result indicated that UV/H_2O_2 can accelerate the removal of metformin cause the creation of more toxic intermediate.

In the aspect of wavelength, three types of UV radiation included UVA, UVB, and UVC exist. UVA is the longest wavelength, which has a wavelength of 315–400 nm, and useful for photocatalysis using titanium dioxide (TiO_2). The most important resources of producing UV are the regular Mercury vapor lamps which have a big size, have a short lifetime, low efficiency, high energy usage, low resistance against strike and shock, high thermal sensibility and the potential of contamination because of the poisonous feature of mercury. Therefore, we used the ultraviolet-light-emitting diode (UV-LED) for metformin removal.

Emerging contaminants have been interested in recent years, as uncontrolled, chemical or biological combinations that have not been traced or standardized and may cause water resources to be polluted. According to the definition and classification of emerging contaminants, PPCPs are classified as a group of emerging contaminants. In this study, pharmaceuticals are interested and from that metformin was selected, at least because of the following reasons:

- A huge amount of consumers all over the world.
- Hazardous potential for human health because of its endocrine disrupting (ED). As metformin is a kind of hormone that is soluble in water instead of fat, and because of

the high rate of renal excretion, it is predicted that there is an interesting amount of it that exists in water resources.
- Many pieces of evidence indicate that this drug cause bio-accumulation and persistence in aquatic bodies and may some dysfunction on wildlife. However, metformin found in low concentration in freshwater environments, and its metabolisms may be active biologically on the aquatic organism accumulation of metformin has been reported in muscular tissues of fish [11].
- Toxicity is one of the disadvantages of many PPCPs because these products are targeted for maximum daily activity in low doses and accumulation and persistence may cause some disorders on untargeted metabolisms. Finally, a study of the removal of metformin from synthetic wastewater using TiO_2 and UV-LED has not been reported in the literature.

The main objective of this study was to determine the feasibility of metformin removal from synthetic wastewater in a batch reactor using both TiO_2 and amended TiO_2 photocatalyst with light-emitting diode (LED) lamps.

Also, the following were some of the detail objectives of the study:

- Investigating the effect of several parameters such as the concentration of catalyst, initial concentration of metformin in synthetic wastewater and wastewater conditions, such as pH, effect and presence of ions, as well as the time of processing on the decomposition rate, the kinetics of the reaction and achieving optimal efficiency conditions.
- Study on the absorption of metformin on the surface of the nanocatalysts.
- Selection of the process which has the highest efficiency of metformin removal from synthetic wastewater analysis.

2. Material and methods

2.1. Experimental setup

A batch reactor using LED lamps was prepared. The selected arrangement of the LED lamps was circular, with three distinct circuits, including a single LED lamp in the center, six LED lamps at the middle ring and 12 LED lamps at the peripheral ring. In such a way that the operation of each of the circuits was created individually and in combination with the rest to achieve different radiation intensities. It was assumed that this arrangement creates a uniform radiation source at the surface. For this purpose, a series of 1, 6 and 12 lamps were connected in parallel and operated with a direct current supply of 220 V.

The batch reactor consists of a glass container with 9 cm in diameter and 1 cm in depth. A 2 mm thick quartz plate was placed between the radiation source and the glass reactor to prevent water contact with a source of radiation. The UV-LEDs used with a wavelength of 365–370 nm were manufactured by SUN LED Corporation in China with the following specifications:

Power was 3 W and IV (MW) was 280–320 IF (mA) was 500 and the holder was copper. AU > 99.99% and WD (nm) was 365–370 VF was 3.3–3.6 V and chip size was 45 mm × 45 mm. Chip's name was Epistar. Fig. 2 indicates the picture of the reactor under study.

2.2. Sample preparation

Pure metformin, with a purity of 100, was prepared by the Hakim Pharmaceutical Company (Teheran, Iran), and after dissolving it in distilled water, a standard solution for calibration was prepared.

A stock solution was made of pure metformin dissolved in distilled water, with a concentration of 100 mg L^{-1}. For this purpose, 50 mg of metformin powder was dissolved in a 500 cubic centimeter of distilled water. This stock solution was used for each of the related tests, after dilution (Table 1). The stock solution before the dilution was stored in dark conditions at 4°C. The final volume of the samples was assumed to be 20 ml based on the volume of the Batch reactor.

Different concentrations of the TiO_2 catalyst were measured by direct weighing of nanoparticles and added to the reactor vessel. We used TiO_2 and FeFNS-doped TiO_2 (named m-TiO_2) with a similar characteristic of works of Hossaini et al. [12] and Shafeei et al. [13]. To prevent sedimentation in the batch reactor and having suspension during the experiment, the batch reactor was placed on a magnetic stirrer (styrene).

2.3. Photocatalytic removal experiment

For testing, metformin, and photocatalyst solution were blended into the reactor under ultraviolet radiation. Various parameters were investigated in these experiments, including the time of the experiment, metformin concentrations, photocatalyst concentrations, different radiation intensity, the effect of anion and pH. At each stage, after the time taken for the photocatalytic process, the suspension was passed through a filter of 0.22-micron polyvinylidene difluoride membrane. Then the filtered specimen was injected into High-performance liquid chromatography (HPLC) (made

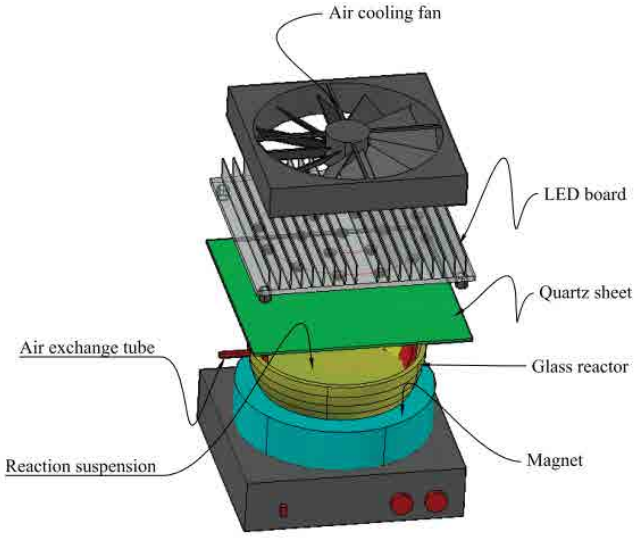

Fig. 2. 3D picture of the batch reactor under study.

Table 1
Design of experiment

No.	Step	Run	Description	Variable Index	Calculating concentration of MTF (mg L^{-1})	Calculating the concentration of catalyst (g L^{-1})	Time (min)	Initial pH
1–8	1	First	Initial (LED photolysis)	Time	10	–	0, 5, 10, 120, 30, 40, 50, 60	7.40
9–20	2	First, second and third	LED photolysis, LED + TiO_2 photocatalysis, and darkness, respectively	pH	10	–0.5	30	4, 7, 8 and 10
21–33	3	Initial		pH	10	–	–	7.4
		First, second and third	LED photolysis, LED + TiO_2 photocatalysis, and darkness		10 10 10	0 to 0.5	30	4, 7, 8 and 10
34–54	4	Initial		pH	10	–	–	7.4
		First to fifth Second Third Second Third	LED photolysis, LED + TiO_2, photocatalysis darkness, LED + TiO_2, (modified) photocatalysis, Darkness, and (modified TiO_2), respectively		10	–0.5	30	4,7,8 and 10 in each run
55	5	Initial		Concentration of catalyst	10	–	–	7.40
56–71		First, to the third run	LED + TiO_2 photocatalysis, LED + TiO_2 (modified) photocatalysis and darkness		10	0.1, 0.2, 0.4, 0.6, 0.8 and 1 in each run	30	7.4
72 and 73						0.8 1		7.4
74–80		Forth and Fifth	Darkness (modified TiO_2) and LED photolysis, respectively		10	0.1, 0.2, 0.4, 0.6, 0.8 and 1 in each run	30	7.4
86–90		First	LED + TiO_2 (modified) photocatalysis		2,4,6,8 and 10	0.8	30	
91–94		Second	Darkness (modified TiO_2)		4, 6,8,10 and 2,4,6 8, 10 in each run	0.8	30	7.4
–								
95–100		Third	LED photolysis			0.8	30	

101–109	7	Initial	Time	10	0.8	5, 10, 15, 20, 30, 40, 50 and 60	7.4		
		LED + TiO_2 (modified) photocatalysis							
110–119	8	12	Radiant intensity ($\mu w\ cm^{-2}$)	10	0.8	30	7.4		
		84							
		228							
	9	Initial	Anion	10	–	–	7.4		
		Chloride, Nitrate, Sulfate, Bi-carbonate, Carbonate, and Tap water		10	0.8	30	7.4		
		–							
120–122	10	Initial	Scavenger	10	1	30	7.40		
		Methanol and Salicylic acid respectively	LED + TiO_2 (modified) photocatalysis						

by HACH) apparatus and the metformin concentration was reported based on the calibration curve.

The photocatalytic process involves two sections of decomposition and absorption. This means that part of the pollutant is decomposed by direct ultraviolet collisions, and the other part is absorbed by the catalyst [12]. Therefore, to determine the removal efficiency in each of these processes, all experiments were performed in the off state of the radiation source and the surface adsorption was measured. Also, to investigate the effect of photolysis on reducing the amount of metformin from synthetic wastewater, the experiments were carried out in the presence of a radiation source without adding a catalyst. From three types of experiments, including photocatalyst, photolysis and absorption, the photocatalytic process efficiency, was calculated by computing the catalytic potential according to the following equation [12]:

$$R_{obs} = R_{pco} - \left(R_{ads} + R_{led}\right) \quad (1)$$

where R_{obs} is degradation efficiency of metformin in photocatalytic removal with photocatalyst and LED; R_{LED} is a degraded performance of metformin without any photocatalyst and under the LED radiation and R_{ads} is adsorption by photocatalyst. The R_{obs} is synergy efficiency.

The catalytic potential is a sign of the effect of the synergy of the efficacy of photolysis and adsorption.

2.4. Effect of different parameters on photocatalytic reactor effect

2.4.1. pH

To study the effect of pH on photocatalytic removal of metformin from synthetic wastewater, pH 4, 7, 8, and 10 were investigated. In this regard, the pH was adjusted using a Hydrochloric acid solution and 0.1 M NaOH. The pH of the solution measured by a pH meter (Model HQ40D, USA).

The constants of these experiments were the initial concentration of metformin, 10 mg L^{-1}, the catalyst concentration of 0.5 g L^{-1} and the time of the experiment, time of 30 min, and the intensity of radiation of 228 $\mu W\ cm^{-2}$. These experiments were performed one time when the radiation source is on without adding a catalyst.

Samples were injected into the HPLC apparatus. Photocatalyst experiments were also repeated in the above pHs to measure total organic carbon (TOC).

2.4.2. Time

Photolysis experiments were carried out to evaluate the effect of time at 5, 10, 15, 20, 30, 40, 50 and 60 min. In this set of experiments, we used natural pH and radiation intensity of 228 $\mu W\ cm^{-2}$. Photocatalytic experiments with modified photocatalyst were performed at a rate of 0.8 g L^{-1} at the mentioned time and some samples were selected for TOC measurement.

2.4.3. Radiation intensity

Lamps installed on different circuits were tested in different modes, including central single lamp, intermediate ring (with 6 lamps), peripheral ring (with 12 lamps) and their

combination, to create different intensities. In this group, which was tested at natural pH, the initial concentration of metformin solution was 10 mg L^{-1}, the modified catalyst concentration was 0.8 g L^{-1} and the time duration was 30 min.

2.4.4. Catalyst concentration

Different amounts of catalysts were investigated at concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 g L^{-1} with both modified TiO_2 and TiO_2 catalysts. In photocatalytic experiments, which was conducted to study the effect of catalyst concentration, the intensity of radiation was 228 μW cm^{-2}, the initial concentration of metformin was 10 mg L^{-1}, pH was natural and time duration was 30 min. Absorption and photolysis experiments were also carried out with both catalysts.

2.4.5. Initial concentration of metformin

The effect of the initial concentration of metformin in synthetic wastewater was tested for amounts of 2, 4, 6, 8 and 10 mg L^{-1}. In this regard, the modified catalyst concentration was 0.8 g L^{-1}, pH was natural, the time of the experiment was 30 min and radiation intensity was 228 μW cm^{-2}. Also, absorption and photolysis experiments were carried out in the above conditions.

2.4.6. Presence of ions and radicals' scavengers

The effect of nitrate, sulfate, phosphate, chloride, carbonate and bicarbonate anions were investigated. In this regard, for photocatalyst experiments, an anion concentration of 100 mg L^{-1}, metformin concentration of 10 mg L^{-1}, modified catalyst concentration of 0.8 g L^{-1}, natural pH, 30 min and radiation intensity of 228 μW cm^{-2} were considered. Also, the effect of adding salicylic acid and methanol to 0.1 g was observed at metformin concentration of 10 mg L^{-1}, modified catalyst concentration of 1 g L^{-1}, natural pH, 30 min and radiation intensity of 228 μW cm^{-2} were tested.

2.4.7. Tap water instead of distilled water

To investigate the efficacy of photocatalytic removal of metformin in natural waters, tap water from the city of Tehran was used. By the way, the concentration of metformin was 10 mg L^{-1}, the modified catalyst concentration was 0.8 g L^{-1}, pH was natural, time duration was 30 min and the radiation intensity was 228 μW cm^{-2}.

2.4.8. Modified catalyst

As all the mentioned parameters, all experiments were also performed with modified TiO_2.

Table 1 indicates the design of experimental work.

3. Results and discussion

3.1. Effect of pH on the removal of metformin

Fig. 3 indicates the results of metformin removal from synthetic wastewater using 0.5 g L^{-1} TiO_2 catalyst in the solution when pH was differing. The concentration of metformin

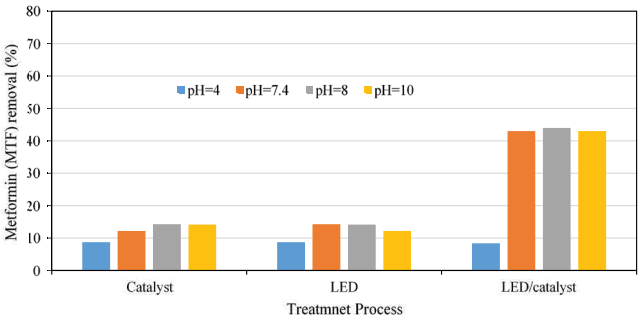

Fig. 3. Effect of pH on the removal of metformin from synthetic wastewater in absorption, photolysis, and photocatalysis.

in was 10 mg L^{-1}, and radiation intensity was 228 μW cm^{-2}. Experimental work was including three processes mentioned as absorption (only in the presence of a catalyst), photolysis (only in presence of LED lamp) and photocatalysis (using catalyst in presence of LED lamp).

Accordingly, the efficiency of photocatalytic removal of metformin from synthetic wastewater at pH 4, 7.4 (natural), 8 and 10 was 8.4%, 43.0%, 44.0%, and 43.0%, respectively. As indicated in Fig. 4, an excess of 40% removal occurred at pH between 7 and 8.

Shafeei et al. [13] studied the removal of Ibuprofen in a concentration of 5 mg L^{-1} from synthetic wastewater using TiO_2. They achieved the highest efficiency of 24.3%, in natural pH (7).

3.2. Effect of m-TiO_2

As higher removal efficiency was obtained when the modified catalyst (m-TiO_2) was used, we experimented with other tests using m-TiO_2 instead of TiO_2. These series of experiments were executed when metformin (MTF) concentration was 10 mg L^{-1} and radiation intensity was 228 μW cm^{-2}. As illustrated in Fig. 4, catalyst modification indicated an increased efficiency in removing metformin from synthetic wastewater

While we used the m-TiO_2 in presence of LED lamp, the efficiency of the photocatalytic process in the metformin removal at pH of 4, 7.4, 8 and 10 were 58.5%, 63%, 65% and 47.5% respectively, which indicated an increase of about 50% efficiency at pH ranging from 7 to 8.

Hossaini et al. [12] also indicated that the highest efficiency of 87.6% obtained in the natural pH at the concentration of 5 mg L^{-1} using m-TiO_2.

3.3. Synergy of LED/catalyst process

Fig. 5 presents the synergies for both TiO_2 and m-TiO_2 catalyst. This diagram indicates that the efficiency of the photocatalysis process is greater than the total efficiency of the photolysis and the absorption process. Also, it shows that in the pH range of 7.4 to 10, the natural pH is the most justifiable. In m-TiO_2 usage; however, the amount of synergy at pH 4 was higher, but because pH of 7.4 was closer to pH of natural water and to reduce the actual costs of tests due to pH changes, the normal pH was considered as the test conditions. Investigating changes before and after the process

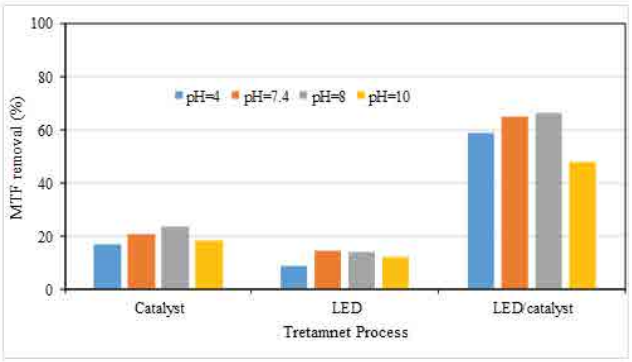

Fig. 4. Effect of pH on the removal of metformin from synthetic wastewater in absorption, photolysis, and photocatalysis.

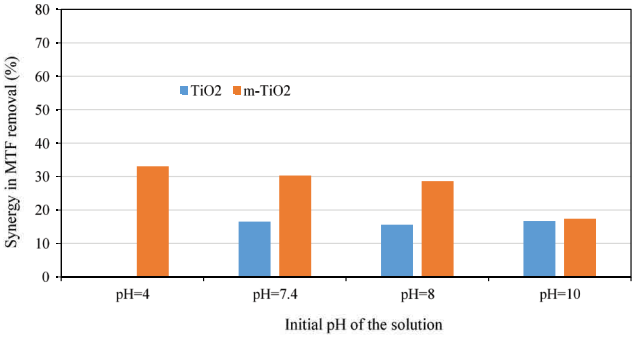

Fig. 5. The synergy of photocatalysis process for removal of metformin from synthetic wastewater.

showed that the addition of nanoparticles did not have a significant effect on the pH of the solution.

3.4. Effect of catalyst concentrations

Fig. 6 illustrates the removal of metformin from synthetic wastewater using 0.1, 0.2, 0.4, 0.6, 0.8 and 1 g L^{-1} of the TiO_2 catalyst. As indicated in Fig. 6, increasing the concentration of the TiO_2 catalyst from 0.1 to 1 g L^{-1} resulted in an increase of 4% to 17% in the removal of metformin from synthetic wastewater.

For removal of diazinon, Hossaini et al. [12] obtained an increase in the removal of diazinon while the rate of catalyst concentration increased and the highest efficiency was 15% while using 200 mg L^{-1} of the catalyst.

3.5. TiO_2/LED process

Fig. 7 presents the removal efficiency of a 10 mg L^{-1} metformin solution with natural pH and intensity of radiation of 228 Mw cm^{-2} using TiO_2 photocatalyst ranging from 0.1 to1 g L^{-1}. As illustrated in Fig. 7, in higher concentrations, the rate of efficiency of metformin removal of synthetic wastewater decreases, which may be due to the increased turbidity of the solution due to the high concentration of the catalyst and the prevention of UV absorption [9].

We applied the maximum efficiency was obtained at concentrations of 0.6 and 0.8 g L^{-1} with 51% removal of

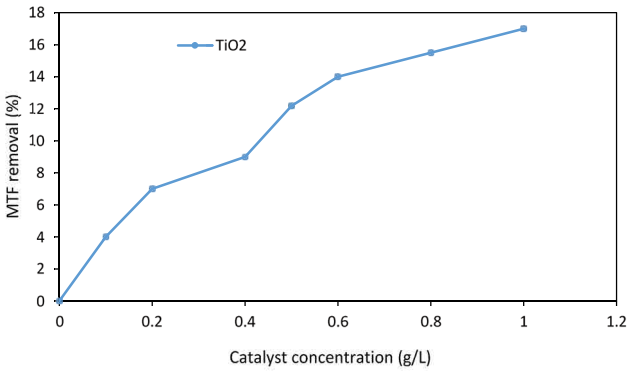

Fig. 6. Effect of changes in TiO_2 concentration in the metformin removal from synthetic wastewater.

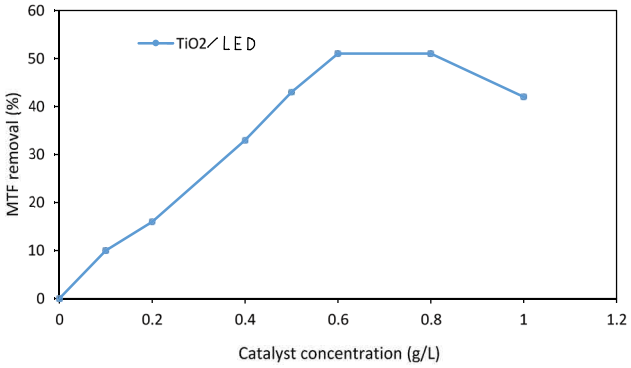

Fig. 7. Effect of variations in catalyst concentration in metformin removal during the photocatalysis process.

metformin and then, with increasing concentration from 0.8 to 1 g L^{-1}, the efficiency of metformin elimination was decreased.

3.6. Photocatalysis

3.6.1. Adsorption

We used m-TiO_2, which indicates the effect of adsorption on a catalyst with different concentrations (Fig. 8). As presented in Fig. 8, the adsorption process increased with increasing catalyst concentration and changed from 7% for the concentration of 0.1 g L^{-1} m-TiO_2 to 28% for the concentration of 1 g L^{-1}, which on average increased by more than 60% related to unmodified TiO_2 catalyst indicates in Fig. 8. The concentration of metformin was 10 mg L^{-1}.

Fig. 9 presents removing metformin from artificial wastewater during the photocatalysis process using modified TiO_2. While, the concentration of catalyst increased up to 0.8 g L^{-1}, the efficiency of removal raised. However, using 10 mg L^{-1} metformin, the rate of removal decreased when we used between 0.8 to 1 g L^{-1} of catalyst. The maximum removal efficiency was at concentrations of 0.8 g L^{-1}. Fig. 10 illustrates the effect of metformin concentration in removal of it from artificial wastewater. As indicated in Fig. 10, increasing of metformin in the wastewater decreased removal efficiency. As mentioned in the case of the TiO_2 catalyst, increased

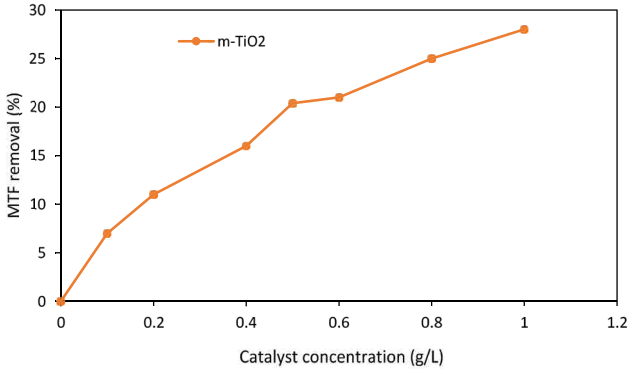

Fig. 8. Effect of m-TiO_2 concentration in the adsorption process.

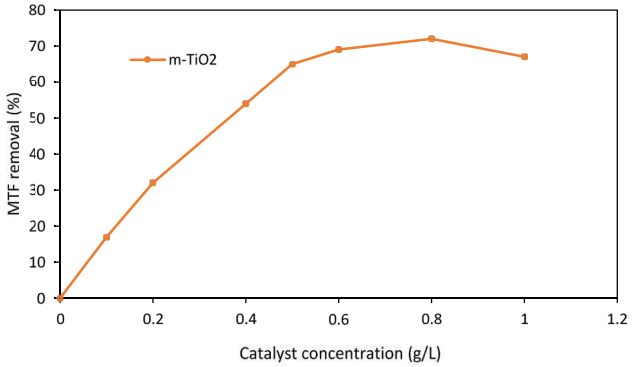

Fig. 9. Effect of the amount of m-TiO_2 in the photocatalysis process.

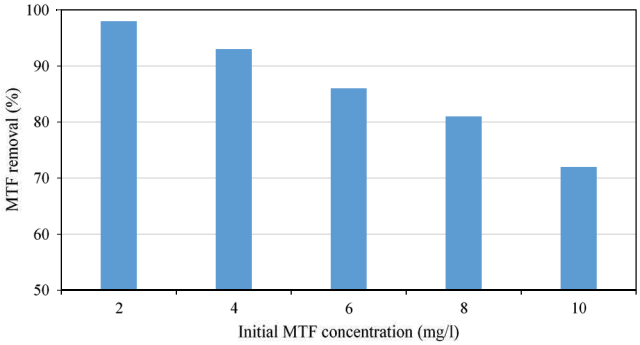

Fig. 10. Effect of metformin concentrations in the m-TiO_2/LED process.

turbidity of the solution may be a factor in reducing process efficiency. According to Fig. 11, a concentration of 0.8 g L^{-1} was selected as optimal catalyst concentration to continue the experiments. Also, due to the significant increase in removal efficiency of metformin using m-TiO_2, only the modified catalyst was used for the photocatalysis process.

Hossaini et al. [12] likewise indicated that for removal of diazinon using modified TiO_2 by increasing catalyst concentration from 25 to 300 mg L^{-1}, the photocatalysis process efficiency increased from 44% to 96.3%. After investigation of the effect of synergy, the concentration of 100 mg L^{-1} of modified

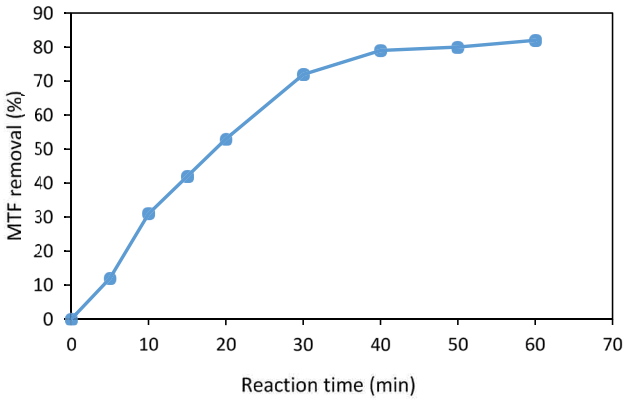

Fig. 11. Effect of time on the removal of metformin from artificial wastewater using m-TiO_2/LED.

TiO_2 indicated the most efficiency for the removal of diazinon [12]. Also, Shafeei et al. [13] presented that for the removal of Ibuprofen at a concentration of 5 mg L^{-1} and at pH 7, using 0.2 g L^{-1} modified TiO_2, reached 47.5% of efficiency [13].

3.7. Effect of metformin concentrations in the m-TiO2/LED process

A concentration of 0.8 g L^{-1} of modified catalyst and natural pH (7.4) was selected for metformin removal from synthetic wastewater. The initial concentrations of metformin were considered to be 2, 4, 6, 8, and 10 mg L^{-1}. As indicated in Fig. 12, increasing the initial concentration of metformin directly effects on the reduction of the photocatalytic removal efficiency, resulting in the removal of 98% of metformin at 2 mg L^{-1} concentration and 72% at the concentration of 10 mg L^{-1}.

The reason for removal, reduction may be the decreasing on the ability of a constant amount of the catalyst and, as a result, a constant amount of radical hydroxyl cannot remove more amount of contaminants under the same conditions of other parameters [9].

Similar results were obtained in Hossaini et al. [12] research, in which changing the initial concentration of diazinon from 1.5 to 14 mg L^{-1}, lead to a reduction of the removal percentage from 87.6% to 32.8%.

3.8. Effect of reaction time on the m-TiO_2/LED process for metformin removal

In these experiments, the modified catalyst concentration was 0.8 g L^{-1}, in natural pH, and the initial concentration of metformin was 10 mg L^{-1}. Photocatalytic tests were performed in 5, 10, 15, 20, 30, 40, 50 and 60 min. Fig. 11 indicates the effect of time of the process for up to 60 min for the photocatalytic removal of metformin from the synthetic wastewater. As illustrated in Fig. 11, the photocatalytic process efficiency, increased from 0% to 82%, with an increase of up to 60 min, due to increased exposure time to hydroxyl radicals.

Based on Fig. 11, the slope of the graph is as high as possible for 30 min. Considering that higher times, reduce lamp lifetime and increase energy consumption; therefore, all the time tests were selected 30 min.

3.9. Mineralization of metformin

Metformin mineralization amount was evaluated at different times by measuring the amount of TOC (Fig. 12). As indicated in Fig. 12, the process of mineralization with increasing reaction time is always ascending and is obtained from 3% for 5 min to 41% after 60 min. But the gradient of the graph is the highest up to 30 min, and after 30 min the mineralization rate reached 70% of its final value.

3.10. Effect of anions on the m-TiO_2/LED process

The increase in ions in the solution of synthetic wastewater led to a reduction of the efficiency of metformin removal (Fig. 13)

Considering Fig. 13, the most significant reduction in metformin removal from synthetic wastewater is caused by the sulfate ion due to adsorption on the catalyst surface, which causes the catalyst active surface to be occupied. As a result, the production of hydroxyl radicals is reduced due to the reduction of active sites on the catalyst surface. Nitrate also produces less radical by absorbing ultraviolet radiation and reducing the amount of radiation received by the catalyst; therefore, the efficiency of metformin removal decreases. Existing carbonate, bicarbonate and chloride ions in the reaction medium, which are considered as scavenger radical and react with radical hydroxyl, reduce the amount of hydroxyl radical available for decomposing the pollutant, and thus reduces the removal efficiency. Also, the presence of anions in tap water, in the experiments carried out with it, reduced the efficiency of effluent. (pH = 7.3, chloride = 58 mg L^{-1}, sulfate = 16 mg L^{-1}, alkalinity = 160 mg L^{-1} as $CaCO_3$)

3.11. Effect of intensity of radiation on the m-TiO_2/LED process

The effect of two different radiation intensities (84 and 228 μW cm^{-2}) on the photocatalytic removal of metformin from synthetic wastewater under initial concentration of 10 mg L^{-1} of metformin in the solution, a duration of 30 min, natural pH and 0.8 g L^{-1} of catalyst were measured (the radiation intensity of each lamp was 12 μW cm^{-2} at the quartz plate). The photocatalytic removal efficiency of metformin from synthetic wastewater at a radiation intensity of 84 and 228 μW cm^{-2}, was equal to 33% and 72% respectively.

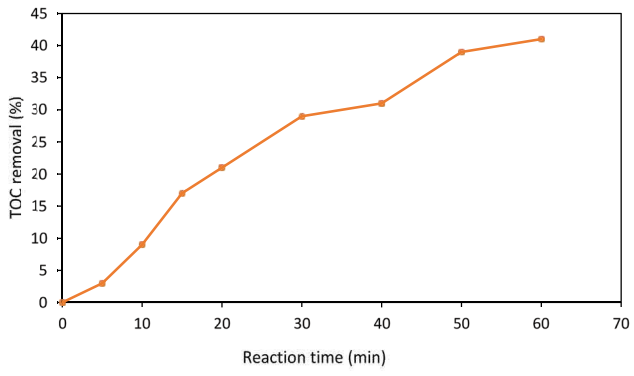

Fig. 12. Effect of time on metformin mineralization.

The one-lamp in the middle practically caused no tangible result. This means that radiation intensity is important for the removal of metformin.

3.12. Effect of Radical scavenger on the m-TiO_2/LED Process

In these experiments, two radical's scavenger of salicylic acid and methanol (MeOH) were used. In theory, if the efficiency of removal is reduced after adding radicals, it can be concluded that radical hydroxyl was produced sufficiently [8]. In the first photocatalytic experiment with natural pH conditions, the initial concentration of 10 mg L^{-1} of metformin, a concentration of 0.8 g L^{-1} of catalyst and time of 30 min, efficiency was 72%. After adding 0.1 g of methanol to the Batch reactor, efficiency was reduced to 57%, and Adding 0.1 g of salicylic acid (SA) to one reactor vessel yielded 26% of efficiency (Fig. 14).

Radical scavenger when added to the system, caused a reduction of the amount of metformin removal from synthetic wastewater. Because it reduced the number of hydroxyl radicals, and this confirms that the removal process was performed through photocatalytic activity.

3.13. Kinetics of metformin decomposition from artificial wastewater

In these experimental works, the removal efficiency of metformin from synthetic wastewater was a function of time.

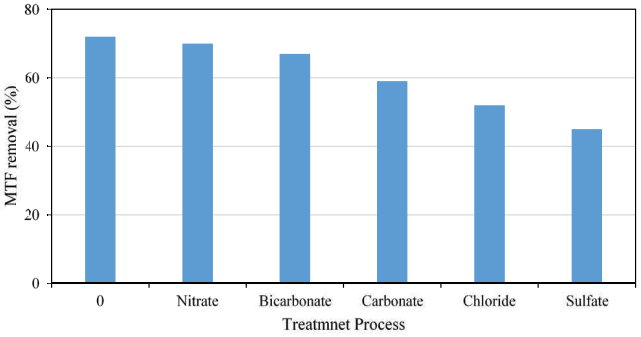

Fig. 13. Effects of anions on metformin removal from synthetic wastewater in the m-TiO_2/LED process.

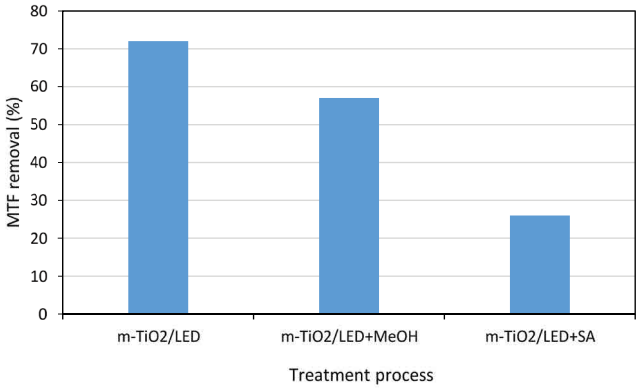

Fig. 14. Effect of radical scavenger on the removal of metformin from synthetic wastewater.

We applied the Lagergren first-order kinetic model according to Eq. (2):

$$\ln\left(\frac{C_t}{C_0}\right) = -K_{app} \quad (2)$$

where C_t is the metformin concentration in the synthetic wastewater at the time t. C_0 is the initial concentration of metformin in the synthetic wastewater and K_{app} (1/d) is the rate of adsorption of metformin which is constant during photocatalysis. As indicated in Fig. 14, the coefficient of determination (R^2) between the Lagergren first-order model and experimental data was equal to 0.9784. Based on the gradient of the line drawn in Fig. 14, the K_{app} reaction was 0.0501 (Fig. 15).

3.14. Kinetics of metformin mineralization

Modeling the data obtained from TOC experiments indicates that the model with R^2 = 0.972 follows a Lagergren first-order model. Based on the gradient of the line drawn on the graph, the reaction constant is 0.0091(Fig. 16).

4. Discussions

Oosterhuis et al. [14] studied metformin and some other medicine removal in sewage treatment in Enscheda and Ootmarsum. The two sewage treatment plant was not the same as each other. In the first one chain of treatment included anaerobic denitrification process and in the second treatment plant, in addition to the mentioned process, UF membrane and sand filtration existed. They found 98% and 99% removal for Enscheda and Ootmarsum, respectively. In this research, 98% of metformin removal is achieved while the influence of our batch reactor was 2,000 μg L^{-1}. The influences of both treatment plants were 73.73 and 84.4 ng L^{-1}, respectively. With consideration of the presence of anions in the experiment, removal of metformin from artificial wastewater using modified TiO_2 photocatalyst is still higher than the mentioned study. The advantages of their study were working on a full scale of sewage treatment plants.

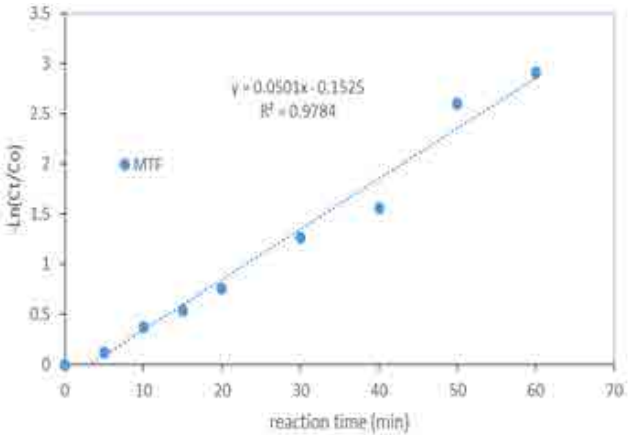

Fig. 15. Kinetics of metformin decomposition in synthetic wastewater.

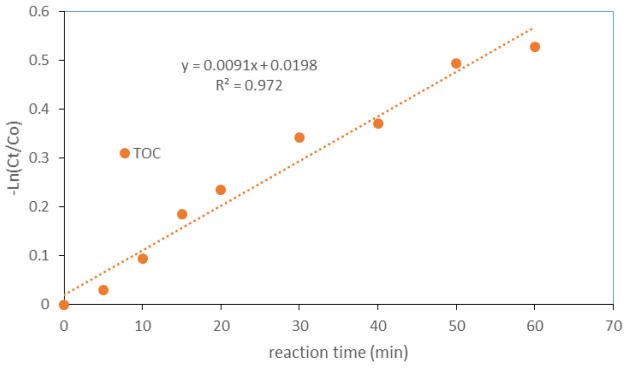

Fig. 16. Metformin mineralization kinetics.

Kim et al. [15] influenced of MBR wastewater treatment plants ranging from 10,000 to 100,000 ng L^{-1} for acetaminophen, caffeine, metformin, 2-hydroxyibuprofen, paraxanthine, and effluent of MBR for removal of metformin was 99%. The efficiency of 98% for metformin removal in this study is achieved for concentrations of 20 to 200 times higher than Kim et al. study [15]. Therefore, the efficiency of removal of metformin from synthetic wastewater using m-TiO_2/LED or TiO_2/LED was higher than their work.

Zhu et al. [16] studied metformin removal from wastewater using graphene oxide. They reached 80% removal of metformin within 20 min. However, we obtained 98% removal of metformin within 30 min using synthetic wastewater containing 20 mg L^{-1} metformin.

5. Conclusions

The keys finding from the study of the removal of metformin from synthetic wastewater in a batch reactor in the presence of LED lamps and m-TiO_2 catalyst are as follows:

- The best removal efficiency of metformin from synthetic sewage was obtained at an approximate pH of 8, but as the pH of contaminated water is often neutral, the pH suitable for this removal process was selected in the natural range of 7.4.
- Increasing the catalyst concentration from 0.1 to 1 g L^{-1} in the adsorption process resulted in increased metformin removal from artificial wastewater from 4% to 12% while 10 mg L^{-1} of metformin exists in the synthetic wastewater.
- The maximum removal efficiency in the photocatalytic process with a modified catalyst was obtained at a concentration of 0.8 g L^{-1} of catalyst. The reason for the reduction of metformin removal at concentrations higher than 0.8 g L^{-1}, maybe due to increased turbidity of the synthetic wastewater and thus reduced the process efficiency due to the prevention of radiation penetration into the solution of synthetic wastewater.
- Increased initial concentrations of metformin in artificial wastewater were effective in reducing its removal efficiency, so that at a concentration of 0.8 g L^{-1} of modified TiO_2 catalyst when metformin was 2 mg L^{-1}, the removal efficiency was 98% and while the amount of metformin was 10 mg L^{-1}, the removal efficiency reduced to 72%.
- Increasing the removal time with a modified TiO_2 catalyst at a concentration of 0.8 g L^{-1}, the natural pH and initial concentration of metformin of 10 mg L^{-1} for 5, 10, 15, 20,

30, 40, 50 and 60 min resulted in increased metformin removal efficiency from synthetic wastewater between 0 up to 80%.

- Metformin degradation from synthetic wastewater persuades a Lagergren's first-order model with R^2 = 0.9784 and a rate constant of 0.0501 h^{-1} obtained from kinetic study for m-TiO_2/LED and the kinetics of metformin mineralization obtained from TOC experiments indicate that the model with R^2 = 0.972 followed a Lagergren's first-order model and the reaction constant was equal to 0.0091 h^{-1}.
- The effect of radiation intensity on the m-TiO_2/LED process with 84 and 228 μW cm^{-2} intensities in the removal of metformin from synthetic wastewater at an initial concentration of 10 mg L^{-1} of metformin, a duration of 30 min, natural pH and 0.8 g L^{-1} catalysts were 33% and 72% respectively. The one-lamp in the middle practically caused no tangible results.
- Presence of anion in synthetic wastewater caused decrease metformin removal. Sulfate reduced metformin removal higher than other anions such as nitrate, bicarbonate, carbonate, and chloride. Sulfate ion has the greatest effect on reducing efficiency because it is absorbed on the surface of the catalyst and causes its active sites to be occupied. Therefore, radical production decreases due to the reduction of active sites on the catalyst surface.
- Using tap water instead of distilled water in synthetic wastewater reduced the removal efficiency of metformin. This reduction of efficiency is due to the presence of various anions in the tap water.

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