

PAPER



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Optimization by central composite design (CCD)-response surface methodology (RSM) of the highly selective molecularly imprinted Ni and F co-doped TiO₂ photocatalyst for photocatalytic degradation of bisoprolol

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Molecularly imprinted Ni and F co-doped TiO₂ nanoparticles were synthesized *via* the sol–gel method. The nanoparticles displayed high photocatalytic activity under both sunlight and artificial visible light for degradation of bisoprolol. Characterization of the nanoparticles was carried out using XRD, FE-SEM, TEM, FT-IR, DRS, EDX and BET-BJH. The effects of different operational variables on the photocatalytic activity were optimized using the response surface methodology (RSM). The optimal experimental conditions for achieving the highest photocatalytic efficiency (72.5% by a desirability function value of 1.0) are as follows: pH = 5.9, photocatalyst mass = 83.42 mg, bisoprolol concentration = 16.2 mg L^{−1}, and irradiation time = 137 min. The selectivity of the photocatalyst was investigated against pantoprazole. The excellent photocatalytic activity is attributed to the doping of Ni and F dopants into the TiO₂ structure. The investigation of the mechanism of the photocatalytic reaction revealed that the main active species involved in the degradation of bisoprolol are OH• radicals.

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1. Introduction

One of the most important concerns, especially among industrial countries, is environmental pollution.¹ Every day, millions of liters of toxic organic pollutants are discharged into the environment.² Many people suffer from the lack of hygienic and safe drinking water. Pharmaceutical chemicals are a group of important organic pollutants. Some pharmaceuticals are supposed to affect the endocrine system of fish and they can also favor the development of multi-resistant strains of microorganisms.^{3,4} These pharmaceutical contaminants are frequently released into the aquatic environment from manufacturing facilities, consumer use, disposal and hospital waste.^{3,5,6} Therefore, an efficient and cost-effective method is required to remove pharmaceutical contaminants from water and also assure the quality of water.³ One of these pharmaceutical contaminants is bisoprolol, which is a selective β₁-blocker, a class of drugs used primarily in CVDs. β-Blockers are among the most widely prescribed of all drug classes and recommended as first-line drugs to treat patients with numerous diseases such as hypertension, angina, and heart failure.⁷

Advanced oxidation processes (AOPs) have been considered as an efficient and promising method to mineralize pollutants in aqueous media and turn them into less toxic and biodegradable compounds.^{8–14} The photocatalytic process is one of the most interesting AOPs, which is based on the production of highly reactive radicals (OH•, O₂•[−], *etc.*) to oxidize organic pollutants. In the photocatalytic process, a semiconductor is activated by absorbing a light beam with an energy greater than the band gap of the semiconductor. During the activation, electrons and holes are produced in conduction and valence bands, respectively. The electrons and holes perform redox reactions with the adsorbed species to form reactive radicals.² Among semiconductor photocatalyst materials, TiO₂ is the most widely used semiconductor due to its specific benefits including efficiency, non-toxicity, durability, reasonable price, high oxidation potential, and stability.^{8,15,16} Despite the advantages of TiO₂ semiconductors, there are noticeable drawbacks that limit their photocatalytic applications. TiO₂ can only be activated by absorption of UV irradiation due to its large band gap (3.2 eV), which is the most important restriction.¹⁷ Another limitation of TiO₂ is the high rate of electron–hole recombination, which results in reduction of the photocatalytic activity.¹⁸ Many strategies have been considered to help solve the limitations of TiO₂.¹⁹ Doping TiO₂ with metal and nonmetal impurities

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decreases its band gap energy and, in turn, improves the photocatalytic activity.^{11,20,21} Nonmetal impurities such as N, B, S, and F have been widely used to improve the photocatalytic efficiency of TiO₂.^{22–24} Extension of the photoresponse of TiO₂ into the visible light region has been reported using transition metal dopants.²⁵ In this regard, many transition metals such as Cr, Mn, Co, Mo, Ni, Cu and Zn have been used to modify the band gap of TiO₂ and increase its photocatalytic activity under visible light irradiation.^{26,27} Poor selectivity is another limitation of the TiO₂ photocatalyst to degrade target molecules. It is of the highest priority to absorb and degrade more toxic components compared to less toxic ones in contaminated water.²⁸

The molecular imprinting technique is an excellent method to prepare molecularly imprinted polymers with particular molecular recognition sites. The molecular imprinting technique provides highly selective binding sites and spatial structure corresponding to the target molecule.²⁹ This approach can be used in surface modification and to improve the selectivity of the TiO₂ photocatalyst toward a specific target pollutant. In this regard, Liu and co-workers reported a highly selective Ag₂S–TiO₂ photocatalyst prepared using the molecular imprinting technique.³⁰

It is crucial to achieve the highest photocatalytic efficiency by optimization of parameters and experimental conditions. Response surface methodology (RSM) has been mostly used to optimize variables and attain maximum efficiency in photocatalytic systems.³¹

In this research, we prepared molecularly imprinted Ni and F co-doped TiO₂ nanoparticles (Ni–F–TiO₂) using the facile sol–gel method. The properties of the prepared nanoparticles were accurately investigated. The photoactivity of the prepared nanoparticles was studied for visible light degradation of bisoprolol. The influencing factors including the irradiation time, photocatalyst amount, the pH of bisoprolol solution and its concentration were optimized using the RSM method.

2. Materials and methods

2.1. Materials

All chemical substances were purchased from Merck Company and no further purification was performed before use. Bisoprolol was bought from Modava Pharmaceutical Company in Iran.

2.2. Synthesis of the molecularly imprinted Ni and F co-doped TiO₂ photocatalyst

The sol–gel method was used to synthesize the molecularly imprinted Ni and F co-doped TiO₂ (Ni–F–TiO₂) photocatalyst. Initially three solutions were prepared as follows: solution (a) was prepared by thoroughly mixing 20 mL of *n*-tetrabutyl titanate (used as the titanium source as well as precursor of functional monomer), 5 g of bisoprolol (used as the template), 10 mL glacial acetic acid 100% (17.5 M) and 40 mL absolute ethanol. Solution (b) was prepared by mixing 20 mL of double distilled deionized water and 5 g NH₄F (used as the source of

fluorine). Also, solution (c) was prepared by mixing 24 mL of double distilled deionized water, 20 mL anhydrous ethanol, 5.5 mL nitric acid 65% (15.6 M) and 5 g nickel nitrate hexahydrate (used as the source of nickel). Then, under extreme stirring, solution (c) was added dropwise into solution (a). Then solution (b) was added dropwise into solution (a). After complete mixing of solutions, stirring was carried out for nearly 2 hours. Then, the resulting solution was kept constant without movement in the dark for 2 days. The solution was filtered using a filter paper and then dried in an oven at 120 °C. The obtained solid was well ground using a mortar. After that, to eliminate the bisoprolol template and form recognition sites, the powdered sample was placed in a furnace at 200 °C for 1 hour and then at 500 °C for 2 hours. The same procedure was followed without addition of Ni and F dopants to prepare un-doped molecularly imprinted TiO₂.

2.3. Characterization of the synthesized photocatalyst

The crystal structure of the prepared samples was determined using X-ray diffraction (XRD) (Philips PW1730, CuK_α radiation ($k_{\alpha} = 1.54 \text{ \AA}$)). The morphology and composition of the prepared nanoparticles were studied using field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) spectroscopy using Tescan-Mira2 (Czechia). Also, the transmission electron microscopy (TEM) images of the prepared nanoparticles were obtained using Philips CM120. N₂ adsorption and desorption isotherms were analyzed using a BEL instrument manufactured in Japan with the model of “BELSORP mini II” and a “BELPREP VAC II” degassing device under vacuum heating up to 450 °C. The pore size distributions and the specific surface areas of the samples were determined using desorption data according to the Barrett–Joyner–Halenda (BJH) method and Brunauer–Emmett–Teller (BET) method, respectively. An AvaSpec-2048-TEC spectrometer (Avantes Company) in the range of 200–800 nm was utilized to perform UV-visible diffuse reflectance spectroscopy (DRS) of the samples. A “Thermo” spectrometer in the range of 500–4000 cm^{−1} was utilized to record the Fourier transform infrared (FTIR) spectra of the prepared samples to characterize their structures. The final solutions were analyzed using an Agilent HPLC with a UV detector (model: 1260 DADVL).

2.4. Photocatalytic activity of the synthesized photocatalyst

To conduct the photocatalytic reaction, we used a sealed box equipped with LED lamps (irradiation wavelength ranges between 410 and 420 nm) to illuminate an Erlenmeyer flask containing bisoprolol as the pollutant and the photocatalyst material. The mixture was constantly stirred during the photocatalytic reaction. The distance between the Erlenmeyer flask and LED lamps was kept constant at 20 cm.

Before illumination, the mixture of the pollutant (bisoprolol) and photocatalyst was kept in the dark for 30 minutes to achieve adsorption/desorption equilibrium between pollutant molecules and the surface of the photocatalyst particles.

The concentration of bisoprolol was monitored at predetermined time intervals. The photocatalyst particles were collected

using centrifugation at 6000 rpm for 15 min. Then, the solution was analyzed by HPLC.

The chromatographic conditions for analysis of bisoprolol by HPLC were as follows: mobile phase containing a mixture of a 1 L portion of the diluent (a mixture of water and acetonitrile (65 : 35)), 5 mL of heptafluorobutyric acid 100% (7.71 M), 5 mL of diethylamine, and 2.5 mL of formic acid 98% (26.45 M). The liquid chromatograph was equipped with a 273 nm UV detector and a 4.6 mm $\times$ 12.5 cm column that contained packing L7. The flow rate was about 1 mL per minute.

Also, the chromatographic conditions for analysis of pantoprazole during the selectivity study were as follows: the mobile phase was a mixture of 86% solution A and 14% solution B, for 10 minutes, followed by a mixture of 42% solution A and 58% solution B, for 35 minutes, where solution A was an acetonitrile–methanol mixture and ammonium phosphate buffer (15 : 85) and solution B was an acetonitrile–methanol mixture. Ammonium phosphate buffer was prepared by dilution of 1.32 g L⁻¹ dibasic ammonium phosphate in water, adjusted with phosphoric acid to a pH of 7.5 and the ratio of the acetonitrile–methanol mixture was 7 : 3. The diluent was prepared by dilution of 25 mL of ammonium hydroxide with water to 500 mL. The liquid chromatograph was equipped with a 285 nm UV detector and a 3.9 mm $\times$ 15 cm column that contained packing L1 (4 μ m). The flow rate was about 1 mL per minute. The autosampler and column temperatures were 4 and 30 °C, respectively.

The experimental design was employed to conduct the photocatalytic reactions under different conditions including different bisoprolol concentrations, photocatalyst masses, pH values and irradiation times. In addition, the same experiments were also done under daylight irradiation for comparison with the results of photocatalytic reactions under LED light.

2.5. Design of experiments

Central composite design (CCD) is one of the most applicable approaches for simultaneous optimization under response surface methodology. Also, it has the ability to estimate the individual effects of variables and their interactions on the performance of the process through the response. Moreover, this method is more cost-effective due to providing a lower number of required experiments.³²

The Design-Expert software (version 11) was utilized to optimize the operational parameters by employing the response surface methodology (RSM) based on central composite design (CCD). The general equation of the response surface is described as follows:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

where Y indicates the predicted response (*i.e.*, dependent variable, which is the degradation percentage), k is the number of patterns (dependent variables), i and j are the index numbers for patterns, β_0 is the free term (*i.e.*, offset term), $X_1 \dots X_k$ are coded independent variables, which here are supposed to be

pH, photocatalyst mass, bisoprolol concentration and irradiation time, β_i is the first-order effect (*i.e.*, linear, primary effect), β_{ii} is the quadratic effect (*i.e.*, squared effect), β_{ij} represents the interaction effect, and ε is the random error accounting for the discrepancies or uncertainties between predicted and observed values.^{32,33} This may account for the possible interactions between the variables.

Independent parameters were selected as follows: X_1 (pH), X_2 (irradiation time), X_3 (photocatalyst mass), and X_4 (bisoprolol concentration). Determination of these parameters is the fundamental and most critical step of the experimental design procedure.

These independent parameters were determined at five levels. Table 1 presents the central composite design matrix (chosen independent variables and their levels). A primary study was first carried out to attain critical parameters and their appropriate ranges. However, relevant studies have also been considered in order to determine the ranges of selected parameters.³⁴

Moreover, Table 1 provides the results of the experimental runs for four parameters and obtained responses. The CCD method was used to find the optimal experimental conditions for the highest degradation efficiency of bisoprolol.

3. Results and discussion

3.1. Characterization

3.1.1. XRD analysis. The crystal structures of the synthesized nanoparticles including molecularly imprinted Ni and F co-doped TiO₂ (Ni-F-TiO₂) and un-doped TiO₂ were studied using XRD analysis. Fig. 1 presents the XRD patterns of Ni-F-TiO₂ and un-doped TiO₂ photocatalysts.

Fig. 1 shows the diffraction patterns of the Ni-F-TiO₂ nanoparticles which are clearly consistent with the diffraction pattern of the anatase phase of TiO₂ (Ref. code: 98-001-1629).⁸ Moreover, there is no observable diffraction peak related to the NiO phases, which confirms the successful embedding of Ni impurities into the TiO₂ crystal structure. Also, Fig. 1 shows the XRD pattern of molecularly imprinted un-doped TiO₂ which reveals the anatase phase of TiO₂ without any impurities. However, there seem to be extra peaks in the XRD pattern of Ni-F-TiO₂, but they are not observed for the other compound and are not vivid in un-doped TiO₂ due to broadening of peaks.

The average crystallite size of the synthesized nanoparticles was calculated with the Scherrer equation (eqn (2)) using the main peak of anatase TiO₂.⁸

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

where D represents the average crystalline domain size of the synthesized samples, λ is the X-ray wavelength, and β is the full width at half maximum (FWHM) of the diffraction peak in radian.⁸

Using the Scherrer equation, the average crystallite sizes of the synthesized Ni-F-TiO₂ and un-doped TiO₂ nanoparticles were 23 nm and 25 nm, respectively.

Table 1 Matrix for the central composite design

Factor	Name	Unit	Type	Factor 2		Factor 3		Factor 4		Maximum	Coded low	Coded high	Mean	Std. dev.
				A: pH	B: irradiation time (min)	C: photocatalyst mass (mg)	D: bisoprolol concentration (mg L ⁻¹)	Actual value	predicted value					
A	pH		Numeric	4.3	97.5	151.25	23.8	74.5	11.00	-1 ↔ 4.25	+1 ↔ 8.75	6.50	2.05	
B	Irradiation time	min	Numeric	8.8	272.5	151.25	23.8	-8.7	360.00	-1 ↔ 97.50	+1 ↔ 272.50	185.00	79.60	
C	Photocatalyst mass	mg	Numeric	4.3	97.5	151.25	11.3	73.2	200.00	-1 ↔ 53.75	+1 ↔ 151.25	102.50	44.35	
D	Bisoprolol concentration	mg L ⁻¹	Numeric	4.3	272.5	53.75	11.3	98.0	30.00	-1 ↔ 11.25	+1 ↔ 23.75	17.50	5.69	
				6.5	185.0	102.50	5.0	74.5						
				8.8	272.5	53.75	11.3	78.9						
				2.0	185.0	102.50	17.5	64.5						
				6.5	185.0	5.00	17.5	49.6						
				4.3	272.5	151.25	23.8	38.2						
				6.5	185.0	102.50	17.5	59.6						
				4.3	97.5	53.75	23.8	78.4						
				4.3	97.5	53.75	11.3	74.5						
				6.5	185.0	200.00	17.5	43.8						
				8.8	272.5	151.25	11.3	22.4						
				8.8	97.5	151.25	11.3	34.6						
				6.5	185.0	102.50	17.5	69.8						
				4.3	272.5	53.75	23.8	74.5						
				11.0	185.0	102.50	17.5	4.8						
				8.8	97.5	151.25	23.8	55.0						
				6.5	185.0	102.50	17.5	74.0						
				8.8	97.5	53.75	11.3	12.0						
				6.5	185.0	102.50	30.0	74.5						
				8.8	97.5	53.75	23.8	40.9						
				6.5	185.0	102.50	17.5	72.7						
				6.5	185.0	102.50	17.5	73.7						
				4.3	272.5	151.25	11.3	69.9						
				8.8	272.5	53.75	23.8	58.7						
				6.5	360.0	102.50	17.5	52.5						
				6.5	185.0	102.50	17.5	64.7						
				6.5	10.0	102.50	17.5	84.8						

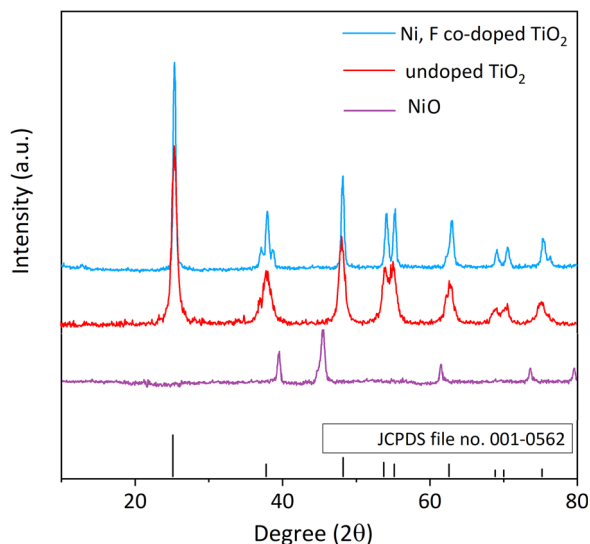


Fig. 1 XRD patterns of the synthesized molecularly imprinted Ni and F co-doped TiO_2 photocatalyst and un-doped TiO_2 and NiO nanoparticles.

3.1.2. Morphological and compositional studies. The morphology and surface properties of the prepared Ni-F- TiO_2 nanoparticles were studied by FE-SEM as shown in Fig. 2a and b. The FE-SEM images display the micro-size agglomerated particles and also the bulk material, which are fully constituted by fine and spherical nanoparticles in the size range below 100 nm.

EDX analysis was carried out to identify the elemental composition of the synthesized Ni-F- TiO_2 . The EDX spectrum (Fig. 3) obviously reveals the presence of Ti, O, Ni, and F elements in the structure of the prepared Ni-F- TiO_2 nanoparticles. Moreover, the elemental distribution of components was studied using EDX mapping as shown in Fig. 2c–f.

Fig. 4a and b present the TEM images of the molecularly imprinted Ni-F- TiO_2 nanoparticles. The TEM images show some irregular shapes which are spotted with some cylindrical structure, which is normal, and are not impurities. Totally, the spherical morphology of the prepared molecularly imprinted Ni-F- TiO_2 is obvious.

3.1.3. N_2 adsorption/desorption analysis. The nitrogen adsorption/desorption isotherms of the synthesized molecularly imprinted Ni-F- TiO_2 nanoparticles and the curve of BJH pore size distribution are presented in Fig. 5a and b, respectively. Fig. 5b discloses the mesoporous structure of the prepared Ni-F- TiO_2 nanoparticles. The BET surface area (SBET) ($\text{m}^2 \text{g}^{-1}$) and average pore diameter (nm) of both molecularly imprinted un-doped and Ni and F co-doped TiO_2 nanoparticles are provided in Table 2. In general, the surface area depends on the particle size and pore size. The results reveal that the surface area of the molecularly imprinted Ni and F co-doped TiO_2 photocatalyst is more than the surface area of the molecularly imprinted un-doped TiO_2 photocatalyst. Doping of Ni and F results in a large surface area due to decreased crystallite size which confirms the results of XRD analysis. With higher specific surface areas, there is an increase in photocatalyst

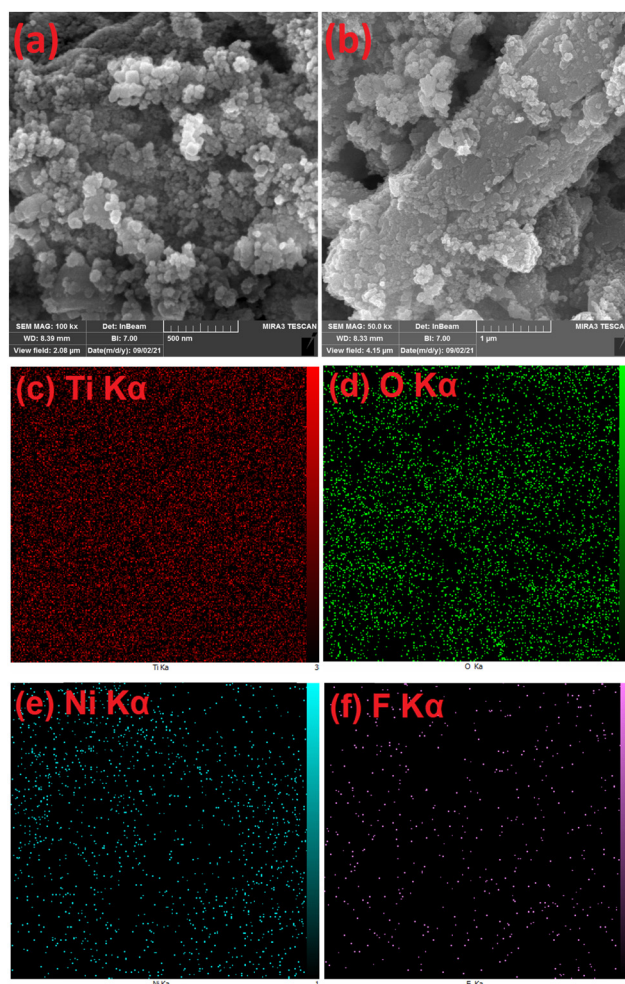


Fig. 2 FE-SEM images of the synthesized molecularly imprinted Ni-F- TiO_2 nanoparticles (a) and (b) and elemental mapping of Ni-F- TiO_2 (c)–(f).

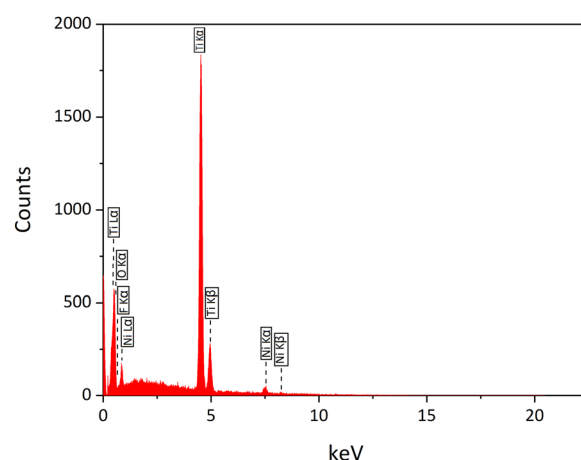


Fig. 3 EDX graph of the synthesized molecularly imprinted Ni-F- TiO_2 photocatalyst.

activities since it provides additional sites for the adsorption of light.³⁵ In addition, the pore size and hence the pore volume

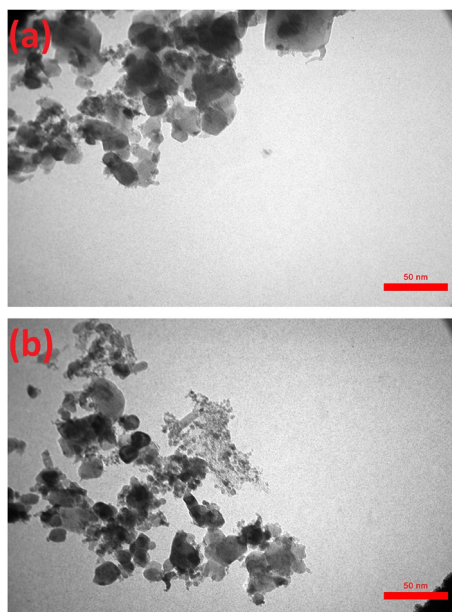


Fig. 4 TEM images of synthesized molecularly imprinted Ni-F-TiO₂ nanoparticles (a, b).

increase with a certain level of dopant concentration. An increased pore volume is another confirmation of the enhanced adsorption performance of the molecularly imprinted Ni and F co-doped TiO₂ photocatalyst and also it implies merging of small pores.

3.1.4. UV-Vis DRS analysis. The DRS spectra of the prepared samples are shown in Fig. 6 which clearly reveals that Ni-F-TiO₂ has higher absorption in the wavelength range of 200–800 nm. The band gap of the prepared samples was calculated using the following equation:

$$\alpha h\nu^2 = B(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, B is the proportionality constant, ν is the frequency of photons, and E_g is the absorption band gap.

The $\alpha h\nu^2$ versus $h\nu$ plot is shown in the inset of Fig. 6. The direct band gap of both doped and un-doped molecularly imprinted TiO₂ was calculated using the intercept of the straight line at ($\alpha = 0$). As can be seen, the introduction of Ni and F dopants has a noticeable effect on the band gap energy of the prepared samples, so that the calculated band gap for Ni-F-TiO₂ is 2.81 eV. In contrast, un-doped TiO₂ has a band gap of 3.27 eV. Therefore, it can be concluded that the doping of Ni and F elements into the TiO₂ structure substantially improves the visible light photocatalytic activity of the synthesized photocatalyst.

3.1.5. Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectra of the prepared Ni-F-TiO₂ and un-doped TiO₂ are presented in Fig. 7. As can be clearly seen, the FT-IR spectra of both samples show two absorption peaks in the ranges of 3300–3450 cm⁻¹ and 1620–1635 cm⁻¹ which belong to the stretching and bending vibrations of O–H bonds,

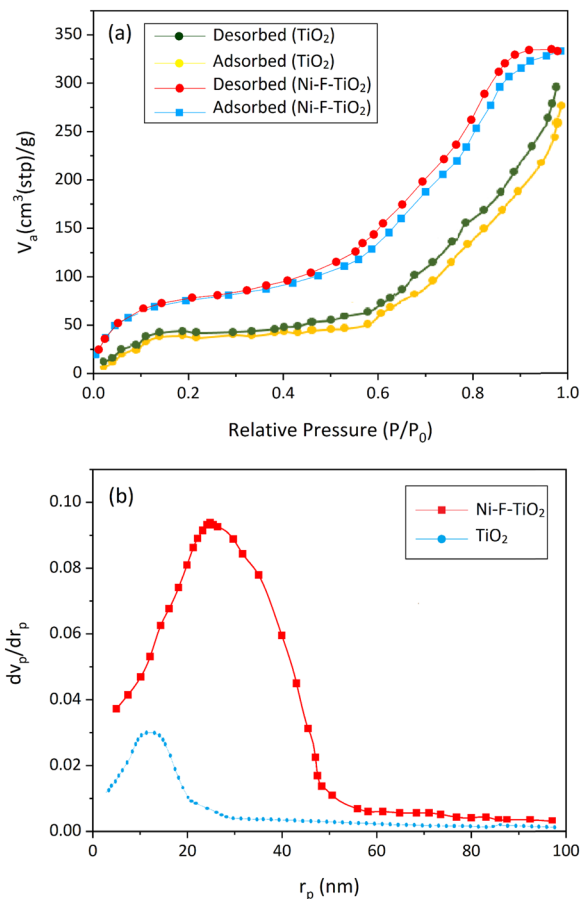


Fig. 5 N₂ adsorption-desorption isotherms (a) and BJH pore size distribution (b) of TiO₂ and the synthesized molecularly imprinted Ni-F-TiO₂ nanoparticles.

respectively.⁸ The characteristic peak related to the Ti–O bonds appears at 600 cm⁻¹.²² In addition, the peak at 1384 cm⁻¹ belongs to the stretching vibration of carboxylate groups.³⁰

3.2. Photocatalytic reaction mechanism of the synthesized photocatalyst

As shown in Table 1, thirty separate experiments were performed with an applied amount for each central composite design matrix (chosen independent variables and their levels). The photocatalytic efficiency for degradation of bisoprolol was evaluated under defined experimental conditions including the pH of bisoprolol solution, irradiation time, bisoprolol concentration and photocatalyst amount. A wide range of bisoprolol concentrations was used to investigate the capability of the prepared photocatalyst material toward degradation of a high content of bisoprolol solution. Being able to efficiently degrade the high concentration of pollutant is important to implement the photocatalytic approach for the large-scale application of pollutant treatment.

The photocatalytic efficiency for degradation of bisoprolol was calculated using the following equation:^{18,36}

$$\% \text{ Paracetamol degradation} = 1 - \frac{A_t}{A_0} \times 100 \quad (4)$$

Table 2 Physical properties of the prepared samples

Samples	BET surface area (SBET) (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
Molecularly imprinted un-doped TiO ₂ photocatalyst	215.54	0.38	8.95
Molecularly imprinted Ni and F co-doped TiO ₂ photocatalyst	257.7	0.45	9.26

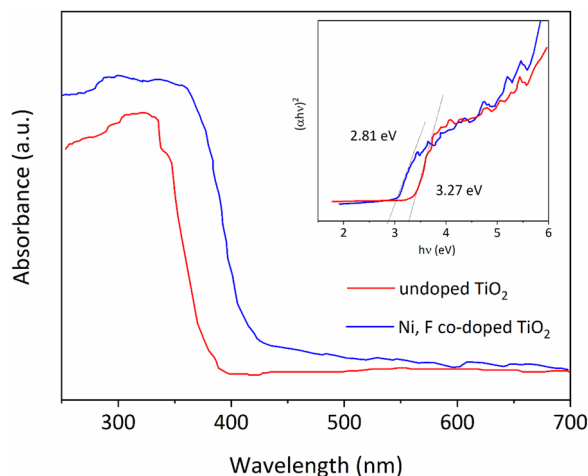


Fig. 6 DRS spectra of the synthesized molecularly imprinted Ni-F-TiO₂ nanoparticles and un-doped TiO₂ nanoparticles. The inset shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for calculating the band gap of the samples.

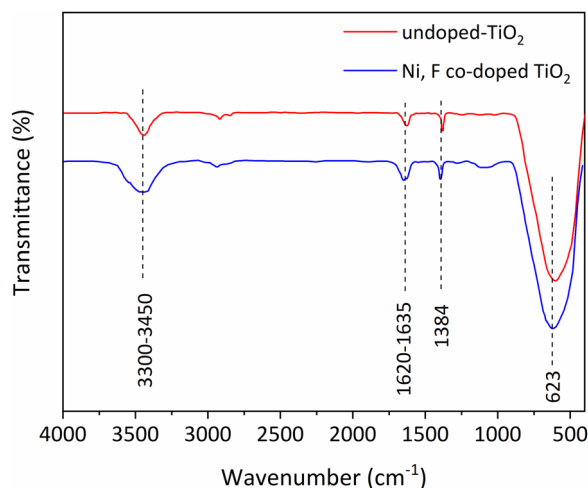


Fig. 7 FTIR spectra of the synthesized molecularly imprinted Ni and F co-doped TiO₂ and un-doped TiO₂ nanoparticles.

where A_0 is the initial absorbance and A_t is the absorbance after time t at $\lambda_{\max}$ of bisoprolol.

3.3. Analysis of variance (ANOVA)

In order to examine the model quality and the most effective parameters and also to search the extent to which the variables interact with each other and to explore the level of significance of each parameter, the analysis of variance (ANOVA) of regression factors according to the response surface quadratic model was applied and the results are tabulated in Table 3.

The significant model terms are A , C , BC , BD , A^2 and C^2 , where A is the pH, B is the irradiation time, C is the catalyst mass and D is bisoprolol concentration. The impact of a parameter with a P -value less than 0.05 indicates that the parameter has significant impact on the response.³⁷ The F -value and P -value of the model are 10.32 and <0.0001 , respectively, which indicates the significance of the model. The “lack of fit” F -value of 4.59 implies that the lack of fit is not significant and the model is appropriately fit.

The acceptable value of the correlation coefficient ($R^2 = 0.9060$) and the value of adj- R^2 (0.8182) confirm the validity of the model. Table 3 shows the P -values of the model, indicating its high validity. The signal-to-noise ratio demonstrates adequate precision of the model. A ratio greater than four is desirable and depicts the appropriate distinction of the model.

The adequate precision is 13.3409, which shows an adequate signal and appropriate distinction of the model. Therefore, this model can be used to navigate the design space. The quadratic equation for bisoprolol degradation is as follows:

$$\begin{aligned} \text{Bisoprolol degradation percentage} = & +69.08 - 16.95A - 3.16B \\ & - 7.02C - 2.16D + 1.80AB - 1.10AC + 3.00AD - 13.74BC \\ & - 10.05BD - 1.89CD - 8.86A^2 - 0.3470B^2 - 5.83C^2 + 1.12D^2 \end{aligned} \quad (5)$$

where A is the pH, B is the irradiation time, C is the photocatalyst mass and D is the bisoprolol concentration.

Fig. 8 depicts the perturbation diagram for bisoprolol. The sharpest curve is related to parameter A which indicates the pH. Therefore, the most effective parameter with the greatest efficiency of bisoprolol degradation is parameter A . Parameter D , which is related to bisoprolol concentration, is less sharp. Therefore, the parameter of photocatalyst mass has the least impact on bisoprolol degradation.

3.4. Response surfaces, 3D surface plots and contour plots

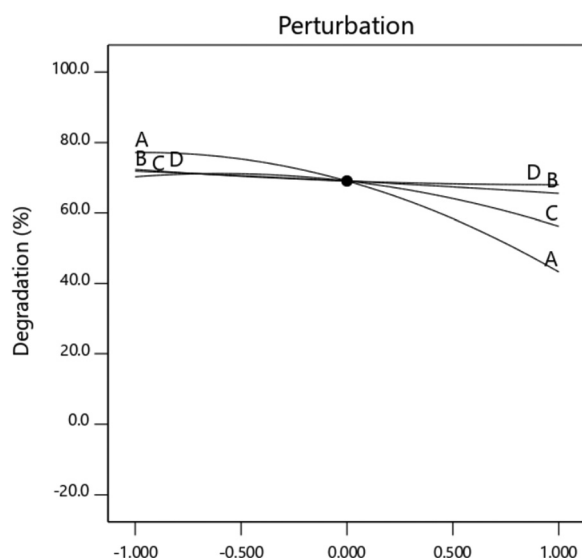
Three-dimensional response surfaces clearly depict the interactions between variables. 3D surface plots are used to indicate the simultaneous effects of two factors on the degradation efficiency of bisoprolol at zero level of the other variables (Fig. 9).

The photocatalytic efficiency of the prepared photocatalyst is inversely affected by the pH of bisoprolol solution. So, the photocatalytic activity is high in an acidic pH of bisoprolol solution compared to the alkaline condition.

A possible explanation for the decline in the photocatalytic activity under alkaline conditions is that the negatively charged surface of the photocatalyst particles has less affinity for absorbing the bisoprolol molecules (Fig. 9a, b, c, g, h, and i). Also, from the experimental results, the optimum pH of

Table 3 ANOVA and model statistics summary of the quadratic model for decomposition of bisoprolol

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	16360.96	14	1168.64	10.32	<0.0001	Significant
A – pH	6894.92	1	6894.92	60.89	<0.0001	
B – irradiation time	240.22	1	240.22	2.12	0.1659	
C – photocatalyst mass	1182.59	1	1182.59	10.44	0.0056	
D – bisoprolol concentration	111.93	1	111.93	0.9885	0.3359	
AB	51.66	1	51.66	0.4562	0.5097	
AC	19.38	1	19.38	0.1712	0.6849	
AD	143.94	1	143.94	1.27	0.2773	
BC	3021.43	1	3021.43	26.68	0.0001	
BD	1615.84	1	1615.84	14.27	0.0018	
CD	56.96	1	56.96	0.5031	0.4890	
A ²	2151.66	1	2151.66	19.00	0.0006	
B ²	3.30	1	3.30	0.0292	0.8667	
C ²	932.50	1	932.50	8.24	0.0117	
D ²	34.21	1	34.21	0.3021	0.5907	
Residual	1698.44	15	113.23			
Lack of fit	1531.73	10	153.17	4.59	0.0531	Not significant
Pure error	166.71	5	33.34			
Cor. total	18059.41	29				
Statistical quality of the model						
Std. dev.	10.64		R ²		0.9060	
Mean	57.95		Adjusted R ²		0.8182	
C.V.%	18.36		Predicted R ²		0.4982	
Adeq. precision	13.3409					

**Fig. 8** Perturbation plot for degradation of bisoprolol by the synthesized molecularly imprinted Ni and F co-doped TiO₂ photocatalyst. (A): pH, (B): irradiation time, (C): photocatalyst mass and (D): bisoprolol concentration.

bisoprolol to achieve the highest photoactivity is 5.9 (Fig. 9a, b, c, g, h, and i).

An increase in the concentration of bisoprolol leads to a decrease in the photocatalytic efficiency which is related to the decrease in the available active sites on the surface of photocatalyst particles. Even so, the bisoprolol concentration has no significant effect on the photocatalytic activity. In addition, increasing the amount of the photocatalyst material leads to a decrease in the photocatalytic activity, which is due to a decline in the penetration of the light beam into turbid solution (Fig. 9c, e, f, i, k, and l).

Also, we examined the effect of irradiation time on the photocatalytic efficiency for degradation of bisoprolol. As can be seen, the photocatalytic efficiency increases with increasing irradiation time which is related to the enhanced exposure of pollutant molecules to the light-activated photocatalyst particles (Fig. 9e and k).

3.5. Optimization

From the experimental results, the optimal conditions to attain the highest photocatalytic efficiency are 16.2 mg L⁻¹, 5.9, 83.42 mg and 137 min for the bisoprolol concentration, pH, photocatalyst mass and irradiation time, respectively.

The maximum photocatalytic decomposition rate was 72.5% which was achieved by utilizing Design-Expert software (version 11), and a desirability function value of 1.0 was applied to optimize variables including the pH, irradiation time, photocatalyst mass and bisoprolol concentration. It should be noted that the minimum, middle and maximum values for desirability were set as 0.0, 0.5 and 1.0, respectively. A value closer to 1.0 means that the corresponding operating conditions are optimum.

3.6. Reusability of the prepared molecularly imprinted Ni-F-TiO₂ photocatalyst

Because the stability of a photocatalyst is an important factor for its industrialization, reusability experiments were carried out for the prepared molecularly imprinted Ni-F-TiO₂ photocatalyst toward degradation of bisoprolol under optimal experimental conditions. The reusability experiments were conducted in six successive reaction cycles. After each reaction, the photocatalyst particles were collected using centrifugation, washed with distilled water and ethanol solution and then dried at 60 °C in an oven.

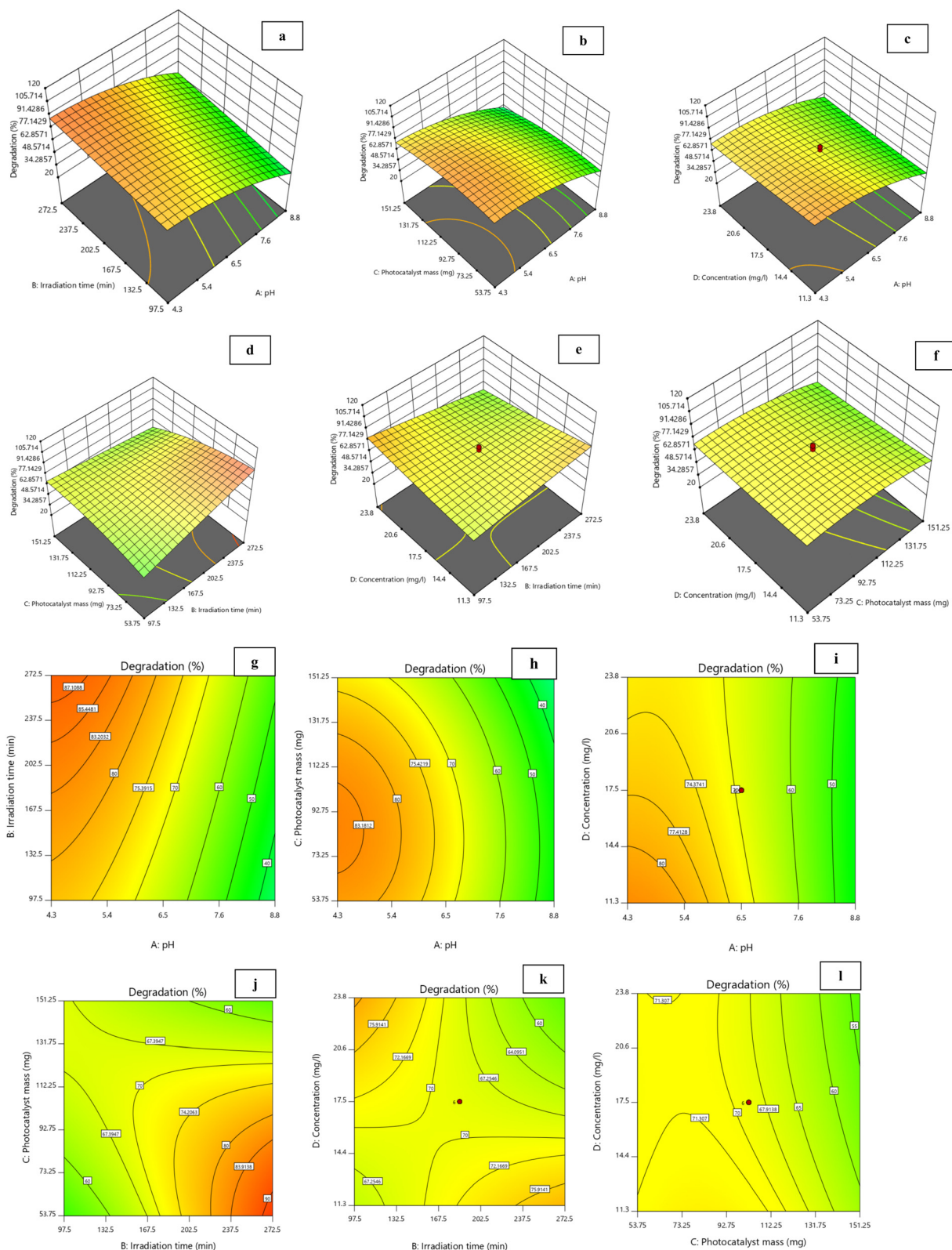


Fig. 9 Response surfaces; 3D (a)–(f) and contour (g)–(i) plots for the efficiency of bisoprolol degradation. Legend: (color scale)

As shown in Fig. 10, the loss of the photocatalytic efficiency is negligible after 3 reaction cycles. However, the decline in the photocatalytic activity is more pronounced

in the next 3 successive reaction cycles which is due to the loss of the prepared photocatalyst material during reaction cycles. Even so, the prepared molecularly imprinted

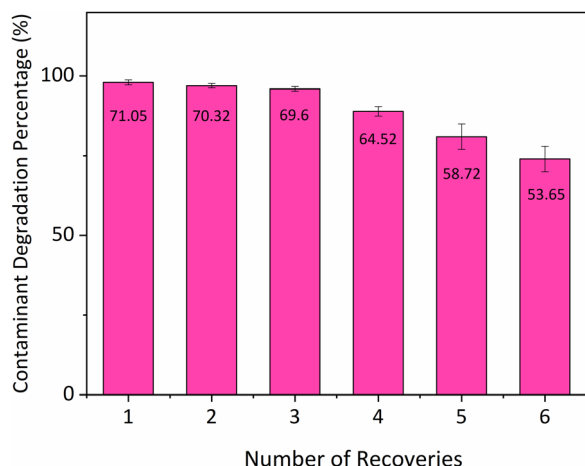
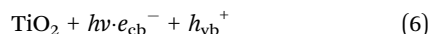


Fig. 10 Effect of the number of reusability cycles of the synthesized molecularly imprinted Ni and F co-doped TiO₂ photocatalyst on the bisoprolol degradation percentage.

Ni-F-TiO₂ demonstrates suitable stability for photodegradation of bisoprolol.

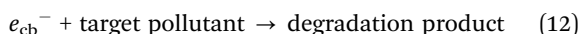
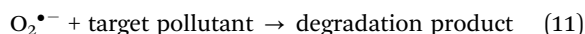
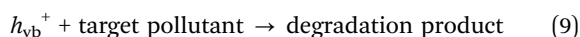
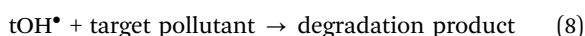
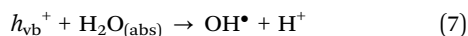
3.7. Contributions of different reactive species

Illumination of TiO₂ by light beams with an energy greater than its band gap (3.2 eV) results in generation of electrons and holes in the conduction and valence bands, respectively:



The photogenerated valence-band holes can react with the adsorbed water to form highly reactive hydroxyl radicals. Both the hydroxyl radicals and valence-band holes may cooperate to mineralize the target contaminants.

On the other hand, the photogenerated conduction-band electrons can react with the adsorbed molecular oxygen on the surface of TiO₂ to produce radical superoxide anions. The produced superoxide radical anions undergo oxidation reactions with the target contaminants to generate mineralized products. Eqn (7)–(12) demonstrate the mentioned mechanisms.



The photocatalytic reactions occur *via* participation of reactive oxygen species (ROS) such as hydroxyl radicals (OH[•]), superoxide radical anions (O₂^{•−}), holes (h⁺), and electrons (e[−]). Different radical scavenging agents were used to identify the most dominant reactive species.

Fig. 11 shows the photocatalytic activity of the prepared photocatalyst toward degradation of bisoprolol in the presence

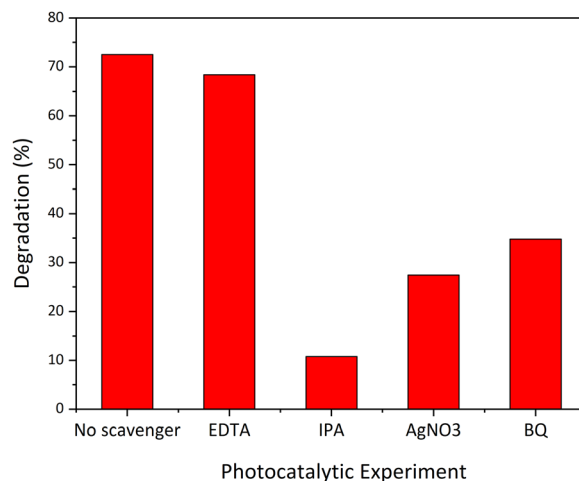


Fig. 11 The degradation efficiency of bisoprolol using the synthesized molecularly imprinted Ni-F-TiO₂ photocatalyst in the presence of different scavengers.

of various radical scavenging agents. Ethylenediaminetetraacetic acid (EDTA), *p*-benzoquinone (BQ), isopropanol (IPA) and AgNO₃ were utilized as h⁺, O₂^{•−}, OH[•] and e[−] scavengers, respectively.

The photocatalytic degradation efficiency decreases after addition of the abovementioned radical scavengers. However, using isopropanol causes a significant decline in the degradation efficiency of bisoprolol which implies that the photocatalytic reaction is proceeded predominantly by hydroxyl radicals.

3.8. Photocatalytic activity of the synthesized samples under solar light

Under the same optimal conditions, the photocatalytic activity of the molecularly imprinted Ni-F-TiO₂ photocatalyst toward degradation of bisoprolol under sunlight was analyzed.

As illustrated in Table 4, bisoprolol can be degraded from aqueous solution under both LED lamps and solar light by the molecularly imprinted Ni-F-TiO₂ photocatalyst nanoparticles.

3.9. Selectivity study of the synthesized molecularly imprinted Ni-F-TiO₂ photocatalyst

The ability of the prepared molecularly imprinted Ni-F-TiO₂ photocatalyst to select a particular target pollutant was investigated using photocatalytic degradation of pantoprazole under optimal conditions. For this purpose, two separate photocatalytic reactions were conducted using bisoprolol and pantoprazole as pollutants. All influencing factors were kept constant as follows: pollutant concentration = 16.2 mg L^{−1}, pH = 5.9, irradiation time = 137 min and photocatalyst amount = 83.42 mg.

After 137 min irradiation, the photocatalytic efficiency was investigated using HPLC with a UV detector at wavelengths of 273 nm and 285 nm for bisoprolol and pantoprazole, respectively.

The selectivity experiments disclose that the photocatalytic efficiency of the prepared photocatalyst is 71.4% and 7.89% for bisoprolol and pantoprazole, respectively.

Table 4 Percentages of bisoprolol removal through different irradiation sources

Photocatalyst	Bisoprolol degradation percentage (%) under LED lamp irradiation	Bisoprolol degradation percentage (%) under sunlight irradiation	Bisoprolol degradation percentage (%) without irradiation
Molecularly imprinted Ni-F-TiO ₂ photocatalyst	70.37	68.27	8.42

4. Conclusions

The sol-gel method was used to synthesize the novel molecularly imprinted Ni and F co-doped TiO₂ photocatalyst. Characterization of the prepared photocatalyst nanoparticles was carried out by XRD, FESEM, TEM, FTIR, DRS, EDX and BET-BJH. The photocatalytic activity of the prepared photocatalyst was studied by degradation of the aqueous solution of bisoprolol under artificial visible light (LED lamps).

The operational parameters including the irradiation time, pH, photocatalyst mass and bisoprolol concentration were optimized using the central composite design under response surface methodology. After 137 min illumination, approximately 72.5% of bisoprolol (16.2 mg L⁻¹, pH = 5.9) was degraded using 83.42 mg of the prepared photocatalyst.

Adequate selectivity of the synthesized photocatalyst against pantoprazole was confirmed. The great reusability of the synthesized molecularly imprinted Ni-F-TiO₂ photocatalyst was confirmed for up to 6 reaction cycles. The excellent photocatalytic performance of the prepared photocatalyst was attributed to the co-doping of Ni and F elements into the TiO₂ structure. Using different radical scavenging agents, it was identified that the primary active species involved in the degradation of bisoprolol are hydroxyl radicals. In addition, the prepared photocatalyst showed great photoactivity under sunlight irradiation.

Author contributions

All authors contributed to study conception, design, material preparation, and data collection and analysis. The first draft of the manuscript was written by Nasim Asadbeigi and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript and gave explicit consent to submit this article.

Conflicts of interest

There are no conflicts to declare.

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