Photocatalytic degradation of cephalexin by $Ag/Ag_2O/TiO_2$ catalyst thin film in a spinning disc reactor

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Abstract
This study investigated the photodegradation of cephalexin (CPX) using a spinning disc photocatalytic reactor (SDPR). To this end, visible light-activated $Ag/Ag_2O/TiO_2$ thin film was immobilized on a ceramic disc by the sol-gel spin coating method. The response surface methodology (RSM) on the basis of the central composite design (CCD) was utilized to evaluate the impact of the operational factors (e.g. illumination duration, rotational speed, solution flow rate, and initial CPX concentration) on the efficiency of CPX photodegradation. The removal efficiency in optimal conditions for CPX was obtained 96.06% upon implementing the following conditions: illumination time: 60 min, the rotational speed: 215 rpm, the solution flow rate: 0.6 L/min, and initial CPX concentration: 30 mg/L.

Keywords: Spinning disc reactor, Photodegradation, $Ag/Ag_2O/TiO_2$, Cephalexin, Blue LED illumination

Introduction
The release of pharmaceutical contaminants to the environment has endangered the aquatic ecosystems leading to adverse impacts on human health. Antibiotics are categorized as emerging pollutants and generally produced by the pharmaceutical, agriculture, and biomanufacturing industries and discharged into the environment [1]. Cephalexin (CPX) is the first generation of cephalosporin that widely used for treating a variety of infections of body systemsuch as ear, skin, and soft tissue, skeletal, urinary and respiratory tract [2].Thanks to its unique properties such as strong oxidation ability, ease of operation, and excellent reaction rate, photocatalysis is one of the most effective AOPs techniques for the degradation of different antibiotics [3-5]. In this regard, titanium dioxide (TiO_2) is a non-toxic, chemically stable, easily-preparable, and environmentally-benign semiconductor photocatalyst with extensive applications in the field of photocatalysis [6, 7]. The photocatalytic behavior of TiO_2 is, however, limited by its relatively wide bandgap (3.2 eV) and poor quantum efficiency [8]. Silver-based semiconductor photocatalysts have been recently developed due to their narrow bandgap and enhanced absorption [9]. The sol-gel method is a facile and low-temperature route to fabricate thin films with increasing popularity due to its cost-effectiveness [10]. The reactions in a catalyst-immobilized reactor often suffer from mass

transfer restrictions which can be resolved by the use of SDRs due to its highly sheared thin films with improved mass transfer performance, especially in solid-liquid systems [11,12]. Based on our literature review, no research has investigated the CPX elimination by a photocatalytic SDR incorporating photocatalysts immobilized on the ceramic disc substrate upon visible light exposure. Therefore, the present research is aimed to assess the performance of an SDPR in CPX degradation. In this context, the major targets of this wok can be listed as (i) immobilization of $Ag/Ag_2O/TiO_2$ thin film on a spinning ceramic disc through sol-gel spin coating, (ii) exploring the impact of the operational factors on the photocatalytic performance of AMX through studying CCD as a branch of RSM.

Experimental

Materials and characterization

All the employed chemicals such as tetra butyl orthotitanate (TBOT), isopropanol, hydrochloric acid, sodium hydroxide, acetic acid and silver nitrate were supplied from Merck Company (Germany). Polyvinylpyrrolidone (PVP) was also provided by Sigma-Aldrich (USA). CPX was supplied by Farabi Pharmaceutical Company (Iran). A UV-Vis spectrophotometer (V-530, Jasco, Japan) was employed to evaluate the optical absorption of the CPX solution. The surface morphological properties of the specimens were assessed by the field emission scanning electron microscopy (FESEM: Sigma, Zeiss) combined with an energy dispersive X-ray Spectrophotometer (EDS) to examine the chemical composition of the samples.

Synthesis of $Ag/Ag_2O/TiO_2$ thin film

A three-step route followed by the sol-gel spin coating was employed to prepare the $Ag/Ag_2O/TiO_2$ thin films and immobilize them on the ceramic disc. First, 0.2 g PVP was added to 10 ml isopropanol and mixed at ambient temperature for 20 min. Afterward, 3 ml TBOT was incorporated into the mixture under 30 minute stirring at room temperature to reach a transparent TiO_2 solution (Sol A). In the next stage, 0.1 g silver nitrate was dissolved in double-distilled water (Sol B) and dropwise added to Sol A under vigorous stirring. The second step involved the coating of the ceramic disc through a spin-coater operating at 700 rpm for 60 seconds followed by drying at room temperature under a fume-hood. In the third step, the as-prepared films were annealed at 500 ℃ for 3 h to enhance their adhesion to the ceramic substrate as well as eliminating the residual organic components.

Photocatalytic reactor setup and experimental procedure

The photocatalytic reactions were tested in a spinning disc photocatalytic reactor (SDPR) as schematically illustrated in Fig. 1. The experimental setup had several sections: (1) glass cylindrical vessel, (2) spinning ceramic disc, (3) blue LED light source, (4) motor, (5) aeration pump, (6) flow meter, (7) reservoir, (8) stirrer, (9) liquid pump, (10) control valves, (11) sampler valve and (12) control panel. The CPX solution from the stirred tank reservoir was then transferred to the center of the spinning ceramic disc by a liquid distributor equipped with a pipe. The flow rate was regulated by a flow meter. Before each run, the adsorption-desorption equilibrium was attained by 30-minute rotation of the ceramic disc at the speed of 100 rpm at the darkness, then the LED illumination initiated and the reaction occurred. In a typical experiment, 3 ml of solution was collected from the sampler valve at the given intervals. Then the CPX concentration was measured by the calibration UV-Vis absorption curve at 200-400 nm. The photodegradation percentage can be estimated by:

$$P\% = (C_0-C_t)/C_0 \times 100 \quad (1)$$

Where, P shows the degradation percentage (%), and C_0 and C_t denote the CPX concentration of at the beginning of the procedure and the certain time (t), respectively. The characteristic UV-Vis absorption peak of CPX in water is depicted in Fig. 2.

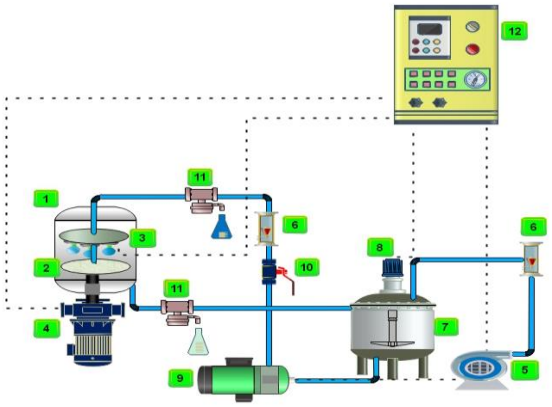

Fig. 1 Spinning disc photocatalytic reactor setup

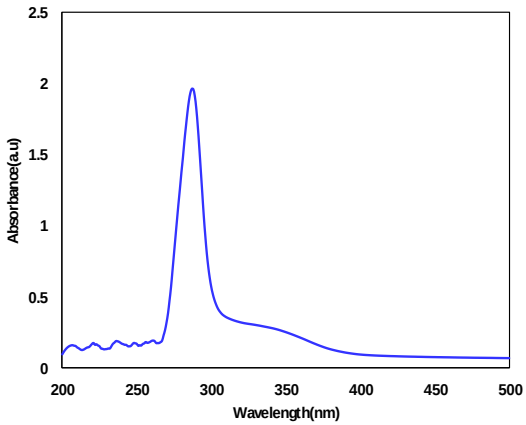

Fig. 2 UV-Vis absorption spectrum of CPX in water.

Statistical analysis and design of experiments

The influence of 4 prominent variables (e.g. illumination time, rotational speed, solution flow rate, and CPX concentration) on the efficiency of photocatalytic CPX removal was assessed at five levels through the use of the response surface methodology (RSM) according to the central composite design (CCD) with a minimum number of experimental runs. The levels of the studied factors are listed in Table 1. A quadratic polynomial model equation was implemented to explore the interactive impacts between the independent variables and their corresponding responses. The model equation can be expressed as [13]:

$$Y = \beta_0 + \sum_{i=1}^{6} \beta_i X_i + \sum_{i=1}^{6}\sum_{j=1}^{6} \beta_{ij} X_i X_j + \sum_{i=1}^{6} \beta_{ii} X_i^2 + \varepsilon \quad (2)$$

in which Y shows the predicted response (CPX removal efficiency); while X_i and Xj denote the independent variables. β_0, β_i, β_{ii}, β_{ij}, and ε also stand for the constant, linear, quadratic, and interaction coefficients, and the residual term, respectively.

Table1: The range and levels of operational parameters.

Factors	Levels				
	Low (-1)	Central (0)	High (+1)	-α	+α
X_1: Illumination Time (min)	35	50	65	20	80
X_2: Rotational Speed (rpm)	80	125	170	35	215
X_3: Solution Flow rate (L/min)	0.4	0.6	0.8	0.2	1.0
X_4: CPX Concentration (mg/L)	20	30	40	10	50

Results and discussion

Statistical analysis of the photocatalytic degradation of CPX

The interaction among the operational factors, including illumination time, rotational speed, solution flow rate, and CPX concentration the on the degradation efficiency (%) of CPX was assessed by CCD using RSM. It is observed that under certain experimental conditions the degradation efficiency ranges from 55.68 to 96.06%. This showed that these operating factors

have a strong impact on the degradation (%) of CPX. Based on experimental results a second order polynomial equation was derived in terms of the independent variables and their interactions.

$$P\%_{CPX}=93.14+10.51X_1+2.93X_2+3.72X_3-2.12X_4+2.27X_1X_2+1.08X_1X_3+0.71X_2X_4+0.81X_2X_4-2.60X_1^2-1.51X_2^2-2.53X_3^2-2.38X_4^2 \quad (2)$$

The model F-value (52.42) suggests that this model is significant and there is a chance of 0.01% chance that F-value of Model might occur as a result of noise. The R^2 value of 0.9789 indicated the high quality of the developed model. This recommended that variation of 97.89% for CPX degradation was explicated with the help of independent factors is in the studied range. Another essential measure to express the variation in the fitted model is lack of fit. For CPX degradation, the value of 3.31 indicated the non-significant lack of fit relative to pure error when the value of p is 0.1077. This illustrates a good predictability of the model.

Response Surface Analysis

The relationship between operational parameters was studied using three-dimensional response surface graphs (Fig. 3). Fig. 3a illustrates the combined influence of the illumination time and solution flow rate on CPX removal efficiency. As it can be understood from Fig. 3a, CPX removal efficiency, was increased while the illuminitaion time increases. On the other hand, the CPX removal efficiency increased with the increase of solution flow rate up to about 0.6 L/min and then decreased. Higher flow rates are associated with strong reduction in intrfacial area between photocatalytic thin film and pollutants and significantly reduce the mass transfer rate [14]. Penetration of light in thick film is short and subsequently photocatalysts located in inner layers cannot be activated and the photodgradation efficiency is decreased. Fig. 3b shows the interaction between rotational speed and CPX concentration on CPX removal efficiency.The effect of rotational speed indicates a positive effect on photodegradation efficiency. Under this condition, micro mixing and turbulency lead to breaking solution thin film to thin layers and droplet shape. In this regard, reduction in thickness of liquid film causes the reduction in mass transfer resistance. Rotational speed is an important parameter in SDR due to its intensification role in mass transfer operation and operational costs. At a lower concentration more photodegradation efficiency was achived. The increase of concentration of CPX in solution, the solution becomes thick and dark. In this condition the penetration depth of light decreases, consequently caused reduction in photodegradation efficiency.

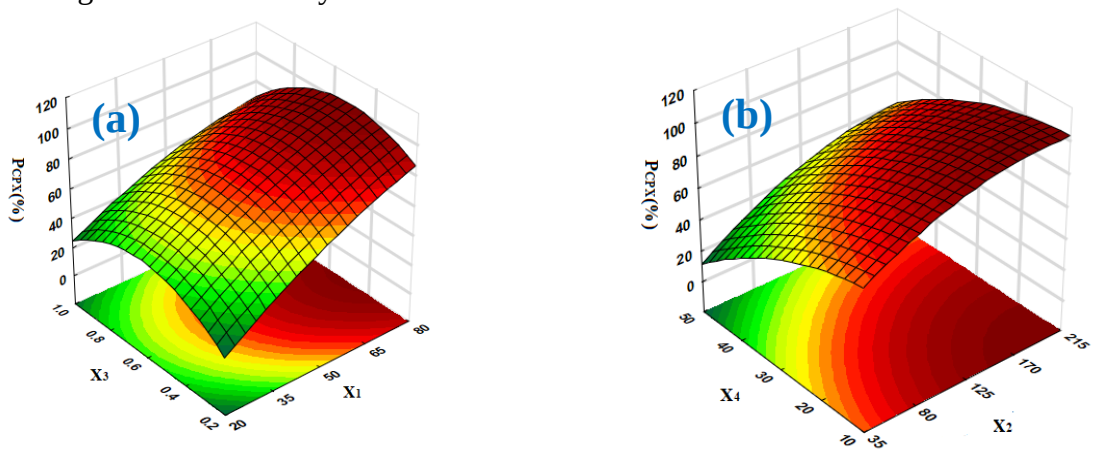

Fig.3 Response surface (3D) plots for CPX removal versus independent variables.

The experimental results were optimized by Design-Expert software. Using the highest removal efficiency of CPX as the optimization target, the optimized conditions were obtained as follows: illumination time of 60 min, rotational speed of 215 rpm, solution flow rate of 0.6 L/min, and CPX concentration of 30 mg/L. The evolutions in the absorption spectra of the CPX solution under the optimum operating conditions are shown in Fig. 4.

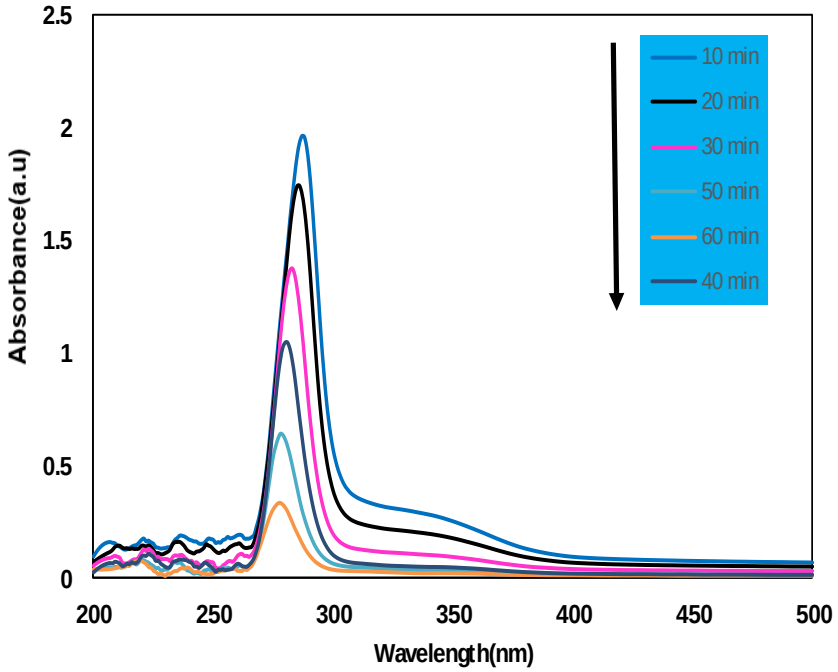

Fig.4 UV-visible absorption spectra of CPX at optimal conditions.

Conclusions

The performance of a innovative SDR was evaluated for photocatalytic degradation of CPX using $Ag/Ag_2O/TiO_2$ thin film coated on a ceramic disc under visible light and the influence of the illumination time, rotational speed, solution flow rate, and CPX concentration on photocatalytic degradation efficiency was studied to find the optimum operational conditions using response surface methodology. The results indicated that designed system leads to high degradation efficiency up to 96.06%. The high performance of designed system proved that SDR is very efficient because of its high mass transfer rate as well as short requirements of irradiation time. Furthermore, using of visible light source is advantageous due to less energy consumption and more environmental-friendly entity.

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