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Zeolite 4A supported CdS/g-C₃N₄ type-II heterojunction: A novel visible-light-active ternary nanocomposite for potential photocatalytic degradation of cefoperazone



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ABSTRACT

The CdS/g-C₃N₄ heterojunction photocatalyst supported on 4A zeolite was successfully synthesized using a simple chemical precipitation method. The physicochemical characteristics of the as-prepared ternary composite were assessed using X-Ray diffraction (XRD), field emission- scanning electron microscopy (FE-SEM), energy dispersive X-Ray (EDX), transmission electron microscopy (TEM), N₂ adsorption-desorption, differential reflectance spectroscopy (UV-Vis-DRS), and photoluminescence (PL) techniques. The results confirmed the successful synthesis of the CdS/g-C₃N₄/4AZ nanocomposite and introduction of the CdS and $g-C_3N_4$ on the substrate of 4A zeolite. Cefoperazone (CFP) antibiotic was tested as the model pollutant to assess the photocatalytic performance of the synthesized nanocomposite under visible light irradiation. The response surface methodology (RSM) and artificial neural network (ANN) showed desirable reasonability for the prediction of the CFP degradation efficiency. More than 93% of CFP with a concentration of 17 mg L^{-1} degraded in the presence of the 0.4 g L^{-1} of the catalyst at pH of 9 after 80 min treatment time (RSM-based optimization results). The pH of the solution, irradiation time, catalyst dosage, and the initial concentration of the CFP affected degradation efficiency with a percentage impact of 37, 29, 19, and 15 %, respectively (ANN-based modeling results). The addition of 1 mM of isopropanol, benzoquinone, and sodium oxalate reduced the CFP degradation efficiency from 93.23% to 85.18, 41.16, and 32.47%, respectively, proving the decisive role of the \circ O₂ and h⁺ in the photodegradation process. The kinetic studies indicated the following of the process from the Langmuir-Hinshelwood's pseudo-first-order model ($k_{app} = 3.71 \times 10^{-2} \text{ min}^{-1}$). The structure of the identified by-products using GC-MS analysis confirmed that CFP mainly decomposed through the cleavage of C-S, C-N, and N-N bonds. Moreover, the formation of the aliphatic compounds and carboxylic acids as by-products confirmed nearly complete mineralization of the CFP to non-toxic products.

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1. Introduction

Recently, the unsafe direct discharge of the pharmaceuticalcontaining wastewaters compounds attracted global concerns. Wastewaters containing pharmaceutical effluents from domestic, hospitals, and pharmaceuticals industries lead to serious damages to physicochemical characteristics and also microorganisms of the receptor water [1–3]. Cephalosporins are the frequently used antibiotics to treat bacteria-caused infections. The extensive usage of these β -lactam antibiotics may cause severe negative impacts on flora and fauna such as increased bacteria resistance or disturbance on the photosynthesis [4,5]. These organic effluents are resistant to

* Corresponding author. *E-mail address:* mehrizad@iaut.ac.ir (A. Mehrizad). classical degradation techniques such as adsorption and biodegradation. Recent studies on the development of the effective purification techniques come an end to great attracts to advanced oxidation processes (AOPs) as the favorable techniques to solve the environmental problems. The non-selective decomposition of the wide diversity of the organic molecules using produced powerful radicals is the basic principle of the AOPs. Photocatalysis is one of the most powerful AOPs with a high mineralization degree, which utilized a semiconductor as the catalyst under ultraviolet or visible light irradiation. In this regard, wide ranges of the semiconductors such as metal oxides, metal sulfides, and their composites have been applied as the catalysts [6–9]. The nanostructured metal sulfides such as CdS [10–13], ZnS [14], CuS [15], FeS₂ [16], and their composites are desired photocatalysts owing to the high absorption coefficient and suitable band gap energy. CdS acts as



catalyst in visible-light region with a narrow band gap (~ 2.1 -2.4 eV), low toxicity, fast charge transfer, high chemical and thermal durability. Unfortunately, the widespread application of the CdS is restricted because of the high recombination rate of the generated charge carriers [17]. Coupling with other semiconductors, doping, and surface modification are some of the techniques used to tackle this problem [18-22]. Graphitic carbon nitride $(g-C_3N_4)$ with high availability, thermal and chemical stability as well as appropriate band gap (\sim 2.7 eV) is one of the suitable candidates to form heterojunctions with other narrow band gap semiconductors such as CdS nanostructures to lowering the charge carrier's recombination and intensifying the photocatalytic performance [23–25]. Coupling of g-C₃N₄ nanosheets with CdS resulting in the formation of the type-II or Z-scheme heterojunctions with accelerated charge transfer rate and decreased charge recombination rate [4.10.26.27]. The limited accessibility to catalyst active sites of the nanostructured semiconductors due to the accumulation of the nanocatalyst particles is another crucial issue that should be addressed. In this regard, stabilizing of the nanostructured catalysts on the suitable substrates with ordered and porous structure possess valuable characteristics in catalytic activities [3,28]. The fundamental of the synthesis of the photocatalyst semiconductors within the pores of the zeolites has been investigated by Herron et al. [29]. Zeolite 4A with the chemical formula of Na₁₂ [AlO₂. SiO₂]₁₂·27H₂O, high porosity, thermal, mechanical, and chemical stability provides suitable substrates for the embedding of the catalyst particles [30]. Based on our knowledge, the embedding of the CdS/g-C₃N₄ photocatalyst on the substrate of the 4A zeolite and its application as photocatalyst has not been reported yet. Different approaches have been reported in order to synthesis of the CdS/ g-C₃N₄ composite, including solvothermal [31], ultrasoundassisted technique [32], and hydrothermal [33]. Most of these techniques are energy and time-consuming. Co-precipitation technique provides a simple and low-cost procedure to preparation of the wide range of the nanomaterials.

The large-scale application of the various treatment techniques required detailed information about the interactions of the operational variables to reach the highest performance. Evaluating the impact of each influential parameter with the classical onefactor-at-a-time method is very time-consuming, and even the interaction of the variables cannot be described in this method. Applying the developed optimization and modeling methods such as response surface methodology (RSM) and artificial neural network (ANN) can effectively decrease the number of tests [3,34].

Based on the above mentioned the most important research topics of this research study can be described as follows: (1) increasing the photocatalytic performance of the CdS by coupling with g-C₃N₄ nanosheets and stabilizing on the substrate of the zeolite 4A; (2) potential application of the synthesized nanocomposite for photodecomposition of the cefoperazone (CFP) antibiotic as the representative of cephalosporins; (3) optimization and modeling of the degradation process of the CFP using RSM and ANN methods and comparison of the two used approaches; (4) investigation the impact of the scavengers on the produced radicals and electron-hole pairs; (5) kinetic studies of the degradation process; and (6) identification of by-products from photocatalytic degradation of CFP using GC-MS analysis.

2. Material and methods

2.1. Chemicals

All the used analytical grade chemicals were provided by Merck Co. (Germany) and used without any purification. Cefoperazone sodium (CFP) with the chemical structure illustrated in Fig. S1 was purchased from Wellona Pharma Co. (India). All the experiments were carried out using doubled-distilled water.

2.2. Synthesis of CdS/g-C₃N₄/4AZ ternary composite

The g-C₃N₄ nanosheets were prepared by thermal polymerization of 5 g of melamine at 520 °C for 4 h. A two-step synthesis technique was applied to the preparation of the CdS/g-C₃N₄/4AZ composite. In the first step, 1 g of CdCl₂·H₂O was dissolved in 50 mL distilled water in a 250 mL flask under vigorous stirring. Then 0.08 g of synthesized g-C₃N₄ powder homogeneously dispersed in 20 mL ethanol under ultrasonic irradiation (ultrasonic bath (Ultra 8060, England) with a frequency of 36 kHz, volumetric capacity of 3 L and output intensity of 150 W) and added to the above solution. Then 50 mL of sodium sulfide solution with concentration of 0.1 M was added dropwise to the mixture and stirred for 1 h. The as-obtained product was centrifuged for 10 min at 5000 rpm followed by washing with ethanol and distilled water. In the next step, 1 g of 4A zeolite was dispersed in 100 mL distilled water and sonicated for 30 min. The resultant powder from the first step was added to the zeolite solution and stirred for another 2 h. Finally, the as-prepared CdS/g-C₃N₄/4AZ composite was dried and calcinated at inert atmosphere for 1 h at 500 °C in a furnace.

2.3. Characterization of the CdS/g-C₃N₄/4AZ composite

The XRD (X-ray diffraction) analysis was applied to observe the crystalline structure of the as-synthesized CdS/g-C₃N₄/4AZ composite applying a PHILIPS (PW1730, Nederland) with Cu-kα radiation (λ = 1.54 A°, 40 kV, 30 mA). The FE-SEM (scanning electron microscopy), and TEM (transmission electron microscopy) analysis were used to study the morphology of the prepared nanocomposite using TESCAN, MIRA III and LEO 906 E (100 kV), respectively. The chemical composition and surface properties of the prepared nanocomposite were evaluated using EDX (Energy Dispersive X-Ray) and BET (Brunauer, Emmett and Teller) analysis using a TES-CAN, MIRA III equipped with SAMX detector and BELSORP MINI II, respectively. The photoluminescence (PL) spectra of the assynthesized nanocomposite were recorded using Shimadzu spectrofluorometer (CARY ECLIPSE/Vaian) with the excitation wavelength of 325 nm.

2.4. Assessment the photocatalytic performance of the CdS/g-C₃N₄/4AZ composite

The aqueous solution of cefoperazone (CFP) was chosen as the model effluent to investigate the photocatalytic performance of the synthesized CdS/g-C₃N₄/4AZ nanocomposite under visible light irradiation. A 300 W halogen lamp (OSRAM, Germany) was selected as a visible light source with a glass optical filter for cut off the components with $\lambda > 420$ nm. In each experiment, the desired amount of the as-synthesized ternary composite was added to the 100 mL of the CFP solution with a specified concentration and pH value. Before starting each run, to establish the adsorption/desorption equilibrium, the antibiotic-photocatalyst mixture was magnetically stirred in the dark for 60 min. The pH of the solution was adjusted using NaOH and HCl solutions with a concentration of 0.1 M. At specific time intervals, 5 mL of the solution was extracted from photo-reactor and the residual amount of CFP antibiotic was measured spectrophotometrically using a single beam spectrophotometer (Shimadzu UV- Mini-1240) at λ_{max} = 229nm. Eq. (1) was used to calculate the degradation percentages of the CFP.

$$Degradation(\%) = \frac{[CFP]_0 - [CFP]_t}{[CFP]_0} \times 100$$
(1)

In this equation, $[CFP]_0$ and $[CFP]_t$ represent the initial and residual concentration of the CFP in the solution (mg L⁻¹), respectively.

To probe the degradation mechanism of the CFP in the photocatalytic process, the effect of the addition of the three different scavengers, including isopropanol (IPA), benzoquinone (BQ), and sodium oxalate (NaOx) was investigated on the degradation performance.

An Agilent 6890 gas chromatograph with a 30 m to 0.25 mm HP-5MS capillary column along with an Agilent 5973 mass spectrometer (Canada) was applied to determine the produced intermediates from photodecomposition of CFP.

2.5. Optimization and modeling of the process

The response surface methodology (RSM) and artificial neural network (ANN) were used for the optimization and modeling of the involved photocatalytic process whose details of these approaches are given in the Supplementary Text 1.

2.5.1. Central composite design

To decrease the number of experiments, investigate the impact of the influential parameters, and optimization of the process, a series of the experiments were designed applying Design-Expert11 (DX11) software based on the central composite design (CCD, as a subset of RSM). Table 1 listed the domain of the experimental parameters.

2.5.2. Artificial neural network

Ranking of the operational parameters influence on the degradation efficiency of the CFP was performed employing MATLAB R2020 b software based on ANN toolbox. Similar to the CCD method, the catalyst dosage, initial CFP concentration, pH, and time were the input variables of the ANN model and the CFP degradation efficiency (%) was the output of the model.

3. Results and discussion

3.1. Characterization of the CdS/g-C₃N₄/4AZ nanocomposite

The crystallographic structure of the as-prepared CdS/g-C₃N₄/4AZ nanocomposite was studied by XRD analysis as depicted in Fig. 1. The peaks related to pure CdS and g-C₃N₄ were also shown in Fig. 1. As can be seen, the successful formation of the CdS/g-C₃N₄/4AZ was indicated by the results. The peaks related to hexagonal CdS (JCPDS Card No. 41-1049) and g-C₃N₄ nanosheets (JCPDS Card No. 87-1526) can be observed in the XRD pattern of the CdS/g-C₃N₄/4AZ with lower intensity, confirming the presence of both phase in the composite [4]. The diffraction peaks located at about 18.60° (420), 30.75° (642), and 32.85° (840) are related to the presence of the 4A zeolite (JCPDS Card No. 43-0142) in the structure of the nanocomposite [30]. The observed decrease in the intensity of the CdS and g-C₃N₄ peaks is related to their interactions with 4A zeolite. The crystallite size of the CdS in pure CdS and composite structure using the Scherrer equation was obtained

Table	1
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The domain	of experimental	parameters.



Fig. 1. The XRD patterns of the (a) CdS, (b) g-C₃N₄, and (c) CdS/g-C₃N₄/4AZ.

as 21.15 and 18.56 nm, confirming the decrease in the size of the CdS in the presence of the 4A zeolite.

Fig. 2(a) shows the morphology of the as-synthesized CdS/g-C₃N₄/4AZ composite. The spherical-shaped CdS particles and also g-C₃N₄ nanosheets can be observed in FE-SEM images. Furthermore, the successful introduction of the CdS nanoparticles and g- C_3N_4 sheets on the surface of the 4A zeolite can be seen. The SEM image of the commercial 4A zeolite was also shown in Fig. 2 (b), showing a typical cubic morphology with homogeneous size distribution. Using the SEM images (Fig. 2a and S2) and Digimizer software the mean particle size of the CdS in the pure CdS, CdS/g-C₃N₄, and CdS/g-C₃N₄/4AZ composite was obtained as 59.81, 53.23, and 48.30 nm. These findings confirmed that in the presence of the g-C₃N₄ and 4A zeolite the number of the CdS nucleation site decreased resulted in declined particle diameter. The chemical composition of the prepared CdS/g-C₃N₄/4AZ ternary composite was observed by EDX analysis, as shown in Fig. 2(c). As can be seen, the elemental composition of the synthesized composite contains all the Cd, S, C, N, O, Na, Si, and Al atoms, confirming the successful formation of the CdS/g-C₃N₄/4AZ composite.

The TEM analysis was conducted to better investigate the morphology of the as-prepared CdS/g-C₃N₄/4AZ composite, as exhibited in Fig. 3. The results of the TEM analysis confirmed the successful synthesis of the nanocomposite below 100 nm. Furthermore, the presence of the spherical-shaped CdS particles and gC_3N_4 sheets on the surface of the 4A zeolite cubic particles was also confirmed.

The porosity and pore structure of the CdS/g-C₃N₄ and CdS/g-C₃N₄/4AZ were investigated by N₂ adsorption–desorption isotherms and the results was illustrated in Fig. 4. The assynthesized nanocomposites showed a type III isotherm (IUPAC), confirming the low adsorption of the N₂ (22.17 and 44.78 cm³ g⁻¹ for CdS/g-C₃N₄ and CdS/g-C₃N₄/4AZ, respectively) on the surface of the catalyst [35]. The specific surface area of the CdS/g-C₃N₄ and CdS/g-C₃N₄/4AZ nanocomposites (S_{BET}) was obtained as 0.92 and 6.43 m² g⁻¹, respectively, indicating the increase in avail-

Parameters	Real and coded values of levels					
	-2	-1	0	+1	+2	
A-[Catalyst] ₀ (g L ⁻¹)	0.1	0.2	0.3	0.4	0.5	
$B-[CFP]_0 (mg L^{-1})$	5	10	15	20	25	
С-рН	3	5	7	9	11	
D-Time (min)	20	40	60	80	100	



Fig. 2. The FE-SEM images of (a) CdS/g-C₃N₄/4AZ and (b) 4A zeolite; (c) the EDX spectrum of the CdS/g-C₃N₄/4AZ.



Fig. 3. The TEM analysis of the CdS/g-C₃N₄/4AZ nanocomposite.

able active surface sites of the ternary composite with embedding of the CdS/g-C_3N_4 on the substrate of the 4A zeolite.

The photocatalytic property of the CdS/g-C₃N₄/4AZ nanocomposite was investigated by the band-gap energy (E_g), which was determined by UV–Vis spectrophotometer, as shown in Fig. 5. According to Fig. 5, the Tauc-Mott's equation was applied to calculate the E_g of the catalyst using extrapolating of the linear parts of the (Ahv)² versus hv according to (Ahv)² = B (hv-E_g), where A is the absorbance (a.u.), hv is the photon energy (eV), B is the propor-



Fig. 4. The N_2 adsorption-desorption isotherms of the CdS/g-C_3N_4 and CdS/g-C_3N_4/ 4AZ.

tional constant, and E_g is the band gap energy (eV) [36]. The E_g value for the CdS/g-C_3N_4/4AZ photocatalyst was achieved as



Fig. 5. The (a) absorption curve and (b) band-gap energy of the CdS-g/C₃N₄/4AZ nanocomposite.

2.10 eV, illustrating the capability of the synthesized nanocomposite to act as a visible-light responsive photocatalyst. Furthermore, the E_g value of the CdS, $g-C_3N_4$, and CdS/ $g-C_3N_4$ were obtained as 2.42, 2.7, 2.45 eV, as reported in our previous research work [4]. The decrease in band gap value and resulting increase in photocatalytic performance of the CdS/ $g-C_3N_4$ /4AZ nanocomposite could be related to the structural properties of the 4A zeolite which acts as a rough surface facilitating light reflection and scattering [3,30].

3.2. The photocatalytic performance of the as-prepared $CdS/g-C_3N_4/4AZ$ nanocomposite towards the degradation of CFP

3.2.1. Process optimization by CCD

Table 2 shows the designed 30 experiments using the CCD for photocatalytic degradation of CFP antibiotic in the presence of the CdS/g-C₃N₄/4AZ nanocomposite as the catalyst.

After performing the proposed runs and importing the experimentally results in the software, the relationship between CFP degradation efficiency (%) and the influential parameters was suggested in terms of coded factors:

Degradation (%) =
$$+73.52 + 2.17 \text{ A} - 0.53 \text{ B} + 3.53 \text{ C}$$

+ 4.83 D - 0.50 AB + 2.11AC - 1.36 AD - 0.65 BC + 0.54 BD
+ 5.95 CD - 1.21 A² - 0.32 B² + 3.37 C² + 0.98 D²
(2)

where +73.52 is a constant and the numbers in front of terms are coefficients for linear, quadratic, and interaction effects (see general form of Eq. (2) in the Supplementary Text 1).

According to Eq. (2), the dosage of the photocatalyst (A), pH (C), and irradiation time (D) present more significant effects on the CFP degradation efficiency. Running of the backward step in the DX11 software led to the elimination of nonsignificant variables in the quadratic polynomial model and it was reduced to Eq. (3) [29]:

As it was inference from Eq. (3), the variation of antibiotic concentration (B) and its quadratic and interaction impacts (B^2 , AB, BC, and BD) had no effect on the CFP degradation efficiency.

Table S1 shows the analysis of variance (ANOVA) results for the evaluation of the model's fitness. As can be observed from the results, the Fisher distribution (F test) value of the model (87.70)

is statistically significant, indicating the proposed model is well fitted to the experimental data. The insignificance of the lack of fit also confirms it. The R^2 value was obtained as 0.9744, indicating the possibility of the prediction the 97.44% of the CFP removal variations in the photocatalytic degradation process using independent parameters.

Another important factor to examine the adequacy of the model is the normal plot of residuals, which shows the differences between the predicted and experimental values. Fig. S3 (a) shows the residual plots for CFP degradation in the photocatalytic process, indicating the formation of the straight line in the normal probability plot. Furthermore, the plot of residuals versus run in Fig. S3 (b) doesn't show a specific trend and the points are randomly distributed with a zero mean, indicating the adequacy and reasonability of the CCD model.

Since all the model statistics and diagnostic plots were OK, the study continued by evaluating the interaction between the influential parameters.

Considering the aforementioned descriptions, it can be concluded that three independent variables including the dosage of the photocatalyst (A), pH (C), and irradiation time (D) and their interactions are significant in predicting the CFP degradation efficiency. Hence, the interaction between these parameters was illustrated as response surfaces (Fig. 6).

Fig. 6(a) shows the impact of the CdS/g-C₃N₄/4AZ content and irradiation time on the degradation efficiency of CFP in the photocatalytic process. As Fig. 6(a) shows, the increase in the dosage of the catalyst along with the increase in irradiation time leads to the gradual increase in CFP degradation efficiency. This could be related to the following reasons. Firstly, the increase in the number of the photocatalyst particles results in increased physical adsorption of the pollutant molecules on the active surface sites of the catalyst as well as the number of photons absorbed. Secondly, the presence of more catalyst particles in the solution provides additional reactive radical species to degrade of the constant amount of the pollutant molecules. In fact, the greater catalyst/pollutant ratio provides additional available active sites for the production of the reactive radicals in the solution, resulting in enhanced degradation efficiency. On the other hand, the increase in catalyst dosage more than 0.4 g L⁻¹ adversely affected on CFP degradation efficiency, probably due to the accumulation of the nanocomposite in high dosage and resulting decline in the available active surface sites [37].

The impact of the solution pH and catalyst dosage on the CFP degradation efficiency was shown in Fig. 6 (b). As clearly seen,

Table 2

The experimental matrix designed by CCD and results of the CFP degradation.

Run	A: [Catalyst] ₀ (g L ⁻¹)	B: $[CFP]_0 (mg L^{-1})$	C: pH	D: Time(min)	Degradation (%)		
					Experimental	Predicted	
						RSM	ANN
1	$0.2^{*}(-1)^{**}$	10 (-1)	5 (-1)	40 (-1)	72.15	72.59	72.87
2	0.3 (0)	15 (0)	7 (0)	60 (0)	75.11	73.16	75.83
3	0.3 (0)	25 (+2)	7 (0)	60 (0)	71.08	73.16	71.80
4	0.3 (0)	5 (-2)	7 (0)	60 (0)	72.91	73.16	73.63
5	0.2 (-1)	20 (+1)	5 (-1)	80 (+1)	74.22	73.08	74.94
6	0.2 (-1)	10 (-1)	9 (+1)	80 (+1)	88.09	87.84	88.81
7	0.2(-1)	10 (-1)	9 (+1)	40 (-1)	65.58	63.54	66.30
8	0.3 (0)	15 (0)	11 (+2)	60 (0)	93.51	93.88	94.23
9	0.3 (0)	15 (0)	7 (0)	60 (0)	75.31	73.16	70.03
10	0.2 (-1)	20 (+1)	5 (-1)	40 (-1)	73.18	72.59	73.90
11	0.4 (+1)	20 (+1)	5 (-1)	80 (+1)	70.61	70.48	71.33
12	0.2 (-1)	20 (+1)	9 (+1)	40 (-1)	61.54	63.54	62.26
13	0.4 (+1)	10 (-1)	9 (+1)	80 (+1)	95.09	93.66	95.81
14	0.3 (0)	15 (0)	7 (0)	60 (0)	75.38	73.16	76.10
15	0.4 (+1)	10 (-1)	5 (-1)	40 (-1)	76.39	75.45	77.11
16	0.4 (+1)	10 (-1)	5 (-1)	80 (+1)	70.44	70.48	71.16
17	0.4 (+1)	20 (+1)	9 (+1)	40 (-1)	73.21	74.82	73.93
18	0.3 (0)	15 (0)	3 (-2)	60 (0)	79.99	79.76	80.71
19	0.3 (0)	15 (0)	7 (0)	100 (+2)	86.43	88.92	87.15
20	0.3 (0)	15 (0)	7 (0)	60 (0)	70.01	73.16	70.73
21	0.4 (+1)	20 (+1)	9 (+1)	80 (+1)	92.23	93.66	92.95
22	0.5 (+2)	15 (0)	7 (0)	60 (0)	73.23	72.83	73.95
23	0.3 (0)	15 (0)	7 (0)	60 (0)	72.16	73.16	72.88
24	0.2 (-1)	10 (-1)	5 (-1)	80 (+1)	72.11	73.06	72.83
25	0.1 (-2)	15 (0)	7 (0)	60 (0)	63.61	64.15	64.33
26	0.2 (-1)	20 (+1)	9 (+1)	80 (+1)	88.45	87.84	89.17
27	0.4 (+1)	20 (+1)	5 (-1)	40 (-1)	73.78	75.45	74.59
28	0.3 (0)	15 (0)	7 (0)	20(-2)	67.95	67.60	68.67
29	0.3 (0)	15 (0)	7 (0)	60 (0)	73.16	73.16	73.88
30	0.4 (+1)	10 (-1)	9 (+1)	40 (-1)	76.41	74.82	77.13

* Real value.

** Coded value.

the increase in solution pH and catalyst dosage favored the degradation efficiency of the CFP. This could be linked to the electrostatic interactions between the catalyst surface and pH of solution [38,39]. For CdS/g-C₃N₄/4AZ, the pHpzc, measured by the method explained in the Supplementary Text 2, was 10.5 (i.e., composite's surface has positively charged at pH < 10.5 and negatively charged at pH > 10.5, Fig. S4). CFP has two pK_a values ($pK_{a1} = 4.5$ and $pK_{a2} = 6.5$). In other words, this chemical compound is mainly cationic (CFP⁺), zwitterionic (CFP^{\pm}), and anionic (CFP⁻) at pH < 4.5, 4.5 < pH < 6.5, and pH > 6.5, respectively [40]. Hence, the electrostatic interactions between the positive charge of catalyst's surface and CFP^{\pm} at the pH range of 4.5–6.5 led to the approach of the CFP to the CdS/g-C₃N₄/4AZ surface, which was followed by an intense electrostatic attraction between the positive charge of catalyst surface and the anionic CFP (CFP⁻) at the pH range of 6.5-10.5. Furthermore, the alkaline pH intensifies the hydrolysis of the CFP due to the instability of the beta-lactam ring [41].

The interaction of irradiation time and pH on CFP degradation was shown in Fig. 6(c). It is clear that the increase in duration and pH have a synergic effect on the degradation of antibiotic, as previously interpreted.

At the end of this section the RSM-based optimal conditions was proposed to reach the highest CFP degradation efficiency and the obtained results were summarized in Table 3. The degradation experiment of CFP was conducted under the optimum conditions and the results showed that degradation of 93.23% of CFP was occurred with the insignificant difference compared with the predicted value. The CFP degradation using CdS/g-C₃N₄ was performed in the determined optimum condition and 81.34 % degradation efficiency was achieved. The higher degradation rate in the pres-

ence of the CdS/g-C₃N₄/4A composite confirmed the better photocatalytic performance.

The kinetics of the CFP degradation in the photocatalytic process was investigated at the determined RSM-based optimum conditions utilizing the Langmuir–Hinshelwood model (described in the Supplementary Tex 3) and Fig. S5 illustrates the plot of the lnC₀/Ct versus irradiation time (t). The results demonstrated that the kinetics of the involved photocatalytic process obeys from the Langmuir-Hinshelwood's pseudo-first-order model. From the slope of Fig. S5, the apparent rate constant (k_{app}) of the degradation reaction of the CFP in the photocatalytic process was obtained as $3.71 \times 10^{-2} \text{ min}^{-1}$.

3.2.2. ANN modeling

The catalyst dosage, initial CFP concentration, pH, and irradiation time were input variables of the ANN model and the CFP degradation efficiency (%) was the output of the model. The experimental data reported in Table 2 were normalized and used to training, validating, and testing of the ANN model.

The number of neurons in the hidden layer was selected by examining various numbers from 2 to 10 and the topology with the number of neurons 1:9:4 in the input, hidden, and output layers was selected as the optimized ANN structure for CFP degradation prediction by the photocatalytic process. Table 4 listed the connection weights of the layers of the developed ANN model.

To validate the designed ANN model, the values of the regression (R^2) for the plots between outputs and targets were calculated and reported in Fig. 7. The results showed good agreement between the estimated values by the ANN model and the results of the experiments, as reported in Table 2, confirming the reasonability of the model.



Fig. 6. Response surface plots for degradation efficiency of CFP as a function of (a) catalyst dosage-irradiation time, (b) catalyst dosage-pH, and (c) pH- irradiation time. (The values of the other two parameters in each graph have been considered equal to the average of their ranges).

Table 3

The optimized values for highest CFP degradation (%) by photocatalytic process.

[Catalyst] ₀ (g L ⁻¹)	[CFP] ₀ (mg L ⁻¹)	рН	Time (min)	Degradation (%)	
				Predicted	Experimental
0.4	17	9	80	95.66	93.23

Table 4

The	matrix	of the	e connection	weights	of the	layers	of the	develop	oed ANN	model.

LW _{j,i}	$IW_{j,i}^{*}$				Neurons
Degradation (%)	Time	рН	[CFP] ₀	[Catalyst] ₀	
0.151	0.209	1.912	1.170	1.402	1
0.822	1.532	2.892	-0.208	-0.133	2
0.082	-0.214	0.611	1.933	-1.234	3
-0.223	-0.192	0.005	1.683	1.594	4
0.130	-2.039	1.252	0.489	0.884	5
-0.665	-1.035	1.333	0.474	-0.634	6
-0.308	-2.138	0.197	-0.725	-2.290	7
0.028	-0.799	2.228	0.260	0.671	8
-0.315	1.929	1.626	0.476	0.799	9

W_{j,i}*: weights between the hidden and the input layers.

W_{i,i}^{**}: weights between the hidden and the output layers.

For better expression the impact of the variables on the degradation efficiency of the CFP antibiotic in the photocatalytic process, the percentage analysis of each factor was performed applying Garson's method (described in the Supplementary Tex 1), and the result was shown as a radar chart in Fig. 8. As can be observed in Fig. 8, the pH of the solution, irradiation time, nanocomposite dosage, and the initial concentration of the CFP affected antibiotic degradation efficiency with a percentage impact of 37, 29, 19, and 15 %, respectively.



Fig. 7. Regression plots for validation of ANN model.



Fig. 8. The relative importance of the input variables on the degradation of CFP analyzed by ANN model.

3.2.3. Comparison of the CCD and ANN

In this section, a comparative study was performed to compare the accuracy of the two CCD and ANN approaches for the prediction of the degradation efficiency of the CFP in the photocatalytic process. As can be seen from Fig. S6, both methods are worthwhile, but a closer look reveals that the ANN model is more susceptible to predict the variation in CFP degradation by the photocatalytic process compared.

3.3. Mechanism of the photocatalytic process

Three steps were taken to suggest a plausible photocatalytic mechanism. (i) The PL analysis was carried out to study the separation and recombination processes of the produced e^-h^+ pairs. As Fig. 9 (a) shows, the ternary nanocomposite showed a weaker emission peak compared with CdS/g-C₃N₄, confirming the decrease in recombination rate of the photoexcited charge carriers. This can be attributed to the presence of the zeolite in the composite texture, which leads to decreasing the recombination of the charge carriers and consequently intensifying the photocatalytic activity of the as-synthesized nanocomposite. Furthermore, the position of the PL peak for CdS/g-C₃N₄/4AZ nanocomposites shifted to the red region, confirming the increased visible-light activity of the ternary composite. (ii) The role of the active species during the



Fig. 9. The PL spectra of the CdS/g-C₃N₄ and CdS/g-C₃N₄/4AZ (a); The impact of the scavengers on the CFP degradation efficiency by the photocatalytic process under RSM-based optimized conditions (b).

photocatalytic CFP degradation over CdS/g-C₃N₄/4AZ was monitored using the addition 1 mM of the IPA, BQ and NaOx as °OH, $^{\circ}O_{2}^{-}$, and h⁺ scavengers, respectively. The results presented in Fig. 9(b) show that IPA as the hydroxyl radical scavenger applied the less scavenging effect with about 8 % decline, whereas the presence of the BO and NaOx decreased the CFP degradation efficiency from 93.23 to 41.16 and 32.47%, respectively, confirming that the superoxide anion radicals and photogenerated holes were the main responsible species in the decomposition of the CFP by the photocatalytic process [3]. The claim has been authenticated from the photoluminescence studies in an alkaline solution of terephthalic acid as described in the Supplementary Text 4 [42]. Fig. S7 showed that there was no significant change in the intensity of the PL spectrum during the time, indicating hydroxyl radicals are inefficacious in the involved photocatalytic process and the produced h^+ can directly oxidized CFP molecules [21,43]. (iii) The relative position of conduction and valence band edges of CdS and $g-C_3N_4$ was established based on our previous study (E_{CB}/E_{VB} of CdS and g- C_3N_4 was -0.36/1.98 eV and -1.11/1.54 eV, respectively) [4]. Undoubtedly, the position of energy band alignments favors the formation of staggered gap (type-II) heterojunction [44]. Unless there is a compelling reason to violate it.

According to the above description, Fig. 10 illustrates a schematic mechanism diagram for photodegradation of CFP antibiotic using CdS/g-C₃N₄/4AZ nanocomposite as the catalyst. As shown, the irradiation of the visible light to CdS/g-C₃N₄/4AZ semiconductor resulted in the excitation of CdS and g-C₃N₄. The excited electrons (e⁻) moved from conduction band (CB) of the g-C₃N₄ to CB of CdS. At the same time, the holes (h⁺) transferred from the valance band (VB) of CdS to VB of g-C₃N₄. Since CB position of CdS (-0.36 eV) is more negative than the standard redox potential of $O_2/^{\circ}O_2^-$ (-0.33 eV) [45], superoxide anion radicals can be easily produced from O₂ molecules reduction. On the other hand, VB position of $g-C_3N_4$ (+1.54 eV) is more negative than the standard redox potential of H₂O/°OH (+2.27 eV) and OH⁻/°OH (+2.38 eV) [46], as a result, photogenerated holes cannot oxidize H₂O or OH⁻ to hydroxyl radicals and they play a direct role in CFP molecules eradication.

The above interpretations confirm the formation of the type-II heterojunction, which lowering the recombination of the produced e^--h^+ pairs and intensifying the photocatalytic activity of the assynthesized nanocomposite. Not to mention that depending on the prevailing conditions, the CdS/g-C₃N₄ composites can have



Fig. 10. The proposed schematic illustration for the mechanism of the studied photocatalytic process.

other configurations such as Z-scheme. The main reason can be incompatibility the relative position of conduction and valence band edges of semiconductors with standard redox potential of $O_2/^{\circ}O_2^-$, $H_2O/^{\circ}OH$, $OH^-/^{\circ}OH$, H^+/H_2 , etc. In addition, the presence of a mediator between the CdS and g-C₃N₄ can lead to the Z-scheme structure [6,7,27,45–47].

Since none of these exceptions has been observed in the present study, it can be firmly accepted that a type-II heterojunction is preferred, which agrees with previously reported articles [48,49].

3.4. Intermediates determination during the CFP photocatalysis

The produced intermediates during degradation of the CFP in the photocatalytic process in the presence of the CdS/g-C₃N₄/4AZ nanocomposite were identified using GC-MS analysis. The list of the major produced by-products during degradation of CFP with m/z ratio and related retention time (R_t) were summarized in Table 5. The structure of the produced intermediate compounds confirmed that the CFP molecules decomposed mainly through

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Table 5

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m/z	R _t	Chemical structure	Name and chemical formula*	No.
59	2.82	т Т	Ethyl Formate $(C_3H_6O_2)$	1
101	3.14	но ог ог он	5-Hydroxy-4-oxopentanoic acid $(C_5H_8O_4)$	2
59	3.53	но	2,3-Dimethyl-2-pentanol (C ₇ H ₁₆ O)	3
31	3.67	НО	1-Methoxy-2-methyl-2-propanol $(C_5H_{12}O_2)$	4
60	7.99		3-Pyrrolidinecarboxylic acid $(C_5H_9NO_2)$	5
203	20.30		2-Methylthiazole-4-carbonitrile $(C_5H_4N_2S)$	6
201	23.11		1,3-dimethyl-1H-pyrazol-5(4H)-one $(C_5H_8N_2O)$	7

* Based on national institute of standards and technology (NIST) library.

the cleavage of the C-S, C-N and, N-N bonds. Production of the different intermediates with various structures confirmed the complexity of the CFP degradation procedure. The formation of the aliphatic compounds and carboxylic acids indicated the mineralization of the CFP to non-toxic products.

3.5. Stability of the CdS/g-C₃N₄/4AZ nanocomposite

Finally, the stability and reusability of the as-prepared CdS/g-C₃N₄/4AZ nanocomposite as the important factor in long-term application of the catalysts was evaluated and the results are presented in Fig. S8. The degradation experiments were performed at the determined optimal conditions ([Catalyst]₀ = 0.4 g L⁻¹, [CFP]₀ = 17 mg L⁻¹, pH = 9, time = 80 min). The nanocomposite was used at 3 repetitive run after washing with distilled water and drying. As can be seen, the insignificant decrease in the performance of the nanocomposite was observed after 3 run, confirming good stability of the nanocomposite and capability to reuse in practical applications. Furthermore, the XRD patterns of the fresh and used catalyst were recorded and reported in Fig. S 8, confirming no meaningful changes in the crystalline structure of the catalyst.

4. Conclusion

The CdS/g-C₃N₄ type II heterojunction supported on 4A zeolite was successfully synthesized as a fascinating visible light responsive composite semiconductor. The photodecomposition of the CFP antibiotic using the as-prepared catalyst under visible light irradiation was studied and the impact of the operating variables optimized using RSM and ANN approaches. The highest degradation efficiency of CFP was obtained as 93.23 % under optimized condition ([Catalyst]₀ = 0.4 g L^{-1} , [CFP]₀ = 17 mg L^{-1} , pH = 9, time = 80 min). The results of the ANN model indicated that pH with a percentage impact of 37 % was the most influential variable in the degradation of the CFP. Based on the results of the scavenger experiments, it was concluded that the produced superoxide radicals and holes were the main responsible species in degradation process. The pseudo-first-order model of the photodegradation process was confirmed by the result of the kinetic studies. Finally, the structure of the formed intermediated during the degradation of the CFP showed that the decomposition of the CFP mainly occurred through the cleavage of the of C-S, C-N, and N-N bonds.

CRediT authorship contribution statement

Naime AttariKhasraghi: Investigation, Writing – original draft. Karim Zare: Resources, Supervision. Ali Mehrizad: Supervision, Software, Formal analysis, Writing – review & editing. Nasser **Modirshahla:** Methodology, Conceptualization. **Mohammad Ali Behnajady:** Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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