

## **Binary Antibiotics Degradation Employing an Efficient Direct Z-Scheme Ti(VI)-Salen Complex Loaded on Dendritic Fibrous Nano-Silica**

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Abstract The degradation of the antibiotics discharged into water, and wastewater has become a challenge in environmental engineering. A new Z-scheme nanocomposite was designed, synthesized, and characterized for photooxidative degradation of the binary antibiotics (doxycycline and tetracycline) in an aqueous solution simultaneously. Firstly, the proposed nanocomposite was created from dendric fibrous nano-silica (KCC-1), as support, improved with Ti(VI)-salen, as an organometallic complex, and its structural and morphological properties were investigated. The band-gap energy achieved from the Tauc equation was in good accordance with the calculated one by the Gaussian software. Analysis of the band structure was used to deduce the probable

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Z-scheme heterojunction mechanism for the proposed photocatalyst. The photodegradation procedure was studied in terms of pH (2.0-6.0), catalyst amount  $(1.5-7.5 \text{ mg mL}^{-1})$ , the concentration of H<sub>2</sub>O<sub>2</sub> (0-0.08% w/v), and irradiation time (5-25 min) under UV light. In optimal conditions, employing the simplex non-linear optimization algorithm, the photodegradation of doxycycline and tetracycline showed efficiencies higher than 95%. Optimal circumstances leading to the maximum simultaneous removal of doxycycline and tetracycline were discovered as pH of 3.6, catalyst dose of 6 mg mL<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> amount of 0.06%w/v, and irradiation time of 16 min. Under the optimal circumstances, the kinetics data for investigated antibiotics were fitted employing a pseudo-firstorder model. The nanocomposite could successfully remove doxycycline and tetracycline contaminations. Regarding the high degradation efficiency as well as fast kinetics, the observations suggest that the proposed photocatalyst has a significant capability of reducing antibiotic pollutants.

**Keywords** Pharmaceutical pollutants · KCC-1 · Salen ligand · Z-scheme mechanism · Oxidative photodegradation

## **1** Introduction

The reusing of treated wastewater, which possesses a potential role as an alternative water source, has been widely recognized and can be incorporated into recycling and safety strategies. Coordinated efforts worldwide try to increase the reuse of wastewater significantly (Patel et al., 2019). Environmental pollutants such as pesticides, pharmaceuticals, fragrances, additives, preservations, and disinfectants are critically detrimental to wastewaters regarding their adverse effects on human health (Abolhasani et al., 2019; Nivetha et al., 2022; Omrani et al., 2022). The pharmaceuticals such as antibiotics, antidepressants, antihypertensives, analgesics, bronchodilators, and cardiovascular and lipid regulators have been repeatedly detected in various wastewaters at different concentration levels (Patel et al., 2019; Shahbeig et al., 2017). Among them, antibiotics such as amoxicillin, cephalexin, cefaclor, ciprofloxacin, clindamycin, doxycycline, penicillin, sulfamethoxazole, and tetracycline are being used vastly to treat human and animal diseases and have been appeared broadly in wastewaters (Nekouei & Nekouei, 2018; Pakzad et al., 2020). The tetracycline class is known as the second largest group of antibiotics, which are being produced and used extensively (Pulicharla et al., 2015). Doxycycline (DOX) and tetracycline (TC) are two types in this class causing bioaccumulation and promoting ecological system resistance, which poses biological risks in humans and animals (Kim et al., 2013).

Various approaches include ion-exchange (T. Wang et al., 2017), reverse osmosis (Lan et al., 2019), membrane separation (J. Liu et al., 2020), photodeg-radation (P. Chen et al., 2023a, 2023b; Das et al., 2023; Doan et al., 2021; Hemmat et al., 2021; Panchal et al., 2023), and adsorption (Lye et al., 2020) have been used to treat the wastewater containing DOX and TC. Among these approaches, adsorption and photodegradation are considered the most proper methods to remove them from aqueous solutions. However, the adsorption procedure has some drawbacks, because of the antibiotic contaminations introduced into the adsorbents after completing this process, so different integration layouts are required for the effective removal of antibiotics.

Heterogeneous catalytic photodegradation has received much attention due to its high efficiency, cost-effectiveness, and safe by-products (such as  $CO_2$ ,  $H_2O$ , etc.) regarding the degradation of various pollutants (Doan et al., 2021; X. Liu et al., 2022). In addition, this layout uses renewable solar energy, so it has been developed as a feasible alternative for high-energy processes. This method works by absorbing photons that contain energy equal to or greater than the catalytic band-gap energy (Shao et al., 2020). After energy absorption, the electrons ( $e^-$ ) of the catalyst move from the valence band to the conduction band, creating photogenic holes ( $h^+$ ) in the valence band. It oxidizes water molecules to generate hydroxyl radical (OH<sup>•</sup>), a powerful oxidant in aqueous media. Lastly, the OH<sup>•</sup> radicals produced can oxidatively decompose many organic compounds such as DOX and TC antibiotics (Hemmat et al., 2021).

 $TiO_2$  as a semiconductor is widely used in the photodegradation process because of its ability for pollutant decomposition, low toxicity, long-term chemical stability, costly effectiveness, superior photocatalytic activity, and ambient operative conditions (S. S. Tan et al., 2006). However, poor active sites and wide band-gap are significant limitations (Fauzi et al., 2022). Moreover, most of generated  $e^-$  and  $h^+$ pairs recombine and dissipate as heat which reduces  $TiO_2$  efficiency (Y. Liu et al., 2014). To address and reduce these problems, researchers have made efforts such as (i) introducing C, N, S, etc., as doping elements into  $TiO_2$ , (ii) modifying  $TiO_2$  with Ag, Au, Cu, Pt, Pd, etc., and (iii) coupling TiO<sub>2</sub> with PbS, CuO, FeTiO<sub>3</sub>, and other semiconductors to make heterogeneous junctions, reduce the band-gap, improve light absorption, inhibit the possibility of e<sup>-</sup> and h<sup>+</sup> pairs recombination, and increase photocatalytic activity (Y. Liu et al., 2014). Furthermore, reported TiO<sub>2</sub>-loaded silica as a photocatalyst exhibited high active sites because of its fibrous morphology (Alamgholiloo et al., 2022; Fauzi et al., 2018). This morphology increases the accessible oxygen vacancies and enhances photodegradation (Fauzi et al., 2018). Recently, a direct Z-scheme silica-based heterostructure system has presented promising superior separation of photo-generated e<sup>-</sup> and h<sup>+</sup> pairs reducing their recombination (Fauzi et al., 2018; Fu et al., 2019; Swedha et al., 2022).

Mesoporous nano-silica (KCC-1) by fibrous morphology, a type of SiO<sub>2</sub> nanoparticles, has been taken as a catalyst-supporting material due to its high specific surface area and permanent porosity. Various heterogeneous catalysts, which exhibited excellent catalytic activity, were designed using KCC-1 as support which have preferable activity compared to conventional mesoporous silica materials (Irfan et al., 2017). Since KCC-1 has a neutral framework, it is necessary to modify the KCC-1 surface to gain access to the active sites and increase the catalytic and photocatalytic activities. This task could be achieved by elemental, organic complex, and semiconductor structure coatings (Najafi Chermahini et al., 2016). Several materials, such as Ag, TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>, and Al, have been utilized for KCC-1 modification (Singh et al., 2016; Zarei et al., 2019). Regarding the modification of these mesoporous materials, Schiff bases, which show a broad range of applications in biology, inorganics, catalysts, clinical, and chemical analysis, can be employed (Da Silva et al., 2011). Moreover, Schiff's base metal complexes are utilized as precursors for the synthesis of different metal oxides, including oxides of Fe, Co, Cu, Ni, Mg, Ti, V, Cd, Zn, Hg, and various ferrites (Ali et al., 2022). However, reports on synthesizing nano-scale structures using Schiff bases or metal complexes derived from Schiff bases as precursors are scarce (Ayodhya et al., 2015a, 2015b). In particular, far less research has been conducted on preparing semiconductor nanoparticles on various Schiff bases and their metal complexes (Ayodhya et al., 2015a, 2015b). Salen ligands, which can be synthesized by condensing 1,2-diamine with two equivalents of salicylaldehyde, are a particular class of tetradentate chelating bis-Schiff base (Cheng et al., 2013). They contain two covalent and two coordinate covalent sites in a planar array, which could incorporate into many metal ions, leaving the two axial sites open for ancillary ligands (Cheng et al., 2013). So far, no study has been reported on using heterogenous Ti(VI)-salen complexes pertinent to modified KCC-1 in photodegradation treatments. Therefore, the synergistic alteration of heterojunction KCC-1 by immobilizing salen ligands and complexing with suitable photocatalytic active metals could be interesting. This could provide a higher surface area and narrower band-gap, forming a Z-scheme heterojunction which inhibits recombination of e<sup>-</sup> and h<sup>+</sup> pairs improving photogenerated charge. This ameliorating in properties leads to increasing photodegradation efficiency.

In this study, KCC-1 was modified with a salen ligand and then complexed with Ti(VI) to produce a novel Z-scheme Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst. The advanced Z-scheme photocatalyst was employed for the DOX and TC photodegradation. Under UV light illumination, it provided us with quantitative removal of DOX and TC. For comparison, the photodegradation capability of KCC-1, NH<sub>2</sub>-KCC-1, and salen@NH<sub>2</sub>-KCC-1 was also examined. The characterization of the synthesized Z-scheme Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst was achieved by FTIR, TGA, XPS, SEM/EDX, HR-TEM, BET, and XRD techniques. The DOX and TC photodegradation pathway and mechanism of Ti(IV)salen@NH<sub>2</sub>-KCC-1 were investigated based on the Z-scheme heterojunction theory in the presence of  $H_2O_2$  as reactive oxygen species (ROS). Furthermore, the impacts of various variables on the photocatalytic degradation of DOX and TC were evaluated by the central composite design (CCD) technique, and the kinetic property of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst was also investigated. The reusability of Ti(IV)-salen@NH2-KCC-1 was also clarified. It is hoped that the present study in the preparation and introduction of Z-scheme Ti(IV)-salen@NH2-KCC-1 photocatalyst will lead to the unique design of photocatalyst for multiple applications.

## 2 Experimental

## 2.1 Chemicals

Cetyltrimethylammonium bromide (CTAB), urea, 3-aminopropyl tri-ethoxy silane (APTES), tetraethyl orthosilicate (TEOS), cyclohexane, 1-pentanol, sodium sulfate, and ethanol were purchased from Merck Co. (Germany) with purities higher than 98%. Salicylaldehyde, DOX, and TC (purity  $\geq$  98%) were obtained from Sigma-Aldrich Co. (US). The solutions were prepared daily using double-distilled water (DDW). The pH values of the solutions were adjusted by hydrochloric acid and sodium hydroxide solutions (1.0 M), which were acquired from Merck Co. (Germany).

## 2.2 Apparatus

The surface morphology study and characterization of the synthesized materials were carried out by several advanced techniques. A scanning electron microscope with energy dispersive X-ray analysis (SEM/EDX, TECSAN VEGA3 model, Czech Republic) was used to determine the morphology and surface structure of the prepared photocatalyst. Transmission electron microscopy was conducted by a high-resolution microscope (HR-TEM, A Carl Zeiss SMT AG Co., ZEISS LIBRA 200 FE, Germany). The Brunauer–Emmett–Teller (BET) isotherm analysis was performed using BELSORP MINI (Osaka, Japan). X-ray diffraction (XRD) study was accomplished by XRD (Bruker, AXS-D8 Advance, US, and Cu K<sub> $\alpha$ </sub> radiation K=1.5406 Å) to detect changes in the crystalline structure of photocatalyst nanoparticles.

To study the type of functional group and qualitative identification, a Fourier transform infrared spectrometer (FTIR, Perkin Elmer, Spectrum 65, US) was used at 4000 to 400 cm<sup>-1</sup> wave number range. The probe of organic matter supported on nanoparticles and thermal stability was conducted with thermogravimetric analysis (TGA, Q600, TA Instrument, US). The X-ray photoelectron spectroscopy studies were acquired by XPS (Thermo Scientific, Nexsa G2, USA). The concentrations of DOX and TC were determined by a UV–Vis spectrophotometer (AnalyticJena, Specord 210, Germany) and an HPLC system (Agilent 1200, USA).

## 2.3 Synthesis Procedures

## 2.3.1 Synthesis of KCC-1 and NH<sub>2</sub>-KCC-1

The hydrothermal method was used for the synthesis of KCC-1 (Bayal et al., 2016; Polshettiwar et al., 2010). Briefly, 2.0 g of CTAB and 2.4 g of urea were dissolved in a beaker with 100 mL of DDW. The prepared solution was stirred at room temperature for 15 min. Then, a mixture of 10 mL of TEOS and 10 mL of cyclohexane was added dropwise to the previous solution. Finally, 6 mL of 1-pentanol was slowly added to the beaker and stirred at room temperature for 20 min to obtain a homogenous solution. The solution was placed in a Teflon-sealed microwave reactor (120 °C and 800W) for 1 h. After the reaction was completed, the mixture was cooled to room temperature, separated by centrifugation, washed with DDW and ethanol, and then dried at 120 °C for 8 h. The final obtained powder was calcined at 550 °C for 5 h (Bayal et al., 2016; Polshettiwar et al., 2010). To activate the KCC-1 surface, 0.3 g of KCC-1 and 0.282 mL of APTES were added to 30 mL of dried toluene in a round-bottomed flask, refluxed at 105 °C for 10 h, the solution was filtered, and finally, the filtrate was dried in a vacuum oven at 80 °C to obtain NH<sub>2</sub>-KCC-1.

## 2.3.2 Synthesis of Salen Ligand

## a) Synthesis of 2-hydroxy-5-chloromethylbenzaldehyde

2-hydroxy-5-chloromethylbenzaldehyde was synthesized and purified as described by Wang et al. (Q. Wang et al., 2006). Briefly, in a roundbottomed flask, 0.25 mmol salicylaldehyde, 0.15 mmol para-formaldehyde, and 150 mL of HCl 0.10 M were refluxed at 70 °C for 48 h, then two drops of sulfuric acid 0.10 M were added to the solution. After that, the obtained solution was cooled to room temperature, followed by the addition of 20 mL of both DDW and dichloromethane. The organic layer was separated and then purified by a crystallization method using absolute hot ethanol to obtain 2-hydroxy-5-chloromethylbenzaldehyde (purple solid, 98% yield).

## b) Synthesis of 2-hydroxy-5-chloromethylsalicylaldehyde salen

Here, 5 mmol of phenylenediamine was dissolved in 30 mL of anhydrous chloroform in a beaker. Then in a separate beaker, 5 mmol of previously acquired 2-hydroxy-5-chloromethylbenzaldehyde was dissolved in anhydrous chloroform. The obtained solution was added dropwise to the first beaker at 0 °C while stirring for 6 h, which led to a yellow product. The solvent was removed using a rotary evaporator. Afterward, 30 mL of absolute ethanol was added to the obtained product. Then, a solution containing 5 mmol salicylaldehyde dissolved in 20 mL of ethanol was added dropwise to the mixture, following refluxing for 2 h to yield the final salen ligand. This brown precipitate was dried in a vacuum oven at 80 °C for 12 h.

## 2.3.3 Synthesis of Ti(VI)-Salen@NH<sub>2</sub>-KCC-1 Photocatalyst

As described in the literature, the synthesized salen ligand was chemically immobilized onto the  $NH_2$ -KCC-1 surface (Nasseri et al., 2019). Briefly, 1.5 g of the prepared  $NH_2$ -KCC-1 was sonicated in 100 mL dry toluene in a beaker for 2 h. Then, 0.5 g of homogeneous salen ligand was added, and the mixture was stirred and refluxed under an inert atmosphere for 48 h. The mixture was washed with dry toluene and ethanol. Then, the crude product

was further purified by Soxhlet extraction using dichloromethane and methanol solvents, and finally, the obtained salen@NH<sub>2</sub>-KCC-1 nanomaterial was dried at 150 °C for 12 h. Finally, 0.3 g of the compound was dissolved in THF, followed by dropwise addition of 1.12 mmol TiCl<sub>4</sub>. The developed Z-scheme Ti(VI)-salen@NH<sub>2</sub>-KCC-1 photocatalyst was washed with acetone and dried in a vacuum oven at 80 °C for 12 h as an end product (Nasseri et al., 2019).

## 2.4 Photodegradation Experiments

The photodegradation experiments were performed as follows. Firstly, 50 mg of the synthesized Ti(VI)salen@NH<sub>2</sub>-KCC-1 photocatalyst was uniformly dispersed in aqueous solutions containing DOX and TC, and stirred at predetermined times in the dark to establish an adsorption-desorption equilibrium. Then, the suspension in the reactor was irradiated for a particular time under UV irradiation to investigate the photodegradation properties. Solid particles of Ti(VI)-salen@NH<sub>2</sub>-KCC-1 were removed by centrifuging at 9000 rpm for 10 min. The absorbance of the aqueous solution was determined by UV-Vis spectrophotometer at 275 and 357 nm for DOX and TC, respectively, to calculate the degradation efficiencies. For real samples, an HPLC system (Agilent 1200, US) was used to evaluate the remained DOX and TC.

## 2.5 Measurements of pH<sub>ZPC</sub> for Ti(IV)-Salen@ NH<sub>2</sub>-KCC-1

The point of zero charge  $(pH_{ZPC})$  is the pH where the actual charge on the substrate surface is zero. In solutions with  $pH^{>}pH_{ZPC}$ , the surface charge is negative, and it is positive at  $pH^{<}pH_{ZPC}$ . To obtain the  $pH_{ZPC}$  of the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst, five Erlenmeyers were filled with 10 mL of DDW at different pH of 3, 5, 7, 9, and 11. Then, 0.1 g of the synthesized photocatalyst was added to each solution, followed by shaking at 250 rpm for 24 h, and recording their final pHs.

To measure  $pH_{ZPC}$ , according to the method described above, the final pH values were measured and compared to the initial pHs. The  $pH_{ZPC}$  or isoelectric point of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 was 2.1.

#### 2.6 Optimization Procedure

The chemometric approach was performed using a central composite design (CCD) under response surface methodology (RSM). Analysis of the experimental data was supported by the Design-Expert software (Trail Version 12, Stat-Ease, Inc., Minneapolis, USA). Effects of four independent parameters, i.e., initial pH, photocatalyst dose (mg mL<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub> concentration (%w/v), and irradiation time, on the photodegradation process were evaluated in detail using CCD, and the photodegradation efficiencies of DOX and TC were selected as the responses of proposed models. The four chosen parameters (A, B, C, D) were converted to the coded values at levels: -2, -1, 0, +1, and +2, which are presented in Table S1.

## **3** Results and Discussion

## 3.1 Characterization

## 3.1.1 FTIR Analysis

The FTIR spectra were employed (Fig. 1) to demonstrate the chemical structure and functional groups of KCC-1, NH<sub>2</sub>-KCC-1, and Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst. The FTIR spectrum of synthesized salen shown in Fig. 1a illustrates two characteristic peaks at 1459 and 748 cm<sup>-1</sup>, which correspond to methylene groups ( $-CH_2-$ ) in meta substitution and stretching vibration of C-Cl group, respectively. Also, the C=N stretching band vibrations were observed at 1606 cm<sup>-1</sup>.

The FTIR spectra of KCC-1 and NH<sub>2</sub>-KCC-1 samples are shown in Fig. 1b, c, respectively. The peak at 3440–3220 cm<sup>-1</sup> is related to O–H stretching band, and the O–H bending vibration has appeared at 1630 cm<sup>-1</sup>. The peaks at 1091–1200 cm<sup>-1</sup> represent the Si–O–Si asymmetric stretching, while the peak at 816 cm<sup>-1</sup> is attributed to Si–O–Si symmetric vibrations (Fig. 1b) (Fauzi et al., 2018). The APTES bonding to the silica surface confirmed by the Si–O–Si asymmetric stretching peak (1091–1200 cm<sup>-1</sup>) is much sharper than that of KCC-1 (Fauzi et al., 2018). Also, the peaks at 2923 and 2851 cm<sup>-1</sup> are related to the stretching vibration of aliphatic C–H bonds (Fig. 1c).

**Fig. 1** FTIR spectra of the synthesized KCC-1, NH<sub>2</sub>-KCC-1, and Ti(IV)salen@NH<sub>2</sub>-KCC-1



Figure 1d demonstrates the FTIR spectrum of the synthesized Ti(IV)-salen@NH<sub>2</sub>-KCC-1. The absorption peak at 1606 cm<sup>-1</sup> is attributed to C = N stretching band vibrations in salen ligand. At 3347 cm<sup>-1</sup>, the O–H stretching of absorbed water molecules has a broad absorption peak (Nasseri et al., 2019). The peak of Si–O–Si at 1097 cm<sup>-1</sup> confirms the successful immobilization of the homogeneous salen ligand on the KCC-1 surface. The new firm peaks at 811 and 899 cm<sup>-1</sup> could have corresponded to Ti–O–C and Ti–Cl, which indicates the fixed position of Ti on the Ti(IV)salen@NH<sub>2</sub>-KCC-1 surface.

## 3.1.2 XRD Analysis

The patterns of XRD at the  $2\theta$  range of  $10-80^{\circ}$  for KCC-1 and Ti(IV)-salen@NH<sub>2</sub>-KCC-1 are presented in Fig. 2. The presence of a broad peak between  $2\theta = 15-30^{\circ}$  for KCC-1 sample (Fig. 2) signifies the existence of amorphous nature of silica (JCPDS No. 29–0085) (Le et al., 2015). This broad peak decreases in the case of Ti(IV)-salen@NH<sub>2</sub>-KCC-1, suggesting the disruption of the fibrous nano-silica framework and successful loading of Ti(IV)-salen on the KCC-1. Moreover, the appearance of new peaks at  $2\theta = 37.5$ , 47.9,



Fig. 2 XRD pattern for the synthesized KCC-1, and Ti(IV)-salen@NH $_2$ -KCC-1

and 53.3° in the XRD pattern of Ti(IV)-salen@ NH<sub>2</sub>-KCC-1 (JCPDS No. 96–231-0711) corresponds to the diffraction from the <101>, <210>, and <211> planes, respectively, confirming the successful immobilization of Ti(IV)-salen complex on the surface of NH<sub>2</sub>@KCC-1(Roy et al., 2008).

## 3.1.3 UV–Vis Diffuse Reflectance Spectroscopy and Photoluminescence Analysis

The UV–Vis diffuse reflectance spectroscopy (DRS) for the prepared KCC-1, Ti(VI)-salen complex, and Ti(IV)-salen@NH<sub>2</sub>-KCC-1 were further carried out to calculate band-gap energy ( $E_g$ ) (see Fig. 3). Whenever, light with ho energy irradiated on a substance, depending on the magnitude of the energy, it can pass through the layer, reflect, or absorb. If the energy of the landing photons is less than the band-gap, it passes while absorbs when it is higher than the band-gap energy.

As it can be seen from Fig. 3a, KCC-1 has the lowest UV light harvest, while its visible light absorption is almost zero. On the other hand, the UV light absorption for Ti(VI)-salen complex and Ti(IV)salen@NH<sub>2</sub>-KCC-1 is much higher than KCC-1, and for Ti(IV)-salen@NH<sub>2</sub>-KCC-1, visible light absorption can be seen to demonstrate the extension of light-responsive region. Therefore, light absorption efficiency improved with immobilizing Ti(IV)-salen complex on KCC-1.

Using the absorption coefficient,  $\alpha$ , the band-gap of thin layers can be studied with the help of the Tauc equation (Eq. 1).



Fig. 3 (a) UV–Vis, (b) DRS, and (c) PL analyses for KCC-1 and Ti(IV)-salen@NH $_2$ -KCC-1

$$\alpha h v = A \left( h v - E_g \right)^{1/m} \tag{1}$$

$$A(hv - E_g) = (\alpha hv)^m \tag{2}$$

where  $\alpha$ , *A*, *hv*, and  $E_g$  are absorption coefficient, constant amount, photon energy, and band-gap energy, respectively. For m = 0.5 or 2.0 (Eq. 2), there will be a direct or indirect transition type, respectively.

The band-gap energies obtained by extrapolating the linear part of the  $(\alpha hv)^m$  with the horizontal axis *hv* graph (m=2, see Fig. 3b) are  $E_g=4.04$ , 3.27, and 3.08 eV for KCC-1, Ti(VI)-salen complex, and Ti(IV)-salen@NH<sub>2</sub>-KCC-1, respectively (Dong et al., 2014). In addition, the conduction band (CB) and valence band (VB) positions of the Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst sample are calculated based on the Eqs. 3 and 4.

$$E_{CB} = X - E_e - 0.5E_g$$
(3)

$$E_{\rm VB} = E_{\rm CB} + E_g \tag{4}$$

X is electronegativity for compositions, which were obtained by Gaussian software. The kinetic energy of electrons,  $E_e$ , is the free-electron energy of the hydrogen which is usually 4.50 eV. For Ti(IV)salen complex, the obtained  $E_{CB}$  and  $E_{VB}$  were – 1.58 and 1.69 eV, respectively. For comparison, the  $E_{CB}$  and  $E_{VB}$  for KCC-1 were – 0.03 eV, and 4.01, respectively.

The HOMO and LUMO energies were also calculated by Gaussian software, and energies difference (i.e.,  $E_g$ ) was 3.93, 3.30, and 3.17 eV for KCC-1, Ti(IV)-salen complex, and Ti(IV)-salen@ NH<sub>2</sub>-KCC-1 which was in good agreement with the obtained  $E_g$  using the Tauc equation.

Also, to evaluate the separation efficiency of photo-generated  $e^-$  and  $h^+$  pairs, the photoluminescence (PL) analysis of KCC-1, salen ligand, Ti(VI)salen complex, and Ti(IV)-salen@NH<sub>2</sub>-KCC-1 was investigated (Fauzi et al., 2022; Y. Liu et al., 2014). As illustrated in Fig. 3c, the PL intensity of Ti(IV)salen@NH<sub>2</sub>-KCC-1 was lower than others which demonstrates more charge transfer efficiency preventing recombination of  $e^-$  and  $h^+$ . Therefore, loading of Ti(VI)-salen complex on KCC-1 improves Z-scheme photocatalyst mobility and reduces photo-generated carrier recombination which will be resulted in higher photocatalytic activity of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 (Fauzi et al., 2022; Y. Liu et al., 2014).

## 3.1.4 BET Analysis

Specific surface area and pore size distribution of the prepared Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst were measured using adsorption–desorption isotherm of nitrogen at 77 K. The BET unique surface area of KCC-1 was 1349 m<sup>2</sup> g<sup>-1</sup>, which means it is a suitable substrate for catalyst. After the addition of NH<sub>2</sub> to KCC-1, the achieved surface area was 854 m<sup>2</sup> g<sup>-1</sup>. Finally, the surface area for Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst was 326 m<sup>2</sup> g<sup>-1</sup>. The relatively high specific area of Ti(IV)salen@NH<sub>2</sub>-KCC-1 exhibits that chemical immobilization of Ti(IV)-salen on the KCC-1 surface has genuinely occurred.

#### 3.1.5 Morphology and Elemental Analysis

The surface morphology and elemental analysis of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 were characterized by HR-TEM, SEM, and EDX analysis. Figure 4a–f illustrates the surface morphology of the KCC-1 supported Ti(IV)-salen complex by SEM and HR-TEM.

As depicted in Fig. 4e, the lattice fringe image (d=19.7 Å) reaffirms the crystalline structure of Ti on the KCC-1 surface. These spacings between planes, which are clearly illustrated in Fig. 4d, e, are ascribed to the <101>, <210>, and <211> planes that are following the XRD patterns. These observations are enough to conclude that the Ti(IV)-salen complex was chemically bonded on the NH<sub>2</sub>@KCC-1 surface. The EDX spectrum (Fig. 5), shows the elemental composition (atomic percentage of Ti) for Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst that confirms the presence of Ti in the desired weight percent.

## 3.1.6 TGA Analysis

TGA analysis was conducted to study the thermal stability of Ti(IV)-salen@NH2-KCC-1 structure under nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup> over a temperature range of 40–900 °C (Fig. 6). As can be observed from Fig. 6, there is a weight loss of about 40% in the TGA curve at three stages. A slight weight change (7%) in the TGA curve of the photocatalyst indicates the presence of physically adsorbed solvents. The second 25% weight loss could have possibly pertained to the decomposition of Ti(IV)-salen@NH2-KCC-1, which starts after 100 °C, and the TGA curve descends swiftly up to 400 °C. This mass change is due to both disintegration of the salen group of the ligand and the complex and also the loss of the hydroxyl group from KCC-1. A slight weight loss (8%) is observed gradually from 400 to about 800 °C.



Fig. 4 SEM (a, b, and c), and HR-TEM (d, e, and f) images for the synthesized Ti(IV)-salen@NH<sub>2</sub>-KCC-1

## 3.1.7 XPS Characterization

The chemical environment and elemental composition studies of the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst were conducted by XPS analysis. As illustrated in Fig. 7, the survey scanning spectrum testifies the existence of C, O, N, Si, Cl, and Ti in the synthesized Z-scheme heterostructure photocatalyst in the  $Si_{2p}$ ,  $Cl_{2p}$ ,  $C_{1s}$ ,  $N_{1s}$ ,  $Ti_{2p}$ , and  $O_{1s}$  binding energy regions.  $Si_{2p}$  shows the peaks at 103.05 eV for O-Si-C (Bouhrara et al., 2013). The C-C, C=O, and C=N-C bonds appear clearly at 284.86 eV, and the Cl<sub>2p</sub> peak at 198.44 eV belongs to Ti-Cl (Cao et al., 2020). The peaks regarding N<sub>1s</sub> emerged at 399.7 and 398.45 eV for N-H and C = N-C, respectively, for Ti(IV)-salen@NH<sub>2</sub>-KCC-1 structure (Bouhrara et al., 2013). The  $O_{1s}$ peaks indicated at 530.9 and 530.9 eV for Ti-O-C and Si-O-C, respectively (Bouhrara et al., 2013). Also, Fig. 7 shows the high-resolution XPS data in the region of the Ti<sub>2p</sub> peaks, located at 464.43 and 458.65 eV, which corresponds to the  $2p_{1/2}$  and  $2p_{3/2}$  spin-orbit-split peaks of Ti(IV), respectively (Cao et al., 2020).

## 3.2 Photocatalytic Activity

To investigate the capability of the synthesized photocatalyst, the photocatalytic activity of Ti(IV)-salen@ NH<sub>2</sub>-KCC-1 was tested for DOX and TC photodegradation in the aqueous solutions containing 100 mg  $L^{-1}$  of these antibiotics. The initial experiments were performed under UV light and dark ambient to compare the adsorption and photodegradation properties of the synthesized photocatalyst.

As seen from Fig. 8, in the dark position (0-10 min), due to the adsorption property, less than 20% removal of DOX and TC was accomplished. In the presence of irradiation (20 min), exponential photodegradation was acquired, and the degradation reached about 80%. Also, the removal efficiencies were examined in the presence of KCC-1 and NH<sub>2</sub>-KCC-1. In the case of KCC-1, the removal efficiencies were approximately constant (Fig. 8). On the other hand, the removal efficiencies for NH<sub>2</sub>-KCC-1

**Fig. 5** SEM–EDX analysis of proposed Ti(IV)-salen@ NH<sub>2</sub>-KCC-1 nanocomposite



79 0

Ó

1.7





6.8

8.5

10.2

11.9

13.6

15.3

5.1

3.4



Fig. 7 XPS analysis for the synthesized Ti(IV)-salen@NH<sub>2</sub>-KCC-1 nanocomposite

were increased from 10 to 25%, which is pertaining to the H-bonding interactions. According to obtained results, the Ti(IV)-salen@NH<sub>2</sub>-KCC-1 has higher photodegradation properties under UV light compared with KCC-1 and NH<sub>2</sub>-KCC-1 (Fig. 8). Therefore, it seems that immobilization of Ti(VI)-salen complex onto the KCC-1 support has a significant impact on photodegradation properties.

## 3.3 Effect of ROS

In the present research, the presence of  $H_2O_2$  as ROS was used to probe the effect of reactive oxygen (T. Tan et al., 2003). The experiments were performed with and without  $H_2O_2$ , and as illustrated in Fig. 9, the  $H_2O_2$  showed high DOX and TC degradation efficiencies. When the  $H_2O_2$  was used, about 90% degradation efficiencies were obtained after 15 and 20 min for DOX and TC, respectively. Therefore, the presence of ROS can improve the DOX and TC

photodegradation processes, and  $H_2O_2$  was chosen for further experiments (Fig. 9).

## 3.4 Model Establishment and Analysis

Traditionally, one variable at a time is usually used for optimization, which requires much experimentation. This optimization method increases time and cost, and also does not consider the interaction of variables. On the other hand, multivariate methods provide fast and efficient tools for optimizing multiple variables at once. In this work, the CCD, which is a separate square design tool, was used. In addition, various variables, i.e., sample pH, Ti(IV)salen@NH<sub>2</sub>-KCC-1 dose, H<sub>2</sub>O<sub>2</sub> amount, and radiation time, have the most critical effects on the DOX and TC photocatalyst degradation. Therefore, their impact on degradation efficiencies as responses were probed using a CCD-based model. Finally, an analysis of variance (ANOVA) was performed and



Fig. 8 Effect of irradiation time on the DOX and TC degradations using KCC-1, NH<sub>2</sub>-KCC-1, and Ti(IV)-salen@NH<sub>2</sub>-KCC-1. Degradation process condition: photo-catalyst dose =  $2.5 \text{ mg mL}^{-1}$ , drug concentration =  $100 \text{ mg L}^{-1}$ , without H<sub>2</sub>O<sub>2</sub>



**Fig. 9** Effect of  $H_2O_2$  on the capability of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 in (**a**) DOX, and (**b**) TC degradations. Degradation process condition: photo-catalyst dose = 2.5 mg mL<sup>-1</sup>, drug concentration = 100 mg L<sup>-1</sup>,  $H_2O_2$  amount = 0.02% w/v

applied to evaluate the models. Due to the limited number of variables that must be optimized, the screening step was skipped, and CCD was applied directly. For k variables, the required run design points (N) were obtained by the following equation (Eq. 5):

$$N = 2^k + 2k + N_0 (5)$$

where k and  $N_{\rm o}$  represent the number of variables and the numbers of center point replicates, respectively. Using this formula, the number of experiments required was determined based on the CCD and randomized into three blocks (4 replicas in each block). Table S1 shows the appropriate range of parameters. The experiment was conducted based on the software design matrix. As the result of analysis of variance (ANOVA) and CCD analysis, the following coded quadratic polynomial models were achieved for DOX and TC degradation efficiencies (Eqs. 6 and 7). To avoid overlapping, the insignificant terms of the models were ignored based on the backward elimination in multiple regression.

TC degradation (%) =89.0 - 2.4A + 1.9B

+ 
$$12.4C + 3.1D - 2.4AD + 1.1BC$$
 (7)  
-  $2.7A^2 - 2.3B^2 - 6.1C^2 - 5.3D^2$ 

Positive and negative values for each model terms represent their effects on the efficiencies as responses. For both of investigated antibiotics, initial pH has negative impact on photodegradation, and photocatalyst dose,  $H_2O_2$  amount, and radiation time affect positively.

Table 1 The ANOVA for DOX and TC removal efficiencies using Ti(VI)-salen@NH2-KCC-1

Source	DOX					TC				
	SS <sup>a</sup>	df <sup>b</sup>	MS <sup>c</sup>	F value	p value	SS	df	MS	F value	p value
Block	86.24	2	43.12			93.16	2	46.58		
Model	5072.13	14	362.30	197.30	< 0.0001	4493.15	14	320.94	133.27	< 0.0001
А	120.74	1	120.74	65.75	< 0.0001	129.44	1	129.44	53.75	< 0.0001
В	102.32	1	102.32	55.72	< 0.0001	79.84	1	79.84	33.15	< 0.0001
С	3033.77	1	3033.77	1652.12	< 0.0001	2652.92	1	2652.92	1101.66	< 0.0001
D	280.45	1	280.45	152.73	< 0.0001	229.90	1	229.90	95.47	< 0.0001
AB	3.46	1	3.46	1.89	0.1856	0.4753	1	0.4753	0.1974	0.6619
AC	0.0058	1	0.0058	0.0031	0.9559	0.7705	1	0.7705	0.3200	0.5782
AD	61.52	1	61.52	33.50	< 0.0001	91.79	1	91.79	38.12	< 0.0001
BC	0.5840	1	0.5840	0.3180	0.5794	10.72	1	10.72	4.45	0.0484
BD	11.95	1	11.95	6.51	0.0195	7.03	1	7.03	2.92	0.1039
CD	29.78	1	29.78	16.22	0.0007	6.23	1	6.23	2.59	0.1243
$A^2$	237.35	1	237.35	129.26	< 0.0001	237.35	1	237.35	98.56	< 0.0001
$\mathbf{B}^2$	180.47	1	180.47	98.28	< 0.0001	167.46	1	167.46	69.54	< 0.0001
$C^2$	1294.76	1	1294.76	705.10	< 0.0001	1085.29	1	1085.29	450.68	< 0.0001
$D^2$	1030.53	1	1030.53	561.20	< 0.0001	890.87	1	890.87	369.94	< 0.0001
Residual	34.89	19	1.84			45.75	19	2.41		
LOF <sup>d</sup>	24.47	10	2.45	2.11	0.1377	31.04	10	3.10	1.90	0.1746
Pure error	10.42	9	1.16			14.72	9	1.64		
Cor total	5193.26	35				4632.07	35			

<sup>a</sup> Sum of squares

<sup>b</sup> Degree of freedom

<sup>c</sup> Mean square

<sup>d</sup> Lack of fit

The ANOVA results for DOX and TC photodegradation (Table 1) are based on F values, and the mean squares are used to estimate the effect of each parameter compared to residuals and the models. F values of 197.30 and 133.27 for DOX and TC exhibit statistical significance. For lack of fit, F values of 2.11 and 1.90 for DOX and TC indicate the validity of the quadratic model for the experimental data, confirming the insignificance of deleted terms.

The  $R^2$  values (i.e., 0.9924 and 0.9867) for DOX and TC degradations reflect the agreement between the experimental and predicted results. Furthermore, the predicted  $R^2$  (i.e., 0.9720 and 0.9521) have consented sensibly with the adjusted  $R^2$  (0.9885 and 0.9810), because their differences are less than 0.2. The normal probability of residuals (shown in Fig. S1) reflects an inconsiderable violation of the basic assumptions. As illustrated in Fig. S1, the residuals follow random distributions around zero in the plots of the residuals against the number of experiments which indicates the accuracy of the models. These good normal distributions of the results prove the validity of the assumptions and the independency of the earlier residuals.

The response surface plots of the models were utilized to consider the interactions between the variables and provide a visual overview of their effects on photodegradation. These three-dimensional plots show minor interaction between dose and time in the case of DOX and dose and H<sub>2</sub>O<sub>2</sub> amount for TC. Meanwhile, the pH-radiation time for both DOX and TC, and H<sub>2</sub>O<sub>2</sub> amount-radiation time for DOX confirm intense interactions, which were proved in the ANOVA table. On the other hand, the strong effect of the  $H_2O_2$  amount on the degradation efficiencies of both investigated antibiotics is also evident. The coefficients related to the H<sub>2</sub>O<sub>2</sub> amount term in the models are also confirmatory. Also, as could be observed from Figs. 10 and 11, the DOX and TC photodegradation efficiencies increase with decreasing sample pH and enhancing photocatalyst dose, the H<sub>2</sub>O<sub>2</sub> amount, and radiation time. It is clear that the last three variables have positive effects on the efficiency process. Nonetheless, the H<sub>2</sub>O<sub>2</sub> amount has an impressive effect, and the low effects of the photocatalyst dose and radiation time are apparent.

The photodegradation time of up to about 15 min has a cumulative effect on efficiency and then becomes constant. In contrast, the sample pH has a negative impact on photodegradation efficiencies. However, at pH values below 4.0, the efficiency is constant. At pH values less than 4.0, the hydrogen bonding between the DOX or TC and synthesized Ti(IV)-salen@NH<sub>2</sub>-KCC-1 probably has a pronounced effect. These interactions could increase the speed of catalytic degradation by elevating the antibiotics transfer rate from the bulk solution to photocatalyst surface. Although, lowering the pH generally involves introducing electrostatic interactions between the DOX and TC molecules and the photocatalyst according to the pH<sub>ZPC</sub>.

Regarding the  $H_2O_2$  amount, it is evident that by increasing the  $H_2O_2$  concentration, the photodegradation rate efficiently increases. This was assigned to the inhibition of  $e^-$  and  $h^+$  recombination at the semiconductor outer layer by acquiring a photoelectron formed from the conduction band and, therefore, elevating charge separation.

Finally, under the application of a non-linear optimization approach according to the Simplex algorithm, the optimum condition was found to be pH=3.6, photocatalyst dose=6.0 mg mL<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> amount=0.06% w/v, and radiation time=16 min to obtain maximum DOX and TC degradation efficiencies which predicted as 98.2 and 95.6%, respectively, for 100 mg L<sup>-1</sup> solution. These are in agreement with the experiments, which achieved  $95.4 \pm 5.1\%$  and  $96.7 \pm 4.2\%$ , showing excellent agreement between experiments and CCD models.

#### 3.5 Kinetic Studies

Under the defined optimal condition, the data obtained from DOX and TC photodegradation process was adapted to the zero-order (Eq. 8), pseudo-first-order (Eq. 9), and pseudo-second-order (Eq. 10) kinetic models following the linearized integrated equations.

$$C_0 - C_t = k_{\rm app} t \tag{8}$$

$$\ln\left(\frac{C_0}{C_t}\right) = k_{\rm app}t\tag{9}$$

$$\frac{1}{C_t} - \frac{1}{C_0} = k_{\rm app}t \tag{10}$$



Fig. 10 3D surface plots, illustrating the correlations between the input parameters and DOX photodegradation by Ti(IV)-salen@  $NH_2$ -KCC-1 nanocomposite



Fig. 11 3D surface plots, illustrating the correlations between the input parameters and TC photodegradation by Ti(IV)-salen@NH<sub>2</sub>-KCC-1 nanocomposite

Here,  $k_{app}$  is the apparent rate constant, the product of  $k_{obs}$  and  $K_{an}$ . Also,  $k_{obs}$  is the rate constant, and  $K_{an}$ is the adsorption–desorption equilibrium constant.  $C_0$ and  $C_t$  (mg L<sup>-1</sup>) are solution antibiotic concentrations at initial and time t. At predetermined optimum conditions, the kinetic photodegradation of DOX and TC under UV light was studied. Based on the Eqs. 8–10, the linearized plots for kinetics of DOX and TC photodegradation process using Ti(IV)-salen@NH2-KCC-1 are depicted in Fig. S2. As clearly illustrated, the pseudo-first-order kinetic model with  $R^2$  values of 0.9916 and 0.9930 for DOX and TC describes the photodegradation process thoroughly. Also, the  $k_{\rm app}$  values attained from the slope of the plots were 0.3411 and 0.1774 min<sup>-1</sup> for DOX and TC photodegradation, respectively. The  $k_{app}$  values show that the DOX photodegradation is about 2 times faster than TC degradation.

#### 3.6 Proposed Mechanism

As discussed in Sect. 3.2 and Fig. 9, photodegradation of DOX and TC was negligible in the presence of  $H_2O_2$  or Ti(IV)-salen@NH<sub>2</sub>-KCC-1, while in the presence of  $H_2O_2$  and Ti(IV)-salen@NH<sub>2</sub>-KCC-1 under irradiation, above 95% of these antibiotics photodegraded in only 16 min under UV light.

When the radiation energy is higher than the bandgap,  $e^-$  or  $h^+$  is formed in a semiconductor and can start heterogeneous photocatalysis reaction. In summary, the oxidation of DOX and TC over photocatalyst in an aerated aqueous solution could involve direct reactions with hydroxylradicals (OH<sup>•</sup>). The OH<sup>•</sup> can be formed by the reaction of the valence band holes ( $h_{VB}$ ) with adsorbed water ((H<sub>2</sub>O)<sub>ads</sub>) forming surface adsorbed OH<sup>•</sup> radicals ((OH<sup>•</sup>)<sub>ads</sub>) in chemical reactions. The rise in the reaction rate with increasing H<sub>2</sub>O<sub>2</sub> amount was also attributed to the increased concentration of hydroxyl radicals. The conversion of H<sub>2</sub>O<sub>2</sub> to OH<sup>•</sup> radicals was significantly accelerated under UV light irradiation (see Eq. 11).

$$H_2O_2 + e_{CB \text{ of } Ti(VI)-salen \text{ complex}}^- \rightarrow 20H^{\bullet}$$
 (11)

$$H_2O_2 + e_{CB \text{ of } KCC-1} \rightarrow 20H^{\bullet}$$
(12)

Also, the dissolved  $O_2$  in the reaction media can interact with conduction band electrons and produce  $O_2^{\bullet-}$ .

$$O_2 + e_{CB \text{ of } Ti(VI)-salen \text{ complex}}^- \to O_2^{\bullet-}$$
 (13)

However, when high concentrations of  $H_2O_2$  are used, the photodegradation efficiencies are almost flat because it may act as a hydroxyl radical scavenger reducing the number of radicals available for destroying the DOX and TC molecules (Eq. 14) (Monteagudo et al., 2005).

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O$$
(14)

Although, other radicals are formed, i.e.,  $HO_2^{\bullet}$ , their oxidation ability is much lower than the OH<sup>•</sup> species (Ramirez et al., 2005).

Based on the above description, the most probable photodegradation process could be described as following, which is shown briefly in Fig. 12.

- When Ti(IV)-salen@NH<sub>2</sub>-KCC-1 absorbs UV light, the VB electrons of both KCC-1 and Ti(VI)-salen complex, in the photocatalyst structure, are excited to their CB and donate holes on their VB.
- Excited electrons on CB of KCC-1 migrate to VB of Ti(IV)-salen complex via the Z-scheme route illustrated in Fig. 12.
- iii) Since the position of CB in Ti(IV)-salen complex (-1.58 eV) is lower than -0.13 eV, O<sub>2</sub> molecules reduce to HO<sub>2</sub><sup>•</sup> followed by generation of O<sub>2</sub><sup>•-</sup>. Also, the H<sub>2</sub>O<sub>2</sub> molecules reduce to HO<sup>•</sup> based on Eqs. 11 and 12.
- iv) Holes on the VB of KCC-1 (4.01 eV) are powerful enough for oxidizing H<sub>2</sub>O molecules and hydroxyl anions to OH<sup>•</sup> radicals, or directly oxidize the DOX and TC molecules.
- v) It is most probable that  $OH^{\bullet}$ ,  $O_2^{\bullet-}$ , and  $h^+$  contribute to photodegradation. The oxidizing ability of  $h^+$  on the VB of KCC-1 (4.01 eV) is applied fully because of  $e^-$  quenching by  $H_2O_2$ , and so it seems that the  $h^+$  contributes more in photodegradation.



Fig. 12 Schematic of proposed Z-scheme mechanism for DOX and TC photodegradation under UV light

## 3.7 Reusability Studies

The reusability of a photocatalyst is a critical feature that could be considered for long-term use that saves cost and energy. The reusability of the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 was examined by five repeated cycles of DOX and TC photodegradation under UV irradiation to verify the photocatalyst stability. At the end of each cycle, the photocatalyst used was collected with centrifugation, washed with DDW, dried at 80 °C, and reused for a new antibiotic photodegradation procedure. The reusability investigation results revealed that the photodegradation efficiencies remain above 80% (see Fig. 13a). This slight decrease in photodegradation can be attributed to the loss of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 in its collecting procedure. The results confirm that the proposed Z-scheme photocatalyst is attractive in wastewater treatment.

## 3.8 Photodegradation Studies on Real Samples

In order to prove the practical ability of the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst for DOX and TC degradation, tap water (Birjand, South Khorasan, Iran) and tailing stream of a pharmaceutical factory (Daropakhsh Pharmaceutical Chemical, Karaj, Tehran, Iran) were used as simulated real samples. It should be pointed out that no DOX and TC were found in both water and wastewater samples. Figure 13b shows the results of DOX and TC photodegradation from these real samples spiked with 50 Fig. 13 (a) Reusability tests of Ti(IV)-salen@  $NH_2$ -KCC-1, and (b) performance of Ti(IV)-salen@  $NH_2$ -KCC-1 in two real samples



and 100 mg L<sup>-1</sup> by Ti(IV)-salen@NH<sub>2</sub>-KCC-1, indicating that the developed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 has effectively degraded DOX and TC from these spiked water and wastewater samples. This suggests that the high content of various interfering species in real samples has no significant impact on photodegradation efficiencies, especially in the case of DOX. Therefore, the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst has great potential for application in water and wastewater processing.

# 3.9 Comparison with Other Reported Nanocomposites

In Table 2, the properties of the synthesized Ti(IV)salen@NH<sub>2</sub>-KCC-1 for the removal of DOX and TC are compared with other reported efficient nanocomposites (Chen et al., 2023a, 2023b; Han et al., 2022; Hemmat et al., 2021; Rahman & Raheem, 2022; Srivastava et al., 2022; Tian et al., 2023). The photocatalytic capability is the most crucial advantage of Ti(IV)-salen@NH<sub>2</sub>-KCC-1 compared to the reported adsorbents (Rahman & Raheem, 2022; Srivastava et al., 2022). As a result of catalytic degradation, DOX and TC contamination is removed from the environment, while in the case of adsorption removal, the reported substrates only adsorb antibiotics on the surface. Therefore, pollution is transferred from a large volume to a small volume.

Compared with the catalysts, as summarized in Table 2, the proposed Ti(IV)-salen@NH<sub>2</sub>-KCC-1 can simultaneously degrade 100 mg L<sup>-1</sup> of each DOX and TC in only 16 min, providing excellent photodeg-radation kinetics and unique properties (Chen et al., 2023a, 2023b; Han et al., 2022; Hemmat et al., 2021; Tian et al., 2023).

4	Conc	lusion	s
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In summary, a novel Ti(IV)-salen@NH<sub>2</sub>-KCC-1 photocatalyst was prepared, characterized, and proposed for the photodegradation of some model antibiotics. To track the step-by-step formation of Ti(IV)-salen@ NH<sub>2</sub>-KCC-1 photocatalyst, various characterization analyses were conducted, which proved the successful immobilizing of Ti(VI)-salen onto KCC-1. Ti(VI)-salen on fibrous KCC-1 photocatalyst provides an excellent photocatalytic activity for DOX and TC degradation under UV light. Different variables, which affected the photocatalytic activity of Ti(IV)salen@NH<sub>2</sub>-KCC-1 on DOX and TC degradation, were modeled by CCD and then optimized. Under the defined optimum condition, i.e., pH=3.6, photocatalyst dose = 6.0 mg mL<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub> amount = 0.06% w/v, and radiation time = 16 min, the DOX and TC photodegradation could be reached up to 99%. It should be stated that the underlying mechanism of DOX and TC degradation in this research is oxidation due to positive holes (h<sup>+</sup>) with maximum oxidation potential. It acts as a producer of hydroxyl radical on Ti(IV)salen@NH<sub>2</sub>-KCC-1 surface from water molecules and the generation of radical hydroxyl in a neutral solution. The studied kinetic models explained that the photocatalytic reactions follow the pseudo-firstorder equation showing surface reaction being the rate-determining step. The results of the present study provide a new method for the synthesis of a very novel photocatalyst with good reusability, and the extension of its practical usage in environmental remediation.

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Author Contribution FD: conceptualization, methodology, investigation, writing-original draft, writing-review and editing, visualization. AA: conceptualization, review and editing, supervision, funding acquisition. AA: conceptualization, review and editing, advisor.

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Data Availability All data generated or analyzed during this study are included in this manuscript.

Code Availability Not applicable.

**Table 2** Comparison of Ti(VI)-salen@NH<sub>2</sub>-KCC-1 with other renorted nanocomposites in DOX and TC removing

•	1				)		
Antibiotic	Nanocomposite	Removal mecha- nism	Hq	Dose (mg mL <sup>-1</sup> )	Initial con- centration $(mg L^{-1})$	Time (min)	Ref
TC	Birnessite	Photocatalytic	8.0	0.67	50	30	(Chen et al., 2023a, 2023b)
TC	Ce/Fe	Catalytic	7.0	2.0	10	60	(Han et al., 2022)
TC	Graphene oxide@Fe-Cu-Ag	Catalytic	2.0	3.0	50	30	(Hemmat et al., 2021)
DOX	Schwertmannite	Catalytic	2.0	1.6	20	120	(Tian et al., 2023)
DOX	Graphene oxide/Mg-Zn-Al	Adsorptive	8.0	1.5	100	06	(Rahman & Raheem, 2022)
DOX	Iron modified wood biochar	Adsorptive	7.0	1.0	20	60	(Srivastava et al., 2022)
DOX & TC	Ti(VI)-salen@NH2-KCC-1	Photocatalytic	3.6	6.0	100	16	This work

#### Declarations

**Ethical Approval** This article does not contain any studies with human or animal subjects.

Consent to Participate Not applicable.

**Consent for Publication** The authors hereby consent to the publication of the work.

**Conflict of Interest** The authors declare no competing interests.

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