Efficient degradation of doxycycline and ofloxacin in an aqueous environment using Fe and Cu doped TiO₂-SiO₂ photocatalyst under sunlight

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ABSTRACT

Several drugs have sparked interest as potential COVID-19 treatment options. Doxycycline (DOX) has been widely used with other potential agents to reduce COVID-19-induced inflammation. DOX and OFLX, both well-known antimicrobial and anti-inflammatory drugs, were chosen as model pollutants. Fe, Cu-codoped TiO₂-SiO₂ was synthesised as a novel photocatalyst active under sunlight irradiation to treat model pollutants. The synthesised catalyst samples were meticulously characterised using various techniques to evaluate their morphological, optical, and structural properties. The results of BET analysis showed that the TSFC1 sample has a large specific surface area of 288 m²g⁻¹. Maximum degradation of DOX and OFLX (about 98%) was achieved with the TSFC1 catalyst. The photocatalytic reusability was investigated for up to seven successive cycles, and the composite particles maintained their high photodegradation activity for DOX and OFLX. TSFC1 composite, in particular, demonstrated high catalytic activity as well as excellent recovery potential, and its combination with solar light, silica, and dopants can be introduced as a promising strategy for efficiently destroying both DOX and OFLX antibiotics. This study highlights the feasibility of hybridising doped dual semiconductor nanostructures in implementing solar light-powered pharmaceutical wastewater degradation.

Keywords: Doping, Doxycycline, Nanoparticles, Ofloxacin, Photocatalysis, TiO₂-SiO₂

1. Introduction

The presence of pharmaceutical contaminants within water sources is a serious matter of concern worldwide. Among all the categories of pharmaceuticals, antibiotics hold importance due to their widespread use in animals and humans. The estimated worldwide average antibiotic consumption is more than 100 × 10⁶ kg every year [1]. Even at trace concentrations (ngL⁻¹) from industries and municipal wastewater, antibiotic residues may cause the proliferation of bacteria with antibiotic-resistant and thus threaten human health and degrades water quality. Out of the various antibiotics, DOX and Ofloxacin (OFLX) are well-known for their antimicrobial and anti-inflammatory capabilities [2]. In the class of antibiotics, Doxycycline (DOX) and Ofloxacin (OFLX) are also recognised as highly refractory and persistent in aquatic water systems. SARS-CoV-2 (COVID-19) pandemic, which has killed

and infected people in 216 countries/territories, has become the most significant pandemic of the century [3]. More than 1.5 Lakhs people are infected daily in India, and more than 1.5 Lakhs people are also recovering. The Medical Council of India (MCI) prescribed doxycycline (DOX) as the best antibiotic for the COVID-19 cure. DOX, a tetracycline antibiotic, combined with other drugs, has been widely used to minimise COVID-19-induced inflammation in 2020 [3]. So, of a sudden, the demand and production of DOX have increased many folds. Due to the high consumptions, there are many chances that DOX will come in effluent treatment through the urinal of COVID-19 patients.

Furthermore, this will also come in wastewater of pharmaceutical industries, which are producing DOX antibiotics. These compounds can enter water resources through various channels, including human waste and inefficient industrial wastewater treatment [4]. DOX is also used to treat chest, skin, and dental infections,

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whereas OFLX is used to treat pneumonia, skin, and urinary tract infections. These pharmaceutical compounds enter water resources in various ways, such as human and animal excretions and inefficient industrial wastewater treatment [4]. They also enter the environment due to the improper disposal of expired pharmaceuticals in the garbage or sewage system.

The traditional methods for treating such wastewater like coagulation, flocculation, or precipitation lacks efficiency and cannot remove them completely [5-7]. On the other hand, biological treatments are time-consuming and produce a large quantity of sludge that cannot be used further [8]. However, most of these technologies have been reported to have drawbacks such as low efficiency, secondary pollution, and high capital costs. As a result, it is necessary to develop practical technologies based on modern world engineering science to find a better and more cost-effective solution to treat water and wastewater for human consumption. In recent years, advanced oxidation processes (AOPs) have piqued the interest of many researchers due to their potential application in the efficient mineralisation of refractory substances [9], more effective and sustainable in the long term [10, 11]. This technology uses potent oxidising agents (O_3 , H_2O_2) and/or catalyst (TiO_2 , ZnO) in the presence of irradiation sources generating highly reactive hydroxyl radicals ($\bullet OH$), which can mineralise organic compounds that are present in industrial effluents [5].

Among various advanced oxidation processes (AOPs), heterogeneous photocatalysis, using semiconductor materials like TiO_2 nanomaterials as the photocatalyst, appears to be the most efficient technology. The main advantage of the photocatalytic process is its inherently non-hazardous nature: it can be carried out under optimal conditions and leads to complete mineralisation of organic carbon into carbon dioxide [12]. TiO_2 serves as an efficient photocatalyst for air and water purification; its strong oxidation activity and super hydrophilicity can be used as an antibacterial agent [13]. TiO_2 shows relatively high chemical stability and reactivity under ultraviolet light ($\lambda < 387$ nm) but have several practical issues like low catalytic activity under solar light due to the high recombination rate of electrons and photons and the wide energy band gap (3.2 eV for anatase phase) [13-15], secondary pollution production, difficult recovery, aggregation and accumulation of catalyst particles, and the use of excessive amounts of materials and energy [16]. However, a single semiconductor photocatalyst cannot usually perform the transformations satisfactorily in light absorption, efficiency, and selectivity, among other things [17, 18]. Bashiri et al. [12] synthesised graphene decorated TiO_2 for catalytic degradation of metronidazole under visible light and achieved a maximum surface area of $55.04 \text{ m}^2\text{g}^{-1}$. Babaei et al. [11] synthesised FOCT/UV/PS hybrid system to remove 4-chlorophenol, demonstrating catalyst reusability up to five consecutive cycles. The development of novel catalysts with high-efficiency photocatalytic performance under sunlight is significant for removing pharmaceutical compounds and further improving pilot photocatalytic performance [19]. Mesoporous composites have been proposed as a more efficient photocatalyst due to their ordered porous structure, eco-friendliness, larger surface area and pore volume, resulting in an increase in active surface sites and improved mass transport [20]. To address these issues, various approaches have been taken, such as surface modification of TiO_2 by incorporating

defects, adding oxygen vacancies, and/or Ti^{3+} using different treatment methods [21], phase structure modulation of TiO_2 (ratio of anatase and rutile) [22] and doping TiO_2 with different transition metals/non-metals [23]. The annihilation of aggregation and improvement of light absorption is an important approach for extending the application of TiO_2 .

In light of this, preparing TiO_2 and supporting/loading an absorbent such as silicon dioxide could be a useful measure [23]. Silica is one of the most efficacious agents combined with TiO_2 because it reduces the bandgap, enhances its specific surface area, and prevents photocatalyst transformation from anatase to rutile phase in the prepared photocatalysts [24]. The accumulation of SiO_2 into TiO_2 lattice increased the degradation activity of rhodamine-6G three times compared to unmodified TiO_2 [25]. Islam et al. [26] reported TiO_2/SiO_2 hybrid nanoparticle films prepared using the sol-gel method that resulted in a less aggregated and homogeneous surface. The addition of SiO_2 enhances the photoactivity and surface area of titanium dioxide. Wang et al. [27] synthesised TiO_2/SiO_2 mesoporous nanocomposites for photocatalytic degradation of arsenic and achieved a maximum surface area of $58 \text{ m}^2\text{g}^{-1}$. Zhang et al. [28] formulated TiO_2-SiO_2 composite with a mesoporous structure, better anatase phase and thermal stability [20]. Like TiO_2 , however, the photocatalyst TiO_2-SiO_2 can only be excited under UV light because the energy of the TiO_2 bandgap is 3.2 eV. Therefore, a growing interest in modifying TiO_2-SiO_2 mixed oxides by doping to improve their visible and solar photocatalytic performance.

Transition metals have received considerable attention in photocatalysis due to their physicochemical properties [15, 29, 30]. As a result, doping TiO_2 with transition metal is an effective and commonly used method for extending light response and preventing recombination of photo-generated electron-hole pairs, resulting in outstanding photocatalytic performance [31]. Concerning the latest approach, Cu and Fe have been reported widely to be the most enticing for this objective [22, 32, 33] and has shown exemplary behaviour, in both the UV and visible light illumination, in degrading environmental pollutants [34], NO_x removal [35], CO_2 reduction [36], and lately, in water splitting for hydrogen production [32, 37]. TiO_2 doped with metal ion species improves the electron-hole recombination rate and decreases its bandgap energy by generating shallow charge-trapping centres into TiO_2 lattice [38]. TiO_2 doped with metal ion species improves the electron-hole recombination rate and decreases its bandgap energy by generating shallow charge-trapping centres into TiO_2 lattice which, results in enhancement of its photocatalytic activity, which results in enhancement of its photocatalytic activity. [39] synthesised P-doped TiO_2-SiO_2 , phosphate modification enhanced charge separation and increased specific surface area. [40] prepared exhibited the highest pore volume and visible-light-driven photocatalytic degradation efficiency for the pollutant Rhodamine B. Li, Qiu et al. [41] synthesised S-Bi-F- TiO_2/SiO_2 catalyst for degradation of acrylonitrile. They achieved a lower bandgap with increased utilisation of the visible light. [42] fabricated $BiOBr/FeWO_4$ composite and achieved maximum degradation of 90% of DOX in 1h under visible light. [43] constructed a system of $\alpha-Bi_2O_3/g-C_3N_4$ coupled with H_2O_2 and achieved maximum degradation of 80% of DOX in 30 min under visible light.

The main focus of this research is to degrade DOX (the most prescribed antibiotic in the treatment of COVID-19) using the novel method, i.e., $\text{TiO}_2\text{-SiO}_2$ based photocatalysis. This study also found that the physio-chemical properties of $\text{TiO}_2\text{-SiO}_2$ (like lower specific surface area, lower bandgap, the poor separation efficiency, and recyclability limit associated with the powder form of the TiO_2 catalyst) were also improved. Furthermore, to overcome the concerns for the activation under visible light and solar light, the $\text{TiO}_2\text{-SiO}_2$ photocatalyst was doped and codoped with iron and copper metal ions. This work will help in the advancement of ongoing efforts to prepare modified photocatalysts to enhance their solar light activity. This study proposes a water purification strategy that is efficient, clean, and recyclable for removing antibiotic contaminants. This research article includes the complete characterisation of synthesised catalyst and degradation efficiency like kinetic study, scavenger study, hydroxyl radical study, TOC study (for complete mineralisation).

2. Materials and Methods

2.1. Chemicals

All of the chemicals used in this study were of analytical grade and were not purified further. The materials used are Titanium tetra isopropoxide (TTIP), and Tetraethylorthosilicate (TEOS), which were purchased from Sigma-Aldrich, absolute ethanol, Hydrochloric acid, Copper nitrate, and Ferric nitrate were bought from LOBA Chemie, Mumbai and used as a source of Fe and Cu. Doxycycline (DOX) and Ofloxacin (OFLX) were kindly supplied from nearby industries. Double-distilled water was used in all of the experiments.

2.2. Synthesis of Doped and Codoped TiO_2 Nanoparticles

The following steps were taken to synthesise doped and codoped TiO_2 nanoparticles: A 0.01 mol of TTIP ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$) was gradually added into 40 mL of ethanol under vigorous stirring until a translucent sol named as 'A' was obtained. The appropriate amount of dopant solutions of copper nitrate ($\text{Cu}(\text{NO}_3)_2$) and Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were prepared with ethanol ($\text{C}_2\text{H}_5\text{OH}$), hydrochloric acid (HCl) and distilled water. The prepared dopant solution was added to prepared sol 'A' to yield doped and codoped TiO_2 nanoparticles. The gel was kept for 24 h before being dried in an oven at 100°C for 6 h. The samples were dried before being crushed into powder with a mortar pestle and calcined at 350°C .

2.3. Synthesis of Doped and Codoped TS Nanoparticles

The synthesis of doped and codoped TS nanoparticles was carried out as follows: TEOS ($\text{SiC}_8\text{H}_{20}\text{O}_4$) precursor for silica was added under constant magnetic stirring to 20 mL of ethanol to obtain a translucent sol named 'B'. The above prepared doped and codoped TiO_2 nanoparticles were added to the sol 'B' in different ratios, followed by the addition of hydrochloric acid, distilled water and kept on stirring overnight. The obtained gel was dried in the oven at 100°C for 5 h. The sample dried in the oven was calcined in a muffle furnace at 800°C for 2 h. The resulting doped samples

$\text{TiO}_2\text{-SiO}_2\text{-Fe}$ 1%, $\text{TiO}_2\text{-SiO}_2\text{-Fe}$ 2%, $\text{TiO}_2\text{-SiO}_2\text{-Fe}$ 3%, $\text{TiO}_2\text{-SiO}_2\text{-Cu}$ 1%, $\text{TiO}_2\text{-SiO}_2\text{-Cu}$ 2% and $\text{TiO}_2\text{-SiO}_2\text{-Cu}$ 3% were named as TSF1, TSF2, TSF3, TSC1, TSC2, and TSC3. The resulting codoped samples $\text{TiO}_2\text{-SiO}_2\text{-Fe, Cu}$ (0.5, 1.5)%, $\text{TiO}_2\text{-SiO}_2\text{-Fe, Cu}$ (1.5, 0.5)%, and $\text{TiO}_2\text{-SiO}_2\text{-Fe, Cu}$ (1, 1)% were named as TSFC1, TSFC2, and TSFC3. A preparatory schematic has been added in supplementary as Fig. S1 to help you understand the process.

2.4. Assessment of Photocatalytic Activity

For comparison, the photocatalytic experiments were investigated under visible, UV, and solar light (on sunny days). The prepared doped and codoped TS nano photocatalyst were used in the photocatalytic degradation of DOX and OFLX (model compounds). Photocatalytic experiments were performed in a shallow pond slurry reactor made of borosilicate glass, measuring 5 cm in height and 10 cm in diameter, with a capacity of 250 mL and continuous magnetic stirring (150 rpm). The stock solution of each DOX and OFLX were made in distilled water ($20\text{ mg}\cdot\text{L}^{-1}$). The 100 mL of each DOX and OFLX solution was used for all the slurry experiments. In a typical photocatalytic experimental run, weighed amount of each doped and codoped photocatalyst with different dopant concentrations were transferred to the batch reactor, respectively. Magnetic stirring was employed to ensure that the catalyst was evenly dispersed. The pH value of the OFLX solution was altered using 0.1 M of HCl and NaOH solution. The blank solution was kept aside to note the zero-time reading. Aliquots of 5 mL of each sample were taken at different time intervals, filtered using micro syringe filters, and centrifuged to remove catalyst particles. The concentration of DOX and OFLX was measured continuously using a UV-Vis spectrophotometer with a wavelength range of 175-900 nm (L850, Perkin Elmer). As a UV light source, the eight UV tubes, 16 W each with wavelength (365 nm), were kept positioned parallel to the reactor and visible light, a total of 100 small led bulbs of 1.5 W each with wavelength (450 nm) were used.

2.5. Identification of Reactive Intermediate Species

Radical trapping experiments were conducted to assess the contribution of $\bullet\text{OH}$ radicals, h^+ , O_2 , and $(\bullet\text{O}_2^-)$ generated during solar light irradiation. t-Butanol was added to the solution to recognise hydroxyl radicals ($\bullet\text{OH}$) influence. To evaluate the participation of holes, potassium iodide (KI) was added, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was added as an e^- scavenger, benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$) and sodium azide (NaN_3) were added $\bullet\text{O}_2^-$ and O_2 scavengers. Throughout the experiments, the concentration of scavenging agents remained constant ($0.5\text{ mol}\cdot\text{L}^{-1}$) [20].

2.6. Instrumentation

The prepared catalyst samples were characterised using different techniques. The surface properties of the synthesised photocatalysts were characterised using a Field emission scanning electron microscope (FESEM) (Nova NanoSEM 450) equipped with energy dispersive X-ray for elemental composition (EDX, Bruker Nano GmbH). The sample's crystal phase arrangement was characterised with X-ray diffractometry (XRD) using $\text{Cu-K}\alpha$ radiations (Smart Lab 9 kW rotating anode x-ray diffractometer) crystalline

phases correlated with standard ICSD file. To identify the chemical compositions and bond structure of the prepared catalysts, Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer SPECTRUM GX) was used. The photocatalysts optical band gap was evaluated using Diffused reflectance spectroscopy (DRS) (Shimadzu UV-1900i). A UV-Visible spectrophotometer (Agilent Technology-Cary-60) was used to determine the extent of degradation of DOX and OFLX. The nanoparticles' size and structure were estimated using a High-Resolution Tunnelling electron microscope (HRTEM) (CM10 Philips). Raman spectroscopy (RS) was carried out using (Horiba Lab RAM HR evolution) for phase determination of the prepared catalyst. The prepared samples' photoluminescence (PL) emission spectra were measured using an Agilent Technology-Cary Eclipse. The pore size distribution was determined using Barrett-Joyner-Helenda (BJH) plot, and the physical solid surface was assessed using N₂ adsorption-desorption (Brunauer-Emmett-Teller (BET)) isotherms at 77 K using a quantachrome analyser (Autoabsorb iQ).

3. Results and Discussions

3.1. Characterisation

3.1.1. XRD analysis

The characteristics of as-prepared TS and TSFC1 were investigated using X-ray diffraction analysis, as shown in Fig. 1(a). The anatase phase is the most active between the three polymorphs of TiO₂ in photocatalysis [44]. The resulting diffractogram showed consistency with the Inorganic Crystal Structure Database (ICSD) 01-084-1286 and 01-089-0553 for anatase and rutile TiO₂ structures, respectively. Titanium dioxide crystal showed a peak pattern with

peaks at $2\theta = 25.3^\circ, 37.8^\circ, 48.07^\circ, 55.1^\circ, 62.7^\circ, 68.8^\circ, 70.3^\circ$, and 74.1° might belong to (101), (004), (200), (211), (204), (116), (220), and (206) crystal planes of anatase phase respectively. Furthermore, peaks at $27.4^\circ, 36.1^\circ, 41.2^\circ, 44.05^\circ$, and 54.3° denotes to (110), (101), (111), (210), and (211) planes of the rutile phase. An additional peak at 23.7° , which was ascribed to the (011) amorphous SiO₂ phase, was determined for both TS and TSFC1 composites. However, an increase in anatase phase content was observed for TSFC1 compared to the unmodified TS sample. Also, careful analysis of the prominent peak (101) of the anatase and (110) of the rutile (inset Fig. 1(b) and (c)) stated a slight shift to the higher angle of the anatase peak and a slight shift to the lower angle of the rutile peak, especially for the TSFC1 catalyst. It has previously been reported that metal doping disrupts the arrangement of TiO₂ octahedral units in the rutile structure and disrupts the overall crystallite structure [33]. This observation indicates lattice distortion in both anatase and rutile structure by incorporating dopants, which may have decreased the crystallite size [45]. Moreover, a careful examination of the XRD profiles shows no hint of Fe and Cu characteristic peaks, suggesting that dopants were doped in the lattice of the crystal structure [33]. The anatase/rutile phase ratio has been shown in Table S1. This indicates that the addition of dopants plays influences the formation of TiO₂ anatase and rutile phases. At the same calcination temperature (800°C), 80% TiO₂:20% SiO₂ showed an appropriate amount of SiO₂ that could effectively suppress the rutile phase ratio. Furthermore, the crystallite size was evaluated using the Debye-Scherrer equation [46]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Where θ is Bragg angle, λ is the X-ray wavelength, D is the

Fig. 1. XRD patterns of as-prepared (a) TSFC1 and TS catalyst calcined at 800°C (b) and (c) shows the shift in anatase (101) and rutile (110) peak.

average crystallite size, and β is the half-width full maximum (HWHM) of the prominent peak anatase or rutile phases. Eq. (1) reveals that the average crystallite size in both TS and TSFC1 was around 25 and 21 nm, respectively. The crystallite size of the TSFC1 composite decreased as compared to TS due to the addition of dopants. This would be due to the formation of complexes between Fe, Cu, and Ti atoms, which efficiently repressed the agglomeration and growth of titanium dioxide particles [47].

3.1.2. FESEM and EDS analysis

Field emission scanning electron microscopy (FESEM) analysis was carried out to determine the prepared catalyst's surface morphology, as illustrated in Fig. 2(a) and (b). Unmodified TS photocatalyst exhibits large irregular particles (Fig. 2(a)). However, Fe and Cu codoped TiO₂-SiO₂ (TSFC1) formed a microsphere structure of uniform size. The particle size was reduced with Fe and Cu doping, which can be attributed to Fe and Cu ions, which constrain grain growth by providing distinct boundaries [48].

The qualitative analysis with Energy Dispersive X-ray Spectroscopy (EDS) was performed to determine the composition and elemental identification of TSFC1. This analysis is based on the X-ray radiations emitted by the atoms in the sample. The

EDS pattern and the elemental map of TSFC1 illustrated in Fig. 2(c)-(h) show that Ti, Si, O, Fe, and Cu were distributed uniformly in the catalyst samples. The weight percentage of Ti, Si, O, Cu, and Fe in TSFC1 was found to be 44.31%, 7.45%, 46.9%, 1.02%, and 0.32%, respectively. This results in a good agreement with the weight ratio of TSFC1 (TiO₂ = 80%, SiO₂ = 20%, Fe = 0.5%, and Cu = 1.5%), which confirms the consistency with designed ratio and actual ratio.

3.1.3. HRTEM analysis

The high resolution TEM images further illustrate the fine morphology and crystallinity of TSFC1, composed of several small nanoparticles. According to Fig. 3(a) and (b), the average particle size is around 20 nm. Moreover, as shown in Fig. 3(c), the SAED pattern indicates distinct rings, corresponding to the high crystallinity of TSFC1. The computed d-spacing values agreed within reasonable limits with the reported d-spacing values for anatase and rutile TiO₂ phases in ICPSD 01-084-1286 and 01-089-0553, respectively. The FESEM and HRTEM analysis of the synthesised photocatalyst showed that the presence of Fe and Cu ions improves photocatalyst dispersion, resulting in more active sites and surface area. The increased photocatalyst dispersion and thermal stability

Fig. 2. FESEM images of (a) TS (b) TSFC1, (c)~(g) corresponding elemental mapping, and (h) EDS of TSFC1.

Fig. 3. (a), (b) HRTEM images and (c) SAED pattern of TSFC1.

can be attributed to a smaller particle size of the anatase phase and the defects formation on the surface of TSFC1. The interplanar distancing and their respective planes show that Fe and Cu are appropriately doped, and these results agree well with the XRD results [49].

3.1.4. UV DRS analysis

The optical properties of TSFC1 and TS catalyst were determined using UV-Vis spectra analysis. When the semiconductor material is exposed to photons with an energy greater than its band gap, the electron in the valence band (VB) is transferred to the conduction band (CB). Therefore, we observe an increase in absorption at the corresponding wavelength (λ). It should be noted; however, that absorption is calculated by low and high energy when the photon energy is higher than the bandgap (E_g) of the semiconductor; absorption increases linearly with an increase in photon energy [50]. While the photon energy is lower than E_g , the observed absorption diverges from linearity and showcases photonic absorp-

tion corresponding to the defect levels between the sample's CB and VB. The energy bandgap of the catalyst was evaluated as the Kubelka-Munk (KM) function [50]:

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

Where R here represents the absolute reflectance of the sample

Fig. 4(a) shows the absorption spectra and bandgap estimation of TS and TSFC1 as a KM function plot vs energy (eV). The tangent line is drawn along the spectra's slope, which extrapolates to the horizontal axis provides the band gap value E_g . The prepared samples' band gap energy was found to be 3.01 eV and 2.86 eV, respectively, for TS and TSFC1. Fe and Cu codoping observed a substantial narrowing of the bandgap and an extensive absorption edge in the spectrum's visible region. The increase in visible light absorption increased the separation of electron-hole pairs at heterojunctions during the photocatalytic process [51].

Fig. 4. (a) DRS spectra of TSFC1 and TS, TSC2, TSF2 (inset) (b) FTIR spectra of TSFC1, TSF2, TSC2 and TS.

3.1.5. FTIR analysis

The bonds formation and structural changes of as-prepared photocatalysts were characterised using FTIR spectrum in the range of $4,000\text{--}400\text{ cm}^{-1}$. The FTIR spectra of the TS, TSF2, TSC2 and TSFC1 samples are shown in Fig. 4(b). The dominant and strong absorption peak found in wavenumber $1,080\text{--}1,100\text{ cm}^{-1}$ is the Si-O-Si bond's asymmetrical stretching [52]. The peak around $1,600\text{--}1,650\text{ cm}^{-1}$ and $3,400\text{--}3,460\text{ cm}^{-1}$ denotes the bending and stretching vibration of the O-H bond of molecular water. All nanoparticles have been prepared in an aqueous solution, so O-H bonds are expected due to the surface hydroxyl group, and the hydroxyl ion content is essential for photocatalysis. The holes resulting from photogeneration on the catalytic surface react with hydroxyl ions to form $\bullet\text{OH}$ radicals strong oxidants [53]. The FTIR spectrum of TS, TSF2, TSC2, and TSFC1 shows broad peaks at $608\text{--}668\text{ cm}^{-1}$ assigned to Ti-O and Ti-O-Ti bonds, respectively [53]. Interestingly, for the doped and codoped $\text{TiO}_2\text{-SiO}_2$ nanoparticles, a shift from this band position to a lower wavenumber was observed, indicating the presence of a structural defect. [54, 55]. We believe that this band shift was responsible for forming Cu-O and Fe-O bonds following the incorporation of Ti^{4+} with Fe^{3+} and Cu^{3+} within the TiO_2 matrix, aligned with the XRD results [55]. The prepared catalysts contained a typical titanium dioxide and silica band, indicating that catalyst formation was successful. All of the prepared samples showed O-H bending and stretching vibrations. The appearance of Ti-O-Si bonds in the IR spectrum at $950\text{--}970\text{ cm}^{-1}$ has been used to characterise the formation of TS composites [56]. Furthermore, due to their low weight percentages, no other significant peaks corresponding to doped or codoped metal oxides were observed. Table S2 shows the types of bonds present in TS, TSF2, TSC2, and TSFC1 catalyst. The Ti-O-Si vibrational peak in all of the synthesised samples indicated that the interaction in TiO_2 and SiO_2 was a chemical reaction process rather than a simple physical mixing process.

3.1.6. BET analysis

The N_2 desorption/adsorption isotherms of the synthesised samples are depicted in Fig. 5. Besides, the BJH pore size distribution curves TS and TSFC1 from the adsorption branch are shown in

the insets of Fig. 5(a) and (b), indicating their mesoporous structure. The surface area of the prepared nanocomposites with and without the dopants are tabulated in Table S1. The isotherms of the TS and TSFC1 catalyst are type IV with a hysteresis loop type H_2 supporting good connectivity between the pores and numerous mesopores in the bulk phase of TS and TSFC1 according to the IUPAC classification [57]. It was found that the TS had six times larger surface ($275\text{ m}^2\text{g}^{-1}$) than that of the TiO_2 ($46.77\text{ m}^2\text{g}^{-1}$) as reported in the literature [58]. This implies that adding TiO_2 to SiO_2 increased its surface area. When Fe and Cu were doped into the composite, the surface area of the TSFC1 ($288\text{ m}^2\text{g}^{-1}$) was found to be slightly more significant than that of the TS catalyst. This increase in the surface area provided more adsorption sites for the reactants, promoting photocatalytic activity. These specific surface area values indicate that the photocatalytic material was effectively dispersed in the translucent silica matrix [48].

3.2. Photocatalytic Performance

3.2.1. Preliminary experiments

The set of experiments were performed to study the impact of darkness, catalyst, and light on DOX and OFLX degradation when used individually and in combinations, as shown in Fig. S6 (a)-(b). It was found out that individual treatment could not yield effective degradation results. The percentage decrease (9% and 8%) in the concentration of DOX and OFLX during the studies under the dark conditions (TS and TSFC1 only) was due to the contaminant adsorption onto the catalyst surface [1]. The formation of contaminant monolayer on the surface of the catalyst may have occupied all its active sites, and therefore no more adsorption was observed. It was determined that the combination of TSFC1 and solar light resulted in significant degradation of DOX and OFLX ($20\text{ mg}\cdot\text{L}^{-1}$) over 15 and 20 min. Hence, preliminary experiments clearly illustrate the requirement of efficient treatment for the complete degradation and mineralisation of both compounds.

3.2.2. Comparison study of doped and undoped TS catalyst under solar light

The degradation of DOX and OFLX have been studied with only

Fig. 5. N_2 adsorption /desorption isotherm of (a) TS (b) TSFC1 (inset BJH pore distribution curve)

TS and codoped TS photocatalyst. The DOX and OFLX (initial concentration $20 \text{ mg}\cdot\text{L}^{-1}$) were allowed to undergo photocatalytic treatment for 15 and 20 min using optimum catalyst concentration ($0.1 \text{ g}\cdot\text{L}^{-1}$) and pH (5.6 & 5 for DOX and OFLX), respectively. It has been observed (Fig. S7(a)) that 98% of OFLX and 98.6% of DOX were degraded in 15 and 20 min, respectively, using Fe, Cu- codoped TS (TSFC1) photocatalyst under natural solar irradiation. Only (20%) of OFLX and (24%) of DOX were degraded using TS photocatalyst, which showed that the introduction of metal dopant into the crystal lattice increased the efficiency and lowered the bandgap energy of TS photocatalyst.

3.2.3. Effect of UV/visible/solar light irradiation

Effect of UV, visible and solar light irradiation for the photocatalytic degradation of OFLX and DOX using $0.1 \text{ g}\cdot\text{L}^{-1}$ TSFC1 catalyst dose, initial concentration ($20 \text{ mg}\cdot\text{L}^{-1}$) and pH (5 and 5.6 for OFLX and DOX), respectively are presented in (Fig. S7(b)). The photocatalytic degradation of DOX and OFLX was higher under solar light than UV and visible light. The maximum degradation of OFLX under UV, visible, and solar light after 20 minutes of reaction time with TSFC1 was 20%, 42.2%, and 98%, respectively. Maximum DOX degradation under visible, UV and solar light were found to be 24%, 45.6%, and 98.6% after 15 min of reaction time using TSFC1.

3.2.4. Effect of dopant concentration

Metal-dopant concentration plays a pivotal role in photocatalytic activity. As shown in Fig. 6(a)-(b), the dopant metal concentration was varied from 1 to 3% by weight. A doping concentration of 2% by weight resulted in the greatest photocatalytic degradation. Increasing the dopant concentration above 2% by weight corresponds to a reduction in degradation efficiency. At lower concentrations, metal ions begin to act as trapping centres for photo-generated (h^+) and/or (e^-) within the titania bandgap, thereby increasing the recombination period of e^-/h^+ pairs. These initially trapped charges may migrate to the semiconductor's surface, where a further redox reaction occurs and photocatalytic activity increases. A higher concentration of dopant ions, on the other hand, may

result in photo-generated e^- and h^+ recombination. There is the best concentration of metal-dopant ions. The concentrated quantity of h^+ and/or e^- is confined without recombination; when the amount of dopant ions exceeds above the best concentration, the recombination rate increases due to a decrease in photocatalytic activity [59].

3.2.5. Kinetic study of DOX and OFLX

As it can be seen from Fig. 7(a) and (b) that the performance of degradation of DOX and OFLX reached 98.6% and 98% for TSFC1, respectively, after 15 and 20 min of sunlight illumination. These results show that the photocatalytic efficiency of TS photocatalyst was improved significantly after doping with Fe and Cu, as predicted by the PL results. The reaction kinetics were investigated using the Langmuir-Hinshelwood first-order kinetic model, expressed by the equation below [46]:

$$r_o = \frac{-dc}{dt} = kC \quad (3)$$

where r_o denotes the initial photocatalytic degradation reaction rate ($\text{mg}\cdot\text{L}^{-1}\cdot\text{min}^{-1}$), and k denotes the rate constant of a first-order reaction. At the beginning of the reaction, $t = 0$, $C_t = C_0$, the equation can be obtained after integration

$$\ln \frac{C_0}{C_t} = -kt \quad (4)$$

where C_0 and C are the initial and final concentration ($\text{mg}\cdot\text{L}^{-1}$) of DOX or OFLX; the solution at t min and k (min^{-1}) are the rate constant.

Fig. 7(a) and (b) shows a linear relationship between $\ln (C_0/C)$ and time (min) for both DOX and OFLX. The correlation coefficients had R^2 values greater than 0.9, and the first-order kinetic model fit the experimental data well. The first-order rate constants (k) were determined from the slope of the linear plots, and they were found to be $3.1 \times 10^{-1} \text{ min}^{-1}$ and $1.9 \times 10^{-2} \text{ min}^{-1}$ for TSFC1, and $1.6 \times 10^{-2} \text{ min}^{-1}$ and $9.8 \times 10^{-3} \text{ min}^{-1}$ for TS photocatalysts. The obtained values of k specified that the kinetics of DOX and

Fig. 6. Effect of dopant concentration in degradation of (a) DOX (b) OFLX under natural solar light.

Fig. 7. First order kinetic plots of (a) DOX (b) OFLX for TSFC1 catalyst.

OFLX photodegradation TSFC1 was two times faster than that of TS photocatalyst. The photocatalyst performance exposed to solar light irradiation has a better photodegradation than those not exposed to solar irradiation (dark conditions). This means that the photocatalytic performance of the catalyst in the degradation of DOX and OFLX is determined by photons. The degradation mechanism of DOX and OFLX by $\bullet\text{OH}$ radicals concerning TSFC1 catalyst illustrated as follow:

When the photocatalyst surface is exposed to solar light illumination, the photodegradation process begins. The TSFC1 catalyst absorbs photons with energies greater than the photocatalyst bandgap. Consequently, the electron in the valence band jumps to the conduction band, leaving a hole in the conduction band (h_{vb}). The electrons present in the conduction (h_{vb}) and valence band (e_{cb}) will react with oxygen (O_2) and water (H_2O) molecules which are absorbed by the photocatalyst and lead to the formation of $\bullet\text{OH}$ radicals which react with DOX and OFLX. When the photocatalyst was kept in the dark and not exposed to UV, Visible or solar light, no photons are produced that activate the photocatalysts performance. As a result, no photodegradation was observed under these conditions. The slight reduction in concentration could have resulted from the adsorption process, which was insignificant. A plausible reaction mechanism has been added as Fig. S3 in supplementary data.

3.2.6. Scavenger study

When exposed to light, the semiconductor photocatalyst generates

various reactive intermediates in the photocatalytic degradation of organic compounds. The effects of different scavenging agents on the function of each active species in the photocatalytic cycle of DOX and OFLX have been investigated. In order to evaluate the involvement of holes (h^+), KI was added. t-butanol was added to recognise the impact of $\bullet\text{OH}$ radicals, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was added as an e^- scavenger, sodium azide (NaN_3) and benzoquinone ($\text{C}_6\text{H}_4\text{O}_2$) as radical scavengers for O_2^- and O_2 to examine specific reactive species [20]. Because of the TSFC1 catalyst's high efficiency, the photocatalytic efficiency of the TSFC1 catalyst in the presence of these scavengers was measured. Degradation efficiency was noted after the addition of each scavenger, and the results were shown in Fig. S8(a). According to the results, the addition of $\text{C}_6\text{H}_4\text{O}_2$ and NaN_3 did not change the degradation rate of both DOX and OFLX, whereas, in the presence of KI, $\text{K}_2\text{Cr}_2\text{O}_7$ and t-butanol degradation were found to be decreased. The quenching of the photocatalytic reaction clearly stated that the main reactive species accountable for the degradation process are $\bullet\text{OH}$, h^+ , and e^- , respectively.

3.2.7. Hydroxyl radical study

The hydroxyl radicals are produced when the photocatalyst surface is illuminated with photons. The $\bullet\text{OH}$ radicals are strong oxidising species, with an oxidation potential of approximately 2.8 volts (as opposed to Normal hydrogen electrode (NHE)), which may increase total pollutant mineralisation. Typically, the higher the rate of formation of $\bullet\text{OH}$ radicals, the greater the separation efficiency of electron-hole pairs. Thus, there is a correlation between the increased photocatalytic activity and the rate of formation of $\bullet\text{OH}$ radicals. Using salicylic acid as a probe molecule, the effect of different Fe and Cu concentrations on the amount of $\bullet\text{OH}$ radicals was measured [60]. The salicylic acid in reaction with the $\bullet\text{OH}$ radicals form 2, 3-dihydroxybenzoic acid. The amount of $\bullet\text{OH}$ radicals absorbed by the solution at a wavelength of 510 nm was assessed after 20 minutes of reaction. Before the addition of the photocatalyst, a blank experiment was carried out. There was no change in absorbance when exposed to natural solar irradiation, indicating no photolysis reaction of salicylic acid. Fig. S8(b)

Fig. 8. (a) TOC removal percentage of DOX and OFLX in the presence of TSFC1 under solar light irradiation (b) Recyclability study of TSFC1 catalyst.

depicts the hydroxyl radical with varying Fe and Cu content. As the Cu content increases, the quantity of hydroxyl radicals increases. The hydroxyl radical generation of TSFC1 was extremely high, indicating that the sample has a high electron and hole separation rate. However, if the Fe content is too high, the number of hydroxyl radicals was discovered to decrease through the experiment. The reason may be that because of excess Fe content, the number of electrons generated began to accumulate immediately at the Fe_2O_3 conduction band so that some photoelectrons recombine with holes indirectly [61]. As a result, doping with an appropriate amount of Fe and Cu can enhance the separation rate of photoinduced charge carriers.

3.2.8. TOC analysis

In the early stages of degradation, the mineralisation process may not be completed. Using TOC measurements, the formation and mineralisation of fragmented organic intermediates were evaluated. It examines the presence of C-C bonds within the organic compounds. It is noted that the process of degradation differs entirely from the total elimination of the antibiotics. The sequential growth of the catalyst degradation efficiency was calculated using the following equation:

$$\text{TOC (\%)} = \frac{\text{TOC}}{\text{TOC}_0} \times 100 \quad (10)$$

The obtained results are plotted in Fig. 8(a) where TOC and TOC_0 are the concentrations of organic carbon present in the solution before and after the reaction's saturation point. The chemical bond cleavage of the DOX and OFLX molecules occurs by the degradation due to the light illumination. At the same time, the degradation of by-products was left in the reaction solution. The TOC removal rate of DOX and OFLX using TSFC1 attained about 69.4% and 72.13% after 15 and 20 min, respectively. Notably, the photocatalytic DOX and OFLX degradation percentage of TSFC1 was higher than the TOC removal percentage upon 15 and 20 min of reaction time, which implies that both the antibiotics are

mineralised to CO_2 and H_2O through serial radical intermediate degradation route instead of direct decomposition [62]. As the time increased to 40 min, TOC removal percentage for both DOX and OFLX increased up to 89.36% and 92.69%, both the drugs were extensively mineralised to CO_2 and H_2O by the photocatalytic process over the as-prepared TSFC1.

3.2.9. Reusability of catalyst

One of the most important practical issues for industrial applications is the reusability of a catalyst. So, the photocatalytic activity of TSFC1 was determined under sunlight. The result is shown in Fig. 8(b). It was found that after the reaction for seven cycles, the catalyst maintained good photocatalytic activity with the degradation efficiency of approximately 80% for both DOX and OFLX after radiating for 120 min. Considering the high stability of the TSFC1 catalyst, the observed reduction in photocatalyst performance is most likely related to the unpreventable loss of material during centrifugation and due to the presence of organic impurities adsorbed on the TSFC1 surface, blocking its photoactive sites [28]. Although after each cycle, we performed photocatalytic reactivation by UV-induced self-cleaning to improve photocatalytic removal of any organic impurities adsorbed to TSFC1, it appears that after repeated photocatalytic cycles, the build-up of such impurities appears to have a slight impact on photocatalytic performance. We recuperated batches of used photocatalyst material to validate this hypothesis and tried to reactivate/clean their surface by calcination for 2 h at 400°C .

Interestingly, the photocatalytic activity of these reactivated samples was the same (cycle 5) as the initial photocatalyst material (cycle 1), meaning that the adsorbed organic impurities can be removed from TSFC1 by a simple calcination step. Following the recycle experiment, the FESEM analysis of the TSFC1 photocatalyst was performed and compared to raw photocatalyst. It confirmed that the photocatalyst's structure had not changed significantly. In the supplementary data, the image has been added as Fig. S4.

3.2.10. Comparative study

The solar photocatalytic degradation process consists of several degradation mechanisms. Various experiments were conducted under optimum operational parameters to discover the contribution of each driving force (light and catalyst) and their synergetic effect on DOX and OFLX degradation efficiency. The maximum degradation of DOX and OFLX under solar light was 20% and 24%, with TS and 98% and 98.6% with TSFC1, respectively. The DOX and OFLX degradation efficiency using TS under solar light demonstrated these processes' low oxidative species production. The removal rates of 8% and 9% for DOX, 9% and 10% for OFLX were reached through TS and TSFC1, respectively, demonstrating synthesised photocatalysis's adsorption potential. Note that the adsorption potential of catalysts was too lower than their catalytic performance for degradation studies. The TSFC1 catalyst had the highest DOX and OFLX degradation rate due to effective interactions of Fe, Cu, SiO₂, and TiO₂ in the heterojunction catalysis. The degradation rate of DOX and OFLX under the solar-TSFC1 system considerably increased due to the synergetic effect between solar light illumination and catalyst powder. The prominent proficiency of the solar-TSFC1 system indicated the favourable visions of high oxidant species production. Also, the TSFC1 catalytic potential (%) was studied using equation 10 by comparing DOX and OFLX removal in a different experiment [63].

$$\text{Catalytic potential (\%)} = S_{\text{solar-TSFC1}} - (S_{\text{solar light}} + S_{\text{TSFC1}}) \quad (10)$$

Where, $S_{\text{solar-TSFC1}}$, $S_{\text{solar light}}$, and S_{TSFC1} denote the DOX and OFLX degradation rates (%) achieved under optimum degradation parameters with varying degradation driving force. Based on equation 10, the solar-TSFC1 system had a catalytic potential of 89.5% and 88.1% for DOX and OFLX, demonstrating that the combination of solar light illumination and TSFC1 is a promising procedure for the efficient degradation of pharmaceutical pollutants.

4. Cost Analysis

Even though it is impossible to scale up lab-scale trials with precise cost analysis due to the scaling-up studies energy-intensive parameters, the cost is an essential factor for the field scale application process. Efforts were made to estimate the total cost of TSFC1 as presented in Table S3.

5. Conclusions

Fe, Cu doped, and codoped TiO₂-SiO₂ (TSF1, TSF2, TSF3, TSC1, TSC2, TSC3, TSFC1, TSFC2, and TSFC3) catalysts were prepared using the sol-gel method. Prepared nanoparticles were investigated for the photocatalytic degradation of DOX and OFLX. Out of the various catalysts prepared, TSFC1 performed well without the oxidants, depicted good stability, and did not lose significant activity after re-use until seven cycles. The total cost, reaction rate, and recyclability studies make TSFC1 a promising catalyst for photocatalytic degradation of DOX and OFLX. Furthermore, the appropriate dopant amount in TiO₂-SiO₂ was conducive to enhanc-

ing sunlight photocatalytic activity proposing a promising environmentally compatible technology. Furthermore, this approach is simpler and provides new thinking to design high-efficiency solar light catalysts for ecological applications, specifically treating pharmaceutically contaminated water applications.

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Author Contributions

S.R. (Ph.D) carried out the experiments, collected and analysed the data and wrote the manuscript. A.G. (Assistant Professor) supervised the project, revised, and approved the manuscript to be published. N.S. (Associate Professor) commented and contributed to the final manuscript.

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