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# Hydrothermally synthesized mesoporous CS-g-PA@TSM functional nanocomposite for efficient photocatalytic degradation of Ciprofloxacin and treatment of metal ions



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#### ABSTRACT

Tin-based ternary inorganic semiconductors enable new opportunities for the development of functional hydrogel nanocomposites to cope with environmental pollution. In this regard, we have synthesized highly functionalize CS-g-PA@TSM nanocomposites by the impregnation of Tin- Si/Mo (TSM) semiconductor in the matrix of chitosan/polyacrylamide (CS-g-PA) using the hydrothermal route. Multifunction platform showed ammonia vapor sensing, fluorescent detection as well as removal and exchange recovery of lead ions from wastewater and its photocatalytic behavior towards antibiotic degradation. The CS-g-PA@TSM nanocomposite achieved almost 96% photodegradation towards Ciprofloxacin (CIP) after 130 min of irradiation which was further monitored and confirmed by 3-D excitation-emission matrix fluorescence and GC-MS techniques, respectively. The photocatalytic mechanism of the CS-g-PA@TSM under visible light irradiation was clarified, which established the generation of  $O_2^-$  /  $O_2^-$  /  $O_2^-$  /  $O_2^-$  /  $O_2^-$  /  $O_2^$ improved photocatalytic performance of CS-g-PA@TSM could be attributed to enhance the optical absorption and efficient separation along with the migration of photoinduced charge carriers. The nanomaterial also exhibits significant  $Pb^{2+}$  recovery (95.6%) from wastewater with a limit of detection (LOD) and limit of quantification (LOQ) as 3.38  $\mu$ g L<sup>-1</sup> and 9.34  $\mu$ g L<sup>-1</sup>, respectively. The CS-g-PA@TSM nanocomposite was successfully employed up to five regeneration cycles with 98% regeneration capacity. Thus, the finding of the present study establishes that the multifunctional CS-g-PA@TSM nanocomposite platform could be used for the treatment of antibiotics (CIP), ammonia, and Pb<sup>2+</sup> from wastewater.

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## 1. Introduction

The emission of environmental pollutants consisting of metal ions, emerging contaminants (ECs), and organic pollutants to the water bodies has disturbed the aquatic ecosystem, which severely affects the environment and human health [1,2]. Ingestion of these pollutants through water, food, and the air is injurious to health as they interrupt normal body function by damaging soft body parts (e.g., liver, kidney, brain, and reproductive systems, etc.) [3,4]. On the other hand, hospital sewage having ECs such as pharmaceutical compounds [anti-inflammatory drugs (NSAIDs), steroidal

\* Corresponding author. E-mail address: amjad.mt.khan@gmail.com (A.M. Khan). hormones, and antibiotics (e.g., ciprofloxacin, tetracycline, amoxicillin, salbutamol, estrone, etc.)] have been detected in the wastewater around the world [5-8]. Therefore, it is necessary to apply an effective technology to treat wastewater consisting of these pollutants from wastewater before being used for any useful purpose. Among various used techniques, removal and recovery of environmental contaminants using functional nanocomposites has attracted more attention owing to its low cost, energy-savings, and higher efficiency [9]. Degradation of environmental pollutants using photocatalytic oxidation under visible light irradiation is gaining considerable interest to utilize maximum energy sources [10-12]. Alternatively, cation exchange-based photocatalysis has proved to be a promising green technology to counter global issues related to detoxification and degradation of organic pollutants. Recently, transition metal salt (TMS) doped with semiconductors

such as silicon have been attracted more research interest worldwide owing to their environmental benignity and significant electronic conductivity [13]. In particular, metal silico/molybdates (M (Si/Mo)xOy = Zn, Ti, Mg, Sr, Ba, Ni, Co, Pb, Ca, Cd, Cu, Sn, and so forth) are one of the most significant families of inorganic materials that have been widely used in various fields. Among them, Si intercalated tin molybdate (Tin(Si/Mo)xOy) is found an interesting inorganic material due to its excellent peculiar properties such as optical and electronic structure [14]. The treatment of these semiconductors with proton indicates a reversible bandgap with improved activity for H<sub>2</sub> production [15] which confirms that the polymeric semiconductor has potential to cover a wide range of potential applications [16].

Recently, hydrogel-based nanocomposites represent an innovative class of materials that has attracted attention because of their thermal and chemical stability and synergic effect of nanoparticles (inorganic fillers) in the polymer matrix. Hydrogel nanocomposites exhibit multi-functional and stimuli-responsive properties due to the interconnectivity of the hydrogel network with inorganic NPs. In the current study, a facile approach was used to synthesize Chitosan-g-Polyacrylamide@Tin (Si/M o)xOy (CS-g-PA@TSM) nanocomposite via radical-polymerization. Further, the CS-g-PA@TSM nanocomposite was developed, followed by using a "bottom-up" approach involving in-situ hydrothermal deposition of TSM in the matrix of the porous hydrogel. These composite materials could be used in different fields because of multifunctionality. This study also provides a deep understanding and feasible methods to prepare efficient, recyclable material in terms of ecological restoration. The CS-g-PA@TSM nanocomposite is expected to enhance thermal stability, biocompatibility, porosity and maintain high capacity along with high surface area while simultaneously persisting/maintaining the inbuilt properties of the inorganic Sn(IV) complex.

#### 2. Experimental

Chemicals and reagents (S-2.1), Instrumentation (S-2.2), Photodegradation of Ciprofloxacin (S-2.3), Gas chromatography-mass spectrometry (S-2.4), fluorescence method for  $Pb^{2+}$  sensing (S-2.5), Removal of  $Pb^{2+}$  from wastewater (S-2.6), Swelling study (S-2.7), Gas vapor sensing behavior (S-2.8), Optical properties (S-2.9), Ion-exchange capacity (S-3.0) along with Sorption studies (S-3.1), and quantitative separation of metal ions from synthetic and real water samples (S-3.2) were carried out are described in the supplementary file.

## 2.1. Nanocomposites preparation

2.1.1. Synthesis of chitosan grafted polyacrylamide hydrogel (CS-g-PA) The polymeric-matrix hydrogel was synthesized by using the precursors of AA wM, and CS via the free-radical graft copolymerization method. In a typical procedure, a mixture of acrylamide (5%) and N, N methylene bisacrylamide (0.1 M) was added dropwise to the micellar media containing transparent chitosan solution. Potassium persulfate (KPS) prepared in 1 M HCl was added dropwise to the above solution as an initiator. The mixture was heated in a thermostat shaker at 70 °C for 2 h to obtain the viscous gel. Finally, the product was filtered off and washed with deionized water, dried in a vacuum, and stored in a desiccator for further use [17,18].

#### 2.1.2. Synthesis of CS-g-PA@TSM nanocomposite

Chitosan/polyacrylamide @Tin(IV) silicomolybdate (CS-g-PA@TSM) nanocomposites were synthesized using the hydrothermal method. In this method, chitosan-grafted polyacrylamide gel (CS-g-PA) as prepared in Section 2.1.1 was used as a host, whereas the inorganic precipitate of Tin(IV)Si/Mo)xOy (TSM) was employed as the guest (filler). The inorganic precipitate of tin silicomolybdate (TSM) was mixed dropwise (using different mixing ratios) in the matrix of CS-g-PA under vigorous stirring at 70 °C for 3 h. The N, N methylene bisacrylamide crosslinking agent was employed to couple organic-inorganic species [19]. Hence, the redox initiator (KPS) generates hydroxyl radicals (•OH), which then produce active free-radical sites on PA. These sites then undergo graft copolymerization with CS biopolymer to create CS-g-PA hydrogel three-dimensional (3D) network of cross-linked polymer matrices. The resultant precipitate of CS-g-PA@TSM was inserted into a Teflon-lined autoclave and heated at 120 °C for 24 h. Afterward, it was allowed to cool down at room temperature. The precipitate (gel) was washed with deionized water trice and finally dried at  $40 \pm 2$  °C in an electrically controlled oven. The nanocomposite was stored in a desiccator for further use as shown in Scheme 1a.

## 3. Results and discussion

#### 3.1. FTIR, XRD and TGA-DTA analyses

The mixing of inorganic precipitate (TSM) into the matrix of chitosan/ polyacrylamide (CS/PA) hydrogel using a sol-gel route followed by hydrothermal method results in the formation of CS-g-PA@TSM nanocomposite. Thus, by varying the mixing ratio of acrylamide and chitosan, different samples of CS-g-PA@TSM were synthesized (as listed in Table S-1). Among different prepared samples, the CS-g-PA@TSM showed the highest capacity along with better optical property (the lowest band gap = 2.45 eV). It might be due to the existence of a functional group; therefore, sample S-3\* (CS-g-PA@TSM) was chosen for detailed studies. The FTIR spectra were examined to identify changes in the functional group of prepared nanomaterials. Comparative FTIR spectra of CS-g-PA, TSM, PTSM, and CS-g-PA@TSM nanocomposite are presented in Fig. 1a. The broadband in the region of 3401  $cm^{-1}$  is attributed to the hydroxyl group of water [20]. Another sharp band at 1622 cm<sup>-1</sup> is ascribed due to H–O–H bonding [21]. Other medium intensity bands at 1633 cm<sup>-1</sup> and 1504 cm<sup>-1</sup> are accredited to amine and amide groups of chitosan of CS-g-PA@TSM. The peak at  $1404 \text{ cm}^{-1}$  is indicated the presence of a considerable amide in CS-g-PA@TSM and PTSM composites. Other sharp frequency bands at 1109 cm<sup>-1</sup> and 943 cm<sup>-1</sup> are related to the silicate and molybdate groups, respectively. The peak at 561 cm<sup>-1</sup> represents the Sn-O-Sn vibrations of CS-g-PA@TSM and PTSM. Shifting of H<sub>2</sub>N-COband to 1630 cm<sup>-1</sup> is possibly due to the interfacial electrostatic interaction between nitrogen group of co-polymer matrix of CSg-PA (amine and imine groups) and inorganic complex of Tin(IV) silicomolybdate (TSM) as shown in Scheme S-1b.

The result of DTA-TGA analysis of CS-g-PA@TSM nanocomposite is shown in Fig. 1b. The TGA curve of CS-g-PA@TSM showed ~8.52% weight loss up to 180 °C due to the elimination of water molecules [22]. Another moderate loss in weight (~26%) from 180 to 250 °C was attributed to the conversion of the silicate group to pyrosilicate as a result of the hydroxyl group due to condensation. Onwards, the decomposition of CS-g-PA@TSM was found at 350 °C, which may be owing to the formation of metal oxide. DTA measurements of CS-g-PA@TMS nanocomposite exhibited one endothermic peak at 80.3 °C (transition temperature) and two sharp exothermic peaks at 319.8 and 500 °C due to the loss of adsorbed water molecules and dehydration and decomposition of CS-g-PA@TMS, respectively [23]. Additionally, the TGA-DTA curves of CS-g-PA hydrogel revealed significant weight loss (30%) in the temperature range of 300-550 °C because of CS-g-PA hydrogel decomposition (Fig. 1c).



Scheme 1a. Schematic for synthesis of CS-g-PA@TSM nanocomposite.



Fig. 1. (a, b, c, d, e, f). FTIR spectra of CS-g-PA, PTSM, CS@PTSM (a); TGA-DTA curves of CS-g-PA and CS-g-PA@TSM (b,c); and XRD pattren of TSM, PTSM and CS-g-PA@TSM (d).

# 3.2. Morphological categorization

The amorphous or crystalline nature of synthesized TSM, PTSM, and CS-g-PA@TSM nanohybrid materials was analyzed using XRD analysis as shown in Fig. 1 **d**. The X-ray diffraction spectra of CS-g-PA@TSM showed a high-intensity peak at  $2\theta$  = 26.2° compared

with PTSM, which suggested a higher degree of crystallinity in CS-g-PA@TSM. A typical XRD pattern of the Tin(IV) molybdosilicate was showed crystalline nature. The Bragg reflections at  $2\theta = 28.6^{\circ}$ ,  $35.5^{\circ}$ , and  $53.5^{\circ}$  can be indexed to the (110), (200), and (211) orientation, respectively [24]. These peaks confirm the complex formation of the Tin(IV) on the silicate/molybdate surfaces. For

composite material polyacrylamide Tin(IV)silicomolybdate (PTSM), well-defined peaks with 20 values at 11.8°, 28.8°, 35°, and 53.3°, respectively, ascribed to the association of polyacry-lamide with Tin(IV) silicomolybdate (TSM). Additionally, high-intensity peaks at 20 = 28.4°, 31.0°, 33.2°, 51.5°, and 65.3° were responsible for intercalated TSM with CS/PA composites which confirmed its crystalline nature. The XRD result revealed the crystalline nature of CS-g-PA@TSM nanocomposite enhanced by impregnation of TSM in the matrix of CS@PA hydrogel.

From XRD analysis, considering the peak position at degrees, average particle size has been calculated by using Debye–Scherrer formula

$$D = \frac{K\lambda}{\beta COS\theta}$$

where 'K' is a dimensionless shape factor, with a value close to unity, the shape factor has a typical value of about 0.9, ' $\lambda$ ' is the wavelength of X-ray (0.154 nm), ' $\beta$ ' is the FWHM (full width at half maximum), ' $\theta$ ' is the diffraction angle and 'D' is particle diameter size. The crystallite size of CS-PA@TSM particles was found in the range of 15–20 nm. Further, the particles size of TSM and PTSM was 30 and 40 nm, respectively.

SEM images of CS-g-PA@TSM, CS-g-PA, and PTSM are shown in Fig. 2 a-d. The particle size of CS-g-PA@TSM was almost uniform with 10–19 nm. However, the morphology of PTSM (Fig. 2b) was found different than that of CS-g-PA@TSM (Fig. 2 c, d). The SEM images of CS-g-PA@TSM nanocomposite have well-defined spherical microspheres. In addition, SEM images demonstrated interaction and nucleate of CS-g-PA co-polymer around TSM particles due to the coordination of tin (Sn<sup>4+</sup>) with silicate and molybdate (Mo<sup>6+</sup>) at the surface of TSM [25]. This established the excellent intercalation between the inorganic TSM particles and CS@PA copolymer matrix. Association of CS-g-PA with TSM was further proven by the EDX analysis (as shown in Fig. 2 j and k).

A higher percentage of carbon was found in CS-g-PA@TSM as compared to C PTSM sample, and the elemental mapping showed uniform distribution of CS-g-PA on the surface of TSM particles (Fig. 2i). The strong association of CS-g-PA co-polymer hydrogel with TSM was further confirmed by TEM analysis (Fig. 2 e, f, g, h). TEM studies revealed the spherical surface morphology of the



Fig. 2. (a, b, c, d). SEM images for (a) Chitosan -g-polyacrylamide hydrogel; (b) PTSM; (c, d) CS-g-PA@TSM; TEM micrographs of PTSM (e), TEM micrographs of CS-g-PA@TSM at different magnifications (f, g, and h). Mapping analysis of Cs-g-PA@TSM (i), EDS spectrum of PTSM (j), and CS-g-PA@TSM (k).

CS-g-PA@TSM in comparison with PTSM nanocomposite. It is confirmed by analyzing TEM images that confirmed that the average size of spherical CS-g-PA@TSM nanocatalyst (Fig. 2 **f**, **g**, **h**) was found to be in the range of 10–20 nm, smaller than the average diameter of PTSM composite (Fig. 2**e**). The crystalline transformation might be due to the impregnation of CS@PA co-polymer to the inorganic counterpart TSM. TEM images of the CS-g-PA@TSM composites also illustrated the association of TSM with CS-g-PA matrix, which is uniformly dispersed onto its surface (Fig. 2**f**). The interlayer spaces of the lattice fringe of CS-g-PA@TSM were 0.366 and 0.263 nm, which were similar to the XRD spaces of the (003) and (015) planes of TSM (2 $\theta$  = 11.3°, d = 0.3 nm and 2 $\theta$  = 25.9°, d = 0.264 nm), respectively. The oxidation state and elemental composition of CS-g-PA@TSM were investigated by XPS analysis as shown in Fig. 3 (a-f). The full scan spectrum of CS-g-PA@TSM (Fig. 3a) approves the presence of C, Mo, Sn, N, Si, and O elements in CS@PTSM which agreed with the EDS data. Fig. 3b shows high resolution of N 1 s spectrum, which was fitted with four peaks. The four observed peaks correspond to -N < at 394.9 eV, -N-H at 397.8 eV, C-N-H at 399.8 eV, and -N = at 405.3 eV, respectively. The XPS spectrum of Sn showed two sharp peaks at 487.1 and 495.4 eV corresponding to the Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$  spin–orbit levels of Sn<sup>4+</sup>. For molybdenum, the XPS spectrum of Mo can be well fitted by two peaks at 230.1 eV and 234.2 eV corresponding to the  $3d_{5/2}$  and  $3d_{3/2}$  states of Mo<sup>6+</sup>, respectively (Fig. 3 c, d) [26]. The XPS spectrum of oxygen (different oxidation states) was found on the range of 529, 531, and 533 eV, which provide information about the lattice oxygen as chemisorbed oxygen and



Fig. 3. (a, b, c, d, e): X-ray photoelectron scanning spectra (a) and N. 1s (b) Sn 3d (c), Mo2p core level regions (d), O 1 s (e), and Si 2P (f).

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adsorbed water molecules via C-O, O–M, and M-O-H, respectively (Fig. 3e) [27]. Fig. 3f corresponds to the high resolution of Si 2p spectrum was fitted with two peaks appear at 101.3 and 103.1 eV. The first peak is believed to arise from Si-O bonding and the second peak at 101.3 eV is representative of Si-C bonding [28]. The surface area and pore size of CS-g-PA @TSM were analysed by BET. According to N<sub>2</sub> adsorption/desorption measurement, the BET surface area was found to be (165 m<sup>2</sup> g<sup>-1</sup>), indicating a high porosity of the CS-g-PA @TSM nanocomposite. The total pore volume of CS-g-PA @TSM was found to be ( $5.6 \times 10^{-3} \text{ cm}^3 \text{ g}^{-1}$ ),

and the average pore size 4.4 to 7.5 nm. These results prove the mesoporous nature of CS-g-PA@TSM.

The optical property, EPR, CV, and PL studies

The UV–Vis diffuse reflectance spectra of nanocomposites were measured to study the electronic structure and optical absorption properties. The UV–vis. ranges of TSM, PTSM and, CS-g-PA @TSM nanocomposite are presented in Fig. 4**a**<sub>0</sub>. The TSM nanoparticles showed a strong bandgap at about 400 nm (2.85 eV). The UV absorption capacities might be produced due to band transition from O<sub>2</sub> (2p) to Sn<sup>4+</sup> (5p), while the visible-light absorption is



**Fig. 4**. (a<sub>0</sub>, b<sub>0</sub>, a, c, d): UV–Vis diffuses reflectance spectra (DRS) (a<sub>0</sub>); and band gap of CS-g-PA@TSM (b<sub>0</sub>); EPR spectra of CS-g-PA@TSM fresh catalyst (a); recycled catalyst after forth run corresponding spin densities and g ~ values (b), CV of CS-g-PA@TSM (red) and Pb<sup>2+</sup> /CS-g-PA@TSM (black) (c); Photoluminescence spectra of CS-g-PA@TSM and CS-g-PA (d).

associated with the transition from the valence band to (Sn<sup>4+</sup> 5p) conduction band [29]. Therefore, better optical properties of CSg-PA@TSM were achieved as compared to both PTSM and TSM. The direct bandgap of the samples was evaluated by plotting the modified Kubeka-Munk function  $[F(R) \times hv]$  versus photon energy (hv) (Fig. 4  $\mathbf{b_0}$ ) [30–32]. The coupling of TSM with polyacrylamide demonstrates that no change was found in the bandgap absorption of (TSM). However, in the case of TSM impregnated with CS-g-PA to form (CS-g-PA @TSM) nanocomposite, the bandgap absorption was extended into the visible light region (about 440 nm). Interestingly, a moderate redshift towards the visible region was observed in the CS-g-PA@TSM nanocomposite. It might be due to the quantum size effect of TSM nanoparticles deposited on the CS-g-PA hydrogel support. Moreover, the potent interfacial interaction between CS-g-PA and TSM plays an important role in tailoring their band structure. This characteristic of CS-g-PA @TSM nanocomposite assists in improving its photo-activity under visible light irradiation. The bandgap of the TSM, PTSM, and CS-g-PA @TSM nanocomposite was found as 2.85, 3.25, and 2.45 eV, respectively, which confirms that TSM particles were successfully immobilized onto the CS-g-PA co-polymer hydrogel network.

From the UV (DRS) data, the bandgap values were found suitable and lie within the range of semiconductors; this feature makes CS-g-PA@TSM a promising material that can be used as an efficient photocatalyst. The EPR spectroscopy provided clear evidence about the existence of unpaired electrons in any system. The EPR spectra of CS-g-PA@TSM before and after CIP degradation, along with other related parameters (spin population, g-value) are shown in Fig. 4a, **b** [33,34]. The EPR analysis results revealed that oxygen vacancies create reactive sites on Tin (IV) surface, which are responsible for the degradation of CIP [35]. The EPR spectra of CS-g-PA@TSM showed a sharp and distinct EPR line centered at g ~2.00254, attributed to the unpaired electrons trapped in surface oxygen vacancies by adsorbed oxygen (O<sub>2</sub>), which proves that tin assists in the formation of oxygen vacancies during the degradation of CIP (Fig. 4a) [36]. The electrochemical measurements of the CS-g-PA@TSM were performed with a potential of -1.0 to 0.1 V at the scan rate of 100 mVs<sup>-1</sup> using a three-electrode system (modified GCE, Ag/AgCl, and KCl act as working, reference, and counter electrode). Cyclic voltammograms of CS-g-PA@TSM exhibited wellseparated redox peaks located near -0.46 V and -0.60 V, respectively (Fig. 4c). Shifting of these peaks at higher potential -0.40 V and -0.50 V, respectively, was found due to the presence of metal ions (Pb<sup>2+</sup>). The PL spectrum of CS-g-PA@TSM nanocomposite was analyzed to determine the generation of electrons and holes together with their recombination efficiency. The PL emission peaks of CS-g-PA and CS-g-PA @TSM (excitation wavelength of 325 nm) are shown in Fig. 4 d.

The PL spectrum of CS-g-PA@TSM showed the emission peak at ~410 nm, which might be due to the electronic behavior of Tin. In the spectra, the CS@PA showed the highest at 420 nm, while for CS@PA-TSM it is comparatively lower. Hence, the PL peak intensity is preferably reduced which results in efficient charge transfer over the catalyst surface. Besides, the emission data of the CS-g-PA@TSM catalyst slightly shifted to the blue wavelength side (~410 nm) is attributed to the defect trap state due to the quantum confinement effect. The PL is found well-matched with the UV-vis-DRS absorption analysis. It assures electron transfer from the conduction band of the photoexcited TSM (core) to the CS-g-PA (shell). This efficient charge transfer by TSM prevented electron-hole recombination, resulted in enhancing the photo-activity of CS-g-PA@TSM nanocomposite. The present study confirmed the suppression of the recombination of electrons and holes on the surface of the CS-g-PA@TSM compared to the bare CS-g-PA. Finally, we can conclude that all UV-vis DRS, PL, CV, and EPR test/ studies provided powerful evidence that widens visible light absorption, higher separation, and faster transfer of photogenerated electron-hole pairs, responsible for the promoted photocatalytic activity of CS-g-PA@TSM nanocomposites.

## 4. Applications

### 4.1. As a photocatalyst

The photocatalytic degradation of CIP was carried out under visible light to examine the efficiency of nanocomposites (TSM, PTSM, and CS-g-PA@TSM). The results of CIP photodegradation are shown in Fig. 5 (a, b, c, d). Interestingly, no photolysis of CIP was found in the absence of a catalyst (CS-g-PA@TSM) (Fig. 5 b). However, the CS-g-PA@TSM achieved significant photocatalytic activity (96.1%) as compared to PTSM (63.4%), TSM (52.1%), and CS-g-PA (44.3%) 130 min.

The improvement in CIP degradation using nanocatalysts is attributed to the superior visible light absorption ability and effective separation of photo-generated electron-hole pairs. Furthermore, the large surface area provided by CS/PA on which Sn(Si/Mo)xOy complex was immobilized showed enhancement in photocatalytic degradation efficiency. Generation of free radicals (during photocatalysis) from Sn(Si/Mo)xOy was possibly transferred owing to the amino groups of CS-g-PA. The electrons trapped in this process (transferred to  $O_2$  molecules) were further adsorbed on the surface and produce reactive species (.OH, e<sup>-</sup>,  $O_2^-$  and h<sup>+</sup>). Because of the above observations, a reasonable photocatalytic degradation mechanism of CS-g-PA@TSM core/shell nanocomposite is illustrated by the **schematic in** Fig. 5e.

The suggested mechanism of the degradation of CIP can be displayed as [37]:

CS-g-PA@TSM + 
$$h\nu \rightarrow$$
 CS-g-PA@TSM \* +  $e^-$  +  $h^+$   
 $h^+$  +  $H_2O \rightarrow .OH$  +  $H^+$   
 $e^-$  +  $O_2 \rightarrow .O_2^-$   
 $.O_2^-$  +  $.OH$  +  $H^+ \rightarrow H_2O_2$  +  $O_2$   
 $.O_2^-$  +  $.OH$  +  $h^+$  + CIP  $\rightarrow$  intermediate  $\rightarrow CO_2$  +  $H_2O$  +  $F^-$ 

From Fig. 5 **c**, it is observed that the photocatalytic degradation of CIP followed pseudo first order kinetics. The k values were determined from the slopes of the straight lines for PTSM, CS-g-PA, TSM, and CS-g-PA@TSM (as listed in **Table S-1**), and the plots of  $\ln C/C_0$  vs. time are shown in Fig. 5 **c**. The degradation efficiency of CIP was studied over a wide pH range (3–10), as shown in Fig. 5 **d**. It is inferred from the pH study that the degradation efficiency of CIP increases with increasing the solution pH up to 7 [38]. On the other hand, in basic medium, CIP molecules and the photocatalyst attain a negative charge, which leads to repulsion, thereby reducing the degradation efficiency.

At neutral pH (7), the surface of photocatalyst remains slightly positive with the CIP, which enhanced degradation efficiency of CIP owing to the degradation of CIP on the surface of the nanocomposite. Accordingly, the synergistic effect of the CS-g-PA@TSM photocatalyst for CIP degradation was observed at neutral pH. As displayed in Fig. S-1a, a positive zeta potential of CS-g-PA@TSM was found at low pH, which gradually became negative with increasing pH. The pH<sub>PZC</sub> value of CS-g-PA@TSM is noticed as ~8, and pH < 8, suggests that the surface of composite bears a positive charge. Meanwhile, CIP as an amphoteric substance has two pKa values that confirm three species (i.e., CIP<sup>+</sup>, CIP<sup>+-</sup>, and CIP<sup>-</sup>) at different pH levels.



**Fig. 5.** (a, b, c, d, e) UV-vis absorbance spectra of Ciprofloxacin photocatalytic degradation (15 mg/L; pH 7) with CS-g-PA @TSM catalyst (a). photocatalytic activity of CS-g-PA @TSM with bare TSM, and PTSM (b); Kinetic of CS-g-PA @TSM towards photocatalytic degradation of CIP (c); The effect of pH for photocatalytic degradation of CIP with CS-g-PA @TSM (d); Reactive species rules on the photocatalytic degradation of CIP using the CS-g-PA@TSM (e).

The degradation of CIP onto CS-g-PA@TSM initially increased with pH; however, (as shown in Fig. 5d), it decreased at high pH (pH = 10), which indicates that the maximum degradation of CIP occurred at pH 6–8 (when CIP was zwitterion). The hydrophobic

interaction and  $\pi$ - $\pi$  bonding dominated under this condition as a result of the high surface area of CS-g-PA@TSM. For detecting the main reactive species in the CIP decomposition, the scavenging experiment was carried out under identical experimental

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conditions. Isopropanol (IPA), disodium ethylenediaamine tetraaceticacid (Na<sub>2</sub>-EDTA), p-benzoquinone (BQ) and formic acid (FA) were chosen as .OH,  $h^+$ ,  $.O_2^-$  [39] and  $e^-$  [40] scavengers, respectively. The experimental results for the scavenging test showed that the reaction rate was relatively retained upon using formic acid (10.50 mM) reflecting the negligible effects of  $e^-$  species. However, in the case of IPA (1.60 mM), Na<sup>2</sup>-EDTA (12.60 mM), and (60  $\mu$ M)BQ scavengers were indicated a significant decrement proposing the influential effect of .OH,  $h^+$ , and  $.O_2^-$  [41].

The CIP degradation efficiency decreases in the presence of different scavengers (IPA, Na2-EDTA, BQ, and FA) to be ca. 27.3%, 33.1%, 19.7%, and 74.3% respectively, which established the formation of  $h^+$ , .OH and  $.O_2^-$  during CIP photodegradation process (**Fig. S-1b**).

## 4.1.1. Mechanism of CIP degradation

To identify various photocatalytic decomposition pathways, the formation of intermediates produced during the degradation of CIP was analyzed by the GC–MS technique. A proposed scheme in Fig. 6e illustrates fragmentations of seven major during the degradation. The cleavage of the C–N and C–C bonds resulted in by-products formation which may be converted into CO<sub>2</sub> and H<sub>2</sub>O through mineralization of the CIP [42]. For more details, the path-



Fig. 6. (a, b, c, d, e): Three-dimensional excitation-emission matrix fluorescence spectra (3D) of the CIP solution after visible light irradiation durations at different time intervals 0 (a), 20 (b), 60 (c), and 100 min. (d), Proposed degradation pathway of CIP (e).

ways of the cleavage piperazine ring and decarboxylation of quinolone ring in CIP were evaluated (**FigS-5 a,b**). Specifically,  $O_2^-$  radical prefers to attack the piperazine side chain to produce oxidative intermediates A (*m*/*z* 362). Then, intermediates B1 (*m*/*z* 333) were derived from the loss of formyl group (-CO) during the piperazinyl rings broken as described in pathway I. The intermediates B2 (m/z **316**) arose from the decarboxylation of quinolone as reported by Deng et al., [43]. The secondary degradation pathway corresponded to continue cleavage of the -C-N bond on the piperazine ring (related to further radical attacks) leading to the formation of the intermediates C with (m/z = 277), while the loss of "-CH<sub>2</sub>NH<sub>2</sub> fragment was attributed to the photo h<sup>+</sup> oxidation to produce intermediate D (m/z 262) [42]. The intermediates E (m/z 234) was derived from the loss of the -CO group during the cleavage of piperazinyl rings. Finally, intermediates F(m/z = 207) and E might be transformed into small molecules such as  $CO_2$ ,  $H_2O$ , and  $F^-$  [44]. All suggested pathways were compatible with previously reported work [44,45]. In order to confirm the photodegradation of Ciprofloxacin, a three-dimensional (3D) (excitation-emission matrix fluorescence spectra) technique was performed (Fig. 6a-d). Pure CIP solution exhibited multiple fluorescence peaks (Ex/Em = 250-300 /425–475 and Ex/Em = 300–350/425–475 nm) as shown in Fig. 6a [46]. Under visible light irradiation, the emission peak intensity decreased with time thereby suggesting the decrease in the concentration of CIP (Fig. 6b, c). After 100 min, a negligible peak in the emission spectra of CIP was found indicating the complete degradation of CIP (Fig. 6d). Therefore, 3D FL study results further confirmed that the CIP molecules could be degraded by photocatalytic processes.

## 4.1.2. Re-usability of nanocomposite catalyst

The surface morphology of catalyst greatly affects the performance of photocatalysts. The recycling behavior of CS-g-PA@TSM catalyst was examined towards the degradation of CIP (as shown in Fig. 7 **a**, **b**). The photocatalytic performance in term of recycability revealed that after 4 times repeatedly used, the CS-g-PA@TSM nanocatalyst retained almost 92% of its initial activity. Slight aggregation of the CS-g-PA@TSM even after 4 cycles indicated excellent stability and durability of the CS-g-PA@TSM catalyst. The high catalytic efficiency and stability of CS-g-PA @TSM could be explained due to the highly dispersed state of chitosan biopolymer, abundant oxygen vacancies on the TSM support, and the strong metal-



**Fig. 7.** (a, b, c, d) Degradation (%) of CIP using CS-g-PA @TSM with bare TSM, CS/PA and PTSM under visible light irradiation (a), Cyclic stability for photodegradation of CIP using the recycled CS-g-PA @TSM nanocomposite (b), FL spectra of the CS-g-PA @TSM in the absence and presence of Pb<sup>2+</sup> (pH 7.0),  $\lambda_{max}$  = 320 nm (c), Stern Volmer (1-F/F<sub>0</sub>) vs concentration of CS@PTSM and CS-g-PA samples (d).

Table 1

Comparison of various photocatalyst systems for CIP degradation.

Ref.
[48]
[38]
[49]
[50]
[41]
[42]
This study
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support interaction between chitosan/PA and TSM [47]. Comparative catalytic performance of some reported nanocomposites in comparison to our prepared nanocomposite is listed in Table 1.

## 4.2. As a sensor for the detection of $Pb^{2+}$

Luminescence studies were carried out to analyze the selective behavior of CS-g-PA@TSM for the detection of Pb<sup>2+</sup> in real water at ultra-low trace levels. Different concentrations of Pb<sup>2+</sup> were mixed with CS-g-PA@TSM (individually) and fluorescence spectra were recorded at  $\lambda_{max}$  = 389 nm. The fluorescence intensity of the CS-g-PA@TSM nanocomposite was decreased by 58% in the presence

of 140  $\mu$ M of Pb<sup>2+</sup>. To explain the mechanism of Pb<sup>2+</sup>-CS-g-PA@TSM interaction, the fluorophore units of CS-g-PA @TSM dispersed in the solution and the increasing the concentration of Pb<sup>2+</sup> ions trigger the aggregation of CS-g-PA@TSM probe to form a complex structure which led to destroying the stability of the colloidal solution and the fluorescence signal decreased markedly [51,52].

As illustrated in Fig. 7 **c**, **d**, the FL intensity of CS-g-PA @TSM was linearly decreased with increasing Pb<sup>2+</sup> concentration (1–10 ppm). Moreover, the linear response was observed in the range from 1.1 to 2  $\mu$ M (by plotting (1 – F/F<sub>0</sub>) against the logarithmic values of Pb<sup>2+</sup> concentration, as shown in Fig. 8**a**. The value of



**Fig. 8.** (a, b, c, d); Plot of (1-F/F<sub>0</sub>) for the FL intensities of CS-g-PA@TSM at 389 nm against the log value of Pb<sup>2+</sup> ions (a); Temperature dependence of the electrical conductivity of CS-g-PA@TSM nanocomposite (b) Resistivity response of CS-g-PA@TSM nanocomposite towards different concentrations of ammonia vapours with respect to time (c); Reversible resistivity response of CS-g-PA@TSM nanocomposite on intermittent exposure to 0.2 N ammonia (d).

 Table 2

 Compilation of Pb<sup>2+</sup> adsorption using different types of adsorbents.

S. No.	Composite Material	$Pb^{2+}(mg/g)$	Time (min)	Removal efficiency (%)	Reference
1	CS-PAA/GO	138.89	270	74.4	[61]
2	EDTA/MCS-GO	206.70	240	84.0	[62]
4	PEI-PD/GO	113.89	180	90.0	[63]
5	$Zr(WO_4)(IO_3)(PO_4)$	82.30	540	96.0	[64]
7	PEI-RCSA	234	480	81.76	[65]
8	CS-g-PA@TSM	238.30	180	95.6	The present study

limit of detection (LOD) was found to be  $1.98\times 10^{-8}$  M and correlation coefficient (R<sup>2</sup>) of 0.97, which was lower than that of the other reported Pb<sup>2+</sup> sensors [53,54]. The selectivity of CS-g-PA@TSM for Pb<sup>2+</sup> detection was examined by investigating its capability with other environmentally relevant metal cations (Na<sup>+</sup>, K<sup>+</sup>, Sr<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, and Ba<sup>2+</sup>). No fluorescent signal variations were observed in the presence of these interfering species, indicating that the CS-g-PA@TSM fluorescence probe exhibits promising results for Pb<sup>2+</sup> sensing with high selectivity. The results indicated that the proposed method (fluorescence sensing) is comparable with that of the AAS method (LOD =  $3.38\mu gL^{-1}$ ). It established that the prepared composite with multifunctional behavior could be employed for various practical applications.

#### 4.3. As a gas sensor

The relation between electrical resistivity and temperature was studied with the help of the Arrhenius equation by plotting a graph of  $ln\sigma$  versus 1000/T (**Fig. S-1c**). The electrical conductivity of CS-g-PA @TSM core-shell nanocomposite was found to be increased with increasing the temperature which revealed the 'thermal activated behavior" of nanocomposite due to improvement in charge transfer between TSM and co-polymer chains as presented in Fig. 8b [55]. Furthermore, temperature-dependent electrical conductivity results indicated that the thermal treatment affects the polymer's chain alignment, which results in the increment of conjugation length that brings about the increment electrical conductivity of the composite. Moreover, molecular reorder on heating enhances the molecular conformation for electron delocalization [56].

The degree of the conductivity depends on both the number of charge carriers and their mobility. It has been observed that mobility of charge carriers increases with increasing temperature leading to the improvement in conductivity similar to the reported POA-TP nanocomposite [57]. The electrical resistivity response of CS-g-PA @TSM nanocomposite as a function of time demonstrated remarkable changes in exposure to various concentrations of ammonia gas (0.05, 0.10, 0.15, and 0.20 N) as illustrated in Fig. 8c. The results indicated that the CS-g-PA @TSM nanocomposite exhibits a relatively fast response towards NH<sub>3</sub> vapors at 0.2 N and the resistivity can be recovered on flushing in air. Fig. 8d illustrates response characteristic curves of CS-g-PA @TSM sensor on exposure ammonia vapors (0.2 N) by a 4-in-line- electrical conductivity probe (using laboratory-made apparatus set up).

Mesoporous CS-g-PA@TSM nanocomposite covered a significant sensitivity ( $R_{air}/R_{gas} \sim 1.3$ ) on the exposure of ammonia vapors in the concentration range from 0.05 to 0.20 N. The resistivity response of the CS-g-PA@TSM nanocomposites reflected its potential in gas sensing [58]. The gas sensing of CS-g-PA@TSM is related to the change in electrical resistance between the material surface and target gas molecules due to interaction (gas adsorption, desorption, and charge transfer). Depletion of ammonia vapors on the surface and interfacial region causes changes in the resistivity of CS-g-PA @TSM nanocomposite as illustrated in **Fig S-2c**.

# 4.4. As an ion-exchanger for removal and recovery of metal ions

## 4.4.1. Removal of Pb<sup>2+</sup> in wastewater

In this study, we applied the recommended column procedure to test this method's applicability for the analysis of lead ions in Iheel Lake and groundwater (U.P., Aligarh, India). The optimum conditions (pH and temperature) were adjusted prior to the experiment. The concentration of lead in wastewater and groundwater samples was analyzed using the FAAS method as reported earlier [59], by spiking  $(3.0 \ \mu g)$  of lead was water samples as listed in Table S-5. The limit of detection for lead ions was found to be 3.38  $\mu$ g L<sup>-1</sup> with its corresponding better limit of quantification value (LOQ = 9.34  $\mu$ g L<sup>-1</sup>) than previously reported study for detection  $Pb^{2+}$  [60]. A compilation of relevant literature for the  $Pb^{2+}$ adsorption using different adsorbents is summarized in Table 2. The adsorption capacity of CS-g-PA@TSM was higher than most other adsorbents with an excellent removal percentage of 95.6% having a high sorption capacity of 238.3 mg  $g^{-1}$  which is closer to the maximum sorption capacity as described by the Langmuir equation and plotted in (Fig. S-3 and Fig. S-4). These findings indicated that the practical applicability of CS-g-PA@TSM nanocomposite exhibited excellent removal performance of Pb<sup>2+</sup> from the real wastewater samples also showed the feasibility of CS-g-PA@TSM for use in industrial purposes.

#### 4.4.2. Regeneration efficiency

The reusability of CS-g-PA@TSM was studied by performing multiple cycles for the removal of Pb<sup>2+</sup>. Nitric acid and deionized water were used to rinse Pb<sup>2+</sup> loaded CS-g-PA@TSM. The CS-g-PA@TSM showed 98% recycle efficiency even after five cycles having significant precision (2.65% RSD). After each set of adsorption/ desorption experiments, distilled water was used to remove excess acid from the surface of the composite. These results established that CS-g-PA@TSM has excellent regeneration capacity.

#### 4.5. Swelling behavior and valuable economic

Swelling ratios of the CS-g-PA@TSM with different TSM contents at pH 7.4 are listed in Table S-6. The swelling capacity of CS-g-PA@TSM decreased with increasing TSM contents. Under swelling conditions (pH 7.4 and 37 °C), the CS-g-PA@TSM had a lower swelling ratio than CS-g-PA (Fig. S-2b). As reported by Fan et al., [66], the suppression of swelling for nanocomposites hydrogel and degree of swelling help in maintaining their initial shape and retain their mechanical property. Hydrogel-based nanomaterials are regarded as economic, eco-friendly, and prime candidates to create a green and sustainable environment. However, due to high cost, their applications are limited. Presently the cost of hydrogelbased nanocomposites prepared by supercritical drying is about \$2870 per kg, while hydrogel-nanocomposites are made from chitosan-g-polyacrylamide NCs is found only \$176 per kg, thereby making the latter commercially important. Moreover, hydrogelbased nanocomposites are economical, and their efficiency in environmental clean-up is also high.

## 5. Conclusions

A novel CS-g-PA@TSM nanocomposite was successfully synthesized by the hydrothermal method with excellent photodegradation of CIP compared with pristine TSM and PTSM. The improved photocatalytic activity and stability of 3D CS-g-PA@TSM hydrogel nanocomposite established three aspects: (i) The introduction of Chitosan (CS) biopolymer matrix reinforced the strength of the polyacrylamide to produce the hydrogel, thereby enhanced the catalytic performance of the system; (ii). The 3D network structure provided more reactive sites and medium transport channels; (iii). The interactions between CS-g-PA gel and semiconductor TSM, enhances the efficiency of the migration and separation of photogenerated charge carriers owing to trapping of excited electrons on the surface of CS-g-PA@TSM. Besides, experimental results indicated that  $.O_2^-$ ,  $h^+$  and .OH species played a major role in the photodegradation of CIP. Hence, the CS-g-PA@TSM nanocomposite has potential in the oxidation of organic pollutants in aqueous phases due to its high photocatalytic activity. The porous structure of CSg-PA@TSM facilitated the sorption and exchange capacity of various metal ions within the surface. The CS-g-PA@TSM was found to be highly efficient for the removal of Pb<sup>2+</sup> from wastewater. The presence of various functional groups (such as hydroxyl, carboxyl, and amide) in the matrix of hydrogel-based nanocomposite (CS-g-PA) resulted in high adsorption capacity (95.6%) of  $Pb^{2+}$  from wastewater.

#### **CRediT** authorship contribution statement

Yahiya Kadaf Manea: Conceptualization, Methodology, Investigation, Writing - original draft, Writing. Amjad Mumtaz Khan: Supervision. Ajaz Ahmad Wani: Data curation. Mohsen T.A. Qashqoosh: Validation. Mohammad Shahadat: Visualization, - review & editing. Mansour A.S. Salem: Software.

## **Declaration of Competing Interest**

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

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#### **Appendix A. Supplementary material**

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