Degradation of ciprofloxacin by TiO$_2$/Fe$_2$O$_3$/zeolite catalyst-activated persulfate under visible LED light irradiation

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The activation of persulfate (PS) by metal catalysts under visible light is expected to offer a promising oxidation reaction for the removal of contaminants from water. Herein, we investigated activated PS systems under visible light irradiation for the generation of reductive species to decompose ciprofloxacin (CIP). Improved PS activation using TiO$_2$/Fe$_2$O$_3$/zeolite ($n$)TiFeZ under visible light irradiation favorably leads the reaction to generate reductive radicals. The enhanced degradation efficiencies of the ($n$)TiFeZ–PS system for CIP removal was due to the extended absorbance in the visible-light region and improved space separation of photo-induced charge carriers. The $4$TiFeZ catalyst exhibited better performance for CIP removal as compared to the other samples. The CIP was completely degraded in 120 min using 1 g L$^{-1}$ ($4$)TiFeZ and 5.0 mM PS at pH 7.0. The characterization and electron paramagnetic resonance (EPR) of ($n$)TiFeZ suggested that CIP was mainly degraded by surface-adsorbed radicals generated from the reaction between PS and Fe(s) on the samples under visible light. The reductive systems coupled with ($n$)TiFeZ exhibited high CIP degradation efficiency and high potential for the decomposition of other antibiotic compounds.

1. Introduction

Ciprofloxacin (CIP; C$_{17}$H$_{18}$O$_3$N$_3$F) is one of the most frequently prescribed human-use fluoroquinolone all over the world.$^1$ It was often detected in the effluent of wastewater treatment plants due to its high aqueous solubility under various pH conditions and high stability in wastewater. Various treatment processes have been applied to remove CIP from water. Especially, advanced oxidation processes (AOPs) contain promising, efficient, and environmentally friendly methods involving the generation of highly reactive radicals to decompose organic pollutants. Thus, AOPs are attractive treatment methods for CIP removal. Among AOPs, activated persulfate (PS, S$_2$O$_8^{2-}$) oxidation is gaining importance in water treatment because PS is stable at ambient temperatures, highly soluble in water, and much cheaper than peroxymonosulfate (PMS) and H$_2$O$_2$.1–4 Various iron-bearing catalysts through the incorporation of iron into various supports, such as mesoporous silica, clay, and carbon, have been explored to activate PS to generate sulfate radicals.$^5$–$^7$ The application of supports is beneficial for high mineralization of organic contaminants and easy separation from treated wastewater without causing secondary metal ion pollution. CIP has multiple ionisable functional groups. At neutral pH, the largely dominant species is zwitterionic, whereas the cationic form and the anionic form predominately in acidic and in basic solutions, respectively. Thus, it can exist as a cation, zwitterion, and anion under aqueous pH conditions. Previous studies show that CIP molecules react with supports by cation exchange rather than cation bridging or surface complexation.$^8$ Depending on the regularly arranged cavities and crystal structure of zeolites, zeolites can be used as hosts to accommodate nano-sized iron materials and support to remove CIP.$^9$ Various physical and chemical methods have been explored to activate PS to generate sulfate radicals.$^{10}$ Especially, activation under light irradiation is more attractive than thermal or chemical activation for producing SO$_4^{2-}$ with high efficiency.

Semiconductor materials have played an important role in activation under light irradiation. TiO$_2$ has been applied to photocatalytic processes due to its non-toxicity, low cost, and high stability.$^{11}$–$^{13}$ The major limitations of TiO$_2$ are its difficult separation from water and large $E_g$ value ($E_g = 3.2$ eV), which inhibits the absorption of the visible light. Therefore, to increase the visible light absorption of TiO$_2$, its coupling with lower band gap semiconductors, such as Fe$_2$O$_3$, Cu$_2$O, CuO, CdSe, and CdTe, can spatially separate electron–hole pairs and thereby decrease the recombination rates.
composite can be more efficient photocatalysts than pure TiO₂ towards organic compound degradation in the UV-vis region of the spectrum due to the narrow band gap (Eg = 2.2 eV), low cost, and high stability of Fe₃O₄.²⁴ To date, various TiO₂-supported catalysts have been developed to activate PS under UV light for the degradation of organics. However, to the best of our knowledge, very limited information on TiO₂/Fe₂O₃-supported zeolite/PS oxidation of CIP in water under visible light is available although it is a likely option for the treatment of CIP-induced water pollution. It is interesting to explore the activation of persulfate with TiO₂/iron-modified zeolite under visible light irradiation for CIP removal.

In addition, the visible light-emitting diodes (LEDs) extensively used in interior and exterior lighting offers a new alternative to conventional light sources due to their narrow spectrum of light, long life span, high spectral purity, small size, and lack of requirement for cooling. Thus, they appear ideal candidates for environmental remediation procedures with reduced power consumption and greater potential for flexible configuration.

To date, many studies have been reported on the UV/PS, UV-vis/catalyst/PS, UV or vis/catalyst/H₂O₂ processes; however, studies on the vis/catalyst/PS system have not been reported. It is the first time that TiO₂/Fe₂O₃/zeolite catalysts have been combined with PS and vis light for the removal of non-biodegradable organics. In this study, we fabricated TiO₂/Fe₂O₃-supported zeolites [(n) TiFe-Z] as catalysts to activate persulfate under visible LED light irradiation. The mechanisms of PS activation and radical reaction were investigated, and the possible degradation pathway was revealed by identification of the reaction intermediates. Moreover, the effects of pH, catalyst loading, PS dosage, and radical scavengers on the oxidation efficiencies were systematically investigated. This study was aimed at providing a green, novel, and highly-efficient PS activation technology for sulfate radical-based oxidation.

2. Experimental
2.1 Materials and chemicals
CIP hydrochloride was purchased from the Sigma-Aldrich Corporation. Commercial P25 TiO₂ (80% anatase and 20% rutile, BET = ca. 270 m² g⁻¹) was purchased from Degussa. Nanoscale zero valent iron particles Fe⁰ (NZVI) were purchased from Fisher Scientific. The size of NZVI was 50 nm. Sodium silicate solution, sodium aluminate, sodium hydroxide, hydrochloric acid, and ferric nitrate were purchased from Fisher Scientific. Sodium oxalate (Na₂C₂O₄), benzoquinone (BQ), ascorbic acid (AsA), dimethyl sulfoxide (DMSO), methanol, and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were purchased from Aladdin, China. All the chemicals were of analytical grade and used without further purification. Milli-Q ultrapure water (18.2 MU cm) was used for all the experiments.

2.2 Synthesis of (n)TiFe-Z
Sodium silicate, sodium aluminate, and sodium hydroxide were mixed in water, and a white gel was formed. The molar ratio of Na₂O : Al₂O₃ : SiO₂ : H₂O was 7.15 : 1 : 2.2 : 122. The gel was heated to boiling for 1 h to produce the precursors of zeolite X. Then, 4 wt% of TiO₂ and various weight percentages of NZVI (4, 8, 16, and 24 wt%) were added to the precursors of zeolite X and then stirred to be homogenized. The gel was crystallized by the Teflon-lined stainless autoclave at 343 K for 3 h and then at 368 K for 2 h. The autoclave was naturally cooled down to room temperature. Finally, the product was washed with deionized water and calcined at 673 K for 3 h to obtain the TiO₂/Fe₂O₃-supported zeolites [(n) TiFe-Z]. The value of n, which was 1, 2, 4, and 6, presented the ratio of the weight percentage of NZVI to that of the TiO₂. The zeolite X was prepared by the same method without adding TiO₂.

2.3 Characterization and analysis
A D/MAX-2500 diffractometer (Rigaku, Japan) was applied to characterize the crystalline phases of the final products using Ni-filtered CuKα radiation and a scan range of 10–80° at a scanning rate of 0.02° s⁻¹. The Brunauer-Emmett-Teller (BET) surface areas were characterized using a N₂ adsorption-desorption isotherm (ASAP-2020 Micromeritics Co., USA) and calculated from the linear part of the BET plot. The sample structure was observed using a JEOL H-8100 field emission scanning electron microscope (FESEM). Photoluminescence (PL) spectra of the sample was obtained using a Perkin Elmer LS55 fluorescence spectrometer with the excitation wavelength of 320 nm at room temperature. The sample was pressed into a thin disk and fixed on a quartz cell. The infrared absorption spectra were obtained by a Nicolet 6700 Fourier transform infrared (FT-IR) spectrophotometer and after the spectrum scan of the blank pure KBr pellet. The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) measurements were conducted using a Hitachi UV-3600 UV-vis spectrophotometer in the range of 200–800 nm, and BaSO₄ was used as a reflectance standard. X-ray photoelectron spectroscopy (XPS) was performed using an ESCA 3000 spectrometer to characterize the chemical state of the elements in the samples. The CIP concentration was determined by ultra-performance liquid chromatography (UPLC) (Waters, USA). The flow rate was 0.8 mL min L⁻¹ and the wavelength of the ultraviolet (UV) detector was set at 355 nm. The mobile phase was 1% ethyllic acid solution (80%) and methanol (20%). The correlation coefficient of the standard curve (n = 10) was more than 0.999. All the TC concentrations were measured in triplicate and mean values were used. The iron concentration in the solution was measured by inductively coupled plasma mass spectrometry (ICP-MS) using Agilent HP 4500.

2.4 The batch experiments
The CIP degradation performance of samples was evaluated under 50 W 455 nm LED light irradiation. The experiments were carried out in a reactor containing 0.1 g sample, 100 mL 500 mg L⁻¹ aqueous solution of CIP, and 5 mM Na₂S₂O₃ solution. The pH of the TC solution was adjusted by adding one or two drops of 0.1 mol L⁻¹ HCl or NaOH solution. The distance between the LED light source and the reactor was 5 cm. Then,
the reactor was exposed to the LED light irradiation. The reactor
was continuously agitated by a magnetic stir bar. All the
experiments were conducted in duplicates, and the results
showed that the experimental errors were less than 5%.

3. Results and discussion

3.1 Physicochemical characterization

3.1.1 XRD. The XRD profiles of (1)TiFeZ, (2)TiFeZ, (4)TiFeZ,
(6)TiFeZ, and zeolite X are shown in Fig. 1. The signal peak at
25.4° indicated the planes of anatase. The most intense peaks
of the anatase phase (48.0° and 54.5°) can also be identified in
the pattern of the sample (n)TiFeZ, overlapping with the zeolite
reflections. The structures of zeolite X were not altered by TiO2
and NZVI loading because no significant shift in the zeolite X
peaks of (n)TiFeZ was observed as compared to that of pure
zeolite X.

The characteristic peak of NZVI was observed at 45°. The
intensity of the reflection at 45° was increased with the
increasing weight percentage of NZVI. This indicated that some
NZVI were coated on the surface of the zeolite X. As TiO2 and
NZVI loading was increased, the diffraction peaks of TiO2 and
NZVI became wider and sharper.

3.1.2 FESEM. The FESEM images of zeolite X and (4)TiFeZ
are shown in Fig. 2. The particle size was uniform and about 4
mm. The morphology of (4)TiFeZ was different from that of
zeolite X. In addition, the surface of (4)TiFeZ was rough, and the
small particles were coated on the surface of (4)TiFeZ; this
indicated that some of TiO2 and NZVI particles were immobi-
lized on the surface of (4)TiFeZ.

3.1.3 Specific surface area and pore diameter. As shown in
Table 1, the specific surface area of (n)TiFeZ increased from
0.0844 to 0.1837 m² g⁻¹ as the weight percentage of TiO2
increased. The average pore diameters of the samples were
between 0.743 and 0.969 nm, and the average pore diameter of
zeolite X was 0.743 nm. The impregnation of NZVI and TiO2 had
an influence on the specific surface areas and pore diameters
and volumes of the samples.

3.1.4 UV-vis DRS spectra. As shown in Fig. 3, the absor-
bance of Ag/AgCl(x)Fe-ZX in the visible light region was
enhanced as the weight percentage of NZVI increased.

3.1.5 Photoluminescence (PL). As shown in Fig. 4, the PL
spectrum intensity of the (n)TiFeZ samples decreased when the
weight percentage of NZVI increased. There was a large decrease
in the PL intensity of (n)TiFeZ. This suggested that as the weight
percentage of NZVI increased, the recombination of the photo-
electron and hole pairs of (n)TiFeZ was more inhibited. (6)TiFeZ
possesses much better optical and photoluminescence behav-
iors than the other samples.

3.2 Evaluation of CIP degradation

3.2.1 The effect of NZVI on CIP adsorption. Table 2 shows
the maximum adsorption capacities Qmax of (n)TiFeZ and the
Langmuir adsorption constants (Kads). The correlation coe-
cfficients R² of the linear form of the Langmuir model were close
to 1. This suggested that the Langmuir model could describe CIP
adsorption. It also showed that the CIP adsorption process
occurred on the homogeneous surface by monolayer adsorp-
tion. The Qmax of (n)TiFeZ increased from 354.6 mg g⁻¹ to
435.2 mg g⁻¹ when the weight percentage of NZVI was increased
from 1% to 4%. However, the Qmax of (n)TiFeZ decreased as the
weight percentage of NZVI was increased from 4% to 6%.

3.2.2 Comparison of CIP removal efficiency by (n)TiFeZ. As
shown in Fig. 5A and B, the photocatalytic performances of the
prepared samples were studied by the removal of CIP under
visible light illumination with and without PS. Without any
catalyst and PS, CIP was fairly stable, and the self-degradation of
CIP through photolysis was negligible (<0.1% over 4 h).

The pseudo-first order equation could be applied to describe
the CIP photocatalytic kinetics by the catalysts. The equation is
as follows:

$$\ln \left( \frac{C_0}{C} \right) = k_1 t$$

(1)
where \( C_0 \) is the initial concentration of CIP (mg L\(^{-1}\)), \( C \) stands for the CIP concentration (mg L\(^{-1}\)) at reaction time \( t \), and \( k_3 \) represents the pseudo-first order rate constant (min\(^{-1}\)).

In the present study, the pseudo-first-order kinetics model, as shown in eqn (1), was used to study the degradation of CIP by the photocatalyst under visible light illumination without PS (Fig. 5C) and with PS (Fig. 5D). The values of correlation coefficient \( R^2 \) were above 0.9, confirming that the removal profiles in all the cases could be well expressed with the pseudo-first-order kinetics. From Fig. 5C, based on the equation, the slopes of the fitted lines were the \( k_3 \) values. The \( k_3 \) values were calculated to be 0.356, 0.405, 0.509, and 0.474 for (1)TiFeZ, (2)TiFeZ, (4)TiFeZ, and (6)TiFeZ, respectively. Compared with those obtained using other samples, the rate constant of CIP degradation obtained using (4)TiFeZ was higher.

From Fig. 5D, the \( k_3 \) values were calculated to be 0.3966, 0.4816, 0.7134, and 0.6013 for (1)TiFeZ, (2)TiFeZ, (4)TiFeZ, and (6)TiFeZ, respectively. The order of the CIP removal efficiencies by (n)TiFeZ under visible light was (4)TiFeZ > (6)TiFeZ > (2)TiFeZ > (1)TiFeZ. The \( k_3 \) value of (n)TiFeZ-PS under visible light was more than that of (n)TiFeZ-PS in the dark. This indicated that the PS activation was promoted under visible light.

3.2.3 The effect of pH. The (n)TiFeZ sample was applied for the pH studies because its CIP degradation efficiency was more
than that of the other samples. Fig. 6 presents the effect of pH on the CIP degradation efficiency of (n)TiFeZ. As the pH increased from 3 to 7, the CIP degradation efficiency decreased. It showed that as the pH was decreased, the breakdown of persulfate into sulfate free radicals could be further promoted. More SO$_4^{2-}$ radicals were produced to enhance the TC degradation efficiency. The reaction equations are shown below:

\[
\text{S}_2\text{O}_8^{2-} + \text{H}^+ \rightarrow \text{HS}_2\text{O}_5^- \\
\text{HS}_2\text{O}_5^- \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{SO}_4^{2-} \\
\]

Fe$^{2+}$ ions were more easily produced from NZVI at lower pH. The homogeneous Fe$^{2+}$ ions activated persulfate by the following reaction:

\[
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \\
\]

The precipitation of Fe$^{2+}$ and Fe$^{3+}$ ions might occur at pH 5.5–7.5. When the pH increased, more sulfate radicals could be transformed to hydroxyl radicals through the following reaction:

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}^+ \\
\]

There were more sulfate radicals generated at lower pH and there were more hydroxyl radicals generated at higher pH. The reduction potential of the sulfate radicals was higher than that of the hydroxyl radicals at higher pH, and their reduction potentials were similar at lower pH. Thus, the CIP degradation efficiency decreased as the pH increased.
3.2.4 The stability of \((n)\)TiFeZ. From Fig. 7, the iron ion concentration was measured during the process of CIP degradation. The maximum concentration of leached iron ion was only 0.15 mg L\(^{-1}\), which was far below the European Union standard (2 mg L\(^{-1}\)); compared with the iron content of \((n)\)TiFeZ, the content of leached iron ion was negligible. Thus, \((n)\)TiFeZ is a sustainable and environmentally friendly catalyst.

3.3 Mechanism discussion

XPS could provide chemical state information of the surface components. According to the characterization results, there were NZVI particles coated on the surface of zeolite X. As shown in Fig. 8, the binding energies of 710.33 eV and 710.59 eV present the binding energies of Fe(II) and Fe(III) in the Fe 2p core level photoelectron spectra, respectively. It suggests that on the surface of \((4)\)TiFeZ, the oxidation states of iron are +II and +III. The peak area ratios of Fe(III) to Fe(II) before and after CIP degradation were 9.12 and 7.22, respectively. This is because after the heterogeneous photocatalytic reaction, the proportion of Fe(III) was reduced as compared to that of Fe(II). Fe(III) could trap and transfer electrons and holes to inhibit the recombination of photo-excited holes and electrons. This suggested that at the interface between Fe(III) and TiO\(_2\), there was effective heterojunction electric field produced to make the photo-generated electrons and holes significantly strengthened. It promoted the reaction between Fe(III) and TiO\(_2\), there was effective heterojunction electric field produced to make the photo-generated electrons and holes significantly strengthened. It promoted the reaction between Fe(III) and S\(_2\)O\(_8\)\(^{2-}\) ions. The separation of the photo-electrons and holes was significantly strengthened. The formation efficiency of SO\(_4\)\(^{-}\) enhanced to make the photocatalytic efficiency increase.

The Na\(_2\)C\(_2\)O\(_4\), BQ, AsA, and DMSO scavengers were applied to determine the type of reactive oxygen species (ROS) produced in the \((n)\)TiFeZ-PS system. The various inhibitory effects of the different radical scavengers on CIP degradation are presented in Fig. 9. As BQ and Na\(_2\)C\(_2\)O\(_4\) were added, there were remarkable inhibitory effects on CIP degradation. As AsA and DMSO were added, there were moderate effects. This indicated that \(^{\cdot}\)OH was one of the predominant oxidative species for oxidizing CIP, produced by the reaction between \(^{\cdot}\)O\(_2\) and H\(_2\)O\(_2\). \(^{\prime}\)H reduction in the CIP removal was observed as an \(^{\cdot}\)H\(^{\prime}\) scavenger (Na\(_2\)C\(_2\)O\(_4\)) was added that verified the contribution of \(^{\cdot}\)H\(^{\prime}\) in Cl\(^{\prime}\) production for CIP oxidation.

The radical quenching experiments were first conducted to study whether the radicals were produced or not. As observed

![Graph showing iron ion concentration in water during CIP degradation by \((n)\)TiFeZ.](image)

**Fig. 7** Iron ion concentration in water during CIP degradation by \((n)\)TiFeZ.

![Graph showing Fe 2p core level photoelectron spectra.](image)

**Fig. 8** Fe 2p core level photoelectron spectra of \((n)\)TiFeZ before (A) and after (B) CIP degradation.

![Graph showing effect of reactive radical scavengers on CIP degradation by \((n)\)TiFeZ-PS after 3 h (CIP concentration, 500 mg L\(^{-1}\); dosage of catalyst, 1 g L\(^{-1}\); and pH, 7.0).](image)

**Fig. 9** Effect of reactive radical scavengers on CIP degradation by \((n)\)TiFeZ-PS after 3 h (CIP concentration, 500 mg L\(^{-1}\); dosage of catalyst, 1 g L\(^{-1}\); and pH, 7.0).
from Fig. 10, when 2 M methanol was added to the reaction, the CIP removal was slightly decreased by 10%. The radicals produced were tested by EPR experiments. Furthermore, the free radicals such as superoxide radicals (O$_2^{-}$) and hydroxyl radicals (OH$^-$) played a vital role in the photocatalytic process. The hydroxyl radicals generated in the photocatalytic process were measured by the EPR spectra. As shown in Fig. 11, more OH$^-$ were generated by (4)TiFeZ–PS than by (4)TiFeZ–PS–methanol under visible light irradiation. This suggested that methanol did not capture the surface-adsorbed radicals completely and 10% of CIP degradation was scavenged by the addition of 2 M methanol. This indicated that the CIP was degraded by the surface radicals.

In Fig. 12, a possible mechanism is proposed to explain the CIP degradation process by (n)TiFeZ. First, cationic CIP ions were adsorbed on the surface of (n)TiFeZ through an ion exchange reaction. Under visible light, TiO$_2$ and Fe$_2$O$_3$ nanoparticles on the surface of (n)TiFeZ could be excited to produce electron–hole (e$^-$/h$^+$) pairs (eqn (2)). During the process, the Fe(III)/Fe(II) cycle reaction enhances the space separation efficiency of the photo-induced charge carriers. This is because the impregnation with NZVI could cause a more efficient utilization of solar energy to accelerate this reaction. The conduction band (CB) electrons of TiO$_2$/Fe$_2$O$_3$ excited by visible light shifted to Fe(III) on the surface of (n)TiFeZ. Fe(III) could act as an electron trap to make the formation of Fe(II). Fe(II) was less stable than Fe(III) because of the half-filled stable d$^5$ configuration. Therefore, the trapped charges could be released to generate stable Fe$^{3+}$ ions (eqn (3)). During the process, it caused the formation of O$_2^-$ and SO$_4^{2-}$ superoxide radicals for the degradation of CIP (eqn (4) and (5)). The radicals O$_2^-$ and SO$_4^{2-}$ could react with H$_2$O to generate the OH$^-$ radical (eqn (6) and (7)). The CIP molecule was oxidized by these superoxide species to intermediates and finally...
completely mineralized (eqn (8)). The reactions are presented by the following equations:

\[
(n)\text{TiFeZ} + hv \rightarrow e^- + h^+ \tag{2}
\]

\[
\text{Fe(III)} + e^- \rightarrow \text{Fe(II)} \tag{3}
\]

\[
\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{O}_2^- \tag{4}
\]

\[
\text{Fe(II)} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe(III)} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \tag{5}
\]

\[
\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}^+ \tag{6}
\]

\[
\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ \tag{7}
\]

\[
\text{CIP} + \text{OH}^- \rightarrow \text{intermediates} + \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_3^- \tag{8}
\]

4. Conclusion

In conclusion, the catalysts ([n]TiFeZ) were synthesized by a facile hydrothermal method followed by the calcination method. The (4)TiFeZ catalyst showed better performance than other samples for CIP removal. The CIP degradation could be achieved in 2 h using 1 g L\(^{-1}\) (4)TiFeZ and 5.0 mM PS at pH 7.0. As the pH increased, the CIP degradation efficiency decreased. "O\(_2^-\)" and SO\(_4^{2-}\) were the predominant reactive oxygen species for CIP removal. After NZVI impregnation, the enhancement of the photocatalytic activity was mainly due to the extended absorption in the visible light region and the efficient space separation of photo-induced charge carriers. This study may expand the further development of zeolite-based heterogeneous catalysts for the degradation of organic pollutants through the activation of PS under visible light.

Conflicts of interest

There are no conflicts to declare.

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