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# Transition metal doped CeO<sub>2</sub> for photocatalytic removal of 2-chlorophenol in the exposure of indoor white light and antifungal activity

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Besides natural sunlight and expensive artificial lights, economical indoor white light can play a significant role in activating a catalyst for photocatalytic removal of organic toxins from contaminated water. In the current effort, CeO<sub>2</sub> has been modified with Ni, Cu, and Fe through doping methodology to study the removal of 2-chlorophenol (2-CP) in the illumination of 70 W indoor LED white light. The absence of additional diffractions due to the dopants and few changes such as reduction in peaks' height, minor peak shift at 2θ (28.525°) and peaks' broadening in XRD patterns of modified CeO<sub>2</sub> verifies the successful doping of CeO<sub>2</sub>. The solid-state absorption spectra revealed higher absorbance of Cu-doped CeO<sub>2</sub> whereas a lower absorption response was observed for Ni-doped CeO<sub>2</sub>. An interesting observation regarding the lowering of indirect bandgap energy of Fe-doped CeO<sub>2</sub> (~2.7 eV) and an increase in Ni-doped CeO<sub>2</sub> (~3.0 eV) in comparison to pristine CeO<sub>2</sub> (~2.9 eV) was noticed. The process of  $e^{-}$   $h^{+}$ recombination in the synthesized photocatalysts was also investigated through photoluminescence spectroscopy. The photocatalytic studies revealed the greater photocatalytic activity of Fe-doped CeO<sub>2</sub> with a higher rate (~3.9 × 10<sup>-3</sup> min<sup>-1</sup>) among all other materials. Moreover, kinetic studies also revealed the validation of the Langmuir-Hinshelwood kinetic model (R<sup>2</sup> = 0.9839) while removing 2-CP in the exposure of indoor light with a Fe-doped CeO<sub>2</sub> photocatalyst. The XPS analysis revealed the existence of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> core levels in doped CeO2. Using the agar well-diffusion method, the antifungal activity was assessed against the fungus M. fructicola and F. oxysporum.

Compared to CeO<sub>2</sub>, Ni-doped CeO<sub>2</sub>, and Cu-doped CeO<sub>2</sub> nanoparticles, the Fedoped CeO<sub>2</sub> nanoparticles have outstanding antifungal properties.

KEYWORDS

modified  $CeO_2$ , band gap energy, photocatalytic removal, 2-chlorophenol, nanocompoiste, antifungal activity

# Introduction

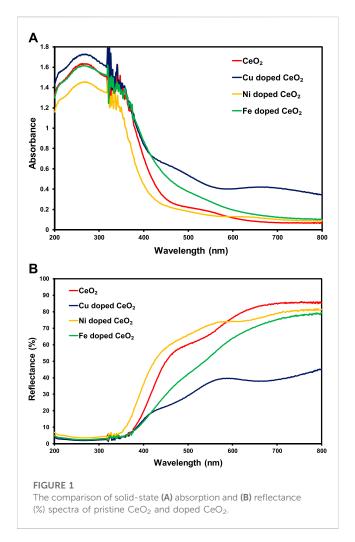
A major environmental threat that humanity faces today is the contamination of water caused by hazardous chemicals released into the environment by industrial processes. Routine daily activities can cause hazardous materials to be introduced into natural water resources, such as aquifers, lakes, oceans, rivers, and groundwater aquifers. Continually introducing such contaminants into natural water can result in an alteration of the characteristic features of natural water as well as polluted water. This is extremely unsuitable for human health. Chemical pollutants like dyes for textiles, halogenated compounds, substituted phenols, insecticides, pesticides, weed killers, and herbicides are known to be carcinogenic and pose major health risks to humans (Anku et al., 2017; Samanta et al., 2019; Brillas and Garcia-Segura, 2020; Kanan et al., 2020; Rafiq et al., 2021). Among toxic organic pollutantschlorophenols and nitrophenols, because of their stable structure, toxic and carcinogenic effects on the human being, have been a remaining area under concern (Chiou et al., 2008; Adewuyi et al., 2016; Umukoro et al., 2017; Sharma et al., 2019; Barakat et al., 2020). Therefore, it is highly desirable to remove these toxins effectively from the polluted water.

The structural properties of these phenols and their derivatives have made them difficult to remove from the polluted water by classical methods, i.e., activated carbon adsorption, chemical oxidation, and biological treatment. Because activated carbon adsorption leads to phase separation without degradation of injurious pollutants, the chemical oxidation method is unable to remove pollutants efficiently, and biological treatments are slow and pH and temperature dependent, while the advanced oxidation process seems to be better for effective removal of such sort of destructive pollutants using light (Eryılmaz and Genç, 2021; Ren et al., 2021; Saputera et al., 2021).

Advanced oxidation leads to the formation of highly reactive species which ultimately react with organic pollutants to degrade them successfully (Mazivila et al., 2019; Du and Zhou, 2021; Gallo-Cordova et al., 2021; Huang et al., 2021; Luo et al., 2021). Among advanced oxidation processes, photocatalytic degradation and mineralization are efficient methods of converting highly toxic organic pollutants to harmless species under ambient conditions using light and a photocatalyst through homogeneous or heterogenous photocatalysis. In addition, heterogeneous photocatalysis is considered advantageous over homogenous photocatalysis due to an easy retrievability of a catalyst from the reaction mixture and then the reusability of a catalyst (Gisbertz and Pieber, 2020). Following the concept of the advanced oxidation process, the heterogeneous photocatalytic reaction starts with the generation of H<sub>2</sub>O<sub>2</sub>, OH, O<sub>2</sub>, HOO and H<sup>+</sup> species by the absorption of a photon having energy equal to or greater than the band gap energy of the photocatalyst which is being used (Loeb et al., 2019; Pandey et al., 2020; Serrà and Philippe, 2020; Danish et al., 2021). In addition, hydroxyl and superoxide anion radicals react with phenols, depending on the position and nature of substituent groups on ph enols, to degrade them into some oxygenate intermediates and consequently, these oxygenates mineralize to their respective harmless species (Qamar et al., 2017a; Qamar et al., 2017b; Alhogbi et al., 2020).

Metal oxide-assisted photocatalytic wastewater treatment is a relatively prospective subject and growing rapidly to remove hazardous pollutants from contaminated water. In this context, metallic oxide semiconductors such as TiO2, ZnO, Fe2O3, SnO2, WO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Cu<sub>2</sub>O, NiO, etc. have been studied extensively both in artificial and natural light sources to acquire pollution free water (Ahmed et al., 2010; Oturan and Aaron, 2014; Wang et al., 2014; Qamar et al., 2015; Zangeneh et al., 2015; Aslam et al., 2018). However, exploration of a potential photocatalyst for the effective removal of toxic pollutants from the wastewater has not over yet and researchers are paying attention to study the photocatalytic properties of CeO2-based photocatalysts for the abatement of organic pollutants. Although, bare CeO2 has wide application in electrocatalysis, solar cells, fuel cells and photocatalysis due to its high chemical stability, low toxicity and greater oxygen storage capacity (Ma et al., 2019; Fauzi et al., 2022). However, its performance in photocatalysis is unsatisfactory due to greater photo excitons' recombination, lower absorption cross-section of light spectrum and higher band gap (2.8-3.1 eV) energy (Ma et al., 2019; Fauzi et al., 2022). Therefore, it is a need to modify CeO<sub>2</sub> in order to increase its utilization as a photocatalyst for removal of organic toxins. The unique thing of this study is the introduction of transition metals into CeO<sub>2</sub> without significantly changing the cubic structure of CeO2 photocatalyst for the removal of 15 ppm 2chlorophenol in the illumination of 70 W indoor white light.

Previously, researchers utilized expensive artificial light sources such as solar simulator, Hg and Xe lamps for photocatalytic degradation of various organic toxins using variety of photocatalysts (Tang et al., 2004; Hao et al., 2015; Aslam et al., 2016; Xu et al., 2017). In addition, a few studies are available for the photocatalytic removal of 2-CP using CeO2-based photocatalysts such as  $CeO_2$ ,  $g-C_3N_4(0.94)/CeO_2(0.05)/Fe_3O_4(0.01)$ ,  $TiO_2-CeO_2-CeO_3$ ZrO<sub>2</sub> (Aslam et al., 2016; García-Hernández et al., 2019; Rashid et al., 2019). However, various combinations of CeO<sub>2</sub> with metals, non-metals and photocatalysts such as Ag<sub>2</sub>CO<sub>3</sub>, rGO, CdS, AgBr, SrFe<sub>12</sub>O<sub>9</sub>, BiOCl, g-C<sub>3</sub>N<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub>, etc., are reported for the photocatalytic removal of organic dyes, phenols and pharmaceutical ingredients (Ma et al., 2019; Yao et al., 2021; Fauzi et al., 2022). Moreover, literature reveals that a photocatalysis setup while using an economical 70 W indoor white light for the removal of 2-CP over the proposed composition of CeO2-based photocatalysts has not been reported before.

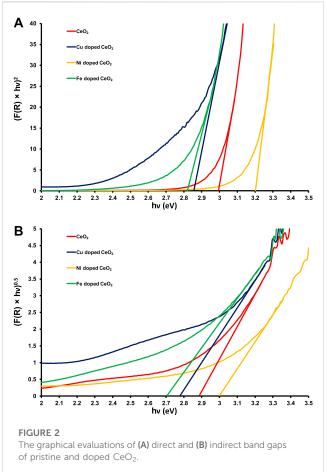


In this study, CeO<sub>2</sub> has been synthesized using a co-precipitation methodology and its modification was executed through doping with transition metals, i.e., Fe, Ni and Cu because 3d transition metals are considered capable dopants in tuning the properties of CeO<sub>2</sub> for catalysis applications (Yue and Zhang, 2009; Elias et al., 2014; Qi et al., 2019). The spectral response and bandgap of the synthesized materials were evaluated using UV-visible diffuse reflectance spectroscopy (UV-visible DRS) whereas photoluminescence (PL) fluorometer was used to investigate e- $-h^+$  recombination. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the structural and chemical characterization of synthesized materials. The photocatalytic activity of the synthesized photocatalysts was studied for the removal of 2-chlorophenol (2-CP) the kinetics for the photodegradation of 2-CP were also investigated.

# **Experimental**

# **Materials**

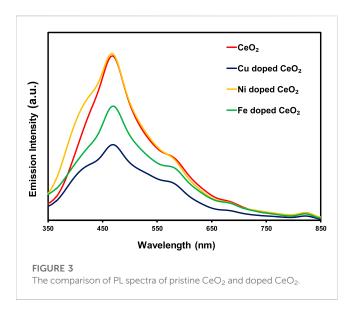
Cerium (III) nitrate hexahydrate  $[Ce(NO_3)_3.6H_2O, Sigma-Aldrich, \ge 99\%]$ , iron (III) nitrate non-ahydrate  $[Fe(NO_3)_3.9H_2O, Sigma-Aldrich, \ge 99\%]$ 

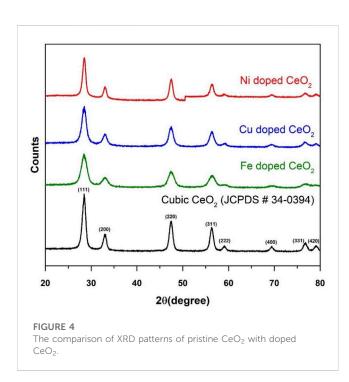


Sigma-Aldrich, 99.95%], nickel (II) nitrate hexahydrate [Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Sigma-Aldrich,  $\geq$ 99%], copper (II) nitrate trihydrate [Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O, Sigma-Aldrich, 99.99%], ethanol (C<sub>2</sub>H<sub>5</sub>OH, Sigma-Aldrich,  $\geq$ 99.8%), nitric acid [HNO<sub>3</sub>, Sigma-Aldrich, 70%], acetone [CH<sub>3</sub>COCH<sub>3</sub>, Sigma-Aldrich], potassium hydroxide [KOH, Sigma-Aldrich, 99.5%] and triton X-100 [Tx-100, Sigma-Aldrich] were used without further purification for the synthesis of photocatalysts.

# Synthesis of pristine CeO<sub>2</sub>

In a typical synthesis of CeO<sub>2</sub>, 30 g Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O was dissolved in 100 mL distilled water with continuous stirring until the formation of a clear solution. After complete dissolution, 3 mL Triton X-100 was added to the clear solution under continuous stirring for 30 min at room temperature. To hydrolyze the solution, 0.1M potassium hydroxide (KOH) was added to the solution dropwise till the formation of yellow precipitate near pH 9 at 50°C. The mixture containing the yellow precipitate, surfactant and KOH content was washed several times with distilled water and then with ethanol/water (30:60) mixture to remove surfactant and basic contents present in the mixture until the mixture attained the neutral pH. The precipitate was separated from the reaction mixture through filtration and the obtained yellow precipitate was again washed with ethanol/water (30:60) mixture and dried overnight at 100°C in a vacuum oven





and then calcined in a muffle furnace for 4 h at 400 $^{\circ}$ C. The calcined material was ground using mortar and pestle to get fine powder of CeO<sub>2</sub> photocatalyst.

### Synthesis of modified CeO<sub>2</sub>

For the synthesis of Cu doped  $CeO_2$ , 0.381 g  $Cu(NO_3)_2.3H_2O$  and 30.681 g  $Ce(NO_3)_3.6H_2O$  were dissolved separately in distilled water with continuous stirring at room temperature till the formation of clear solutions and marked solution A and B, respectively. Then, solution A was added slowly into the beaker having solution B with continuous stirring at 50°C for 10 min followed by the addition of 3 mL Triton X-100 under continuous

stirring for 30 min. The mixture of both precursors and surfactant was then hydrolyzed with the slow addition of 0.1M KOH till the formation of precipitate at pH 9. The formed precipitate was separated through filtration, washed with water and ethanol/ water (30:60) mixture, and dried overnight in a vacuum oven at 100 °C. The dried sample was then subjected to the muffle furnace for calcination at 400°C for 4 h. The calcined material was ground using mortar and pestle to get fine powder of Cu doped CeO2 photocatalyst. The same procedure was applied for the synthesis of Ni-doped CeO2 and Fe-doped CeO2 except for the different amounts of precursors, e.g., 0.496 g Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 0.723 g Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O about the Ni and Fe contents, respectively for 30.681 g of Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O. The synthesized photocatalytic materials were characterized by UV- visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence (PL), X-ray Diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS).

# Photocatalytic studies

The photocatalytic performance of transition metal doped CeO<sub>2</sub> was studied for the removal of 15 ppm 2-chlorophenol under the illumination of 70 W indoor white light (800  $\times$  10<sup>2</sup> lx) at room temperature. In this context, the synthetic wastewater containing 15 ppm 2-chlorophenol was prepared in the laboratory, and the dose of the photocatalyst was optimized by exposing the suspension having 100 mL of pollutant with varying amounts of CeO2 photocatalyst (50, 100, 150, and 200 mg) in a glass reactor of 14 cm (diameter) and 2 cm (height) to the indoor white light for 3 h and the samples were collected and filtered using 0.20 µm syringe filter. The filtered samples were then subjected to UV-visible spectrophotometer for the monitoring of photodegradation of 2-CP and 100 mg of the photocatalyst was found to be the optimum dose of catalyst in 100 mL of pollutant. The optimized amount, i.e., 100 mg/100 mL of all four photocatalysts was further used for the evaluation of their photocatalytic degradation efficiency in removing 2-CP under the exposure of 70 W indoor LED white light (800  $\times$  10<sup>2</sup> lx, 400-800 nm, Opple Lighting Co., Ltd. China) at room temperature and samples were collected after 30, 60, 90, 120, 180 and 240 min and filter using 0.20 µm syringe filter for UVvisible spectrophotometric analysis to evaluate the kinetic of photodegradation.

To study the removal of the target pollutant from the polluted water, the samples were collected using a syringe filter from the suspension exposed to the light after a regular interval and were subjected to UV-visible spectrophotometer for the determination of the concentration of the removed pollutant which ultimately led to the % removal of target pollutant by the photocatalyst under the exposure of light using the following equation.

$$\% removal = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

Here,  $C_o$  is the pollutant initial concentration whereas  $C_t$  is the concentration of the pollutant after exposure time "t." Moreover, the validity of Langmuir Hinshelwood (L-H) kinetic models was also

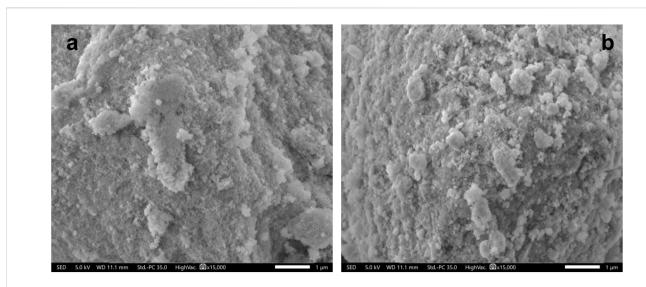
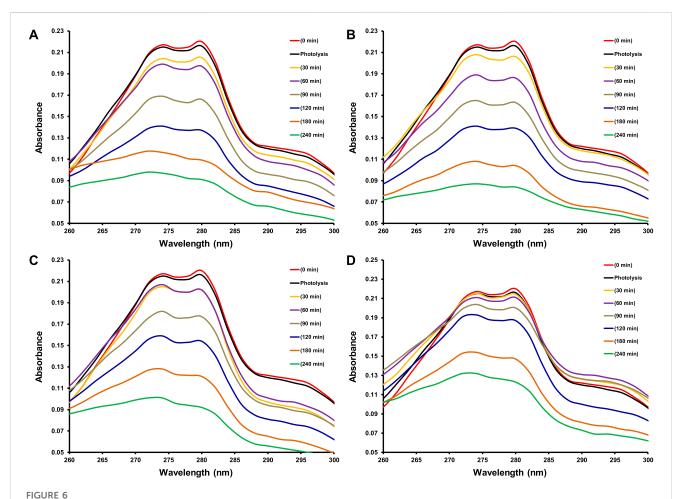
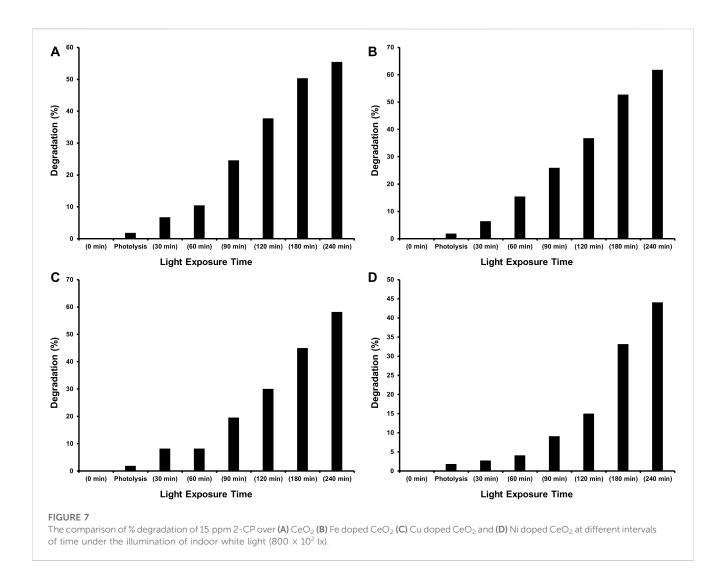


FIGURE 5
The comparison of scanning electron micrographs of (A) pristine CeO<sub>2</sub> and (B) Fe doped CeO<sub>2</sub>.



The comparison of absorption spectra for photocatalytic degradation of 15 ppm 2-CP over (A)  $CeO_2$  (B) Fe doped  $CeO_2$  (C) Cu doped  $CeO_2$  and (D) Ni doped  $CeO_2$  at different intervals of time under the illumination of indoor white light (800  $\times$  10<sup>2</sup> k).



studied using the following equation to evaluate the kinetics of photocatalytic removal of organic pollutants under exposure to light.

$$ln \frac{C_o}{C_t} = k \times t \tag{2}$$

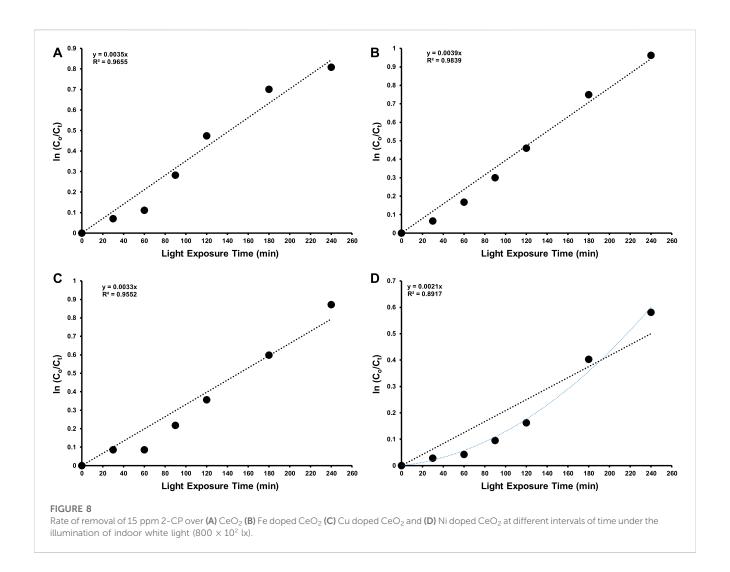
Here, k is the rate constant which was determined from the slope by plotting  $\ln \frac{C_o}{C}$  Vs. t.

### Results and discussion

The solid-state absorption response of the pristine  $CeO_2$  compared to the modified  $CeO_2$  is presented in Figure 1A in UV (200–400 nm) as well as visible (400–800 nm) regions of the spectrum. Wherein, Cu-doped  $CeO_2$  shows higher absorbance in both UV and visible regions than other synthesized materials. Interestingly, Cu-doped  $CeO_2$  and Fe-doped  $CeO_2$  showed higher absorbance of visible light than  $CeO_2$  and Ni-doped  $CeO_2$  whereas in the UV region of the spectrum only Cu-doped  $CeO_2$  presented higher absorbance than other photocatalysts. So, the insertion of Cu and Fe content into the structure of  $CeO_2$  leads to an increase in the

spectral response of  $CeO_2$  whereas the same amount of Ni content has a detrimental effect on the spectral response of the pristine  $CeO_2$ . Moreover, the response of these photocatalysts in reflecting the light spectrum has also been explored in Figure 1B. Wherein, lower reflectance (%) was noticed for  $CeO_2$  having copper contents followed by Fe and Ni contents in the lower energy region of the spectrum. This higher absorbance and lower reflectance (%) were attributed to the higher absorbance ability of copper content present in the structure of  $CeO_2$  as compared to Fe and Ni.

The direct and indirect band gap evaluations (Figures 2A, B) reveal a lowering in the band gap energy of Cu and Fe-doped CeO<sub>2</sub> photocatalysts as compared to pristine CeO<sub>2</sub> was noticed which may be attributed to the shifting of conduction band edges to lower energy due to the addition of Cu and Fe contents in the structure of CeO<sub>2</sub> (Yue and Zhang, 2009; Qi et al., 2019). Whereas a significant increase in the band gap energy of Ni-doped CeO<sub>2</sub> was observed. The direct and indirect band gaps of the pristine CeO<sub>2</sub> were noticed at ~3.0 and ~2.9 eV, respectively which have good agreement with the literature values (Aslam et al., 2016). Moreover, the direct band gap energies found for Cu, Fe, and Ni-doped CeO<sub>2</sub> photocatalysts are ~2.85, ~2.8, and ~3.2 eV whereas evaluated indirect band gap energies are ~2.78, ~2.7, and ~3.0 eV, respectively as shown in



Figures 2A, B. A greater decrease in the band gap energy was noticed for Fe doped CeO<sub>2</sub> as compared to other photocatalysts which reveal that this photocatalyst requires lower energy as compared to pristine and other modified photocatalysts to make good use of excitons for the removal of organic toxins under the illumination of light.

Photoluminescence analysis is a promising technique to study the emission intensity of the excited electron under the illumination of light which ultimately leads to the study of  $e^-h^+$  recombination process. Figure 3 depicts the comparison of photoluminescence spectra of pristine and doped CeO<sub>2</sub> photocatalysts, wherein a significantly lower emission intensity was noticed for Cu and Nidoped CeO<sub>2</sub> as compared to unmodified CeO<sub>2</sub>. The relative decrease in emission intensities of the Cu and Fe doped CeO<sub>2</sub> as compared to CeO<sub>2</sub> is strong evidence for lowering  $e^-h^+$  recombination rate than pristine CeO<sub>2</sub> which favors the photocatalytic degradation of organic toxins. Moreover, the decrease in strong emission bands around 470 nm is attributed to the trapping of photoexcitons by the surface defects generated due to the insertion of Cu or Fe into the structure of CeO<sub>2</sub> (George et al., 2020).

The comparison of x-ray diffraction patterns of the modified  $CeO_2$  with pristine  $CeO_2$  is presented in Figure 4 and the cubic phase of the synthesized  $CeO_2$  was confirmed by matching diffractions planes (111), (200), (220), (311), (222), (400), (331), and (420) with

literature and JCPDS 34-0394 (Aslam et al., 2016). The absence of additional diffraction peaks related to the dopant entities in the respective diffraction patterns verifies the successful doping of CeO<sub>2</sub> with Cu, Ni, and Fe. Moreover, few changes such as reduction in few peaks' height, minor peak shift at 2θ (28.525°) and peaks' broadening in XRD patterns of modified CeO2 as compared to pristine CeO2 also favour the introduction of dopants in CeO<sub>2</sub> (Kumar et al., 2010). Moreover, the successful insertion of dopants into CeO2 without significantly altering its structure were also evident from the micrographs as shown in Figure 5. The average crystallite size of the photocatalytic materials was calculated using a high-intensity diffraction peak at 2θ (28.525°) with the help of the Debye-Scherrer equation. The calculated crystallite sizes were 9.76, 3.46, 4.97, and 8.28 nm for pristine CeO<sub>2</sub>, Fe doped CeO<sub>2</sub>, Cu doped CeO<sub>2</sub>, and Ni doped CeO2, respectively. Moreover, a significant difference in doped CeO2 as compared to unmodified CeO2 were also reported in literature which support the changes in crystallite sizes of Fe and Cu doped CeO<sub>2</sub> (Yue and Zhang, 2009; Kumar et al., 2010; Qi et al., 2019).

As this study was designed to investigate the effect of transition metal dopants on the photocatalytic performance of CeO<sub>2</sub> under the illumination of indoor white light for the degradation of 15 ppm 2–CP. Before the exposure of suspension containing photocatalyst

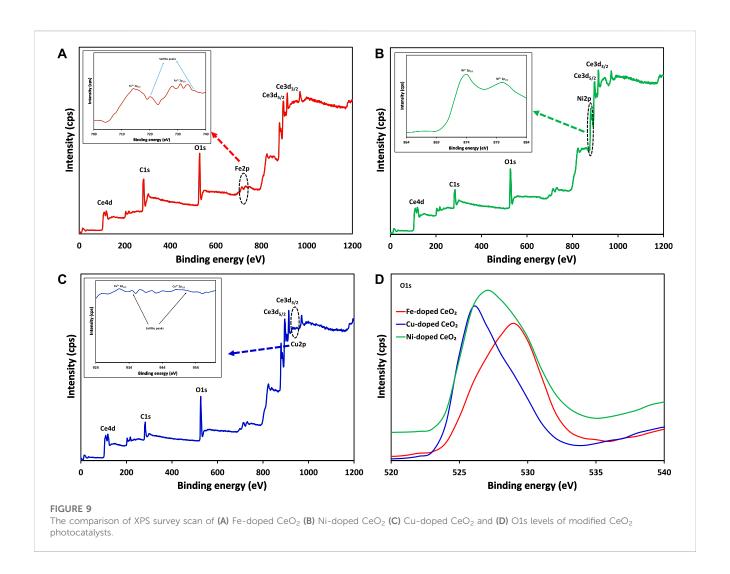


TABLE 1 Agar Well cut diffusion method zone of inhibition for the antifungal action of CeO<sub>2</sub>, Fe-doped CeO<sub>2</sub>, Ni-doped CeO<sub>2</sub> and Cu-doped CeO<sub>2</sub>.

Antifungal performance			
Bacterial strains	Samples	Blank	Zone of inhibition (mm)
M. fructicola	CeO <sub>2</sub>	0	17.4
	Fe-doped CeO <sub>2</sub>	0	25.3
	Cu-doped CeO <sub>2</sub>	0	21.1
	Ni-doped CeO <sub>2</sub>	0	12.2
F. oxysporum	CeO <sub>2</sub>	0	15.7
	Fe-doped CeO <sub>2</sub>	0	23.1
	Cu-doped CeO <sub>2</sub>	0	19.4
	Ni-doped CeO <sub>2</sub>	0	10.3

and 2-CP to light as mentioned in the experimental section, the suspension was kept in dark for 30 min to establish an equilibrium between pollutant and catalyst. The photolysis of 2-CP was also

evaluated by recording the absorption spectrum of the substrate after 240 min of light exposure without the presence of a photocatalyst. The amount of photocatalyst was also optimized

(100 mg of photocatalyst) while studying the photocatalytic removal of 15 ppm 2-CP with varying doses of  $CeO_2$  catalyst under the illumination of indoor white light. The comparison of absorption spectra of photocatalytic removal of 2-CP over pristine  $CeO_2$ , Fe doped  $CeO_2$ , Cu doped  $CeO_2$ , and Ni-doped  $CeO_2$  under the illumination of indoor white light  $(800 \times 102 \text{ lx})$  is provided in Figure 6, respectively at different exposure time. Whereas the photocatalytic degradation (%) of 2-CP at different exposure over the pristine and modified  $CeO_2$  photocatalysts is given in Figure 7, respectively and highest photodegradation  $(\sim 65\%)$  was noticed for Fe doped  $CeO_2$  followed by Cu doped  $CeO_2$   $(\sim 60\%)$ , pure  $CeO_2$   $(\sim 59\%)$  and Ni doped  $CeO_2$   $(\sim 45\%)$  under the exposure of white light after 240 min of exposure. The decreasing trend of removal efficiency (%) of the photocatalysts is given below.

### Fe doped $CeO_2 > Cu doped CeO_2 > CeO_2 > Ni doped CeO_2$

Moreover, the rate of photodegradation of 15 ppm 2-CP over synthesized photocatalysts was also investigated and higher photocatalytic removal efficiency with rate constant (k =  $3.9 \times 10^{-3}$  min $^{-1}$ ) was observed by Fe doped CeO<sub>2</sub> than others as shown in Figure 8. The calculated bandgap energy values as shown in Figure 2 also support the possible higher photodegradation efficiency of Fedoped CeO<sub>2</sub> due to its lower bandgap energy than CeO<sub>2</sub>. Moreover, a lower photo-excitons' recombination in PL spectra presented by Fedoped CeO<sub>2</sub> also arguments its higher removal efficiency due to the possible charge transferability for the generation of ROS. The decreasing trend of rate of removal of 2-CP by different photocatalysts is provided below.

### Fe doped $CeO_2 > CeO_2 > Cu$ doped $CeO_2 > Ni$ doped $CeO_2$

The kinetic study also reveals that the photocatalytic removal of 2-CP by Fe doped  $CeO_2$ , pure  $CeO_2$ , Cu doped  $CeO_2$  followed Langmuir Hinshelwood (L-H) kinetic model whereas the photocatalytic removal of 2-CP by Ni doped  $CeO_2$  did not follow Langmuir Hinshelwood (L-H) kinetic model. Previously, Zhang et al. (2022) reported a decrease in degradation rate of 2-CP removal in the illumination of 5W LED white light as compared to 300 W Xe arc lamp. In another study,  $BiFeO_3/Bi_2Fe_4O_9$  heterojunctions were able to remove 95% of the 2-CP in the exposure of 150W LED white light (Wang et al., 2022).

In this study, x-ray photoelectron spectroscopy (XPS) was also carried out to investigate the chemical and electronic states of the elements in modified materials as shown in Figure 9. The presence of Ce3d<sub>3/2</sub>, Ce3d<sub>5/2</sub>, Fe2p<sub>1/2</sub>, Fe2p<sub>3/2</sub>, Cu2p<sub>1/2</sub>, Cu2p<sub>3/2</sub>, Ni2p<sub>1/2</sub>, Ni2p<sub>3/2</sub> core levels and O1s levels in the synthesized photocatalysts can be seen in Figure 9, which confirm the existence of dopants (Fe<sup>3+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>) in doped CeO<sub>2</sub> as shown in inset figures. Moreover, the effect of dopants was also verified by the appearance of peak correspond to O1s level at different binding energies which ultimately confirm the different environment of oxygen.

# Antifungal activity

Using the agar well-diffusion method and amphotericin B as a reference, CeO<sub>2</sub>, Fe-doped CeO<sub>2</sub>, Ni-doped CeO<sub>2</sub>, and Cu-doped

 ${\rm CeO_2}$  nanoparticles were further assessed for their antifungal activity against M. fructicola and F. oxysporum. Table 1 provides a summary of the outcomes. According to the antifungal activity data (Table 1), Fe-doped  ${\rm CeO_2}$  nanoparticles exhibit greater toxicity when compared to  ${\rm CeO_2}$ , Ni-doped  ${\rm CeO_2}$ , and  ${\rm Cu-doped}$   ${\rm CeO_2}$  nanoparticles, with zone inhibition values of 25.3 and 23.1 mm. Due to their small particle size, the Fe-doped  ${\rm CeO_2}$  nanoparticles easily pass through the fungal cell membrane, attach to functional protein groups as well as substances that contain phosphorus and sulphur, including DNA, and ultimately result in fungal cell death. The improved antifungal impact was caused by the synergistic interaction of Fe-doped  ${\rm CeO_2}$  nanoparticles and decreased size.

# Conclusion

In conclusion, cubic  $CeO_2$  was doped successfully with Fe, Cu and Ni through co-precipitation method followed by calcination at  $400^{\circ}$ C for 4 h. The crystallite sizes were reduced from 9.76 to 3.46 nm by incorporating 3d transition metals into  $CeO_2$ . Solid-state absorption analysis revealed a better spectral response and lower bandgap energy of Fe and Cu-doped  $CeO_2$  than unmodified  $CeO_2$  whereas increase in bandgap energy was noticed for Ni-doped  $CeO_2$ . Moreover, the insertion of Cu and Fe into  $CeO_2$  suppressed its  $e^-h^+$  recombination process by generating trapping sites for photoexcitons. Among the synthesized photocatalysts in this study, Fedoped  $CeO_2$  is excellent for the removal of 2-CP in the illumination of 70 W indoor LED white light.

# Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

### **Author contributions**

MQ: Conception, design of study, writing-original draft preparation. SI: Interpret the data, performed major experimental works, writing-original draft preparation and editing. MA: He wrote the antifungal analysis part in the manuscript, interpreted the data and critical revision. AA: He wrote the UV-vis application part in the manuscript, interpreted the data and critical revision. ABi: Conception, performed dye degradation analysis, acquisition of data, interpret the data. KR: She wrote the PL analysis part in the manuscript, interpreted the data and critical revision. HF: degradation analysis, Performed reviewed manuscript and critical revision. TS: Reviewed original manuscript, and critical revision. ABa: He performed synthesis methodology. NA: Visualization of data, XRD analysis, funding acquisition, writing reviewing, and editing. HI: Conception, visualization of data, performed bandgap analysis, funding acquisition. RA: She wrote the SEM analysis part in the manuscript, funding acquisition, interpreted the data and critical revision. EE: Visualization of data, reviewed original manuscript and critical revision.

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# Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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