

Aluminium Doped Cerium Oxide as an Efficient Nanophotocatalyst for the Elimination of Rhodamine B Dye Present in Water

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Received: 13 January 2023; Accepted: 11 February 2023; Published online: 30 March 2023;	AJC-21185
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The photodegradation efficiency of rhodamine B (RhB) dye present in water using aluminium-doped CeO₂ (Ce_{1-x}Al_xO_{2- δ}; *x* = 0, 0.1, 0.2, 0.3, 0.4 and 0.5) nanoparticles was studied in this work. The synthesis of nanoparticles was done by simple wet chemical precipitation route. The photochemical characteristics of Al doped CeO₂ was studied by UV-visible (UV) and photoluminescence (PL) techniques. The photocatalytic removal of RhB dye was studied using the above nanomaterials as photocatalysts and the degradation efficiency was optimized by varying the pH and the concentration of dye solution under UV light. Among the samples studied, 0.02 g of sample with the composition of Ce_{0.50}Al_{0.50}O_{2- δ} exhibited a higher photocatalytic degradation efficiency of 70.94% against RhB dye having concentration of 0.05 g/L at the pH of 11 under UV irradiation for 60 min at room temperature.

Keywords: Al doped CeO₂, Rhodamine B, photocatalytic degradation, UV irradiation.

INTRODUCTION

In current environment, the removal of contaminants from water bodies is an advanced technology [1-4]. Water pollution is a very serious concern, which is mainly due to the discharge of hazardous chemicals into the waterbodies by textile, pharmaceutical, petrochemical and fine chemical industries. Through this global problem, the living things, such as, fauna and flora which present in the ecosystem are severely affected [5]. The advanced oxidative process is a best method for the removal of industrial waste compared to the biological and adsorption methods [6]. In this method, the OH• active radical species are generated from common oxidants O_2 , O_3 and H_2O_2 . This process is improved with the doping of transition metals and by the irradiation of light sources like UV, visible light and γ -rays. This will lead to the enhancement in the gener-ation of OH• radicals [7,8].

 CeO_2 is a known semiconductor that has been used widely as catalysts [9-12], photocatalysts [13-16] and fluorescent materials [17]. The variable valence state of cerium (+3 and +4) in CeO₂ is responsible for its excellent oxygen ion conduction [18-20]. The aluminium based nanoparticles were found to be the perfect catalysts in specific applications such as antimicrobial and biomedical fields [21,22]. To improve the photocatalytic efficiency of CeO₂, different metals, *e.g.* chromium [23], copper [24], cobalt [25], *etc.* were doped. However, aluminium doped TiO₂ samples exhibited better photocatalytic efficiency [26]. Rhodamine B (RhB) dye is a toxic dye which is mainly used in textile industry. This dye can easily enter the body of humans through food and can cause carcinogenic diseases so it needs to be removed from water sample [27] by an efficient method. In this work, the chemical precipitation has been adopted to synthesize Ce_{1-x}Al_xO_{2-δ} nanoparticles and the prepared materials have been utilized to degrade the RhB dye present in water sample.

EXPERIMENTAL

The Al doped ceria nanoparticles were prepared by simple wet chemical precipitation route using metal nitrate salts and sodium hydroxide precipitant and their physico-chemical

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characteristics were already reported [28]. The photocatalytic characteristics of Al doped CeO₂ nanophotocatalysts to degrade RhB dye present in water were studied by using a simple photoreactor equipped with the UV light source. For each experiment, 0.02 g of photocatalyst (Al doped CeO₂ nanoparticles) was suspended in 50 mL of 0.0005% RhB dye aqueous solution. After mixing the same in dark for about 60 min, it was subjected to UV irradiation. The sampling was done at regular time intervals, *viz.* 0, 15, 30, 45 and 60 min. The solution (3 mL) after centrifugation was subjected to UV measurements at the wavelength of 554 nm. The percentage of degradation of dye was calculated as per eqn. 1:

Degradation of dye (%) =
$$\frac{C_o - C_t}{C_o} \times 100$$
 (1)

where C_o is the absorbance of the dye solution initially and C_t is the absorbance after a particular time interval, t.

Photochemical evaluation of Al doped CeO₂ nanoparticles: The absorbance spectra of the aluminium doped ceria samples were examined by UV-visible spectrophotometer (Shimadzu 1800), whereas the photoluminescence (PL) spectral analysis of the materials was studied by spectrofluorometer (JASCO) at room temperature.

RESULTS AND DISCUSSION

UV-visible studies: Fig. 1 shows that the UV absorption region of CeO₂ and Al doped CeO₂ nanoparticles exhibited a broad peak between 330-350 nm with the maximum value at 340 nm approximately. The absorption energy band gap (E_g) of the materials was calculated using Tauc method [29]. The plot drawn between $(\alpha hv)^2$ versus hv is shown in Fig. 2. E_g value for pure CeO₂ was found to be 3.0 eV and for Al doped CeO₂ was found to be in the range between 1.5 and 2.7 eV. The E_g value of Co-doped CeO₂ was reported earlier as 1.61 eV [30].





 $\begin{array}{lll} \mbox{Fig. 2.} & \mbox{Band gap curves obtained on CeO_2 based nanoparticles (a) pure CeO_2;} \\ & (b) $Ce_{0.90}Al_{0.10}O_{2\text{-}6}$; (c) $Ce_{0.80}Al_{0.20}O_{2\text{-}6}$; (d) $Ce_{0.70}Al_{0.30}O_{2\text{-}6}$; (e) $Ce_{0.60}Al_{0.40}O_{2\text{-}6}$; (f) $Ce_{0.50}Al_{0.50}O_{2\text{-}6}$ \\ \end{array}$

Photoluminescence (PL) studies: The PL spectra obtained on pure CeO₂ and Al doped CeO₂ nanoparticles are shown in Fig. 3. Since defects in the materials are formed in response to dopant concentration, the PL spectra were found to be extremely dopant concentration dependent. The Al doped CeO₂ nanoparticles exhibited peaks at 420, 445 and 480 nm, which are related with blue emission. These characteristics of the materials may be due to their structural behaviour and the charge transfer occurs between cerium and oxygen ions as reported [31,32]. Based on the PL spectra, the UV light source has been recommended for further studies.



Fig. 3. PL spectra obtained on CeO₂ based nanoparticles (a) pure CeO₂; (b) Ce_{0.90}Al_{0.10}O₂₋₆; (c) Ce_{0.80}Al_{0.20}O₂₋₆; (d) Ce_{0.70}Al_{0.30}O₂₋₆; (e) Ce_{0.60}Al_{0.40}O₂₋₆; (f) Ce_{0.50}Al_{0.50}O₂₋₆

Photocatalytic studies: Fig. 4 shows the photocatalytic degradation graphs obtained in this research work. The results revealed that the highest photodegradation (56.92%) was exhi-



Fig. 4. Photodegradation curves obtained in presence of CeO₂ based nanophotocatalysts with RhB dye and RhB dye alone without nanophotocatalysts (a) RhB alone in dark, (b) RhB alone in light, (c) pure CeO₂; (d) Ce_{0.90}Al_{0.10}O₂₋₆; (e) Ce_{0.80}Al_{0.20}O_{2-δ}; (f) Ce_{0.70}Al_{0.30}O_{2-δ}; (g) Ce_{0.60}Al_{0.40}O_{2-δ}; (h) Ce_{0.50}Al_{0.50}O_{2-δ}

bited by $Ce_{0.50}Al_{0.50}O_{2-\delta}$ catalyst after 60 min of UV irradiation. The photodegradation data are presented in Table-1. The efficiency of the catalyst was based on the type and structure of dyes used [33]. Hence, 50 mol% of Al doped CeO₂ nanophotocatalyst ($Ce_{0.50}Al_{0.50}O_{2-\delta}$) was further used as an optimized composition to examine the photocatalytic behaviour with respect to the change in pH and by changing the dye concentration. A plot of ln C₄/C₀ vs. time is displayed in Fig. 5. The kinetics data obeyed the pseudo-first order reaction mechanism as reported by Langmuir and Hinshelwood (eqn. 2) [34].

$$\ln \frac{C_{t}}{C_{o}} = -kt$$
 (2)



Fig. 5. First order kinetic plot of RhB dye using (a) RhB alone in the absence of photocatalyst; (b) pure CeO₂; (c) Ce_{0.90}Al_{0.10}O_{2.6}; (d) Ce_{0.80}Al_{0.20}O_{2.6}; (e) Ce_{0.70}Al_{0.30}O_{2.6}; (f) Ce_{0.60}Al_{0.40}O_{2.6}; (g) Ce_{0.50}Al_{0.50}O_{2.6}

TABLE-1		
PERCENTAGE DEGRADATION OF RhB DYE IN		
PRESENCE OF PURECERIA AND ALUMINIUM DOPED		
CERIA NANOPHOTOCATALYSTSAFTER 60 min		
OF UV LIGHT IRRADIATION		
Sample	Percentage degradation after	
	60 min of UV light irradiation	
CeO ₂	35.46	
$Ce_{0.90}Al_{0.10}O_{2-\delta}$	49.26	
$Ce_{0.80}Al_{0.20}O_{2-\delta}$	46.43	
$Ce_{0.70}Al_{0.30}O_{2-\delta}$	47.54	
$Ce_{0.60}Al_{0.40}O_{2-\delta}$	49.09	
$Ce_{0.50}Al_{0.50}O_{2-\delta}$	56.92	

The rate constant (k) values were reported to be 0.08 min⁻¹ (CeO₂), 0.024 min⁻¹ (Ce_{0.90}Al_{0.10}O_{2-δ}), 0.014 min⁻¹ (Ce_{0.80}Al_{0.20}O_{2-δ}), 0.01 min⁻¹ (Ce_{0.70}Al_{0.30}O_{2-δ}), 0.016 min⁻¹ (Ce_{0.60}Al_{0.40}O_{2-δ}) and 0.014 min⁻¹ (Ce_{0.50}Al_{0.50}O_{2-δ}) in this research work. Possible mechanism of the photocatalytic reaction can be explained as follows (eqns. 3-7):

$$Ce_{1-x}Al_xO_{2-\delta} + h\nu \longrightarrow e_{CB}^- + h_{VB}^+$$
(3)

$$H_2O + h_{VB}^{+} \longrightarrow H^{+} + OH^{\bullet}$$
(4)

$$O_2 + e_{CB}^{-} \longrightarrow O_2^{-\bullet}$$
(5)

$$Dye + OH^{\bullet} \longrightarrow Degradation of dye$$
 (6)

$$Dye + O_2^{-\bullet} \longrightarrow Degradation of dye$$
(7)

When Al doped CeO₂ was subjected to UV light at the wavelength of 340 nm, electrons were moved from valence band (VB) to conduction band (CB). This will result in the formation of electron-hole pair. Then, the e_{CB}^- (electrons in the CB) and h_{VB}^+ (holes in the VB) will move to the surface of the catalyst (Al doped CeO₂). There h_{VB}^+ will react with surface bound water moisture (H₂O) to form hydroxyl radicals (OH[•]) at the surface and the e_{CB}^- (electrons at the CB) will reduce O₂ as O₂^{-•}. Finally, OH[•] and O₂^{-•} will react with the RhB dye molecule and make the dye to undergo degradation reaction. This will result in the decolouration of dye [35].

Effect of pH: The effect of pH value on the photocatalytic efficiency of RhB dye using Ce_{0.50}Al_{0.50}O_{2-δ} nanophotocatalyst is displayed in Fig. 6. The initial pH value of RhB is 4.3. Either dilute HCl or KOH solution was utilized to change the pH of the solution as per requirement. The dye solution with varying pH values of (2.5, 4.3, 6.5, 9 and 11) was prepared. The prepared dye solutions were subjected to UV light irradiation for 60 min in presence of Ce_{0.50}Al_{0.50}O₂₋₈ nanophotocatalyst and then their photocatalytic behaviour was studied. It was found that the degradation efficiency of RhB dye solution increased till the pH of 4.3 and then the degradation efficiency reduced with increase in pH of the solution. The photocatalytic behaviour was lower at the pH of 6.5 and resulted with optimum degradation at pH 11. The optimum RhB degradation (70.94%) found at the pH value of 11 may be due to the enhancement of photocatalysis by the Al doped CeO₂ photocatalysts and photolysis reaction of RhB [36]. In the basic medium, OH[•] radicals can be generated easily by the OH⁻ ions available on the surface of the Al doped CeO₂ and this may the reason for higher photodegradation at the pH of 11 [37].



Fig. 6. Effect of pH value on the degradation efficiency of RhB in presence of $Ce_{0.50}Al_{0.50}O_{2.\delta}$ photocatalyst material at different pH = 2.5, 4.3, 6.5, 9 and 11

The percentage photodegradation of RhB dye using $Ce_{0.50}Al_{0.50}O_{2-\delta}$ nanophotocatalyst with respect to different pH is presented in Table-2.

TABLE-2 PERCENTAGE PHOTODEGRADATION OF RhB DYE USING Ce _{0.50} Al _{0.50} O2.& NANOPHOTOCATALYST WITH RESPECT TO DIFFERENT pH VALUES		
pH	Percentage degradation after 60 min of UV light irradiation	
2.5	38.32	
4.3	56.92	
6.5	22.90	
9.0	23.17	
11.0	70.94	

Effect of dye concentration: The photocatalytic degradation of Ce_{0.50}Al_{0.50}O_{2-δ} was examined at a standardized pH value of 11 with different concentrations of RhB dye *viz.*, 0.0025 g/L, 0.005 g/L, 0.0075 g/L and 0.01 g/L for 60 min under UV light irradiation (Fig. 7). The effect of initial concentration of dye on the photodegradation of RhB using Ce_{0.50}Al_{0.50}O_{2-δ} nanophotocatlyst at pH of 11 is presented in Table-3. The efficiency of photodegradation of Ce_{0.50}Al_{0.50}O_{2-δ} (best material) was optimum with the dye concentration of 0.005 g/L at pH 11. At this condition, the photodegration efficiency of Ce_{0.50}Al_{0.50}O_{2-δ} nanophotocatalyst was reported to be 70.94%. Above this concentration, RhB dye molecule may not have active sites for the effective

TABLE-3 EFFECT OF INITIAL CONCENTRATION OF DYE ON THE PHOTODEGRADATION OF RhB USING Ce _{0.50} Al _{0.50} O _{2.8} NANOPHOTOCATLYST AT pH 11		
RhB dye concentration (g/L)	Percentage degradation after 60 min of UV light irradiation	
0.0250	69.66	
0.0050	70.94	
0.0075	64.31	
0.0100	51.76	



Fig. 7. Effect of initial concentration of dye in the photodegrdation of RhB dye in presence of Ce_{0.50}Al_{0.50}O_{2.8} photocatalyst material at pH 11

adsorption of hydroxyl radicals because of higher turbidity level and as a result degradation efficiency got reduced [38-40].

Conclusion

Phase pure CeO₂ and Al-doped CeO₂ (Ce_{1-x}Al_xO_{2- δ}; where x = 0, 0.10, 0.20, 0.30, 0.40 and 0.50) nanoparticles were synthesized by simple chemical precipitation method. The UV visible spectra of the samples showed a maximum absorption (λ_{max}) at 340 nm. The band gap of the samples was reported to be 3.0 eV for pure CeO_2 and in the range of 1.5 to 2.7 eV for the Al doped CeO_2 samples. The photoluminescence (PL) spectra of Al doped CeO₂ particles resulted with three peaks, viz. at 420, 445 and 480 nm, which are relevant to blue emission. Among the samples studied, photodegradation efficiency of 56.92% was shown by $Ce_{0.50}Al_{0.50}O_{2-\delta}$ nanophotocatalyst after 60 min of UV irradiation. The photocatalytic reaction obeyed pseudo first order reaction mechanism. Under the optimum conditions (at the pH of 11 and with concentration of dye of 0.005 g/L), highest percentage photodegradation (70.94%) of rhodamine B (RhB) dye was achieved using the optimized $Ce_{0.50}Al_{0.50}O_{2-\delta}$ nanophotocatalyst at the room temperature after 60 min of UV irradiation.

ACKNOWLEDGEMENTS

The authors thank Karunya Institute of Technology and Sciences (KITS) for providing the necessary research facilities to complete this research work.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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