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Synthesis, Characterization and Photocatalytic Study of Cerium Oxide/Zeolite-NaX Catalyst with Brilliant Green Dye Degradation

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ABSTRACT

Synthesis of zeolite NaX (Zeo-NaX) from coal fly ash and its development into a photocatalyst is a rarely studied current research field. The present work focuses on this field by using cerium oxide photosensitizer over Zeo-NaX. The ceria supported zeolite-NaX (CeO_2/Zeo-NaX) was prepared by introducing nanosize CeO_2 into Zeo-NaX framework through ion-exchange method. The prepared catalysts were characterized by FT-IR, XRD, SEM, EDX, BET Surface area, and DRS techniques. Photocatalytic degradation of brilliant green dye (BG; 10 ppm) over the synthesized photocatalyst was studied with visible light irradiation (100 W tungsten lamp). The effects of pH, dye concentration, and catalyst dosage were also studied on the degradation reaction of BG. By varying the pH, dye concentration, and catalyst dosage, the observed percentage of photocatalytic degradation of BG are (28-100 %), (80-94 %) and (77-94 %) respectively. Thus the present work established the development of nano zeolite photocatalyst with CeO_2 photosensitizer.

1. Introduction

Coal Fly ash (CFA) is a major solid waste from coal-firing power stations. In India, more than 112 million tons of fly ash is generated every year and there is a tendency to increase every year [1]. Since only about 20-30 % of the generated fly ash is used as an additive in cement and concrete manufacture, the management of fly ash is a global concern from both environmental and economic points of view. Fly ash consists of crystalline aluminosilicate, mullite and α-quartz with trace amounts of metal oxides depending on the origin of coal [2]. Because of high silica and alumina content, fly ash can be converted into zeolite material by hydrothermal treatment, and subsequently it can be used as adsorbents, ion–exchangers, catalysts etc., [3, 4].

Presently there is a growing interest in using coal fly ash derived zeolite for adsorption and degradation of dyes. The incorporation of light-absorbing transition metal heteroatoms in the framework of zeolites could make the structure photoactive [5]. Most of the previous studies reported the degradation of dyes using metal ions supported commercial zeolite and registered a high catalytic activity [6, 7, 8].

Advanced oxidation process (AOP), especially photocatalysis, is one of the few prominent methods available for wastewater treatment because it can degrade contaminants into stable inorganic compounds, such as carbon dioxide and water. The abundance of hydroxyl radicals generated by the AOPs plays an important role in oxidizing the organic species present in wastewater into harmless species [9]. Heterogeneous photocatalysis by semiconductor materials, such as TiO_2, ZnO, Fe_2O_3, CdS, GaP, CeO_2 and ZnS, have been widely used in toxic pollutant degradation [10]. In our previous work [11] we developed iron oxide/Zeo-NaX photocatalyst material and observed a high photocatalytic activity in methylene blue dye degradation.

In the present work zeolite is first prepared from the waste material coal fly ash and then CeO_2 is incorporated into it. The resulting nano CeO_2/Zeo-NaX photocatalyst is assessed for its visible light activity by the photocatalytic degradation of brilliant green (BG) dye. The results show that the developed zeolite photocatalyst material is in nano form and has greater efficiency in BG dye pollutant degradation.

2. Experimental Methods

2.1 Materials

F-type coal fly ash sample was kindly provided by the electrostatic precipitators of Tuticorin Thermal Power Station (TTPS), Thoothukudi, Tamil Nadu, India. Brilliant green dye, NaOH, HCl (39%) and H_2O_2 were obtained from LOBA Chemie, Mumbai. $(NH_4)_2Ce(NO_3)_6$ was obtained from Sigma-Aldrich. All the chemicals used in the study were of AR grade and the water used was a distilled one.

2.2 Synthesis of Zeolite from Coal Fly Ash

The raw fly ash sample was initially screened through a mechanical siever of 75 µm size, to eliminate the larger particles. The unburnt carbon (3 %) along with other volatile materials present in fly ash were removed by calcination at 800 (±10 °C) for 2 h. A mixture of sodium hydroxide and fly ash (1.2:1) was fused at 550 °C for 1 h in a silica crucible. The products obtained after the fusion process were cooled to room temperature, ground further and dissolved in water (10 g fly ash / 100 mL water). The slurry thus obtained was agitated mechanically for 8 h. Crystallisation of the sodium aluminosilicate gel thus obtained was then performed under static condition of 90 °C in an oven for 6h without any disturbance. The resultant precipitate was washed several times with distilled water to remove excess NaOH, filtered and dried. The dried powder (Zeo-NaX) was characterized for finding the nature of zeolite.

2.3 Synthesis of CeO_2/Zeolite-NaX

About 2 g of $(NH_4)_2Ce(NO_3)_6$ and 1 g of Zeo-NaX were dispersed in 30 mL of water and gently stirred at 333 K for 2 h. The obtained and Ce^{4+} incorporated Zeo-NaX was filtered through whatman No.1 filter paper, washed thoroughly with distilled water and finally dried at 353 K overnight. Lastly the sample was calcined at 550 °C for 4 h, in order to obtain ceria-incorporated zeolite (CeO_2/Zeo-NaX) material.

2.4 Characterization of the Synthesized Materials

FTIR spectra of the powdered zeolite samples were recorded using Jasco FTIR spectrophotometer model 410 in the wavenumber range 400–4000 cm^{-1}. X-ray diffraction (XRD) was recorded for $2\theta = 10–80°$ in a step of 0.05° using PANalytical Expert Pro-MPG with generator set at 30 mA and 40 kV and Cu Kα radiation ($\lambda = 1.5406$ Å). SEM images of the sample were observed with Jeol JSM-6390 instrument operating at 20 kV after

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coating the samples with gold. The samples were characterized by BET surface area analysis by nitrogen adsorption at 77 K using an ASAP-2010 Porosimeter by Micrometrics Corporation. Diffuse reflectance spectra were recorded with UV–vis spectrophotometer, Shimadzu model UV-2550 against $BaSO_4$ white background.

2.5 Photocatalytic Process

The photocatalytic activity of the prepared material was investigated by following the degradation of brilliant green dye in aqueous solution. In a typical experiment, 200 mL of BG dye solution (10 ppm) containing 100 mg of the photocatalyst was stirred. Then the solution was irradiated for 3 h with visible light (cut off with filter for UV; intensity = 4.61×10^{-4} W/cm^2 at 555 nm using 200 K Kusam-Meco Luxmeter) from 100 W tungsten lamp at its natural pH 6.9. A uniform dispersion of photocatalyst particles was ensured by stirring with a magnetic bar and also with air bubbling into the solution, which also provided a constant supply of oxygen. Dye sample (2 mL) withdrawn at regular time intervals was centrifuged and the absorbance of the supernatant solution was read out spectrophotometrically at 625 nm (Perkin Elmer Lambda 3B) in matched 1 cm quartz cuvettes. The experiment was repeated twice/thrice with the same material catalyst and the efficiency was monitored on reuse. The effect of rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, and volume of H_2O_2 on the photodegradation of BG was also studied.

3. Results and Discussion

3.1 FT-IR Characterization

The FTIR spectra of the synthesized materials are presented in Fig. 1. The spectrum of Na-X zeolite (Fig. 1b) exhibits absorptions at 461, 565, 674, 754, 980, 1082 and 1198 cm^{-1}. The bands in the region at 980 cm^{-1} and 1082 cm^{-1} respectively represent the characteristic asymmetric stretching of Si–O–Al tetrahedral silica framework and Si-O-Si silica framework in the formed zeolite [12]. The broad band at 3470 cm^{-1} is attributed to the stretching vibrations of O-H group present in the original IR spectrum. The weak band at 1646 cm^{-1} arises from the bending mode of water molecules**.** All these characteristic observations confirm the formation of zeolite (Zeo-NaX) on alkali treatment of fly ash [12, 13]. The spectrum of CeO_2/Zeo-NaX (Fig. 1c) exhibits the characteristic peaks at 433, 465, 533, 741, 1018 and 1634 cm^{-1}. This shows the blue shift in the characteristic peaks of Na-X zeolite by 5-10 cm^{-1} upon CeO_2 incorporation [14]. That means Ce has some influence on the zeolite framework. Thus the IR spectra provide evidence for Zeo-NaX and CeO_2/Zeo-NaX materials and confirm their synthesis.

3.2 Powder XRD Analysis

Powder XRD patterns of the prepared photocatalysts are displayed in Fig. 2. In Fig. 2a fly ash shows the diffraction peaks at 2θ = 26.50°, 39.30° and 40.78° [15]. In Fig. 2b the presence of diffraction peaks at 2θ = 15.47°, 23.37° 26.72°, 31.03° and 51.70° confirms the formation of Na-X crystals in the fly ash derived zeolite. X-ray diffraction pattern given in Fig. 2c confirm the presence of CeO_2 through peaks at 2θ = 29.20 °, 48.39° and 57.93°. These low intensity peaks represents the less crystalline nature of CeO_2. The zeolite peaks are not distinctly seen in both fresh and spent CeO_2/Zeo-NaX (Fig. 2c & 2d). This shows the formation of CeO_2 layer over the formed zeolite framework. The average crystallite sizes (D) of the photocatalysts are: fly ash = 40.83 nm, Zeo-NaX = 61.44 nm, CeO_2/Zeo-NaX = 4.40 nm, CeO_2/Zeo-NaX-S (spent catalyst) = 4.40 nm. Therefore the formed CeO_2 is in amphorous and nano form. Thus IR spectra and XRD patterns confirm the formation of zeolite materials (Zeo-NaX, and CeO_2/Zeo-NaX) from coal fly ash.

3.3 SEM and EDX Studies

The SEM images of the prepared materials are displayed in Fig. 3. Fly ash particles are predominantly spherical in shape (Fig. 3a) with relatively smooth surface and few micron sizes. The prepared zeolite Na-X image (Fig. 3b) shows the presence of fine spherical nano size (~100 nm) primary particles [13]. As observed in Fig. 3c, CeO_2/Zeo-NaX has morphology similar to Zeo-NaX (Fig. 3b) except some agglomeration leading to bigger secondary particles. That means CeO_2 incorporation through the pores of Zeo-NaX does not alter the morphology of zeolite material but facilitates agglomeration. The elemental analysis data of SEM EDX given in Table 1 clearly suggest the presence of required elements and the chemical composition of the materials. The Si/Al ratio is conserved in the formed zeolite from fly ash. The presence of 12.45 atomic % of Ce confirms the encapsulation of CeO_2 layer in the zeolite material.

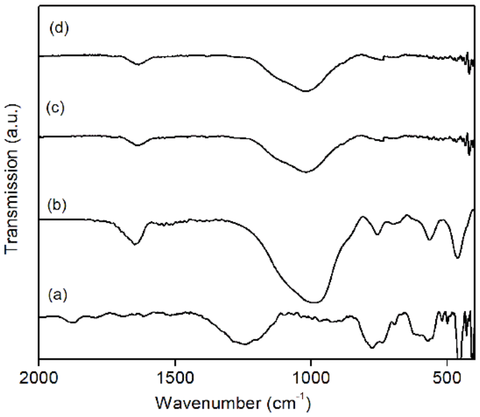

Fig. 1 FTIR spectra of (a) fly ash, (b) Zeo-NaX, (c) CeO_2/Zeo-NaX and (d) CeO_2/Zeo-NaX-S

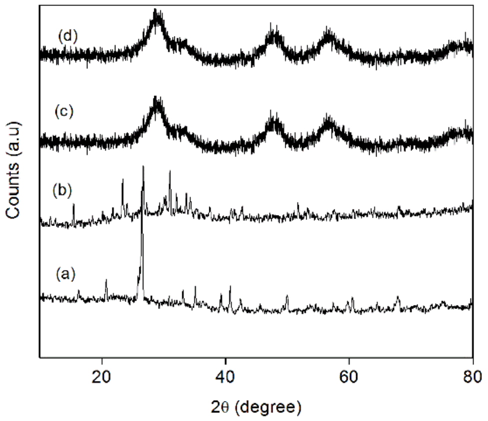

Fig. 2 PXRD patterns of (a) fly ash (b) Zeo-NaX (c) CeO_2/Zeo-NaX and (d) CeO_2/Zeo-NaX-S

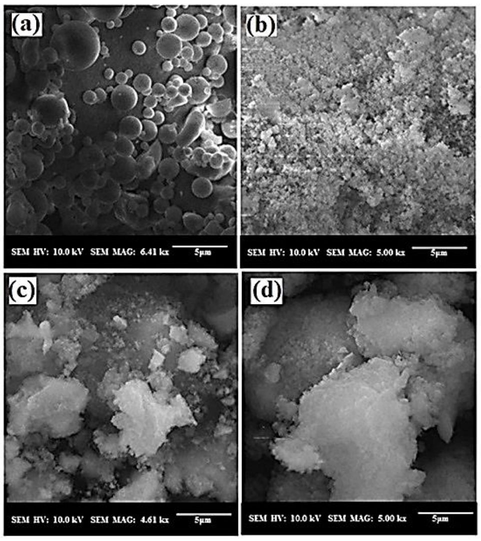

Fig. 3 SEM images of (a) fly ash, (b) Zeo-NaX, (c) CeO_2/Zeo-NaX and (d) CeO_2/Zeo-NaX-S

Table 1. Elemental composition of the materials from SEM-EDX analysis

Material	Element (atomic %)				
	Si	Al	Ce	O	Si/Al
Fly ash	15.77	13.11	0.00	58.56	1.203
Zeo-NaX	14.06	11.92	0.00	55.05	1.179
CeO_2/Zeo-NaX	12.21	10.64	12.45	56.39	1.147
CeO_2/Zeo-NaX-S	11.73	10.29	4.82	54.34	1.139

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3.4 Surface Area Characterization

Surface area data of the synthesized materials are given in Table 2. Surface area of Zeo-NaX enormously increases while pore volume increases and pore size considerably decreases when compared to fly ash. The greater surface area of CeO_2/Zeo-NaX than that of Zeo-NaX indicates that on CeO_2 incorporation zeolite particles have become finer. This is consistent with SEM images (Fig. 3). But there is a slight increase in pore volume and considerable decrease in pore size. That means pores/channels are occupied by CeO_2.

Table 2. Surface area, pore volume and pore size of zeolite materials

Material	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
Fly ash	0.795	0.002	161.33
Zeo-NaX	28.72	0.163	101.96
CeO_2/Zeo-NaX	94.58	0.176	31.98

3.5 Diffuse Reflectance Spectral Study

Diffuse reflectance spectra (DRS) of the materials are plotted in Fig. 4 and the band gap energy (E_g) values are obtained from the average of both direct and indirect band gap energies. Fly ash exhibits a band gap value (E_g) of 2.599 eV which is increased on the formation of zeolite (3.08 eV). The synthesized CeO_2/Zeo-NaX system has a lower E_g value of 1.95 eV due to the incorporation of CeO_2 particles in zeolite. The spent catalyst CeO_2/Zeo-NaX-S having a marginal effect of lower E_g value (1.924 eV) suggests the stable nature of the synthesized system. The DRS study clearly shows that Zeo-NaX synthesized from coal fly ash is a poor visible light absorbing material while CeO_2 incorporation and zeolite conversion to CeO_2/Zeo-NaX greatly enhances its visible light absorption.

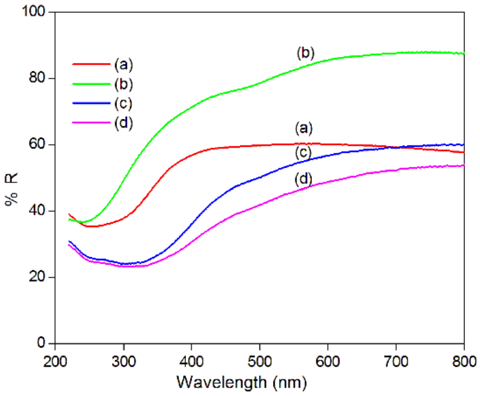

Fig. 4 DRS of (a) fly ash, (b) Zeo-NaX, (c) CeO_2/Zeo-NaX and (d) CeO_2/Zeo-NaX-S

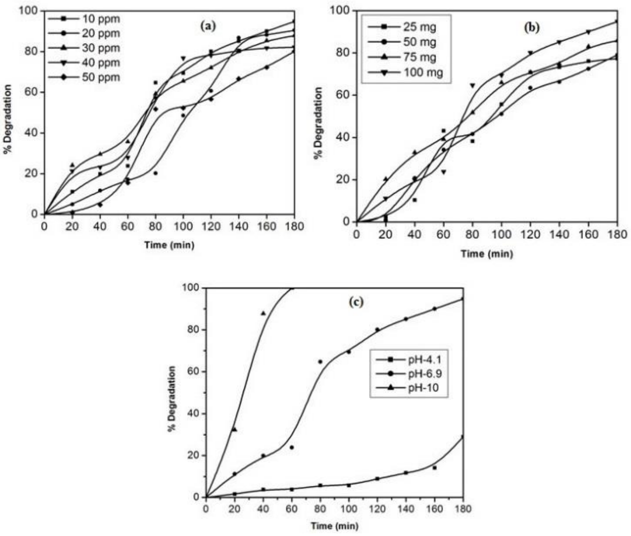

Fig. 5 Effect of reaction parameters (a) dye concentration, (b) catalyst amount and (c) pH on the photocatalytic degradation of BG

3.6 Photocatalytic Degradation of BG

Fig. 5a clearly depicts the dependence of degradation efficiency of the catalyst CeO_2/Zeo-NaX on dye concentration. The degradation efficiency is found to decrease with an increase in dye concentration. The percentage degradation of BG dye in the concentration range 10, 20, 30, 40 and 50 ppm is 94.81 %, 90.43 %, 87.83 %, 82.11 %, and 80.13 % respectively at natural pH 6.9, 100 mg catalyst. The active surface of the catalyst available for reaction is an important factor, but as the dye concentration is increased and the catalyst amount is kept constant, such condition results in fewer active sites per dye molecule during the reaction [16]. Further, with increased dye molecules the solution becomes more intense coloured and the path length of photons entering the deep solution is thus decreased. Thereby only fewer photons could reach the catalyst in the bulk of the solution. Therefore 10 ppm of the initial dye concentration is considered for further parametric optimization.

The effect of catalyst loading was studied by varying the catalyst amount from 25 to 100 mg maintaining other optimized parameters (dye concentration = 10 ppm) at natural pH. From Fig. 5b, it is noted that the degradation efficiency increases, of course, marginally with increase in the amount of catalyst. The values of % of degradation are 77.24 %, 78.97 %, 85.78 % and 94.81 % for 25, 50, 75 and 100 mg respectively. This may be due to an increase in the active sites available on the catalyst surface for the reaction.

The pH is one of the most important factors for controlling the degradation of dye. The pH of brilliant green solution was adjusted in the range of 4 to 10 by adding HCl and NaOH (0.05 M) [17]. The reaction was carried out with acidic pH 4.1, neutral natural pH 6.9 and alkaline pH 10 keeping the amount of catalyst (100 mg),) and dye concentration (10 ppm) as constant and the data are depicted in Fig. 5c. The percentage of BG degradation at this experimental condition is 28.98%, 94.81 % and 100 % at pH 4.1, 6.9 and 10.0 respectively. An increase in pH of the medium increases the degradation efficiency. This may be due to the generation of more OH radicals at higher pH by the reaction between OH^- ions and hole (h^+) of the semiconductor [17].

3.7 Reuse of Catalyst

The CeO_2/Zeo-NaX used in the photocatalytic process was filtered, washed with water and dried at 80 °C in a hot air oven and calcined at 550 °C for 4 h before it was reused as such in the succeeding photocatalytic experiment. The fresh CeO_2/Zeo-NaX exhibited 94.81 % degradation efficiency and the first recycled CeO_2/Zeo-NaX-S shows 75.45 % degradation efficiency in 3 h (Fig. 6). Therefore it is clear that the photocatalyst CeO_2/Zeo-NaX can be reused without any drastic change in its catalytic activity. The retainment of photoactivity in used/spent CeO_2/Zeo-NaX catalyst could be explained by the maintenance of chemical, physical and morphological characteristics of the material even after two uses. The FTIR spectrum (Fig. 1d), XRD pattern (Fig. 2d), SEM image (Fig. 3d) and elemental composition (Table.1) all confirm this statement, because these characteristics of the spent catalyst CeO_2/Zeo-NaX-S are similar to those of fresh catalyst. Only in Ce content, a deviation/decline is noticeable with spent catalyst (Table 1).

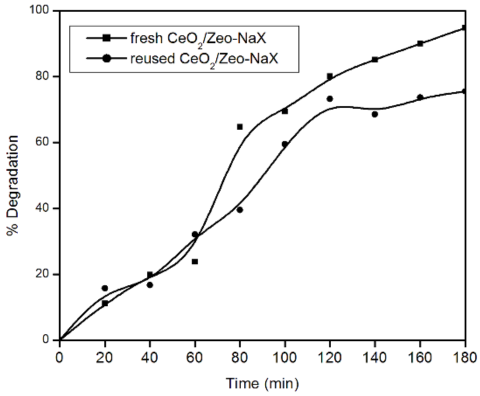

Fig. 6 Effect of recycling the catalyst

4. Conclusion

The present work is an attempt to a novel visible light active zeolite photocatalyst designed and synthesized from the waste material coal fly ash. FTIR, XRD and DRS characterizations confirm the formation of zeolite photocatalyst while SEM studies provide evidence for the existence of nanoparticles photocatalyst. Zeo-NaX prepared from waste coal fly ash

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and incorporated with cerium oxide has a considerable level of photocatalytic activity for brilliant green dye degradation. In view of environmental and economic aspects, production of fly ash converted Zeo-NaX from fly ash may provide cost-effectiveness to commercial zeolites. Hence, the novel catalyst has many potential applications because of its good structural stability, simple preparation, and stable catalytic activity in a repetitive reaction cycle and reusability.

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