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Influence of Pollutants Ionic Charge on Their Photodegradation by Fly Ash Derived CeO_2/Zeolite-NaX Catalyst

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ABSTRACT

The management of waste material for the environmental remediation is the fast growing field of research. Dyes and organic molecules are extensively used in the textile industry and unused content is discharged into the nearby water resources. This creates severe problems in the aquatic system. In this direction, our recently synthesized photocatalyst CeO_2/Zeo-NaX derived from coal fly ash is employed for the visible light degradation of cationic charged dye methylene blue, anionic charged dye methyl orange and neutral organic compound p-nitroaniline. The study reveals that the photocatalyst is more efficient towards the degradation of cationic dye (methylene blue) over anionic dye (methyl orange) and neutral organic molecule (p-nitroaniline).

1. Introduction

In our world today, there is an increasing necessity for access to clean and safe water both for domestic use and for other purposes [1]. The demand for clean water surpasses its supply. In this scenario it is imperative that wastewater released from industries should be recycled, purified and later used for other purposes [2]. The pollution that accompanies the dye industry is of great significance and imminent attention. This is particularly because of the non-biodegradable nature of the dyes and the accompanying acid/alkali, toxic trace metals and carcinogenic aromatic amines in the effluent [3]. Biological treatment is a technique broadly applied to the treatment of wastewater from urban areas. It uses microorganisms to metabolize the pollutants. However a large number of compounds are not biodegradable or cannot be destroyed by biological treatment due to their toxicity [4-6]. More than 15% of the total world production of dyes is lost during the dyeing process and is released as a source of textile industry pollution [7]. Wastewater from dyeing industry is thus known to contain considerable amounts of non-fixed dyes, especially cationic and anionic dyes, and huge amounts of inorganic salts [8].

p-nitroaniline (p-NA) is an important compound either manufactured or used as an intermediate in the synthesis of dyes, antioxidants, pharmaceuticals, gum inhibitors, poultry medicines, pesticides etc., [9]. Unfortunately, p-NA has been found to be harmful to aquatic organisms and may cause long-term damage to the environment [10]. It is highly toxic with a TLV (threshold limit value) of 0.001 kgm^{-3} [11], which is lower than that of aniline (0.002 kgm^{-3}). The presence of a $-NO_2$ group in the aromatic ring enhances its stability to resist chemical and biological oxidation degradation, while the anaerobic degradation produces nitroso- and hydroxylamine compounds which are known as carcinogens [12, 13]. Therefore, chemical remediation of p-NA contained wastewater is one of the main targets in modern environmental chemistry [9-11].

Advanced oxidation process (AOP), especially photocatalysis, is one of the few prominent methods available for wastewater treatment because it is a green method under solar/visible light and it can degrade contaminants into stable inorganic compounds, such as carbon dioxide and water. The abundance of hydroxyl radicals generated in the AOPs and their reactivity play an important role in oxidizing the organic species present in wastewater into harmless species [14]. Heterogeneous photocatalysis by semiconductor materials, such as TiO_2, ZnO, Fe_2O_3, CdS, GaP, CeO_2 and ZnS is widely used in toxic pollutants degradation [15].

Among the various metal oxide semiconductor photocatalysts CeO_2 is relatively new and its reactive potential remains largely untapped. CeO_2 impregnated MCM-41/MCM-48 was employed for the photocatalytic degradation of Congo red [16]. The CeO_2 coated zeolite has been applied for sensing dimethylmethylphosphonate [17]. We recently developed a photocatalyst CeO_2/Zeolite-NaX utilizing fly ash and evaluated its photoactivity over visible light degradation of a dye brilliant green [18]. Herein we extend the study of this photocatalyst to three different types of organic compounds, namely methylene blue (MB; a cationic dye), methyl orange (MO; an anionic dye) and p-nitroaniline (p-NA; a neutral molecule). The study yields interesting results concerning the influence of charge of the pollutants on their visible light photocatalytic degradation by CeO_2/Zeo-NaX catalyst.

2. Experimental Methods

2.1 Materials

F-type coal fly ash sample was kindly gifted from the electrostatic precipitators of Tuticorin Thermal Power Station (TTPS), Thoothukudi, Tamil Nadu, India. $(NH_4)_2Ce(NO_3)_6$ was obtained from Sigma-Aldrich. Methylene blue (Ranbaxy), p-Nitroaniline (SISCO Chem), H_2O_2, NaOH, HCl and methyl orange (LOBA Chemie) were of AR grade and used without further purification.

2.2 Synthesis of Zeolite and CeO_2/Zeolite-NaX from Coal Fly Ash

The zeolite (Zeo-NaX) was synthesised from fly ash via alkaline fusion method followed by the hydrothermal treatment as per our earlier report [18]. The dried zeolite powder (Zeo-NaX) obtained was dispersed and treated with 2 g of $(NH_4)_2Ce(NO_3)_6$ via gentle stirring at 333 K for 2 h. The obtained Ce^{4+} incorporated Zeo-NaX was filtered, washed, dried at 353 K for overnight and finally calcined at 550 °C for 4 h to get ceria-incorporated zeolite (CeO_2/Zeo-NaX) material.

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2.3 Characterization of the Synthesized Materials

The chemical composition of fly ash, Zeo-NaX, and CeO_2/Zeo-NaX was analyzed by wavelength dispersive X-ray fluorescence spectroscopy (XRF) (ASM 100 T). The materials were characterized using BET surface area (ASAP-2010 Micromeritics), SEM (Jeol JSM-6390) and FTIR (Jasco Spectrophotometer – 410).

2.4 Photocatalytic Process

The overall photocatalytic activities of the photocatalysts were investigated by following the degradation of methylene blue, methyl orange and p-nitroaniline in aqueous solution. In a typical experiment, 200 mL of 10 ppm dye solution (MB or MO or p-NA) containing 100 mg of the photocatalyst was stirred for 1h to attain adsorption equilibrium. Then the solution was irradiated for 3 h with visible light (cut off with filter for UV; intensity = 4.61 x 10^{-4} W/cm^2 at 555 nm using 200K 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 665, 465 and 375 nm respectively for MB, MO and p-NA compounds (Perkin Elmer Lambda 3B) in matched 1 cm quartz cuvettes.

3. Result and Discussion

3.1 XRF Analysis

Table 1 presents the chemical composition of various materials, derived from XRF analysis. As can be seen from Table 1, the fly ash sample used is of class F type with SiO_2, Al_2O_3 and iron oxide as the major components. A perusal of data in Table 1 reveals the following: 1. Alkali fusion and hydrothermal treatment of fly ash has considerably increased the content of Na_2O (from mere 0.56 to 4.19%); 2. However, Ce^{2+} ion exchange has substantially removed Na_2O by substituting with CeO_2. Other metal oxides have also undergone considerable decrease in their content increasing the proportion of CeO_2 (~36%). This reveals that major portion of the CeO_2 is placed at the surface of the material. Thus the synthesis process and the expected chemical change in each and every step of CeO_2/Zeo-NaX synthesis are confirmed and validated by XRF analysis.

Table 1 Chemical composition (wt%) of fly ash, Zeo-NaX and CeO_2/Zeo-NaX

Chemical composition	Weight %		
	Fly ash	Zeo-NaX	CeO_2/Zeo-NaX
SiO_2	57.23	60.32	33.59
Al_2O_3	31.30	22.47	15.87
Na_2O	0.56	4.19	1.35
Fe_2O_3	4.72	7.91	4.65
TiO_2	1.84	2.89	1.28
CaO	1.19	1.50	0.82
MgO	0.62	0.00	0.00
K_2O	1.34	0.54	5.86
P_2O_5	0.93	0.10	0.30
MnO	0.02	0.05	0.05
CeO_2	0.00	0.00	36.19

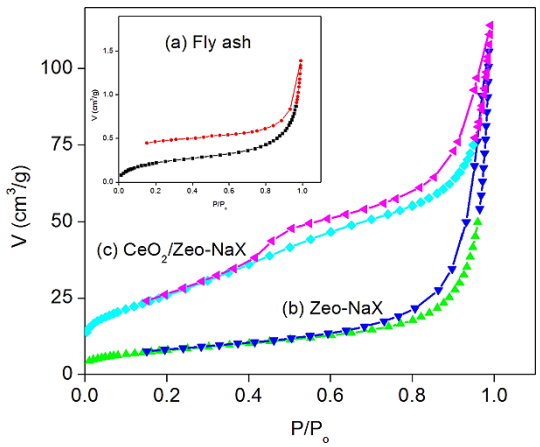

Fig. 1 BET isotherms of (a) Fly ash, (b) Zeo-NaX and (c) CeO_2/Zeo-NaX

3.2 Surface Area Characterization

The BET isotherms of the synthesized catalysts are shown in Fig. 1. Fly ash exhibits an incomplete adsorption desorption isotherm (Fig. 1a) with very low surface area of 0.79 m^2/g. The formation of zeolitic structure in fly ash creates type III isotherm (Fig. 1b) and loading of CeO_2 modifies the isotherm into type II (Fig. 1c). The formation of zeolite structure has enormously increased the surface area of fly ash to 28.72 m^2/g. The addition of CeO_2 in to zeolite structure followed by its calcination has further improved the surface area to 94.58 m^2/g [18].

3.3 SEM Study

The SEM images of the prepared materials are displayed in Fig. 2. Fly ash particles are predominantly spherical in shape (Fig. 2a) with relatively smooth surface and few micron sizes. The prepared zeolite NaX image (Fig. 2b) shows the presence of fine spherical nano size (~100 nm) primary particles [19]. As observed in image Fig. 2c, CeO_2/Zeo-NaX has morphology similar to Zeo-NaX (Fig. 2b) 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.

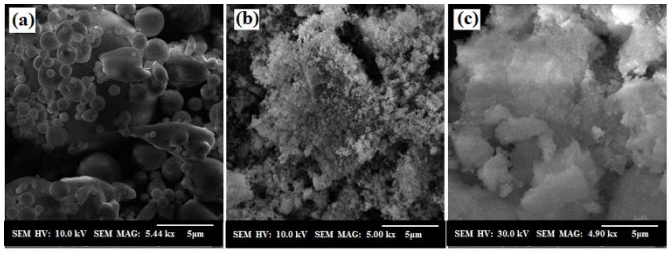

Fig. 2 SEM images of (a) Fly ash, (b) Zeo-NaX, and (c) CeO_2/Zeo-NaX

3.4 Photocatalytic Degradation of MB, MO and P-NA

The photocatalytic degradation was studied by visible light degradation of MB using CeO_2/Zeo-NaX catalyst and the data are given in Fig. 3 and in Table 2. The dye undergoes self-degradation to an extent of 21.8% under visible light irradiation from 100 W tungsten lamp and the presence of H_2O_2 enhances the degradation to 30.3%. However the presence of zeolite (Zeo-NaX) inhibits the self-degradation of MB down to 18.6%. This shows that the zeolite itself is not a photocatalyst but functions as an adsorbent and protects MB from degradation. However, the presence of CeO_2/Zeo-NaX photocatalyst is found effective for MB degradation (nearly twice as that of light*) and ineffective for MO and p-NA. The data for recycled catalyst ensure the sustainable activity of CeO_2/Zeo-NaX toward visible light degradation of MB.

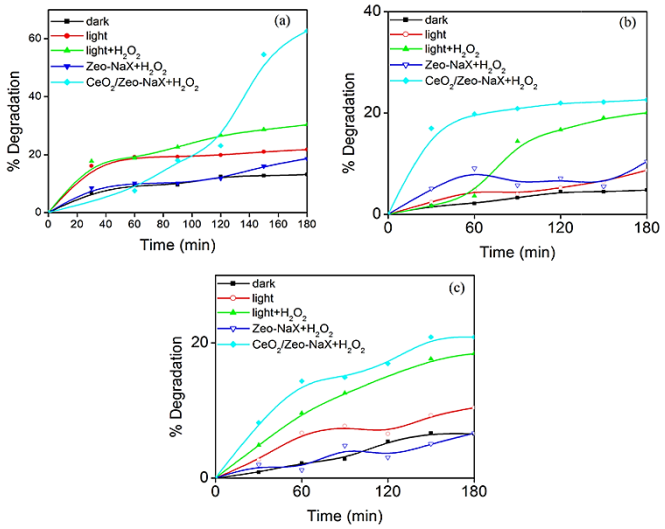

Fig. 3 Degradation profiles of (a) MB (b) MO and (c) p-NA with/without catalyst, light and H_2O_2

Among the three pollutants taken for degradation, i.e. MB, MO and p-NA, the catalyst CeO_2/Zeo-NaX degrades only the cationic charged MB and the efficiency is nearly twice as that of light + H_2O_2 (light*) ; for MO and p-NA the % degradation values are almost close to light*. The effectiveness

or ineffectiveness of the catalyst could be explained on the basis of charge on the catalyst and the pollutants. Having aluminosilicate network structure zeolite has negative charge and the same is counter-balanced by interlying metallic cations [20, 21]. This negative charge easily attracts the positively charged MB dye and either repels or does not show any influence with the negatively charged MO dye or the neutral p-NA molecule respectively. Similar type of observation has been made in previous studies. For example, Jaffer et al [22], in their study on photodegradation of methyl orange with α-Fe_2O_3/HY zeolite, have observed that a strong electrostatic field between the positively charged catalyst surface and the negatively charged methyl orange as well as the iron cations inside zeolite affect the photocatalytic degradation of methyl orange. At pH-2 because of strong electrostatic attraction the degradation is more than that at alkaline pH where electrostatic interaction is absent. Muduli at al [23] have noted that the ligand-to-metal charge transfer mechanism involving the positively charged Rhodamine-B dye (ligand) and n-type cerium oxide photocatalyst is operative. Thus the present work enlightens that charge on the pollutant and the zeolite plays a crucial role in deciding the photoactivity.

Table 2 Degradation data of MB, MO and p-NA

Catalyst	Degradation (%)		
	MB	MO	p-NA
Dark	13.1	4.80	6.5
Light	21.8	8.72	10.4
Light*	30.3	20.03	18.4
Zeo-NaX*	18.6	10.4	6.6
Ce-oxide/Zeo-NaX*	62.7	22.5	20.8
Ce-oxide/Zeo-NaX**	55.9	19.6	18.8

*Reaction condition: [MB], [MO] and p-NA = 10 ppm (200 mL), Catalyst amount = 100 mg, Time = 3 h, pH = 6.9, *H_2O_2 = 2 mL, ** Third recycled catalyst*

3.4 Reused Catalyst FT-IR

The FTIR spectra of the fresh and reused catalyst materials are presented in Fig. 4. The spectrum of CeO_2/Zeo-NaX (Fig. 4a) exhibits absorptions at 433, 465, 533, 741, 1018 and 1634 cm^{-1}. The peak position of the broader peak at 1018 cm^{-1} gets shifted by 60-80 cm^{-1} to the longer wavenumber side in spent catalyst. This suggests hydration of zeolitic framework during the reaction.

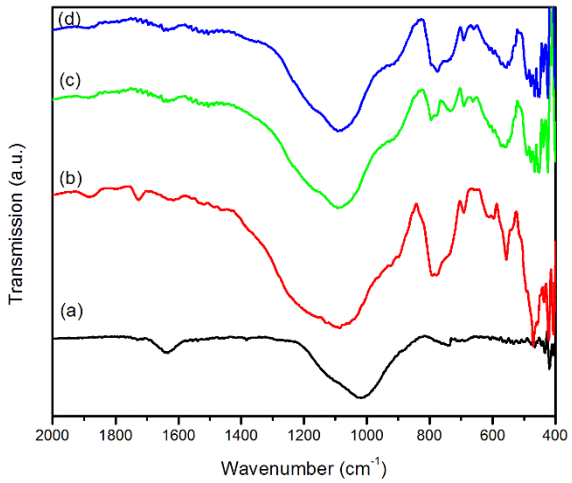

Fig. 4 FTIR spectra of (a) CeO_2/Zeo-NaX (b) reused MB-CeO_2/Zeo-NaX (c) reused MO- CeO_2/Zeo-NaX and (d) reused p-NA-CeO_2/Zeo-NaX

4. Conclusion

In the present work, the efficiency of visible light photocatalyst CeO_2/Zeo-NaX is tested over cationic and anionic dyes and over neutral p-NA. The results show that the catalyst is effective only for cationic dye MB and not for anionic MO/neutral p-NA molecule photodegradation. Thus the present work enlightens that pollutant charge plays a crucial role is deciding its photodegradation with CeO_2/Zeo-NaX.

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