Journal of Water Process Engineering xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe

Modification of the photocatalytic performance of various metal oxides by the addition of β-cyclodextrin under visible light irradiation

Sakthivel Pitchaimuthu [1], Ponnusamy Velusamy *

Centre for Research and Post-Graduate Studies in Chemistry, Ayya Nadar Janaki Ammal College, Sivakasi, 626 124, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 31 December 2015
Received in revised form 14 October 2016
Accepted 31 October 2016
Available online xxx

Keywords:
Photodecoloration
Neutral Red
β-CD
CeO_2
TiO_2
ZnO

ABSTRACT

The photocatalytic decoloration of Neutral Red (NR) dye in aqueous solutions on various metal oxide (MO) photocatalysts (such CeO_2, TiO_2 and ZnO) has been investigated under visible light irradiation. The significance of addition of β-Cyclodextrin (β-CD) on the photocatalytic performance of the above catalysts has also been investigated. The interaction between semiconductors and β-CD were characterized in detail by FE-SEM, X-ray diffraction, and UV-vis Diffuse Reflectance spectral analyses. The analytical results indicated that the addition of β-CD shows no change in the lattice structure, crystalline features of semiconductors. The experiments were carried out to study the factors influencing the photocatalytic decoloration, such as the initial concentration of dye solution, catalyst concentration, illumination time and pH. The experimental results show that catalytic system bounded with β-CD exhibits superior photocatalytic activity than that of bare catalyst systems. The decoloration rate was pH dependent.

1. Introduction

Nowadays, with the development of modern society, water pollution has become an increasingly serious problem with hazardous heavy metal ions and organic dyes as common pollutants [1]. Dyes are one of the most hazardous chemical compound classes which found in industrial effluents need for their treatment treated since their presence in water bodies reduces light penetration, precluding the photosynthesis of aqueous flora [2,3]. Dyes can cause allergy, dermatitis, skin irritation [4] and also provoke cancer [5] and mutation in humans [6]. They are also aesthetically objectionable for drinking and other purposes [7]. It is estimated that 15% of the total dye production is lost during the dyeing process and is released into the textile effluents [8]. Several physico-chemical and biological methods have been developed to treat dye-containing wastewaters. Each technique has its own advantages as well as drawbacks.

In recent years, a great deal of efforts has been devoted to decompose the harmful organic pollutants [9]. Compared with the conventional oxidation processes, semiconductor photocatalysis is an attractive candidate because of its various advantages, such as complete mineralization of the pollutants, application of the UV or solar light, low cost [10,11]. Considering the sunlight contains only 5% ultraviolet light (λ < 380 nm), visible-light-responsive photocatalysts with high activity are urged to be developed [12].

Cyclodextrin (CD) modified semiconductor photocatalysts, a typical type of host modified photocatalyst, have attracted significant interest because of their unique properties [13–15]. As one of the most common host molecules, cyclodextrin does not only modify the external morphology of the photocatalyst, [16–18] but also the intrinsic properties including photoactivity, photoelectric activity, energy transfer [14]. More importantly, photocatalyst can be endowed with the recognition ability for certain guest molecules after the modification with cyclodextrins [13,19,20], which can lead to more guest-targeting and efficient functions of the photocatalyst that play a role as a 'channel or bridge between the guest molecules and the surface of the photocatalysts. All previous work suggests that β-CD plays electron-donating and hole-capturing roles when linked to TiO_2 colloids, which lead to charge-hole recombination restriction and photocatalytic efficiency enhancement. Some previous papers have reported the stimulative effect of cyclodextrins on the photocatalytic degradation of organic pollutants in TiO_2 suspensions [13–20]. Our previous works have also accounted for the stimulative effect of β-CD on the photocatalytic degradation of dye in ZnO, TiO_2 and CeO_2 suspensions under different light radiations [21–24]. In this study, the activity of different metal oxide catalysts (such as CeO_2, TiO_2, ZnO) and the effect of additon of β-CD with the metal oxide catalysts on photocatalytic decoloration of NR dye

* Corresponding author.
E-mail addresses: velusamyanjac@rediffmail.com, velmuruga@rediffmail.com (P. Velusamy).
[1] Present address: Department of Chemistry, Thiagarajar College, Madurai, 625 009, TN, India.

http://dx.doi.org/10.1016/j.jwpe.2016.10.009
2214-7144/

solution under visible light radiation have been investigated and the results are well documented.

2. Experimental

2.1. Materials

The commercial organic dye Neutral Red (NR) (Molecular Formula $C_{15}H_{17}ClN_4$, λ_{max} = 540 nm) obtained from Loba Chemie was used as such. The metal oxide (MO) photocatalysts (such as CeO_2, TiO_2 and ZnO) were purchased from Merck Chemicals. β-Cyclodextrin was received from Himedia chemicals. All other chemicals were of the Analytical grade, received from Merck Chemicals and used without further purification. Double distilled water was used throughout the study for the preparation of all the experimental solutions.

2.2. Characterization

FE-SEM was used to investigate the morphology of the samples *viz.* β-CD, MO and MO-β-CD. FE-SEM images were obtained on a Carl ZEISS (ΣIGMA Series, Germany) microscope taken at an accelerated voltage of 2 kV. X-ray diffraction patterns of powdered samples were recorded with a high resolution powder X-ray diffractometer model RICH SIERT & Co with CuK_α radiation as the X-ray source ($\lambda = 1.5406 \times 10^{-10}$ m). UV–vis Diffuse Reflectance Spectra were recorded on a Shimadzu 2550 UV–vis spectrophotometer with $BaSO_4$ as the background between 200 and 700 nm. UV–vis spectra were recorded by a UV–vis spectrophotometer (Shimadzu UV-1700) and the scan range was from 400 to 700 nm. FT-IR spectra were recorded using FT-IR spectrometer (Shimadzu model 8400S) in the region of 4000 − 400 cm^{-1} using KBr pellets.

2.3. Preparation of MO-β-CD and NR-β-CD samples for characterisation

In order to study the interaction of β-CD on MO surface, a suspension containing 2.0 g/L MO and 10.0 g/L β-CD was magnetically stirred for 24 h, centrifuged, and then the solid phase was collected. After being centrifuged, the solid phase of the suspension was carefully washed with double distilled water. Eventually, the MO-β-CD sample was dried at 50 °C. The sample prepared in this way was used for FESEM, XRD and UV–vis DRS analysis.

For studying the inclusion complex between β-CD and NR dye, to a saturated solution of β-CD in distilled water, equimolar amount of NR dye was added and stirred continuously for 24 h. The formed β-CD-NR dye complex powder was filtered, washed with diethyl ether to remove uncomplexed NR dye and dried in an air oven at 50 °C for about 24 h. The resultant complex obtained was used as such for FT-IR spectral analysis.

2.4. Experimental conditions

Photocatalytic decoloration experiments were carried out under visible light irradiation. Heber Annular type visible (500 W, OSRAM) photoreactor was used as light source in the central axis. NR dye solutions containing the photocatalysts of either MO or MO-β-CD were prepared. The pH values of dye solutions were adjusted using digital pen pH meter (Hanna Instruments, Portugal) depending on desired values with HCl and NaOH solution as their effect on the adsorption surface properties of MO is negligible [34]. Prior to irradiation experiment, reaction suspensions were kept in dark for 10 min to get adsorption-desorption equilibrium (The dye is adsorbed onto the MO or MO–β-CD surface and attain adsorption-desorption equilibrium between dye and MO/visible or MO-β-CD/visible light system). After adsorption the equilibrium concentration of the dye solution is determined and it is considered as the initial dye concentration for kinetic analyses. The reaction vessels were taken out at different intervals of time and the solutions were centrifuged. The supernatant liquid was collected for the determination of concentrations for the remained dye by measuring its absorbance (at λ_{max} = 540 nm) with visible spectrophotometer (ELICO, Model No. SL207). In all the cases, exactly 50 mL of the reactant solution was irradiated with required amount of photocatalysts. Chemical oxygen demand (COD) was determined by open reflux method [21–23]

By keeping the concentrations of NR dye-β-CD as constant with the molar ratio of 1:1, the effects of the other experimental parameters on the rate of photocatalytic decoloration of NR dye solutions were investigated. The natural pH of NR dye solution was 7.0 and the irradiation time was fixed as 120 min.

3. Results and discussion

3.1. Catalyst characterisation

3.1.1. Field emission scanning electron microscopy (FESEM)

Fig. 1(a–g) depicts FESEM micrograph of the bare β-CD, bare MO and MO-β-CD. Bare CD shows amorphous surface. The surfaces of bare MO and MO-β-CD exhibit a similar morphology which indicates that the morphology of MO has not been affected by its complexation with β-CD. However, the surfaces of the MO-β-CD were conspicuously different from MO. This may be due to the aggregation of MO and β-CD particles as the surfaces of the particles are very loose. This kind of surface structures can provide a better adsorption environment and more active site for the photocatalytic reaction.

3.1.2. X-ray powder diffraction patterns (PXRD)

The X-ray powder diffraction patterns of β-CD, MO and MO-β-CD are presented in Fig. 2. The XRD analysis of TiO_2 reveals that the sample exhibits single-phase belongs to anatase-type TiO_2 which is identified by comparing the spectra with the

JCPDS file #21-1272. Diffraction peaks at 25.38°, 37.9°, 48.07°, 53.94° and 55.18° correspond to (101), (004), (200), (105) and (211) planes of TiO_2 respectively. The X-ray powder diffraction patterns of ZnO expose that, all the diffraction peaks of the samples can be indexed as the wurtzite structured hexagonal ZnO with lattice (JCPDS, No.36-1451), which indicate that the sample ZnO is in pure form. Diffraction peaks at 31.73°, 34.45°, 36.28°, 47.51° and 56.68° correspond to (100), (002), (101), (102) and (110) planes of ZnO respectively. The X-ray powder diffraction patterns of CeO_2 depicts that, all the diffraction peaks of the samples belongs to the fluorite type oxide structure of CeO_2 (JCPDS, No. 34-394). Diffraction peaks at 28.26°, 32.85°, 47.25°, 56.06° and 58.90° correspond to (111), (200), (220), (311) and (222) planes of CeO_2 respectively and thus no effect on the crystalline form of MO. Moreover, the addition of β-CD does not cause any shift in the peak positions of phases of MO. The results also demonstrated that the MO conserved their respective crystal features.

3.1.3. UV–vis analysis

The molecular structure of β-CD allows various guest molecules with suitable dimensions to accommodate into its torous cavity form host/guest inclusion complexes. In this study, the inclusion complex between β-CD and NR dye was characterized with UV–vis spectra as given in Fig. 3. It depicts that the absorbance of inclusion complex increases with increasing the concentration of β-CD [25]. In this work, the optimum molar ratio between β-CD and NR dye was fixed as 1:1.

Please cite this article in press as: P. Sakthivel, P. Velusamy, Modification of the photocatalytic performance of various metal oxides by the addition of β-cyclodextrin under visible light irradiation, J. Water Process Eng. (2016), http://dx.doi.org/10.1016/j.jwpe.2016.10.009