



Solar photocatalytic activity of nano-ZnO supported on activated carbon or brick grain particles: Role of adsorption in dye degradation

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ABSTRACT

In precedent work, nano-ZnO was supported on activated carbon or brick grain particles using simple co-precipitation method. Successful formation of ZnO-activated carbon (ZnO-AC) and ZnO-brick grain particle (ZnO-BGP) nanocomposites was ascertained by various spectral techniques. Scanning electron microscope (SEM) images revealed that ZnO particles were highly dispersed in activated carbon/brick grain particles. The size of ZnO-AC and ZnO-BGP was found to be 70 and 80 nm, respectively. Both ZnO-AC and ZnO-BGP exhibited excellent adsorption and photocatalytic activity for malachite green (MG) and congo red dye (CR) degradation. The adsorption data for MG and CR removal followed pseudo second order kinetic model. The adsorption capacity followed the order: ZnO-AC > ZnO-BGP > ZnO. The effect of adsorption on photocatalysis was explored under different reaction conditions. Simultaneous adsorption and photocatalysis (A + P) exhibited promoting effect on dye degradation. While adsorption followed by photocatalysis (A – P) had retarding effect on dye removal. ZnO-AC/A + P system emerged as highly efficient for MG and CR degradation. The rate of photodegradation followed pseudo first order kinetics. Using ZnO-AC/A + P system, 99 and 92% of COD removal was attained for MG and CR degradation, respectively. The oxidative degradation mainly occurred through hydroxyl radicals. The prepared nanocomposites possessed higher recyclability and could be easily separated from solution by sedimentation.

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1. Introduction

Since the first pioneering work in 1970s, semiconductor based heterogeneous photocatalytic processes have shown high efficiency for degradation of organic pollutants in aqueous phase [1–4]. Binary metal oxides such as TiO₂, ZnO, Cu₂O, WO₃, V₂O₅, NiO, ZrO₂, CeO₂, Ga₂O₃, etc. have been synthesized and investigated for photocatalytic water purification [5,6]. Among various semiconductor photocatalysts, ZnO has been attracting worldwide attraction due to its optical, electronic properties (band gap = 3.37 eV), low cost, high level of photocatalytic activity, chemical stability and non-toxicity [7,8]. In previous studies, the small particle size of nano-photocatalysts resulted in greater

photocatalytic activity for dye degradation [9–11]. However, the size of nano-photocatalyst is so small that it was difficult to recover catalyst from aqueous medium. Therefore, nano-photocatalysts need to be immobilized on organic/inorganic materials to improve liquid–solid separation and re-cyclization efficiency for efficient degradation process [12–16].

Generally, the mechanism of visible light assisted photocatalytic dye degradation is based on three steps. Firstly, the dye molecules are adsorbed onto the surface of the catalyst [17–19]. Then, the adsorbed dye molecules are excited by visible light so as to inject electrons into the conduction band of the semiconductor photocatalyst to form conduction band electrons (e_{CB}^-). The conduction band electrons are scavenged by O₂ to generate hydroxyl radicals (OH•). Finally, hydroxyl radicals degrade dye molecules into innocuous product [20–22]. Among above steps, adsorption of dyes onto catalyst surface is a prerequisite for highly efficient photodegradation under visible light [23]. Hung et al. explored photocatalytic activity of activated carbon and

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TiO₂ based nanocomposites for enhanced dye degradation [24]. Shobana and Swaminathan investigated photocatalytic activity of ZnO-AC composite for dye degradation [25]. Recent studies also concluded that high adsorption could enhance the photodegradation rate [26,27], whereas some authors claimed that the adsorbed molecules might have detrimental effect on the degradation process [28]. Taking into account the porous nature of activated carbon and brick grain particles, they may possess higher adsorption ability to certain contaminants, and adsorption may also play significant role in photodegradation reaction. Nevertheless, as far as we know, very few works have been done with the effect of actual adsorption of the organic contaminants in photocatalysis mediated with nano-ZnO immobilized on activated carbon or brick waste.

Malachite green dye (MG) is an *N*-methylated diaminotriphenylmethane. MG is used extensively in textile industry for dyeing leather, silk, cotton, wool and jute. MG is extremely toxic to mammalian cells and reproductive problems in rabbit, fish, etc. [29]. Congo red (CR) is toxic to many organisms and is suspected mutagen and carcinogen [30]. This work was focused on the preparation of ZnO-activated carbon (ZnO-AC) and ZnO-brick grain particles (ZnO-BGP) nanocomposites for efficient MG and CR degradation. ZnO, ZnO-AC and ZnO-BGP were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron energy microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), elemental dispersive X-ray spectroscopy (EDX) and UV-Visible spectroscopy (UV-Vis). Malachite green (MG) and congo red (CR) dyes were selected as model pollutant due to their severe impact and strong resistance to biochemical oxidation. In particular, co-operative action between adsorption of MG/CR and their photodegradation was discussed in detail. Additionally, the recovery and recyclability of ZnO-AC and ZnO-BGP was also examined.

2. Experimental

2.1. Material and methods

2.1.1. Chemicals

Zinc nitrate [Zn(NO₃)₂·6H₂O], sodium hydroxide (NaOH), malachite green and congo red were purchased from CDH Company, India. Commercial activated carbon (200 mesh) was obtained from Merck, India. Brick grain particles (BGP) were collected from local construction site at Shoolini University, Solan, Himachal Pradesh, India. Brick grain particles were washed with distilled water to remove adhered impurities and dried. Brick grain particles were ground and sieved to a fragment size less than 200 mesh. All the solutions were prepared in doubly distilled water.

2.2. Preparation of ZnO-AC, ZnO-BGP and ZnO

ZnO-AC nanocomposite was prepared with little modifications in co-precipitation method [31]. In a typical procedure, 0.45 M aqueous solution of zinc nitrate [Zn(NO₃)₂·6H₂O] and 1.0 M aqueous solution of sodium hydroxide (NaOH) were separately prepared in 100 mL distilled water. 1 g of activated carbon was added to 100 mL of zinc nitrate solution. To resulting solution, 100 mL of NaOH was added dropwise at 70 °C with constant stirring. The solution was centrifuged at 4000 rpm to obtain precipitated ZnO-AC. ZnO-AC were washed with distilled water and ethanol then dried in air atmosphere at about 350 °C for 4 h. ZnO-BGP was synthesized using brick grain particles in place of activated under identical reaction conditions. ZnO nanoparticles were prepared by adopting same methodology with no addition of activated carbon or brick grain particles.

2.3. Characterization of ZnO, ZnO-AC and ZnO-BGP

Fourier transform infrared (FTIR) spectra were obtained using Perkin Elmer spectrometer (Spectrum 400, USA). EDX analysis was performed at randomly selected locations on the solid surfaces. EDX mapping was carried out at 1000× magnification under vacuum conditions. The powder samples were attached onto adhesive carbon tapes supported on metallic disks. Scanning electron microscope (Quant-250, model 9393) was used to obtain SEM micrographs. Sample surfaces were observed at different magnifications and SEM images were recorded. The structure of prepared nanocomposites and ZnO was analyzed using transmission electron microscopy (TEM) (Tecnai 20 G2 Plate/CCD Camera). XPERT-PRO diffractometer was used for powder XRD analysis. Cu Kα radiations (wavelength of 1.54 Å) were used as source of X-rays. Samples were placed in glass holder and were recorded over 2-theta (2θ) range of 10°–100°. Crystallite size of nanocomposites was calculated using Debye–Scherrer formula (Eq. (1)):

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D = the thickness of the nanocrystal, k (constant) = (0.9), λ = wavelength of X-rays (1.54 Å). β = width at half maxima of reflection at Bragg's angle 2θ (θ = Bragg's angle).

2.4. Adsorption and photocatalytic experiments

Adsorptional and photocatalytic experiments were performed in a double walled pyrex vessel (ht. 7.5 cm × dia. 6 cm) surrounded by thermostatic water circulation arrangement to keep temperature in the range of 30 ± 0.3 °C. During adsorption and equilibration experiments, the slurry composed of dye solution (50 mL) and catalyst suspension was continuously stirred. For the photocatalytic studies, suspension composed of dye and catalyst was exposed to solar light with continuous stirring. At specific time intervals, aliquot (3 mL) was withdrawn and centrifuged for 2 min to remove catalyst particles from aliquot. The absorbance of malachite green and congo red dye in supernatant liquid was measured at 620 nm and 490 nm, respectively. The solar light intensity was measured by digital lux-meter (35 × 10³ ± 1000 lx). Photocatalytic experiments were performed between March to May 2013 (11 am to 2 pm). All the experiments were undertaken in triplicate with errors below 5% and average values were reported. The chemical oxygen demand (COD) was measured by closed reflux method. The unreacted oxidant was determined by titrating sample with ferrous ammonium sulphate using ferroin indicator [32]. The removal efficiency was calculated using Eq. (2):

$$\% \text{ removal efficiency} = \frac{C_0 - C_t}{C_0} \quad (2)$$

where C_0 is the initial concentration/COD and C_t is instant concentration/COD of sample.

2.5. Determination of pH of zero point charge

pH of zero point charge (pH_{pzc}) was estimated by pH drift method [33,34]. For this purpose, 0.01 M sodium chloride (50 mL) solutions were adjusted to different initial pH values between 2 and 12. Then, photocatalyst (0.10 g) was added into solutions. After 48 h, final pH of all the solutions was measured and plotted against initial pH. pH at which the curve crossed the line of equality was taken as pH_{pzc} of catalyst.

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