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Effect of the supported ZnO on clinoptilolite nano-particles in the photodecolorization of semi-real sample bromothymol blue aqueous solution

Mohsen Bahrami [a], Alireza Nezamzadeh-Ejhieh [a,b,*]

[a] Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O Box 311-86145, Shahreza, Isfahan, Iran
[b] Razi Chemistry Research Center (RCRC), Shahreza Branch, Islamic Azad University, Isfahan, Iran

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ABSTRACT

Photodecolorization of bromothymol blue (BTB) aqueous solution using supported ZnO onto clinoptilolite nanoparticles (NCP) under Hg lamp irradiation was studied. NCP was prepared by a mechanical method using a planetary ball mill. ZnO supported samples (ZnO–NCP) were obtained by calcinations at 450 °C for 12 h followed by ion exchanging of the parent NCP with zinc(II) nitrate aqueous solutions (0.1, 0.2, 0.3 and 0.5 M) for 24 h. Raw and modified samples were characterized by XRD, FT-IR, DRS, TEM, SEM and BET. The degradation extent was monitored by UV–vis absorption as well as COD. The decolorization kinetics was fitted well to the Langmuire–Hinselwood first order rate law.

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1. Introduction

Due to daily increase of industrial units, pollution of water resources by industrial effluents is hazardous for human and environmental health. Most of dyes, as one of the most groups of water pollutants, have very low biological capability analysis and some of them are hazardous to marine biological activity. Presence of dyes even less than 1 mg/L is important from a visible appearance point of view [1,2]. Presence of dyes in the water can significantly absorb a major part of arrived sunlight, which in turn causes to lesser photosynthesis process to carry out. This in turn causes rapid growth of some types of algae and hence reduces the dissolved oxygen in water and the life of aquatic animals like fish endangers [3,4]. Thus, due to limited water resources, different methods such as: biological and chemical adsorption, ion exchange, coagulation, oxidation, membrane separation, Fenton and electrochemical have been used for removing dyes or other organic pollutants from water and wastewater [5]. The dyes pollutants are generally resistant to aerobic biodegradation and not removable with conventional biological purification processes. Probable cause is the lack of enzymes necessary for the analysis of the dyes in biological systems [6]. Advanced oxidation processes are among the newest methods and technologies that can make various organic pollutants into inorganic materials. The mechanism of this process is ultraviolet or visible irradiation of a semiconductor substance and excitation of electrons from capacity band into the conduction band. Excitation of electrons leads to produce hydroxyl radicals in aqueous environment which is a strong oxidizing agent. Low cost, stability and high efficiency are important advantages of this process [7,8].

ZnO, with a direct band gap energy of 3.3 eV and a binding energy of 60 meV, is an attractive material for fundamental research and industrial application [9,10]. Due to its unique optical and electrical properties, it is very useful for solar cells, gas sensors, nanolasers,

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* Corresponding author at: Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O Box 311-86145, Shahreza, Isfahan, Iran. Tel.: +98 31 53292515/98 3153292500; fax: +98 31 53291018.
E-mail address: arnezamzadeh@iaush.ac.ir (A. Nezamzadeh-Ejhieh).

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piezoelectric nanogenerators, etc. [10]. Moreover, its high chemical stability and low toxicity make it suitable for UV screening applications. Further, nanoparticulate ZnO is a bactericide and inhibits both Gram-positive and Gram-negative bacteria [11]. It is widely used as a photocatalyst due to its unique chemical and physical properties, environmental stability, in-expensiveness, strong oxidizing power, non-toxicity and long term photostability as compared to other metal oxides [12,13]. The biggest advantage of ZnO compared with TiO_2 is that it absorbs over a larger fraction of the UV–vis spectrum than TiO_2. Hence, the application of TiO_2 is limited under solar light [14–17]. In general, ZnO nanoparticles which have special fine nanostructure and large specific surface area are more effective than the bulk one because the photocatalysis always begins at interfaces between the catalyst and organic pollutants [12,18]. However, the low dimensional nanoscaled building blocks tend easily to aggregate during the preparation and photocatalysis processes which reduce their surface area and photocatalytic efficiency. Therefore, three-dimensional (3D) ZnO materials with a hierarchical structure have aroused great concern due to their fine structure and larger size that can avoid the aggregation of low dimensional nanoblocks in the commercial application as photocatalysts [19,20]. The photocatalytic activity of ZnO depends significantly on its structure and physical properties because the photocatalytic reactions mostly take place on the surface of ZnO catalysts [21]. On the other hand, the ZnO surface area is a key factor in the kinetic and efficiency of photocatalytic reaction. It is known that supported photocatalysts with high adsorption ability can (a) attract the pollutant substances near the reactive surface of the catalyst particles where the hydroxyl radicals produce, (b) create a lot of active sites for adsorption of intermediates, (c) extend life time and reusability of the photocatalyst and (d) decrease the recombination rate of photogenerated electron–hole pairs. These finally can promote the degradation rate and enhance the photocatalytic activity of ZnO [22,23].

Many materials have been used as photocatalyst supports; among them zeolites are very important. Properties such as high surface area, individual micro-pores, owing Lewis acid sites, a variety of channels and high resistance make zeolites as very useful materials in industrial applications and academic research. In addition antibacterial activity of zeolite-based compounds has recently been reported [24–30]. Moreover, their inorganic framework preserves them from photo-decay. Natural zeolites, with respect to the synthetic group, are cheaper and more abundant, but have smaller channels and more impurities. Clinoptilolite, a typical chemical formula of $Na_6[(AlO_2)_6(SiO_2)_{30}]\cdot 24H_2O$, is the most abundant zeolite in nature and isostructural with heulandite (as the alkali-rich and silica-rich member of the heulandite group with $Si/Al > 4$). It has a monoclinic framework consisting of a 10-membered ring (7.5 × 3.1 Å) and two eight member rings (4.6 × 3.6 Å, 4.7 × 2.8 Å). The used clinoptilolite in this work has a SiO_2/AlO_2 ratio of 4.84 which shows good agreement with the literature [31].

In the present work, the photo-catalytic activity of zinc oxide supported on clinoptilolite nanoparticles, as a cheap and the most abundant zeolite in Iran, was studied for photodegradation of bromothymol blue (BTB) aqueous solution. BTB with the molecular formula of $C_{27}H_{28}Br_2O_5S$ was used as a dye for painting plant tissue (cell wall and nucleus) and in fish breathing tanks to determine the amount of carbonic acid. BTB stimulates the respiratory, digestive, skin and eye diseases [32,33].

2. Experimental

2.1. Materials and preparation of the catalyst

Bromothymol blue and other used analytical grade chemicals were obtained from Merck. Natural clinoptilolite, belonging to the Semnan region in the north-east of Iran, was purchased from Afrand Tuska Company (Isfahan, Iran). The pH of solutions was appropriately adjusted with sodium hydroxide or hydrochloric acid solution. Distilled and tap water were used for preparation of BTB solutions.

Natural clinoptilolite was mechanically pretreated, by crushing in an agate mortar and sieving in analytical sieves, for separating the particles $\leq 100\ \mu m$. The obtained powder was used to prepare nanoparticles of zeolite using a planetary ball mill (PM100; Retsch Corporation). The particles smaller than 100 μm were used for dry milling during 6 h. In order to remove any water soluble and also the magnetic impurities, the obtained nanoparticles were heated at 70 °C in distilled water under magnetical stirring for 24 h. This step was repeated to complete removal of the magnetic impurities by magnet.

The ZnO/NCP catalyst was prepared in the following steps. For ion exchange experiments, 50 mL of 0.1, 0.2, 0.3 and 0.5 M Zn(II) (as nitrate salt) was added to 2 g NCP and stirred at room temperature for 24 h. The samples were centrifuged, re-suspended in water, re-centrifuged and dried at room temperature. The obtained sample was referred as Zn–nanoclinoptilolite zeolite (Zn–NCP). Finally, the obtained Zn–NCP sample was calcined at 450 °C in a furnace for 12 h to form ZnO–nanoclinoptilolite catalyst (ZnO–NCP).

2.2. Catalyst characterization

The amount of zinc in the prepared catalysts and in the solutions was measured using an atomic absorption spectrometer (Analyst 300, Perkin-Elmer Co. USA, Air–C_2H_2, $\lambda = 324.8$ nm). For this goal, 2 mL 1:1 concentrated HNO_3:$HClO_4$ was added to an accurate amount of each catalyst in polyethylene beakers and heated until dried. This process was repeated 3 times and then 2 mL HF was added and heated to destroy the zeolitic framework. Finally, 10 mL diluted HCl was added and heated for 20 min. The obtained solution was filtered and diluted in a 50 mL volumetric flask and finally used for the determination of zinc [8]. The structure of the raw and modified clinoptilolite nanoparticles was analyzed by X-ray powder diffraction (XRD) patterns, using an X-ray diffractometer (Philips, Xpert PW3719, X-ray tube anode: Co Kα wavelength: 1.79 Å) in 2θ range of 5–70°. Infrared spectroscopy (FT-IR) spectra of the samples on KBr pellets were recorded with a Nicollet single beam FT-IR (Impact 400D) spectrometer in the range of 400–4000 cm^{-1} at room temperature. The surface morphology of samples

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