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Sunlight photodecolorization of a mixture of Methyl Orange and Bromocresol Green by CuS incorporated in a clinoptilolite zeolite as a heterogeneous catalyst

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ABSTRACT

Photocatalytic activity of CuS incorporated into an Iranian clinoptilolite (CuS-Cp) was studied for decolorization of a mixture of Methyl Orange and Bromocresol Green under sunlight irradiation. All samples were characterized by XRD, FTIR, DRS and TG/DTG techniques. The effect of some key experimental parameters such as: amount of the catalyst (0.05–5 g L^{-1}), initial concentration of dyes (5–30 mg L^{-1}), solution pH (1–11) and also dosage of H_2O_2 and $KBrO_3$ was studied on the decolorization extent. The extent of decolorization was estimated from the residual concentration by spectrophotometrically and it was confirmed by the reduction of chemical oxygen demand (COD).

1. Introduction

Most of the colors in the effluent from textile or dye industries involve aromatic compounds which are chemically stable and harmful to human health when they enter into aquatic system [1–4]. Advanced oxidation processes (AOPs) involve the generation of highly reactive radical species by several ways [5,6]. These techniques are based on the production of reactive species such as hydroxyl radicals ($HO^{\bullet}$), which are powerful oxidizing agents and capable of attacking a wide variety of organic molecules [7]. AOPs photocatalysis systems include combination of semiconductors and light and semiconductor and oxidants. Heterogeneous photocatalysis is the most promising method of AOPs for wastewater treatments with low-organic contents [8,9]. In addition, use of solar irradiation instead of UV radiation, to these systems could diminish the energy consumption required for generating of hydroxyl radicals [10]. Band gap-illumination of semiconductor crystals generates electron–hole pairs, electrons in the conduction band and holes in the valence band. While a fraction of these pairs diffuse out to the crystal surface and involve in redox reactions leading to photocatalysis, the recombined pairs cause a decrease in the photocatalytic efficiency [11].

CuS with a layered structure is a transparent p-type semiconductor with a band gap above 3.1 eV. The top of the valence band is primarily composed of well-hybridized states of Cu 3d and S 3p states, while the bottom of the conduction band consists mainly of Cu 4s state. The band gap of CuS was found to be a direct-allowed transition type through the analysis of the symmetry of these states. It was also found that the dispersion of the valence band is relatively large due to the considerable hybridization of Cu 3d and S 3p states. This dispersed valence band is responsible for the emergence of p-type electrical conduction in this material. On the other hand, the dispersion of the conduction band is rather small, probably because of the layered structure, in comparison with typical n-type conducting materials. This small dispersion of the conduction band leads to the wide band gap and high stability of excitons in CuS [12].

In zeolite-based photocatalysis, zeolite increases the adsorption of pollutants as a useful stage for degradation process. Zeolites can delocalize excited electrons of the supported semiconductors, such as CuS, on their surfaces and minimize e^-/h^+ recombination [13,14].

In this work, the photo-efficiency of the CuS incorporated into an Iranian clinoptilolite was studied in the decolorization extent of an aqueous solution containing Methyl Orange (MO) and Bromocresol Green (BCG). Methyl Orange is a widely used colored compound in dyeing and printing textiles. It is also known as Acid Orange52 and the C.I. no. is 13025, Helianthine B, Orange III, Gold orange and Tropaeolin D. This dye is an azo dye and also used in textile, foodstuffs, pulp and paper, and leather industry [15]. Bromocresol Green (BCG) belongs to the tri phenyl methane family (triaryl methane dyes), and has been used as a pH indicator and as a tracking dye for DNA agarose gel electrophoresis. MO and BCG dyes have different molecular structure and different functional groups. The release of these complex dyes and their products in the environment causes some environmental problems.

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Efficiency of various semiconductor photocatalysts such as: NiO, CdO, ZnO, FeO, CuS, NiS, CdS, ZnS and FeS as doped into clinoptilolite was compared in the decolorization of aqueous solution of the proposed mixture. After the selection of CuS-Cp as more effective catalyst than others, some experiments were performed to investigate the effects of various experimental parameters including catalyst loading, pH of the solution and initial dye concentration on the efficiency of photodecolorization process. The effect of direct photolysis and surface adsorption was also investigated. The mixture of the dyes was used to reach more similarity to a wastewater sample.

2. Experimental

2.1. Materials and preparation

Zeolite clinoptilolite was obtained from Semnan region in the north-east of Iran. Copper(II) nitrate trihydrate, sodium sulfide, Bromocresol Green and Methyl Orange dyes, H_2O_2 (46%), $KBrO_3$ (99%) and other reagents used in the present study were obtained from Merck. pH of the dye solutions was appropriately adjusted by hydrochloric acid or sodium hydroxide solution. Distilled water was used throughout the experiments.

Natural clinoptilolite zeolite was mechanically pretreated, by crushing in an agate mortar and sieving in analytical sieves, for the separation of the $\leq 100\ \mu m$ particle-size fractions. To remove water soluble and also probably magnetic impurities, the obtained powder was refluxed at 70 °C for 3 days while it was stirred magnetically and renewing of its water contents daily. After filtration, washing and drying, the purified material was stored for next experiments.

2.2. Preparation of the catalyst

In this paper, the various doped semiconductors such as: NiO, CdO, ZnO, FeO, CuS, NiS, CdS, ZnS and FeS doped into zeolite clinoptilolite were prepared by calcination (for oxide forms) and sulfurization (for sulfide forms) methods followed by ion exchange processes. The general procedure for ion exchanging of Ni^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, and Cd^{2+} ions with clinoptilolite zeolite is described as follows: 2 g of clinoptilolite zeolite was added to 50 mL nitrate salts of the above mentioned metals (0.3 M) and the obtained suspensions were shaken for 24 h in polyethylene bottles at room temperature. At the end of period, the solid phases were separated from the solutions by filtering, washed with water and dried at room temperature for 12 h. For preparing metal oxides the resulting exchanged zeolites were calcined at 550 °C in a furnace for 8 h. For preparing the metal sulfide forms of catalysts, the related exchanged zeolites were added to 1 M sodium sulfide aqueous solutions for 30 min. After this time, the suspensions were filtered and washed with copious water until to obtain the sulfide free filtrates. Finally, remained solids were dried at room temperature for 8 h. The effect of CuS loaded into the zeolite was also investigated by preparing the different catalysts by ion exchanging the raw zeolite in 0.1, 0.2, 0.3, 0.4 and 0.5 M copper nitrate solutions.

2.3. Characterization techniques

All samples were analyzed by XRD by using a diffractometer Bruker, D8ADVANCE, X-ray tube anode: Cu, wavelength: 1.5406 Å (Cu Kα-radiation); filter: Ni, in the 2θ range of 5-70°. Infrared spectra were recorded using a Nicolet single beam FT-IR (Impact 400D) spectrometer in the range of 400–4000 cm^{-1} by using KBr pellet. Diffuse reflectance UV–vis spectra were recorded by using a Shimadzu UV-3101PC spectrometer equipped with an integrating sphere. Differential scanning calorimetry (DSC), TG and DTG thermograms were performed by using a Model Setaram (STA) unit in the range of 50–600 °C and a temperature rise of 10 °C min^{-1}. Amount of copper was measured by atomic absorption spectrometer, PerkinElmer Analyst 300 (Air–C_2H_2 = 324.8 nm) and was 4.41% of Cu^{2+} cation (corresponds to 6.6% CuS). The absorption spectra were recorded in the wavelength range of 185–900 nm on a double beam spectrophotometer (Carry 100 Scan) in surpassed quartz cells of 1 cm optical path length.

2.4. Irradiation experiments

As mentioned above, decolorization efficiency of various photocatalysts were compared and zeolite containing CuS was selected as more efficient catalyst. Prior to carrying photocatalytic experiments, surface adsorption extent of BCG and MO onto the CuS-Cp catalyst was measured under dark condition. For this purpose, an appropriate amount of the photocatalyst (0.1 g L^{-1}) was added to 20 mL of a solution containing 10 mg L^{-1} both BCG and MO mixture. The suspension was shaken in regular time intervals and then centrifuged for determining the remained concentration of both dyes spectrophotometrically. Direct photolysis of the mixture was also studied by subjecting it to solar irradiation in the absence of the photocatalyst.

For photodecolorization experiments, the suspensions containing 0.1 g L^{-1} photocatalyst in 20 mL of 10 mg L^{-1} aqueous solutions of each BCG and MO dyes were irradiated under solar light in conditions of sunny days of July–August 2010 between 10 AM and 3 PM when the solar intensity fluctuations were minimal. During irradiation, the suspensions were sampled at regular intervals and centrifuged to remove any suspended solid particles. The decolorization extent was calculated in terms of changing in the absorbance intensity at λ_{max} of the dyes. It shows main absorption peaks (λ_{max}) at 617 nm for BCG and 466 nm for MO in the visible region. The λ_{max} of both BCG and MO do not change after mixing. The decolorization efficiency of dyes was calculated by the following equation:

$$\text{Decolorization}\% = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t are the initial and final absorbance values of dyes, which respectively relate to the initial (C_o) and final (C) concentrations according to Beer–Lambert law.

To confirm the extent of mineralization of the mixture, COD was also measured at regular time intervals using closed reflux titrimetric method [16].

3. Results and discussion

3.1. Characterization

3.1.1. XRD patterns

The XRD patterns of various samples including purified natural clinoptilolite (Cp), Cu-exchanged clinoptilolite (Cu-Cp) and its sulfurized form (CuS-Cp), in the 2-theta degrees covering the range of 5–70°, are shown in Fig. 1. The pattern (a) in Fig. 1 shows the characteristic lines of clinoptilolite with good agreement to the XRD pattern of clinoptiloite in the literature [17]. By ion exchanging the parent zeolite with Cu(II), some slight changes taken place in the XRD pattern, so, the peaks located in 2θ degrees of 12, 28.2 and 41.5 show the presence of copper into zeolite structure. This is also in agreement with the literature [18]. The XRD pattern of Cu-Cp and CuS-Cp samples is well matched with the pattern of clinoptilolite. This indicates that the framework