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Research paper

Photocatalytic decolorization of cationic and anionic dyes over ZnO nanoparticle immobilized on natural Tunisian clay

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ABSTRACT

In the present work we describe a simple and low-cost method for the decolorization of textile dyeing and printing wastewaters, using ZnO as photocatalyst supported on natural Tunisian clay (ZnO/Clay). This composite ZnO/Clay material was synthesized through a sol–gel method. X-ray diffraction (XRD), Nitrogen Physisorption (BET), Infrared Spectroscopy (FTIR), Scanning Electronic Microscopy (SEM) and High-Resolution Transmission Electron Microscopy (HRTEM) linked with Energy Dispersive X-ray (EDX), were performed in order to explain the characteristics of the ZnO/Clay photocatalyst. The XRD patterns, pointing to the presence of ZnO of very small crystal sizes, i.e. highly dispersed on the clay surface. The photocatalytic activity of ZnO/Clay was assayed in the decolorization of a cationic dye (Malachite Green, MG) and anionic dyes (Red Congo, RC) in aqueous solution as models pollutants under UV irradiation. In addition, the effects of different parameters such as pH of the solution, catalyst dosage, concentration of the dyes, irradiation source, as well as the influence of the presence of inorganic ions were investigated. The ZnO/Clay photocatalyst exhibited high photocatalytic activity of MG and CR decolorization under simulated solar compared to UV irradiation. The recyclability of the ZnO/Clay photocatalyst was as well validated.

1. Introduction

Azo and triphenylmethane dyes, Malachite Green and Red Congo, are two of the most widely used colorants in various industries such as the textile, cosmetic, food, printing, paper and leather industries (Forgacs et al., 2004). Congo Red (CR), an anionic diazo dye, can be metabolized into benzidine, a well-known human carcinogen (Ong et al., 2016). Malachite Green (MG), a cationic triphenylmethane dye, is resistant to fading on exposure; when this dye is discharged into water it affects the aquatic life and can cause detrimental effects in the gills, intestine, liver, kidney and gonadotrophic cells (Bel Hadjltaief et al., 2013; Saikia et al., 2015). These pollutants are quite refractory to both aerobic and anaerobic digestions, and stable to light, heat, and moderate oxidizing agents, being thus difficult to remove (Bel Hadjltaief et al., 2013; Saikia et al., 2015). Therefore, the elimination of these pollutants from wastewater remains a very challenging task.

A wide range of methods have been developed aiming to the removal of Malachite Green and Red Congo dyes from the wastewaters such as adsorption, membrane separation, ion exchange, photocatalytic degradation and biological treatments (Bel Hadjltaief et al., 2013). Among these methods, semiconductor photocatalytic processes, show important removal efficiencies and have an important potential for industrial application. Photocatalytic proceses moreover allow full water decontamination under relative mild operation conditions (Bel Hadjltaief et al., 2014b).

Zinc oxide as a semiconductor, (ZnO, 3.37 eV), has been historically used for the removal of CR or MG from water due to its high photo sensitivity, large band-gap, stability and relatively low toxicity (Saikia et al., 2015; Balcha et al., 2016; Ong et al., 2016). Aiming to its practical utilization, ZnO has been immobilized on various supports such as zeolites (Nezamzadeh-Ejhieh and Khorsandi, 2014), activated carbon (Muthirulan et al., 2013; Soltani et al., 2014) and clay (Fatimah et al., 2011; Motshekga et al., 2013; Li et al., 2014; Ye et al., 2015; Zhou et al., 2015; Xu et al., 2015).

In particular, clay-based catalysts, i.e. metal oxide supported clays, have been frequently used in heterogenous photocatalytic applications (Bel Hadjltaief et al., 2014b; Bel Hadjltaief et al., 2016). These catalysts have been employed in the photocatalytic degradation of organic

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pollutants such as phenol and of some phenolic derivates (Zhou et al., 2015; Ye et al., 2015), organic dyes (Motshekga et al., 2013; Li et al., 2014; Xu et al., 2014; Xu et al., 2015) and other persistent compounds (Dhakshinamoorthy et al., 2011; Abedi et al., 2015). For example, Xu and co-workers reported the preparation of a composite material consisting in ZnO loaded onto the surface of commercial Bentonite following an in situ sol–gel technique. Compared with the original raw clay and pure ZnO, the composite material exhibited considerably higher photocatalytic activity in the photodecomposition of Acid Red 35 in water solution under ultraviolet irradiation (Xu et al., 2015). In another study, ZnO particle supported on commercial Rectorite (ZnO/rectorite) was prepared through sol-gel synthesis using zinc acetate and lithium hydroxide as raw materials and Rectorite as support (Li et al., 2014). The photo-catalytic performance of such ZnO/rectorite was investigated in the removal of Methylene Blue under simulated solar irradiation. So far, to the best of our knowledge and according to the literature research, using ZnO supported on natural Tunisian clays has never been considered and used as a photocatalyst in the decolorization of organic dye-containing waters, under solar and UV irradiation.

In the present work, natural Tunisian clay was therefore used as a support for the immobilization of ZnO following a sol-gel method. The photocatalytic activity of this clay-supported ZnO was assayed in the decolorization of water containing both cationinc (Malachite Green, MG) and anionic dyes (Red Congo, RC). The influence of key operational parameters, such as pH, catalyst dosage, initial dye concentration, has been considered. In addition, the potential interference of inorganic ions such as NO_3^-, SO_4^{2-}, HCO_3^- and Cl^- on the photocatalytic performance of ZnO/clay was also investigated.

2. Experimental

2.1. Materials and chemicals

The natural red clay (NC) used in this study was sampled in Jebel Tejera-Esghira deposits located in the Southeast of Tunisia from the area of Medenine (Bel Hadjltaief et al., 2017). From geological point of view, those clays were attributed to the Lower Triassic. It is a very thick series with dominant of sandstone alternating with red clays and with some silty intercalations. The outcrops extended from the Beni Kheddache cliff to the J. Tebaga of Medenine; it occupies the anticline of the J. Tajera site. The outcropping feature of the Jebel Tajera-Esghira was estimated to 80 m-thick deposits of ferruginous clays (Bel Hadjltaief et al., 2017). The procedures used for its purification and Na-ion exchange from its surface have been previously described elsewhere (Bel Hadjltaief et al., 2014a; Bel Hadjltaief et al., 2016).

Zinc acetate dehydrate (zinc nitrate ($Zn(NO_3)_2$), 98%, Sigma–Aldrich, purity: 97%) was used as ZnO source for the preparation of the photocatalyst. Commercial ZnO (Merck, BET: 10 m^2/g) was used as a basis for comparison with our synthesized ZnO/Clay photocatalyst. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), sodium bicarbonate ($NaHCO_3$) and sodium nitrate ($NaNO_3$) were provided by Merck Chemical Company. All the chemicals were used as received without further treatment. Red Congo (RC) and Malachite Green (MG) dyes were used; both supplied by Sigma Aldrich. The absorption peaks at 618 and 499 nm were used to monitor the discoloration of MG and RC, respectively.

2.2. Synthesis of photocatalyst

The ZnO/Clay was synthesized via an optimized sol–gel method (Abedi et al., 2015). To do so, 4.38 g of dehydratedzinc acetate were dissolved in 100 mL of ethanol and stirred in a water bath at 50 °C. Then, 2.98 g of tri-ethanolamine were subsequently added to the solution while stirring continuously stirring for 1 h. The mixture was then placed under vibration and heated for 0.5 h at 40 °C, resulting in a colorless and transparent sol. At this instant, 3 g of natural clay were added to this sol. The dispersion was further agitated under vibration for another 0.5 h, filtered, dried and calcined for 4 h at 400 °C.

2.3. Raw clay and photocatalysts physico-chemical characterization

Several techniques were employed for the characterization of both the natural clay and ZnO/Clay catalyst. The identification of the different phases and crystal structures contained in the ZnO/Clay catalysts was performed through XRD analysis. An X-ray diffractometer (Philips PW 1710, Japan) was used with CuKα (λ = 1.54056 Å) radiation over a range of 2θ angles from 10 to 70, with a step size of 0.02°/s. The Scherrer equation was applied for estimation of the crystal size of ZnO on clay based catalyst.

Nitrogen adsorption–desorption isotherms for the different materials were acquired at − 196 °C on a Micromeritics ASAP 2010, after outgassing (10^{-5} Pa) for 24 h at ambient temperature. Surface areas were calculated using the BET equation, whereas mean pore size, pore size distribution and pore volume were estimated using the BJH method (Bel Hadjltaief et al., 2016).

The surface functional groups were studied using Fourier transform infrared (FT-IR) spectroscopy (IR, Digilab Excalibur FTS 3000 spectrometer). 1 mg of the clay fraction (> 2 μm) was diluted in 200 mg KBr to quantify the superficial reactive sites.

The morphology of the natural and ZnO supported clay was studied using scanning electronic microscopy (SEM, Hitachi SU-70) and High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM 2011) coupled by EDX microanalyzer (PGT IMIX PC) to evaluate the chemical composition.

The zero point charge (pH_{ZPC}) of the prepared material was determined following the method described by Bouzid et al. (2008).

2.4. Photocatalytic activity and irradiation experiments

Photocatalytic discoloration experiments were performed in an open Pyrex-glass cell with 250 mL capacity (of 5cminside diameter and 11 cm height). A detailed description of photocatalytic reactor was reported in an earlier study (Bel Hadjltaief et al., 2013; Bel Hadjltaief et al., 2016). Irradiation was carried out using an UV-lamp (Black-Ray B 100WUV-lamp, V-100AP series) with a wavelength of 365 nm. The experiments under natural solar radiation were carried out during the month of September 2016 during sunny days in our laboratory Sfax (Tunisia) in front of the Chemistry Department without any obstacle and were started at 11:00 am for a total duration of 2 h.

For the discoloration of MG or RC under UV irradiation, 150 mg of ZnO/clay was added to 100 mL of each dye aqueous solutions (50 mg/L) at room temperature. The resulting suspension was first magnetically stirred for 60 min in the dark, in order to reach adsorption-desorption equilibrium. At specific time intervals 2–3 mL of sample was withdrawn and catalyst was filtered using PTFE filters (0.45 μm). Concentration of MG and RC was then measured by means of UV–vis spectrophotometer (Shimadzu UV–vis spectrophotometer model 160A (Kyoto, Japan)), at the maximal adsorption wavelengths of RC and MG, λ_{max} = 497 nm and λ_{max} = 617 nm, respectively. Therefore, the dye discoloration efficiency was calculated as follows:

$$\text{Discoloration efficiency (\%)} = \left(1 - \frac{A_t}{A_0}\right) \times 100 \quad (1)$$

where A_0 represents the initial absorbance of the RC or MG solution, and A_t its absorbance after t minutes of irradiation/reaction.

The experimental work of this study involved several parameters on discoloration of the RC and MG dyes was studied. Firstly, the influence of the dye solution pH was assayed. The solution pH was adjusted from 2 to 12 using HCl (0.1 M) and NaOH (0.1 M), while fixing the dye concentration at 50 mg/L for either RC or MG and of the ZnO/clay catalyst at 1 g/L. The influence of the catalyst dosage, the ZnO/clay