High efficient photocatalytic activity of Zn-Al-Ti layered double hydroxides nanocomposite

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Abstract. This work establishes a simple method for synthesising layered double hydroxides (LDHs) powders with coprecipitation. The characteristics of the samples were investigated y X-ray diffraction (XRD), scanning electron microscopy (SEM) and spectrophotometer UV–Vis (DRS). Non-uniform distribution was shown for LDHs samples by SEM. Photocatalytic efficiencies were tested using methylene blue (MB) dye as a model contaminant under UV irradiation. In particular, Zn–Al-Ti LDH exhibited an excellent performance towards MB degradation compared with commercial TiO_2 nanoparticles. Methylene blue removal percentage was reached at almost 100%, whereas commercial TiO_2 reached a removal rate of only 66% under the same conditions within 20 min. The aim of the current work is to prepare Zn-Al-Ti layered double hydroxides nanocomposite and to evaluate their photocatalytic activity in the removal of methylene blue under UV irradiation.

1 Introduction

Over the past few decades, several researches focusing on photocatalysis have been investigated as an alternative method to eliminate the organic dye pollutant [1–2]. In the last years, the synthesis of layered materials has attracted a considerable attention and was widely used in photocatalysis process due to their stability, their simple preparation method and their low cost [3].

Lamellar double hydroxides (LDH) were synthesized for the first time by Feitknecht [4]. Their development was then amplified by the work of Miyata [5-7] on the $[Zn_3Al(OH)_8][X.\ nH_2O]$ phase. These compounds have been the subject of numerous studies and have been widely described in the literature because of the numerous possibilities of application of these materials in a wide range of fields: catalysis, environment, polymer and health…These materials consist of positively charged sheets containing divalent and trivalent cations. The electro-neutrality of the material is ensured by the presence of intercalary anions, solvated by molecules of water [8]. LDHs associated with zinc, used as an addition because of its photocatalytic activity in order to contribute to the overall activity of the new Ti-Zn-Al nanocomposite [9]. ZnO is often considered as an alternative to TiO_2 because it can absorb a greater energy fraction of the solar spectrum and more quanta of light [10]. Enormousres researches have reported that LDH photocatalysts presented an effective removal performance of organic contaminants [11, 12]. Furthermore, enormous LDH photocatalysts were reported that Zn-Ti LDH exhibited the highest photocatalytic performance in the degradation of organic pollutants [11, 13].

2 Experimental

Zn-Al LDH was synthesized by the simultaneous addition of $Zn(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$ ($4cm^3$/min) with a basic solution of 0.67 Na_2CO_3 and 2,25 of NaOH at constant pH 9-9.5 and constant temperature of 45 °C for 10 hours. At the end of the stirring, a white gel is precipitated, aged for 12 hours at 100°C and then calcined for 5 hours at 500 °C. The dried samples were

denoted as Zn-Al LDH. To bind the titanium oxide in the previous nanocomposite, a wet impregnation of TiO_2 on Zn-Al LDH was used for the preparation of Zn-Al-Ti LDH; diluted TiO_2 suspension (3wt%) and 0.67 M of Na_2CO_3 basic solution are charged to the Zn-Al LDH calcined powder and removed in a stove at 100°C.The obtained sample was dried for 12 hours at 100 °C, calcined for 5 hours at 500 °C and denoted as Zn-Al-Ti LDH.

The photocatalytic activities of materials were assessed via the photocatalytic degradation of methylene blue (MB) under UV light irradiation using a 125Wlamp.Photocatalytic reaction was carried out in a Pyrex reactor containing10 ppm of MB and 0.5g/L of the photocatalyst. The mixture was vigorously stirred in the dark for 60 minutes in order to reach the adsorption-desorption equilibrium, and then the aqueous samples were filtered. The concentration of the suspension was analyzed using the UV/vis spectrometer.

X-ray diffraction (XRD) was acquired using a Siemens D5000 diffractometer. This unit uses the mounting BRAGG-BRENTANO (θ/2θ). UV/vis spectrophotometer was performed using the UV–vis spectrometer UV2300 Spectrophotometer. The morphology of samples was examined by scanning electron microscopy (SEM) using Jeol JSM-7000F FE-SEM, Japan.

3 Results and discussion

LDHs samples and commercial TiO_2 presented in fig. 1 were analyzed by XRD. ZnO and $Zn_6Al_2O_6$ were the dominant phase detected in Zn-Al LDH and Zn-Al-Ti LDH samples, whereas ZnO phase originates from Zn-Al LDH [14]. After the impregnation, the intensity of TiO_2 peak is weak comparing with others due to their very small amount. The anatase phase in Zn-Al-Ti LDH sample has been detected in DRX diffractogram. Although the formation of Zn_2TiO_4 phase is due to the reaction between ZnO and TiO_2. Formation of very weak peaks intensity were observed in Zn-AL Ti LDH sample calcined at 500 °C, where as Yee-Shin Chang et al., reported that from 700 °C, some peaks correlated to Zn_2TiO_4 were shown in the XRD pattern [15].

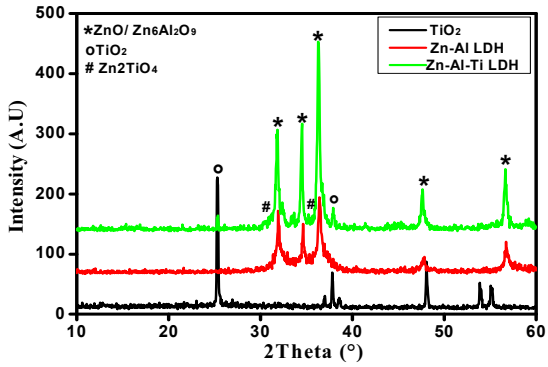

Fig. 1. XRD patterns of Zn-Al-Ti LDH, Zn-AL LDH and TiO_2.

SEM photographs of Zn–Al LDH and Zn-Al-Ti LDH are shown in Figs. 2a and 2b respectively.SEM of LDHs samples showed non-uniform distribution. Furthermore, the images show that all samples were agglomerated and possessed large and lumpy particles.SEM analysis revealed the same morphology for Zn–Al LDH and Zn-Al-Ti LDH.

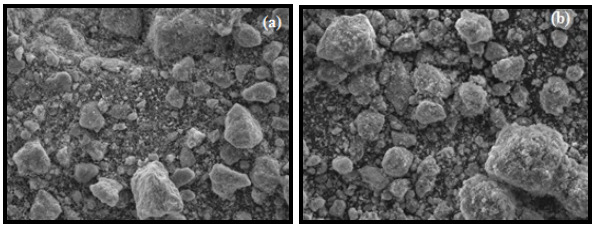

Fig. 2. SEM photographs of (a) Zn-Al LDH and (b) Zn-Al-Ti LDH

The evaluation of optical absorption spectra was recorded by UV–Vis DRS. The optical absorbance versus wavelength plots for as-prepared samples are presented in fig.3. It was observed that the optical absorption of LDH materials was estimated to be 404 nm and 411 nm for Zn-Al LDHs and Zn-AL-Ti LDHs, respectively. Their band gaps were estimated to be 3.06eV and 3.01eV.However, the absorption edge of the commercial TiO_2 is about 3.26 nm [16]. This change of the band gap, indicating that photocatalytic activity enhancement was directly ascribed to the band gap.

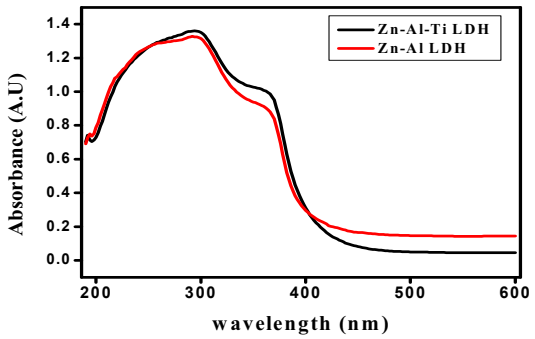

Fig. 3. UV-vis absorption spectra of Zn-Al-LDH and Zn-Ti LDH composites.

The study of methylene blue degradation (MB) was used in order to evaluate the photocatalytic performance of as-prepared samples. The results presented in Fig.4showthat MB concentrations were decreased. Before photocatalytic tests, adsorption performance was conducted.Fig.4 shows the linear plot of MB degradation, which follows a pseudo- first-order kinetic be havior by the equation below [17]:

$$Ln(C/C_0) = -Kt$$

Where C_0 and C are the initial concentration of MB and the concentration at time t, respectively, K is the photocatalytic reaction rate constant (min^{-1}).

Fig. 4 shows the photocatalytic degradation of methylene blue, under UV irradiation. It was remarkable that all the samples exhibited high photocatalytic activity

but Zn-Al-Ti LDH present the highest performance. Therefore, it may be concluded that samples prepared using LDH play an important role in the degradation of MB. It has been observed that samples synthesized using LDH exhibit much higher photocatalytic activity than commercial TiO_2.

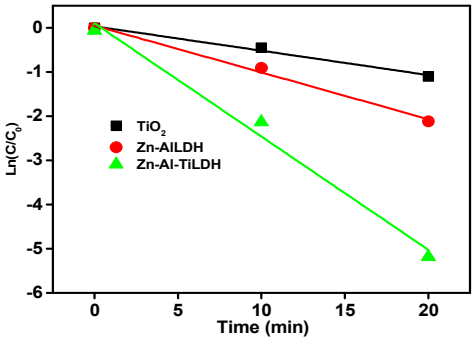

Fig. 4. Photocatalytic performance of as-prepared photocatalysts.

The methylene blue was degraded around 99% in 20 min for Zn-Al Ti LDH. It could be assigned to the fact that LDH materials are rich in OH groups which favor the titania activity. However, at the same photocatalytic time, the degradation rate of Zn-Al LDH and TiO_2 was only 87% and 66%, respectively. The increase in the photocatalytic activity, could be assigned to the rapid electron and hole separation efficiency. Zn-Al-Ti LDHs showed higher degradation which was greater compared with other samples. Many researchers have reported and discussed the photocatalytic performances of Zn type LDH [18, 19]. Zn–Al LDH could have two active species such as superoxide O2•- and hydroxyl radicals OH• under UV irradiation for the removal of MB. Mohapatra et al., and Li et al., [19, 20] have proven thatO2•- plays the key role in the initiation of the photocatalytic process in LDH photocatalytic systems.

Conclusion

Layered double hydroxide was synthesized using simple coprecipitation method. A slight decrease in the band gap of Zn-Al-Ti LDHs was observed by the introduction of TiO_2. All the samples presented a high photocatalytic activity and produced 100% removal of MB. The enhancement of photocatalytic performance could be assigned to the enhanced of the electron–hole pair formation. The photocatalytic process matched pseudo-first-order kinetic model.

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