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TAILORING PHOTOCATALYSTS NANOARCHITECTONICS FOR DEGRADING INDUSTRIAL DYES

BY

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Abstract. In this work we report novel photocatalysts based on Zn - based layered double hydroxides (LDHs), as active photocatalysts for degrading the following industrial dyes: drimaren red (DR), drimaren navy (DN) and nylosan (NYL).

X-ray diffraction (XRD), IR spectroscopy (FTIR), and UV–vis analyses were used to investigate the structure, composition and photoresponsive features of the catalysts. The catalysts photoefficiency was analyzed by UV–vis following the absorbance (A) at 283 nm, 277 nm and 567 nm characteristic to DR, DN and NYL, respectively.

The results point out that the studied LDHs present high photocatalytic activity for the degradation of the dyes; such that the maximum photocatalytic efficiency was about 80%. The catalytic performances of ZnAlLDH and the derived mixed oxides are a function of the specific composition of the clay.

Keywords: layered double hydroxides; industrial dyes; photocatalysts; environmental catalysis.

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1. Introduction

Nowadays the industrial dyes and garment industries are big concerns for water pollution (Meng, 2015). Photocatalysis has been established as an effective tool for removing various toxic pollutants from contaminated wastewaters by using efficient catalysts that are active under irradiation with solar or Uv light. In recent years, the scientific community has been increasingly interested in the novel emerging technologies that might guarantee an efficient mineralization of a wide variety of toxic organic pollutants in less harmful products (Abderrazek *et al.*, 2017).

Layered double hydroxides (LDHs) are also known as hydrotalcites or anionic clays. They are denoted by the general formula $[M^{II}_{1-x} M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ where M^{II}, M^{III} are the divalent respectively trivalent cations and A^{n-} is the interlayer anion with n- valence (Klemkaite *et al.*, 2011; Muhhamad *et al.*, 2016; Zhao *et al.*, 2002). The nature of the interlayer anions might take a high diversity, such that, LDHs with different type of anions like organic, inorganic, biomolecules, polyoxometalates has been reported (Cavani *et al.*, 1991).

The properties of LDHs and the oxides derived after their calcination can be adapted by varying the nature of Me^{2+} and Me^{3+} in the brucite-like layers, the molar ratios of Me^{2+}/Me^{3+} and the nature of the A^{n} in the interlayers. Recently, much effort has been focused on the study of LDHs as environmentally friendly materials that can be used as photocatalysts or photocatalytic support (Carja *et al.*, 2013).

Furthermore, LDHs are relatively simple and inexpensive mesoporous materials be obtained that can be facile synthesized in both laboratory and industrial scale (Forano *et al.*, 2006). The most common methods of preparation of LDHs are: co-precipitation method, ion exchange method and reconstruction method (He *et al.*, 2006). Thermal treatment of LDHs at 550ºC destroys their layered brucite-like structure and and gives rise to mixture of mixed oxides. LDHs have shown a unique property known as "structural memory effect" that represents the ability of LDHs to restore their initial layered structure when the mixed oxides, obtained by calcination, are introduced in aqueous solutions containing anions. The nature of anions used in the reconstruction process can be different from the initial ones (Cârjă *et al.*, 2011). After calcination at temperatures higher then 550ºC the layered structure cannot be restored the LDHs lose their memory to reconstruct their initial structure.

Zinc-based LDHs ($ZnMe^{3+}$LDHs) are widely studied as photocatalysts for the degradation of organic compounds from aqueous solutions. Recent results point out that ZnTiLDHs has significant catalytic activity in the degradation of the Methylene Blue dye under irradiation in the presence of visible radiation (Shao *et al.*, 2011). Furthermore, ZnTiLDHs preserves its photocatalytic stability over five cycles with almost constant degradation yield, which means that Zn-TiLDH does not deactivate during the photocatalytic process (Shao *et al*., 2011). Zn-based LDHs in combination with different series of Me^{3+} (*e.g.*: Al, Fe, Co) have been studied in photocatalytic degradation of Rhodamine B (RB) using irradiation with Vis light (Xia *et al*., 2013).

This work aims to study the removal of three industrial dyes such that: Drimaren Red (DR), Drimaren Navy (DN) and Nylosan Navy (NYL) from water solutions by using ZnAlLDH and the mixed oxides obtained by calcination at 550°C and 750°C, as novel photocatalysts.

2. Experimental

2.1. Synthesis

ZnAlLDH was synthesized by coprecipitation method. Metal salts solution composed from $Zn(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ with a molar ratio $Zn^{2+/}Al^{3+} = 4{:}1$ together with precipitants $NaOH/Na_2CO_3$ were added dropwise at a constant pH equal of 8.3. The precipitate formed was aged about 24 h at room temperature, separated by filtration, washed with distilled water and dried at 80°C in an oven (Rivers, 2001). Then, the solid was calcined at 550°C and 750°C (10°C min^{-1}) for 5 h. The resulting samples were denoted ZnAl550 and ZnAl750.

2.2. Characterization

The structural analysis of the samples was performed by powder X-ray Diffraction (XRD) using an X-ray diffractometer (PANalytical X'Pert PRO MPD) equipped with CuKα radiation ($\lambda = 0.15406$ nm); measurements were done in the 2θ range from 5° to 80°. DRIFT spectra were acquired using a Nicolet 6700 FT-IR spectrometer. The samples were mixed (2 wt%) with dry KBr and pure KBr was used as reference. For each sample, 200 scans were averaged and a resolution of 4 cm^{-1} was applied. UV-Vis analyses were recorded on a Jasco V550 spectrophotometer with integration sphere. TG/DTG analysis was performed on Perkin-Elmer Pyris Diamond TG/DTA thermogravimetry.

2.3. Photocatalytic Tests

The photocatalytic activity was tested for the photodegradation of three industrial dyes: Drimaren red (DR), Drimaren navy (DN) and Nylosan navy (NYL). The initial concentration of dyes was 0.1 g/L while 1 g/L of photocatalyst was used in each photocatalytic experiments. Before the photocatalytic run, the catalyst was dispersed in the dye compound solution was stirred in the dark for 1 h to reach the adsorption–desorption equilibrium between the solid surface and the adsorbate molecules. Afterwards, the dye solutions were irradiated with a solar simulator (Unnasol US800, 180 W). The reactor volume was 250 mL. Samples of about 3 mL were withdrawn from the reactor every 30 min up to 240 min from the beginning of the photocatalytic run. The catalyst photo efficiency was monitored by UV–vis analysis following the absorbance (A) at 283 nm, 277 nm and 567 nm, characteristic to DR, DN and NYL, respectively.

3. Results and Discussion

3.1. Characterization of Catalysts

XRD spectra of the as-synthesized ZnAl-LDH and the derived mixed oxides are presented in Fig. 1. It shows the characteristic peaks of LDHs that are assigned to the basal reflections (003), (006) and (009) at lower 2θ degrees and non-basal reflections (015), (018), (110) and (113) for higher 2θ degrees. All the peaks are sharp, especially one from (003) and shows a strong intensity, revealing the high crystallinity of the catalyst (Seftel *et al*., 2008).

Further, ZnAlLDH was calcined at two different temperatures (550ºC and 750ºC) in order to form the derived mixed oxides. Results of XRD analysis reveal that after the thermal treatment ZnAlLDH was transformed into a mixture of zinc oxides and zinc aluminate $ZnAl_2O_4$.

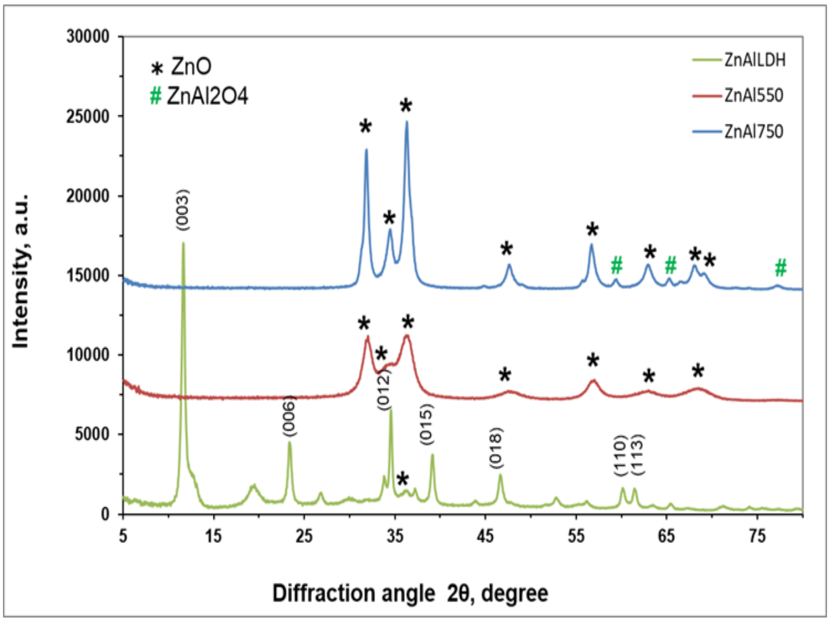

Fig. 1 – The X-ray diffraction patterns of the as synthesized and the calcined catalysts.

The FTIR spectra of the tested catalysts (Fig. 2) is defined by an intense absorption band around 3450 cm^{-1} that can be assigned to O-H groups from the brucite layer and the phisysorbed H_2O molecules. The H-O-H bending vibration, assigned to the interlayer water is represented by an absorption peak around 1630 cm^{-1}. FTIR results demonstrate that CO_3^{2-} is present as the interlayer anion thus, the corresponding symmetric and asymmetric stretching modes appear around 1360 cm^{-1}and 1500 cm^{-1}, respectively. Between 800-400 cm^{-1} the characteristic signals for M-O-M and M-O can be clearly identified (Seftel *et al*., 2007; Lin *et al*., 2017). In the case of the derived mixed oxides it can be noticed a significant decreasing of the intensity for O-H and CO_3^{2-} groups because of the water removal and the decarboxylation of the layered double hydroxide during the calcination process. The intensity of the band at 686 cm^{-1}, due to the lattice vibration modes of Al–O in octahedral coordination state, increases after calcination at 750°C, suggesting the formation of a $ZnAl_2O_4$ spinel phase.

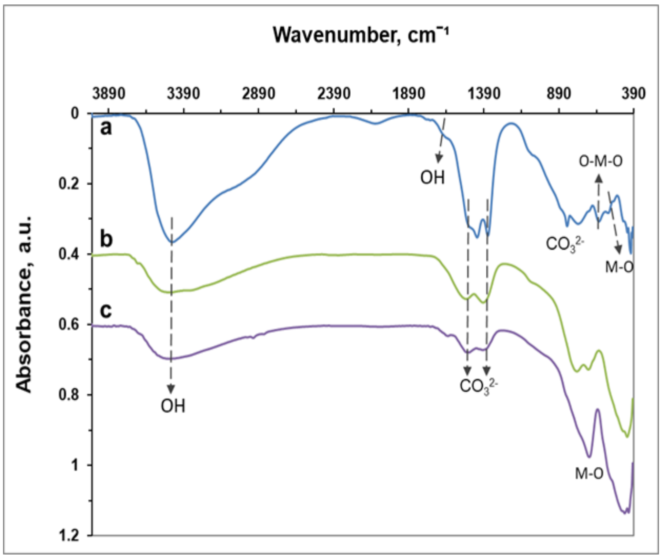

Fig. 2 – The results of FTIR analyses for ZnAlLDH (a), ZnAl550 (b) and ZnAl750 (c).

The optical properties of catalysts were studied by UV-Vis spectrophotometry and the results are given in Fig. 3. ZnAlLDH does not show any adsorption bands in UV range which reveals that it is optical transparent but after 350 nm a small band is present. Unlike the LDHs precursor, the mixed oxides obtained by calcination present a broad band around 340 nm revealing, in agreement to the XRD results, the presence of ZnO (Khodam *et al*., 2015). For ZnAl750 the band from 340 nm is a bit shifted to the right due to the formation of the spinel phase $ZnAl_2O_4$.

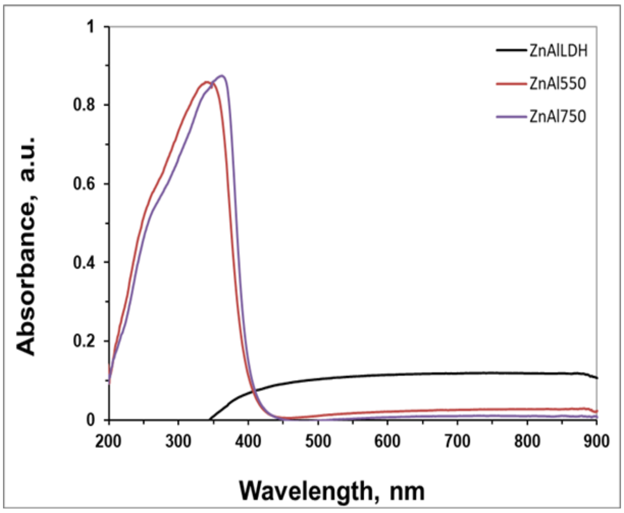

Fig. 3 – UV-Vis absorption profiles of the studied catalysts.

TG/DTG analysis of ZnAlLDH (Fig. 4) indicate three stages of mass loss; this is typical for the LDHs-like materials. The first stage of the thermal degradation might be attributed to the removal of the surface and interlayer water from the LDHs structure (30-185°C) and shows a mass loss of 9.3%. The next step corresponds to the dehydration of the LDH within the temperature range (180-268°C) with a mass loss of 25.87%. Further the third stage may be assigned to the decomposition of the anions from the interlayers (268-530°C) and shows a 30.39% mass loss (Pușcașu *et al.*, 2017).

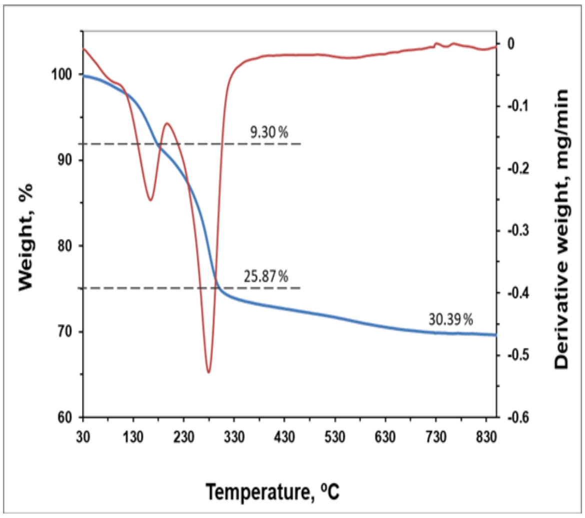

Fig. 4 – Thermal analysis profiles of ZnAlLDH.

3.2. Photocatalytic Results

To study the photocatalytic response of the tested materials we have investigated the photodegradation of three industrial dyes from the aqueous solutions under irradiation with solar light. A dark test was performed in order to achieve the sorption-desorption equilibrium. Further, a blank test without catalyst were done to see the stability of dyes under solar irradiation.

Fig. 5 shows the UV-vis evolution spectra as a function of time for drimaren red (A), drimaren navy (B), nylosan navy (C) and the corresponded degradation curves (D). First at all results revealed that the intensity of representative peaks for dyes decreases after the irradiation starts.

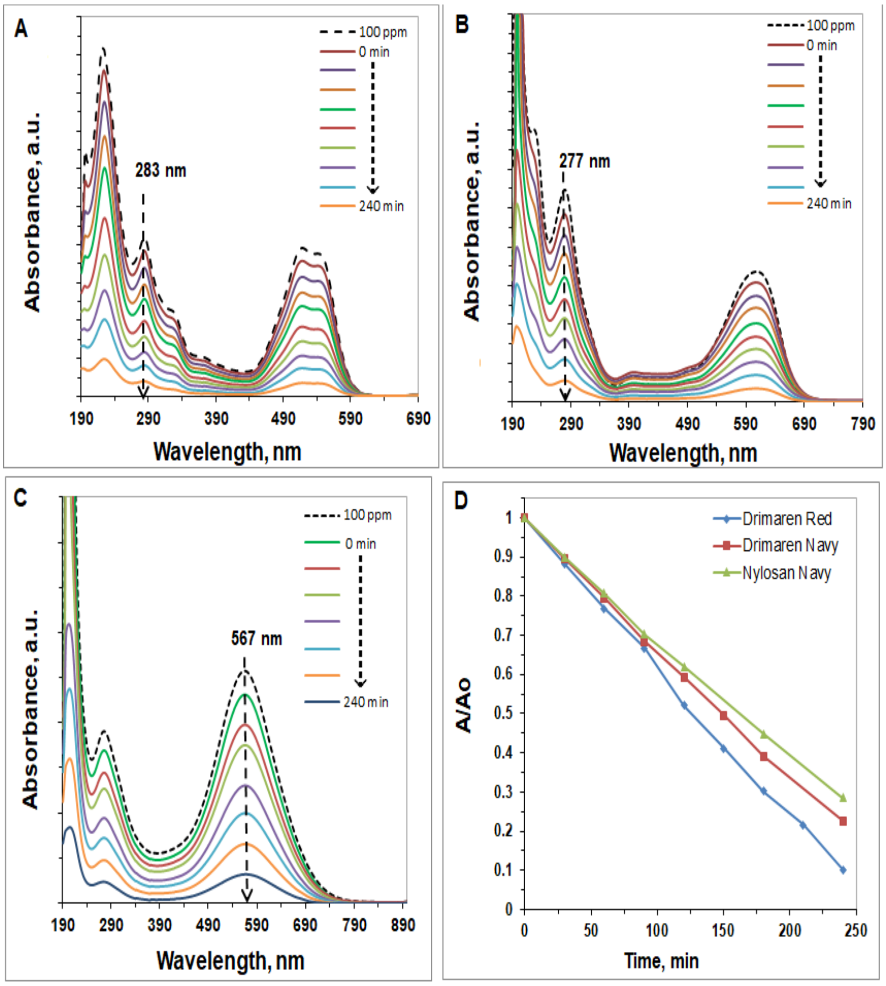

Fig. 5 – UV-vis evolution spectra in time for drimaren red (A), drimaren navy (B), nylosan navy (C) and degradation curves (D) on ZnAl750.

For $ZnO/ZnAl_2O_4$ mixed oxides demonstrated a higher photocatalytic activity in the destruction of dyes. Hence the photocatalytic activity has been improved when for the mixed oxides derived by calcination at 550°C and 750°C. After 4 h of irradiation can be noticed (Fig. 6) that ZnAlLDH achieved an efficiency less than 15.8% while for ZnAl550 the dyes were degraded almost 50% while for ZnAl750 the degradation efficiency was higher than 80%.

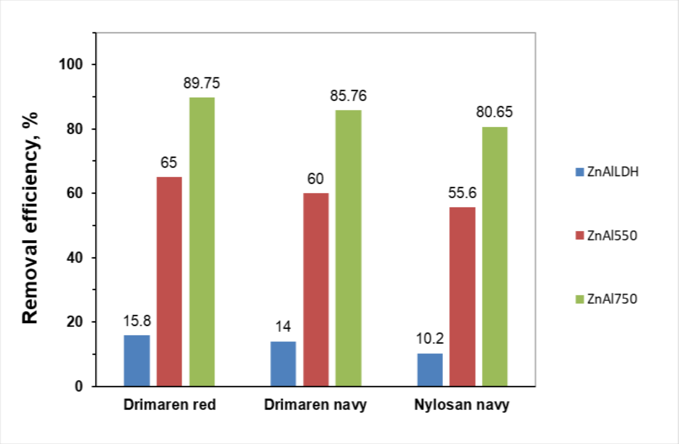

Fig. 6 – The removal efficiency of the tested dyes after 4 h of irradiation under solar light.

4. Conclusions

ZnAlLDH ($Zn^{2+}/Al^{3+}= 4$) was fabricated by the co-precipitation method and the derived mixtures of mixed oxides were obtained by a thermal treatment at 550°C and 750°C, respectively. Detailed physical-chemical characterization by XRD, UV-vis, FTIR-DRIFT and TG/DTG analyses showed the successful formation of layered LDH- brucite-like layers and their optical characteristics. The photocatalytic results show that the best catalyst for the photodegradation of Drimaren Red, Drimaren Navy and Nylosan Navy, under the experimental details used in this study, is ZnAl750ºC that showed an efficiency higher than 80% for the degradation of all of the dyes, after 4 h of irradiation.

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ADAPTAREA FOTOCATALIZATORILOR NANOARHITECTONICI PENTRU DEGRADAREA COLORANȚILOR INDUSTRIALI

(Rezumat)

În această lucrare raportăm noi formulări active de fotocatalizatori bazați pe hidroxizi dubli lamelari, pentru degradarea coloranților industriali Drimaren red (DR), Drimaren navy (DN) și Nylosan navy (NYL), sub iradiere cu lumină solară. Difracția de raze X (XRD), spectroscopia IR (FTIR) și analiza UV-vis au fost utilizate pentru a investiga structura, compoziția și proprietățile fotoresponsive ale probelor. Eficiența fotocatalitică a fost monitorizată prin analiza UV-vis urmărind absorbția (A) la 283 nm, 277 nm și 567 nm caracteristică DR, DN și respectiv NYL.

Rezultatele arată că ZnAlLDH și oxizii micști derivați prezintă o activitate fotocatalitică ridicată în degradarea coloranților; eficiența fotocatalitică maximă a fost de aproape 80%.