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PHOTOCATALYTIC AND PHOTO-FENTON DEGRADATION OF IBUPROPHEN UNDER SOLAR LIGHT IRRADIATION

BY

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Abstract. In this work, the degradation of pharmaceutical agent ibuprofen by photocatalysis and photo-Fenton catalysis, using artificial visible light irradiation and H_2O_2 as Fenton reagent, was carried out. Two efficient Fe/LDHs photocatalysts with different iron content were fabricated. First, the LDH precursor with Zn^{2+} and Al^{3+} as di- and trivalent brucite-like cations ($\text{Zn}^{2+}/\text{Al}^{3+} = 3/1$) was obtained by co-precipitation method and denoted as Zn3Al. Then, by the structural reconstruction of the calcined Zn3Al in aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, two Fe/LDH- based nanocomposites were obtained and denoted as Fe(1%)Zn3Al and Fe(4%)Zn3Al. The structural and optical properties of the samples were studied by XRD, FTIR and UV-Vis techniques. The photocatalytic tests were performed using a solar simulator as irradiation source. Photocatalytic results showed that the novel catalysts is efficient for the ibuprofen degradation. A remarkable enhancement of Ibuprofen degradation was obtained in the case of photo-Fenton process, up to 89% by Fe(1%)Zn3Al nanocomposite. Increasing the content of Fe in the catalysts showed an insignificant effect in enhancing the catalyst efficiency for ibuprofen removal.

Keywords: photocatalyst; ibuprofen; photo-Fenton; solar photodegradation.

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1. Introduction

The widespread of pharmaceuticals products in wastewaters represents a current worldwide issue for the environment safety, since the exact impact and possible toxic effects of these compounds on the aquatic fauna and water quality is still unknown (Yuan *et al.*, 2009). Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) are the most used pain killers in the world and the most frequently detected pharmaceuticals in the aquatic system, respectively (Zhang *et al.*, 2011). Hence, they are considered a new class of pollutants (Calza *et al.*, 2006). One of the most representative example pharmaceutical from NSAIDs class is the analgesic drug ibuprofen. Studies reported the presence of ibuprofen in the environment in concentration in the range of [169 $\mu\text{g/L}$ - 10 mg/L] (Santos *et al.*, 2007). Although is a biodegradable compound, the concern is about the ecological effects caused by the main biological oxidation by products (hydroxyl-IBP and carboxy-IBP) (Mendez-Arriaga *et al.*, 2010).

Advanced oxidation processes (AOPs), such as heterogeneous photocatalysis, ozonation, photo-Fenton catalysis etc., are environmentally friendly techniques characterized by the generation of hydroxyl radicals ($\cdot\text{OH}$), a strong oxidant capable to react with organic pollutants. Photo-Fenton reactions are based on redox reaction of Fe(II) and H_2O_2 and the photolysis of H_2O_2 under light irradiation to generate an increased amount of $\cdot\text{OH}$ (Guinea *et al.*, 2008; Secula *et al.*, 2008; Sheng *et al.*, 2015). Photocatalysis is a catalytic process occurring on the surface of semiconductor materials under light irradiation, generating electron-hole pairs that react with water and the dissolved oxygen to form hydroxyl radicals ($\cdot\text{OH}$) and super oxide radicals ($\text{O}_2^{\cdot-}$) capable of degrading organic compounds (Park *et al.*, 2016).

Recently, the attention is focused on photocatalytic processes that use the solar light as an inexhaustible, low-cost, environmentally-friendly energy resource (Wang *et al.*, 2014). Among efficient semiconductors for the removal of organic pollutants from the environment, layered double hydroxides (LDHs) are considered promising photocatalysts not only in the UV region, but also in the visible region due to their specific structure, versatile composition, morphology and semiconductor properties (Muresanu *et al.*, 2017; Puscasu *et al.*, 2015).

Layered double hydroxides or hydrotalcite-like compounds are natural or synthetic anionic clays with a brucite-like lamellar structure represented by the general chemical formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+} (\text{A}^n)_{x/n} \cdot y\text{H}_2\text{O}$ (Ahmed *et al.*, 2012). The partial replacement of divalent cations (M^{II}) by trivalent cations (M^{III}) gives the brucite-like sheets a positive surface charge that is counterbalanced by anions located in the space between two brucite-like layers (known as gallery or interlamellar space) along with water molecules (Bouariu *et al.*, 2013). A wide range of divalent/trivalent cations, such as Mg^{2+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , Al^{3+} , Fe^{3+} , Ni^{3+} , Ga^{3+} can be incorporated in the brucite-like

layers (Carja *et al.*, 2011; Morimoto *et al.*, 2011) and even tetravalent and monovalent cations (such Ti^{4+} , Sn^{4+} , Li^+) are reported (Mingos *et al.*, 2006; Velu *et al.*, 1999; Gupta *et al.*, 2012). The anions located in the gallery can be any anion (organic, inorganic, biomolecules, polyoxometalates etc.) as long as it does not abstract the metal cation from the layer and has a sufficient charge density (Rivers *et al.*, 2014). By incorporating specific metal-cations, multi-component LDHs can also be obtained. All these possibilities and combinations give rise to a large variety of LDH materials with a versatile and flexible chemical composition (Zhao *et al.*, 2016).

LDHs are low-cost, biocompatible and environmental friendly materials with specific properties as lamellar structure, high surface area, positive surface charge, high anion exchange capacity that make them suitable materials in application for catalysis, adsorption processes, medicine, removal of organic pollutants from the environment and nanotechnology (Carja *et al.*, 2013; Bouariu *et al.*, 2013; Sajid *et al.*, 2016; Xu *et al.*, 2011).

Synthetic LDHs are simple to prepare and the most common way is the coprecipitation method (Cavani *et al.*, 1991). By calcination at certain temperatures, anionic clays transform into a mixed metal oxide that have the ability to regenerate their layered structure when exposed to an aqueous solution (Reichle *et al.*, 1986). This unique property called “structural memory effect” gives layered double hydroxides the ability to form nanoparticles of metals or metal oxides-LDH (Me or MeO_x-LDH) as self-assembly (Carja *et al.*, 2010; Muresanu *et al.*, 2017). The presence of nanoparticles onto LDH surface facilitates the migration and separation of electron-hole pair, avoiding the rapid recombination of photo-generated charge-carriers (Muresanu *et al.*, 2017) and thus enhancing the photocatalytic performance of the catalyst.

The aim of this work has been to study the degradation of pharmaceutical agent ibuprofen by means of photocatalysis and photo-Fenton catalysis processes using the solar simulator as irradiation source, Fenton reagent - hydrogen peroxide (H_2O_2) and iron nanocomposites based on layered double hydroxides as visible light-driven photocatalysts.

2. Experimental

2.1. Catalysts Synthesis

ZnAlLDH clay precursor containing Zn^{2+} and Al^{3+} ($\text{Zn}^{2+}/\text{Al}^{3+} = 3/1$) as cations of the LDH layers was obtained via co-precipitation method at constant pH of 8.0. The procedure involved the slow addition of a mixed metal nitrate solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to a $\text{Na}_2\text{CO}_3/\text{NaOH}$ solution under vigorous stirring, at 65°C (Rivers *et al.*, 2001). After the aging process for 24 h the final precipitate was filtered under vacuum, washed two times with deionized water and dried in the oven at 80°C. The sample was denoted Zn3Al.

Based on the structural “memory effect” of anionic clays, using the reconstruction method, the obtained clay was then used as a precursor in the preparation of Fe(x%)/Zn3Al nanocomposites with two different iron content. More precisely, a proper amount of calcinated clay (1.2 g at 500°C for 12 h) was added, under stirring, in two vessel reaction containing 200 mL aqueous solution of FeSO₄·7H₂O, at two different concentrations. The final pH of both reconstruction solution was 9. The final product was aged for 5 h, separated by centrifugation and dried at 80°C. The samples were denoted as Fe(1%)Zn3Al and Fe(4%)Zn3Al.

2.2. Characterization of the Catalysts

These materials were further characterized by X-ray diffraction (XRD), FT-IR spectroscopy and solid phase UV-Vis spectrophotometry in order to obtain informations about their structure and optical proprieties. Structural characteristics and the optical proprieties of our catalysts were investigated using a D8 ADVANCE XRD diffractometer at a Bragg angle (θ_B) of $2\theta_B = 3^\circ\text{--}60^\circ$ with a scan step of 0.01° and a scan rate of 5 s per step. The measurements were performed at 40 kV and 40 mA using Cu K α emission and a nickel filter. UV-Vis absorption profiles were recorded at room temperature, using a Jasco V-550 Spectrophotometer, within the wavelength range 190–900 nm. FT-IR spectra were measured in a KBr phase, on a Perkin Elmer Spectrum 100 spectrophotometer, in the frequency range of 400–4000 cm⁻¹, at a resolution of 4 cm⁻¹.

2.3. Photocatalytic Experiments

The obtained catalysts were further used for the degradation of ibuprofen by photocatalysis either by photo-Fenton catalysis, under artificial visible light irradiation, using a solar simulator UNNASOL (US800, 250 W). The photocatalytic experiments under artificial solar light were performed in batch mode with a 0.1 g catalyst dose added to 200 mL aqueous solution of 0.1 g/L ibuprofen. Prior to the irradiation, the mixture was stirred in dark for 30 min in order to establish the adsorption-desorption equilibrium between the pollutant and the catalyst surface, until the pollutant remained constant. For photo-Fenton catalytic tests, a proper amount of H₂O₂ was added in the mixture immediately just before exposure to irradiation. After the light irradiation was turned on, 1 mL of sample was withdrawn at given time intervals, diluted in 6 mL of distilled water, centrifuged to remove the catalyst and analyzed by UV-Vis spectrophotometer following the absorbance at 219 nm, characteristic for

Ibuprofen. The Fenton reagent hydrogen peroxide was used in excess to ensure efficient $\cdot\text{OH}$ radicals production. All the photocatalytic tests were conducted at room temperature. The blank test was also performed following the same procedure, without adding catalyst or H_2O_2 , to investigate the photostability of the pollutant and to evaluate the role of the catalyst.

3. Results and Discussions

3.1. Catalysts Characterization

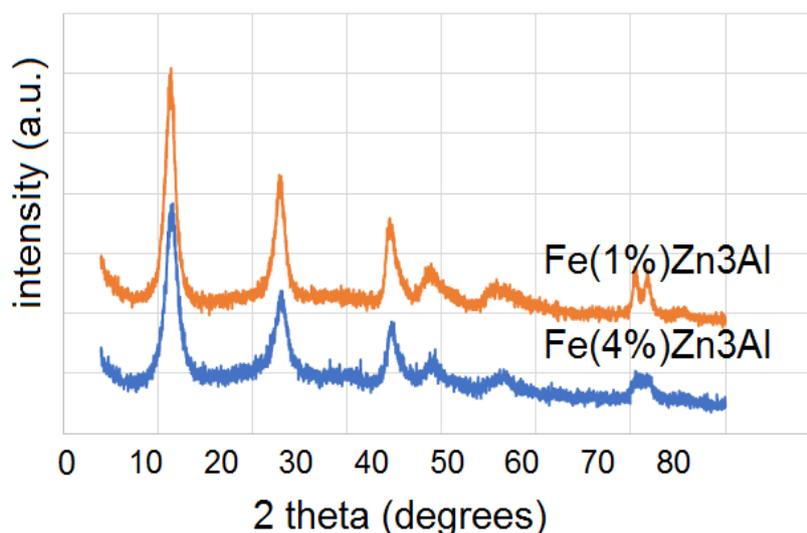


Fig. 1 – The XRD patterns of the reconstructed LDHs.

The powder X - ray diffraction patterns of the as - synthesized and reconstructed clays are depicted in Fig. 1. A single crystalline phase is observed for all the samples. The diffraction peaks in the 2θ range of $4 - 70^\circ$ correspond to the characteristic reflections of hydrotaalcite - like clay with a series of $(00l)$ peaks appearing as symmetric sharp lines at low angles (arising from the basal reflections of $(00l, l = 3, 6)$ planes) and broader and less intense reflections for the nonbasal $(01l, l = 2, 5, 8)$ planes.

The FT-IR characterization of the parent clay Zn_3Al is represented in Fig. 2. The spectrum of LDH precursors shows a broad band around 3450 cm^{-1} , corresponding to the stretching vibrations of OH groups in the brucite-like layers and the interlamellar water molecules. The broadening of the band is due to hydrogen-bond formation (Parida *et al.*, 2010). The band at 1435 cm^{-1} and 1384 cm^{-1} is assigned to the ν_3 stretching vibration of the CO_3^{2-} anion in the LDH interlayer region.

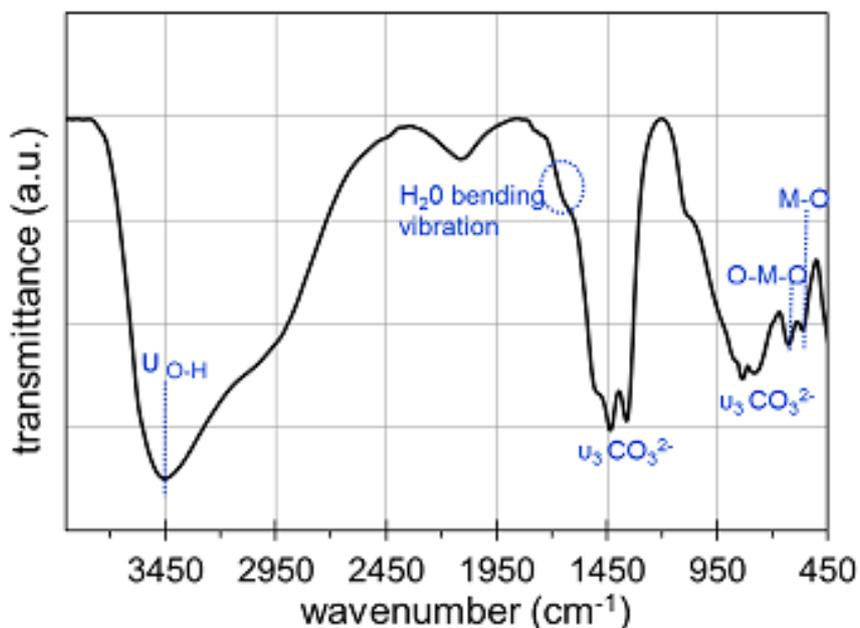


Fig. 2 – FT-IR spectrum of the Zn₃Al clay.

The 840–820 cm⁻¹ bands are also assigned to the stretching vibrations of the CO₃²⁻ groups. The bands in the low wavenumber region, at approximately 640 cm⁻¹ and 550 cm⁻¹ arise from the M-O-M and M-O vibrations in the brucite-like layers. The FT-IR analysis confirms the general structure of the layered double hydroxides for the Zn₃Al clay with carbonate anion (CO₃²⁻) located in the gallery region (Mendoza-Damian *et al.*, 2015; Arizaga *et al.*, 2009).

The optical properties of the catalysts were investigated by UV-Vis spectroscopy. Results in Fig. 3 show that Zn₃Al is almost optically transparent in the UV region (Zhou *et al.*, 2015), while in the visible region very little absorption it can be seen. After the calcination of the clays and their structural reconstruction in FeSO₄ aqueous solutions at two different molar ratios, wider absorption bands and higher intensities in the UV-Vis are observed. Both reconstructed clays have an absorption peak centered at 350 nm and a shoulder at 450 – 500 nm. It can also be observed that for the sample with a higher iron concentration, the absorption is more shifted toward the visible range in comparison with the iron based nanocomposite in a smaller concentration, although the intensity is lower.

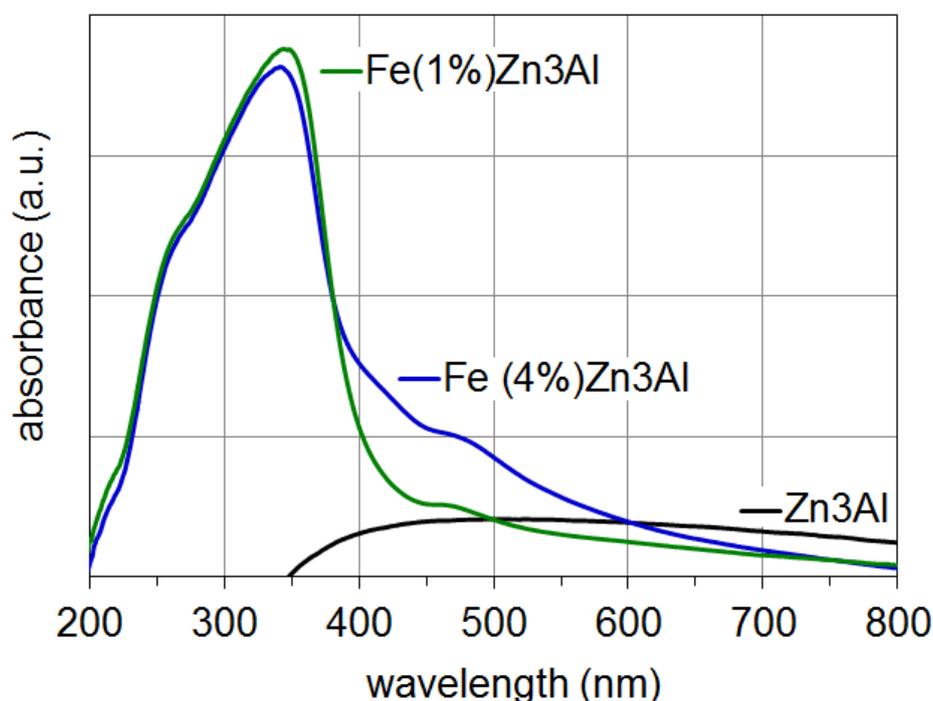


Fig. 3 – Solid-phase UV-Vis absorption profiles of the catalysts.

3.2. Photocatalytic Activity of the Nanocomposites

The photocatalytic activity of the samples was tested in the degradation of 1 g/L aqueous solution of ibuprofen with 1 g/L catalyst dose through photocatalysis and photo-Fenton catalysis processes, using simulated solar light as a source of irradiation.

Fig. 4 presents the UV-Vis evolution spectra for Ibuprofen degradation under visible light irradiation in presence and absence of photo-Fenton reagent. Results point out that after the adsorption equilibrium between the catalyst and pollutant is established, the degradation of ibuprofen molecule begins once the irradiation is started. Ibuprofen shows three peaks: the first two peaks located at 195 nm and 219 nm undergo a linear decrease during light excitation, while the third peak located at 263 nm has an increase, probably as a consequence of by-product formation that cannot be degraded by this photocatalytic system. An enhancement in ibuprofen degradation can be observed after H_2O_2 is added (Fig. 4 b).

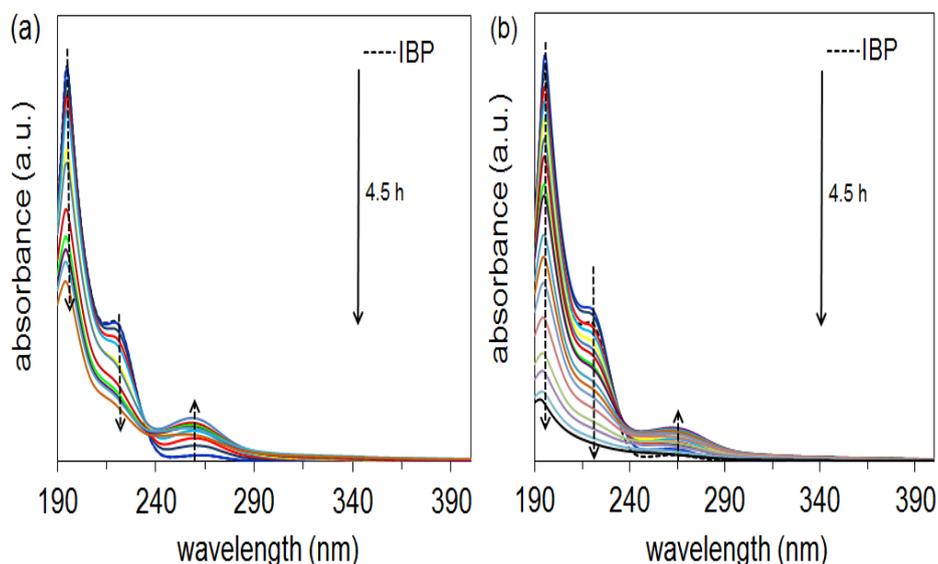


Fig. 4 – Uv-Vis spectra evolution during ibuprofen degradation by Fe(4%)Zn3Al: (a) photocatalysis; (b) photo-Fenton.

Fig. 5 describes the parallel evolution of normalized absorbance of ibuprofen degradation. In the absence of H_2O_2 , results show no major difference between the two samples in the photocatalytic removal of ibuprofen, which means that the increase of iron concentration in the nanocomposite has no significant influence on pollutant removal.

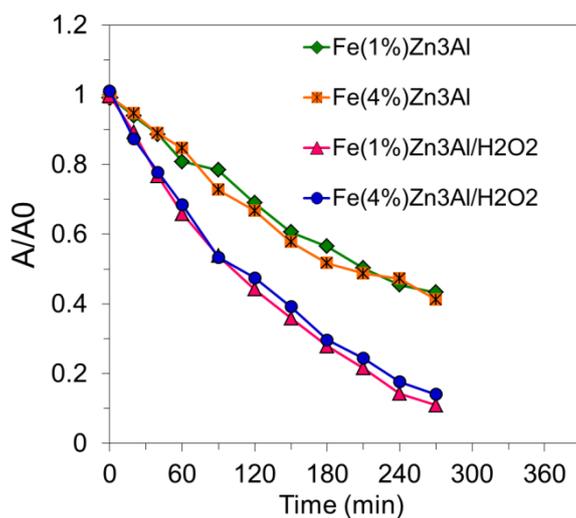


Fig. 5 – Ibuprofen degradation by photocatalysis and photo-Fenton process.

On the other hand, after H_2O_2 is added in the system, a significant pollutant removal can be observed for both samples. This is due to the iron reaction with H_2O_2 and also to the photolysis of H_2O_2 under light irradiation to generate an increased amount of $\cdot OH$ radicals, leading further to higher and faster degradation rates of the pollutant.

An overview of the photocatalytic performance in ibuprofen removal is presented in Fig. 6. After 4.5 h of irradiation, in the absence of the H_2O_2 , both samples have approximate removal efficiency, with a slightly increase of 2% for Fe(4%)Zn3Al. The small increase can be explained by the extended absorption of Fe(4%)Zn3Al sample toward visible region, as seen in Fig. 3.

After the addition of H_2O_2 , the fastest degradation was obtained in case of Fe(1%)Zn3Al nanocomposite, with 89% removal efficiency. It can be seen that a greater amount of iron in the nanocomposite doesn't necessarily leads to a greater amount of hydroxyl radicals as would be expected. On the contrary, the catalytic performance is slightly lower for the iron based nanocomposite with a higher content.

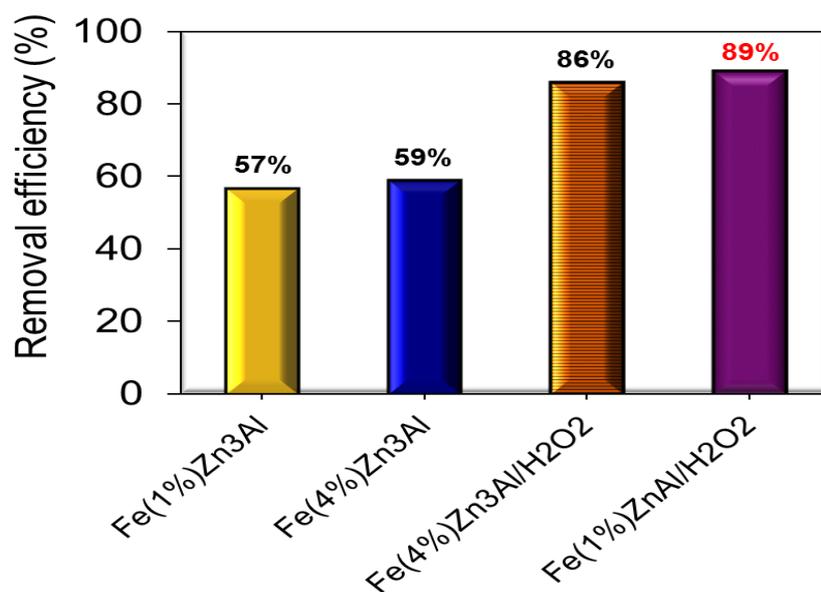


Fig. 6 – Removal efficiency of Ibuprofen after 4.5 h of irradiation.

These results are in good agreement with our expectation of the synergistically effect of combining light irradiation, photo-Fenton reagent and iron based LDH nanocatalysts.

4. Conclusions

In this study, Fe/LDH-based nanocomposites at two different values of iron weight concentration were tested in the degradation of ibuprofen pharmaceutical agent by photocatalysis and photo-Fenton catalysis, using simulated solar light and H₂O₂ as a Fenton reagent. Zn₃Al clay precursor at a molar ratio of Zn²⁺/Al³⁺ = 3 was obtained by co-precipitation method. Based on the structural “memory effect” of anionic clays, by calcination of Zn₃Al at 500°C and immersion in aqueous solution of FeSO₄·7H₂O at two different concentrations, two types of iron based nanocomposites were obtained and denoted as: Fe(1%)Zn₃Al and Fe(4%)Zn₃Al. Uv-Vis, FT-IR and XRD characterization techniques confirmed the general layerd structure and their optical properties. The photocatalytic results showed that different concentration of iron in the nanocomposites has an insignificant impact on photocatalytic activity of the samples. A remarkable enhancement of ibuprofen removal takes place when H₂O₂ is added. After 4.5 h of irradiation, the higher degradation of Ibuprofen was observed in case of Fe(1%)Zn₃Al nanocomposites.

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DEGRADAREA FOTOCATALITICĂ ȘI FOTO-FENTON A IBUPROFENULUI PRIN IRADIERE CU LUMINĂ SOLARĂ

(Rezumat)

În prezenta lucrare, s-a studiat degradarea compusului farmaceutic ibuprofen prin procese de fotocataliză și foto-Fenton, utilizând ca sursă de radiație lumina solară artificială și H₂O₂ ca agent Fenton. În acest context, s-a urmărit sinteza a două nanocompozite semiconductoare de tipul Fe/ZnAILEDH, utilizând două concentrații diferite de fier. Mai întâi a fost preparată argila precursoră cu cationi divalenți de Zn²⁺

și, respectiv, cationi trivalenți de Al^{3+} în straturile LDH (raport molar $Zn^{2+}/Al^{3+} = 3/1$). Proba a fost notată Zn3Al. Utilizând efectul de memorie structurală a argilelor anionice, prin calcinarea probei Zn3AlLDH și imersarea într-o soluție apoasă de $FeSO_4 \cdot 7H_2O$, în două concentrații diferite, s-au obținut nanocompozitele de tipul Fe/LDH, notate Fe(1%)Zn3Al, respectiv Fe(4%)Zn3Al. Proprietățile structurale și optice ale probelor au fost studiate utilizând ca tehnici de caracterizare: XRD, FT-IR și UV-Vis. Testele fotocatalitice au fost realizate utilizând ca sursă de iradiere o lampă solară. Rezultatele fotocatalitice au arătat că materialele sintetizate sunt fotocatalizatori eficienți în degradarea ibuprofenului. Cea mai mare performanță fotocatalitică s-a obținut prin intermediul proceselor foto-Fenton, pentru nanocompozitul Fe(1%)Zn3Al, cu un randament de degradare de 89%. Rezultatele au arătat că introducerea fierului în concentrații diferite în argila precursoră nu a avut un efect semnificativ asupra performanței fotocatalitice a probele în degradarea ibuprofenului.