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EFFICIENT FENTON-LIKE CATALYSIS FOR IBUPROFEN DEGRADATION UNDER SOLAR LIGHT USING IRON AND MANGANESE SUPPORTED ON ZnAl/LAYERED DOUBLE HYDROXIDES

BY

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Abstract. Herein we report the fabrication of efficient photocatalysts for degrading ibuprofen from aqueous solutions by solar light by photocatalysis and photo-Fenton catalysis processes. Heterostructures composites of iron or iron-manganese (Fe = 10 wt%; Mn = 4 wt%) self-supported on the surface of zinc-based layered double hydroxides (LDHs) were synthesized by exploiting the manifestation of the LDHs “structural memory” effect in aqueous solutions of iron and manganese salts and further tested as catalysts. ZnAl anionic clay (as Zn^{2+}/Al^{3+} molar ratio = 3) was obtained by coprecipitation method. The characteristics of Fe-Mn/ZnAl and Fe/ZnAl heterostructures were described by X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) and solid-phase UV-Vis spectrophotometric analyses. Photocatalytic and photo-Fenton studies were performed in batch mode using appropriate amounts of catalysts and H_2O_2 as Fenton reagent. The UNNASOL (US800, 250 W) solar simulator was used as an irradiation source and an UV-Vis spectrophotometer to monitor the ibuprofen concentration. The present study indicate that ibuprofen degradation for photo-Fenton process reached a high efficiency in the presence of Fe-Mn/ZnAl and Fe/ZnAl photocatalysts.

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Keywords: nanocomposite; ibuprofen; Fenton; solar light; photodegradation.

1. Introduction

The contamination of water around the globe is a constant concern nowadays. The pharmaceutical industry is a worldwide pollution source for the environment with a negative impact especially for the aquatic system (Yuan *et al.*, 2009). The most common used and frequently detected drugs in the wastewaters belong to the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) class (Calza *et al.*, 2006; Keen *et al.*, 2013; Zhang *et al.*, 2011). Ibuprofen represents one of the most consumed NSAIDs. The global consumption of NSAIDs is estimated to create wastewaters with ibuprofen concentration between 10 ngL^{-1} and 169 μgL^{-1}. Although is a biodegradable compound, the main issue remains the possible toxic effects upon aquatic fauna caused by the ibuprofen biological oxidation by-products (hydroxyl-IBP and carboxy-IBP) (Méndez-Arriaga *et al.*, 2010).

In recent years, many methods have been investigated in order to remove pharmaceutical pollutants from the environment. Advanced oxidation processes (AOPs) such as heterogeneous photocatalysis, photolysis, ozonation, photo-Fenton catalysis, homogeneous Fenton etc. are efficient methods to decompose and remove such compounds (Epold *et al.*, 2012; Secula *et al.*, 2008). Among these methods, photocatalysis and photo-Fenton processes represent promising alternatives with great potential for the environment protection. Photocatalysis is a process that involves the presence of a semiconductor material and a source of light. Semiconductors are a type of solids with an electronic structure characterized by a valence band (VB) and conduction band (CB) separated by a band gap (Eg) with specific energy for each semiconductor. When irradiated with light energy higher than their band gap energy, these materials generate charge carriers of electron-hole pairs (e^-/h^+) able to migrate to the surface of the solid and to react with water and the adsorbed molecular oxygen to form hydroxyl radicals (·OH) and super oxide radicals (O_2*). These strong oxidizing species are capable of degrading organic pollutants adsorbed at the surface of the catalysts from the contaminate waters (Herrmann, 1999; Lacombe and Keller, 2012). Photo-Fenton is also an oxidative process capable to produce ·OH radicals. This process, besides illumination source, requires the presence of Fe and H_2O_2 in order to promote redox reactions and photolysis of H_2O_2 under light irradiation that generates an increased amount of ·OH oxidative species able to decompose organic pollutants from contaminated waters (Secula *et al.*, 2008).

Among the many known semiconductors, Layered double hydroxides (LDHs) represent a class of efficient photocatalysts. LDHs or hydrotalcite-like compounds are anionic clays with a lamellar structure formed by the partial substitution of divalent cations (M^{2+}) with trivalent cations (M^{3+}) along with the intercalation of anions and water molecules (Morimoto *et al.*, 2011). LDHs are biocompatible and environmental friendly materials with a versatile and flexible chemical composition suitable for many applications, such as catalysis, adsorption processes, medicine, removal of organic pollutants from the environment and nanotechnology (Bouariu *et al.*, 2013; Carja *et al.*, 2013).

LDHs are semiconductor materials widely studied for the removal of various organic pollutants from the environment. The structural features and the unique property of “structural memory effect” of LDHs materials allow them to give rise to a wide new range of photresponsive compositions such as NPs/LDHs self-assemblies. The synthesis procedure of NPs/LDHs self-assemblies involves the calcination of the LDHs and the immersion of the resulted mixed metal oxide to an aqueous solution containing anions (Carja *et al.*, 2015; Carja *et al.*, 2008). Based on the property of “structural memory effect”, the layered structure regenerates and the remaining cations in the solution self-organize on their surface giving rise to new nanocomposites with enhanced photocatalytic properties (Seftel *et al.*, 2015).

This work aims to fabricate the self-assemblies of Fe and Mn nanoparticles (NPs) with ZnAl as novel heterostructured photocatalysts and photo-Fenton catalysts. The assemblies of Fe and Mn nanoparticles with ZnAl were obtained by reconstruction method (Bouariu *et al.*, 2013; Carja *et al.*, 2013). The photocatalytic activity was studied for the removal of ibuprofen from aqueous solution for photocatalysis and photo-Fenton processes. The study was conducted using simulated solar light as an irradiation source and H_2O_2 as a typical Fenton reagent.

2. Experimental

2.1. Samples Synthesis

Two NPs/LDHs self-assemblies of FeNPs and Fe-MnNPs supported on the surface of ZnAl layered double hydroxide were prepared via reconstruction method using the structural “memory effect” of LDHs materials (Carja *et al.*, 2009). For this purpose, first ZnAl precursor with a molar ratio of 3 was obtained by coprecipitation method described elsewhere (Carja *et al.*, 2011), at constant pH of 8.5 and vigorous stirring. In this case, the procedure involved the slow addition of a mixed metal solution of $Zn(NO_3)_2 \cdot 6H_2O/Al(NO_3)_3 \cdot 9H_2O$ to a Na_2CO_3/NaOH solution and the aging of the mixture for 24 h. The final precipitate was then filtered under vacuum, washed with deionized water, dried in the oven and labeled as ZnAl. Further, 2.4 g of ZnAl was calcined at 550°C for 12 h and added in two vessel reaction containing 200 mL aqueous solution of $FeSO_4 \cdot 7H_2O$ (Fe wt% = 10). In addition, for the preparation of Fe-Mn/ZnAl, a proper amount of $C_4H_6MnO_4 \cdot 4H_2O$ (Mn wt% = 4) was also added.

Both mixtures were aged for 5 h under vigorous stirring and the final precipitates were separated by centrifugation and dried in the oven. The as-prepared catalysts were denoted as Fe/ZnAl and Fe-Mn/ZnAl.

2.2. Characterizations

The structural and optical properties of the as-obtained catalysts were investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and solid phase UV-Vis spectrophotometry. X-ray diffraction patterns were recorded on a D8 ADVANCE XRD diffractometer at a Bragg angle (θ_B) of $2\theta_B$=3°–60° with a scan step of 0.01° and a scan rate of 5 s/step. The measurements were performed at 40 kV and 40 mA using Cu Kα emission and a nickel filter. The UV-Vis absorption profiles of the solids were measured on a Jasco V-550 Spectrophotometer equipped with an integrating sphere attachment. Measurements were done at room temperature, within the wavelength range of 250–850 nm. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrophotometer, in a KBr phase, in the frequency range of 400 – 4000 cm^{-1}, at a resolution of 4 cm^{-1}.

2.3. Photocatalytic Experiments

The photocatalytic and photo-Fenton tests were done using a UNNASOL (US800, 250 W) solar simulator and H_2O_2 as Fenton reagent for the degradation of ibuprofen from aqueous solution. Both experiments were carried out in batch mode, at room temperature, with 0.02 g of catalyst added to 200 mL solution of 0.1 g/L ibuprofen. Before irradiation, the mixtures were stirred in dark for 30 min in order to establish the adsorption-desorption equilibrium between the pollutant and the catalyst surface. For the photo-Fenton experiments, a proper amount of 100 mg/L of H_2O_2 solution was added into mixture right before irradiation to provide efficient ·OH radicals formation. When light irradiation was turned, 1 mL of sample was withdrawn at certain time intervals, diluted in 6 mL of distilled water, centrifuged to remove the catalyst and analysed by UV-Vis spectrophotometer following the characteristic absorbance of ibuprofen at 219 nm.

3. Results and Discussions

3.1. Catalysts Characterization

The XRD patterns of the as - synthesized self-assemblies are shown in Fig. 1. Samples present the diffraction lines typical for hydrotalcite-like materials with a single crystalline phase. Results indicate a series of sharp and symmetric planes in the low 2θ region corresponding to the basal reflections of the (00ℓ, ℓ = 3, 6, 9) planes and broad and less intense reflections at higher 2θ angles attributed to the non-basal (01ℓ, ℓ = 2, 5, 8) planes. The two peaks around 2θ = 60° represent the (110) and (113) characteristic LDH reflections (Morimoto *et al.*, 2011).

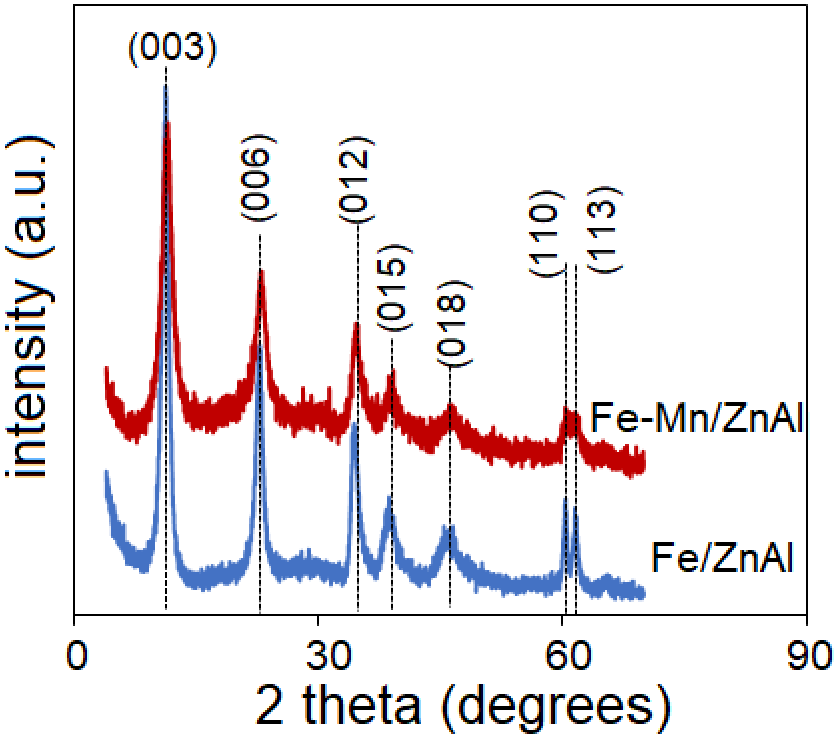

Fig. 1 – XRD patterns of the Fe/ZnAl and Fe-Mn/ZnAl nanocomposites.

Fig. 2 shows the FT-IR spectra of the samples. The broad band around 3450 cm^{-1} is due to the O-H groups stretching vibrations in the brucite-like layers and the interlamellar water molecules. The peak at 1384 cm^{-1} is attributed to the v_3 stretching vibration of the NO_3^- anions present between LDH sheets. The band located around 830 cm^{-1} is assigned to D_{3h} symmetry LDHs with NO_3^- anions intercalated between layers (Arizaga *et al.*, 2009). The band at 630 cm^{-1} arise from the M-O vibration modes in the LDHs layers (Santos *et al.*, 2017). The FT-IR profile of Fe/ZnAl nanocomposite show similar peaks to that of the original LDHs indicating the regeneration of the hydrotalcite lamellar structure after the reconstruction process of ZnAl precursor in $FeSO_4$ aqueous solution. In addition, a new band around 1100 cm^{-1} occurs. This band is associated with υ_3 stretching vibration of SO_4^{2-} ions (Mahjoubi *et al.*, 2017). In conclusion, FT-IR analysis confirms the general structure of the layered double hydroxides for both samples, with (NO_3^-) species located in LDH gallery and additional SO_4^{2-} ions for the nanocomposites after the structural reconstruction in $FeSO_4$ solution.

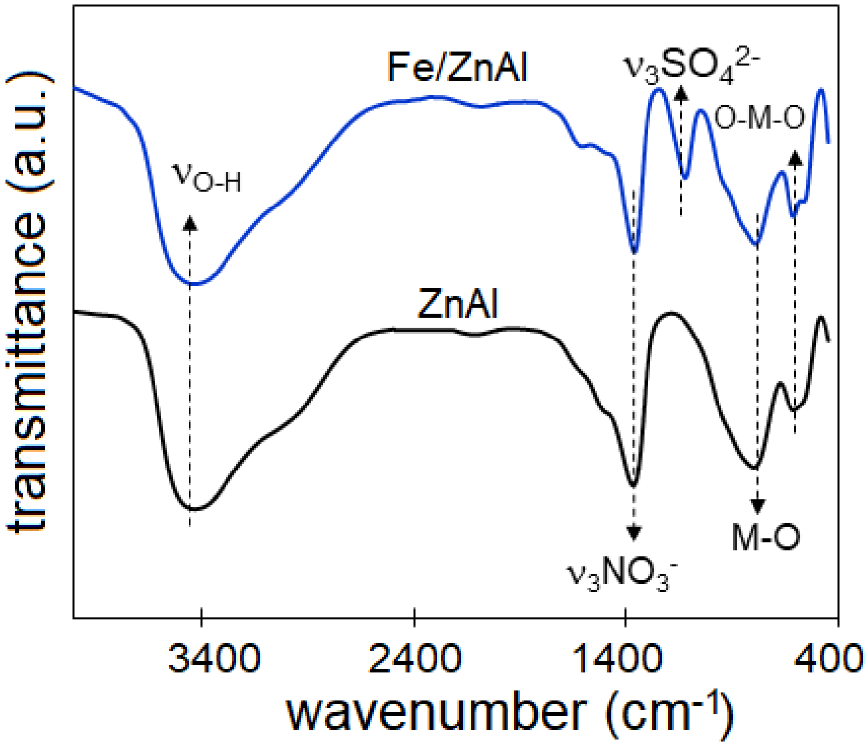

Fig. 2 – The FT-IR spectra of the samples.

UV-Vis spectroscopy technique was used in order to investigate the optical properties of the as-obtained catalysts. Fig. 3 shows the UV-Vis spectra of the samples. At it can be seen, simple ZnAl clay shows almost no absorption at all within the measured wavelength range. However, after the structural reconstruction of the sample, the absorption spectra became wider and with higher intensities in the UV-Vis region. The absorption band at 270 nm and the shoulder located around 450–500 nm are assigned to Fe^{3+} ions octahedral coordinated in the LDH structure (Heredia *et al.*, 2013). The absorption located at 360 nm is attributed to the ZnO phase, formed during the calcination of the clay (Heredia *et al*., 2011). UV-Vis measurements confirm that the deposition of FeNPs and MnNPs on the ZnAl surface improve the optical properties of the samples which leads to a better absorption of the photons and an enhanced photocatalytic activity.

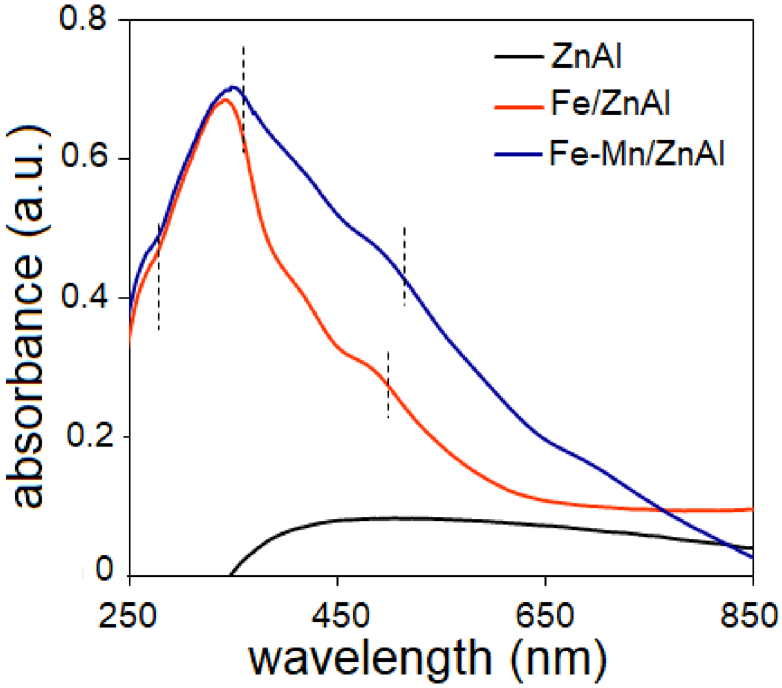

Fig. 3 – The UV-Vis spectra of the catalysts.

3.2. Photocatalytic Activity of the Nanocomposites

The photocatalytic activity of the nanocomposites was studied for the degradation of ibuprofen from aqueous solution, using artificial solar light and H_2O_2 as Fenton reagent. First, the mixture of catalyst and pollutant is stirred in dark to establish the adsorption-desorption equilibrium. Then, the irradiation is turned on and aliquots are taken from time to time, centrifuged and analyzed using a UV-Vis spectrophotometer. For the photo-Fenton tests, a proper amount of H_2O_2 is added into the mixture prior to irradiation. The evolution of photocatalytic process was monitored by following the characteristic absorption maxima of ibuprofen (219 nm) using an UV-Vis spectrophotometer. Results show an enhanced removal efficiency of ibuprofen when H_2O_2 is added into the system.

The UV-Vis absorption profile of the ibuprofen degradation upon solar irradiation in the presence of the Fe/ZnAl and Fe-Mn/ZnAl and H_2O_2 is shown in Fig. 4. It can be observed both catalysts manifest good removal efficiency of ibuprofen by means of photo-Fenton process.

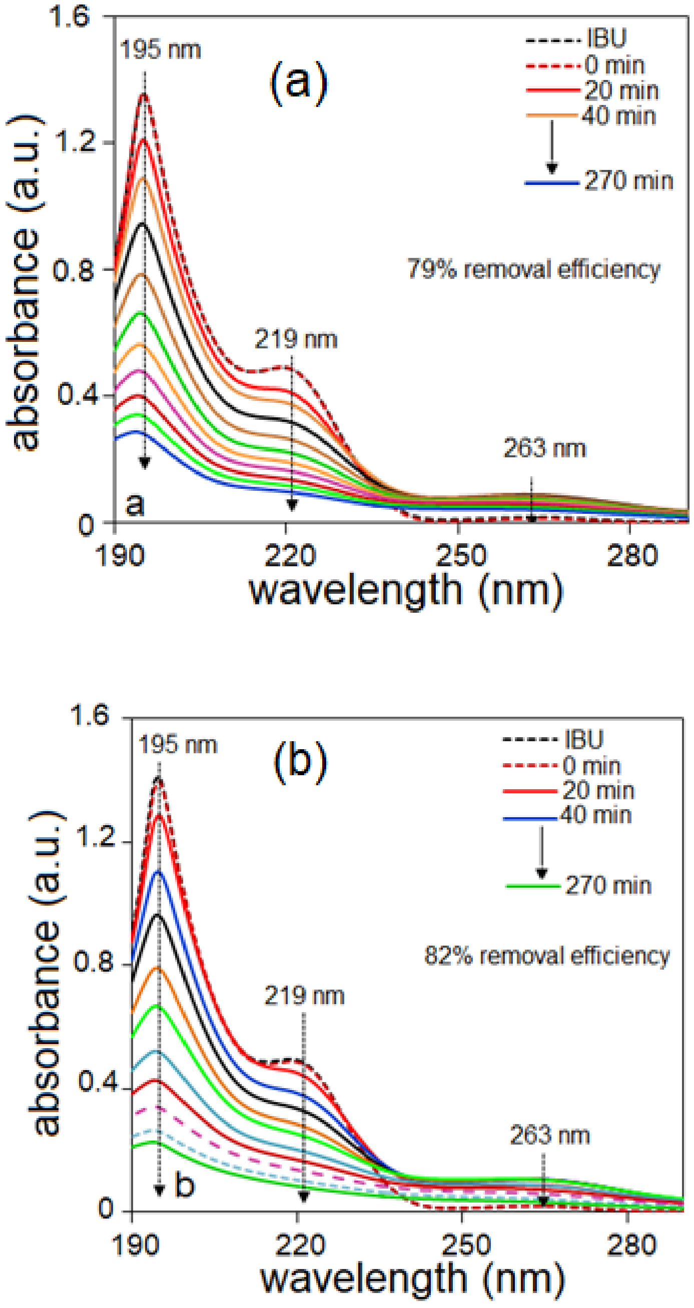

Fig. 4 – UV-Vis spectra of ibuprofen degradation in the presence of: (*a*) Fe/ZnAl/H_2O_2 and (*b*) Fe-Mn/ZnAl/H_2O_2.

In aqueous solution, ibuprofen shows the characteristic peak at 219 nm, along with two additional peaks at 195 nm and 263 nm, respectively. In dark conditions, no electronic modification occurs in the pollutant molecule in the presence of catalyst. Fig. 4*a* and *b* point out that after irradiation is turned on and H_2O_2 is added into the system, the three peaks from 195 nm, 219 nm and 263 nm gradually start to decrease in time. Results show that after 4.5 h of solar irradiation the best catalytic performance is achieved in the case of photo-Fenton system with 82% degradation efficiency for Fe-Mn/ZnAl and 79% degradation efficiency for Fe/ZnAl in the presence of H_2O_2.

4. Conclusions

The present study demonstrates the potential of the nanostructured assemblies of Fe/ZnAl and Fe-Mn/ZnAl as photocatalysts and photo-Fenton catalysts for ibuprofen degradation using simulated solar light. Results showed that the photo-Fenton removal of ibuprofen was higher with almost 20% in comparison with the photocatalytic process. Based on the reaction of Fe and Fe-Mn supported upon ZnAl surface and the H_2O_2 Fenton reagent under solar irradiation, a higher amount of OH· species were formed, hence, the efficiency of ibuprofen degradation from aqueous solution by solar light irradiation increased up to 82%.

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DEGRADAREA SOLARĂ A IBUPROFENULUI PRIN CATALIZA FENTON UTILIZÂND HIDROXIZI DUBLU LAMELARI ZnAl IMPREGNAȚI CU FIER ȘI MANGAN

(Rezumat)

Lucrarea prezintă noi formulări catalitice pentru degradarea ibuprofenului prin procese de fotocataliză și foto-Fenton sub iradiere cu lumină solară artificială. Catalizatorii sunt descriși de auto-ansamble formate din nanoparticule de Fe și Mn (Fe = 10 wt%; Mn = 4 wt%) depuse pe suprafața argilei ZnAl. Argila ZnAl a fost preparată la un raport molar Zn^{2+}/Al^{3+} de 3 utilizând metoda coprecipitării. Matricea precursoare ZnAl a fost calcinată şi apoi utilizată pentru prepararea nanocompozitelor de tip Fe/ZnAl și Fe-Mn/ZnAl prin reconstrucție în soluții apoase de săruri de Fe și Mn. Materialele astfel obținute au fost caracterizate prin tehnici specifice de analiză de XRD, FT-IR și UV-Vis. Testele fotocatalitice și foto-Fenton au fost realizate utilizând lumină solară simulată, obținută la simulatorul solar UNNASOL (US800, 250 W) și cantități optime de catalizator și reactiv Fenton (H_2O_2). Pe parcursul experimentelor, concentrația ibuprofenului din soluție a fost monitorizată cu ajutorul spectrofotometrului UV-Vis. Rezultatele au arătat randamente ridicate de degradare a ibuprofenului, egale cu 82% for Fe-Mn/ZnAl și 79% pentru Fe/ZnAl, în prezența H_2O_2 ca reactiv Fenton.