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Photo-responsive behavior of γ -Fe₂O₃ NPs embedded into ZnAlFe-LDH matrices and their catalytic efficiency in wastewater remediation

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Abstract

We present here a fast, facile and cost-effective route to design efficient semiconductor/LDHs heterojunction photocatalysts based on γ -Fe₂O₃ nanoparticles (NPs)/ZnAlFe-LDHs matrices and their use as novel photocatalytic systems for wastewater remediation. Different compositions of ZnAlFe-LDHs were tailored by controlling the isomorphous substitution of Al³⁺ with Fe³⁺ as well as by the modulation of the Zn²⁺/(Al+Fe)³⁺ cationic ratio within the layers of the hydrotalcite-like matrix. The lowered band gap of the γ -Fe₂O₃NPs/ZnAlFe-LDHs enhanced the electron-hole pair formation under light illumination and increased the photocatalysts performances. The photodegradation studies on aqueous media containing several phenolic compounds (phenol, 4-nitrophenol and 2,4-dinitrophenol) revealed that the γ -Fe₂O₃NPs/LDHs assemblies show high catalytic efficiency producing the

total degradation of the toxic organic compounds in short times. Further, this study provides new insights into the photodegradation mechanism of the phenolic compounds in aqueous media.

Keywords: Fe₂O₃ nanoparticles, Layered Double Hydroxide matrices, heterojunction, photocatalysis

1. Introduction

The family of iron oxides includes a large variety of forms; among these, the semiconductor oxides maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃) are of high importance for industrial applications. These forms of Fe₂O₃ differ in their unit cell coordination, *e. g.* γ -Fe₂O₃ is cubic, with both octahedrally and tetrahedrally coordinated Fe³⁺ sites (defect spinel structure), while α -Fe₂O₃ has a hexagonal unit cell with entirely octahedrally coordinated Fe³⁺ sites (corundum structure) [1, 2].

The electronic structure of Fe₂O₃ offers them strong absorptivity in the UV (ligand-to-metal charge-transfer transitions) and visible range (Fe³⁺ ligand field transitions and excitations involving coupled adjacent Fe³⁺ cations), which together with their low cost, has stimulated a considerable interest for their use in photocatalytic applications [3].

The abundant α -Fe₂O₃ is one of the cheapest semiconductor materials available which manifest strong absorptivity and is a promising candidate for the visible-light photocatalysis [4, 5].

But the highly valuable maghemite γ -Fe₂O₃ itself does not show an excellent photocatalytic activity because of its low charge carrier mobility and/or rapid recombination of the photogenerated charge carriers. An efficient way to overcome these issues is the

manipulation of the photogenerated charge dynamics by the so-called *band-gap engineering*. This involves the formation of heterostructured nanomaterials with adjacent domains where heterojunctions can increase the lifetimes of the photogenerated charge carriers leaving them available for participating in redox reactions with surface adsorbed species [6-8].

A high interest exists in obtaining stable nanoparticles (NPs) of Fe_2O_3 , though the procedures that have been reported so far involve the use of very sophisticated reagents, the presence of organic templates for directing the growth of NPs, multiple and time consuming synthetic steps which usually require special equipment, high temperatures or autogeneous conditions [2, 9-13]. Moreover, the post-synthetic treatments, the removal of the templates and/or the formation of toxic by-products make the overall synthetic process of Fe_2O_3 NPs inefficient and difficult to up-scale to an industrial application. Here we present a fast, facile and cost-effective route to obtain $\gamma\text{-Fe}_2\text{O}_3$ NPs organized on layered double hydroxides (LDHs) hosts. The synthesis procedure is directed at room temperature and doesn't involve the use of any organics products and no post-synthesis treatments.

Layered double hydroxides (LDHs) are a class of naturally occurring anionic clays. Their structure arises from the isomorphous substitution of a divalent cation with a trivalent or tetravalent cation in the brucite mineral ($\text{Mg}(\text{OH})_2$) leading to the formation of positively charged brucite-like sheets held together by the anions located in the interlayer gallery, along with the crystallization of water molecules. They are represented by general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+} \cdot \text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$, where the divalent M^{II} and trivalent M^{III} cations may be Mg^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Al^{3+} , Fe^{3+} , etc, and the A^{n-} can be almost any organic or inorganic anion [14, 15].

These materials may bring several advantages due to the following main aspects, such as (i) the versatility of the brucite-like sheets composition which may allow the insertion of key cations (e.g. Fe^{3+}) within the LDH network and thus might act as charge separation centers, (ii) supply a good metal dispersion within the brucite-type layers, and as a consequence the formation of an intimate contact at atomic level between the generated semiconductor phases, (iii) the layered structures are composed of highly hydroxylated surfaces which may enhance the photocatalytic activity and (iv) interesting textural features, such as micro- and/or mesoporous features, tailored surface area and pore size and shape. These unique features make LDHs interesting candidates in the formation of powerful complex photocatalysts with combined active sites.

The controlled thermal treatment of the LDHs matrices destroys the layered structure with the concomitant formation of a solid solution of mixed oxides. Based on a unique property called structural memory effect, the initial layered structure can be reformed when this solid solution of mixed oxides is placed in the vicinity of aqueous solutions containing anions [16-18]. In the same reconstruction process, the leftover cations in the solution are able to organize in oxide form on the layered sheets, leading thus to new and complex nanoarchitectures [19, 20].

In this work we have studied the formation of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles – ZnAlFe-LDH self-assemblies obtained during the structural reconstruction process of the LDHs by an impregnation induced memory effect procedure. The structural identification, spectral and porosity features of the $\gamma\text{-Fe}_2\text{O}_3$ NPs/LDHs formulations were studied by the combination of XRD, FTIR, UV-vis DR and N_2 sorption techniques, while their photocatalytic performances were investigated for the photodegradation phenol and nitro-phenols from aqueous media.

2. Experimental procedures

2. 1. Synthesis of Fe_2O_3 /LDHs self-assemblies

The ZnAlFe-LDH matrices defined by a cationic ratio $\text{Me}^{2+}/\text{Me}^{3+}$ equal of 3/1 and 2/1, respectively were synthesized using the co-precipitation method at constant pH [14]. This involved the slow addition of a mixed $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (1 M in total) to a $\text{Na}_2\text{CO}_3/\text{NaOH}$ solution under magnetic stirring. During the synthesis the pH value was kept constant at 9 by manipulating the flows of metallic salts and carbonate/hydroxide solutions, respectively. The resulting slurry was aged about 24 h at room temperature, recuperated by filtration, washed several times with distilled water and dried at room temperature overnight. After their calcination at 500°C , the obtained mixed oxides were introduced in a $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution for 1.5 h at room temperature. During this procedure, the reconstruction of the original layered structure, the formation of Fe_2O_3 nanoparticles and their organization on the layered sheets were realized in a single synthetic step. The samples were denoted as $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ ($\text{Zn} : \text{Al} : \text{Fe} = 2 : 0.5 : 0.5$) and $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ ($\text{Zn} : \text{Al} : \text{Fe} = 3 : 0.5 : 0.5$), respectively.

2. 2. Photocatalytic experiments

The photocatalytic activity for all catalysts was evaluated in the photodegradation reaction of phenol, 4-nitrophenol and 2,4-dinitrophenol in aqueous solution under ultraviolet irradiation. In a batch-type reactor, 0.5 g/L catalyst dose was added together with an aqueous solution of pollutant (25 mg/L). The mixture was vigorously stirred in dark for 30 min in order to establish the adsorption – desorption equilibrium between the pollutant and the catalyst surface. Then the reaction mixture (800mL) was stirred under UV light for several hours using a Pen-Ray-Power Supply lamp (UVP Products, TQ 718, 700W) at room

temperature. From time to time, 4 mL of reaction mixture was sampled, separated by centrifugation and the solution was analyzed using a UV-vis spectrophotometer following the absorbance at 270 nm (phenol), at 317 nm (4-nitrophenol) and at 356 nm (2,4-dinitrophenol), respectively. After the analysis, the solution was added back into the photocatalytic reactor to maintain the total volume and solid/liquid ration at a constant value.

2. 3. Characterization techniques

XRD power diffraction patterns were recorded with a PANalytical X'Pert PRO MPD diffractometer with filtered Cu α radiation. Measurements were done in the 2 θ mode using a bracket sample holder with a scanning speed of 0.04/4s in continuous mode. Fourier transform infrared (FT-IR) spectra, in a KBr phase, were recorded on a Perkin Elmer Spectrum 100 spectrophotometer in the frequency range of 400–4000 cm⁻¹, at a resolution of 4 cm⁻¹. UV-vis spectra were obtained at room temperature with a Jasco V-550 Spectrophotometer with integration sphere. Textural properties were determined from the nitrogen adsorption isotherm using a Quantachrome Quadrasorb SI automated gas adsorption system with an AS-6 degasser. Prior to the measurement the materials were outgassed at room temperature for 16 h. Afterwards, N₂-sorption was carried out at –196°C. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. The volume adsorbed at a relative pressure $p/p_0 = 0.97$ was used to determine the total pore volume.

3. Results and Discussions

3. 1. Structural characterization

The XRD patterns recorded for the obtained nanocomposites are presented in Figure 1. The patterns show the characteristic reflections of layered double hydroxides with the basal reflections corresponding to the (003), (006) planes and the non-basal reflections attributed to the (110) and (113) planes [14, 15]. The (003) reflections give information on the interlayer thickness and stacking order, and allow us to calculate the 'c' unit cell parameter. The reflection corresponding to the (110) crystallographic plane provides information on the brucite-like sheets (average metal-metal distance within the sheets) and allows the calculation of the 'a' unit cell parameter value. These results are included in Table 1. It can be observed that the 'a' unit cell parameter increases from 0.308 nm (in the Zn₂AlFe-LDH sample) to 0.310 nm (for the Zn₃AlFe-LDH sample). In the present study, the variation of this parameter is related with the Zn²⁺ cations of which ionic radius is $r_{\text{Zn}^{2+}} = 0.074$ nm. Therefore, the change of the 'a' unit cell size may be correlated with the Zn content in the samples. The 'c' unit cell parameter value increased from 2.3 nm, in the initial material which contains carbonate anions, to 2.7 nm which correspond well with the formation of sulphate containing LDH matrices [21, 22]. On the other hand, the 'a' unit cell parameter value remains constant after the deposition of the γ -Fe₂O₃ NPs showing that the brucite-like sheets preserve their structure, and the cations are not leaching out of the structure during the reconstruction process.

Figure 1.

The XRD patterns also confirm the assembly of LDH and iron oxide nanoparticles towards the formation of well-defined heterostructures as indicated by the presence of reflections attributed to the (220), (311), (400), (422) and (511) planes characteristic of maghemite γ -Fe₂O₃ [2, 23].

Table 1.

Further investigation on the spectroscopic characteristics was obtained using the infrared and UV-vis Diffuse Reflectance Spectroscopy technique. Figure 2 displays the FTIR and UV-vis DR spectra for the studied nanocomposites. The FTIR spectra highlight the presence of both LDH and γ -Fe₂O₃ NPs as also observed from the XRD results. The broad band centered at 3460 cm⁻¹ may be attributed to the stretching vibrations of surface and interlayer water molecules and hydroxyl groups [24, 25]. Also the weaker band at 1647 cm⁻¹ may be attributed to bending mode of the water molecules. The bands centered at 1115 cm⁻¹, 988 cm⁻¹ and 623 cm⁻¹ are attributed to the ν_3 (antisymmetric stretching), ν_1 (symmetric stretching) and ν_4 vibration modes manifested by the sulphate anions in the restricted environment between the brucite-like sheets of the LDH phase lowering its symmetry from T_d to C_{3v} [26-28].

Figure 2.

Two bands at 584 cm⁻¹ and 462 cm⁻¹ are identified in the low frequency region in the IR spectra. These bands may be attributed to the Fe-O stretching and bending vibration modes, respectively of the γ -Fe₂O₃ NPs [2, 9]. The optical properties of the nanocomposite samples in comparison with the initial LDH matrices were evaluated by UV-Vis DR spectroscopy and the results are included in Figure 2B. The Fe³⁺ species in the octahedral environment within the LDH lattice also manifest a strong characteristic absorption profile in the UV-Vis DR spectra [29, 30]. Therefore, the nanocomposites were analyzed with respect to the initial LDH matrices to evaluate the contribution of the Fe₂O₃ NPs on the nanocomposites. The UV-vis DR spectra of the LDH matrices (Figure 2B, a and b) exhibit a main absorption band with a maximum centered at ~280 nm which is typically assigned to the Fe³⁺ species octahedrally

coordinated within the brucite-like sheets of the LDH matrices [31]. The calculated band-gap energies are in the range of 2.4 – 2.5 eV which correspond well with the literature reported values for the ZnFe-LDH materials [29]. After the Fe₂O₃ NPs were loaded on the LDH matrices, the absorption profile becomes broader and shifts towards the visible range. This absorption profile is typical for the γ form of Fe₂O₃ NPs due to the d-d transitions of Fe³⁺ ions between 350 and 550 nm [31, 32]. The calculated band gap energy values are listed in Table 1. The wavelength of the absorption edges were determined by extrapolating the sharply rising and horizontal portions of the UV–vis curves and defining the edges as the wavelengths of the intersection. Such low band gap energies can indicate also a fast recombination rate of the generated charges, but the LDH support contains well-dispersed octahedral coordinated Zn²⁺, Al³⁺ and Fe³⁺ ions. Among these, the Zn²⁺ and Fe³⁺ ions may play an important role in the photocatalytic process. The low band gap energy of γ -Fe₂O₃ NPs can act as a sink for the photogenerated electrons and the holes may be trapped within the LDH structure (schematically illustrated in the inserted picture in Figure 2B). The interface between the LDH and the γ -Fe₂O₃ nanoparticles may facilitate the electron/hole transfer increasing therefore the charge separation efficiency. The results indicate the formation of semiconductor/LDHs heterojunction (straddling gap semiconductors – type I heterojunction) nanocomposites and high photocatalytic activities are expected, respectively.

3. 2. Photocatalytic studies

The photocatalytic features of the obtained nanocomposites were evaluated for the photodegradation of phenol and nitrophenols, e. g. 4-nitrophenol (4-NP) and 2,4-dinitrophenol (DNP) in aqueous solution. Initially, the mixture of catalyst and phenolic solution (25mg/L) is stirred in dark for 30min in order to establish the adsorption-desorption

equilibrium between the pollutant and the catalyst surface. Further, when the UV light is turned on, modifications in the absorption profiles and intensities are observed for all the studied phenolic pollutants indicating the formation of radical intermediary species. Therefore, the UV-Vis absorption spectra were recorded in the 190 – 500 nm region in order to investigate the evolution of the photocatalytic process. The results indicate a fast and complete removal of all the phenolic compounds under the UV illumination.

3. 2. 1. Photocatalytic degradation of phenol (Ph)

The photocatalytic degradation process of phenol in the presence of the parent $\text{Zn}_x\text{FeAl-LDHs}$ and the obtained nanocomposites may be visualized in Figure 3, where the removal efficiency together with the absorption spectra of the phenolic solutions in different times of reactions are presented. No modifications in the phenol absorption profile occur during the first 30 min. of irradiation in dark. Only a slight difference in the phenol absorption onto the catalyst surface is observed and can be attributed to the higher specific surface area measured for the $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ sample (Table 1). After the UV lamp was turned on, the absorption profile broadens with a slight shift from 270 nm to 265 nm. This band together with the one located at 198 nm may be interpreted as the cleavage of the aromatic ring with the concomitant formation of biodegradable aliphatic acids, e. g. muconic acid (MA) and further oxalic and formic acids [20, 33] as schematically represented in Figure 3D. The total efficiency for the photocatalytic phenol removal is 96% within 180min. of irradiation when using the Fe_2O_3 NPs were loaded on the layered matrices, while only ~70% phenol is degraded by the unloaded LDH matrices. It should be noted that the data included in Figure 3A considers the percentage of phenol removed within 180 min. of UV irradiation. The

parent $\text{Zn}_x\text{FeAl-LDHs}$ could also achieve almost total phenol photodegradation when the phenol/catalyst mixtures were exposed for longer UV irradiation times, e. g. 300min.

Figure 3.

3. 2. 2. Photocatalytic degradation of 4-nitrophenol

The photocatalytic degradation results of 4-nitrophenol (4-NP) in the presence of the obtained nanocomposites are shown in Figure 4. Both catalysts manifest a strong photocatalytic effect, being able to totally degrade 4-NP within 130 min. They both reach the same degradation efficiency, but the $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ nanocomposite is able to promote the photocatalytic reaction faster than its homologue $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$. A plausible explanation is the higher specific surface area, as also pointed out for the phenol photodegradation process, which allows a better contact of the 4-NP molecules with the catalyst surface, but most likely the cationic content within the LDH matrices plays the major role in the degradation process.

Figure 4.

This hypothesis may be explained by the closer examination of the UV-vis absorption profiles of the 4-NP solutions at different times of the photodegradation process (Figure 4 B and C). Initially, the 4-NP molecules exhibit an absorption maxima at 317 nm [34]. After the catalyst is added and stirred in dark for 30 min., the band at 317 nm decreases in intensity and another band appears at 404 nm (bathochromic effect). This new band may be assigned to the electronic modifications in the 4-NP molecules and the formation of the 4-nitrophenolate ions which indicate the beginning of the decomposition process [34, 35]. The concentration of these species decreases fast under UV irradiation highlighting the strong

photocatalytic activity of the $\text{Fe}_2\text{O}_3/\text{LDHs}$ assemblies. It can be observed that the percentage of the 4-nitrophenolate ions produced initially by the $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ sample is higher than the one obtained for the $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ which can explain the faster decomposition process observed in the first case. This behavior may be assigned to the different composition of the LDH matrices demonstrating again that the LDH support participates also in the catalytic process like also deduced from the UV-Vis DR results. The total degradation efficiency for the photocatalytic 4-nitrophenol removal is 100% within 130 min. of irradiation when using the Fe_2O_3 NPs were loaded on the layered matrices, while only ~70% 4-nitrophenol is degraded by the unloaded LDH matrices. Like also noted in the case of phenol, the data included in Figure 4A considers the percentage of 4-NP removed within 130 of UV irradiation. The parent $\text{Zn}_x\text{FeAl-LDHs}$ could also achieve almost total 4-NP photodegradation when the 4-NP/catalyst mixtures were exposed for longer UV irradiation times, e. g. 240min.

3. 2. 2. Photocatalytic degradation of 2,4-dinitrophenol

The photocatalytic degradation results and the evolution of the absorption profiles of 2,4-dinitrophenol (DNP) in the presence of the obtained nanocomposites are shown in Figure 5.

It can be observed that both nanocomposites manifest strong oxidation effect under the present experimental conditions.

Figure 5.

In both cases, the reaction starts by the formation of the 2,4-dinitrophenolate ions which may be correlated with the observed hyperchromic effect in the absorption profiles measured during the photocatalytic tests (Figure 5 B and C). The hyperchromic effect

indicates electronic modifications in the DNP molecule which lead to an apparent increase of the concentration but this can be actually correlated with the formation of different chromosphere groups and the formation of intermediary species [36-38]. After this step, the DNP photodegradation reaction occurs very fast, total degradation being achieved within maximum 80min. of irradiation with no major difference between the nanocomposites. The parent Zn_xFeAl -LDHs could also achieve almost total DNP photodegradation when the DNP/catalyst mixtures were exposed for longer UV irradiation times, e. g. 180min.

3. 2. 3. Reusability of the catalysts

In order to verify the reusability of the photocatalysts, the Fe_2O_3/Zn_xAlFe -LDH samples were recuperated after the 1st use, dried in air and subsequently reused with a fresh batch of pollutant, e. g. phenol, 4-nitrophenol and 2,4-dinitrophenol, respectively. It is important to note that small amounts of solid were lost during the separation after the 1st catalytic run, but the ratio of catalyst/pollutant solution was kept the same in the 2nd run as that used in the 1st run. In this way, the reusability of the as-prepared $Fe_2O_3/ZnAlFe$ -LDHs photocatalysts was checked for three cycles. As it can be observed in Figure 6, after three cycles of use, the activity of both Fe_2O_3/Zn_2AlFe -LDH and Fe_2O_3/Zn_3AlFe -LDH photocatalysts decreases with only 4% when tested for the phenol photodegradation. In the case of both 4-NP and DNP, the loss in activity is even less, e. g. 1%. Therefore, we may conclude that the loss of the photocatalytic activity is minimal indicating the possibility of sustainable use of the photocatalysts.

Figure 6.

Conclusions

Self-assemblies of γ -Fe₂O₃ nanoparticles and ZnAlFe-LDHs were synthesized by a simple and cost effective route. This involves an impregnation-induced memory effect procedure in which the calcined layered matrices are reconstructed, by using the LDHs structural “memory” in Fe₂SO₄ aqueous solution at room temperature. The structural and textural features were confirmed by different characterization techniques. Furthermore, the prepared γ -Fe₂O₃/LDH nanocomposites are endowed with powerful catalytic properties being able to completely remove very toxic, persistent and non-biodegradable pollutants like phenol, 4-nitrophenol and 2,4-dinitrophenol. This is attributed to the synergistic effect of the γ -Fe₂O₃ nanoparticles and LDH matrices which are combined in one heterojunction nanocomposite, enabling the electron/hole transfer and consequently an increased charge separation efficiency with high photocatalytic efficiency.

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415 **Table caption**

416 Table 1. Structural and textural characteristics of the Fe₂O₃/LDH nano-assemblies.

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433 Table 1.

Sample	c, nm	a, nm	^a D _{Fe₂O₃} , nm	E _g , eV	S _{BET} , m ² /g	TV _p , cm ³ /g
Zn ₂ AlFe-LDH	2.3	0.308	-	2.5	65	0.18
Zn ₃ AlFe-LDH	2.3	0.310	-	2.4	81	0.33
Fe ₂ O ₃ /Zn ₂ AlFe-LDH	2.7	0.307	4.8	1.95	43	0.15
Fe ₂ O ₃ /Zn ₃ AlFe-LDH	2.7	0.310	6.1	1.88	74	0.22

434 c = 3d₀₀₃, a = 2d₁₁₀, ^a Crystallite sizes (LDH and Fe₂O₃, respectively) calculated using the Scherrer
 435 equation [24], E_g – band gap energy, S_{BET} – specific surface area calculated using the BET method, TV_p
 436 – total pore volume measured at p/p₀ of 0.97.

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Figure caption

Figure 1. The XRD patterns of the (a) $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ and (b) $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ samples.

Figure 2. Spectroscopy profiles of the materials A: FTIR spectra of the (a) $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ and (b) $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ samples; B: UV-Vis DR spectra of the (a) $\text{Zn}_2\text{AlFe-LDH}$, (b) $\text{Zn}_3\text{AlFe-LDH}$, (c) $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ and (d) $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$ samples.

Figure 3. Photocatalytic results for the degradation of phenol: A: photo-bleaching and photo-degradation efficiency of phenol in the presence of $\text{Fe}_2\text{O}_3/\text{Zn}_x\text{AlFe-LDH}$ and compared with the parent $\text{Zn}_x\text{AlFe-LDH}$ samples (phenol: 25mg/L; catalyst dose 0.5g/L; time: 180min); B and C: UV-Vis absorption spectra of the phenol solution during the photocatalytic tests in the presence of $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ and $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$, respectively, and D: schematic representation of the photodegradation pathway.

Figure 4. Photocatalytic results for the degradation of 4-NP: A: photo-bleaching and photo-degradation efficiency of 4-NP in the presence of $\text{Fe}_2\text{O}_3/\text{Zn}_x\text{AlFe-LDH}$ and compared with the parent $\text{Zn}_x\text{AlFe-LDH}$ samples (4-NP: 25mg/L; catalyst dose 0.5g/L; time: 130min); B and C: UV-Vis absorption spectra of the 4-NP solution during the photocatalytic tests in the presence of $\text{Fe}_2\text{O}_3/\text{Zn}_2\text{AlFe-LDH}$ and $\text{Fe}_2\text{O}_3/\text{Zn}_3\text{AlFe-LDH}$, respectively, and D: schematic representation of the photodegradation pathway.

Figure 5. Photocatalytic results for the degradation of DNP: A: photo-bleaching and photo-degradation efficiency of DNP in the presence of $\text{Fe}_2\text{O}_3/\text{Zn}_x\text{AlFe-LDH}$ and compared with the parent $\text{Zn}_x\text{AlFe-LDH}$ samples (DNP: 25mg/L; catalyst dose 0.5g/L; time: 80min); B and C: UV-Vis absorption spectra of the DNP solution during the photocatalytic tests in the presence of

480 Fe₂O₃/Zn₂AlFe-LDH and Fe₂O₃/Zn₃AlFe-LDH, respectively, and D: schematic representation of
481 the photodegradation pathway.

482 Figure 6. Reusability tests realized for the A: Fe₂O₃/Zn₂AlFe-LDH and B: Fe₂O₃/Zn₃AlFe-LDH
483 photocatalysts.

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Supplementary Interactive Plot Data (CSV)

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