

## Article

# Layered Double Hydroxide-Based Composites for Concerted Decontamination of Water

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**Abstract:** A series of composites was prepared starting from five types of LDHs, which were then exchanged with three types of metallo-phthalocyanines, and, in the end, magnetic nanoparticles were attached. In the case of LDHs containing Fe, characterization data showed that there was a partial oxidation from Fe<sup>2+</sup> to Fe<sup>3+</sup>. Samples containing evident LDH structures performed better in general than the ones containing iron oxide mixtures, the composites being more active towards amoxicillin removal compared with ampicillin removal. The nature of the phthalocyanine did not have such a great influence, although some differences in the activity were observed. The removal was a combination between adsorption and photocatalytic degradation. The best composites for this application were those based on Mg<sub>0.325</sub>Fe<sub>0.325</sub>Al<sub>0.25</sub>-LDH prepared by co-precipitation in the presence of NaOH and Na<sub>2</sub>CO<sub>3</sub>. They presented high adsorption capacity in 10 min and, at the same time, high photocatalytic activity for both amoxicillin and ampicillin.

**Keywords:** hydrotalcite; mechanochemical; organic alkali; phthalocyanine; antibiotics; adsorption; photocatalysis



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## 1. Introduction

Active pharmaceutical compounds are important for public health and quality of life. However, like many things, we consume these compounds, but they are not completely absorbed or metabolized in organisms. Moreover, these compounds can reach the environment without modifications or being non-metabolized. Among the pharmaceutical compounds which can cause major damage to the environment, antibiotics have an important contribution due to their high consumption rate in both veterinary and human medicine [1,2]. Antibiotics act as important drugs to inhibit the growth of bacteria and eliminate or kill microbes. As such, antibiotics have been classified upon on their chemical structure, spectrum, mechanism of action, method of administration, and effect. However, classification based on mechanism of action is the most common [3]. These are used in present in large quantities and because of that they have become a focal point in the research regarding the resistance of pathogens to antibiotics and, in recent years, in environmental research [4].

Although they are used as a treatment for many human or animal diseases, antibiotics from the pharmaceutical industry, animals, poultry, households, hospitals, and aquaculture or livestock farms represent a challenge [5]. Hence, efforts towards removing antibiotics from water were made, although several limitations (incomplete removal, lack of sustainability, cost, and production of toxic side products) remain. Compared to the general water treatment techniques, photocatalytic degradation of antibiotics is still an efficient method

used to remove them from water systems [6]. However, the use of “classical” photocatalysts such as  $\text{TiO}_2$  has limitations, mostly due to their large band-gap (3.2 eV), which makes them efficient only under UV irradiation.

The catalytic systems which involve supramolecular chemistry concepts use chromophores as photosensitizers. For example, metallo-phthalocyanines (MPcs) are electron donors that play the role of a substrate that can absorb the radiation in the visible range. Phthalocyanines, with planar structure, can incorporate either two hydrogen atoms to form metal-free phthalocyanine ( $\text{H}_2\text{Pc}$ ) or a transition metal atom in the center of their circular structure to form metal-organic complexes [7]. Complexes or phthalocyanines containing metal cations with complete electron shells or d-orbitals such as  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  [8] present catalytic activity. Layered double hydroxides (LDHs), which belong to the anionic clays [9], can act with good results in the degradation of these drugs, showing the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}\text{A}^{n-}_{x/n}\cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are, respectively, divalent and trivalent metallic cations (e.g.,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ),  $\text{A}^{n-}$  is an anion,  $x$  is the mole ratio (varies between 0.2 and 0.33), and  $m$  is the number of molecules of water of crystallization within the inter lamella. LDHs can be prepared in the laboratory in an easy and timely way [10,11]. Positively charged octahedral sheets are obtained when  $\text{M}^{2+}$  cations from brucite,  $\text{Mg}(\text{OH})_2$ , are replaced by  $\text{M}^{3+}$  cations [12]. Further, charge-compensating anions ( $\text{A}^{n-}$ ) are incorporated into the interlayer in order to maintain charge balance [13]. LDHs can precipitate heavy metal cations in aqueous solutions (acid buffer role) [14] as a result of their alkaline nature. There are several categories of LDH: Mg/Al-LDH, Ca/Al-LDH, Mg/Fe-LDH, or Cu/Al-LDH [15,16]. The representative material of this class of compounds is hydrotalcite, in which  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are present as cations. Traditionally, these materials are obtained with the tandem co-precipitation method and inorganic alkalis [17]. A new approach which is a viable alternative to the traditional one is the use of the mechanochemical synthesis method but also the use of organic alkalis [11,18]. However, using organic alkalis presents several advantages, such as the elimination of the possibility of contamination of the final material with alkaline cations, fewer steps in the synthesis process, the low amount of energy involved and also of water used, etc.

Organic-inorganic hybrid supramolecular systems are developed by encapsulating the metallo-phthalocyanines into a layered double hydroxide (LDH) structure [19,20]. To avoid conventional catalyst-separation methods (filtration, centrifugation), magnetic nanoparticles (MNPs) were considered as alternative catalytic supports [21]. MNPs represent a widely used class of nanoparticles due to their medical and pharmaceutical applications. The main representatives are magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ). They are ferrite colloids that present a spinel crystal structure with oxygen ions forming a close-packed cubic lattice with iron ions located at the interstices [22,23]. The antiferromagnetic coupling (super exchange through oxygens) that takes place between the  $\text{Fe}^{3+}$  ions in the octahedral and tetrahedral interstices leads to the magnetization of  $\text{Fe}_3\text{O}_4$  [22].

This research aimed to synthesize different magnetic-Fe-containing LDH systems incorporating different metallo-phthalocyanines (Pcs) and their application into the removal of  $\beta$ -lactam antibiotics from water through a simple and environmentally friendly method. The preparation method for the LDHs and the nature of the precipitating agent were studied in order to achieve efficient photocatalytic systems and to determine the most efficient method from an environmental point of view.

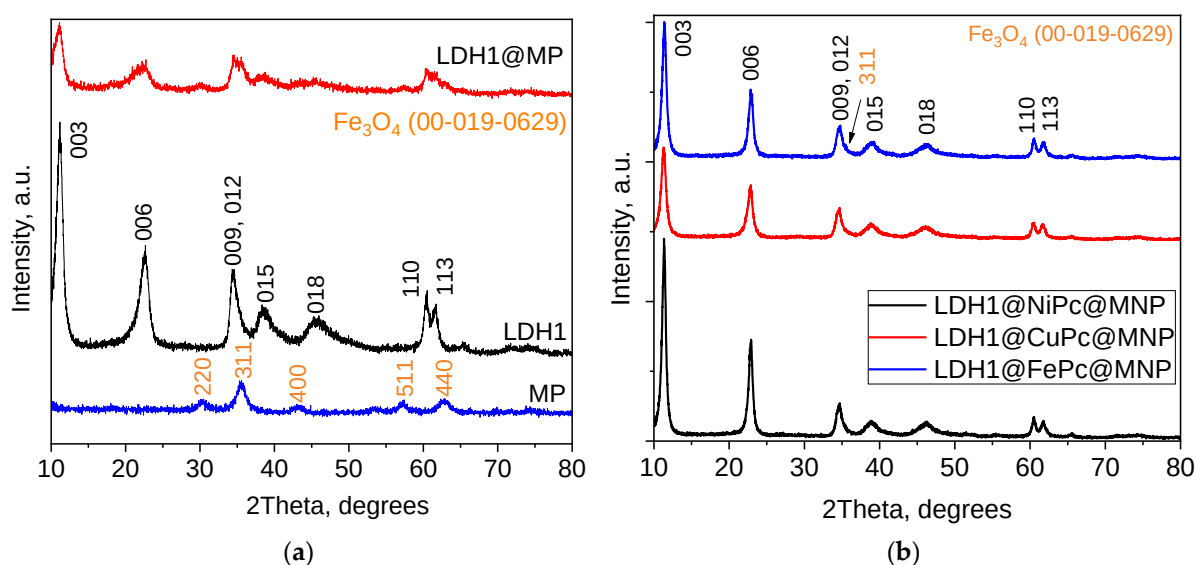
## 2. Results and Discussion

### 2.1. Characterization of the Materials

#### 2.1.1. X-ray Diffraction (XRD)

X-ray patterns obtained for magnetic particles ( $\text{Fe}_3\text{O}_4$ ) and hydrotalcite (Mg, Al) prepared by co-precipitation and hydrotalcite (Mg, Al) deposited on magnetic particles are typical of these materials (Figure 1). The X-ray diffractograms show narrow and intense diffraction lines located at low angles of 2 theta and broad and less intense lines at high diffraction angles, with this behavior corresponding to LDH-type layered mate-

rials [13]. The diffraction lines from approximately  $2\theta(^{\circ})/d(\text{\AA}) = 30/2.91766$ ;  $36/2.52937$ ;  $43/2.10491$ ;  $57/1.60640$ ; and  $63/1.46029$  corresponding to the crystal planes (220), (311), (400), (511), and (440) of  $\text{Fe}_3\text{O}_4$  are clearly observed. The diffractogram of the hydrotalcite deposited on the magnetic particles does not show other phases than those associated with the two components. As presented in the experimental section,  $\text{LDH}_x\text{@MPc@MNP}$  ( $x = 1\text{--}5$ ;  $m = \text{Fe, Cu, Ni}$ ) represents  $\text{Mg}_{0.75}\text{Al}_{0.25}\text{-LDH}$  synthesized by traditional co-precipitation (LDH1),  $\text{Mg}_{0.325}\text{Fe}^{\text{II}}_{0.325}\text{Fe}^{\text{III}}_{0.25}\text{-LDH}$  (LDH2) synthesized by traditional co-precipitation,  $\text{Mg}_{0.325}\text{Fe}^{\text{II}}_{0.325}\text{Fe}^{\text{III}}_{0.25}\text{-LDH}$  synthesized by the mechanochemical method (LDH3),  $\text{Mg}_{0.325}\text{Fe}_{0.325}\text{Al}_{0.25}\text{-LDH}$  synthesized by traditional co-precipitation (LDH4), or  $\text{Mg}_{0.325}\text{Fe}_{0.325}\text{Al}_{0.25}\text{-LDH}$  synthesized by co-precipitation with TMAH (LDH5), on which the metallo-phthalocyanine (MPc) was drafted and attached with magnetic nanoparticles (MNPs).

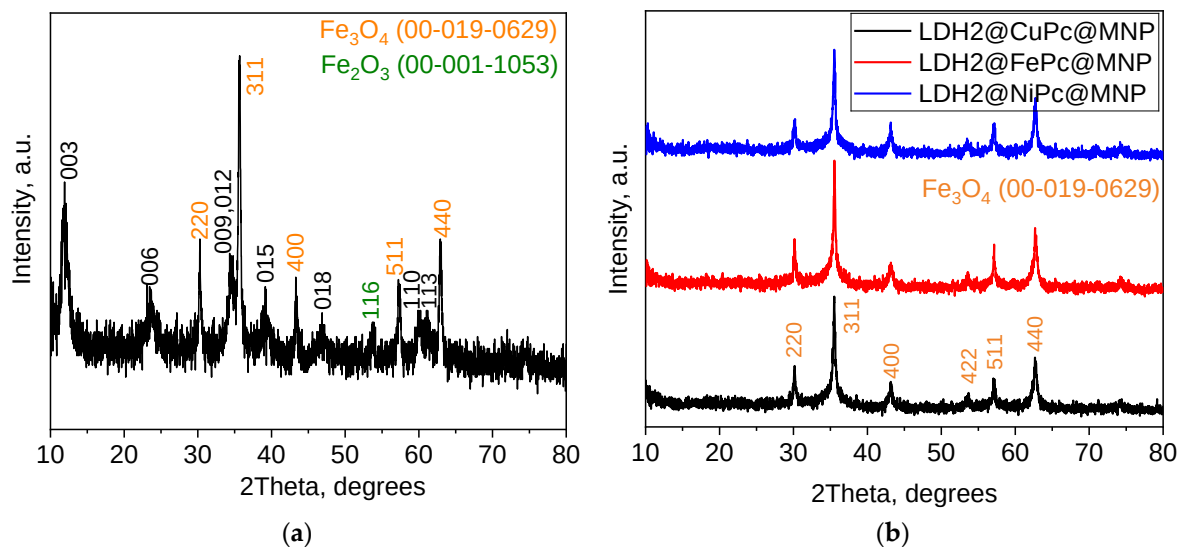


**Figure 1.** X-ray diffractograms of (a) individual magnetic nanoparticles (MNPs), MgAl LDH (LDH1), and MgAl LDH-magnetic nanoparticle composite (LDH1@MP); (b) LDH1 containing Ni, Fe, or Cu phthalocyanine (LDH1-Ni, -Fe, or -Cu) and LDH1 phthalocyanine-magnetic nanoparticle composite (LDH1-Fe-MNPs or Cu-MNPs).

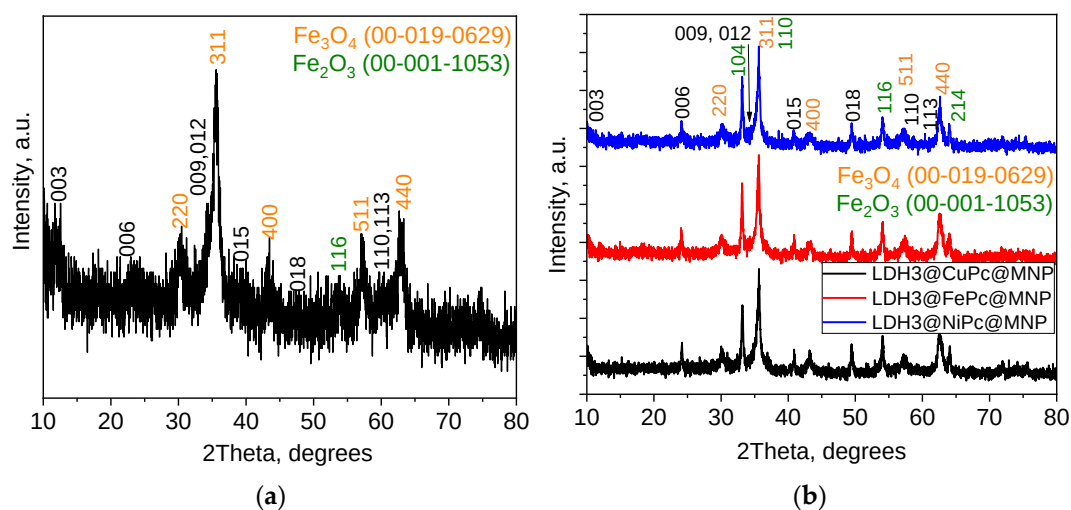
In all Fe-LDH samples (LDH2 and LDH3), shown in Figures 2 and 3, the  $\text{Fe}_3\text{O}_4$  (ICDD 00-019-0629) lines are easily distinguishable (intense line for 311 and weaker ones for 220, 400, 511, 440), together with the characteristic lines of the LDHs, which highlights the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  similar with obtaining stable structures ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ). This synthesising approach does not seem to allow protection against this oxidation, especially considering that all solid syntheses were carried out in an air atmosphere.

In comparison with LDH2, in the case of LDH3 (mechanochemical preparation), after the insertion of phthalocyanines and the deposition of magnetic particles, the LDH structure is visible, along with the lines of iron oxides, as can be seen in Figure 3b, which indicates its reconstruction during the rehydration of the mixed oxides.

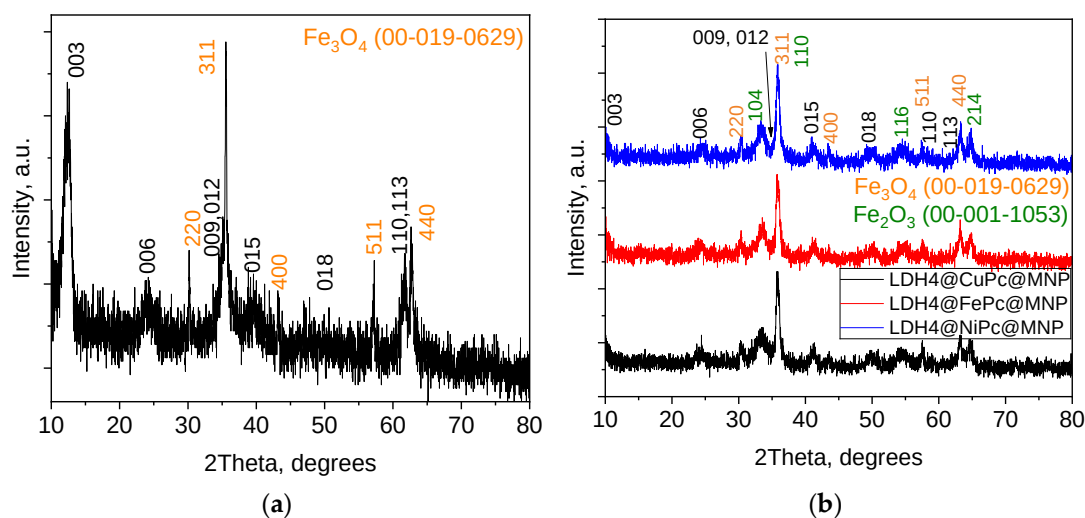
For LDH4 or LDH5 samples, the  $\text{Fe}_3\text{O}_4$  (ICDD 00-019-0629) lines (Figures 4 and 5) are easily distinguishable (the intense line 311, together with weaker ones for 220, 400, 511, 440), which highlights the partial oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , similar to obtaining stable structures ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ). LDH5-based composites present a structure similar to LDH2, which corresponds to a mixture of oxides with less evident LDH arrangements.



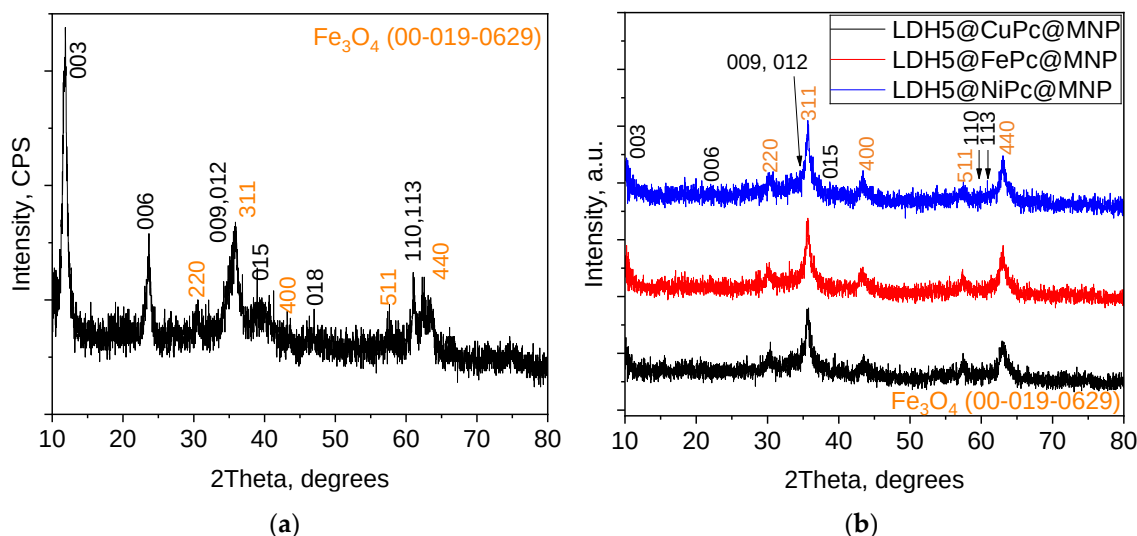
**Figure 2.** X-ray diffractograms of (a) as-prepared LDH2; (b) LDH2@Fe, Cu, or NiPc@MNP.



**Figure 3.** X-ray diffractograms of (a) as-prepared LDH3; (b) LDH3@Fe, Cu, or NiPc@MNP.



**Figure 4.** X-ray diffractograms of (a) as-prepared LDH4; (b) LDH4-Fe, Cu, or Ni-phthalocyanine MNPs.



**Figure 5.** X-ray diffractograms of (a) as-prepared LDH5; (b) LDH5@Fe, Cu, or NiPcMNP.

The network parameter “*a*”, Table 1, indicating the average cation-cation distance in the layered network, is similar for all samples, so no change of the cations in the octahedral positions takes place. Moreover, partial replacement of  $\text{Mg}^{2+}$  from LDH1 with  $\text{Fe}^{2+}$  in LDH4 and LDH5 confirm the oxidation of  $\text{Fe}^{2+}$  at  $\text{Fe}^{3+}$  considering their ionic radius ( $\text{Mg}^{2+} = 0.72 \text{ \AA}$ ;  $\text{Fe}^{2+} = 0.78 \text{ \AA}$ ;  $\text{Fe}^{3+} = 0.64 \text{ \AA}$ ) is presented already in the XRD pattern [24]. The same phenomenon is also observed also for the “*c*” parameter. The ratio between the intensity of the first harmonic and the second,  $I_{003}/I_{006}$ , indicates the non-existence of any other impurity phase inside the LDH lamellar layer. The crystallite size estimated using the Scherrer equation suggested a different crystallinity for the three types of LDHs, with the most crystalline samples being the LDH2. The IFS parameter, which represents the interplanar distance between two consecutive layers, is close in all cases, showing that phthalocyanine prefers a similar intercalation position regardless of the LDHs. Therefore, the phthalocyanine is positioned parallel to the hydrotalcite layers or anchored to its lamellar edges.

**Table 1.** Cell parameters, IFS values, and crystallite size for prepared composites.

| LDH Sample                 | Parameters   |                            | IFS <sup>1</sup> (Å) | $I_{003}/I_{006}$ | $I_{003}/I_{110}$ | FWHM <sub>003</sub> (°) | 2 Theta (°) | D <sup>2</sup> (nm) |
|----------------------------|--------------|----------------------------|----------------------|-------------------|-------------------|-------------------------|-------------|---------------------|
|                            | <i>a</i> (Å) | <i>c</i> (Å)/ <i>d</i> (Å) |                      |                   |                   |                         |             |                     |
| LDH1@CuPc@MNP <sup>1</sup> | 3.059        | 23.249/7.75                | 2.95                 | 2.22              | 6.42              | 0.621                   | 11.40       | 13                  |
| LDH1@FePc@MNP <sup>1</sup> | 3.059        | 23.304/7.77                | 2.97                 | 1.96              | 4.61              | 0.860                   | 11.38       | 9                   |
| LDH1@NiPc@MNP <sup>1</sup> | 3.057        | 23.215/7.73                | 2.94                 | 2.06              | 7.30              | 0.706                   | 11.44       | 11                  |
| LDH2@CuPc@MNP <sup>1</sup> | 3.054        | 23.104/7.70                | 2.90                 | 1.00              | 1.00              | 0.319                   | 35.52       | 26                  |
| LDH2@FePc@MNP <sup>1</sup> | 3.064        | 23.612/7.87                | 3.07                 | 1.17              | 0.70              | 0.287                   | 35.54       | 29                  |
| LDH2@NiPc@MNP <sup>1</sup> | 3.035        | 23.259/7.75                | 2.95                 | 1.20              | 1.00              | 0.365                   | 35.51       | 23                  |
| LDH3@CuPc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.493                   | 35.60       | 17                  |
| LDH3@FePc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.461                   | 35.57       | 18                  |
| LDH3@NiPc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.492                   | 35.58       | 17                  |
| LDH4@CuPc@MNP <sup>1</sup> | 2.94         | 23.561/7.85                | 3.05                 | 0.85              | 0.31              | 0.360                   | 10.48       | 22                  |
| LDH4@FePc@MNP <sup>1</sup> | 2.94         | 22.861/7.62                | 2.82                 | 1.18              | 0.37              | 0.053                   | 11.22       | 26                  |
| LDH4@NiPc@MNP <sup>1</sup> | 2.94         | 23.098/7.70                | 2.90                 | 0.73              | 0.31              | 0.280                   | 10.88       | 28                  |
| LDH5@CuPc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.053                   | 10.11       | 30                  |
| LDH5@FePc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.099                   | 10.21       | 35                  |
| LDH5@NiPc@MNP <sup>2</sup> | -            | -                          | -                    | -                 | -                 | 0.235                   | 10.16       | 33                  |

<sup>1</sup> For LDH; IFS = interlayer free spacing. <sup>2</sup> For iron oxide.

It should be noted that the sample obtained in the presence of TMAH (LDH5) shows the more intense diffraction lines compared with LDH4. The X-ray diffractograms of the LDH4@Cu, Fe, or NiPc@ MNPs and the calculation of the IFS parameter show that the anchoring of phthalocyanines occurs mostly on the edges of the hydroxide lamellae.

### 2.1.2. Diffuse-Reflectance UV-Vis Spectroscopy (DR-UV-Vis)

The DR-UV-Vis spectra of parent LDH1, LDH2, LDH3, LDH4, and LDH5 (Figure S1) prove the simultaneous presence of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species. Due to the presence of  $\text{Fe}^{3+}$  species, all samples exhibited a strong absorption around 500 nm [23], which decreases their band-gaps compared with the LDH without iron, increasing their absorption capabilities in the visible domain. These values are sensibly smaller compared with the ones reported in the literature [25]. However, several specific species can be distinguished, e.g., in the form of isolated  $\text{Fe}^{3+}$  (247–252 nm),  $\text{Fe}_x\text{O}_y$  oligomers (369–389 nm), and  $\text{Fe}_2\text{O}_3$  particles (472–478 nm) [26]. The presence of  $\text{Fe}^{3+}$  in LDH4 and LDH5 was also confirmed by Raman spectroscopy (Figure S2).

The DR-UV-Vis spectra of the final composites (Figure 6) show a part of the strong absorption bands of phthalocyanine in the 350–450 nm region due to their B bands attributed to  $\pi$ – $\pi^*$  transitions in the macrocyclic ring [27], overlapping those of  $\text{Fe}_2\text{O}_3$ , and also in the 500–900 nm region due to their Q bands [28]. The blue color appearing at ligand  $\pi$ – $\pi^*$  transitions is characteristic of both the free and the encapsulated complexes.

The band around 700 nm, a Q band typical of metallo-phthalocyanines, represents the contribution of electron transfer between the orbitals of the aromatic 18-electron  $\pi$  system and the overlapping orbitals of the central metal [29]. Absorption has been confirmed for many phthalocyanine complexes and is related to the formation of singlet excitons [30,31]. The absorption maxima in the range 600–645 nm is characteristic of the presence of high-order aggregated or dimer phthalocyanines [32,33], while the Q band located around the 700 nm region is attributed to the presence of monomeric phthalocyanines. These bands are less evident for the composites based on LDHs containing iron (LDH2-LDH5).

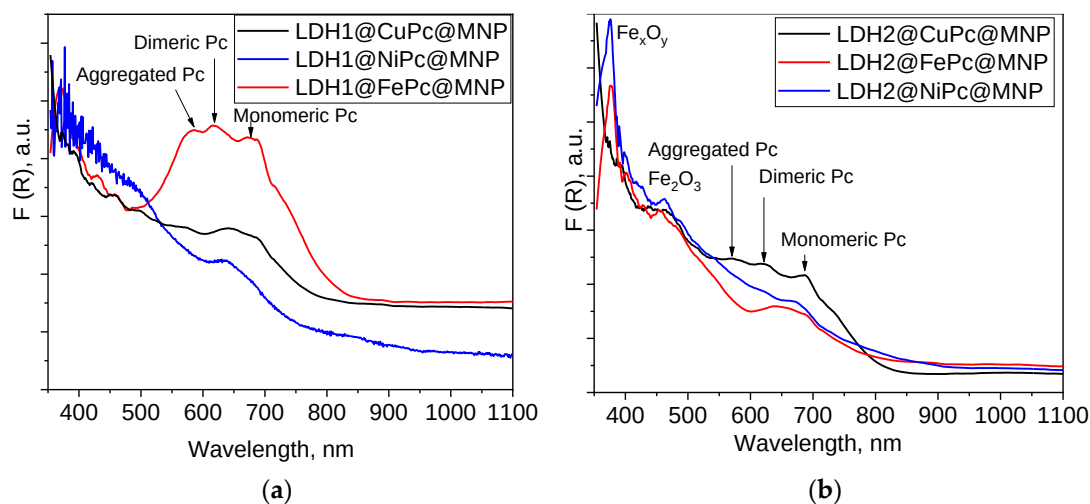
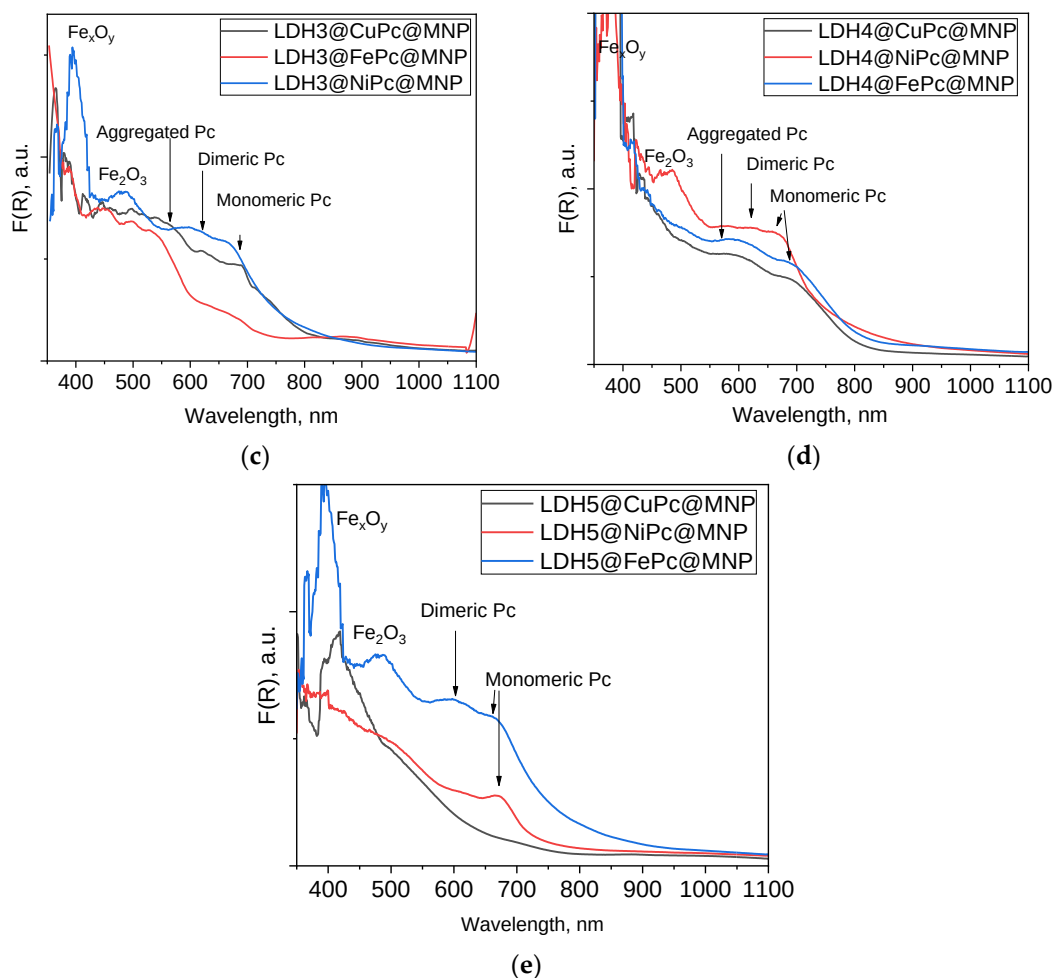


Figure 6. Cont.

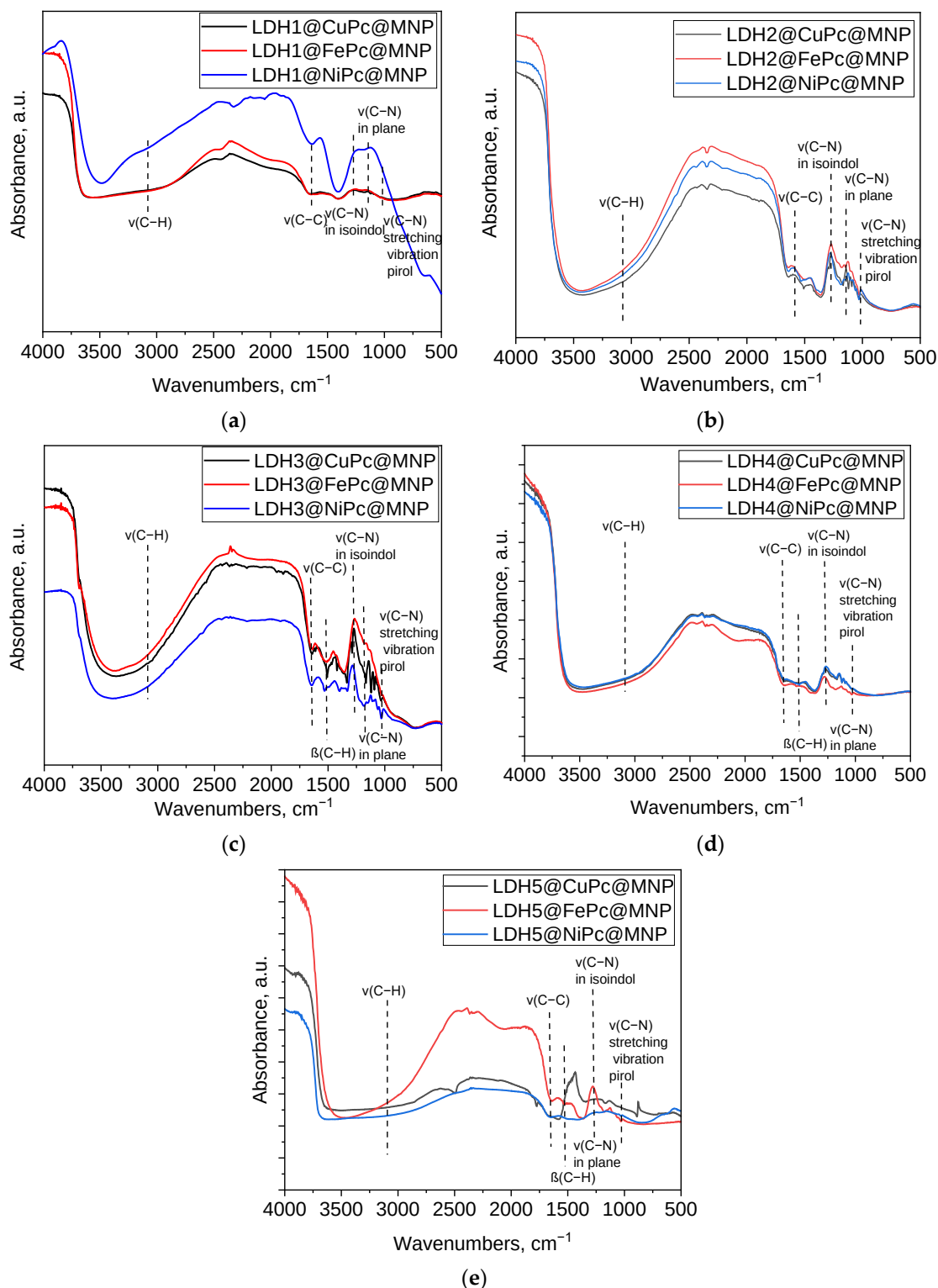


**Figure 6.** DR-UV-Vis spectra of (a) LDH1@MPc@MNP; (b) LDH2@MPc@MNP; (c) LDH3@MPc@MNP; (d) LDH4@MPc@MNP; and (e) LDH5@MPc@MNP.

### 2.1.3. Diffuse-Reflectance Infrared Spectroscopy (DRIFTS)

In Figure 7, a broad absorption band is observed in the  $3700\text{--}3400\text{ cm}^{-1}$  area corresponding to the vibrations of the OH groups,  $\nu(\text{O--H})$ , while the band at  $3000\text{ cm}^{-1}$  is assigned the presence of hydrogen bonds between  $\text{H}_2\text{O}$  groups and the residual carbonate anion from co-precipitation, both located in the interplanar space [28]. The band at  $1638\text{--}1650\text{ cm}^{-1}$  corresponds to the H-O-H bending. The band located between  $1100$  and  $650\text{ cm}^{-1}$  is attributed to the vibrations of the carbonic groups, while the bands below the value of  $600\text{ cm}^{-1}$  correspond to M-O (M = Mg, Fe or Al) bonds.

The success of the preparation of the composites and the presence of phthalocyanine in them was also confirmed by the presence of specific bands in the infrared spectra [30]. The DRIFT spectra of the investigated materials (Figure 7) show the typical bands of the metal complexes, confirming their presence in the supported catalysts:  $1287$ ,  $1333$ ,  $1418$ ,  $1468$ ,  $1495$ , and  $1515\text{ cm}^{-1}$  in the corresponding catalysts. For example, the band at approximately  $1650\text{ cm}^{-1}$  can also be assigned to the C=N bond, the band at  $1120\text{ cm}^{-1}$  can be assigned to the S=O bond, and the bands at  $730$ ,  $1033$ , and  $1090\text{ cm}^{-1}$  can be attributed to the C-H bond. The very low intensity of these bands shows the existence of very small amounts of phthalocyanines in the chosen support.



**Figure 7.** DRIFTS spectra of (a) LDH1@MPc@MNP; (b) LDH2@MPc@MNP; (c) LDH3@MPc@MNP; (d) LDH4@MPc@MNP; and (e) LDH5@MPc@MNP.

#### 2.1.4. Textural Properties

The textural properties of the composites are presented in Table 2. The composites based on LDH2 and LDH3 present the lowest surface areas. This is a consequence of the structure and composition of the parent LDHs, those two having a predominant iron oxide composition with almost no evident LDH layered structure, as seen in XRD. The pore size

is larger than that for the composites based on LDH1, LDH4, and LDH5. However, this can reflect the inter-particle voids.

**Table 2.** Textural characteristics of the final composites.

| Composite     | Surface Area<br>(m <sup>2</sup> g <sup>−1</sup> ) | Pore Volume<br>(cm <sup>3</sup> g <sup>−1</sup> ) | Pore Size<br>(nm) |
|---------------|---------------------------------------------------|---------------------------------------------------|-------------------|
| LDH1_FePc_MNP | 220                                               | 0.50                                              | 35, 54, 124       |
| LDH1_NiPc_MNP | 210                                               | 0.45                                              | 35, 57, 125       |
| LDH1_CuPc_MNP | 236                                               | 0.54                                              | 36, 55, 125       |
| LDH2_FePc_MNP | 91                                                | 0.22                                              | 39, 480           |
| LDH2_NiPc_MNP | 59                                                | 0.17                                              | 36, 504           |
| LDH2_CuPc_MNP | 84                                                | 0.22                                              | 36, 506           |
| LDH3_FePc_MNP | 90                                                | 0.28                                              | 38, 158, 295      |
| LDH3_NiPc_MNP | 73                                                | 0.24                                              | 36, 160, 293      |
| LDH3_CuPc_MNP | 79                                                | 0.26                                              | 36, 155, 300      |
| LDH4_FePc_MNP | 225                                               | 0.51                                              | 33, 93, 177       |
| LDH4_NiPc_MNP | 214                                               | 0.47                                              | 33, 100, 177      |
| LDH4_CuPc_MNP | 231                                               | 0.53                                              | 33, 88, 177       |
| LDH5_FePc_MNP | 133                                               | 0.32                                              | 36, 130           |
| LDH5_NiPc_MNP | 166                                               | 0.36                                              | 40, 155           |
| LDH5_CuPc_MNP | 159                                               | 0.34                                              | 37, 142           |

The composites based on LDH1 and LDH4 present similar surface areas, although the latter present sensibly larger pores. At the same time, although TMAH can also act as a template molecule, besides being a synthesis agent, the surface area of the composites based on LDH5 is smaller to the one of the composites starting from the LDH4, having the same composition but prepared using NaOH as precipitating agent. In all cases, the surface area of the composites increased compared with the rehydrated initial LDHs, while the pore distribution became multimodal. The textural properties of the final composites, which also contain magnetic particles, are not influenced by the crystallite size of the parent LDHs.

#### 2.1.5. Elemental Analysis

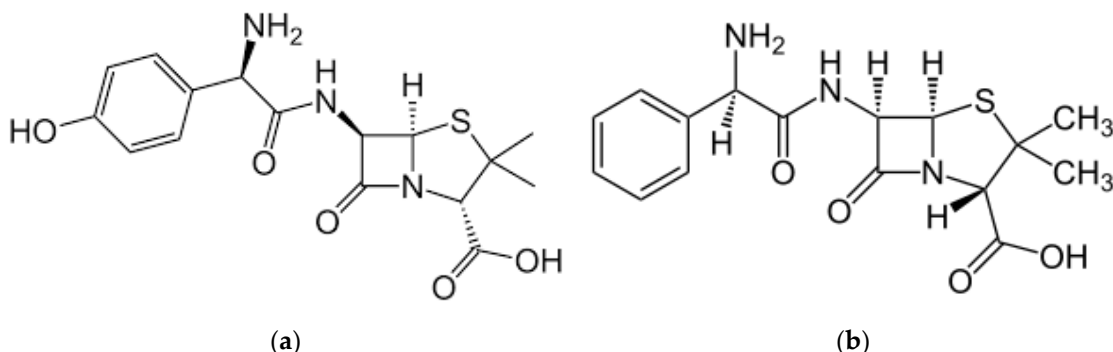
The amount of phthalocyanines calculated from the elemental analysis of selected samples, Table 3, showed no significant differences for LDH1-, LDH4-, and LDH5-based samples, while for the composites derived from LDH2 or LDH3, the amount of photosensitizer was lower.

**Table 3.** Amount of Cu or Ni-phthalocyanine determined in MNP@Cu or NiPc@ LDH4.

| Composite     | Amount Pc (mol/g Composite) |
|---------------|-----------------------------|
| LDH1_FePc_MNP | $6.5 \times 10^{-5}$        |
| LDH1_NiPc_MNP | $6.6 \times 10^{-5}$        |
| LDH1_CuPc_MNP | $6.7 \times 10^{-5}$        |
| LDH2_FePc_MNP | $3.9 \times 10^{-5}$        |
| LDH2_NiPc_MNP | $4.1 \times 10^{-5}$        |
| LDH2_CuPc_MNP | $4.2 \times 10^{-5}$        |
| LDH3_FePc_MNP | $3.8 \times 10^{-5}$        |
| LDH3_NiPc_MNP | $4.1 \times 10^{-5}$        |
| LDH3_CuPc_MNP | $4.3 \times 10^{-5}$        |
| LDH4_FePc_MNP | $5.1 \times 10^{-5}$        |
| LDH4_NiPc_MNP | $5.6 \times 10^{-5}$        |
| LDH4_CuPc_MNP | $6.1 \times 10^{-5}$        |
| LDH5_FePc_MNP | $4.2 \times 10^{-5}$        |
| LDH5_NiPc_MNP | $4.4 \times 10^{-5}$        |
| LDH5_CuPc_MNP | $4.7 \times 10^{-5}$        |

## 2.2. Antibiotic Removal Tests

The prepared samples were tested in the removal of two  $\beta$ -lactam antibiotics from water, namely amoxicillin and ampicillin (Figure 8).



**Figure 8.** Structures of (a) amoxicillin and (b) ampicillin.

Around 50% of the amoxicillin was removed after 10 min of stirring in dark for samples based on/starting from MgAl LDH and prepared by classical co-precipitation using NaOH as precipitating agent (LDH1 and LDH4), highlighting the adsorption ability of these composites (Figure 9). In contrast, LDH5, which was prepared in the presence of TMAH, exhibited a lower adsorption capability, being correlated with its textural properties. The composites containing FePc performed slightly worse than those containing CuPc or NiPc for all three starting LDHs.

All three types of composites presented a lower adsorption capability of ampicillin, which can underline the importance of the antibiotic structure, with even only one hydroxyl group influencing this phenomenon. However, the photocatalytic contribution seems to have a slightly higher magnitude for amoxicillin.

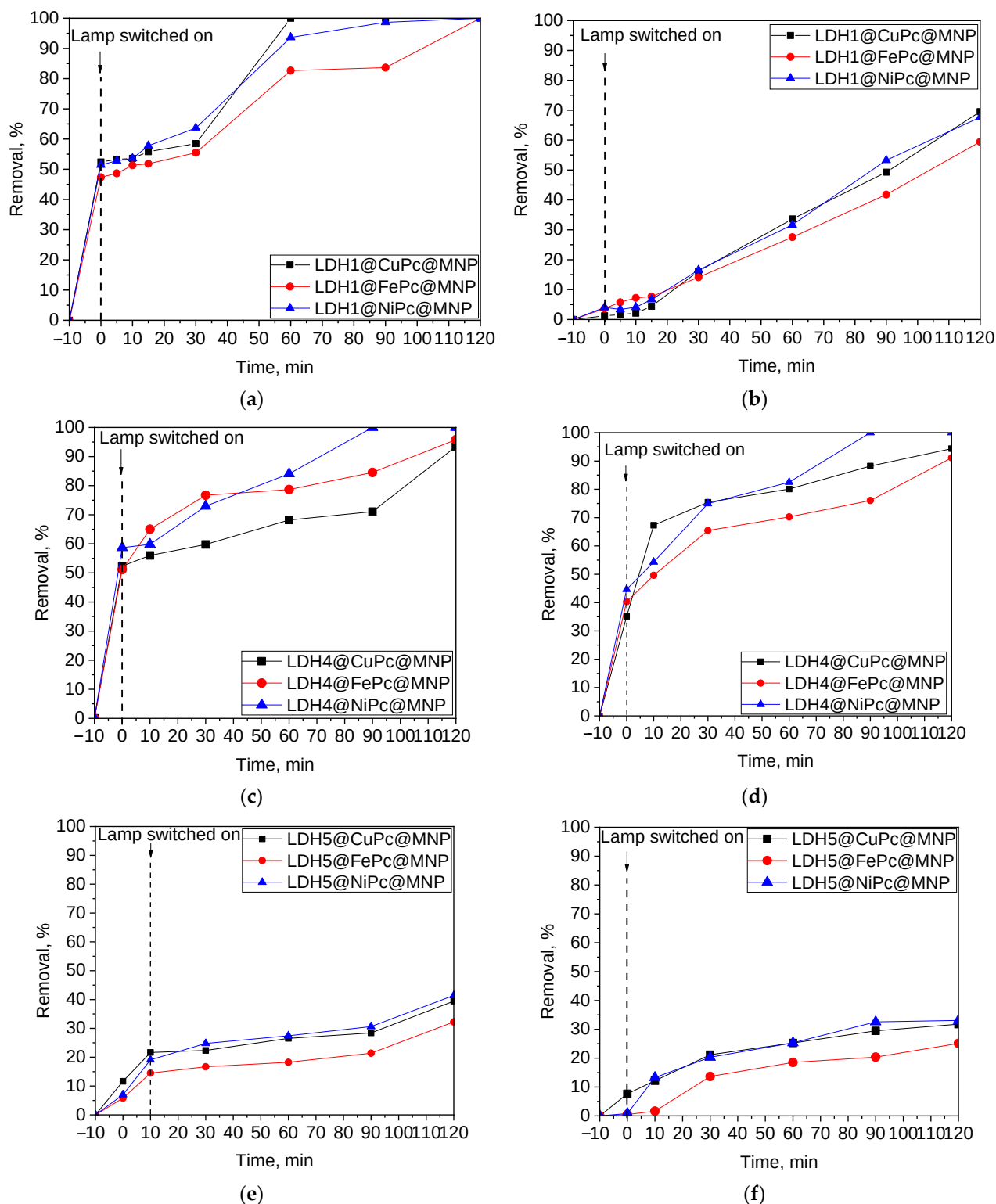
The composites based on LDH2 and LDH3 presented, in general, lower activity than the other composites (Figure 10). The adsorption capability was lower. At the same time, the trend related to the nature of the substrate was preserved, the amoxicillin being removed in a larger amount.

No significant differences were observed between the two sets of composites, although the one prepared by the mechanochemical method exhibited a slightly higher activity.

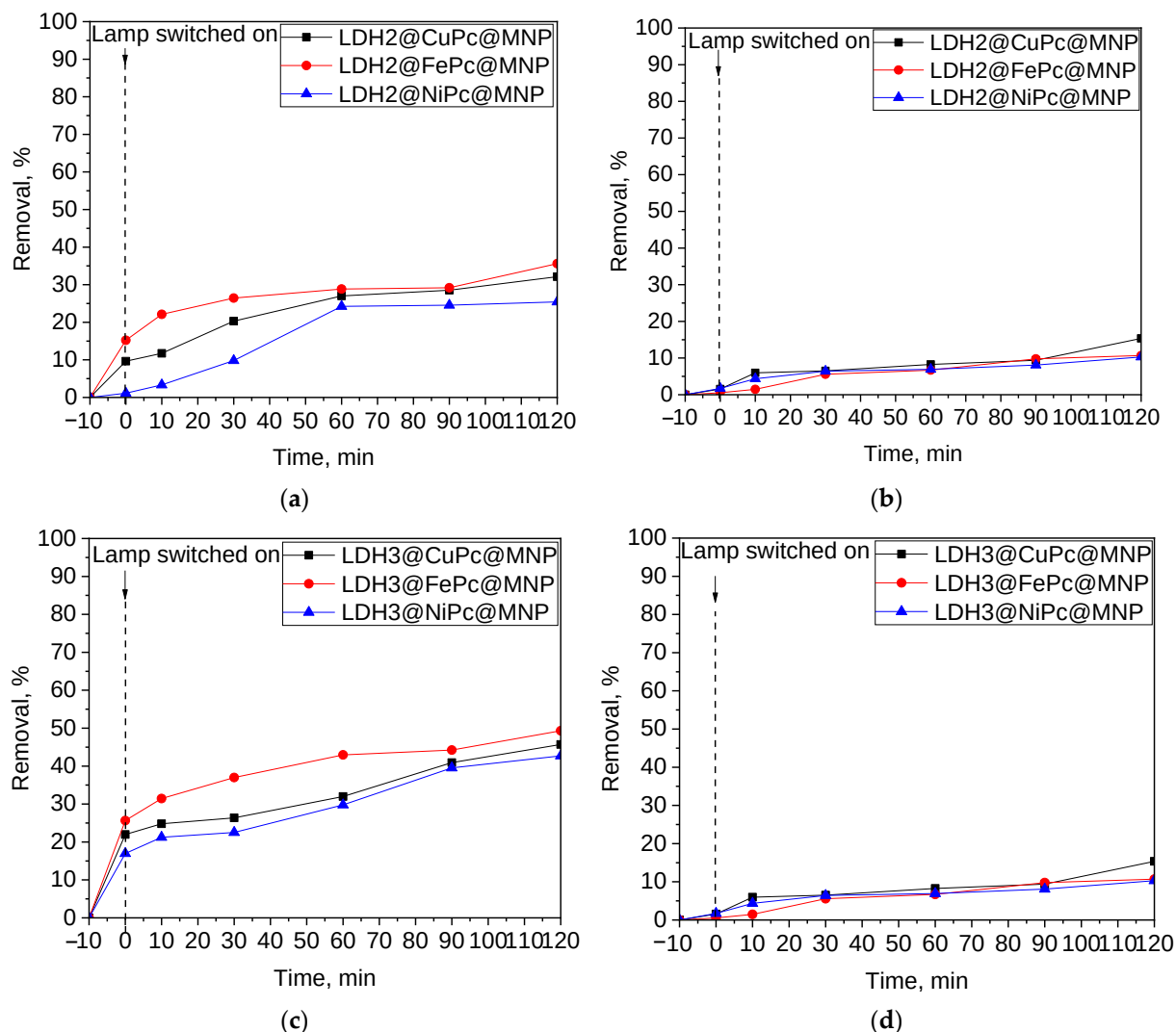
If only the photocatalytic contribution to the removal process is considered (Figure S3), it can be concluded that in this step, phthalocyanine is responsible for the performance of the composites. The degree of removal depends mainly on the amount of MPc and it does not follow the variation in the band-gap of the parent LDHs.

There are two trends which can be observed by summarizing the results. First of all is the dependence of the removal degree on the nature of the composite. This is a consequence of the two phenomena involved: adsorption and the photocatalytic reaction. The different adsorption is mainly a consequence of the textural properties of the composites. At the same time, the literature states that for mesoporous supports with larger pores (above 200 nm), as it is the case for the composites based on LDH1 and LDH4, the amount of ampicillin (and this can be extended also to amoxicillin) adsorbed does not depend on the pore size and is only related to the surface charge density ( $\sigma$ ) of the adsorbent surface [34]. In addition, in the case of LDHs, it was found that the adsorption uses a chemisorption mechanism, following the pseudo-second order [35,36]. However, for all the composites, the adsorption degree of amoxicillin was higher than for ampicillin, and this is the second trend observed. Hydrogen bonds, electrostatic repulsion, electrostatic attraction, competition of excess -OH and weak van der Waals forces are responsible for the adsorption [35,36]. The only difference in the structure of the two antibiotics is the presence of the hydroxyl group attached to the aromatic ring in the case of amoxicillin, which offers a more hydrophilic character to amoxicillin compared to ampicillin. This hydroxyl group offers an additional

bonding capacity for amoxicillin. This hydroxyl group is also responsible for the higher degradation of amoxicillin compared with ampicillin, a trend which is in accordance with the literature [1,37]. In the same time, this hydroxyl group increases the electron density of the aromatic ring through resonance and inductive effects, making it more reactive towards oxidation.



**Figure 9.** Removal % of amoxicillin using (a) LDH1, (c) LDH4, and (e) LDH5 and removal % of ampicillin using (b) LDH1-, (d) LDH4-, and (f) LDH5-based composites.



**Figure 10.** Removal % of amoxicillin using (a) LDH2 and (c) LDH3 and the removal % of ampicillin using (b) LDH2- and (d) LDH3-based composites.

In all the removal tests presented, although in some cases the removal of the antibiotic reached 100%, total decomposition of the antibiotic (mineralization) is not reached. We can assume that a longer irradiation time can achieve total mineralization or at least a higher degree of removal; however, from a practical point of view, this can be unfeasible. The literature presents two pathways of degradation: (i) hydroxylation and (ii) beta-lactam ring opening [38]. The FTIR-ATR spectra of amoxicillin solutions recorded every 30 min showed the continuous increase in the number of functional groups and bonds related to the degradation of the antibiotics (Figure S4). This is proof that the antibiotics are degraded to smaller molecules. However, the fact that the bands associated with these bonds are not decreasing after a certain point is an indication that these molecules are not totally degraded. Some authors concluded that the degradation intermediates still present toxicity due to the carboxyl groups generated during the degradation process [39].

### 3. Materials and Methods

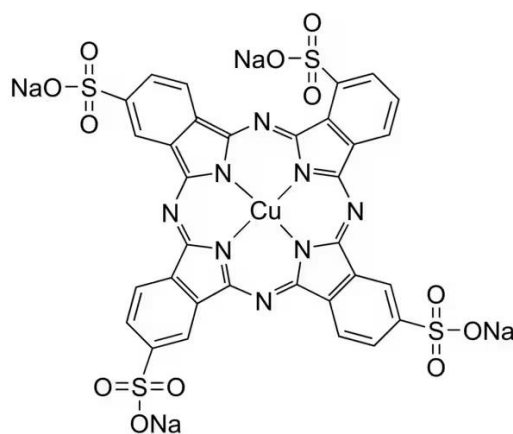
#### 3.1. Preparation of the Composites

$\text{Mg}_{0.75}\text{Al}_{0.25}\text{-LDH}$  (LDH1) and  $\text{Mg}_{0.325}\text{Fe}^{\text{II}}_{0.325}\text{Fe}^{\text{III}}_{0.25}\text{-LDH}$  (LDH2) were synthesized using the traditional co-precipitation method, while  $\text{Mg}_{0.325}\text{Fe}^{\text{II}}_{0.325}\text{Fe}^{\text{III}}_{0.25}\text{-LDH}$  was synthesized using the non-traditional mechanochemical method (LDH3), using inorganic

alkali for pH adjustment. In addition,  $\text{Mg}_{0.325}\text{Fe}_{0.325}\text{Al}_{0.25}$ -LDH was synthesized using co-precipitation by inorganic (LDH4) or organic alkali (LDH5).

The preparation was achieved by mixing two solutions. The first solution consisted of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in a molar ratio of 0.325/0.325/0.25. The second solution contained 0.23 moles NaOH and 0.092 moles  $\text{Na}_2\text{CO}_3$  (1M in  $\text{Na}_2\text{CO}_3$ ) for LDH1, LDH2, and LDH4 or Tetra Methyl Ammonium Hydroxide (TMAH), 25% in water, for LDH5. Both solutions were mixed at 600 rpm and pH 10 at room temperature. The solutions were mixed with a feed rate of  $60 \text{ mL} \cdot \text{h}^{-1}$  each. At the end of the precipitation, the suspension was aged in air for 18 h at  $80^\circ\text{C}$ , then cooled to room temperature and filtered, washed with bi-distilled water until pH 7 and, finally, dried for 24 h in air at  $120^\circ\text{C}$  (LDH1, LDH2, LDH4, LDH5). The synthesis in the presence of TMAH required a significant decrease, of almost 10 times, in the amount of bi-distilled water used for washing compared to the synthesis with inorganic alkali (NaOH). The non-traditional mechanochemical method for obtaining LDH3 was performed by a direct mortaring of the aforementioned precursors for 1 h at a pH of 10, and then the obtained solid was washed and filtered.

For the insertion of phthalocyanine in the LDH structure, the latter's memory effect was exploited. Thus, the hydrotalcites were calcined at  $460^\circ\text{C}$  after which they were cooled in a desiccator. The hydrotalcites were placed directly in a solution of Cu or Ni-phthalocyanine 3,4',4'',4'''-tetrasulfonic acid and left to stir for 12 h. After, the phthalocyanine-containing hydrotalcite was filtered off and dried at  $120^\circ\text{C}$  for 24 h in an air atmosphere (LDH1@Fe, Cu or NiPc, LDH2@Fe, Cu or NiPc, LDH3@Fe, Cu or NiPc, LDH4@Fe, Cu or NiPc, LDH5@Fe, Cu or NiPc). For the synthesis of LDH@Fe, Ni or CuPc@MNP,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  were added to a suspension of Ni or CuPc@LDH (for a mass ratio  $\text{MPC@Fe-LDH}/\text{Fe}_3\text{O}_4 = 3/1$ ). The suspension was heated to  $70^\circ\text{C}$ , after which the iron was precipitated by adding 30 mL of NaOH (0.15M). The obtained material was removed with the help of a magnet, washed with water and dried at  $70^\circ\text{C}$  for 12 h. (LDH1@Fe, Cu or NiPc@MNP, LDH2@Fe, Cu or NiPc@MNP, LDH3@Fe, Cu or NiPc@MNP, LDH4@Fe, Cu or NiPc@MNP, LDH5@Fe, Cu or NiPc@MNP). Figure 11 shows Cu-phthalocyanine 3,4',4'',4'''-tetra sulfonic acid as model for the phthalocyanines used.



**Figure 11.** Cu-phthalocyanine 3,4',4'',4'''-tetrasulfonic acid.

### 3.2. Characterization Techniques

#### 3.2.1. X-ray Diffraction (XRD)

XRD data were collected with the Shimadzu (Kyoto, Japan) XRD-7000 diffractometer, with the monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV, 40 mA) at a scanning rate of  $0.1^\circ/\text{min}$  in the range  $2\theta = 10\text{--}90^\circ$ . The size of the crystallites was estimated using Scherrer's equation.

### 3.2.2. Diffuse-Reflectance UV-Vis Spectroscopy (DR-UV-Vis)

The DR-UV-Vis spectra were collected using a Specord 250 (Analytic Jena, Jena, Germany) spectrometer equipped with an integrating sphere as a measuring device in the reflectance mode. MgO was used as reference material.

### 3.2.3. Diffuse Reflectance Infrared Spectroscopy (DRIFT)

Infrared spectra were collected with a Bruker (Billerica, MA, USA) Tensor II equipped with a Harrick Praying Mantis Diffuse Reflectance attachment. A Perkin-Elmer Spectrum Two with Attenuated Total Reflection Fourier (ATR) cell with diamond crystal was also used to collect the spectra. The final spectra are the average of 20 scans with a resolution of  $4\text{ cm}^{-1}$ .

### 3.2.4. Textural Analysis

The textural characteristics of the catalysts (surface area, pore volume, and pore size) were determined from adsorption-desorption isotherms of nitrogen at  $-196\text{ }^{\circ}\text{C}$  using a Micromeritics (Norcross, GA, USA) ASAP 2020 Surface Area and Porosity Analyzer. The samples were outgassed for 12 h at  $120\text{ }^{\circ}\text{C}$  before nitrogen adsorption.

### 3.2.5. Elemental Analysis

The elemental analysis (CHNS) of the final composites was performed using a EuroVector (Pavia, Italy) EuroEA EA3000 Series analyzer.

## 3.3. Antibiotic Removal Tests

The irradiation of the composites has been carried out using a sunlight simulator Sciencetech (London, ON, Canada) SF150-A Small Collimated Beam Solar Simulator (Air Mass AM1.5G Filter and Light-Tight Reaction Chamber). The advance of the reaction was monitored by liquid chromatography using an Agilent (Santa Clara, CA, USA) HPLC equipped with a Agilent Zorbax SB-C18 column ( $4.6 \times 150\text{ mm}$ , 5 microns); the mobile phase was  $25\text{ mM KH}_2\text{PO}_4\text{:ACN} = 60\text{:}40$ , under a flow of  $0.5\text{ mL min}^{-1}$ , column temperature  $60\text{ }^{\circ}\text{C}$ , and with DAD detection at  $204\text{ nm}$ . For the experiments,  $15\text{ mL}$  of a prepared  $0.17\text{ mM}$  solution of antibiotic and  $60\text{ mg}$  of catalyst were added into quartz test tubes. Before turning on the lamp, the samples were kept in the dark, under stirring, for  $10\text{ min}$  to reach the absorption-desorption equilibrium.

## 4. Conclusions

A series of composites was prepared starting from five types of LDHs (co-precipitated in the presence of inorganic or organic alkali and the mechanochemical method), which were then exchanged with three types of metallo-phthalocyanines. In the end, magnetic nanoparticles were attached. LDHs containing Fe showed a partial oxidation from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . The final composites presented a multimodal pore distribution. Samples containing evident LDH structures performed better in general than the ones containing iron oxide mixtures, the composites being more active towards amoxicillin removal compared with ampicillin. The nature of the phthalocyanine did not have such a great influence, although some differences in the activity were observed. The removal was a combination between adsorption and photocatalytic degradation. However, FTIR-ATR analysis of the antibiotic solutions at different reaction times suggest that the total decomposition is not reached, or at least not to an important extent, after the two hours of irradiation. The best composites for this application were those based on LDH4 ( $\text{MgFe}^{2+}\text{Al}$  prepared by co-precipitation in the presence of NaOH), which presented high adsorption capacity in  $10\text{ min}$  and, at the same time, high photocatalytic activity for both amoxicillin and ampicillin. Although the composite based on LDH1 ( $\text{MgAl}$  prepared by co-precipitation in the presence of NaOH) presented similar performance in the removal of amoxicillin, it performed poorly for the removal of ampicillin. This difference is the result of both adsorption and photocatalytic decomposition, which are affected by the structure of the target molecules. The use of

TMAH as template and precipitating agent does not lead to an increase in performance for the LDH5-based ( $\text{Mg}_{0.325}\text{Fe}_{0.325}\text{Al}_{0.25}$ -LDH prepared by co-precipitation) composites due to the oxidation of  $\text{Fe}^{3+}$  and formation of mixed oxides during rehydration. The poor performance of the composites based on  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  simultaneous doping of LDH (LDH2 and LDH3), in comparison with the composites doped only with  $\text{Fe}^{2+}$  (LDH4 and LDH5), is related mainly to their structure and composition. The first are mixtures of iron oxides, compared with the real LDH structure of the latter. However, the solid prepared by mechanochemical reaction (LDH3) presents some degree of layered structure as seen by XRD. This is also reflected in the textural properties of the material.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14100668/s1>, Figure S1: DR-UV-Vis spectra of as-prepared (a) LDH1; (b) LDH2; (c) LDH3; (d) LDH4; (e) LDH5; Figure S2: Raman spectroscopy of (A) LDH4 and (B) LDH5; Figure S3: Photocatalytic contribution to the removal % of amoxicillin using (a) LDH1; (c) LDH4; (e) LDH5; (g) LDH2; (i) LDH3 and ampicillin using (b) LDH1; (d) LDH4; (f) LDH5; (h) LDH2; (j) LDH3-based composites; Figure S4: FTIR-ATR Spectra of amoxicillin solutions at selected reaction times. References [40–42] are cited in the Supplementary Materials.

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