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\textbf{A B S T R A C T}

In this study, ZnFe-layered double hydroxides were synthesized by a chemical co-precipitation method with different intercalated anions, including chloride and sulfate. They were then modified with graphene oxide to obtain ZnFe–Cl-LDH/GO and ZnFe–SO\textsubscript{4}-LDH/GO photocatalysts. The as-synthesized samples were characterized by XRD, SEM, EDX, TEM, FTIR, BET, UV-Vis DRS, XPS, and PL analyses and evaluated for the decomposition of ofloxacin (OFX) under visible light irradiation. OFX is a persistent and resistant emerging pollutant in an aqueous solution. Among the photocatalysts synthesized, the photocatalytic activity of ZnFe–SO\textsubscript{4}-LDH/GO was highest (71.19% after 150 min irradiation) under optimum conditions. This observation is ascribed to the synergistic impact of swift separation rates of the photo-generated electrons that extend the longevity of charge carriers resulting from the heterostructures created between pure ZnFe–SO\textsubscript{4}-LDH and GO. The results indicate that a pseudo-first-order kinetic model can determine the kinetics of the OFX-degrading system. Based on the results of scavengers, \textsuperscript{•}OH radicals and h\textsuperscript{+} were the major species for OFX degradation. Moreover, a possible photocatalytic mechanism is proposed for the degradation of OFX. Gas chromatography-mass spectrometry (GC–MS) was employed to recognize the by-products formed in solution by the dissociation of OFX. The chemical oxygen demand (COD) was analyzed to evaluate the mineralization of the OFX solution. Furthermore, the reusability and photostability of the photocatalyst were examined. The leaching zinc and iron concentrations in the aqueous phase were measured within five consecutive examinations.

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1. Introduction

Ecosystems are facing increasing threats due to the widespread use of antibiotics, which are poorly biodegradable [1,2]. To examine the environmental consequences of antibiotics, studies have focused on their impacts on the ecosystem and human health [1,3]. Different sources can easily discharge antibiotic residues into the environment, including production sites, hospital wastewater, and post-administration drug excretion [4,5]. Fluoroquinolones are broad-spectrum synthetic antibiotics that have extensive applications in both human antimicrobial treatments and veterinary medicine [1,5,6]. The most commonly used fluoroquinolone antibiotic is ofloxacin (OFX), which is normally identified in water and wastewater because of its difficult dissociation by biological water and wastewater treatment methods [1,7,8].

Wastewaters containing antibiotics such as OFX result in chronic toxicity, which leads to the growth of bacterial resistance to antibiotics [9]. Accordingly, researchers have sought to discover techniques for the degradation of OFX from solutions [1,5,10]. Physicochemical and biological methods for the removal of antibiotics from wastewater have been proven to be ineffective because of both technical disadvantages and antibiotic stability against degradation. This is supported by positive results reported for many antibiotics that are present at concentrations of as much as nanograms per liter to as high as 100 mg/L in numerous sewer waters sampled from wastewater treatment plants [4,11].

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Advanced oxidation processes (AOPs) are capable of generating highly reactive oxygen species (ROS), such as hydroxyl radicals (•OH), which can quickly and non-selectively decompose intractable organic pollutants. AOPs have displayed potential applications in the decomposition of antibiotics [10, 12–14]. Great attention has been given to photocatalysis, particularly due to its inexpensive, high-throughput, and eco-friendly performance [15, 16]. Moreover, a variety of photocatalysts have been used to eradicates OFX contaminants, including BiO2/TiO2 [5], La2Ti2O7 [17], Gd2Ti2O7/HZSM-5 [18], Bi2MoO6 nanosheets [19], CdS/TiO2 [20], ordered mesoporous g-C3N4 [21], TiO2 NT-based SnO2-Sb/polytetrafluoroethylene resin (FR-PbO2) [22], zinc oxide-exopolyhipapatite [23], and many others. These catalysts have shown promising degradation efficiency in aqueous solution. Furthermore, substantial interest has been shown towards novel, effective, simple, and low-cost approaches to control the discharge of antibiotics.

Recently, layered double hydroxides (LDHs) have been gaining extensive attention for use as photocatalysts due to their high anion exchange capacity, large specific surface area, and convenient synthesis method [24, 25]. As anionic clays, LDHs have a general formula of \([\text{M}^{n+}x\cdot \text{M}^{n+}y(\text{OH})z_{x\cdot z'}^{\cdot z''}\text{Cl}^{z''}H_2O]\), where \(\text{M}^{n+}\) denotes divalent cations (Cu2+, Ni2+, Mg2+, Zn2+, etc.), \(\text{M}^{n+}\) indicates trivalent cations (Fe3+, Al3+, Cr3+), etc., \(x\) represents interlayer anions (CO3\(^2\), Cl\(^-\), NO3, SO4\(^2\), etc.), and \(y\) is the amount of water molecules present in the layered structure. Therefore, layers that are positively charged compensate by the intercalation of hydrated anions [26]. Nonetheless, bare LDHs typically have lower quantum yield under ultraviolet and visible light irradiation because of their poor charge carrier mobility, rapid recombination of photo-induced charges, and lower electron–hole \((e^-\cdot h^+)\) transfer [27, 28]. The performance of LDHs as nanophotocatalysts can be efficiently enhanced through various modifications, such as doping and combination with various semiconductors and immobilization on preferred substrates [29].

Materials based on graphene oxide (GO) have received extensive attention for wide application in environmental remediation processes [30–34]. The reason behind this lies in their outstanding charge carrier mobility, high electrical conductivity to accept photogenerated electrons from the conduction bands of most of the semiconductors, acting as electron receivers and donors [35, 36], and interesting nanostructure [37]. This two-dimensional carbon material is produced by various techniques, including exfoliation, oxidation–reduction, ultrasonic, and thermal exfoliation. Nevertheless, ultrasonically prepared GO generally shows aggregation during the drying process due to the liquid phase reaction [37].

However, the thermal exfoliation method is able to yield comparatively fluffy GO, but with fewer functional groups on its surface. Consequently, making a dispersion of GO in aqueous and organic solutions is difficult and seriously restricts its functionalization for several specific purposes [38]. Various amendments have been used to improve the solubility of GO [39–42]. Oxidation methods are the easiest techniques to covalently attach chemical groups that lead to the formation of carboxyl and hydroxyl groups on the surface of GO [39, 42]. These methods include liquid oxidation, oxygen plasma treatment, and ozone modification. However, they have some intrinsic disadvantages. For instance, liquid oxidation methods require intricate processing stages and are relatively time consuming [38]. Plasma treatment has several other problems, including an inappropriate degree of oxidation and an inability to yield the large quantities required [37].

In recent years, ozone treatment has been applied as a fairly novel and simple method to modify carbon materials, such as active carbon, carbon black, and carbon fiber [43–45]. Carbon exposure to ozone may result in the creation of carboxylic, hydroxyl, ether, and carbonyl groups. The features of ozone oxidation include a simple experimental set up, ease of use, low cost, and efficiency compared to the two previous oxidation methods. In addition, mass production is achievable with this method, in contrast to plasma treatment. Simultaneous processing using ozone oxidation can also be obtained by regulation of the system temperature, the addition of water vapor, or ultraviolet irradiation as auxiliary conditions, which result in multifactor synergetic improvements including a significant improvement in the oxidation level [39, 46, 47].

The GO-based nanophotocatalysts have enhanced physicochemical properties compared to graphene and can also combine the advantages of GO along with other nanomaterials [48–50]. A variety of LDHs and modified LDHs have been applied as photocatalysts. For instance, Shao et al. used Zn/Ti LDH [51]. Parida et al. studied the photocatalytic activity of Zr–Cr LDH for the photodegradation of organic contaminants [52]. Similarly, Parida and Mohapatra reported on the photocatalytic performance of carbonate intercalated Zn/Fe LDH in the photodegradation of azo dyes [53]. Mantilla et al. used Mg/Al LDH for the photo-assisted dissociation of 4-chlorophenol and p-cresol [54]. Khodam et al. studied the photocatalytic performance of Nd-doped CoAl-mixed metal oxides in the removal of two pharmaceutical pollutants ciprofloxacin and ibuprofen [55].

It seems that there has been no research on the use of graphene-based LDH for the photocatalytic dissociation of contaminants. This study reports the successful synthesis of two different chloride (Cl\(^-\)) and sulfate (SO4\(^2\)) anions intercalated into Fe3-LDH, ZnFe2–Cl-LDH/GO, and ZnFe2–SO4-LDH/GO, which were characterized by several techniques. The as-synthesized samples were assessed in terms of their photocatalytic performance in the photocatalytic degradation of OFX as a target antibiotic pollutant. The main operating factors were tested, such as the photocatalyst dosage, OFX concentration, initial pH, effect of scavengers, and the durability of the photocatalyst in repeated trials. A mechanism is also suggested to illustrate the substantial improvements of the photocatalytic activity for the degradation of OFX from an aquatic phase under visible light irradiation.

2. Experimental

2.1. Materials

Sodium nitrate (NaNO3, 99%), iron (II) sulfate (FeSO4•7H2O, 99.5%), zinc (II) sulfate (ZnSO4•7H2O, 99.5%), iron (III) chloride (FeCl3•6H2O, 99%), zinc (II) chloride (ZnCl2, 100%), sodium hydroxide (NaOH, 99%), formic acid (CH2O2, 98–100%), 2-propanol (C3H6O, 99%), 1,4-benzoquinone (C6H4O2, 99%), and diethyl ether (C2H5OEt, 99%) were provided by Merck (Germany). Ethanol (C2H5OH, 96%) was supplied by Sigma Aldrich (USA). Hydrochloric acid (HCl, 38%) was obtained from Royalax (India). GO nanoplasts (99+%, 3.4–7 nm, 6–10 layers) were obtained from US Research Nanomaterials (USA). OFX was obtained from Rouz Darou Laboratories (Iran). The properties of OFX are presented in Table 1.

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<th>Chemical structure</th>
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Table 1

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<th>Physical/chemical properties of antibiotic ofloxacin.</th>
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<td>λ_max (nm)</td>
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2.2. Synthesis of the samples

2.2.1. Synthesis of modified GO

GO (0.02 g) was dispersed in distilled water (150 mL) by ultrasonication (ULTRA 8060 D-H, England), which resulted in stable aqueous-dispersed GO. The GO was modified under a continuous flow rate of ozone (30 L/h) in a cylindrical Pyrex reactor. Ozone was generated in an ozone generator (BE-72, Iran) using oxygen gas, which was supplied by an oxygen generator (Airsep, USA). The cylindrical reactor was placed in a water bath, and the temperature was adjusted. The obtained solution was then dried in an oven, and the precipitates were collected. The experimental conditions of ozone modification of GO are shown in Table 2.

2.2.2. Synthesis of ZnFe–Cl-LDH and ZnFe–SO4-LDH

For ZnFe–Cl LDH, FeCl3·6H2O (0.001 mol) and ZnCl2 (0.003 mol) were dissolved in a molar ratio of 3:1 in 40 mL of distilled water. The solution was titrated slowly with NaOH solution (2 mol/L) until the pH reached 8 at room temperature and under Ar atmosphere. The solution was then stirred for 24 h. The precipitates were centrifuged and dried in an oven at 60 °C. Zn/Fe–SO4 LDH was also prepared by the method described using FeSO4·7H2O (0.001 mol) and ZnSO4·7H2O (0.003 mol).

2.2.3. Synthesis of ZnFe–Cl-LDH/GO and ZnFe–SO4-LDH/GO

ZnFe–Cl-LDH/GO was synthesized through the chemical co-precipitation method. For the synthesis of ZnFe–Cl LDH-GO, a distinct proportion of FeCl3·6H2O, ZnCl2, and 0.04 g of modified GO were dissolved in 40 mL of distilled water. The solution was titrated slowly with NaOH solution (2 M) until the pH reached 8. After that, the solution was stirred for 12 h under Ar atmosphere, and the precipitates were centrifuged and dried in an oven at 60 °C. ZnFe–SO4-LDH/GO was also prepared by the method described using FeSO4·7H2O and ZnSO4·7H2O.

2.3. Instrumentation

The crystallographic characteristics of the samples were analyzed by an X-ray diffraction (XRD) (PANalytical X’Pert PRO, Germany, Cu Kα radiation: 0.15406 nm; 45 kV, 40 mA). The surface area of the samples was tested by the Brunauer-Emmett-Teller (BET) method using a 3 Flex instrument (Micromeritics, USA). Scanning electron microscopic (SEM) micrographs of the samples were obtained using a Tescan Mira3 microscope (Czech Republic). Energy-dispersive X-ray (EDX) spectroscopy of the samples was performed using a Zeiss Sigma 300. High-resolution transmission electron microscopy (HRTEM) (FEI, TALOS F200S, Netherlands) was performed at 200 kV. Diffuse reflectance spectrophotometer (DRS) spectra of the samples were recorded on an Analytik Jena spectrophotometer (S 250, Germany) to measure the band gap.

X-ray photoelectron spectroscopy (XPS) (K-Alpha, Thermo Scientific, U.K.) was used to investigate the changes of the composition. Atomic absorption spectroscopy (AAS) (NovAA 400, Analytik Jena, Germany) was used to study the leaching concentrations of zinc and iron. The functional groups of samples were measured by an FTIR spectrometer (Tensor 27, Bruker, Germany) in the range of 400–4000 cm⁻¹ by the KBr disk method. The chemical oxygen demand (COD) of the OFX solution was determined before and after the treatment process using standard method 5220 with a Palin test apparatus (United Kingdom). The photoluminescence (PL) spectra of the as-synthesized samples were measured by a spectrometer (Perkin Elmer LS45, USA). Gas chromatography–mass spectrometry (GC–MS) was used to determine the intermediate by-products produced during OFX degradation. The characteristics of the GC–MS instrument are provided in the supporting materials.

2.4. Evaluation of the photocatalytic performance

OFX was selected as a model pollutant to study the photocatalytic activity of ZnFe–Cl-LDH, ZnFe–SO4-LDH, ZnFe–Cl-LDH/GO, and ZnFe–SO4-LDH/GO photocatalysts. The reactions were performed under a 10-W LED lamp as a visible light source at ambient temperature. In photocatalytic trials, a predetermined amount of photocatalyst was added in a 100-mL aqueous OFX solution (20 mg/L). The pH of OFX solution was adjusted using NaOH and HCl solutions (1 M) and measured with a pH meter (Ohaus 3100, USA). Before the irradiation, the OFX solution was agitated for 30 min in the dark to obtain an adsorption–desorption equilibrium between the photocatalysts and OFX. The OFX concentration was determined using an ultraviolet-visible (UV-Vis) spectrophotometer (SU-6100, Philler scientific, USA) at a maximum wavelength of 288 nm. The degradation efficiency (DE (%)) was calculated using the following equation:

\[
DE(\%) = 1 - \frac{A_t}{A_0} \times 100
\]

where \(A_t\) and \(A_0\) are the initial absorbance of OFX and its absorbance after the photocatalytic process, respectively.

3. Results and discussion

3.1. Characterization

As shown in Fig. S1, the qualitative validation of oxygen-containing functional groups was performed on the GO surface using FTIR spectra. In the unmodified GO sample, the peaks located at 1049 and 1519 cm⁻¹ are related to C–O and C=–O, respectively [37]. Following the treatment with ozone, the C=–C peak was slightly weaker, and C=–H and C–O–C peaks were observed at 966 and 1296 cm⁻¹, respectively. After the ozone treatment, there was a clear peak at 3429 cm⁻¹, which is related to the functional group of OH [37]. The intensity of these peaks was enhanced by prolonging the ozone treatment time and increasing the temperature. Notably, the intensity of the C=–O peak at 1683 cm⁻¹ and the C–O peak at 1076 cm⁻¹ was increased after the ozone treatment, which is attributed to the stretching mode of the –COOH group [37, 56]. According to the FTIR spectra, there were many oxygen functional groups of –OH, C=–O, and C=–O, which were derived from COOH groups on the surface, which probably resulted from the ozone oxidation [37]. The results showed that the modified GO samples are burned, and low-intensity peaks are generated after 15 min of treatment time at a reaction temperature of 75 °C. Consequently, 15 min and 75 °C were selected as the optimum conditions for ozone treatment.

Additionally, the changes in the oxidation degree and chemical components of GO were assessed by XPS throughout the ozonation
In Fig. S2, the survey spectrum shows that the intensity of the 0 1s peak is notably enhanced for the modified GO compared to the unmodified GO. The elemental contents of the unmodified and modified GO are shown in Table S1. The percentage of oxygen in the samples was clearly enhanced from 32.82% to 59.94% after ozone modification for 15 min, and the atomic ratio of O/C was enhanced as well. In addition, C 1s peaks were investigated for detailed studies.

Fig. S3 and Table S2 demonstrate the C 1s peaks of XPS spectra of the GO before and after ozone modification. The C 1s spectra of both samples were deconvoluted into five peaks, which were attributed to C=O-C in aromatic rings (284.3–284.4 eV), a C-CH bond (285.1–285.2 eV), a C-O-C group (286.4–286.7 eV), a C-O group (287.4–288.5 eV), and an extra COOH group (288.5–290.3 eV) [37]. Because of the ozonation process, the percentage of C=O-C was increased, while the percentage of oxygen-containing functional groups increased for the unmodified GO, which was also compatible with the O 1s spectra of GO (Fig. S4). When the temperature was increased to 75 °C, the oxygen-containing functional groups on the surface of GO changed. When comparing the C 1s spectra for samples, it can be clearly seen that ozone modification at 75 °C increased the C–OH, C–O–C, and C=O and decreased the C=C/C=C [37, 57]. Particularly, when ozone modification was carried out at 75 °C for 15 min, C–OH, C–O–C, and C=O were increased.

Fig. 1 shows the XRD patterns of ZnFe–Cl-LDH, ZnFe–SO₄-LDH, ZnFe–Cl-LDH/GO, and ZnFe–SO₄-LDH/GO samples. For the ZnFe–Cl-LDH and ZnFe–Cl-LDH/GO samples (Fig. 1(a)), the measured XRD patterns show the characteristic diffraction peaks of the LDH structure via a hexagonal phase. The peaks at 11.44°, 19.89°, 22.54°, 28.44°, 30.59°, 32.84°, 34.84°, 37.39°, 38.59°, and 61.04° are readily indexed to the (002), (006), (110), (101), (009), (012), (015), (018), (110), and (113) planes, respectively, which correspond to the characteristic model of hydrotalcite structure [58, 59]. For the ZnFe–SO₄-LDH and ZnFe–SO₄-LDH/GO samples (Fig. 1(b)), the peaks located at 12.54°, 19.94°, 24.69°, 33.34°, 34.54°, 50.59°, 59.24°, and 61.44° correspond to the reflections of the (003), (006), (110), (009), (012), (018), (110), and (113) planes of LDH, which are typical of the characteristic pattern of hydrotalcite [58]. The (003) and (006) planes indicate incorporation of carbonate ions and H₂O in the LDH lattice [60]. Successful formation was observed for the LDH crystal phase. For ZnFe–Cl-LDH/GO, the diffraction peak of the (001) plane (2θ=9°) with d-spacing of 9.84 Å and ZnFe–SO₄-LDH/GO (2θ=10°) with d-spacing of 8.85 Å correspond to GO. These results indicate the integration of GO into the LDHs and confirm the successful synthesis of ZnFe–Cl-LDH/GO and ZnFe–SO₄-LDH/GO. The basal spacing of ZnFe–SO₄-LDH/GO (7.22 Å) was lower than that of ZnFe–Cl-LDH/GO (7.53 Å), which is in accordance with the higher sulfate charge density [53]. The lattice parameters c and a can be calculated from the diffraction peaks of the (003) and (110) crystal planes using the equations: \( c = 3d_{(003)} \) and \( a = 2d_{(110)} \). The parameter c is three times the basal spacing of the adjacent brucite-like layers [58]. The average crystal size of all the samples is calculated for the high-intensity peak that emerged at (003) by using the Scherrer equation [61]. The average crystallite size and lattice parameters are listed in Table 3.

The particle size distribution and the surface morphology of the samples were evaluated using SEM images. A smooth layered structure with large stacks was found for GO (Fig. 2(a) and (b)), whereas the SEM images of modified GO revealed close individual layers of GO, which indicate the successful exfoliation of graphite layers (Fig. 2(c) and (d)). The as-synthesized ZnFe–Cl-LDH (Fig. 2(e) and (f)) and ZnFe–SO₄-LDH (Fig. 2(i) and (j)) exhibited characteristic hexagonal plate-like LDH sheets and predominately smooth texture. The SEM images of modified LDHs (Fig. 2(g) and (h)) showed perfect sheet shapes for the ZnFe–Cl-LDH/GO and ZnFe–SO₄-LDH/GO samples, which have naturally uniform surface structures with thicknesses of the platelets of 31 nm and 33 nm, respectively. These images confirm the intercalation of GO into the LDH samples, which differ from the surface of LDHs.

The elemental composition of the as-synthesized samples was determined by EDX microanalysis, and the results are shown in Fig. 3. The EDX analysis revealed the changes occurred in the elemental composition of the GO after modification (Fig. 3(a) and (b)). An increase in the amount of oxygen indicates a successful oxidation process. The EDX spectra of ZnFe–Cl-LDH and
Fig. 2. SEM images of (a, b) GO, (c, d) modified GO, (e, f) ZnFe–Cl–LDH, (g, h) ZnFe–Cl–LDH/GO, (i, j) ZnFe–SO₄–LDH, and (k, l) ZnFe–SO₄–LDH/GO samples.
Fig. 2. Continued
ZnFe–SO₄-LDH confirmed the presence of O, Cl, S, Fe, and Zn in the as-synthesized samples. The EDX spectra of the modified LDHs (Fig. 3(d) and (f)) were compared with those of pure LDHs, from which it can be concluded that ZnFe–Cl-LDH and ZnFe–SO₄-LDH were successfully incorporated onto the GO surface.

The size and morphology of as-synthesized samples were measured by HRTEM. The TEM images of ZnFe–Cl-LDH/GO and ZnFe–SO₄-LDH/GO (c) and (d) with different magnifications are shown in Fig. 4. Both ZnFe–Cl-LDH and ZnFe–SO₄-LDH had uniform distributions on the surfaces of the graphene layers, and the dark
parts with LDH platelets had an even distributions on the wrinkled surfaces of the graphene.

Fig. 5 shows the FTIR spectra of ZnFe–Cl-LDH, ZnFe–Cl-LDH/GO, ZnFe–SO₄-LDH, and ZnFe–SO₄-LDH/GO. The broad, strong bands in the range of 3413–3450 cm⁻¹ for all of the samples are assigned to the stretching vibrations of −OH with hydrogen bonding and surface water molecules [62]. The bands in the range of 1623–1643 cm⁻¹ are associated with the bending mode of interlayer water molecules [62]. In the spectra of ZnFe–Cl-LDH and ZnFe–Cl-LDH/GO, bands appeared at 723 and 732 cm⁻¹, respectively, which are attributed to chloride ions [53, 63]. The bands around 600–800 cm⁻¹ are related to the stretching and vibration mode of M–O in the hydrotalcite, and the bands at 400–500 cm⁻¹ are related to the vibration mode of O–M–O, where M denotes the cations of Zn²⁺ and Fe³⁺ [63]. In the case of ZnFe–SO₄-LDH and ZnFe–SO₄-LDH/GO, the bands located at 1116 and 1118 cm⁻¹, respectively, are related to sulfate ions (Fig. 5(b) and (d)) [64].

Both modified LDHs samples present the same absorption peaks as the pure LDHs. In the spectra of ZnFe–Cl-LDH/GO (Fig. 5(c) and ZnFe–SO₄-LDH/GO (Fig. 5(d)), the relatively broad bands at about 3444 and 3438 cm⁻¹, respectively, are associated with the stretching mode of COOH [62,65]. In addition, the peaks around 1515 cm⁻¹ could be due to the CO₂⁻ anions located in the LDH interlayers [63]. The absorption bands at 1741 and 1739 cm⁻¹ are attributed to the stretching vibration of C=O for ZnFe–Cl-LDH/GO and ZnFe–SO₄-LDH/GO, respectively (Fig. 5(c) and (d)) [62]. These bands indicated that GO is successfully intercalated in the LDHs. The bands located at 1018 and 1055 cm⁻¹ are associated with C–O bending vibration (Fig. 5(c) and (d)) [62].

The light-harvesting feature of synthesized photocatalysts is a crucial parameter for a photocatalytic process [35]. Hence, UV-Vis DRS was applied to record the optical characteristics of the as-synthesized samples. The band gaps of the samples were calculated using the Tauc equation:

\[(\alpha h\nu)^2 = K(h\nu - E_g)\]  

In this equation, \(E_g\), \(\alpha\), \(h\nu\), and \(K\) are the band gap energy, absorption coefficient, photon energy (eV), and absorption index, respectively. This equation is used to obtain the optical band gap from UV-Vis DRS data by plotting \((\alpha h\nu)^2\) versus the photon energy \((h\nu)\) and then extrapolating the linear part of the plot to the energy \((h\nu)\) axis (Fig. 6).
To investigate the surface area and pore structure of the samples, N\textsubscript{2} adsorption–desorption experiments were carried out. Since the number of active sites and adsorption activity of a photocatalyst are directly affected by the surface area size, the photocatalytic degradation efficiency is highly influenced by the surface area of the photocatalyst [66]. The detailed parameters of the pore structure are listed in Table 4. The experimental data revealed that the isotherms of the modified GO and as-synthesized photocatalysts have type IV behavior with an H\textsubscript{3} hysteresis loop, which indicates that all the samples have mesoporous structures (Fig. 7).

The modified GO has the lowest specific area of 6.17 m\textsuperscript{2}/g. The samples of ZnFe–Cl-LDH and ZnFe–SO\textsubscript{4}-LDH show BET surface areas of 131.33 m\textsuperscript{2}/g and 31.26 m\textsuperscript{2}/g, respectively, which are larger than that of ZnFe–Cl-LDH/GO (124.67 m\textsuperscript{2}/g) and ZnFe–SO\textsubscript{4}-LDH/GO (27.47 m\textsuperscript{2}/g). This decline can be attributed to the GO intercalation and pore blockage. Table 4 reveals that the pore diameter in all samples was 6 to 16 nm, with minimum in the ZnFe–Cl-LDH sample and the maximum in the ZnFe–SO\textsubscript{4}-LDH/GO. The interparticle pore enlargement with increased LDH grains after their intercalation with GO could lead to increased mean pore diameter of the modified LDHs. Based on our results, it can be inferred that high photocatalytic performance occurred due to the alteration in the surface area of the as-synthesized photocatalysts.

The PL behavior shows the separation and recombination process of photo-generated electron–hole pairs (e\textsuperscript{−}–h\textsuperscript{+}). The PL spectra of modified GO, ZnFe–SO\textsubscript{4}-LDH, and ZnFe–SO\textsubscript{4}-LDH/GO samples were recorded at an excitation wavelength of 315 nm to investigate the photocatalytic activities (Fig. 8). The ZnFe–SO\textsubscript{4}-LDH/GO has weaker intensity than the modified GO and ZnFe–SO\textsubscript{4}-LDH, suggesting the possible reduction of e\textsuperscript{−}–h\textsuperscript{+} recombination of the ZnFe–SO\textsubscript{4}-LDH/GO and the best photocatalytic degradation performance (Fig. 8(a)). Fig. 8(b) indicates that the PL spectra changes through the photocatalytic process with terephthalic acid solution for the ZnFe–SO\textsubscript{4}-LDH/GO photocatalyst at different time intervals. The formation of *OH radicals was enhanced by increasing the irradiation time.

### 3.2. Photocatalytic oxidation of OFX

Photocatalysis is one of the essential characteristics of a catalyst in a photocatalytic process. Therefore, effective irradiation has to be provided to activate the catalyst and to form e\textsuperscript{−} – h\textsuperscript{+} pairs. In addition, some of the other necessities are effective absorption of light, application of photo-generated charge carriers in redox reactions before recombination, and high surface area. Preparations of pure ZnFe–Cl-LDH, ZnFe–SO\textsubscript{4}-LDH, ZnFe–Cl-LDH/GO, and ZnFe–SO\textsubscript{4}-LDH/GO photocatalysts were applied in photocatalytic OFX degradation using visible-light irradiation. As shown in Fig. 9(a), the resulting OFX degradation efficiency was examined as a function of irradiation time for different photocatalysts. The inset indicates that the type of catalyst influenced the degradation. Higher activities were recorded for both modified LDH photocatalysts compared to ZnFe–Cl-LDH (23.52%) and ZnFe–SO\textsubscript{4}-LDH (25.40%) towards OFX degradation under visible light irradiation. The photocatalytic performance was higher for ZnFe–SO\textsubscript{4}-

![Fig. 5. FTIR spectra of (a) ZnFe–Cl-LDH, (b) ZnFe–SO\textsubscript{4}-LDH, (c) ZnFe–Cl-LDH/GO, and (d) ZnFe–SO\textsubscript{4}-LDH/GO samples.](image-url)

### Table 4

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>Average pore diameter (nm)</th>
<th>Total pore volume (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{m} (cm\textsuperscript{3}/(STP)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified GO</td>
<td>6.17</td>
<td>15.240</td>
<td>0.0235</td>
<td>1.418</td>
</tr>
<tr>
<td>ZnFe–Cl-LDH</td>
<td>131.33</td>
<td>6.934</td>
<td>0.2276</td>
<td>0.3972</td>
</tr>
<tr>
<td>ZnFe–SO\textsubscript{4}-LDH</td>
<td>31.26</td>
<td>11.246</td>
<td>0.0878</td>
<td>0.1503</td>
</tr>
<tr>
<td>ZnFe–Cl-LDH/GO</td>
<td>124.67</td>
<td>8.078</td>
<td>0.2517</td>
<td>0.4558</td>
</tr>
<tr>
<td>ZnFe–SO\textsubscript{4}-LDH/GO</td>
<td>27.47</td>
<td>9.100</td>
<td>0.0625</td>
<td>0.1499</td>
</tr>
</tbody>
</table>
LDH/GO (71.19%) than ZnFe–Cl-LDH/GO (43.29%) after a similar irradiation period.

To investigate the adsorption capability, suspensions of photocatalyst and OFX solution were kept in a dark place, and their adsorption capability was measured, as shown in Fig. 9(b). The modified GO, ZnFe–Cl-LDH, ZnFe–SO₄-LDH, ZnFe–Cl-LDH/GO, and ZnFe–SO₄-LDH/GO adsorbed 43.73%, 33.00%, 27.54%, and 41.77% of 20 mg/L OFX, respectively. According to the results, the intercalation of GO into pure LDHs promoted the adsorption and photocatalytic activities of the modified LDHs. Therefore, ZnFe–SO₄-LDH/GO was chosen as an appropriate catalyst for further examinations.

3.3. Effect of the operational parameters

3.3.1. Effect of photocatalyst dosage

It is crucial to determine the optimal catalyst dosage because it has a major contribution to the robust degradation efficiency of photocatalysis [67]. Accordingly, a catalyst dose of 0.3–2.5 g/L was examined in a series of experiments for the decomposition of 20 mg/L of OFX at pH 8 and 150 min of light exposure. The degradation efficiency was highest with 1.5 g/L and dropped thereafter with increasing photocatalyst dosage (Fig. 9(c)). The increased photocatalytic degradation efficiency from 0.3 g/L to 1.5 g/L is principally ascribed to the increase in active sites and total surface area, which became accessible on the catalyst surface after increasing the catalyst dose. The catalyst doses of 1.5–2.5 g/L resulted in a considerable reduction in degradation efficiency, which was possibly caused by a decline in light penetration. High concentrations of catalyst cause more turbidity in solution, thereby blocking the penetration of incident visible and impairing the efficiency of the photocatalytic process [15,68]. Thus, a photocatalyst dose of 1.5 g/L was selected as the optimum level for further applications.

3.3.2. Effect of the initial OFX concentration

The dependency of photocatalytic dissociation on the concentration of aqueous pollutants is one of the most important factors in our investigation [15]. The degradation of OFX was investigated while altering its original concentration ranging from 10 to 50 mg/L. As shown in Fig. 9(d), the performance of the process dropped from 87.99% to 22.78% with increasing OFX concentration from 10 mg/L to 50 mg/L. A reduction in the original OFX concentration was associated with an increase in the probability of the reaction between OFX and oxidizing species, which led to greater degradation efficiency. Nevertheless, the excess OFX concentration decreased the degradation efficiency.

At lower OFX concentration, sufficient active sites on the surface of the photocatalyst could interact with comparatively few OFX molecules in the solution, resulting in high OFX degradation.
Fig. 7. $N_2$ adsorption–desorption isotherms of (a) modified GO, (b) ZnFe–Cl-LDH, (c) ZnFe–SO$_4$-LDH, (d) ZnFe–Cl-LDH/GO, and (e) ZnFe–SO$_4$-LDH/GO samples.
efficiency. However, there was a surplus of concentrations with increasing OFX level in the aqueous phase. In such a situation, some of the OFX can only interact with inadequate active sites on the surface of the photocatalyst, which decreases the efficiency of OFX degradation at higher initial concentrations.

3.3.3. Effect of solution pH

The photocatalytic process can be significantly affected by the solution pH [13, 69]. The influence of the initial pH on the degradation efficiency of OFX was evaluated in the range of pH 4–10 (Fig. 9(e)). According to the results, the degradation efficiency increased with the solution pH up to 7.2 and then dropped afterwards. It is very difficult to clarify how pH affects the photocatalytic process due to its multiple roles, including electrostatic interactions between the catalyst surface, solvent molecules, substrate, and charged radicals generated throughout the reaction process [15].

The surface properties of heterogeneous catalysts markedly influence the decomposition process, particularly the surface charge. Thus, the pH at the point of zero charge (pH_{pzc}) was determined for ZnFe–SO₄-LDH/GO to identify its surface charge. A pH_{pzc} of 7.2 was detected for ZnFe–SO₄-LDH/GO, indicating positive charge (pH < 7.2) and negative charge (pH > 7.2) at the surface of the sample (Fig. S5). OFX, however, had a positive charge at pH levels lower than pKₐ₁ (6.05), a negative charge at pH levels over pKₐ₂ (8.11), and zwitterions at pH levels between pKₐ₁ and pKₐ₂ [68]. Therefore, acidic and alkaline pH values are not advantageous for OFX to be adsorbed on the surface of ZnFe–SO₄-LDH/GO.

The decreased photodegradation efficiency observed at low pH values is attributable to the repelling effect between OFX and the positively charged surface of the photocatalyst. In contrast, both ZnFe–SO₄-LDH/GO and OFX have negative charges in alkaline conditions, which cause electrostatic repulsion between them and lower OFX photodegradation efficiency. Both the photocatalyst and OFX present neutral forms at pH 8, where no repulsion occurs between them.

3.3.4. Performance of various processes

Fig. 9(f) presents the results of a comparative study on the contribution of each process to OFX removal via to find the most effective system. According to the figure, the photolysis process was able to remove only 17.26% of the OFX, suggesting inefficiency of the visible light in dissociating OFX molecules. The degradation efficiency of OFX in the dark (i.e., the adsorption process) resulted in about 2.4 times higher performance than the blank test (i.e., the photolysis process). Furthermore, visible light irradiation significantly increased the efficiency of the system containing ZnFe–SO₄-LDH/GO photocatalyst, with which 71.19% of OFX was degraded within 150 min.

The synergistic effect of light and catalyst in the efficient dissociation of OFX was confirmed by comparing the efficiency of the processes and the corresponding decomposition rates. In addition to the involvement of photolysis and adsorption in the degradation process, the incident light provides considerable energy to the catalyst to generate reactive oxygen species (ROSs), resulting in the effective oxidation of OFX molecules.

Visible light irradiation triggers the transfer of excited electrons to the conduction band (CB), leaving h⁺ in the valence band (VB), in which photo-generated e⁻–h⁺ pairs move to the GO and react with O₂ and H₂O molecules to form *OH radicals and O₂⁻ radical anions, respectively [35]. The synergistic factor was assessed for the photocatalytic system of ZnFe–SO₄-LDH/GO/visible light using Eq. (3). The pseudo-first-order kinetic model (Eq. (4)) assessed the OFX removal rate via adsorption, photolysis, and photocatalysis processes, as well as corresponding reaction rates (kₚₛ). The calculated regression coefficients (R²) were close to one in all of the processes, indicating the ability of the pseudo-first-order kinetic model to characterize the process of OFX decomposition well.

\[
\text{Synergy index} = \frac{k_{\text{app, photolysis}}}{k_{\text{app, adsorption}} + k_{\text{app, photolysis}}} 
\]

\[
\ln \left( \frac{A_0}{A} \right) = k_{\text{app}}t 
\]

kₚₛ is the reaction rate (1/min), and A₀ and A are the initial and final absorbance of OFX at 0 and t min, respectively. A value of 1.81 was calculated for the synergy index of the photocatalytic process, which indicates intimate interaction between light and the catalyst for effective decomposition of OFX.

3.4. Effect of scavengers

Generally, ROSs act as the main contributors in the oxidation of target pollutant in photocatalytic reactions under visible light.
Fig. 9. Performance of different catalysts in the decomposition of OFX. (a) photocatalytic, (b) adsorption, (c) effect of ZnFe–SO₄–LDH/GO dosage ([OFX]₀ = 20 mg/L and pH = 8); (d) effect of OFX concentration ([ZnFe–SO₄–LDH/GO] = 1.5 g/L and pH = 8); (e) effect of initial pH of solution ([ZnFe–SO₄–LDH/GO] = 1.5 g/L and [OFX]₀ = 20 mg/L); (f) degradation potential of OFX by various systems ([OFX]₀ = 20 mg/L and pH = 8).
Fig. 10. Effect on the OFX degradation efficiency of different scavengers with molar ratios of (a) 1:1, (b) 1:10, and (c) 1:20. Experimental condition: [ZnFe-SO$_4$-LDH/GO] = 1.5 g/L, [OFX]$_0$ = 20 mg/L, and pH = 8.

ROS-trapping experiments were carried out by adding various scavengers to determine their roles in the photodegradation of OFX. 1,4-benzoquinone (BQ), isopropanol alcohol (IPA), and formic acid (FA) were employed as scavengers for $\cdot$OH, $\cdot$O, and h$^+$, respectively [35,70]. To evaluate the photocatalytic activity inhibition of individual compounds, their impacts were controlled without the use of scavengers. The presence of all scavengers reduced the photocatalytic activity of ZnFe-SO$_4$-LDH/GO, but the most noticeable outcomes were obtained with the use of $\cdot$OH and h$^+$ scavengers (Fig. 10(a)). A 10 to 20-fold increase in the amounts of scavengers greatly decreased the performance, as shown in Fig. 10(b) and (c). These observations confirm the roles of $\cdot$OH radicals and h$^+$ as the key species in OFX disintegration over photo-activated ZnFe-SO$_4$-LDH/GO photocatalyst. A second role was played by O$_2^-$ radicals as well.

3.5. Ofoxacin degradation intermediates

The by-products of OFX degradation through the photocatalytic process were identified by GC–MS. Table 5 lists eight compounds distinguished as intermediates. It was possible to assume the cleavage of C–O, C–N, and C–C bonds to be the early reaction stages leading to the destruction of some rings with the likely production of compounds such as six-membered aromatic rings containing N and O heteroatoms. There also might be other compounds resulting from OFX dissociation, which were not recognized prior to the formation of the detected compounds. Low-carbon-content aliphatics including acetimidic acid, malonic acid, acetic acid, and acetamide are generated by additional oxidation of these cyclic intermediates via cleavage of the rings by consecutive attacks of ROSs. Finally, partial mineralization of all these aliphatic compounds into H$_2$O, CO$_2$, and inorganic ions is plausible.

The formation of various intermediate compounds (e.g., carboxylic acids and amides) induces the mineralization of an organic contaminant containing N and S heteroatoms, which eventually transforms into CO$_2$, H$_2$O, and inorganic ions [71]. Accordingly, rising concentrations of inorganic ions along with a drop in COD concentration in the treated solution can be regarded as acceptable indices of contaminant mineralization [72]. At an OFX concentration of 20 mg/L with optimized parameters, the photocatalytic process
efficiency was tested by COD analyses [73]. The result was a COD degradation efficiency of 51.85% during 300 min of treatment.

In addition, concentrations of dissolved iron and zinc ions were measured with AAS to investigate the photocatalyst stability and whether the photocatalyst was dissolved in the solution phase or if it was stable under the experimental conditions. The concentrations of released iron and zinc were 0.43 mg/L and 1.19 mg/L, respectively. Since each experiment used a ZnFe–SO₄-LDH/GO photocatalyst concentration of 1.5 g/L, it can be concluded that the ZnFe–SO₄-LDH/GO could preserve the main parts of iron and zinc in its structure, and hence, the catalyst can be regarded as a stable catalyst.

3.6. Reaction mechanism of OFX degradation

Based on the findings, Fig. 11 displays the proposed detailed mechanisms of ZnFe–SO₄-LDH/GO photocatalyst for OFX degradation under visible light irradiation. Upon illumination with visible light, electrons (e⁻) in the VB of ZnFe–SO₄-LDH are rapidly induced to the CB with concurrent generation of holes (h⁺) in the VB. As a visible light-driven system, electron and hole pairs are formed in the as-synthesized photocatalyst. Overall, the ZnFe–SO₄-LDH and GO components had major contributions to the catalytically active ZnFe–SO₄-LDH/GO photocatalyst, in which electrons in the CB of ZnFe–SO₄-LDH are transferred to the CB of GO since the CB level of GO is lower than that of ZnFe–SO₄-LDH.

Moreover, the longevity of charge carriers was increased by the GO sheets by trapping the photo-driven electrons [35]. Subsequently, the formed electrons reduce the adsorbed O₂ molecules to extremely reactive superoxide radical anions (O₂⁻) and ·OH radicals, which in turn attack OFX molecules and destroy them. Furthermore, OFX can either be directly oxidized by the photoinduced holes, or the holes can produce ·OH radicals after reacting with water molecules. Ultimately, the reactive species react with OFX molecules to generate harmless molecules.

3.7. Reusability and stability of the ZnFe–SO₄-LDH/GO

The reusability of a photocatalyst in full-scale uses is among the important factors for long-term applications of the photocatalyst [55,74]. Photocorrosion within consecutive examinations typically reduces the photocatalytic performance of most photocatalysts. Accordingly, the reusability of ZnFe–SO₄-LDH/GO was examined using an OFX concentration of 20 mg/L and reaction time of 150 min. The loss in the OFX degradation efficiency following each run was evaluated through five consecutive experiments. As depicted in Fig. 12(a), the decrease in DE (%) of OFX was not significant after five cycles. The five cycles of photocatalysis with ZnFe–SO₄-LDH/GO photocatalyst yielded degradation efficiencies of 71.19%, 68.32%, 65.23%, 61.28%, and 58.21%, respectively, which clearly reveals the robustness of the photocatalyst for the degradation of the target pollutant from a water solution.

The nature of the recovered photocatalyst was also assessed. As depicted in Fig. 12(b) and (c), the XRD and FTIR results of the photocatalyst after the five cycles resemble those of the fresh photocatalyst. Such an outcome confirms there are no significant structural changes in the ZnFe–SO₄-LDH/GO photocatalyst and that it has suitable stability throughout the photocatalytic process. The iron and zinc released in the solution during OFX degradation were assessed as well. The insignificant amount of iron and zinc released indicate high physico-chemical durability of the ZnFe–SO₄-LDH/GO. The leached amounts of zinc and iron after 5 cycles (Table 6) were less than 0.068 mg/L and 0.184 mg/L, which are lower than the maximum acceptable iron (i.e., 0.3 mg/L) and zinc (i.e., 3 mg/L) concentrations in drinking water. This indicates that ZnFe–SO₄-LDH/GO does not cause secondary pollution.

### Table 5
Identified intermediates during degradation of OFX by photocatalytic process.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>tₑ (min)</th>
<th>Main fragments (<a href="%25">m/z</a>)</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetimidic acid</td>
<td>3.794</td>
<td>147.10 (100.00%), 75.10 (44.50%), 73.10 (33.21%), 116.10 (22.78%), 148.10 (18.26%)</td>
<td>![Structure of Acetimidic acid]</td>
</tr>
<tr>
<td>2</td>
<td>Butane-1,3-diol</td>
<td>4.005</td>
<td>75.10 (100.00%), 116.10 (66.67%), 147.10 (49.83%), 73.10 (15.27%), 76.10 (8.56%)</td>
<td>![Structure of Butane-1,3-diol]</td>
</tr>
<tr>
<td>3</td>
<td>Acetamide</td>
<td>4.149</td>
<td>75.10 (100.00%), 116.10 (69.07%), 147.10 (40.35%), 73.10 (14.92%), 76.10 (8.61%)</td>
<td>![Structure of Acetamide]</td>
</tr>
<tr>
<td>4</td>
<td>Acetic acid</td>
<td>4.293</td>
<td>75.10 (100.00%), 116.10 (70.44%), 147.10 (34.83%), 73.10 (14.57%), 76.10 (8.65%)</td>
<td>![Structure of Acetic acid]</td>
</tr>
<tr>
<td>5</td>
<td>Malonic acid</td>
<td>9.198</td>
<td>147.10 (100.00%), 75.00 (23.18%), 148.10 (18.38%), 70.10 (10.07%), 56.10 (9.91%)</td>
<td>![Structure of Malonic acid]</td>
</tr>
<tr>
<td>6</td>
<td>2-methyl-5-(prop-1-en-2-yl)cyclohex-2-one</td>
<td>10.074</td>
<td>82.10 (100.00%), 147.10 (78.63%), 75.00 (59.19%), 108.10 (42.97%), 93.10 (41.35%)</td>
<td>![Structure of 2-methyl-5-(prop-1-en-2-yl)cyclohex-2-one]</td>
</tr>
<tr>
<td>7</td>
<td>2,6-di-tert-butyl-4-methylphenol</td>
<td>16.400</td>
<td>205.20 (100.00%), 220.20 (31.12%), 206.20 (17.52%), 145.10 (9.30%), 147.10 (8.60%)</td>
<td>![Structure of 2,6-di-tert-butyl-4-methylphenol]</td>
</tr>
<tr>
<td>8</td>
<td>2-((2-ethylhexyl)oxy)carbonyl)benzoic acid</td>
<td>30.581</td>
<td>149.00 (100.00%), 167.00 (34.07%), 57.10 (14.28%), 279.20 (13.28%)</td>
<td>![Structure of 2-((2-ethylhexyl)oxy)carbonyl)benzoic acid]</td>
</tr>
</tbody>
</table>

*a* Value corresponding to the trimethylsilyl derivative.

*b* Value corresponding to the dimethylsilyl derivative.
Fig. 11. Illustration of photocatalytic reaction mechanism over ZnFe–SO₄-LDH/GO photocatalyst under visible light irradiation.

Fig. 12. (a) Reusability of ZnFe–SO₄-LDH/GO photocatalyst, (b) XRD, and (c) FTIR pattern of ZnFe–SO₄-LDH/GO before and after five photocatalytic experiments.
4. Conclusions

An efficient and simple chemical co-precipitation method was applied for the synthesis of three photocatalysts: ZnFe-CI-LDH, ZnFe–SO₄-LDH, ZnFe-CI-LDH-GO, and ZnFe–SO₄-LDH-GO. Comparison of the photocatalytic activity of the as-synthesized photocatalysts demonstrated the high performance (71.9%) of the ZnFe–SO₄-LDH-GO photocatalyst in the degradation of OFX molecules under visible light irradiation. Such a result was obtained with 150 min of visible light irradiation, 1.50 g/L of ZnFe–SO₄-LDH-GO, and an OFX initial concentration of 20 mg/L at pH 8. The high performance corresponds to the synergistic effect of the rapid separation rates of photo-generated electrons and extended longevity of the charge carriers caused by the formation of heterostructures between the pure ZnFe–SO₄-LDH and GO.

Furthermore, the addition of isopropanol, 1,4-benzoquinone, and formic acid scavengers decreased the performance of the system, particularly at an [OFX]:[scavenger] ratio of 1:20. According to the results of the scavengers, the •OH radicals and h⁺ were the main reactive species for OFX degradation. The reusability experiments showed that the reusable ZnFe–SO₄-LDH-GO photocatalyst provides effective wastewater treatment with low zinc and iron leaching. Based on the GC–MS results, OFX molecules are decomposable into a group of non-toxic by-products. Additionally, COD analysis confirmed the mineralization of OFX. Therefore, the present study provides new insights into the practical development of photocatalysts based on LDHs for the decomposition of pollutants under visible-light irradiation for wastewater remediation.

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Supplementary material


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