Zinc-chromium layered double hydroxides anchored on carbon nanotube and biochar for ultrasound-assisted photocatalysis of rifampicin

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A B S T R A C T

In this study, ZnCr layered double hydroxide (LDH), ZnCr LDH/carbon nanotube (CNT), and ZnCr LDH/Biochar (BC) were synthesized and characterized by various analyses. The successful synthesis and the great crystallinity of the samples were consented by XRD analysis. SEM and TEM were applied to study the morphology of the synthesized samples. The simultaneous presence of C, Zn, and Cr elements was well confirmed by EDX and dot mapping analyses demonstrating the successful preparation of nanocomposites. According to the BET analysis, ZnCr LDH nanocomposites with BC and CNT had more specific surface area compared to ZnCr LDH alone. The catalytic performances of the samples were determined for the degradation of rifampicin (RF). The degradation efficiency of the sonophotocatalytic process in the presence of 0.6 g L⁻¹ of ZnCr LDH/BC toward 15 mg L⁻¹ of RF under 150 W ultrasound and visible light irradiation was found to be about 100% within 40 min. The influence of the reactive species on the sonophotocatalytic process was assessed via the addition of different scavengers (para-benzoquinone (p-BQ), formic acid (FA), isopropyl alcohol (IPA)), and enhancers (hydrogen peroxide and potassium persulfate). The GC-MS analysis was carried out and eleven by-products during the RF decomposition were detected.

1. Introduction

Refractory organic compounds (ROCs) including pharmaceuticals, endocrine disruptors, pesticides, and so forth still frequently are used and discharged into the water which is capable of posing critical threats to human beings as well as the aquatic environment. With the extension of industrialization and urbanization, ROC-containing wastewaters have become a challenging issue worldwide during the recent decades [1,2]. Rifampicin (RF), a common and potent antibiotic mostly utilized to treat tuberculosis, has received extensive attention due to its poor biological stability, high solubility in water, and antimicrobial resistance. Besides, RF may trigger serious toxicity in humans and aquatic species if it discharges into surface and groundwater used for food production or drinking. As a result, providing a method for the disintegration of RF is considered essential to minimize the adverse risks on the ecosystem and human health [3].

Conventional treatment methods such as coagulation-sedimentation, adsorption, and biological techniques are widely used. Even so, the main bottlenecks that restrict the application of these techniques are inefficiency and high energy consumption [4]. As such, advanced oxidation processes (AOPs) that can provide remarkable degradation efficiency (DE%) are highly desired according to the generation of reactive oxygen species (ROSs). During the AOPs, refractory pollutants can be turned into none/low toxic small structures, or even simple compounds such as carbon dioxide and water [5,6]. The combinations of various AOPs have recently been applied, mainly to treat detrimental compounds from wastewater. It is noteworthy that, the DE% of organic compounds is promoted with the combination of ultrasonic (US) with light irradiation [7]. Hence, sonophotocatalysis can specifically manifest the high degradation of a broad domain of contaminants. The
ultrasonic process is accomplished based on the cavitation phenomenon, which includes the growth, nucleation, and collapse of the solution microbubble [8,9]. The cleavage of water and dissolved oxygen molecules to reactive radicals like 'OH and O$_2^-$ can cause the decomposition of organic pollutants [10].

Among heterogeneous catalysts, LDHs, as anionic clays appear more promising alternatives for environmental remediation [11]. LDHs are widely used as catalysts in wastewater treatment owing to some characteristics including layered and porous structures, high specific surface area, and interlayer anion mobility. What’s more, LDHs are a type of outstanding and broadly used adsorbent in wastewater treatment that can be used to eliminate a variety of substances including nitrate, phosphate, heavy metals, etc [12]. However, bare LDHs typically own low charge carrier mobility, which resulted in rapid electron-hole recombination and low quantum yield under light irradiations. In an attempt to solve this problem, various modifications, like doping and combination with diverse semiconducting, magnetic, and carbonaceous materials are used. In this way, LDH-based nanocomposites can play a decisive role in the treatment processes as an eminent catalyst according to high stability, conductivity, and catalytic performances [13,14].

Nowadays, studies are reported with literature describing the extensive application of carbon-enriched materials in environmental remediation processes [15-17]. BC can be attained from diverse natural or waste sources under restricted oxygen conditions and exhibits tremendous potential for nanocomposite synthesis owing to its significant features including enriched surface functional groups, high porosity, and high surface area [18,19]. Recent research has revealed that biochar (BC) is more than just an adsorbent; it is also a catalytically active material capable of participating in electron transfer and redox reactions due to its abundance of redox-active moieties [20]. Ye et al. [21] deduced that the catalytic performance of CoFe-LDH@BC was more than CoFe-LDH and BC, which can be related to the redox-active moieties from BC and the electron transferability. As another carbon-based material, carbon nanotubes (CNTs) demonstrate significant thermal and electrical conductivity, which can reinforce the charge mobility of the composites [22].

To date, existing kinds of literature still lack a comprehensive application of CNT or BC-based ZnCr LDH in the sonophotocatalytic processes. In the present study, ZnCr LDH was prepared via the co-precipitation method and then the CNT/BC-based composites were synthesized. To shed light on the characterization of the catalysts, X-ray diffraction (XRD), Fourier transform infrared spectrometer (FTIR), scanning electron microscope (SEM), energy dispersive X-Ray (EDX), Brunauer–Emmett–Teller (BET), elemental dot mapping, transmission electron microscope (TEM), and differential reflectance spectroscopy (DRS) analyses were carried out. Then the corresponding influencing factors on the sonophotocatalytic process for the decomposition of RF molecules in the presence of the optimum catalyst (ZnCr LDH/BC nanocomposite) were thoroughly examined. Also, attempts were made to delineate the role of the ROSs and a plausible mechanism for the degradation of RF in the presence of different scavengers, photoluminescence (PL), and GC–MS analyses, respectively. Interestingly, the present work provides a new viewpoint and theoretical support for using ZnCr LDH/BC as an efficient sonophotocatalyst for the degradation of hazardous contaminants.

2. Materials and methods

2.1. Chemical agents

Hydrochloric acid (38%) was purchased from Royalex (India). Chromium (III) nitrate nonahydrate, zinc nitrate hexahydrate, sodium hydroxide pellets, hydrogen peroxide (30%), potassium peroxydisulfate, formic acid (FA), parabenzquinonone (p-BQ), and isopropanol (IPA) were procured from Merck (Germany). Biochar was synthesized by flame curtain pyrolysis of pine-tree (Pinus halepensis) which was described in a study conducted by Cornelissen et al. [23]. MWCNT was supplied from Cheap Tubes (USA). RF was obtained from Kocak Farma Pharmaceutical and Chemical Industry Co. (Turkey).

2.2. Synthesis methods

2.2.1. The synthesis of ZnCr LDH, ZnCr LDH/BC, and ZnCr LDH/CNT

ZnCr LDH was prepared by the simple co-precipitation method, as mentioned in our previous paper [24]. Firstly, 7.85 g of Zn(NO$_3$)$_2$·6H$_2$O and 4.57 g of Cr(NO$_3$)$_3$·9H$_2$O were dissolved in deionized water. Dropwise additions of NaOH were made to the resultant solution under argon atmosphere and stirring to attain the pH of 9. The obtained suspension was then agitated for another 24 h at ambient temperature. The powder of the synthesized ZnCr LDH was collected using the centrifuge at 25000 rpm for about 5 min. Then, the gathered powder was washed with deionized water and dried. Finally, about 3.5 g of ZnCr LDH powder was achieved in each synthesis.

Ultrasonically dispersed BC solution was prepared by the dilution of 0.08 g BC in 10 mL distilled water. The pH of the solution containing Zn(NO$_3$)$_2$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O was raised to 9 by adding NaOH solution (2 mol L$^{-1}$). The BC solution was added and agitated for another 30 min before being moved to a Teflon-lined stainless-steel autoclave. The autoclave was put in a pre-heated oven at 90 °C for 24 h. Synthesized ZnCr LDH/BC nanocomposite was collected using the centrifuge at 25000 rpm for about 5 min. The sediment was rinsed with deionized water and dried for 18 h in a 60 °C oven. Finally, about 4.5 g of ZnCr LDH/BC nanocomposite was obtained. It should be noted that the molar ratio of BC/ZnCr LDH is about 1:150.

For the modification of CNT, initially, CNT was refluxed in a round bottom flask for 6 h with concentrated nitric acid and the modified CNT was filtered and washed until the pH level reached 7. The obtained sediment was dried at 60 °C for 24 h. A similar trend was followed for the preparation of ZnCr LDH/CNT with the addition of modified CNT instead of BC dispersion along with Zn(NO$_3$)$_2$·6H$_2$O and Cr(NO$_3$)$_3$·9H$_2$O solutions. In the end, approximately 4.5 g of ZnCr LDH/CNT was collected. Moreover, the molar ratio of CNT/ZnCr LDH is about 1:150.

2.3. Characterisation methods

To record the XRD patterns of the catalysts, D8 Advance, Bruker (Germany) apparatus with monochromatic high-intensity Cu Kα radiation (l = 1.5406 nm), an accelerating voltage of 45 kV, and an emission current of 40 mA was applied. The functional groups of synthesized samples were analyzed with a Bruker FT-IR model Tensor 27 (Germany). The SEM, EDX, and TEM images of the synthesized samples were detected on the Tescan apparatus with a model of MIRA 3 (Czech Republic) and JEOL JEM-2100 apparatus acting at 200 kV (Japan), respectively. In addition, the N$_2$ adsorption/desorption isotherms of the prepared materials were determined using the Micromeritics instrument (Gemini VII (USA)). DRS UV–Vis spectra of the synthesized materials were determined using Analytik Jena spectrophotometers model S 250 (Germany). The PL spectra were recorded by a Perkin Elmer spectrometer with the model LS45 (USA). Gas chromatography-mass spectrometry (GC-MS) analysis was accomplished with Agilent 6890 gas chromatograph along with an Agilent 5973 mass spectrometer (Agilent Technologies, Palo Alto, Canada).

2.4. Hydroxyl radical recognition

The PL method was used to detect the hydroxyl radicals produced during the sonophotocatalytic process. For this purpose, the specific quantity of catalyst was added to 100 mL of a terephthalic acid solution containing 5 × 10$^{-7}$ mol L$^{-1}$ of terephthalic acid and 2 × 10$^{-3}$ mol L$^{-1}$ of NaOH. The obtained suspension was subjected to ultrasonic irradiation and visible light, and a certain volume of the solution was withdrawn at predetermined times.
2.5. Sonophotocatalytic tests

An ultrasonic bath (150 W, 36 kHz, Ultra 8060, England) and a light-emitting diode (LED, 30 W lamp were used to study the sonophotocatalytic destruction of RF molecules. Actually, the RF solution was subjected to solely light irradiation and ultrasound in the case of photolysis and sonolysis, respectively. At 10-minute intervals, the residual concentration of RF has been examined via sampling and
filtering about 3 mL of solution. Philler Scientific UV–Vis spectrophotometer with the model of SU-6100 (USA) was used to analyze the concentration of RF at \( \lambda_{\text{max}} = 334.5 \) nm.

3. Results and discussion

3.1. Characterization of ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC

The crystalline structure of ZnCr LDH/CNT and ZnCr LDH/BC was assessed using XRD analysis, and the patterns are shown in Fig. 1a. The characteristic bands at 2\( \theta \) of 10.1°, 20.0°, 32.5°, 34°, 39.5°, 48.5°, and 60.6° refer to the 003, 006, 101, 012, 015, 018, and 110 reflection planes of ZnCr LDH, respectively (JCPDS standard card 51–1525) [24]. The presence of the aforementioned characteristic bands in XRD patterns of ZnCr LDH/CNT and ZnCr LDH/BC confirms the successful synthesis of ZnCr LDH in the presence of CNT and BC. Considering that the amount of the CNT and BC is much lower than ZnCr LDH in the nanocomposites, the characteristic bands of CNT and biochar have not appeared in XRD patterns.

The FT-IR spectra of the prepared ZnCr LDH, ZnCrLDH/CNT, and ZnCr LDH/BC are shown in Fig. 1b. Some characteristic bands can be seen in wavenumber ranging from 400 to 800 cm\(^{-1}\) which can be assigned to the vibration of metal–oxygen (M–O) and metal-hydroxide (M–OH) bonds [25]. The bands recorded at about 1380 cm\(^{-1}\) and 2430 cm\(^{-1}\) can be attributed to the interlayer nitrate anions [26]. Owing to the stretching and bending vibration of O–H bonds in LDH lattice and adsorbed water molecule, two bands were detected at 3454 cm\(^{-1}\) and 1630 cm\(^{-1}\), respectively.

The morphology of the prepared ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC was assessed using SEM analysis. As can be seen in Fig. 2a and b, the ZnCr LDH has been synthesized in layered morphology with an average width of 20 nm. Figs. S1a and b demonstrate tubular and honeycomb structures of the pure CNT and BC, respectively. In SEM images represented in Fig. 2d and e, the CNTs with tubular morphology can be seen along with the layers of ZnCr LDH, confirming the successful preparation of ZnCr LDH/CNT nanocomposite. Moreover, the formation of ZnCr LDH layers on the surface and inside the pores of the BC can be observed in the SEM images of ZnCr LDH/BC nanocomposite shown in Fig. 2g and h.

Further investigation on the morphology of the prepared ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC was carried out by TEM analysis. The sheets of the ZnCr LDH can be seen in Fig. 2c, confirming the layered
The morphology of the synthesized LDH. In the TEM image of ZnCr LDH/CNT shown in Fig. 2f, the simultaneous presence of tubular CNTs and layered LDH is clear evidence of successful synthesis of the nanocomposite. Moreover, the formation of the LDH with layered morphology on the BC can be observed in Fig. 2i.

The EDX spectra and elemental dot mapping images of the ZnCr LDH nanocomposites with CNT and BC are represented in Fig. 3. The simultaneous presence of C, Zn, and Cr elemental peaks in EDX spectra of ZnCr LDH/CNT and ZnCr LDH/BC demonstrates the successful synthesis of these nanocomposites. The uniform hybridizing of the component of the nanocomposite is a key factor affecting its properties and activity. Homogeneous distribution of the elements without any agglomeration can be seen in EDX dot mapping images of the nanocomposites. This confirms the uniform hybridizing of ZnCr LDH layers with CNT and BC in ZnCr LDH/CNT and ZnCr LDH/BC nanocomposites, respectively.

The N\textsubscript{2} adsorption–desorption isotherms of the prepared samples were obtained to study the specific surface area (Fig. 4a-c). According to IUPAC classification, the isotherm type IV was detected for ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC, establishing the mesoporous nature of the synthesized materials [27]. Also, similar studies reported isotherm type IV for the ZnCr LDH [28,29]. The BET surface area of 1.2 m\textsuperscript{2} g\textsuperscript{-1} was obtained for ZnCr LDH which increased to 5.0 m\textsuperscript{2} g\textsuperscript{-1} and 7.0 m\textsuperscript{2} g\textsuperscript{-1} via hybridizing with CNT and BC, respectively.

The bandgaps of the prepared samples were determined as 2.46, 2.22, and 1.60 eV, respectively, using UV–Vis DRS analysis. For this purpose, the linear area in the curve of (αhv\textsuperscript{2}) versus hv was extrapolated, where α, h, and v are absorbance coefficient, Plank constant, and light frequency, respectively (Fig. 4d–f) [30,31]. As shown, the hybridizing of ZnCr LDH with CNT and BC decreased its band gap value, accelerating the production of electron-hole pairs under ultrasonic irradiation and light source.

The PL spectra of the prepared samples were recorded at the excitation wavelength of 390 nm, and the results are shown in Fig. S2a. As can be observed in recorded spectra, the PL intensity of the ZnCr LDH weakened via hybridizing with the CNT and BC, indicating that the sonophoto-induced electron-hole pairs can be efficiently separated in the presence of carbonous materials. As can be seen, the electron-hole pairs can be separated more efficiently in ZnCr LDH/BC nanocomposite compared with ZnCr LDH/CNT nanocomposite. Therefore, higher sonophotocatalytic activity is expected for ZnCr LDH/BC nanocomposite. In addition, the PL analysis was applied to evaluate the hydroxyl radical’s production during the sonophotocatalytic process (Fig. S2b). For this purpose terephthalic acid was used as a fluorescence probe. More intensive PL spectrum was detected for 40 min compared with 20 min of reaction time, demonstrating that the hydroxyl radicals increased via time passing during the sonophotocatalytic process. Our obtained results are in good consistency with the outcomes reported in the other papers [13].

3.2. The sonophotocatalytic destruction of RF

3.2.1. Effect of diverse processes on the degradation efficiency of RF

The effects of ZnCr LDH and its nanocomposites on the degradation efficiency of RF through diverse processes were studied (Fig. 5). Initially, the degradation efficiencies of RF (15 mg L\textsuperscript{-1}) in the absence of the catalysts and via photolysis, sonolysis, and sonophotolysis were evaluated. According to the findings in Fig. 5a, the lowest DE% (about 15% within 40 min) belongs to the photolysis, confirming that the RF molecules have a resistant chemical structure. By transferring the ultrasound through the water, bubbles form, grow, and eventually collapse, resulting in the formation of high-temperature reaction sites (~5000 K) and high pressure (~1000 atm), named as hot spots [32,33]. Through the pyrolysis of water molecules in hot spot regions during sonolysis, hydrogen and hydroxyl radicals can be generated, resulting in the increment of DE% up to 26% within 40 min (Eq. (1)). Only 33% of the RF was degraded via sonophotolysis when visible light and ultrasound irradiation were used simultaneously, which can be attributed to insufficient hydroxyl radical generation.
Fig. 5. The comparison of the DE% of RF via diverse processes (a) in the absence of catalyst, (b) in the presence of ZnCr LDH, (c) in the presence of ZnCr LDH/CNT, (d) in the presence of ZnCr LDH/BC, and (e) the probable mechanism involved in the sonophotocatalytic degradation of RF by ZnCr LDH/BC. (Experimental condition: [RF]₀ = 15 mg L⁻¹, [catalyst] = 0.6 g L⁻¹, power of ultrasonic = 150 W, pH = 8, and under visible light).
Table 1
Comparing the catalytic activity of ZnCr LDH/BC with different catalysts during various AOPs for 40 min.

| Catalyst       | AOP               | Pollutant                  | Parameters                                                                 | DE (%) | Refs. |
|----------------|-------------------|----------------------------|---------------------------------------------------------------------------|--------|-------|
| NiAl LDH       | Catalytic ozonation | Methyl orange             | [pollutant] = 500 mg L$^{-1}$, [catalyst] = 1 g L$^{-1}$, ozone flow rate = 109 mg h$^{-1}$. | -85    | [36]  |
| ZnO            | Sonophotocatalysis | Methyl orange             | [pollutant] = 50 mg L$^{-1}$, [catalyst] = 0.1 g L$^{-1}$, light source = 300 W, ultrasonic power = 200 W. | -42    | [37]  |
| ZnCr LDH       | Photocatalysis     | Rhodamine B, Rhodamine 6G, 4-chloro 2-nitro, phenol | [pollutant] = 100 mg L$^{-1}$, [catalyst] = 1 g L$^{-1}$, light source = visible light. | -57    | [38]  |
| WS$_2$         | Sonocatalysis      | Methylene blue            | [pollutant] = 10 mg L$^{-1}$, [catalyst] = 1 g L$^{-1}$, ultrasonic power = 250 W. | -30    |       |
| FeAl LDH/ Hydrochar | Photocatalysis   | Diethyl phthalate         | [pollutant] = 20 mg L$^{-1}$, [catalyst] = 1 g L$^{-1}$, light source = 500 W Xenon lamp. | -25    | [40]  |
| ZnCr LDH/BC    | Sonophotocatalysis | Rifampicin                | [pollutant] = 15 mg L$^{-1}$, [catalyst] = 0.6 g L$^{-1}$, light source = visible light, ultrasonic power = 150 W. | 98     | Present study |

Fig. 6. The impact of (a) RF concentration, (b) ZnCr LDH/BC dosage, (c) power of ultrasonic, (d) pH, and (e) determination of pH$_{pzc}$ (Experimental condition: [ZnCr LDH/BC] = 0.6 g L$^{-1}$, [RF]$_0$ = 15 mg L$^{-1}$, power of ultrasonic = 150 W, pH = 8, and under visible light).
H₂O + Ultrasonic waves → OH + H

Afterward, the adsorption, photocatalysis, sonocatalysis, and sonophotocatalytic activities of the ZnCr LDH and its nanocomposites for the decomposition of RF were evaluated and the obtained outcomes are reported in Fig. 5b–d. During 40 min, the adsorption of the RF molecules was negligible by ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC. Based on the previously-reported results, the hollow and layered structure of CNTs endows large surface area as well as high sorption potentials for different contaminants [34]. So, ZnCr LDH/BC owns high DE% through the adsorption process compared to the other nanocomposites.

The photocatalytic properties of the synthesized samples were studied as illustrated in Fig. 5b–d. Amongst, superior photocatalytic activity belongs to the ZnCr LDH/BC, according to the low bandgap energy (1.60 eV) which can facilitate the electron transfer from the valence band to the conduction band. These electrons can react with molecules of oxygen to generate hydroxyl radicals (Eqs. (2)–(4)). Moreover, produced holes can be reacted with water molecules which resulted in the generation of excess amounts of hydroxyl radicals (Eq. (5)). On the other hand, electron-hole recombination can be prevented by the usage of carbon-based materials. Besides, the nanosheet aggregation of ZnCr LDH will be hindered in the presence of BC and CNT. The probable catalytic mechanism was depicted in Fig. 5e.

\[
\begin{align*}
O_2 + \text{electron} & \rightarrow O_2^- \quad (2) \\
2H^+ + 2O_2^- & \rightarrow O_2 + H_2O_2 \quad (3) \\
H_2O_2 + \text{electron} & \rightarrow \text{OH} + \text{OH}^- \quad (4) \\
\text{Holes} + H_2O & \rightarrow H^+ + \cdot OH \quad (5)
\end{align*}
\]

While the sonocatalytic process, the DE% of RF was increased from 37.4% to 61.2% and 81.2% in the presence of ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC, respectively. It was proved that utilizing heterogeneous catalysts can boost DE% through improving the generation of cavitation bubbles as well as contributing a large number of nuclei which results in the high generation of hydroxyl radicals. According to the possible sonoemulsion mechanism, electron-hole pairs can be created via the emission of ultrasonic waves, too (Eq. (6)). Furthermore, the increment in the DE% during sonocatalysis may be assigned to the high amounts of ROSs, cleansing influence of sonication on the composite surface, high mass transportability among the reaction media/catalyst surface, and catalyst aggregation prevention by ultrasonic waves which eventuate in the augmentation of the accessible active sites [35].

\[
\text{ZnCr LDH} \xrightarrow{\text{US}} \text{ZnCr LDH} (\text{electron} + \cdot H^+) \quad (6)
\]

The sonophotocatalytic activities of prepared nanocomposites were evaluated under ultrasound and light irradiation. The degradation efficiency was promoted from 66.3% to 77% and 98% within the insertion of ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC, respectively to the reaction media during 40 min, and the outcomes are displayed in Fig. 5b–d. Moreover, the synergy factor (SF) was calculated as 1.44, 1.19, and 2.08 for ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC, respectively by Eq. (7) which, unveiled the effective interaction of catalyst, light, and ultrasound irradiation for powerful degradation. In Eq. (7), \( k_{\text{app} (\text{vis})} \), \( k_{\text{app} (\text{US})} \), and \( k_{\text{app} (\text{vis-US})} \) are the rate constants of photocatalysis, sonocatalysis, and sonophotocatalysis, respectively. The presented degradation efficiency compared with similar studies, which have evaluated the efficiencies of diverse AOPs in the presence of carbon-based LDHs for the decomposition of various pollutants (Table 1). The outcomes indicated that the ZnCr LDH/BC nanocomposite has high catalytic potential for the degradation of antibiotics. Subsequently, ZnCr LDH/BC was chosen as the optimum sonophotocatalyst for the decomposition of RF during 40 min, complementary experiments were performed to specify the operational parameters.

\[
\text{SF} = \frac{k_{\text{app} (\text{vis-US})}}{k_{\text{app} (\text{vis})} + k_{\text{app} (\text{US})}} \quad (7)
\]

### 3.2.2. Effect of RF concentration

The impact of RF concentrations in the range of 10–30 mg L\(^{-1}\) on the DE% was investigated, as represented in Fig. 6a. Under sonophotocatalysis, the DE% was lowered from 98.9% to 53.5% by increasing the RF concentration from 10 to 30 mg L\(^{-1}\) within 40 min. This could be attributed to the occupancy of the catalyst’s active sites with RF molecules, inhibiting the absorption of generated energy and heat from bursting the cavitation bubbles. Furthermore, excessive levels of the RF molecules prevent light from penetrating the solution media and reaching the catalyst surface, resulting in a reduction in DE%. Owing to the limited amount of ROSs generated at the constant light intensity, ultrasonic power, time, and catalyst dosage, competition among the RF molecules and the produced intermediates occurs, which is another reason for the decrement of DE%. Also, other studies have reported similar behavior [13,41].

### 3.2.3. Effect of the amount of catalyst

Fig. 6b depicts the influence of ZnCr LDH/BC dosage on the sonophotocatalytic degradation of RF. The DE% raised from 35.5% to 98% by enhancing the catalyst concentration from 0.2 to 0.6 g L\(^{-1}\). This can be attributed to the generation of the high quantities of reactive species including ‘OH, O\(_2\)\(^{-}\), and holes that participate in the degradation process. However, at dosages greater than 0.6 g L\(^{-1}\), the DE% represented a significant decrease, which can be attributed to the catalyst accumulation, which results in a decrease in active sites and generated ROSs. Furthermore, an increase in catalyst concentration may inhibit heat and energy conduction near the catalyst surface [42]. Accordingly, additional tests were performed with 0.6 g L\(^{-1}\) of catalyst as optimum dosage.

### 3.2.4. Power of ultrasonic irradiation

Exploring the effect of ultrasonic power on DE% of RF during sonophotocatalysis is important according to the alterations in the number of active cavitation bubbles. Hence, the influences of 150, 200, and 300 W ultrasonic power on the decomposition of 15 mg L\(^{-1}\) of RF at pH 8 and ZnCr LDH/BC dosage of 0.6 g L\(^{-1}\) were assessed (Fig. 6c). Raising the ultrasonic power to 300 W may lead to a high generation of cavitation bubbles, enhancing the system turbulence, improving the mass transfer rate of RF to the catalyst surface, and finally the cleansing effect of US irradiations on the catalyst active sites [43]. The reason for selecting the 150 W as the optimum ultrasonic power was reducing the cost of energy consumption and also there wasn’t any remarkable difference among the DE% when using 150, 200, and 300 W.

### 3.2.5. Initial pH

Generally, the performance efficacy of the sonophotocatalytic process is greatly affected by pH alterations [44]. As a result, the influence of pH on the DE% of RF in the range of 4–12 was evaluated and illustrated in Fig. 6d. The obtained results represented that the DE% decreased above and below the pH = 8 (the natural pH of RF). Hence, the pH at the point of zero charge (pH\(_{\text{pzc}}\)) was calculated to interpret this trend (Fig. 6e). A pH\(_{\text{pzc}}\) of 4.96 was obtained in which the surface of the catalyst is negatively charged at 4.96 < pH and a positive charge at pH < 4.96. Moreover, the reported pK\(_a\) for RF is 7.9 indicating that the RF molecules have negative charges at pH > 7.9 and have positive charges at pH < 7.9. So, as a result of the proper absorption of RF molecules on the ZnCr LDH/BC surface, the pH = 6 and pH = 8 indicated a high DE%. In acidic and basic pHs, electrostatic repulsion prevents RF adsorption on the catalyst, resulting in a decrease in DE%.
3.2.6. Main species involved in sonophotocatalysis: The effects of scavengers and enhancers

ROSs are primarily regarded as prominent contributors to the degradation of refractory pollutants through AOPs. In this case, experiments to trap ROSs were carried out by adding diverse scavengers including \(\text{p-BQ}, \text{FA}, \text{IPA}\), and others. Thus, \(\text{p-BQ}, \text{FA}, \text{IPA}\) were added to assess the presence of superoxide anion radicals, holes, and hydroxyl radicals, in that order (Fig. S3a). The DE% was reduced from 98% to 61.4%, 50.6%, and 27% by the addition of \(\text{p-BQ}, \text{FA}, \text{IPA}\), respectively. According to the decrement by applying IPA, it is obvious that hydroxyl radicals play a significant role in RF disintegration during sonophotocatalysis. A second role was played by generated holes as well. Also, superoxide radicals have some positive effects on increasing DE% during sonophotocatalysis, too.

Oxidant species such as hydrogen peroxide (\(\text{H}_2\text{O}_2\)) and potassium persulfate (\(\text{K}_2\text{S}_2\text{O}_8\)) can accelerate the decomposition processes through the generation of excessive amounts of free radicals [45]. Hence, the effects of \(\text{K}_2\text{S}_2\text{O}_8\) and \(\text{H}_2\text{O}_2\) were evaluated and the results are represented in Fig. S3b. Considering the high rate of the processes in the presence of enhancers, reaction time was reduced to 20 min to proper evaluation. The DE% improved from 80% in the absence of an enhancer to 87.5% and 98% in the presence of \(\text{H}_2\text{O}_2\) and \(\text{K}_2\text{S}_2\text{O}_8\), respectively. Evidently, the observed improvement in DE% can be attributed to the production of hydroxyl radicals as a result of the reaction among \(\text{H}_2\text{O}_2\), ultrasound waves, and light irradiation (Eqs. (8) and (9)).

\[
\text{H}_2\text{O}_2 \xrightarrow{\text{US}} 2 \text{OH} \quad (8)
\]

\[
\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{OH} + \text{H}_2\text{O} \quad (9)
\]

Similarly, by subjecting persulfate ions to ultrasound cavitation, sulfate radicals (\(\text{SO}_4^{2-}\)) can be yielded (Eq. (10)). The RF molecules can be disintegrated to form simple-structured intermediates as shown in Eq. (11).

| No. | Compound Names | Structures | \(t_0\)(min) | Main fragments (m/z)(percent) |
|-----|---------------|------------|--------------|-------------------------------|
| 1   | Acetamide     | \(\text{H}_2\text{N} = \text{O}\) | 2.396 | 130.10 (100.00%), (73.10 68.12%), 75.10 (18.21%), 59.10 (17.12%), 145.10 (16.98%) |
| 2   | 1,3-Pentadiene| \(=\text{H} \quad \text{H}\) | 3.583 | 141.10 (100.00%), 75.00 (87.78%), 73.10 (24.86%), 99.00 (24.51%), 156.10 (12.22%) |
| 3   | Acetic acid   | \(\text{H}_3\text{C} = \text{O}\) | 3.927 | 75.10 (100.00%), 116.10 (95.77%), 73.10 (14.58%), 117.10 (12.76%), 76.10 (10.62%) |
| 4   | Ethanimidic acid| \(\text{H}_3\text{C} = \text{O}\) | 4.338 | 147.10 (100.00%), 73.10 (69.55%), 203.10 (44.63%), 148.10 (40.81%), 188.10 (24.57%) |
| 5   | Ethylamine    | \(\text{H}_3\text{C} = \text{NH}_2\) | 4.404 | 174.10 (100.00%), 100.10 (85.56%), 73.10 (70.12%), 147.10 (53.71%), 75.00 (50.29%) |
| 6   | Propionic acid| \(\text{H}_3\text{C} = \text{O}\) | 4.482 | 75.10 (100.00%), 73.10 (67.67%), 144.10 (55.49%), 116.10 (45.75%), 147.10 (43.46%) |
| 7   | Butanoic acid | \(\text{H}_3\text{C} = \text{OH}\) | 4.815 | 115.10 (100.00%), 75.10 (96.99%), 159.10 (58.10%), 73.00 (52.83%), 116.10 (40.27%) |
| 8   | Pentanoic acid| \(\text{H}_3\text{C} = \text{OH}\) | 4.815 | 115.10 (100.00%), 75.10 (96.99%), 159.10 (58.10%), 73.00 (52.83%), 116.10 (40.27%) |
| 9   | Pentane       | \(\text{H}_3\text{C} = \text{OH}\) | 5.991 | 115.10 (100.00%), 75.10 (85.24%), 73.10 (56.43%), 131.00 (41.95%), 86.10 (34.54%) |
| 10  | Phenol        | \(\text{H}_3\text{C} = \text{OH}\) | 17.465 | 205.20 (100.00%), 293.20 (52.90%), 251.10 (29.10%), 73.10 (28.82%), 252.10 (27.71%) |
| 11  | Benzene       | \(\text{H}_3\text{C} = \text{OH}\) | 36.318 | 207.00 (100.00%), 281.00 (44.66%), 55.10 (41.37%), 57.10 (41.36%), 69.10 (32.75%) |

Table 2
Identified intermediates via the decomposition of RF. (\([\text{RF}]_0 = 15 \text{mg L}^{-1}, [\text{ZnCr LDH/BC}] = 0.6 \text{g L}^{-1}, \text{pH} = 8\), under visible light, and ultrasonic power = 150 W.)
40 min. Furthermore, the synergy factor of 2.08 confirmed the effective interaction of photocatalysis and sonocatalysis in the presence of ZnCr LDH/BC. The strategic role of BC as a charge separator that provided the weakest bonds e.g. N-C, C→O, and so on. Consequently, acids can be converted to CO2, H2O, and so on.

\[ \text{SO}_4^{2-} + \text{RF} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{intermediates} \]  
\[ \text{S}_2\text{O}_8^{2-} \rightarrow \text{2SO}_4^{2-} \] (10) (11)

3.2.7. Reusability and stability of ZnCr LDH/BC

The stability and durability of the catalysts are regarded as the most important parameters for long-term applications from the economic and environmental viewpoint. In this study, 0.6 g L⁻¹ of ZnCr LDH/BC was reused during four successive tests, and the DE% during sonophotocatalysis was determined. For this, ZnCr LDH/BC was separated after each test, rinsed, dried, and applied in the subsequent runs. As depicted in Fig. S4, the DE% decrement was not significant (about 19%) following four cycles. This apparently revealed the robustness of ZnCr LDH/BC for the disintegration of similar refractory organic contaminants.

3.3. Mineralisation and generated intermediates

GC-MS analysis was used to further investigate the sonophotocatalytic ability of ZnCr LDH/BC and propose a possible mechanism to recognize the generated by-products encompass sonophotocatalysis. In the present study, eleven main molecules were explored and the retention time (tR), the chemical structure of the fragments (m/z), and the relative percentages are shown in Table. 2. Accordingly, a plausible mechanism for the decomposition of RF during sonophotocatalysis was postulated (Fig. 7b). Obviously, some intermediates may be missed owing to the fast oxidation. Based on the discovered mechanism, the weakest bonds e.g. N-C, C = C, N-CH3, etc. are vulnerable to ROSs attacks. Subsequent reactions may result in opening up aromatic rings and oxidizing –CH3 to –COOH groups. Ultimately, acids can be converted to simple organic compounds which may be altered to CO2, H2O, and so on.

4. Conclusion

Successful preparation of the ZnCr LDH, ZnCr LDH/CNT, and ZnCr LDH/BC was developed and diverse analyses were operated to characterize the resulting samples. The XRD analysis confirmed the proper synthesis of the carbon-based nanocomposites of the ZnCr LDH. The observation of layered ZnCr LDH along with the tubular CNTs and porous BC in SEM and TEM images revealed the successful preparation of ZnCr LDH/CNT and ZnCr LDH/BC nanocomposites. Moreover, homogeneous distribution of the Zn, Cr, and C was seen in the EDX dot mapping images of ZnCr LDH/CNT and ZnCr LDH/BC nanocomposites, manifesting the uniform hybridizing of the components.

Then, the sonophotocatalytic properties of the samples were evaluated for the disintegration of RF. ZnCr LDH/BC with the dosage of 0.6 g L⁻¹ illustrated the exceptional activity (DE% = 98%) toward 15 mg L⁻¹ of RF, pH of 8, ultrasonic power of 150 W, and under visible light within 40 min. Furthermore, the synergy factor of 2.08 confirmed the effective interaction of photocatalysis and sonocatalysis in the presence of ZnCr LDH/BC. The strategic role of BC as a charge separator that provided favorable reaction sites can be regarded as the dominant reason for the increase in DE%. Among various scavengers, IPA significantly decreases the DE%, manifesting a greater contribution of hydroxyl radicals in the decomposition of RF. Interestingly, according to the reusability tests, ZnCr LDH/BC can be introduced as a stable and cost-effective catalyst. Eventually, the current research introduced the carbon-based ZnCr LDHs as sonophotocatalysts capable of decomposing refractory pollutants in mild conditions. Additional researches on the roadmap of sonophotocatalytic properties of carbon-based LDH nanocomposites is required for environmental remediation.

CRediT authorship contribution statement

Tannaz Sadeghi Rad: Writing – original draft. Alireza Khataee: Supervision, Writing – review & editing. Samin Sadeghi Rad: Writing – original draft. Samira Arefi-Oskoui: Writing – original draft. Erhan Gencge: Resources, Investigation, Validation. Mehmet Kobya: Resources, Investigation, Validation. Yejoon Yoon: Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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