Application of CoMn/CoFe layered double hydroxide based on metal–organic frameworks template to activate peroxymonosulfate for 2,4-dichlorophenol degradation

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ABSTRACT
Metal–organic frameworks (MOFs) have unique properties and stable structures, which have been widely used as templates/precursors to prepare well developed pore structure and high specific surface area materials. In this article, an innovative and facile method of crystal reorganization was designed by using MOFs as sacrificial templates to prepare a layered double hydroxide (LDH) nano-layer sheet structure through a pseudomorphic conversion process under alkaline conditions. The obtained CoMn-LDH and CoFe-LDH catalysts broke the ligand of MOFs and reorganized the structure on the basis of retaining a high specific surface area and a large number of pores, which had higher specific surface area and well developed pore structure compared with LDH catalysts prepared by traditional methods, and thus provide more active sites to activate peroxymonosulfate (PMS). Due to the unique framework structure of MOFs, the MOF-derived CoMn-LDH and CoFe-LDH catalysts could provide more active sites to activate PMS, and achieve a 2,4-dichlorophenol degradation of 99.3% and 99.2% within 20 minutes, respectively. In addition the two LDH catalysts displayed excellent degradation performance for bisphenol A, ciprofloxacin and 2,4-dichlorophenoxyacetic acid (2,4-D). X-ray photoelectron spectroscopy indicated that the valence state transformation of metal elements participated in PMS activation. Electron paramagnetic resonance manifested that sulfate radical (SO\textsuperscript{\cdot}\textsuperscript{-}/CO\textsuperscript{4}) and singlet oxygen (\textsuperscript{1}O\textsubscript{2}) were the main species for degrading pollutants. In addition, after the three-cycle experiment, the CoMn-LDH and CoFe-LDH catalysts also showed long-term stability with a slight activity decrease in the third cycle. The phytotoxicity assessment determined by the germination of mung beans proved that PMS activation by MOF-derived LDH catalysts can basically eliminate the phytotoxicity of a 2,4-D solution. This research not only developed high-activity LDH catalysts for PMS activation, but also expanded the environmental applications of MOF derivants.

Key words: catalysis, degradation, layered double hydroxide (LDH), MOF derived, peroxymonosulfate

HIGHLIGHTS
• LDH derived from MOFs through a pseudomorphic conversion process.
• LDH showed excellent activity to activate PMS to degrade 2,4-DCP and other pollutants.
• CoMn-LDH and CoFe-LDH exhibited high stability and reusability.
• High specific surface area and well developed pore structure of LDH provide more active sites.
• Phytotoxicity assessment displayed the practical application value of LDH.

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1. INTRODUCTION

Chlorophenol organics are widely used in oil refining, coking, papermaking, plastics, printing and dyeing industries (Yu et al. 2018; Xie et al. 2020). Because of their carcinogenic, teratogenic, mutagenic potential toxicity and refractory properties, they are listed as priority pollutants. 2,4-Dichlorophenol (2,4-DCP), as a typical chlorophenol pollutant, widely exists in industrial wastewater (Yuan et al. 2017; Tian et al. 2019) and shows significant impact on the water environment and human health. Therefore, it is urgent to solve the problem of water pollution caused by chlorophenols. At present, various methods have been used to remove 2,4-DCP and multiple organic pollutants, including membrane separation (Yin et al. 2021), electrochemistry (Ma et al. 2021), adsorption (Liu et al. 2009), and photodegradation (Hou et al. 2021a, 2021b). However, these methods often have shortcomings such as low efficiency, secondary pollution, or complicated operation (Olmez-Hanci et al. 2013). Therefore, it is urgent to seek the more efficient ways to eliminate the hazards of 2,4-DCP.

In recent years, the advanced oxidation techniques (SR-AOPs) based on sulfate radicals ($SO_4^{•-}$) has attracted extensive research due to their higher standard reduction potential (2.5–3.1 V) compared with hydroxyl radicals ($^•OH$) (1.8–2.7 V), which have been widely used for degradation of various organic substances. $SO_4^{•-}$ can be produced by activation of peroxymonosulfate (PMS) and peroxydisulfate (PS) through ultraviolet light (Wang et al. 2017), heat (Pan et al. 2018), electrocatalysis (Ahman et al. 2021), transition metal catalysts (Wang & Wang 2018) and other ways (Ahman et al. 2020b, 2020c). Among different methods, the transition metal catalysts, such as Ag(I), Co(II), Fe(II/III), Ce(IV), Mn(IV), etc., which were widely used activate PMS for degradation of organic compounds, and theoretically most refractory organics could be degraded through PMS activation (Yang et al. 2009; Ji et al. 2014; Huang et al. 2017). Among transition metals, Co(II)/PMS homogeneous system has received extensive attention from researchers due to the advantages of high activity and low cost (Hu & Long 2016; Xiao et al. 2018). In previous studies, it was found that homogeneous transition metal catalysts are difficult to recycle and thus cause secondary pollution. Compared with homogeneous Co(II) catalysts, heterogeneous catalysts have the advantages of easy separation and recycling, which shows more potential for PMS activation. Therefore, to design a stable, low-loss heterogeneous transition metal catalyst with high catalytic performance is the key to improve catalyst performance and promote industrialization of PMS activation.
Transition metal catalysts are generally used for PMS activation and other catalytic reaction in the form of oxides (Wang et al. 2022), sulfides (Li et al. 2021), hydroxides (Yang et al. 2021a), supported catalysts (Ahsan et al. 2020a), perovskite (Geng et al. 2020), and so on. As a typical anion layer material, layered double hydroxides (LDHs) are often referred to as hydrotalcite-like compounds, consisting of a body laminate with metal hydroxide and an interlayer region containing compensating anions and solvated molecules (Daud et al. 2016). At present, transition metal-based LDHs are widely used for PMS activation because of their unique structure and relatively simple synthesis method (Chen et al. 2019; Cao et al. 2020a). Generally, LDH was mainly prepared by hydrothermal methods (Huang et al. 2021), precipitation methods (Xiao et al. 2019) and other traditional methods, but the specific surface area, morphology and structure of the LDH samples obtained by these methods are difficult to accurately control. Seeking a facile method to prepare LDH with controlled specific surface area and specific structure is the key to study the structure–activity relationship between the catalyst structure and catalytic performance, thus further improving the activity of the LDH catalyst.

Metal–organic frameworks (MOFs) are crystalline porous materials with periodic network structure formed by self-assembly of metal ions and organic bridging ligands (Yaghi et al. 1995; Liu et al. 2017). MOFs have the advantages of large specific surface area, metal center variability, organic ligand diversity, large pore volume, high stability, and these special properties make MOFs an ideal sacrificial template or precursor for preparation of nanomaterials with specific structure, such as porous carbon (Zhang et al. 2014; Lai et al. 2016), metal oxides (Yu et al. 2016; Yuan et al. 2017) and metal sulfides (Li et al. 2016; Jin et al. 2017). Furthermore, MOFs can also be used as sacrificial precursors to synthesize LDH samples with good pore structure and high specific surface area. Existing research showed that MOF-derived LDH has been widely used as a catalyst (Yang et al. 2021b; Yusuf et al. 2021), supercapacitors (Xiao et al. 2019; Liu et al. 2022), sensors (Qin et al. 2021; Shen et al. 2021) and so on. Xiao and colleagues (Xiao et al. 2019) prepared LDH samples by replacement of the organic ligands in MOFs with OH\(^{-}\) under alkaline conditions, which obtained a larger surface area and high porosity and exhibited excellent electrochemical performance. Based on the above research, MOFs can be used as precursors to prepare high-performance LDH catalysts by etching under alkaline conditions, applicable in the field of PMS activation for pollutants elimination.

In this article, CoMn-LDH and CoFe-LDH catalysts with high specific surface area and well developed pore structure were prepared though a pseudomorphic conversion process by using CoMn-MOF and CoFe-MOF as precursors through replacing the organic ligands by OH\(^{-}\). The MOF-derived LDH catalysts were used to activate PMS for degradation of 2,4-DCP and other pollutants. Different factors (temperature, pressure, PMS and catalyst dosage) affecting PMS activation were systematically studied. In addition, the stability and reusability of two LDH samples were tested. Radical scavenger test, electron paramagnetic resonance (EPR) experiments and X-ray photoelectron spectroscopy (XPS) characterization were also performed to elucidate the types of reaction species and PMS activation mechanism. Moreover, total organic carbon (TOC) test and phytotoxicity assessment were conducted in order to determine the mineralization of the organic pollutant and the toxicity of the degraded organic pollutant. This study provides a promising insight for the precise design of PMS activation catalysts with specific structures, and further broadens the application of MOF derivatives.

2. MATERIALS AND METHODS

2.1. Chemical reagents

All chemical reagents were used without further purification. Ferric nitrate nonahydrate (Fe(NO\(_3\))\(_3\)-9H\(_2\)O, ≥99.99%), cobalt nitrate hexahydrate (Co(NO\(_3\))\(_2\)-6H\(_2\)O, ≥99.99%), manganese nitrate solution (Mn(NO\(_3\))\(_2\), 50 wt% solution), polyvinylpyrrolidone (PVP, K29-32), potassium peroxomonosulfate (PMS, ≥42.8%), L-histidine (≥99%), p-benzoquinone (≥99%), 2,4-DCP, (≥98%), 2,4-dichlorophenoxyacetic acid (2,4-D, ≥98%), ciprofloxacin (CIP, ≥98%), bisphenol A (BPA, ≥99%), hydrogen peroxide solution (H\(_2\)O\(_2\), 3 wt% in water), 5,5-dimethylpyrroline-oxide (DMPO, ≥97%), 4-amino-2,2,6,6-tetramethylpiperidine (TEMP, ≥98%) and 1,4-benzenedicarboxylic acid (H\(_2\)BDC, ≥99%) were purchased from Aladdin Industrial Corporation. Sodium hydroxide (NaOH, ≥98%), N\(_2\)N dimethylformamide (DMF, ≥99.5%), tert-butyl alcohol (TBA, ≥99%), ethanol (≥99.7%), formic acid (1% w/v), acetic acid (99.8%), high-performance liquid chromatography (HPLC) grade acetonitrile (≥99.9%) and HPLC grade methanol (≥99.9%) were purchased from Sinopharm Chemical Regent Co. Ltd. Mung beans were purchased from a local store.

2.2. Synthesis of MOF-derived LDH catalysts

CoMn-MOF was prepared by the solvothermal method: 2 mmol Mn(NO\(_3\))\(_2\)-6H\(_2\)O, 4 mmol Co(NO\(_3\))\(_2\)-6H\(_2\)O, 1.2 g PVP (K29-32) and 0.6645 g H\(_2\)BDC were added in the solution containing 30 mL DMF and 20 mL ethanol, and then stirred for 1 hour at
room temperature. After that, the mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave and kept at 120 °C for 24 h. After cooling to room temperature, the product was centrifuged, then repeatedly washed with ethanol and then dried at 70 °C overnight. The obtained CoMn-MOF precipitate was immersed in 50 mL 2 M NaOH aqueous solution and stirred at room temperature for 3 h to prepare CoMn-LDH. After that, the product was washed with deionized water to remove excess NaOH. Finally, the MOF-derived LDH sample was obtained after drying at 70 °C overnight. The CoFe-LDH catalyst was prepared using the same methods but by using 2 mmol Fe(NO₃)₃·9H₂O instead of Mn(NO₃)₂·6H₂O.

2.3. Characterization
The X-ray diffraction (XRD) pattern of the sample was measured on a Bruker D8 advanced X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology and structure of LDHs were observed by using an Hitachi S-4800 field emission scanning electron microscope (SEM). The transmission electron microscopy (TEM) was tested by using a JEOL JEM-2100 instrument to further observe the nanostructures. The specific surface area was measured by using Micromeritics ASAP 2020 equipment to perform nitrogen adsorption–desorption measurements at 77 K (Micromeritics, USA) and the sample was determined according to Brunauer–Emmett–Teller (BET) (Benselka-Hadj Abdelkader et al.) analysis. Through Thermo Fisher ESCALABXi+ XPS and Al-K (1,486.6 eV) as the X-ray source, the surface composition and electronic state of Co, Fe, Mg, O and other elements were recorded then analyzed. The FT-IR spectrum was measured at 4,000–400 cm⁻¹ using a PerkinElmer Frontier FT-IR spectrometer. EPR (Bruker EMX/plus) was used to detect reaction species generated by the reaction through DMPO and TEMP as spin-trapping agents. The concentrations of cobalt, manganese and iron were determined by the solution and used inductively coupled plasma mass spectroscopy (ICP-MS) (Scientific iCAP RQ). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were tested on a Mettler Toledo TGA-1 thermal analyzer in a dynamic N₂ atmosphere and the heating rate was 10 °C/minute.

2.4. Catalytic degradation experiments
In a typical degradation experiment unless otherwise specified, 10 mg of catalyst (0.2 g/L) was dispersed into 50 mL of 2,4-DCP solution (20 mg/L), and then stirred for 30 minutes to eliminate the effect of adsorption. After reaching adsorption–desorption equilibrium, a 1.0 mL of PMS solution (10 mg/mL) was added into above solution to start the PMS activation reaction. After that, a 1.0 mL sample was taken into a centrifuge tube every 5 minutes, and immediately mixed with 1.0 mL methanol to stop the catalytic reaction. Then, the collected sample was filtered through a 0.22-μm filter membrane into an HPLC vial. Unless otherwise stated, the catalytic performance of all catalysts was evaluated in a beaker at room temperature (25 ± 1 °C), and all tests were conducted in deionized water with an initial pH (pH₀) of 6.5. The effects of different influence factors (catalyst dosage, PMS dosage, temperature) on the PMS activation and the stability and reusability of the catalysts were also tested. In order to study the reusability of the catalyst, the catalyst was collected by centrifugation, washed several times with ethanol and deionized water and dried for the next cycle. The concentrations of 2,4-DCP and other pollutants were measured by HPLC (LC-20A) on an instrument equipped with a Phenomenex C18 column under a UV detector and the specific test conditions for these are shown in Table 1. TOC was measured by using a TOC analyzer (TOC-L, CPH, Shimadzu).

| Organic pollutants                | Mobile phase (v/v)    | Flow rate (mL/min) | Detection wavelength (nm) | References               |
|-----------------------------------|-----------------------|--------------------|---------------------------|--------------------------|
| 2,4-Dichlorophenol (2,4-DCP)      | Methanol/Water = 70/30| 1                  | 283                       | Wang et al. (2021)       |
| 2,4-Dichlorophenoxyacetic acid (2,4-D) | Acetonitrile/0.2% Formic acid = 40/60 | 1              | 284                       | Li et al. (2020a)        |
| Ibuprofen (IBP)                   | Methanol/0.1% Acetic acid = 60/40 | 1              | 210                       | Nawaz et al. (2020)      |
| Ciprofloxacin (CIP)               | Acetonitrile/0.1% Formic acid = 20/80 | 1              | 278                       | Mukherjee et al. (2021)  |
2.5. Phytotoxicity assessment

The toxicity test was based on the germination rate and radicle length of mung beans (Peng et al. 2020). At the first, mung bean seeds were sterilized with 3% H2O2, and rinsed with ultrapure water several times. Then 100 cleaned mung beans were taken and placed on the filter paper as a carrier. The seeds were cultured by using the undegraded 2,4-D solution (20 mg/L), the 2,4-DCP solution degraded by CoMn-LDH, the 2,4-DCP solution degraded by CoFe-LDH and ultrapure water. An appropriate amount of the solution was replenished into a Petri dish twice a day during the culture process. Mung beans were incubated in the dark (25 ± 1 °C, 24 h) for 7 days. The germination rate of mung bean seeds was recorded every 24 hours, and 20 seedlings were randomly selected from each Petri dish after 7 days to count the radicle length.

2.6. Statistical analysis

All the measured experimental results were expressed as the mean ± SD (standard deviation) of repeated experiments. The physicochemical parameters adopted one-way ANOVA. Tukey's post-hoc and SPSS (version 19.0) were used to compare significant differences. When the hypothesis did not satisfy homogeneity of variance and normality, the Kruskal–Wallis test was used for data analysis, and then the Dunn multiple comparison test was adopted. The R language was used to perform Levene’s test to confirm the homogeneity of variance, and Kolmogorov–Smirnov test was adopted to confirm normality (p-value > 0.05). If the p-value was <0.05, the experimental data were considered to be statistically significant.

3. RESULTS AND DISCUSSION

3.1. Characterization of MOF-derived LDH catalysts

The samples obtained were initially characterized and analyzed by SEM, TEM XRD and TG. The CoMn-LDH and CoFe-LDH samples were obtained by in-situ etching under alkaline conditions, and the hydroxyl groups were used to replace the organic ligands in MOFs. During the etching process for the ligands, crystal structures with special shapes were formed, which also created complex and hierarchical structures. As shown in Figure 1(a) and 1(b), the surface of CoMn-LDH became rough and porous, which inferred that a large number of pores were produced in the process of replacing organic ligands with hydroxyl groups. The high magnification SEM image of CoMn-LDH (Figure 1(c)) further showed that there were large numbers of porous structures on the surface and arranged at layered forms. Compared to the CoMn-LDH sample, the CoFe-LDH exhibited different morphological features. The low magnification SEM images (Figure 1(d) and 1(e)) manifested the formation of the porous stacked sheet structures. The high magnification image in Figure 1(e) further revealed that there were irregular flake nanostructures with a width of about 500 nm on the surface. For comparison, the SEM images of used CoMn-LDH and CoFe-LDH were also taken. As shown in Supplementary Material, Figure S1, the two used LDH catalysts still maintained stable layered morphology, indicating the high structural stability of two LDH catalysts. TEM (Supplementary Material, Figure S2) pictures also showed that the two fresh LDH catalysts were stacked in layered forms, which conforms to the traditional structure of LDHs. Combining SEM images with TEM images, it could be manifested that the LDH structure with layered structure has been successfully prepared.

In the XRD spectrum of CoMn-LDH (Figure 2(a)), it can be seen that the peak of the crystal appeared obvious and the characteristic peaks can be matched with Co(OH)2 (JCPDS: 51-1731) and Mn(OH)2 (JCPDS: 18-0787). Similarly, the XRD spectra of CoFe-LDH (Figure 2(b)) peaks were obvious and the characteristic peaks of Co(OH)2 (JCPDS: 74-1057) and Fe(OH)2 (JCPDS: 13-0089) could be better matched. Combined with the analysis of SEM and XRD patterns, it can be concluded that the organic ligands in MOFs were replaced by hydroxyl groups and the layered amorphous hydroxycarbonate-like structures were successfully synthesized, in which the reconstruction and deconstruction of the structure occurred simultaneously (Zhang et al. 2018).

As shown in the FT-IR spectra (Figure 3(a)), CoMn-LDH had a broad adsorption peak from 2,500 to 3,600 cm⁻¹, which was related to the absorption of the -OH group (Shakeel et al. 2019). The characteristic peak of CoMn-LDH appeared at about 1,650 cm⁻¹ and was associated with -COO-. The bands between 900 and 1,500 cm⁻¹ should be a strong absorption band of terephthalic acid ligands, but there was almost no absorption in the spectrum, which meant the organic ligands had been basically removed. Thereby, the band at 1,650 cm⁻¹ can be attributed to the CO3²⁻ ions existing in the LDH interlayer. For CoFe-LDH, there was a strong absorption peak at 3,631 cm⁻¹, which could be associated to the stretching vibration of -OH. The absorption of 3,596 cm⁻¹ was also due to the absorption of the -OH group. The existence of the absorption peak from 1,550 to 1,650 cm⁻¹ indicated that the terephthalic acid ligand had been basically removed and the existence of the -COO- group. This also confirmed the presence of CO3²⁻ ions. For CoMn-LDH and CoFe-LDH, the strong absorption
around 600 cm$^{-1}$ could be attributed to the M-O and O-M-O stretching vibrations in LDHs (M = Co & Mn & Fe). The FT-IR results proved that the hydrotalcite structure had been synthesized and there were inorganic anions that could be exchanged between layers and externally.

The specific surface area and pore structure of CoMn-LDH and CoFe-LDH samples were evaluated by N$_2$ adsorption–desorption isotherm and the results are shown in Figure 3(b). The specific surface area, average pore diameter and pore volume of CoMn-LDH were 43.1 m$^2$/g, 33.9 nm and 0.37 cm$^3$/g, respectively. Almost all pores existed in the form of mesopores. In comparison, CoFe-LDH had a higher specific surface area of 169.9 m$^2$/g, a smaller average pore size of 2.9 nm,
and a pore volume of 0.25 cm$^2$/g. In particular, the BET specific surface area of CoFe-LDH with MOFs as the precursor is much higher than that with other traditional synthesis methods (Table 2). The increased surface area of CoFe-LDH made PMS and organic pollutant molecules easier to diffuse and interact with the reaction sites, thereby increasing the reaction rate.

TGA is an effective way to assess thermostability of materials, which is shown in Supplementary Material, Figure S3. Due to the dihydroxylation of the hydroxide in LDHs (Benselka-Hadj Abdelkader et al. 2011), the total weight loss of CoMn-LDH and CoFe-LDH were 15.1% and 21.2% respectively, and reached stable states at 460 and 710 °C. After that, the further increase in temperature did not cause continued quality loss.

The surface element composition and metal valence of CoMn-LDH and CoFe-LDH were obtained by XPS. As shown in Figure 3(c), the peaks of CoMn-LDH were mainly attributed to the C 1s, N 1s, O 1s, Mn 2p and Co 2p regions. The spectrum of Co 2p shown in Figure 3(d) was made up of two main peaks, Co 2p$^{3/2}$ (779.4 eV) and Co 2p$^{1/2}$ (794.3 eV). The main peak with a binding energy of 779.4 eV can be decomposed into two peaks, Co$^{3+}$ at the peak of 779.2 eV and Co$^{2+}$ at the peak of 780.2 eV. As shown in Figure 3(e), the Mn 2p spectrum was composed of Mn 2p$^{3/2}$ (641.6 eV) and Mn 2p$^{1/2}$ (653.2 eV), and the two main peaks can be divided into four peaks in total. The peaks at 642.8 eV and 653.9 eV were attributed to the Mn$^{4+}$ species, and the peaks at 641.0 eV and 652.5 eV can be attributed to the Mn$^{2+}$/Mn$^{3+}$ species. According to the peak area of different species, it can be found that Co$^{3+}$/Co$^{2+}$ was 1.1, indicating that both Co$^{3+}$ and Co$^{2+}$ existed and the composition was basically the same. Furthermore, the proportion of Mn$^{2+}$/Mn$^{3+}$ to Mn$^{5+}$ was 2.1, indicating that Mn species was mainly in the form of Mn$^{2+}$/Mn$^{3+}$. The atomic ratio of Mn to Co was 1:2.6. The XPS results conformed to the basic characteristics of LDH and the distribution of element valence states, and matched well with the XRD result. Figure 3(f) shows the valence and composition of the elements in CoFe-LDH. It can be seen that the peaks were mainly composed of C 1s, N 1s, O 1s, Fe 2p and Co 2p. As shown in Figure 3(g), Co 2p mainly consisted of two main peaks and two larger satellite peaks. The main peak of Co 2p$^{3/2}$ at 780.2 eV can be divided into 779.8 eV and 781.2 eV. At the same time, the positions of the two satellite peak bands appeared at 785.4 eV and 802.3 eV. These values matched well with the reported Co(OH)$_2$ data, which meant that the Co species in the compound presented a high-spin Co$^{2+}$ state (Ma et al. 2011), which further confirmed the existence of Co(OH)$_2$. The XPS spectrum of Fe 2p is shown in Figure 3(h), where the Fe 2p orbital peaks were asymmetrical and there were splits and overlaps, therefore it was difficult to determine the specific composition of Fe (Biesinger et al. 2011). Generally, the appearance of satellite peaks beside the main peak meant the presence of Fe$^{3+}$ in the compound. Peak splitting could prove that Fe$^{2+}$ existed in the compound at the same time, which was consistent with formed Fe(OH)$_2$ detect by XRD results. The atomic ratio of Fe to Co is 1:3.4. These results showed that Co$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ are simultaneously present in the prepared CoFe-LDH, which also conformed the existence of hydrotalcite-like structures. The XPS graphs of used CoMn-LDH and CoFe-LDH are shown in Figure S4, after activating PMS to degrade organic pollutants, the valence state of LDHs has changed significantly, which showed that the transition of element valence states in the reaction process was inseparable from the PMS activation process.
Figure 3 | FT-IR spectra (a) and N₂ adsorption–desorption isotherms (b) of CoMn-LDH and CoFe-LDH, XPS spectrum of CoMn-LDH; (c) survey spectra: Co 2p (d) and Mn 2p (e); XPS spectrum of CoFe-LDH; (f) survey spectra: Co 2p (g) and Fe 2p (h).
3.2. Catalytic performance

The following section describes the 2,4-DCP degradation via PMS activated by CoMn-LDH and CoFe-LDH catalysts under different conditions. In order to ensure the accuracy of the experimental results, each experiment was tested three times without special requirements and the average value has been taken.

After mixing CoMn-LDH and CoFe-LDH catalysts and 2,4-DCP solution, the 2,4-DCP concentration in the adsorption process was monitored. It could noted from Figure 4(a) that the adsorption equilibrium was reached within 15 minutes, and the

| Table 2 | The BET specific surface area of CoMn-LDH and CoFe-LDH derived from MOFs and by other traditional methods |
|---|---|---|
| Samples | Specific surface area (m²/g) | References |
| MOF-derived CoMn-LDH | 43.2 | (This work) |
| MOF-derived CoFe-LDH | 169.9 | (This work) |
| CoMn-LDH | 41.6 | Zhang et al. (2021) |
| Zn-Co-LDHs | 4.9 | Jiehu et al. (2020) |
| Ni/Fe-LDH (3:1) | 20.1 | Sun et al. (2018) |
| Ni₅₀Co₅₀-LDH | 48 | Soltani et al. (2021) |
| Mn₄Al₁-500 | 23.4 | Wu et al. (2019) |
| Mg-Fe-OH-LDH | 42.8 | Cao et al. (2020b) |

Figure 4 | Adsorption–desorption balance of CoMn-LDH and CoFe-LDH (a); catalytic degradation of 2,4-DCP using different catalysts (b); TOC removal of 2,4-DCP of CoMn-LDH and CoFe-LDH (c); The concentration of cobalt ions, manganese ions and iron ions in solution (d). The diagram is the average value of the triplicate and the error bars represent SD. Reaction conditions: [2,4-DCP]₀ = 20 mg/L, [PMS]₀ = 0.2 g/L, [catalyst]₀ = 0.2 g/L, pH₀ = 6.5 and T₀ = 25 °C.
adsorption rates of 2,4-DCP by CoMn-LDH and CoFe-LDH were stable at 24.2% and 19.1%, respectively. In order to eliminate the interference of adsorption on the catalytic performance, the mixture of LDH catalysts and 2,4-DCP solution were stirred for 30 minutes before PMS addition. In addition, only 10.2% of 2,4-DCP was degraded by PMS self-activation without addition of LDH catalysts, which indicated that PMS had a weak self-activation ability to degrade pollutants. The ability of CoMn-LDH and CoFe-LDH to adsorb dyes was weak in the absence of PMS, so catalyst adsorption effect can be excluded. In Figure 4(b), after PMS and catalyst were added simultaneously, 2,4-DCP degradation reached 95.4% and 89.4% within 10 minutes and reached 99.3% and 99.2% within 20 minutes by CoMn-LDH and CoFe-LDH catalysts, respectively. The results showed that CoMn-LDH and CoFe-LDH exhibited excellent performance to activate PMS for 2,4-DCP degradation. In addition, MOF-derived LDHs were more prominent in terms of pollutant removal rate compared with other LDH catalysts (Table 3).

In order to study the mineralization degree of the reaction, the TOC of the 2,4-DCP solution was detected after 30 minutes of reaction. The removal rate of TOC reached 77.1% and 69.6% in systems of CoMn-LDH/PMS and CoFe-LDH/PMS, respectively (Figure 4(c)). The results indicated that the PMS activated by LDH catalysts had high removal rates of TOC, and 2,4-DCP was degraded into small molecules and then mineralized.

During the degradation reaction, transition metals in LDH catalysts may enter the solution in the form of ions. In order to determine the degree of loss of metal ions during the catalysis process and the influence of the homogeneous catalysis of metal ions on the experimental results, the concentrations of Co ions, Mn ions and Fe ions in the reaction system were determined by ICP-MS. As shown in Figure 4(d), only 0.10 mg/L of Co ions and 0.092 mg/L Mn ions were detected in the CoMn-LDH/PMS system after 30 minutes of reaction and only 0.091 mg/L Co ions and 0.11 mg/L Fe ions were detected in the CoFe-LDH catalytic system. Such a low metal ion concentration had a negligible effect on the catalytic activity. The results proved that the MOF-derived LDH catalysts with stable structure and excellent performance were successfully synthesized.

3.3. Influence of 2,4-DCP degradation parameters

In order to further research PMS activation performance of CoMn-LDH and CoFe-LDH, a series of 2,4-DCP degradation experiments was carried out under different conditions (PMS concentration, catalyst dose, reaction temperature). 2, 4-DCP degradation by CoMn-LDH/PMS and CoFe-LDH/PMS at different PMS concentrations is shown in Figure 5(a) and 5(b). As the PMS concentration increased from 0.1 g/L to 0.2 g/L (catalyst concentration: 0.2 g/L), the removal rate of 2,4-DCP increased gradually. However, when the PMS concentration was further increased to 0.4 g/L, no significant improvement in 2,4-DCP degradation was observed. It can be concluded that at the PMS concentration of 0.2 g/L, LDHs achieved the highest catalytic efficiency. Too high PMS concentration would produce excess reaction species, which may undergo a self-scavenging reaction, resulting in no significant improvement for 2,4-DCP degradation (Oh et al. 2016). As shown in Equations (1) and (2):

\[
\text{HSO}_5^- + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{SO}_5^{4-} \quad (1) \\
\text{SO}_5^{4-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-} \quad (2)
\]

The amount of catalyst could determine the number of active sites for PMS activation. Figure 5(c) and 5(d) shows the effect of catalyst concentration on the PMS activation to degrade 2,4-DCP. After addition of the catalyst, the removal rate of 2,4-

| Catalyst            | Catalyst dosage | PMS concern | Organic pollutant | Removal efficiency | Ref.        |
|---------------------|-----------------|-------------|-------------------|--------------------|------------|
| MOF-derived CoMn-LDH| 0.2 g/L         | 0.2 g/L     | 2,4-DCP (20 mg/L) | 99.3% (20 min)     | This work  |
| MOF-derived CoFe-LDH| 0.2 g/L         | 0.2 g/L     | 2,4-DCP (20 mg/L) | 89.2% (10 min)     | This work  |
| AlCo-LDH            | 0.2 g/L         | 0.4 g/L     | TC (30 mg/L)      | 49.1% (30 min)     | Cao et al. (2020a) |
| DOM-LDH             | 0.2 g/L         | 0.2 g/L     | BPA (20 mg/L)     | 95% (60 min)       | Ye et al. (2020) |
| Fe-Mn-LDH           | 0.4 g/L         | 0.4 g/L     | ODA (10 mg/L)     | 85.5% (5 min)      | Chen et al. (2019) |
| AC@CoFe-LDH         | 0.2 g/L         | 1.0 g/L     | LMF (5 mg/L)      | 92.0% (60 min)     | Ma et al. (2020) |
Figure 5 | Catalytic degradation of 2,4-DCP under different conditions. PMS dosage (a, b), catalyst dosage (c, d), temperature (e, f) of CoMn-LDH and CoFe-LDH, respectively. The diagram is the average value of triplicates and the error bars represent SD. Reaction conditions: [2,4-DCP]₀ = 20 mg/L, [PMS]₀ = 0.2 g/L, [catalyst]₀ = 0.2 g/L, pH₀ = 6.5 and T₀ = 25 °C.
DCP increased sequentially. When the amount of LDHs was increased from 0.1 g/L to 0.4 g/L (PMS concentration: 0.2 g/L), 2,4-DCP degradation by CoMn-LDH and CoFe-LDH increased from 66.9% to 77.6% and 56.2% to 78.7%, respectively, within 5 minutes. In fact, more catalyst provided more active sites for PMS activation, thereby further promoting the degradation of 2,4-DCP. However, the amount of catalyst only increased the initial degradation rate, but did not significantly affect the final degradation of 2,4-DCP. The results showed 0.1 g/L catalyst could provide enough active sites to activate PMS for degrading 2,4-DCP.

It can be seen from Figure 6(e) and 6(f) that when CoMn-LDH and CoFe-LDH were used as catalysts, increasing the reaction temperature can increase the degradation rate of 2,4-DCP. In the first 10 minutes, the increase of the reaction temperature had a more obvious increase in the degradation rate, because the PMS activation is an endothermic reaction. However, after 10 minutes, the degradation rate at different temperatures tended to be the same, indicating that the temperature was not the rate determining step of the catalytic reaction.

3.4. Degradation test of multiple pollutants

In order to further broaden the actual application value of MOF-derived LDHs, degradation tests of bisphenol A (BPA), ciprofloxacin (CIP) and 2,4-D were carried out. In the CoMn-LDH/PMS system, the degradation rates of BPA, CIP and 2,4-D reached 92.7%, 77.7% and 73.1% after 15 minutes of reaction, and 98.4%, 94.5% and 93.9% within 30 minutes, respectively. It can be seen that the pollutants have been basically removed. In CoFe-LDH/PMS system, the degradation rates of BPA, CIP and 2,4-D reached 96.8%, 93.7% and 92.3%, respectively, within 30 minutes. The above results indicated that MOF-derived LDHs manifested excellent catalytic performance for different organic pollutants, indicating that LDHs showed great potential in environmental fields.

3.5. Stability and reusability of LDHs

The reusability of the catalyst is one of the important factors to measure the stability and activity of the catalyst. Under the same reaction conditions, repeated experiments were set up to investigate the reusability of CoMn-LDH and CoFe-LDH catalysts. As shown in Figure 7(a) and 7(b), after three cycles, 2,4-DCP degradation by CoMn-LDH and CoFe-LDH was still as high as 99.5% and 97.2%, respectively. The results showed that the MOF-derived CoMn-LDH and CoFe-LDH catalysts exhibited extremely high activity, stability and practical application value.

3.6. Identification of reaction species and possible mechanism

MOF-derived CoMn-LDH and CoFe-LDH catalysts showed excellent catalytic performance for PMS activation to degrade 2,4-DCP and multiple pollutants. It is particularly important to understand the PMS activation mechanism by LDH catalysts. PMS can generate sulfate radical (SO\textsuperscript{4}·), and can also react with H\textsubscript{2}O or OH\textsuperscript{−} to generate hydroxyl radicals (\textbullet OH) (Equations (3) and (4)), which can also degrade 2,4-DCP. Furthermore, during the PMS activation process, singlet oxygen (\textcircled{1}O\textsubscript{2}) and superoxide radicals (O\textsuperscript{2−}) may be generated to degrade 2,4-DCP. In order to determine which kind of reaction

Figure 6 | The degradation of different pollutants by CoMn-LDH (a) and CoFe-LDH (b). The diagram is the average value of the triplicate and the error bars represent SD. Reaction conditions: [pollutants]\textsubscript{0} = 20 mg/L, [PMS]\textsubscript{0} = 0.2 g/L, [catalyst]\textsubscript{0} = 0.2 g/L, pH\textsubscript{0} = 6.5 and T\textsubscript{0} = 25 °C.
species generated in the PMS/LDH system, active reaction species quenching experiments were carried out. TBA, ethanol, L-Histidine and \( p \)-benzoquinone were used as alternative active species scavengers to detect the existence of \( \cdot \)OH, \( \text{SO}_4^{\cdot -} \) and \( \text{O}_2^{\cdot -} \). Ethanol can fast react with \( \cdot \)OH and \( \text{SO}_4^{\cdot -} \) to quench free radicals. TBA can react quickly with \( \cdot \)OH radical, but hardly reacts with \( \text{SO}_4^{\cdot -} \). In addition, the generated singlet oxygen (\( \text{O}_2^{\cdot -} \)) and superoxide radicals (\( \text{O}_2^{\cdot -} \)) can be scavenged by L-histidine and \( p \)-benzoquinone:

\[
\text{SO}_4^{\cdot -} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \tag{3}
\]

\[
\text{SO}_4^{\cdot -} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} \tag{4}
\]

As shown in Figure 8(a) and 8(b), addition of ethanol and l-histidine significantly reduced 2,4-DCP degradation by the CoMn-LDH/PMS system and the CoFe-LDH/PMS system, while the system with TBA and \( p \)-benzoquinone had relatively small reduction in the removal rate of pollutants. In the system with CoMn-LDH as the catalyst, after adding 10 mM TBA, 10 mM ethanol, 10 mM l-histidine and 10 mM \( p \)-benzoquinone, the removal rate of 2,4-DCP dropped from 99.9\% to 99.1\%, 40.2\%, 15.9\% and 92.5\% within 30 minutes, respectively. At the same time, in the system with CoFe-LDH as the catalyst, the removal rate of 2,4-DCP declined from 99.1\% to 97.9\%, 42.9\%, 34.0\% and 94.6\% within 30 minutes, correspondingly. In the CoMn-LDH/PMS system and the CoFe-LDH/PMS system with addition TBA and \( p \)-benzoquinone, 2,4-DCP was almost completely degraded within 30 minutes, but the degradation rate decreased significantly. It can be clearly seen that the inhibitory effect of l-histidine and ethanol on 2,4-DCP removal was significantly greater than TBA and \( p \)-benzoquinone, and the inhibitory effect of l-histidine on 2,4-DCP degradation was most obvious. Therefore, it can be concluded that \( \cdot \)HO, \( \text{SO}_4^{\cdot -} \), \( \text{O}_2^{\cdot -} \) also can be generated by the activation of LDH catalysts, but non-radical pathways \( (\text{O}_2^{\cdot -}) \) and free radical pathways \( (\text{SO}_4^{\cdot -}) \) played significant roles in 2,4-DCP degradation.

In order to further demonstrate the types of reaction species involved in the degradation reaction, electron paramagnetic resonance experiments were performed using spin-trapping agents DMPO and TEMP, which are shown in Figure 8(c)–8(f). When only 2,4-DCP and PMS were added to the system, no signal was observed using TEMP and DMPO, which indicated that reaction species can only be produced in large quantities after catalyst activation. TEMP can be used as trapping agents for detecting \( \text{O}_2^{\cdot -} \) (Luo et al. 2020). When CoMn-LDH and CoFe-LDH were added to the system with TEMP as the trapping agent, a representative signal with a signal intensity ratio of 1:1:1 was detected (Figure 8(c) and 8(d)), which showed that the PMS was activated and produced a large amount of \( \text{O}_2^{\cdot -} \). In the system with DMPO as the trapping agent, when CoMn-LDH and CoFe-LDH were added, a weak signal was detected in the CoMn-LDH system and no reaction species signal was detected in the reaction with CoFe-LDH as catalyst (Figure 8(e) and 8(f)). According to the above results, both \( \text{SO}_4^{\cdot -} \) and
Figure 8 | Scavenger quenching on 2,4-DCP degradation by ethanol, tert-butyl alcohol l-histidine, p-benzoquinone of CoMn-LDH (a) and CoFe-LDH (b); EPR spectra of CoMn-LDH catalyst in TEMP solutions (c) and in DMPO solutions (d); EPR spectra of CoFe-LDH catalyst in TEMP solutions (e) and in DMPO solutions (f). The diagram is the average value of the triplicates and the error bars represent SD. Reaction conditions: [2,4-DCP]₀ = 20 mg/L, [PMS]₀ = 0.2 g/L, [catalyst]₀ = 0.2 g/L, pH₀ = 6.5 and T₀ = 25 °C.
\(^1\text{O}_2\) participated and played more important roles in the PMS activation reaction, which was consistent with the results shown in Figure 8(a) and 8(b).

In order to explain the production of \(^1\text{O}_2\) and the reason why \(\text{SO}_4^{2-}\) were only detected in small amounts, the production pathway of \(\text{SO}_4^{2-}\) and \(^1\text{O}_2\) was further studied. Under normal circumstances, \(^1\text{O}_2\) can be slowly generated by the self-decomposition of PMS, but the production of \(^1\text{O}_2\) can be significantly promoted in the presence of carbon-based PMS activation catalysts. The C–O bond, as sp2 carbon electron-rich oxides, was identified as the active sites for PMS activation to generate non-radical reaction species (Li et al. 2020b). In addition, the presence of N atoms in CoMn-LDH and CoFe-LDH catalysts can attract the electrons of surrounding C atoms, and the positively charged C can increase the production of \(^1\text{O}_2\) (Du et al. 2021). In addition, the electron-rich N group can also provide the electrons to break the O–O bond of PMS to generate \(^1\text{O}_2\).

Based on the above research results, a possible reaction mechanism for the catalytic activation of PMS by MOF-derived LDH was proposed. The activation of PMS was mainly completed by the non-radical \(^1\text{O}_2\) pathway and the free radical \((\text{SO}_4^\cdot\text{O})\) pathway (Geng et al. 2021). For CoFe-LDH system, PMS reacted with \(\text{Co}^{2+}\) to generate sulfate radicals \((\text{SO}_4^\cdot\text{O})\) and hydroxyl radicals \((^\cdot\text{HO})\), accompanied by one electron loss of \(\text{Co}^{2+}\) to form \(\text{Co}^{3+}\) (Equation (5)). \(\text{Fe}^{2+}\) also lost an electron and reacted with PMS to generated \(\text{SO}_4^\cdot\text{O}\) and \(^^\cdot\text{HO}\) (Equation (7)). The transformation between \(\text{Co}^{2+}\) and \(\text{Co}^{3+}\) can be realized through Equations (5) and (6) and \(\text{SO}_4^\cdot\text{O}\) can be formed at the same time. Then under the conditions of MOF-derived LDH, large amounts of HSO\(_5\) and \(\text{SO}_4^\cdot\text{O}\) were converted to \(^1\text{O}_2\) (Equation (8)). Therefore, because large amounts of \(\text{SO}_4^\cdot\text{O}\) were converted into non-radical species \(^1\text{O}_2\) through the above-mentioned pathways, the number of \(\text{SO}_4^\cdot\text{O}\) radicals decreased which made it more difficult to detect. Finally, non-radicals \((^1\text{O}_2)\) and free radicals \((\text{SO}_4^\cdot\text{O})\) attack the chemical bonds of 2, 4-DCP to form small molecules or other intermediates, which were further mineralized into \(\text{CO}_2\), \(\text{H}_2\text{O}\) or \(\text{Cl}^-\) (Equation (9)). According to the standard reduction potentials of metals (Equations (10)–(12)), it can be considered that the redox between \(\text{Co}^{2+}\) and \(\text{Fe}^{3+}\) is thermodynamically favorable (Su et al. 2013):

\[
\text{Co}^{2+} + \text{HSO}_5^- \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \quad (5)
\]

\[
\text{Co}^{3+} + \text{HSO}_5^- \rightarrow \text{Co}^{2+} + \text{SO}_4^{2-} + \text{H}^+ \quad (6)
\]

\[
\text{Fe}^{2+} + \text{HSO}_5^- \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \quad (7)
\]

\[
\text{HSO}_5^- + \text{SO}_4^{2-} \rightarrow \text{SO}_4^{2-} + \text{H}^+ + ^1\text{O}_2 \quad (8)
\]

\[
\text{SO}_4^{2-} + ^1\text{O}_2 + 2, 4\text{DCP} \rightarrow [\text{intermediates}] \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^- \quad (9)
\]

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}, E^0 = 0.77 \text{ V} \quad (10)
\]

\[
\text{Co}^{2+} + e^- \rightarrow \text{Co}^{3+}, E^0 = 1.83 \text{ V} \quad (11)
\]

\[
\text{Fe}^{3+} + \text{Co}^{2+} \rightarrow \text{Fe}^{2+} + \text{Co}^{3+}, E^0 = 1.04 \text{ V} \quad (12)
\]

### 3.7. Phytotoxicity assessment

2,4-D is a chlorophenoxy herbicide (CPHs), which is widely used to control the growth of various broad-leaved weeds. In order to study the toxicity of 2,4-D and its degradation intermediates, mung bean seeds were cultured in degraded 2,4-D solution for 7 days by measuring its germination rate and radicle length. It can be seen from Figure 9(a) that the germination rate of mung bean seeds cultured in pure water exceeded 90% within 2 days, and the germination rate of mung in degraded 2,4-D solution by CoMn-LDH and CoFe-LDH decreased slightly. However, undegraded 2,4-D had a significant inhibitory effect on the germination rate of mung. Furthermore, as shown in Figures 9(b), 10 and 11, the average radicle length of mung bean seeds germinated in pure water, degraded 2,4-D solution (CoMn-LDH), degraded 2,4-D solution (CoMn-LDH) and undegraded 2,4-D solution were 10.3 cm, 7.4 cm, 7.0 cm and 1.1 cm. After degradation via PMS activation by LDH catalysts, the toxicity of the 2,4-D solution decreased greatly, but it still had certain inhibitory effects on the germination of mung bean, which may be due to the leakage of a small part of metal ions or the degradation of 2,4-D intermediates affecting the growth of radicles (Kumar et al. 2021).
4. CONCLUSIONS

In this work, MOF-derived CoMn-LDH and CoFe-LDH catalysts with high activity and high specific surface area were successfully prepared through the pseudomorphic transformation process under alkaline conditions. SEM and TEM manifested that the two LDH catalysts have a stable layered structure, and the morphology basically did not change even after use. BET results showed that two LDHs have well developed porous structures and high specific surface area, which could provide more active sites to activate PMS. As a result, the two LDH samples demonstrated high catalytic performance to activate PMS for the degradation of 2,4-DCP and other organic pollutants. 2,4-DCP degradation by CoMn-LDH/PMS system and

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**Figure 9** | The germination rate (a) and average radicle length (b) of mung beans cultivated in degraded 2,4-D solution by CoMn-LDH, degraded 2,4-D solution by CoFe-LDH, undegraded 2,4-D solution and ultrapure water. The diagram is the average value of the triplicate and the error bars represent SD.

**Figure 10** | Phytotoxicity assessment of mung beans cultivated in degraded 2,4-D solution by CoMn-LDH, degraded 2,4-D solution by CoFe-LDH, undegraded 2,4-D solution and ultrapure water.
CoFe-LDH/PMS system reached 99.3% and 99.2% within 20 minutes, respectively. The moderate increase in PMS concentration, catalyst dosage and reaction temperature all have a positive effect on the degradation of 2,4-DCP. After three cycles, CoMn-LDH and CoFe-LDH catalysts could still obtain 2,4-DCP degradation of 99.5% and 97.2%, indicating that MOF-derived LDH catalysts are stable and excellent candidates for PMS activation. In addition, these two LDH catalysts also showed excellent catalytic performance for the degradation of other different types of pollutants, such as BPA, CIP, 2,4-D. The high activity of the two LDH catalysts was attributed to the large specific surface area, hierarchical structure, and redox reaction. The scavenger experiments and EPR results showed that $^{1}$O$_2$ and SO$_{4}^{2-}$ were the main active substance in 2,4-DCP degradation. In addition, phytotoxicity assessment of mung beans confirmed the significant enhancement in mineralization degree and reduction toxicity of the degraded 2,4-D solution by two LDH catalysts. In summary, this research provided a facile method to design transition metal-based LDH samples and expands the scope of MOF derivants for PMS activation in organic wastewater treatment.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Ahsan, M. A., Imam, M. A., Puente Santiago, A. R., Rodriguez, A., Alvarado-Tenorio, B., Bernal, R., Luque, R. & Noveron, J. C. 2020a Spent tea leaves templated synthesis of highly active and durable cobalt-based trifunctional versatile electrocatalysts for hydrogen and oxygen evolution reactions. Green Chemistry 22 (20), 6967–6980.
Ahsan, M. A., Puente Santiago, A. R., Rodriguez, A., Maturano-Rojas, V., Alvarado-Tenorio, B., Bernal, R. & Noveron, J. C. 2020b Biomass-derived ultrathin carbon-shell coated iron nanoparticles as high-performance tri-functional HER, ORR and Fenton-like catalysts. Journal of Cleaner Production 275, 124141.
Ahsan, M. A., Santiago, A. R. P., Nair, A. N., Weller, J. M., Sanad, M. F., Valles-Rosasles, D. J., Chan, C. K., Sreenivasan, S. & Noveron, J. C. 2020c Metal-Organic frameworks-derived multifunctional carbon encapsulated metallic nanocatalysts for catalytic peroxymonosulfate activation and electrochemical hydrogen generation. Molecular Catalysis 498, 111241.
Ahsan, M. A., Puente Santiago, A. R., Sanad, M. F., Mark Weller, J., Fernandez-Delgado, O., Barrera, L. A., Maturano-Rojas, V., Alvarado-Tenorio, B., Chan, C. K. & Noveron, J. C. 2021 Tissue paper-derived porous carbon encapsulated transition metal nanoparticles as advanced non-precious catalysts: Carbon-shell influence on the electrocatalytic behaviour. Journal of Colloid and Interface Science 581 (Pt B), 905–918.
Benselka-Hadj Abdelkader, N., Bentouami, A., Derriche, Z., Bettahar, N. & de Ménorval, C. 2011 Synthesis and characterization of Mg-Fe layer double hydroxides and its application on adsorption of Orange G from aqueous solution. Chemical Engineering Journal 169 (1–3), 231–238.

Biesinger, M. C., Payne, B. P., Grosvenor, A. P., Lau, L. W. M., Gerson, A. R. & Smart, R. S. C. 2011 Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe and Ni. Applied Surface Science 257 (7), 2717–2730.

Cao, J., Sun, L., Li, X., Zhang, Y., Xiong, W., Wu, Y., Jia, M., Zhou, Y., Zhou, C. & Zhang, Y. 2020a Efficient charge transfer in aluminum-cobalt layered double hydroxide derived from Co-ZIF for enhanced catalytic degradation of tetracycline through peroxymonosulfate activation. Chemical Engineering Journal 382, 122802.

Cao, Y., Guo, Q., Liang, M. & Sun, W. 2020b Sh(III) and Sh(V) removal from water by a hydroxyl-intercalated, mechanochemically synthesized Mg-Fe-LDH. Applied Clay Science 196, 105766.

Chen, G., Nengzi, L. C., Li, B., Gao, Y., Zhu, G. & Cheng, X. 2019 Octadecylamine degradation through catalytic activation of peroxymonosulfate by FeMn layered double hydroxide. Science of the Total Environment 695, 133963.

Daud, M., Kamal, M. S., Shehzad, F. & Al-Harthi, M. A. 2016 Graphene/layered double hydroxides nanocomposites: a review of recent progress in synthesis and applications. Carbon 104, 241–252.

Du, N., Liu, Y., Li, Q., Miao, W., Wang, D. & Mao, S. 2021 Peroxydisulfate activation by atomically-dispersed Fe-Nx on N-doped carbon: mechanism of singlet oxygen evolution for nonradical degradation of aqueous contaminants. Chemical Engineering Journal 413, 127545.

Geng, G., Cai, M., Fang, R., Luan, Q., Zhang, Z., Song, J. & Zhang, J. 2020 Metal-organic frameworks-derived perovskite catalysts for efficient degradation of 2,4-dichlorophenol via peroxymonosulfate activation. Applied Surface Science 534, 147467.

Geng, G., Gao, Y., Zhang, Z., Gao, K., Zhang, W. & Song, J. 2021 Renewable and robust biomass waste-derived Co-doped carbon aerogels for PMS activation: catalytic mechanisms and phytotoxicity assessment. Ecotoxicology and Environmental Safety 220, 112381.

He, S., Li, Z., Wang, J., Wen, P., Gao, J., Ma, L., Yang, Z. & Yang, S. 2016 MOF-derived NiCo1−x(OH)2 composite microspheres for high-performance supercapacitors. RSC Advances 6 (35), 49478–49486.

Hou, C., Liu, H. & Li, Y. 2021a The preparation of three-dimensional flower-like TiO2/TeO2 photocatalyst and its efficient degradation of tetracycline hydrochloride. RSC Advances 11 (25), 14957–14969.

Hou, C., Liu, H. & Mohammad, F. B. 2021b Preparation of ordered mesoporous F−H2Ti3O7 nanosheets using orthorhombic HTIO3 as a precursor and their highly efficient degradation of tetracycline hydrochloride under simulated sunlight. Journal of Solid State Chemistry 300, 122288.

Hu, P. & Long, M. 2016 Cobalt-catalyzed sulfate radical-based advanced oxidation: a review on heterogeneous catalysts and applications. Applied Catalysis B: Environmental 181, 103–115.

Huang, G. X., Wang, C. Y., Yang, C. W., Guo, P. C. & Yu, H. Q. 2017 Degradation of Bisphenol A by Peroxymonosulfate Catalytically Activated with Mn1.4Fe1.6O4 Nanospheres: synergism between Mn and Fe. Environmental Science and Technology 51 (21), 12611–12618.

Huang, C., Nie, J., Xu, Z., Zhang, X., Tang, J., Wang, B., Huang, J., Du, C. & Chen, J. 2021 One-step hydrothermal synthesized 3D P-MoO4/FeCo LDH heterostructure electrocatalysts on Ni foam for high-efficiency oxygen evolution electrocatalysis. International Journal of Hydrogen Energy 46 (24), 12992–13000.

Ji, F., Li, C., Liu, Y. & Liu, P. 2014 Heterogeneous activation of peroxymonosulfate by Cu/ZSM5 for decolorization of Rhodamine B. Separation and Purification Technology 135, 1–6.

Jiehu, C., Chunlei, W., Ming, Z., Jie, Z., Li, F., Xiuhong, D., Leiming, C. & Chunguang, L. 2020 2D to 3D controllable synthesis of three Zn-Co-LDHs for rapid adsorption of MO by TEA-assisted hydrothermal method. Applied Surface Science 534, 147564.

Jin, M., Lu, S.-Y., Ma, L., Gan, M.-Y., Lei, Y., Zhang, X.-L., Fu, G., Yang, P.-S. & Yan, M.-F. 2017 Different distribution of in-situ thin carbon layer in hollow cobalt sulfide nanocages and their application for supercapacitors. Journal of Power Sources 341, 294–301.

Kumar, A., Prasad, B. & Garg, K. K. 2021 Enhanced catalytic activity of series LaCuFe1−xFe2O3 (x = 0.2, 0.4, 0.6, 0.8) perovskite-like catalyst for the treatment of highly toxic ABS resin wastewater: phytotoxicity study, parameter optimization and reaction pathways. Process Safety and Environmental Protection 147, 162–180.

Lai, Q., Zhao, Y., Liang, Y., He, J. & Chen, J. 2016 In situ confinement pyrolysis transformation of ZIF-8 to nitrogen-enriched mesoporous carbon frameworks for oxygen reduction. Advanced Functional Materials 26 (45), 8334–8344.

Li, G.-C., Liu, M., Wu, M.-K., Liu, P.-F., Zhou, Z., Zhi, S.-R., Liu, R. & Han, L. 2016 MOF-derived self-sacrificing route to hollow NiS2/ZnS nanospheres for high performance supercapacitors. RSC Advances 6 (103), 103517–103522.

Li, W., Li, Y., Zheng, D., Lan, Y. & Guo, J. 2020a CuO-Co3O4@CeO2 as a heterogeneous catalyst for efficient degradation of 2,4-dichlorophenoxyacetic acid by peroxymonosulfate. Journal of Hazardous Materials 381, 121209.

Li, Y., Li, J., Pan, Y., Xiong, Z., Yao, G., Xie, R. & Lai, B. 2020b Peroxymonosulfate activation on FeCo2S4 modified g-C3N4 (FeCo2S4-CN): mechanism of singlet oxygen evolution for nonradical efficient degradation of sulfamethoxazole. Chemical Engineering Journal 384, 123561.

Li, M., Zhong, H., He, Z., Hu, L., Sun, W., Loganathan, P. & Xiong, D. 2021 Degradation of various thiol collectors in simulated and real mineral processing wastewater of sulfdie ore in heterogeneous modified manganese slag/PMS system. Chemical Engineering Journal 413.

Liu, G., Ma, J., Li, X. & Qin, Q. 2009 Adsorption of bisphenol A from aqueous solution onto activated carbons with different modification treatments. Journal of Hazardous Materials 164 (2–3), 1275–1280.


Liu, X., Zhou, Y., Zhang, J., Tang, L., Luo, L. & Zeng, G. 2017 Iron containing metal-organic frameworks: structure, synthesis, and applications in environmental remediation. *ACS Appl Mater Interfaces* **9** (24), 20255–20275.

Liu, M., Wang, L., Yu, X., Zhang, H., Zhang, H., Li, S. & Huang, F. 2022 Introducing oxygen vacancies for improving the electrochemical performance of CoOx@NiCo-LDH nanotube arrays in flexible all-solid battery-capacitor hybrid supercapacitors. *Energy* **238**, 121761.

Luo, J., Bo, S., Qin, Y., An, Q., Xiao, Z. & Zhai, S. 2020 Transforming goat manure into surface-loaded cobalt/biochar as PMS activator for highly efficient ciprofloxacin degradation. *Chemical Engineering Journal* **395**, 125063.

Ma, R. Z., Liang, J. B., Takada, K. & Sasaki, T. 2011 Topochemical synthesis of Co-Fe layered double hydroxides at varied Fe/Co ratios: unique intercalation of triiodide and its profound effect. *Journal of the American Chemical Society* **133** (3), 613–620.

Ma, Q., Nengzi, L.-c., Li, B., Wang, Z., Liu, L. & Cheng, X. 2020 Heterogeneously catalyzed persulfate with activated carbon coated with CoFe layered double hydroxide (AC@CoFe-LDH) for the degradation of lomefloxacin. *Separation and Purification Technology* **235**, 116204.

Ma, Y., Gu, Y., Jiang, D., Mao, X. & Wang, D. 2021 Degradation of 2,4-DCP using persulfate and iron/E-carbon micro-electrolysis coupling system. *Journal of Hazardous Materials* **413**, 125381.

Mukherjee, A., Mullick, A., Moulik, S. & Roy, A. 2021 Oxidative degradation of emerging micropollutants induced by rotational hydrodynamic cavitation device: a case study with ciprofloxacin. *Journal of Environmental Chemical Engineering* **9** (4), 105652.

Nawaz, M., Khan, A. A., Hussain, A., Jang, J., Jung, H. Y. & Lee, D. S. 2020 Reduced graphene oxide-TiO2/sodium alginate 3-dimensional structure aerogel for enhanced photocatalytic degradation of ibuprofen and sulfamethoxazole. *Chemosphere* **261**, 127702.

Oh, W.-D., Dong, Z. & Lim, T.-T. 2016 Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: current development, challenges and prospects. *Applied Catalysis B: Environmental* **194**, 169–201.

Olmez-Hanci, T., Arslan-Alaton, I. & Gene, B. 2013 BispHENol A treatment by the hot persulfate process: oxidation products and acute toxicity. *Journal of Hazardous Materials* **265 Pt 2**, 283–290.

Pan, X., Yan, L., Qu, R. & Wang, Z. 2018 Degradation of the UV-filter benzophenone-3 in aqueous solution using persulfate activated by heat, metal ions and light. *Chemosphere* **196**, 95–104.

Peng, J., Zhang, C., Zhang, Y., Shao, S., Wang, P., Liu, G., Dong, H., Liu, D., Shi, J., Cao, Z., Liu, H. & Gao, S. 2020 Efficient removal of triclosan via peroxymonosulfate activated by a ppb level dosage of Co(II) in water: reaction kinetics, mechanisms and detoxification. *Ecotoxicology and Environment Safety* **198**, 110676.

Qin, Y., Ding, W. & Zhao, R. 2021 ZIF-8-derived ZnTi-LDHs with unique self-supported architecture and corresponding LDHs/rGO hybrid for gas sensor applications. *Chemical Physics Letters* **781**, 138965.

Shakeel, M., Arif, M., Yasin, G., Li, B. & Khan, H. D. 2019 Layered by layered Ni-Mn-LDH/g-C3N4 nanohybrid for multi-purpose photoelectrocatalysis: morphology controlled strategy for effective charge carriers separation. *Applied Catalysis B: Environmental* **242**, 485–498.

Shen, M., Li, W., Chen, L., Chen, Y., Ren, S. & Han, D. 2021 NiCo-LDH nanoflakes arrays-supported Au nanoparticles on copper foam as a highly sensitive electrochemical non-enzymatic glucose sensor. *Analytica Chimica Acta* **1177**, 338787.

Soltani, R., Peralak, R., Pishnamazi, M., Marjani, A., Sarkar, S. M., Albadarin, A. B. & Shirazian, S. 2021 Novel bimodal micro-mesoporous Ni50Co50-LDH/UiO-66-NH2 nanocomposite for Ti(I) adsorption. *Arabian Journal of Chemistry* **14** (4), 103058.

Su, S., Guo, W., Leng, Y., Yi, C. & Ma, Z. 2013 Heterogeneous activation of oxone by Co0.1Fe0.93-xO4 nanocatalysts for degradation of rhodamine B. *Journal of Hazardous Materials* **244–245**, 736–742.

Sun, J., Li, Y., Chen, C., Qi, T., Xia, D., Mao, W., Yang, T., Chen, L., Shen, W. & Tang, S. 2018 Magnetic Ni/Fe layered double hydroxide nanosheets as enhancer for DNA hairpin sensitive detection of miRNA. *Talanta* **187**, 265–271.

Tian, N., Tian, X., Nie, Y., Yang, C., Zhou, Z. & Li, Y. 2019 Enhanced 2,4-dichlorophenol degradation at pH 3–11 by peroxymonosulfate via controlling the reactive oxygen species over Ce substituted 3D Mn2O3. *Chemical Engineering Journal* **355**, 448–456.

Wang, J. & Wang, S. 2018 Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chemical Engineering Journal* **334**, 1502–1517.

Wang, F., Wang, W., Yuan, S., Wang, W. & Hu, Z.-H. 2017 Comparison of UV/H2O2 and UV/PS processes for the degradation of thiampenicol in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry* **348**, 79–88.

Wang, Y., Wang, L., Zhang, Y., Mao, X., Tan, W., Zhang, Y., Wang, X., Chang, M., Guo, R. & Xi, B. 2021 Perdisulfate-assisted advanced oxidation of 2,4-dichlorophenol by bio-inspired iron encapsulated biochar catalyst. *Journal of Colloid and Interface Science* **592**, 358–370.

Wang, Q., Xu, Z., Cao, Y., Chen, Y., Du, X., Yang, Y. & Wang, Z. 2022 Two-dimensional ultrathin perforated Co3O4 nanosheets enhanced PMS-Activated selective oxidation of organic micropollutants in environmental remediation. *Chemical Engineering Journal* **427**, 131953.

Wu, X., Feng, Y., Liu, X., Liu, L., Du, Y. & Li, Z. 2019 Redox & acidity optimizing of LDHs-based CoMnAl mixed oxides for enhancing NH3-SCR performance. *Applied Surface Science* **495**, 143513.

Xiao, R., Luo, Z., Wei, Z., Luo, S., Spinney, R., Yang, W. & Dionysiou, D. D. 2018 Activation of peroxymonosulfate/persulfate by nanomaterials for sulfate radical-based advanced oxidation technologies. *Current Opinion in Chemical Engineering* **19**, 51–58.

Xiao, Z., Mei, Y., Yuan, S., Mei, H., Xu, B., Bao, Y., Fan, L., Kang, W., Dai, F., Wang, R., Wang, L., Hu, S., Sun, D. & Zhou, H. C. 2019 Controlled hydrolysis of metal-organic frameworks: hierarchical Ni/Co-layered double hydroxide microspheres for high-performance supercapacitors. *ACS Nano* **15** (6), 7024–7030.
Xie, M., Tang, J., Fang, G., Zhang, M., Kong, L., Zhu, F., Ma, L., Zhou, D. & Zhan, J. 2020 Biomass Schiff base polymer-derived N-doped porous carbon embedded with CoO nanodots for adsorption and catalytic degradation of chlorophenol by peroxymonosulfate. *Journal of Hazardous Materials* **384**, 121345.

Yaghi, O. M., Li, G. & Li, H. 1995 Selective binding and removal of guests in a microporous metal–organic framework. *Nature* **378** (6558), 703–706.

Yang, Q., Choi, H., Al-Abed, S. R. & Dionysiou, D. D. 2009 Iron–cobalt mixed oxide nanocatalysts: heterogeneous peroxymonosulfate activation, cobalt leaching, and ferromagnetic properties for environmental applications. *Applied Catalysis B: Environmental* **88** (3–4), 462–469.

Yang, Z., Li, X., Huang, Y., Chen, Y., Wang, A., Wang, Y., Li, C., Hu, Z. & Yan, K. 2021a Facile synthesis of cobalt-iron layered double hydroxides nanosheets for direct activation of peroxymonosulfate (PMS) during degradation of fluoroquinolones antibiotics. *Journal of Cleaner Production* **310**, 127584.

Yang, Z., Yan, X., Tang, Z., Peng, W., Zhang, J., Tong, Y., Li, J. & Zhang, J. 2021b Facile synthesis of hemin-based Fe-N-C catalyst by MgAl-LDH confinement effect for oxygen reduction reaction. *Applied Surface Science* **573**, 151505.

Ye, Q., Wu, J., Wu, P., Wang, J., Niu, W., Yang, S., Chen, M., Rehman, S. & Zhu, N. 2020 Enhancing peroxymonosulfate activation of Fe-Al layered double hydroxide by dissolved organic matter: performance and mechanism. *Water Research* **185**, 116246.

Yin, X., Ma, X., He, Y., Li, H., Fan, Y., He, T., Guo, X. & Chen, L. 2021 Robust self-cleaning urchin-like Ni/Co LDH stainless steel mesh for gravity-driven oil/water emulsion separation and catalytic degradation of aromatic dyes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **627**, 127186.

Yu, D., Wu, B., Ge, L., Wu, L., Wang, H. & Xu, T. 2016 Decorating nanoporous ZIF-67-derived NiCo2O4 shells on a Co3O4 nanowire array core for battery-type electrodes with enhanced energy storage performance. *Journal of Materials Chemistry A* **4** (28), 10878–10884.

Yu, X., Cabooter, D. & Dewil, R. 2018 Effects of process variables and kinetics on the degradation of 2.4-dichlorophenol using advanced reduction processes (ARP). *Journal of Hazardous Materials* **357**, 81–88.

Yuan, J., Liu, Q., Li, S., Lu, Y., Jin, S., Li, K., Chen, H. & Zhang, H. 2017 Metal organic framework (MOF)-derived carbonaceous Co3O4/Co microframes anchored on RGO with enhanced electromagnetic wave absorption performances. *Synthetic Metals* **228**, 32–40.

Yusuf, S., Dinari, M. & Moheb, A. 2021 Facial synthesis of V-containing CuMgAl-LDHs as a new catalyst for the phenol hydroxylation. *Chemical Physics* **546**, 111183.

Zhang, P., Sun, F., Xiang, Z., Shen, Z., Yun, J. & Cao, D. 2014 ZIF-derived in situ nitrogen-doped porous carbons as efficient metal-free electrocatalysts for oxygen reduction reaction. *Energy & Environmental Science* **7** (1), 442–450.

Zhang, B., Qi, Z., Wu, Z., Lui, Y. H., Kim, T.-H., Tang, X., Zhou, L., Huang, W. & Hu, S. 2018 Defect-rich 2D material networks for advanced oxygen evolution catalysts. *ACS Energy Letters* **4** (1), 328–336.

Zhang, G., Xing, J., Zhao, Y. & Yang, F. 2021 Hierarchical N,P co-doped graphene aerogels framework assembling vertically grown CoMn-LDH nanosheets as efficient bifunctional electrocatalyst for rechargeable zinc-air battery. *Journal of Colloid and Interface Science* **590**, 476–486.

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