

ACTIVATION OF PEROXYMONOSULFATE BY CuCoFe LAYERED DOUBLE HYDROXIDE FOR THE DECOMPOSITION OF LEVOFLOXACIN

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Abstract

In this study, we synthesized CuCoFe-LDH bilayer hydroxide catalysts in different Cu:Co:Fe ratios (1:1:1; 1:2:1, and 1:3:2) by hydrothermal method and applied them to activate peroxymonosulfate (PMS) for decomposing levofloxacin. The obtained LDH samples were characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The results showed that CuCoFe-LDH (1:3:2) has the strongest ability to activate PMS and degrade levofloxacin. After 10 minutes of reaction (catalyst content of 200 mg/L, PMS concentration of 1.629 mM, pH 7, at 30°C), the decomposition efficiency was 64.89, 83.93, and 92.58% for LDH with ratios of 1:1:1, 1:2:1, and 1:3:2, respectively. The influence of PMS concentration and reaction temperature on levofloxacin degradation was investigated. PMS at high concentrations was beneficial for the formation of active oxygen species. The degradation rate of levofloxacin was affected by temperature and the activation energy was 34.04 kJ/mol.

Keywords: CuCoFe-LDH; PMS; levofloxacin.

1. Introduction

With the rapid development of the pharmaceutical industry and the increasing consumption of drugs, pharmaceutical and personal care products are released into the aquatic environment causing inevitable harm to the ecosystem and human health. In recent years, fluoroquinolones (FQ) have become a new class of organic pollutants of great interest due to their wide use and high frequency of detection [1]. Levofloxacin (LFV) (Fig. 1) is a typical antibiotic of the fluoroquinolone group widely used in the treatment of respiratory tract, urinary tract, skin infections, and other diseases [2]. However, due to the stable molecular structure, it is difficult to decompose in the natural aquatic environment. Its residues and derivatives also pose a serious threat to human

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health and ecological safety. To date, many technologies have been developed to remove antibiotics from the environment such as advanced oxidation, adsorption, and biological treatment [3].

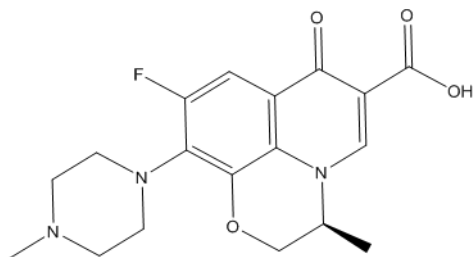


Fig. 1. Molecular structure of levofloxacin.

Advanced oxidation processes (AOPs) based on peroxymonosulfate (PMS) activation by heterogeneous catalysis of transition metals form reactive oxygen species (ROS) with strong oxidizing properties such as $\text{SO}_4^{\bullet-}$, $\text{HO}^{\bullet}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$. In these processes, one radical can be converted into another and participate in the decomposition of organic pollutants. Among them, the sulfate radical ($\text{SO}_4^{\bullet-}$) is known to have a higher redox potential ($E_0 = 2.5 - 3.1 \text{ V}$) than the traditional hydroxyl radical ($\text{HO}^{\bullet}$) ($E_0 = 1.8 - 2.8 \text{ V}$), a longer half-life (30 - 40 μs) than the hydroxyl radical (1 μs), a wider pH range, and a higher selectivity in the degradation of organic pollutants [2, 4]. Therefore, the activation of PMS to form sulfate radicals has been widely applied to degrade organic pollutants in water. The sulfate radical can be formed by peroxymonosulfate (PMS) activation by heat, ultrasound, UV radiation, and transition metal ion catalysis. Among these methods, catalytic PMS activation based on transition metals is highly effective in removing organic pollutants [5].

Layered double hydroxides (LDHs) have the general formula $[\text{M}_{1-x}^{2+} \text{M}_x^{3+} (\text{OH})_2]^{x+} [(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}]^{x-}$. M^{2+} and M^{3+} are divalent and trivalent metals, respectively, and x is the ratio $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ and usually ranges from 0.2 - 0.4 [6]. There are many choices of M^{2+} and M^{3+} in the layered structure, especially the transition metals, giving LDHs diversity and flexibility, and becoming a heterogeneous catalyst with high PMS activation for the degradation of organic pollutants in water. Compared with other transition metals, Cu^{2+} , Co^{2+} , and Fe^{2+} ions are more favorable for redox properties and can have high catalytic efficiency to activate PMS to decompose organic pollutants. Based on the Fenton-like reaction, there have been several publications on LDH of Cu, Co, and Fe elements that activate PMS to degrade antibiotics in water such as CuCo-LDH [7, 8], CoFe-LDH [9, 10], and CuCoFe-LDH [11-14]. Using ternary LDHs based on Cu, Co, and Fe to activate PMS gives a synergistic effect between single metals and better

catalytic activity as compared to binary LDHs. Besides, ternary LDHs reduce Jahn-Teller reaction efficiency, leading to a decrease in the structural deformation of LDHs [11].

In previous studies, we synthesized CuCoFe-LDH by hydrothermal and co-precipitation and applied it to activate PMS that effectively degrades glyphosate and water-based antibiotics [11, 15]. In this study, we report the influence of the ratio of Cu, Co, and Fe precursors, PMS content, and reaction temperature of CuCoFe-LDH/PMS system to degrade levofloxacin antibiotic.

2. Experiments

2.1. Chemicals and reagents

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, NH_4F , urea, levofloxacin (LFV), potassium peroxymonosulfate (PMS, Oxone) was bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Other chemicals such as NaOH and H_2SO_4 were bought from Shanghai Macklin, Co., Ltd. All chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis of CuCoFe-LDH

CuCoFe-LDHs with different Cu/Co/Fe ratios were synthesized via the hydrothermal method according to our previous publication [11]. For CuCoFe-LDH (Cu:Co:Fe = 1:3:2), $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.25 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.75 mmol), and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.5 mmol) were dissolved in 70 mL of double-distilled water and added with 0.8 g of NH_4F and 3 g of urea under stirring until completely dissolved. The solution was then transferred to a 100 mL autoclave and hydrothermally treated at 90°C for 12 h. Next, the resulting product was washed several times with double distilled water and ethanol until neutral. Finally, CuCoFe-LDH was vacuum-dried at 90°C for 24 h. Different LDHs Cu/Co/Fe ratios (1:2:1 and 1:1:1) were synthesized based on the methods described above.

2.3. Characterization of material

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$, voltage/current 40kV/40mA, step scan of 0.02°, step time of 1 second). The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan) with EDS (JEM-2100, JEOL Corporation, Japan). In addition, Fourier-transform infrared spectroscopy (FTIR) was investigated using an FTIR spectrometer (FT-IR, Perkin Elmer, USA) in the range 4000 - 400 cm^{-1} . LFV concentrations at different reaction times were analyzed using a UV-Vis spectrophotometer (Biochrom Model SP-60, Biochrom Ltd., UK) with 1.0 cm matched quartz cells [16]. For LFV degradation, all batch experiments

were conducted in a 250 mL beaker containing 100 mL of 10 mg/L LFV at 30°C using a water bath.

2.4. Degradation experiments

In the experiments, CuCoFe-LDH suspension (200 mg/L) and PMS (1.629 mM) were added to the LFV solution and stirred with a magnetic stirrer at 400 rpm. The initial pH of the LFV solution (pH = 7) was adjusted with 0.1 M NaOH or 0.1 M H₂SO₄ solution. At certain time intervals, 3.00 mL of sample solution was taken from the beaker and immediately filtered through a 0.22 µm filter and analyzed by UV-Vis method at 295 nm.

The decomposition efficiency of LFV is calculated by the equation

$$H(\%) = (1 - C_t/C_0) \times 100 = (1 - A_t/A_0) \times 100 \quad (1)$$

where C_0 and A_0 are the concentration and absorbance of LFV at the initial time, respectively. C_t and A_t are the concentration and absorbance of LFV at a given time, respectively. All experiments were carried out in triplicate and the results were the averaged data with standard deviations.

The rate constant of LFV decomposition by the CuCoFe-LDH/PMS system is calculated according to the equation.

$$\ln C_t/C_0 = -k.t \quad (2)$$

The activation energy E_a is determined by the equation.

$$\ln k = \ln A - E_a/R.T \quad (3)$$

where k is the reaction rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature (in Kelvin).

3. Results and discussions

3.1. Material characterization

XRD patterns of CuCoFe-LDH samples are shown in Fig. 2a. For CuCoFe-LDH with ratio of 1:2:1 and 1:3:2, peaks are observed at 2θ of 11.6, 23.6, 33.9, 38.7, 46.4, 52.8 and 60.4°, corresponding to the crystal planes of (003), (006), (012), (015), (018), (110), and (113), which is the characteristics of LDHs (JCPDS No. 50- 0235) [17]. In addition, the characteristic malachite phase (Cu)₂(OH)₂(CO₃) was also observed at 2θ of 14.6, 17.4, 18.5, 20.82, 24.1, 31.2, and 35.7 (JCPDS 41-1390), the formation of the malachite phase can be explained by its low solubility product value, with a K_{sp} of $10^{-33.78}$ [18]. Among the above ratios, CuCoFe-LDH with a ratio of 1:3:2 had better crystallinity than the 1:2:1 ratio, which can be explained by the ratio of precursor $M^{2+}/M^{3+} = 2$ leading to the formation of stable LDH structure with high crystallinity [11]. Furthermore, the 1:1:1 ratio appears a high-intensity doping of the malachite phase, which can be explained by the Jahn-Teller effect that appears at high Cu content [11, 19].

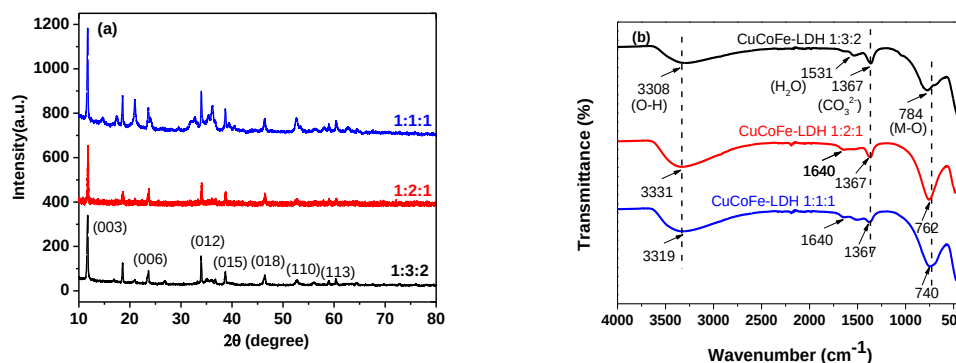


Fig. 2. XRD patterns (a) and FT-IR spectra of CuCoFe-LDH at different ratios (b).

The surface functional groups of the prepared CuCoFe-LDH were further analyzed by FTIR (Fig. 2b). The absorption peak at 740 - 784 cm^{-1} is attributed to metal-oxygen-metal bonding (Cu-O, Co-O, and Fe-O) in the catalyst. The 1367 cm^{-1} peak is attributed to the vibration of the intercalated carbonate layer. The peaks at 1531 - 1640 cm^{-1} characterize the bending vibration of the interlayer or adsorbed water. The high intensity and wide peak at 3308 cm^{-1} can be attributed to hydrogen bonding vibrations of the hydroxide layers [20].

The morphology of a catalyst affects its catalytic activity. The morphology of CuCoFe LDH samples in different ratios is shown in Fig. 3. For CuCoFe-LDH 1:1:1, there are porous microspheres with unequal sizes of 1 - 2 μm in diameter. The CuCoFe-LDH 1:2:1 is observed in the form of plates and rods. The morphology of the sample CuCoFe-LDH 1:3:2 is a dense microsphere mixed with filaments, and the average diameter of the microsphere is about 2.5 μm . Precursors such as urea and NH_4F used in the synthesis of LDH have different roles. Here, urea was used as a precursor to provide CO_3^{2-} anion. Meanwhile, NH_4F was used as a morphology-oriented inorganic surfactant for LDH because it has many advantages over organic surfactants, such as being environmentally friendly, cheap, and easy to find [11]. Meanwhile, the EDX spectra of CuCoFe-LDH 1:3:2 (Fig. 4a) and EDX mapping (Fig. 4b) confirm the presence and uniform distribution of Cu, Co, Fe, O, and C elements.

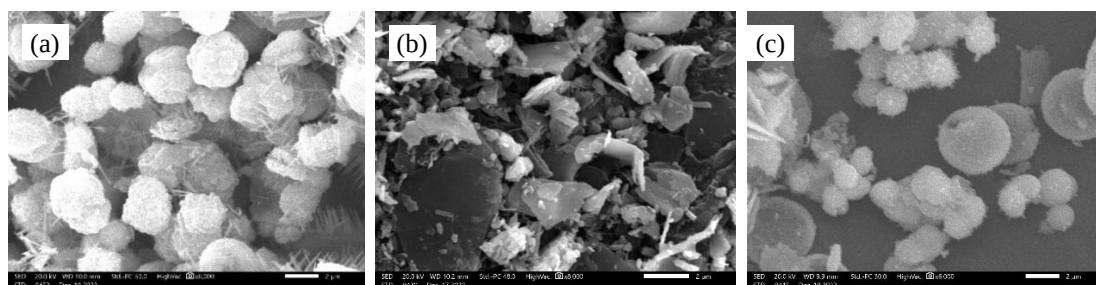


Fig. 3. SEM images of CuCoFe-LDH at ratios of 1:3:2 (a), 1:2:1 (b), and 1:1:1 (c).

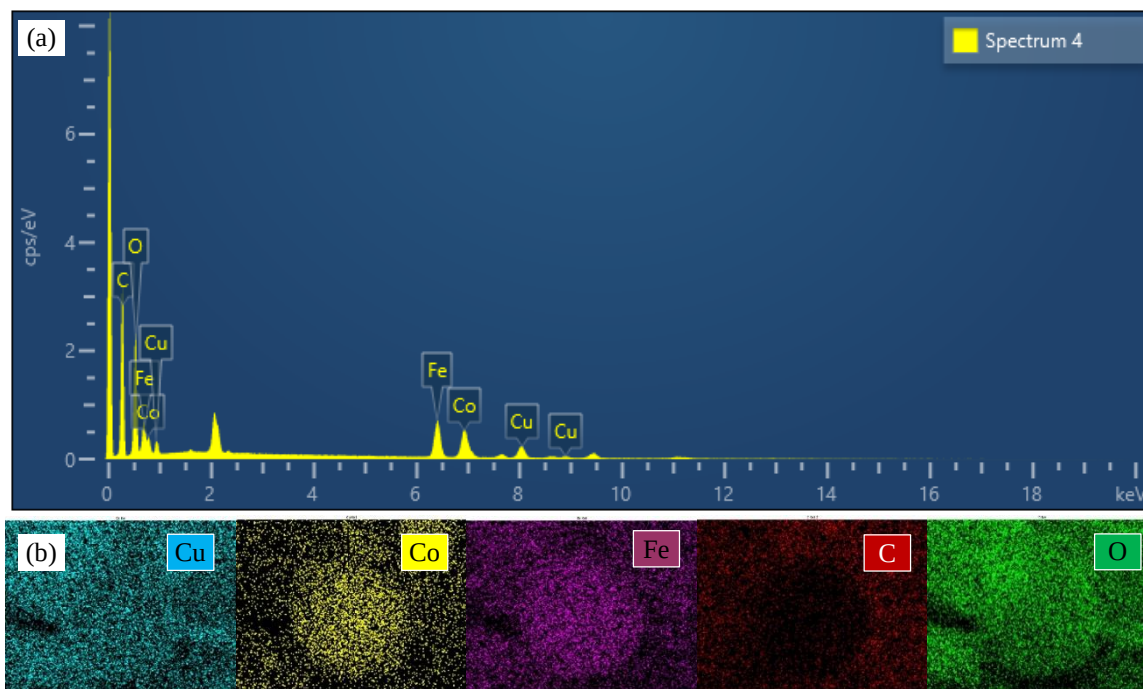


Fig. 4. EDX (a) and elemental mapping of CuCoFe-LDH 1:3:2 (b).

3.2. Catalytic abilities of LDH material

Experiments were performed to test the catalytic efficiency of the materials in different systems including CuCoFe-LDH and CuCoFe-LDH/PMS (Fig. 5). For 10 min, CuCoFe-LDH exhibited poor adsorption for LFV. When increasing the Co content in the LDHs in the ratio 1:1:1; 1:2:1, and 1:3:2, the decomposition efficiency of LFV in CuCoFe-LDH/PMS systems was in the range of 64.89, 83.93, and 92.58%, respectively (Fig. 5a). Among LDHs, CuCoFe-LDH ratio 1:3:2 had the highest LFV decomposition efficiency of 92.58% in the presence of a catalyst content of 200 mg/L, 1.629 mM of PMS, and solution pH = 7.0. The rate constant of LFV decomposition by CuCoFe-LDH (1:3:2)/PMS system was 2 times higher than that of CuCoFe-LDH (1:1:1)/PMS (Fig. 5b). This result is explained by Co(II) having very strong catalytic activity towards PMS, which is consistent with the report of Anipsitakis and Dionysiou [21] in which the ability to activate PMS of transition metal ions in the order $\text{Ni}^{2+} < \text{Fe}^{3+} < \text{Mn}^{2+} < \text{V}^{3+} < \text{Ce}^{3+} < \text{Fe}^{2+} < \text{Ru}^{3+} < \text{Co}^{2+}$.

In the CuCoFe-LDH/PMS system, PMS acts as a precursor to form different types of reactive oxygen species (ROSs). Therefore, the concentration of PMS has a great influence on the LFV decomposition. Fig. 6 shows that the LFV decomposition efficiency increased from 48.36 to 92.58% when the PMS concentration changed from 0.162 to 1.629 mM. In general, more PMS favors the formation of ROSs, thereby increasing the

catalytic capacity of LDH. However, when increasing PMS to 2.442 mM, no significant change in LFV removal was observed. Therefore, the optimal amount of PMS of 1.629 mM was selected in the subsequent tests.

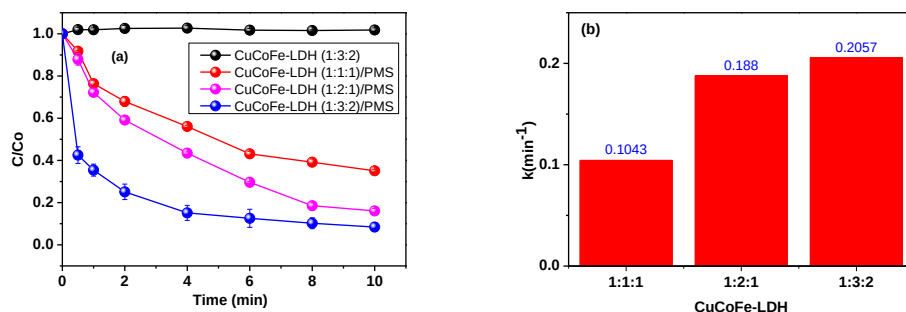


Fig. 5. LFV decomposition efficiency (a) and rate constants of CuCoFe-LDH/PMS systems (b) ([LFV] = 10 mg/L, [CuCoFe-LDH] = 200 mg/L, [PMS] = 1.629 mM, pH = 7.0, T = 30°C).

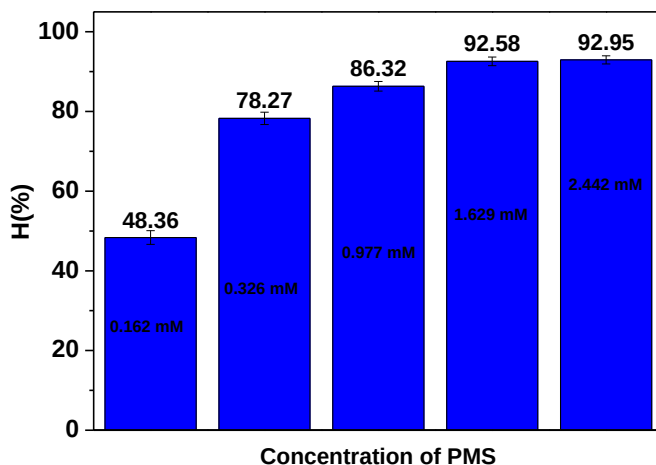


Fig. 6. Effect of PMS content on LFV decomposition efficiency ([LFV] = 10 mg/L, [CuCoFe-LDH] = 200 mg/L, [PMS] = 0.162 - 2.442 mM, pH = 7.0, T = 30°C).

The effect of different temperatures (30, 40, and 50°C) on LFV decomposition is shown in Fig. 7. The amount of CuCoFe-LDH (200 mg/L), PMS (1.629 mM), and LFV (10 mg/L) was fixed. The decomposition efficiency of LFV has relatively obvious changes at different temperatures. Specifically, after 10 minutes of reaction, the LFV decomposition efficiency reached 92.58%, 95.88%, and almost completely at 30, 40, and 50°C. On the other hand, the LFV decomposition rate constant increased from 0.2057 to 0.5063 min⁻¹ when the temperature increased from 30 to 50°C. LFV was decomposed rapidly after 4, 2, and 1 min when increasing the temperature from 30 to 50°C, showing

that temperature plays an important role in PMS activation and LFV degradation. The increased decomposition efficiency of LFV at high temperatures may be due to the acceleration of ROSs due to the endothermic nature of PMS activation, which is consistent with previous publications on tertiary LDH [22, 23]. Furthermore, the activation energy E_a of the LFV decomposition is determined through the Arrhenius equation based on the reaction rate constant and the temperature. The results show that the $\ln k - 1/T$ curve has a good linear correlation coefficient ($R^2 = 0.988$), proving that the kinetics of the LFV decomposition reaction by the CuCoFe-LDH/PMS system can be correlated with the temperature through the Arrhenius equation. The activation energy for LFV decomposition is calculated as 34.04 kJ/mol, which is much higher than the activation energy of the controlled diffusion reactions (10 - 13 kJ/mol). Thus, the LFV degradation rate of the CuCoFe-LDH/PMS system is dominated by the intrinsic chemical reaction rate on the CuCoFe-LDH catalyst surface [24]. This activation energy value is lower than some MgCuFe-LDH/PMS systems for Rhodamine B of 30.8 kJ/mol [22], CoMgAl-LDH/PMS for phenol of 65.19 kJ/mol [23], MgCoAl-LDH/PMS for methylene blue of 70.81 kJ/mol [25].

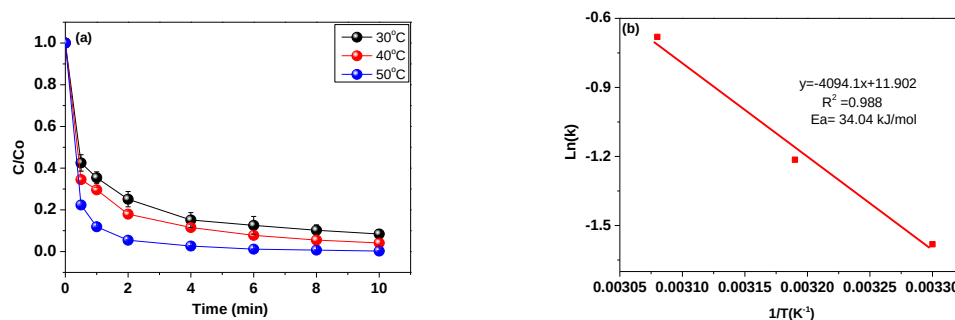


Fig. 7. Effect of reaction temperature on LFV decomposition efficiency (a) and activation energy E_a (b) ($[LFV] = 10 \text{ mg/L}$, $[CuCoFe-LDH] = 200 \text{ mg/L}$, $[PMS] = 1.629 \text{ mM}$, $pH = 7.0$, $T = 30 - 50^\circ\text{C}$).

4. Conclusion

Advanced oxidation process (AOP) based on peroxymonosulfate is an effective method to treat organic pollution in water. In this work, CuCoFe-LDH in different ratios were successfully synthesized by hydrothermal method and characterized by XRD, FTIR, SEM, EDX, and elemental mapping. The material was then applied for high catalytic activation of PMS to degrade levofloxacin in water under different conditions of Cu:Co:Fe ratio (1:1:1, 1:2:1, and 1:3:2), PMS concentration (0.162 - 2.442 mM), and reaction temperatures (30 - 50°C). At the optimum condition of pH 7, PMS dosage of 1.629 mM, and CuCoFe-LDH content (1:3:2) of 200 mg/L, 92.58% levofloxacin was decomposed after 10 minutes of reaction. The LFV decomposition rate constant of CuCoFe-LDH(1:3:2)/PMS was 2 times higher than that of

CuCoFe-LDH(1:1:1)/PMS ratio. The activation energy (E_a) calculated by the Arrhenius equation in the temperature range of 30 - 50°C was 34.04 kJ/mol. This study further expands the applications of LDH-based heterogeneous catalysis for PMS activation.

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References

- [1] Y. Zhong, K. Shih, Z. Diao, G. Song, M. Su, L. a. Hou, D. Chen, and L. Kong, Peroxymonosulfate activation through LED-induced $ZnFe_2O_4$ for levofloxacin degradation, *Chemical Engineering Journal*, Vol. 417, 2021, 129225. DOI: 10.1016/j.cej.2021.129225
- [2] Y. He, J. Qian, P. Wang, J. Wu, B. Lu, S. Tang, and P. Gao, "Acceleration of levofloxacin degradation by combination of multiple free radicals via MoS_2 anchored in manganese ferrite doped perovskite activated PMS under visible light," *Chemical Engineering Journal*, Vol. 431, 2022, 133933. DOI: 10.1016/j.cej.2021.133933
- [3] L. Saya, V. Malik, D. Gautam, G. Gambhir, Balendra, W. R. Singh, and S. Hooda, "A comprehensive review on recent advances toward sequestration of levofloxacin antibiotic from wastewater," *Science of The Total Environment*, Vol. 813, 2022, 152529. DOI: 10.1016/j.scitotenv.2021.152529
- [4] L. Chang, X. Xue, Q. Deng, X. Xie, X. Zhang, C. Cheng, H. Chai, and Y. Huang, "Modulating the electronic structure of Co center via $MgO@C$ co-doping for PMS activation to remove levofloxacin," *Separation and Purification Technology*, Vol. 321, 2023, 124151. DOI: 10.1016/j.seppur.2023.124151
- [5] F. Ghanbari and M. Moradi, "Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review," *Chemical Engineering Journal*, Vol. 310, pp. 41-62, 2017. DOI: 10.1016/j.cej.2016.10.064
- [6] Z.-z. Yang, C. Zhang, G.-m. Zeng, X.-f. Tan, H. Wang, D.-l. Huang, K.-h. Yang, J.-j. Wei, C. Ma, and K. Nie, "Design and engineering of layered double hydroxide based catalysts for water depollution by advanced oxidation processes: A review," *Journal of Materials Chemistry A*, Vol. 8, pp. 4141-4173, 2020. DOI: 10.1039/C9TA13522G
- [7] R. Guo, Y. Zhu, X. Cheng, J. Li, and J. C. Crittenden, "Efficient degradation of lomefloxacin by Co-Cu-LDH activating peroxymonosulfate process: Optimization, dynamics, degradation pathway and mechanism," *Journal of Hazardous Materials*, Vol. 399, 2020, 122966. DOI: 10.1016/j.jhazmat.2020.122966

- [8] R. Guo, Y. Li, Y. Chen, Y. Liu, B. Niu, J. Gou, and X. Cheng, "Efficient degradation of sulfamethoxazole by CoCu LDH composite membrane activating peroxymonosulfate with decreased metal ion leaching," *Chemical Engineering Journal*, Vol. 417, 2020, 127887. DOI: 10.1016/j.cej.2020.127887
- [9] Z. Yang, X. Li, Y. Huang, Y. Chen, A. Wang, Y. Wang, C. Li, Z. Hu, and K. Yan, "Facile synthesis of cobalt-iron layered double hydroxides nanosheets for direct activation of peroxymonosulfate (PMS) during degradation of fluoroquinolones antibiotics," *Journal of Cleaner Production*, Vol. 310, 2021, 127584. DOI: 10.1016/j.jclepro.2021.127584
- [10] M. Fu, J. Yan, B. Chai, G. Fan, D. Ding, and G. Song, "In situ synthesis of CoFe-LDH on biochar for peroxymonosulfate activation toward sulfamethoxazole degradation: cooperation of radical and non-radical pathways," *New Journal of Chemistry*, Vol. 47, pp. 4018-4032, 2023. DOI: 10.1039/D2NJ05132J
- [11] N. Q. Tung, D. T. C. Van, D. X. Thang, N. T. K. An, T. T. Trang, B. D. Nhi, N. P. Thao, L. T. Son, N. N. Huy, and N. T. Dung, "Hydrothermal synthesis of CuCoFe layered double hydroxide and its performance in the degradation of antibiotics: Influencing factors, degradation pathways, and reaction mechanism," *Journal of Environmental Chemical Engineering*, Vol. 11, 2023, 110127. DOI: 10.1016/j.jece.2023.110127
- [12] H. Lu, M. Sui, B. Yuan, J. Wang, and Y. Lv, "Efficient degradation of nitrobenzene by Cu-Co-Fe-LDH catalyzed peroxymonosulfate to produce hydroxyl radicals," *Chemical Engineering Journal*, Vol. 357, pp. 140-149, 2019. DOI: 10.1016/j.cej.2018.09.111
- [13] L. Wu, T. Jin, D. Li, L. Wang, and Y. Sun, "Heterogeneous activation of permonosulfate by biochar supporting CuCoFe layered double hydroxide for rapid degradation of phenanthrene," *Journal of Environmental Chemical Engineering*, Vol. 11, 2023, 110718. DOI: 10.1016/j.jece.2023.110718
- [14] S. Wang, T. Li, X. Cheng, R. Zhu, and Y. Xu, "Regulating the concentration of dissolved oxygen to achieve the directional transformation of reactive oxygen species: A controllable oxidation process for ciprofloxacin degradation by calcined CuCoFe-LDH," *Water Research*, Vol. 233, 2023, 119744. DOI: 10.1016/j.watres.2023.119744
- [15] N. T. Dung, V. D. Thao, and N. N. Huy, "Decomposition of glyphosate in water by peroxymonosulfate activated with CuCoFe-LDH material," *Vietnam Journal of Chemistry*, Vol. 59, pp. 813-822, 2021. DOI: 10.1002/vjch.202100045
- [16] Y. Zhao, X. Yuan, L. Jiang, X. Li, J. Zhang, and H. Wang, "Reutilization of cathode material from spent batteries as a heterogeneous catalyst to remove antibiotics in wastewater via peroxymonosulfate activation," *Chemical Engineering Journal*, Vol. 400, 2020, 125903. DOI: 10.1016/j.cej.2020.125903

- [17] T. Li, X. Du, J. Deng, K. Qi, J. Zhang, L. Gao, and X. Yue, "Efficient degradation of Rhodamine B by magnetically recoverable Fe₃O₄-modified ternary CoFeCu-layered double hydroxides via activating peroxymonosulfate," *Journal of Environmental Sciences*, Vol. 108, pp. 188-200, 2021. DOI: 10.1016/j.jes.2021.02.020
- [18] D. Chen, X. Wang, X. Zhang, W. Wang, Y. Xu, Y. Zhang, and G. Qian, "In situ growing Cu₂(OH)₂CO₃ on oxidized carbon nitride with enhanced photocatalytic hydrogen evolution and pollutant degradation," *International Journal of Hydrogen Energy*, Vol. 45, pp. 24697-24709, 2020. DOI: 10.1016/j.ijhydene.2020.06.225
- [19] G. Chen, L.-c. Nengzi, B. Li, Y. Gao, G. Zhu, and X. Cheng, "Octadecylamine degradation through catalytic activation of peroxymonosulfate by FeMn layered double hydroxide," *Science of the Total Environment*, Vol. 695, 2019, 133963. DOI: 10.1016/j.scitotenv.2019.133963
- [20] C. Xue, Z. Cao, X. Tong, P. Yang, S. Li, X. Chen, D. Liu, and W. Huang, "Investigation of CuCoFe-LDH as an efficient and stable catalyst for the degradation of acetaminophen in heterogeneous electro-Fenton system: Key operating parameters, mechanisms and pathways," *Journal of Environmental Management*, Vol. 327, 2023, 16787. DOI: 10.1016/j.jenvman.2022.116787
- [21] G. P. Anipsitakis and D. D. Dionysiou, "Radical generation by the interaction of transition metals with common oxidants," *Environmental Science & Technology*, Vol. 38, pp. 3705-3712, 2004. DOI: 10.1021/es035121o
- [22] J. Zhu, Z. Zhu, H. Zhang, H. Lu, and Y. Qiu, "Efficient degradation of organic pollutants by peroxymonosulfate activated with MgCuFe-layered double hydroxide," *RSC Advances*, Vol. 9, pp. 2284-2291, 2019. DOI: 10.1039/C8RA09841G
- [23] Z. Liao, J. Zhu, A. Jawad, J. Muzi, Z. Chen, and Z. Chen, "Degradation of Phenol Using Peroxymonosulfate Activated by a High Efficiency and Stable CoMgAl-LDH Catalyst, *Materials*," Vol. 12, 2019, 968. DOI: 10.3390/ma12060968
- [24] S. Zhu, Z. Wang, C. Ye, J. Deng, X. Ma, Y. Xu, L. Wang, Z. Tang, H. Luo, and X. Li, "Magnetic Co/Fe nanocomposites derived from ferric sludge as an efficient peroxymonosulfate catalyst for ciprofloxacin degradation," *Chemical Engineering Journal*, Vol. 432, 2022, 134180. DOI: 10.1016/j.cej.2021.134180
- [25] J. a. Sun, L. Wang, Y. Wang, W. Lv, and Y. Yao, "Activation of peroxymonosulfate by MgCoAl layered double hydroxide: Potential enhancement effects of catalyst morphology and coexisting anions," *Chemosphere*, Vol. 286, 2022, 131640. DOI: 10.1016/j.chemosphere.2021.131640

HOẠT HÓA PEROXYMONOSULFATE BẰNG HYDROXIT PHÂN LỚP KÉP CuCoFe ĐỂ PHÂN HỦY LEVOFLOXACIN

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Tóm tắt: Trong nghiên cứu này, chúng tôi báo cáo về các chất xúc tác hydroxit phân lớp kép CuCoFe-LDH theo các tỉ lệ Cu:Co:Fe khác nhau (1:1:1; 1:2:1 và 1:3:2) được tổng hợp bằng phương pháp thủy nhiệt và ứng dụng để hoạt hóa PMS phân hủy levofloxacin. Các mẫu LDH thu được được đặc trưng bởi nhiễu xạ tia X (XRD), quang phổ hồng ngoại biến đổi Fourier (FT-IR), kính hiển vi điện tử quét (SEM) và phổ tán sắc năng lượng tia X (EDX). Kết quả chỉ ra CuCoFe-LDH tỉ lệ 1:3:2 có khả năng hoạt hóa PMS và phân hủy levofloxacin mạnh nhất. Sau 10 phút phản ứng, trong điều kiện hàm lượng xúc tác 200 mg/L, nồng độ PMS 1,629 mM, pH = 7, ở 30°C, hiệu quả phân hủy các LDH lần lượt là 64,89%; 83,93 và 92,58% tương ứng với các tỉ lệ 1:1:1; 1:2:1 và 1:3:2. Ảnh hưởng của các yếu tố nồng độ PMS và nhiệt độ phản ứng đến hiệu quả phân hủy LFV đã được khảo sát. PMS ở hàm lượng cao sẽ có lợi cho hình thành các loại oxy hoạt động. Tốc độ phân hủy của levofloxacin bị ảnh hưởng bởi nhiệt độ và năng lượng hoạt hóa là 34,04 kJ/mol.

Từ khóa: CuCoFe-LDH; PMS; levofloxacin.

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