

**This is the preprint of the contribution published as:**

**Keyikoğlu, R.,** Khataee, A., Orooji, Y. (2023):

Degradation of emerging pollutants on bifunctional ZnFeV LDH@graphite felt cathode through prominent catalytic activity in heterogeneous electrocatalytic processes

*J. Environ. Manage.* **342** , art. 118090

**The publisher's version is available at:**

<https://doi.org/10.1016/j.jenvman.2023.118090>

**Degradation of emerging pollutants on bifunctional ZnFeV LDH@graphite  
felt cathode through prominent catalytic activity in heterogeneous  
electrocatalytic processes**

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## ABSTRACT

The heterogeneous Electro-Fenton (EF) process is a promising wastewater treatment technology that can generate onsite  $\text{H}_2\text{O}_2$ , and operate in a wide pH range without generating a metal sludge. However, the heterogeneous EF process needs bifunctional cathode electrodes that can have high activity in  $2\text{e}^-$  oxygen reduction reaction and  $\text{H}_2\text{O}_2$  decomposition. Herein, ZnFeV layered double hydroxide (LDH), as a heterogeneous catalyst, was coated on the graphite felt (ZnFeV LDH@GF) cathode using the electrophoretic deposition method. ZnFeV LDH@GF cathode was able to generate  $59.8 \pm 5.9 \text{ mg L}^{-1} \text{ H}_2\text{O}_2$  in 90 min under a constant supply of  $\text{O}_2$ . EF process with ZnFeV LDH@GF cathode exhibited  $89.8 \pm 6.8\%$  removal efficiency for pharmaceutical (ciprofloxacin) at neutral pH. Remarkably, the apparent reaction rate constant ( $k_{\text{app}}$ ) of the ZnFeV LDH@GF-EF was 2.14 times that of the EF process with pristine GF. ZnFeV LDH coating increased the hydroxyl radical ( $\cdot\text{OH}$ ) production of the EF process from 1.74 mM to 3.65 mM. The pathway of  $\cdot\text{OH}$  production is thought to be a single electron transfer from redox couples of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{V}^{4+}/\text{V}^{5+}$  to  $\text{H}_2\text{O}_2$ . After 10 reuse cycles, the ZnFeV LDH@GF cathode retained 90.2% of its efficiency. Eight intermediate compounds were identified by GC-MS including cyclic compounds and aliphatic compounds.

**Keywords:** Electrophoretic deposition; Ciprofloxacin; Graphite felt; Layered double hydroxide; Water treatment

## 1. Introduction

The emergence of pharmaceuticals in water resources is currently the focus of researchers due to their unknown biological and ecotoxicological effects. When pharmaceuticals enter ordinary wastewater treatment facilities, their bioactive components can remain unaffected, or worse, transform into more toxic intermediates (Davey et al., 2022). Advanced oxidation processes (AOPs) have transformed the treatment of water that contains persistent organic pollutants with benefits like a fast reaction rate, strong oxidation ability, and practicality (Xing et al., 2018). Among AOPs, the Fenton reaction relies on the generation of  $\cdot\text{OH}$  through the reaction of  $\text{Fe}^{+2}$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) at highly acidic pH conditions (2-3) (Fenton, 1894). Recently, the electro-Fenton (EF) process has gained popularity owing to the electrochemical generation of  $\text{H}_2\text{O}_2$  through the two-electron oxygen reduction reaction (ORR) (Eq. 1) (El Kateb et al., 2019; Ganiyu et al., 2018b). In situ production of  $\text{H}_2\text{O}_2$  in the EF process eliminates the risk involved with the storage, shipping, and handling of hazardous  $\text{H}_2\text{O}_2$  (Nada et al., 2021; Orimolade et al., 2020). In the presence of a suitable catalyst such as  $\text{Fe}^{2+}$ , the-produced  $\text{H}_2\text{O}_2$  produces a strong radical,  $\cdot\text{OH}$  ( $E^\circ = 2.80 \text{ V/SHE}$ ) that can attack pollutants unselectively (Eq. 2). Another advantage of EF is the regeneration of oxidized  $\text{Fe}^{3+}$  via cathodic reduction, further increasing the process efficiency (Eq. 3) (Ganiyu et al., 2018b). As for the type of catalyst used in the EF process, heterogeneous catalysts overcome some of the disadvantages of traditional homogeneous catalysts, such as overcoming sludge build-up, narrow operating pH, and one-time use of the catalyst (Zhu et al., 2019).



Layered double hydroxides (LDHs) are two-dimensional layered nanomaterials and are a member of the anionic clay family. LDHs are known by the general formula of

65  $[M_{1-x}^{2+}M_x^{3+}OH_2]^{x+}[A_{x/n}^{n-}\cdot yH_2O]^{x-}$ , where  $M^{2+}$  is a divalent cation,  $M^{3+}$  is a trivalent cation,  $x$   
 66 is the molar ratio of  $M^{3+}/(M^{3+} + M^{2+})$ , and  $A^{n-}$  is an anion (Lv et al., 2019; Zhou et al., 2021).  
 67 The layered structure of LDHs consists of brucite-like positively charged cationic layers and  
 68 interlayer hydrated anions that balance the total charge. The application of LDHs as a  
 69 heterogeneous catalyst has received much interest owing to their large surface area, abundant  
 70 catalytic active sites, and thermal and chemical stabilities (Fan et al., 2014). Various LDHs  
 71 have been previously explored for their catalytic activities for the heterogeneous Fenton  
 72 process. For example, CuFe LDH has shown 91.3% removal efficiency when used as a powder  
 73 catalyst in the EF process (Ghasemi et al., 2019). Copper-modified MgFe LDH achieved  
 74 complete removal of antibiotic sulfathiazole in 90 min at pH 7.5. Thus, LDHs offer high  
 75 stability and catalytic effectiveness at circumneutral pH values for the removal of various  
 76 pollutants (Xue et al., 2023). However, the heterogeneous Fenton process still abides by the  
 77 rule of the classical Fenton process and thus experiences lowered performance under neutral  
 78 conditions. Worse still, they require excess  $H_2O_2$  above the stoichiometric amount because of  
 79 the mass transfer limitations and low reduction rate of  $\equiv M^{3+}$  to  $\equiv M^{2+}$  ( $M$  stands for metal  
 80 species). Developing co-catalytic systems is a good strategy to boost the  $Fe^{2+}/Fe^{3+}$  cycle (Zhu  
 81 et al., 2019). Cocatalyst is a material that has low activity on its own but improves the properties  
 82 of the active catalyst such as electronic structure, valance state, stability, etc (Xiang et al.,  
 83 2022a). Literature classifies heterogeneous catalysts into two groups: (i) non-metallic  
 84 cocatalysts such as phosphorous, boron, and carbon materials, and (ii) transition metal  
 85 cocatalysts including nickel (Ni), tungsten (W), molybdenum (Mo), or vanadium (V), etc.  
 86 (Liang et al., 2017). For example, rich reductive active sites on the surface of Mo-based ( $M^0$ ,  
 87  $M^{4+}$ ) and W-based materials ( $W^0$ ,  $W^{4+}$ ) induce the  $Fe^{3+}$  conversion to  $Fe^{2+}$  (Yan et al., 2020).  
 88 Similarly, V as a transition metal has multiple valance states ( $V^{3+}$ ,  $V^{4+}$ ,  $V^{5+}$ ) making it a suitable

cocatalyst for Fe. Recent studies have shown that various vanadium oxides ( $V_2O_3$ ,  $VO_2$ ,  $V_2O_5$ ) can activate  $H_2O_2$  for the removal of pollutants (Fang et al., 2018, 2017; Liang et al., 2022).

In EF processes, the highly porous structure of graphite felt (GF) serves as a medium for the exposure of more catalytically active sites. Depositing nanomaterials on the surface of GF is a good strategy to increase the specific surface area. In this work, we present a binder-free formation of self-standing ZnFeV LDH@GF electrode through the electrophoretic deposition (EPD) method. The great number of active sites owing to the embedded LDH particles are expected to provide reaction sites for  $H_2O_2$  adsorption and subsequent decomposition. Furthermore, the use of a catalyst-coated cathode, where  $H_2O_2$  is continuously produced, is expected to reduce the mass transfer limitations for  $\cdot OH$  generation. The efficiency of the ZnFeV LDH@GF-EF process was evaluated in the degradation of ciprofloxacin (CIP) as a model pollutant. The effects of process performances such as CIP concentration, reaction pH, applied voltage, and type of gas injection were studied. We also aimed to investigate the reaction mechanism of the ZnFeV LDH@GF-EF process in the degradation of CIP.

## 2. Materials and methods

### 2.1. Materials

Iron (III) chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ,  $\geq 99\%$ , CAS-Number: 10025-77-1), zinc chloride ( $ZnCl_2$ ,  $\geq 98\%$ , CAS-Number: 7646-85-7), vanadium (III) chloride ( $VCl_3$ , 97%, CAS-Number: 7718-98-1), hydrogen peroxide ( $H_2O_2$ , 30%, CAS-Number: 7722-84-1), nitric acid ( $HNO_3$ , 70%, CAS-Number: 7697-37-2), sodium hydroxide pellets ( $NaOH$ , 99%, CAS-Number: 1310-73-2), sulfuric acid ( $H_2SO_4$ , 95.0-98.0%, CAS-Number: 7664-93-9),  $Mg(NO_3)_2 \cdot 6H_2O$  ( $\geq 99\%$ , CAS-Number: 13446-18-9), 1,4-benzoquinone ( $C_6H_4O_2$ , 99%, CAS-Number: 106-51-4), diethyl ether ( $(C_2H_5)_2O$ ,  $\geq 99\%$ , CAS-Number: 60-29-7), N, O-bis-(trimethylsilyl)-acetamide ( $\geq 95\%$ , CAS-Number: 10416-59-8), o-phenylenediamine (OPD, 99.5%, CAS-Number: 95-54-

5), KI (Potassium iodide,  $\geq 99.0\%$ , CAS-Number: 7681-11-0), ammonium molybdate tetrahydrate  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$ ,  $\geq 99.0\%$ , CAS-Number: 12054-85-2), potassium hydrogen phthalate (KHP, CAS-Number: 877-24-7), ethanol ( $\text{EtOH}$ ,  $\geq 99.5\%$ , CAS-Number: 64-17-5), and isopropanol  $((\text{CH}_3)_2\text{CHOH})$ ,  $\geq 99.5\%$ , CAS-Number: 67-63-0) were purchased from Merck, Germany. Graphite felt electrode was supplied from SGL Sigratherm (Germany). A platinum (Pt) plate electrode was obtained from DiaCCon GmbH (Germany). Ultra-high purity oxygen and nitrogen gases were obtained from Hatgrup (Turkey).

## 2.2. Development of ZnFeV LDH@GF cathode

ZnFeV LDH was synthesized using the co-precipitation method (Keyikoğlu et al., 2022). Appropriate amounts of  $\text{ZnCl}_2$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{VCl}_3$  were dissolved in ultrapure water that was previously purged with  $\text{N}_2$  for 30 mins. The molar ratio of  $\text{Zn}/(\text{Fe}+\text{V})$  was adjusted to 3. The precipitator agent,  $\text{NaOH}$ , was slowly added to the above solution under vigorous stirring to raise the pH to around 8. Following an aging period of 24 h, a centrifuge was used to separate the solid phase. The remaining solid was washed with pure water several times to remove the impurities.

The EPD method was adopted to coat the GF electrode with LDH nanoparticles (Figure 1a) (Tada and Onoda, 2002). Before coating, GF was treated with ethanol, acetone, and deionized water for 15 min, respectively, in an ultrasonic bath (Elmasonic P120H, 37 kHz, Germany). The pre-treated GF was then subjected to acid treatment using a hydrothermal method and dried in an oven at  $60^\circ\text{C}$  (Keyikoğlu et al., 2022). A colloidal suspension of LDH was prepared by adding 0.1 g LDH and  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  into 40 mL of 2-propanol. The mixture was sonicated in an ultrasonic bath for 30 mins to achieve a homogenous suspension of LDH particles. The resulting solution was put into a glass electrochemical cell that was connected to a DC power supply (Aim-TTi, TSX3510, UK). The GF and stainless steel (SS, 316 AISI SS, Turkey) were placed vertically into the cell with a 1 cm interelectrode distance and connected

to the negative and positive poles of the power supply, respectively. For the electrodeposition of LDH particles, the voltage was set to 40 V for 7 min. The prepared ZnFeV LDH-coated GF is denoted as ZnFeV LDH@GF. The pristine GF, which is denoted as PGF, was also subjected to pretreatment and hydrothermal treatment.

### 2.3. Characterization studies

The crystalline and phase structure of the ZnFeV LDH was investigated using an X-ray diffraction (XRD) instrument (Empyrean diffractometer PANalytical B.V., Holland)) that has Cu K $\alpha$  radiation ( $\lambda$  =0.15406 nm; 40 kV, and 40 mA). The morphological features and the elemental analysis of the material were done using the scanning electron microscope (SEM) instrument Philips XL30 FEG (the Netherlands) coupled with energy-dispersive X-ray spectroscopy (EDS). High-resolution transmission electron microscopy (HR-TEM) images were taken using JEOL JEM-2100 Plus (Japan) operated at 200 kV. Functional groups and the interactions between the intercalated anions and the brucite layers of the ZnFeV LDH were determined using a Fourier-transform infrared (FTIR) instrument (Perkin Elmer Spectrum 100, Germany). The specific surface area, pore volume, and pore diameter of the catalyst were analyzed by Brunauer–Emmett–Teller (BET) method using the data collected from the N<sub>2</sub> adsorption-desorption analyzer (BELSORP Mini II, Japan). The surface composition and surface chemistry of the catalyst were further analyzed by XPS (Kratos Analytical Ltd. Axis Ultra, Manchester, UK) with a monochromatic Al excitation source.

The intermediate products of the CIP were detected using a Gas Chromatography/Mass Spectrometry (GC-MS) instrument (Agilent 6890N, USA) (Keyikoğlu et al., 2022). Heavy metals leaching from the ZnFeV LDH during the electro-Fenton process was determined by Inductively coupled plasma-optical emission spectrometry (ICP-OES) analyses (Perkin-Elmer Optima 7000 DV, USA). The composition of the synthesized material was verified by the

digestion of a known amount of solid material in nitric acid and H<sub>2</sub>O<sub>2</sub> solution and analysis by ICP-OES. Electrochemical properties of the ZnFeV LDH@GF electrode were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in a three-electrode potentiostat (Metrohm Autolab PGSTAT302N, the Netherlands), where the Pt wire, Ag/AgCl, and GF were used as a counter, reference, and working electrodes, respectively. The concentration of H<sub>2</sub>O<sub>2</sub> in the EF cell was determined according to the iodide method (Klassen et al., 1994). A spectrophotometric method that is based on the reaction of <sup>•</sup>OH and OPD was used to determine <sup>•</sup>OH generated in the EF process (Text S1) (Fang et al., 2009; Sun et al., 2021).

#### **2.4. Application of ZnFeV LDH@GF cathode in EF process**

EF experiments were conducted in a cylindrical glass cell with a volume of 150 mL. The EF process consisted of ZnFeV LDH@GF (6 cm × 5 cm) and Pt (6 cm × 5 cm) plate electrodes that were located vertically parallel to each other with a 1.5 cm distance. Electricity was supplied using a DC power supply (Aim-TTi TSX3510, UK). In a typical treatment, 50 mM Na<sub>2</sub>SO<sub>4</sub> was added as a supporting electrolyte to 100 mL CIP solution. Pure oxygen was supplied to the bottom of the cathode for electrochemical H<sub>2</sub>O<sub>2</sub> production. The concentration of CIP was analyzed using a UV-Vis spectrophotometer (Perkin Elmer, lambda 25) at the wavelength of 278 nm. The solution pH was measured by a pH meter (Mettler Toledo Seven Compact, USA) and was adjusted using 0.1 M H<sub>2</sub>SO<sub>4</sub> or NaOH. The removal of CIP by the ZnFeV LDH@GF-EF process was also tested in real wastewater collected from a wastewater treatment plant on the Kocaeli University (Turkey) campus, where a university hospital, university buildings, and residential complexes are located. The characteristic of the real wastewater is given in Table S1. The synergy factor of the process was calculated using Eq.4.

$$\text{Synergy factor} = \frac{k_{\text{app}}(\text{ZnFeV LDH@GF} - \text{EF})}{k_{\text{app}}(\text{PGF} - \text{EF}) + k_{\text{app}}(\text{Adsorption})} \quad (4)$$

where  $k_{\text{app}}$  is the apparent rate constant. The energy efficiency of CIP removal by the developed process was evaluated by calculating the specific energy consumption (SEC) according to Eqs. 5 and 6 (Turan et al., 2020).

$$\text{SEC (kWh m}^{-3}\text{)} = \frac{U \times i \times t}{10^3 \times V} \quad (5)$$

$$\text{SEC (kWh kg}^{-1}\text{)} = \frac{U \times i \times t}{10^3 \times V \times (C_0 - C_t)} \quad (6)$$

where  $i$  is current (A),  $U$  is cell voltage (V),  $t$  is operating time (h),  $V$  ( $\text{m}^3$ ) is the volume of treated solution, and  $C_0$  and  $C_t$  ( $\text{kg/m}^3$ ) are the CIP concentration at time zero and at a specified time.

### 3. Results and discussions

#### 3.1. Characterization studies

According to the SEM images, ZnFeV LDH particles have a lamellar flake morphology (Figures 1b and c) (Yong Yang et al., 2019). The particles are uniformly distributed and have an average thickness of 25 nm. TEM images of the LDH sample show well-defined plate-like material that is specific to LDH materials. The interplanar spacing of the lattice plane (101) was determined as 0.20 nm (Figure 1d and e) (Bao et al., 2022). According to the EDS elemental analysis, ZnFeV LDH contains Zn, Fe, V, Cl, and O atoms without other impurities (Figure S1). The weight percentages of the elements are given in the inset figure, which is very close to the ratios of the prepared precursors. The metallic composition analysis by ICP-OES showed the amount of Zn, Fe, and V metals in the LDH as 79.13%, 11.82%, and 9.05%, respectively.

XRD analysis of the sample indicates a high crystalline material with diffraction peaks at 11.52° (003), 23.13° (006), 28.46°(110), 30.69°(101), 32.95°(009), 34.97°(012), 37.47°(015), 48.9° (018), 58.71°(110), 60.12° (113), which agrees with the Zn type LDH materials (Keyikoğlu et al., 2022) (Figure 1f). The average crystallite size of the ZnFeV LDH was determined as 14 nm using Debye-Scherrer's equation. According to Bragg's equation ( $\lambda=2 \cdot d \cdot \sin\theta$ ), where 'λ' is the wavelength of X-ray, the crystal plane distance (d) of ZnFeV LDH is 0.76 nm, which agrees with the literature (Wang et al., 2021). In the FTIR spectrum of the ZnFeV LDH (Figure 1g), the metal-oxygen bands of the brucite layers appear as several stretching and bending modes below 1000 cm<sup>-1</sup> (Ganiyu et al., 2018a). The characteristic stretching of O-H between 2670-3700 cm<sup>-1</sup> indicates the presence of surface hydroxyl ions and the inter-gallery water molecules. Furthermore, angular deformation of the water molecules causes a band around 1674 cm<sup>-1</sup> (Tichit et al., 2019). BET surface area (S<sub>BET</sub>), total pore volume, and average pore diameter of the ZnFeV LDH are 125.38 m<sup>2</sup> g<sup>-1</sup>, 28.81 cm<sup>3</sup> g<sup>-1</sup>, and 13.9 nm, respectively.

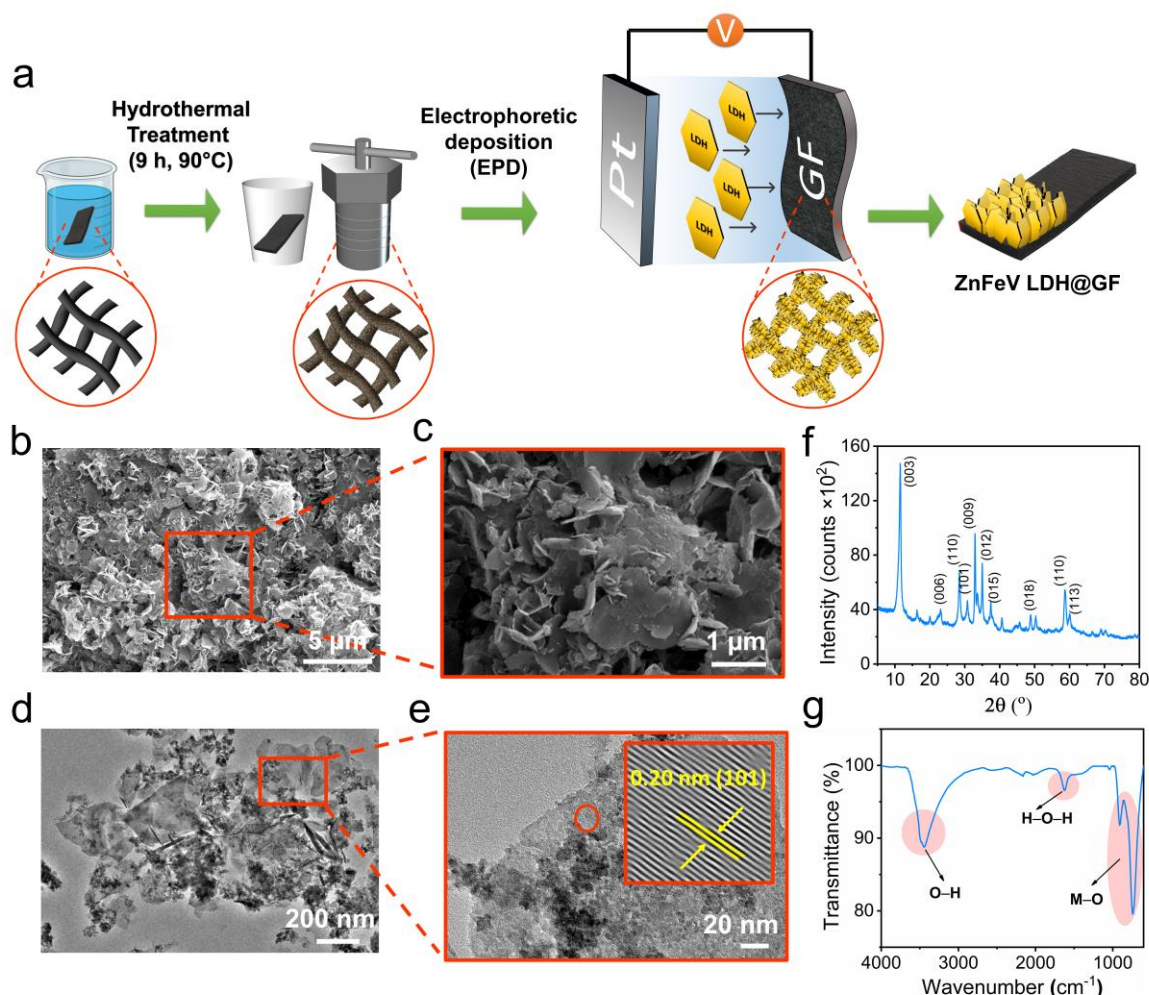


Figure 1. a) The production scheme of ZnFeV LDH@GF cathode using electrophoretic deposition (EPD) method; b-c) Scanning electron microscope (SEM) images d-e) high-resolution transmission electron microscopy (HR-TEM) images (inset-e shows the lattice spacing); f) X-ray powder diffraction (XRD) spectrum and, g) Fourier-transform infrared (FTIR) spectrum of ZnFeV LDH.

The surface chemical composition of the ZnFeV LDH was investigated by XPS analysis (Figure 2). The survey spectrum of the material shows the presence of Zn, Fe, V, O, and Cl as the constituents of the LDHs and not other impurities (Figure 2a). Deconvoluted O1s peak consisted of three components with the binding energies of 530.4 eV, 531.8 eV, and 533.1 eV, which can be assigned to lattice oxygen ( $\text{O}_2^{2-}$ ), chemisorbed and dissociated oxygen caused by species such as adsorbed water molecules or adsorbed oxygen, and the surface  $\text{OH}^-$  groups of

metal centers, respectively (Figure 2b) (Keyikoglu et al., 2022). The two peaks in the Fe 2p XPS signal at the binding energies of 711.1 eV and 724.9 eV along with a satellite peak at 718.2 eV (Figure 2c) (Li et al., 2018). These observed peaks separated by a  $\Delta 13.8$  eV were assigned to the  $2p_{3/2}$  and  $2p_{1/2}$  spin state of  $Fe^{3+}$  in the ZnFeV LDH structure. The high-resolution signal of V2p consisted of V  $2p_{3/2}$  and V  $2p_{1/2}$  peaks that are separated by 7.33 eV spin-orbit splitting (Figure 2d) (Biesinger et al., 2010; Liu et al., 2021). The two components of V  $2p_{3/2}$  having binding energies of 516.5 eV and 517.4 eV were assigned to  $V^{4+}$  and  $V^{5+}$  species, respectively (Li et al., 2018), which confirms the redox couple of  $\equiv V^{4+}/\equiv V^{5+}$ .

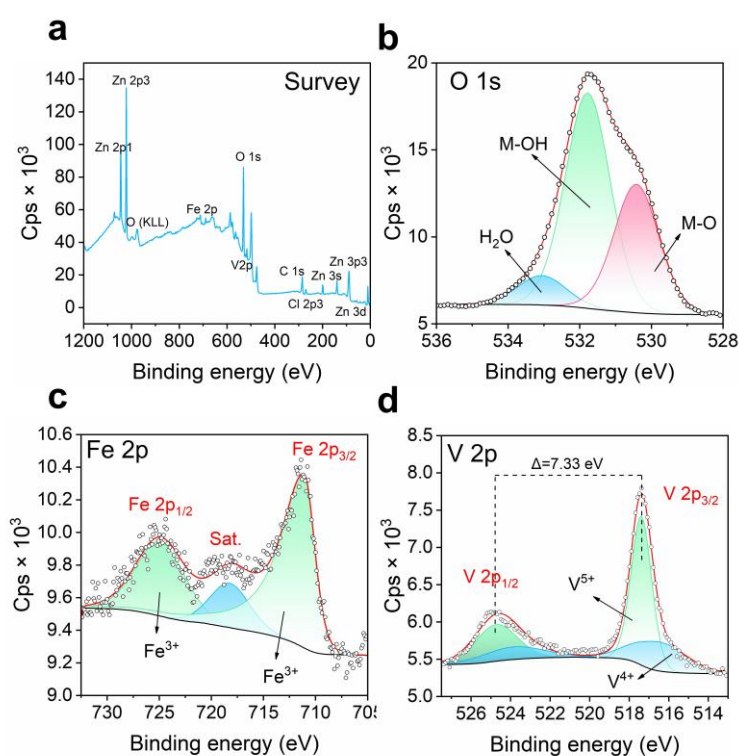


Figure 2. X-ray photoelectron spectroscopy (XPS) analysis of the ZnFeV LDH: a) Survey spectrum, b) O1s, c) Fe 2p, and d) V 2p.

Figures 3a-d show the SEM images of the ZnFeV LDH@GF electrode at different magnifications. GF fibers were uniformly covered with flake-like LDH particles. Furthermore, the morphology of the ZnFeV LDH remained the same after the EPD coating.

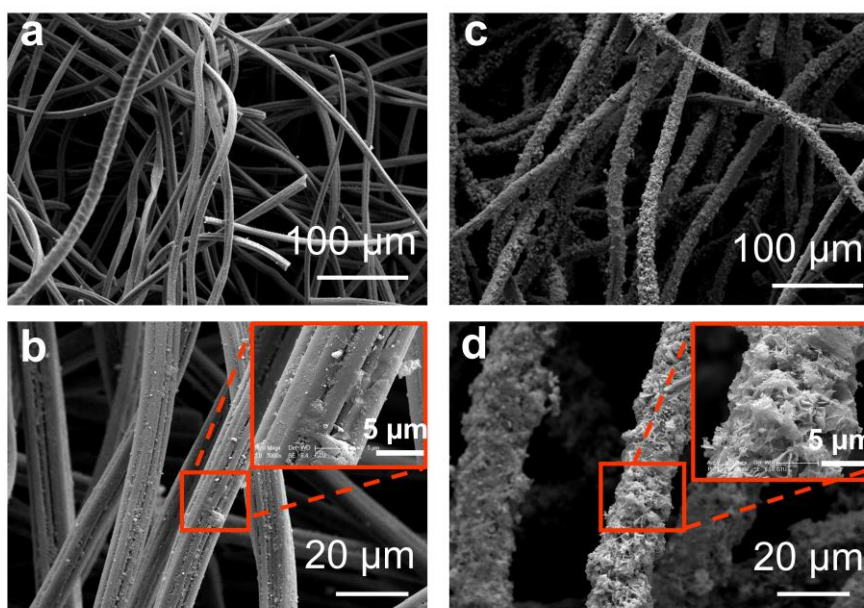


Figure 3. a-b) SEM images of pristine graphite felt (PGF) and c-d) ZnFeV LDH@GF cathodes.

To investigate the electrochemical characteristics of the pristine GF and ZnFeV LDH@GF, we have employed cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). According to the Nyquist plot, the semicircle of the PGF significantly decreases after GF was coated with ZnFeV LDH. This indicates that ZnFeV LDH@GF has lower charge transfer resistance ( $R_{ct}$ ) and enhanced electrical conductivity, which can facilitate the electron transfer rate of the electrode (Figure 4a) (Zhou et al., 2022). Similarly, the CV curve of ZnFeV LDH@GF had a higher redox peak current and bigger peak area than that of the pristine GF, which shows that ZnFeV LDH enhances the electron transfer rate of the pristine GF (Figure 4b). Similar findings were also reported for catalyst-coated carbon-felt electrodes (Xie et al., 2019). Moreover, the CV curve of the ZnFeV LDH@GF remained relatively stable after 100

CV cycles in  $K_4[Fe(CN)_6]$  solution, which implies the electrode is suitable for long-term applications (Figure 4c).

In the EF process, the generation of  $H_2O_2$  takes place at the cathode through the reduction of  $O_2$ . Therefore, the modified cathode should produce enough  $H_2O_2$  for the Fenton reaction. As Figure 4d shows that the amount of  $H_2O_2$  accumulated in the reaction cell was  $81.0 \pm 3.6$  mg  $L^{-1}$  at 2 V voltage, whereas only  $14.8 \pm 3.8$  mg  $L^{-1}$  accumulated at 1 V voltage in 90 min by PGF. Furthermore,  $H_2O_2$  accumulation declined to  $59.8 \pm 5.9$  mg  $L^{-1}$  when ZnFeV LDH@GF was employed as the cathode. The lower  $H_2O_2$  yield of the ZnFeV LDH@GF is due to the presence of LDH as a heterogeneous catalyst on the cathode surface that can directly decompose  $H_2O_2$  to  $\cdot OH$ , as reported in catalyst-loaded cathodes (Dung et al., 2022; Qi et al., 2021).

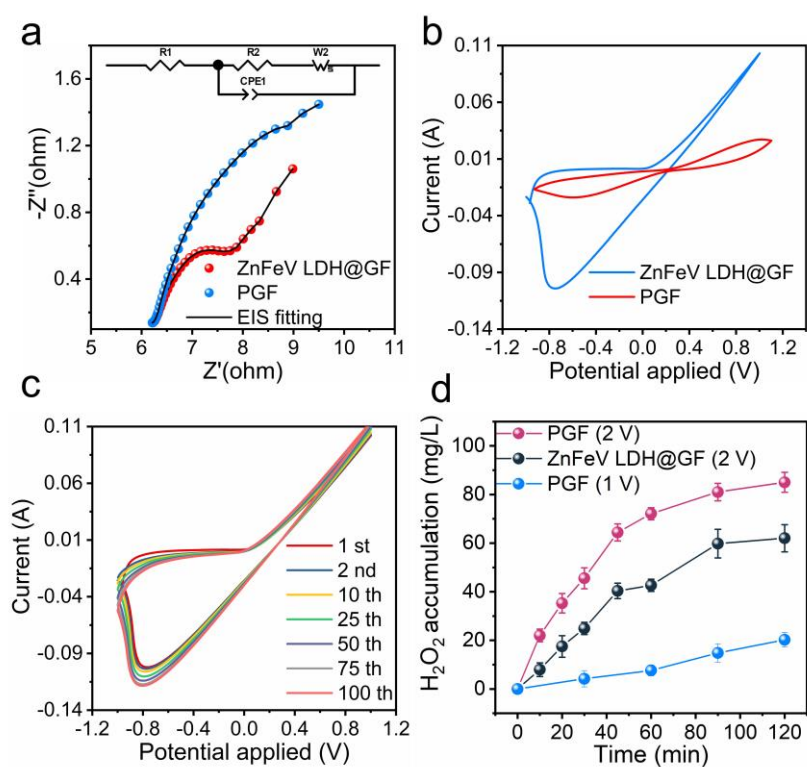


Figure 4. a) Nyquist plots and b) cyclic voltammograms (scan rate= $0.04 \text{ V s}^{-1}$ ) of the PGF and ZnFeV LDH@GF electrodes; c) stability test of ZnFeV LDH@GF (c) in 0.1 M

K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution; d) H<sub>2</sub>O<sub>2</sub> production tests of the PGF and ZnFeV LDH@GF cathodes in neutral 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution.

### **3.2. The effects of the operational parameters**

#### **3.2.1. The pollutant concentration**

Increasing the initial concentration of CIP adversely affected the degradation efficiency of the ZnFeV LDH@GF-EF process (Figure 5a). The process achieved almost complete removal of CIP when the initial concentration was 5 mg L<sup>-1</sup>. A gradual increase in the initial CIP concentration resulted in a decrease in the removal efficiency. Still, the ZnFeV LDH@GF-EF process could achieve 75% removal efficiency at 30 mg L<sup>-1</sup> initial CIP concentration. This occurrence is related to the production rate of <sup>•</sup>OH in the EF process. The EF process is incapable of competing with the increasing amount of pollutant molecules when <sup>•</sup>OH generation remains constant (Qi et al., 2021). Secondly, the surplus amount of CIP molecules can cover the surface-active sites of ZnFeV LDH, which reduces the catalytic conversion of H<sub>2</sub>O<sub>2</sub> to <sup>•</sup>OH. At the same time, as the number of pollutant molecules increases, so as the generation of intermediate products that compete with the parent molecule to consume <sup>•</sup>OH (Keyikoğlu et al., 2022).

#### **3.2.2. The solution pH**

Solution pH strongly influences the efficiency of the Fenton reaction and the rate of H<sub>2</sub>O<sub>2</sub> production (Ganiyu et al., 2018b). Although acidic pH values are favorable for the effective Fenton reaction, it's always desirable to run the process at circumneutral pHs. As Figure 5b shows, ZnFeV LDH@GF worked well on a wide pH scale. Even under neutral pH values, CIP removal efficiencies remained close to 90%. Only when the pH was adjusted to 10, the performance of ZnFeV LDH@GF-EF decreased to 55%. The lower performance of the process

at alkaline pH values is because of the lower oxidation potential of  $\cdot\text{OH}$  (Zhang et al., 2021). At the same time, alkaline pH conditions cause  $\text{H}_2\text{O}_2$  to decompose into  $\text{O}_2$  and  $\text{H}_2\text{O}$  at a faster rate, which is detrimental to the process performance (Yang et al., 2021). In conclusion, the ability of the ZnFeV@GF-EF process to function at wide pH windows implies that the process will be resistant to abrupt pH changes that could be experienced in real-life conditions. Considering that the LDHs are susceptible to acidic pH values, neutral pH values are also beneficial to the service life of the cathode.

### 3.2.3. Voltage

Applied voltage plays a decisive role in the treatment performance of electrochemical processes. Its role in the EF process is even greater with both controlling the  $\text{H}_2\text{O}_2$  generation rate and the anodic oxidation of pollutants (Xiang et al., 2022b). EF process performed better in removing CIP at higher voltages (Figure 5c). Decreasing the applied voltage resulted in a deterioration of the process performance. The CIP removal efficiency of the EF process dropped lower than 50% at a voltage of 1V. This is because of the significantly lower conversion rate of an  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  as shown in the previous section (Figure 4d). Additionally, higher voltage boosts the charge passing through the ZnFeV LDH@GF cathode and regenerates the LDH catalyst at a faster rate (Xie et al., 2019). Running the EF process at a voltage of 2V resulted in the best CIP removal efficiency as well as the greatest  $\text{H}_2\text{O}_2$  generation rate. However, undesired side reactions may dominate in the EF process at elevated voltages. While  $\text{O}_2$  evolution may compete with the  $\text{M}(\cdot\text{OH})$  at the anode, the hydrogen evolution reaction suppresses the ORR at the cathode (Ganiyu et al., 2018b).

#### 3.2.4. Dissolved gasses

Unlike the classical Fenton process, in which  $\text{H}_2\text{O}_2$  was externally added, the EF process requires an oxygen supply to produce in-situ  $\text{H}_2\text{O}_2$ . The performance of the ZnFeV LDH@GF-EF process was investigated under different gas supply conditions (Figure 5d). The process with pure oxygen gas achieved the best CIP removal efficiency. Air injected process performed worse than the  $\text{O}_2$ -injected process due to the lower  $\text{O}_2$  content of the air. In contrast, running the process without any gas supply caused a significant reduction in performance. The EF process supplied with  $\text{N}_2$  performed even worse than the process without any gas supply, which could be due to the stripping of the  $\text{O}_2$  that was already present in the solution (Gao et al., 2020).

#### 3.2.5. Radical scavengers

Scavenger agents can rapidly react with radical species, quenching their oxidative abilities. Therefore, the level of removal efficiency reduction caused by a radical scavenger can provide information regarding the pollutant oxidation done by the target radical. In this regard, PBQ and Isopropanol were added to the EF process to quench superoxide ( $\cdot\text{O}_2$ ), and  $\cdot\text{OH}$ , respectively (Figure 5e) (M. Guo et al., 2022; Mi et al., 2019). The greatest inhibition occurred in the presence of ethanol, which confirms  $\cdot\text{OH}$  was the most active species in the removal of CIP (Mi et al., 2019). PBQ reduced the CIP removal efficiency by 4%, suggesting a small amount of  $\cdot\text{O}_2$  production in EF through the single electron reduction of  $\text{O}_2$  (Xie et al., 2019). Figure 5f shows the UV-Vis spectra of OPD-trapped  $\cdot\text{OH}$ . The intensification of the peak at 418 nm as a function of time suggests continuous production of  $\cdot\text{OH}$  throughout the EF process by ZnFeV LDH@GF cathode. Moreover, ZnFeV LDH coating increased the hydroxyl radical ( $\cdot\text{OH}$ ) production of the EF process from 1.74 mM to 3.65 mM.

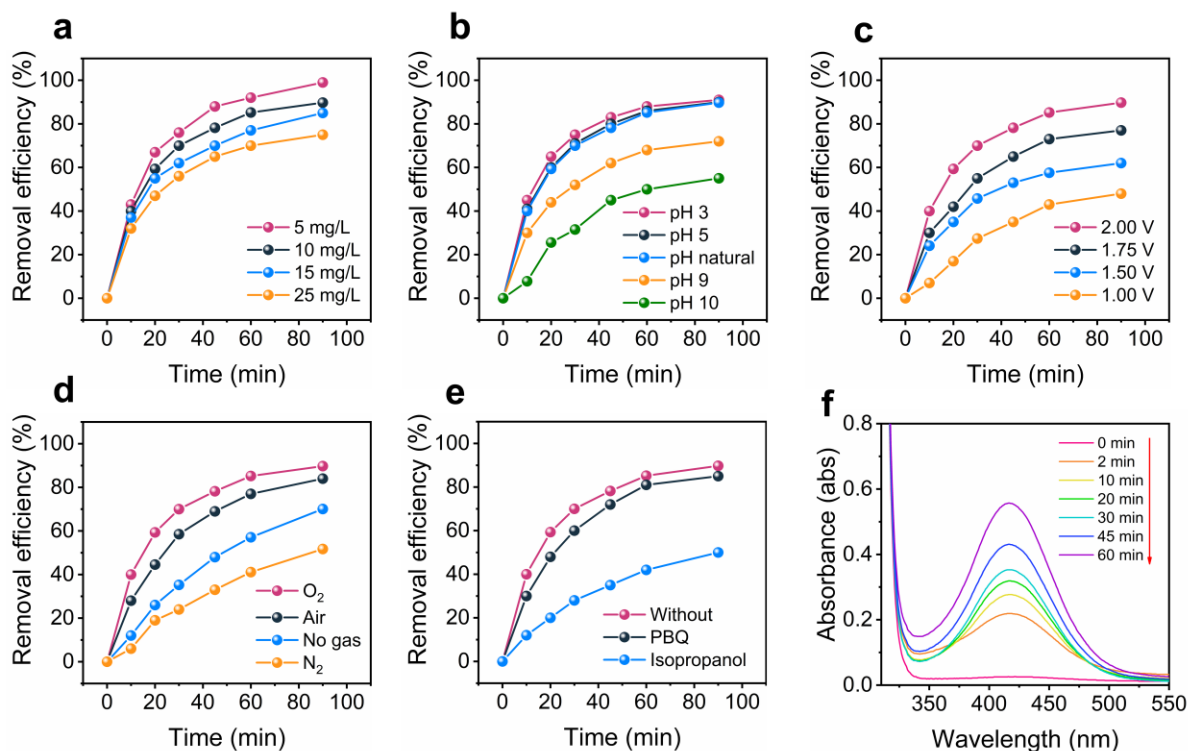


Figure 5. The effect of operational parameters on the removal efficiency of ciprofloxacin (CIP) by ZnFeV LDH@GF-EF process: a) initial pollutant concentration, b) initial pH, c) applied voltage, d) different gas supplies; e) Radical trapping experiments using various scavengers and (f) UV-vis spectrum of OPD-trapped  $\cdot\text{OH}$  (Experimental conditions:  $[\text{CIP}] = 10 \text{ mg L}^{-1}$ ,  $\text{pH} = \text{natural}$ , and voltage = 2 V).

### 3.3. Catalytic activity of ZnFeV LDH@GF cathode

We have compared the performance of the ZnFeV LDH@GF-EF process with adsorption and anodic oxidation- $\text{H}_2\text{O}_2$  (PGF-EF) processes (Figure 6a). Adsorption of CIP by the ZnFeV LDH@GF cathode accounted for  $20.5 \pm 1.7\%$  and the apparent reaction rate ( $k_{\text{app}}$ ) constant was  $3.1 \pm 0.5 \times 10^{-3} \text{ min}^{-1}$ . PGF-EF achieved  $69.7 \pm 4.9\%$  removal efficiency, which could be due to the anodic oxidation by the Pt anode and the  $\text{H}_2\text{O}_2$  oxidation (M. Guo et al., 2022). Remarkably, with the use of ZnFeV LDH@GF cathode in EF, the  $k_{\text{app}}$  increased from  $14.6 \pm 1.3 \times 10^{-3} \text{ min}^{-1}$  to  $31.7 \pm 6.3 \times 10^{-3} \text{ min}^{-1}$  (Figure 6b). The results are in line with the previously reported trends for the removal of pollutants by the heterogeneous EF process (Fu et al., 2022;

J. Guo et al., 2022; Qi et al., 2021). The rate constant of the combined process is much greater than the sum of the individual processes, pointing out a synergistic action in the presence of ZnFeV LDH as a catalyst. Therefore, the synergy factor (SF) of the process was calculated as  $1.8 \pm 0.4$  using Eq (4).

The ZnFeV LDH@GF-EF process was explored for its ability to remove different types of pollutants such as textile dye (Methylene blue), pesticide (Pymetrozine), and pharmaceuticals (Ciprofloxacin, and Phenazopyridine). The process achieved complete removal of methylene blue and phenazopyridine in 1 h and achieved 95% removal efficiency of pesticide (Figure 6c). The results indicate that ZnFeV LDH@GF-EF has broad applicability in the treatment of different types of pollutants.

We further investigated the removal of CIP in real wastewater by the ZnFeV LDH@GF-EF process (Figure S2). The ZnFeV LDH@GF-EF process achieved 59.3 % TOC removal and complete removal of CIP in 360 min and 240 min, respectively. The longer duration of CIP removal from wastewater is because of constituents of real wastewater that can compete with CIP molecules and scavenge the radical species. The degradation products of CIP generated by the ZnFeV LDH@GF-EF process were detected by GC-MS analysis. Eight intermediate products were found by comparing their spectra to those in the MS library. (Table S2). The opening of aromatic generated many different compounds.

#### **3.4. Stability, reusability of the ZnFeV LDH@GF cathode**

The attachment of the catalyst to the surface of the cathode eliminates the need for a separation process to recover the catalyst. Still, the modified cathode must retain its integrity during consecutive uses in the water treatment process. We have tested the reusability of ZnFeV LDH@GF cathode in the EF process by monitoring the CIP removal efficiency decrease after 10 reuse cycles (Figure 6d). ZnFeV LDH@GF experienced approximately a 9.8% reduction in

the CIP removal efficiency after the 10<sup>th</sup> use. The observed reduction in the performance of the electrode might be due to the mechanical wearing of the catalyst from the GF surface due to stirring or the gas bubbling from the bottom of the electrode. This is also evident in the photograph and SEM images of the electrode after 10 use (Figure S3). Compared to the fresh electrode, the surface of the used electrode shows minor wear marks and sparse areas on the surface.

It's desirable for any process to avoid secondary pollution during water treatment. Unlike the classical homogenous Fenton process, the heterogeneous EF process has the advantage of avoiding iron sludge formation (Ganiyu et al., 2018b). However, concerns over heavy metal pollution may arise for heterogeneous catalysts having low stability. According to the ICP-OES analysis, heavy metal leaching from the ZnFeV LDH@GF was 1.034 mg L<sup>-1</sup>, < 0.3 µg L<sup>-1</sup>, 0.02 mg L<sup>-1</sup>, for Zn, Fe, and V, respectively, which are below the permissible limit of WHO (WHO Press, 2011). These leaching findings are much lower than our previous study, where a heterogeneous catalyst was used in powder form (Keyikoğlu et al., 2022). The stability of ZnFeV LDH@GF suggests that the attachment of the catalyst on the cathode is an effective way to reduce heavy metal leaching.

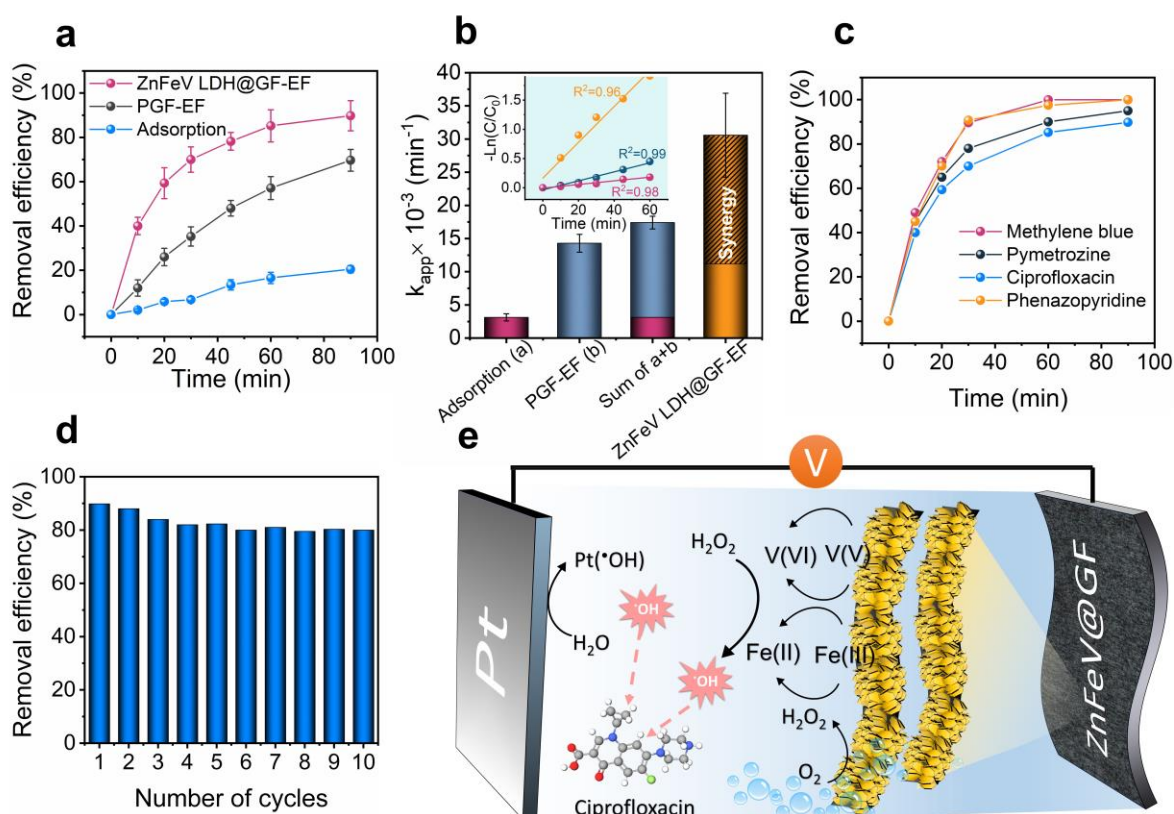


Figure 6. a) Removal of CIP by different process combinations and b) pseudo-first-order kinetic rate constants; c) Removal of different pollutant types by ZnFeV LDH@GF-EF process; d) reusability of ZnFeV LDH@GF over 10 reuse cycles; e) The proposed reaction mechanism of the degradation of ciprofloxacin in the ZnFeV-EF process (Experiment conditions: [Ciprofloxacin]=10 mg L<sup>-1</sup>, Voltage=2 V, pH=natural, and [Na<sub>2</sub>SO<sub>4</sub>]=50 mM).

### 3.5. Energy efficiency and toxicity evaluation of the process

SEC value of the ZnFeV LDH@GF-EF process for the degradation of CIP was calculated to be 0.3 kWh m<sup>-3</sup> and 32.15 ± 2.5 kWh · kg<sup>-1</sup> CIP. In terms of energy efficiency, our study shows significantly lower energy consumption than that of the majority of studies reported in the literature (Table S3). In terms of stability, the developed cathode shows a 9.8% reduction in performance after 10 cycles, which is similar to the values reported in the literature. Overall,

our study shows promising results with low energy consumption and comparable performance and stability to other studies in the field.

The acute and chronic toxicities of CIP and its degradation products were studied across three trophic levels of aquatic organisms, namely fish, daphnia, and green algae to evaluate their potential toxicity (Ghasemi et al., 2020; Liu et al., 2022). The ECOSAR software was used to forecast the potential acute toxicity (LC50 or EC50) and chronic toxicity of CIP and its degradation products, which are presented in Table S4. Based on the classification criteria of the European Union for dangerous chemical substances (No. 67/548/EEC) (Directive, 1967; Nations, 2011), most of the degradation products and CIP are harmless. However, the degradation of the CIP resulted in the generation of some products that may be potentially harmful such as the degradation products of D1, D2, and D7 in terms of acute and chronic toxicities. The increase in the toxicity of degradation products compared to the less toxic parent compounds is a noteworthy observation, and this phenomenon has been observed previously in the advanced oxidation of CIP (Li et al., 2020; Liu et al., 2022). Thus, effective treatment of emerging water contaminants should not only focus on their removal but also include detoxification.

### **3.6. Mechanism discussion**

Initially, in-situ  $\text{H}_2\text{O}_2$  production takes place on the ZnFeV LDH@GF cathode through a 2-electron reduction of oxygen that diffused into the GF. The  $\cdot\text{OH}$  production via metal oxide-catalyzed activation of  $\text{H}_2\text{O}_2$  follows similar steps as the classical Fenton reaction proposed by the Harber-Weiss theory (Haber and Weiss, 1934). At circumneutral pH values, the activation of  $\text{H}_2\text{O}_2$  should be a surface-catalyzed process (Ganiyu et al., 2018a) taking place on the LDH that was located at the inner and outer matrix of GF. Given that octahedral sites are highly exposed on the surface of LDHs, the catalytic activity of the ZnFeV LDH should involve

octahedral cations (Figure 6e) (Yibin Yang et al., 2019). In LDHs, the most dominant form of V is its high oxidation state ( $V^{4+}$ ). In this regard, the pathway of  $\cdot OH$  production is thought to be a single electron transfer from redox couples of  $\equiv Fe^{2+} / \equiv Fe^{3+}$  and  $\equiv V^{4+} / \equiv V^{5+}$  to  $H_2O_2$  (Eqs. 7-8). The reaction between the oxidized species ( $\equiv Fe^{3+}$  and  $\equiv V^{5+}$ ) and the  $H_2O_2$  results in the regeneration of  $\equiv Fe^{2+}$  and  $\equiv V^{4+}$  Eqs. (9-10) (Deng et al., 2008; Fang et al., 2018; Zhang et al., 2020). Given that the standard redox potential of  $Fe^{3+}/Fe^{2+}$  (0.771 V) is lower than that of the  $V^{5+}/V^{4+}$  (0.91 V), regeneration of  $Fe^{2+}$  is thermodynamically possible through the reduction of  $Fe^{3+}$  by  $V^{5+}$  according to Eq. (11) (Liang et al., 2010; Zhang et al., 2020). Similarly, the strong catalytic activity resulting from transitional metal doping due to electron transfer has been reported (Liang et al., 2022, 2010). Simultaneously, anodic oxidation by Pt also contributes to the pollutant degradation Eq. (12) (M. Guo et al., 2022).



#### 4. Conclusions

This work reported the development of ZnFeV LDH@GF cathode using the EPD method. Two-dimensional flake-like LDH nanoparticles homogeneously covered the GF fibers, providing active sites for the decomposition of cathodically produced  $H_2O_2$ . ZnFeV LDH@GF-EF process achieved around  $89.8 \pm 6.8\%$  CIP removal efficiency in 90 min at natural pH conditions. The high efficiency of the cathode was attributed to the high  $H_2O_2$  yield ( $59.8 \pm 5.9$

mg L<sup>-1</sup>) and <sup>•</sup>OH production (3.65 mM). Remarkably, the  $k_{app}$  of the ZnFeV LDH@GF-EF process was twice that of the EF treatment with pristine GF. Energy consumption of the ZnFeV LDH@GF-EF process for the degradation of CIP was calculated to be 0.3 kWh m<sup>-3</sup> and 32.15 ± 2.5 kWh kg<sup>-1</sup> CIP. After 10 consecutive reuse cycles, the ZnFeV LDH@GF retained 90.2% of its original efficiency, which shows the suitability of the cathode for practical applications. The heavy metal leaching experiments further confirmed the stability of the produced cathode. Furthermore, the ZnFeV LDH@GF-EF achieved complete removal of CIP in real wastewater in 210 min. The process proved its effectiveness in the removal of different pollutant types including dyes, pharmaceuticals, and pesticides, with removal efficiencies almost higher than 90% at neutral conditions.

## Acknowledgment

We would like to thank Gebze Technical and University of Tabriz for the support.

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