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Hierarchical CoFe-Layered Double Hydroxide Modified Carbon-felt Cathode for Heterogeneous Electro-Fenton

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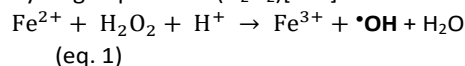
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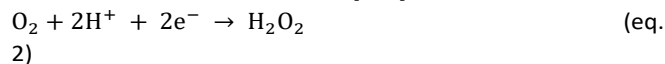
Hierarchical CoFe-Layered Double Hydroxide (CoFe-LDH) was grown on carbon felt (CF) as heterogeneous catalyst by *in-situ* solvothermal growth. The CoFe-LDH/CF serves as cathode as well as Fe²⁺ (catalyst) source in electro-Fenton (EF) process. A combined structural and electrochemical characterization revealed highly ordered and well crystallized CoFe-LDH anisotropically grown on CF substrate with highly dense urchin-like structures that were highly stable at circumneutral pH. EF experiments with CoFe-LDH/CF cathode showed excellent mineralization of Acid Orange II (AO7) over a wide pH range (2 – 7.1). The mineralization of AO7 with CoFe-LDH/CF was by both homogeneous and surfaced catalyzed process at low acidic pH, whereas only surface catalyzed process occurs at circumneutral pH due to stability of the LDH as well as precipitation of the catalyst. Higher mineralization was achieved with CoFe-LDH/CF compared to homogeneous EF with raw CF using Fe²⁺/Co²⁺ catalyst at all pH studied and the TOC removal with CoFe-LDH/CF cathode was at least 1.7 and 3.5 times higher than homogeneous system with Fe²⁺/Co²⁺ at pH 5.83 and 7.1 respectively. The enhanced performance observed with CoFe-LDH/CF was ascribed to (i) surface-catalyzed reaction occurring at the surface of the cathode which can expand the working pH window and avoiding the precipitation of iron sludge as pH increases, (ii) enhanced generation of H₂O₂ due to improved electroactive surface area of the cathode and (iii) co-catalyst effect of the Co²⁺ in the LDH that can promote regeneration and additional production of Fe²⁺ and hydroxyl radical, respectively. The CoFe-LDH/CF cathode exhibited relatively good reusability as the TOC removal after 2 h was still above 60% after 7 cycles of degradation, indicating that the prepared CoFe-LDH/CF is a promising cathode for the removal of organic pollutants by EF technology.

Introduction

Electro-Fenton process (EF) is an eco-friendly electrochemical advanced oxidation process (EAOP) based on classical Fenton's reaction chemistry in which organic contaminants are destroyed by *in-situ* homogeneously generated hydroxyl radical (**•OH**) from the Fenton's reaction (eq. 1) between Fe²⁺ ion and hydrogen peroxide (H₂O₂) [1–4].

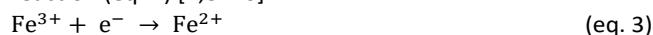


The *in-situ* production of H₂O₂ by 2e⁻ reduction of dissolved oxygen (eq. 2) at the cathode has great influence on the efficiency of the EF process and the production rate depends on the nature of cathode materials [5–7].



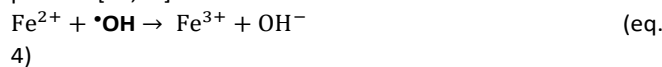
An interesting characteristic of EF process is that only catalytic quantity of Fe²⁺ is required because it can be regenerated at the cathode by e⁻ reduction of Fe³⁺ (eq. 3) formed from Fenton's

reaction (eq. 1) [1,8–10].



The *in situ* electrogeneration of H₂O₂ (eq. 2) and the electro-regeneration of Fe²⁺ from Fe³⁺ produced in Fenton's reaction (eq. 3) allow continuous formation of **•OH** that is able to destroy any organic pollutant [1,11].

The major challenges of homogeneous EF with Fe²⁺ are the narrow working pH window and non-reusability of the catalyst in several runs [12–14]. Optimization of the quantity of Fe²⁺ is another problem because excessive quantities of Fe²⁺ in the solution may promote the wasting reaction (eq. 4) that consumes the generated **•OH**, thus reduce the efficiency of the process [15,16].



To avoid these problems, heterogeneous EF with Fe containing solid catalyst or modified electrodes has been developed for the effective oxidation of organic pollutants over a wide range of pH with excellent stability and reusability of the catalyst. Heterogeneous catalyst such as pyrite [17,18], magnetite [19] goethite [20], Fe/Mn-loaded alginate [21] and Fe-carbon PTFE [22] have been studied in EF treatment of organic pollutants. Fe@Fe-oxides functionalized cathodic materials such as pyrrhotite grafted on graphite by conductive silver paste [23], Fe@Fe₂O₃ nanowires mixed with carbon nanotubes and fixed on tetrafluoroethylene (PTFE) [12], activated carbon-supported nano-goethite (FeOOH) [20], Fe-modified activated carbon [24,25] and Fe-impregnated carbon-felt [26] electrodes have

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been investigated as catalyst source as well as cathode for EF oxidation at a wider pH range. Recently, Ferrite-carbon [14], FeCuC [27] and Fe₃O₄-C [28,29] aerogel have been synthesized in either one pot or more complex method and studied as efficient cathode materials to enhanced electro-Fenton reactivity at acidic and neutral pHs.

The development of new electrodes that incorporates electrochemically active second phase containing transition metal oxides/hydroxides coated on carbon based matrixes for pseudo-capacitors used in energy conversion/storage devices [30,31] and electrochemical water oxidation [32,33] may be of great application in Fenton based EAOPs. The transition metals in the carbon based matrix electrode can act as heterogeneous catalyst which reacts with *in-situ* generated H₂O₂ in a Fenton or Fenton-like reaction. Layered double hydroxides (LDHs) are anionic clay materials that contain a brucite sheets of metallic cations (M^{II} and M^{III}) octahedrally coordinated by hydroxyl groups, forming M^{II}(OH)₆/M^{III}(OH)₆ octahedral with charge-compensating anions positioned within the interlayer space [34,35]. Transition metal based LDHs possess tunable compositions and high dispersion of cations in their octahedral sheets which sometimes gives them astonishing electrochemical properties and have found several applications such as biosensors, alkaline secondary batteries, supercapacitors and recently used as electrocatalyst in water splitting/oxidation reaction [36,37]. These properties can also be harness for electrochemical wastewater treatment, with the transition metals catalyzed the process in a heterogeneous EF process. The possibility of using other transition metals such as copper, cobalt, and manganese [38–40] that have been tested as co-Fenton catalyst with Fe to improve the efficiency of EF process will be an added advantage of using LDH incorporated carbon based matrix cathode.

Additionally, the modification of carbon based matrix electrodes with LDH may also enhanced the generation of H₂O₂ due to increased electroactive surface area [41]. In fact, *Le et al.* [42] have shown that graphene modified carbon-felt cathode achieved better mineralization of azo-dye Acid Orang II (AO7) compared to raw carbon-felt due to the increase in electroactive surface area, which in turn enhance *in-situ* generation of H₂O₂. Therefore, this present study investigates for the first time, the use of hierarchical CoFe-LDH grown on carbon-felt cathode for efficient degradation and mineralization of a model organic pollutant. The modified cathode was prepared by *in-situ* solvothermal process. The structural and electrochemical properties of the prepared cathode were examined by XRD, SEM-EDX, FTIR, XPS and cyclic voltammetry and electrochemical impedance spectroscopy. AO7, a common azo-dye found in high concentration in wastewater and effluent discharge from textile industries [43,44] was used as model pollutant. Besides, the influence of hydrothermal treatment parameters such as temperature, initial concentration of growth solution and treatment time on the performance of the prepared cathode was extensively studied. More importantly, the mineralization of AO7 solution by heterogeneous EF over a wide pH range as well as the leaching of the Co/Fe in the treated solution was systematically examined. For comparison,

analogous studies were made with raw CF using externally added 0.2 mM Fe²⁺, Co²⁺ or Co²⁺/Fe²⁺ (1:1 and 2:1) as this value was reported in literature as the optimum concentration of Fe²⁺ for EF process [45].

Experimental

1. Reagents and Materials

Carbon felt was obtained from Alfa Aesar. Cobalt II nitrate tetrahydrate, Co(NO₃)₂·4H₂O (> 99% purity); iron III nitrate nonahydrate, Fe(NO₃)₃·9H₂O (98% purity); iron II sulfate heptahydrate, FeSO₄·7H₂O (> 99% purity); urea, CO(NH₂)₂ and ammonium fluoride, NH₄F (99% purity) were purchased from Sigma Aldrich and used in the synthesis of LDH coated on the carbon-felt without further purification. AO7, C₁₆H₁₁N₂NaO₄S (Orange II sodium salt) and sodium sulfate, NaSO₄ (anhydrous, 99-100%) were also supplied by Sigma Aldrich. All solutions were prepared with ultra-pure water obtained from a Millipore Milli-Q system with resistivity > 18 MΩ cm at room temperature.

2. Electrode preparation

The CoFe-LDH modified carbon felt (CoFe-LDH/CF) cathode was prepared by *in-situ* solvothermal process [46,47] in which CoFe-LDH was grown on CF substrate. The growth solution contains Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, NH₄F (0.125 M) and CO(NH₂)₂ (0.5 M) dissolved in 100 mL of Milli-Q water with molar ratio of Co/Fe = 2:1 (*n/n*). The homogeneous solution was vigorously stirred for 30 min before transferred into a Teflon-lined stainless steel autoclave. Raw CF substrate (6.0 cm length × 1.0 cm width × 1.27 cm thickness) was pretreated with concentrated HNO₃ and then washed in turn in ultrasonic bath with deionized water, acetone, ethanol and deionized water for 15 min each. The clean CF was immersed into the growth solution in Teflon autoclave for hydrothermal treatment at predetermined temperature and period. Subsequently, both the substrate coated with LDH and the solid LDH suspension were separated from the solution, washed extensively with distilled water followed by Milli-Q water and oven dried at 40 °C. The sample used for studying leaching of catalyst and reusability were dried at 80°C

3. Characterization

The surface morphology of the as-prepared cathode was analyzed by SEM (Hitachi S-4800), with an accelerating voltage of 10 kV, combined with EDX. TEM images were taken with a PHILLIP-CM 20. XRD were recorded on a BRUKER S5000 diffractometer, using Cu-Kα radiation (0.15418 nm) at 40 kV and 20 mA. FTIR pattern of the powder LDH was performed on NEXUS FTIR (ThermoFisher). The surface chemistry of the prepared sample was analyzed by XPS (ESCALAB 250 Thermal Electron) with AlKα (1486.6 eV). Cyclic voltammetry (CV) experiments were carried out in solution of 50 mM Na₂SO₄ using μ3AUT70466 Autolab System (Eco Chemie BV, Netherlands) without external addition Fe²⁺ source. A Three-electrodes cell consisting of CoFe-LDH/CF as a working

electrode, Pt foil and Saturated Calomel Electrode (SCE) as a counter and reference electrodes respectively was used to conduct the CV experiments. The electrical conductivity of the prepared cathode was determined by measuring electrode interfacial-charge transfer resistance using electrochemical impedance spectroscopy (EIS). The EIS was performed at an open circuit voltage with voltage amplitude of 10 mV in a frequency range of 50 kHz to 100 MHz.

4. EF experiment

The EF experiments were performed in an open, undivided cylindrical glass cell of diameter 4 cm and 300 mL capacity equipped with platinum (Pt) gauze anode, placed in parallel to the cathode (4.5 cm × 1 cm × 1.27 cm) made of CoFe-LDH/CF at a distance of 2 cm. All experiments with CoFe-LDH/CF cathode were performed with 150 mL AO7 solutions (0.1 mM) containing 0.05 M Na₂SO₄ as supporting electrolyte. The solution was constantly stirred by PTFE magnetic bar to ensure mass transfer towards the electrodes. Compressed air was continuously bubbled into the solution at about 1 L min⁻¹, starting at 10 min prior to electrolysis to maintain a stationary O₂ level.

5. Instrument and analytic procedure

All electrolyses experiments were performed with Lambda single power supply (Lambda Electronique, USA) at constant applied current of -40 mA. AO7 solution pH was adjusted with 1 M H₂SO₄ or NaOH and was measured with a pH 209 pH-meter from HANNA Instruments (Romania). The mineralization of the AO7 solutions was assessed from the decay of dissolved organic carbon, which can be considered as the total organic carbon (TOC) for highly water soluble organic compounds. The TOC of initial and electrolyzed samples were measured on a Shimadzu TOC-L CSH/CSN analyzer. Reproducible TOC values with ± 2% accuracy were obtained using the non-purgeable organic carbon method. Calibration curves for total organic (TC) and inorganic carbon (IC) analysis were built up by automatic dilution of standards solutions containing potassium hydrogen phthalate and sodium hydrogen carbonate for TOC and IC, respectively. Percentage of TOC removal was calculated from the following equation:

$$\text{TOC removal (\%)} = \frac{\Delta(\text{TOC})_{\text{exp}}}{\text{TOC}_0} \times 100 \quad (\text{eq. 5})$$

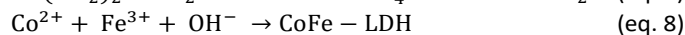
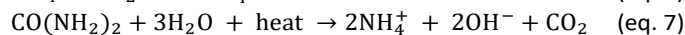
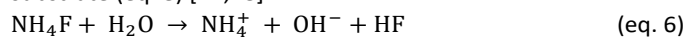
where $\Delta(\text{TOC})_{\text{exp}}$ is the experimental TOC decay at electrolysis time t (mg L⁻¹) and TOC_0 is the corresponding initial value prior to electrolysis.

The leaching of both Co and Fe from as-prepared CoFe-LDH/CF cathode into the treated solution was monitored by Optima 8300 Optical Emission Spectrometer with Inductively Coupled Plasma (ICP-OES) (Perkin Elmer) at absorption wavelength of 230 and 239 nm for Co and Fe respectively. Standard solutions of different concentrations were prepared with Perkin Elmer IV (1000 ppm) by dilution with acidified Milli-Q water. The organic intermediate formed after 20 min of electrolysis were identified by GC-MS.

Results and discussion

1. Preparation of CoFe-LDH/CF electrode

CF, a well-known carbonaceous cathode for Fenton based EAOPs was used as a substrate for *in-situ* growth of CoFe-LDH multiwall, which serves as heterogeneous catalyst/co-catalyst for EF process. The reactions at hydrothermal temperature mainly involve progressive hydrolysis of NH₄F and decomposition of CO(NH₂)₂ to NH₄OH (eq. 6 and 7). The resulting alkaline solution induces homogeneous nucleation, crystallization and growth of metallic hydroxides on the substrate (eq. 8) [47,48]:



The CF immersed in the growth solution acts as high energy sites for the nucleation and growth of the LDH on its surface compared to other sites in the growth solution.

2. Structural and morphological properties of the CoFe-LDH/CF

SEM image of pretreated CF shows that it is clean, without organic and inorganic impurities that may have inherited during production process (Figure 1a). After solvothermal synthesis, there was anisotropic growth of hierarchical CoFe-LDH on the CF as shown in Figure 1b-h, with the density/quantity of coating on the CF substrate closely related to the hydrothermal treatment temperature, time and initial concentration of the growth solution. In fact, treatment at 70 °C and 25:12.5 (*n/n*) initial Co²⁺/Fe³⁺ concentration yielded a growth of fine but low dense LDH wall on the CF (Figure 1b), indicating only nucleation of the LDH particles with limited crystal growth. The quantity of CoFe-LDH deposited on the CF at this temperature was not sufficient enough as it showed little enhancement of mineralization of organic pollutant (as demonstrated in section 3.4.2). Synthesis made at higher temperature of 90 °C with similar concentration for period of 4 h produced a highly dense and extensive growth of LDH on the CF substrate with formation of few urchin-like structures (Figure 1c). These urchin-like structures extensively grown and increased in quantity for synthesis at 90 °C but longer period of time (7 h) (Figure 1d). For these synthesis conditions, it can be observed that the CF strands were entirely coated with CoFe-LDH, which are adhesively grafted on the CF. The magnified image (Figure 1e) revealed that the CoFe-LDH wall and urchin-like structures are distributed across the entire surface of each CF strand, interconnected with each other, highly rough and porous which can enhance the diffusion of substance within the electrode. Further increase in hydrothermal treatment period to 21 h (Figure 1f) as well as temperature (120 °C) (Figure 1g) at this concentration shows little or no change in the morphology of the CoFe-LDH coated on CF substrate. Additionally, as shown in Figure 1h, the increase in the initial concentration of the growth solution (i.e. 50:25) does not enhance the quantity of CoFe-LDH deposited on the CF substrate. The surface compositions of the LDH coated CF were analyzed by EDX and the elemental peaks of C, O, Fe and Co were obtained. Interestingly, the molar ratio of Co to Fe was found to be 2.17, consistent with the initial and

normal molar ratio of M^{II}/M^{III} in LDH. Besides, elemental peak of F was detected, which may be one of the interlayer anions that neutralized the excess positive charge of LDH layers. The O peak emanates mainly from octahedral -OH and interlayer water.

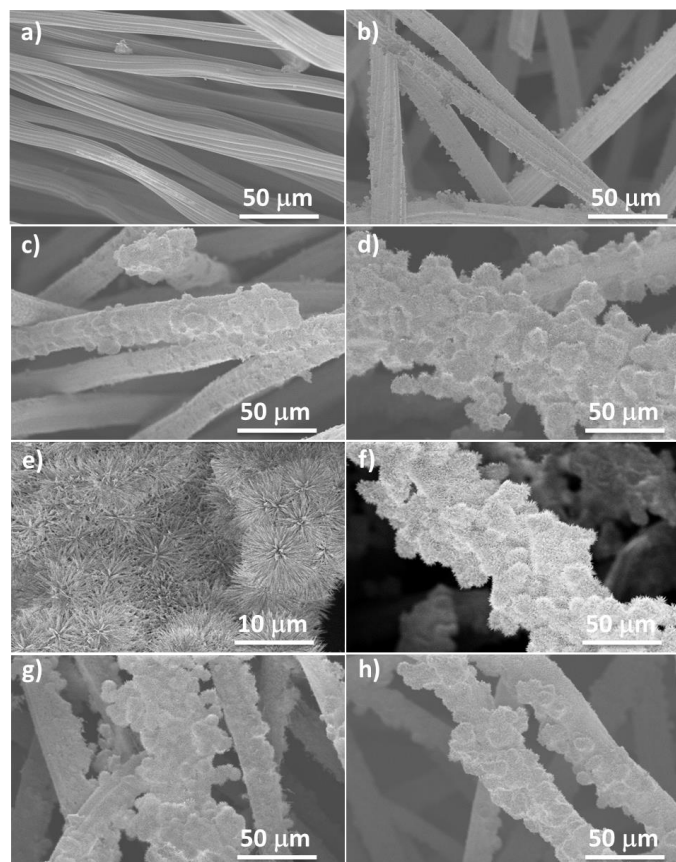


Figure 1. SEM images of (a) raw CF, (b) CoFe-LDH/CF – 70 °C for 7 h (c) CoFe-LDH/CF – 90 °C for 4 h (d) CoFe-LDH/CF – 90 °C for 7 h (e) magnified image of (d), (f) CoFe-LDH/CF – 90 °C for 21 h (g) CoFe-LDH/CF – 120 °C for 7 h and (h) CoFe-LDH/CF – 90 °C for 7 h. Note: (a-f) – 25:12.5 and (h) – 50: 25 (Co^{2+}/Fe^{3+})

The TEM images (Figure 2) of CoFe-LDH deposited on CF showed rod-like structures with average width of 30–40 nm and lengths up to 400 nm. The CoFe-LDH plates were intercalated with each other to form a hierarchical network, which provide both high specific surface area and fast diffusion of substance within the structure for excellent electrochemical reactions.

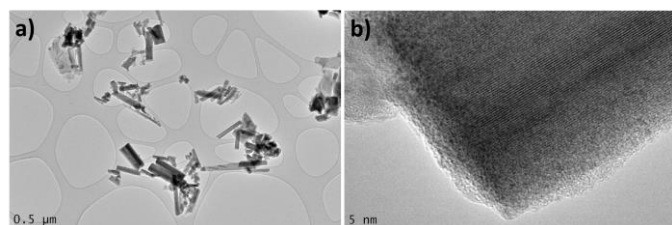
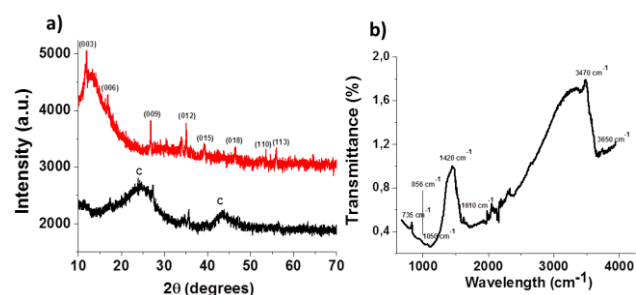


Figure 2. TEM images of CoFe-LDH.

The XRD patterns of the CoFe-LDH powder (Figure 3a, upper diffractogram) and CoFe-LDH/CF cathode (Figure 3a, lower

diffractogram) showed characteristic reflections corresponding to the crystal planes (003), (006), (009), (012), (015), and (018), of a typical layered hydroxide phase. A good symmetry was obtained in the as-prepared LDH and LDH/CF as shown by the weak peaks at $2\theta = 54.9^\circ$ and 57° , assigned to (110) and (113) crystal planes [49,50]. The broad peak at $2\theta = 23.4^\circ$ and 43.7° in lower diffractogram of Figure 3a was characteristic of carbon substrate on which the LDH was grown. It is important to note that no other crystalline phase was detected, indicating the high purity of the LDH phase grown on the CF substrate. The functional groups present in the as-prepared LDH/CF were examined from ATR FT-IR spectrum (Figure 3b) of the powder CoFe-LDH using diamond indenter. The FT-IR spectrum was recorded in the wavelength range of $400 - 4000\text{ cm}^{-1}$. As could be seen from the FTIR spectrum, a narrow band observed at around 3690 cm^{-1} was associated to the stretching vibration of non-hydrogen bonded O–H groups (OH in the brucite sheet). The second band located at 3470 cm^{-1} could be ascribed to the stretching vibration mode of hydrogen bonded O–H groups (interlayer water) in the CoFe-LDH [50,51]. The bands between $2400 - 1900\text{ cm}^{-1}$ were due to diamond indenter of the FT-IR. A small absorption band located at 1610 cm^{-1} was assigned to the bending vibration of adsorbed water molecules onto the CoFe-LDH via hydrogen bonding. The strong absorption band at 1420 cm^{-1} is characteristic of N–O stretching mode of the surface adsorbed and interlayer nitrate species, which is predominantly from the starting reactants in growth solution (i.e. $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$). Additionally, CO_3^{2-} may also be identified as adsorbed or interlayer anions as shown by small band at 1050 cm^{-1} , which may come from adsorption of CO_2 either from the atmosphere or during the synthesis from the decomposition of urea [49]. Other bands observed in the lower wavelength region (856 and 735 cm^{-1}) can be associated with stretching vibration of M–OH and M–O bondings (M = Co and Fe) in the brucite sheet of the LDH [52].



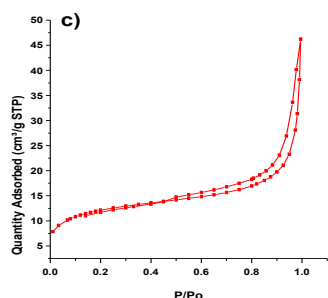


Figure 3. (a) XRD pattern of the powder CoFe-LDH (red curve) and CoFe-LDH/CF electrode (black curve), (b) FTIR – spectrum of the powder CoFe-LDH and (c) N_2 adsorption isotherm of CoFe-LDH.

The N_2 adsorption-desorption result for CoFe-LDH showed type IV isotherm with hysteresis loop typical of mesoporous material. The BET surface area was $42.9 \text{ m}^2 \text{ g}^{-1}$ and the total pore volume $0.18 \text{ cm}^3 \text{ g}^{-1}$.

The chemical composition and electronic states at the surface of the as-prepared CoFe-LDH on CF were analyzed by XPS, as shown in Figure 4a and b, the Co 2p core lines split into Co 2p_{3/2} (782.5 eV) and Co 2p_{1/2} (798.2 eV) peaks with the later accompanied by a satellite band at 803.4 eV (Figure 4a), demonstrative of a high-spin Co^{II} state in the LDH material [50,53]. Similarly, the peaks of Fe 2p_{3/2} and Fe 2p_{1/2} emanates from the splitting of Fe 2p lines are located at 711.3 and 724.8 eV (Figure 4b) respectively, having a spin energy separation of 13.5 eV [54]. The XPS spectra showed C1s core line at 287.5 eV, confirming the existence of carbon (Figure 4c). Existential state of other elements such as N, O and F in the CoFe-LDH/CF were confirmed by XPS as shown in Figure 4d.

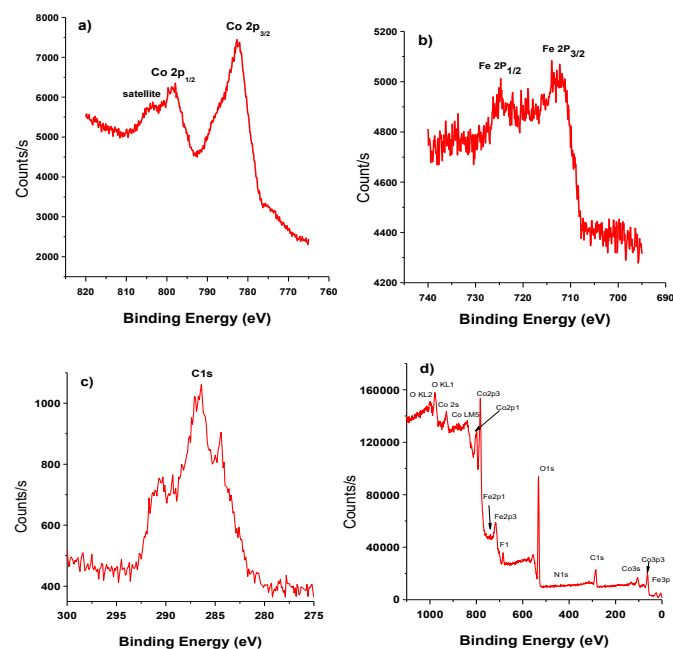


Figure 4. XPS spectra for (a) Co 2p, (b) Fe 2p, (c) C1s and (d) existential state of Co, Fe, C, O and N of CoFe-LDH/CF

3. Electrochemical behavior of the CoFe-LDH/CF

Cyclic voltammetry of the CoFe-LDH/CF (25:12.5, 90 °C and 7 h treatment) in 50 mM Na_2SO_4 aqueous electrolyte at different pHs were shown in Figure 5a. This study was essential in order to determine the contribution of the homogeneous Fenton's oxidation to the overall mineralization of the pollutants and the stability of the prepared cathode with pH. Two pairs of redox peaks at $\sim 0.25 \text{ V vs. SCE}$ and $\sim 0.56 \text{ V vs. SCE}$ during the anodic and cathodic sweeps were clearly observed at pH 2 and 3, indicating iron reduction and oxidation respectively ($\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple). This implies that Fe^{III} was leached into the solution. The peak current increased with the decrease of pH, revealing the gradual leaching of Fe and Co into the solution since LDH became less stable as the solution becomes more acidic. The presence of Co in the solution could lead to extra reversible conversion redox processes via reduction of Fe^{3+} by Co^{2+} [52]. No redox peak was observed at pH 5.83, indicating high stability of the CoFe-LDH coat on CF with negligible leaching of the metal ions into the solution

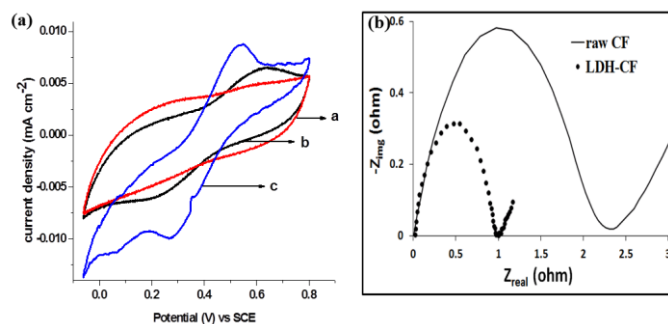


Figure 5. (a) CVs of CoFe-LDH/CF (synthesized at 90 °C for 7 h), in 50 mM Na_2SO_4 at scan rate 50 mVs^{-1} : Curves at (a) pH 5.83, (b) pH 3 and (c) pH 2; and (b) EIS spectra of raw and CoFe-LDH modified CF.

Generally in EF process, excellent electrochemical properties (i.e. conductivity) of the electrode are as essential as the Fenton catalytic activity. The interface properties and potential of electron transfer between the electroactive substance and the prepared electrode was investigated by EIS. Figure 5b shows the electrochemical impedance spectra of raw and CoFe-LDH modified CF electrodes. The Nyquist plots presents suppressing semicircle arcs corresponding to the interfacial charge-transfer resistance (R_{ct}) with the intercepts on the real axis provides the actual value of R_{ct} (i.e. the diameter of the semicircle). As can be seen in Figure 5b, There was increase of interfacial resistance and in turn, decrease of electrical conductivity of the CF cathode after the modification with CoFe-LDH as shown by increase of the intercept of the Nyquist plot. However, the R_{ct} obtained was 0.97 and 2.3Ω for raw CF and CoFe-LDH/CF respectively, indicating that the CF still maintains excellent conductivity after been modified with CoFe-LDH. The increase in R_{ct} of CF from 0.97 to 2.3Ω after modification with CoFe-LDH was expected since the LDH coating is non-conducting solid.

4. Mineralization of AO7 by EF process using CoFe-LDH/CF cathode over wide pH range

The performance of the as-prepared CoFe-LDH/CF as a suitable cathode as well as catalyst source for heterogeneous EF process was evaluated by studying the mineralization of AO7 as a model pollutant at pH 2, 3, 5.83 and 7.1. Firstly, the CoFe-LDH/CF showed extremely poor removal of AO7 by adsorption (0 mA) with less than 2% TOC and color removal (Figure 6a). As shown in Figure 6a, high level of mineralization of AO7 was achieved in a wide pH range from 2 to 7.1 in heterogeneous EF oxidation with CoFe-LDH/CF cathode at 40 mA applied current. For instance, TOC removal of 90, 97, 80, and 66% were obtained at pH 2, 3, 5.83 and 7.1 respectively, after 8 h of electrolysis. Based on literature [12,14], the heterogeneous EF reaction occurs on the surface of the CoFe LDH catalyst, thus expanding the working pH range of the EF process without the precipitation of the Fe/Co sludge. It is important to note that at lower pH (i.e. pH 2 and 3) the overall mineralization of the AO7 is a combination of both heterogeneous oxidation at the surface of the cathode and homogeneous oxidation in the bulk solution due to the leaching of the Fe^{III}/Co^{II} from the brucite sheet of the LDH as shown by CV (Figure 5a). The ICP analysis of the treated solutions (Table 1) after 8 h shows significant leaching of the Fe^{III}/Co^{II} in the LDH at pH 2 and 3 (Table 1), confirmed the participation of the homogeneous EF in the mineralization of the AO7. The CoFe-LDH catalyst was highly stable as the pH increases toward basic region as shown by CV results (Figure 5a), where the mineralization was major by heterogeneous EF reaction at the surface of the catalyst. This is apparent from the amount of Fe and Co found in the final solution, which is less than 0.08 mg L⁻¹ at pH 5.83 and 7.1 during the whole EF process (Table 1). The higher performance observed at pH 3 compared to pH 2 was primarily due (i) the preferential formation of peroxonium ions (H₃O₂⁺) which makes the electrogenerated H₂O₂ electrophilic and reduces its reactivity towards Fe²⁺/≡Fe^I/Co^{II}-OH at such low pH [11,55], and (ii) the transformation of [•]OH into HO₂[•] radicals (eq. 9) which decreased the Fenton process efficiency [11, 56]. This implies that H₂O₂ was the limiting reagent at pH < 2.5. Inactivation of surfaced catalyzed process at pH 2 due to high leaching of Co and Fe may contribute to the lower efficiency obtained at this pH, but it is expected to be compensated by homogeneous counterpart promoted by leached Co and Fe.

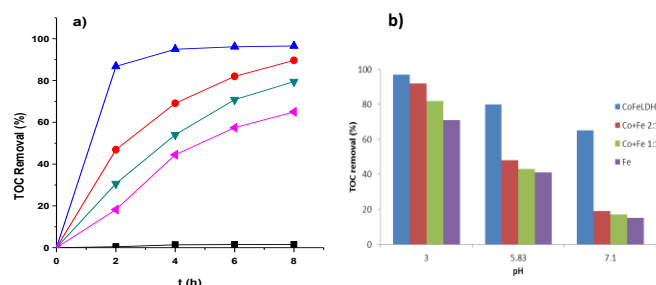
$$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2^{\bullet} + \text{H}_2\text{O} \quad (\text{eq. 9})$$


Figure 6. (a) Effect of initial solution pH on the mineralization of AO7 using CoFe-LDH/CF synthesized at 90 °C, for 7 h and 25:12.5 molar concentration, (■) 0 mA (●) pH 2, (▲) pH 3, (▼) pH 5.83, and (◄) pH 7.1, (b) Comparison between heterogeneous EF with CoFe-LDH/CF cathode and homogeneous EF with raw CF cathode and Fe²⁺/Co²⁺ at different pH. (RSD: 2%).

Comparison studies with traditional homogeneous EF process using 0.2 mM Fe²⁺, Co²⁺ or Fe²⁺/Co²⁺ (1:1 or 1:2 n/n) and raw CF cathode, showed inferior mineralization compared to heterogeneous EF with CoFe-LDH at all pH studied. There was drastic reduction in mineralization efficiency in homogeneous EF system as the pH increases (Figure 6b). After 8 h, TOC removal of 80% was attained at pH 5.83 in heterogeneous catalysis with CoFe-LDH/CF cathode, which is at least 1.7 times that of homogeneous system with Fe²⁺/Co²⁺ at the same pH. Further increase in pH to 7.1 causes more drastic reduction in efficiency of homogeneous system with the TOC removal less than one-third of that of heterogeneous system with CoFe-LDH/CF cathode (Figure 6b). This reduction was mainly due to Fe³⁺/Co³⁺ precipitation which reduce the Fenton's reaction rate. The corresponding AO7 conversion/degradation at pH 3 for the comparison studies showed in Figure 5b is given in Figure 7. Slightly faster degradation of AO7 was observed for homogeneous compared to heterogeneous EF process at the early stage of treatment as expected because the latter was much diffusion dependent compared to the former due to prevailing surfaced-catalyzed process that controlled the oxidation

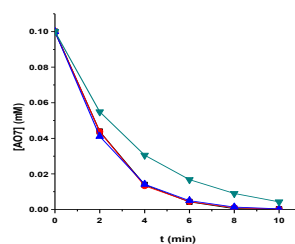


Figure 7. Degradation of AO7 at pH 3 (■) Fe²⁺, (●) Co + Fe (1:1), (▲) Co + Fe (2:1) (▼) CoFe-LDH/CF

Table 1. Concentration of Co and Fe after 8h during EF treatment at different pHs

pH	Co (mg L ⁻¹) RSD =1%	Fe (mg L ⁻¹) RSD =1%
2	13.69	4.58
3	2.02	0.63
5.83	0.075	0.061
7.1	0.041	0.009

The mineralization of AO7 by [•]OH generated by catalytic activity of CoFe-LDH/CF cathode proceeds via the formation of several aromatic/cyclic intermediates such as 4-aminophenol, hydroquinone, 1,4- benzoquinone, 1,2-naphthaquinone, 4-aminobenzosulphonic acid, 4-hydroxylbenzosulphonic acid, 2-hydroxy-1,4-naphthalenedione and its derivatives, 2-formyl benzoic acid, and salicylic acid which have also been reported by previous studies [57,58]. Further oxidation of these intermediates by [•]OH leads to cleavage of their cyclic rings to form several short-chain carboxylic acids which were later oxidized to CO₂ and H₂O₂. The reaction sequence for complete mineralization of AO7 by [•]OH is provided in SI Figure 1.

The efficiency of the as-prepared CoFe-LDH/CF cathode was compared with some recent heterogeneous catalysts or electrodes reported in literature and the summary is presented in Table 2. As shown in Table 2, a very high mineralization efficiency (87% TOC removal after 2 h) was attained with CoFe-LDH/CF compared to previous studies, even though low current density of 4.2 mA cm⁻² was utilized with an “active anode” of Pt, on which there is limited mineralization of organics. Other studies [25, 27, 28] that have reported excellent mineralization of pollutants either: (i) utilized boron-doped diamond anode (BDD) which contributes tremendously to the TOC removal due to the generation of addition hydroxyl radical (BDD(*OH)) at its surface (BDD is highly expensive) or (ii) performed the experiment at high current density [25,28]. Indeed, studies have shown that the BDD(*OH) induced by the boron-doped diamond anode is more efficient in mineralization of refractory carboxylic acids than the Fenton’s generated *OH at the cathode [1,9,10]. Thus the excellent mineralization obtained in those previous studies was majorly due to the contribution of BDD(*OH) produced from water oxidation at the surface of the anode.

Table 2. Summary of some recent studies on heterogeneous EF process

Catalyst/ electrode	Experimental conditions	Summary/comment of the efficiency
CoFe- LDH/CF	40 mg L ⁻¹ of AO7 at pH 3 using Pt mesh at 4.2 mA cm ⁻²	87% TOC removal after 2 h; and 97% after 8h [present study].
Fe ₃ O ₄ C- aerogel	50 mg L ⁻¹ of dimethyl phthalate (DMP) at pH 3 using BDD anode at 50 mA cm ⁻²	65% TOC removal after 2 h with major contribution of oxidation at the surface of BDD anode (BDD(*OH)) [28].
Fe- bentonite	100 mg L ⁻¹ of orange II at pH 3 using graphite anode at 14.29 mA cm ⁻²	71.57% COD removal after 1 h [59]
FeOOH/γ- Al ₂ O ₃	10 mg L ⁻¹ rhodamine B (RhB) at pH 3 using divided cell with Pt anode constant voltage E = -0.5 V	78.82% TOC removal after 2.5 h, with contribution of both adsorption and oxidation [20]
Fe- activated carbon	100 mg L ⁻¹ of <i>m</i> -cresol at pH 2 using BDD anode at constant voltage of 5 V	83% TOC removal after 2 h, however with high contribution from BDD(*OH) [25].
Fe-alginate	20 mg L ⁻¹ indole at pH 3 using Pt anode at 0.53 mA cm ⁻²	90% TOC removal after 7 h [21]
PTFE – modified Fe-carbon	120 mg L ⁻¹ 2,4-dichlorophenol at pH 6.7 using DSA anode at 12.5 mA cm ⁻²	70% TOC removal after 6 h [22].
Fe-CuC aerogel	50 mg L ⁻¹ methylene blue at pH 3 using BDD anode at 5 mA cm ⁻²	82% TOC removal after 1 h with 27% from the oxidation at BDD surface (BDD(*OH))

		[27]
FeS ₂	58 mg L ⁻¹ sulfamethazine at pH 3 using Pt anode at 100 mA applied current	69% TOC removal after 8 h [60]

5. Effect of hydrothermal treatment parameters on mineralization of AO7

The influence of hydrothermal treatment parameters such as temperature, time and initial concentration on the mineralization of AO7 solution was investigated and the results were presented in Figure 8. Overall, the hydrothermal treatment parameters control the loading and the morphology of the CoFe-LDH wall on the CF substrate which in turn affects the mineralization of AO7 because of difference in quantity of catalyst loaded on the CF. Among studied parameters, hydrothermal treatment temperature has the greatest effect on the mineralization of AO7 (Figure 8a) with the highest TOC removal obtained with CoFe-LDH/CF synthesized at 90 °C. It is important to state that the effect of hydrothermal treatment temperature was investigated at initial molar concentration of 25:12.5 (Co²⁺:Fe³⁺) and treatment time of 7 h. The CoFe-LDH/CF synthesized at 70 °C has lower loading of CoFe-LDH compared to those synthesized at 90 or 120 °C. In fact, the loading of CoFe-LDH was found to be 0.540 (± 0.002), 7.2 (± 0.3) and 7.0 (± 0.3) mg cm⁻² for synthesis made at 70, 90 and 120 °C, respectively. At 70 °C, the decomposition of urea and NH₄F into aqueous NH₃, which initiated the concurrent precipitation of Co^{II}/Fe^{III} hydroxides into LDH, was relatively low. As such, very scanty nuclei of CoFe-LDH were formed on the CF substrate with limited growth (Figure 1b). Optimum loading obtained at 90 °C could be attributed to excellent decomposition of both urea and NH₄F at this temperature which ensured high alkalinity of the growth solution, and in turn efficient nucleation and growth of CoFe-LDH on the CF substrate as shown in Figure 1c,d. Although high loading was expected at 120 °C, but the latter was slightly lower compared to the one obtained at 90 °C. This could be explained by excessive growth of the LDH particles into heavy conglomerates which stripped them off from the substrate surface. After 8 h of electrolysis, the TOC removal was 73, 97 and 94% for 70, 90 and 120 °C, respectively. Similar effect was observed with hydrothermal treatment time and initial concentration with optimum loading of CoFe-LDH on CF at 7h and initial molar ratio of 25:12.5 (Co²⁺:Fe³⁺). Synthesis made at lower and longer treatment time than 7 h or initial molar ration other than 25:12.5 (Co²⁺:Fe³⁺) shows less loading, which in turn reduced the efficiency of the heterogeneous EF system

6. Catalyst leaching and reusability of the CoFe-LDH/CF

The leaching of Co^{II} and Fe^{III} from CoFe-LDH/CF cathode investigated by studying EF treatment of AO7 at pH 3 was shown in Figure 9a. Catalytic activity and stability are important features of a good catalyst, which determine its reusability for several cycles [54]. As a heterogeneous catalyst, metal species

leaching from solid to the bulk solution was one key issue, and must be minimized to limit the contribution of homogeneous EF and enhance the reusability of the electrode. The concentrations of both Co and Fe gradually accumulated in the treated solution with electrolysis time and 0.63 and 2.02 mg L⁻¹ of Fe and Co, respectively, were found in the final solution after 8 h of electrolysis (Figure 9a). This implies that the mineralization of the AO7 was mostly due to surface-catalyzed process, even at pH 3. The evidence of leaching at this pH is obvious in the SEM image and XPS analysis of the used CoFe-LDH/CF after 8 h of electrolysis which indicates significant removal of the needlelike structure of the LDH and reduction in XPS spectral of both Co and Fe respectively (SI Figure 2a-c). The stability of the catalytic activity of the prepared CoFe-LDH/CF was even much better at circumneutral pH as the leaching of metal ions from the LDH was less than 0.08 mg L⁻¹ during the whole EF process as shown in Table 1.

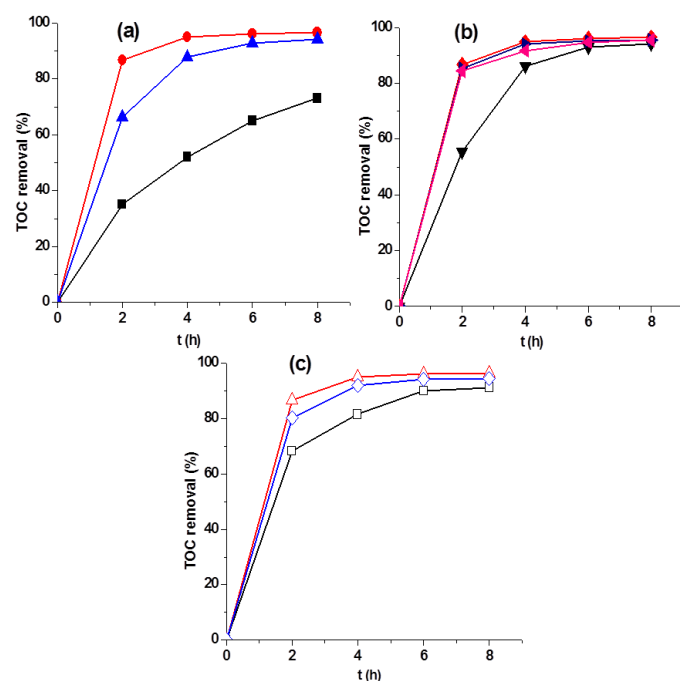


Figure 8. Effect of hydrothermal treatment parameters on the mineralization of AO7 at pH 3: (a) temperature (■) 70 °C, (●) 90 °C and (▲) 120 °C; (b) time (▼) 4 h, (◆) 7 h, (◀) 14 h and (▶) 21 h; and (c) initial molar concentration of growth solution (Co²⁺:Fe³⁺) (□) 10:5, (Δ) 25:12.5 and (◊) 50:25 (Co²⁺:Fe³⁺). (RSD: 2%).

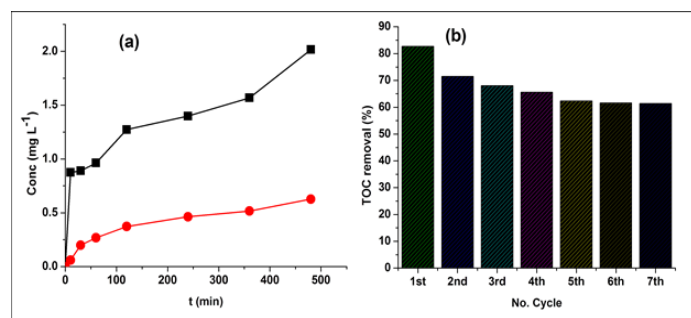


Figure 9. a) Evolution of the concentration of Fenton's catalyst/co-catalyst in the treated solution (RSD: 1%); (■) Co and (●) Fe and (b) TOC removal (RSD: 2%) after 2 h vs number of cycles for the EF treatment using CoFe-LDH/CF synthesis at optimal conditions.

For practical environmental application and scale up, reusability of the prepared cathode was studied at pH 3 using CoFe-LDH/CF (90 °C; 7h and 25:12.5) dried at 80 °C after solvothermal treatment. Preliminary studies (result not reported) showed that drying as-prepared CoFe-LDH/CF at high temperature after solvothermal treatment enhanced the adhesion and stability of the catalytic activity of the CoFe-LDH on the CF substrate but with slight reduction in mineralization efficiency of AO7. Indeed 6% and 10% reduction in mineralization efficiency were observed for sample dried at 80 and 100 °C respectively. This is attributed to the gradual collapse of the porous structure of the LDH into more compacted and less porous structure which hindered the diffusion of substance towards and from the carbon-felt matrix cathode. The production of hydrogen peroxide (H₂O₂) and reduction of leached Fe³⁺ to Fe²⁺ occur in the matrix of the carbon-felt substrate on which the LDH was deposited. As such, compacted LDH structure reduces the diffusion of substance. The reusability of CoFe-LDH/CF with number of cycles is shown in Figure 9b. After the first cycle there was sharp reduction in TOC removal (11%) largely due to mechanical wearing of the loosely bounded CoFe-LDH on CF substrate by the highly stirred treated solution. The TOC removal was almost stable afterward up till seventh (7th) cycle with approximately 10% reduction in TOC removal (Figure 9b). Over 60% mineralization was still feasible after 7th cycle, indicating the good reusability of the prepared cathode.

7. Mechanism of Efficient removal of AO7 with CoFe-LDH/CF cathode in EF oxidation

Previous studies [12,14] have shown that mechanisms of Fenton's catalytic decomposition of H₂O₂ by heterogeneous catalyst can be in two ways, depending on the working pH. Under low acidic pH conditions, the process is controlled by redox cycling of Fe²⁺/Fe³⁺ in the solution and surface catalyzed process by ≡Fe[III]—OH at the surface of the catalyst, with the Fe ions in the bulk comes from the dissolution of the catalyst due to acidic pH. However at circumneutral pH, the catalysis of the H₂O₂ should mainly occur at the catalyst surface with negligible contribution of dissolved Fe – species since Fe³⁺ is insoluble at this pH.

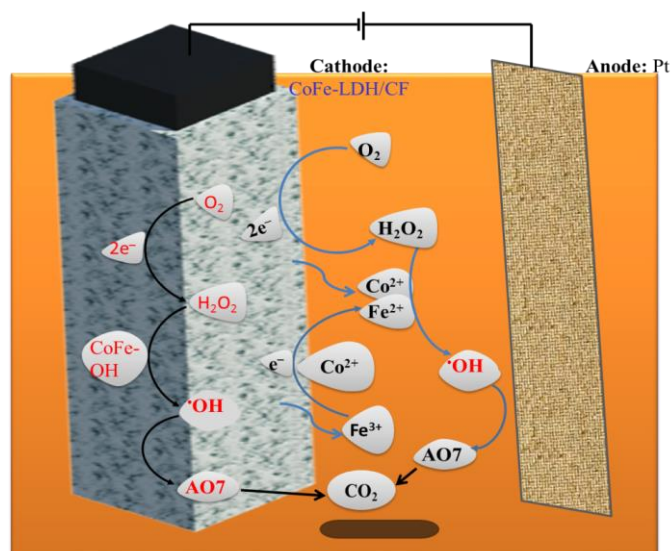
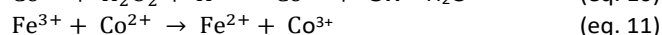
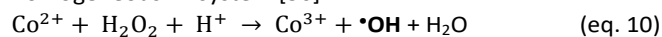
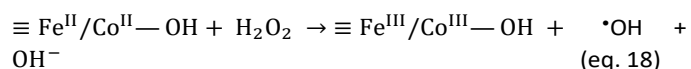
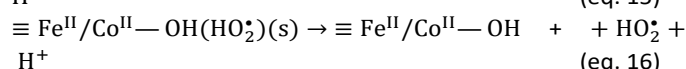
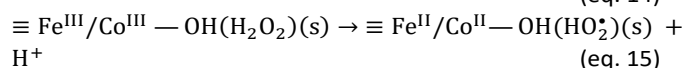
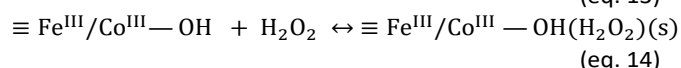
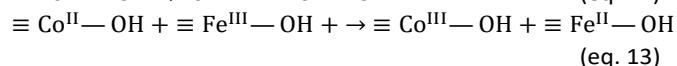
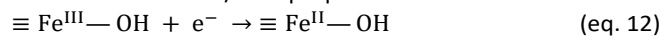


Figure 10. Schematic illustration of AO7 degradation in heterogeneous EF system with CoFe-LDH/CF cathode.

The mineralization of AO7 by CoFe-LDH/CF cathode was proposed based on these two mechanisms. Firstly, H₂O₂ is electrogeneration by 2e⁻ reduction of oxygen adsorbed onto the surface of CoFe-LDH/CF cathode [1, 8–11,41,42,61], and when working at lower pH 2 or 3, concurrent partial leaching of Co^{II}/Fe^{III} occurs. At this pH, both mechanism controls the oxidation of the organics. In the bulk, the leached Fe³⁺ is first reduced to Fe²⁺ by obtaining electron at the cathode, diffused into the solution and, in conjunction with Co²⁺ catalyzed the decomposition of H₂O₂ to produce *OH in Fenton's (eq. 1) and Fenton-like reactions (eq. 9). The catalysis of H₂O₂ is further accelerated by regeneration of Fe²⁺ from reduction of Fe³⁺ by Co²⁺ (eq. 10) in the bulk, has previously reported for homogeneous EF system [36].



The surface catalysis of H₂O₂, which occurs at the surface of CoFe-LDH/CF cathode and the predominant mechanism of mineralization of AO7 at circumneutral pH, also started in similar manner to homogeneous system with the production of H₂O₂ in the carbon matrix of the cathode. The production of *OH from catalytic decomposition of H₂O₂ is strongly correlated to the production rate of H₂O₂ and the catalyst properties. The surface-catalyzed mechanism for the production of *OH at the surface of CoFe-LDH/CF is proposed as follow:



Under circumneutral pH conditions (pH 5.83 and 7.1), the application of applied current to the electrolytic cell immediately resulted in generation of large quantities of H₂O₂ (eq. 2), and ≡Fe^{III}-OH in the LDH obtained an electron to partial reduced to ≡Fe^{II}-OH (eq. 11) [14,20] or via redox reduction by ≡Co^{II}-OH (eq. 12) in a similar manner obtained in homogeneous EF system. The generated H₂O₂ is adsorbed onto the surface of alkaline ≡Fe^{III}/Co^{III} to generate ≡Fe^{III}/Co^{III}-OH(H₂O₂) surface complex as presented in eq. 13, which later undergoes ground-state electron-transfer to form hydrogen peroxy radical complex (eq. 14). The generated Fe^{II}/Co^{II}-OH(HO₂^{*}) at surface of the brucite sheet of the LDH can activated itself to form Fe^{II}/Co^{II}-OH and HO₂^{*} (eq. 15) with the former catalyzes the decomposition of the H₂O₂ generated on the carbon matrix to produced *OH. The AO7 molecules which are diffused towards and in the cathode rapidly oxidized by the generated *OH. Two parallel reaction pathways are possible for the produced *OH: (i) direct oxidation of organic pollutants and (ii) destructive reaction with H₂O₂ to form HO₂^{*} (eq. 20). However, the high diffusion rate of the AO7 to the cathode ensure that the direct oxidation reaction is predominant and prevent the *OH quenching, thus improving the mineralization of the pollutant. Obviously, the ≡Co^{II}-OH in the LDH enhanced the production of *OH via the Fenton-like reaction and regeneration of Fe^{II}-OH (eq. 13).

Conclusions

This study investigated a facile and simple two-steps synthesis route to produce CoFe-LDH on the surface of CF substrate for application as suitable cathode as well as heterogeneous Fenton catalyst source for electrochemical wastewater treatment over a wide range of pH. The structure, morphology and loading of the CoFe-LDH on the CF substrate largely depended on the hydrothermal treatment temperature and time and the best synthesis was obtained at 90 °C for 7 h using initial Co/Fe molar concentration ratio of 25:12.5.

The as-deposited CoFe-LDH/CF cathode exhibited high performance catalytic activity in EF treatment of AO7 over a wide pH range, with superior TOC removal at all pH studied compared to analogous homogeneous treatment with Fe²⁺ and/or Co²⁺ using raw CF cathode. The TOC removal with CoFe-LDH/CF cathode was at least 1.7 and 3.5 times higher than homogeneous system with Fe²⁺/Co²⁺ at pH 5.83 and 7.1 respectively.

The mineralization of AO7 was majorly by surfaced-catalyzed process at circumneutral pH, whereas there is significant contribution of homogeneous EF oxidation when working at low acidic pH of 3 and 2. At circumneutral pH, the catalytic activity of CoFe-LDH was very stable and the quantity of Fe and Co leached into the solution was negligible, thus minimized the anxiety of Co toxicity. Furthermore, the as-prepared CoFe-

LDH/CF showed relatively good reusability at pH 3 with more than 60% TOC removal after 7 cycles of 2 h treatment. Based on the results obtained in this work, the CoFe-LDH/CF is a good cathode material for efficient mineralization of organic pollutants at circumneutral pH.

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Table of content:

LDH films are directly grown on carbon-felt to act as high-performance heterogeneous-catalyst for efficient EF mineralization of organics at near-neutral pH

