Optimization and control of Electro-Fenton process by pH inflection points: A case of treating acrylic fiber manufacturing wastewater

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HIGHLIGHTS

- Identification of the pH inflection points (pH IPs) during Electro-Fenton process.
- Current density, H_2O_2 dosage and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ affect the appearance of the pH IPs.
- Kinetic rate of COD degradation distinctly decreased when the pH IPs appeared.
- The appearance of the pH IP suggests the exhaustion of H_2O_2 during EF process.
- EF process can be optimized via pH monitoring and control by using the pH IPs.

GRAPHICAL ABSTRACT

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ABSTRACT

The Electro-Fenton (EF) process has shown great potential in refractory wastewater treatment. However, its efficiency is highly pH-dependent and the high reagent costs for pH adjustment greatly limit its large-scale application. This study used a bench-scale EF reactor to study pH variation during the treatment of an acrylic fiber wastewater. The appearance of pH inflection points (pH IPs), i.e., sudden changes in pH, under different H_2O_2 dosages, current densities, and ratios of $[\text{Fe}_{\text{theo}}^{2+}]/[\text{H}_2\text{O}_2]$ ($R_{\text{Fe:H}_2\text{O}_2}$), were investigated. The pH IPs appeared on the time scale of 5–7.5 min, and were favored at decreased H_2O_2 dosages (2.5–1.0 mM), increased current densities (3–4.5 mA/cm^2), and elevated $R_{\text{Fe:H}_2\text{O}_2}$ (0.1:1–0.2:1). The appearance of pH IPs was indicative of the exhaustion of H_2O_2 and a significant decrease of COD degradation, as expressed by the pseudo-first order kinetic constant (k) of COD degradation. Besides this, the substitution of $\text{Fe}(\text{OH})_3$ by $\text{Fe}(\text{OH})_2^{2-}$ and $\text{Fe}(\text{OH})_2$ occurred after pH IP appearance, and the dominant mechanism changed from electrochemical oxidation (EO) to electro-coagulation (EC) accordingly. In the presence of sufficient H_2O_2 , the formation of $\text{Fe}(\text{OH})_3$ barely affected pH variation. After H_2O_2 exhaustion, i.e., the appearance of pH IPs, dissolved O_2 rapidly oxidized Fe^{2+} to Fe^{3+} , the hydrolysis of which contributed to immediate pH increase thereafter. The optimization of the EF process may be achieved by adjusting H_2O_2 doses and the control of pH IP appearance.

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1. Introduction

The Electro-Fenton (EF) process has been increasingly employed to treat refractory organic wastewaters, and its *in situ* production

of hydroxyl radical ($\cdot\text{OH}$) enables high reactivity and powerful non-selective oxidation [1]. A well-designed EF process can achieve multiple functions such as electrochemical oxidation (EO), electro-coagulation (EC), electroflotation, and/or electro-reduction. These

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processes act synergistically in removing a wide range of complex contaminants, such as oil wastes, dyes, bromate, chromium, arsenic, and synthetic organic manufacturing waste [2–6]. Among these processes, electrochemical oxidation dominates in EF systems, and is highly affected by the concentrations of hydrogen peroxide (H_2O_2) and ferrous ion (Fe^{2+}), the ratio of $[\text{Fe}_{\text{theor}}^{2+}]/[\text{H}_2\text{O}_2]$ ($R_{\text{Fe:H}_2\text{O}_2}$), and pH [7]. Generally, pH impacts the reaction rate and species hydrolysis in the EF process [8–10]. An undesirable deterioration in removal efficiency sometimes occurs if solution pH is not well controlled.

Acidic pH conditions generally accelerate Fenton reactions in the EF process. However, at an extremely high acidity of $\text{pH} \leq 2$, hydrogen (H_2) evolution occurs on cathode surfaces, and this effect significantly decreases the active sites available for oxygen reduction and electro-regeneration of Fe^{2+} (Eqs. (1) and (2)) [11]. An optimum initial pH, reported to be from 2 to 4, favors the *in situ* production of H_2O_2 and promotes Fenton reactions [12]. Recently, some modified EF processes such as a mixed-valence iron-oxide-based EF process and a bio-EF process have been proposed to achieve Fenton reactions in relatively high pH ranges [13,14]. Most studies have mainly focused on the effects of initial pH on EF efficiency. Generally, solution pH tends to increase markedly with prolonged reaction time in EF processes, and this is mainly attributed to the consumption of H^+ by Fenton reactions. However, the pH variation trends in EF systems are far from well characterized [15,16]. Moreover, pH variation closely relates to the oxidation of free radicals and the hydrolysis of iron ions, and greatly affects the oxidative efficiency thereafter. For example, the efficiency of EF decreased from 7.4×10^{-2} to $2.3 \times 10^{-2} \text{ min}^{-1}$ when pH changed from 7.0 to 10.5 [17,18]. Unfortunately, few studies have investigated the relation between the EF efficiency and pH variation to the best of our knowledge; and a strategy to monitor and optimize pH in the EF process has never been reported:

After the consumption of H_2O_2 , EC plays an important role in the removal of pollutants. The species distribution of iron intermediates and end products, which is highly dependent on pH and DO, affect the effectiveness of EC and the pH variation. Firstly, Fe^{2+} can hardly be hydrolyzed in low pH ranges whereas Fe^{3+} hydrolysis occurs at pH ranging from 3 to 6 with $\text{Fe}(\text{OH})_2^{2+}$ and $\text{Fe}(\text{OH})_3^+$ as its main products. The formation of $\text{Fe}(\text{OH})_3(\text{s})$ at the anode occurs soon after the oxidation of Fe^{2+} by DO, which is highly affected by pH [19]. The diversity of iron hydrolysis products complicates pH variation during the EC process, and there is no consensus on pH variation trends in the EC process. Kobya et al. [20] reported a pronounced increase of pH from 2 to 6.3 in the treatment of poultry slaughterhouse wastewaters by an Fe-EC process. A pH increase from 2.86 to 6.36 was also observed in an air-free Fe-EC reactor to remove chromium and arsenic [3]. However, Chen et al. [21] reported the decrease of pH from 10.2 to 8.8 in a Fe-EC reactor in the removal of restaurant wastewater. It is widely accepted that the Al-EC process plays a neutralization role in terms of pH variation [19], whereas in the Fe-EC process, it is unclear whether this neutralization occurs or not. The understanding of the pH variation trend is valuable in practical optimization of the Fe-EC process.

In this study, a bench-scale EF reactor was developed to treat a typical acrylic fiber wastewater, which contains plentiful toxic and bio-refractory organic contaminants, such as dimethyl formamide (DMF), ethylene diamine tetraacetic acid (EDTA), amine, oil, and low MW polyacrylonitrile (PAN) polymers. These components pose great ecological risk to water environments and should be appropriately treated before being discharged [22]. The EF process may

be adopted as a pre-treatment prior to the biological treatment process to effectively remove refractory organics and to improve their biodegradability. To optimize the EF process, the pH variation trends under different initial H_2O_2 dosages (0–10 mM), current densities ($1.5\text{--}4.5 \text{ mA/cm}^2$), and $R_{\text{Fe:H}_2\text{O}_2}$ values (0–0.8) were investigated. Next, the relationship between COD removal efficiency and pH variation trend was further studied. Subsequently, the pH variation was quantified by the second derivative values of the corresponding pH curve, and sudden variations of this value were referred to as pH inflection points (pH IPs). Finally, the mechanisms involved in the appearance of pH IPs were elucidated and the significance of pH IPs with respect to EF optimization was discussed accordingly.

2. Materials and methods

2.1. Chemicals

All chemicals were at least of analytical grade and used as received. H_2O_2 (30%), Na_2SO_4 (99%), H_2SO_4 (98%) and NaOH (96%) were purchased from Sino pharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water used in all experiments was produced by a Millipore Water Purification System (Advantage A10, Millipore), with a resistivity of $\geq 18.2 \text{ M}\Omega \text{ cm}$. The raw wastewater used in this study was collected from the effluent of a pure oxygen aeration reactor in a typical acrylic wastewater plant in Daqing City, China. The characteristics of this wastewater are illustrated in Table 1.

2.2. Electrochemical apparatus

The electrolytic trial was conducted in an open undivided cylindrical glass cell of 500 mL capacity at $24 \pm 1^\circ \text{C}$. An iron plate anode and stainless steel cathode were used both having an exposed geometric area of $6.5 \times 8.5 \text{ cm}$. Three iron plates were used as induced electrodes in the center of anode and cathode. All the electrodes were pre-polarized in 0.1 M Na_2SO_4 at 150 mA within 30 min of use in order to remove impurities and to activate the electrodes.

For each experiment, the wastewater was stirred by a magnetic bar at 400 rpm to ensure homogenization and transport of reactants toward/from the electrodes. 1 M H_2SO_4 or NaOH was injected to adjust the initial pH to 3, and then H_2O_2 was added only once. Current densities from 1.5 to 4.5 mA/cm^2 were supplied by a constant power source. Samples were collected periodically at intervals and filtered by filter paper ($0.45 \mu\text{m}$) for chemical analysis. For the nitrogen control experiment, the wastewater was pretreated by bubbling with N_2 for 30 min to make sure $\text{DO} < 0.1 \text{ mg/L}$. When the test started, N_2 was supplied for 17.5 min, and then replaced by pure oxygen.

2.3. Analytical methods

An Orion 720A digital pH meter coupled with a combination pH electrode (Thermo Scientific Inc., US) was used to measure the

Table 1
Characteristics of the acrylic wastewater.

Parameters	Units	Average value
pH	–	6.8
COD	mg L^{-1}	315
TOC	mg L^{-1}	110
Total Fe	mg L^{-1}	0
Turbidity	NTU	65
Conductivity	$\mu\text{S cm}^{-1}$	1460

solution pH. Chemical oxygen demand (COD) was measured by a titrimetric method using dichromate as the oxidant in acidic solution at 165 °C for 30 min (HACH Co, US). The samples withdrawn for COD measurement were settled overnight to remove any iron precipitate before analysis. The supernatant was prepared after determining that no H₂O₂ was left by titanium potassium oxalate titration. The molecular size distribution was analyzed via gel permeation chromatograph (GPC), which was performed with a high performance liquid chromatograph (HPLC, Agilent Technologies, USA) equipped with a TSK gel G3000PWXL column (300 mm × 7.3 mm, 12 μm particle size), and UV detector at 254 nm. The eluent was a phosphate buffer (0.1 M NaCl, 0.002 M KH₂PO₄ and 0.002 M Na₂HPO₄, pH = 6.8), and the flow rate was 0.6 mL min⁻¹ with a sample injection of 20 μL. A standard calibration curve was plotted using poly (sodium-p-styrenesulfonate) at four MW points of 16,500, 6400, 4600 and 1370 Da. Fluorescence excitation-emission spectroscopy was carried out using a fluorescence spectrophotometer (Hitachi F-2000), equipped with a 150 W xenon lamp. The filtered sample (3 mL) was scanned in a 1 cm quartz cell at excitation and emission ranging from 200 to 400 nm and from 280 to 550 nm, respectively. The slit was 5 nm for both excitation and emission. Both Raman and Rayleigh scattering were minimized by subtracting the spectrum of pure water blank that was scanned prior to analysis of the samples. The samples were diluted to DOC < 1 mg L⁻¹ to avoid errors associated with inner filter effects. Ultraviolet-visible spectroscopy was determined using an Ultraviolet-visible spectrophotometer (U-3100) (Hitachi High-Technologies Co., Japan), equipped with a deuterium lamp and a tungsten filament lamp. The scanning range was from 190 to 700 nm. The samples were diluted 5 times for UV scanning. Before samples were scanned, a cuvette filled with distilled water was scanned as a blank to provide a spectral background. Each experiment was repeated three times.

2.4. Calculation methods

Electrolysis dissolves elemental iron from iron electrodes to form Fe(II). So the theoretical generation of Fe(II) can be obtained by Faraday's law of electrolysis (i.e. Eq. (3)) [23],

$$C_{\text{Fe}^{2+}} = \frac{n \times I \times t \times M_{\text{Fe}}}{2 \times F \times V} \quad (3)$$

where C represents the concentration of Fe²⁺ (g/L); I is current (A); t means retention time (s); Z is equal to the ferrous valence number; F is Faraday's constant; V represents the volume of the reactor (L).

The geometric meaning of a second derivative was adopted to accurately describe the convexity of a fluctuating curve. For each time-varying pH curve, the pH IPs simply corresponds to the concave/convex information of the curves. Thus the pH IPs can be identified by taking the mathematical second derivative of the pH curve, as shown below:

$$f'(t_0) = \left. \frac{dpH}{dt} \right|_{t=t_0} = \lim_{\Delta t \rightarrow 0} \frac{\Delta pH}{\Delta t} = \frac{pH_{t+\Delta t} - pH_t}{\Delta t} \quad (4)$$

$$f''(t_0) = \left. \frac{d^2 pH}{dt^2} \right|_{t=t_0} = \frac{\Delta pH_{t_0+1} - \Delta pH_{t_0}}{\Delta pH_{t_0} - \Delta pH_{t_0-1}} = W_{t_0} \quad (5)$$

W_t is used to detect the pH IPs. Briefly, a continuous and smooth pH curve results in a series of stable W_t values, which are approximately equal to 1. However, an inflection point appearing at time t_0 leads to a huge change of W_t , possibly much greater than 1.

3. Results

3.1. The pH IPs as the indicator of H₂O₂ residual

As can be seen in Fig. 1a and c, the changes of solution pH were different under various initial H₂O₂ dosages and current densities. Some typical pH IPs can be identified through Eq. (5). Fig. 1b and d shows the corresponding W_t values derived from their corresponding pH curves, respectively. For example, an obvious value of $W_{7.5}$ derived from pH curve-III suggested an appearance of a pH IP at 7.5 min. Similarly, pH curves II and VII both had their corresponding pH IPs at 5 min, respectively. In Fenton reaction system, pH variation has been reported to be highly dependent on the reagents and intermediates involved in the Fenton chain-reactions, such as ·OH, hydroxide ion, and hydrogen ion [24]. In EF reactors, the electrode reactions such as water electrolysis also play an important role [1]. As the only injected species in this EF system, H₂O₂ is the major control factor for pH variation and the effectiveness of EF oxidation. Fig. 2 shows the residual concentration of H₂O₂ during the EF process under different initial H₂O₂ dosages and current densities. As observed from Fig. 2, the residual H₂O₂ varied with different experimental conditions. Specifically, the residual concentrations of H₂O₂ decreased with elevated initial H₂O₂ concentrations and increased current densities. pH IP appearance was observed to be indicative of the exhaustion of H₂O₂. For example, at initial H₂O₂ concentration ([H₂O₂]₀) of 1 mM, the depletion of H₂O₂ at 5 min as indicated in Fig. 2a corresponded to the appearance of a pH IP in Fig. 1a, i.e., pH curve-II. The same results were observed in pH curve-III and -VII, suggesting that the appearance of a pH IP indicates the depletion of H₂O₂.

3.2. Effects on the appearance of pH IPs

3.2.1. Initial H₂O₂ dosages

As mentioned above, the appearance of a pH IP suggested the depletion of H₂O₂. It was found that high initial concentration H₂O₂ dosages delayed the appearance of pH IPs under the same current density. In fact, the dosage was not proportional to the duration time of H₂O₂. As illustrated in Fig. 1a, comparing with pH curve-II and -III, the H₂O₂ duration time was not correlated with the H₂O₂ dose and this was attributed to the reduction of excessive H₂O₂ to H₂O on cathode surfaces at strongly acidic pH (Eq. (6)). Moreover, overdosed H₂O₂ leads to self-oxidation to O₂ via an intermediate HO₂ (Eqs. (7) and (8)) and ·OH scavenging (Eqs. (9) and (10)) at the beginning of EF. These reactions are widely accepted, and contribute to the changes in the solution pH in EF systems [25,26]. It was noted that the elevation of pH exhibited a neutralized trend without H₂O₂ addition (i.e. pH curve-I in Fig. 1a), and this neutralization role of pH is similar to the results reported for chemical iron coagulation [27]:

3.2.2. Current density

Current density is the driving force for the release of Fe²⁺, and indirectly promotes the generation of ·OH and Fe³⁺ from the Fenton reaction. Hence, the current-density-controlled Fe³⁺/Fe²⁺ may have

Fig. 1. Changes of pH during EF process and the corresponding W_t values. (a) H_2O_2 dosage from 0 to 10 mM, initial pH 3 and current density 3.0 mA/cm². (b) The corresponding W_t values under different conditions of H_2O_2 dosages. (c) Current densities from 1.5 to 4.5 mA/cm², initial pH 3 and H_2O_2 dosages 2.5 mM. (d) The corresponding W_t values under different current densities.

great effects on pH variation. Fig. 1c shows the effect of different current densities (from 1.5 to 4.5 mA/cm²) on the pH variation during the electrochemical treatment of wastewater. The results indicated that more utilization of H_2O_2 was obtained under 3.0 mA/cm² compared to 1.5 mA/cm², resulting in the appearance of a pH IP at 7.5 min. Furthermore, the more earlier appearance of a pH IP at 5 min was observed under 4.5 mA/cm², indicating good consistency with previous research showing that the catalytic behavior of the Fe^{3+}/Fe^{2+} couple mainly depended on factors such as pH and electrode potential [7]. High current density contributed to mass electro-regeneration of Fe^{2+} (i.e. 75–98% in the pH 1.0–2.5), which can then react with H_2O_2 to continuously yield $\cdot OH$. The Fe^{3+}/Fe^{2+} cycle significantly controls the Fenton reaction rate and greatly affects the pH variation accordingly. At extremely high current density, some negative effects such as concentration polarization and anodic cleanout of H_2O_2 (i.e. Eq. (7)) are both responsible for Fenton reaction rate decrease [28]. According to this data, our results obtained from Fig. 1c and Table 2 both provide strong evidence: the earlier appearance of a pH IP resulting from the excessive current density of 4.5 mA/cm² compared to that of 3.0 mA/cm² led to the decline of Fenton efficiency from 58.4% to 48.5%.

3.2.3. Fe_{theo}^{2+}/H_2O_2

Another key to pH change is the ratio of $[Fe_{theo}^{2+}]/[H_2O_2]$ (i.e. $R_{Fe:H_2O_2}$), which can be calculated based on the assumption that the theoretical Fe^{2+} dissolution verifies Faraday's law and all the Fe^{2+} reacts with H_2O_2 via Fenton's reaction. Table 2 shows the changes of solution pH under different values of $R_{Fe:H_2O_2}$ from 0 to 0.8. As shown in Table 2, the pH IPs only appeared for ratios ranging from 0.08 to 0.19, meanwhile the COD removal efficiency amounted to

48.5%, 57.2% and 58.4%, respectively. Previous studies had proved that the maximum $\cdot OH$ production from the Fenton reaction occurred when the $R_{Fe:H_2O_2}$ was close to 1:5 (i.e. 0.2), and both lower ratio (i.e. 1:1) and higher ratio (i.e. 1:10) decreased the oxidative efficiency [29]. These different effects of $[Fe^{2+}]/[H_2O_2]$ on the EO process efficiency complicated the appearance of pH IPs. The appropriate values ranging from 0.1 to 0.2 promoted Fenton's reaction, and led to the appearance of pH IPs subsequently. However, as the ratio increased to 0.76, the solution pH increased rapidly (see pH curve-V in Fig. 1a), but the efficiency of EF decreased from 49.9% to 31.4%. The increase of $R_{Fe:H_2O_2}$ resulted in the excess dissolution of iron to form Fe^{2+} , which can react with $\cdot OH$ rapidly (i.e. Eq. (11)). The optimum $R_{Fe^{2+}:H_2O_2}$ is crucially important to control the appearance of pH IPs and to achieve high efficiency for EF reactors:

3.3. COD removal around pH IPs

3.3.1. COD

The COD removal within 15 min was accelerated as H_2O_2 dosages decreased from 10 to 2.5 mM (Fig. SI-1). However, as the dosage further decreased to 1 mM, a slight negative effect was observed. On one hand, according to Eqs. (7)–(10), an appropriate concentration of H_2O_2 was crucial for Fenton reaction. On the other hand, the positive effect of high current density on COD removal was inhibited due to the consumption of $\cdot OH$ by the excessive electro-generated Fe^{2+} . As mentioned before, the appearance of pH IPs did have a close relation with the Fenton reaction rate and COD removal efficiency. Therefore, the initial degradation rates ($k_{initial}$)

Fig. 2. Changes of H₂O₂ during EF process under different (a) initial H₂O₂ dosages and (b) current densities. Unless otherwise specified, the initial solution pH is 3.

Table 2
Single factor experiments used for study.

pH curves	Current density (mA cm ⁻²)	Initial H ₂ O ₂ dosage (mM)	Fe ²⁺ _{theo} /H ₂ O ₂	pH value			COD removal (%)
				Initial	Infective	Final	
I	3.0	0	0	3.00	–	6.30	17.8
II	3.0	1.0	0.08	3.00	3.46	6.26	57.2
III	3.0	2.5	0.19	3.00	3.31	5.73	58.4
IV	3.0	5.0	0.38	3.00	–	4.00	49.9
V	3.0	10.0	0.76	3.00	–	5.49	31.4
VI	1.5	2.5	0.39	3.00	–	3.45	43.2
VII	4.5	2.5	0.09	3.00	3.55	6.20	48.5

were used to quantify the COD removal behaviors (see [Supporting information](#)). The calculated k_{initial} values before pH IP appearance were much higher than those after the appearance of a pH IP, indicating more significant COD removal in the initial stage. Furthermore, the specific details can be further demonstrated in [Fig. 3](#) and [Table 3](#), which both reveal that the evolution of COD during the preliminary EF process was well described by a pseudo-first order kinetic under different initial H₂O₂ dosages and current densities, respectively. As a result, the COD removal within 7.5 min was accelerated with the kinetic rates increased from 0.024 to 0.103 when H₂O₂ dosages decreased from 10 to 2.5 mM, suggesting an appropriate concentration of H₂O₂ might be helpful to the Fenton reaction. However, an obvious decrease in COD removal efficiency was observed after the pH IPs appeared. As shown in [Table 3](#), COD can be well fitted by pseudo-first kinetic modeling prior to the appearance of pH IPs, i.e., the first stage from 0 to 7.5 min, and the k value was determined to be 0.103 ($R_2 = 0.998$) under 2.5 mM dosage of H₂O₂. In comparison, after the appearance

Fig. 3. Pseudo-first order kinetics of COD degradation before and after the pH IPs under different (a) H₂O₂ dosages and (b) current densities. Unless otherwise specified, the initial solution pH is 3.

of the pH IP, the k value significantly decreased to as low as 0.016 ($R_2 = 0.998$) in the subsequent stage from 7.5 to 15 min. This can be mainly attributed to the decline of EF efficiency owing to the exhaustion of H₂O₂, echoing the conclusions reached above. Similar behavior was also found during some electrochemical treatments for chemical industry wastewater [30] and landfill leachate [31].

3.3.2. Components

To provide insights on the organics species transformation before and after the appearance of pH IPs, the characterization methods of EEM, UV–Vis, and GPC were used. As shown in [Fig. 4a](#), the raw water shows four peaks (Ex/Em) at 235/395 and 245/440 in region III, 315/385 and 360/440 in region V, and the fulvic acid-like and humic acid-like substances may be the dominant organics. Prior to the appearance of the pH IP, the EF process contributed to an obvious decrease of the two typical peak intensities from 450.4 to 290.5 and 761.3 to 348 ([Fig. 4b](#)). After that, however, there was a slight blue shift of the typical peaks from 370/440 to 340/405 (region V) and from 245/440 to 225/410 (region III) ([Fig. 4c](#)). This indicated that the transformation of soluble organics in the EF process is highly dependent on the oxidation capability of the EF process. The generated $\cdot\text{OH}$ directly degraded the conjugated structure of acrylonitrile and destroyed its C–N and C=C bonds, and the position of its fluorescence peak shifted accordingly. UV–Vis spectra also indicated similar trends and the UV absorbance at 210, 266, and 284 nm decreased remarkably before the appearance of the pH IP ([Fig. 4d](#)). By comparison, the variation of absor-

Table 3

The calculated pseudo-first-order kinetics rate constants.

pH curves	Current density (mA cm ⁻²)	Initial H ₂ O ₂ dosages (mM)	k (min ⁻¹)/ R^2		
			No pH IPs	The appearance of pH IPs	
				Before	After
I	3.0	0	0.011/ 0.914	–	–
II	3.0	1.0	–	0.092/ 0.965	0.034/ 0.916
III	3.0	2.5	–	0.103/ 0.998	0.016/ 0.998
IV	3.0	5.0	0.045/ 0.993	–	–
V	3.0	10.0	0.024/ 0.989	–	–
VI	1.5	2.5	0.040/ 0.994	–	–
VII	4.5	2.5	–	0.089/ 0.996	0.019/ 0.868

bance at 266 and 284 nm indicated that the removal efficiency remarkably decreased after the appearance of the pH IP. As indicated from the molecular weight distribution by GPC (Fig. 4e and f), the molecular weight of the soluble organics in raw water were approximately 9000, 6000, 2000, 200, 64, and 43 Da. The high-molecular weight (MW) species corresponded to the complex components of 170, 113, and 37 unit polymers of acrylonitrile, and the low-MW substances may be related to EDTA (~290 Da) and acrylonitrile monomer (~53 Da) although further studies are required to confirm this. Before the appearance of the pH IP, the peaks at the MW of 9000, 6000, 2000, 290, and 64 Da decreased significantly and the acrylonitrile monomer was completely degraded, and this suggested a high efficiency in degrading the macromolecular chain by the EF process. Additionally, the peaks at 290 and 64 Da disappeared, and the peaks at 9000, 6000, and 2000 Da attenuated continuously. This corresponded to the mineralization of these low-MW organics by EF oxidation. In particular, after the appearance of the pH IP a new peak at 900 Da was observed, and this corresponded to an oxidation intermediate that was resistant to oxidation by the EF process.

Fig. 4. Changes of the organics characteristics in wastewater before and after pH IP by EEMs, UV-Vis, and GPC. EEMs analysis of (a) Raw water, (b) before pH IP, and (c) after pH IP; (d) UV-Vis analysis of organics before and after pH IP; (e) GPC measurements of organics before and after pH IP. (f) Molecular weight distribution of the organics. The experimental conditions: initial pH 3; H₂O₂ dosage 2.5 mM; current density 3.0 mA/cm².

4. Discussion

4.1. The characteristics of pH IPs

Through the above analysis, the characteristics of pH IPs can be summarized as follows: (1) Instantaneity. The inflection points behave neatly, not sloppily, and the appearance of a pH IP has no predictive sign. (2) No repetitiveness. The entire shape of a pH curve containing a pH IP appears like a “boomerang”. Apparently, the lack of repetition pH IPs can be attributed the fact that only single initial H_2O_2 doses were used. (3) The approximate value of a pH IP is close to the initial value, rather than the final pH. As seen from Table 2, the pH values of the inflection points (i.e. 3.46, 3.31, and 3.55) were much closer to the initial pH of 3, compared with the final pH values of 6.26, 5.73, and 6.20, respectively.

4.2. Proposed mechanism of the appearance of pH IPs

The following discussion is based on the experimental condition of 2.5 mM H_2O_2 dosage and 3 mA/cm² current density. From the above results, the appearance of a pH IP is inferred to be indicative of the depletion of H_2O_2 . During the EF process, the exhaustion of H_2O_2 indicates the transformation of the reaction mechanism from electrochemical oxidation to electrocoagulation. Therefore the mechanism of the changes of pH during the EF process before and after the pH IP should be separately discussed.

4.2.1. Before the appearance of the pH IPs

In the electrochemical oxidation process, the Fenton reaction involves the consumption of hydrogen ions, and leads to a dramatic increase in pH. Theoretically, if a total of 2.5 mM H_2O_2 is involved in the Fenton reaction, the accumulated concentration of OH^- will reach 1.0E–5.60 M. Therefore, the final pH should arrive at 8.4 based on the initial pH of 3. In fact, the actual value of the final pH was only 3.31. The two equivalents of electrons transferred in the dominated electrode reaction allows an accumulation of one equivalent Fe^{2+} and two equivalents of OH^- (Eqs. (11) and (12)) [12], and the generated Fe^{2+} ions start to form $\cdot\text{OH}$ prior to any other reactions due to the high reaction rate ($k_2 = 63 \text{ M}^{-1} \text{ s}^{-1}$, Eq. (13)) [32]. In general, three equivalents OH^- , one of Fe^{3+} and one of $\cdot\text{OH}$ remain in solution, respectively. The higher level and faster speed of Fe(III) hydrolysis in acidic conditions results in prior formation of the polynuclear hydroxyl complexes of iron through hydrolysis, polymerization and sedimentation. Thus, based on the above solution condition, the ratio of $[\text{Fe}^{3+}]/[\text{OH}^-]$ (i.e. 1:3) is preferred, giving priority to the hydrolysis of Fe^{3+} .

Moreover, considering the effects of water alkalinity, the ultimate form of Ferric hydroxyl complexes mainly depends on B and modified B^* [33,34]. The calculated B^* increases from 3.03 to 3.76 (see Supporting information), leading to the main hydrolysis of $\alpha\text{-FeOOH}_{(\text{am})}$ and $\text{Fe(OH)}_{3(\text{am})}$. Therefore, the accumulated OH^- tends to form coordination compounds with Fe(III) , but not to affect pH. As seen from Fig. 1a, pH only slightly increased from 3 to 3.31 before the pH IP appeared. This slight increase in pH can be attributed to the oxidative behavior of $\cdot\text{OH}$ with exposed protons, which are favored to attack the electron clouds with highest density. On one hand, $\cdot\text{OH}$ initially attacks unsaturated carbon bonds, which results in a subsequent electrophilic addition of H^+ provided by acidity following Markovnikov's rule [35]. On the other hand, $\cdot\text{OH}$ abstracts hydrogen atoms from C–H bonds [36]. In general, the oxidation by $\cdot\text{OH}$ results in a slight pH rise in the electrochemical oxidation process in acidic conditions:

$$B = \text{OH}^-/\text{Fe} = [\text{OH}^-]/[\text{Fe}] \quad (15)$$

$$B^* = \left(10^{-\text{pH}} + \text{OH}_{\text{add}}^+ - \text{H}_{\text{add}}^+\right)/[\text{Fe}] \quad (16)$$

4.2.2. After the appearance of the pH IPs

The hydrolysis of iron plays a dominant role in the change of pH during the Fe-EC process [19]. In Fe-EC, although the molar ratio between electro-generated Fe^{2+} and hydroxide ions released from the cathode is still 1:2, it is hard to form Fe(OH)_2 in acidic conditions. Compared to electrochemical oxidation, due to the absence of H_2O_2 , the effects of H_2O_2 on pH can be ignored, and the formation pathway of Fe^{3+} by Fenton oxidation is also blocked. Thus, the only approach for Fe^{3+} generation is the oxidation of Fe^{2+} by dissolved oxygen (DO), ensuring the hydrolysis of Fe^{3+} during the acidic Fe-EC process. The increasing rate of Fe^{2+} oxidation by DO with increasing pH is widely accepted, such that a unit increase in pH accelerates the Fe^{2+} oxidation rate by a factor of 100 according to Eq. (16) [27]. The increased concentration of hydroxide ion distinctly results in measurably greater oxidation of Fe^{2+} to Fe^{3+} . Hence, an abrupt elevation in pH after the pH IPs appears can be attributed to the above reasons. Not coincidentally, a similarly sharp rise in pH has also been reported during Al-EC by Holt et al. [37]:

$$\frac{d[\text{Fe}^{2+}]}{dt} = -k[\text{Fe}^{2+}]P_{\text{O}_2}[\text{OH}^-]^2 \quad (17)$$

Furthermore, in order to clarify the effects of DO on pH change during the whole EF process, a N_2 -purged control experiment ($\text{DO} < 0.1 \text{ mg/L}$) was carried out and the results indicated that the pH IP still existed. However, in the nitrogen-enriched solution, pH increased more rapidly than in the conventional electrochemical solution (Fig. SI-2). As expected, Fe^{2+} was stabilized in solution without any oxidation under N_2 conditions until pH increased to about 6.5. In contrast, Fe^{2+} is prone to oxidation to Fe^{3+} by DO under conventional conditions, leading to Fe^{3+} with a single hydroxyl ligand (i.e. Fe(OH)^{2+} , Figs. SI-3 and SI-4) being dominant at pH 3–4. As a result, at least half of the accumulated hydroxide ions were captured in formation of the iron hydroxide complex, which led to a relatively slow increase in pH compared with the nitrogen-enriched condition. Another interesting phenomenon illustrated in Fig. SI-2 is that Fe-EC seemed to play the role of neutralization of pH when DO increased because the continued uptrend of pH halted after pure oxygen was pumped in at 17.5 min, after which pH began to fall from 9.8 to neutral.

To sum up, as shown in Fig. 5, the mechanism of pH excursions (3–7) during the whole electrochemical process in the conventional EF system can be summarized as follows: (1) At $3 \leq \text{pH} < \text{IP value}$, the complexation of generated Fe^{3+} and OH^- does not contribute to the rise in pH, while the oxidation by $\cdot\text{OH}$ does. (2) At IP value $\leq \text{pH} < 4$, the formation of Fe(OH)^+ is initiated at the anode by direct hydrolysis of Fe^{3+} , which still results in a continuous increase in pH caused by the surplus OH^- . (3) At $4 \leq \text{pH} < 6.5$, Fe(OH)^{2+} , as a dihydroxy complex, gradually becomes dominant in solution. The utilization of OH^- through coordination with Fe^{3+} increases, so the elevation in pH slows down. (4) At $6.5 \leq \text{pH} \leq 7$, the majority of Fe^{3+} hydroxyl complexes are Fe(OH)_4^- . Obviously, the electro-generated OH^- is inadequate for complexing. Hence, the pH plays the role of neutralization.

Fig. 5. Proposed mechanism of pH excursion during the EF process.

4.3. Strategy for EF optimization via pH IPs control

Based on the mechanism of the appearance of the pH IP, it is reasonable that the pH IP is the key factor in regulating and controlling the process of EF. Therefore, using pH monitoring to identify the appearance of a pH IP in order to further control the EF process has its advantages in engineering application. On the one hand, the instantaneous feature of pH IP is beneficial to quickly and accurately indicate the decay of EF efficiency; on the other hand, online pH sensors have come into widespread use for wastewater treatment owing to being cost-effective, durable and sensitive, and have provided technological and engineering supports for precise identification of pH IPs in real time. Thus, to accurately achieve process monitoring of EF in engineering application is no longer difficult.

Furthermore, keeping an optimum concentration of H_2O_2 continuously during the EF process is an effective way to maintain high efficiency of electrochemical oxidation and to avoid the excessive loss of ferrous ion from electro-coagulation. Therefore, when a pH IP is detected through pH monitoring, H_2O_2 should be immediately added to the EF system again. Putting this strategy into practice, this supplementation of H_2O_2 was repeated as soon as the each pH IP appeared. The results indicated that the further removal of COD from 171 to 78 mg/L after 5 min (as a pH IP was found) could be attributed to the timely supplementation of H_2O_2 (Fig. SI-5). But as for a one-time dosage of H_2O_2 , COD only slightly decreased from 180 to 144 mg/L within 5 min. When H_2O_2 was introduced at three intervals, the observed COD removal was 50% higher as compared to that when H_2O_2 was dosed at one time with the same total H_2O_2 dose. Our team has already promoted the implementation of this strategy in the treatment of an acrylic fiber wastewater based on this method. Desired results were achieved and resulted in huge reduction of engineering costs. Therefore, the optimum control of the EF process through a combination of monitoring pH IPs and resupplying H_2O_2 is a promising strategy in engineering application.

5. Conclusions

In this work, we precisely identified the pH IPs under various trends of pH caused by different initial H_2O_2 dosages and current densities during the EF process. Experiments indicated that both decreased dosages of H_2O_2 (2.5–1.0 mM) and increased current densities (3–4.5 mA/cm²) accelerated the appearance of pH IPs. The optimum value of $R_{\text{Fe:H}_2\text{O}_2}$ (0.08–0.19) promoted the efficiency of electrochemical oxidation, meanwhile COD removal efficiency increased from 48.5% to 58.4%, but the appearance of pH IPs was only delayed from 5 to 7.5 min. The appearance of pH IPs corresponded to the exhaustion of H_2O_2 , and after that point electro-coagulation rather than electrochemical oxidation was the dominant mechanism in the EF system. Specifically, the pH showed little variation in the initial EF oxidation stage. However, after the consumption of H_2O_2 , i.e., the appearance of a pH IP, the sensitive oxidation of ferrous to ferric ion by DO contributed to immediate pH increase, and the hydrolysis of ferric ions in electrocoagulation contributed to significant pH increase thereafter. In summary, effective and timely supplementation of H_2O_2 during the EF process as soon as pH IPs appear, as identified by pH monitoring is a promising means of optimizing the EF process of wastewater treatment.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.01.115>.

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