Transformation characteristics of refractory pollutants in plugboard wastewater by an optimal electrocoagulation and electro-Fenton process

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ABSTRACT

The treatment of the plugboard wastewater was performed by an optimal electrocoagulation and electro-Fenton. The organic components with suspended fractions accounting for 30% COD were preferably removed via electrocoagulation at initial 5 min. In contrast, the removal efficiency was increased to 76% with the addition of H_2O_2 . The electrogenerated Fe^{2+} reacts with H_2O_2 and leads to the generation of $\cdot\text{OH}$, which is responsible for the higher COD removal. However, overdosage H_2O_2 will consume $\cdot\text{OH}$ generated in the electro-Fenton process and lead to the low COD removal. The COD removal efficiency decreased with the increased pH. The concentration of Fe^{2+} ions was dependent on the solution pH, H_2O_2 dosage and current density. The changes of organic characteristics in coagulation and oxidation process were differentiated and evaluated using gel permeation chromatography, fluorescence excitation–emission scans and Fourier transform infrared spectroscopy. The fraction of the wastewater with aromatic structure and large molecular weight was decomposed into aliphatic structure and small molecular weight fraction in the electro-Fenton process.

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1. Introduction

Currently, plugboard plants are available in developing countries, and wastewater containing acid, alkali, organic macromolecule compounds and chemical additives is generated by such plants (Metes et al., 2004; Ma and Xia, 2009). Such wastewater is traditionally treated by precipitation and biological methods (Metes et al., 2000). Biological process is not efficient for the removal of refractory pollutants.

Therefore, efforts on coagulation, oxidation and other advanced processes for the plugboard wastewater treatment are examined. Generally, both components that can only be removed via coagulation or via oxidation coexisted in the wastewater. Thus, individual oxidation will destroy both of the components and lead to long treatment time and high cost.

A process with the double function of coagulation and oxidation was desired. Electrochemical technology has reached a promising state of development and can be effectively used for the removal and destruction of organic contaminants (Chen, 2004). Electrocoagulation, a process that generates coagulant electrochemically, has been reported to be efficient in removing a wide range of pollutants from water and wastewater (Mollah et al., 2004). However, organic contaminants with low molecular weight cannot be removed via individual electrocoagulation process. Recently, anodic oxidation

of organic contaminants was largely investigated (Díaz et al., 2011; Garcia-Segura and Brillas, 2011). Application of BDD electrode in treatment of biologically pretreated plugboard wastewater via electrochemical oxidation was reported by Zhu et al. (2009). Unfortunately, anodic oxidation was limited by the long treatment time and low treatment efficiency. Electro-generated chlorine and/or hypochlorite have also found applications as electro-oxidation mediators for wastewater treatment (Panizza and Cerisola, 2003). However, the hypochlorite oxidation process is limited by its low oxidation potential. And, organochlorinated compound is readily generated (Panizza and Cerisola, 2009; Scialdone et al., 2009).

In contrast, H_2O_2 is an environmentally friendly chemical that leaves no hazardous residuals since it decomposes only to water and oxygen. H_2O_2 can be electrogenerated on cathode surface. H_2O_2 can also be added externally to the electrolytic cell sometimes. In both cases, $\cdot\text{OH}$ radicals are generated in the solution by the well-known Fenton's reaction between Fe^{2+} and H_2O_2 (Brillas et al., 2009).

Thus, the refractory components can be removed via electro-Fenton process efficiently. However, nearly no report pays attention on the optimal combination application of electrocoagulation and electro-Fenton from the view of organics characteristics. Herein, an optimal combination process of electrocoagulation and electro-Fenton can efficiently treat the plugboard wastewater in 5 min. The components variation of organic contaminants in the coagulation and oxidation processes were differentiated and analyzed fully. An optimal ratio of $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ was determined.

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2. Material and methods

2.1. Materials

The chemical reagents used in the experiments were of analytical grade. The plugboard wastewater used was obtained from a plugboard plant in Jiangxi Province of China. The wastewater has been treated via biological process. Typical parameters of the wastewater are presented in Table 1.

2.2. Electrochemical apparatus

A schematic diagram of the experimental setup is shown in Fig. SM-1. The $\text{Ti}_{0.7}\text{Ru}_{0.3}\text{O}_2/\text{Ti}$ and stainless steel with an exposed geometric dimension of $60\text{ mm} \times 70\text{ mm}$ was used as the anode or cathode, respectively. Iron electrodes were used as induced electrode in the center of anode and cathode. The experiments were conducted in an undivided cell of 1 L capacity at room temperature.

For each experiment, the wastewater of 1 L volume was stirred by a magnetic stirring bar in the electrochemical process. 1.0 M HNO_3 or NaOH were added into wastewaters to adjust pH of the solutions. Samples were collected from the cell at various intervals for chemical analysis. Two samples were collected at same time, one of which is used to detect the concentration of Fe^{2+} and total Fe at the solution, the other is used to analyze the dissolved chemical oxygen demand (COD) and total COD. For the analysis of COD, the pH of the sample was adjusted to be 8 and the total COD was measured for the supernatant obtained from water sample. The dissolved COD was determined for the sample filtrated by filter paper (0.45 μm) before measurement.

2.3. Analytical methods

All experiments were carried out in duplicate, and the analysis of each parameter was done in triplicate for each run. pH was determined using a pH meter (310P-02, Thermo Fisher, USA). COD was measured by a titrimetric method using dichromate as the oxidant in acidic solution at 150°C for 2 h (Hach Corporation, USA). pH value of the samples were adjusted to be higher than 8.5. After the sedimentation of Fe coagulants and iron oxides, the supernatant was put overnight for the decomposition of the remaining H_2O_2 in Fenton reaction. The Fe^{2+} concentration was obtained via reaction with 1,10-phenanthroline using an UV–Vis spectrophotometer (U-3010, HITACHI). The total Fe concentration was determined using an inductively coupled plasma atomic emission spectroscopy (Plasma Quad 3, VG Corporation, UK).

Molecular size distribution was analyzed via gel permeation chromatograph (GPC), which was performed with high performance liquid chromatography (HPLC, Agilent Technologies, USA) equipped with TSKgel G3000PWXL column ($300\text{ mm} \times 7.3\text{ mm}$, $12\text{ }\mu\text{m}$ particle size), and UV detector at 254 nm. The eluent was a phosphate buffer (0.1 M NaCl , 0.002 M KH_2PO_4 , and 0.002 M

Na_2HPO_4 , pH = 6.8), and the flow rate was 0.6 mL min^{-1} with a sample injection of $20\text{ }\mu\text{L}$. The standard calibration was plotted via poly(sodium-p-styrenesulfonate) at four points of 16500, 6400, 4600 and 1370 Da. Fluorescence excitation–emission spectroscopy was determined 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 nm to 400 nm and from 290 nm to 550 nm, respectively. The slit was 5 nm for both excitation and emission. Both Raman and Rayleigh scatters were minimized by subtracting pure water blank which was scanned prior to analysis of the samples. The samples were diluted to $\text{DOC} < 1\text{ mg L}^{-1}$ to avoid errors associated with inner filter effect. Excitation–emission matrices (EEMs) were plotted to identify compounds based on peaks characterized by Chen et al. (2003). The coagulants in the reaction process were collected and treated via a freeze–drying process. KBr was mixed with the obtained powder with the ratio of 100–1 and the Fourier transform infrared spectroscopy (FTIR) of the mixture were obtained by scanning it with FTIR spectrometer (Thermo Nicolet 5700, USA).

3. Results and discussion

3.1. COD removal by electro-coagulation and electro-Fenton process

The treatment of the wastewater was performed via electrochemical process with the addition of various H_2O_2 dosages. Without the addition of H_2O_2 , it can be seen from Fig. 1 that the COD was reduced to 164 from 232 mg L^{-1} at 5 min. And, COD removal was slightly enhanced with the reaction time up to 30 min. The removal efficiency of COD increased with the addition of H_2O_2 . It is interesting that with the addition of 150 and 600 mg L^{-1} of H_2O_2 , the COD was reduced to 116 and 149 mg L^{-1} at 5 min, respectively. In contrast, the COD can be reduced to 50 mg L^{-1} with 600 mg L^{-1} H_2O_2 at 30 min. With 149 mg L^{-1} of H_2O_2 , the removal of COD was slightly increased at 30 min. The effect of H_2O_2 dosage on COD removal will be discussed below.

The organic substances in the wastewater were divided into two parts via micro-filtration process (0.45 μm): dissolved COD (COD_{Diss}) (about 56%) and suspended COD (COD_{Susp}) (about 44%). Fig. 2 shows that COD_{Susp} can be removed by electrocoagulation process within 5 min, while COD_{Diss} were difficult to be removed only by individual coagulation process; even the reaction time was extended to 30 min. In contrast, in Fenton oxidation process, the organic components can be removed at 5 min with 150 mg L^{-1}

Fig. 1. COD removal from the plugboard wastewater via electrocoagulation and electro-Fenton process. pH = 3; current density 104.2 A m^{-2} .

Table 1
Characteristics of the plugboard wastewater used in the experiments.

Parameters	Unit	Values
pH		6.5
COD	mg L^{-1}	242
$\text{NH}_3\text{--N}$	mg L^{-1}	3.8
Chloride	mg L^{-1}	3618
Cu	mg L^{-1}	1.0
Turbidity	ntu	37
Fe	mg L^{-1}	8.1
Conductivity	$\mu\text{S cm}^{-1}$	1246

Fig. 2. Suspended COD (COD_{Susp}) and dissolved COD (COD_{Diss}) removal in electro-coagulation and electro-Fenton processes at 5 and 30 min (I, 5 min; II, 30 min). pH = 3; current density 104.2 A m⁻².

H₂O₂. Thus, the fractions that cannot be removed by coagulation were efficiently oxidized. In the case of 600 mg L⁻¹ H₂O₂, the removal efficiency of COD_{Susp} and COD_{Diss} were low at 5 min. However, both of the COD were efficiently removed at 30 min.

3.2. Effect of pH on COD removal

pH plays an important role in the electro-Fenton process. The pH of the plugboard wastewater was adjusted to 2.0, 3.0, 4.0 and 6.5 and the wastewater was electrochemically treated at 62.5 A m⁻². The results are illustrated in Fig. 3a. A notable pH effect was found in the electro-Fenton process, reaching its faster degradation at pH 3.0 with a maximum COD removal of 65.5% at 10 min. In contrast, only slight removal of COD was observed at pH 6.5. This result is consistent with the one reported for electro-Fenton treatments of trichlorophenoxyacetic acid (Brillas et al., 2003).

Under various pH conditions, the generated amount of Fe²⁺ was determined. As can be seen from Fig. 3b, the amount of Fe²⁺ at pH 2 is the largest. It can be as high as 150 mg L⁻¹ in 5 min and increases with the time. In contrast, with pH of 3, 4, and 6, the amounts of Fe²⁺ are low and follow the order of pH 3 > pH 4 > pH 6. At high pH (above 3.0 or more) the COD removal rate decreased because the oxidation potential of ·OH and also the dissolved fraction of ferrous species decrease with increasing pH. While at very acidic pH (about pH below 3.0) the H₂O₂ may solvate a proton to form an oxonium ion (H₃O₂⁺) that enhances its stability and reduces the reactivity with ferrous ions and consequently less hydroxyl radicals are produced (Kwon et al., 1999). Meantime, a large amounts of Fe²⁺ generated via chemical dissolution of iron will consume ·OH and lead to the low COD removal at pH 2.

3.3. Effect of H₂O₂ dosage on COD removal

As can be seen from Fig. SM-2a, the dosage of H₂O₂ plays an important role. Without the addition of H₂O₂, nearly no COD_{Diss} removal was observed. In contrast, the removal increases with the addition of H₂O₂. Furthermore, it was the fastest in the initial 5 min. After that, the COD removal efficiency was decreased.

Under various H₂O₂ dosages, the amount of Fe²⁺ concentration was determined. As shown in Fig. SM-2b, the concentration of Fe²⁺ decreases with the increase of H₂O₂ dosage. Thus, it is evident that an important factor for Fenton reaction as the Fe²⁺ is the catalyst for H₂O₂ to generate ·OH. However, overdosage H₂O₂ will consume ·OH and lead to the low COD removal. In the electrochemical

Fig. 3. (a) COD removal from the plugboard wastewater and (b) Fe²⁺ concentration in the electrochemical process under various pH values. Current density 62.5 A m⁻²; H₂O₂ dosage 150 mg L⁻¹.

process, the pH values of the solution increased with the H₂O₂ dosages (Fig. SM-3). The effect of current density on COD removal was also investigated. As shown in Fig. SM-4, the change of current density from 104.2 to 31.3 A m⁻² slightly affects the COD removal, which may mean the current density of 31.3 A m⁻² is enough.

3.4. Components variations of the wastewater in the reaction process

The molecular weight distribution of the reaction solution with the addition of various dosages of H₂O₂ was firstly evaluated via GPC. As shown in Fig. 4a, the molecular weight distribution of the raw water was mainly in 16, 10 and 6 kDa. Without addition of H₂O₂, the peak intensity for the 16 and 6 kDa decreased in 5 min. The peak intensity for the 10 kDa increased at 5 min. Then, the intensity decreased slightly with the reaction evolution. Meantime, the components with molecular weight at about 4 kDa appear at 5 min and increased slightly with the reaction proceed. The above results indicated that the components with large molecular weight were transformed into the components with low molecular weight and these components cannot be removed without the addition of H₂O₂.

As shown in Fig. 4b, with the addition of 150 mg L⁻¹ H₂O₂, the peaks at 16 and 6 kDa disappear at 1 min. The peak at 10 kDa quickly increases at 1 min and decreases with the reaction proceed. The new peak appears at 1 min and increased slightly. An interesting phenomenon was observed in the case of 600 mg L⁻¹ H₂O₂ (Fig. 4c), the peaks remained unchanged within 5 min. Furthermore, the peaks at 16 and 6 kDa disappear at 10 min. The peak intensity at 10 kDa increased. Meantime, a new peak at 4 kDa appears and increases slightly. It can be concluded from the above results that

Fig. 4. Gel permeation chromatograph analysis of the board wastewater in the electrocoagulation and electro-Fenton processes with various H_2O_2 dosages. (a) 0, (b) 150 and (c) 600 mg L^{-1} .

the components with large molecular weight were decomposed into the components with small molecular weight, which can be furthermore decomposed via the electro-Fenton process. In the case of 600 mg L^{-1} H_2O_2 , at the initial 5 min, the overdose H_2O_2 will consume $\cdot\text{OH}$ radicals generated in the electro-Fenton process, leading no change in the molecular weight distribution, which is consistent with the results in Fig. 1.

Fluorescence excitation–emission spectroscopy was used to assess chemical modification of the organic components in the reaction process. The progressive changes observed in EEMs of untreated and treated water with different H_2O_2 dosage at 30 min were presented in Fig. 5. Excitation and emission boundaries were operationally defined into five regions based on the results by Wen et al. (2003). As shown in Fig. 5a, three peaks (excitation (Ex)/emission (Em) (nm)) at 235/303 in Region I, 275/305 in Region IV and 225/440 in Region V were found for raw water. These peaks suggested that the raw water primarily contained aromatic protein-like, soluble microbial by-product like, phenol-like, and humin-like substances. It was shown that the fluorescence intensity of peak in Region IV and Region V decreased within 30 min during electrocoagulation process (Fig. 5b). In addition, the peak in Region I almost

Fig. 5. EMMs of the wastewater in the reaction processes with the reaction time. pH = 3; current density 104.2 A m^{-2} ; reaction time 30 min. (a) Raw water, (b) 0, (c) 500 and (d) 1000 mg L^{-1} H_2O_2 .

disappeared at 30 min during electrocoagulation process. Whereas the fluorescence intensity of these peaks decreased sharply with addition of H_2O_2 , all three peaks of raw water disappeared at 30 min in the presence of 600 mg L^{-1} H_2O_2 (Fig. 5c and d). These results indicated that the electro-Fenton process destroyed the aromatic and conjugated structure of raw water more efficiently than individual electrocoagulation process.

Fig. SM-5 shows the variation of sample fluorescence spectroscopy with the reaction time during electro-Fenton process. It was reported that $f_{450/500}$ corresponded to the ratio of emission intensity at 450 nm over 500 nm at 370 nm excitation and lower $f_{450/500}$ may refer to the compounds with more aromatic structures. The $f_{450/500}$ increased from 1.75 to 1.93 at 30 min during electro-Fenton process. Furthermore, the blue shift of the peak from 255/440 (Ex/Em (nm)) to 250/425 (Ex/Em (nm)) within 30 min was observed. It is recognized that blue shift of Ex/Em reflects the transformation of organic components into small molecular weight

components and a reduction in the degree of the π -electron system (Wen et al., 2003). In addition, the loss of fluorescence of the humin-like peaks (Region V) did not exhibit the simple first-order decay that was observed for the protein-like peak (Region I). This result suggested that humic substances may be more resistant to $\cdot\text{OH}$ oxidation than the protein-like substances. Furthermore, it can be concluded that raw water with the aromatic structure and large molecular weight fraction was decomposed to aliphatic structure and small molecular weight fraction via electro-Fenton process.

FT-IR spectra have been widely used for the characterization of organic substances. Samples exposed to infrared light adsorb energy corresponding to the vibrational energy of atomic bonds. The progressive changes observed in FT-IR spectra of flocs formed in raw and treated water with different H_2O_2 dosage at different reaction time were obtained. As seen in Fig. 6, the raw water showed peaks at 1468, 2850 and 2921 cm^{-1} , which are attributed to C–H deformation in methyl, methylene groups (Valdemar et al., 2009). The raw water was also found to have peaks at 1385, 1646, 1540 and 1075 cm^{-1} , which are assigned to C=O stretching of carboxylic group, C=C stretching vibration, N–H deformation of primary amides and C–O stretching of polysaccharide-like substances, respectively (Hyun and Myong, 2005; Matilainen et al., 2011). These peaks suggested that the raw water primarily contained aromatic and long aliphatic chain organics, which was in agreement with the EEMs results.

It is shown in Fig. 6 that the peak intensity at around 1468, 1540, 1646, 2850 and 2921 cm^{-1} decreased sharply during electrocoagulation and electro-Fenton process. In contrast, the peak intensity in the 460–475 cm^{-1} region increased during the electrocoagulation and electro-Fenton process. In comparison with electrocoagulation process, the peak intensity in the 1040–1125 cm^{-1} region was stronger than for electro-Fenton process. Furthermore, during electro-Fenton process the peak at 1385 cm^{-1} was weaker than for the sample at 30 min than that for 5 min in the presence of 150 mg L^{-1} H_2O_2 . In addition, new peaks in the 600–700 and 1100–1120 cm^{-1} bands appeared at 30 min during electro-Fenton process, which correspond to C–H out-of-plane deformation and

C–O stretching vibration, respectively (Matilainen et al., 2011). These results indicated that electro-Fenton processes primarily destroyed the aromatic and conjugated structure of raw water and transformed large aromatic and long aliphatic chain organic structures to small and hydrophilic organics. In comparison with the individual electrocoagulation, the possible reactions in electro-Fenton process involved the addition of $\cdot\text{OH}$ to aromatic and conjugated structures of raw water, then further oxidation could yield epoxides, alcohols, carboxylic acids and carbohydrates, which may be mineralized finally.

4. Conclusions

The treatment of the plugboard wastewater was achieved via an optimal electro-coagulation and electro-Fenton process. The individual electrocoagulation process can only remove 30% COD nearly. In contrast, the addition of H_2O_2 largely increases the removal efficiency of COD. The in situ generation of Fe^{2+} can react with H_2O_2 to generate $\cdot\text{OH}$, which was responsible for the increase in COD removal. At an optimum pH of 3 and H_2O_2 dosage, the oxidation process rendered 76% COD removal in less than 5 min. The generation of Fe^{2+} ions under various experiments was amounted. The removal of COD was mainly dependent on the ratio of Fe^{2+} ions to H_2O_2 in the reaction process. The wastewater mainly contained aromatic protein-like, soluble microbial by-product like, phenol and humin-like substances. The electro-Fenton process efficiently destroyed the aromatic and conjugated structure of the wastewater.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemosphere.2012.01.054](https://doi.org/10.1016/j.chemosphere.2012.01.054).

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Fig. 6. FTIR spectra of the freeze-dried coagulants in the electrocoagulation and electro-Fenton processes.

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