

# Advanced Treatment of Paper Mill Wastewater Using Electro-Fenton Process with Novel Catalytic Particle Electrodes

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Waste rice straw and iron-containing sludge were converted into catalytic particle electrodes (CPEs). The CPEs were tested for their ability to strengthen electro-Fenton (EF) oxidation of real paper mill wastewater. The prepared CPEs were characterized by different techniques including scanning electron microscopy, X-ray diffraction, BET surface area, and X-ray fluorescence. The CPEs exhibited excellent electro-catalytic activity and appreciably reduced the levels of pollutant parameters during EF process at near neutral pH conditions. Additionally, the treated wastewater was more biodegradable and had lower toxicity, which met Chinese effluent discharge criteria. Optimized treatment conditions used were a current density of 10 mA/cm<sup>2</sup>, a CPEs dosage of 1.0 g/L, and an aeration rate of 5 L/min. Based on the measurements of H<sub>2</sub>O<sub>2</sub> and hydroxyl radicals (<sup>•</sup>OH), the enhancement of catalytic activity was attributed to more *in situ* <sup>•</sup>OH being produced from the H<sub>2</sub>O<sub>2</sub> which was generated from dissolved oxygen (DO). Moreover, the CPEs showed superior stability, and successive recycle runs were completed with efficient and economical application advantages.

*Keywords:* Waste rice straw; Paper mill wastewater; Electro-Fenton; Catalytic particle electrodes; Hydroxyl radicals

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## INTRODUCTION

The paper industry is one of the most water-intensive industries; the industry generates large amounts of wastewater that contains dissolved organics (*e.g.*, lignin and carbohydrates), color, and toxic compounds (Ashrafi *et al.* 2015; Hermosilla *et al.* 2015). Although biological options are efficient and environmentally sustainable for treating paper mill waste effluents, these processes cannot completely degrade toxic and recalcitrant compounds that they may contain (Gönder *et al.* 2011); thus, biologically pretreated paper mill wastewater still contains various contaminants that have lower biodegradability than its untreated counterpart. It is difficult to achieve the increasingly stringent Chinese discharge standards post-treated paper mill effluents (GB/T 3544-2008). Improper pretreatment and discharge of wastewater can cause serious environmental problems (Lucas *et al.* 2012; Hubbe *et al.* 2016). Hence, it is very important to develop an efficient and cost-effective process for advanced treatment of paper mill effluents that have been biologically pretreated.

Electro-Fenton (EF), a promising technology for toxic and refractory wastewater treatment, has received considerable attention. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is formed by the *in situ* two-electron reduction of oxygen (O<sub>2</sub>) at a carbonaceous cathode; the H<sub>2</sub>O<sub>2</sub> is then

catalytically decomposed into hydroxyl radicals by  $\text{Fe}^{2+}$  ions in the pH range of 2 to 4 (Florenza *et al.* 2014; Cruz-Rizo *et al.* 2017). However, the drawbacks of the EF process are the highly acidic pH used and the high amount of iron-containing sludge generated after treatment neutralization; there are several approaches to solve these problems, such as using fluidized-bed reactors or heterogeneous catalysts (Garcia-Segura *et al.* 2016). Especially, the conventional soluble  $\text{Fe}^{2+}$  catalyst can be replaced by a heterogeneous Fe-containing solid, which should promote the life span of catalyst, reduce the concentration of iron ions, and shift the pH range to less acidic conditions (Hou *et al.* 2016). Recently, several studies have focused on the preparation of particle electrodes that can increase interfacial electrode surface area and mass-transfer rates, which perform as efficient Fenton catalysts (*i.e.*, catalytic particle electrodes (CPEs)). CPEs are frequently used in electrode electrochemical reactions and are predominantly made of carbonaceous and metallic materials (Healy *et al.* 2013; Labiadh *et al.* 2015). Up to now, the complicated preparation process and expensive raw materials used to make CPEs have restricted their further development. It is a great challenge to develop more efficient and cost-effective CPEs that can promote electro-Fenton reactions on wastewater at near neutral pH conditions.

Large amounts of agricultural waste, including straw, are produced from the Chinese rice industry. The straw is mostly burned for quick disposal, which results in air pollution emissions. This lignocellulosic material can be converted into activated carbon, which has the advantage of being more environmentally sustainable (Basta *et al.* 2009). Moreover, the homogeneous Fenton process and Fe/C micro-electrolysis process generate massive iron-containing sludge, which contributes to secondary pollution to the environment without appropriate disposal (Hou *et al.* 2016). Thus, integrating waste rice straw and iron-containing sludge composite as CPEs could further enhance EF property and also provide additional economic benefits. Currently, there are no published reports on the use of this new type of CPEs to improve the EF oxidation of industrial paper mill effluents.

This study investigated the effect of novel CPEs (waste rice straw and iron-containing sludge composites) on the EF oxidation of discharged paper mill effluents. The physical and chemical properties of the CPEs were characterized, and the effects of the main operating parameters, such as pH, current density, aeration rate, and CPEs dosage, on the removal of wastewater contaminants were studied. The possible degradation mechanism of the contaminants was considered. In addition, the stability and reuse of the CPEs was evaluated.

## EXPERIMENTAL

### Materials

Biologically treated wastewater from a two-step treatment plant (anaerobic-aerobic) was obtained from an integrated paper mill in Zhejiang province (Jiaying City, China). The characteristics of the wastewater were as follows:  $215 \pm 17$  mg/L COD,  $33 \pm 5$  mg/L BOD<sub>5</sub>, and  $135 \pm 12$  color unit (C.U.);  $30 \pm 5$  °C, and  $6.5 \pm 0.5$  raw pH value. Waste straw from 5-month-old rice plants was pulverized and screened to 0.5 to 2.0 cm in size; the resulting material was washed with distilled water to remove ash and dried. Iron-containing sludge was obtained from a pilot industrial wastewater treatment plant (Hangzhou, China) that was set up with the Fe/C micro-electrolysis process.

## Preparation of the CPEs

The dewatered rice straw, iron-containing sludge, and clay (as adhesive) were impregnated into the  $\text{ZnCl}_2$  solution (3 mol/L) by stirring for 12 h with the weight proportion of 70%, 20%, and 10%, respectively, at room temperature. The supernatant liquid from the above slurry was removed, and the dewatered solids were dried at 95 °C. The subsequently dried solids were pyrolyzed in a muffle furnace under pure nitrogen gas (90 mL/min) in the absence of oxygen. The furnace temperature was gradually increased at a rate of 5 °C/min to 600 °C and maintained at this temperature for 4 h. The resulting residuals were washed with concentrated HCl (36%) to remove inorganic impurities and then thoroughly washed with Milli-Q deionized water until the pH of the rinsed water remained constant. The washed residual was dried. The final product was denoted as a composite of carbon derived from rice straw and iron-containing sludge (RSC-Fe). The above process was repeated again without the addition of iron-containing sludge; the final composite from this process was denoted as carbon derived from rice straw (RSC).

## Experimental Procedures

All batch experiments were performed in a cylindrical Plexiglas reactor with an effective volume of 1 L as a one-compartment electrochemical cell. Less than 3% of COD was removed by adsorption on the polymeric container in Plexiglas reactor during 3 days. There was no serious impact on comparison performance of electro-Fenton with different catalysts. The anode was a boron-doped diamond electrode, and the immersion partial area was  $3 \times 5$  cm. The cathode was the same dimension of active carbon fiber. Both electrodes were fixed on two plastic brackets with the distance of 6 cm. An amount of CPEs (adsorption saturation) were filled between the anode and cathode while switching on the DC current by a DC stabilized power supply (MS155D), and the EF reaction was initiated. Air was bubbled from the bottom of the reactor to provide oxygen and to stir the fluid. In a homogeneous EF process, 3 mmol/L of  $\text{Fe}^{2+}$  was used in place of the CPEs for generating  $\text{HO}^\bullet$  from *in situ* formed  $\text{H}_2\text{O}_2$ . Samples from the reactor were withdrawn at pre-selected time intervals and passed through filter paper (0.45  $\mu\text{m}$ ) prior to analysis.

## Analytical Methods

The BET surface area and pore size distribution of CPEs were determined using nitrogen adsorption-desorption experiments (Micrometrics ASAP 2020, Texas, USA). X-ray fluorescence spectroscopy (XRF) (Axios-pw4400, Almelo, Netherlands) was used to analyze the chemical elements contained in the samples (excluding C, H, and O). The concentrations of the dissolved metal ions in the catalytic electro-Fenton process were analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES) (Optima 5300DU, Perkin Elmer, Massachusetts, USA). The morphology and structure of the prepared catalyst was examined using scanning electron microscopy (SEM) (Phenom ProX, Netherlands). The crystal structure of the catalyst was analyzed using a powder X-ray diffractometer (XRD) (Rigaku D/max-2000, Tokyo, Japan) with monochromatic  $\text{Cu } K\alpha$  radiation (45 kV and 50 mA). Electron spin resonance spectroscopy (ESR) (Bruker model ESP 300E) was used to detect signals of radicals that were trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), as well as to identify the radicals (Yuan and Dai 2014). The COD, biochemical oxygen demand ( $\text{BOD}_5$ ), and color of wastewater were measured in accordance with standard methods as described by Clescerl *et al.* (1998). The acute toxicity of the wastewater was assessed by the *Daphnia magna* test in accordance to the National Standards of China (GB/T 13266 (1991)). All the experiments were replicated three times,

and the results reported are the average of these measurements; measurements had an accuracy of  $\pm 5\%$ .

## RESULTS AND DISCUSSION

### Characteristics of the Prepared CPEs

The SEM images revealed that the morphologies of RSC and RSC-Fe had uneven surfaces with well-developed porous structures. There were few attached particles, which were uniformly distributed onto the RSC surface or embedded inside the carbonized rice straw matrix. This observation indicated the high decentralization of the iron-based catalyst (Fig. 1). As shown in Table 1, RSC exhibited a high specific surface area of  $735.6 \text{ m}^2\cdot\text{g}^{-1}$  and a well-developed mesoporous structure, which was attributed to the activation and pore-forming effects of  $\text{ZnCl}_2$  on the hemicelluloses, cellulose, and lignin of rice straw during the pyrolysis process (Torrellas *et al.* 2015). It was noteworthy that the Fe content increased from 0.24% to 15.8% when iron-containing sludge was added to RSC; this addition did not appreciably change the pore size diameter distribution or the specific surface area.

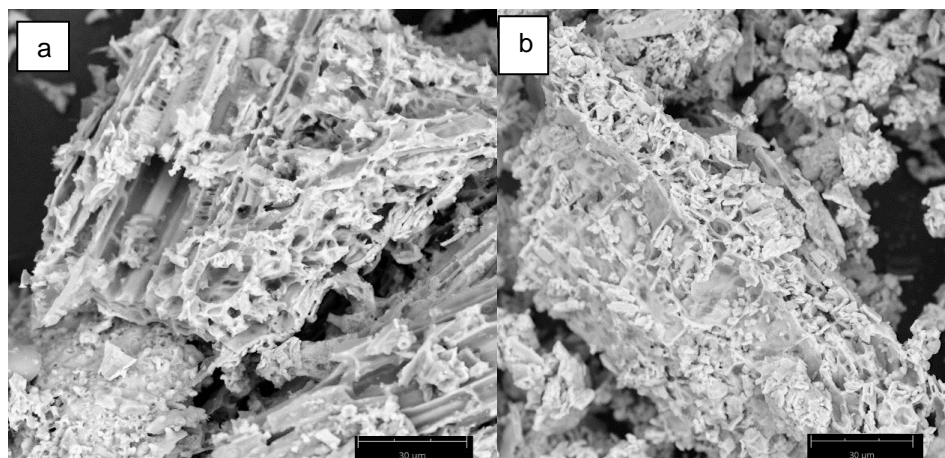


Fig. 1. SEM images of the CPEs: (a) RSC and (b) RSC-Fe

Table 1. Physico-Chemical Properties of the CPEs

Parameters	RSC	RSC-Fe
BET surface area, $S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	735.6	677.3
Mesopore volume, $V_{\text{meso}(\text{macro})}$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	0.341	0.313
Micropore volume, $V_{\text{micro}}$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	0.237	0.201
Pore size width (nm)	4.245	3.512
Fe (wt.%)	0.24	15.77
C (wt.%)	55.83	50.19
H (wt.%)	5.57	4.92
N (wt.%)	1.52	1.29

The XRD patterns of the RSC showed a wide peak at  $23.5^\circ$  that corresponded to a graphite carbon structure, which is similar to activated carbon (Fig. 2). Principally, important diffraction peaks were observed at  $26.3^\circ$ ,  $35.8^\circ$ ,  $43.5^\circ$ ,  $53.5^\circ$ ,  $57.5^\circ$ , and  $63.1^\circ$ ,

which correspond to the diffraction patterns of  $\text{Fe}_3\text{O}_4$  particles reported according to the JCPDS reference database (JCPDS card No. 88-0315).

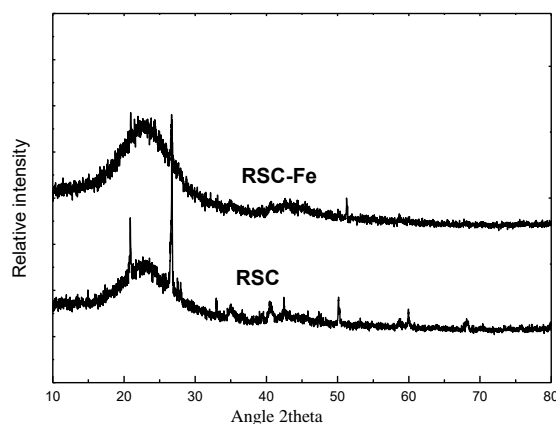


Fig. 2. XRD pattern of the CPEs

### Catalytic Activity of CPEs

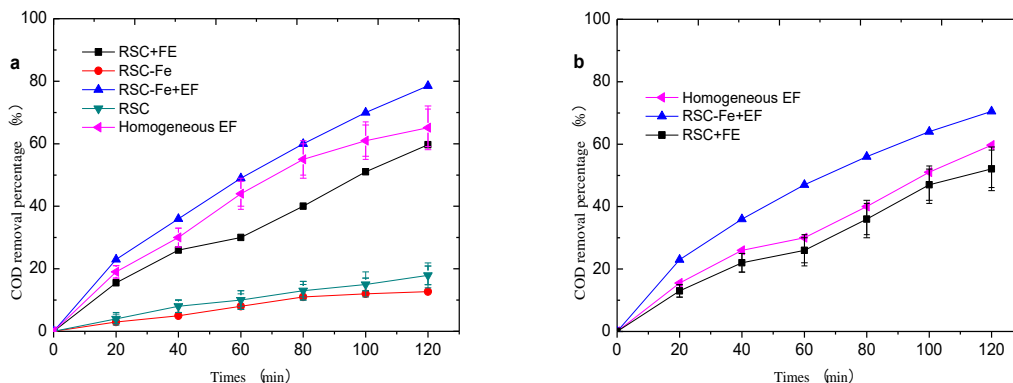
Figure 3a shows that only 12.9% and 17.5% of the original COD load was adsorbed onto the RSC-Fe and RSC particles during the 120 min exposure time while the adsorption was close to saturation. The percentage of COD removal increased appreciably with EF combined with CPEs. COD removal rates were 59.7% and 65.1% with RSC- EF (*i.e.*, 5 L/min aeration rate, 10 mA/m<sup>2</sup> current density, 1.0 g/L catalyst dosage, and raw wastewater at its natural pH) and homogenous EF (*i.e.*, 3 mmol/L of  $\text{Fe}^{2+}$  catalyst dosage, wastewater pH 4, and 120 min), respectively. However, COD removal percentage was dramatically increased during the EF process with RSC-Fe (*i.e.*, 78.5% removal), which indicated that there was electro-catalytic activity.

Meanwhile, the wastewater color removal percentage was about 70% with the EF combined with RSC-Fe, which was higher than other treatments (Fig. 3b). As Table 2 shows, the treated effluent concentrations were 40.5 color units and 46.2 mg/L COD, which met the waste effluent discharge standards set by China for the pulp and paper industry (*i.e.*, GB/T 3544 (2008)).

The high catalytic activity of CPEs is closely related to the availability of high specific surface area, which can provide active sites and drive the production of radicals (Marques *et al.* 2011). Although acceptable reductions of pollutant parameters could be realized by homogeneous EF, the drawbacks of high ferric sludge levels and low pH levels have limited its widespread application (Hou *et al.* 2016).

**Table 2.** Removal Performance for Pollutants in EF Process with RSC-Fe

Wastewater	COD (mg/L)	BOD <sub>5</sub> (mg/L)	color (dilution times)
Before treatment	215±17	33±5	135±12
After treatment	46.2±2	20±2	40.5±1

**Fig. 3.** Effect of catalysts on pollutant removal in EF process: (a) COD removal, and (b) color removal

### Optimization of Important Operating Parameters

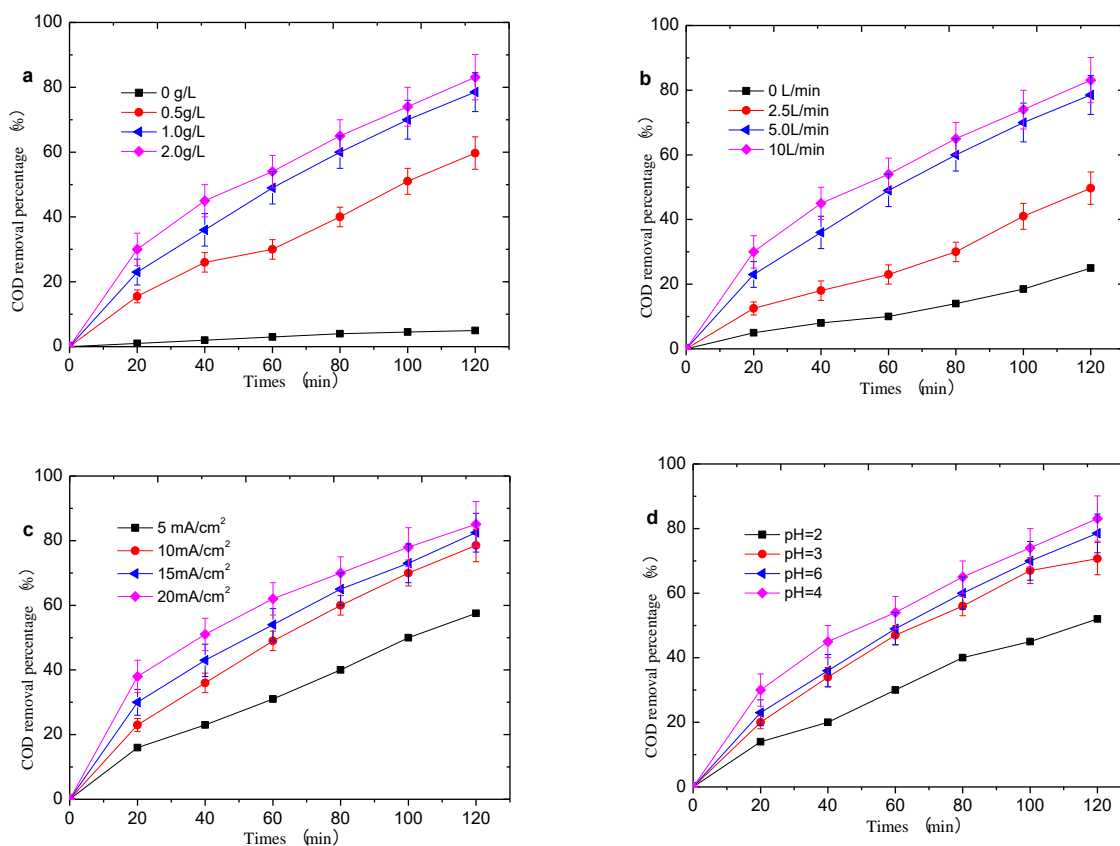
As shown in Fig. 4a, the effect of RSC-Fe dosage on COD removal during the EF process was investigated. While the dosage increased from 0.5 to 1 g/L, the COD removal percentage increased by 21% units, which was higher than when the dosage was increased from 1 to 2 g/L. Without RSC-Fe addition, the anode oxidation only removed 5% of the original COD load. It was noteworthy that higher dosages of CPEs facilitated the improvement of pollutant removal. However, excessive CPE dosages can short circuit the electrical current between the anode and the cathode, which results in lower electrical current flows and lower pollutant removal efficiencies (Hou *et al.* 2016). Hence, the RSC-Fe dosage of 1.0 g/L was deemed a reasonable catalyst addition level.

Dissolved oxygen (DO) levels in the aqueous solutions were elevated by aeration. Oxygen is the raw material that is reduced to form H<sub>2</sub>O<sub>2</sub> during electrolysis. Figure 4b showed that higher aeration rates, from 0 to 5 L/min, appreciably enhanced COD removal efficiencies, from 35.4% to 78.5%. It is speculated that improved COD removal can be chiefly attributed to higher DO levels that are closer to the saturation limit. This increase of DO was in response to the endpoint of the equilibrium state, while the amount of oxygen in the electrolyte is equivalent to the O<sub>2</sub> consumption of the electrochemical reaction. Thus the optimal aeration rate was 5 L/min.

Figure 4c shows that a 78.5% COD removal was achieved with 10 mA/cm<sup>2</sup> in EF process with RSC-Fe; COD removal increased to 86% when the current density was increased to 20 mA/cm<sup>2</sup>. Current density is the driving force for the generation of more H<sub>2</sub>O<sub>2</sub> and hydroxyl radicals. However, exceedingly high current densities enhanced the occurrence of a side reaction, which appeared to scavenge generated radicals by excessive H<sub>2</sub>O<sub>2</sub> production (Garcia-Segura and Brillas 2014; Santos *et al.* 2016). It is possible to

obtain high pollutant removal efficiencies while minimizing energy costs by using 10 mA/cm<sup>2</sup>.

The EF process was sensitive to the initial pH (Fig. 4d). The results indicated that the RSC-Fe had remarkable electro-catalytic activity over a wide pH range. There was only a 3.5% unit drop in COD removal percentage when the initial pH was increased from 4 to 6. This observation could be ascribed to H<sub>2</sub>O<sub>2</sub> being continuously electro-generated on the surface of CPEs. It can be hypothesized that the constant H<sub>2</sub>O<sub>2</sub> was catalyzed by the CPEs, and the precipitation of iron ions never occurred in this heterogeneous EF. The pH of the raw wastewater (*ca.* 6 pH) could be used as the initial pH of the EF process, which would reduce the operational costs associated with wastewater pH adjustment.

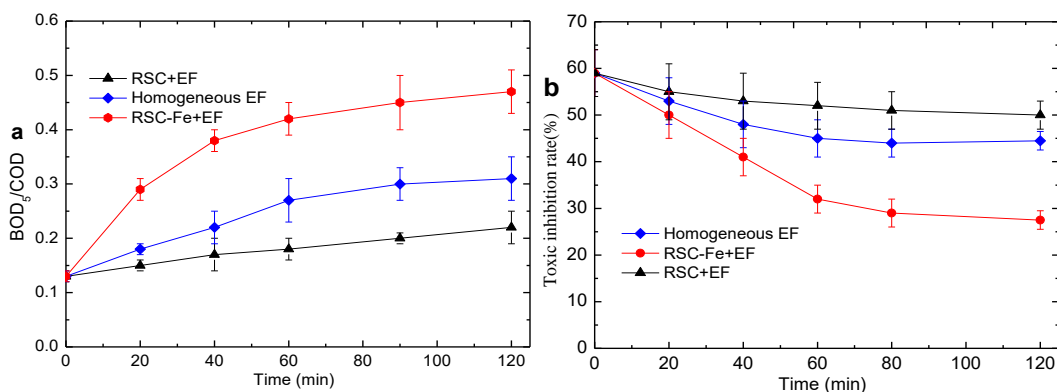


**Fig. 4.** Effect of operating parameters on pollutant removal percentage in EF process: (a) CPEs dosage, (b) aeration rate, (c) current density, and (d) initial wastewater pH

### Biodegradability and Toxicity Analysis

The biologically-pretreated wastewater had low biodegradability (0.15 BOD<sub>5</sub>/COD ratio), and improved biodegradability was clearly observed in the EF process with CPEs process (Fig. 5a). The BOD<sub>5</sub>/COD ratio gradually increased from initially 0.15 to levels of 0.21, 0.34, and 0.43 for 120 min reaction with the addition of RSC, Fe<sup>2+</sup>, and RSC-Fe, respectively. When the BOD<sub>5</sub>/COD ratio is higher than 0.4, the effluent is considered totally biodegradable (Sarria *et al.* 2003; Zhuang *et al.* 2016; Garcia-Segura *et al.* 2017); only EF using RSC-Fe achieved this threshold. Figure 5b showed that the acute toxicities of the treated effluents were decreased by 19.7%, 31.1% and 57.3% for RSC, Fe<sup>2+</sup>, and RSC-Fe additions to the EF process, respectively. These observations suggested that the

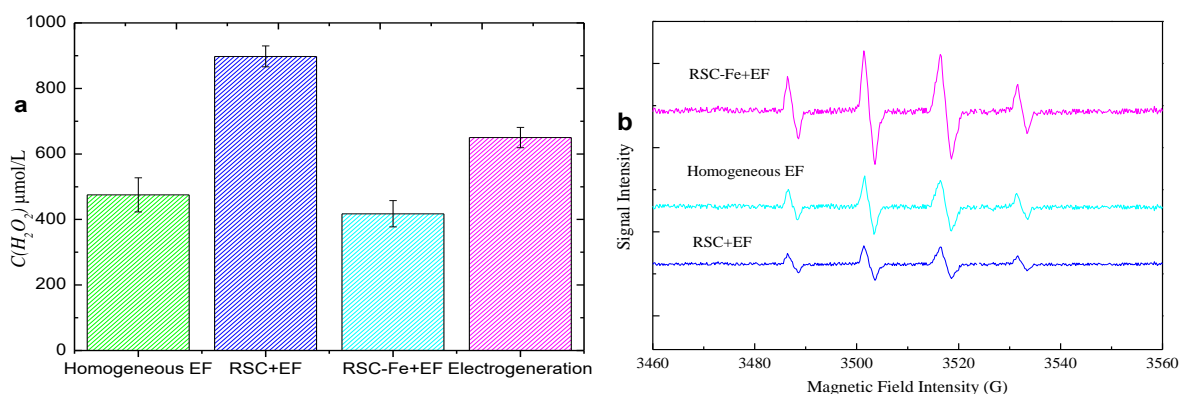
highly toxic pollutants were degraded into less toxic or even non-toxic substances, which suggests the modified EF process has potential to augment pollution removal after biological wastewater pretreatment.



**Fig. 5.** Changes of biodegradability (*i.e.*, BOD<sub>5</sub>/COD ratio) and acute toxicity in EF processes

### Possible Reaction Mechanism

Figure 6a illustrates the amount of H<sub>2</sub>O<sub>2</sub> generated from the homogenous EF process, EF with RSC, and RSC-Fe additions; these processes yielded 435.3, 817.5, and 427.2 μmol H<sub>2</sub>O<sub>2</sub>/L, respectively. The high accumulation of H<sub>2</sub>O<sub>2</sub> was observed with the RSC+EF process because every version of RSC as carbonaceous material cathode formed a micro-electrolysis cell in which the molecular O<sub>2</sub> is reduced to H<sub>2</sub>O<sub>2</sub> by a two-electron process (O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>O<sub>2</sub>) (Liu *et al.* 2016). However, lower concentration of H<sub>2</sub>O<sub>2</sub> was detected with the RSC-Fe+EF process, which is likely attributable to the *in situ* decomposition of H<sub>2</sub>O<sub>2</sub> that forms highly reactive HO<sup>•</sup> by the catalytic Fe ions (Hou *et al.* 2015).



**Fig. 6.** (a) H<sub>2</sub>O<sub>2</sub> concentration levels, and (b) ESR spectra for radicals trapped by DMPO for various EF processes

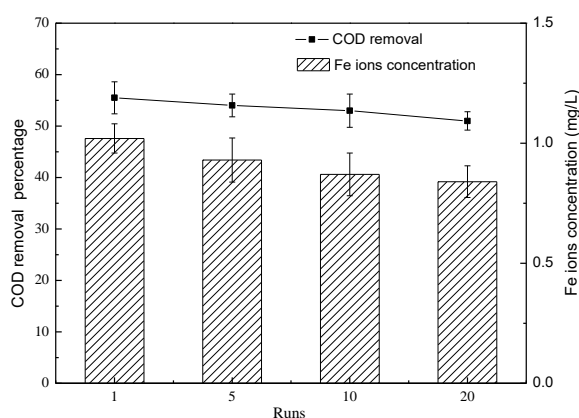
As shown in Fig. 6b, the ESR spectra of the various EF treatments displayed 4-fold peaks that are characteristic of the DMPO-<sup>•</sup>OH adduct (*i.e.*, 1:2:2:1 peak height ratio). No ESR signals of sextet peaks of DMPO-HOO<sup>•</sup> or DMPO-O<sub>2</sub><sup>•-</sup> adducts were observed, which suggested that the generation of <sup>•</sup>OH radicals are the primary active species involved in the EF process with CPEs. The amount of <sup>•</sup>OH radicals (according to peak intensity) followed the order: RSC-Fe +EF > homogeneous EF > RSC+EF. This order seems consistent with



the observed degradation tendencies.

### Stability and Reusability of RSC-Fe

As Fig. 7 shows, there were no remarkable changes in the electro-catalytic activity of recycled RSC-Fe versus virgin RSC-Fe. The COD removal percentage only decreased by 5.6% units after the 20th reuse, which indicated the recovered RSC-Fe had good stability. The stability of RSC-Fe was also evaluated by measuring the concentration of Fe ions, which was just under 0.42 mg/L in successive recycle runs. Thus, the results showed that the EF process with the RSC-Fe could remarkably improve the performance of pollutants removal and biodegradability at near neutral pH condition with stability and low cost. These advantages will facilitate engineering applications that cater to the concept of “using waste to treat waste”.



**Fig. 7.** COD removal efficiencies of the EF process and iron levels of the CPEs after numerous reuses

## CONCLUSIONS

1. Waste rice straw and iron-containing sludge were converted into catalytic particle electrodes (CPEs). These catalysts appreciably improved the performance of electro-Fenton (EF) oxidation of paper mill wastewater at near neutral pH conditions, and chemical oxygen demand (COD) and color of the treated wastewater after 120 min achieved discharge limits set by China. The optimized conditions for the EF process were: current density of 10 mA/cm<sup>2</sup>, CPEs dosage of 1.0 g/L, and aeration rate of 5 L/min.
2. The biodegradability of the EF-treated wastewater was improved considerably as the BOD<sub>5</sub>/COD ratio increased from 0.15 to 0.46, and the acute toxicity decreased by 57.3%.
3. Based on measured H<sub>2</sub>O<sub>2</sub> concentrations and interpreted ESR spectra, the enhanced catalytic activity of RSC-Fe could be attributed to the *in situ* generated H<sub>2</sub>O<sub>2</sub>, which was subsequently degraded into more •OH.
4. CPEs exhibited outstanding stability when recycled, which should make this EF catalyst suitable for industrial utilization with high efficiency.

## ACKNOWLEDGMENTS

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