An activated carbon fiber cathode for the degradation of glyphosate in aqueous solutions by the Electro-Fenton mode: Optimal operational conditions and the deposition of iron on cathode on electrode reusability

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ABSTRACT

An activated carbon fiber (ACF) cathode was fabricated and used to treat glyphosate containing wastewater by the Electro-Fenton (EF) process. The results showed that glyphosate was rapidly and efficiently degraded and the BOD₅/COD ratio was increased to >0.3 implying the feasibility of subsequent treatment of the treated wastewater by biological methods. The results of ion chromatography and HPLC measurements indicated that glyphosate was completely decomposed. Effective •OH generation and rapid recycling/recovery of the Fe²⁺ ions at the cathode were responsible primarily for the high performance of the ACF-EF process. Factors such as inlet oxygen gas flow rate, Fe²⁺ dosage, initial glyphosate concentration, applied current intensity, and solution pH that may affect the efficiency of the ACF-EF process were further studied and the optimum operation condition was established. Results of SEM/EDX, BET and XPS analysis showed the deposition of highly dispersed fine Fe₂O₃ particles on the ACF surface during the EF reaction. The possibility of using the Fe₂O₃-ACF as iron source in the EF process was assessed. Results showed that the Fe₂O₃-ACF electrode was effective in degrading glyphosate in the EF process. The deposition of Fe₂O₃ particles on the ACF electrode had no adverse effect on the reusability of the ACF cathode.

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1. Introduction

Glyphosate is the activate ingredient of Roundup™, marketed as a non-selective, post-emergence, broad-spectrum organophosphate herbicides of wide global agricultural and non-agricultural uses (Neto and de Andrade, 2009; Manassero et al., 2010; Zhang et al., 2011). The US Environmental Protection Agency (US EPA)

has classified glyphosate as an “extremely persistent” chemical and has established a maximum glyphosate concentration in sweet-water of 0.28 mg/L (Neto and de Andrade, 2009). It has been reported that only about 0.1% of the chemical applied in agriculture practice reaches the targets that most of the chemical escapes to the environment (Pimentel, 1995). Since the half-life of glyphosate is about 7–70 days (Frontera et al., 2011), its impact on the environment is moderately significant. Furthermore, improper disposal of glyphosate containing waste can lead to the contamination of soil, groundwater and surface water.

Several conventional methods such as adsorption (Hu et al., 2011; Ren et al., 2014), membrane filtration (Speth, 1993), biological and chemical treatments (Jardim et al., 1997), have been used to

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treat glyphosate containing wastewater. The effectiveness of the above methods is varying. Adsorption and filtration do not transform the chemical nor reduce its toxicity that post-treatment may be needed. Conventional biological processes usually require a long residence time (Zhang et al., 2011). Hence, chemical treatment, especially advanced oxidation process (AOP) has been received great attention in the last decade and electrochemical AOP has become a promising technology due to its simplicity and effectiveness in treating a wide variety of hazardous organic chemicals. There are studies on the electrochemical oxidation of glyphosate using different anodes, such as RuO₂–IrO₂ dimensionally stable anode (DSA) (Neto and de Andrade, 2009) and boron doped diamond (BDD) anode (Rubí-Juárez et al., 2016). Electrochemical mineralization of herbicide can occur through direct withdrawing of electron or indirect generation of oxidation species such as hydroxyl radicals, peroxocarbonate, peroxosulfate and hypochlorite dependent on the type of supporting electrolyte. The electro-generated oxidants are mostly responsible of herbicide degradation and achieve a complete mineralization of glyphosate. Heterogeneous photocatalysis, using UV–TiO₂ (Echavia et al., 2009), titania nanotubes (Zhang et al., 2012), and mesoporous graphite-like carbon supporting SnO₂ (Chen et al., 2015) as photocatalysts, have also showed promising potential for the degradation of glyphosate.

Electro-Fenton process, as an advanced oxidation process, has been used to degrade toxic and refractory organic pollutants based on the incipiently electro-generated H₂O₂ from the two-electron reduction of O₂ on the cathode and ferrous ions in acidic aqueous medium (eq. (1)–(3)) (Labiadh et al., 2015; Mousset et al., 2016).

Boron-doped diamond electrode (BDD), graphite or carbon-PTFE, most often used cathode (Do and Chen, 1993; Harrington and Pletcher, 1999; Brillas et al., 2004), is too expensive for large scale application. Recently, three-dimensional (3D) carbon electrode, namely, activated carbon fiber (ACF), has been reported to exhibit excellent performance in cathodic oxidation of hazardous chemicals (Wang et al., 2010). However, the following questions remain unanswered regarding the feasibility of the ACF-based EF technology: Can one reuse the ACF electrode? What is the effect of iron deposition on the ACF surface on the performance of the ACF electrode? Can Fe²⁺ be regenerated and recycled *in situ* and (*vis a viz* eq. (2) and eq. (3)) at the cathode surface?

In order to answer the above questions, this research was to evaluate the efficiency of the degradation of hazardous chemicals by electro-Fenton (EF) process using ACF as cathode exemplified by glyphosate. Major factors such as inlet gas, pH, applied current, Fe²⁺, and glyphosate concentration that may affect the performance of the ACF-EF process and the role of iron chemistry, i.e., Fe²⁺ and Fe³⁺, were explored. Additionally, the biodegradability of ACF-EF treated glyphosate was characterized in terms of change in BOD₅/COD ratio. Finally, the optimum reaction condition for the ACF-EF degradation of glyphosate was established. Finally, the effect of iron oxide deposition on the ACF surface and its effect on the reusability of the ACF electrode for continuing degradation of glyphosate were also investigated.

2. Materials and methods

2.1. Materials and reagents

Glyphosate (purity 99.6%) was purchased from Sigma Company. Iron (II) sulfate heptahydrate (99%, Wako) and sodium sulfate (anhydrous, 99%, Wako) were used as supporting electrolyte. High purity nitrogen and oxygen gas, and compressed air were purchased from Beijing Feda Hight-Tech Gas Co., Ltd and used directly. All of other reagents were of analytic grade. All solutions were prepared with ultrapure water ($\geq 18 \text{ M}\Omega$, Milli-Q, Millipore).

2.2. Equipment and procedures

Fig. 1 shows the sketch of the 400-mL undivided cell with two-electrode and a magnetic stirring bar. The anode was a 6.5 cm × 7.0 cm RuO₂/Ti mesh and the cathode was ACF felt coated RuO₂/Ti mesh with the same area as the anode. The DC power was provided by a power supply (DH1718E-4, Dahua Instrument Co., Beijing). The synthetic wastewater was consisted of a pre-determined amount of glyphosate in 0.1-M Na₂SO₄ supporting electrolyte. Unless otherwise specified, pure O₂ was fed into the solution at 100 mL/min. At given times, samples were taken and filtrated through 0.45-μm membrane for the analysis of residual glyphosate. The pH of the reaction solution was adjusted by 0.1 M NaOH and H₂SO₄ solutions.

2.3. Characterization of the electrode

The electrode was characterized by scanning electron microscopy (SEM, Hitachi S-3000N), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX) analysis, and electrochemical workstation (CHI 660E, Chenhua, Shanghai). Specific surface area was determined by nitrogen adsorption/desorption using a Micromeritics ASAP2000 analyzer (Micromeritics Co., USA). The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument from Kratos using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C1s hydrocarbon peak at 284.80 eV.

Fig. 1. Experimental setup of the electrochemical reactor: (1) DC power supply, (2) RuO₂/Ti anode, (3) ACF felt cathode, and (4) Magnetic stirrer.

2.4. Analytical chemical method

Glyphosate was analyzed by ion chromatography with an Ion PacAG19-HC (4 mm × 250 mm) guard column, an AS19A-HC (4 mm × 50 mm) separating column, and an ion self-regenerating suppressor (Alltech DS-Plus). KOH solution (30 mM) was used as eluent at a flow rate of 1.2 mL/min (Lan et al., 2013). The injection volume was 25 μ L with a suppress current of 90 mA. The concentration of intermediates was analyzed using high-performance liquid chromatography (1200 series; Agilent, Santa Clara, CA) with a HPLC organic acid analysis column (Aminex HPX-87H Ion Exclusion Column, 7.8 mm × 300 mm). COD, BOD₅ and iron ion concentration were measured according to the according to Standard Methods (A.P.H.A., 1998). The total organic carbon (TOC) content of the solution was analyzed using a Phoenix 8000 TOC analyzer. Determination of hydroxyl radicals and H₂O₂ was performed with a photometric method (Babbs and Gale, 1987; Steiner and Babbs, 1990; Klassen et al., 1994): methanesulfinic acid (MSA) generated from the reaction of $\cdot$ OH and DMSO can then react with fast blue BB salt to form a yellow diazosulfone compound. Hence, $\cdot$ OH concentration was measured quantitatively by determining the maximum absorbance wavelength at 425 nm. Hydrogen peroxide was determined by the iodide method as follows. Aliquots (1.5 mL) of samples were added in 10 mm quartz cuvettes, and 0.75 mL 0.1 M potassium biphthalate and 0.75 mL of iodide reagent (0.4 M potassium iodide, 0.06 M NaOH, $\approx 10^{-4}$ M ammonium molybdate) were then added. The absorbance of the treated solution was measured with a UV–visible spectrophotometer (Hitachi 3010) at $\lambda = 352$ nm $\epsilon = 26,400$ M⁻¹ cm⁻¹). While the Fe²⁺ and Fe³⁺ concentration in solution was measured by determination of the absorbance at 514 nm of the complex of Fe²⁺ and 1,10-Phenanthroline. The Fe³⁺ amount was calculated as follows: the total amount of iron (Fe²⁺ and Fe³⁺) was measured by reducing Fe³⁺ to Fe²⁺ by hydroxylamine hydrochloride; after measuring the amount of Fe²⁺ in solution (without Fe³⁺ reduction), so that $[\text{Fe}^{3+}] = \text{total} [\text{Fe}] - [\text{Fe}^{2+}]$. All of the experiments were repeated three times.

3. Results and discussion

3.1. Comparative degradation of glyphosate in different EAOP processes

Fig. 2 shows results of glyphosate degradation by (a) RuO₂/Ti anodic oxidation (AO); (b) oxidation by electro-generated H₂O₂ in the absence of Fe²⁺ (AO-H₂O₂); and (c) electro-Fenton process. As shown in Fig. 2A, only 10% of glyphosate was removed after 120 min by anodic oxidation. It could be speculated that the RuO₂/Ti mesh anode had a high electrochemical activity toward oxygen evolution thereby exhibiting low chemical reactivity for glyphosate oxidation. The AO-H₂O₂ system exhibited a slightly greater glyphosate oxidation at 25% (Fig. 2A b) compared to that of the RuO₂/Ti electrode (Fig. 2A a). In addition to direct AO oxidation, H₂O₂ generated at the cathode played the major role on the removal of glyphosate.

In contrast, the EF process exhibited the highest glyphosate oxidation capacity at ca. 85% after 120 min (Fig. 2A c). Moreover, the degradation rate of glyphosate reached 75% after 10 min. It must be noted that the degree of glyphosate degradation was parallel to that of the formation of $\cdot$ OH radical (Inset, Fig. 2A). Much more $\cdot$ OH radicals was generated in the EF process than the other two systems and reached the steady state level at 30 min, whereas the amount of $\cdot$ OH generated in the AO-H₂O₂ system was notably lower and there was almost no $\cdot$ OH formation in the AO system compared to the ACF-EF system. Hence, the extent of $\cdot$ OH generation facilitated glyphosate degradation in the EF process per the Haber and Weiss

Fig. 2. Glyphosate degradation and $\cdot$ OH generation (inset) at different processes: (a) AO oxidation over RuO₂/Ti, (b) AO-H₂O₂ and (c) electro-Fenton. (B) Changes of glyphosate biodegradability in different processes and the inset is the COD removal of glyphosate solution in electro-Fenton process.

mechanism.

BOD₅/COD ratio is an engineering indicator of the degree of biodegradability. It has been reported that BOD₅/COD > 0.3–0.4 represents complete biodegradation of the organic compounds (Chamarro et al., 2001). Fig. 2B shows the change in BOD₅/COD ratio and thus biodegradability of glyphosate in different EAOPs. The results indicated that after 360 min (6 h) 72% of total COD was removed (Inset, Fig. 2B), and the BOD₅/COD was greater than 0.3, which indicated that the ACF-EF treated wastewater was amenable to biological treatments.

3.2. Parameters affecting the performance of the ACF-EF process

Based on the above results, the ACF-EF process was proven to be the most effective method for glyphosate degradation. The parameters affecting the performance of the ACF-EF process with respect to glyphosate degradation was investigated. Firstly, the cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) analysis suggested the feasibility of ACF cathode for the production of H₂O₂ through the electrochemical reduction (Fig. S1). In this experiment, different gases were introduced into the system to ensure dissolved gases saturation before reaction. Fig. 3 shows the accumulation of O₂, H₂O₂ and the corresponding $\cdot$ OH formation as a function of reaction time in the presence of different inlet gases. Results clearly indicated that H₂O₂ and $\cdot$ OH increased quickly with

Fig. 3. The influence of oxygen purity on the (A) DO concentration (current intensity = 0.36 A, pH = 3.0, gas flow = 100 mL/min); (B) the correspondingly generated H₂O₂ (current intensity = 0.36 A, pH = 3.0, gas flow = 100 mL/min); and (C) •OH generation in electrochemical process (Fe²⁺ dosage = 1.0 mM, current intensity = 0.36 A, pH = 3.0, gas flow = 100 mL/min).

time until a steady state was achieved and followed the order: N₂ < air < O₂, which was a reflection of the DO concentration in the solution. The steady-state DO concentration was measured as 12, 14.5 and 45 mg/L when sparging with N₂, air, and pure oxygen, respectively. The quick increase of DO in the N₂ atmosphere after applying power supply could be attributed to the anodic oxygen evolution. Hence, unless otherwise stated, O₂ was always chosen as the inlet gas in all following experiments.

The effect of Fe²⁺ and glyphosate concentration, applied current

density, and solution pH on glyphosate degradation was also evaluated in terms of TOC removal by the ACF-EF process. Fig. 4A shows TOC change as affected by Fe²⁺ dose (from 0 to 1.0 mM) at pH 3.0 and current intensity of 0.36 A in the presence of 0.1 mM of glyphosate after 360 min (6 h) of treatment. The TOC removal was increased from 20 to 50% when the Fe²⁺ dosage was increased from 0 to 1 mM, correspondingly. The effect of the initial concentration of glyphosate on its mineralization was studied in four concentrations in the presence of 1 mM of Fe²⁺ with a pH of 3.0 and current

Fig. 4. The influence of different parameters on the glyphosate removal efficiency by electro-Fenton process: (A) Fe²⁺ dosage (B) initial glyphosate concentration, (C) applied current, (E) initial solution pH. (D) and (F) represent the H₂O₂ generation under different applied current and initial solution pH.

intensity of 0.36 A (Fig. 4B). After 360 min (6 h) of electrolysis, the TOC removal was 50.4, 48.5, 46.9, and 43.0% at initial glyphosate concentration of 0.1, 0.5, 1.0 and 1.5 mM, respectively. In general, the TOC removal was not sensitive to the initial glyphosate concentration in the range studied, presumably due to the presence of excess H_2O_2 or hydroxyl radical. The effect of applied current on TOC removal was also examined at 0.12, 0.24 and 0.36 A in the presence of 0.1 mM glyphosate and pH 3.0.

As shown in Fig. 4C, 26.25, 39.26 and 48.45% of TOC was removed after 360 min (6 h), in the presence of 0.12, 0.24 and 0.36 A of current intensity, respectively. It was found that increasing the current intensity in the range 0.12–0.36 A significantly enhanced the mineralization of glyphosate. The enhanced glyphosate removal by increasing the current density could be attributed to the increase in the production of H_2O_2 (Fig. 4D), subsequently, which resulted in the enhancement of $\cdot\text{OH}$ generation since the production of $\cdot\text{OH}$ is proportional to the H_2O_2 concentration (Qiu et al., 2015; Wang et al., 2016). A notable pH effect on the degradation of glyphosate was observed (Fig. 4E), reaching a maximum TOC removal of 48.45% at pH 3.0 in 360 min (6 h). It is noted that there was no significant difference in H_2O_2 generation within the range of solution pH studied (Fig. 4F). Hence, at pH > 3.0 decrease in glyphosate decomposition could be due to a weakening of the oxidation potential of $\cdot\text{OH}$ and a decrease in Fe^{2+} concentration due to pH-dependent Fe(II) speciation. Our result was in total agreement with those reported in the literature on the degradation of organic pollutants by electro-Fenton method. Furthermore, the optimum pH of 2.8 was consistent with typically reported value for maximum Fenton's reaction (Sun and Pignatello, 1993; Panizza and Cerisola, 2009). Based on the above results, the optimum reaction condition for the present ACF-EF process was: applied current intensity = 0.36 A, pure O_2 flow rate = 100 mL/min, $[\text{Fe}^{2+}] = 1.0 \text{ mM}$, $[\text{glyphosate}] = 0.1 \text{ mM}$, and pH < 3.0.

3.3. The mechanism on the degradation of glyphosate

The intermediates of the degradation of glyphosate were further monitored using ion chromatography (inorganic ions) and HPLC (small molecular organic acid) (Fig. 5). Obviously, the concentration of ammonium, nitrate, and phosphate were increased with reaction time, which indicated that the primary chemical structure of glyphosate was destroyed and that ammonium was oxidized to nitrite and finally to nitrate. The nitrite was not detected in the system probably due to its quick oxidation to nitrate by $\cdot\text{OH}$. The increase in acetic acid and oxalic acid concentration during glyphosate degradation also proved the cleavage of the C–P and

Fig. 6. The proposed reaction mechanism of glyphosate degradation in electro-Fenton process.

C–N bond of glyphosate and subsequent generation of aliphatic acids. Based on the experimental results, the reaction mechanism of the ACF-EF process, a preliminarily proposed glyphosate degradation pathway could be proposed (Fig. 6). First, oxygen was adsorbed onto the ACF surface and H_2O_2 was then efficiently generated through the reduction of oxygen on cathode. Meanwhile, Fe^{2+} immediately and catalytically decomposed H_2O_2 to generate hydroxyl radicals presumably through the Haber-Weiss mechanism. The regeneration of Fe^{2+} ions could be mainly brought by a direct cathode reaction via electro-reduction of Fe^{3+} ions. The degradation of glyphosate started with breaking the C–N and C–P bond to form acetic acid and oxalic acid. Finally, most of the organic intermediates were converted to carbon dioxide and inorganic ions, respectively. For instance, the nitrogen atom was released as ammonium and nitrate ions, and the P atom was converted to phosphate.

3.4. Iron deposition on ACF and its effect on electrode reusability

In the ACF-EF process, Fe^{3+} or Fe^{2+} ion, as Fenton or Fenton-like catalyst, was beneficial to $\cdot\text{OH}$ generation. Therefore, it is justified to investigate the iron cycle further. Fig. 7A shows the change of iron ion concentration upon the addition of Fe^{2+} to the reaction system.

Fig. 5. The formation of intermediates in electro-Fenton degradation of glyphosate: (A) inorganic ions and (B) small molecular organic acid. Experimental conditions: $C_0 = 0.5 \text{ mM}$, Fe^{2+} dosage = 1.0 mM, current intensity = 0.36 A, pH = 3.0, and $\text{O}_2 = 100 \text{ mL/min}$.

Fig. 7. The change of iron ion concentration when (A) Fe²⁺ and (B) Fe³⁺ was added into the electro-Fenton process: Experimental conditions: Fe ion dosage = 1.0 mM, current intensity = 0.36 A, pH = 3.0, and O₂ = 100 mL/min.

There was a rapid decay of Fe²⁺ concentration and simultaneous increase in Fe³⁺ content. The steady state was achieved quickly in about 15 min for both Fe²⁺ and Fe³⁺, which agreed with the results of $\cdot$ OH generation and glyphosate degradation (Fig. 2). On the other hand, when Fe³⁺ was added to the reaction system, it was also reduced quickly to Fe²⁺ and reached the steady state condition in about 10 min as well (Fig. 7B). Fast regeneration of Fe²⁺ species at the ACF electrode is essential for sustaining the oxidation capacity of the ACF-EF system, since Fe²⁺ ion is needed to form $\cdot$ OH per the Fenton's reaction (Sires et al., 2007; Oturan et al., 2008).

According to Fig. 7, the total amount of iron (Fe²⁺ and Fe³⁺) was decreased with reaction time regardless of the form of the iron species, i.e., Fe²⁺ or Fe³⁺, added to the system, which indicated

clearly that some iron oxide should be deposited onto the ACF electrode surface as verified by SEM imaging (Fig. 8A and B). As shown in Fig. 8A & B, some white clusters appeared on the ACF surface after the electro-Fenton reaction. Based on the EDX analysis (Inset, Fig. 8A and B), iron element indeed was present on the ACF electrode surface at atomic ratio of 0.59% compared to fresh ACF after the cathodic process period.

Fig. 8C shows the N₂ adsorption-desorption isotherms. The iron deposition did not change significantly the pore size distribution of ACF. The BET surface area of the ACF electrode before and after EF reaction was 1053 and 940 m²/g, respectively. The N₂ adsorption-desorption isotherms followed type III with hysteresis loops, which implies the presence of mesoporous structure after EF

Fig. 8. SEM images of ACF before (A) and after (B) being used in electro-Fenton reaction. (C) Pore size distribution of the ACF electrode (a) before and (b) after the electro-Fenton reaction. The inset shows the nitrogen adsorption-desorption isotherm of the used ACF. (D) XPS spectra of Fe 2p of iron deposited on the surface of ACF.

reaction. Moreover, the XPS peaks (Fig. 8D) at 711, 719, and 725 eV were assigned to the binding energy of Fe2p_{3/2}, shake-up satellite Fe2p_{3/2} and Fe2p_{1/2} (Lan et al., 2015), suggesting the existence of Fe₂O₃. The above results indicated that Fe₂O₃ with small particle size was highly dispersed on the ACF surface and that the deposition of Fe₂O₃ did not change the ACF pore structure. It is necessary to investigate the possibility of Fe₂O₃/ACF reuse in EF catalytic degradation of glyphosate.

Fig. 9 depicts the electro-Fenton activity of Fe₂O₃/ACF electrode (used as iron ion source) in the catalytic degradation of glyphosate. The reused operation procedure of iron oxide deposited ACF (Fe₂O₃/ACF) was provided as followed: after the EF process, the used ACF (Fe₂O₃/ACF) was taken out from the reaction mixture and rinsed twice with deionized water. It was then reused directly in EF process without the addition of any Fe²⁺ or Fe³⁺. The experimental conditions were as followed: C₀ = 0.5 mM, current intensity = 0.36 A, pH = 3.0, and O₂ = 100 mL/min. The mineralization of glyphosate by the Fe₂O₃/ACF electrode was comparable with the ACF electrode (run 1) and more significant (run 2 & 3) than the AO and AO-H₂O₂ process (inset, Fig. 9). The oxidation capacity of the Fe₂O₃/ACF electrode decreased slightly with recycle time, which was parallel to •OH generation under same experimental conditions. Since part of iron oxides remained on the ACF surface, the high efficiency of the Fe₂O₃/ACF-EF system could be brought by the H₂O₂ activation to generate •OH at the iron sites on the electrode surface (Zhao et al., 2012). Dissolution of iron oxide occurred at acidic pH of 3.0, which ultimately deactivate the oxidative function of the Fe₂O₃/ACF electrode. The results in Fig. 9 indicated that the deposition of Fe₂O₃ particles on the ACF surface had almost no influence on the cycle/reuse of ACF as cathode. Dissolution of iron oxide to yield soluble iron ions from the Fe₂O₃/ACF electrode could aid in the glyphosate gradation in the EF process.

4. Conclusion

EF reaction was efficient for the degradation of glyphosate using ACF as cathode in an acidic aqueous solution. During the degradation process, the C–N and C–P bond were broken and acetic acid and oxalic acid were then formed. The nitrogen atom in glyphosate was released as ammonium and nitrate ions, while the

phosphorous atom was converted into phosphate. After reaction for 6 h, the remaining intermediates from glyphosate degradation was biodegradable as the BOD₅/COD ratio was >0.3. •OH radical generated from the H₂O₂ activation by Fe²⁺ and the quick conversion of iron species at the cathode were responsible for the high performance of the electro-Fenton process. The optimum reaction condition for the present ACF-EF process was: [applied current] = 0.36 A, O₂ flow rate = 100 mL/min, [Fe²⁺] = 1.0 mM, and pH = 3.0. Moreover, based on the SEM/EDX, BET and XPS analysis, Fe₂O₃ in small particles was deposited and highly dispersed on the ACF surface during the EF reaction. Fe₂O₃/ACF could be used as iron source in the EF process for efficient degradation of glyphosate; hence the deposition of Fe₂O₃ particles on ACF surface had almost no influence on the cycle/reuse of ACF as cathode.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.09.036>.

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Fig. 9. •OH generation with the repeated times when Fe₂O₃/ACF was reused in EF process. The inset shows the comparison of glyphosate removal efficiency by different reaction systems. Experimental conditions: C₀ = 0.5 mM, current intensity = 0.36 A, pH = 3.0, and O₂ = 100 mL/min.

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