Electro-Fenton for control and removal of micropollutants – process optimization and energy efficiency

E. Mousset, Z. Wang and O. Lefebvre

ABSTRACT

The removal of micropollutants is an important environmental and health issue. Electro-Fenton offers an electrochemical advanced treatment that is particularly effective for the breakdown of aromatic contaminants. Due to the wide variety of chemicals, it is preferable to analyze model contaminants, such as phenol, when optimizing and assessing the efficacy of a novel treatment process. In this study, we therefore made use of innovative types of electrode material and optimized operating parameters (current density and aeration rate) for the removal of phenol by electro-Fenton, with a view to maximize the energy efficiency of the process. By determining the best current density (1.25 mA cm^{-2}), frequency of aeration (continuous) and by using a boron-doped diamond (BDD) anode, it was possible to achieve over 98.5% phenol (1 mM) removal within 1.5 h. BDD further outcompeted platinum as anode material in terms of mineralization rate and yield, and displayed low energy consumption of 0.08 kWh (g-TOC)$^{-1}$, about one order of magnitude lower than other advanced oxidation processes, such as UV/TiO$_2$ and UV/O$_3$. Furthermore, a carbon cloth anode proved even more cost-effective than BDD if the end goal is the removal of phenol by electro-Fenton instead of complete mineralization.

Key words | advanced oxidation processes, aeration rate, anodic oxidation, carbon-based anode, electro-Fenton, industrial micropollutants

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INTRODUCTION

Humans have found or made over 50 million different chemicals, the vast majority over the last few decades. Many of these are resistant to microbial degradation, pass unaltered through wastewater treatment plants (WWTPs) and end up as micropollutants in surface waters (Ternes & Joss 2006). To minimize the discharge of industrial contaminants from WWTPs into the receiving waters and thus prevent adverse ecological and health effects, there have been discussions on upgrading WWTPs with advanced treatment processes (tertiary treatment). Advanced physico-chemical processes such as advanced oxidation processes (AOPs) have gained popularity because they allow the generation of hydroxyl radical ($\bullet$OH), a non-selective oxidant that can react very quickly with many biorefractory organic compounds and particularly with aromatic molecules (Oturan & Aaron 2014).

With new chemicals being isolated or synthesized every 2.6 seconds on average, it is impossible to study all of them and there is a need to work with model contaminants, when optimizing and assessing the efficacy of advanced treatment processes. Phenol is a common choice to represent aromatic molecules of industrial origin. Phenolic compounds are widely used in the manufacture of antioxidants, biocides, disinfectants, pesticides, polymeric resins, dyes, pulp, paper, pharmaceuticals, and other synthetic materials. They are therefore commonly found in industrial wastewater streams from oil refineries, petrochemical and coal conversion plants, and other chemical industries (Gernjak et al. 2003). Another advantage of using phenol as a model molecule is that not only is it a relevant industrial compound, but its wide use in many studies enables comparison between different treatment processes. Phenol has indeed been frequently used as a model molecule for testing the efficacy of many AOPs, including ozonation, chlorination and the Fenton reaction (Lee & von Gunten 2010).

A novel approach is the electrochemical generation of OH radicals. Electrochemical treatments present the benefits of using a clean reagent (electrons), reaching high degrees of

mineralization and degrading a wide array of contaminants over a broad range of organic loads (chemical oxygen demand between 0.01 and 100 g-O$_2$ L^{-1}), making them equally useful as primary and as tertiary treatments (Sirés *et al.* 2014). Electro-Fenton has emerged as the most promising among electrochemical technologies. In contrast with the conventional Fenton's process, the Fenton's reagent (H$_2$O$_2$ and Fe^{2+}) is generated electrocatalytically and *in situ* at the cathode of the electro-Fenton reactor. Other advantages include the electrochemical regeneration of iron, meaning that it can be provided at only a catalytic amount – unless present in wastewater (Huguenot *et al.* 2015) – and without sludge production (Brillas *et al.* 2009). Electro-Fenton has proven to be effective even with the most recalcitrant pollutants and streams, including pesticides and landfill leachates (Mousset *et al.* 2014; Rodrigo *et al.* 2014; Oturan *et al.* 2015).

Several aspects of electro-Fenton still require further development, mostly in terms of energy efficiency. On top of the current density, energy is also required for aeration in order to electrogenerate H$_2$O$_2$, and most electro-Fenton studies continuously supply an external source of O$_2$ (Brillas *et al.* 2009; Nidheesh & Gandhimathi 2012). However, it is known that O$_2$ is produced at the anode of the system too. Considering that aeration often constitutes the biggest expense for wastewater treatment, it appears important to figure out the economy that could be made if only partial aeration was provided. Exploration of novel electrode materials could further contribute to cost reduction, and platinum (Pt) – conventionally employed in electro-Fenton research (Sopaj *et al.* 2014) – should be avoided. A cheaper and more effective anode in the form of boron-doped diamond (BDD) has been developed over the last decade (Panizza & Cerisola 2009); yet it remains quite expensive (Cañizares *et al.* 2009; Sirés *et al.* 2014). Carbon-based electrodes, on the other hand, are cheap and scalable and have shown good performance as cathodes in electro-Fenton (Brillas *et al.* 2009). However, their use as anode is yet to be evaluated from a cost-effectiveness point of view. In particular, carbon cloth is a commonly used anode material in the emerging field of microbial fuel cells (galvanic process) (Thepsuparungsikul *et al.* 2014) and their use could be evaluated in electrolytic mode for electro-Fenton.

In this context, this study focuses on the opportunity to use electro-Fenton for the removal of phenol, and optimize the process from a cost-effectiveness point of view by studying the effects of (i) applied current density, (ii) aeration rate, and (iii) anode materials. The energy requirements are taken into account in this cost-efficiency study in order to determine the optimal operating parameters.

METHODS

Electro-Fenton set-up

Electrochemical experiments were run under controlled conditions of temperature (35 ± 0.1 °C) in a 0.6-L (working volume of 0.4 L) open undivided tempering glass reactor (Figure 1). The electrochemical cell was monitored by a power supply (HAMEG 7042-5, Germany) and the applied current density varied in the range of 0.625–2.5 mA cm^{-2}. The solutions were continuously stirred at 500 rpm. The cathode was made of carbon fibers (SGL group (USA)) shaped as a brush (8 cm length; 5 cm diameter). Three different anode materials were employed: a piece of platinum (30 cm^2) supplied by Manilal Maganlal & Co. (India), a piece of carbon cloth (5 × 13.5 cm) treated with polytetrafluoroethylene provided by Fuel Cell Earth (USA) and a single-side BDD plate (2.5 × 8 cm) coated on niobium substrate (0.2 cm of thickness) obtained from Condias (Germany). K$_2$SO$_4$ (0.050 M) was added as electrolyte and FeSO$_4$ as a source of Fe^{2+} catalyst for the Fenton's reaction, at the optimal concentration of 0.1 mM, as optimized by Pimentel *et al.* (2008). The pH was adjusted to 3.0, corresponding to the optimal value for electro-Fenton (Brillas *et al.* 2009). In all experiments, compressed air was bubbled into the solution at a flow rate of 0.2 L min^{-1} for 20 min in
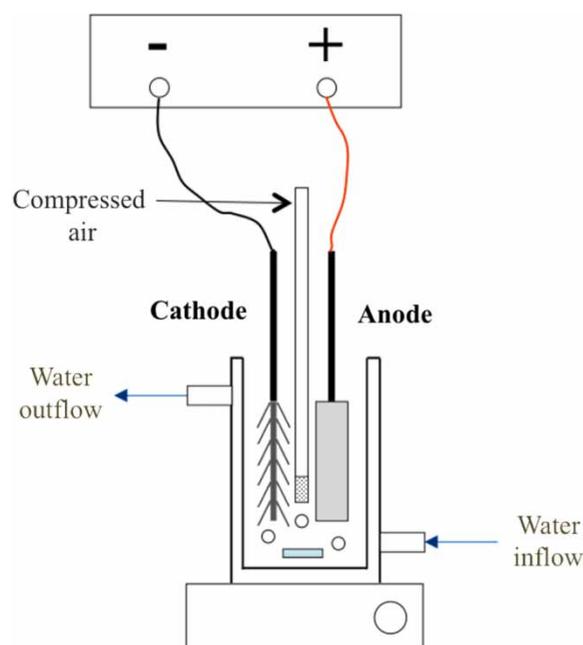

Figure 1 | Schematic diagram of the electro-Fenton apparatus used in this study.

order to ensure consistent initial dissolved O_2 concentration (Pimentel *et al.* 2008; Mousset *et al.* 2016a).

Sequential aeration was performed by bubbling for 10 min at different frequencies: every 1, 2, 3 and 4 h. For continuous aeration experiments, compressed air was provided throughout the electrochemical treatment period.

Analyses

Phenol decay was followed by reversed phase high performance liquid chromatography (Shimadzu SCL-10A, Japan) coupled with a UV-absorbance detector (Shimadzu SPD-M10A, Japan) (Mousset *et al.* 2016a). A Zorbax® C-18 column (15 cm length, 5 μm of stationary phase thickness) (Agilent, USA) was used and placed in an oven and set at 40.0 °C. The mobile phase was a mixture of ultrapure water and acetic acid (1%)/methanol (75:25 v/v) and the flow rate was set at 0.25 mL min^{-1}. Analyses were carried out at isocratic elution mode. The UV detection was set at 280 nm.

Total organic carbon (TOC) analyses were performed to quantify the mineralization degree during the electro-Fenton treatment of phenol. The TOC values were determined by thermal catalytic oxidation (680 °C) using a Shimadzu V$_{CSH}$ TOC analyzer (Japan).

RESULTS AND DISCUSSION

Influence of current density on the electro-Fenton treatment

For initial experiments, the carbon fiber brush cathode was associated with the cloth anode. The influence of current density on phenol removal is depicted in Figure 2. When the current density increased from 0.625 mA cm^{-2} to 2.5 mA cm^{-2}, the phenol concentration after 3 h of treatment

decreased from 1 mM to 0.1 mM (90.7% removal efficiency) and 0.001 mM (99.9% removal efficiency), respectively (Figure 2(a)). Increasing the current density allowed amplification of the *in situ* generation of Fenton reagent (H_2O_2 and Fe^{2+}) at the cathode through Equations (1) and (2):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{2}$$

The reaction between H_2O_2 and Fe^{2+} then stimulated the production of $\cdot$OH through the Fenton reaction (Equation (3)):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + HO^- \tag{3}$$
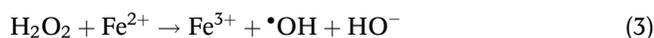
Therefore, the increase of Fenton reagent increased the production of OH and phenol degradation up to 2.5 mA cm^{-2}; however, increasing the current density further to 3.75 mA cm^{-2} did not increase the removal yield of phenol and this could be explained by parasitic reactions at the cathode (Equations (4) and (5)), at the anode (Equations (6) and (7)) and in the bulk solution (Equation (8)) (Brillas *et al.* 2009):
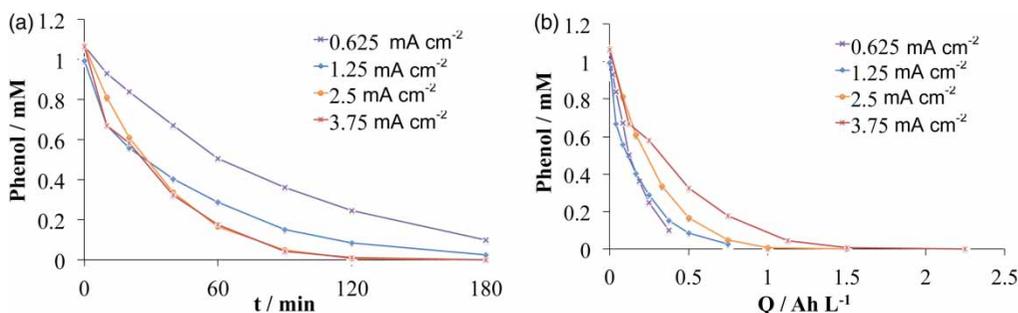
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{4}$$

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{5}$$

$$H_2O_2 \rightarrow HO_2^\cdot + H^+ + e^- \tag{6}$$

$$HO_2^\bullet \rightarrow O_2 + H^+ + e^- \tag{7}$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{8}$$

Figure 2 | Impact of current density on phenol removal as a function of (a) time and (b) specific charge.

A current density of 2.5 mA cm^{-2} maximized the phenol removal efficiency, in accordance with the findings of Pimentel et al. (2008); however, this also raised the specific charge required to degrade the pollutant (Figure 2(b)). Therefore, based on energy requirements, a current density of 1.25 mA cm^{-2} seemed the best – allowing 98.0% phenol removal in 3 h – and was therefore selected for subsequent experiments.

Influence of continuous vs sequential aeration on the electro-Fenton treatment

In order to optimize energy requirements for electro-Fenton further, the influence of continuous vs sequential aeration on the process was assessed for the first time. The experiments were performed with a carbon fiber brush cathode and a carbon cloth anode at a current density of 1.25 mA cm^{-2} and by bubbling compressed air into the solution at a flow rate of 0.2 L min^{-1}, which is conventional for electro-Fenton (Pimentel et al. 2008; Zhou et al. 2013; Yu et al. 2015; Mousset et al. 2016a). In fact, Zhou et al. (2013) reported that at higher air flow rate, the excessive mass of bubble increased the resistance of the medium and decreased H$_2$O$_2$ generation yield.

The results are displayed in Figure 3.

Sequential aeration clearly improved phenol degradation, with removal efficiencies after 8 h of 73%, 90%, 95% and 99.5% when bubbling every 4, 3, 2 and 1 h, respectively. Continuous bubbling further shortened the treatment time and 99% removal efficiency was achieved in barely 3 h. It is clear that bubbling air into the solution improved the process efficiency by increasing the amount of O$_2$ that can adsorb to the active sites of the cathode surface for its subsequent reduction into H$_2$O$_2$ (Equation (1)) (Yu et al. 2015).
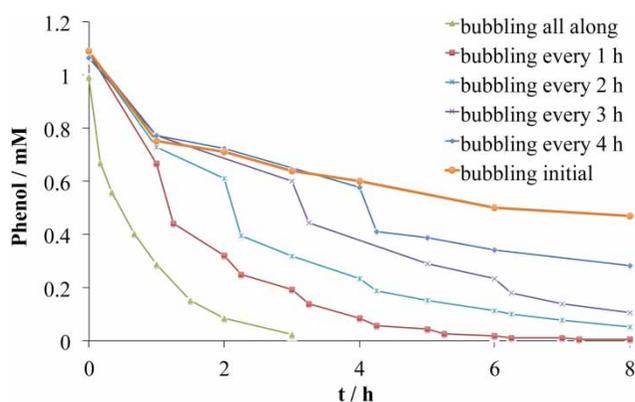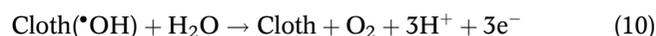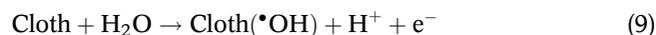

Figure 3 | Impact of aeration on phenol removal.

The low removal efficiency in the absence of aeration (only initial bubbling for 20 min) highlighted that the amount of O$_2$ provided by the low O$_2$-overvoltage carbon cloth anode through water oxidation (Equations (9) and (10)) was insufficient to ensure optimal production of H$_2$O$_2$ generated at the cathode.

$$Cloth + H_2O \rightarrow Cloth(^{\bullet}OH) + H^+ + e^- \qquad (9)$$

$$Cloth(^{\bullet}OH) + H_2O \rightarrow Cloth + O_2 + 3H^+ + 3e^- \qquad (10)$$

The energy requirements for electrolysis and aeration were further calculated following the method of Brillas et al. (2009) and the results are presented in Table 1, in order to achieve 50% phenol removal.

It is obvious from Table 1 that increasing the frequency of aeration decreased the overall energy consumption from 12 kWh m^{-3} to 0.9 kWh m^{-3}. This can be explained by the longer time needed to treat the contaminant at lower aeration rates, resulting in unacceptable electrolysis costs. It is therefore obvious that for electrochemical treatments, it is essential to achieve rapid treatment as the cost of electrolysis is higher than the cost of aeration. Therefore, this study demonstrates for the first time that the addition of a continuous external source of O$_2$ improves the cost-effectiveness of the process and that the oxygen required for the cathode reaction cannot be supplied efficiently by the anode reaction. Under the best conditions, the aeration represents about ¼ of the total energy cost and electrolysis ¾.

In Table 1, we deliberately ignore the cost of pH acidification because, even without such adjustment, Mousset et al. (2016b) have shown that the pH was found to decrease until a plateau around 3 is reached, corresponding to the average acid dissociation constant (pK_a) values of the carboxylic acids formed during electro-Fenton treatment of wastewater. This makes electro-Fenton suitable even at an initial circumneutral pH.

There could, however, be a cost for adjusting the pH back to 6–7 following electro-Fenton, as generally required for secondary treated effluent discharge into a watercourse. Finally, another possible cost would be related to the removal of excess iron, which is generally considered a macronutrient (Tchobanoglous et al. 2004) but is nevertheless sometimes controlled. For example, in Singapore the limit pertaining to iron discharge in watercourses is generally 10 mg L^{-1}, but can be as low as 1 mg L^{-1} for a controlled watercourse (used for potable water supply). In the latter case, the Fe(II) concentration employed in this

Table 1 | Impact of aeration on energy required for the removal of 50% of phenol by electro-Fenton process

Frequency of aeration	No aeration	Every 4 h	Every 3 h	Every 2 h	Every 1 h	Continuous aeration
Half-life time of phenol (h)	5.3	3.7	2.5	1.8	1.0	0.46
Energy for aeration (kWh m^{-3})	0	0.02	0.1	0.3	0.6	0.2
Energy for electrolysis (kWh m^{-3})	12.0	6.8	4.9	3.0	1.6	0.7
Total (kWh m^{-3})	12.0	6.8	5.0	3.3	2.2	0.9

study could be in excess of the discharge limits and could lead to increased expenses. More investigation is needed to follow the fate of iron in a continuous electro-Fenton treatment system and also to optimize the iron concentration depending on the nature of the watercourse. It should be noted here that the cost of iron removal would anyway remain much lower for electro-Fenton than for the conventional (chemical) Fenton's process, for which the iron concentration is typically an order of magnitude higher (Maciel *et al.* 2004).

Influence of anode materials on the electro-Fenton treatment

The performance of carbon cloth as an anode was compared to that of Pt and BDD for the first time. The results in terms of phenol degradation are shown in Figure 4. Carbon cloth and Pt achieved 98% and 99% phenol removal efficiency in 3 h and the treatment was faster with BDD with 98.5% phenol removal in just 1.5 h. According to the trend of the phenol decay in Figure 4(a), its reaction with •OH was considered to be a pseudo-first-order kinetic model, assuming a quasi-stationary state for •OH concentration ([•OH]). •OH are continuously produced and destroyed at a similar rate to attain a steady-state concentration in the bulk and/or the vicinity of the electrodes, so that their concentration

can be considered constant as shown in Equation (11) (Brillas *et al.* 2009):

$$\frac{d[Phenol]}{dt} = -k_{abs}[\bullet OH][Phenol] = k_{app}[Phenol] \quad (11)$$

where k_{abs} is the absolute rate constant of phenol decay and k_{app} is the pseudo-first-order rate constant of phenol decay.

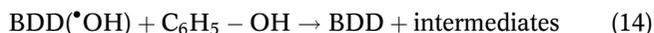After integration of Equation (11), Equation (12) was obtained:

$$\ln\left(\frac{[Phenol]_0}{[Phenol]}\right) = k_{app}t \quad (12)$$

k_{app} values were calculated from linear regression of the semi-logarithmic plots and ranked as follow: 0.035 min^{-1} (BDD, half-life time of 20 min) > 0.025 min^{-1} (cloth, half-life time of 28 min) > 0.021 min^{-1} (Pt, half-life time of 33 min). Correlation coefficients (R^2) of 0.995, 0.985 and 0.990 were achieved for BDD, cloth and Pt, respectively, which validate the pseudo-first-order kinetic model. The rate of phenol degradation with BDD was 1.4-fold to 1.6-fold higher than cloth and Pt, respectively. The kinetic analysis therefore confirms the superiority of BDD, which can be explained by its O$_2$-overvoltage (2.3 V vs SHE), high enough to produce physisorbed hydroxyl radicals (BDD (•OH)) at the surface of the anode (Equations (13) and
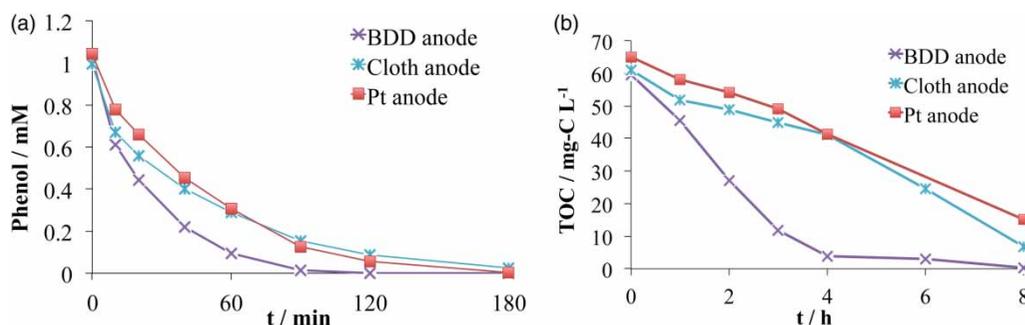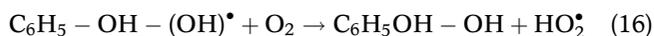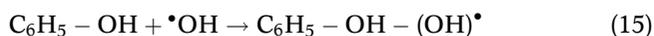

Figure 4 | Influence of anode material on (a) phenol and (b) TOC removal.

(14)), a process referred to as anodic oxidation (Panizza & Cerisola 2009):

$$BDD + H_2O \rightarrow BDD(^\bullet OH) + H^+ + e^- \tag{13}$$

$$BDD(^\bullet OH) + C_6H_5 - OH \rightarrow BDD + \text{intermediates} \tag{14}$$

Therefore, the combination of electro-Fenton and anodic oxidation resulted in a paired electrocatalysis process, which allowed generation of homogeneous $^\bullet OH$ radicals in the bulk solution via the Fenton reaction (Equation (3)) and heterogeneous $^\bullet OH$ radicals at the anode surface. Thanks to the existence of two sites of $^\bullet OH$ production, the degradation efficiency with BDD was much higher than with the other anode materials.

A yellow coloration also appeared in solution after 10 min of electrolysis with the three anode materials and the color was more pronounced with BDD. This coloration was caused by para-benzoquinone, an intermediate of phenol hydroxylation following oxidation with $^\bullet OH$ through reactions 15 and 16 (Brillas *et al.* 2009):

$$C_6H_5 - OH + ^\bullet OH \rightarrow C_6H_5 - OH - (OH)^\bullet \tag{15}$$

$$C_6H_5 - OH - (OH)^\bullet + O_2 \rightarrow C_6H_5OH - OH + HO_2^\bullet \tag{16}$$

According to the ortho and para directing effect of the hydroxyl group (–OH) during hydroxylation of aromatic compounds, catechol and hydroquinone appeared as the major hydroxylated aromatic by-products (Mousset *et al.* 2016a). As the medium was strongly oxidizing, hydroquinone was quickly oxidized to para-benzoquinone (Pimentel *et al.* 2008). The stronger coloration observed with BDD at the beginning of the treatment implied that higher concentrations of para-benzoquinone were formed, which corroborates the higher degradation efficiency of this material.

The superiority of BDD was further confirmed by TOC removal (Figure 4(b)). The mineralization with BDD was more efficient than with other anode materials and resulted in treated effluent TOC as low as 0.6 mg-C L^{-1} (94% mineralization) in 4 h, as compared to 3.8 mg-C L^{-1} (94% mineralization) and 6.8 mg-C L^{-1} (90% mineralization) in 8 h, with Pt and carbon cloth, respectively.

In terms of energy requirements, BDD also outcompeted carbon cloth and Pt: 0.08 kWh (g-TOC)$^{-1}$ was needed to achieve 90% of phenol mineralization as compared to 0.12 kWh (g-TOC)$^{-1}$ and 0.14 kWh (g-TOC)$^{-1}$ with Pt and cloth, respectively. Comparatively, conventional AOPs such as UV/TiO$_2$ and UV/O$_3$ require about 1.00 kWh (g-TOC)$^{-1}$ and 1.19 kWh (g-TOC)$^{-1}$, respectively, to reach lower phenol mineralization yields of 40% as shown by the experiments of Suzuki *et al.* (2015). Our study therefore demonstrates the superiority of electro-Fenton, especially with BDD, resulting in 12 to 15 times lower energy consumptions.

Further investigation should be done to continue improving the cost-effectiveness of electro-Fenton, for example by combining it with biological treatment in order to be even more competitive from an energy-efficiency point of view (Mousset *et al.* 2014). In such a configuration, the electrochemical treatment would aim at enhancing the effluent biodegradability instead of achieving complete mineralization. A rapid comparison of Figure 4(a) and 4(b) shows quite clearly that, with such an approach, carbon cloth would very likely be competitive with BDD as an anode, with equivalent energy consumptions for both electrode materials as low as 0.009 kWh (g-phenol)$^{-1}$ in order to degrade 50% of the phenol. Considering its low cost – about eightfold cheaper than BDD, carbon cloth could prove more cost-effective than BDD and Pt, which are generally considered in the literature (Ganzenko *et al.* 2014; Mousset *et al.* 2014).

CONCLUSIONS

In this study, electro-Fenton demonstrated promise for the removal of phenol used as a model pollutant, with great prospect for many other micropollutants from industrial origin. Degradation and mineralization yields as high as 99% were achieved in the best conditions of current density, aeration and electrode materials. After considering cost-effectiveness, we reach the following conclusions: (i) the current density was an important factor and the best value (1.25 mA cm^{-2}) was determined experimentally based on energy consumption and removal efficiency; (ii) providing continuous aeration was more cost-effective than the absence of aeration even after considering the costs of aeration (0.9 vs 12 kWh m^{-3}); (iii) a BDD anode demonstrated the best mineralization efficiency (98.5% after 1.5 h). However, considering its cost-effectiveness and good performance, we recommend the use of a carbon cloth anode over BDD if the end goal is the removal of phenol by electro-Fenton instead of complete mineralization, for example if a co-treatment alongside biological treatment would be considered.

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