



# Electrochemical advanced oxidation processes as decentralized water treatment technologies to remediate domestic washing machine effluents

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## Abstract

Water scarcity is one of the major concerns worldwide. In order to secure this appreciated natural resource, management and development of water treatment technologies are mandatory. One feasible alternative is the consideration of water recycling/reuse at the household scale. Here, the treatment of actual washing machine effluent by electrochemical advanced oxidation processes was considered. Electrochemical oxidation and electro-Fenton technologies can be applied as decentralized small-scale water treatment devices. Therefore, efficient decolorization and total organic abatement have been followed. The results demonstrate the promising performance of solar photoelectro-Fenton process, where complete color and organic removal was attained after 240 min of treatment under optimum conditions by applying a current density of  $66.6 \text{ mA cm}^{-2}$ . Thus, electrochemical technologies emerge as promising water-sustainable approaches.

**Keywords** Advanced oxidation processes · Azo dyes · Boron-doped diamond · Solar photoelectro-Fenton · Wastewater treatment · Decentralized water treatment

## Introduction

Water directly from the tap is a *fait accompli* and perfectly assumed as a fundamental need of the welfare society. However, the droughts, the limited water resources, and water pollution can endanger or limit this certainty. The water shortage is a worldwide concerning issue that is propitiating the consideration of alternative sources of water commodities

such as urban and domestic wastewater (Fragkou and McEvoy 2016; Hoekstra 2016). The assurance of water for domestic and urbane usage could be sustainably planned by considering new systems capable of reducing and recycling the water resources (Pedro-Monzonis et al. 2015; Garcia and Pargament 2015). However, this ambitious goal faces two great challenges: (i) social perception of wastewater reuse and (ii) development of novel water treatment technologies and decentralized devices.

Although the reutilization of wastewater can give rise to certain social concern, it is important to remark that downstream river influents are in certain cases upper-stream wastewater (Rice et al. 2016). It is here, where appropriate methods in wastewaters and drinking water treatment plants (WWTP) are crucial to ensure water reuse. Unfortunately, the high physical footprint of WWTP hinders the application of water recycling principles at the household scale (Martínez-Huitle et al. 2015). In this context, the development of small decentralized systems appears as a possible solution to household closed-loop water reuse systems as an alternative sustainable water resource (Piratla and Goverdhanam 2015; Leong et al. 2017; Hussien et al. 2017). The correct environmental

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management of water could also reduce water consumption and human activity impact on the ecosystems.

Household decentralized systems have to be compact, automatized, and easy to operate/maintain. To be useful in practice, moreover, these systems have to avoid the production of biosolids or wastes (Hocaoglu 2017). Nonetheless, the major challenge is related to the highly differentiated domestic wastewater containing food residues, urine, surfactants, or dyes among others (Heberer and Feldmann 2005; Kim et al. 2015; Richards et al. 2015; Butkovskiy et al. 2016). Then, the big question mark is how to treat efficiently such discriminated water matrices. An interesting approach could consist of the development of compact devices optimized to treat efficiently and independently each one of those differentiated effluents.

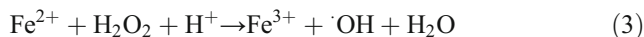
Indeed, one of the most water-consuming home appliances is washing machines. The water consumption usually associated to washing machines represents ~6 L of water per kilogram of laundry. The effluents from washing machines usually contain organic dyes and microfibers from clothes. Organic dyes are emerging pollutants of concern that not only generate visual pollution but also are suspected carcinogenic compounds (De Souza et al. 2007; Couto et al. 2013; Brillas and Martínez-Huitle 2015). Thereby, the removal of such noxious species from water is mandatory if we are considering the reuse of water in closed loops. In this frame, electrochemical advanced oxidation processes (EAOPs) have been previously considered to treat industrial effluents of the textile industry demonstrating great performance on the abatement of organic pollutants and dye containing solution decolorization (Panizza and Oturan 2011; Aquino et al. 2012; Solano et al. 2016; Garcia-Segura and Brillas 2017).

Electrochemical oxidation (EO) is the most studied EAOPs on the abatement of azo dyes. The EO consists of the electrogeneration of hydroxyl radical (OH) as intermediate of the water oxidation from Eq. (1), which remains physisorbed on the anode surface (Rodrigo et al. 2010; Martínez-Huitle et al. 2015; Salazar et al. 2016; Garcia-Segura et al. 2018). The ·OH is a highly oxidant species ( $E^\circ(\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V}$ ) that conducts to the complete mineralization of organic pollutants.

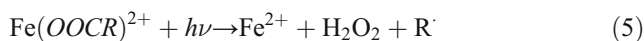


Alternatively, indirect EAOPs are those based on the Fenton process and considered a novel approach for treating effluents. Electro-Fenton (EF) technologies produce in situ hydrogen peroxide from oxygen reduction reaction (Eq. (2)) on the cathode surface. In its turn, hydrogen peroxide yields homogeneous ·OH from the Fenton reaction (Eq. (2)) when it reacts with iron(II) in the solution (Barhoumi et al. 2017; Li et al. 2017; Florenza et al. 2014). Besides, the iron catalyst is

regenerated by electrochemical reduction (Eq. (4)) (Rego et al. 2014; Garcia-Segura et al. 2016b).



The performance on the mineralization of organic pollutants of EF process can be considerably enhanced by the simultaneous irradiation with UV or natural sunlight (Garcia-Segura and Brillas 2014; Vidal et al. 2016; Gozzi et al. 2017). The irradiation with light sources leads to the photolysis of some highly stable iron complexes, such as carboxylate complexes, following general expression (Eq. (5)). The EF process conducted under solar irradiation is better known as solar photoelectro-Fenton process (SPEF).



Taking into account that electrochemical treatment systems are compact and easy to automatize (Martínez-Huitle et al. 2015; Moreira et al. 2017; Fajardo et al. 2017), the development of small-scale electrochemical water treatment devices to depollute and reuse washing machine effluents could become an interesting alternative to be explored. In this work, we present a proof of concept to demonstrate the viability and possibilities of electrochemical technologies within this context. An actual effluent was collected after a complete cleaning cycle and was treated by means of EO and EF technologies considering different operational variables.

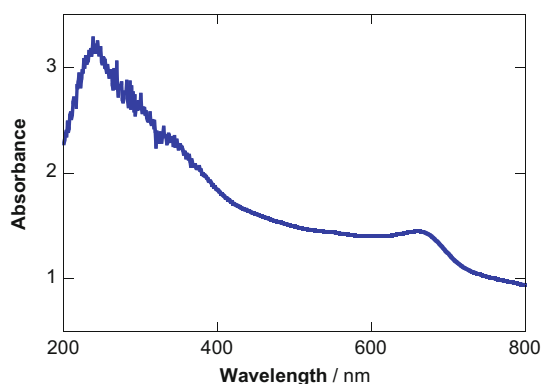
## Experimental

### Actual wastewater effluent

Blue jeans were submitted to a complete washing machine cycle with cold tap water without the addition of detergents and/or softeners. The addition of detergents and/or softeners has not been considered in order to ease the understanding of the results obtained in this first approach that aims to elucidate the applicability of electrochemical technologies as proof of concept by treating a simpler complex water matrix. Further studies will consider the treatment of effluents containing different surfactants. The resultant blue-colored effluent of the washing machine was collected and treated by means of different electrochemical technologies. The main characteristics of the wastewater effluent obtained are summarized in Table 1. The water matrix corresponds to a characteristic soft water with hardness below  $60 \text{ mg L}^{-1}$  of  $\text{CaCO}_3$  and natural pH 6.0. The high content of ca.  $300 \text{ mg L}^{-1}$  of total organic carbon (TOC) that can be

**Table 1** Washing machine effluent characteristics prior to treatment. Below, the characteristic UV-vis spectra of the colored effluent after the washing cycle is depicted

Parameter	Characteristics
TOC	315 mg L <sup>-1</sup>
Turbidity	382.5 UT
Conductivity	880 μS cm <sup>-1</sup>
pH	5.95
NO <sub>3</sub> <sup>-</sup>	0.99 mg L <sup>-1</sup>
Cl <sup>-</sup>	52.02 mg L <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	197.36 mg L <sup>-1</sup>
Hardness	27.72 mg L <sup>-1</sup>
A <sub>0</sub> λ=660 nm	1.45
DFZ <sub>436</sub>	155 m <sup>-1</sup>
DFZ <sub>525</sub>	145 m <sup>-1</sup>
DFZ <sub>620</sub>	138 m <sup>-1</sup>



preeminently associated to the leached organic dyes from the textiles during the washing process is noticeable. Anionic species, such as nitrate, chloride, and sulfate, are a typical content in tap water and, in this case, with concentrations of about 0.99, 52.02, and 97.36 mg L<sup>-1</sup>, respectively. Sodium sulfate (Merck) was added reaching a final concentration of 197.36 mg L<sup>-1</sup> to enhance the conductivity up to 880 μS cm<sup>-1</sup> to allow electrochemical treatment (Martínez-Huitle et al. 2015; De Vidales et al. 2017). The final sulfate concentration was below the recommended concentrations in drinking waters (a more stringent water quality condition) by the World Health Organization (500 mg L<sup>-1</sup>) (World Health Organization 2004). Nevertheless, it is important to remark that the reuse of the treated water in a closed-loop circuit would be the final desired usage. Furthermore, in Table 1, the characteristic UV-vis spectrum of the colored effluent with a discrete maximum of absorbance at 660 nm (blue color) is depicted but with a considerable width due to the complex dying mixture used to dye jeans.

## Electrochemical systems, apparatus, and analytical procedures

Comparative experiments to treat 100 mL of actual effluent were conducted at bench scale using a monocompartmental electrochemical cell thermostated at 35 °C. Temperature was kept at 35 °C to carry out experiments under reproducible and comparable conditions avoiding influences of temperature on degradation kinetics. A carbon polytetrafluoroethylene air diffusion electrode (ADE) mounted as described elsewhere (Dos Santos et al. 2016) was used as cathode. An air pump coupled to the cathode ensured the feed of air at 300 mL min<sup>-1</sup> through the ADE in order to electrogenerate H<sub>2</sub>O<sub>2</sub> from Eq. (2) while a platinum plate or a boron-doped diamond (BDD) thin film was employed as anode. The electrodes presented a geometric area of 3 cm<sup>2</sup> being the inter-electrode gap kept at 1 cm. Prior to the treatments, the effluent pH was adjusted to 3.0 using a pH meter Tecnonon mPA-210 by using H<sub>2</sub>SO<sub>4</sub> or NaOH of analytical grade supplied by Sigma-Aldrich to avoid iron catalyst precipitation during EF and SPEF treatment. The solutions treated by EO were adjusted to pH 3.0 to conduct experiments under identical comparable conditions, although EO can be carried out under natural pH conditions. Catalytic concentrations of 0.5 mM of Fe<sup>2+</sup> (Merck) were used to perform EF and SPEF. The treatments were carried out in the dark conditions for EF or under direct natural sunlight irradiation, in the case of SPEF treatment, respectively. Treated solutions were kept under vigorous stirring circumstances with a magnetic bar at 800 rpm to ensure homogenization and that reactants transport towards/from the electrodes.

The absorbance was determined by using an UV-vis spectrophotometer Analytikjena SPECORD 210 PLUS at a solution characteristic maximum absorptivity of λ<sub>max</sub> = 660 nm (cf. Table 1). Tap water used in the washing cycle was used as blank in the UV-vis analysis. From the registered UV-vis spectra, the percentage of color removal of the solution during the electrochemical treatments was estimated from Eq. (6) (Dos Santos et al. 2016; Brillas and Martínez-Huitle 2015):

$$\% \text{ Color removal} = \frac{A_0 - A_t}{A_0} \times 100 \quad (6)$$

where A<sub>0</sub> is the initial absorbance and A<sub>t</sub> the absorbance at the electrolysis treatment time *t*. However, the solution coloration was analyzed also according to the international standard DIN EN ISO 7887 (2012-04) of water quality concerning the examination and determination of color (DIN EN ISO 7887 (2012-04)) by the estimation of the parameter DFZ (Deutsche Farb Zah) (m<sup>-1</sup>) from the solution absorbance at characteristic λ = 436 nm, λ = 525 nm, and λ = 620 nm from

Eq. (7). The estimation of DFZ allows the evaluating of the effluent coloration in complex case scenarios by considering these different characteristic wavelengths.

$$DFZ = \frac{A}{D} \tag{7}$$

where  $A$  is the absorbance and  $D$  is the optical path length of the cuvette expressed in meters. According to the German textile wastewater discharge standards, released effluents should present values below the maximum DFZ values of  $7\text{ m}^{-1}$  for 436 nm,  $5\text{ m}^{-1}$  for 525 nm, and  $3\text{ m}^{-1}$  for 620 nm, respectively (Salim et al. 2016; DIN EN ISO 7887 (2012–04)). TOC abatement was monitored with a Shimadzu VCSN TOC analyzer from 50  $\mu\text{L}$  aliquots with reproducible TOC values (precision of  $\pm 1\%$ ). The content of inorganic ionic species in the water matrix was assessed by means of ion chromatography system Dionex model ICS-2000 with a Dionex Ion Pac AS 11 analytical column ( $2 \times 250\text{ mm}$ ) coupled to a Dionex DS6 thermostated conductivity cell detector. Aliquots of 20  $\mu\text{L}$  were injected using a Dionex EGC III KOH solution at  $0.25\text{ mL min}^{-1}$  as mobile phase. Determination of turbidity was done by using a portable turbidimeter Hanna HI 98703 while the conductivity was measured by employing a pH/conductometer CD 4301 Procyon. Water hardness (APHA 2005) was determined with the concentrations of calcium and magnesium by using ICP spectrometer iCAP 6000 series from Thermo Scientific (hardness, mg equivalent  $\text{CaCO}_3/\text{L} = 2.497 \times [\text{Ca, mg L}^{-1}] + 4.118 \times [\text{Mg, mg L}^{-1}]$ ).

## Results and discussion

### Decolorization of washing machine effluent by different electrochemical methods

The blue-colored actual effluent was treated by different electrochemical approaches at  $66.6\text{ mA cm}^{-1}$ . Figure 1 depicts the solution decolorization attained by means of EO with Pt anode, EO with BDD anode, EF, and SPEF with BDD anode, respectively. Noticeable differences were observed between the anodic materials employed in EO. While a 55.5% color removal was attained using BDD anode, only a discrete 14.9% was obtained by using Pt anode. Both anodes were capable of electrogenerating  $\cdot\text{OH}$  from water oxidation reaction (Eq. (1)); nevertheless, the different electrocatalytic characteristics led to this differentiated behavior. In general, it has been reported that BDD anodes present higher pollutant removal capacity due to their lower enthalpy of adsorption of  $\cdot\text{OH}$  (Kapalka et al. 2009; Rocha et al. 2014; Garcia-Segura et al. 2015; Martínez-Huitle et al. 2015). Meanwhile; those radicalary species became strongly adsorbed onto

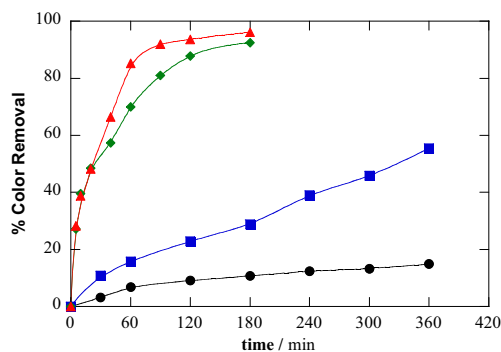
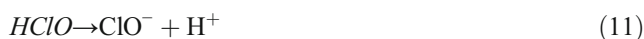


Fig. 1 Percentage of color removal attained during the electrochemical treatment of an actual washing machine effluent at pH 3.0 and  $66.6\text{ mA cm}^{-2}$  by EO with Pt anode (circle), EO with BDD anode (square), EF with BDD anode (diamond), and SPEF with BDD anode (triangle)

the Pt surface, where higher oxides became the main oxidant mediators from Eq. (8) (Panizza and Cerisola 2009).



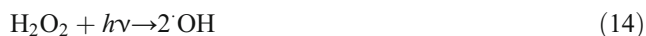
The weakly adsorbed  $\cdot\text{OH}$  radicals are more reactive and more highly oxidant than the strongly chemisorbed radicals, which can explain the major removal attained by BDD anodes (Kapalka et al. 2009; Garcia-Segura et al. 2015; Martínez-Huitle et al. 2015). However, the pollutant oxidation mediated by the strongly adsorbed oxidant  $\cdot\text{OH}$  is strongly limited, in kinetic terms, by mass transfer. It is important to remark that the electrogeneration of weaker oxidants is also feasible from the oxidation of electrolytes present in the water matrix. Chloride anion can be oxidized on the anode surface yielding active chlorine species  $\text{Cl}_2$  and  $\text{HClO}/\text{ClO}^-$  from Eqs. (8) to (10) (Martínez-Huitle et al. 2015; De Vidales et al. 2016; Lan et al. 2017) whereas peroxodisulphate can be released from the oxidation of sulfate according to Eq. (11) (Thiam et al. 2015; Lan et al. 2017).



On the other hand, indirect electrochemical processes based on the Fenton reaction attained almost complete removals of coloration in ca. 180 and 120 min of treatment by EF and SPEF, respectively. The faster removal kinetics can be explained by the higher generation of  $\cdot\text{OH}$  from Fenton’s reaction (Eq. (3)), and the homogeneous character of the radicals was generated in situ (Brillas and Martínez-Huitle 2015; Martínez-Huitle et al. 2015). Thereby, from these results, it can be concluded that EF technologies are capable of efficiently decolorizing actual



effluents after short treatment times. Note that blank experiments, where washing machine effluents were solely submitted to natural irradiation, did not result in any kind of decolorization (data not shown). In fact, organic dyes are widely considered to be highly photostable species (Florenza et al. 2014; Solano et al. 2016). The enhanced performance on decolorization can be associated to the major release of  $\cdot\text{OH}$  from iron(III) hydroxocomplexes photoreduction by Eq. (13) and  $\text{H}_2\text{O}_2$  photodecomposition by UVC irradiation (Eq. (14)) (Garcia-Segura and Brillas 2014). It is important to remark that the natural solar ultraviolet radiation in Natal (Brazil) has UVC contribution, which has been associated to the increasing number of new cases of non-melanoma skin cancer (Corrêa 2015). Furthermore, the activation of persulfate yielding sulfate radical by Eq. (15) is feasible (Criquet and Leitner 2009; De Vidales et al. 2017).

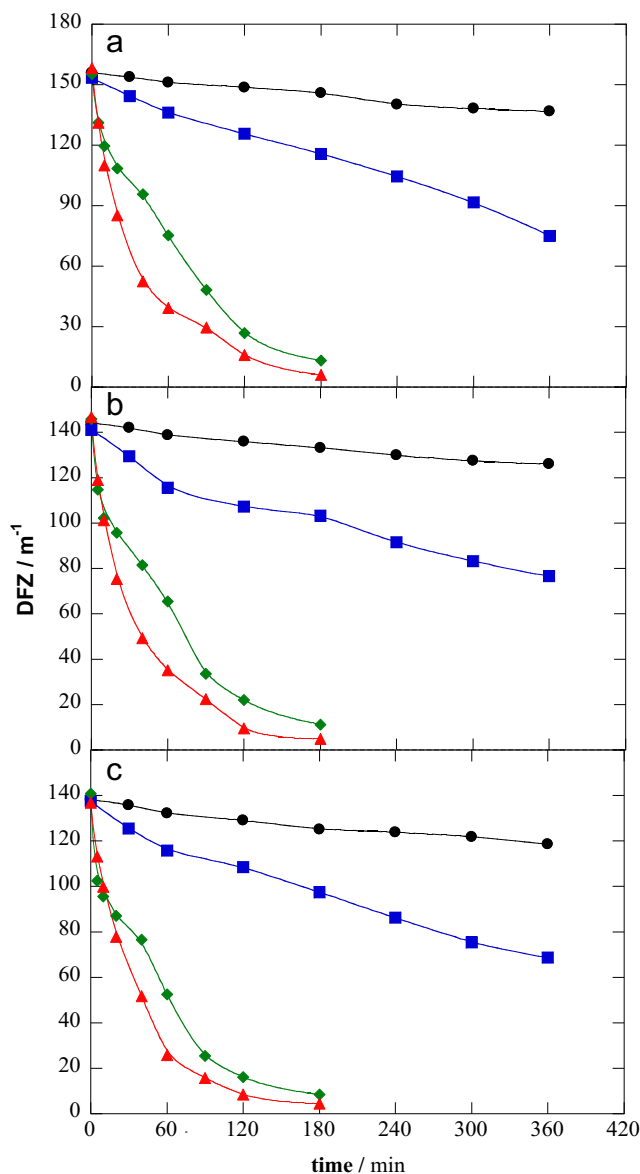


The evaluation of the color through the parameter DFZ (cf. Fig. 2) showed that only EF technologies reached the maximum acceptable values for effluent release after 180 min of treatment, achieving values of  $\sim 6.0\text{ m}^{-1}$  for 436 nm,  $\sim 4.8\text{ m}^{-1}$  for 525 nm, and  $\sim 2.8\text{ m}^{-1}$  for 620 nm, respectively. Meanwhile, the diminution of coloration attained by EO methods, using either Pt or BDD anodes, stands for values about one order of magnitude superior than the maximum limits accepted by law.

### Effect of applied current density on decolorization rate

The applied current density ( $j$ ) is related to the number of electrons circulated through the system and consequently the amount of oxidizing mediator species electrogenerated (Martínez-Huitle et al. 2015; Vidal et al. 2016; Barhoumi et al. 2017). Therefore,  $j$  is one of the most influential parameters on electrochemical kinetics of EAOPs.

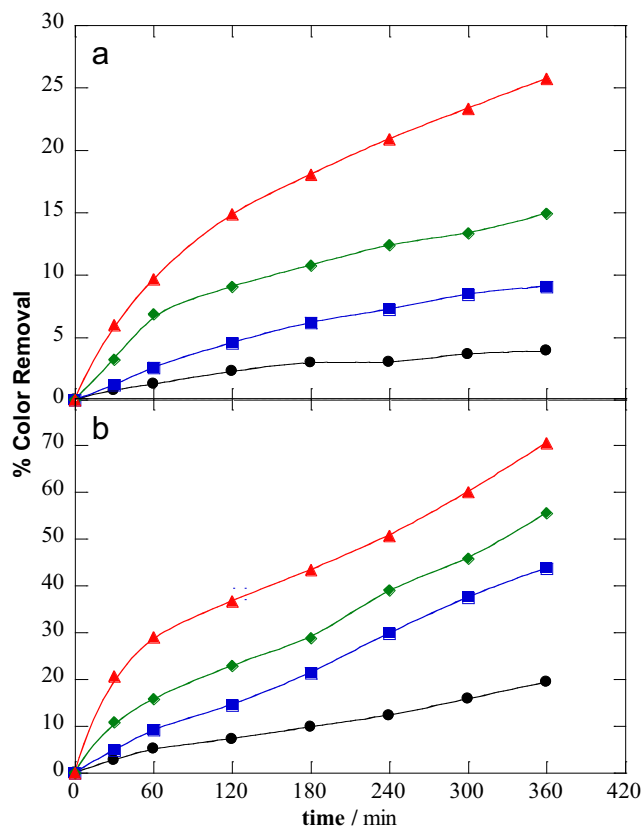
Figure 3 depicts the influence of  $j$  on the decolorization performance of EO process using Pt and BDD anodes. The increase in applied  $j$  allowed attaining higher percentage of color removal under similar operational times for both anodic materials. The increase of  $j$  from 16.6 to 100  $\text{mA cm}^{-2}$  during the EO with Pt accelerated the decolorization rate, increasing decolorization rate constants ( $k_{\text{dec}}$ ) by one magnitude order from  $1.8 \times 10^{-6}$  to  $1.3 \times 10^{-5}\text{ s}^{-1}$ . This trend is also observed during the treatment with BDD anodes where the  $k_{\text{dec}}$  increased fourfold from  $1.0 \times 10^{-5}\text{ s}^{-1}$  at 16.6  $\text{mA cm}^{-2}$  up to  $4.3 \times 10^{-5}\text{ s}^{-1}$  at



**Fig. 2** Evolution with electrolysis time of washing machine effluent DFZ determined at **a** 436 nm, **b** 525 nm, and **c** 620 nm. Electrochemical treatment: EO with Pt anode (circle), EO with BDD anode (square), EF (diamond), and SPEF (triangle)

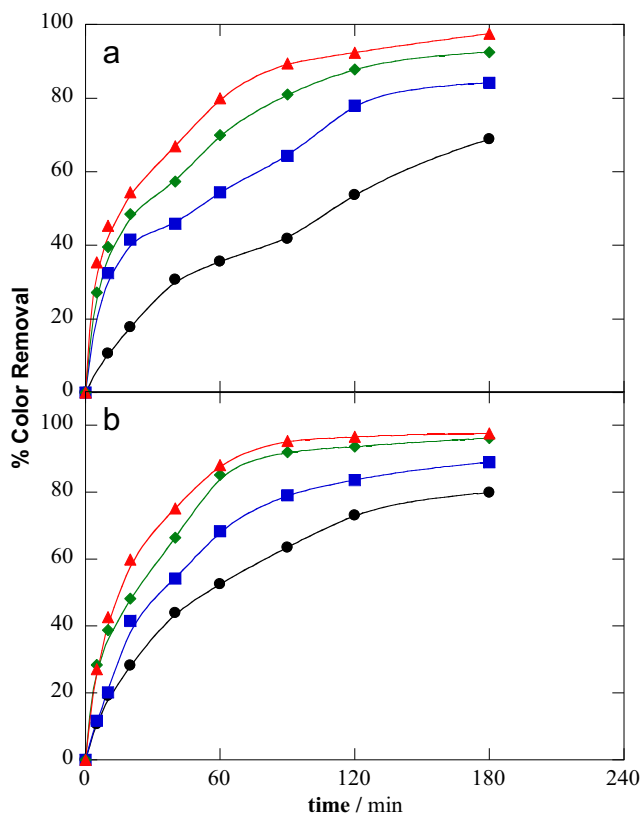
$100\text{ mA cm}^{-2}$ . The comparison between the experimental  $k_{\text{dec}}$  values of Pt and BDD anodes is in accordance with the results previously reported, where BDD presented a greater oxidative power. As discussed above, the electrocatalytic properties of these anodic materials affect the availability of electrogenerated  $\cdot\text{OH}$  radicals and consequently the overall EO treatment performance (Kapalka et al. 2009; Garcia-Segura et al. 2015).

Nonetheless, 70.5% of color removal achieved after 360 min by EO-BDD at  $100\text{ mA cm}^{-1}$  is far from the almost complete decolorization attained by EF and SPEF, which was achieved only in 180 min. The outstanding results obtained by EF and SPEF processes were attained with lower



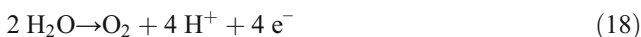
**Fig. 3** Influence of applied current density on the washing machine effluent decolorization by **a** EO with Pt and **b** EO with BDD. Applied current density: 16.6 mA cm<sup>-2</sup> (circle), 33.3 mA cm<sup>-2</sup> (square), 66.6 mA cm<sup>-2</sup> (diamond), and 100.0 mA cm<sup>-2</sup> (triangle)

applied  $j$ , as collected in Fig. 4. The complete decolorization attained during the treatment suggests that the homogeneous  $\cdot\text{OH}$  radicals yielded by Fenton's reaction were the main oxidizing species involved in the decolorization process. Similar to the EO treatment, the increase in applied  $j$  accelerated the color removal, as can be deduced from estimated  $k_{\text{dec}}$  values. However, only a slight difference can be observed at higher applied  $j$ . This effect was more notorious in SPEF where the increase in  $j$  from 66.6 to 100 mA cm<sup>-2</sup> supposes a 1.2-fold increase on the  $k_{\text{dec}}$ . Even though the electrogeneration of in situ oxidants increases with applied  $j$ , parasitic side reactions that consume  $\cdot\text{OH}$  are simultaneously enhanced (Martínez-Huitle et al. 2015; Salazar et al. 2016; Gozzi et al. 2017). Thereby, further increases in  $j$  upon the maximum decolorization rate attain results in an unnecessary consumption of energy and consequently an undesired rise in the treatment cost. The most common parasitic reactions consume  $\cdot\text{OH}$  releasing weaker oxidant species such hydroperoxyl radical ( $\text{HO}_2\cdot$ ) ( $E^\circ(\text{HO}_2\cdot/\text{H}_2\text{O}) = 1.65 \text{ V}$ ) from Eq. (16) or hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) ( $E^\circ(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.76 \text{ V}$ ) from  $\cdot\text{OH}$  radical dimerization according to Eq. (17) (Florenza et al. 2014; Brillas and Martínez-Huitle 2015). Furthermore, the release of  $\text{O}_2$  from complete



**Fig. 4** Influence of applied current density on the washing machine effluent decolorization by **a** EF and **b** SPEF. Applied current density: 16.6 mA cm<sup>-2</sup> (circle), 33.3 mA cm<sup>-2</sup> (square), 66.6 mA cm<sup>-2</sup> (diamond), and 100.0 mA cm<sup>-2</sup> (triangle)

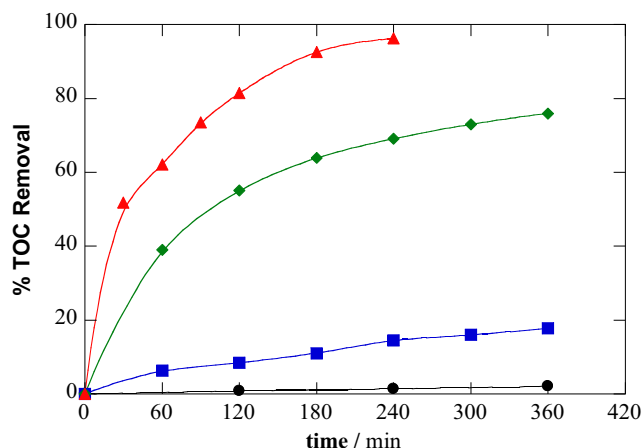
water oxidation (Eq. (18)) was observed at high applied  $j$  on the anode surface (Panizza and Cerisola 2009).



According to the trends observed, when analyzed in terms of electric charge consumed, the optimal operational  $j$  can be selected as 66.6 mA cm<sup>-2</sup> for EF and SPEF processes. The use of 66.6 mA cm<sup>-2</sup> allows to achieve complete decolorization in shorter treatment times ( $\approx 180 \text{ min}$ ) with almost identical results than 100 mA cm<sup>-2</sup> but with lower energy consumption and higher faradaic efficiencies. Moreover, EF and SPEF processes present a considerably greater performance than EO under similar treatment conditions.

### Organic compound abatement during electrochemical treatment

In a complex water matrix including a mixture of organic compounds, the TOC is one of the most useful parameters to envision the effective removal of such undesired species (Martínez-



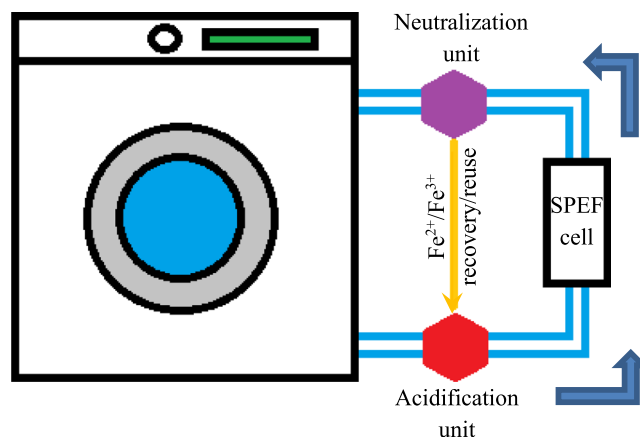
**Fig. 5** TOC removal achieved during the electrochemical treatment of an actual washing machine effluent at pH 3.0 and  $66.6 \text{ mA cm}^{-2}$  by EO with Pt anode (circle), EO with BDD anode (square), EF (diamond), and SPEF (triangle)

Huitle et al. 2015; Garcia-Segura and Brillas 2017). Therefore, the decolorization cannot be considered the unique parameter on the evaluation of electrochemical technologies such as decentralized water treatment systems. Figure 5 shows the TOC removal attained during the electrochemical treatment of the collected effluent under optimal applied  $j$  of  $66.6 \text{ mA cm}^{-2}$ . The initial organic load of  $315 \text{ mg L}^{-1}$  of TOC (cf. Table 1) was reduced by the oxidation of organic pollutants to  $\text{CO}_2$  by  $\cdot\text{OH}$ . However, the performance of each one of the electrochemical processes considered was completely different.

The initial TOC of the blue-colored effluent remained practically constant ( $< 2\%$  removal) after 360 min of EO treatment with Pt anode. The slight decolorization of  $14.9\%$  attained with Pt anodes suggests that even though the chromophore groups can be removed, the recalcitrant organic by-products and intermediates remained in the solution. Conversely,  $17.8\%$  TOC removal was achieved when a BDD anode is used. Higher removals attained are related to the large generation of  $\cdot\text{OH}$  on the BDD surface from water oxidation reaction (Eq. (1)) (Rodrigo et al. 2010; Aquino et al. 2012; Martínez-Huitle et al. 2012). There, the non-active character of BDD anodic material results in a major mineralization of organic pollutants in solution  $\cdot\text{OH}$  (Kapalka et al. 2009; Martínez-Huitle et al. 2015; Garcia-Segura et al. 2015). The percentages of decolorization (Fig. 1) and TOC abatement (Fig. 5) by EO with BDD increase with electrolysis time without reaching a plateau. These results clearly indicate that complete mineralization and color removal are achieved after long treatment times. Unfortunately, considering the large volumes of effluent generated per washing cycle, the requirement of long operational times is unpractical, but if the reactor is scaled up to improve its hydrodynamic conditions and, consequently, its efficacy to treat this kind of effluent, a new scenario can be expected (Martínez-Huitle et al. 2015).

The electrochemical processes based on Fenton's chemistry, EF and SPEF, showed a greater performance in comparison to EO. The washing machine effluent treatment by EF attained  $76\%$  of TOC abatement after 360 min of electrolysis and complete decolorization in 180 min. It can be observed in Fig. 5 that after 180 min of treatment, the TOC removal kinetics was slower in reaching a semi-plateau. This behavior is in agreement with the trends observed in synthetic effluents (Florenza et al. 2014; Solano et al. 2016; Salazar et al. 2016). The degradation of the main pollutants (usually aromatic compounds) in solution resulted in the yield of short-linear carboxylic acids such oxalic or oxamic acids. Carboxylic acids, although biodegradable, are highly recalcitrant organic species hardly mineralized by  $\cdot\text{OH}$  released by Fenton's reaction (Eq. (3)) and are slowly oxidized on BDD anodes. Moreover, carboxylic acids form stable complexes with iron(III) and Cu(II) species which reduces the extension of Fenton's reaction (García-Segura and Brillas 2014; Garcia-Segura et al. 2016a; Vidal et al. 2016). These complexes were easily photolyzed by solar radiation conducting to their complete mineralization along with the catalyst regeneration according to Eq. (5), which allows attaining almost complete TOC removals in short treatment times of 180–240 min by SPEF.

This proof of concept identified SPEF process as the most effective EAOP on the treatment of an actual household effluent collected from a washing machine. In Fig. 6, a scheme of a SPEF decentralized device is envisioned where the water can be reused in a closed loop. Note that since Fenton processes are conducted in acidic media, acidification and neutralization units could be required. Fortunately, these elements can be considered as consumables that could be easily interchanged by the users. The concentrations of iron used as catalyst are small as  $0.5 \text{ mM}$  which, although superior to the one suggested in secondary limits for drinking waters ( $0.3 \text{ mg L}^{-1}$ ) (EPA 2017), can be found in some natural waters in Brazil



**Fig. 6** Scheme of the possible decentralized electrochemical water treatment device

(Souza et al. 2016). It is important to note that the treated water is expected to be reused in a closed-loop cycle and not released as effluent after treatment. In the decentralized system, an iron catalyst recovery system is envisioned. The recovery of the catalyst for reuse can lead to effluents containing small amount of iron that would not compromise the quality of the subsequent washing cycles. Possible alternatives to be explored are the use of ferromagnetic nanoparticle catalysts that can be recovered by magnets or the use of heterogeneous iron catalyst in a fluidized bed that would minimize the requirement of the recovery unit (Garcia-Segura et al. 2016b). If the treated effluent is discarded after the use of low amounts of iron, it would be diluted within the sewage system. The complexity of SPEF devices that include the requirement of sunlight delivery systems to the reactors can hinder its application. Thus, the development and enhancement of simpler EO treatments or alternative processes such H<sub>2</sub>O<sub>2</sub>/UVC with in situ electrogenerated H<sub>2</sub>O<sub>2</sub> should be further explored and considered. Further studies to develop these complementary decentralized electrochemical water treatment units are required.

## Conclusions

To solve water scarcity, the water recycling/water reuse approach by the use of decentralized water treatment devices is suggested. Here, the applicability of EAOPs on the treatment of actual household effluents is considered as a proof of concept. Experimental results on the treatment of an actual effluent of washing machine evidence the superior performance of electrochemical technologies based on Fenton's process over conventional EO. Discrete decolorization of 14.9% and TOC abatement < 2% were attained after 360 min of EO treatment with Pt anodes at 66.6 mA cm<sup>-2</sup>. Higher removals were achieved by using BDD anodes, attaining 55.5% of effluent decolorization and 17.8% of TOC removal. The better results obtained with BDD anodes can be explained by the more highly oxidant character of the physisorbed ·OH on the BDD surface than the one strongly chemisorbed on the Pt surface. Both electrogenerated ·OH species are considered heterogeneous oxidants, and the EO process is limited by mass transfer. In contrast, homogenous ·OH yielded by Fenton's reaction in EF and SPEF methods presents faster degradation and decolorization kinetics. Indeed, complete decolorizations are attained by both methods in solely 180 min of treatment. Different performances were observed on the TOC abatement, where 76% of removal is attained by EF in 360 min while almost complete abatement is observed for SPEF after 180–240 min of treatment. Thus, SPEF emerges as the most efficient EAOP to reduce the organic load, associated mainly to organic dyes, of washing machine effluents. However, the complexity of SPEF device design that includes the

requirement of sunlight delivery systems to the reactors can hinder its application. Thus, the development and enhancement of simpler EO treatments or alternative processes such H<sub>2</sub>O<sub>2</sub>/UVC with in situ electrogenerated H<sub>2</sub>O<sub>2</sub> must be explored and considered. These novel results demonstrated a proof of concept on the feasible application of small-scale electrochemical devices to recycle household water sources. Nevertheless, further pre-analysis must be considered to evaluate the influence of the variability of the effluent matrix composition (detergent, softener, organic load, water hardness, and so on). The engineering of this process has been outlined, although the scaling up and application should be faced before technology transfer.

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