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1	Novel bio-electro-Fenton technology for azo dye wastewater treatment using
2	microbial reverse-electrodialysis electrolysis cell
3	Xiaohu Li, Xiangdan Jin [#] , Nannan Zhao [#] , Irini Angelidaki, Yifeng Zhang*
4	Department of Environmental Engineering, Technical University of Denmark, DK-2800 Lyngby,
5	Denmark
6	
7	*Corresponding author:
8	Dr. Yifeng Zhang
9	Department of Environmental Engineering, Technical University of Denmark, Denmark
10	Tel: (+45) 45251429.
11	Fax: (+45) 45933850.
12	E-mail address: <u>yifz@env.dtu.dk</u>
13	[#] Both authors contributed equally to this work
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19 Abstract

Development of sustanaible technologies for treatment of recalcitrant pollutants containing 20 21 wastewaters has long been of great interest. In this study, we proposed an innovative concept of using microbial reverse-electrodialysis electrolysis cell (MREC) based Fenton process to 22 treat azo dye wastewater. In such MREC-Fenton integrated process, the production of H₂O₂ 23 which is the key reactant of fenton-reaction was driven by the electrons harvested from the 24 25 exoelectrogens and salinity-gradient between sea water and fresh water in MREC. Complete decolorization and mineralization of 400 mg L⁻¹ Orange G was achieved with apparent first 26 order rate constants of 1.15 ± 0.06 and 0.26 ± 0.03 h⁻¹, respectively. Furthermore, the initial 27 28 concentration of orange G, initial solution pH, catholyte concentration, high and low concentration salt water flow rate and air flow rate were all found to significantly affect the 29 dye degradation. This study provides an efficient and cost-effective system for the 30 degradation of non-biodegradable pollutants. 31

32 Key words: Microbial Reverse-electrodialysis Electrolysis cell (MREC), Fenton reaction,
33 Salinity gradient, Azo dye, Wastewater

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42 **1. Introduction**

Azo dyes are the most important synthetic dyes in textile industries. During textile 43 coloration processing, approximately 10-15% of azo dyes are lost in the discharged effluents 44 45 (Pearce, 2003; Solanki et al., 2013). Textile wastewaters if not efficiently treated would consititue a serious environmental issue for water pollution (Wang & Bai, 2016). Most of azo 46 dyes have complex structures and are toxic, which makes them difficult to be degraded by 47 biological processes (Banerjee et al., 2015). Electro-Fenton reaction as one of typical 48 advanced oxidation processes has been extensively studied as a promising and efficient 49 method for treatment of dyes wastewater (Nidheesh & Gandhimathi, 2012). The most 50 51 important advantages of Electro-Fenton technology are high efficiency and mild operating conditions (Martinez-Huitle et al., 2015). However, there are still several shortcomings such 52 as short lifetime of catalyst, costy electrode materials and high energy consumption (ranges 53 from 87.7 to 275 kWh kg TOC⁻¹), which hinder the industrial application (Gao et al., 2015; 54 Martinez-Huitle et al., 2015; Nidheesh & Gandhimathi, 2012; Rosales et al., 2012). 55

More recently, bioelectrochemical systems (BES) such as microbial fuel cell (MFC) and 56 microbial electrolysis cell (MEC) based Electro-Fenton systems have been demonstrated as 57 58 promising alternative method to the traditional Electro-Fenton process for the degradation of azo dyes (Feng et al., 2010; Solanki et al., 2013; Zhang et al., 2015b). In such systems, the 59 electrons used for H₂O₂ production at the cathode are fully or partly derived from organic 60 61 wastes by bacteria in the anode. Thus, the catalyst cost and energy-consumption have been greatly reduced. The BES-Fenton process not only can remove the biodegradable organics in 62 anode chamber, but also can remove the biorefractory pollutants in cathode chamber (Solanki 63 64 et al., 2013; Xu et al., 2011; Zhuang et al., 2010). However, there are still several challenges

65 which need to be addressed before field application. For example, high mineralization efficiency has been mainly achieved at low dye concentration ($\leq 100 \text{ mg L}^{-1}$) in the MFC-66 Fenton process due to the extreme low H₂O₂ production (Asghar et al., 2014; Fu et al., 2010). 67 Comparatively, MEC-Fenton system could be more efficient due to much higher and faster 68 H₂O₂ production (Zhang et al., 2015b). However, the requirement of external power supply 69 for MEC may add the capital and operational costs and also complicate the whole system. 70 Thus, there is a great research and practical interest to develop more economical and efficient 71 72 BES-Fenton system for dye wastewater treatment.

Recently, a novel type of BES system called microbial reverse-electrodialysis electrolysis cell (MREC), which combines a reverse electrodialysis stack (RED) and MEC have been developed to drive H_2 or CH_4 generation (Kim & Logan, 2011a; Luo et al., 2014). In our previous study, the MREC system has been demonstrated as one promising system to produce high concentration of H_2O_2 with low electrical energy consumption. Therefore, intergration of MREC and Fenton process could be an ideal technology to remove azo dye, which has never been previously reported.

80 In the present study, we developed one novel MREC-Fenton system for the treatment of wastewater containing Orange G which is a typical model azo dye used in dyeing the textile 81 82 fabrics (Banerjee et al., 2015; Cai et al., 2016). The effects of main process paremeters such as the wastewater pH, initial Orange G concentration, HC and LC flow rate, and air flow rate 83 were investigated. Furthermore, its concentration on the system performance was also 84 investigated. It is the first time that MREC-Fenton system was used to degrade azo dye 85 wastewater. This new system may offer a potential platform technology for azo dye 86 87 wastewater treatment.

4

88 2. Materials and Methods

89 2.1. Configuration and operation of MREC-Electro-Fenton system.

The MREC consists of anode and cathode chamber which were separated by a RED stack 90 (Fig.1). The anode and cathode chamber had a working volume of 50 mL (5 cm \times 5 cm \times 2 91 cm) separately. The anode was a carbon fibre brush (5.0 cm diameter, 5.0 cm length, Mill-92 Rose, USA), which was heated to 450 °C for 30 min in a muffle furnace before use (Zhang & 93 Angelidaki, 2015b). The anode was first enriched with biofilm in a MFC using domestic 94 wastewater collected from primary clarifier (Lyngby Wastewater Treatment Plant, 95 Copenhagen, Denmark) together with acetate sodium (20 mM) as substrate (Zhang & 96 Angelidaki, 2015a), and then transferred into the anode chamber of MREC. The cathode was 97 a graphite plate (3 cm \times 3 cm). In order to avoid anode substrate limitation on the system 98 99 performance, the anode chamber was continuously fed with domestic wastewater amended with acetate sodium (~1.6 g COD L^{-1}) at 100 mL d⁻¹. The cathode chamber was filled with 40 100 mL Orange G-containing synthetic wastewater and operated in batch mode. Air was bubbled 101 into the catholyte continuously at the rate of 8 mL min⁻¹ expect otherwise mentioned. HC and 102 LC solutions was $35g L^{-1}$ and $0.35g L^{-1}$ NaCl, respectively. All experiments were carried out 103 104 in duplicate at room temperature $(22\pm 2^{\circ}C)$.

105 *2.2. Analytical methods.*

The concentration of Orange G was determined by a UV-vis spectrophotometry (Spectronic 20D+, Thermo Scientific) at 478 nm (Banerjee et al., 2015). The mineralization rate of orange G in the wastewater during the degradation experiment was estimated through the analysis of total organic carbon (TOC) of the samples measured by shimadzu TOC 5000 A. The pH was measured using a pH meter (PHM 210 pH meter, Radiometer). Chemical oxygen demand (COD) was measured according to the Standard Method (A.W.W.A, 1998). The voltage across on the external resistor (10 Ω) was monitored with 30 min intervals using a digital multimeter (model 2700, Keithley Instruments, Inc., Cleveland, OH, USA). Current density was calculated base on the surface area (3 cm × 3 cm) of cathode. Coulomic efficiency (CE) were calculated as previous reported (Kim & Logan, 2011a).

116 The apparent decolorization rate constant (K_{app}) and mineralization rate constant (K_{TOC}) 117 were determined according to Eq. 1 and Eq. 2

118
$$\ln \frac{C_0}{C_t} = K_{app}t \tag{1}$$

119
$$\ln \frac{TOC_0}{TOC_t} = K_{TOC}t$$
(2)

where $C_0 (mg L^{-1})$ and $C_t (mg L^{-1})$ are the Orange G concentrations at time 0 and reaction time t, respectively. TOC₀ (mg L⁻¹) and TOC_t (mg L⁻¹) are the TOC concentrations at time 0 and reaction time t, respectively.

The TOC removal and corresponding electrical energy consumption were evalutated to determine whether the MREC-Fenton process is economical. Electrical energy consumption in the MREC system was mainly due to the pumping system for supply of anolyte, high concentration (HC) and low concentration (LC) solution and the aeration of catholyte. The specific electrical energy consumption was calculated in terms of the removal of 1 kg of TOC from dye wastewater by the MREC-Fenton process (kWh kg⁻¹) using Eq. 3.

129 Energy consumption =
$$\frac{100000 \text{ W}}{TOC_0 \times V_0 - TOC_t \times V_t}$$
 (3)

where W (kWh) is the total electrical energy consumption, which was measured by a spar meter (Type NZR230, S.L. Energitekinik, Denmark). V_0 (L) and V_t (L) are the volume of dye wastewater at time 0 and reaction time t, respectively.

133 **3. Results and discussion**

134 *3.1. System performance*

Fig. 2 shows the decolorization and minerlization of orange G in the cathode of MREC-135 Fenton system with the initial Orange G concentration of 100 mg L⁻¹. The decolorization 136 efficiency of Orange G reached to about 70% within one hour, and 88% of Orange G was 137 removed after 3 hours (Fig. 2A). Comparatively, the decoloriezation efficiency of 10% was 138 observed after 5 hours under open circuit condition (control 1), which could be due to the 139 140 absorption on the electrode material and the anion membrane (the side closed to the cathode chamber). The Orange G decolorization efficiency without air flow in cathode chamber 141 (control 2) and without Fe^{2+} addition in catholyte (control 3) only reached about 32% and 142 143 45%, respectively, after 5 hours. The minerlization of Orange G in terms of TOC removal showed similar trend as decoloration. As shown in Fig. 2B, the TOC removal efficiency could 144 reach to 87% after 5h, which was only 16% and 13% in control 2 and 3, respectively. The 145 146 slight decolorization observed in control experiments could be due to the reduction of Orange G as electron acceptor at the cathode. This is supported by the observation that Orange G 147 could be decomposed to colorless shorter organic molecules without dissolved O_2 in control 2 148 and lack of the Fenton regent (Fe^{2+}) in control 3. Similar behaviour from other azo dyes (e.g., 149 Orange 7 and Methylene Blue) have been previously observed in BES system (Li et al., 2016; 150 Mu et al., 2009; Zhang et al., 2015a). On the other hand, the results also confirmed that the 151 removal of Organge G was mainly due to the Fenton reaction driven by the energy from 152

153 anodic bacteria and salinity gradient (Luo et al., 2011). In addition, based on the experiment data the degradation kinetics of Orange G dye were studied, which showed that degradation 154 of Orange G dye followd a first-order reaction (Fig. 2). The decolorization rate constant (K_{app}) 155 and mineralization rate constant (K_{TOC}) were 1.22 h⁻¹ and 0.46 h⁻¹, respectively. In recent 156 studies for oxidization of Methylene blue (a compound similar to Orange G dye) in MFC-157 MEC-Fenton system, K_{app} of 0.43 h⁻¹ and K_{TOC} of 0.22 h⁻¹ were reported, which were much 158 lower than that observed in this study (Zhang et al., 2015b). Feng et al. (2010) also reported a 159 first order removal reaction of Orange II with K_{app} of 0.212 h^{-1} and K_{TOC} of 0.0827 h^{-1} in 160 MFC-Fenton system. These results demonstrated that the MREC-Fenton system could be 161 more efficient than other BES system for azo dye wastewater treatment. 162

163 *3.2.* The effect of initial wastewater pH on the system performance

164 Degradation performance of organic compounds by Electro-Fenton technologies are often found to be dependent on the wastewater pH, and for different dyes in different degradation 165 systems, the effect of wastewater pH was found to vary greatly. On the other hand, the actual 166 167 dye wastwaters may have variable pH values. Therefore, the effect of initial pH on the Orange 168 G wastewater degradation in the MREC-Fenton system was examined. As shown in Fig.S1 (Supplementary data), the decolorization and TOC removal were greatly affected by the initial 169 pH of the wastewater. The increasing of initial pH from 2 to 7 caused a decrease in 170 decolorization rate and TOC removal rate. The highest removal rate of Orange G was found at 171 pH 2 (79 \pm 0.8 mg L⁻¹ h⁻¹) in the first hour, and the maximum decolorization efficiency 172 reached to 100% after 4 h reaction. The decolorization and TOC removal rate decreased with 173 further increasing of the initial pH from 3 to 7. For example, when the pH increased to above 174 4, the decolorization rate of Orange G started to decline. When the pH increased to above 7 175

(Fig. S1) during the reaction, the decolorization process continued with a rate of 4.9 ± 0.4 mg 176 L^{-1} h⁻¹, which was much lower than 32 mg L^{-1} h⁻¹ (average in 3 hours) at pH 2. However, the 177 TOC was not decreasing with the reaction time when the initial pH was above 4. Moreover, 178 the pH also increasing along the reaction time in all tests (Fig.S1). In general, the 179 decolourization efficiency was higher than the TOC removal at all the tested initial pH. That 180 is because the azo bond could be first cleaved by hydroxyl radical, resulting in the formation 181 of colorless shorter organic molecules. The results observed was in line with the conventional 182 Fenton process for Orange G degradation (Cai et al., 2016). Even though the acidic 183 environment is benefitting the cleavage of the azo bond and mineralization of azo dye, initial 184 pH lower than 2 may counteract generation of hydroxyl radical. Thus, pH 2 was adopted for 185 186 the following test, unless otherwise stated.

187 *3.3. Effect of initial Orange G concentration*

The performance of azo dyes removal by the BES-Fenton process is often found to be 188 independent on the dye concentration (Asghar et al., 2014). In this section, the initial 189 concentration of Orange G was varied from 100 to 500 mg L⁻¹ to explore its impact on the 190 system performance. The time course of Orange G dye degradation is shown in Fig. 3. For 191 initial Orange G concentrations of 100, 200, 300, and 400 mg L⁻¹, the degradation efficiency 192 after 6 h was about 100%, while degradation efficiency of 94.4% was obtained at 500 mg⁻¹ 193 (Fig.3A). However, the Kapp and KTOC decreased with the increasing of Orange G 194 concentration (Fig.3B). For example, the K_{app} of 1.15 \pm 0.04 h⁻¹ and K_{TOC} of 0.46 \pm 0.05 h⁻¹ 195 were observed at initial concentration of 100 mg L⁻¹, while only 0.59 ± 0.03 h⁻¹ and $0.21 \pm$ 196 0.01 h⁻¹ were obtained at 500 mg L⁻¹. The behaviour was consistent with that observed in 197 MEC-Fenton and classical Fenton process (Zhang et al., 2015b). 198

The current density of MREC increased with increasing of Orange G concentration 199 (Fig.3C). Similar to electro-Fenton and photoelectro-Fenton processes, relatively higher 200 201 current density was benefical for the degradation of Orange G (Pereira et al., 2016). Interestingly, the current density decreased along with decolorization of Grange G wastewater. 202 For example, the current density decreased from 1.73 ± 0.04 to 1.26 ± 0.02 A m⁻² with the 203 reaction time at the initial Grange G concentration of 400 mg L^{-1} . This observation was 204 different with previous report in which the current density was stable at same initial 205 206 methylene blue concentration in MEC-Fenton system (Zhang et al., 2015b). The higher concentration Orange G lead to higher current density, which could support the conclusion 207 that the Orange G might also function as electron acceptor at the cathode. Moreover, we can 208 209 hereby deduce that Orange G might be a stronger electron acceptor than oxygen in the cathode chamber, which still needs to be clarified in future work. 210

211 *3.4. Effect of cathode electrolyte on degradation of Orange G.*

It was previously shown that the supporting electrolyte can affect the Electro-Fenton process 212 213 (Bakheet et al., 2013; Pajootan et al., 2014). In addition, the current density achieved in the 214 MREC can also be increased by enhancing the concentration of the cathode supporting electrolyte (Nam et al., 2012). It is therefore of great interest to evaluate the effects of the 215 cathode supporting electrolyte (Na₂SO₄) on Orange G removal. In this investgation, the initial 216 concentration of Orange G was kept at 400 mg L⁻¹, while the concentration of NaSO₄ varied 217 from 0, 25, 50, 75, to 100 mM. Parameters describing the treatment performance such as 218 decolorization, minerlization and current density were shown in the Fig.4. No significant 219 difference on the final decolorization and minerlization efficiency was observed (Fig.4A and 220 4B) which was consistent with that observed in other Electro-Fenton systems (Bakheet et al., 221

222 2013). However, the K_{app} and K_{TOC} (the slopes of the inserted figure) increased with the 223 increasing of NaSO₄ concentration and reached maximum value at 50 mM NaSO₄ (0.86 and 224 0.24 h⁻¹). However, there was no further increas when the catholyte concentration was higher 225 than 50 mM. In comparison, the current density increased slightly with the increasing of the 226 concentration of NaSO₄ within the tested range (Fig.4C). This is probably because higher 227 concentration of the catholyte could enhance the conductivity and thereby lowering the 228 overall resistance (D'Angelo et al., 2015).

3.5. Effect of HC and LC flow rate on the system performance.

High flow rates of HC and LC solutions can improve the cell potential of MREC (Kim & 230 Logan, 2011b). However, increasing flow rates could also increase energy consumption on 231 pumping the HC and LC solutions through the RED stack. The energy required for pumping 232 233 is an important cost for the MREC operation. Thus there is a trade off between pumping and treatment performance. The optimal flow rates of HC and LC solutions were different for 234 various MREC systems (D'Angelo et al., 2015; Kim & Logan, 2011a; Watson et al., 2015). In 235 this study, an increase in the flow rate of the HC and LC from 0.2 to 0.5 mL min⁻¹ improved 236 237 the decoloration and the mineralization rate (Fig. 5). Notably, there was no remarkable difference on degradation rate when the HC and LC flow rate was between 1.0 and 1.5 mL 238 min⁻¹. The current density increased with the increasing of HC and LC flow rate (Fig. 5C), 239 which implied that the increase of HC and LC flow rate were able to accelerate the cathode 240 reaction. The behavior was consistent with that observed in the MRC for electrical power 241 production (Kim & Logan, 2011b). Therefore, pumping intensity could be used as a control 242 for the degradation of azo dye in the MREC. On the other hand, the decoloration and the 243 244 mineralization rate might not always be improved by increasing solution flow rates. It could

be due to that the HC and LC flow rate was no longer the predominate limiting factor when it
over a certain level (e.g., 1.0 mL min⁻¹ in this study), since the electrical energy output in
RED depends on the predominate resistance at a given HC and LC flow rate (Zhu et al., 2015).
Considering both the Orange G degradation and energy consumption, the optimal flow rate
was considered to be 0.5 mL min⁻¹.

250 *3.6. Effect of air flow rate on the system performance.*

251 The effect of air flow rate on decolorization rate are shown in Fig. 6. As presented in Fig. 6, it was clearly shown that the Orange G degradation rate was greatly affected by the air flow 252 rate. The K_{app} and K_{TOC} increased with the air flow rate and reached the maximum value at 16 253 mL min⁻¹. When the air flow rate was further increased to 32 mL min⁻¹, no further increase in 254 K_{app} was observed, while K_{TOC} decreased slightly. The observation indicates that both 255 inadequate and excessive air supply could deteriorate the mineralization. Moreover, the 256 enhanced air flow rate could increase the current density (Fig. 6B), which was consistent with 257 what has been observed in Electro-Fenton processes (Tian et al., 2016). The air flow rate 258 259 could also affect the total electrical energy consumption. Thus, setting an optimum air flow 260 rate may not only improve the H_2O_2 production but also reduce the operating cost of the system (Tian et al., 2016; Zhou et al., 2013). 261

262 *3.7. Columbic efficiency and energy consumption*

The coulombic efficiency (CE) was $15.56 \pm 0.76\%$ at the air flow rate 16 mL min⁻¹ and HC and LC solution flow rate of 0.5 mL min⁻¹, while the COD removal reached $81.16 \pm 1.85\%$ in the anode fed with domestic wastewater. The low CE could be due to the oxidation of organic matter by the non-exoelectrogenic microorganisms from wastewater. The anolyte pH was 267 maintained at 6.7-7.9, which exclude inhibition of anodic biofilm by non optimal pH (Kim &268 Logan, 2011b).

Energy consumption is one of the major concerns for wastewater treatment using Electro-269 Fenton technology, especially for recalcitrant pollutant degradation (Liu et al., 2015). In this 270 271 MREC-Fenton process, the current density for Orange G decolorization was in the range of 1.27-1.37 A m⁻² (Fig. 6B), which is much lower than that required by Electro-Fenton process 272 (500 A m⁻²) (Pereira et al., 2016). The MREC-Fenton process was driven by renewable 273 energy derived from domestic wastewater and salinity gradient, which are abundant and 274 relatively unlimited (Kim & Logan, 2011a; Zhu et al., 2014). The costs of the MREC-Fenton 275 system mainly includ capital and operating costs. The MREC capital costs are approx. 930 € 276 m⁻³ (in Denmark) (Zhang & Angelidaki, 2016). The operating costs mainly include reagent 277 costs and energy consumption for pumping. The MREC-Fenton system required energy 278 consumption of 25.93 kWh (kg TOC)⁻¹, which is much lower than for traditional Electro-279 Fenton peocess treat Orange 7 with a cost of 865 kWh (kg TOC)⁻¹ (Xu et al., 2008). It was 280 also much lower than that required by sequential Electro-Fenton process (45.8 kWh (kg 281 TOC)⁻¹) (Gao et al., 2015). However, our estimates were based on small laboratory-scale 282 reactor and more accurate assessment is required. The above results suggest that the MREC-283 284 Fenton system could be a potentially cost-effective method for azo dye degradation.

285 *3.8. Practical significance and perspectives*

The results in this study demonstrated that the MREC-Fenton system was environmentfriendly, efficient and low-cost compared to conventional Electro-Fenton system. In this process, the MREC not only can treat domestic wastewater in anode chamber, but also degrade Orange G in cathode chamber. Compared to other bioelectro-Fenton system such as 290 MFC and MEC, the MREC has its own merits. Firstly, the degradation rate was greatly improved by employing the RED stacks between the anode and cathode, compared to MFC. 291 292 Secondly, unlike MEC based Fonton process, the electric energy was mainly produced by RED stack using the renewable salinity-gradient energy which replaced the electrical grid 293 power source. Furthermore, salinity-gradient, as source of energy, is abundant, which could 294 be regenerated using waste heat and thermolytic solutions or seawater and river water (Kim & 295 Logan, 2011a; Nam et al., 2012; Zhu et al., 2014). Thirdly, the energy consumption was only 296 25.93 kWh (kg TOC)⁻¹ under optimal operation condition, indicating that the MREC is a low-297 cost biolectro-Fenton system with efficient mineralization. Though promising, more efforts 298 should be made to accelerate the industrial application. First of all, this system has the 299 300 potential to degrade many refractory compounds, so other nonbiodegradable and toxic pollutants such as nitrobenzene and phenol should be tested for their potential degradation by 301 this system. Although the decalorisation rate was high, the TOC removal rate was low. For 302 improving the TOC removal rate, development of a more cost-effective and efficient MREC 303 reactor configuration is required. Moreover, the CE was relatively low which could probably 304 305 be improved by process optimisation. Lastly, large scale system with continuous-flow operation should be tested in order to validate the technology at industrial scale conditions. 306

307 4. Conclusions

This study demonstrated that the MREC-Fenton system is an effective and environmentally friendly technology for azo dye wastewater treatment. In such system, Orange G (400 mg L⁻¹) was not only effectively degraded with first order kinetic constant of $1.15 \pm 0.06 \text{ h}^{-1}$, but also highly mineralized with TOC removal efficiency of 99.6% and K_{TOC} of $0.26 \pm 0.02 \text{ h}^{-1}$ at pH 2. Notably the energy consumption was only 25.93 kWh (kg TOC)⁻¹. This work provides a 313 cost-effective method for azo dye degradation, which is also attractive and applicable for314 efficient degradation of recalcitrant pollutants.

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320 **References**

- A.W.W.A. 1998. American Public Health Association, Water Pollution Control Federation,
 Standard Methods for the Examination of Water and Wastewater, nineteenth.
 American Public Health Association, Washington, DC.
- Asghar, A., Abdul Raman, A.A., Daud, W.M.A.W., 2014. Recent advances, challenges and
 prospects ofin situproduction of hydrogen peroxide for textile wastewater treatment in
 microbial fuel cells. J. Chem. Technol. Biotechnol. 89(10), 1466-1480.
- 327 3. Bakheet, B., Yuan, S., Li, Z., Wang, H., Zuo, J., Komarneni, S., Wang, Y., 2013. Electro328 peroxone treatment of Orange II dye wastewater. Water Res. 47(16), 6234-6243.
- 4. Banerjee, S., Chattopadhyaya, M.C., Chandra Sharma, Y., 2015. Removal of an azo dye
 (Orange G) from aqueous solution using modified sawdust. J. Water. Sanit. Hyg. De.
 5(2), 235-242.
- 5. Cai, M., Su, J., Zhu, Y., Wei, X., Jin, M., Zhang, H., Dong, C., Wei, Z., 2016.
 Decolorization of azo dyes Orange G using hydrodynamic cavitation coupled with
 heterogeneous Fenton process. Ultrason. Sonochem. 28, 302-310.
- 6. D'Angelo, A., Galia, A., Scialdone, O., 2015. Cathodic abatement of Cr(VI) in water by
 microbial reverse-electrodialysis cells. J. Electroanal. Chem. 748, 40-46.
- 7. Feng, C.H., Li, F.B., Mai, H.J., Li, X.Z., 2010. Bio-Electro-Fenton Process Driven by
 Microbial Fuel Cell for Wastewater Treatment. Environ. Sci. Technol. 44(5), 18751880.

- 8. Fu, L., You, S.J., Zhang, G.Q., Yang, F.L., Fang, X.H., 2010. Degradation of azo dyes
 using in-situ Fenton reaction incorporated into H₂O₂-producing microbial fuel cell.
 Chem. Eng. J. 160(1), 164-169.
- 9. Gao, G., Zhang, Q., Hao, Z., Vecitis, C.D., 2015. Carbon nanotube membrane stack for
 flow-through sequential regenerative electro-Fenton. Environ. Sci. Technol. 49(4),
 2375-83.
- 10. Kim, Y., Logan, B.E., 2011a. Hydrogen production from inexhaustible supplies of fresh
 and salt water using microbial reverse-electrodialysis electrolysis cells. Proc. Natl.
 Acad. Sci. 108(39), 16176-16181.
- 11. Kim, Y., Logan, B.E., 2011b. Microbial reverse electrodialysis cells for synergistically
 enhanced power production. Environ. Sci. Technol. 45(13), 5834-5839.
- 12. Li, N., An, J., Zhou, L., Li, T., Li, J., Feng, C., Wang, X., 2016. A novel carbon black
 graphite hybrid air-cathode for efficient hydrogen peroxide production in
 bioelectrochemical systems. J. Power Sources 306, 495-502.
- 13. Liu, Y., Chen, S., Quan, X., Yu, H., Zhao, H., Zhang, Y., 2015. Efficient Mineralization
 of Perfluorooctanoate by Electro-Fenton with H2O2 Electro-generated on
 Hierarchically Porous Carbon. Environ. Sci. Technol. 49(22), 13528-13533.
- 14. Luo, X., Zhang, F., Liu, J., Zhang, X., Huang, X., Logan, B.E., 2014. Methane production
 in microbial reverse-electrodialysis methanogenesis cells (MRMCs) using thermolytic
 solutions. Environ. Sci. Technol. 48(15), 8911-8918.
- 15. Luo, Y., Zhang, R., Liu, G., Li, J., Qin, B., Li, M., Chen, S., 2011. Simultaneous
 degradation of refractory contaminants in both the anode and cathode chambers of the
 microbial fuel cell. Bioresour Technol. 102(4), 3827-3832.
- 16. Martinez-Huitle, C.A., Rodrigo, M.A., Sires, I., Scialdone, O., 2015. Single and Coupled
 Electrochemical Processes and Reactors for the Abatement of Organic Water
 Pollutants: A Critical Review. Chem. Rev. 115(24), 13362-13407.
- 17. Mu, Y., Rabaey, K., Rozendal, R.A., Yuan, Z., Keller, J., 2009. Decolorization of Azo
 Dyes in Bioelectrochemical Systems. Environ. Sci. Technol. 43, 5137-5143.
- 18. Nam, J.Y., Cusick, R.D., Kim, Y., Logan, B.E., 2012. Hydrogen generation in microbial
 reverse-electrodialysis electrolysis cells using a heat-regenerated salt solution. Environ.
 Sci. Technol. 46(9), 5240-5246.

- 19. Nidheesh, P.V., Gandhimathi, R., 2012. Trends in electro-Fenton process for water and
 wastewater treatment: An overview. Desalination 299, 1-15.
- 20. Pajootan, E., Arami, M., Rahimdokht, M., 2014. Application of Carbon Nanotubes Coated
 Electrodes and Immobilized TiO₂ for Dye Degradation in a Continuous
 Photocatalytic-Electro-Fenton Process. Ind. Eng. Chem. Res. 53(42), 16261-16269.
- 21. Pearce, C., 2003. The removal of colour from textile wastewater using whole bacterial
 cells: a review. Dyes Pigments 58(3), 179-196.
- 22. Pereira, G.F., El-Ghenymy, A., Thiam, A., Carlesi, C., Eguiluz, K.I.B., Salazar-Banda,
 G.R., Brillas, E., 2016. Effective removal of Orange-G azo dye from water by electroFenton and photoelectro-Fenton processes using a boron-doped diamond anode. Sep.
 Purif. Technol. 160, 145-151.
- 23. Rosales, E., Pazos, M., Sanroman, M.A., 2012. Advances in the Electro-Fenton Process
 for Remediation of Recalcitrant Organic Compounds. Chem. Eng. Technol. 35(4),
 609-617.
- 24. Solanki, K., Subramanian, S., Basu, S., 2013. Microbial fuel cells for azo dye treatment
 with electricity generation: a review. Bioresour Technol. 131, 564-571.
- 25. Tian, J., Zhao, J., Olajuyin, A.M., Sharshar, M.M., Mu, T., Yang, M., Xing, J., 2016.
 Effective degradation of rhodamine B by electro-Fenton process, using ferromagnetic
 nanoparticles loaded on modified graphite felt electrode as reusable catalyst: in neutral
 pH condition and without external aeration. Environ. Sci. Pollut. Res. 23(15), 1547115482.
- Wang, J., Bai, R., 2016. Formic acid enhanced effective degradation of methyl orange dye
 in aqueous solutions under UV-Vis irradiation. Water Res. 101, 103-113.
- Watson, V.J., Hatzell, M., Logan, B.E., 2015. Hydrogen production from continuous flow,
 microbial reverse-electrodialysis electrolysis cells treating fermentation wastewater.
 Bioresour Technol. 195, 51-56.
- 28. Xu, L., Zhao, H., Shi, S., Zhang, G., Ni, J., 2008. Electrolytic treatment of Acid Orange 7
 in aqueous solution using a three-dimensional electrode reactor. Dyes Pigments 77(1),
 158-164.
- 29. Xu, N., Zhou, S., Yuan, Y., Qin, H., Zheng, Y., Shu, C., 2011. Coupling of anodic
 biooxidation and cathodic bioelectro-Fenton for enhanced swine wastewater treatment.
 Bioresour Technol. 102(17), 7777-7783.

- 30. Zhang, B., Wang, Z., Zhou, X., Shi, C., Guo, H., Feng, C., 2015a. Electrochemical
 decolorization of methyl orange powered by bioelectricity from single-chamber
 microbial fuel cells. Bioresour Technol. 181, 360-362.
- 406 31. Zhang, Y., Angelidaki, I., 2015a. Bioelectrochemical recovery of waste-derived volatile
 407 fatty acids and production of hydrogen and alkali. Water Res. 81, 188-195.
- 32. Zhang, Y., Wang, Y., Angelidaki, I., 2015b. Alternate switching between microbial fuel
 cell and microbial electrolysis cell operation as a new method to control H₂O₂ level in
 Bioelectro-Fenton system. J. Power Sources **291**, 108-116.
- 33. Zhang, Y., Angelidaki, I., 2016. Microbial Electrochemical Systems and Technologies: It
 Is Time To Report the Capital Costs. Environ. Sci. Technol. 50(11), 5432-5433.
- 413 34. Zhou, L., Zhou, M., Zhang, C., Jiang, Y., Bi, Z., Yang, J., 2013. Electro-Fenton
 414 degradation of p-nitrophenol using the anodized graphite felts. Chem. Eng. J. 233,
 415 185-192.
- 35. Zhu, X., Hatzell, M.C., Logan, B.E., 2014. Microbial Reverse-Electrodialysis Electrolysis
 and Chemical-Production Cell for H₂ Production and CO₂ Sequestration. Environ. Sci.
 Technol. Lett. 1(4), 231-235.
- 36. Zhu, X., He, W., Logan, B.E., 2015. Reducing pumping energy by using different flow
 rates of high and low concentration solutions in reverse electrodialysis cells. J.
 Membrane Sci. 486, 215-221.
- 37. Zhuang, L., Zhou, S., Yuan, Y., Liu, M., Wang, Y., 2010. A novel bioelectro-Fenton
 system for coupling anodic COD removal with cathodic dye degradation. Chem. Eng.
 J. 163(1-2), 160-163.
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431 **Figure Captions**

Fig. 1. Schematic illustration of the MREC-Fenton reactor. LC: low concentration NaCl
solution; AEM: anion exchange membrane; CEM: cation exchange membrane; HC: high
concentration NaCl solution.

Fig. 2. The decolorization and mineralization of Orange G. Control 1, open circuit; Control 2,
without air flow in cathode; Control 3, without Fe²⁺ addition in azo dye wastewater. MREC-F
(MREC-Fenton) conditions: Fe²⁺ concentration of 10 mM, initial pH 3, air flow rate of 8 mL
min⁻¹, HC and LC flow rate of 0.5 mL min⁻¹.

Fig. 3. The effect of initial Orange G concentration on the degradation of Orange G in the
MREC. Operational conditions: initial pH 2, Fe²⁺ of 10 mM, HC and LC flow rate of 0.5 mL
min⁻¹, and air flow rate of 8 mL min⁻¹.

442 Fig. 4. The effect of cathode electrolyte concentration (Na₂SO₄) on the degradation of Orange 443 G in the MREC. Conditions: Orange G concentration of 400 mg L^{-1} , initial pH 2, HC and LC 444 solutions flow rate of 0.5 mL min⁻¹, and air flow rate of 8 mL min⁻¹.

- **Fig. 5.** The effect of solution flow rate on the Orange G degradation in the MREC. Conditions: Orange G concentration of 400 mg L^{-1} , initial pH 2, Fe²⁺ of 10 mM, NaSO₄ concentration of 50 mM, and air flow rate of 8 mL min⁻¹.
- **448 Fig. 6.** The effect of air flow rate on the Orange G degradation in the MREC. Conditions: 449 Orange G concentration of 400 mg L^{-1} , initial pH 2, Fe²⁺ of 10 mM, HC and LC solutions 450 flow rate of 0.5 mL min⁻¹, NaSO₄ concentration of 50 mM.
- 451



Fig. 1.



Fig. 2.



Fig. 3.





Fig. 4.



Fig. 5.



Fig. 6.

Supplymentary data Click here to download Electronic Annex: Supplementary data.docx