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1 Novel bio-electro-Fenton technology for azo dye wastewater treatment using  
2 microbial reverse-electrodialysis electrolysis cell

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19 **Abstract**

20 Development of sustainable technologies for treatment of recalcitrant pollutants containing  
21 wastewaters has long been of great interest. In this study, we proposed an innovative concept  
22 of using microbial reverse-electrodialysis electrolysis cell (MREC) based Fenton process to  
23 treat azo dye wastewater. In such MREC-Fenton integrated process, the production of H<sub>2</sub>O<sub>2</sub>  
24 which is the key reactant of fenton-reaction was driven by the electrons harvested from the  
25 exoelectrogens and salinity-gradient between sea water and fresh water in MREC. Complete  
26 decolorization and mineralization of 400 mg L<sup>-1</sup> Orange G was achieved with apparent first  
27 order rate constants of  $1.15 \pm 0.06$  and  $0.26 \pm 0.03$  h<sup>-1</sup>, respectively. Furthermore, the initial  
28 concentration of orange G, initial solution pH, catholyte concentration, high and low  
29 concentration salt water flow rate and air flow rate were all found to significantly affect the  
30 dye degradation. This study provides an efficient and cost-effective system for the  
31 degradation of non-biodegradable pollutants.

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

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## 42 **1. Introduction**

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

56 More recently, bioelectrochemical systems (BES) such as microbial fuel cell (MFC) and  
57 microbial electrolysis cell (MEC) based Electro-Fenton systems have been demonstrated as  
58 promising alternative method to the traditional Electro-Fenton process for the degradation of  
59 azo dyes (Feng et al., 2010; Solanki et al., 2013; Zhang et al., 2015b). In such systems, the  
60 electrons used for H<sub>2</sub>O<sub>2</sub> production at the cathode are fully or partly derived from organic  
61 wastes by bacteria in the anode. Thus, the catalyst cost and energy-consumption have been  
62 greatly reduced. The BES-Fenton process not only can remove the biodegradable organics in  
63 anode chamber, but also can remove the biorefractory pollutants in cathode chamber (Solanki  
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  
66 efficiency has been mainly achieved at low dye concentration ( $\leq 100 \text{ mg L}^{-1}$ ) in the MFC-  
67 Fenton process due to the extreme low  $\text{H}_2\text{O}_2$  production (Asghar et al., 2014; Fu et al., 2010).  
68 Comparatively, MEC-Fenton system could be more efficient due to much higher and faster  
69  $\text{H}_2\text{O}_2$  production (Zhang et al., 2015b). However, the requirement of external power supply  
70 for MEC may add the capital and operational costs and also complicate the whole system.  
71 Thus, there is a great research and practical interest to develop more economical and efficient  
72 BES-Fenton system for dye wastewater treatment.

73 Recently, a novel type of BES system called microbial reverse-electrodialysis electrolysis  
74 cell (MREC), which combines a reverse electrodialysis stack (RED) and MEC have been  
75 developed to drive  $\text{H}_2$  or  $\text{CH}_4$  generation (Kim & Logan, 2011a; Luo et al., 2014). In our  
76 previous study, the MREC system has been demonstrated as one promising system to produce  
77 high concentration of  $\text{H}_2\text{O}_2$  with low electrical energy consumption. Therefore, intergration of  
78 MREC and Fenton process could be an ideal technology to remove azo dye, which has never  
79 been previously reported.

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

## 88 **2. Materials and Methods**

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

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

### 105 *2.2. Analytical methods.*

106 The concentration of Orange G was determined by a UV-vis spectrophotometry (Spectronic  
107 20D+, Thermo Scientific) at 478 nm (Banerjee et al., 2015). The mineralization rate of orange  
108 G in the wastewater during the degradation experiment was estimated through the analysis of  
109 total organic carbon (TOC) of the samples measured by shimadzu TOC 5000 A. The pH was

110 measured using a pH meter (PHM 210 pH meter, Radiometer). Chemical oxygen demand  
 111 (COD) was measured according to the Standard Method (A.W.W.A, 1998). The voltage  
 112 across on the external resistor (10  $\Omega$ ) was monitored with 30 min intervals using a digital  
 113 multimeter (model 2700, Keithley Instruments, Inc., Cleveland, OH, USA). Current density  
 114 was calculated base on the surface area (3 cm  $\times$  3 cm) of cathode. Coulomic efficiency (CE)  
 115 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

$$118 \quad \ln \frac{C_0}{C_t} = K_{app} t \quad (1)$$

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

120 where  $C_0$  (mg L<sup>-1</sup>) and  $C_t$  (mg L<sup>-1</sup>) are the Orange G concentrations at time 0 and reaction  
 121 time t, respectively.  $TOC_0$  (mg L<sup>-1</sup>) and  $TOC_t$  (mg L<sup>-1</sup>) are the TOC concentrations at time 0  
 122 and reaction time t, respectively.

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

$$129 \quad \text{Energy consumption} = \frac{1000000 \text{ W}}{TOC_0 \times V_0 - TOC_t \times V_t} \quad (3)$$

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

### 133 **3. Results and discussion**

#### 134 *3.1. System performance*

135 Fig. 2 shows the decolorization and minerlization of orange G in the cathode of MREC-  
136 Fenton system with the initial Orange G concentration of  $100 \text{ mg L}^{-1}$ . The decolorization  
137 efficiency of Orange G reached to about 70% within one hour, and 88% of Orange G was  
138 removed after 3 hours (Fig. 2A). Comparatively, the decolorieization efficiency of 10% was  
139 observed after 5 hours under open circuit condition (control 1), which could be due to the  
140 absorption on the electrode material and the anion membrane (the side closed to the cathode  
141 chamber). The Orange G decolorization efficiency without air flow in cathode chamber  
142 (control 2) and without  $\text{Fe}^{2+}$  addition in catholyte (control 3) only reached about 32% and  
143 45%, respectively, after 5 hours. The minerlization of Orange G in terms of TOC removal  
144 showed similar trend as decoloration. As shown in Fig. 2B, the TOC removal efficiency could  
145 reach to 87% after 5h, which was only 16% and 13% in control 2 and 3, respectively. The  
146 slight decolorization observed in control experiments could be due to the reduction of Orange  
147 G as electron acceptor at the cathode. This is supported by the observation that Orange G  
148 could be decomposed to colorless shorter organic molecules without dissolved  $\text{O}_2$  in control 2  
149 and lack of the Fenton reagent ( $\text{Fe}^{2+}$ ) in control 3. Similar behaviour from other azo dyes (e.g.,  
150 Orange 7 and Methylene Blue) have been previously observed in BES system (Li et al., 2016;  
151 Mu et al., 2009; Zhang et al., 2015a). On the other hand, the results also confirmed that the  
152 removal of Organge G was mainly due to the Fenton reaction driven by the energy from



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

### 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  
165 found to be dependent on the wastewater pH, and for different dyes in different degradation  
166 systems, the effect of wastewater pH was found to vary greatly. On the other hand, the actual  
167 dye wastewaters 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  
169 (Supplementary data), the decolorization and TOC removal were greatly affected by the initial  
170 pH of the wastewater. The increasing of initial pH from 2 to 7 caused a decrease in  
171 decolorization rate and TOC removal rate. The highest removal rate of Orange G was found at  
172 pH 2 ( $79 \pm 0.8 \text{ mg L}^{-1} \text{ h}^{-1}$ ) in the first hour, and the maximum decolorization efficiency  
173 reached to 100% after 4 h reaction. The decolorization and TOC removal rate decreased with  
174 further increasing of the initial pH from 3 to 7. For example, when the pH increased to above  
175 4, the decolorization rate of Orange G started to decline. When the pH increased to above 7

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

### 187 *3.3. Effect of initial Orange G concentration*

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

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

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

212 It was previously shown that the supporting electrolyte can affect the Electro-Fenton process  
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  
215 electrolyte (Nam et al., 2012). It is therefore of great interest to evaluate the effects of the  
216 cathode supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>) on Orange G removal. In this investigation, the initial  
217 concentration of Orange G was kept at 400 mg L<sup>-1</sup>, while the concentration of Na<sub>2</sub>SO<sub>4</sub> varied  
218 from 0, 25, 50, 75, to 100 mM. Parameters describing the treatment performance such as  
219 decolorization, mineralization and current density were shown in the Fig.4. No significant  
220 difference on the final decolorization and mineralization efficiency was observed (Fig.4A and  
221 4B) which was consistent with that observed in other Electro-Fenton systems (Bakheet et al.,

222 2013). However, the  $K_{app}$  and  $K_{TOC}$  (the slopes of the inserted figure) increased with the  
223 increasing of  $NaSO_4$  concentration and reached maximum value at 50 mM  $NaSO_4$  (0.86 and  
224  $0.24\ h^{-1}$ ). However, there was no further increase 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  $NaSO_4$  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).

### 229 *3.5. Effect of HC and LC flow rate on the system performance.*

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

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

### 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,  
252 it was clearly shown that the Orange G degradation rate was greatly affected by the air flow  
253 rate. The  $K_{app}$  and  $K_{TOC}$  increased with the air flow rate and reached the maximum value at 16  
254 mL min<sup>-1</sup>. When the air flow rate was further increased to 32 mL min<sup>-1</sup>, no further increase in  
255  $K_{app}$  was observed, while  $K_{TOC}$  decreased slightly. The observation indicates that both  
256 inadequate and excessive air supply could deteriorate the mineralization. Moreover, the  
257 enhanced air flow rate could increase the current density (Fig. 6B), which was consistent with  
258 what has been observed in Electro-Fenton processes (Tian et al., 2016). The air flow rate  
259 could also affect the total electrical energy consumption. Thus, setting an optimum air flow  
260 rate may not only improve the H<sub>2</sub>O<sub>2</sub> production but also reduce the operating cost of the  
261 system (Tian et al., 2016; Zhou et al., 2013).

### 262 *3.7. Columbic efficiency and energy consumption*

263 The coulombic efficiency (CE) was  $15.56 \pm 0.76\%$  at the air flow rate 16 mL min<sup>-1</sup> and HC  
264 and LC solution flow rate of 0.5 mL min<sup>-1</sup>, while the COD removal reached  $81.16 \pm 1.85\%$  in  
265 the anode fed with domestic wastewater. The low CE could be due to the oxidation of organic  
266 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).

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

### 285 *3.8. Practical significance and perspectives*

286 The results in this study demonstrated that the MREC-Fenton system was environment-  
287 friendly, efficient and low-cost compared to conventional Electro-Fenton system. In this  
288 process, the MREC not only can treat domestic wastewater in anode chamber, but also  
289 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  
291 improved by employing the RED stacks between the anode and cathode, compared to MFC.  
292 Secondly, unlike MEC based Fonton process, the electric energy was mainly produced by  
293 RED stack using the renewable salinity-gradient energy which replaced the electrical grid  
294 power source. Furthermore, salinity-gradient, as source of energy, is abundant, which could  
295 be regenerated using waste heat and thermolytic solutions or seawater and river water (Kim &  
296 Logan, 2011a; Nam et al., 2012; Zhu et al., 2014). Thirdly, the energy consumption was only  
297 25.93 kWh (kg TOC)<sup>-1</sup> under optimal operation condition, indicating that the MREC is a low-  
298 cost bioelectro-Fenton system with efficient mineralization. Though promising, more efforts  
299 should be made to accelerate the industrial application. First of all, this system has the  
300 potential to degrade many refractory compounds, so other nonbiodegradable and toxic  
301 pollutants such as nitrobenzene and phenol should be tested for their potential degradation by  
302 this system. Although the decolorisation rate was high, the TOC removal rate was low. For  
303 improving the TOC removal rate, development of a more cost-effective and efficient MREC  
304 reactor configuration is required. Moreover, the CE was relatively low which could probably  
305 be improved by process optimisation. Lastly, large scale system with continuous-flow  
306 operation should be tested in order to validate the technology at industrial scale conditions.

#### 307 **4. Conclusions**

308 This study demonstrated that the MREC-Fenton system is an effective and environmentally  
309 friendly technology for azo dye wastewater treatment. In such system, Orange G (400 mg L<sup>-1</sup>)  
310 was not only effectively degraded with first order kinetic constant of  $1.15 \pm 0.06 \text{ h}^{-1}$ , but also  
311 highly mineralized with TOC removal efficiency of 99.6% and  $K_{\text{TOC}}$  of  $0.26 \pm 0.02 \text{ h}^{-1}$  at pH  
312 2. Notably the energy consumption was only 25.93 kWh (kg TOC)<sup>-1</sup>. This work provides a

313 cost-effective method for azo dye degradation, which is also attractive and applicable for  
314 efficient degradation of recalcitrant pollutants.

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431 **Figure Captions**

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

435 **Fig. 2.** The decolorization and mineralization of Orange G. Control 1, open circuit; Control 2,  
436 without air flow in cathode; Control 3, without  $\text{Fe}^{2+}$  addition in azo dye wastewater. MREC-F  
437 (MREC-Fenton) conditions:  $\text{Fe}^{2+}$  concentration of 10 mM, initial pH 3, air flow rate of 8 mL  
438  $\text{min}^{-1}$ , HC and LC flow rate of 0.5 mL  $\text{min}^{-1}$ .

439 **Fig. 3.** The effect of initial Orange G concentration on the degradation of Orange G in the  
440 MREC. Operational conditions: initial pH 2,  $\text{Fe}^{2+}$  of 10 mM, HC and LC flow rate of 0.5 mL  
441  $\text{min}^{-1}$ , and air flow rate of 8 mL  $\text{min}^{-1}$ .

442 **Fig. 4.** The effect of cathode electrolyte concentration ( $\text{Na}_2\text{SO}_4$ ) on the degradation of Orange  
443 G in the MREC. Conditions: Orange G concentration of 400 mg  $\text{L}^{-1}$ , initial pH 2, HC and LC  
444 solutions flow rate of 0.5 mL  $\text{min}^{-1}$ , and air flow rate of 8 mL  $\text{min}^{-1}$ .

445 **Fig. 5.** The effect of solution flow rate on the Orange G degradation in the MREC. Conditions:  
446 Orange G concentration of 400 mg  $\text{L}^{-1}$ , initial pH 2,  $\text{Fe}^{2+}$  of 10 mM,  $\text{NaSO}_4$  concentration of  
447 50 mM, and air flow rate of 8 mL  $\text{min}^{-1}$ .

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  $\text{L}^{-1}$ , initial pH 2,  $\text{Fe}^{2+}$  of 10 mM, HC and LC solutions  
450 flow rate of 0.5 mL  $\text{min}^{-1}$ ,  $\text{NaSO}_4$  concentration of 50 mM.

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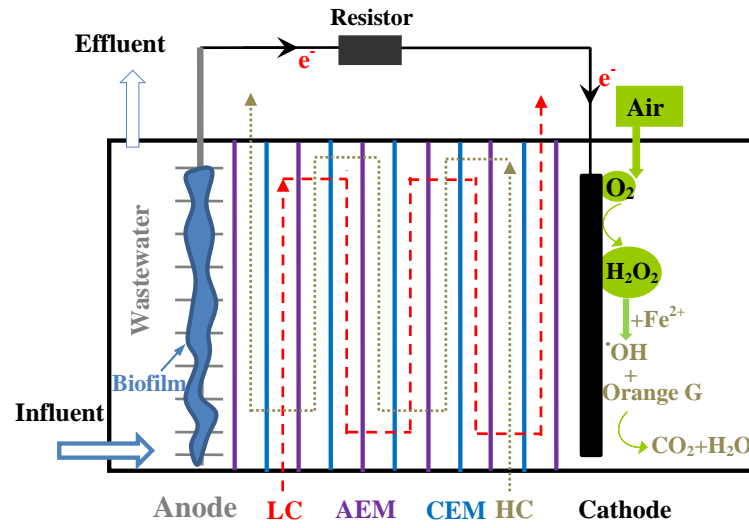
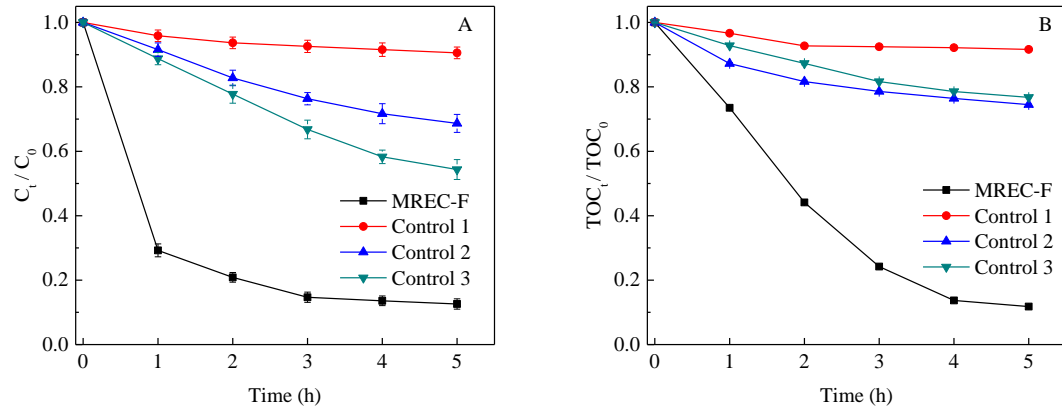


Fig. 1.



**Fig. 2.**

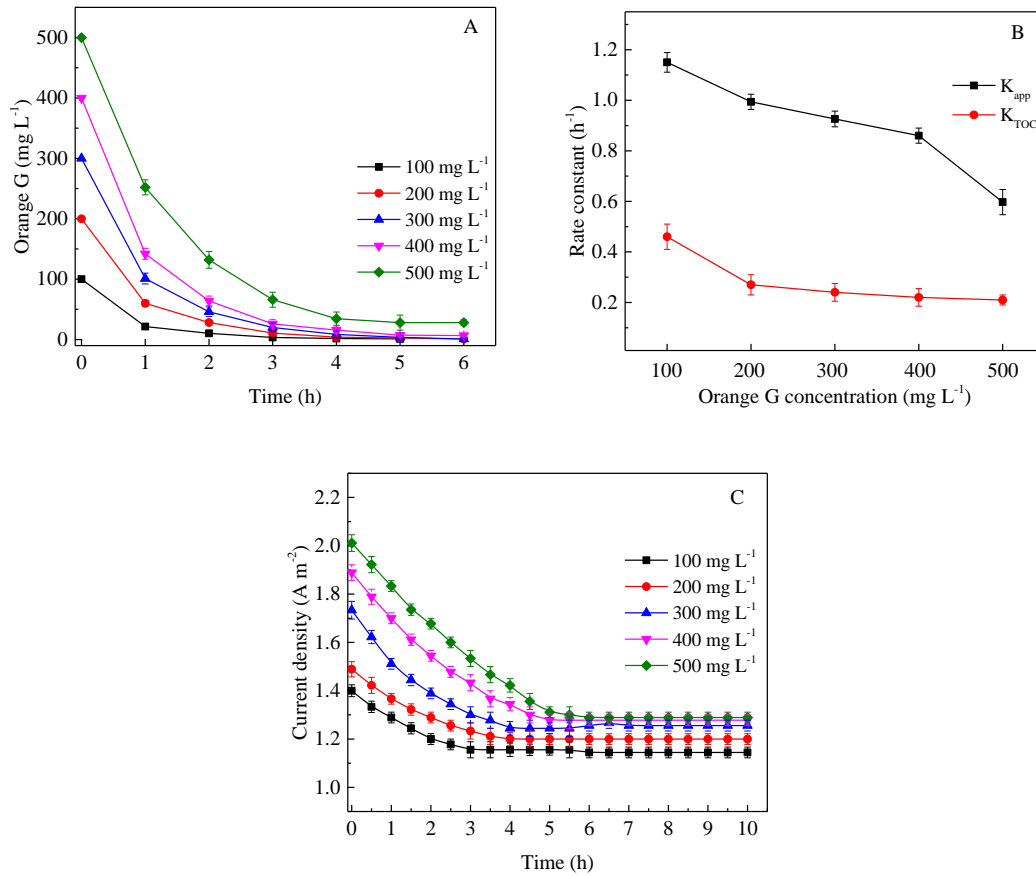


Fig. 3.

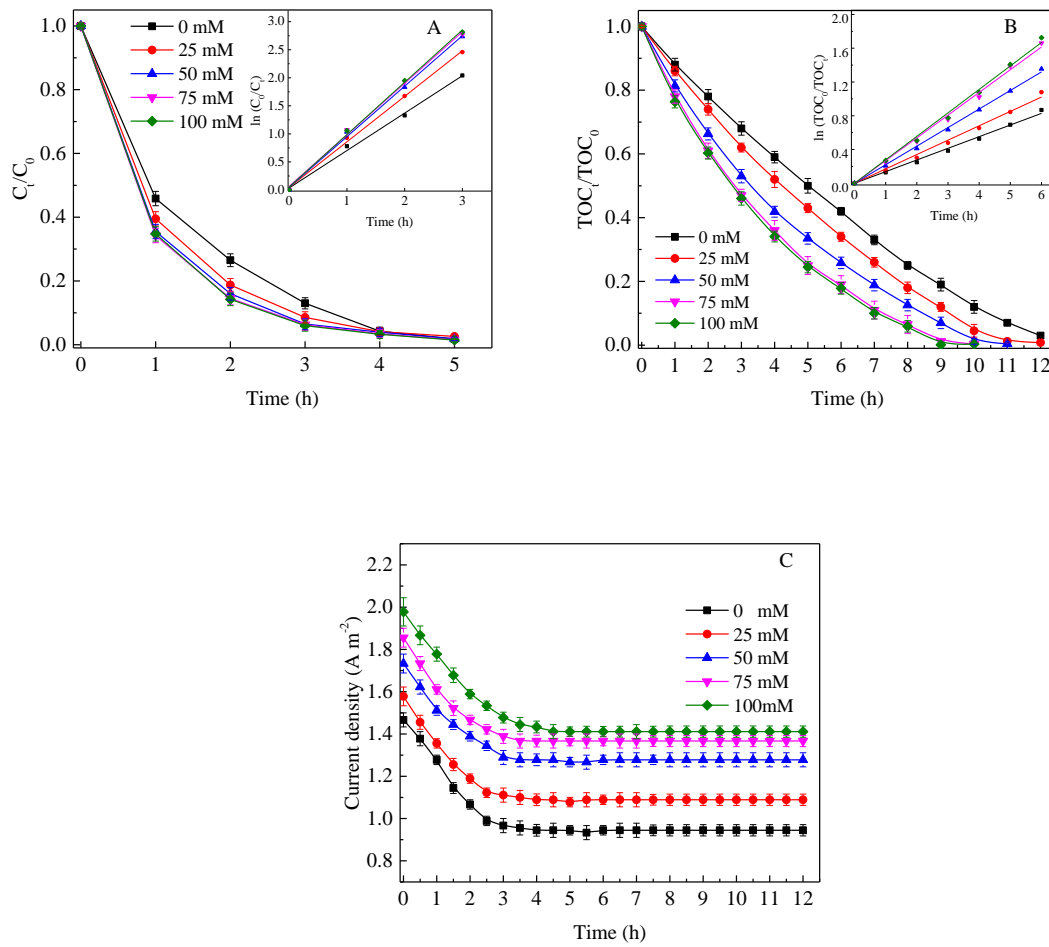


Fig. 4.



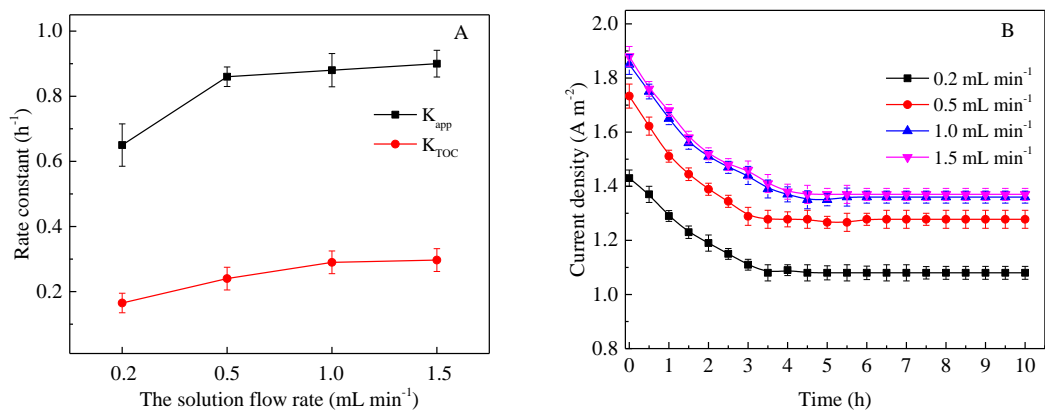


Fig. 5.

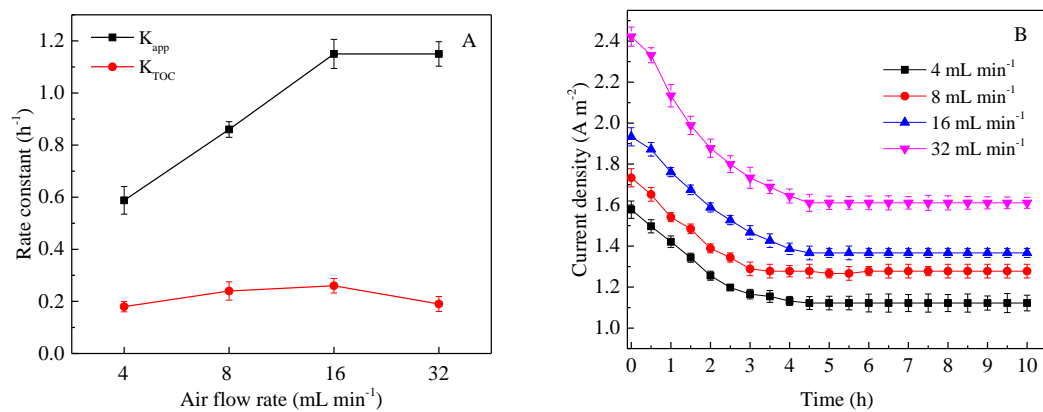


Fig. 6.

**Supplementary data**

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