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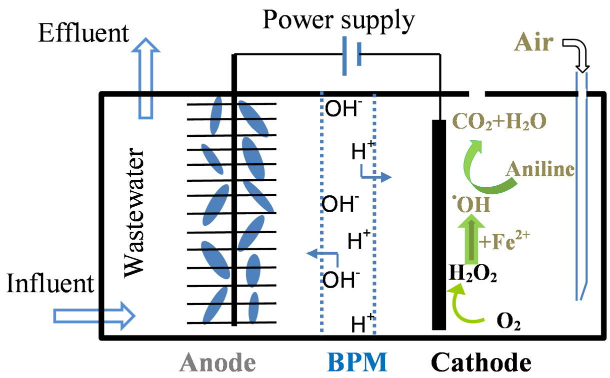

Power supply
Effluent
Air
Wastewater
Influent
OH-
H+
CO2+H2O
Aniline
•OH
+Fe2+
H2O2
O2
Anode
BPM
Cathode

Submission to Water Research

Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-Fenton system

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Abstract

Aniline-containing wastewater can cause significant environmental problems and threaten the humans's life. However, rapid degradation of aniline with cost-efficient methods remains a challenge. In this work, a novel microbial electrolysis cell with bipolar membrane was integrated with Fenton reaction (MEC-Fenton) for efficient treatment of real wastewater containing a high concentration (4460 ± 52 mg L^{-1}) of aniline. In this system, H_2O_2 was in situ electro-synthesized from O_2 reduction on the graphite cathode and was simultaneously used as source of $^{\bullet}OH$ for the oxidation of aniline wastewater under an acidic condition maintained by the bipolar membrane. The aniline was effectively degraded following first-order kinetics at a rate constant of 0.0166 h^{-1} under an applied voltage of 0.5 V. Meanwhile, a total organic carbon (TOC) removal efficiency of 93.1±1.2% was obtained, revealing efficient mineralization of aniline. The applicability of bipolar membrane MEC-Fenton system was successfully demonstrated with actual aniline wastewater. Moreover, energy balance showed that the system could be a promising technology for removal of biorefractory organic pollutants from wastewaters.

Keywords: Microbial electrolysis cell; Fenton reaction; Aniline; Industrial wastewater; Bipolar membrane; H_2O_2

1. Introduction

Aniline ($C_6H_5NH_2$) has been widely used for various industries producing dyes, pesticides, rubber chemicals, and pharmaceuticals. Considering the biological accumulation, long term residue and carcinogenic properties, aniline-contained wastewater is categorized as hazardous waste (Li et al., 2016a; Wang et al., 2016). Biological methods have been widely used to treat aniline wastewater at low concentration (0-1000 mg L^{-1}) (Jin et al., 2012; Liu et al., 2015), during which the aniline can be completely mineralized into CO_2 and N_2/NO_x (Wang et al., 2016). However, most conventional biological methods cannot treat high concentration (＞2000 mg L^{-1}) aniline wastewater due to the toxicity of aniline (Chen et al., 2007; Jin et al., 2012). In the past years, advanced oxidation processes especially the Electro-Fenton process have been recognized as attractive method for aniline degradation due to its high efficiency (Anotai et al., 2010; Brillas and Casado, 2002). However, there are still several shortcomings such as high cost electrode materials, high electrical energy consumption and required thoroughly pH control (at 2-3.5), which hinder industrial application (Brillas et al., 2009).

Recently, Bio-Electro-Fenton systems such as integrated microbial fuel cell-Fenton systems (MFC-Fenton) and Microbial Electrolysis Cell-Fenton systems (MEC-Fenton) have been demonstrated as promising alternative and cost-effective methods to traditional Electro-Fenton process for degradation of organic pollutants, such as azo dyes (Li et al., 2017b; Zhang et al., 2015), P-nitrophenol (Tao et al., 2013), Estrone (Xu et al., 2013), Bisphenol A, Sulfamethazine and Triclocarban (Wang et al., 2017). Though promising, there are still challenges which need to be addressed and validation is needed before commercial application. For instance, high mineralization efficiency has only been achieved with synthetic wastewater and/or at low pollutant concentration (Asghar et al., 2014; Xu et al., 2015). Furthermore, most of the bio-Electro-Fenton systems use cation exchange membrane (CEM) as a separator, which has difficulty to maintain low catholyte pH and thus may cause inhibition on the Fenton process. The pH rise could also cause extensive iron precipitation which in return may damage the CEM and cathode (Ter Heijne et al., 2006). Therefore, a bio-Electro-Fenton system that can treat real and high concentration wastewater without causing pH issues is needed.

In this study, an innovative bio-Electro-Fenton system using bipolar membrane was developed to treat real industrial wastewater containing high concentration of aniline. The bipolar membrane has been shown to be an effective ion separator in previous MFC studies (Ter Heijne 2010), which could prevent pH elevation in the catholyte and pH drop in the anolyte (Ter Heijne et al., 2006; Ter Heijne et al., 2010; Zhang and Angelidaki, 2015). To the best of our knowledge, bipolar membrane has never been applied in bio-Electro-Fenton system. Furthermore, this is the first time that the MEC-Fenton system was applied for treatment of real industrial aniline wastewater. To optimize the conditions for the MEC-Fenton degradation of aniline, the effects of pH value, air flow rate and applied voltage on aniline degradation were investigated. This work offers an efficient and cost-effective approach for the removal of biorefractory organic pollutants from industrial wastewaters.

2. Material and methods

2.1. Reactor setup

The schematic diagram of the bipolar membrane MEC-Fenton system is shown in Fig. 1. The MEC consisted of two chambers which were separated by a bipolar membrane (BPM, fumasep® FBM, FuMA-Tech GmbH, Germany). The membrane was used to maintain low cathode pH and avoid H^+ leakage to the anode (Zhang et al., 2015). The working volume of anode and cathode chamber was 100 mL (5 cm × 5 cm × 4 cm). The anode electrode was made of a carbon fiber brush (5.9 cm diameter, 6.9 cm length, Mill-Rose, USA), which was pretreated at 450 ^{o}C for 30 min and then pre-cultivated with mature biofilm in a MFC reactor before transferring to the MEC (Zhang et al., 2015). The cathode electrode was a graphite plate (3.5 cm × 4 cm). Cathode potential was measured versus a reference electrode (Ag/AgCl electrode, +197 mV vs SHE). Titanium wire was used to connect the cathode and anode electrode to the circuit.

Fig. 1. is here

2.2. Characterization of domestic wastewater and aniline wastewater

Domestic wastewater was collected from primary clarifier (Lyngby Wastewater Treatment Plant, Copenhagen, Denmark). The characteristics of the wastewater were as following: chemical oxygen demand (COD) of 386 ± 32 mg L^{-1}, pH 8.1, conductivity of 1.7 mS cm^{-1}, stored at 4 ^{o}C before use. The aniline wastewater was provided by Vandrens A/S, Denmark and then stored at 4 ^{o}C before use. The characteristics of the aniline wastewater were: Aniline concentration of 4460 ± 52 mg L^{-1}, TOC of 3360 ± 80 mg L^{-1}, COD of 10930 ± 110 mg L^{-1} and pH = 7.2. The aniline wastewater was amended with 50 mM Na_2SO_4 and 10 mM $FeSO_4$ before each batch run.

2.3. Reactor operation

In this study, the research focused on the performance of aniline degradation in the cathode chamber. In order to avoid the influence from anode side, the anode chamber was continuously fed with domestic wastewater amended with sodium acetate (~1.6 g COD L^{-1} in total) at 100 mL d^{-1}. At the same time the domestic wastewater was recirculated from a feed reservoir (liquid volume of 300 mL) through anode at a recirculation rate of 20 mL min^{-1} using a peristaltic pump (OLE DICH, Instrument makers APS, Denmark). The anode chamber and reservoir were purged with nitrogen gas before start new batch cycle. The cathode chamber was filled with 80 mL aniline wastewater and operated in batch mode. During the treatment process, fresh air was bubbled into the cathode providing oxygen at the rate of 16 mL min^{-1} except otherwise mentioned. All experiments were carried out in duplicate at ambient temperature (20 ± 2 ^{o}C). The cathode and anode were connected to a battery test system (Neware Battery Testing System TC53, Shenzhen, China), which was used as a power source (PS) to control the applied voltage and record the current of MEC (Li et al., 2014).

2.4. Analytical methods

The samples were taken from the MEC cathode chamber, and then were filtered through 0.45 µm filters. The H_2O_2 concentration was measured by UV-vis spectrophotometry (spectronic 20D+, Thermo Scientific) at 400 nm, using potassium titanium (IV) oxalate as colored indicator (Sellers, 1980). The concentration of aniline was determined by high performance liquid chromatography (HPLC) (Wang et al., 2011). The pH was measured using a pH meter (PHM 210 pH meter, Radiometer). Whereafter adding 1 M NaOH solution in the samples to adjust the pH at 11 to stop the Fenton reaction. Chemical oxygen demand (COD) was measured according to the standard method (A.W.W.A., 1998). The total organic carbon (TOC) was measured by Shimadzu TOC 5000 A. Current density was calculated based on the surface area of cathode. Energy consumption was mainly due to the pumping system besides power supply. The energy consumption for pumping system was estimated according to previous report (Zhang and Angelidaki, 2015). The calculations of degradation rate constant of aniline (k), COD and TOC removal efficiencies are shown in the Supplementary data.

3. Results and discussion

3.1. Performance of aniline wastewater treatment in MEC-Fenton

To evaluate the feasibility of this MEC-Fenton system for aniline wastewater treatment, aniline removal was conducted at 0.5 V, 16 mL min^{-1} air flow rate, 10 mM Fe^{2+} and initial pH 3. As shown in Fig. 2, aniline was rapidly degraded with removal efficiency of 97.1 ± 1.2% in 6 days, while the removal efficiency was only 8% for the system without Fe^{2+} (Control 1) and 3% for the system without cathodic aeration (Control 2). The results imply that the bipolar membrane MEC-Fenton system was efficient for aniline degradation.

Fig. 2. is here

3.2. Effect of initial pH

The electro-Fenton processes are generally performed at low pH to avoid the precipitation of ferric hydroxides. This requires pH adjustment before and after wastewater treatment. To study the effect of wastewater pH on the aniline removal, a group of experiments were conducted under various initial pH values (2, 3, 5 and 7.2) of aniline containing wastewater. The results are illustrated in Fig. 3. Firstly, experiments were performed without any pH adjustment at 7.2, which is the native pH value of aniline wastewater. The aniline removal efficiency just was 8% at this pH value. Comparatively, decrease of the initial pH value from 7.2 to 3 led to a sharp increase in the degradation efficiency of aniline. When the pH was decreased to 2, the aniline degradation efficiency of 97.1 ± 1.2% was obtained (Fig. 3a). The differences observed here may result from the different efficiency of Fenton reaction at different initial pH values. The results demonstrated the MEC-Fenton system constructed with bipolar membrane can be used to treat high concentration aniline wastewater efficiently with initial pH 2-3.

The variation trend of catholyte pH is shown in Fig. 3b. It was observed that pH of aniline wastewater in the cathode chamber increased slowly to 5.6 from the initial value of 3 after 6 days treatment. The pH increased to 10.7 from the initial values of 5 and 7.2 after 6 days. In order to investigate the effect of bipolar membrane on the cathodic pH, cation exchange membrane was used in a MEC as reference experiment, where the obvious removal of aniline was only observed for three days in MEC-Fenton with cation exchange membrane (Fig. S1. see Supplementary data). Furthermore, when using cation exchange membrane instead of bipolar membrane, ferric hydroxide was found in the cathode chamber after three days. The results demonstrated that the bipolar membrane could be used to help sustaining a lower catholyte pH without the need of extra acid dosage when the initial pH was 3. On the other hand, the formation of short-chain carboxylic acids during the mineralization of aniline such as maleic acid and oxalic acid (Anotai et al., 2006) could also contribute to the acidic pH. The anodic pH was maintained at 7.3-7.7 without significant changes. These results further demonstrated that the bipolar membrane is an effective separator in MEC-Fenton system.

Fig. 3. is here

3.3. Effect of air flow rate

The effect of air flow rate in the cathode on the degradation of aniline was investigated. It can be seen in Fig. 4, the optimum air flow rate observed was 16 mL min^{-1}. It could be due to that the increase of dissolved O_2 and mass transfer rate in the aniline wastewater improved the H_2O_2 production, and thus promoted the Electro-Fenton process. The decrease of aniline decay rate at a higher air flow rate can be explained as following. There was a saturated state for dissolved O_2 in the MEC-Fenton system, thus the accumulations of H_2O_2 hardly increased after dissolved O_2 was saturated (8.6 ± 0.2 mg L^{-1}). In addition, the resistance of the aniline wastewater also increased with the excessive mass of O_2 bubble in the cathode chamber, which could lead the less negative cathode potential (Fig. S2). As a result, slightly drop in the removal efficiency of aniline was observed at the higher air flow rate. Similar phenomena were observed in the Electro-Fenton system (Zhou et al., 2013). The trend of COD and TOC removal efficiency in Fig. 4b was consistent with the evolution of aniline concentration. The mineralization rate at 4, 8, 16 and 50 mL min^{-1} was 43.5 ± 2.3%, 68.2 ± 1.8%, 93.1 ± 1.2% and 83.9 ± 1.9% after 6 days, respectively. Moreover, the air flow rates could also affect the energy consumption in terms of pumping. These results indicated that setting an optimum air flow rate in the MEC-Fenton system could not only improve the treatment efficiency of the aniline wastewater but also reduce treatment cost.

Fig. 4. is here

3.4. Effect of applied voltage

Applied voltage is a critical parameter affecting the effectiveness of Electro-Fenton process as it controls the production of hydroxyl radicals. Therefore its influence on the degradation of aniline in the MEC-Fenton system was investigated under the optimal air flow rate of 16 mL min^{-1} and initial pH 3. As shown in Fig. 5, aniline removal efficiency was significantly enhanced when the applied voltage was increased from 0.3 to 0.5 V. However, further increase of applied voltage to 0.7 V led significantly in decrease of the aniline removal efficiency, which was probably due to the relatively faster increase of pH in the cathode (Fig. S3). In addition, the current density increased from 1.47 ± 0.03 to 3.35 ± 0.03 A m^{-2} with the increasing of applied voltage from 0.3 to 0.7 V (Fig. 5b). The cathode potential was -0.31 ± 0.01, -0.45 ± 0.01 and -0.60 ± 0.02 V at 0.3, 0.5 and 0.7 V (Fig. 5c), respectively. The corresponding COD removal efficiencies are presented in Fig. 5d. Similar behavior of aniline removal efficiencies under different applied voltages were observed. The trend was different with Electro-Fenton processes for aniline wastewater treatment. It could be due to that the performance of Electro-Fenton for pollutants degradation was highly dependent on the H_2O_2 production rate and hydroxyl radical ($^{\bullet}OH$) generation from the reaction between Fe^{2+} and H_2O_2 (Eq. 1). The •OH generation rate would increase with the increasing of H_2O_2 production rate. According to our previous study (Li et al., 2017a), the optimal cathode potential of the graphite plate for H_2O_2 production is ranging from -0.4 V to -0.5 V. Thus, the applied voltage of 0.5 V was the optimal for the aniline degradation in the bipolar membrane MEC-Fenton system.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (1)$$

Mineralization of organic pollutants with fast kinetics is highly desirable for contamination control. Here, the TOC removal efficiency was tested to evaluate the performance of MEC-Fenton for aniline mineralization (Fig. 5d). The TOC removal efficiency was 66.8 ± 3.1, 93.1 ± 1.2, 51.2 ± 1.9% at 0.3, 0.5 and 0.7 V after 6 days, respectively. The higher mineralization rate of aniline at 0.5 V could be due to the faster H_2O_2 production rate which is dependent mainly on the cathode electrode potential regulated by the external applied voltage. The results are similar with the trend of aniline removal efficiency. The removal rate constant of aniline degradation was 0.0097, 0.0166 and 0.0066

h^{-1} at 0.3, 0.5 and 0.7 V, respectively (Fig. S4). These results imply that aniline can be efficiently mineralized by the MEC-Fenton technology at 0.5 V. This behavior can be ascribed to the greater production rate of H_2O_2 at 0.5 V. The residual H_2O_2 in the treated aniline wastewater at different applied voltage were also measured (Fig. S5). The residual H_2O_2 concentration after MEC-Fenton treatment was less than 10 mg L^{-1}. The results also demonstrated the feasibility of the bipolar membrane MEC-Fenton system for efficient control of residual H_2O_2 level during aniline wastewater treatment.

Fig. 5. is here

3.5. Energy efficiency for aniline wastewater treatment

Energy consumption is one of the major concerns for wastewater treatment using Electro-Fenton technology, especially for recalcitrant pollutant degradation. In this bipolar membrane MEC-Fenton process, the optimal external voltage for aniline wastewater treatment was 0.5 V, which was much lower than that required for conventional Electro-Fenton process. The costs of the MEC-Fenton system mainly include the capital costs and the operating costs. The bipolar membrane MEC reactor capital costs are approx. 5544 € m^{-3} (in Denmark) (Zhang and Angelidaki, 2016). The operating costs mainly include reagent costs and energy consumption of the external power supply. The MEC-Fenton system degrade aniline only required energy consumption of 0.728 kWh kg^{-1}-aniline from the external power over a fed batch cycle, which was much lower than classical Electro-Fenton process treat aniline with a cost of 74 kWh kg^{-1}-aniline (Brillas and Casado, 2002). The energy consumption for pumping would be 0.374 kWh kg^{-1}-aniline. Meanwhile our estimates were based on small laboratory-scale reactor and did not include reagent, e.g.,

Na_2SO_4, $FeSO_4$. Nevertheless the above results suggest that the bipolar membrane MEC-Fenton system was a cost-effective method for aniline wastewater treatment.

3.6. Perspectives

The results in this study demonstrated that the bipolar membrane MEC-Fenton system was environment-friendly, efficient and low cost compared to conventional Electro-Fenton system. In this process, the MEC besides treating domestic wastewater in the anode chamber (the COD removal efficiency reached 80.5 ± 2.2% under 0.5 V), also mineralizes aniline from wastewater in the cathode chamber. It was proven that the operation of bipolar membrane MEC-Fenton greatly enhanced the treatment of aniline wastewater. Compared to other bio-Electro-Fenton system such as MFC-Fenton system, the bipolar membrane MEC-Fenton system has its own merits. Firstly, the degradation efficiency was greatly improved by adding low applied voltage (0.5 V) compared to MFC (Zhang et al., 2015). Secondly, the MEC-Fenton reactor with bipolar membrane requires lower dose of acid to adjust and control the pH of the aniline wastewater. Thirdly, the energy consumption was only 1.423 kWh kg^{-1}-TOC under optimal operation condition, which was much lower than that in Electro-Fenton process (45.8 kWh kg^{-1}-TOC) (Gao et al., 2015). In addition, compared with other methods for aniline removal (see table 1), the MEC-Fenton system has relative high removal rate, especially higher than that of the biodegradation method. All these advantages together suggest that the MEC-Fenton system has potential for cost-effective and efficient degradation of recalcitrant organic pollutants. Finally, this system also can be extended to treat other industrial wastewater such as pharmaceuticals wastewaters. Though promising, more efforts should be made to accelerate the industrial application, such as development of large scale system with continues-flow operation. Future work also should focus on the development of low cost cathode electrode with large surface such as three dimensional electrode, which may improve the H_2O_2 production rate and further enhance the aniline removal rate.

4. Conclusions

This study demonstrated that the MEC-Fenton system is an effective and environmentally friendly technology for aniline containing wastewater treatment. In such system, high concentration (4460 ± 52 mg L^{-1}) aniline was not only effectively degraded with removal rate of 30.1 ± 0.4 mg L^{-1} h^{-1}, but also highly mineralized with TOC removal efficiency of 93.1 ± 1.2% and k of 0.0166 h^{-1} at initial pH 3. Notably the energy consumption was only 1.423 kWh kg^{-1}-TOC. This work provides a cost-effective method for aniline degradation, which is also attractive and applicable for efficient treatment of industrial wastewater.

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Table 1. Performance of aniline removal using different technologies.

Method	Concentration (mg L^{-1})	Removal efficiency	Removal rate (mg L^{-1} h^{-1})	Energy consumption kWh kg^{-1}-aniline	Reference
Fenton	930	85.9%	798.9	-	(Anotai et al., 2006)
Electro-Fenton	1000	63%	315	74	(Brillas and Casado, 2002)
Biodegradation	300	87%	2.175	-	(Jin et al., 2012)
Fluidized-bed Fenton	930	97%	1804.2	-	(Anotai et al., 2010)
MFC-biodegradation	260.4±9.3	91.2±2.2%	1.65±0.04	-	(Cheng et al., 2015)
Electrocatalytic	3500	97.7%	683.9	36.2	(Li et al., 2016b)
Electrodialysis	1000	100%	6792.4	2.86	(Wang et al., 2016)
MEC-Fenton	4460±52	97.1±1.2%	30.1±0.4	1.10	This study

-: no report the energy consumption.

Figure Captions

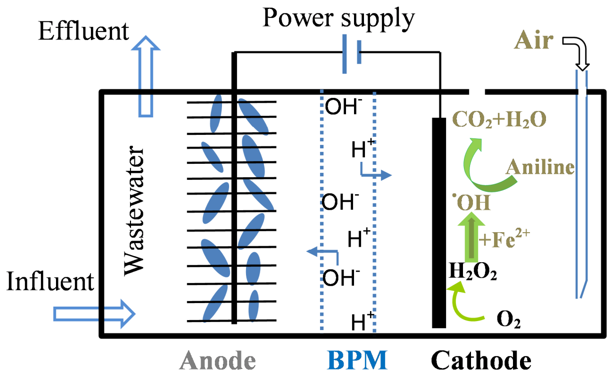
Fig. 1. Schematic illustration of the MEC-Fenton reactor with bipolar membrane (BPM).

Fig. 2. The performance of bipolar membrane MEC-Fenton system on the aniline degradation. Conditions: E =0.5 V, initial pH = 3 and air flow rate of 16 mL min^{-1}. (Control 1: without Fe^{2+}; Control 2: without cathodic aeration)

Fig. 3. The effect of initial pH on the performance of bipolar membrane MEC-Fenton system. Conditions: E = 0.5 V, air flow rate of 16 mL min^{-1}.

Fig. 4. The effect of air flow rate on the performance of bipolar membrane MEC-Fenton system. Conditions: E = 0.5 V, initial pH = 3.

Fig. 5. The effect of applied voltage on the bipolar membrane MEC-Fenton degradation of aniline.



Power supply
Effluent
Air
Wastewater
Influent
OH-
H+
OH-
H+
OH-
H+
CO2+H2O
Aniline
•OH
+Fe2+
H2O2
O2
Anode
BPM
Cathode

Fig. 1.

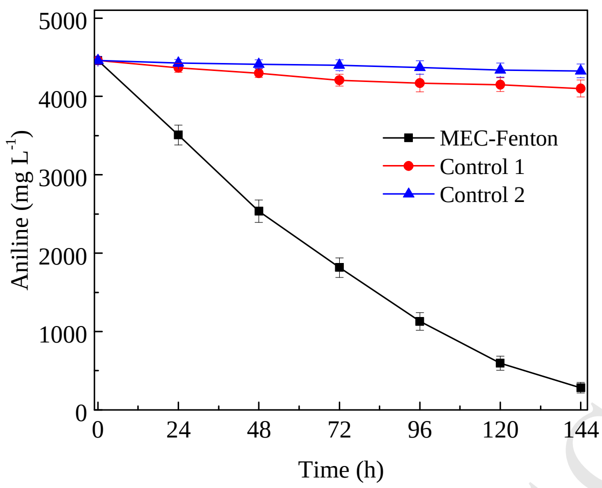

5000
4000
3000
2000
1000
0
Aniline (mg L-1)
0
24
48
72
96
120
144
Time (h)
MEC-Fenton
Control 1
Control 2

Fig. 2.

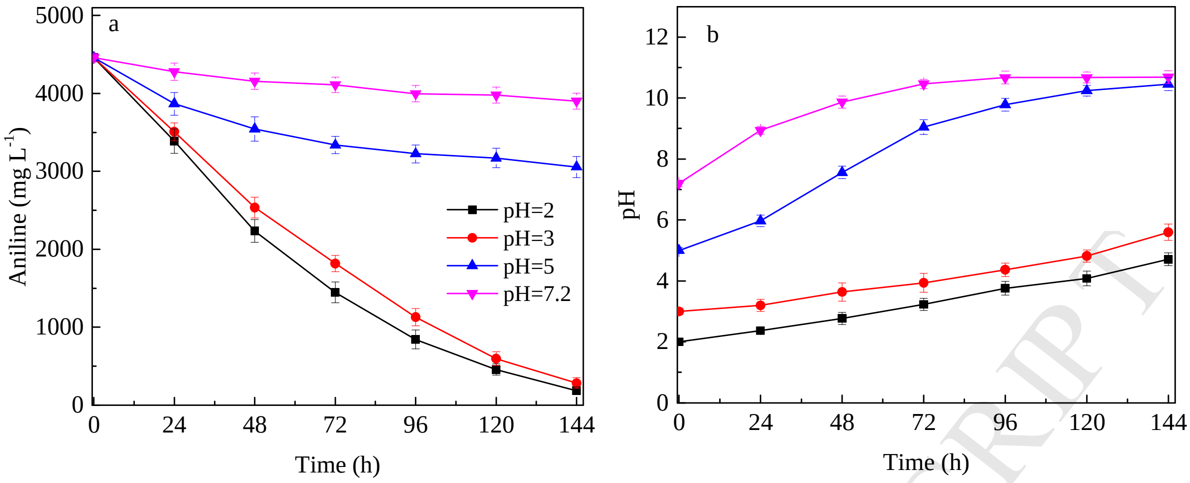

a
5000
4000
3000
2000
1000
0
Aniline (mg L-1)
pH=2
pH=3
pH=5
pH=7.2
0
24
48
72
96
120
144
Time (h)
b
12
10
8
6
4
2
0
pH
Time (h)

Fig. 3.

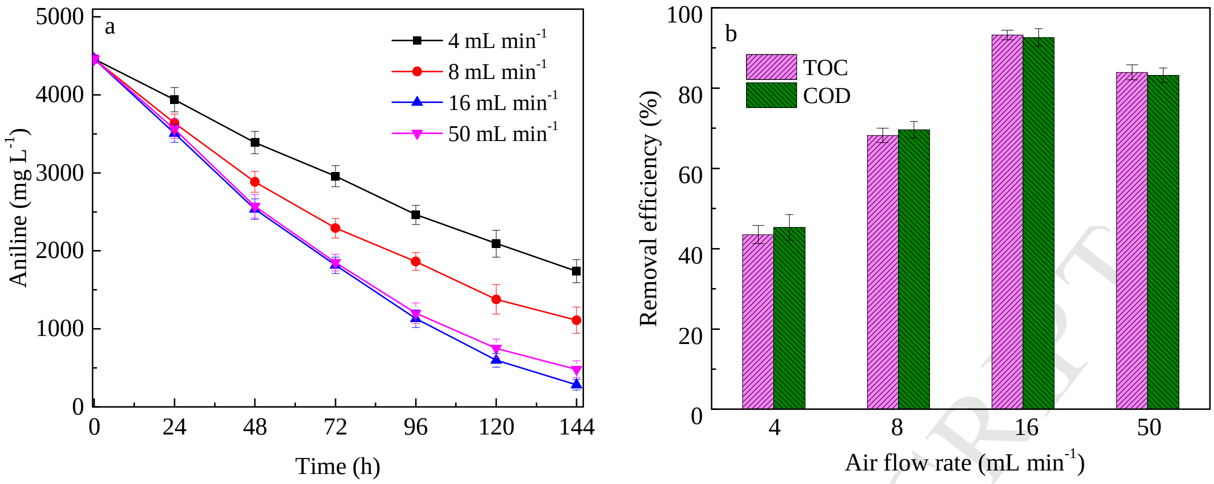
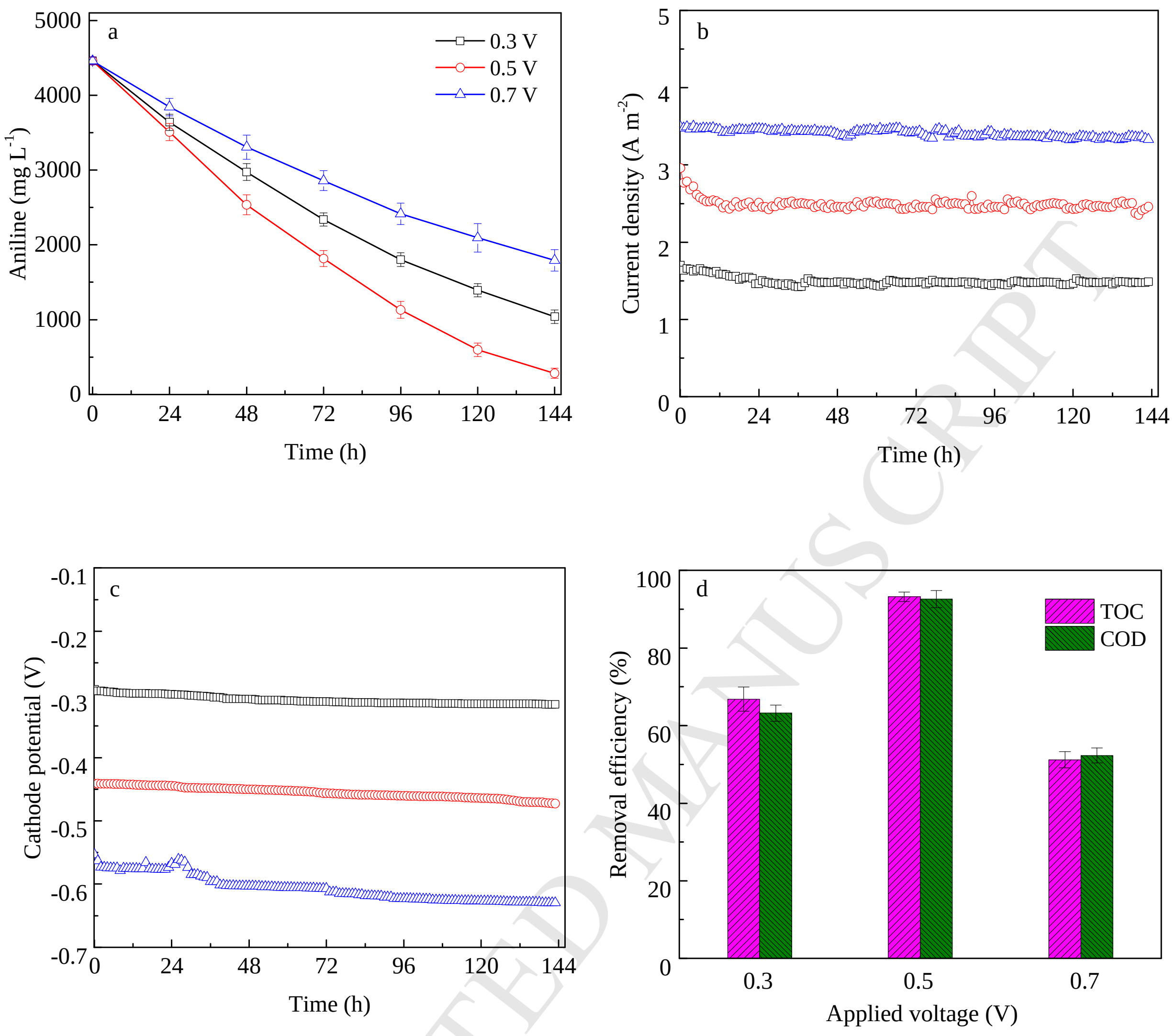

5000
4000
3000
2000
1000
0
Aniline (mg L-1)
0
24
48
72
96
120
144
Time (h)
a
4 mL min-1
8 mL min-1
16 mL min-1
50 mL min-1
100
80
60
40
20
0
Removal efficiency (%)
b
TOC
COD
4
8
16
50
Air flow rate (mL min-1)

Fig. 4.



a
5000
4000
3000
2000
1000
0
Aniline (mg L-1)
0.3 V
0.5 V
0.7 V
0
24
48
72
96
120
144
Time (h)
b
5
4
3
2
1
0
Current density (A m-2)
Time (h)
c
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
Cathode potential (V)
Time (h)
d
100
80
60
40
20
0
Removal efficiency (%)
TOC
COD
0.3
0.5
0.7
Applied voltage (V)

Fig. 5.

Highlights

- Novel MEC-Fenton process for the treatment of real aniline-contained wastewater.
- The bipolar membrane was an effective pH separator in MEC-Fenton process.
- High removal efficiency was achieved at relatively higher aniline concentration.
- Identified key factors affecting the aniline degradation in MEC-Fenton system.
- Efficient removal of aniline with low energy consumption in MEC-Fenton system.