



Degradation of organics in reverse osmosis concentrate by electro-Fenton process

Minghua Zhou^{a,b,*}, Qingqing Tan^{a,b}, Qian Wang^{a,b}, Yongli Jiao^{a,b}, Nihal Oturan^c, Mehmet A. Oturan^c

^a Key Laboratory of Pollution Process and Environmental Criteria, Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

^b Key Laboratory of Urban Ecology Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

^c Université Paris-Est Marne-la-Vallée, Laboratoire Géomatériaux et Environnement (LGE), 5 Boulevard Descartes, Marne-la-Vallée Cedex 2, France

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ABSTRACT

The present work studied, for the first time, the removal of organic pollutants from a high-salinity reverse osmosis (RO) concentrate by electro-Fenton approach using a graphite-felt as cathode. To gain insights into the process, the in situ generation of hydrogen peroxide was also investigated. The COD removal efficiency and energy consumption were optimized by investigating the effects of some important operating parameters such as ferric ion concentration, initial pH and cathodic potential. Under the conditions of cathodic potential at -0.72 V and Fe^{3+} concentration 0.2 mM, more than 62% COD could be removed in 3 h treatment, meeting the local wastewater discharge requirement (COD <50 mg/L). It confirmed the feasibility of electro-Fenton process for the treatment of RO concentrate accounting for its cost-effectiveness in wide pH ranges.

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1. Introduction

The ever-increasing application of reverse osmosis (RO) in municipal and industrial wastewater treatment has provided an affordable alternative for the sustainable reclamation of water resource, but simultaneously has brought about a large yield of RO concentrate, which is normally 5–25% of the feed stream and 4–20 times of the feed water in concentration [1]. The organic pollutants in the RO concentrate are difficult to be treated by conventional methods since this wastewater typically contains elevated salinity and many kinds of recalcitrant organics such as natural organic matters, pharmaceuticals and personal care products (PPCPs) and persistent organic pollutants (POPs) such as pesticides and/or synthetic dyes [2–4]. The direct discharge of RO concentrate to the aquatic environment will certainly cause severe ecotoxicological risk and environmental impact, and consequently it is vital to explore appropriate processes for the effective abatement of organics under an acceptable level.

Advanced oxidation processes (AOPs), generating hydroxyl radicals ($\cdot\text{OH}$) as non-selective oxidants, have been established to be highly efficient for the degradation of various refractory pol-

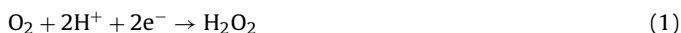
lutants. Several processes including ozonation [5], heterogeneous photocatalysis (UV/TiO₂) [6], sonolysis and their combination processes [7] have been investigated to be feasible in RO concentrate disposal. Recently, electrochemical advanced oxidation processes (EAOPs) have attracted considerable interests due to their simplicity and high efficiency in the electrochemical production of hydroxyl radical [2,4,8–10]. Hege et al. compared four anode materials for the electro-oxidative abatement of low-salinity RO concentrates, and verified boron doped diamond (BDD) was the best in successful elimination of the COD and color [8]. Dialynas et al. studied the treatment of dissolved organic carbon (DOC) in the RO concentrate by electrolysis, and observed up to 36% DOC removal at 17.8 A after 30 min treatment [9]. And more recently, the electrochemical destruction of N-nitrosodimethylamine in RO concentrates using BDD electrode has been investigated, demonstrating advantages over other AOPs [10]. Pérez et al. confirmed that the electrochemical oxidation on BDD was effective in eliminating COD and 10 emerging pollutants from RO concentrates that generated in tertiary water treatment [4]. In our previous work, the feasibility of the electrochemical treatment of RO concentrate was studied on BDD and two dimensionally stable anodes (DSAs), and revealed that the Ti/IrO₂-RuO₂ electrode showed the greatest potential for industrial application [2].

Compared to these anodic oxidation processes, electro-Fenton seems to be more attractive owing to its high mineralization effectiveness, no harmful chemicals additions and environmental compatibility, in which hydrogen peroxide is generated in situ by the reduction of oxygen on the cathode (Eq. (1)) and thus Fenton

* Corresponding author at: Key Laboratory of Pollution Process and Environmental Criteria, Ministry of Education, College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China. Tel.: +86 22 23507800; fax: +86 22 66229619.

E-mail addresses: zhoumh@nankai.edu.cn, skynumen@yahoo.com (M. Zhou).

reaction takes place in the bulk solution in the presence of ferrous ions (Eq. (2)) [11–15]:



In addition to the in situ and controlled production of H_2O_2 , one other particular advantage of this technology over conventional Fenton process is that, the Fenton reaction is more powerful since the continuous production of hydroxyl radical can be fulfilled by the electro-regeneration of ferrous ion through the cathodic reduction of Fe^{3+} (Eq. (3)) formed by Fenton's reaction (Eq. (2)) and thus decline the production of iron sludge.



Up to now, this process has been employed to degrade many kinds of organic pollutants including phenol and phenolic compounds, pesticide, dyes and PPCPs [11–13,16–18], however, to the best of our knowledge, no study on the RO concentrate treatment by this efficient process was well reported.

Therefore, in the present work, the objective was to study the viability of removing organic pollutants from a RO concentrate by the electro-Fenton process using a graphite-felt cathode to meet the local wastewater discharge requirement (i.e., chemical oxygen demand (COD) <50 mg/L). The effect of some operating parameters such as ferric ion (catalyst) concentration, pH, and cathodic potential on the COD removal and the energy consumption were investigated. To further gain insights into the application of electro-Fenton process, the generation of hydrogen peroxide and its current efficiency under different conditions were also disclosed.

2. Experimental

2.1. RO concentrate

The RO concentrate was collected from a RO process in a local steel plant in Tianjin, China. This wastewater was closed to neutral (pH 7.2–7.6) with a very high conductivity of 22300 $\mu\text{S}/\text{cm}$ due to the presence of Cl^- , Ca^{2+} and Mg^{2+} ions. The organic pollutants in the RO concentrate were complicated and biorefractory, identified mainly to be some straight-chain alkanes (e.g., eicosane, docosane and tetracosane) by GC–MS. The suspended solid (SS) was rather lower than 25 mg/L. The COD and BOD of the wastewater were about 120–150 mg/L and 15–18 mg/L, respectively, and total organic carbon (TOC) was about 25–35 mg/L. Therefore this wastewater was not easily to be treated to meet the local wastewater discharge requirement (COD <50 mg/L) by traditional methods such as biological treatment.

2.2. Experimental procedure

The experiments for hydrogen peroxide generation were conducted at room temperature in an undivided electrochemical cell using a CHI600D electrochemical workstation (Shanghai Chenhua, China) in a conventional three-electrode cell. The cathode of graphite-felt (Carbone Loraine, 15 cm \times 4 cm \times 0.5 cm) was selected as the working electrode, a platinum wire electrode (0.5 (i.d.) mm \times 37 mm) as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The counter electrode was placed in the centre with an inter-electrode distance of 2.45 cm to the cathode that covered the inner wall of the electrochemical cell. The experiments were performed in a 200 mL solution comprising Na_2SO_4 or NaCl as the supporting electrolyte in a batch mode with a constant magnetic stirring (300 rpm). Prior to the experiment, the solution pH was adjusted to 3 using H_2SO_4 or NaOH , and oxygen was sparged near the cathode at a desired flow rate for 10 min.

Then the experiment started once the electrochemical workstation turned on and the cathodic potential was kept at a suitable value. The electrochemical reactor was similar with our previous work and the sketch of could be seen in Ref. [19].

The procedures for wastewater treatment were similar, except that the solution used was the RO concentrate. After the pH adjusted to a desirable value, suitable amount of ferric sulfate (analytical grade, Tianjin Chemicals Co.) were introduced into the solution. At certain time intervals, samples were taken from the solution and then filtered by 0.45 μm membrane for analysis, and the electric charges were recorded.

2.3. Analysis methods

Hydrogen peroxide concentration was determined spectrophotometrically using the potassium titanium (IV) oxalate method ($\lambda = 402 \text{ nm}$) [20]. The current efficiency (CE) for hydrogen peroxide generation is defined as follows [15]:

$$\text{CE} = \frac{nF c_{\text{H}_2\text{O}_2} V}{\int_0^t I dt} \times 100 \quad (4)$$

where $c_{\text{H}_2\text{O}_2}$ is the concentration of H_2O_2 (mol/L), F is the Faraday constant (96,486 C/mol), n is the number of electrons transferred for oxygen reduction to H_2O_2 , V is the bulk volume (L), I is the applied current (A), and t is electrolysis time (s).

The COD test is difficult due to the large content of Cl^- , therefore, a new method of COD test for the wastewater with high salinity and low COD has been applied [21]. The COD was measured by a commercial COD detector (HACH, DRB 200, DR/890 Colorimeter, USA).

The general current efficiency (GCE) for the RO wastewater treatment was calculated using the following equation:

$$\text{GCE} = \frac{(\text{COD}_0 - \text{COD}_t)}{8It} \cdot F \cdot V \cdot 100\% \quad (5)$$

where $(\text{COD})_0$ and $(\text{COD})_t$ are the COD (g/L) value at initial time and given time t , respectively, and other parameters are the same as described above.

The electrochemical energy consumption (EEC, kWh/kg COD) was determined according to:

$$\text{EEC} = \frac{I \times U \times t \times 1000}{(\text{COD}_0 - \text{COD}_t) \times V} \quad (6)$$

where U is the applied voltage (V), and other parameters are the same as stated above.

3. Result and discussion

3.1. Hydrogen peroxide generation

The performance of wastewater treatment by electro-Fenton is deemed to be related with hydrogen peroxide, which determines the amount of hydroxyl radical that generated. Fig. 1 shows the generation of hydrogen peroxide under different sparged oxygen flow rates. Unsurprisingly, it increased with the sparged oxygen flow rate until 0.6 L/min, after which the enhancement was not so obvious. This behavior could be explained by the increase in dissolved oxygen concentration for hydrogen peroxide synthesis. These outcomes could also be verified by the tendency for current efficiency (CE) under different oxygen sparged flow rates (Fig. 1b), which showed no substantial difference under the oxygen sparged flow rate of 0.6 and 0.7 L/min. That meant the value of 0.6 L/min was enough to saturate the solution. At the oxygen sparged flow rate of 0.6 L/min, the CE decreased dramatically from about 55% to about 30% in 1 h, and then kept relatively stable at about 25%. Therefore,

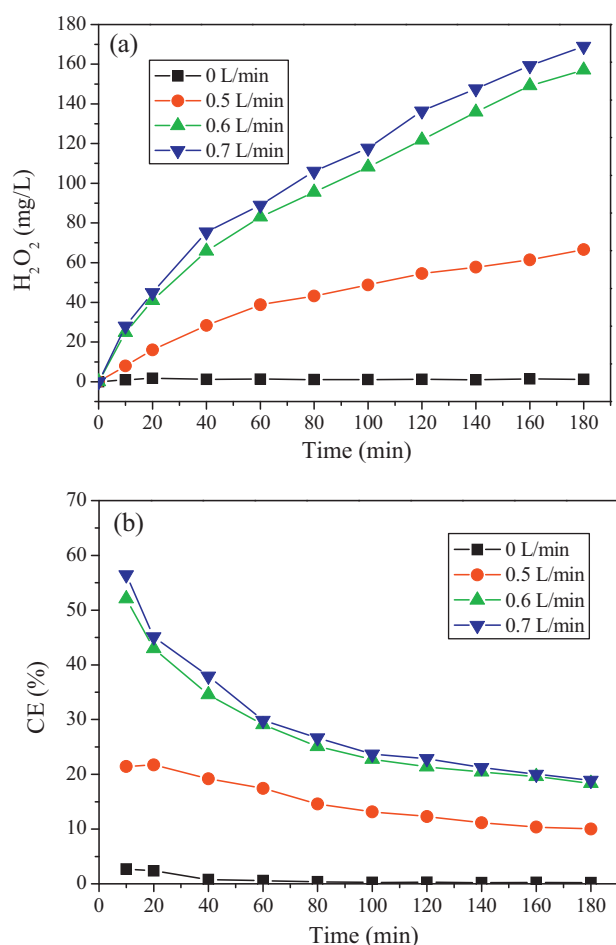


Fig. 1. The evolution of H₂O₂ (a) and CE in function of oxygen sparged rates. Operating conditions: pH=3, [Na₂SO₄]=0.1 mol/L, V=0.2 L, and cathode potential = -0.72 V.

in the following experiments, we adopted the oxygen sparged flow rate at 0.6 L/min in consideration of cost.

It was also observed that the hydrogen peroxide generation rate was relatively high in the first 60 min but after that the accumulation rate was decreased. This phenomenon had been observed by many other investigators, and they attributed it to the self-decomposition of hydrogen peroxide at higher concentrations (Eq. (7)) [15,22],



Another reason may be hydrogen peroxide oxidation at the anode:



The sparged oxygen flow rate being larger, no plateau corresponding to the steady-state H₂O₂ concentration was observed as acknowledged in some other works [15,22], since the generation rate was higher than that of decomposition during the investigated time periods.

It has been verified that cathode material plays an important role on the generation rate of hydrogen peroxide. In literature, graphite [23,24], graphite-PTFE [15], gas diffusion electrode [24,25], reticulated vitreous carbon [26], activated carbon fiber felt [27], carbon-felt [28,29] as well as graphite-felt [30] and carbon sponge [22] have been explored as cathode materials. Pozzo et al. concluded that the gas diffusion electrode displayed a higher selectivity for hydrogen peroxide production than that a graphite

Table 1

The evolution of hydrogen peroxide and CE in two electrolytes.

Time (min)	H ₂ O ₂ (mg/L)		CE (%)	
	Na ₂ SO ₄	NaCl	Na ₂ SO ₄	NaCl
10	24.77	13.24	52.06	32.96
20	40.87	20.36	42.96	25.34
40	65.78	36.55	34.57	22.75
60	82.96	51.78	29.07	21.48
80	95.49	70.04	25.09	21.79
100	108.1	84.05	22.73	20.92
120	121.8	98.04	21.35	20.34
140	135.8	106.1	20.40	18.86
160	149.2	113.6	19.60	17.68
180	157.0	123.0	18.35	17.01

Conditions: oxygen sparging rate 0.6 L/min, cathodic potential -0.72 V, initial pH 3, supporting electrolyte: 0.1 M, stirring rate 300 rpm.

electrode [24]. Gallegos and Pletcher adopted a reticulated vitreous carbon cathode to generate H₂O₂ in a divided system using a relatively expensive membrane, which should restrict its practical application in wastewater treatment, though the H₂O₂ generation rate was high up to 7.3 mg/L/h/cm² [26]. Wang et al. used an activated carbon fiber as the cathode, obtaining a H₂O₂ generation rate of about 0.34 mg/L/h/cm² [27]. In the present work, a H₂O₂ generation rate of about 0.88 mg/L/h/cm² (157 mg/L for 60 cm² cathode in 3 h) was achieved on this commercial graphite-felt cathode in an undivided cell. This graphite-felt cathode with a large tri-dimension active surface was verified to be efficient on ferric ion electrochemical reduction to ferrous ion [25]. Our previous work confirmed that the reduction of ferric ion at the graphite-felt cathode was very fast, and only ferrous ion was detected after electrolysis 20 min [31]. Thus the Fenton reaction could be propagated in a catalytic way from Fe²⁺ regeneration, and promoted the organics degradation rate by avoiding formation of stable Fe³⁺ complexes and thus the production of iron sludge [11,19]. Therefore, the present electrode system was easy to be scale up with a satisfactory performance.

Due to the presence of NaCl in the RO concentrate, it is necessary to explore the effect of electrolytes on hydrogen peroxide generation. Table 1 lists the formation of hydrogen peroxide in two electrolytes of NaCl and Na₂SO₄ with the same concentration of 0.1 M. It was observed that both H₂O₂ generation and its current efficiency were similar in tendency but a little different on quantity. After 3 h electrolysis, the hydrogen peroxide generated in the NaCl solution was about 123 mg/L, which was 21.7% less than that in the Na₂SO₄ electrolyte. This fact agreed well with other previous finding [22], and might be due to the difference of the ionic strength of these two supporting electrolytes.

3.2. Effect of Fe³⁺ concentration on RO concentrate treatment

In a conventional Fenton reaction, the molar ratio of H₂O₂/Fe²⁺ was very crucial in wastewater treatment. This is not the case of electro-Fenton process, because H₂O₂ reacts with Fe²⁺ (in excess in solution) since its formation, following to Fenton's reaction, its concentration is very low and thus avoiding the scavenging reaction with •OH (Eq. (9)). It was reasonable to assume that the electrochemical formation of hydrogen peroxide was equal under the same operating parameters such as pH, cathodic potential and oxygen sparged flow rate. Fig. 2 shows the effect of Fe³⁺ on the removal of COD in the RO concentrate under the same other operating parameters. The results also indicated that suitable Fe³⁺ addition is very important in electro-Fenton process. In the case of low Fe³⁺ concentration, the generation of Fe²⁺ (Eq. (3)) would be also relatively slow, which indicating the H₂O₂ would be over amount. It supposed that hydrogen peroxide would react with the hydroxyl

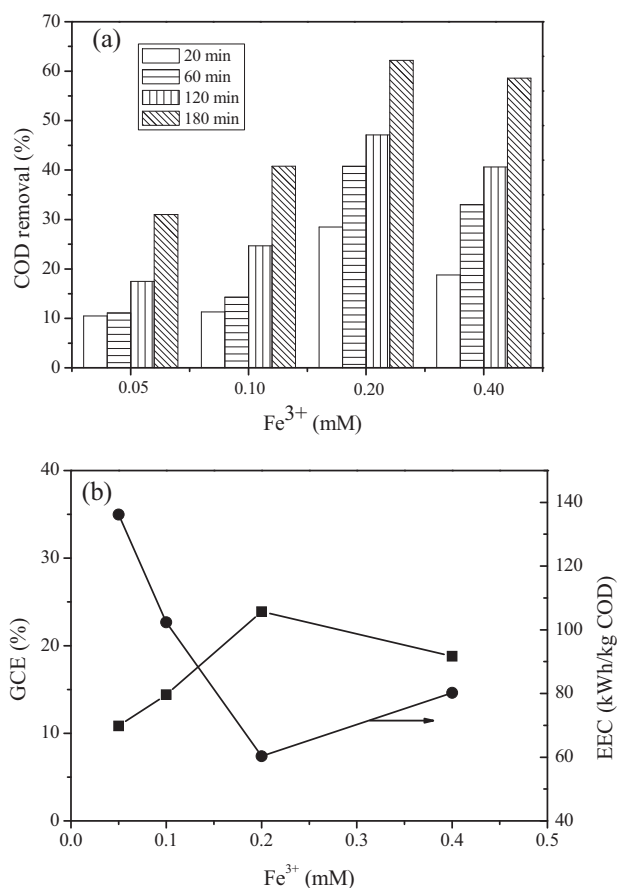


Fig. 2. Effect of Fe³⁺ (as catalyst) concentration on COD removal (a) and ICE, EEC (b). Operating conditions: pH = 3, V = 0.2 L, O₂ sparged flow rate = 0.6 L/min, stirring rate = 300 rpm, and cathode potential = -0.72 V.

radical that produced by Fenton's reaction in the following way (Eq. (9)),



This scavenging reaction consuming hydroxyl radical led to the decay of COD removal performance since HO₂· was regarded as an oxidant with less oxidation power than hydroxyl radical. With the increase of Fe³⁺ concentration from 0.05 mM to 0.2 mM, more hydroxyl radical was produced by the Fenton's reaction, and consequently an enhanced COD removal efficiency was observed. In this case, more than 62% COD was removed, i.e., the effluent COD could reach lower than the local wastewater discharge limit (COD < 50 mg/L). However, when Fe³⁺ concentration was higher than 0.2 mM, the COD removal efficiency was found decreased, which might be elucidated that an excess of ferric ion (also excess of ferrous ion formed continuously following electrochemical reduction of ferrous ions (Eq. (3))) would consume the strong oxidant (hydroxyl radical) in the following way (Eq. (10)) [12,16].



Such a phenomena was also observed on other kinds of wastewater treatment (e.g., dye) using the same cathode of graphite-felt [22,29].

Fig. 2b shows the effect of Fe³⁺ on GCE and electrochemical energy cost (EEC) evolution, supporting that ferric ion of 0.2 mM is the optimum concentration value. At a low ferric concentration, the GCE was relatively low (about 10%), while the EEC was higher than 140 kWh/kg COD. At the ferric ion of 0.2 mM, the GCE was the highest and the EEC was about 60 kWh/kg COD. In our previous work

on the similar RO wastewater treatment by BDD anodic oxidation, though the wastewater could reach the local discharge limitation, the EEC would be higher than 200 kWh/kg COD. And the anodic oxidation on Ti/IrO₂-RuO₂ and Ti/IrO₂-Ta₂O₅ could not reach the wastewater discharge level though the EEC could be lower than 50 kWh/kg COD under the low current of 25 mA [2]. These results comparison confirmed that the electro-Fenton process was more cost-effective.

3.3. Effect of cathodic potential

The cathodic potential determines the formation and current efficiency of hydrogen peroxide, and thus affects the wastewater treatment performance. As shown in Fig. 3a, the COD removal at the cathodic potential of -0.6 V was observed about 15–25% less than that at -0.72 V. However, for the cathodic potential at -0.86 V, the enhancement on the COD removal was insignificant. This can also be confirmed by the GCE and EEC in Fig. 3b. A higher cathodic potential also led to a higher current, this was why the GCE for the cathodic potential at -0.86 V was a little lower than that at -0.76 V.

To better disclose the performance difference among three cathodic potentials (-0.60, -0.72 and -0.86 V), the formation and current efficiency of hydrogen peroxide in 0.1 M Na₂SO₄ were investigated, as shown in Fig. 3c and d, respectively. It was observed that both the hydrogen peroxide concentration and CE greatly improved when the cathodic potential decreased from -0.6 V to -0.72 V, which was in agreement with the trend for the COD removal. This fact was reasonable since a higher current density was observed when applied a more negative cathodic potential. And our previous work also supported that high current density benefited the formation of hydrogen peroxide [29]. However, as shown in Fig. 3d, the CE enhancement was insignificant when further applied the cathodic potential at -0.86 V. This might be related with side reactions because further decrease in the cathodic potential would lead to the enhancement of side reactions of hydrogen or water formation as shown in Eqs. (11) and (12) [15,26],



These side reactions probably induced the decrease of the GCE for the degradation of organics, and thus the increase of EEC. Account for these effects, it would be optimum to select the suitable cathodic potential of -0.72 V for the RO concentrate treatment.

3.4. Effect of pH

It is well recognized that pH plays much important role in Fenton and electro-Fenton process, and pH around 3 has been widely accepted as the optimum condition for wastewater treatment [32]. Fig. 4a shows the effect of initial pH on the COD removal in the RO concentrate. It also verified that the wastewater treatment performed the best at initial pH 3. However, the performance difference between 3 and 7 was not so obvious, also confirmed by GCE and EEC in Fig. 4b. These outcomes might be explained by the following two aspects.

The first aspect is related to the formation of hydrogen peroxide. As shown in Fig. 4c and d, it indicated that the solution pH did not dramatically influence the generation of H₂O₂ in 0.1 M Na₂SO₄, and favored its accumulation at high initial pH. In agreement with the findings of Özcan et al. [22], this effect might be owned to the decrease of side reactions (Eqs. (12) and (13)) when the solution pH increased.



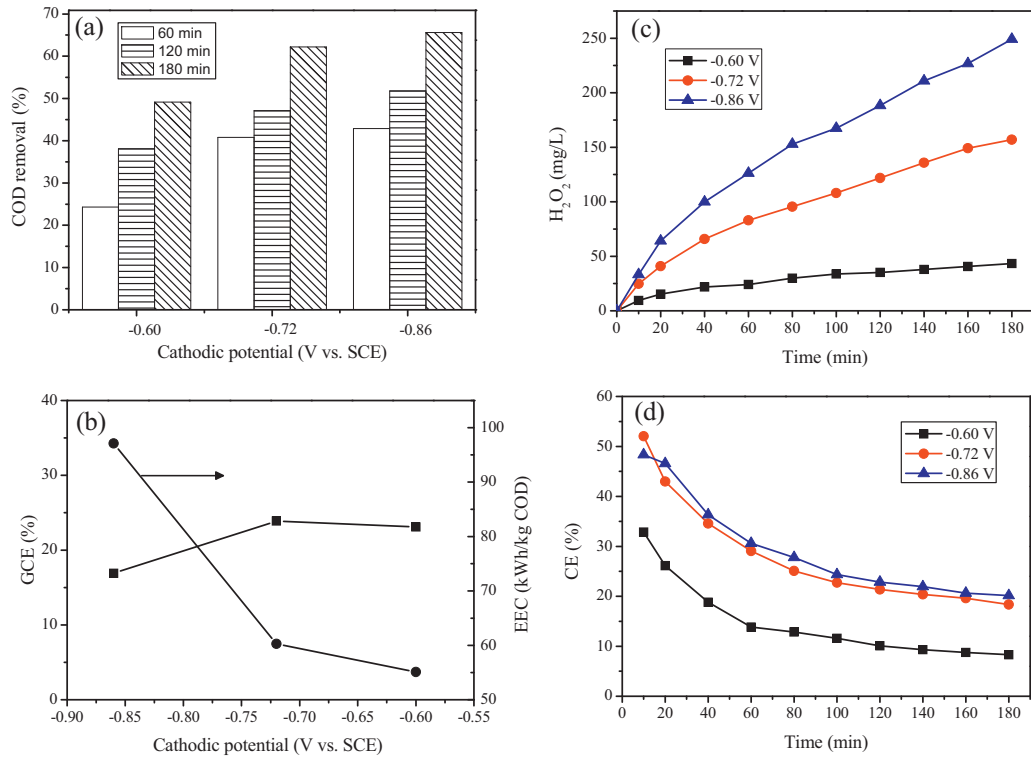


Fig. 3. Effect of cathode potential on COD removal (a), ICE and EEC (b), hydrogen peroxide (c) and EC evolution (d). Operating conditions: pH = 3, V = 0.2 L, O₂ sparged flow rate = 0.6 L/min, initial Fe³⁺ concentration = 0.2 mM, and stirring rate = 300 rpm.

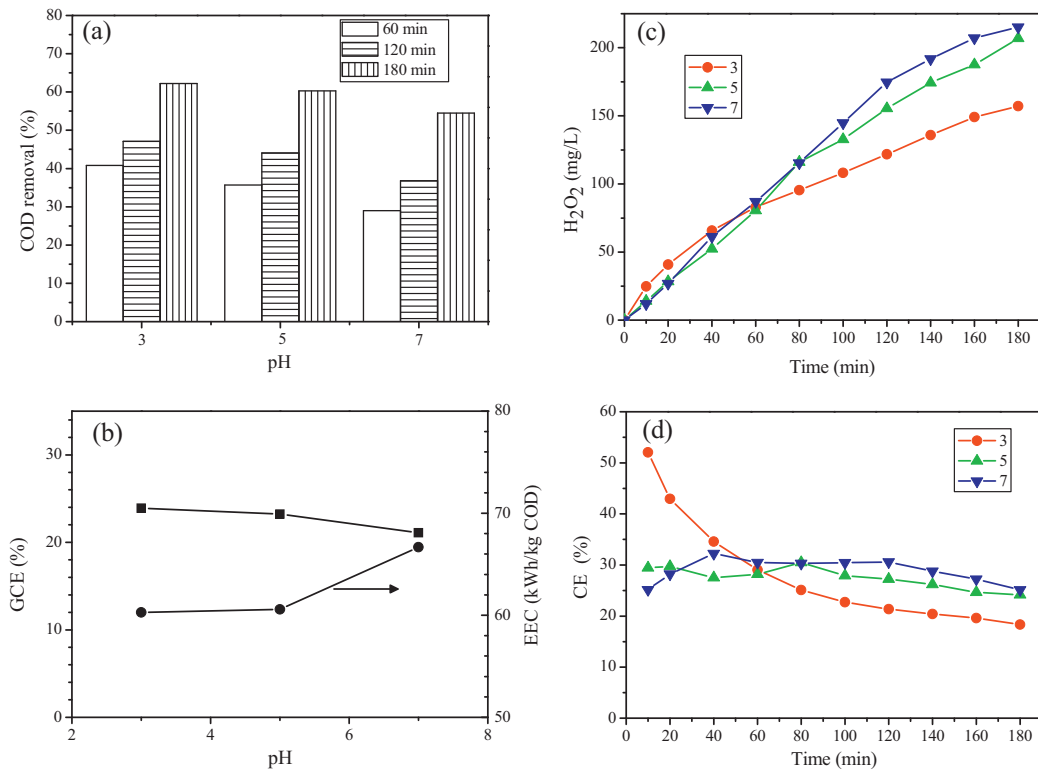
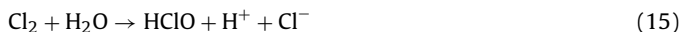


Fig. 4. Effect of initial pH value on COD removal (a), ICE and EEC (b), hydrogen peroxide (c) and EC evolution (d). Operating conditions: V = 0.2 L, O₂ sparged flow rate = 0.6 L/min, initial Fe³⁺ concentration = 0.2 mM, stirring rate = 300 rpm, and cathode potential = -0.72 V.

The second aspect might be related to the generation of active chlorine by anodic oxidation. The presence of chloride in RO concentrate facilitates indirect oxidation by the electro-generation of active chlorines (Eqs. (14) and (15)) such as hypochlorite, chlorine dioxide and chlorine, which could greatly improve the overall electrochemical abatement of organic pollutants [33,34].



It is known that the predominant chlorine species present at the pH range 1–3 is chlorine, at pH range 5–7 is HClO, while above 8 it is ClO^- [35]. So in the present work, the main product at pH 5–7 should be HClO, which greatly improved the indirect oxidation, by balancing the negative effect on treatment efficacy due to the decrease of irons in the solution by increasing the pH.

These two effects made the electro-Fenton performed not much different at initial pH 3–7, supporting that this process was cost-effective for RO wastewater treatment since no pH adjustment was necessary.

4. Conclusions

The removal of organics from the RO concentrate was firstly carried out by electro-Fenton process using a graphite-felt cathode, and the following conclusions could be drawn,

- (1) The hydrogen peroxide could be effectively generated using this cathode. Under the conditions of cathodic potential -0.72 V , initial pH 3 and the oxygen sparged flow rate of 0.6 L/min , the hydrogen peroxide concentration could reach over 150 mg/L in 3 h.
- (2) Parameters such as Fe^{3+} (catalyst) concentration and cathodic potential strongly influenced the performance of RO concentrate treatment by electro-Fenton process. Suitable Fe^{3+} additions and cathodic potential would help to improve the treatment efficiency. Moreover, the process showed a stable performance in a wide pH range 3–7.
- (3) The COD removal achieved the best performance under the conditions of cathodic potential -0.72 V , Fe^{3+} concentration 0.2 mM , initial pH 3, in which more than 62% COD could be removed, and could meet the local wastewater discharge requirement. The energy consumption for this wastewater can be lower than 60 kWh/kg COD .

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