Journal of Applied Electrochemistry (2007) 37:385–393
DOI 10.1007/s10800-006-9268-y

The "In-cell" and "Ex-cell" Fenton treatment of phenol, 4-chlorophenol and aniline

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Received 7 March 2006; accepted in revised form 17 October 2006

Key words: aniline, electro-Fenton, gas-diffusion electrodes, hydrogen peroxide, phenol, 4-chlorophenol

Abstract

A comparative study of phenol, 4-chlorophenol and aniline degradation with the electro-generation of H_2O_2 at gas-diffusion electrodes was carried out under three different conditions: electro-Fenton® treatment in an undivided cell; electro-Fenton treatment in the catholyte of a membrane cell divided by a proton-exchange membrane (in-cell electro-Fenton membrane process); and a treatment of polluted solution in the cathode space of a membrane cell with the generation of H_2O_2, followed by the addition of Fe(II) salt in the other reactor (ex-cell electro-Fenton process). An optimized cell design with no gap between the membrane and the anode, along with the appropriate choice of supporting electrolytes, ensured a voltage reduction with a membrane cell in comparison with that of an undivided cell. The accumulation of hydrogen peroxide in concentrations sufficient for the almost complete destruction (90–98%) of aromatic organic pollutants was achieved in all cases but the ex-cell process with the preparative electrolysis in the pilot scale membrane reactor separated by the proton-exchange membrane MK-40 showed higher treatment efficiency and lower specific energy consumption in comparison with known technologies. Damage of the gas-diffusion layer was observed in some tests which could be caused by alkaline conditions in the pores of the gas-diffusion cathode (GDE). The pH indicator paper showed a color specific for alkaline media in contact with the GDE treated in the solution with pH 3 in the bulk. A possible explanation could be that even in acid media, hydrogen peroxide generation in pores of the gas diffusion layer proceeds with formation of HO_2^- which is common for alkaline media and consecutive protonation occurs at the interface with the acid solution.

1. Introduction

The hydroxyl radical, a powerful oxidant ($E^0_{\mathrm{pH}}\,0 = 2.8$ V vs. SHE) obtained in the Fenton reaction by the catalytic destruction of hydrogen peroxide with Fe^{2+} [1, 2] is known to be effective in the mineralization of the aromatic organic substrates present in effluents with the conversion of organic carbon into carbon dioxide [3]. The Fenton treatment includes the reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^- \quad k = 76.5\,M^{-1}\,s^{-1} \tag{1}$$

$$Fe^{2+} + OH^* \rightarrow Fe^{3+} + OH^- \tag{2}$$

$$H_2O_2 + OH^* \rightarrow HO_2^* + H_2O \tag{3}$$

$$Fe^{2+} + HO_2^* \rightarrow Fe^{3+} + HO_2^- \quad k = 1.2 \times 10^6\,M^{-1}\,s^{-1} \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^* + H^+ \quad k = 2 \times 10^{-3}\,M^{-1}\,s^{-1} \tag{5}$$

$$Fe^{3+} + HO_2^* \rightarrow Fe^{2+} + H^+ + O_2 \tag{6}$$

The on-site generation of hydrogen peroxide by means of the electrochemical reduction of oxygen

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \text{ (acid solutions)}, \quad E^0 = 0.67\text{V (SHE)} \tag{7}$$

proceeds with commercially viable current densities at a gas-diffusion cathode (GDE) which is characterized by an extended intrinsic surface area of the catalytically active hydrophilic layer on the side of the carbon cloth matrix facing the solution. The PTFE impregnated hydrophobic reverse side of the GDE serves to supply oxygen to the 3-phase interface.

Brillas and co-workers [4–8] were first to use gas-diffusion electrodes in effluent treatment processes. The results of the systematic investigation of H_2O_2 generation at the GDE in the treatment of 4-chlorophenol, aniline and 4-chloroaniline with Fe^{2+} ions added to a 0.05 M Na_2SO_4 solution in an undivided cell prior to electrolysis (electro-Fenton® process) were reported. They also reported the results of H_2O_2 generation combined with Fe^{2+} generation by means of the anodic dissolution of an iron electrode ("Peroxi-coagulation" process), and electro-Fenton processes with UV radiation ("Photoelectro-Fenton"). The peroxi-coagulation process was found to have the highest oxidative power allowing the removal of 91% of 1000 ppm aniline at 20 A load in 1 h at 39 kW h m^{-3} energy cost and some intermediates coagulated with $Fe(OH)_3$.

The electrogeneration of hydrogen peroxide for the mineralization of formaldehyde, phenol, cresol, catehol, quinon, hydroquinon, aniline, oxalic acid and azo-dyes using Fe(II) as a catalyst was studied by Pletcher et al. [9, 10].

Taking into account that the subsequent Fenton reactions of the electro-generated hydrogen peroxide with iron salts can proceed both inside the electrochemical cell (in-cell electro-Fenton process) and in a separate reactor (ex-cell process), a comparative study of the phenol, 4-chlorophenol and aniline degradation was carried out with the electrogeneration of the H_2O_2 at the GDE for three different conditions:

1. Electro-Fenton® treatment of polluted water in an undivided cell with a 2 mm inter-electrode gap with the addition of 1 mM Fe (II) in 1 g l^{-1} Na_2SO_4 supporting electrolyte.
2. In-cell electro-Fenton treatment of polluted water in a cathode compartment of the membrane cell divided by the MK-40 PEM with the addition of 1 mM Fe(II) to the catholyte with 1 g l^{-1} NaCl supporting electrolyte and 1 M H_2SO_4 used as an anolyte;
3. Ex-cell Fenton treatment of the polluted solution with H_2O_2 electrogenerated in 1 g l^{-1} NaCl catholyte of a membrane cell and with the addition of ferrous salt in Fe(II) : H_2O_2 = 1:1 molar ratio and mixing for 1 h in an other reactor.

One g l^{-1} NaCl was used as a supporting electrolyte in the cathode chamber of a membrane cell as it is cheaper, has higher electrical conduction, and bears a greater similarity to the practical conditions of industrial wastewater than the 0.05 M Na_2SO_4 used in previous studies. The price of 7.1 kg m^{-3} sodium sulfate makes the electrochemical generation of H_2O_2 non-competitive with the price of commercially available hydrogen peroxide produced in industry by means of the chemical reduction of oxygen by hydrogen with antraquinone as a catalyst (cyclic reduction of antraquinone by hydrogen and oxidation of antrahydroquinone). Additional contamination of the wastewater with this salt is another drawback. On the other hand, the addition of sodium chloride to the undivided cell is not reasonable as interference with the produced hypochlorite ion leads to the destruction of the electro-generated hydrogen peroxide:

$$H_2O_2 + NaClO \rightarrow NaCl + O_2 + H_2O \qquad (8)$$

This reaction does not occur in the catholyte of the membrane cell which makes sodium chloride desirable as a supporting electrolyte.

2. Experimental

2.1. *Chemicals and analytical procedures*

All solutions were prepared using distilled water and chemical grade reagents. Sulfuric acid was supplied by PFP, phenol, 4-chlorophenol and aniline by Junsei Chem Co., iron (II) sulfate by Shinyo Pure Chem. Co. Ltd, (Japan) and sodium chloride and sodium sulfate by Jin Chemical Pharm.Co. Ltd (S. Korea).

The solution pH was measured using an ORION 420A + pH meter. The hydrogen peroxide concentration was measured using a standard potassium permanganate titration method. The organic content of the solution was measured by Chemical Oxygen Demand (COD), which was monitored by a standard method based on the oxidation of the organic content of the sample with potassium dichromate in 50% sulfuric acid [11, 12] using a Hach model DR/4000 U spectrophotometer. A total organic carbon (TOC) analysis was carried out with a Shimadzu 5000 A analyzer.

2.2. *Electrochemical reactor and electrodes*

Pilot tests were carried out using a filter-press type cell [13]. The solution was re-circulated between the reservoir and an undivided cell. The membrane cell had a 2 mm gap between the gas-diffusion electrode and the proton-exchange membrane. In all cases we used GDE supplied by Electrocell AB (Sweden) which consisted of carbon-PTFE cloth coated with Black Pearls 2000 carbon black. The MK-40 type PEM was fixed with no gap on the surface of a Ti-IrO_2-SnO_2 catalytic stable mesh anode manufactured by TECHWIN Co. Ltd. [14–16]. Both the anode and the cathode were of 100 cm^2 (10 × 10 cm) visible surface area. 1 M H_2SO_4 anolyte was recirculated between the reverse side of the anode and the reservoir. O_2 gas of 95% purity was supplied to the GDE gas chamber at 2 l min^{-1} at 0.1–0.14 atm pressure from a WH-7 type Pressure Swing Adsorption (PSA) oxygen generator produced by Won Hi Tech. Corp. DC power was taken from a HS-SCP type rectifier (Hyun Sung Co.)

3. Results and discussion

3.1. *Phenol treatment*

Results of the COD removal in the electro-Fenton® treatment of 282 ppm C_6H_5OH in 1 g l^{-1} Na_2SO_4

supporting electrolyte in an undivided cell at pH 3 and 20 °C are shown in Figure 1(a), curve 1. These tests were carried out using a current density of 0.05 A cm^{-2} (current 5 A) and at 7.5–6.6 V.

Curve 2 of Figure 1(a), shows the results of the in-cell electro-Fenton treatment in the cathode department of the membrane cell with 1 g l^{-1} NaCl as supporting electrolyte and 1 mM $FeSO_4$ added at 4.64–4.54 V, while curve 3 of Figure 1(a) shows the results of the ex-cell Fenton treatment at Fe (II) : H_2O_2 = 1:1 molar ratio of the solution, treated previously in the cathode chamber with the same initial amount of NaCl and phenol (Table 1). 1 l of solution was electrolyzed in all three cases in batch re-circulation mode and the decay of the volume (50 ml on the each sample) was taken into account when the energy cost and treatment efficiency were calculated according to the equations suggested in [8] with COD instead of TOC:

$$\text{Energy cost (kW h m}^{-3}) = [\text{U (V)} \times \text{I (A)} \times \text{t (h)/volume (l)}] \times [\text{COD}_{\text{in}}/\Delta(\text{COD})_{\text{exper}}] \quad (9)$$

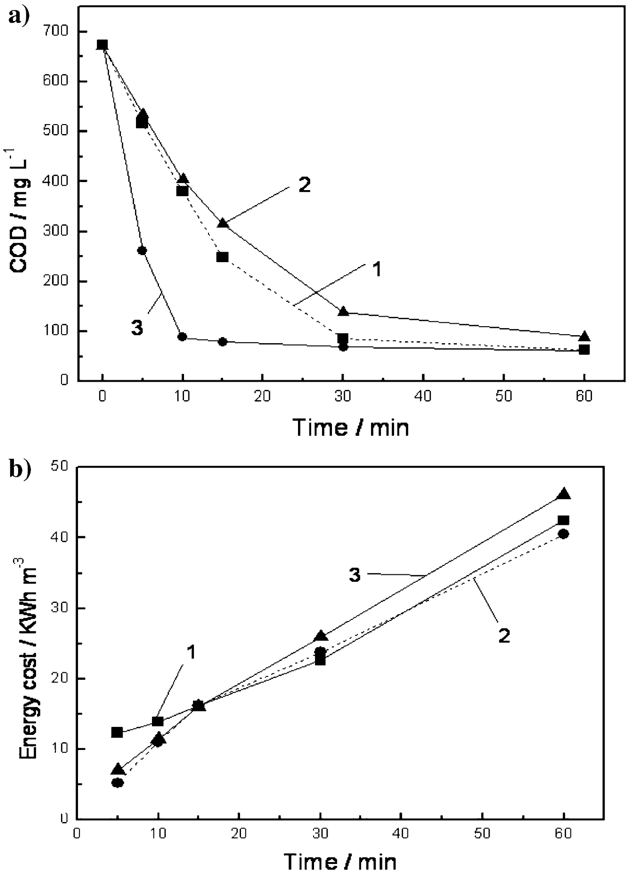

Fig. 1. COD (a) and the energy cost (b) as a function of electrolysis time in tests of phenol removal in the electro-Fenton®, carried out at 5 A current in the undivided cell (1), same in the cathode compartment of the membrane cell (2) and in the ex-cell Fenton treatment of the catholyte from the membrane cell with the Fe^{2+} (3).

where U is voltage, I is current, $\Delta(COD)_{exper}$ is experimental decay in COD with time t.

87–90% of the initial COD was removed during 1 h with a 5 A current in the membrane cell with 40 kWh m^{-3} energy consumption, whereas the same process took 30 min of electro-Fenton treatment in an undivided cell with 22 kW h m^{-3} consumption, while only 10 min of electrolysis with a 5 kWh m^{-3} power cost was needed when the electrolyzed solution was treated with Fe(II) : H_2O_2 = 1:1 molar ratio addition outside the cell (ex-cell Fenton treatment). It is evident that the latter case is preferable.

The addition of 1 mM Fe(II) gives 90% COD removal in all three cases after 1 h of electrolysis. But the treatment efficiency in the initial stages of the electro-Fenton treatment in the membrane cell can be improved when higher amounts of ferrous salts are used. More than 80% of the COD removal was achieved during 15 min treatment at 16 kWh m^{-3} when 10 mM $FeSO_4$ was added to the electrolyte (curve 3, Figure 2 (a)). Only 53–59% COD removal was obtained in the initial 15 min with the same energy consumption when 1 mM and 5 mM Fe(II) was added to the solution (curves 1,2, Figure 2 (a) and (b)).

A comparison of treatment efficiencies (Figure 3) was used to evaluate the extent of formation of polymers and/or precipitates of intermediates together with $Fe(OH)_3$ as related to mineralization according to Equation 11:

$$C_6H_5OH + 11H_2O \rightarrow 6CO_2 + 28H^+ + 28e^- \quad (10)$$

$$\text{Treatment efficiency (TE, \%)} = [\Delta(\text{COD})_{\text{exper}}/\Delta\text{COD}_{\text{theor}}] \times 100 \quad (11)$$

where ΔCOD_{theor} is a theoretical value, calculated assuming that one molecule of phenol requires 28 electrons to be completely mineralized (Equation 12) and consumes seven molecules of dioxygen according to Equation 13:

$$C_6H_5OH + 7O_2 \rightarrow 6CO_2 + 3H_2O \quad (12)$$

The theoretical current efficiency may be as high as 200% in the case of an undivided cell, where anodic oxidation of phenol is possible, but only 100% can be achieved in the other two cases where the solution is treated only in the cathode department of the membrane cell. The extent of the co-precipitation of intermediates with $Fe(OH)_3$ and polymerization, detected in the first stages in ex-cell Fenton treatment, is also observed in electro-Fenton processes, but the advantage of the addition of Fe(II) to the electrolyte before electrolysis is eliminated because of the higher energy cost due to voltage increase which was observed in tests with a higher concentration of ferrous salt. It is evident that ferric hydroxide deposition at the cathode surface takes

Table 1. Results of the "ex-cell" and "in-cell Fenton"treatment of the 282 ppm phenol + 1 g l^{-1} NaCl, pH 3 solution at 0.05 A cm^{-2} current density. Anolyte–1 M H_2SO_4

Time of H_2O_2 electro-generation/min	ex-cell Fenton treatment of solutions with electrogenerated H_2O_2				In-cell Fenton treatment in the membrane cell	
	Voltage/V	H_2O_2/g in the 50 ml sample	$FeSO_4 \cdot 7H_2O$/g added to the sample	COD/mg l^{-1}	Voltage/V	COD/mg l^{-1}
0	–	–	–	674	–	673
5	4.64	0.019	0.156	261	4.47	534
10	4.63	0.034	0.278	88.5	4.41	404
15	4.64	0.053	0.434	79.5	4.33	315
30	4.60	0.087	0.712	69.0	4.24	139
60	4.54	0.146	1.198	62.5	4.34	89

place which results in the decay of real surface area due to pore obstruction.

The influence of the anodic oxidation of phenol in electro-Fenton processes performed in an undivided cell was studied in a test carried out with the addition of 282 ppm of phenol to the anolyte of the membrane cell, which contained 1 M H_2SO_4. A reduction of 10% (60 mg l^{-1}) of the initial COD (670 mg l^{-1}) was observed after 1 h, which does not make up for the deficiencies of the electro-Fenton treatment in an undivided cell. The ex-cell Fenton treatment of a solution with electro-generated hydrogen peroxide is preferable in all cases.

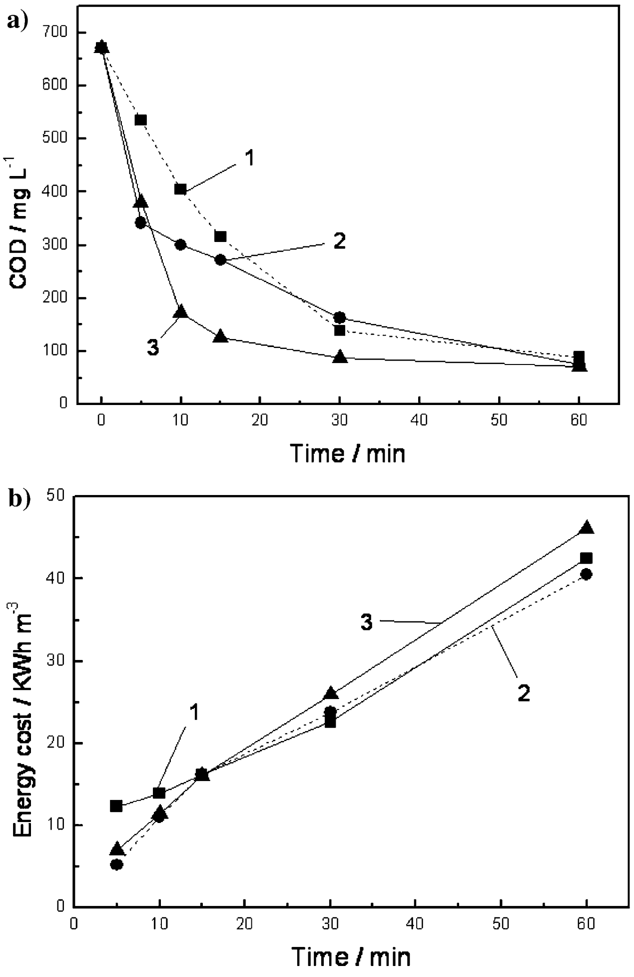

Fig. 2. COD removal (a) and energy cost (b) over time in the in-cell electro-Fenton treatment at a 0.05 A cm^{-2} current density in the membrane cell of the 1 g l^{-1} NaCl solution with 282 ppm phenol and Fe(II): 1–1 mM; 2–5 mM; 3–10 mM.

3.2. *4-Chlorophenol treatment*

The mineralization of chlorophenol proceeds according to the reaction:

$$Cl-C_6H_4OH+11H_2O \rightarrow 6CO_2+HCl+26H^++26e^- \tag{13}$$

Test results are shown in Table 2 and in Figure 4. Electro-generation of 0.8 g l^{-1} H_2O_2 was obtained even at 3 A in 30 min in the solution with initial COD = 178 ppm. 75–80% treatment efficiency was achieved in subsequent 1 h ex-cell Fenton treatment of this solution with a 1:1 molar ratio of Fe(II):H_2O_2.

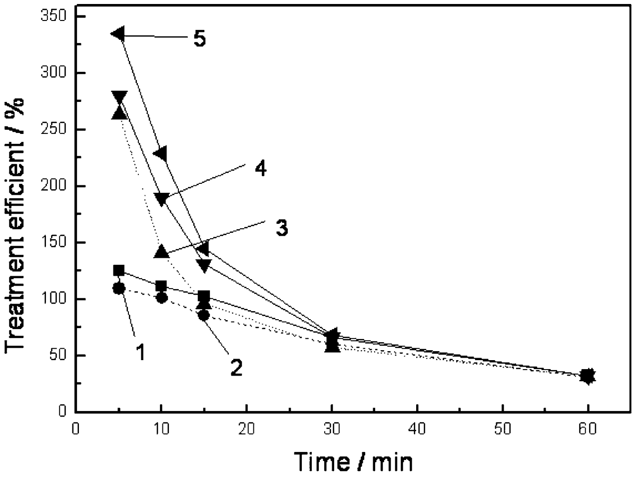

Fig. 3. Variation of the treatment efficiency with time in tests, performed with 1 mM Fe^{2+} and 1 g l^{-1} Na_2SO_4 addition into the solution treated in the electro-Fenton® regime in the undivided cell (1); in-cell electro-Fenton process in the membrane cell with Fe^{2+} addition, mM: 1–(2); 5–(3); 10–(4); ex-cell treatment of the electrolyzed solution with Fe^{2+}:H_2O_2 = 1:1 molar ratio (5). Supported electrolyte 1 g l^{-1} NaCl, pH 3, temperature 20 °C; current density 0.05 A cm^{-2} (current 5 A).

Table 2. Results of the "ex-cell" and "in-cell Fenton"treatment of the 178 ppm chlorophenol + 1 g l^{-1} NaCl, pH 3 solution treatment with variation of current density and of the $FeSO_4 \cdot 7H_2O$ addition. Anolyte–1 M H_2SO_4

Current density /A cm^{-2}	Time of H_2O_2 electro-generation /min	ex-cell Fenton treatment of solutions with electrogenerated H_2O_2				In-cell Fenton treatment in the membrane cell.		
		Voltage/V	H_2O_2/g in the 50 ml sample	$FeSO_4 \cdot 7H_2O$/g added to the sample	COD/mg l^{-1}	Added $FeSO_4 \cdot 7H_2O$/g l^{-1}	Voltage/V	COD/mg l^{-1}
0.03	0	–	–	–	289	1	–	289
	30	4.02	0.04	0.33	38.4	1	4.24	51.2
	60	3.97	0.074	0.605	36.4	1	4.21	35.6
	120	3.6	0.136	1.112	33.6	–	4.28	32.4
	180	4.04	0.192	1.57	20	–	4.3	29.6
0.05	0	–	–	–	290	1	–	287
	30	5.74	0.06	0.5	29	1	5.75	41.2
	60	5.71	0.125	1.022	28	1	6.38	38.4
	120	5.69	0.257	2.1	20	1	6.4	36
	180	5.82	0.327	2.67	16	–	6.9	29.6
0.07	0	–	–	–	290	10	–	287
	30	6.81	0.087	0.711	34.8	1	10.97	75
	60	6.67	0.187	1.53	30	1	11.0	41.6
	120	6.68	0.364	2.976	13.6	–	9.66	16
	180	6.81	0.5	4.088	10	–	9.5	20.8
0.1	0	–	–	–	290	10	–	287
	30	8.7	0.128	1.05	25.6	1	13.5	96
	60	8.51	0.243	1.98	20	1	14	62.5
	120	8.6	0.45	3.68	11.6	1	12.4	22.4
	180	8.41	0.59	4.82	10.8	–	13.6	27.2

The transparent initial solution with 178 ppm chlorophenol became dark brown in a few minutes after hydrogen peroxide electrogeneration. It changed to light brown after 1 h of electrolysis, with the simultaneous formation of gas bubbles in the bulk solution. In contrast, the initial content of chlorophenol did not change and coloration was not observed in the control test when 5 g l^{-1} hydrogen peroxide was added to the same 178 ppm chlorophenol solution. The solution remained transparent even after 24 h of mixing. The oxidation of 4-chlorophenol with the formation of colored compounds, observed in electrochemical generation tests, may be caused by the participation of intermediate species (O_2^-, $^*OH_2$ and $^*OH$) formed on the carbon black surface of the GDE [2, 17].

The in-cell electro-Fenton process was carried out at an initial concentration of 178 ppm of 4-chlorophenol and 1 g l^{-1} $FeSO_4{\cdot}7H_2O$. Different quantities (1–15 g l^{-1}) of ferrous salt were added to the catholyte during the electrogeneration of the hydrogen peroxide. 50 ml samples were removed every 30 min and after 1 h of mixing were neutralized, filtered and analyzed for COD.

Though the shapes of the COD removal curves are similar and the rapid removal of 82~88% of organics occurs during the first 25–30 min in both ex-cell and in-cell Fenton treatment processes (Figure 4, (a) and (b)), the cell voltage was higher in the in-cell process, especially in tests where a high quantity of Fe^{2+} was introduced.

The final COD level is also higher and visual observation of the GDE after electrolysis showed that brown iron compounds covered the electrode surface in

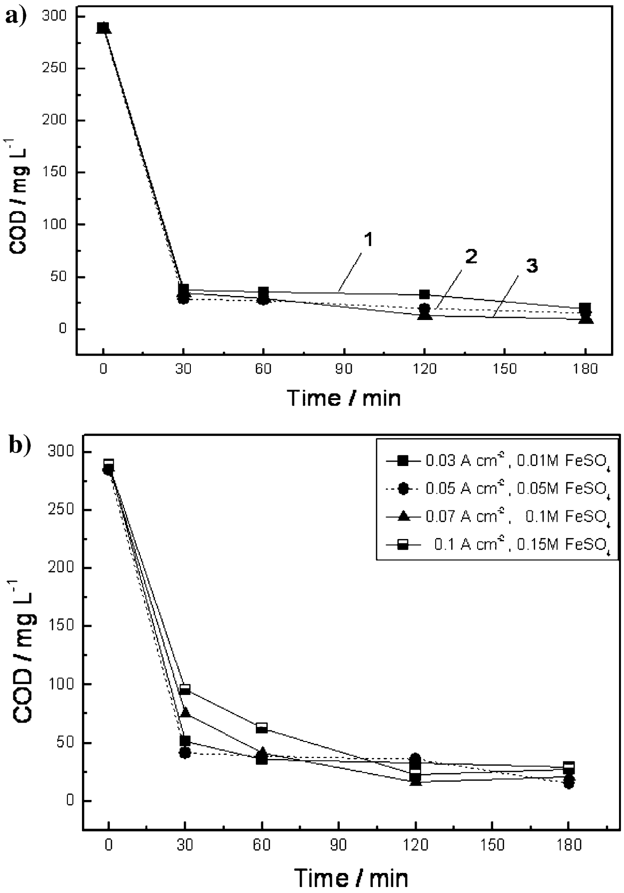

Fig. 4. Influence of current density variation on COD removal vs. electrolysis time curves, when 1 l of 178 ppm 4-chlorophenol + 1 g l^{-1} NaCl, pH 3 solution was added as a catholyte, with a consecutive "ex-cell" Fenton reaction (a) and when different amounts of the $FeSO_4$ were added to the solution, which was treated in the electro-Fenton regime (b).

the in-cell electro-Fenton process which emphasizes the advantages of the ex-cell Fenton treatment.

The variation of COD, treatment efficiency and of energy cost over time in the electro-Fenton® treatment of 1 l solution of 178 ppm 4-chlorophenol, 1 mM $FeSO_4$ and 1 g l^{-1} Na_2SO_4 at pH 3, 20 °C temperature and 5 A current (0.05 A cm^{-2}) in an undivided cell are shown in curves 1 of Figure 5 (a), (b) and (c) respectively.

Curves 2 in the same figures illustrate the ex-cell Fenton treatment of the solution with an initial content of 178 ppm 4-chlorophenol and 1 g l^{-1} NaCl, after H_2O_2 electrogeneration in the membrane cell. The comparison of these data shows that though the treatment efficiency is similar in both cases, the energy cost is nearly two times lower in the ex-cell Fenton treatment.

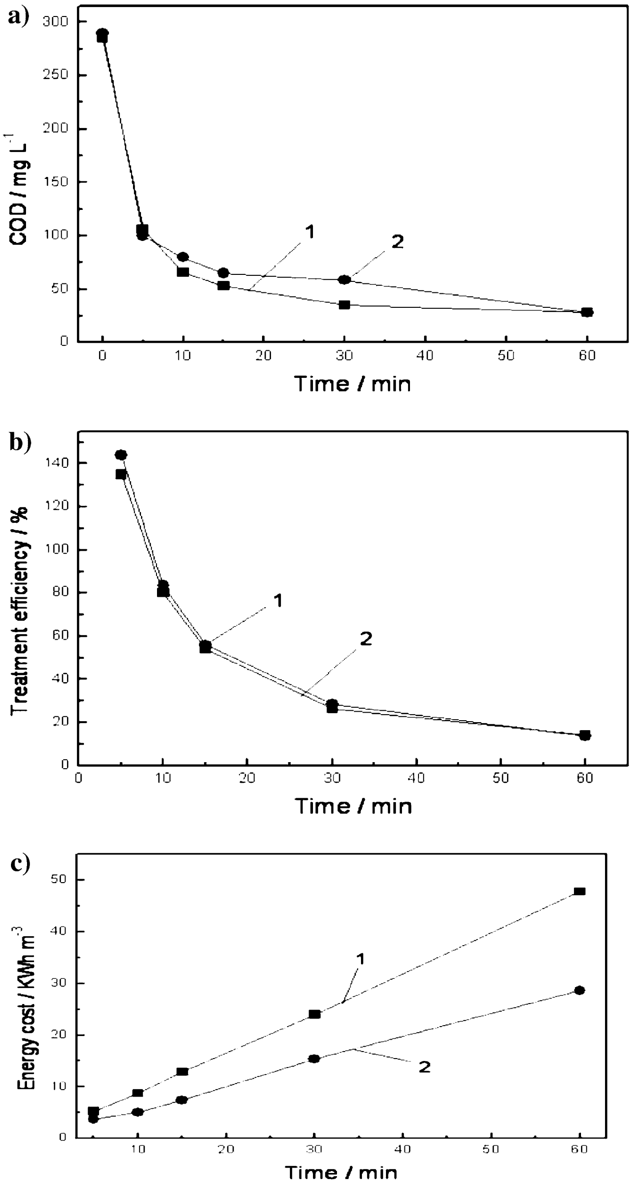

Fig. 5. COD removal (a), treatment efficiency (b) and energy cost (c) over time in the electro-Fenton® treatment in the undivided cell (1) and in the ex-cell Fenton treatment (2) in membrane cell.

3.3. *Treatment of Aniline*

The results of the ex-cell Fenton treatment at H_2O_2:Fe^{2+} = 1:1 molar ratio of the solution with an initial content of 1000 ppm of aniline and 1 g l^{-1} NaCl, electrolysed in the cathodic department of the membrane cell are summarized in Table 3.

The in-cell electro-Fenton process was carried out with the addition of 1 mM Fe^{2+} to the 1 g l^{-1} NaCl catholyte at pH 3. The initially transparent solution became colored dark red and changed to dark violet after 30 min. Black precipitates were found on the bottom of the recirculation tank and a white film covered the surface of the solution after 30 min. However, these precipitates vanished after 120 min of electrolysis. An excess of hydrogen peroxide was found in all tests after 30 min of treatment and no iron (II) salts were observed. So ex-cell addition of $FeSO_4$ became necessary for the elimination of H_2O_2 interference on the COD analysis results. Therefore the results of COD analysis in these cases (marked by * in Table 3) can be considered to be results of combined in-cell and ex-cell treatment.

Further tests were performed with 2.7 g (17 mM) $FeSO_4$ addition. Fe^{2+} was found in all samples after 4 h electro-Fenton treatment of 1 litre of solution. Though the final level of COD removal after 3 h treatment was found to be the same in the in-cell and ex-cell Fenton processes (136 and 145 mg l^{-1} residual), a decrease to 960 mg l^{-1} from the initial level was detected in the in-cell electro-Fenton treatment after first 30 min, in contrast to 310 mg l^{-1} in the ex-cell process (Figure 6). In the ex-cell Fenton case the cell voltage was almost two times lower. This is probably caused by coverage of the GDE surface with ferric hydroxide, resulting in a decrease in surface area of the porous electrode.

The treatment efficiency and energy cost variation over time (Figure 7 (a) and (b)) obtained after the substitution of TOC with COD in Equation 9 and 10 illustrates the advantages of ex-cell Fenton treatment.

For comparison, the electro-Fenton® treatment was carried out under conditions close to those described in [8]. The tests were carried out at 5 A in an undivided cell with a 2 mm inter-electrode gap between the Ti-IrO_2-SnO_2 mesh anode and the Black Pearls 2000 GDE cathode. The solution of 1000 ppm aniline, 1 mM Fe^{2+} and 1 g l^{-1} Na_2SO_4, pH 3 taken as a supporting electrolyte was circulated at 60 l min^{-1} and 20 °C between the cell, the heat-exchanger and the reservoir by means of a centrifugal pump. The results are shown in Table 4. In these tests the pH falls with time. The voltage also falls due to increased electrolyte conduction, but COD removal up to the final level (92–93%) was obtained only after 120 min, whereas with the membrane cell this level was achieved with a nearly twice lower energy consumption after 60 min electrolysis and then 60 min of ex-cell Fenton treatment (see Table 3).

Table 3. Results of the “ex-cell” and “in-cell” electro-Fenton process of the 1000 ppm aniline + 1 g l^{-1} NaCl solution at pH 3 with variation of current density and amount of $FeSO_4 \cdot 7H_2O$. Anolyte −1 M H_2SO_4

Current density/A cm^{-2}	Electro-lysis time/min	ex-cell Fenton					In-cell electro-Fenton in the membrane cell (+ex-cell Fenton in tests, signed with*)				
		Voltage/V	H_2O_2/g in 100 ml sample	$FeSO_4 \cdot 7H_2O$/g added to 100 ml sample	COD/mg l^{-1}	COD Removal/%	Fe^{2+}/mM added	Voltage/V	H_2O_2/g in 100 ml sample	COD/mg l^{-1}	COD Removal/%
0.03	0	–	–	–	2400	–	1	–	–	2400	–
	30	4.04	0.094	0.765	560	76.6	–	3.57	0	395	83.54
	60	4.12	0.192	1.564	180	92.5	–	3.64	0.02	160*	93.3
	120	4.14	0.39	3.17	165	93.1	–	3.74	0.11	80*	96.6
	180	4.17	0.596	4.87	150	93.7	–	3.86	0.19	93*	96.1
0.05	0	–	–	–	2400	–	1	–	–	2400	–
	30	5.47	0.153	1.25	310	87.1	–	5.15	0.085	125*	94.8
	60	5.48	0.31	2.54	178	92.6	–	5.38	0.17	122*	94.9
	120	5.46	0.652	5.33	155	93.6	–	5.52	0.34	80*	96.6
	180	5.49	0.955	7.82	145	93.9	–	5.11	0.476	82*	96.5
0.05	0	–	–	–	–	–	17	–	–	2400	–
	30	–	–	–	–	–	–	10.8	–	960	60.0
	60	–	–	–	–	–	–	11.3	–	485	79.8
	120	–	–	–	–	–	–	9.75	–	224	90.6
	180	–	–	–	–	–	–	7.47	–	136	94.3
0.1	0	–	–	–	2400	–	–	–	–	–	–
	30	8.47	0.306	2.5	158	93.4	–	–	–	–	–
	60	8.52	0.574	4,69	145	93.9	–	–	–	–	–
	120	8.62	1.125	9.2	140	94.2	–	–	–	–	–
	180	9.08	1.585	12.96	106	95.5	–	–	–	–	–

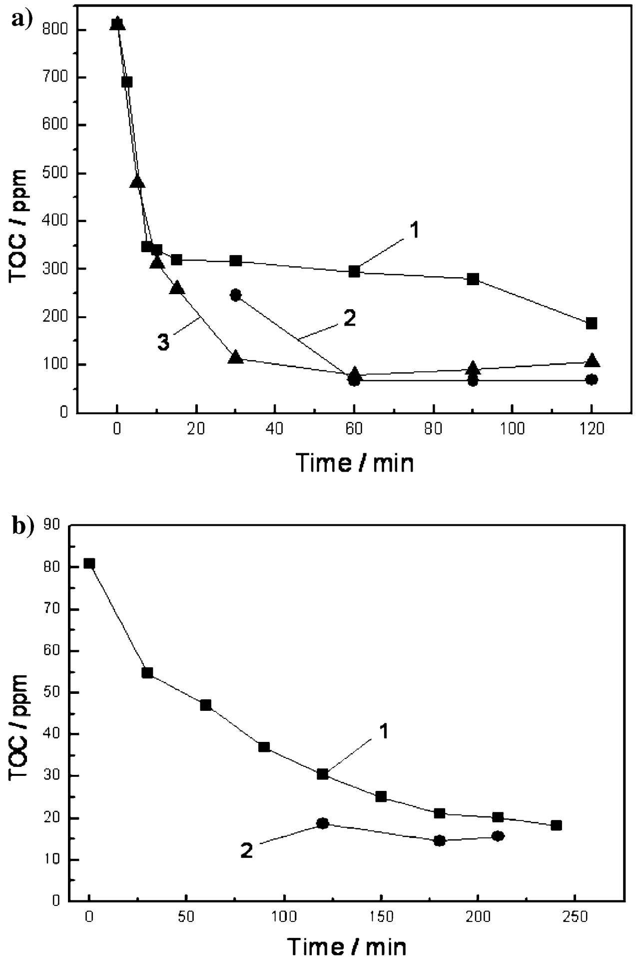

Fig. 6. TOC removal over time in tests of 1 g l^{-1} NaCl solution treatment as a catholyte in the membrane cell:. 1– in cell electro-Fenton; 2– additional ex-cell chemical treatment with Fe(II) after the electro-Fenton. 3– ex-cell Fenton treatment after the H_2O_2 electro-generation: (a) treated solution volume 1 l, initial aniline concentration 1000 mg l^{-1}; (b) solution volume 30 l, initial aniline concentration 100 mg l^{-1}.

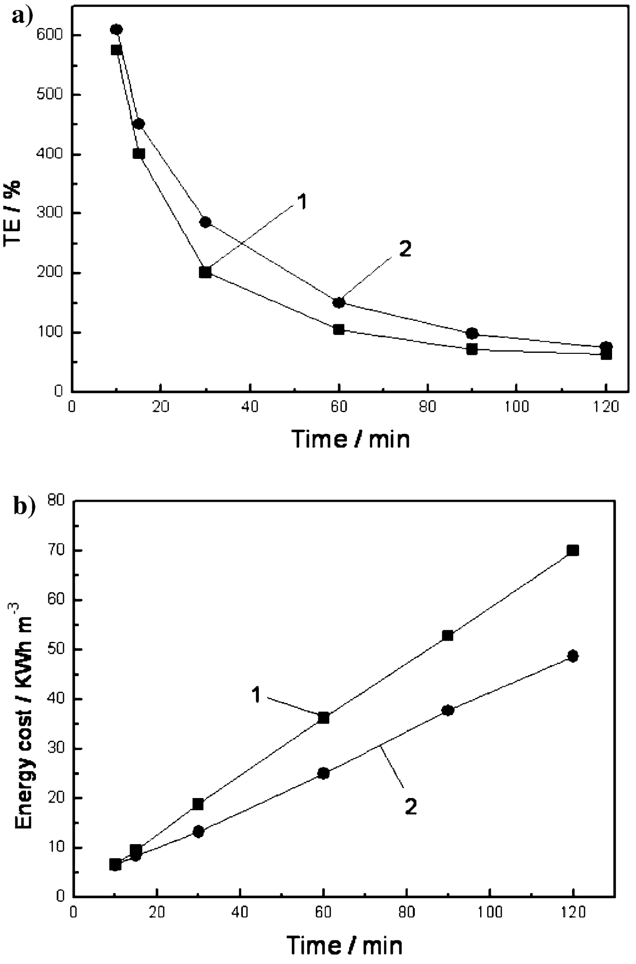

Fig. 7. Treatment efficiency (a) and the energy cost (b) variation with time in the electro-Fenton treatment in the in-cell (1) and ex-cell(2) Fenton treatment of the 1 l 1 g l^{-1} NaCl + 1 mM Fe^{2+} solution with the initial content 1000 ppm aniline at pH 3, temperature 20 °C. Current 5 a; catholyte flow rate 1 l min^{-1}. Anolyte–1 M H_2SO_4.

One more drawback of the electro-Fenton® process is the loss of Fe^{2+} in an undivided electrochemical cell due to the anodic oxidation of Fe^{3+} instead of participation of iron (II) in the reaction (1). In this case, the positive effect of the direct oxidation of organic pollutants at the Ti-IrO_2 anode [18] is also reduced by the oxidative anodic decomposition of hydrogen peroxide.

The significant economy of specific energy consumption (29.4 kW h m^{-3} for 92.6% COD removal against 39 kW h m^{-3} for 91% TOC removed) was achieved in the present study for the ex-cell treatment even when compared with peroxi-coagulation, the best of all three methods studied in [8]. The complicated design of the electrochemical reactor represents a disadvantage of this technology as the sacrificial Fe anodes must be changed frequently. There is a loss of oxygen at the anode which comprises up to 50% of the gas consumed by the cathode process on GDE. On the other hand, as shown by Agladze et al., even the corrosion of iron scrap in a separate vessel is enough for Fenton-like chain reactions to proceed, and this can be used instead of the anodic dissolution of iron electrodes [19, 20].

Iron (II) is the most effective catalyst only when dilute solutions of H_2O_2 are used. At higher concentrations of hydrogen peroxide (>1 mg l^{-1}) iron (III) is a more effective catalyst for a superoxide/perhydroxyl driven reaction (5) [21]. But regulation of iron salt addition, which is easy to accomplish in a chemical Fenton reaction outside the electrochemical cell, cannot be carried out effectively by means of changing the rate

Table 4 Conditions and results of the electro-Fenton® treatment of the solution with 1 g l^{-1} Na_2SO_4, + 1000 ppm aniline and 1 mM Fe^{2+} in the undivided cell

Current density/ A cm^{-2}	Time/min	Voltage/V	pH	COD/mg l^{-1}	COD removal/%
0.05	0	–	3	2400	–
	30	7.38	2.34	578	75.9
	60	6.6	2.25	382	84.1
	120	5.8	2.20	158	93.4
	180	5.0	2.15	156	93.5

(current) of the anode dissolution in an electrochemical cell as it may change the generation of H_2O_2 at the cathode.

GDE damage was observed after a number of tests. As a result the nickel mesh was corroded by the penetrating acid solution. However the pH indicator paper showed an alkaline media in contact with the GDE which was taken out from the reactor after treatment of the solution with pH 3. A possible explanation could be that even in acid media, hydrogen peroxide generation in pores of the gas diffusion layer proceeds with formation of HO_2^- which is common for alkaline media and consecutive protonation occurs at the interface with the acid solution.

4. Conclusions

A 90–98% destruction of aromatic organic substances was achieved in solutions where hydrogen peroxide was electrogenerated at a GDE in the cathodic chamber of a cell separated by a proton-exchange membrane both in ex-cell and in-cell Fenton treatment, but higher rates of decomposition were achieved in the former process. Nearly twice less energy cost was achieved with a membrane cell in comparison with an undivided cell.

A substantial reduction in specific energy consumption was achieved in ex-cell treatment even in comparison with the results of peroxi-coagulation, known as the best of three methods [8].

A simple and compact cell design, the possibility of using anodically generated oxygen gas for the GDE feed, and the addition of iron salts or even the corrosion of scrap iron in a vessel separate from the electrochemical reactor can be used effectively instead of the anodic dissolution of iron electrodes for the Fenton-like chain reactions.

At present the lifetime of the GDE is the main problem in electro-Fenton treatment. Damage of the gas-diffusion layer was observed in some tests. The destruction of hydrogen peroxide in alkaline conditions presents another problem. The pH indicator paper showed a color specific for alkaline media in contact with the GDE treated in the solution with pH 3 in the bulk. A possible explanation could be that even in acid media, hydrogen peroxide generation in pores of the gas diffusion layer proceeds with formation of HO_2^- which is common for alkaline media and consecutive protonation occurs at the interface with the acid solution.

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