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Comparative study of chemical and electrochemical Fenton treatment of organic pollutants in wastewater

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Abstract The technological and economic aspects of using the Fenton process to treat industrial wastewater containing morpholyne and diethylethanolamine, as well as sodium salts of naphthalene sulfonic acid and of ethylenediaminetetraacetic acid based on data obtained in pilot tests are discussed. Chemical Fenton technology was tested using commercial 30–35% solutions of H_2O_2 and iron (II) salts, which was followed by the additional electrochemical destruction of organic pollutants in an undivided reactor with catalytic stable anodes (CSA) and 1 g L^{-1} NaCl as a supporting electrolyte and a source of active chlorine. An alternative electrochemical method involving the electrogeneration of hydrogen peroxide in polluted water at the gas-diffusion cathode was studied both with the addition of ferrous salt to the electrolyte prior to electrolysis (in-cell electro-Fenton) as well as with the post-electrolysis addition of Fe^{2+} in another reactor (ex-cell electro-Fenton). The accumulation of hydrogen peroxide in concentrations sufficient for the mineralization of organic pollutants was achieved in both cases with near 100% current efficiency. In comparison with wastewater treatment processes which use a purchased hydrogen peroxide reagent, the Fenton-like processes achieved an economic savings of as much as 64.5% in running costs due to the on-site electrochemical generation of H_2O_2. Preparative electrolysis in the membrane reactor showed higher current efficiencies and lower specific energy consumptions for H_2O_2 electrogeneration in comparison with the results of tests carried out in an undivided cell.

Keywords Electro-Fenton · Gas-diffusion electrode · Hydrogen peroxide · Proton-exchange membrane · Wastewater treatment

1 Introduction

Fenton [1] was the first to study the catalytic destruction of hydrogen peroxide by Fe^{2+} ions (reaction 1), a process which is now used on a commercial scale in wastewater treatment:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3} + {}^{*}OH + OH^{-} \quad (1)$$

Concentrated (35–70%) solutions of hydrogen peroxide are produced commercially by the chemical reduction of oxygen with hydrogen using anthraquinone as a catalyst [2]. The main drawbacks of this method are the relatively high price of the hydrogen peroxide solution, and the fact that it experiences a continuous decrease in oxidizing power during transportation and storage. High investment costs coupled with the necessity of hydrogen feedback dictates that hydrogen peroxide production using the ''Anthraquinone'' process be limited to a few industrial sites. This makes the handling and delivery of hazardous and unstable H_2O_2 solutions to wastewater treatment facilities both dangerous and uneconomical.

An alternative process is the on-site generation of hydrogen peroxide solutions through the electrochemical reduction of oxygen at the cathode of the electrochemical reactor:

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

$$O_2 + H_2O + 2e^- \rightarrow H_2O^- + OH^-(\text{alkaline solutions}),\quad E^\circ = -0.065\ \text{V} \tag{3}$$

Due to the limited solubility of oxygen in aqueous solutions, three-dimensional electrodes with enlarged real surfaces are needed for the industrial implementation of this process using commercially reasonable current densities. The application of gas-diffusion electrodes (GDE) for hydrogen peroxide electrosynthesis has also been studied [3–11].

The present work makes a comparison of the chemical and electrochemical methods of H_2O_2 production taking the example of wastewater treatment processes used at a Korean construction plant. The wastewater contained morpholyne and diethylethanolamine, as well as sodium salts of naphthalene sulfonic acid and of ethylenediaminetetraacetic acid, which were used as modifiers of concrete hardness and bondability. The initial chemical oxygen demand (COD) level found in the wastewater was in the range 250–275 mg L^{-1} at pH 12. The chemical Fenton treatment, followed by an electrodestruction process which is described in detail in Sect. 1.1, was implemented at the construction plant on a large scale (13 m^3 h^{-1}) while the electro-Fenton processes were tested on a small pilot scale (5–6 L h^{-1}). This discrepancy makes an accurate comparison of investment costs more complicated. The main investment in the electro-Fenton treatment lies in the price of GDEs, which still need to be tested in a continuous mode in order to determine their lifetime. The E-TEK Co. Ltd.—a commercial producer of GDE for H_2O_2 electrogeneration indicates a current efficiency of between 85 and 95% over 9,000 test hours in alkaline solutions. The data for prolonged tests in acid solutions is not available at the present time and consequently the comparison made in this work is based only on the running costs of electricity and chemicals.

2 The chemical Fenton treatment followed by electrodestruction

The overall wastewater treatment process carried out at the construction plant involved the following steps:

1. Chemical treatment;
2. Dissolved air flotation;
3. Fenton process: the reaction between H_2O_2 and ferrous salt ($FeSO_4$ or $FeCl_2$) resulting in the production of (*OH), which affects refractory organics in solution;
4. Sedimentation and filtration of the $Fe(OH)_3$ sludge;
5. Electrodestruction: direct anodic treatment, combined with the action of the hypochlorite-ions that, due to the addition of NaCl to the solution, are electrogenerated in the undivided electrochemical reactor.

The removal of suspended solids, oils, etc., was achieved by means of dissolved air flotation, coagulation and sedimentation, which decrease the average COD to 195 mg L^{-1}. The chemical Fenton reaction of hydrogen peroxide and ferrous salt and final ED in the undivided reactor with Ti-RuO_2-IrO_2 CSA [11] and stainless steel cathodes with 1 g L^{-1} NaCl as a supporting electrolyte and a source of active chlorine are responsible for the removal of refractory organics to the targeted level of $COD_{Mn} \leq 50$ mg L^{-1}. Each of these steps requires pH adjustment by addition of alkali $Ca(OH)_2$ or acid H_2SO_4 or HCl. The consumption and costs of the reagents and power used in this process are shown in Table 3, Sect. 4.

3 The electro-Fenton treatment

The principal possibility for economizing running costs occurs when the chemical Fenton and ED processes are replaced by the combined electro-Fenton process. In these cases the electrogeneration of H_2O_2 at the cathode of an undivided or membrane electrochemical reactor results in either a simultaneous reaction (in-cell electro-Fenton process), or a consequent reaction between cathodically electrogenerated hydrogen peroxide and ferrous salt in a separate vessel (ex-cell Fenton process), which generates the hydroxyl radicals (*OH) that treat wastewater contaminants. The anodic process may also be used for the electrodestruction of pollutants, which means that power will be consumed for the generation of desired products both at the anode and the cathode.

These processes were studied in the experimental part of the present work. Though the pressure swing adsorption (PSA) oxygen generator was used as a source of oxygen, air could also be used for this purpose without significant changes to H_2O_2 current efficiency, as shown previously [15].

Pilot tests on the hydrogen peroxide electrogeneration process were carried out with the batch recirculation of wastewater at a 360 L h^{-1} flow rate in a filter-press type Electro-MP cell (Fig. 1) with a 3 mm gap between parallel electrodes possessing 100 cm^2 visible surface area (10 × 10 cm) each: the gas-diffusion cathode, a polytetrafluoroethylene (PTFE) impregnated carbon sheet coated with Black Pearls 2000 carbon black (all supplied by

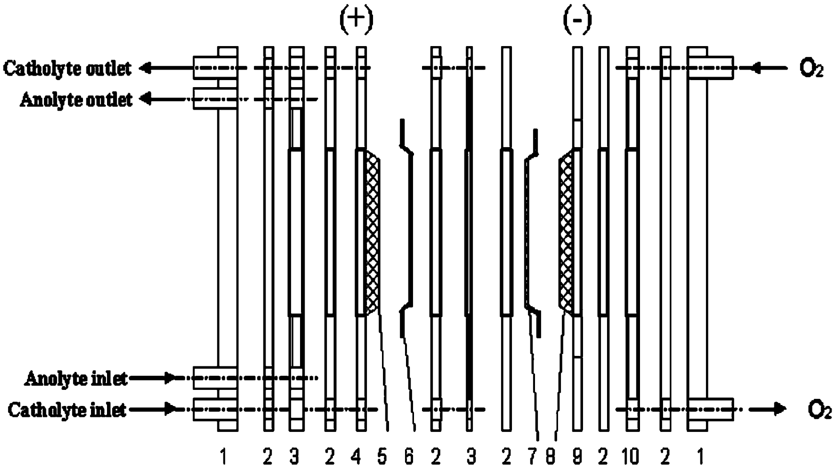

Fig. 1 Set-up and components of the electrochemical cell. Legend: (1) plastic plates with manifolds for electrolyte and gas inlet and outlet, (2) rubber gaskets, (3) plastic frame with spacer for electrolyte flow, (4) titanium frame as a current feeder, (5) Ti-IrO_2-SnO_2 catalytic stable anode mesh, (6) proton-exchange membrane, (7) gas-diffusion electrode, (8) titanium mesh as a cathode current distributor, (9) titanium frame as a current feeder, (10) plastic frame as a gas chamber. Stainless steel end plates and bolts through holes are not shown

Electrocell AB) and a meshed Ti-IrO_2-SnO_2 catalytic-stable anode (CSA) supplied by TECHWIN Co. Ltd. [11–14].

The GDE was hot-pressed on the nickel mesh, which together with the graphite frame acted as a current feeder. On-site generation of O_2 of 95% purity for the GDE supply was obtained from a WH-7 type pressure swing adsorption (PSA) oxygen generator produced by Won Hi Tech; oxygen was fed to a gas chamber next to the cathode. The cation-exchange membrane (CEM) was fixed between the spacer, used for the catholyte flow and the meshed anode, so the anolyte flowed on the reverse side of the CSA, while the treated solution (catholyte) flowed through the spacer between the GDE and CEM. A 10% H_2SO_4 solution with a pH of 1.5 was used as anolyte, which was continuously re-circulated from the special reservoir. The series of tests was also performed in the undivided cell in which the cathode and anode compartments were not separated by the membrane. DC power was supplied to the cell from an HS-SCP type rectifier (Hyun Sung Co.).

3.1 Chemicals and analytical procedures

All solutions were prepared with distilled water and with chemical grade reagents, except for the real wastewater samples which were supplied from industrial sites. Sulfuric acid was supplied by PFP Co.; iron (II) sulfate was supplied by Shinyo Pure Chem. Co. Ltd, (Japan); and sodium chloride and sodium sulfate were supplied by Jin Chemical Pharm.Co. Ltd, (S. Korea).

The solution pH was measured with an ORION 420A+ pH meter. The hydrogen peroxide concentration was measured using a standard titration method with potassium permanganate. The organic content of the solution was measured by COD, which was monitored by a standard permanganate method based on the oxidation of the organic content of the sample with potassium permanganate in H_2O_2, Cl^- and Fe (II)-free solutions, as these can interfere with the titration of organics by permanganate [10].

3.2 Ex-cell electro-Fenton process

The initial tests were carried out with the electrochemical generation of hydrogen peroxide in complex wastewater with an initial COD in the range 250–275 mg L^{-1} at pH 12. Prior to electrolysis, wastewater was treated with flocculants and polymer coagulants for suspended solid and oil contaminant removal at pH 7. The specific conductivity of the resulting solution with COD = 184 mg L^{-1} was 3.26 mS cm^{-1}, which increased to 5–6 mS cm^{-1} at pH 3. This solution was treated in the electrochemical reactor with a 10 × 10 cm Ti/IrO_2 anode, and the GDE (Black Pearls 2000) as cathode. 1 L of solution was re-circulated at a 60–90 L h^{-1} between the reservoir and a plastic spacer of 3 mm thickness, which was fixed between the anode and the cathode. Oxygen was supplied to the GDE from the PSA generator at 0.5 L min^{-1} and excess oxygen was discharged into the atmosphere.

As soon as 0.5–0.55 g L^{-1} residual H_2O_2 generation was achieved after treatment at different currents, the solution was discharged from the electrochemical cell to the other reactor, where it was stirred for 1 h at 22–23 °C, pH 3 with 0.05 A cm^{-2} current density and 1.5 L min^{-1} flow rate, with the addition of ferrous sulfate in H_2O_2/Fe^{2+} = 1:1

Table 1 Influence of current density and temperature on H_2O_2 electrogeneration in the undivided cell at 20 °C with consecutive Fenton treatment of the electrolyzed wastewater (ex-cell Fenton process). Initial COD = 184 mg L^{-1}

Current Density/A cm^{-2}	Temperature/ °C	Electrolysis Time/min	H_2O_2 after electrolysis/g L^{-1}	COD after Fenton reaction/mg L^{-1}	Power on electrolysis/W h L^{-1}
0.03	20	25	0.535	31.2	6.53
0.03	30	25	0.454	39.2	5.67
0.03	40	25	0.400	48.0	5.25
0.05	20	15	0.563	34.4	9.62
0.05	30	15	0.527	29.50	8.21
0.07	20	10	0.547	36.8	10.96
0.07	30	10	0.493	29.6	9.33

molar ratio. Then, after the addition of sodium hydroxide, the precipitated ferrous hydroxide sludge was separated by filtration at pH 7. The conditions and results of the tests with 1 L of wastewater with initial COD = 184 mg L^{-1} treatment are shown in Table 1.

Table 2 illustrates treatment results of wastewater where the initial COD = 148 mg L^{-1}. Fe (II) was added in a $FeSO_4$:H_2O_2 = 1:1 molar ratio to the 100 mL samples, which had been taken from the solution once every 2.5 min during electrolysis. Tests were performed at 22–23 °C, pH 3 with 0.05 A cm^{-2} current density and 1.5 L min^{-1} flow rate. As in the previous case, the final COD was determined in iron-free solutions.

As the targeted COD of 50 mg L^{-1} was achieved after 5 min of treatment, the results obtained after this time are useful for comparing running costs and thus for assessing the economic viability of the undivided cell process. Along with the fact that no hydrogen peroxide needs to be purchased (an expense which, in the standard wastewater treatment process, accounts for 48.1% of the total running costs for chemicals and power), the fact that sodium sulfate salt was not used during the electrochemical treatment reduces the cost input by another 4.52%, while the difference in power consumption in the electrolysis constitutes a savings of (0.27–0.144) = 0.126 US \$ per m^3 of wastewater, or 7% of the total cost. Combined, we find a total savings of 59.62% on the running costs of chemicals and power in the case of the undivided cell. The cost of oxygen (or air) supply should be assessed by taking into account specific conditions and prices at the site (which are negligible in the case of the existing plant). While the investment costs of the other system components are minimal, the lifetime and price of the GDE itself still needs to be optimized and established.

The results of the tests carried out with Fe^{2+} ions added to the plant wastewater during electrolysis in the undivided cell (electro-Fenton® process) are discussed later (Sect. 3.3) in comparison with the results of the tests performed in the membrane cell. It should be noted that in all cases a higher treatment efficiency was achieved with each consecutive Fenton treatment of plant wastewater. Possible reasons for this include the partial oxidation of Fe (II) at the anode (which decreases the amount of reagent available for the reaction), and the possible reduction of Fe (III) at the cathode with the precipitation of ferric hydroxide in the pores of the GDE, where the pH remains alkaline even at acidic conditions in the bulk of the flowing electrolyte, along with other factors which are discussed in our previous publications [15, 16].

3.3 Plant wastewater treatment in the membrane cell

Results of tests performed using the electro-Fenton treatment in a cell divided by a MK-40 type proton-exchange membrane (PEM) are shown in Fig. 2. A solution of 100 g L^{-1} H_2SO_4 served as an anolyte and 1 L of wastewater with an

Table 2 Results of H_2O_2 electrogeneration in the undivided cell at 5 A with consecutive Fenton treatment of electrolyzed wastewater. Initial COD = 148 mg L^{-1}

Time of electrolysis/min	H_2O_2 after electrolysis/g L^{-1}	Voltage/V	COD final/ mg L^{-1}	Power on electrolysis/W h L^{-1}	Price of power on electrolysis/US \$ m^{-3}
5	0.27	6.37	45.2	2.65	0.144
7.5	0.40	6.50	38.8	4.06	0.220
10	0.48	6.53	37.6	5.44	0.296
12.5	0.67	6.60	26.4	6.87	0.375

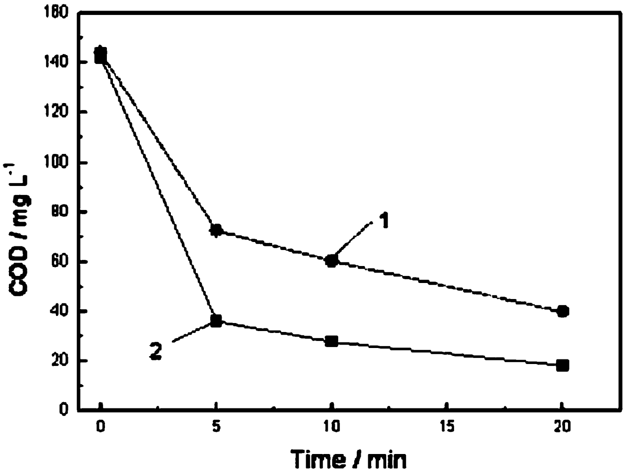

Fig. 2 Variation of COD in tests of 1 L of the plant wastewater treatment at 0.05 A cm^{-2} current density (5 A current) with time of electrolysis: 1-the in-cell electro-Fenton process with 3 g L^{-1} $FeCl_2$ addition into the cathode department of the membrane cell; 2-electrogeneration of the H_2O_2 in the plant wastewater, followed by ex-cell Fenton treatment in the other reactor

initial COD of 144 mg L^{-1} was treated at pH 3 as a catholyte. The addition of NaCl was avoided due to the significant conductivity of the salts present in the wastewater (4.91 mS cm^{-1} at pH 2.9). The electrolyte temperature was 22–23 °C, and the catholyte flow rate was 1 L min^{-1}. 1 g L^{-1} $FeCl_2$ was added prior to electrolysis, and two more 1 g L^{-1} portions were subsequently added, after 5 and 10 min of treatment respectively, so the total amount of added $FeCl_2$ equaled 3 g. 50 mL samples were removed from the cell and analyzed.

The best results were achieved in tests (illustrated in Fig. 2, curve 2) which were performed in the following conditions: 1 L of wastewater with COD = 142 mg L^{-1} and a specific conductivity of 4.32 mS cm^{-1} was treated at 22 °C and pH 3, with a 5 A current (0.05 A cm^{-2} current density), 4.33 V and a 1.5 L min^{-1} flow rate in the cathodic compartment of the membrane cell separated by an MK-40 PEM. After 5 min of hydrogen peroxide electrogeneration (in which 0.25 g L^{-1} residual C_{H2O2} was achieved with 1.8 W h L^{-1} of specific energy consumption), 0.2 g $FeSO_4 \cdot 7H_2O$ was added to a 100 mL sample of that solution and stirred for 1 h in another reactor. A resulting COD of 36 mg L^{-1} was determined analytically in the neutralized and filtered solution.

3.4 Tests with electrodestruction in the anolyte followed by in-cell electro-Fenton treatment in the catholyte of the membrane cell

The electrodestruction of organic pollutants by the active chlorine electrogenerated in the anolyte, followed by a secondary electro-Fenton treatment as a catholyte of the membrane cell, was tested in the next trial. Wastewater with an initial COD = 184 mg L^{-1} was supplied initially to the anode chamber of the divided cell, where pH 1.5 was achieved with the addition of hydrochloric acid solution. At that time, pH 3 wastewater was used as a catholyte. After 30 min of electrolysis using a 10 A current with 8.5 V cell voltage, a COD of 84 mg L^{-1} was found in the anolyte. Thus, the partial oxidation of pollutants was obtained through active chlorine action electrogenerated at the anode chamber. This treated anolyte solution was used for the dilution of another portion of the initial electrolyte (in a ratio of 1:4), resulting in pH 3 and a COD of 121 mg L^{-1} in the mixed solution.

1.3 g of $FeCl_2$ per liter of that solution was added and supplied for treatment to the cathode chamber, while the anode chamber was filled with a new portion of initial solution for treatment. 27.2 mg L^{-1} was found for COD in samples after 10 min, and 22 mg L^{-1} after 20 min of electrolysis at 10 A current. As the targeted level was 50 mg L^{-1}, the combined method with the initial electrodestruction of organics by the active chlorine generated at the anode, and consecutive treatment in the cathode chamber by the hydrogen peroxide electrogenerated at the cathode could be also suggested based on these results. Current is used for the electrochemical treatment processes both at the anode and at the cathode, which is the significant advantage of this method in comparison with electrodestruction in the undivided cell, where the hydrogen gas produced at the cathode is not only wasted, but also needs to be diluted with air to reach a non-explosive concentration

4 Comparison of running costs

A comparative economic analysis of the running costs of H_2O_2 electrogeneration in the membrane cell followed by the ex-cell Fenton treatment of plant wastewater, with the costs of the process described in Sect. 2 (chemical Fenton followed by electrodestruction) was carried out based on the test results illustrated in Fig. 2, curve 2, Sect. 3.3.

Due to a lower ohmic drop in the highly acidic solution, the voltage was lower in the membrane cell than it was in the undivided cell. This indicates a savings of 8.15% in the amount of power needed for electrolysis. This is in addition to the 48.1% savings incurred by not having to purchase hydrogen peroxide, as well as further savings of 4.52% on sodium salt, and 3.8% on sulfuric acid which is generated in the anodic department in amounts sufficient for the pH adjustment of the overall process. This results in a total wastewater treatment cost of 0.825 $ per 1 m^3, compared with 2.326 $ per 1 m^3 using the existing technology. This

Table 3 Consumption and prices of chemicals and power for the plant wastewater treatment process

Existing technology (chemical Fenton & electrodestruction (ED))						Proposed Technology (H_2O_2 electrogeneration in the membrane cell with ex-cell Fenton treatment)	
Chemicals	Solution/%	Unit price/US \$ kg^{-1}	Consumption/ kg m^{-3}	Price of chemicals/ US \$ m^{-3}	cost/%	Price of chemicals/S \$ m^{-3}	cost/%
H_2SO_4	70%	0.15	0.589	0.088	3.80	–	–
HIPAC	17%	0.24	0.960	0.230	9.90	0.230	27.86
Polymer	–	3.40	0.004	0.014	0.60	0.014	1.7
$FeCl_2$	30%	0.11	2.288	0.252	10.83	0.252	30.52
H_2O_2	35%	0.55	2.034	1.119	48.10	–	–
$Ca(OH)_2$	75%	0.13	1.667	0.217	9.32	0.217	26.28
NaCl	–	0.21	0.500	0.105	4.50	–	–
HCl	–	0.35	0.003	0.001	0.05	–	–
Power per electrolysis on ED				0.300	12.9	0.1125	13.63
Total				2.325	100	0.8255	100

gives a total savings of 64.57% when compared with the process currently being implemented in the industry (Table 3).

5 Conclusions

The systematic study of hydrogen peroxide electrogeneration at the GDE in plant wastewater, which contained morpholyne and diethylethanolamine, as well as sodium salts of naphthalene sulfonic acid and ethylenediaminetetraacetic acid, was carried out at different current densities and solution temperatures at pH 3. A decay of current efficiencies was observed at elevated temperatures (60 °C), as well as at high current densities (0.2 A cm^{-2}). Hydrogen peroxide generation proceeded at the initial period with almost 100% current efficiency in solutions polluted by organic substances, with H_2O_2 accumulation in concentrations sufficient for its mineralization in consecutive Fenton reactions, as well as in simultaneous electro-Fenton treatment.

Results obtained with a membrane cell divided by a proton-exchange membrane were found to be preferable to those obtained using an undivided cell. The combined method with the initial electrodestruction of organics by active chlorine generated at the anode, and consecutive treatment in the cathode chamber by the hydrogen peroxide electrogenerated at the cathode could also be suggested for some wastewaters.

Economic analysis taking into account the consumption and price of chemicals used in plant wastewater treatment indicates that up to 64.5% of running costs can be cut when electrochemically generated hydrogen peroxide is used for the Fenton treatment of organic waste in comparison with the use of chemicals purchased for this purpose.

References

1. Fenton HJH (1894) J Chem Soc 65:899
2. Ullmann's Encyclopedia of Industrial Chemistry5th edn (John Willey & Sons, Weinheim, 1989), XV, pp 632
3. Harrington T, Pletcher D (1999) J Electrochem Soc 146:2983
4. Bartlett PhN, Pletcher D, Zeng J (1999) J Electrochem Soc 146:1088
5. Brillas E, Bastida RM, Llosa E (1995) J Electrochem Soc 142:1733
6. Brillas E, Mur E, Casado J (1996) J Electrochem Soc 143:L49
7. Brillas E, Sauleda R, Casado J (1996) J Electrochem Soc 144:2374
8. Brillas E, Sauleda R, Casado J (1998) J Electrochem Soc 145:758
9. Brillas E, Casado J (2002) Chemosphere 47:241
10. Standard Methods of Water Pollution Control. Dong-Wha-Ki Sul. (Korean, 1999) 214
11. Kim KW, Kim J-S, Jung BJ (2003) Fabrication method of catalytic oxide electrode for water treatment. Korean patent 0403235
12. Kim KW, Kim JS, Jung BJ (2003) Catalytic oxide anode manufacturing method by high temperature sintering. Korean patent 0407710
13. Kim KW, Kim JS, Jung BJ (2003) Method for manufacturing catalytic oxide anode using high temperature sintering. Japan patent 3428976
14. Kim KW, Lee EH, Shin KH, Jung BJ (2002) J Electrochem Soc 149:D187
15. Agladze GR, Tsurtsumia GS, Jung BJ, Kim JS, Gorelishvili GG (2007) J Appl Electrochem 37:375
16. Agladze GR, Tsurtsumia GS, Jung BJ, Kim JS, Gorelishvili GG (2007) J Appl Electrochem 37:385