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OXIDISING AND DISINFECTING BY HYDROGEN PEROXIDE PRODUCED IN A TWO-ELECTRODE CELL

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Abstract—Hydrogen peroxide was produced by direct current electrolysis using two electrodes only, a carbon felt cathode and a dimensional stabilised anode (titanium coated with RuO_2), without adding any chemical. The required oxygen was supplied by water oxidation and by transfer from the atmosphere. The intensity should be maintained under a maximum value to avoid peroxide reduction. High peroxide production rate and concentration were then reached. Electroperoxidation partially removed dissolved organic carbon (DOC) contained in solutions of phenol, salicylic acid, benzoic acid and humic acids. The DOC removal in effluent of municipal sewage plant corresponded to a breakage of the double bonds. Real effluents were significantly disinfected owing to the direct effect of electric current and the indirect effect of peroxide. Moreover, a remnant effect was ensured. © 2001 Elsevier Science Ltd. All rights reserved

Key words—disinfection, electrochemical treatment, electrolysis, hydrogen peroxide, oxidation

INTRODUCTION

Conventional techniques of water disinfection are mostly inconvenient. Chlorinating generates hazardous and carcinogenic compounds (Jolley *et al*., 1982). Ozone and ultraviolet light are efficient and produce harmless derivatives but they are more expensive (Christopher and Richard, 1995); moreover, ultraviolet light has no remnant effect. Research of alternative oxidants is actually carried out to identify inexpensive techniques, with remnant effect, producing harmless substances. Such a process could be based on hydrogen peroxide produced by electrolysis.

Hydrogen peroxide is a metastable molecule of high redox potential (1.77 V). Its disinfecting properties result from a direct molecular action (Doré, 1989) but, mostly, from free radicals which are formed by catalysis (Guitonneau *et al*., 1988). Hydrogen peroxide can be chemically produced from peroxigenated compounds or by electrolysis of sulphuric acid or sulphates with a platinum anode (Barbier and Nguyen, 1996). A conventional electrochemical technique reduces oxygen at the cathode with potassium hydroxide as electrolyte (Berl, 1939). Some recent works described peroxide production in a three-electrode cell in presence of Fenton reactive (Oturan, 1999). However, the challenge would be producing hydrogen peroxide in a two-electrode cell without any added chemical. A preliminary voltametric study showed that hydrogen peroxide could be produced in a cell provided with a vitreous carbon cathode and a dimensional stabilised anode (DSA) (Drogui, 1999). This work evaluates the electrochemical peroxide production and its oxidative and disinfecting properties.

MATERIALS AND METHODS

Electrolysis cell

The PVC (0.5 cm thickness) cylindrical electrolysis cell, 30 cm long, had two volume electrodes separated by an electrically insulating porous diaphragm that allowed circulation of the liquid phase (Fig. 1). The electrodes were made with suitable materials identified in a preliminary study (Drogui, 1999). Vitreous carbon was selected as cathode and DSA (titanium coated with RuO_2) as anode. The 177-cm^2 cathode, in carbon felt RVC 4000 provided by Le Carbone Lorraine, of 0.94 porosity, induced low hydraulic resistance. The carbon felt layer (fibres of 10 μm diameter) was 12 mm thick. A steel grid, on the carbon felt, ensured the electric contact. The anode had a solid surface area of 67 cm^2 and a void surface area of 110 cm^2. Another stainless-steel grid, used as cathode, enabled polarising the carbon electrode to ensure elimination of the carbonate deposit when required. The formation of calcium carbonate at the cathode results in one of the following reactions:

$$4HCO_3^- + 4Ca^{2+} + 4e^- \rightarrow 4CaCO_3 + 2H_2$$

$$O_2 + 4HCO_3^- + Ca^{2+} + 4e^- \rightarrow 4CaCO_3 + 2H_2O$$

An inversion of the electrode polarisation and of the liquid circulation, at low flow-rate, ensured anodic dissolution of

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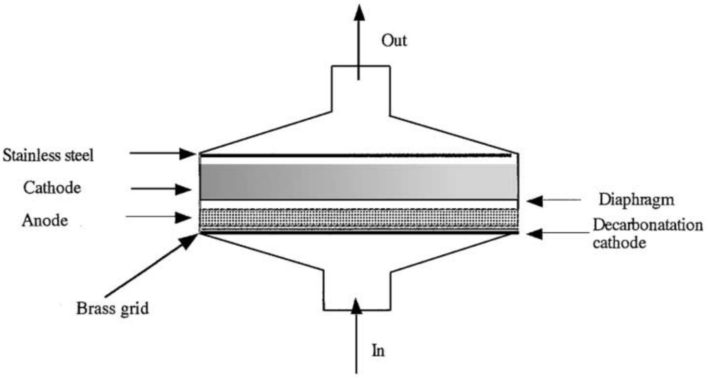

Fig. 1. Electrolysis cell.

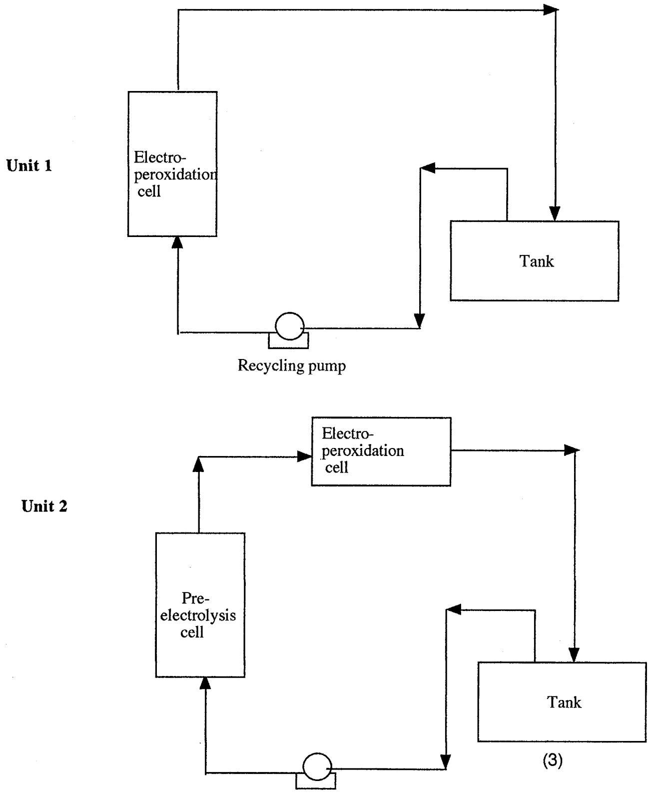

Fig. 2. Experimental units.

the carbonate deposit. The carbon electrode, anodically polarised, produced H^+ ions which react with insoluble $CaCO_3$ giving soluble $Ca(HCO_3)_2$:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

$$2CaCO_3 + 2H^+ \rightarrow Ca(HCO_3)_2 + Ca^{2+}$$

A brass grid (72% Cu, 28% Zn), used to catalyse the formation of free radicals (Doré, 1989), was installed over a layer of rubber foam (0.5 cm thickness) against the cathode, during the disinfection runs (water flows from the steel grid towards the brass grid inside the cell). Hydrogen peroxide is adsorbed on the metal M (McKee, 1969):

$$H_2O_2 + M \rightarrow M(O)H_2O$$

The adsorbed layer M(O) induces a peroxide dissociation:

$$M(O) + H_2O_2 \rightarrow M + O_2 + H_2O$$

During these reactions, many intermediate compounds are produced (OH^0, OH^-, HO_2^-, HO_2, etc.) (McKee, 1969).

Experimental units

Two units were operated. Unit 1 included a 5-litre tank in a closed loop with the electrolysis cell where a recycling induced perfect mixing of the liquid phase (Fig. 2). The turbulence allowed transferring oxygen from the atmosphere to the liquid phase. A second electrolysis cell was installed in the loop of unit 2 (Fig. 2). This cell was provided with a DSA anode and a stainless-steel cathode.

Tested solutions and suspensions

The liquid phase was tap water, without adding any chemical, in all the runs of peroxide production or wastewater treatment. In the oxidation runs of pure compounds, the following substances were dissolved in distilled water: phenol, salicylic acid, benzoic acid and humic acids (Acros Organic). Considering the very low conductivity of distilled water, sodium sulphate (10^{-3} M) was added to reach a suitable conductivity of 250 μS/cm).

The removal of some characteristic microorganisms, usually contained in wastewater, was studied: coliforms, pseudomonas and streptococcus. Non-carbonated natural mineral water was contaminated with the effluent of a municipal wastewater treatment plant including a biological step (Montpellier or Mèze, France). Some experiments were carried out with pure culture of *Pseudomonas aeruginosa*.

Analytical techniques

Hydrogen peroxide concentration was determined by the cerium sulphate technique, which involves peroxide oxidation in the presence of some ferrous orthophenantroline drops (Doré, 1989):

$$2Ce^{4+}+H_2O_2 \rightleftharpoons 2Ce^{3+}+O_2+2H^+$$

Oxygen concentration was given by an oxymeter WTW- SL 340. Dissolved organic carbon (DOC) was measured with a TOC-meter Shimadzu TOC 5000. Turbidity was obtained with a turbidimeter Hach DR 2000. An absorbance of 254 nm was obtained with a spectrophotometer Jasco V-530. Most other parameters, particularly microorganism concentration and chemical oxygen demand (COD), were determined in conformity with the Standard Methods for the Examination of Water and Wastewater (1995).

RESULTS AND DISCUSSION

Hydrogen peroxide production

Many processes are involved in hydrogen peroxide synthesis by cathodic reduction of oxygen. Water oxidation takes place on the anode:

$$2H_2O \rightleftharpoons O_2+4H^++4e^- \tag{1}$$

Even though for most materials (Pt, graphite, Zn, V, Zr, Cu, Hf) dissolved, oxygen reduction occurs theoretically in two steps, only one wave can be observed. These materials would therefore catalyse the peroxide decomposition (Pellequer, 1950). A vitreous carbon cathode induces a two-wave process (Drogui, 1999). Hydrogen peroxide addition to tap water allowed identifying the second step as peroxide reduction. This result is consistent with the following mechanism (Berl, 1939; Trémillon, 1993).

$$O_2+2H^++2e^- \rightleftharpoons H_2O_2 \tag{2}$$

$$H_2O_2+2H^++2e^- \rightleftharpoons 2H_2O \tag{3}$$

A dimensional stabilised anode was selected since the decomposition potentials of water and peroxide are nearly identical (1 V) (Drogui, 1999). Water being in excess, the peroxide oxidation would be limited. Moreover, reaction (3) should also be limited to enhance the peroxide production. A third electrode and a potentiostat, generally expensive, are not required if the electronic balance favours reaction (2). Four electrons are indeed produced on the anode. Two electrons are used to reduce the transferred oxygen, whereas the two others should exclusively reduce the oxygen produced on the anode. This condition is met if the intensity I is less than a maximum value given by:

$$I \leq \frac{QFC}{M_{O_2}} \tag{4}$$

where Q is the flow-rate through the cell, F the Faraday number, M_{O_2} the mass of an oxygen mole and C the oxygen concentration. In all the runs, the flow-rate was 140 l/h. Oxygen concentration varied between 8 and 10 mg/l.

Berl (1939) and McIntyre (1995) studied electroreduction of oxygen in alkaline solution in a two-electrode cell. McIntyre's synthesis was based on the oxidation of sodium hydroxide into oxygen at an anode, whereas hydrogen peroxide was produced via the subsequent reduction of oxygen. Berl (1939) carried out similar experiments with potassium salts as the electrolyte. Both authors obtained a 0.9 current efficiency that is quite higher compared to the 0.21 yield obtained in electroperoxidation (Drogui, 1999). This significant difference is probably due to the high electrical resistance of the electroperoxidation cell in which no chemical was added. For example, McIntyre (1995) operated at a 2 V potential with a current of 5000 A, whereas the electroperoxidation potential was approximately 25 V with a 2 A current. An electrolyte solution allows minimising the ohmic loss.

Without adding any chemical to tap water, the peroxide concentration, in the loop of unit 1, linearly increased with elapsed time then tended towards a plateau due to a limitation by dissolved oxygen concentration and peroxide decomposition (Drogui, 1999) (Fig. 3). The plateau values are significantly high to consider oxidising and disinfecting by this electrochemical process that will be called electroperoxidation. The rate of peroxide production was proportional to current intensity (Drogui, 1999), which is in agreement with the results obtained by Kraft *et al.* (1999). They observed the same dependence on current of the production rate of active chlorine, IrO_2 being used as anode with a 150 mg/l chloride concentration. The current efficiency for iridium oxide, at that chloride concentration, was 41.5%, a high value compared to 20% obtained with electroperoxidation (Drogui, 1999). The current efficiency of electroperoxidation was generally lower than for other electrochemical processes. However, electroperoxidation has many advantages, e.g., it does not induce carcinogenic compounds (Jolley *et al.*, 1982). McIntyre's (1995) and Berl's (1939) synthesis require addition of chemicals. Electroperoxidation allows reducing the operation cost.

Dissolved organic carbon removal

The electrochemical oxidation of dissolved organic substances leads to results similar to chemical oxidation with peroxide (Doré, 1989). Phenol and humic acids were more oxidised and faster than benzoic or salicylic acid but, in all cases, the removal was less than 50% (Fig. 4). Aromatic carriers of electron donor groups (phenol) are more reactive than aromatic carriers of electron attractive groups (benzoic and salicylic acid) and hydroxyl groups (phenol) induce fast oxidation kinetics. (Doré, 1989). Electroperoxidation could also remove dissolved organic carbon, contained in a sewage plant effluent (Fig. 5). The 254-nm absorbance was removed at the same rate (Fig. 5). The 254-nm absorbance is linked to organic compounds with one or many double bonds. Electroperoxidation, therefore, broke the double bonds producing smaller molecules. The oxidation of DOC was not complete because of refractory compounds or insufficient peroxide production. Only 40% of the DOC were removed, which is low compared to the 80–100% abatement obtained with catalytic oxidation (Matatov-Meytal and Sheintuch, 1998). However, catalytic oxidation requires high temperature (800–850°C), high pressure, and metal oxides like Cr_2O_3, CuO or V_2O_5 and metals like Pt or Pd as catalysts. These conditions make catalytic oxidation expensive.

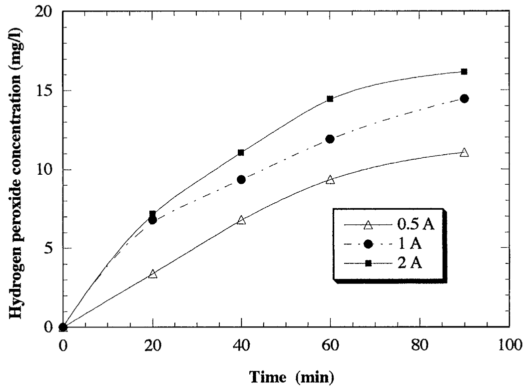

Fig. 3. Hydrogen peroxide concentration against time at different intensities (unit 1, tap water).

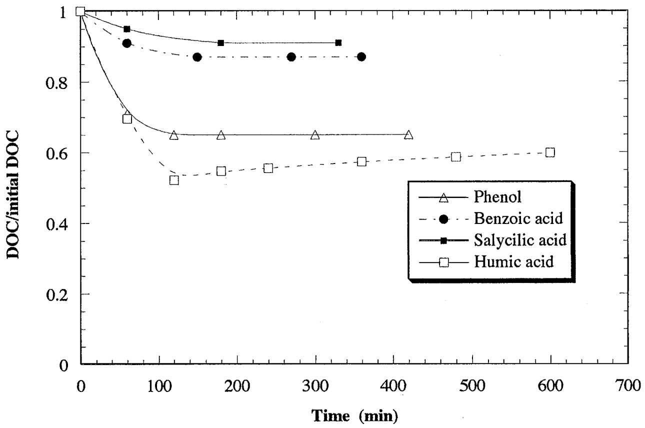

Fig. 4. Oxidation of organic compounds in unit 1 at 1 A (initial DOC concentrations: 35 mg/l (phenol), 31 mg/l (salicylic acid), 26 mg/l (humic acids) and 36 mg/l (benzoic acid)).

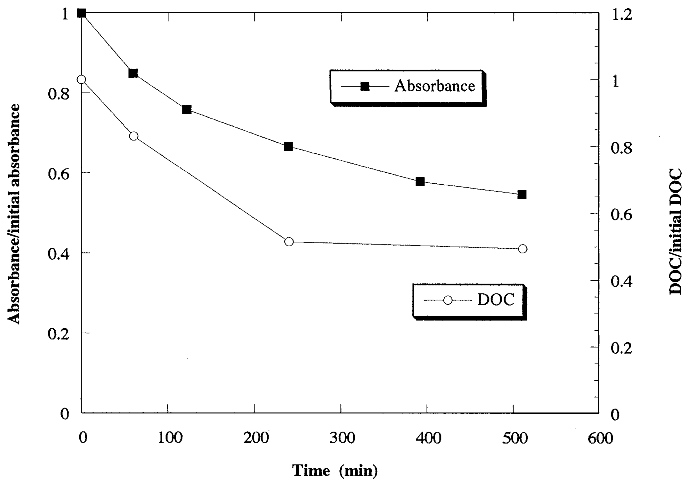

Fig. 5. DOC and 254 nm absorbance removal (effluent of Mèze sewage plant; 40 mg/l initial DOC; unit 1).

Turbidity removal

Turbidity takes into account solid and colloid particles (humic substances, fulvic acid, proteins and microorganisms larger than 0.1 μm). Disinfection is hampered by high turbidity (Logsdon *et al.*, 1985; Montiel and Welte, 1990). Turbidity could protect some microorganisms, e.g., coliforms (Seidler and Evans, 1982). Turbidity contained in the effluent of a municipal wastewater treatment plant was nearly totally removed by electroperoxidation (Fig. 6); moreover, the initial brown colour disappeared and water became transparent. Turbidity was nearly not removed without electric current and the overall abatement cannot be due to filtration of the initial suspension through the porous media contained in the cell (Fig. 6). The generated electric field neutralised the surface charges of the colloid particles inducing their agglomeration and sedimentation; the carbon felt was not fouled. The turbidity decrease was also due to the oxidation of the organic matter and bacteria.

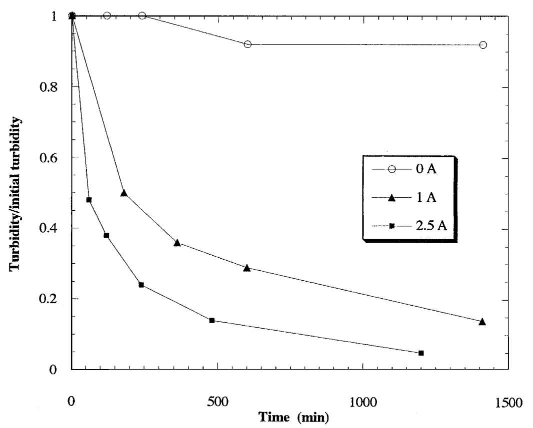

Fig. 6. Turbidity removal (effluent of Montpellier sewage plant; 12 FTU initial turbidity; unit 1).

Disinfection

Microorganism abatement depended on the initial COD concentration since a fraction of the produced peroxide was used to oxidise the dissolved organic substances (Fig. 7). Is disinfection induced by electroperoxidation comparable to disinfecting with the sole hydrogen peroxide? The direct effect of electrolysis corresponds to oxidation or reduction on an electrode. The indirect effect results from the peroxide production. Both effects cannot be separated during electroperoxidation. However, their respective contribution to disinfecting could be evaluated by the following procedure.

Non-carbonated natural mineral water was electrolysed in unit 1, without catalyst, to reach a 12 mg/l plateau concentration of peroxide. Then a sample was taken from the tank, poured in a beaker containing a brass grid, and contaminated with *Pseudomonas aeruginosa*. This sample was therefore treated by the sole effect of chemical hydrogen peroxide and free radicals. The remaining tank content was also contaminated while the electrolysis was maintained in operation in presence of the catalyst; this second sample was therefore submitted to two main processes, i.e., the chemical effect of peroxide and free radicals and the electrical effect. Disinfecting was much more effective with simultaneous electrolysis, which induced more than 3-log difference (Fig. 8). This result can be explained as following.

The vital centres of bacterial cells are protected by a membrane essentially constituted by a bimolecular layer of phospholipids with hydrophobic and hydrophilic parts (Prescott *et al.*, 1995). Protein inclusions, within the membrane, allow ion exchange with the

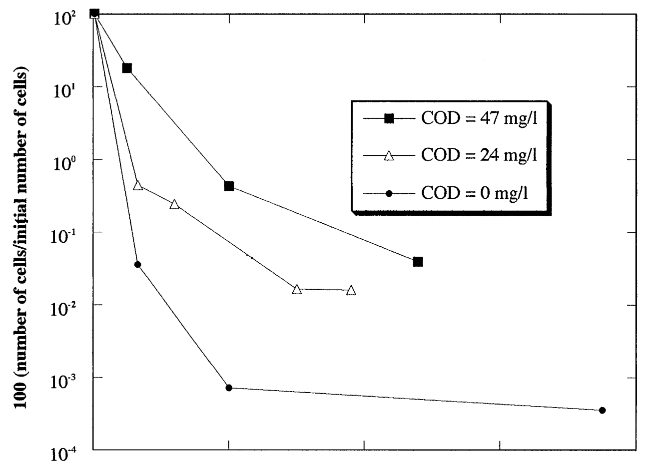

Fig. 7. Faecal coliforms removal for different initial COD: non-carbonated natural mineral water (0 mg/l) and same mineral water mixed with Mèze sewage plant effluent (24 and 47 mg/l) at 1.5 A intensity in unit 1.

cell environment. The phospholipidic membrane is not easily oxidised, whereas the proteins are easily destroyed by the direct effect of electrical current (Pillaud, 1987). The cell cannot then exchange ions. However, it could be re-activated in a more favourable environment (Crémieux and Freney, 1995). Its total destruction requires an oxidant able to cross the membrane and reach its vital centres, which is done by hydrogen peroxide generated at the cathode (Garnerone, 1979). Moreover, the electrolysis induces a pH gradient which affects bacteria (Savluk, 1982; Crémieux, 1995).

Unit 2 offered a double advantage. Oxygen, which was produced on the cathode of the conventional cell, could be used to increase overall peroxide production. Moreover, the direct effect was enhanced while severe pH variations were locally imposed. Disinfecting was indeed higher when the second cell was simultaneously operated; a difference of 2 log units was observed (Fig. 9). In both cases, the maximum abatement was obtained after 1 h treatment. The slight cell number decrease was probably due to retention on the carbon felt.

Another interesting peculiarity of hydrogen peroxide results from its remnant effect. The effluent of a municipal sewage plant was electrolysed in unit 1, during 3 h, at 1.5 A intensity. Then the current was switched off and bacteria and hydrogen peroxide concentrations were monitored starting at that moment. The bacteria concentration rapidly decreased towards a plateau, reached in less than 5 h, while the peroxide concentration remained significant after 20 h (Fig. 10).

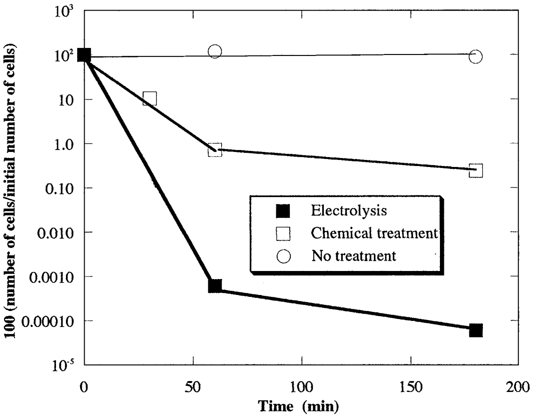

Fig. 8. Compared survival of *Pseudomonas aeruginosa* with electrolysis and chemical oxidation (non-carbonated natural mineral water) at 1.5 A intensity in unit 1.

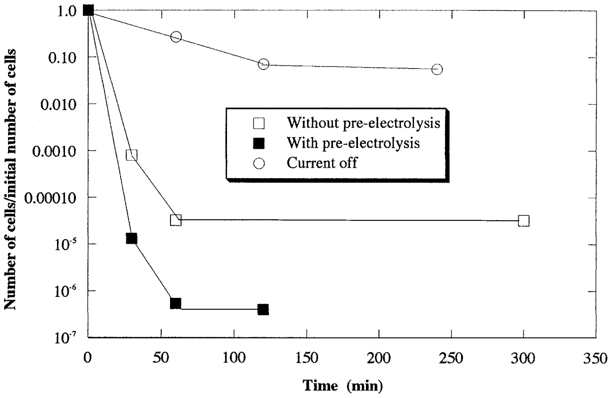

Fig. 9. Compared survival of total coliforms with and without pre-electrolysis (unit 2, 1 A pre-electrolysis, 3 A electroperoxidation).

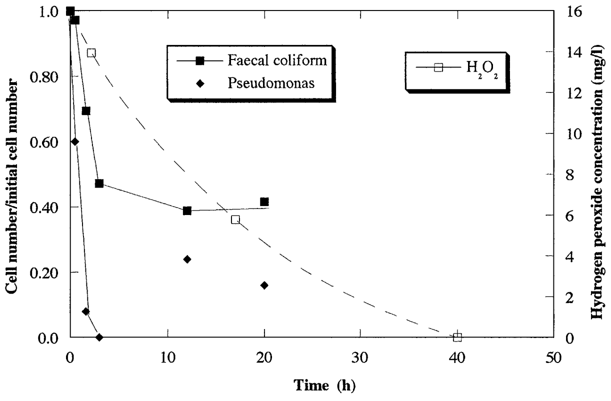

Fig. 10. Disinfecting effluent of Mèze sewage plant: bacteria removal and remnant effect (unit 1, 1.5 A).

CONCLUSIONS

(1) Hydrogen peroxide could be electrochemically generated with a two-electrode cell, without adding any chemical.

(2) Electroperoxidation was effective for removal of dissolved organic carbon.

(3) Electrochemical production of hydrogen peroxide, combined with the effects induced by an electric field, was effective for removal of turbidity and production of a clear effluent.

(4) Disinfecting by electroperoxidation combines the direct effect of electrolysis to the oxidative indirect effect of hydrogen peroxide.

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