A Feasibility Study of Hydrogen Peroxide Electrogeneration in Seawater for Environmental Remediation

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The electrogeneration of hydrogen peroxide in seawater by oxygen reduction on a gas diffusion cathode was investigated considering the feasibility of this process in an undivided reactor. The possible co-presence of different oxidants and the possibility of their synergistic action was evaluated. The loss of hydrogen peroxide due to direct anodic oxidation and to reaction with anodically electrogenerated species was evidenced. To optimize the production efficiencies of both active chlorine and hydrogen peroxide, the influence of electrode materials and current density was studied.
An investigation of the possible analytical interferences was also provided.

1. Introduction

The treatment of effluents from remediation process of contaminated sediments requires the development and application of green technologies aimed at minimizing waste production and mitigating the negative impact with the adoption of environmentally-friendly chemicals.

Hydrogen peroxide, unlike other oxidants, does not pose the risk of gaseous release or chemical residues (Drogui et al, 2001). Moreover, the in situ production, either by catalysed reaction (Biasi et al., 2011) or electrogeneration, avoids the hazard associated to storage, transportation and handling of highly concentrated solutions. In particular the electrogeneration, by means of oxygen cathodic reduction on carbon cathodes, involves the formation of different radical species such as superoxide radicals $O_2^{\cdot-}$ and hydroperoxide radicals $HOO^{\cdot}$ (Alvarez and Pletcher, 1998; Qiang and Huang, 2002). Increasing efficiency and economic save have been obtained by adopting, as the cathode, a gas diffusion electrode either catalysed (Guillet et al, 2006) or uncatalysed (Alcaide et al., 2002). The better performance of a gas diffusion electrode (Da Pozzo et al., 2005) can be attributed to the increased reactive area but also to the porosity that makes gas transport and reagent diffusion easier thus allowing to overcome the difficulty related to the solubility of oxygen into the catholite and its transport from the bulk to the cathode surface.

The cathodic electrogeneration of hydrogen peroxide in aqueous solution has been so far extensively studied mostly considering as main applications the disinfection of drinking water and the electro-Fenton's reaction for the treatment of water and wastewater containing recalcitrant and toxic compounds. However, scarce investigations are still available about electrosynthesis of hydrogen peroxide in seawater. A previous paper (Da Pozzo et al., 2008) indicates that in a two-compartment cell notable concentrations of hydrogen peroxide are obtained with a constant yield in a wide range of charge. However, due to the high salinity of the medium, serious fouling phenomena affect the

membranes used for separation thus resulting in increasing values of cell resistance. Besides in the presence of a separation, high investment and operating cost are needed. The electrogeneration of hydrogen peroxide in undivided reactor is expected to lead to lower concentrations. This is due to numerous reactions such as: anodic oxidation with oxygen evolution, cathodic reduction to water, chemical decomposition in the bulk of solution and chemical reaction with species anodically generated as well as reactions with species cathodically generated (O_2^-, $^\bullet OH$, $O_2H^\bullet$) as suggested by Agladze et al. (2007). However, in the absence of a separation, the simultaneous anodic electrogeneration of different oxidising species, in particular active chlorine (which is a mixture of chlorine, hypoclorous acid and hypochlorite ions), chlorates and bromates, certainly occurs. It is thus worth assessing whether the synergistic action of different oxidants can compensate for the lower concentration of peroxide.

This study was aimed at verifying the feasibility of cathodic electrogeneration of hydrogen peroxide in an undivided electrolyser. The coexistence of different oxidising species and the possibility of their synergistic action were evaluated analyzing the analytical interference in the determination of their concentrations.

2. Experimental

2.1 Materials
Reagents were supplied by Carlo Erba Company and Sigma Aldrich and used in their commercially available form without further purification. To ensure reproducibility, all the electrolyses were conducted on solutions of artificial seawater prepared according to Kester et al. (1967). In this recipe: 47.852 g NaCl, 8.016 g Na_2SO_4, 1.354 g KCl, 0.392 g $NaHCO_3$, 0.196 g KBr, 0.052 g H_3BO_3, 0.006 g NaF, 10.16 g $MgCl_2$, 2.2954 g $CaCl_2$, 0.0284 g $SrCl_2$, were dissolved in two litres of distilled water in the absence of organic constituents. The initial pH was 7.4 - 7.5 while the conductivity was 40 mS.

2.2 Electrochemical apparatus and procedure
Electrolyses were performed under galvanostatic conditions using a potentiostat AMEL 2051.

The electrolyser was an undivided glass cell having a volume of 100 mL. The reactor was thermostated and stirred with a magnetic bar. The cathode was an uncatalysed gas diffusion electrode (GDE). This electrode, described in detail in previous work (Petrucci et al, 2009), had a geometric area of about 5 cm^2 and was fed with air (130 mL/min). It was coated on both sides by hydrophobic Shawinigan acetylene black carbon (SAB) provided by Industrie De Nora (Milan, Italy). The anodes tested were a commercially available Pt wire (supplied by Amel mod. 805/SPG/12J), a home made Pt disk with a total surface area of 5 cm^2, and a Boron-Doped Diamond electrode (supplied by Adamant Technologies) with a total surface area of 5 cm^2. The electrodes were placed vertically at a distance of about 1 cm. Unless differently specified tests were conducted at a current density of 400 A m^{-2}, at ambient temperature at least in triplicate. Samples were withdrawn at defined time intervals during the electrolysis for immediate analysis of active chlorine, hydrogen peroxide and anions content.

2.3 Analyses
pH was measured using a Crison GLP 421 pH meter, conductivity using a HD9213-R1Delta Ohm meter. Hydrogen peroxide concentrations were determined reflectometrically by means of Merck analytical tests based on a peroxidase catalyzed reaction. The active chlorine concentration was determined using the DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (EN ISO 7393/2, 2000). At circumneutral pH, the colourless N,N-diethyl-p-phenylenediamine is oxidised by active chlorine into a coloured product with an absorbance peak at 510 nm measured by means of a PG Instruments T80+ UV/vis Spectrophotometer and quartz cells of 1 cm path length.

Anions were determined using a Dionex 120 ionic chromatograph equipped with an IONPAC AS12A anionic column in isocratic mode and conductometric detector. Fast analyses of perchlorate were carried out using the Ion Chromatograph DX120 equipped with a RFC 30 eluent generator and a IONPAC AS16 anionic column. The conditions adopted were: a gradient from 35 mM at 0 min to 38 mM at 8 min, a flow rate of 1.5 mL min^{-1} and an injection volume of 25 μL.

3. Results

To verify the simultaneous electrogeneration of the oxidants anodically and cathodically produced a preliminary series of tests was conducted to quantify the production of hydrogen peroxide and active chlorine, one at a time. In particular, to evaluate the amount of hydrogen peroxide electrogenerated at the cathode, electrolyses were performed in the absence of chloride, on solutions of Na_2SO_4 0.1M with an initial pH of 6.5. Unless otherwise specified, all the runs were carried out at at room temperature (20 °C) applying a current density of 400 A m^{-2} using a GDE as cathode with a platinum wire as anode. As expected, in the absence of chloride, as shown in Figure 1, there is no production of active chlorine while hydrogen peroxide presents increasing concentration up to 710 mg L^{-1}. The hydrogen peroxide production rate tends to decrease with time while current efficiency, defined as the ratio of the amount of hydrogen peroxide actually produced to the amount theoretically expected from Faraday's law (Da Pozzo et. al, 2008), drops to a value less than 40 % after 1 h of electrolysis. Although hydrogen peroxide is known to be an interfering species in the determination of active chlorine with DPD method, these data exclude the possibility since in the presence of H_2O_2 the amount of active chlorine was always found undetectable. Tests here not reported, verified that the analytical error, due to the presence of hydrogen peroxide in the spectrophotometric determination of active chlorine, becomes appreciable for H_2O_2 concentrations higher than 1000 mg L^{-1}.

To evaluate the concentrations of active chlorine anodically electrogenerated, galvanostatic electrolyses of seawater solutions were conducted at j = 400 A m^{-2}. To avoid the simultaneous production of hydrogen peroxide, a platinum disk was used as cathode. Figure 2 shows that a notable amount of active chlorine is produced during the electrolysis. Moreover, contrary to the expected results, increasing concentrations of hydrogen peroxide was also detected. The test was then repeated under the same operating conditions in the absence of chloride using a 0.1 M Na_2SO_4 solution. The experiment confirmed the inability of platinum cathodes to reduce oxygen to hydrogen peroxide whose detection was solely due to analytical interference of active chlorine on the analytical determination of hydrogen peroxide with the peroxidase based technique. A quantification of the interference was obtained measuring H_2O_2 in solutions containing given concentrations of active chlorine (in the range 0 - 200 mg L^{-1}) in the absence of hydrogen peroxide. A positive linear interference was observed in the range of concentrations studied ($[H_2O_2]_{detected}$=0.1219×[Active chlorine], R^2 = 0.994).

After assessing each single production, a series of tests have been conducted to investigate the oxidants' simultaneous electrogeneration in electrolyses of seawater using a GDE as cathode and a Pt wire anode. The concentration of H_2O_2 (Figure 1) and active chlorine (Figure 2) are found lower than those obtained when electrogenerated alone. However, given that high amounts of active chlorine are produced, it can not be excluded that a reaction with hydrogen peroxide causes the overall depletion of this species and that the content of hydrogen peroxide detected is only due to the analytical interference of the residual active chlorine. To deeply investigate this issue, further electrolyses were performed in seawater enriched with an initial H_2O_2 content of 100 mg L^{-1}, under the same operating conditions previously adopted. The data shown in Figure 1 indicate that after thirty minutes of treatment the concentration of hydrogen peroxide does not present the expected increase, due to the contemporary cathodic electrogeneration and, on the contrary, it is even lower than the initial content. In addition, the amount of active chlorine generated in the presence of an initial concentration of hydrogen peroxide, is considerably less than that detected in electrolyses conducted in the absence of peroxide (Figure 2) suggesting the occurrence of a reaction that involves the two species. This hypothesis was confirmed by carrying out a series of tests where different amount of hydrogen peroxide and active chlorine were mixed in a flask and determined after 5 min. The results indicate that under the adopted conditions a weight ratio $[H_2O_2]$ / [Active chlorine] ≈ 0.5 and a molar ratio (expressing the active chlorine as mgL^{-1} Cl_2) equal to 1 were found. This reaction involves the reduction of the hypochlorite to chloride by oxidizing the peroxide to water and is favored under acidic conditions (results here not reported).
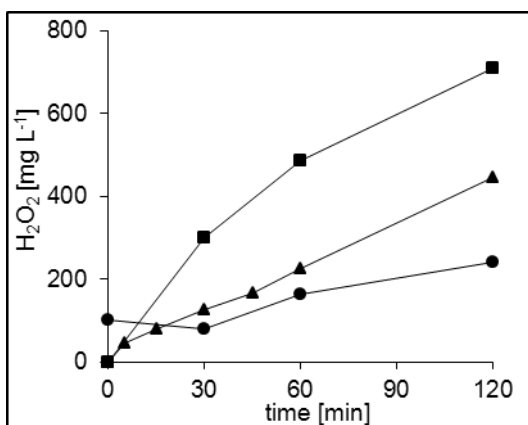
Figure 1: H₂O₂ production in (■) Na₂SO₄ 0.1 M; (▲)seawater; (●)seawater with 100 mg L⁻¹ of initial H₂O₂.

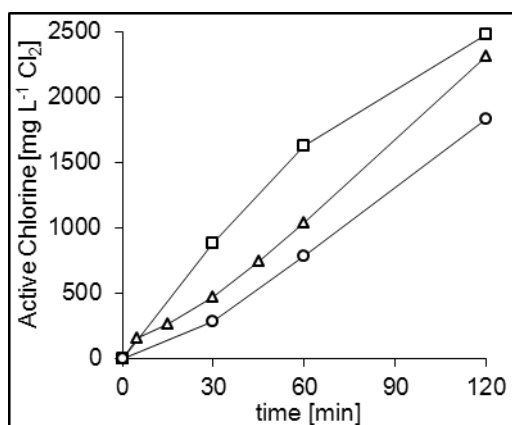*Figure 2: Active chlorine production in (□) Na₂SO₄ 0.1M (cathode: Pt disk); (Δ) seawater and (○)seawater with 100 mg L⁻¹ of initial H₂O₂ (cathode: GDE)*

The results so far illustrated suggest that the use of the undivided cell does not represent a viable possibility to take advantage of a synergistic effect of oxidants. In fact, under the conditions adopted, the high amount of active chlorine produced at the anode and the reaction occurring between this species and the hydrogen peroxide cause a rapid consumption of the latter. Nonetheless the substantial technological and economic benefits deriving from using an undivided cell lead to further investigate the feasibility of this treatment. For this reason the study was focused on determining the operating condition that negatively affect the electrogeneration of active chlorine in order to favour the persistence in solution of the hydrogen peroxide. In particular, the influence of the applied current density on the electrogeneration of active chlorine was investigated in the range 100-800 A m⁻². As shown in Figure 3A, the concentration of active chlorine as a function of the electrolysis time increases with increasing current density while, as reported in the inset of Figure 3A, is unaffected by charge, in the whole range of current density adopted. This can be explained by considering that the amount of chloride ions in seawater is sufficiently high to avoid that the mass transport rate of this ion, from the solution bulk to the anode, limits the electrogeneration of active chlorine even when higher values of current density would favor the occurrence of side reactions (i.e. oxygen evolution).

Besides active chlorine, further products, such as chlorite, chlorate and perchlorate, are expected to be generated by the oxidation of chloride ions. However chromatographic analyses only confirmed the presence of chlorate whose concentration should be strictly controlled, being considered an unwanted product in the aquatic environment. Similarly to what previously reported for active chlorine, also chlorate production is enhanced by increasing current density (Figure 3B) thus suggesting the adoption of 100 A m⁻² as the optimum value. This value also corresponds to the least cell potential (3.7 V) and subsequently to a lower energy consumption. Moreover, a low current density limits the cathodic side reactions such as the evolution of hydrogen whose occurrence severely affect the cathodic production of hydrogen peroxide.

The effect of anodic materials on the production of active chlorine and chlorate was finally considered. A Pt wire, a Pt disk and BDD electrode with a rectangular surface of 5 cm² were used in these trials. Figure 4A illustrates the concentration of active chlorine with time. Data obtained show that lower concentration of active chlorine was produced when the electrochemical cell was equipped with a Pt disk anode. After two hours, a concentration of 500 mg L⁻¹ was detected in solution, while 677 mg L⁻¹ was the final concentration when a Pt wire electrode was used. Considering that the higher surface area of the disk should promote the direct oxidation of chloride ions, this was an unexpected result that will need further investigation. Data collected during the tests conducted with the BDD anode show a particular behavior. Although a high production rate of active chlorine was observed at the beginning of

electrolysis, the final concentration was very similar to that found in tests with Pt wire anode. This result can be explained considering that BDD anodes provide huge amount of ˙OH that easily react with the electrogenerated active chlorine to further produce chlorine species with higher oxidation state. This hypothesis was confirmed by studying the effect of anodic material on chlorate production. As shown in Figure 4B, chlorate concentration is notably promoted by the use of BDD anodes.
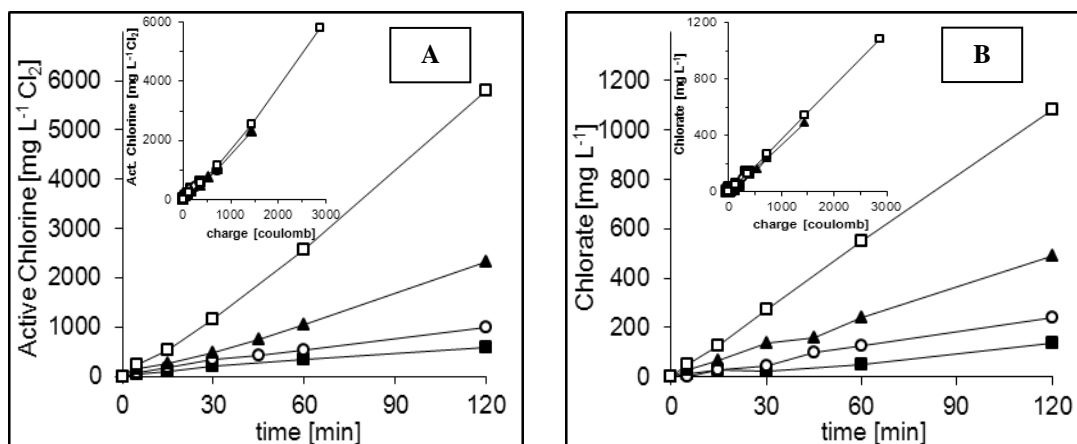

Figure 3: Current density effect on active chlorine (A) and chlorate (B) concentration vs time. Inset: concentration vs charge. (■) 100 A m^{-2}, (○) 200 A m^{-2}, (▲) 400 A m^{-2}, (□) 800 A m^{-2}. Cathode: GDE.
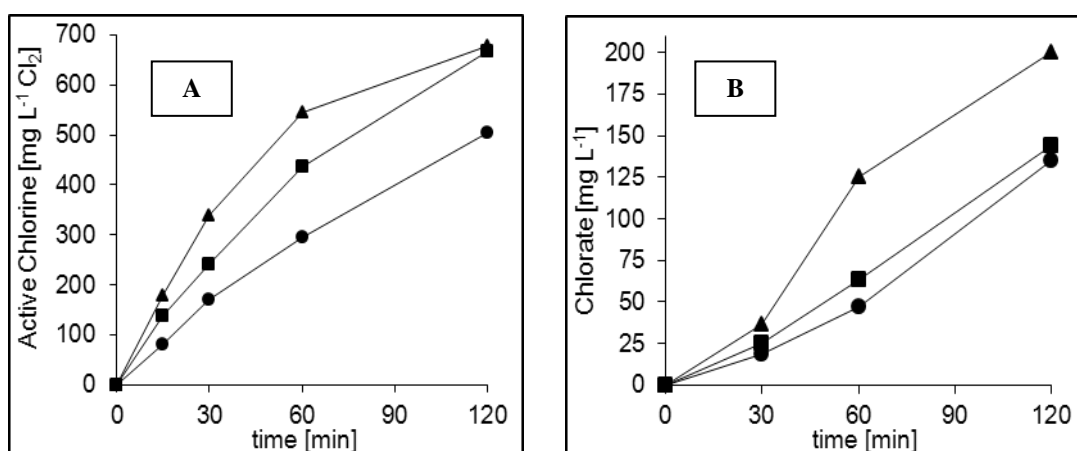

Figure 4: Anodic material effect on active chlorine (A) and chlorate (B) concentration. Anode: (■) Pt wire, (●) Pt disk, (▲) BDD. Cathode: GDE. j=100 A m^{-2}.

Under the conditions adopted, the results obtained exclude the coexistence of the two main oxidants at least in the absence of an oxidisable substrate thus discouraging the adoption of an undivided reactor. The use of a divided cell has to be then reconsidered. Nonetheless, an improvement of the cost-effectiveness can be provided by designing a combined treatment involving the anodic oxidation of the effluent mediated by electrogenerated active chlorine and a subsequent final stage in the cathodic compartment. Here the hydrogen peroxide accumulated contributes either in completing the removal of

pollutants or in removing residual concentration of active chlorine with a totally reagent-free process thus reducing the need for a dechlorination treatment before discharge.

4. Conclusions

The electrogeneration of hydrogen peroxide in seawater was verified using a GDE fed with air in undivided reactor. The simultaneous anodic production of oxidising species, mainly active chlorine, severely affects the stability of hydrogen peroxide due to the chemical reaction between these species. In the absence of a reducing substrate, the fast production rate of active chlorine leads to total depletion of H_2O_2. The investigation of a wider current density range and the adoption of different anode materials were not sufficient to limit the active chlorine production thus suggesting the need for a divided treatment. The results obtained lead to reconsider the H_2O_2 electrogeneration in a two-compartment cell not only to complete the effluent oxidation but also for the mandatory final removal of residual active chlorine thus representing a reagent free alternative to the traditional dechlorination mediated by sulph.

In the range of concentrations studied, an analytical interference of active chlorine on H_2O_2 determination was proved and corrected while the quantification of active chlorine resulted unaffected by the presence of H_2O_2.

5. Acknowledgements

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