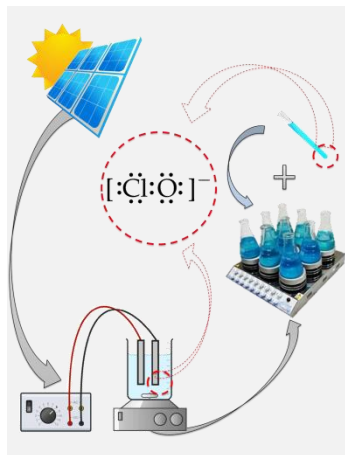


Use of hypochlorite Electrogenerated at MMO-type Electrodes as Ex-Situ Oxidation Approach

ORAL
Ph.D. Student: N
Journal: ESPR

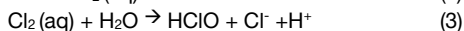
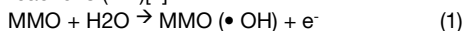
M. B. Ferreira¹, E. C. M. Moura¹, E. V. Dos Santos¹, C. A. Martínez-Huitle² (1) *Renewable Energies and Environmental Sustainability Research Group, Institute of Chemistry, Federal University of Rio Grande do Norte, Campus Universitário, Av. Salgado Filho 3000, Lagoa Nova, CEP 59078-970, Natal, Rio Grande do Norte, Brazil.* (2) *Instituto de Química, Federal University of Rio Grande do Norte, Lagoa Nova, CEP59078-970 Natal, Rio Grande do Norte, Brazil.*



A wide range of synthetic and real effluents have been treated using MMO mediated by electrogenerated reactive active chlorine species (RCS) in situ electrochemically systems to eliminate persistent organic pollutants and microorganisms. Here, an electrochemical MMO-RCS system was evaluated in terms of solution oxidation power as a function of storage temperature, storage time, and ex situ applicability. Results clearly showed that the temperature has an influence on the storage and service-life of the solutions, called as fresh-hypochlorite (25 °C) or cold-hypochlorite (10 °C). Greater stability in the cold-hypochlorite solution was observed, as a function of time, and it was effective in degrading organic pollutants as an ex situ oxidation approach, eliminating above 90% after 15 min for Novacron blue dye and the antibiotic isoniazid. These results contribute to understanding of the fundamentals of chlorine aqueous solutions as precursors of hypochlorite-based oxidizing solutions and their applications.

Introduction

Advanced oxidation processes (AOPs) are used because of their high reactivity, quick reaction times, and lack of secondary pollution to efficiently degrade organic pollutants and other types of persistent compounds. The oxidation path of pollutants can be determined by electrode material, electrolyte composition, and experimental conditions, with highly oxidative species like hydroxyl radicals causing mineralization. MMOs based on RuO₂ have high efficiency in terms of chloride oxidizability or chlorine/hypochlorous acid/hypochlorite reduction and have excellent stability for the chlorine release reaction, for this reason are called MMO-Cl₂ [1]. These species which are frequently electrogenerated in situ (due to the presence of mediators in the solution) and these play an important role in the indirect oxidation of organic molecules. Anodic oxidation process with an MMO-Cl₂ anode involves: (i) the generation of physisorbed •OH at the anode surface, denoted MMO(•OH), from reaction (5), and (ii) the parallel oxidation of Cl⁻ to originate homogeneous free or active chlorine species (Cl₂/HClO/ClO⁻) from reactions (1-4)[2]:



In the literature, many studies have already reported the treatment of effluents containing persistent compounds through the use of MMO anodes. However, information on the storage capacity and shelf life of a solution containing hypochlorite after its electrosynthesis with MMO has not yet been published. For this reason, the objective of this work is to electrosynthesize hypochlorite and evaluate oxidation power of solutions as a function of the temperature of storage, the storage time and to propose MMO-HClO/ClO⁻/Cl₂ system as an ex-situ oxidation tool for environmental applications, such as an off-grid clean water solution.

Material and Methods

Solutions containing sodium chloride, Novacron blue dye (NB), and isoniazid antibiotic (ISO), were prepared with ultrapure water. Purified water was obtained from the Milli-Q system. Hypochlorite electrosynthesis experiments using MMO anode were carried out using a batch cell with a capacity of 1L of solution. The system had Ti/RuO₂-IrO₂-TiO₂ as anode and titanium as cathode, both with an area of 45 cm². Electrolysis of synthetic solution containing with 0.5 M of NaCl was performed carried out at room temperature by applying 30 and 45 mA cm⁻² for 120 min by solar panels. During all experiments, samples were collected at predetermined time intervals and the concentration profiles of oxidants-concentration were obtained.

These aliquots were analyzed by a spectrophotometric method using a UV-vis, the analytical wavelength was fixed at 292 nm [3]. To determine the storage capacity and service-life of the electrosynthetic chlorine-based oxidizing species solution, as a function of time, it was divided in two solutions of 0.5 L each one of them, after its preparation. Subsequently, both solutions were stored in amber reservoirs, at different temperatures: i) at room temperature ($25\text{ }^{\circ}\text{C}\pm 2$) and ii) at $10\text{ }^{\circ}\text{C}\pm 2$ in the refrigerator, which were denominated as fresh-hypochlorite (F-HYP) and cold-hypochlorite (C-HYP) solutions, respectively. Then, its stability was evaluated by determining the concentration profiles of oxidants-concentration for F-HYP and C-HYP solutions, respectively, for 8 days. Meanwhile, the service life of the solutions (oxidation power) was also established by ex situ oxidation tests after their electrosynthesis. 15 ml of F-HYP or C-HYP solutions was added in glass beakers containing with 15 ml of 50 mg L^{-1} of NB or ISO. Both solutions were mixed by using magnetic agitation during 2 h and aliquots were withdrawn at predetermined times to determine the concentration of the target pollutants by as a function of time. In the case of C-HYP solution, it was immediately stored at $10\text{ }^{\circ}\text{C}$ during 2 h, after to be electrosynthesized, before its use. Meanwhile, F-HYP solution was kept to $25\text{ }^{\circ}\text{C}$ and directly used in the oxidation tests.

Results and Discussion

Electrosynthesis tests showed that an increase in j (45 mA cm^{-2}) favors the intensification of hypochlorite concentration, reaching values approximately 5 times greater than when using 30

Conclusions

Electrosynthesis tests showed that an increase in j intensifies hypochlorite concentration, reaching values 5 times greater than the lowest j , after 120 min of electrolysis. Then, the larger the j , the higher concentration of electrogenerated hypochlorite. C-HYP solutions showed greater stability in oxidant concentration values over time, while fresh solutions were unstable and decreased by almost 30% after 24 h. Storage temperature can influence the degradation reaction kinetics of these species. Furthermore, ex situ oxidation tests showed a 90% degradation for both species, NB and ISO, after 10 min.

Acknowledgments

The authors extend their gratitude to PRH-ANP/FINEP 26 for financial support.

References

- [1] J. Y. C. Ribeiro et al., 'Platinum-Modified Mixed Metal Oxide Electrodes for Efficient Chloralkaline-Based Energy Storage', *Catalysts*, vol. 14, no. 2, p. 152, Feb. 2024, doi: 10.3390/catal14020152.
- [2] R. J. A. Felisardo, E. Brillas, L. F. Romanholo Ferreira, E. B. Cavalcanti, and S. Garcia-Segura, 'Degradation of the antibiotic ciprofloxacin in urine by electrochemical oxidation with a DSA anode', *Chemosphere*, vol. 344, p. 140407, Dec. 2023, doi: 10.1016/j.chemosphere.2023.140407.
- [3] M. Scheurer, A. Michel, H. J. Brauch, W. Ruck, and F. Sacher, 'Occurrence and fate of the antidiabetic drug metformin and its metabolite guanilurea in the environment and during drinking water treatment', *Water Res.*, vol. 46, no. 15, pp. 4790–4802, Oct. 2012, doi: 10.1016/J.WATRES.2012.06.019.

mA cm^{-2} after 120 min of electrolysis. The storage capacity of hypochlorite solutions, in terms of oxidant concentration, up to 74 h after their electrosynthesis, were evaluated and a slight variations in the concentration of C-HYP was observed, being a general trend for these solutions independent of j applied. The C-HYP solutions demonstrated greater stability, in terms of oxidant concentration values, as a function of time. Meanwhile, the oxidant concentration in F-HYP solutions was unstable and its concentration decreased significantly after 24 h, with a loss of almost 30% in the concentration of these species. These behaviors are completely associated with effectiveness in the $\text{Cl}_2/\text{HClO}/\text{ClO}^-$ formation as well as the mechanisms involved in the decomposition of these species. Therefore, the storage temperature can influence the degradation reaction kinetics of these species. Ex situ oxidation tests were performed with F-HYP and C-HYP solutions for 120 min, Figure 1. For all experiments, about 90% was degraded after 10 minutes of oxidation for both species, NB and ISO, regardless of j and storage temperature.

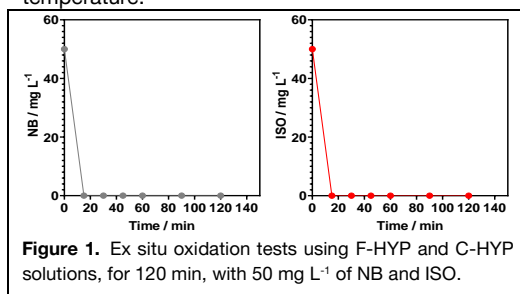


Figure 1. Ex situ oxidation tests using F-HYP and C-HYP solutions, for 120 min, with 50 mg L^{-1} of NB and ISO.