TOWARDS A GREEN PRODUCTION OF CHLORINE DIOXIDE BY CONVERGENT PAIRED ELECTROSYNTHESIS

Rodrigo Mena-Brito, Sebastian Terrazas-Moreno and Jorge G. Ibanez*

Centro Mexicano de Quimica Verde y Microescala, Depto. de Ing. y Ciencias Quimicas
Universidad Iberoamericana, Prolongación Reforma #880, 01219 México, D.F. México

ABSTRACT

As a proof-of-concept, we show that the clean, potent bleaching and disinfecting agent ClO_2 can be produced simultaneously at both electrodes of an electrochemical cell by the anodic oxidation of ClO_2^- ions and the cathodic reduction of ClO_3^- ions in a convergent paired electrosynthesis. This novel approach may lead to important savings in the economy and energy of its production and byproduct reduction.

KEYWORDS: Chlorine dioxide, simultaneous electrosynthesis, paired electrosynthesis, paired electrochemical processes

INTRODUCTION

In the vast majority of electrochemical processes, the desired reaction occurs at one of the electrodes, yet the complementary reaction is not productive. The products of the latter should not interfere with the starting materials, intermediates or products [1]. In fact, the current at the counter electrode is most frequently used to decompose the solvent. In some cases, this last reaction serves the purpose of producing a desired pH in the solution by decomposition of water (production of H^+ or OH^- and the concomitant formation of O_2 or H_2, respectively), although this may translate into energy waste. Several organic and inorganic synthetic processes have been designed to avoid such a waste [2-4]. Besides savings in the economy and energy, benefits of designing and using simultaneous processes also include a reduced use of fossil fuels for producing electricity combined with decrease in pollution. The production of useful substances also avoids the need for waste disposal.

Selected examples of simultaneous processes for environmentally oriented applications are summarized below:

a) Simultaneous removal of copper and chemical oxygen demand [5], as well as reduction of Cu, Ag or Cd ions and oxidation of CN^- ions [6]

b) Simultaneous production of high-purity H_2 gas and solid S from H_2S either through a direct or an indirect process [7-17]

c) Removal of SO_2 by anodic oxidation and the simultaneous water reduction producing H_2SO_4 and H_2, respectively [18, 19]

d) Simultaneous production of O_3 and H_2O_2 in a flow reactor equipped with a proton exchange membrane. This avoids the need for two separate cells to produce these chemicals, whereby O_3 and waste H_2 would be produced in the first one, and H_2O_2 and waste O_2 in the second [20].

e) The production of Fe^{2+} at the anode and reduction of O_2 at the cathode of a cell to produce H_2O_2. A mixture of Fe^{2+} and H_2O_2 is known as *Fenton's reagent* which yields $^{\bullet}OH$ radicals (known to be very powerful oxidizers) and OH^- ions. These ions produce iron hydroxides that form a three-dimensional gel capable of adsorbing a plethora of pollutants, thus producing a decontamination effect [21].

f) An interesting variation of the above process involves the use of boron-doped diamond electrodes whereby hydroxyl radicals can be generated simultaneously by anodic and cathodic processes in order to destroy persistent organics [22, 23].

With this background in mind, we tested the possibility of electrochemically producing a disinfecting agent in a simultaneous fashion. Useful chemical disinfectants have one or more of the following characteristics [24]:

- Deactivate microorganisms strongly, and are also relatively toxic to humans and animals
- Undergo active interaction (normally oxidation or addition) with organic matter and inorganic reducing agents
- Dissolve adequately in aqueous media (except the dihalogens due to their non-polar nature)
- Can penetrate surfaces and cell membranes
- Deodorize well or moderately well

Since chlorine dioxide (ClO_2) has most of these characteristics, we tested it for the purpose of the present study. It can act as an extremely effective biocide, disinfectant and oxidizer under appropriate conditions, and its oxidizing and disinfecting properties remain essentially constant over a wide pH range [25]. The paper and pulp industry utilize it as a bleaching agent and alternative to chlorine for water treatment because it does not undergo hydrolysis in water, but is active, even against some chlorine-resistant pathogens, and does not react with ammonia. In addition, ClO_2 disinfection by-products (DBPs) are substantially fewer than those produced by chlorine. In fact, contrary to Cl_2, the ClO_2 does not react with humic substances to generate toxic species, such as carcinogenic trihalomethane compounds during water disinfection processes. ClO_2 is unable to react with unsaturated bonds in natural organic matter (NOM) on account of its different reaction mechanism (i.e., ClO_2 directly oxidizes organic matter by electrophilic abstraction rather than by the substitution and oxidation pathway of chlorine) [24]. It is also used for taste and odor reduction, algal growth control, as well as for iron and manganese removal by oxidizing them to produce insoluble compounds that can be eliminated easily from an aqueous medium. ClO_2 has been used to disinfect public buildings in the US after terrorist attacks involving liberation of anthrax spores.

Many of the chemical reactions utilized in producing ClO_2 have been discussed and illustrated in our publications elsewhere [24-27]. The main strategies involving electrochemical steps can be grouped as shown below.

1. Anodic processes:

1.1 Electrolysis of a Cl^- solution to produce:

1.1.1 ClO_2 [28]
1.1.2 $ClO_2 + Cl_2$ [29, 30]
1.1.3 ClO_3^-, followed by chemical comproportionation with Cl^- to produce ClO_2 [31-35]
1.1.4 Cl_2, followed by chemical comproportionation with ClO_3^- to produce ClO_2 [36-38]
1.1.5 Cl_2, followed by chemical disproportionation with ClO^- to produce ClO_2 [39]
1.1.6 Cl_2 that oxidizes ClO_2^- to produce ClO_2 [40]

1.2 Electrolysis of a ClO_2^- solution to produce ClO_2 using a cation exchange membrane (CEM) [41]

1.3 Electrolysis of H_2O to produce:
1.3.1 H^+ ions that are fed through a CEM (cation exchange membrane) into an ion exchange compartment to acidify a ClO_2^- solution to produce ClO_2 [42]
1.3.2 H^+ ions that are fed through a solid electrolyte to acidify a ClO_2^- solution to produce ClO_2 [43]
1.3.3 H^+ ions that are fed through a CEM into a compartment containing Cl^-. This acidified solution is sent to a non-electrochemical step to comproportionate with ClO_3^- and produce ClO_2 [44].

2. Cathodic processes:

2.1 Electrolysis of a ClO_3^- solution to produce ClO_2 [45, 46]. The H^+ produced at the anode can be fed through a CEM into the catholyte to acidify the ClO_3^- solution in order to facilitate its reduction to ClO_2. The Cl_2 byproduct is separated and re-fed into the cathode to provide more Cl^- for the reaction [47].

2.2. Electrolysis of H_2O to produce H_2 that reacts with Cl_2 to yield HCl. Then, this HCl comproportionates with ClO_3^- to produce ClO_2 [48, 49].

For our present purpose, we built on the above concepts - namely that ClO_2 can be obtained separately from the cathodic reduction of Cl(V) and the anodic oxidation of Cl(III). Thus, the aim of the present study was to show a proof-of-concept that ClO_2 can be produced simultaneously at both electrodes. This novel, unusual type of process is also termed *convergent paired electrosynthesis* [1]. To the best of our knowledge, this approach has not been attempted before.

Experimental procedure

The strategy for the simultaneous electrochemical production of ClO_2 firstly focused on finding the appropriate experimental conditions to oxidize ClO_2^- ions, to reduce ClO_3^- ions individually, and then to combine both processes. The individual production reactions were performed in a cell composed of two 10-ml vial compartments separated by a cation exchange membrane, CEM (see Fig. 1). The simultaneous production was carried out in a cell composed of two 10-ml glass beakers connected through an ion exchange bridge (as discussed below). The potential for each individual process was selected on the basis of earlier reports and standard potential tables [50, 51], and undesirable reactions (e.g., the reduction of ClO_3^- to Cl^-) can thus be minimized [52]. Regulated potentials and currents were applied with an AMEL potentiostat/galvanostat (model 2049). All the potentials in the present study were referred to Ag/AgCl, and all experiments were run in duplicate or triplicate.

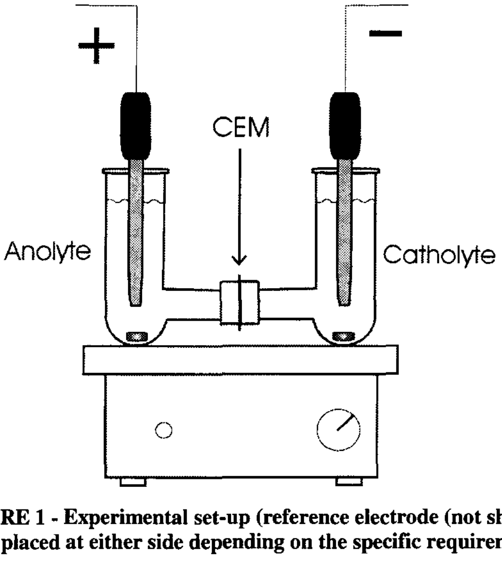

FIGURE 1 - Experimental set-up (reference electrode (not shown) can be placed at either side depending on the specific requirements).

Reagents and Materials

NaCl (J.T. Baker, analytical reagent), $NaClO_2$ (Aldrich, 80% pure), $NaClO_3$ (Sigma, analytical reagent), concentrated H_2SO_4 (J.T. Baker, 96% pure), cation exchange resin, CER (Rohm and Haas, Amberlite Irrono), cation exchange membrane, CEM (Nafion 417, Aldrich), anion exchange membrane (The Electrosynthesis Co.), graphite rods (Steadtler Mars HB, 2 mm in diameter, used as working and counter electrodes), Ag/AgCl reference electrode (BAS, Bioanalytical Systems), phosphate buffer pH 7 (Aldrich).

Specific conditions are indicated below:

a) Individual process for the anodic production of ClO_2

Anolyte: 5 ml of 0.1 M $NaClO_2$

Catholyte: 5 ml of a saturated NaCl solution

The reaction was performed under a potential of 0.7–0.9 V vs. Ag/AgCl, measured at the working electrode. Reaction times varied from 10 to 65 min. The solution was stirred at 5-min intervals.

b) Individual process for the cathodic production of ClO_2

Anolyte: 5 ml of a saturated NaCl solution

Catholyte: 1.5 ml of 3 M $NaClO_3$, 0.1 ml of 0.1 M NaCl, 2 ml of concentrated H_2SO_4, and 3 ml of a 0.001-0.003 M ClO_2 solution, prepared chemically in advance by acidification of a ClO_2^- solution [25]

The reaction was performed under a potential of 0.5 V vs. Ag/AgCl, measured at the working electrode. Reaction times varied from 20 to 120 min.

c) Simultaneous electrochemical production of ClO_2

Anolyte: 6 ml of 3 M $NaClO_2$, 2 ml of a saturated phosphate buffer (pH = 7).

Catholyte: 1.5 mL of 3 M $NaClO_3$, 0.1 ml of 0.1 M NaCl, 4.4 ml of a 0.001-0.003 M ClO_2 solution, prepared chemically in advance by acidification of a ClO_2^- solution (see above), 2 ml of concentrated H_2SO_4.

The reaction was performed under a potential of 0.5 V vs. Ag/AgCl, measured at the cathode. Reaction times varied between 60-120 min. Two 10-ml glass beakers were used (instead of the 10-ml vials employed in the individual ClO_2 preparations). They were connected through a 7 cm tall, 0.4 mm ID glass U-tube packed with Amberlite CER, and they had both ends covered with anion exchange membranes (held in place by small rubber bands). This U-tube/ion exchange system was designed to prevent migration of H^+ from the inherently acidic catholyte towards the anode. Such H^+ ions are known to facilitate the generation of $HClO_2$, which can then decompose to produce ClO_2. This situation would produce erroneous (i.e., high) yields compared to those obtained from a purely electrochemical production, and was thus avoided. Furthermore, to prevent the pH in the anolyte from being drastically affected by this or other unexpected phenomena, we added a small amount of phosphate buffer as described above.

Analytical technique

The quantification of aqueous ClO_2 may be a complicated task since other possible chlorinated species present (e.g., Cl_2, ClO^-, ClO_2^-, and ClO_3^-) can mask some of its analytically useful properties (e.g., redox potential, oxidizing ability, and optical absorbance) [53]. Therefore, we selected the standard method of amperometric titration [54]. Here, a fixed potential is applied between two electrodes and the response current is monitored as a function of the concentration of specific redox species. Successive titrations permit the selective analysis of each chlorinated species. In spite of its time-consuming characteristics, the high selectiveness of the method warrants its use for the present application. Due to the possible co-production of chlorine gas, the analytes of interest for our present purposes were Cl_2 and ClO_2 (see below).

RESULTS AND DISCUSSION

Using the parameters for the individual productions as described above, we obtained the following ClO_2 chemical yields after 1 h of reaction. These are calculated on the basis of the amount of ClO_2 achieved as compared to the initial amount of reagent at the anode or cathode (i.e., ClO_2^- or ClO_3^-, respectively; a) anodic: 12% (at 0.73 V), 9% (at 0.90 V), and b) cathodic: 0.3%). Once we succeeded in producing ClO_2 with each individual process, we proceeded to test the simultaneous process. The ClO_2 yields thus obtained are given in Table 1. Also listed are the results of a blank test performed in the absence of an applied potential so as to evaluate a possible parasitic parallel chemical pathway for the production of ClO_2 that could alter the electrochemical results. These results clearly indicate that ClO_2 was electrochemically obtained at both sides of the electrochemical cell.

TABLE 1 - Experimental results of the simultaneous process (chemical yield is calculated as moles of product/moles of reagent x 100).

Medium	*g/L (average)*	*mmol (average)*	*Chemical yield (%)*
Anolyte			
Cl_2			
60 min	0.04	0.0045	0.03
100 min	11	1.3	7.1
120 min	0.2	0.02	0.1
ClO_2			
60 min	5	0.6	3.3
100 min	9	1.0	5.8
120 min	11	1.3	7.0
Catholyte			
Cl_2			
60 min	0.2	0.02	0.45
100 min	0.09	0.008	0.2
120 min	0.02	0.002	0.05
ClO_2			
60 min	0.3	0.03	0.6
100 min	0.45	0.04	0.95
120 min	0.5	0.05	1.1
Blank test			
Cl_2			
60 min	0.3	0.04	0.8
100 min	0.06	0.007	0.15
120 min	0.06	0.006	0.1
ClO_2			
60 min	0.04	0.004	0.1
100 min	0.08	0.01	0.2
120 min	0.03	0.003	0.07

The yield of the blank test, albeit measurable, was not of significance so as to mask the electrochemical yields. Hydrogen ions are inherently produced at the anode and - as discussed earlier - are known to produce chlorous acid ($HClO_2$) that can disproportionate to yield ClO_2. Further efforts would be required in order to separate this contribution from the pure electron-transfer phenomenon.

We have initiated experiments to take advantage of LeChatelier´s principle by removing the ClO_2 product from the final solution with the aid of an inert gas stream. Preliminary results using this approach in a commercial filter press-type cell are promising.

CONCLUSIONS

We have demonstrated for the first time that ClO_2 can be produced simultaneously at the anode and cathode of an electrochemical cell by the respective oxidation or reduction of ClO_2^- and ClO_3^- ions in a simultaneous, convergent paired electrosynthesis. Even though small yields were obtained under our experimental conditions (ca. 8%), higher yields can undoubtedly be achieved by parameter optimization (e.g., temperature, time, volume per unit area, electrode materials and separation, and flow/mass transfer conditions).

ACKNOWLEDGEMENTS

Funding from CONACYT and the Universidad Iberoamericana is gratefully acknowledged as well as helpful discussions with Ruben Vasquez-Medrano and Arturo Fregoso-Infante. Elizabeth Garcia-Pintor and Samuel Macias provided experimental assistance. This paper is dedicated to Dr. Michael Tausch (University of Wuppertal, Germany) on occasion of his 60th birthday.

REFERENCES

[1] Paddon, C.A., Atobe, M., Fuchigami, T., He, P., Watts, P., Haswell, S.J., Pritchard, G.J., Bull, S.D. and Marken, F. (2006) Towards paired and coupled electrode reactions for clean organic microreactor electrosyntheses. J. Appl. Electrochem. 36, 617-634.

[2] Walsh, F. (1993) A first course in electrochemical engineering. The Electrochemical Consultancy, Southampton, 13-45.

[3] Bersier, P.M., Carlsson, L. and Bersier, J. (1994) Electrochemistry for a better environment. In: Topics in Current Electrochemistry. Vol. 170, Springer Verlag, Berlin, 114-229.

[4] Baizer, M.M. (1991) Paired Electrosynthesis. In: H. Lund, M.M. Baizer (Eds.) Organic electrochemistry. An introduction and a guide, 3rd. ed. Marcel Dekker, New York, 1421-1430.

[5] Kusakabe, K., Nishida, H., Morooka, S. and Kato, Y. (1986) Simultaneous electrochemical removal of copper and chemical oxygen demand using a packed-bed electrode cell. Electrochim. Acta 16, 121-126.

[6] Zhou, C.-D. and Chin, D.-T. (1994) Continuous electrolytic treatment of complex metal cyanides with rotating barrel plater as the cathode and a packed bed as the anode. Plat. Surf. Fin. 81, 70-78.

[7] Mizuta, S., Kondo, W., Fujii, K., Iida, H., Isshiki, S., Noguchi, H., Kikuchi, T., Sue, H. and Sakai, K. (1991) Hydrogen production from hydrogen sulfide by the Fe-Cl hybrid process. Ind. Eng. Chem. Res. 30, 1601-1608.

[8] Alexander, S.R. and Winnick, J. (1994) Electrochemical polishing of hydrogen sulfide from coal synthesis gas. J. Appl. Electrochem. 24, 1092-1101.

[9] Lim, H.S. and Winnick, J. (1984) Electrochemical removal and concentration of hydrogen sulfide from coal gas. J. Electrochem. Soc. 131, 562-568.

[10] Pujare, N.U., Tsai, K.J. and Sammells, A.F. (1989) An electrochemical Claus process for sulfur recovery. J. Electrochem. Soc. 136, 3662-3678.

[11] Petrovic, S., Donini, J.C., Szynkarczuk, J., Thind, S., Hileman, O.E. and Lever, A.B.P. (1992) Liquid phase hydrogen sulphide electrolysis, Abstracts of Papers, Sixth Int. Forum on Electrol. in the Chem. Ind., Fort Lauderdale, FL: The Electrosynthesis Co., November 8-12, 1992.

[12] Kalina, D.W. and Maas, Jr., E.T. (1985) Indirect hydrogen sulfide conversion. 1. An acidic electrochemical process. Int. J. Hydrog. Energy 10, 157-162.

[13] Kalina, D.W. and Maas, Jr., E.T. (1985) Indirect hydrogen sulfide conversion. 2. A basic electrochemical process. Int. J. Hydrog. Energy 10, 163-167.

[14] Oloman, C., Electrochemical synthesis and separation technology in the pulp and paper industry, Abstracts of Papers, Sixth Int. Forum on Electrol. in the Chem. Ind., Fort Lauderdale, FL: The Electrosynthesis Co., November 8-12, 1992.

[15] Weinberg, N.L. (1992) A new air purification technology: The electrocinerator system. In: Genders, D. and Weinberg, N. (Eds.) Electrochemistry for a Cleaner Environment. The Electrosynthesis Co., East Amherst, NY, Chapter 16.

[16] Anani, A.A., Mao, Z., White, R.E., Srinivasan, S. and Appleby, A.J. (1990) Electrochemical production of hydrogen and sulfur by low-temperature decomposition of hydrogen sulfide in an aqueous alkaline solution. J. Electrochem. Soc. 137, 2703-2709.

[17] Weaver, D. and Winnick, J. (1987) Electrochemical removal of H_2S from hot gas streams. J. Electrochem. Soc. 134, 2451-2458.

[18] Van Velzen, D. (1992) Electrochemical processes in the protection of the environment. In: Genders, D. and Weinberg, N. (Eds.) Electrochemistry for a cleaner environment. The Electrosynthesis Co., East Amherst, NY. Chapter 21.

[19] Struck, B.D., Junginger, R., Neumeister, H. and Dujka, B. (1982) A three compartment electrolytic cell for anodic oxidation of sulfur dioxide and cathodic production of hydrogen. Int. J. Hydrogen Energy 7, 43-49.

[20] Tatapudi, P. and Fenton, J.M. (1994) Simultaneous synthesis of ozone and hydrogen peroxide in a proton-exchange-membrane electrochemical reactor. J. Electrochem. Soc. 141, 1174-1178.

[21] Brillas, E., Sauleda, R. and Casado, J. (1997) Peroxi-coagulation of aniline in acidic medium using an oxygen diffusion cathode. J. Electrochem. Soc. 144, 2374-2379.

[22] Brillas, E., Boye, B., Sires, I., Garrido, J.A., Rodriguez, R.M., Arias, C., Cabot, P.L. and Comninellis, C. (2004) Electrochemical destruction of chlorophenoxy herbicides by anodic oxidation and electro-Fenton using a boron-doped diamond electrode. Electrochim. Acta 49, 4487-4496.

[23] Sires, I., Oturan, N., Oturan, M.A., Rodriguez, R.M., Garrido, J.A. and Brillas, E. (2007) Electro-Fenton degradation of antimicrobials triclosan and triclocarban. Electrochim. Acta 52, 5493-5503.

[24] Rajeshwar, K. and Ibanez, J.G. (1997) Environmental electrochemistry: Fundamentals and applications in pollution abatement. Academic Press, San Diego, CA. Chapter 5.

[25] Ibanez, J.G., Navarro-Monsivais, C., Terrazas-Moreno, S., Mena-Brito, R., Pedraza-Segura, L., Mattson, B., Anderson, M.P., Fujita, J. and Hoette, T. (2006) Microscale environmental chemistry, Part 5. Production of ClO_2, an environmentally-friendly oxidizer and disinfectant. Chem. Educ. 11, 174-177.

[26] Ibanez, J.G., Hernandez-Esparza, M., Doria-Serrano, C., Fregoso-Infante, A. and Singh, M.M. (2007) Environmental chemistry: Fundamentals. Springer, New York, 244-245.

[27] Ibanez, J.G., Hernandez-Esparza, M., Doria-Serrano, C., Fregoso-Infante, A. and Singh, M.M. (2008) Environmental chemistry: Microscale laboratory experiments. Springer, New York, 198.

[28] Zhan, H., Ma, X. and Wu, K. (1993) Production of chlorine dioxide from electrolysis of brine. Huanjing Wuran Yu Fangzhi (China) 15, 46-47.

[29] Sweeney, C.T. Generation of chlorine-chlorine dioxide mixtures. U.S. Patent 4324635 (Apr. 13, 1982).

[30] Sweeney, C.T. Generation of chlorine-chlorine dioxide mixtures. U.S. Patent 4308117 (Dec. 29, 1981).

[31] Sweeney, C.T. Generation of chlorine/chlorine dioxide mixtures. U.S. Patent 4248681 (Feb. 3, 1981).

[32] Westerlund, G.O. (1993) Integrated procedure for high-yield production of chlorine dioxide. Can. Pat. Appl. 120:119445.

[33] Hughes, T.D. (1980) Chemetic's integrated chlorine dioxide system boasts success. Pulp & Paper Canada 81, 30-34.

[34] Kushiro, J., Tamura, K. Simultaneous preparation of chlorine dioxide, chlorine, and alkali metal hydroxide. Japanese Patent 52027098 (Mar. 1, 1977).

[35] Westerlund, G.O. Chlorine dioxide. U.S. Patent 3404952 (Oct. 8, 1968).

[36] Nojima, S. and Sato, T. Regeneration of pulping reagents chlorine dioxide and sodium hydroxide. Japanese Patent 48053002 (Jul. 25, 1973).

[37] Nojima, S. and Sato, T. Regeneration of pulping reagents, chlorine dioxide and sodium hydroxide. Japanese Patent 48053001 (Jul. 25, 1973).

[38] Westerlund, G.O. Closed loop system and process for preparing chlorine dioxide and reactants. Canadian Patent 835288 (Feb. 24, 1970).

[39] Taku, K. Disinfection of waters using chlorine dioxide generated from chlorine gas. Japanese Patent 05161890 A2 (Jun. 29, 1993).

[40] Ikeda, T., Inoue, T., Hara, K. and Hirai, R. Production of chlorine dioxide for controlling fungal growth in crop and meat storage. Japanese Patent 63253007 A2 (Oct. 20, 1988).

[41] Taku, K. and Inazumi, Y. Method for producing chlorine dioxide. Japanese Patent 09279376 A2 (Oct. 28, 1997).

[42] Kaczur, J.L. and Cawlfield, D.W. Electrochemical process for producing chlorine dioxide solutions from chlorites. PCT Int. Appl. WO 9109158 A1 (Jun. 27, 1991).

[43] Hirakata, K., Shimoda, S. and Kato, T. Method and apparatus for the electrolytic production of chlorine dioxide from chlorite solution. Japanese Patent 02205693 A2 (Aug. 15, 1990).

[44] Twardowski, Z. Integrated process for the manufacture of chlorine dioxide and sodium hydroxide. U.S. Patent 4806215 (Feb. 21, 1989).

[45] Yuan, B. (1995) Study on preparation of chlorine dioxide by electrolysis of chlorate. Huaxue Shijie (China) 36, 626-628.

[46] Yuan, B. (1995) Preparation of ClO_2 by direct electrolysis of chlorate. Xiandai Huagong (China) 15, 22-23.

[47] Lipsztajn, M., McGilvery, J.D. and Twardowski, Z. Production of chlorine dioxide in an electrolytic cell. Eur. Pat. Appl. 328818 A2 (Aug. 23, 1989).

[48] Lohrberg, K. (1987) Manufacture of chlorine dioxide from chlorine. Svensk Papperstidning (Sweden) 90, 25-27.

[49] Westerlund, G.O. Controlled and efficient preparation of chlorine dioxide. Canadian Patent 809143 (Mar. 25, 1969).

[50] Hardee, K.L., Gordon, A.Z., Pyle, C.B. and Sen, R.K. Method and electrocatalyst for making chlorine dioxide. US Patent 4426263 (Jan. 17, 1984).

[51] Lide, D. (2004-2005). Handbook of Chemistry and Physics, 85th. ed. CRC Press, Boca Raton, FL. 8-24.

[52] Swaddle, T.W. (1997) Inorganic chemistry: An industrial and environmental perspective. Academic Press, San Diego, CA, 224-225.

[53] Aieta, E.M., Roberts, P.V. and Hernandez, M. (1984) Determination of chlorine dioxide, chlorine, chlorite, and chlorate in water. J. Amer. Water. Works Assoc. 76, 64-70.

[54] Greenberg, A., Clesceri, L. and Eaton, D. (1992) Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association, Washington, 4-57.

Received: October 14, 2008
Revised: February 17, 2009
Accepted: April 24, 2009

CORRESPONDING AUTHOR

Jorge G. Ibanez
Centro Mexicano de Quimica Verde y Microescala
Depto. de Ing. y Ciencias Quimicas
Universidad Iberoamericana
Prolongación Reforma #880
01219 México, D.F.
MÉXICO

Phone: +52(55)59504074
Fax +52(55)59504279
E-mail: jorge.ibanez@uia.mx

FEB/ Vol 18/ No 8/ 2009 – pages 1434 – 1438