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Abstract

In this work, the valorization of brines, with concentrations similar to those produced by reverse osmosis or electrodialysis processes, by electrolysis with diamond anodes is evaluated. To do this, synthetic brines made from solutions of NaCl (with concentrations ranging from 1.0 to 5.0 M) were used as the raw material for the electrochemical production of perchlorate using commercial electrochemical cells equipped with boron-doped diamond (BDD) anodes. The effect of key parameters on the rate and efficiency of perchlorate production was evaluated. The results show that it is possible to transform more than 80% of the initial chloride concentration into perchlorate, with current efficiencies higher than 70% regardless of the initial concentration of sodium chloride contained in the brine. Moreover, it was observed that both hypochlorite and chlorate were produced almost simultaneously at the beginning of electrolysis, while perchlorate was only produced when a certain value of applied electric charge was passed through the system. The results obtained were essentially independent of the concentration of NaCl, as the high concentrations used in this study avoided mass transfer limitations. Moreover, the specific energy cost of perchlorate production was estimated to range from 26.14 kWh kg⁻¹ (for 2.0 M and 1000 A m⁻²) to 56.10 kWh kg⁻¹ (for 1.0 M and 2000 A m⁻²).

2). According to the results obtained, the electrochemical production of perchlorate by BDD electrochemical oxidation stands out as a promising novel technology for the valorization of the brine produced in reverse osmosis or electrodialysis processes.

Keywords: boron-doped diamond; perchlorate production; power consumption; electrolysis; desalinization; valorization.

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1. Introduction.

Currently, increasing the sustainability of processes is one of the main targets for chemical and environmental engineers. This increase in sustainability may come from the reduction in the use of resources required for the operation of the process (energy or raw materials) or from the valorization of streams that could otherwise become wastes.

In the context of water scarcity, which is particularly important in several regions of the world such as the Mediterranean region, electrodialysis or reverse osmosis of brackish (or even salty) water may become an important source of drinking water. However, waste brine is a very important environmental issue, particularly when this technology is applied to the inlands because it may contribute to the salinization of the reservoirs (Urtiaga et al., 2013). Because of that, finding promising ways for the valorization of this waste stream could help make this technology more attractive. At this time, the main component of these waste streams is chloride that is transformed into perchlorate, which is a very valuable reagent, and may become a milestone for the technology (Bebelis et al., 2013). Perchlorate is a very strong oxidizing agent ($E^\circ = 1.287 \text{ V}$), despite its slow kinetics at ambient pressure and temperature. However, it has an extremely high reactivity at higher temperatures. Thus, because of its exceptional oxidizing capacity, perchlorate is not only widely used in the manufacture of flares, explosives and fireworks but also used in specific medical applications and in small amounts in other high-volume consumer products.

In the literature, many possible mechanisms are proposed for perchlorate production in aqueous solutions, including electrochemical (electrolytic anodic oxidation of chlorate or chloride), thermal (decomposition of chlorate), or chemical (direct chemical oxidation of chlorates with strong oxidizing agents such as ozone, persulfates, and permanganate) processes. Among them, electrochemical processes have been the focus of scientific

interest in recent years. The anodic material has been demonstrated to be key in the performance of electrosynthesis. The mixed metal oxide (MMO) anodes commonly used in the chloralkali industry (Tran Le et al., 2015) do not seem to be the most appropriate for the synthesis of perchlorate. Thus, with Ru-MMO electrodes, the oxidation of chloride to chlorine and hypochlorite is very efficient, but no perchlorate is formed. However, with non-active electrodes, such as the well-known boron-doped diamond (BDD) electrode, perchlorate becomes the final product in the oxidation of chloride (Yoon et al., 2015). In fact, perchlorate is generally one of the undesirable by-products of the conductive-diamond electrochemical oxidation of urban and industrial wastewater (Bergmann et al., 2009; Bergmann et al., 2015). This change in outcome can be attributed to the effect of hydroxyl radicals that are produced during electrolysis when performed with these electrodes, Eq. (1)-(4) (Canizares et al., 2009).

Generally, the efficiency of the electrochemical process depends on the initial concentration of the raw materials. In previous work (Sánchez-Carretero et al., 2011), we observed that the electrolysis of dilute chloride solutions (0.1 M) with conductive-diamond electrodes led to the production of a chlorine-oxospecies mixture, although perchlorate was the final product, and 100% conversions to perchlorate were achieved when large current charges were passed through the system. Perchlorate production is enhanced at high current density operations and at alkaline conditions. The efficiency of

the perchlorate generation did not depend on the type of chlorine raw materials, but it was limited by the concentration of chlorine raw materials.

The concentration of chloride in brines is usually much higher, and in this work, we aim to go further in the evaluation of the electrochemical synthesis of perchlorate using conductive diamond electrodes by using concentrated chloride solutions with concentrations in the range from 1.0 to 2.0 of sodium chloride. This range of concentrations falls within the range of the highest values usually encountered in rejected streams (Pérez-González et al., 2012), although the aim of this work is not to directly use SWRO rejected streams for the production of perchlorate but to evaluate the viability of the electrochemical production of perchlorate from such high concentration of the raw materials. If a SWRO concentrate was aimed to be used, a previous treatment to remove impurities and other ions (v. g. sulfate, calcium, magnesium or bicarbonate) should be performed first (Pérez-González et al., 2015). To confront the main aim of this work, several tests were carried out in which the key operating parameters, current density and concentration were evaluated. Finally, to confirm the performance of the technique in the target range of concentrations (from 1.0 to 2.0 M), an additional test at an even higher concentration (5.0 M) was performed, and a preliminary evaluation of the estimated energy cost of perchlorate production was performed.

2. Material and methods.

2.1. Analytical procedures

Chlorine anionic species were monitored by ion chromatography using a Shimadzu LC-20A system equipped with a Shodex IC I-524A No. R209105 anionic column. The mobile phase consisted of a 2.5 M solution of phthalic acid at pH 4.0. The flow rate was 0.5 mL min⁻¹, and the injection volume was 200 µL. The temperature of the oven was 30 °C for

the determination of anions. Because the hypochlorite peak interfered with the chloride peak, the hypochlorite concentration was also measured by titration using a Metrohm 702 Titrino with 0.001N As_2O_3 (Fluka), after 0.2 mL of the sample was mixed with 2.0 mL of 2.0 M NaOH. In addition, chloride was also measured by titration with 0.02 N AgNO_3 (PanReac). The sample (0.5 mL) was mixed with 0.25 M K_2CrO_4 , which gave the solution a yellowish colour. Then, the solution was titrated until the colour became white.

2.2. Experimental procedure

The electrolyses were carried out in a bench-scale double-compartment electrochemical cell working under galvanostatic conditions. Boron-doped diamond (BDD) was used as the anode and stainless steel was used as the cathode. The diamond coating (boron content: 500-700 ppm, sp^3/sp^2 ratio: $220 \pm 5\%$, thickness: $2.7 \mu\text{m} \pm 10\%$) was provided by Adamant (Switzerland). Both electrodes were circular (100 mm diameter) with a geometric area of 78.5 cm^2 . A cationic exchange membrane (NAFION N-117) separated the anode and the cathode compartments.

The anolyte consisted of different solutions of sodium chloride with concentrations ranging from 1.0 to 5.0 M, and the catholyte consisted of 1.0 M solutions of sodium hydroxide. The anolyte and catholyte were stored in a dark glass tank and were recirculated towards the electrolytic cell by means of a centrifugal pump. The volumes of anolyte and catholyte were 1.0 L each. The temperature was controlled by a heat exchanger, and it was maintained at 25°C . The pH was regulated at 12.0 by means of a WTW-InoLab pH meter because it was previously reported that alkaline pH values favour the production of perchlorate (Sánchez-Carretero et al., 2011). The current densities applied in the different tests ranged from 7.8 A (1000 A m^{-2}) to 15.7 A (2000 A m^{-2}).

2.3 Calculation of theoretical charge and power consumption

The theoretical value of the concentration of a given oxoanion that would be obtained with 100% current efficiency ($[ClO_x^-]$, mM) has been calculated according to Eq. (5), and it has been included in several figures to compare the actual production with the maximum reachable rate. In Eq. (5), Q is the applied electric charge (Ah L⁻¹), n is the moles of electrons required to oxidize one mole of the oxoanion ($n=2$ for hypochlorite, $n=6$ for chlorate, $n=8$ for perchlorate), F is the Faraday constant (96500 C mol⁻¹) and $3.6 \cdot 10^6$ is a unit conversion factor.

$$[ClO_x^-] = \frac{Q}{n \cdot F} \cdot 3.6 \cdot 10^6 \quad (5)$$

Based on the same concept, the value of the charge required to fully convert the initial chloride to a given oxoanion with 100% current efficiency (Q_0 , Ah L⁻¹) can be obtained from Eq. (6), where $[Cl^-]_0$ is the initial chloride concentration (mM), and the remaining variables are the same as defined for Eq. (5).

$$Q_0 = \frac{[Cl^-]_0 \cdot n \cdot F}{3.6 \cdot 10^6} \quad (6)$$

Finally, the power consumption per unit of mass of perchlorate (kWh kg⁻¹) was also estimated. To compare different experimental conditions, all values of power consumption should be referred to the same value of conversion (arbitrarily fixed to 80% in this work) and can be calculated according to Eq. (7), where $Q_{80\%}$ is the electric charge required to convert 80% of the initial chloride to perchlorate (kAh L⁻¹), V is the average cell voltage throughout the test (V), $[Cl^-]$ is the chloride concentration to be electrolyzed (kmol L⁻¹), 0.8 is the required value of conversion and 99.5 is the molecular mass of perchlorate (kg kmol⁻¹).

$$Power\ consumption = \frac{Q_{80\%} \cdot V}{[Cl^-] \cdot 0.8 \cdot 99.5} \quad (7)$$

3. Results and discussion.

3. 1. Production of chlorine oxoanions from high salinity effluents: General behaviour

As a first step, the production of the three main chlorine oxoanions (*i.e.*, hypochlorite, chlorate and perchlorate) from 1.0 M sodium chloride solutions was evaluated. The concentration of chlorite and chlorine dioxide was not measured, as it has been reported that, at high current densities, the occurrence of these two species is negligible compared to the total active chlorine both due to their electrochemical activity and their chemical reaction pathways in the bulk solution (Sánchez-Carretero et al., 2011; Neodo et al., 2012).

Fig. 1 focuses on the production of hypochlorite, chlorate and perchlorate, respectively, with respect to the applied electric charge for three values of current density (1000, 1500 and 2000 A m⁻²).

Fig. 1. Influence of the current density on the production of hypochlorite (a), chlorate (b) and perchlorate (c) with respect to applied electric charge. Initial NaCl concentration = 1.0 M. ● 1000 A m⁻²; ▲ 1500 A m⁻²; ■ 2000 A m⁻². Discontinuous line: theoretical

concentration with 100% efficiency to this oxidant; Continuous line: guidance to follow the general trend of the results

The first important conclusion that can be drawn from this figure is that electrolysis is selective for hypochlorite production only in the initial moments of the process for applied electric charges lower than 20.0 Ah L^{-1} . Subsequently, the production of hypochlorite and chlorate occurs simultaneously, until reaching the applied electric charge theoretically required to convert the entire chloride concentration to hypochlorite ($Q_0=53.6 \text{ Ah L}^{-1}$ for 1.0 M NaCl and 100% current efficiency for hypochlorite conversion). After this value of charge, the hypochlorite concentration decreases due to its conversion to chlorate, which reaches its maximum concentration, as in the case for hypochlorite, for its corresponding value of Q_0 (160.8 Ah L^{-1} , in this case).

Regarding perchlorate, the concentration is zero until the value of Q_0 is approximately equal to the production of chlorate (160.8 Ah L^{-1}). At this time, the oxidation of chlorate to perchlorate is the only oxidation taking place in the system, reaching a final conversion of 80% of the initial chloride. At high values of electric charge ($> 250 \text{ Ah L}^{-1}$ for these experimental conditions), perchlorate is the main oxoanion present in the reaction media, which indicates that it behaves as the final product, as has been previously reported for BDD electrolysis of chloride in solutions with lower concentrations (Sánchez-Carretero et al., 2011; Lin et al., 2016).

To the best of the authors' knowledge, these results present the highest concentration values of perchlorate reached by electrochemical oxidation with BDD anodes. As was stated in the Introduction section, the vast majority of previously published works are focused on the production of perchlorate as the undesirable by-product of processes to disinfect (Bergmann, 2010; Bergmann et al., 2015) or to degrade organic (Garcia-Segura

et al., 2015a; Cotillas et al., 2016; Lin et al., 2016) or inorganic (Pérez et al., 2012) pollutants. The aim of those works was generally to avoid the production of perchlorate due to the known health risks related to its presence in water (Urbansky and Schock, 1999; Urbansky, 2002; Sirés et al., 2014). However, the aim of the present work is the opposite, that is, to maximize the production of perchlorate as a valuable product for the chemical industry. The results obtained here demonstrate that it is possible to use high-salinity effluents to produce active chlorine to be used in the disinfection or degradation of organic pollutants, avoiding the production of perchlorate. Thus, as it has been determined that the production of perchlorate begins at high applied electric charges, it would be easy to produce active chlorine, while avoiding the occurrence of perchlorate.

Regarding the influence of current density, it can be stated that the profiles previously described for the three current densities tested completely overlapped, and the slight differences observed between the different tests can be attributed to the uncertainty inherent in the analytical methods under such high concentrations. Therefore, this indicates that the current density is not playing an important role when working at high concentrations. This behaviour can be explained in terms of the relationship between mass transfer and current density. In the electrochemical process, it is well-known that the efficiency of a given electrochemical process is affected by the rate at which the raw material is transported to the electrode surface (Panizza et al., 2001; Martínez-Huitle and Ferro, 2006; Scialdone, 2009). The transport rate of a raw material by diffusion through the boundary layer close to the electrode is directly proportional to the concentration of this material in the bulk solution, according to Fick's law of diffusion (Cañizares et al., 2004; Brillas and Sirés, 2015; Cotillas et al., 2016; Raschitor et al., 2017). This means that, at the high concentrations tested in the present work, no mass transfer limitations are expected, and the successive raw materials (chloride for the first step of the oxidation

process; hypochlorite, chlorite and chlorate for the subsequent steps) are fully available to be oxidized at the electrode surface, regardless the value of the current density selected.

3. 2. Influence of the initial NaCl concentration on the production of chlorine-based oxidants

Fig. 2 shows the concentration of hypochlorite (Fig. 2a), chlorate (Fig. 2b) and perchlorate (Fig. 2c) for an initial concentration of NaCl of 2.0 M (117 g L^{-1}).

Fig. 2. Influence of the current density on the production of hypochlorite (a), chlorate (b) and perchlorate (c) with respect to applied electric charge. Initial NaCl concentration = 2 M. ● 1000 A m^{-2} ; ▲ 1500 A m^{-2} ; ■ 2000 A m^{-2} . Discontinuous line: theoretical concentration with 100% efficiency to this oxidant; Continuous line: guidance to follow the general trend of the results

The results presented in Fig. 2 confirm the evolution of the different chlorine oxoanions based on an initial concentration of 1.0 M, that is, the coexistence of the initial formation of hypochlorite and chlorate and the subsequent oxidation of chlorate to perchlorate at

higher values of applied electric charge. Moreover, a negligible influence of the applied current density was observed.

The unique noticeable difference between the initial concentrations is the maximum conversion observed for chlorate, which is higher for the 2 M concentration. To confirm this behaviour, an additional test was performed with an even higher initial concentration (5.0 M NaCl, 292.5 g L⁻¹). In this case, the test was maintained until the concentration of perchlorate began to increase but before a full conversion to perchlorate due to the large amount of charge required for a complete conversion (1072.2 Ah L⁻¹ for 100% current efficiency). Fig. 3 represents the conversion to chlorate (Fig. 3a) and perchlorate (Fig. 3b) with respect to the applied electric charge. The applied electric charge has been referred to the value of Q₀ of chlorate or perchlorate in order to compare in the same figure the results obtained for different initial concentrations of NaCl. In all cases, the selected current density was 2000 A m⁻².

Fig. 3. Influence of the initial NaCl concentration on the conversion to chlorate (a) and perchlorate (b) vs. the applied specific electric charge. 1.0 M (▲); 2.0 M (■); 5.0 M (●). Q₀: applied electric charge for a full conversion to chlorate or perchlorate with 100% current efficiency. j=2000 A m⁻². Continuous line: guidance to follow the general trend of the results

As can be seen, the experiment carried out at the highest concentration confirms the profile of chlorate and perchlorate evolution. Thus, the existence of an applied charge threshold below which the concentration of perchlorate produced is negligible has been verified again.

3. 3. Current efficiency and power consumption in the production of perchlorate

As a final step, the current efficiency and power consumption for the production of perchlorate were evaluated. Thus, Fig. 4 shows the values of current efficiency (together with the conversion) for the production of perchlorate at both 1.0 M (Fig. 4a) and 2.0 M (Fig. 4b) initial NaCl concentrations.

Fig. 4. Influence of the current density on the conversion and current efficiency in the production of perchlorate for 1.0 M (a) and 2.0 M (b) initial NaCl concentrations. Solid symbols: conversion; Open symbols: current efficiency. ● 1000 A m⁻²; ▲ 1500 A m⁻²; ■ 2000 A m⁻². Lines: guidance to follow the general trend of the results

As can be seen, the maximum efficiency obtained is close to the value of Q_0 . The maximum current efficiency is similar in both cases and is close to 70%, for a conversion higher than 80% of the initial chloride (close to 90% for the 2 M concentration). These results emphasize the fact that BDD electrolysis is a powerful and efficient tool for the production of oxidants, even at very high concentrations. Compared to previous work on chlorine-based oxidant synthesis with BDD electrolysis, the values obtained for current

efficiency are greater than those obtained at lower initial concentrations of NaCl (Sánchez-Carretero et al., 2011).

This efficiency can be explained by three factors. First, working with a high concentration ensures full availability of the raw material at the anode surface, avoiding mass transfer limitations, as was previously mentioned. Second, it is known that the ability of BDD to produce a high concentration of available hydroxyl radicals can promote the production of perchlorate, either by direct reaction with chlorate or by the formation of $\text{ClO}_3\cdot$ and its subsequent reaction with $\cdot\text{OH}$ (Azizi et al., 2011). Third, according to the literature, the ability of BDD layers to produce strong oxidants is favoured for lower sp^3/sp^2 ratios, since sp^2 -carbon impurities behave as adsorption sites (in this case, for chlorate) favouring the production of strong oxidants (Watanabe et al., 2014; Garcia-Segura et al., 2015b). As the sp^3/sp^2 ratio of the BDD layer selected in the present work ($220\pm5\%$) can be considered in the low range (Brito et al., 2015), these factors together explain the high values of efficiency obtained.

Finally, the power consumption, together with the average cell voltage, is represented in Fig. 5. The variation in cell voltage, which is represented in Fig. 5 as error bars, was very limited throughout the tests due to the high conductivity of the electrolysis media and the limited variation in electrolysis media conductivity during electrolysis.

Fig. 5. Influence of current density and initial NaCl concentration on specific power consumption and cell voltage for perchlorate production. Conversion to ClO_4^- : 0.8; Power consumption: ● 1 M, ▲ 2 M. Cell voltage: dotted bars 1M, striped bars 2 M. Lines: guidance to follow the general trend of the results

The specific power consumption follows the same trend as the cell voltage does. Both the voltage and power consumption are slightly higher for 1.0 M than for 2.0 M (due to the increase in conductivity in the initial NaCl concentration) and increase for the highest current density. This results in power consumption that ranges from 26.14 kWh kg^{-1} (for 2.0 M and 1000 A m^{-2}) to 56.10 kWh kg^{-1} (for 1 M and 2000 A m^{-2}). Taking into account recently published data on the average cost of energy for non-household consumers in Europe (0.112 € kWh^{-1}) (EUROSTAT, 2017), the estimated energy cost of the electrochemical production of perchlorate is calculated in Table 1.

Table 1. Estimated energy cost of the electrochemical production of perchlorate from NaCl solutions.

j (A m ⁻²) \ [NaCl] ₀	1.0 M	2.0 M
1000	3.70	2.93
1500	3.49	2.99
2000	6.28	4.78

The estimated energy cost ranges from 2.93 € kg⁻¹ to 6.28 € kg⁻¹. Although this estimate does not cover investment costs, and a more detailed estimation of the total cost of production will be handled in the future, this process could be considered of competitive value, especially taking into account that the raw material used may come from the waste streams of water desalination processes. At this time, previous works have indicated that the energy cost of electrochemical environmental processes is approximately 50% of the total cost, including the amortization of the investment, as a rule of thumb. These parameters could be used to gain an initial idea of the total production cost of these valuable products.

4. Conclusions.

- The following conclusions can be gathered from the present work:
- The production of perchlorate from high-salinity effluents by electrolysis with BDD anodes was technically viable and efficient.
- Conversions of chloride to perchlorate from 80% to 90% with 70% current efficiency were obtained.

- A very limited effect of initial NaCl concentration and current density on the profile of the oxoanions produced was observed.
- Hypochlorite and chlorate coexisted during the first part of electrolysis. Conversely, perchlorate was not produced until a certain value of applied electric charge was reached.
- The specific energy consumption of perchlorate production ranged from 26.14 kWh kg⁻¹ (for 2 M and 1000 A m⁻²) to 56.10 kWh kg⁻¹ (for 1 M and 2000 A m⁻²).

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