Electrochemical production of active chlorine using platinised platinum electrodes

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Abstract. This paper presents the results obtained during the electrogeneration of active chlorine species. Active chlorine species were generated through the electrolysis of sodium chloride solutions in an undivided cell, employing two platinised platinum electrodes and a polarity reversal procedure. The electrolytic process was conducted at four current densities (0.05, 0.10, 0.30 and 0.50 A/cm²) and three concentrations (0.1, 0.5 and 1 mole/L) the polarity reversal period being of 5 min. The brine flow rate was kept constant, namely 1.68 L/h. The results showed a maximum active chlorine concentrations for an initial brine concentration of 0.5 mole/L. The overall concentration of dissolved chlorine in water was quantified as active chlorine, defined as the sum of the three possible species (Cl², HClO and ClO⁻).

1. Introduction

Chlorination is one of the most used disinfection methods as it is effective, inexpensive and provides both primary and secondary residual disinfection. Moreover, chlorine acts as an oxidizing agent. One uses the term active chlorine species to designate the chlorine-based compounds used as disinfectants. Active chlorine species refers to dissolved chlorine, hypochlorite ions and hypochlorous acid [1-7]. Nonetheless, the use of chlorine as disinfection agent has several drawbacks. Among these, one mentions unfavourable taste and odour of treated water, resistance of some bacteria to chlorine and the generation of disinfection by-products [4, 8, 9].

In the recent years, studies have focused on new alternative disinfection methods and electrochemical disinfection is a promising alternative, as it generates a mixture of oxidants with bactericidal effect. Generally, the generation of hypochlorite is achieved through the hydrolysis of chlorine in aqueous media. In the electrochemical process, the hypochlorite generation takes place starting from brine solutions. This method has the advantage of on-site production and of solving the issues of storage and handling [4, 10, 11, 12].

Several parameters influence the electrochemical generation of active chlorine species, such as electrode material, electrolyte composition and cell configuration. Several types of electrodes were
used to generate active chlorine species: Ti/IrO$_2$, RuO$_2$-TiO$_2$/Ti, platinum coated titanium, titanium coated with oxides of titanium, ruthenium and iridium, titanium coated with iridium oxide or platinum, Ti/RuO$_2$:2SnO$_2$ and boron doped diamond (BDD) [7, 10, 12-20].

During electrolysis of sodium chloride solutions, chlorine is generated at the anode, while at the cathode hydrogen is produced. The reactions that take place in an undivided electrochemical cell are described by the following equations:

At the anode [10, 12, 17, 20]:

$$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \quad E^0 = 1.35\text{V} \quad (1)$$

At the cathode [17]:

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^0 = 0\text{V} \quad (2)$$

The generated chlorine reacts with water and forms hypochlorous acid which further hydrolyses forming hypochlorite ion. In fact, this is the active bactericidal agent [10-12, 17, 20].

$$\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad (3)$$

$$\text{HClO} \rightarrow \text{ClO}^- + \text{H}^+ \quad (4)$$

Among the uses of electrochemically generated active chlorine species, one mentions the removal of microcystins and reactive dyes, disinfection of water, grey water, textile and pharmaceutical wastewater [5, 14, 16, 17].

The aim of this paper is to present the results obtained during the electrochemical generation of active chlorine species from sodium chloride solutions in an undivided cell. The electrodes were made of platinised platinum and the efficiency of the electrolytic process was increased by applying a polarity reversal procedure.

2. Materials and Methods

The active chlorine species were produced through electrolysis of sodium chloride solutions (0.1, 0.5 and 1 mole/L) according to a procedure similar to the one previously described in [21, 22]. The electrolysis was performed in a modified commercial chlorinator. The electrodes consisted of two Pt sheets of rectangular shaped (each electrode had a total area of 1.3 cm$^2$). The electrodes were platinised using a base solution containing hexachloroplatinic acid (3.5%) and lead acetate (0.005%) according to the procedure detailed by Zoski [23]. The electrolytic process was performed galvanostatically, at four current densities (0.05, 0.10, 0.30 and 0.50 A/cm$^2$). The sodium chloride feed flow rate was kept constant (1.68 L/h). The process efficiency was enhanced by reversing the polarity of the electrodes at every 5 min. The total time of electrolysis was 70 min.

One has monitored the dissolved chlorine concentration using the iodometric titration method [24].

3. Results and discussions

Fig. 1-3 show the time variation of active chlorine concentration generated for all sodium chloride concentrations and current densities.

One has noticed that, for the same feed concentration of sodium chloride solution, the concentration of active chlorine increases as the current density increases.

The active chlorine concentration generated is higher when the feed concentration of sodium chloride solution increases. The maximum concentration was achieved for an initial concentration of sodium chloride solution of 0.5 mole/L and a current density of 0.50 A/cm$^2$.

For a feed concentration of sodium chloride solution of 0.5 and 1 mole/L, one has noticed that the active chlorine concentration increases as the current density increases. However, in the case of an initial concentration of 0.1 mole/L, one may notice that the concentration active chlorine generated at 0.05 A/cm$^2$ is greater than the one generated at 0.10 A/cm$^2$. For a feed concentration of 0.5 mole/L, the
values of active chlorine concentration generated at a current density of 0.30 and 0.50 A/cm$^2$ are relatively close.

Figure 1: The variation of concentration of active chlorine species generated through electrolysis of 0.1 mole/L NaCl solution

Figure 2: The variation of concentration of active chlorine species generated through electrolysis of 0.5 mole/L NaCl solution
Figure 3: The variation of concentration of active chlorine species generated through electrolysis of 1 mole/L NaCl solution

4. Conclusions
The electrochemical generation of active chlorine species was performed in an undivided cell using a pair of platinised platinum electrodes at various constant current densities and initial brine concentration. In order to enhance the efficiency of the electrolytic process and also to avoid deposit formations, one has used a polarity reversal procedure at every 5 min interval for the whole duration of electrolysis.

The results showed that the increase of the current density as well as the increase in the sodium chloride feed concentration caused an increase of the active chlorine concentration, the maximum active chlorine concentration being achieved when the initial sodium chloride solution was 0.5 mole/L and the current density of 0.50 A/cm².

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