

## The Effect of the Pulsed Current Regime on the Electro-combustion of Phenol

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The pulsed current regime is normally used to obtain two or more metals codeposition which have different values of standard electrochemical potential. In this study the same technique has been applied in the electro-combustion of phenol to study its effect.

It is evident that an interaction between the pulsed current and the electro-combustion occurs when the frequency of the applied pulsed current is very close to the inverse of the characteristic time of the electro-combustion process.

In the electro-combustion process the hydroxyl radicals, formed on lead dioxide and diamond doped boron anodes etc, have been considered the oxidized agents. It is probable that some of produced radicals are diffused in the electrolyte and react with the organic species in solution. Then the characteristic time of this process  $\tau_r$ , can be estimated by considering the balance of the phenol and of the radical in this region:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial z^2} - k_1 C_1 C_2$$

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial z^2} - k_1 C_1 C_2 - 2k_2 C_2^2$$

where  $C_1$  and  $C_2$  are the concentration of phenol and hydroxyl radical,  $k_1$  is the kinetic constants of the phenol oxidation by the radical and  $k_2$  the constant of hydrogen peroxide production. The estimate characteristic time of this process was 0,0625 s and consequently a frequency range between 0 and 250 Hz was applied.

A low initial phenol concentration was used ( $63 \text{ mg dm}^{-3}$ ) the electrolyte contain also  $10^{-3} \text{ mole dm}^{-3}$  NaOH and  $0.5 \text{ mole dm}^{-3}$   $\text{Na}_2\text{SO}_4$ . The electrolyte was well mixed and the mass transfer coefficient  $k_m$ , was determined. The applied current density was relatively low ( $6.25$  and  $9.4 \text{ mA cm}^{-2}$ ), but due to the low phenol concentration, the anode operates under mass transfer limitation.

To point out the efficiency of the pulsed technique, despite the mass transfer limitation, the normalized current efficiency  $\phi$  and not the current efficiency  $\eta$ , was used which make also more simple the organic species balance during the electro-combustion, that assume the following form:

$$V \frac{dCOD}{dt} = -\phi k_m S(COD)$$

where  $V$  is the volume of the cell and  $S$  the anodic surface.

If the normalized current efficiency  $\phi$ , is constant, its value can be estimated by using the above differential equation solution:

$$\ln \frac{COD(t)}{COD_0} = -\phi \frac{t}{\tau}$$

where  $\tau = V/k_m S$  ( $= 7500 \text{ s}$ ), is the characteristic time of the electrochemical cell.

The demolition of the organic species vs. specific charge at constant and pulsed current regime has been

reported in Fig. 1. It is interesting to note that in this case the pulsed current regime, at the frequency of 150 Hz, has an evident positive effect on the organic demolition.

Fig. 2 reports the experimental results to calculate  $\phi$ , according the reported solution. The fitting of the experimental  $\phi$  value, indicates that in this case during the electro-combustion the normalized current efficiency  $\phi$ , remain practically constant.

Finally Fig. 3. shows two new cases with constant and pulsed current regime. Also now it is observed that the pulsed current regime is more efficient than the constant one. While the normalized current efficiency  $\phi$ , is not constant, but change with the proceeding of the electro-oxidation process, especially with the pulsed current regime.

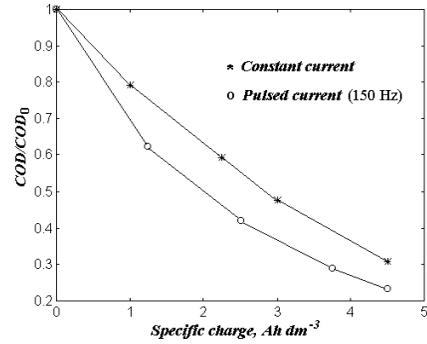


Fig. 1.  $COD/COD_0$  vs. specific charge; duty cycle 0.5, mean current density  $9.4 \text{ mA cm}^{-2}$

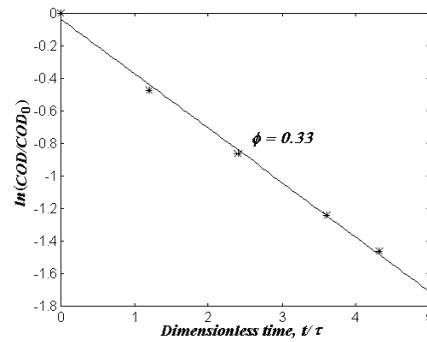


Fig. 2.  $\ln(COD/COD_0)$  vs. dimensionless time; duty cycle 0.5, mean current density  $9.4 \text{ mA cm}^{-2}$ , frequency 150 Hz.,  $\tau = 7500 \text{ s}$ .

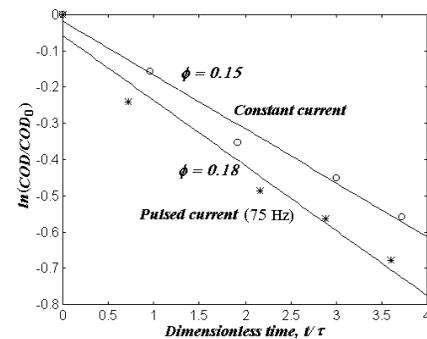


Fig. 3.  $\ln(COD/COD_0)$  vs. dimensionless time; duty cycle 0.5, mean current density  $6.25 \text{ mA cm}^{-2}$ ,  $\tau = 7500 \text{ s}$

The reported results indicate that the pulsed current regime, affects the electro-combustion when its frequency is close to the inverse of characteristic time, of phenol electro-combustion by the deadsorbed hydroxyl radicals.