DIRECT AND MEDIATED ELECTROCHEMICAL OXIDATION OF NAPHTALEN- AND ANTHRAQUINON-SULFONIC ACIDS

Marco Panizza, Giacomo Cerisola

Dipartimento di Ingegneria Chimica e di Processo,
Università di Genova
P.le J.F. Kennedy 1, 16129 Genova,
e-mail: marco.panizza@unige.it

The electrochemical treatment of organic pollutants can be performed by direct and indirect oxidation. In the direct anodic oxidation, pollutants are oxidised on anode surface without the involvement of other chemical reagent. By using these technique, organics are incinerated to CO_2 by hydroxyl radicals electrogenerated from water discharge:

$$2H_2O \rightarrow 2OH^\bullet + 2H^+ + 2e^- \tag{1}$$

Besides direct oxidation, organic pollutants can also be treated by an indirect electrolyses, generating in situ chemical reactants to convert them to less harmful products. Although a large number of electrogenerated inorganic mediators can be used, active chlorine and Fenton's reagent are the most widely employed.

Active chlorine, in the form of chlorine, hypochlorous acid and hypochlorite is electrogenerated in solution containing chloride ions on anode surface by the following reactions:

$$2\,Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{4}$$

Hydrogen peroxide is electrogenerated in acidic solutions by two-electron reduction of oxygen on the cathode surface:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{5}$$

Hydrogen peroxide alone is not a strong oxygen-transfer agent, but the oxidation of organics is improved by the presence of Fe^{2+} ions because the reaction leads to the formation of the highly oxidising $OH^\bullet$ radicals, according to Fenton's mechanism:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{6}$$

The aim of the present study was to compare the efficiency of direct and indirect electrochemical oxidation of a real industrial wastewater containing especially naphthalen- and anthraquinon-sulfonic acids. The direct oxidation was carried out using high oxygen overpotential anodes, such as boron-doped diamond and lead dioxide anodes. The indirect electrolyses were mediated by active chlorine electrogenerated on a platinum anode and on a Ti-Ru-Sn ternary oxide anode, or by hydrogen peroxide electrogenerated on a graphite cathode. Furthermore, for each type of electrolyses the effects of operating factors, such as anode material, current density, chloride concentration, ferrous ions concentrations on COD removal and colour fading were analysed.

The comparison of the results showed that the best electrochemical treatment was obtained by direct oxidation using boron-doped diamond anode at 30 mA cm^{-2}, which resulted in a complete mineralization of the wastewater after about 15 Ah dm^{-3}.

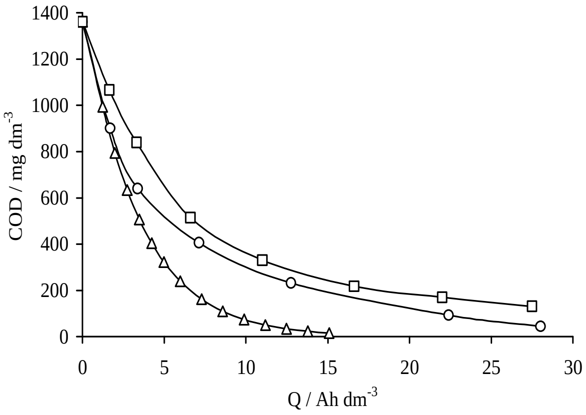

FIGURE 1: Comparison of COD evolution with the specific electrical charge passed during direct and mediated electrolyses. (□) H_2O_2 mediated electrolysis: $FeSO_4$ = 3 g dm^{-3}; (○) chlorine mediated electrolysis: Ti/PtO_x anode; NaCl = 5 g dm^{-3}; i = 30 mA cm^{-2}; (Δ) direct electrolysis: boron-doped diamond anode; i = 30 mA cm^{-2}.

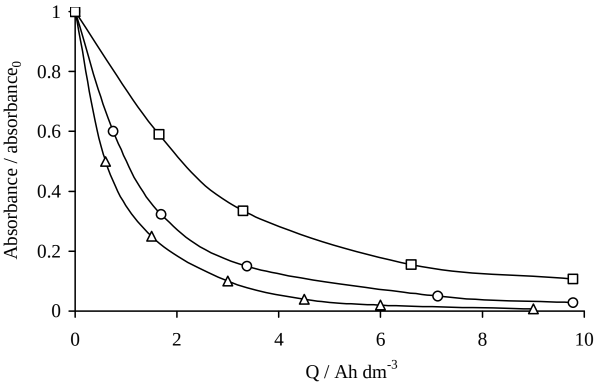

FIGURE 2 - Comparison of colour removal with the specific electrical charge passed during direct and mediated electrolyses. (□) H_2O_2 mediated electrolysis: $FeSO_4$ = 3 g dm^{-3}; (○) chlorine mediated electrolysis: Ti/PtO_x anode; NaCl = 5 g dm^{-3}; i = 30 mA cm^{-2}; (Δ) direct electrolysis: boron-doped diamond anode; i = 30 mA cm^{-2}.