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# Parameter study on bleaching of the organic dye p-nitrosodimethylaniline (RNO) by electrochemical oxidation

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Bleaching of the organic dye p-nitrosodimethylaniline (RNO) is a method widely applied for evaluation of the oxidative performance of electrochemical water treatment systems (Comninellis, 1994; Martinez-Huitle et al. 2004; Tanaka et al. 2004). During the last 15 years, electrochemical oxidation has been developed into a strong physico-chemical oxidation technique for treatment of water utilizing hydroxyl radicals and lattice active oxygen depending on the electrode material used. The present study concerned the use of RNO as a selective probe compound for detection of hydroxyl radicals, an indirect determination method adapted from the cell biology and photobiology fields (Kraljic and Trumbore, 1965). RNO was claimed to act as a selective scavenger towards hydroxyl radicals through oxidation of the chromophore nitroso group, however, bleaching was also observed in Ti/Pt and Ti/$RuO_2$ anode systems utilizing chemisorbed lattice active oxygen (Tanaka et al. 2004) according to the generally accepted models (Comninellis 1994). In addition, several studies reports bleaching of RNO by other strong oxidant as ozone (Wabner and Grambow, 1985) and chlorine (Tanaka et al. 2004). These observations were explained by oxidation mechanisms through radical chain reactions generating intermediate hydroxyl radicals (Fukatsu and Kokot, 2001).

The applied anode material was Ti/$Pt_{90}$-Ir10 and experimental runs in inert 0.050 M sodium sulphate and sodium phosphate electrolytes confirmed bleaching of RNO following first order reaction kinetics. In 0.050 M sodium chloride electrolyte, the bleaching rate was much faster with a shift in kinetics to second order RNO dependence, which confirmed the oxidation of RNO by the generated hypochlorous acid/hypochlorite pair. The electrolytic formation of available free chlorine species in a 0.154 M sodium chloride electrolyte was simulated with addition of alkaline sodium hypochlorite solution in similar amount and rate, in order to compare the oxidation rate of the in-situ generated and the physically added chlorine. The rate of the chemical oxidation obeyed none of the standard kinetic expressions, but comparison of the evolution in the relative RNO concentration revealed a superior oxidation efficiency of the in-situ generated hypochlorous / hypochlorite species. In order to study the role of hydroxyl radicals in the oxidation reactions observed, tertiary butyl alcohol (t-BuOH) was added in excess to remove all hydroxyl radicals if present. In 0.050 M sodium sulphate electrolyte an almost similar evolution in the RNO concentration was found with or without the presence of 0.05 M t-BuOH stating that no hydroxyl radicals was formed by the Ti/$Pt_{90}$-$Ir_{10}$ anode material and that the oxidation was due entirely to lattice active oxygen $MO_{x+1}$. In a similar fashion, the hydroxyl radical chain reaction proposal was rejected since neither 0.05 M nor 0.10 M t-BuOH slowed or even affected the rate of RNO oxidation in the 0.050 M sodium chloride electrolyte. As concluding remark, RNO was both oxidized by lattice active oxygen and chlorine species, and can not be regarded as a fully selective hydroxyl radical probe compound in electrochemical studies. However, it is a very applicable and easy to use compound for evaluation of the electrochemical oxidation potential, taking account of all oxidative species generated in the process.

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