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Electrochemical degradation of anionic surfactants

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Abstract

This study was performed to investigate the electrochemical oxidation of anionic surfactants. In particular, a synthetic solution of sodium dodecyl benzene sulfonate and a real car wash wastewater were treated by galvanostatic electrolysis using a Ti–Ru–Sn ternary oxide and a boron-doped diamond (BDD) anode. Measurements of the Chemical Oxygen Demand (COD) and the concentration of the anionic surfactants were used to follow the oxidation. Using the Ti–Ru–Sn ternary oxide anode, the complete removal of COD and sodium dodecyl benzene sulfonate was obtained only in the presence of chloride ions that act as inorganic mediators. The oxidation rate was almost independent of current density and electrolyte flow rate. In the case of BDD the mineralisation of the sodium dodecyl benzene sulfonate was achieved in all experimental conditions due to reaction with hydroxyl radicals electrogenerated on the diamond surface during electrolysis. The COD removal rate increased with increase in electrolyte flow rate, indicating that the oxidation was mass-transfer controlled. Comparison of the results of the two electrodes showed that chlorine mediated oxidation at the Ti–Ru–Sn ternary oxide anode allowed a faster COD removal of both the synthetic solution and real car wash wastewater.

1. Introduction

Surfactants are the active cleaning ingredients in synthetic detergents used for all kinds of washing. They consist of a water-soluble (hydrophilic) and a water-insoluble (hydrophobic) component. As a result of this structure, the molecules of surfactants align themselves to form micelles able to separate dirt and oily stains. Surfactants are classified according to their ionic properties in the water: anionic (negative charge), cationic (positive charge), non-ionic (no charge) and amphoteric (positive or negative charge). The most common surfactants in use in industrial and household detergents are of the anionic type such as the linear alkyl benzene sulfonate (LAS). Even if they are more easily biodegraded than the highly branched alkyl benzene sulfonate (ABS), their presence in waters favours the formation of stable and highly-difficult-to-separate emulsions. With the increase in the consumption of detergents in car washes, laundries and households, washing waters are becoming a pollution danger.

Many papers have demonstrated that besides the traditional chemical, physical and biological methods, electrochemical technologies can be efficiently applied to the treatment of wastewater containing organic pollutants [1–3].

By means of electrochemical oxidation, pollutants can be completely mineralised using high oxygen overvoltage anodes such as PbO_2 [4–7] and boron-doped diamond (BDD) [8–13]. In fact, using these anodes, organics are incinerated to CO_2 by electrogenerated hydroxyl radicals [14]:

$$2H_2O \rightarrow 2OH^{\bullet}_{ads} + 2H^+ + 2e^- \qquad (1)$$

Studies have shown that organic pollutants can also be mineralised on platinum or dimensional stable anodes (DSA®) by indirect electrolysis, using chloride ions as an inorganic mediator [15–20]. In media containing chloride the oxidation of organics is carried out by active chlorine formed through oxidation of chlorides. Direct and indirect electrochemical oxidation has been used for the combustion of many synthetic solutions and industrial wastewaters. However, up to now little attention has been paid to the possibility of applying electrochemical processes to the degradation of anionic surfactants [21–22].

The aim of this work was to study the electrochemical oxidation of a synthetic solution and of a real car wash wastewater containing anionic surfactants. The electrochemical treatment was performed by direct electrolysis, using a BDD, and indirect electrolysis, generating *in situ* active chlorine, using a Ti–Ru–Sn ternary oxide anode. In particular, the influence of such operating parameters as chloride concentration, current density and mass-transfer coefficient were studied for each electrode, in order to find the optimal conditions for electrolysis.

2. Experimental

The Ti–Ru–Sn ternary oxide anodes, hereafter referred to as $TiRuSnO_2$, were prepared by coating titanium plates by thermal decomposition with a mixture of $TiCl_4$, $RuCl_3 \cdot 3H_2O$ and $SnCl_4 \cdot 5H_2O$ dissolved in propanol–HCl mixture [23]. The titanium plates were subjected to surface pre-treatment with corundum sandblasting and hot hydrochloric acid picking. The precursor solution was painted on the titanium plates, the solvent was evaporated in air at 80 °C and then the precursors were decomposed at 450 °C for 1 h. Thereafter this procedure was repeated until the coating thickness was 50 μm. The nominal composition of the ternary oxide was $Ti/Ti_{0.5}\ Ru_{0.45}\ Sn_{0.05}O_2$.

A BDD thin-film electrode was supplied by CSEM Centre Swiss d'Electronique et de Microtechnique of Neuchâtel. It was prepared by the hot filament chemical vapour deposition technique (HF-CVD) on single crystal p-type Si <100> wafers (1–3 mΩ cm, Siltronix). The diamond film thickness obtained was about 1 μm with a resistivity of 10–30 mΩ cm and the doping level of the boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm.

Bulk oxidation of the anionic surfactants was performed in an undivided electrolytic flow cell under galvanostatic conditions. The BDD or $TiRuSnO_2$ anodes and the stainless-steel cathode were square with a geometric area of 25 cm^2 and an interelectrode gap of 0.5 cm. The solution was stored in a 500 ml thermoregulated glass tank and circulated through the electrolytic cell by a centrifugal pump with different flow rates in the range of 60–180 $dm^3\ h^{-1}$ corresponding to a mass-transfer coefficient in the cell, determined using the Ferri/Ferrocyanide couple, of about 1.1×10^{-5}–1.6×10^{-5} m s^{-1}.

The synthetic solution was prepared dissolving 0.75 g dm^{-3} of sodium dodecyl benzene sulfonate, representing the anionic surfactants, in distilled water in 0.5 N Na_2SO_4. The real wastewater was collected in a car wash installation and it presented a COD of 1150 mg dm^{-3} and concentration of anionic surfactants of 50 mg dm^{-3} and a pH of about 7.8. In order to remove the suspended solids that influence the electrochemical process, the effluent was subjected to a filtration pre-treatment using a 230-mesh screen. The wastewater, after the filtration, presented a COD of 920 mg dm^{-3} and concentration of anionic surfactants of 40 mg dm^{-3}.

During the experiments, samples were drawn from the cell at different times and analysed. The Chemical Oxygen Demand (COD) and the concentration of the anionic surfactant were chosen as parameters in order to evaluate the progress of the oxidation. The instantaneous current efficiency (ICE) for the anodic oxidation of the anionic surfactants was calculated from the values of COD using the relationship [24]:

$$\mathrm{ICE} = \frac{\left[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}\right]}{8 \cdot \mathrm{I} \cdot \Delta t} \cdot \mathrm{F} \cdot \mathrm{V} \tag{2}$$

where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demands at times t and t + Δt (in $gO_2\ dm^{-3}$) respectively, and I is the current (A), F is the Faraday constant (96487 C mol^{-1}), V is the volume of the electrolyte (dm^3).

3. Results and discussion

Figure 1 shows the influence of the chloride ion concentration on the COD removal rate during the oxidation of sodium dodecyl benzene sulfonate at the Ti–Ru–SnO_2 anode. In the absence of chlorides, curve (a), low COD depletion and low current efficiency were obtained, because the major anodic reaction at the Ti–Ru–SnO_2 anode, which has low oxygen evolution overpotential, was oxygen evolution. In contrast, the addition of 1 g dm^{-3} of NaCl in the electrolyte resulted in an increase in COD removal due to the mediation of active chlorine electrogenerated on the anode surface by chloride oxidation:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{3}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^- \tag{4}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{5}$$

Increasing the NaCl up to 2.5 g dm^{-3} accelerated the removal rate, enabling complete mineralisation of the

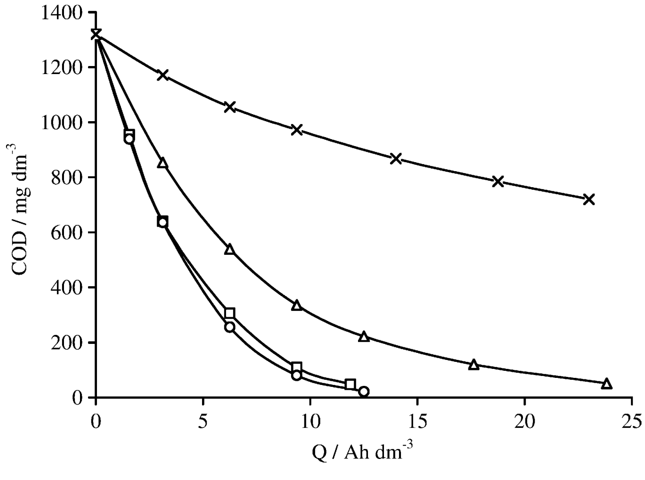

Fig. 1. Influence of chloride ion concentration on the evolution of COD with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene solfonate on the Ti–Ru–Sn ternary oxide anode. Electrolyte: Na_2SO_4 0.5 N; *T* = 25 °C; flow rate: 180 $dm^3\ h^{-1}$; *i* = 75 mA cm^{-2}; NaCl concentration: (×) 0 g dm^{-3}; (Δ) 1 g dm^{-3}; (□) 2.5 g dm^{-3}; (○) 5 g dm^{-3}.

anionic surfactant after 12.5 Ah dm^{-3}. A further increase in the NaCl concentration to 5 g dm^{-3} did not bring about any meaningful improvements, and so the optimum NaCl concentration used in the successive experiments was 2.5 g dm^{-3}.

The influence of the applied current density and electrolyte flow rate on the trend of COD removal versus specific charge passed are shown in Figures 2 and 3. In the range of current density (25–75 mA cm^{-2}) and flow rate (60–180 dm^3 h^{-1}) studied, COD abatement was almost independent of these parameters. This fact can be explained because the oxidation of the surfactant did not occur directly on the electrode surface but in the bulk of the solution due to electrogenerated active chlorine. Moreover, with a concentration of 2.5 g dm^{-3} of NaCl, the electrogeneration of active chlorine is under charge-transfer control and then it mainly depends on the specific charge passed through the cell. It is interesting to observe from Figure 2 that the increase in current density resulted in a moderate increase in COD removal. Although this behaviour could be considered surprising taking into account the possible effect of the secondary reaction of oxygen evolution, similar results were also obtained by Bonfatti et al. [17] during the oxidation of glucose on a Ti/Pt anode.

Since the oxidation of surfactants is due to the mediation of active chlorine, organochlorinated compounds can be formed, resulting in increased toxicity of the wastewater. In fact, the gas chromatograph analysis of the solution revealed the formation of traces of organochlorinated compounds; however they disappeared during the electrolysis.

The results obtained during the oxidation of sodium dodecyl benzene sulfonate on the BDD anode were somewhat different. As shown in Figure 4, the COD of the solution was completely removed even in the absence of the chloride ion mediation. This indicates that using BDD, which is a high oxygen overvoltage anode, sodium dodecyl benzene sulfonate is incinerated by reaction with $OH^{\bullet}$ radicals electrogenerated by water discharge [25]:

$$C_{18}H_{29}SO_3Na \xrightarrow{102\,OH^{\bullet}} 18\,CO_2 + 65\,H_2O + SO_3 + NaOH \tag{6}$$

Moreover, it was observed that an increase in current density resulted in a decrease in current efficiency due to the side reaction of oxygen evolution:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{7}$$

In order to further investigate the effects of operating parameters on the oxidation of sodium dodecyl benzene sulfonate on BDD, electrolysis was performed at different flow rates in the range 60–180 dm^3 h^{-1} (Figure 5). As can be seen from Figure 5, the trend of the COD was strongly influenced by the hydrodynamic conditions and, in particular, the mineralisation of the surfactant was favoured by a high flow rate, indicating that the oxidation on the BDD is a mass-transfer controlled process. Similar results were also obtained by Polcaro et al. [13] during the oxidation of phenolic compounds at a BDD electrode.

Comparison of the trend of the COD, sodium dodecyl benzene sulfonate concentration and current efficiency during the oxidation with Ti–Ru–SnO_2 and BDD anodes, each under its best operating conditions, is presented in Figure 6. These graphs show that faster surfactant mineralisation and higher efficiency were obtained by indirect electrolysis at the Ti–Ru–SnO_2

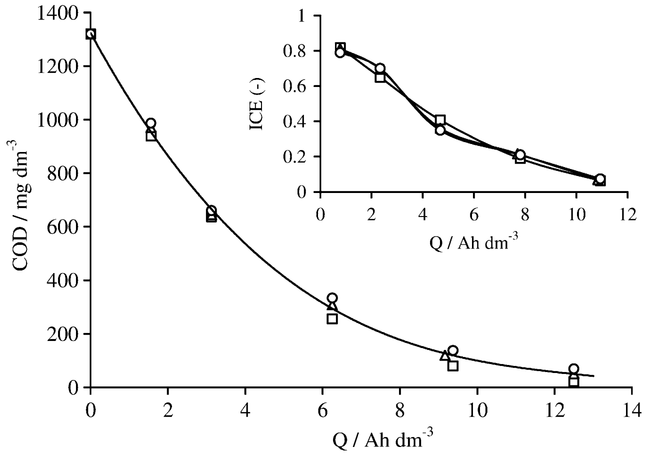

Fig. 2. Influence of applied current density on the evolution of COD and ICE (inset) with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene solfonate on the Ti–Ru–Sn ternary oxide anode. Electrolyte: Na_2SO_4 0.5 N; T = 25 °C; NaCl = 2.5 g dm^{-3}; flow rate: 180 dm^3 h^{-1}; applied current density: (○) i = 25 mA cm^{-2}; (Δ) i = 50 mA cm^{-2}; (□) i = 75 mA cm^{-2}.

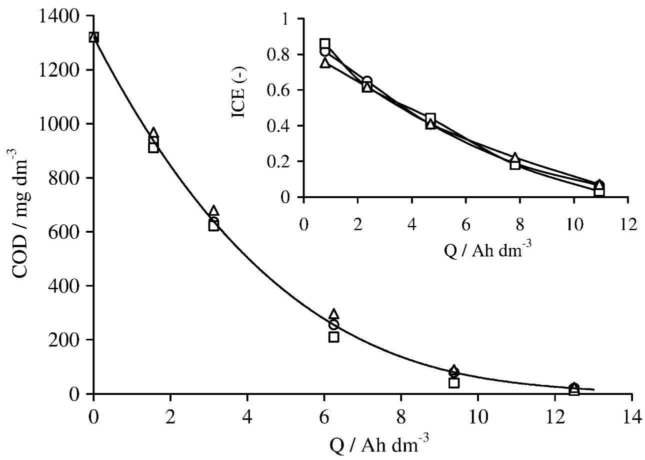

Fig. 3. Influence of electrolyte flow rate on the evolution of COD and ICE (inset) with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene solfonate on the Ti–Ru–Sn ternary oxide anode. Electrolyte: Na_2SO_4 0.5 N; T = 25 °C; NaCl = 2.5 g dm^{-3}; i = 75 mA cm^{-2}; flow rate (Δ) 60 dm^3 h^{-1}; (□) 100 dm^3 h^{-1}; (○)180 dm^3 h^{-1}.

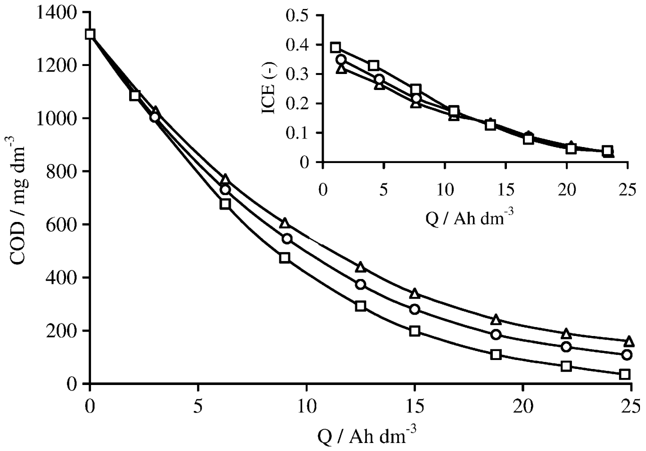

Fig. 4. Influence of applied current density on the evolution of COD and ICE (inset) with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene solfonate on the BDD anode. Electrolyte: Na_2SO_4 0.5 N; T = 25 °C; flow rate: 180 dm^3 h^{-1}; applied current density: (□) i = 25 mA cm^{-2}; (○) i = 50 mA cm^{-2}; (Δ) i = 75 mA cm^{-2}.

anode. From a comparison of the data in Figure 6a and b for the COD and sodium dodecyl benzene sulfonate trend, a steeper decrease in the sodium dodecyl benzene sulfonate concentration is observed, suggesting that it was firstly oxidised to organic intermediates and then to carbon dioxide.

Finally, a real car wash wastewater containing anionic surfactants was treated using Ti–Ru–SnO_2 and BDD anodes in the operating conditions found during the oxidation of sodium dodecyl benzene sulfonate, and the results are presented in Figure 7. Even in this case, faster COD removal and surfactant oxidation were obtained using the Ti–Ru–SnO_2 anode in the presence of 2.5 g dm^{-3}. However, the current efficiency of the Ti–Ru–SnO_2 anode during the oxidation of the real effluent was lower than that obtained during the oxidation of the synthetic solution, due to the presence of heavy metals that cause the decomposition of electrogenerated active chlorine in the car wash wastewater. In contrast, heavy metals did not significantly affect the degradation at the BDD anode. From the data of Figure 7 and of the cell potential, it is possible to estimate that the energetic cost of the electrochemical treatment of a carwash wastewater is about 50 kWh kgCOD^{-1} and 140 kWh kg COD^{-1} using a Ti–Ru–SnO_2 or a BDD anode, respectively.

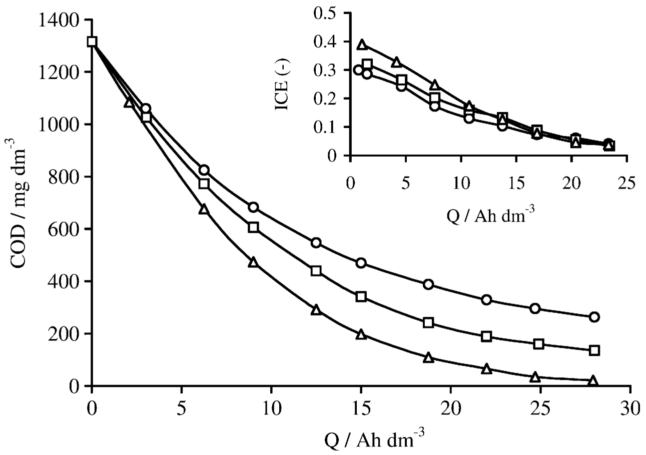

Fig. 5. Influence of electrolyte flow rate on the evolution of COD and ICE (inset) with the specific electrical charge passed during the electrolyses of 750 mg dm^{-3} of sodium dodecyl benzene solfonate on the BDD anode. Electrolyte: Na_2SO_4 0.5 N; T = 25 °C; i = 75 mA cm^{-2}; flow rate (○) 60 dm^3 h^{-1}; (□) 100 dm^3 h^{-1}; (Δ)180 dm^3 h^{-1}.

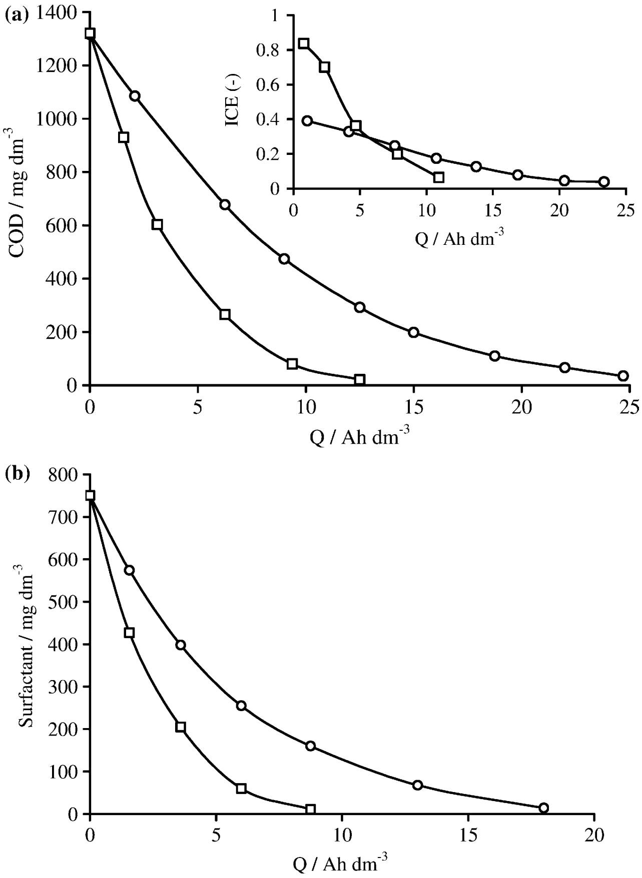

Fig. 6. Comparison of (a) COD and ICE (inset) and (b) sodium dodecyl benzene solfonate concentration with the specific electrical charge passed during the oxidation at the (□) Ti–Ru–Sn ternary oxide anode, NaCl = 2.5 g dm^{-3}; i = 75 mA cm^{-2}; flow rate 180 dm^3 h^{-1}; the (○) BDD anode; i = 25 mA cm^{-2}; flow rate 180 dm^3 h^{-1}.

4. Conclusion

The electrochemical oxidation of a synthetic solution and of a real car wash wastewater containing anionic surfactants on Ti–Ru–SnO_2 and BDD anodes was investigated. Using the Ti–Ru–SnO_2 electrode, which is a low oxygen evolution overpotential anode, the favoured reaction was oxygen evolution, and then the current efficiency for sodium dodecyl benzene sulfonate mineralisation was very low. In contrast, in the presence of chloride ions, the surfactant was completely oxidised because of the mediation of electrogenerated active

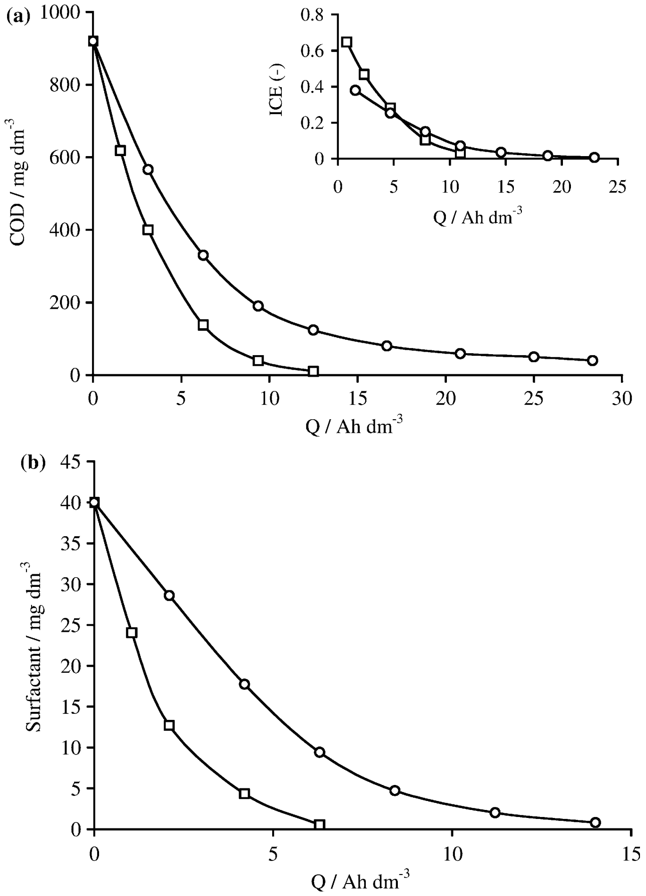

Fig. 7. Comparison of (a) COD and ICE (inset) and (b) anionic surfactant concentration with the specific electrical charge passed during the oxidation at the (□) Ti–Ru–Sn ternary oxide anode, NaCl = 2.5 g dm^{-3}; i = 75 mA cm^{-2}; flow rate 180 dm^3 h^{-1}; the (○) BDD anode; i = 25 mA cm^{-2}; flow rate 180 dm^3 h^{-1}.

chlorine. In particular, the optimal NaCl concentration was 2.5 g dm^{-3}. It was also found that the COD depletion was not influenced by the applied current density or electrolyte flow rate. The results of the electrolyses on BDD have shown that, independently of the experimental conditions, total incineration of sodium dodecyl benzene sulfonate was achieved, due to the formation of hydroxyl radicals from the water discharge. An increase in electrolyte flow rate and a decrease in current density favoured COD removal and current efficiency, meaning that the oxidation was under mass-transport control.

A comparison of the data obtained with the two electrode materials, each under its optimum experimental conditions, showed that faster sodium dodecyl benzene sulfonate mineralisation was achieved at the Ti–Ru–SnO_2 anode. Even in the case of the treatment of a real car wash wastewater, mediated electrolysis at the Ti–Ru–SnO_2 anode allowed faster COD removal even in the presence of heavy metals that catalysed the decomposition of the electrogenerated active chlorine.

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