

Electrochemical Incineration of Glucose as a Model Organic Substrate. I. Role of the Electrode Material

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Electrochemical Incineration of Glucose as a Model Organic Substrate

I. Role of the Electrode Material

F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi, and A. De Battisti^{*,z}

Dipartimento di Chimica, Università di Ferrara, I-44100 Ferrara, Italy

In the frame of study on the electrochemical incineration of organic pollutants, the reactivity of glucose toward mineralization was studied under different electrolysis conditions. The process was followed at Pt, SnO₂-Pt composite, and PbO₂ electrodes, at different current densities and temperatures. In all cases, the supporting electrolyte was 2 N H₂SO₄. Chemical oxygen demand and total organic carbon content of the solutions and amount of oxygen evolved were measured as functions of the electrolysis time. From these data, an initial electrochemical oxidation index (EOI) was evaluated following standard methods. Larger values for this parameter were found at the PbO₂ electrodes under all conditions of current density and temperature. At Pt and SnO₂-Pt, in the room-temperature range, the efficiency of the electrochemical mineralization of glucose was low, particularly at longer electrolysis times. The situation improved by increasing the temperature to 56°C. The extent of mineralization was quite low at SnO₂-Pt electrodes under all conditions explored. At Pt and SnO₂-Pt electrodes, the main oxidation intermediate was glucaric acid, apparently quite stable toward further attack at these electrodes. In the case of PbO₂ electrodes, smaller concentrations of intermediates were detected. Gluconic and 2-ketogluconic acids were also present in amounts comparable with that of glucaric acid. Study of the initial electrochemical oxidation index for gluconic acid and glucaric acid was also carried out, confirming the stability of the latter at Pt and SnO₂-Pt electrodes. At PbO₂, on the contrary, it was found to be even more reactive than glucose. An explanation for the reactivity of carboxylic acids toward mineralization at the PbO₂ electrodes is proposed.

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The possibility of eliminating organic pollutants from industrial wastes by anodic mineralization or "incineration" has been discussed in recent years.¹⁻⁶ The electrochemical wastewater treatment may be of particular interest when the effluent contains biorefractory organics, or any high amounts of organic carbon, and requires some pretreatment to allow further biological purification. The mineralization process takes place as an extreme case of anodic oxidation, together with the oxygen evolution reaction. The formation of adsorbed hydroxyl radicals is a necessary condition for the oxidative attack on the organic substrate to occur and also for oxygen evolution.⁷ At high oxygen overvoltage anodes, like PbO₂ and Sb(V)- or F⁻-doped SnO₂, typically the anodic mineralization of organic substrates takes place with better faradaic yields. In the case of lead dioxide, however, problems of service life and of release of lead ions in the treated effluent may represent serious drawbacks in a practical application. On the other hand, for tin dioxide-based electrodes, the short service life is also an important inconvenience.

While the improvement of these anodes is under investigation in different labs,⁸ it may be of interest to test their efficiency in the electrochemical mineralization of different organic substrates. The investigation of the mechanism of oxidation at different electrode materials, can serve as an important tool in attempts to optimize the process under discussion.

In the present work, glucose was studied as a model substrate, considering that saccharides give the main contribution to the very high chemical oxygen demand (COD) value (30-60 g O₂ dm⁻³) in certain effluents from the food industry (e.g., olive mill wastewaters).

Experiments on electro-oxidation were carried out at different electrode materials, investigating also the role of current density, temperature, and organic concentration. All data were obtained in acidic media.

Experimental

Constant-current electrolyses were performed by an Amel model 553 galvanostat. Experiments were performed in a single-body cell, at 25 and 56°C. The solution volume was 200 mL. The anode was symmetrically positioned between two zirconium plate cathodes, and the solution was vigorously stirred during the electrolysis exper-

iments. Industrial anodes were prepared by deposition of PbO₂, SnO₂-Pt, or galvanic Pt onto Ti plate and hereafter are indicated as Ti/PbO₂, Ti/SnO₂-Pt, and Ti/Pt.

Unless otherwise stated, the initial glucose concentration was 1 g dm⁻³. Supporting electrolyte was 2 N sulfuric acid. The duration of the electrolytic treatments was typically 24 h. The solution composition was tested every hour.

The glucose concentration was followed by high-performance thin-layer chromatography (HPTLC) using silica gel 60 (Merck) plates. 2 µL volumes of the sampled solutions were spotted onto the plates by means of a Linomat IV (Camag) automatic system; the spot analysis was performed by TLC scanner 3 (Camag) instrument and Cats 4.04 software. The plate developments were carried out both isocratically and in gradient mode using an automatic apparatus (AMD Camag). Detailed description of the optimization of the HPTLC separation has been given elsewhere.⁹

Some intermediates of the glucose electro-oxidation were identified by gas chromatography/mass spectrometry (GC-MS). A gas chromatograph (HP 5890 Series II Plus) equipped with an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.23 mm film thickness) was coupled with an HP 5989B mass spectrometer. Ionization was performed by electron impact (70 eV energy).

COD was determined according to the method described by Jirka and Carter.¹⁰ Total organic carbon (TOC) was measured by a TOC-Dohrmann 80 model.

Atomic-absorption measurements, for the determination of lead amount in electrochemically treated solutions, were carried out by a Perkin-Elmer 1100 model equipped with a graphite furnace HGA-500 and an auto-sampler AS40.

Results and Discussion

In the study of electrochemical wastewater treatment, the electrochemical oxidation index (EOI) of a given organic substrate has been proposed as a global parameter supplying information on the reactivity of organics toward oxidative degradation.^{7,11} If evaluated during a sufficiently short time at the beginning of the electrolysis, it can be specific for the substrate itself, assuming that reaction intermediates are still present at very low concentrations. If reasonable assumptions can be made on the nature of the reaction intermediates, it is possible to characterize the reactivity of each of them with the same procedure followed for the initial substrate. In our case, the

* Electrochemical Society Active Member.

^z E-mail: dba@dns.unife.it

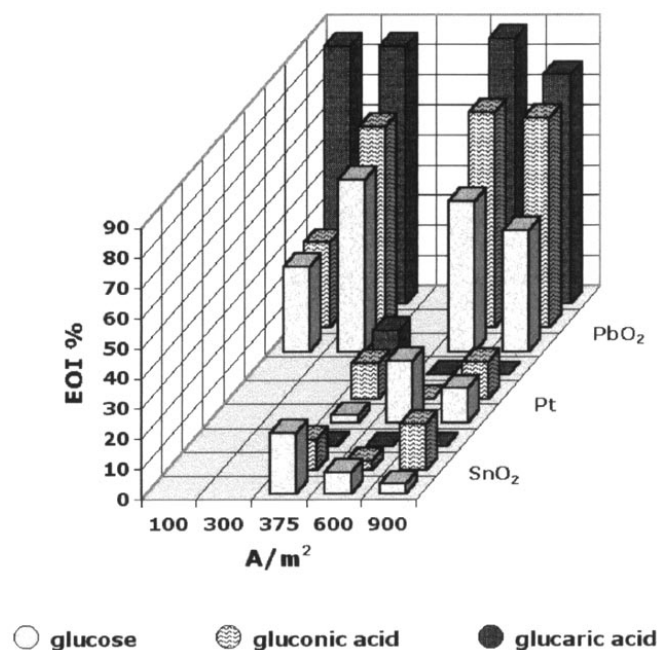


Figure 1. EOI values for glucose, gluconic, and glucaric acid at different electrodes and current densities.

EOI of glucose, gluconic acid, and glucaric acid have been determined under the different experimental conditions described in the Experimental section. The results are shown in Fig. 1.

At Ti/Pt electrodes, the reactivity of glucose is acceptable under all conditions, slightly higher at intermediate current densities. The reactivity of gluconic acid is comparable to that of glucose. Glucaric acid, on the contrary, does not seem to be electroactive. At Ti/SnO₂-Pt electrodes, the highest EOI values for glucose are found at low current densities. Glucose is also apparently the most reactive substrate, and the electrochemical activity decreases with increasing degree of oxidation. Glucaric acid is again practically inert. According to the data of Fig. 1, EOI values at Ti/SnO₂-Pt electrodes are generally lower than at Ti/Pt electrodes. Considering the higher dispersion of Pt in the composite electrodes and the possible occurrence of hydroxyl radical spillover, this is somewhat against expectations and requires further specific investigation.

At Ti/PbO₂ electrodes, high faradaic yields for glucose oxidation are found under all conditions of electrolysis. The highest faradaic yield has been found at 300 A m⁻² current density. As a function of temperature, the highest oxidation rate is attained at 56°C, which allows the use of lower current densities, further improving the yields. The EOI values are high both for glucose and gluconic acid. At variance with the case of the other two electrode materials, at Ti/PbO₂ electrodes for glucaric acid EOI is even higher than for the other substrates. This may be taken as evidence for a substantially different mechanism of electrochemical mineralization at PbO₂ electrodes.

The decrease of glucose content in solution, as a function of charge, at different electrodes and at different current densities, is shown in Fig. 2. Experiments were carried out in 2 N H₂SO₄ at 25°C. The curves exhibit substantially different shapes. Curves related to Ti/PbO₂ electrodes fit an exponential law. All other curves are better fitted by a polynomial function and are characterized by slower rate of decrease of glucose concentration with time. Complete abatement of the glucose content is achieved only at Ti/PbO₂. Increase of current density clearly leads to loss of faradaic efficiency due to the "parasitic" oxygen evolution.

At both Ti/Pt and Ti/SnO₂-Pt, the same situation is encountered, oxygen evolution being more favored anyway, in comparison with the case of Ti/PbO₂ electrodes. At Ti/SnO₂-Pt electrodes, at the intermediate current density of 600 A m⁻², the oxidation rate of glucose is lower than at 375 and 900 A m⁻², which confirms the complexity

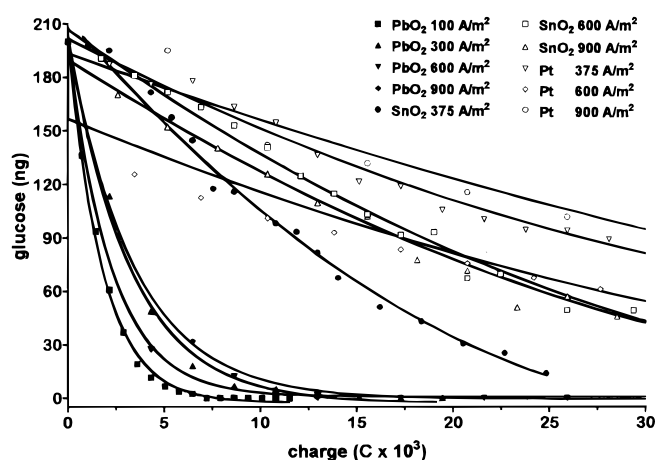


Figure 2. Decrease of glucose content in solution, as a function of charge, at different electrode materials and at different current densities. Solution: glucose 1 g dm⁻³ in 2 N H₂SO₄ at 25°C.

of the process at this electrode. The mechanism of anodic mineralization of organics, based on a higher activity of adsorbed hydroxyl radicals under oxygen evolution conditions, at high-oxygen-over-voltage electrode materials satisfactorily accounts for these results.⁷

The influence of temperature on the glucose oxidation rate has been studied at Ti/Pt and Ti/PbO₂ electrodes. The results are shown in Fig. 3. The solution temperature has an important effect on the glucose oxidation at both electrodes. In the first case the increase from 25 to 56°C causes a decrease to about one half the time required for the complete oxidation of the substrate. The effect at Ti/Pt electrodes is even more evident. Interestingly, at 56°C the shape of the glucose concentration decay changes to exponential. Due to the complex mechanism of the electrochemical mineralization of organics, involving different intermediate oxidation products and a number of adsorbed intermediates, these effects cannot be easily accounted for on the basis of the available results. Furthermore, a different explanation could hold at Ti/PbO₂ and Ti/Pt. In the first case, the formation of hydroxyl radicals is generally assumed to be a difficult step, and the less reactive organic species is glucose. In the second case, under oxygen evolution conditions, high hydroxyl radical coverages are attained, and the less reactive organic species is glucaric acid. Accordingly, it could be tentatively hypothesized that the observed increase of the electrochemical mineralization rate with temperature at Ti/PbO₂ electrodes is due to faster hydroxyl formation. In the case of Ti/Pt electrodes, the behavior of glucaric acid at the Pt/solution

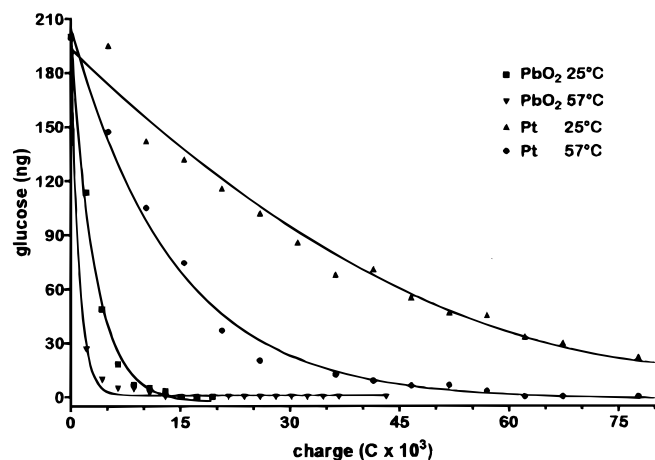


Figure 3. Effect of temperature on glucose mineralization at Ti/PbO₂ (300 A m⁻²) and Ti/Pt (900 A m⁻²).

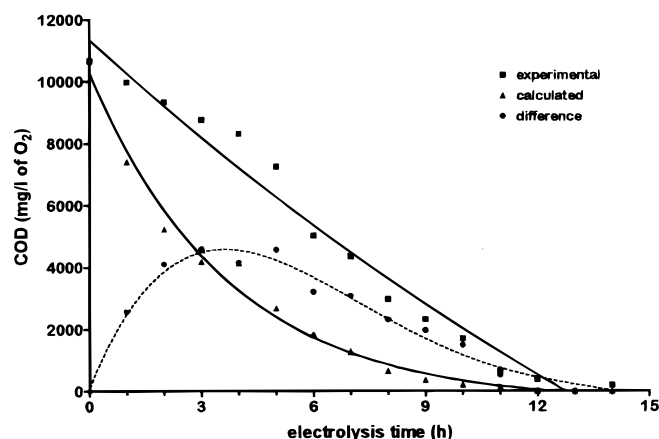


Figure 4. COD as a function of time. Ti/PbO₂ at 300 A m⁻², glucose 10 g dm⁻³ in 2 N H₂SO₄.

interface could play an important role. The high activation energy of some of the steps of the electrochemical incineration justify the observed temperature effects.

Wastewaters from the food industry (e.g., olive mill wastewaters) may contain saccharides at the level of several grams per liter. Accordingly, at Ti/PbO₂ electrodes, the study on glucose electro-oxidation has been extended to the concentration of 10 and 30 g dm⁻³. As might be expected, with increasing substrate concentration, the faradaic yield of the electrochemical oxidation increases. The decay of the glucose concentration as a function of time remains exponential. This suggests that even in the presence of large amounts of the reactant, no accumulation of intermediates takes place and confirms the high reactivity of the intermediate products of glucose anodic oxidation at the Ti/PbO₂ electrode.

The occurrence of corrosion phenomena of different anode materials in the presence of saccharides has been reported in the literature.¹² In our case, measurements have been carried out in the case of lead dioxide anodes, whose dissolution could represent a particularly serious drawback in wastewater treatment. Atomic absorption measurements have been carried out on solutions with an initial glucose content of 10 g dm⁻³, after complete mineralization of organics at 900 A m⁻². An amount of 80 ± 1.5 ppb of lead was found, well below the limits imposed in different countries (e.g., 300 ppb in Italy). Due to the character of standard analysis of the analytical method applied, its precision and accuracy can be estimated to be around 3%.

Global analytical information on the reactivity of glucose and all its oxidation products can be achieved through the study of the

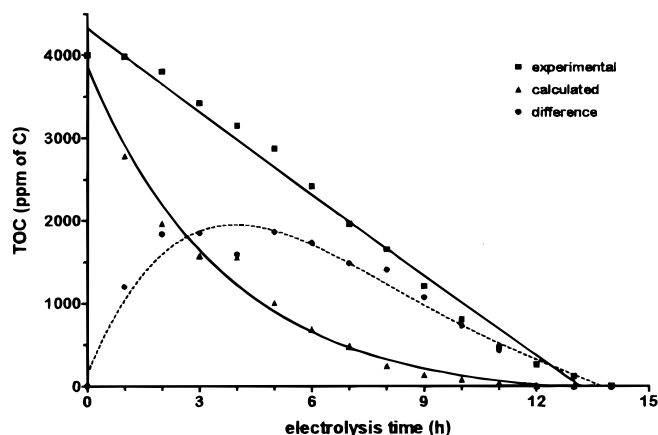


Figure 5. TOC as a function of time. Ti/PbO₂ at 300 A m⁻², glucose 10 g dm⁻³ in 2 N H₂SO₄.

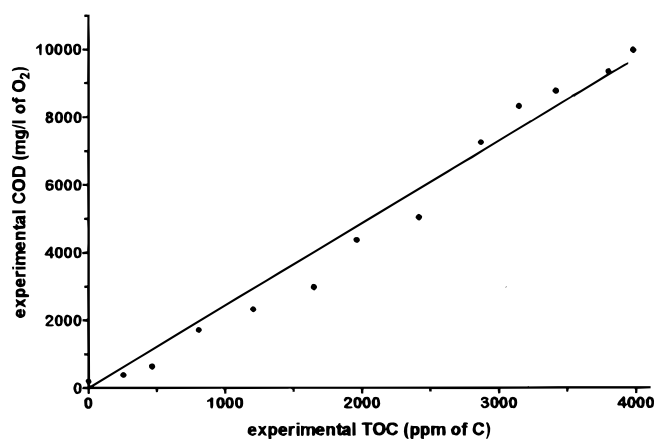


Figure 6. COD-TOC relationship. Ti/PbO₂ at 300 A m⁻², glucose 10 g dm⁻³ in 2 N H₂SO₄.

dependence of COD and TOC, from the different variables of interest. TOC is more directly related to the effective mineralization of organics. Data relative to the anodic oxidation of a solution containing 10 g dm⁻³ at Ti/PbO₂ are shown in Fig. 4 and 5. The calculated COD and TOC contributions due to glucose are shown as well, together with the difference between total COD and residual glucose COD. The latter difference can be ascribed to the contribution due to reaction intermediates.

The correlation between COD and TOC is shown in Fig. 6. It can be observed that the decrease in COD is accompanied by a decrease of TOC. This evidence justifies the assumption that at Ti/PbO₂ anodes, the intermediate products of glucose oxidation are quite reactive themselves toward further oxidation steps. Similar observations have been made by Sharifian and Kirk⁶ for the case of phenol oxidation at PbO₂ electrodes in sulfuric acid media.

The results obtained at Ti/SnO₂-Pt electrodes are quite different. As seen in Fig. 7, the rate of decrease of COD is much lower than the rate of decrease of glucose concentration, also expressed in COD units. This evidence and the previously described initial EOI values show that accumulation of intermediates takes place during the anodic oxidation of glucose. The situation is represented by the curve showing the dependence on time of the difference between total COD and residual glucose to total COD.

The plot of TOC vs. electrolysis time, in Fig. 8, confirms that the electrochemical mineralization at Ti/SnO₂-Pt electrodes is hindered. As expected, the correlation between COD and TOC data is not linear.

Data on the electrolysis at Ti/Pt electrodes are substantially similar to those observed at Ti/SnO₂-Pt film electrodes.

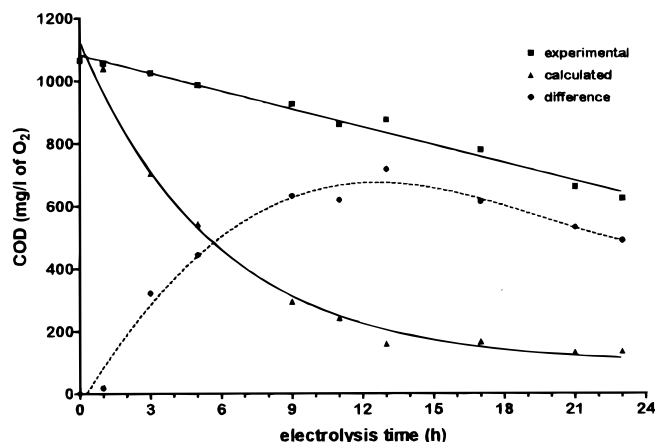


Figure 7. COD as a function of time. Ti/SnO₂-Pt at 900 A m⁻², glucose 1 g dm⁻³ in 2 N H₂SO₄.

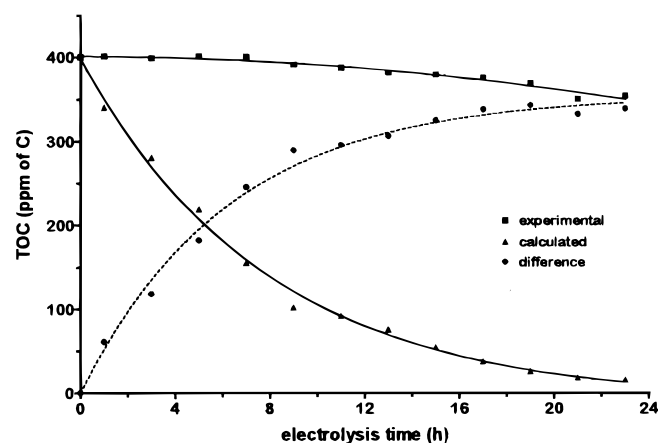


Figure 8. TOC as a function of time. Ti/SnO₂-Pt at 900 A m⁻², glucose 1 g dm⁻³ in 2 N H₂SO₄.

In Fig. 9 the densitograms of samples of solution (glucose 10 g dm⁻³ in 2 N H₂SO₄) after 12 h of electrolysis at Ti/PbO₂ (300 A m⁻²) and Ti/SnO₂-Pt (900 A m⁻²) are shown. In both cases several peaks of different height and shape are present, witnessing to the complexity of the matrix. On the basis of analytical and electrochemical data, glucaric acid can be considered as the main metabolite at the SnO₂-Pt electrode. While its reactivity is low, at this anode material, it is readily oxidized at Ti/PbO₂. Accordingly, metabolite "1", produced in a smaller amount at Ti/SnO₂-Pt, is the main metabolite at the Ti/PbO₂ electrode. On the basis of retention time and of the results of several

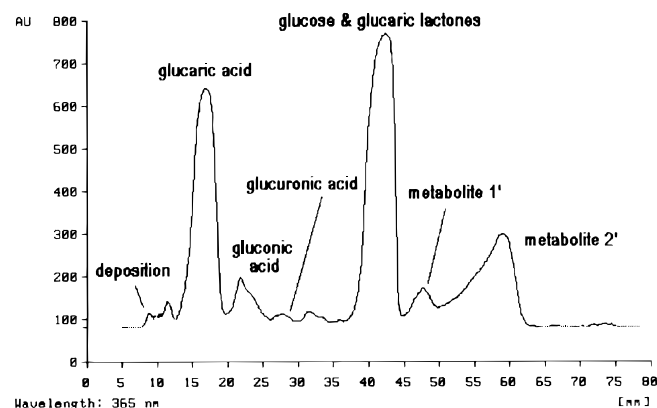
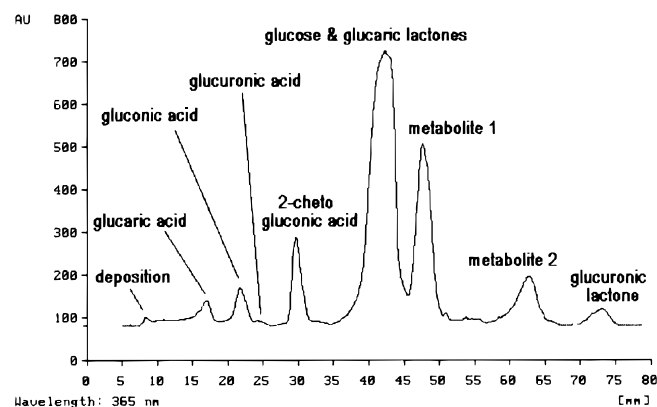


Figure 9. HPTLC densitograms of solution samples after 12 h of electrolysis at Ti/PbO₂ (300 A m⁻²) and Ti/SnO₂-Pt (900 A m⁻²).

qualitative tests, this intermediate was found to be a pentose. GC-MS experiments, carried out on HPTLC spots after trimethylsilylation of the products extracted from the chromatographic plate, confirmed this evidence, indicating that metabolite 1 is arabinose. At a migration distance of about 60 mm, both densitograms show a peak, labeled metabolite "2" at Ti/PbO₂ and "2'" at Ti/SnO₂-Pt. By GC-MS experiments, this product was identified as inositol, an organic compound which can be formed by cathodic reduction and further cyclization of the dicarboxylic derivative of glucose.

In order to confirm the satisfactory efficiency of lead dioxide electrodes for the abatement of organics under conditions more similar to those encountered in real effluents, experiments have been extended to a real effluent from the sugar industry. Due to lengthy preliminary lagoon ageing, the effluent exhibited an average COD value of 400 mg dm⁻³ of oxygen, and a TOC value of 445 mg dm⁻³ of carbon, refractory to further natural oxidative degradation. The effluent pH was 7.7 and its conductivity 3 mS/cm. Anodic mineralization experiments were carried out without addition of electrolyte to increase the latter value. An electrolysis cell consisting of two compartments separated by a Nafion membrane was used. The anode, a PbO₂-coated Ti mesh, had an area of 50 cm². A set of graphite rods was used as cathode. The solution in the cathodic compartment was 1 N sulfuric acid. The volume of the two compartments was 0.5 dm³ (12 × 12 × 3.5 cm). The effluent was continuously fed to the anodic compartment from a 10 dm³ reservoir by means of a pump at a flow rate of 0.9 dm³ min⁻¹. Under the same conditions, 1 N sulfuric acid was fed to the cathodic compartment from a 5 dm³ reservoir.

As a consequence of the low conductivity of the effluent, the initial part of the electrolysis could be carried out at a current density of only 150 A m⁻². Under these conditions the cell potential was about 12 V. The improvement of conductivity during the mineralization process allowed the current density to be increased to 230 A m⁻². Under these conditions, particularly unfavorable for achieving a low COD and with the expected low reactivity of organic components due to the previous natural degradation, an abatement of COD to 110 mg O₂ dm⁻³ in the 10 dm³ reservoir could be attained after 30 h of electrolysis.

Conclusions

Although glucose can be readily oxidized under different conditions,^{13,14} its electrochemical incineration takes place at reasonable rates only at PbO₂ electrodes. At this electrode material, the EOI value remains high in a wide range of current density, temperature, and substrate concentration.

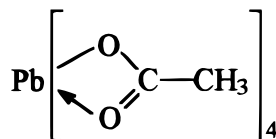
As indicated by the difference in nature of some of the intermediates at the investigated electrode materials and by the different abundance of others, the mechanism of glucose mineralization is strongly electrode-dependent.

At most electrode materials, the further oxidation of the aldaric acid intermediate seems to be the difficult step in the whole process. Once the first oxidation of the carbonylic group and of the terminal alcoholic function is accomplished, attack to secondary alcoholic functions as well as to the carboxylic one seems to be more difficult.

The faster mineralization occurring at lead dioxide electrodes is, in this sense, an exception. The formation of C-5 compounds (arabinose) may be explained assuming that the decarboxylation step is facilitated by some sort of short-range interaction between the carboxylic group and Pb(IV) sites. Some experimental results obtained in the present work support this hypothesis. At PbO₂ electrodes, the initial EOI obtained for glucose, gluconic acid, and glucaric acid indicate an increasing reactivity in the direction aldose-aldonic acid-aldaric acid. On the other hand, the concentration of glucaric acid is always low during the mineralization process. Less direct evidence can be found in the literature. Acetate, tartrate, and citrate ions are added in electrolytic baths for lead dioxide deposition to remove mechanical stress during the oxide film growth, which suggests a strong interaction between carboxylate groups and Pb(IV)¹⁵.

In aqueous acetate solution, oxidation of Pb(II) to Pb(IV), by means of chlorine, leads to lead tetraacetate instead of PbCl₄; analo-

gous carboxylate complexes are obtained in the presence of propionates, stearates, or benzoic acids. In these complexes, dodecahedral coordination is assumed, and each lead ion forms four covalent bonds and four ionic bonds with oxygen atoms in the carboxylic groups



The lower electronic density induced in the carboxylate groups, through the chemisorptive bonds at the Pb(IV), can then allow a facilitated oxidation step. This view is in substantial agreement with the interpretation of the decarboxylation process of the Kolbe reaction in aqueous media. The decrease in electron density in the carboxylate group, leading to the corresponding radical, is enhanced through the strong interaction between carboxylate and Pb(IV) sites under anodic polarization in the case of aldonic/aldaric acids at PbO₂ electrodes.

The observed formation of arabinose suggests that the complete reaction follows, the Hofer-Möst path,¹⁶⁻¹⁸ however, rather than the Kolbe one. These complex aspects of the glucose mineralization require further investigation, better focused on mineralization intermediates.

The oxidative attack to gluconic acid can take place through the C-6 primary alcoholic position or through the carboxylic group itself. In the case of glucaric acid, surface complexes involving both the carboxylic groups can be assumed, with oxidative formation of smaller molecules like oxalic and formic acid.

Although results of the present work seem to indicate that (galvanic) Pt electrodes and tin dioxide based electrodes are not particularly efficient in the electrochemical incineration of organics, further investigation is necessary on these points. As a matter of fact, carrying out the electrolysis at higher temperature seems to improve the performance of the Pt. Also, the tin dioxide based electrodes are

not particularly deeply studied at the moment, and different compositions and preparation conditions should be tested in order to complete the picture. The possibility that dissolution of the anode material can take place to some extent when using lead dioxide electrodes may be a disadvantage preventing their use in electrochemical wastewater treatment. Further research is in progress in our lab on the application of less polluting electrodes in the presence of mineralization mediators.

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