J Appl Electrochem (2010) 40:1743–1750
DOI 10.1007/s10800-010-0134-6

ORIGINAL PAPER

Adsorption layer and its characteristic to modulate the electro-oxidation runway of organic species

Nicolaos Vatistas

Received: 30 December 2009 / Accepted: 7 April 2010 / Published online: 22 April 2010

Abstract Studies of organic compounds oxidation at constant current conditions with different anodes, indicate that the oxidative action of these anodes is related to their absorption characteristic i.e. the low or high difficulty of the generated hydroxyl radicals in reaching the solution. This paper shows that the adsorption does not concern the anodic surface, but an adjacent thin layer (*adsorption layer*) of the aqueous solution. An estimation of the fraction of hydroxyl radicals that move from the adsorption layer to the adjacent reactive/diffusive layer is obtained as well as a suitable tool for comparison the result of this approach with the experimental results. This comparison shows how the adsorption layer modulates the runway of the organic species oxidation.

Keywords Anodes · Adsorption layer · Electro-oxidation · Hydroxyl radicals · Modulation · Oxidation runway

1 Introduction

Experimental results of electrochemical organic species oxidation with BDD anodes indicate that when the anode achieves a sufficiently high potential the oxidation of theses compounds occurs thanks to the generated hydroxyl radicals $HO^{\bullet}$ [1]. Indeed the high oxidative action of BDD anodes is attributed to loosely adsorbed hydroxyl radicals, i.e. to their capacity to leave the anodic surface and to enter in the aqueous solution. The low or high oxidative action of other anodic materials used in this field is also be attributed to the adsorption state of the generated radicals on their surface. The experimentally detected increase of oxidative action of the anodes RuO_2–TiO_2, IrO_2–Ta_2O_5, Pt, PbO_2, SnO_2–Sb_2O_5 and BDD was attributed to the decreasing electrode-hydroxyl radical interaction resulting in a low electrochemical activity for oxygen evolution reaction (OER) and to high chemical reactivity for organics oxidation [2]. The high effect of interaction electrode-hydroxyl radical suggests to study the adsorption process.

The term *adsorption* refers to the process by which species are accumulated on the surface of electrode and form a layer adjacent to this surface (*adsorption layer*). In the case of an electrode the adsorbed species reach this layer from the electrolyte or they are generated by electrochemical reaction. When such adsorption is due to the universal weak van der Waals interaction, a multilayer of these species is formed and it is defined *physical adsorption*, while when a stronger interaction occurs between one species and the electrode, a mono-layer is adsorbed and the process is defined *chemical adsorption*. The interaction, which concerns the adsorbed species has been considered by Gibbs [3], but its measure is not related to its exact structure.

The effect of adsorption on the electro-oxidation will be studied in this manuscript, by assuming that it occurs not on the anodic surface but into a thin adsorption layer adjacent to it. The principal propriety of the adsorption, i.e. the attraction of the species by the anodic surface, will be related to there mobility and then to their diffusion coefficient. Reaction and diffusion mechanisms of hydroxyl radicals, into this layer will be considered in order to establish how many radicals react with the organic species. Available experimental results of organic species oxidation

---

Paper dedicated to Professor Christos Comninellis' 65th birthday

N. Vatistas (✉)
Chemical Engineering Department, University of Pisa,
Via Diotisalvi, 2, 56126 Pisa, Italy
e-mail: vatistas@diccism.unipi.it; vatistas@ing.unipi.it

with PbO_2 and BDD anodes will be considered in order to ascertain if the proposed approach provides to obtain more details concerning the complex mechanisms of organic electro-oxidations.

2 Adsorption layer

The physical adsorption of species on the various electrodes is attributed to the universal van der Waals interaction between the electrode and these species. This interaction, which is due to induced dipole—induced dipole attraction is highly dependent on their distance as well as, on the specific species. In fact the interaction between a molecule and the electrode, expressed as potential energy $w(x)$, depends on such parameters and the interaction is expressed the following equation [4]:

$$w(x) = -\frac{\pi C_{e,i}\rho_e}{6}\frac{1}{x^3} \quad (1)$$

where $C_{e,i}$, is a specific constant related to the considered electrode and the molecule, ρ_e, is the number density of molecules in this anode, and x, is the distance between electrode and this molecule.

When an electrode is immersed in the electrolyte, the intrinsic chaotic motion of species, due to the temperature, has two opposite effects on the adsorption. The positive effect is that such motion allows the species i, to reach the position that optimize the attractive van der Waals interaction. The negative effect is that this motion removes the species i that have just achieved their optimum position. The forward growth rate of the adsorption r_f, is related to the attractive effect, while its backward removal rate r_b, is related to the chaotic motion effect. The stationary state of adsorption is reached when the whole growth rate ($r = r_f - r_b$), becomes zero, and this occurs when a quantity n_a, of molecules has been adsorbed forming a thin adsorbed layer of thickness δ_a.

The main characteristic of the adsorption layer is its higher order respect to the rest of this solution. This makes is easier if its high order is subject to a sharp variation. In order to estimate this variation the attractive potential of the adsorbed layer is considered [4]:

$$w = -\frac{\pi C_{e,i}\rho_e}{6}\int_{x_0}^{\infty}\frac{\rho_i(x)}{x^3}dx \quad (2)$$

where x_0, is the minimum distance electrode—adsorbed species i, while $\rho_i(x)$ concerns the number of adsorbed molecules of species i and x is the distance from the electrode.

As Eq. 2 shows when the distance reaches a specific value $x = \delta_a$, the van der Waals interaction that locates the molecules in their optimum positions, becomes lower than the chaotic motion due to the temperature that remove these species from their optimum position. The consequence is a reduction of the density $\rho_i(x)$, i.e. an additional reduction of the van der Waals interaction. The synergism of two negative effects (longer distance and lower density), suggests that when the distance reaches this specific value (δ_a), a rather sharp transition is observed, i.e. the layer that is inside this distance is ordered while outside this layer the species are subject to a chaotic motion. In the adjacent chaotic layer ($x > \delta_a$), the diffusivity assumes its normal value D_i, while into the adsorbed layer the diffusion coefficient $D_{i,a}$, is related to lower mobility of its ordered state and then a lower value of diffusivity is expected ($D_{i,a} < D_i$) [5].

A low diffusion into the adsorption layer means high residence time of species in this layer. A such higher time increases the fraction of hydroxyl radicals that is degraded into this layer and decreases the fraction of hydroxyl radicals that reaches the adjacent layer. A similar low diffusivity of the organic compounds into the adsorption layer obstruct their entering into this layer where the concentration of hydroxyl radicals is high. More details of the adsorption layer processes are required. This is the object of the following section that consider the simpler case, i.e. when the solution does not contains organic species and other trapping species of hydroxyl radicals.

3 Absence of organic and other reactive species of hydroxyl radicals

The above Eq. 2 shows that the attractive van der Waals interaction as well as the diffusion coefficient of the various species ($D_{i,a}$), decreases in the adsorption layer. In order to allow a simple mathematical treatment of the balance equation in this layer, the mean values of diffusion coefficients will be considered. The adjacent region of the solution was reached by the survival hydroxyl radicals whose reaction continue these (see Fig. 1). The thickness of the said adjacent layer δ_r, is related to the presence of such radicals and its value depends to the operating conditions. The diffusion of the hydroxyl radicals and their reaction occurs into this layer and is defined as *reactive/diffusive layer*. If the solution contains other species the flow of them from the bulk of the solution toward the reactive/diffusive layer occurs in a region that is know as *diffusive layer* which thickness δ_d, is related to the transport of these species. Anode, adsorption layer, reactive/diffusive and diffusive layers are shown schematically in Fig. 1.

If the absence of organic and other trapping species is assumed, the effect of various parameters on the generated hydroxyl radicals can be obtained by their balance into the adsorption and reactive/diffusive layers. The hydroxyl radicals are generated on the anodic surface according the following equation [6, 7]:

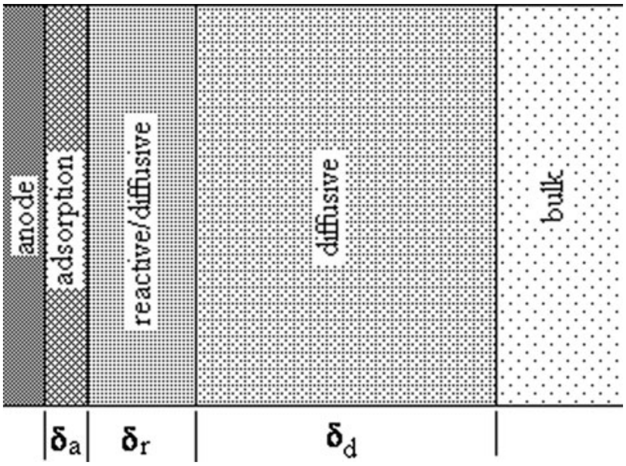

Fig. 1 Scheme of anode with the adjacent layers of the solution (not in scale)

$$H_2O \rightarrow HO^{\bullet} + H^{+} + e^{-}. \tag{3}$$

If the adsorption layer is present the generated hydroxyl radicals enter in the layer and can react with each other to produce hydrogen peroxide, as given by the following equation:

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2. \tag{4}$$

The produced hydrogen peroxide is successively oxidized to oxygen and the whole reaction is the oxygen evolution reaction. The balance of hydroxyl radical into the adsorption layer is applied by considering their consumption due to the reaction (4), and their diffusion. The equation of this balance assumes the following form [6]:

$$D_{HO^{\bullet},a}\frac{d^2C_{HO^{\bullet},a}}{dx^2} = k_{HO^{\bullet},a}C^2_{HO^{\bullet},a}; \quad 0 \le x \le \delta_a. \tag{5}$$

While a similar equation is obtained for the subsequent reactive/diffusive layer:

$$D_{HO^{\bullet}}\frac{d^2C_{HO^{\bullet},r}}{dx^2} = k_{HO^{\bullet}}C^2_{HO^{\bullet},r}; \quad \delta_a \le x \le \delta_r. \tag{6}$$

The balance equation that concern the adsorption layer assumes the following dimensionless form:

$$\frac{d^2y_a}{d\xi_a^2} = y_a^2; \quad 0 \le \xi_a \le \frac{\delta_a}{\lambda_a}. \tag{7}$$

While a formally similar equation is obtained for the successive reactive/diffusive layer:

$$\frac{d^2y_r}{d\xi_r^2} = y_r^2; \quad \frac{\delta_a}{\lambda_a} \le \xi_r \le \frac{\delta_r}{\lambda_a} \tag{8}$$

where y_a and y_r are the dimensionless concentrations of hydroxyl radicals into the adsorption and reactive/diffusive layers:

$$y_a = \frac{C_{HO^{\bullet},a}}{C_{HO^{\bullet}}(0)}, \quad y_r = \frac{C_{HO^{\bullet},r}}{C_{HO^{\bullet}}(0)}. \tag{9}$$

Two characteristic parameters were introduced having the dimension of length, the first concerning the adsorption layer λ_a, and the second the reactive/diffusive layer λ_r. Such parameters are obtained by combining the various parameters of the Eqs. 5 and 6:

$$\lambda_a = \sqrt{\frac{D_{HO^{\bullet},a}}{k_{HO^{\bullet},a}C_{HO^{\bullet}}(0)}}; \quad \lambda_r = \sqrt{\frac{D_{HO^{\bullet}}}{k_{HO^{\bullet}}C_{HO^{\bullet}}(0)}}. \tag{10}$$

The above parameters defined *characteristic lengths*, are used to define the two dimensionless distances into the two adjacent layers: $\xi_a = x/\lambda_a$, and $\xi_r = x/\lambda_r$. The value of λ_a, is a measure of survival distance of hydroxyl radicals while they moved into the adsorption layer, while the value of λ_r, is a measure of survival distance in the reactive/diffusive layer. Available values of the characteristic reactive/diffusive parameters, allow us to estimate the value of its characteristic length λ_r. If we consider a diffusion coefficient $D_{HO^{\bullet}} = 2.2 \cdot 10^{-9}\,m^2\,s^{-1}$, a rate constant $k_{HO^{\bullet}} = 5.5 \cdot 10^6\,m^3\,mol^{-1}\,s^{-1}$, and a concentration $C_{HO^{\bullet}}(0) = 0.1\,mol\,m^{-3}$, this length is $\lambda_r = 32$ nm. Moreover if a value of 0.1 is assumed for the ratio λ_a/λ_r, the characteristic length of adsorption layer is $\lambda_a = 3.2$ nm $= 32$ Å.

The dimensionless ratio δ_a/λ_a relates the thickness of the adsorption layer to the characteristic length of this layer. If the thickness of adsorption layer increases respect to its characteristic length the probability of the hydroxyl radicals to transit this layer and achieve the adjacent reactive/diffusive layer decrease, i.e. an increase of this ratio decreases the fraction of the hydroxyl radicals that achieve the adjacent reactive/diffusive layer.

The previously obtained dimensionless differential equations (7) and (8), that concern the adsorption and reactive/diffusion layers, thanks to the adopted dimensionless variables are reduced to the following single equation:

$$\frac{d^2y}{d\xi^2} = y^2. \tag{11}$$

After its dissolution it is necessary to consider the two different characteristic lengths λ_a and λ_r, in the two consecutive adsorption and reactive/diffusive layers. In the Appendix is reported the method that allow to obtain the analytic solution of the Eq. 11. Its form is:

$$y = \frac{1}{\left(\sqrt{\frac{8}{3}}\xi + 1\right)^2}. \tag{12}$$

The derivative of this concentration that is related to the hydroxyl radical flow into the adsorption and reactive/diffusive layers is given by the following relationship:

$$\frac{dy}{d\xi} = -\frac{\sqrt{\frac{2}{3}\frac{\delta_a}{\lambda_a}}}{\left(\sqrt{\frac{8}{3}\frac{\delta_a}{\lambda_a}}\,\xi + 1\right)^3}. \tag{13}$$

The ratio η_a, of hydroxyl radical flow that reaches the reactive/diffusive layer to the generated radicals on the anodic surface, represents the efficiency of the considered anode to produce free hydroxyl radicals. i.e. the fraction of radicals that reach the reactive/diffusive layer. Its value is related to the previously introduced dimensionless ratio (δ_a/λ_a), and this relationship assumes the following form:

$$\eta_a = \frac{1}{\left(\sqrt{\frac{8}{3}\frac{\delta_a}{\lambda_a}} + 1\right)^3}. \tag{14}$$

The diagram in Fig. 2. indicates that when the dimensionless ratio is low $\delta_a/\lambda_a < 0.01$, the value of η_a is high, i.e. the effect of the adsorption layer is low and then only a small fraction of the generated hydroxyl radicals is degradated into this layer. In the opposite conditions of an adsorption layer that is higher than the characteristic length $\delta_a/\lambda_a > 1$, the value of η_a is low, i.e. a low fraction of these radicals reaches the reactive/diffusive layer. Finally the value of η_a changes significantly when the parameter δ_a/λ_a is in the interval 0.01–1.

As the Eq. 2 indicates the effect of van der Waals interaction that generates the adsorption layer is highly dependent from the distance and the adsorption layer is expected to be thin. To illustrate this Fig. 3. shown an adsorption layer whose thickness assumes values between 1 and 10 Å. Within this thickness range, the value of η_a changes significantly when the ratio λ_a/λ_r assumes values between 0.05 and 0.1. Assuming that the variation is due to the diffusivity into the adsorption layer, its value is respectively 0.0025 and 0.01 times lower than the diffusivity into the solution.

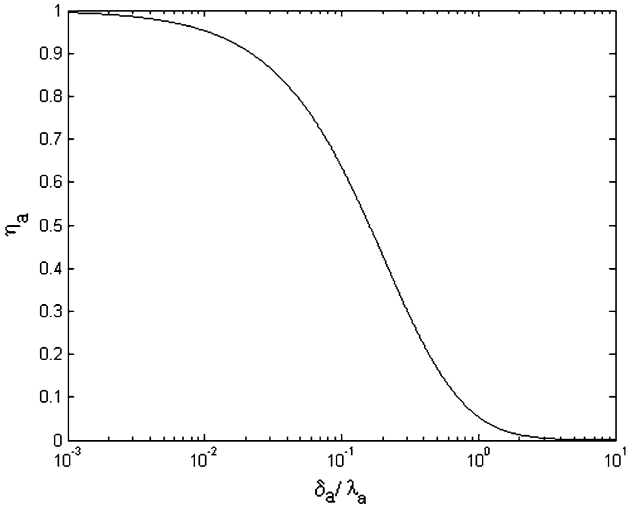

Fig. 2 Free fraction η_a versus dimensionless ratio δ_a/λ_a

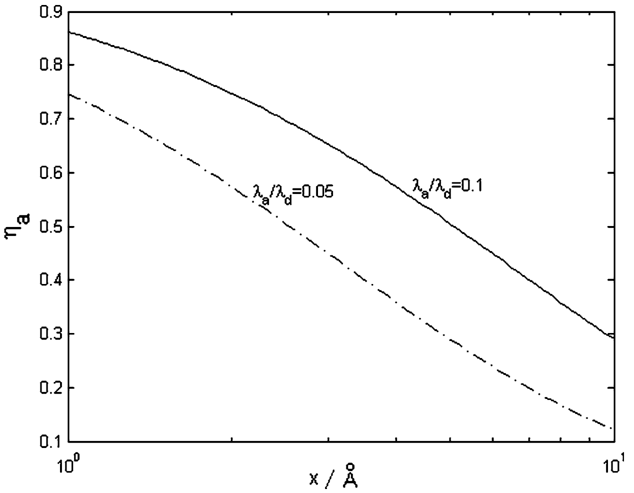

Fig. 3 Free fraction η_r versus adsorption layer thickness δ_a, at two different values of parameter $\lambda_a/\lambda_r = 0.025$, 0.1, and constant characteristic length of reactive reactive/diffusive layer ($\lambda_r = 32$ nm)

The variation of the dimensionless concentration of hydroxyl radicals versus distance from the anodic surface is estimated by means of the Eq. 12 and this variation is reported in Fig. 4. for two different cases: when the adsorption layer is absent ($\delta_a/\lambda_a = 0.0$) and when the adsorption layer is present ($\delta_a/\lambda_a = 0.2$). The comparison of the concentrations obtained in the two cases clearly indicates the high effect of adsorption layer on the concentration of hydroxyl radicals. The same figure also shown a sharp variation of the concentration at the point of the transition from the adsorption to the reactive/diffusive

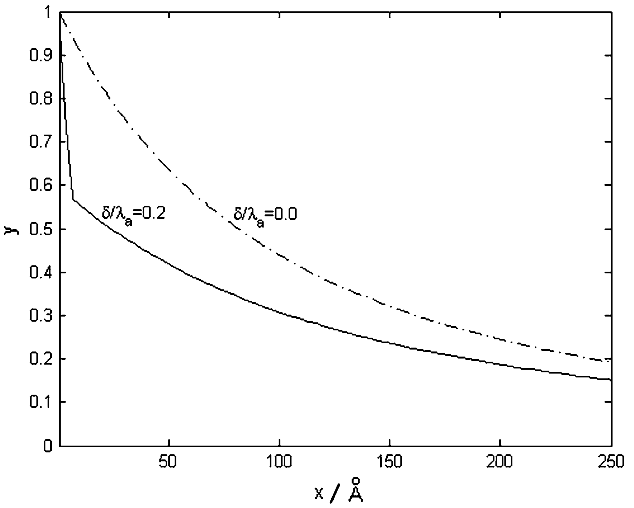

Fig. 4 Dimensionless concentration of hydroxyl radicals versus distance from the anodic surface at two different conditions, without adsorption layer ($\delta_a/\lambda_a = 0.0$) and with adsorption layer ($\delta_a/\lambda_a = 0.2$). Characteristic lengths ratio $\lambda_a/\lambda_r = 0.1$

layer. This sharp variation is due to the continuity of hydroxyl radicals flow at this point ($x = \delta_a$), and to the completely different values of diffusivity at the two adjacent layers ($D_{\mathrm{HO}^\bullet,a} = 0.01 D_{\mathrm{HO}^\bullet}$).

4 Hydroxyl radicals and presence of organic species

When organic species are contained in the solution they reach the anodic region where are subject to oxidation by the hydroxyl radicals. Such oxidation is represented by the following form:

$$R + z\mathrm{HO}^\bullet \rightarrow \text{Oxidation products.} \tag{15}$$

Reaction (15), is consists of several steps. In this paper is assumed that the first step of hydroxyl radicals trapping by the organic species, is very high. The second assumption is that the trapped hydroxyl radicals oxidize efficiently the organic species, however, the rate of this oxidation is not necessarily very high. This second assumption assures that the trapped hydroxyl radicals complete the oxidation even into the bulk of the solution. Despite the previous assumptions, the complexity of the mechanisms that occur into the adsorption and reactive/diffusive layers imposes, to consider a qualitative analysis in order to points out the essential dimensionless parameters that relate their values to the efficiency of electro-oxidation.

The organic species from the bulk of the solution reach the reactive/diffusive layer, where start their oxidation by the hydroxyl radicals that arrive from adsorption layer. The following conditions exclude that the organic species reach in the adsorption layer: (i) The low concentration of organic compounds in the electrochemical wastewater treatments field, that means a low value of organic species flow toward the reactive/diffusive layer. (ii) The oxidation of these organic species in the reactive/diffusive layer that reduce their concentration in this layer and (iii) The low diffusivity of the adsorption layer that obstruct the entrance of said species into the adsorption layer.

The flow of the hydroxyl radicals that enter into the reactive/diffusive layer from the adsorption layer $\dot{m}_a$, and the organic species flow coming from the bulk of the solution $\dot{m}_b$ are the two reactive species of oxidation and their ratio is an essential parameter. This ratio is related to other operating parameters by the following equation:

$$\frac{\dot{m}_b}{\dot{m}_a} = \frac{k_m \left(C_{R,b} - C_{R,r}\right)}{\frac{i_{ap}}{zF}\eta_a} \tag{16}$$

where k_m is the mass transfer coefficient referring to the diffusion layer, i_{ap} is the applied current density, $C_{R,b}$ is the concentration of organic species in the bulk of the solution ($x > \delta_a + \delta_r + \delta_d$), and $C_{R,r}$ the concentration of these species at the point $x = \delta_a + \delta_r$ (see Fig. 1).

4.1 Anode without adsorption layer

If the adsorption layer is absent, all the generated hydroxyl radicals reach the reactive/diffusive layer ($\eta_a = 1$), and two regimes can be observed. The first regime occurs when a sufficiently high concentration of the organic species in the bulk of the solution assures an enough flow of organic species toward the reactive/diffusive layer. In this regime all the hydroxyl radicals that reach this layer are used and then an equivalent flow of organic species is oxidized:

$$\frac{\dot{m}_b}{\dot{m}_a} = \eta_u (= 1) \tag{17}$$

where η_u is the utilization of the hydroxyl radicals into the reactive/diffusive layer, is this regime it achieves its maximum value. Moreover this parameter represents also the current efficiency of the electro-oxidation.

The second regime occurs when the concentration of organic species in the bulk is low. In this case the not enough flow of the organic species imposes a partial use of the hydroxyl radicals that reach the reactive/diffusive layer ($\eta_u < 1$). In this regime the concentration $C_{R,r}$ becomes more smaller than $C_{R,b}$, and then ($C_{R,b} - C_{R,r}$)≈ $C_{R,b}$. Consequently the ratio of the two reactive flows becomes:

$$\frac{\dot{m}_b}{\dot{m}_a} = \eta_u \left(= \frac{k_m C_{R,b}}{\frac{i_{ap}}{zF}} \right). \tag{18}$$

The partial use of the generated hydroxyl radicals ($0 < \eta_u < 1$), also in this regime represents the current efficiency.

If an electro-oxidation is performed at constant applied current, with an anode absent of adsorption layer and with an enough concentration of organic species, at its starting it operates in the first regime and then the current efficiency assumes its maximum value. In this regime the concentration of the organic compounds decrease linearly with time. When the concentration of organic species is reduced to a specific value the limitation of organic species flow toward the anode ($\dot{m}_b$) imposes a decrease of current efficiency, proportional to the concentration into the solution. In this regime an exponential decrease of organic species concentration with time is observed.

4.2 Anode with adsorption layer

The presence of adsorption layer makes the oxidation of the organic species more complex and less efficient. A high concentration of organic species into the solution allows an easy flow of organic species into the reactive/diffusive layer. The quantity of the hydroxyl radicals that reach this layer is lower than the previous case because a portion ($1-\eta_a$), of the generated radicals, is consumed into the adsorption layer.

Their lower flow and their consumption by the organic species, decrease the concentration of these radicals into the reactive/diffusive layer. This decrease in concentration has a positive effect: an increased flow of these radicals are subtracted from the adsorption layer. The final effect is that an increase of the organic species concentration in the bulk increase the capacity of the reactive/diffusive layer to subtract a greater fraction of hydroxyl radicals (η_a), from the adsorption layer. In this case this fraction is related to the previously defined ratio δ_a/λ_a and to organic species concentration in the bulk of the solution $C_{R,b}$:

$$\eta_a = f\left(\frac{\delta_a}{\lambda_a}, C_{R,b}\right). \qquad (19)$$

If the concentration of the organic species achieves low values in the solution, as at the end of a treatment, it is easy to show that the flow of hydroxyl radicals that reach the reactive/diffusive layer $\dot{m}_a$, proves to be higher than the equivalent flow of organic species $\dot{m}_b$. At this condition the electro-oxidation is controlled by the mass transfer and then the current efficiency can be estimated by the Eq. 18. In other words, if the assumption of the complete oxidative action of the trapped hydroxyl radicals is valid, the current efficiency is not related to the presence or absence of adsorption layer

5 Comparison of experimental and theoretical results

The condition obtained on the current efficiency at the end of a treatment suggests to consider the ratio of the experimental obtained values of current efficiency with various anodes to the estimated efficiency by the Eqs. 17 and 18. This efficiency ratio was introduced and defined as *normalized current efficiency* ϕ. Moreover electro-oxidation tests of 4-chlorophenol at constant values of current density were performed using PbO_2 and BDD anodes and the values of the normalized current efficiency at different operating conditions were reported [8].

Values of normalized current efficiency ϕ versus conversion X is reported in Fig. 5. The obtained values of ϕ for BDD anode is close to unity, i.e. the behavior of such anode is close to an anode without adsorption layer. Moreover this result confirms that the assumption of the complete oxidative efficiency of trapped hydroxyl radicals is valid.

The results of PbO_2 anode show a different behavior, the value of ϕ is distant from unity and its value decreases with the decreasing of organics species concentration into the solution. In particular when the concentration achieves low values, ϕ is very distance from unity while, as previously indicated, a value close to this value is expected. In order to see what happen with the PbO_2 and not with BDD anodes is mandatory to focus the attention on the principal difference of the reactive/diffusive layer in the two cases. This layer operates with a high concentration of hydroxyl radicals in the case of BDD and with a low concentration in the case of PbO_2 anode (Fig. 4, offers a clear indication of this difference). More details of the effect of the hydroxyl radicals concentration on the oxidation of organic species are required.

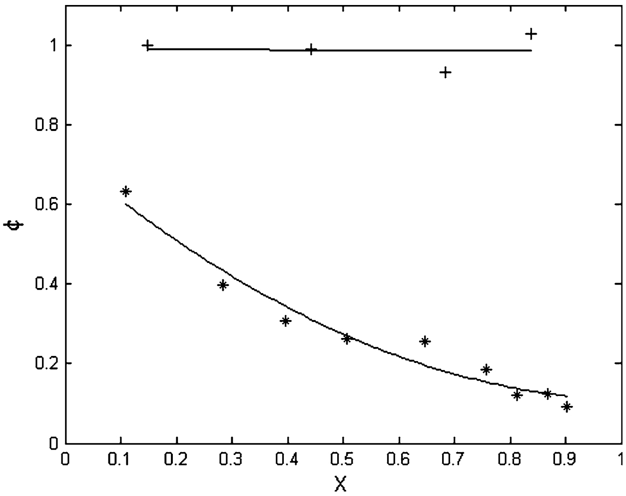

Fig. 5 Normalized current efficiency versus conversion of organic species. [4-chlorophenoc] = 2,000 ppm, i_{ap} = 30 mA/cm^2, +BDD anode, * PbO_2 anode

Experimental electro-oxidation tests of m-cresol with BDD and PbO_2 anodes operating at similar conditions indicate a different values of current efficiency and substantially different concentrations of the produced intermediate species, as well as, different products (polymeric compounds with PbO_2 but not with BDD) [9]. The obtained different intermediates indicates that different oxidation runways occurs with the two types of anodes and this event can be attributed to the different hydroxyl radicals concentrations in the reactive/diffusive layer. Also in the field of electro-oxidation with BDD is known that if a low current density is applied a polymeric phase cover its surface, while the same anode at higher current density oxidize completely the same species [1]. This case more clearly indicates that the different electro-oxidation runways are not due to the anode but to the different values of hydroxyl radicals concentration in the reactive/diffusive layer.

The high activity of the hydroxyl radicals can be modulated by its concentration and then an organic species can be by oxidized by different runways. The characteristic of high activity of hydroxyl radicals is combined with the characteristic of organic species, to be oxidized by a variety of runways. In other words the concentration of hydroxyl radicals becomes the parameter that modulate the runway of the oxidation. This consideration suggests that the initial assumptions of the efficient oxidative action of the trapped hydroxyl radicals is valid by using specific anodes and operating conditions.

6 Conclusions

This paper starts by the generally assumed relationship between efficient action of anodic material used in the field of organic species electro-oxidation and capacity of these materials to adsorb the generated hydroxyl radicals. The universal and attractive var der Waals interaction has been consider in order to obtain enough details on the adsorption layer and to detect its characteristic dimensionless parameters. The fundamental effect of this attractive van der Waals action is the reduction of diffusion coefficient into the adsorption. This reduced value obstructs both hydroxyl radicals toward the reactive/diffusive layer and organic species toward the adsorption layer.

The hydroxyl radicals balance into the adsorption and reactive/diffusive layers has been applied and the fraction of the generated hydroxyl radicals that transit the adsorption layer and achieve the reactive/diffusive layer has been related to the dimensionless parameters of the adsorption layer. The higher effect of adsorption layer, i.e. its capacity to reduce the hydroxyl radicals concentration in the reactive/diffusive layer has been calculated. The effect of organic species flow toward the anode has considered and a previously introduced notion of *normalized current efficiency* has been considered in order to compare the results of the proposed approach to the available experimental results.

The convergence between experimental and theoretical results of the proposed approach in the case of BDD and the divergence in the case of PbO_2 anodes were used to point out that the concentration of hydroxyl radicals into the reactive/diffusive layer has high effect on the oxidation. The elaboration of experimental and theoretical result points out that the concentration of radicals is the modulating parameter of the organic species oxidation runways.

This manuscript make explicit two events that have high effects in the field of the electro-oxidation of organic species, the decrease of the diffusivity in the adsorption layer and the modulating effect of hydroxyl radicals concentration. The adopted approach that is funded on these events offers new tools that can be applied in other electrochemical reactions in order to obtain more details on the mechanisms that catalyse or inhibit the whole electrochemical reaction. Moreover, by considering that the adsorption layer is funded on the universal van der Waals action, this approach can be also applied in many other heterogeneous reactions.

Appendix

The differential equations is of second order:

$$\frac{d^2y}{d\xi^2} = y^2 \tag{20}$$

While the boundary conditions of this equation are:

$$\frac{dy}{d\xi}(\infty) = 0, \quad y(0) = 1 \tag{21}$$

The following new variable $\phi = \phi[y(\xi)]$, is introduced:

$$\phi = \frac{dy}{d\xi} \tag{22}$$

This new variable is elaborated in the following way:

$$\frac{d\phi}{d\xi} = \frac{d\phi}{dy}\frac{dy}{d\xi} = \phi\frac{d\phi}{dy} = \frac{d^2y}{d\xi^2}. \tag{23}$$

Using the obtained relationship in the second order differential equation it is reduced to a first order equation that is separable:

$$\phi d\phi = y^2 dy. \tag{24}$$

The integral of this equation is estimated by assuming as initial values a generic value of y at which correspond a generic value of ϕ, while as final values are zero for both variables. In fact when $\xi \to \infty$ both variables assumes as value zero:

$$\int_{\phi}^{0} \phi d\phi = \int_{y}^{0} y^2 dy \tag{25}$$

And from the solution of this integral the following equation is obtained:

$$\phi^2 = \frac{2}{3}y^3 \tag{26}$$

The new variable ϕ is substituted by $dy/d\xi$:

$$\frac{dy}{d\xi} = \pm\sqrt{\frac{2}{3}}\sqrt{y^3}. \tag{27}$$

And the following integral equation is obtained by considering the initial point (0, 1) and a generic point (ξ, y):

$$\int_{1}^{y} \frac{dy}{\sqrt{y^3}} = \pm\sqrt{\frac{2}{3}}\int_{0}^{\xi} d\xi \tag{28}$$

The solution of this integral is:

$$\frac{1}{\sqrt{y}} = \mp\sqrt{\frac{8}{3}}\xi + 1. \tag{29}$$

And the obtained equation relates the dimensionless concentration y, to dimensionless distance ξ:

$$y = \frac{1}{\left(\mp\sqrt{\frac{8}{3}}\xi + 1\right)^2}. \tag{30}$$

The obtained concentration versus dimensionless distance must be constantly decreasing with the dimensionless distance and then the sign plus can be accepted.

$$y = \frac{1}{\left(\sqrt{\frac{8}{3}}\xi + 1\right)^2}. \tag{31}$$

At the end of adsorption layer $\xi = \delta_a/\lambda_a$, this dimensionless concentration assumes the following value:

$$y(1) = \frac{1}{\left(\sqrt{\frac{8}{3}\frac{\delta_a}{\lambda_a}} + 1\right)^2}. \tag{32}$$

The derivative of this concentration that is proportional to the hydroxyl radical flow is given by the following relationship:

$$\frac{dy}{d\xi} = -\frac{\sqrt{\frac{2}{3}\frac{\delta_a}{\lambda_a}}}{\left(\sqrt{\frac{8}{3}\frac{\delta_a}{\lambda_a}}\,\xi + 1\right)^3}. \tag{33}$$

The ratio of hydroxyl radical flow that reaches the diffusion layer respect to the produced radicals is indicated as efficiency of the considered anode to produce free hydroxyl radicals layer and its value is given by the following relationship:

$$\eta_a = \frac{1}{\left(\sqrt{\frac{8}{3}\frac{\delta_a}{\lambda_a}} + 1\right)^3} \tag{34}$$

References

1. Iniesta J, Michaud PA, Panizza M, Cerisola G, Aldaz A, Comninellis Ch (2001) Electrochemical oxidation of phenol at boron-doped diamond electrode. Electrochim Acta 46:3573
2. Kapalka A, Fóti G, Comninellis Ch (2010) In: Comninellis Ch, Chen G (eds) Electrochemistry for the environment. Springer, New York
3. Gibbs JW (1928) Collected works, vol 1. Longmans and London, New York
4. Israelachvili JN (1992) Intermolecular and surface forces. Academic Press, London
5. Miret-Artés S, Pollak E (2005) Thermodynamics of activated surface diffusion. J Phys 17:S4133
6. Kapalka A, Fóti G, Comninellis Ch (2009) The importance of electrode material in environmental electrochemistry: formation and reactivity of free hydroxyl radicals on boron-doped diamond electrodes. Electrochim Acta 54:2018
7. Enache TA, Chiorcea-Paquim AM, Fatibello-Filho O, Oliveira-Brett AM (2009) Hydroxyl radicals electrochemically generated in situ on a boron-doped diamond electrode. Electrochem Commun 11:1342
8. Gherardini L, Michaud PA, Panizza M, Comninellis Ch, Vatistas N (2001) Electrochemical oxidation of 4-chlorophenol for wastewater treatment. Definition of normalized current efficiency. J Electrochem Soc 148:D78
9. Flox C, Arias C, Brillas E, Savall A, Groenen-Serrano K (2009) Electrochemical incineration of cresols: a comparative study between PbO_2 and boron-doped diamond anodes. Chemosphere 74:1340