Electrochemical conversion/combustion of a model organic pollutant on BDD anode: Role of sp^3/sp^2 ratio

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Abstract

In this work, it is presented critical evidence about the influence of sp^3/sp^2 ratio on the performance of electrochemical oxidation (combustion or conversion) of Rhodamine B (RhB), used as a model organic pollutant. Results demonstrate that the higher the content in diamond-carbon, the greater are the TOC and COD decay rates and hence the oxidation of organic to CO_2. The evidence of chromatographic analysis also indicates that the oxidation carried out by the diamonds with lower content of sp^3-carbon is softer, favoring electrochemical conversion of RhB instead of mineralization. This degradation pathway is followed because higher graphite content on BDD anode leads to a higher direct electrochemical activity. These results are of a paramount significance for the choice of electrodes that could guarantee high efficiencies in wastewater remediation processes; because they clearly indicate that the sp^3-sp^2 carbon ratio should be kept as higher as possible in order to deplete completely pollutants and intermediates from the waste.

Keywords: diamond electrode; conversion; combustion; organic matter, hydroxyl radicals, active and non-active anodes.

1. Introduction

In the last three decades, BDD anode has been defined as non-active electrode, since it is expected that it does not provide any catalytically active site for the adsorption of reactants and/or products in aqueous media [1, 2]. Hydroxyl radical (BDD(•OH)) formed from water discharge on its surface from reaction (physically adsorbed on the anode surface): $H_2O \rightarrow {}^{\bullet}OH + e^- + H^+$, is then considered the responsible species for the electrochemical combustion of organic pollutants, although slower reactions with other reactive oxygen species (H_2O_2 and O_3) and electrogenerated oxidants (active chlorine, peroxodisulphate, peroxodicarbonate or peroxodiphosphate) are also feasible [3-6].

Many research groups have demonstrated that BDD anodes allow complete mineralization up to near 100% of current efficiency of a large number of organic pollutants [4-6]. Unfortunately, most of these studies have been focused on the study of the feasibility of the use of this technology to treat different types of pollutants and on the selection of the experimental conditions to improve the performance of this technique [3-6].

Nevertheless, some authors have questioned the non-active nature of BDD material as well as the reactivity of hydroxyl radicals [7, 8] because some results have demonstrated the occurrence of partial oxidation or complete mineralization of organic pollutants when BDD is used as anode. In this point, it seems reasonable to think that the electrochemical process can be greatly affected by the characteristic of the BDD electrodes used. Therefore, few works have showed that the conductive layer characteristics (sp^3/sp^2 ratio, boron content, BDD layer-thickness) and the substrate

properties (resistivity and roughness of the surface) have an important influence in the bulk electrolysis results [9-11].

The most relevant result supposes that the electrooxidation mechanism is strongly influenced by the BDD characteristics; particularly the ratio diamond/graphite carbon [11]. High graphite content favors direct oxidation of the pollutant on the electrode surface and it leads to the formation of many intermediates. On contrary, high diamond content seems to favor the complete oxidation of the organic to CO_2, thanks to the contribution of the oxidants (hydroxyl radicals and electrogenerated reagents) present in a region close to the electrode surface. However, these assumptions were not completely verified because no quantification of intermediates was performed as well as no complete mineralization was attained, for enrofloxacin oxidation. Also, a limited range of the sp^3/sp^2 ratio was considered (ranging from 45 to 105).

Thus, the goal of this work has been to present critical evidence about the influence of sp^3/sp^2 ratio on the performance of electrochemical oxidation (EO) of a model organic pollutant, RhB. To do this, it has been used BDD samples by one of the more important diamond-electrodes manufacturers with different sp^3/sp^2 ratio, ranging from 165 to 329. Results obtained will help to understand the electrocatalytic properties of BDD in the oxidation of a model pollutant and to elucidate the mechanism involved (electrochemical combustion or conversion).

2. Experimental

2.1. Chemicals

Chemical reagents used in this study were of high purity. RhB solutions with concentration of 2.09×10^{-4} M, for each experiment, were prepared by using Na_2SO_4 as supporting electrolyte (using Milli-Q water).

2.2. Analytical procedures

Color removal was monitored by UV-visible technique using a UV-1603 spectrophotometer Model Shimadizu, at a wavelength of 550 nm. Chemical oxygen demand (COD) was performed by using pre-dosage vials with 2 mL of sample. Samples of 10 mL were collected to determine total organic carbon (TOC) content, using a TOC analysator Multi N/C and the results were obtained through the Analytikjena program. Electrolysis samples before and after the EO of RhB at different diamond anodes were collected and analyzed by HPLC in Agilent 1100 HPLC (Two columns were used (aromatics and aliphatic acids) to determine the intermediates generated). Also, few samples of anolyte were extracted into non-aqueous medium and were subjected to GC-MS analysis using GC-FOCUS and MS-ISQ Thermo Scientific to identify the intermediates (column VF5 ms with a composition of 5% de fenil-arylene and 95% de dimetilpolisiloxane. Program: 40ºC–5 min; 12°C/min–100ºC; 10ºC/min–200ºC and 10ºC/min–270ºC–5 min. Injector: 220ºC. Mode: Splitless. Gas flow: 0.8 mL/min. Transfer line: 270ºC; ions source temperature: 220ºC, Mass range: 40-500 m/z).

2.3. Electrochemical cell and bulk electrolysis

Bulk oxidations were carried out in an undivided electrochemical cell by using different BDD anodes (provided by Adamant Technologies (Neuchatel, Switzerland)

and synthesized by the hot filament chemical vapor deposition technique (HF CVD) monocrystalline *p*-type Si substrate (thickness 2 mm, resistivity 100 mΩcm), diamond coating of 2-3 μm, boron concentration 500 ppm, 78 cm^2 of geometrical area and with distinct sp^3/sp^2 ratio (estimated by Raman spectrometry): BDD_1 = 165, BDD_2 = 176, BDD_3 = 206, BDD_4 = 220, BDD_5 = 262 and BDD_6 = 329. Stainless steel was used as cathode. EO experiments of RhB solutions (1 L) were performed under galvanostatic conditions using a power supply. Experiments were performed at 25°C by applying a current density of 97 mA cm^{-2}. Each one of the experiments was stopped when a value of zero was attained at TOC measurements. Analysis of UV-visible, TOC and HPLC were performed for all samples in order to understand the influence of sp^3/sp^2 ratio on the EO performance (the trueness of the results was evaluated by three independent analyses).

3. Results and discussion

Figure 1 shows the changes in absorbance, TOC and COD, as a function of electric charge passed (Q), during galvanostatic electrolysis of RhB solution (1 L) using different BDD anodes by applying 97 mA cm^{-2} at 25°C. It can be observed that all parameters decrease with the current charge passed in a similar way for all essays performed. For all type of BDD anodes, color decayed continuously until it disappeared after about 25 Ah dm^{-3}, leading to complete discoloration; independent on the sp^3/sp^2 ratio (Fig. 1a). Conversely, discoloration rate seems depends on sp^3/sp^2 ratio, being significant at BDD_6. The absorbance changes were reasonably rapid, indicating that during the first treatment stages there are mechanisms involving dye oxidation to other more simple organics. Oxidation of this complex molecule can

result in formation of many intermediates by chromophore group cleavage by hydroxyl radicals attack prior to production of aliphatic carboxylic acids and CO_2 [4].

On the other hand, TOC results reveal that complete elimination of organic matter is achieved at all BDD anodes. However, highest removal rate is achieved at BDD_6 ($sp^3/sp^2 = 329$), see Fig. 1b, than the rate observed at BDD_1 with lower sp^3/sp^2 ratio. In fact, TOC was completely removed after passing 44 Ah dm^{-3} with BDD_6, while BDD_1 needed 74 Ah dm^{-3} to complete the elimination of TOC. Despite the complete TOC decay seems to indicate that BDD anodic oxidation is a good choice for the removal of this complex pollutant, and it depends on diamond/graphite relation; differences between the results obtained in the electrolysis with the different diamonds are more evident in terms of the COD than in TOC changes. This can be observed in Figure 1c where BDD_6 with high diamond content leads to fast rate and complete organic removal, while diamond with high graphite content favors lower rate degradation. Based on these results, we can suggest that the EO of RhB leads to CO_2 when a diamond anode with high diamond content was used, favoring the electrochemical combustion pathway. It is due to the contribution of the oxidants ($^{\bullet}OH$ and electrogenerated reagents) present on the anode surface and the reaction cage [1, 11]. Conversely, high graphite content favors electrochemical conversion of the pollutant, producing many intermediates. These figures are in convergence with the assumptions suggested by Guinea et al. [11] for the oxidation of enrofloxacin.

Although these affirmations seem feasible, TOC and COD removals are not enough information to confirm these approaches; therefore, qualitative/quantitative analyses would be required to verify these hypotheses. Then, to address these questions, we analyzed the generation of by-products, in terms of chromatographic area of each one

of signals obtained (HPLC) and identification of the intermediates (GC/MS), during the EO of RhB at BDD_6 and BDD_1. Fig. 2 and 3 compare the number of intermediates produced (aromatics and aliphatic acids), as a function of chromatographic area, during EO of RhB by using high diamond (sp^3) and high graphite (sp^2) anodes.

From these results, it is apparent that more aromatic intermediates are formed at BDD_6 (see Fig. 2a), while a minor number of them are produced when BDD_1 was used (Fig. 2b). However, an important observation is the significant chromatographic area achieved by intermediates produced by BDD_1 (Fig. 2b), indicating that high concentration of N-ethyl-N-ethylrhodamine (~27000 units) is attained after 10 min of electrolysis, and it decays slower until 180 min. Other sub-products are produced (intermediates identified as isomer of phthalic acid, benzoic and phthalic acids) but with minor areas. On contrary, BDD_6 produces a large number of by-products (Fig. 2a) including N-ethyl-N-ethylrhodamine, but these intermediates are quickly degraded. This fact can be explained by the effective attack of $^{\bullet}OH$ to N-terminated groups of RhB and to the nature of the $^{\bullet}OH$ produced at different non-active anodes, as already proposed by Bejan and co-workers [8].

Restricting now our analysis to the number of aliphatic acids produced (Figure 3), a lower amount of intermediates (oxalic, formic, acetic and α- hidroxyglutaric acids plus I_2), with low-units of chromatographic area, is produced on BDD_6, being quasi completely oxidized after 60 min of electrolysis (Figure 3a). For the case of BDD_1, a large number of aliphatic acids are generated (malonic, oxalic, formic, succinic, acetic, 2-hydroxypentanedioic, adipic, α- hidroxyglutaric acids and I_1) with a relevant predominance of adipic acid, even after 60 min of electrooxidation (Fig. 3b).

The evidence of chromatographic analysis suggests that the oxidation carried out by the diamond with lower content of sp^3-carbon is softer, favoring electrochemical conversion of RhB. This degradation pathway is followed because higher graphite content on BDD anode leads to a higher direct electrochemical activity [11] that is related to better adsorption of reactants on sp^2 carbon. On the contrary, the high level of electrochemical mineralization obtained by higher diamond content in BDD_6 is caused by the oxidants generated from water electrolysis and supporting electrolyte. Even when the number of aromatic intermediates is formed at this BDD anode, these are oxidized to CO_2. In fact, inorganic carbon measurements showed clearly that higher concentrations of CO_2 are produced at BDD_6 after 15 min of electrolysis (≈4.9 mg dm^{-3}), while at BDD_1, lower concentrations were detected (1.7 mg dm^{-3}).

4. Conclusions

Theoretically, based on the existing literature [2], diamond anode is predominantly considered as an ideal non-active anode. However, our results evidenced that the non-active nature of diamond electrode is strongly influenced by the ratio diamond(sp^3)/graphite(sp^2) carbon content. Higher content in diamond-carbon the greater the TOC and COD decays in the bulk electrolysis by electrochemical combustion (oxidation of organic to CO_2). This may be confirmed by HPLC and GC/MS analyses performed for the intermediates formed. Conversely, high graphite content favors the electrochemical conversion (formation of many intermediates) due to the adsorption of reactants on sp^2 carbon. The sp^2 carbon species can be considered as the primary pathway for the charge transfer process (direct oxidation) [12]. All by-products identified are in accordance with [13].

We cannot be certain about the reactivity of •OH [8], but it could be related with the stability of N-ethyl-N-ethylrhodamine formed at both BDD anodes. Further experiments with BDD_6 and BDD_1 are in progress to clarify this BDD property.

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Figures captions

Figure 1. Effect of the sp^3/sp^2 ratio of the BDD anodes on the absorbance (a), TOC (b) and COD (c) removal, as a function of Q, during electrolysis of RhB solutions.

Figure 2. Chromatographic areas of aromatic intermediates produced, as a function of time, during RhB electrooxidation using BDD_6 (a) and BDD_1 (b). I_1, no identified intermediate.

Figure 3. Influence of sp^3/sp^2 ratio on the production of aliphatic acids, as a function of chromatographic areas and time, during RhB electrooxidation using BDD_6 (a) and BDD_1 (b). I_1 and I_2, no identified intermediates.

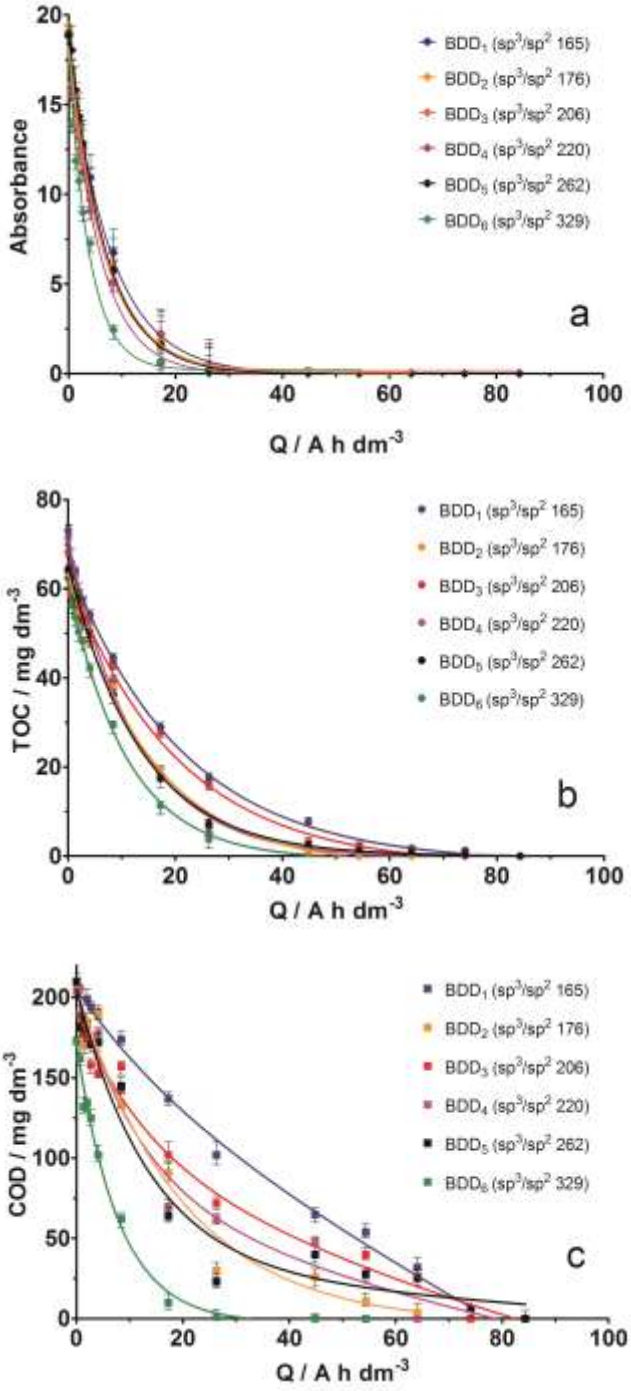
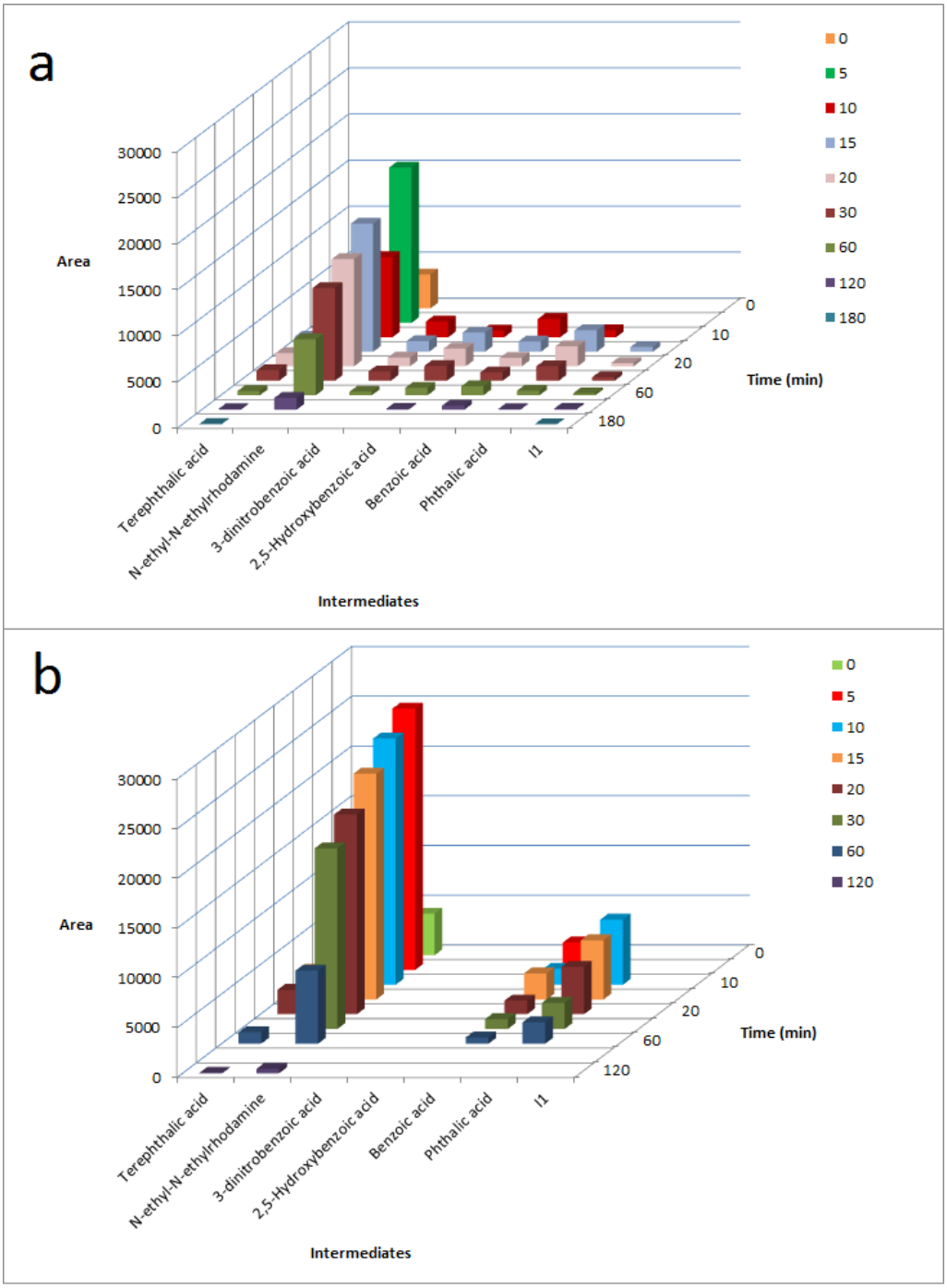

Absorbance
Q / A h dm-3
BDD1 (sp3/sp2 165)
BDD2 (sp3/sp2 176)
BDD3 (sp3/sp2 206)
BDD4 (sp3/sp2 220)
BDD5 (sp3/sp2 262)
BDD6 (sp3/sp2 329)
a
TOC / mg dm-3
Q / A h dm-3
b
COD / mg dm-3
Q / A h dm-3
c

Figure 1


a
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30000
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Terephthalic acid
N-ethyl-N-ethylrhodamine
3-dinitrobenzoic acid
2,5-Hydroxybenzoic acid
Benzoic acid
Phthalic acid
I1
Intermediates
0
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Time (min)
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b
Area
30000
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Terephthalic acid
N-ethyl-N-ethylrhodamine
3-dinitrobenzoic acid
2,5-Hydroxybenzoic acid
Benzoic acid
Phthalic acid
I1
Intermediates
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Time (min)
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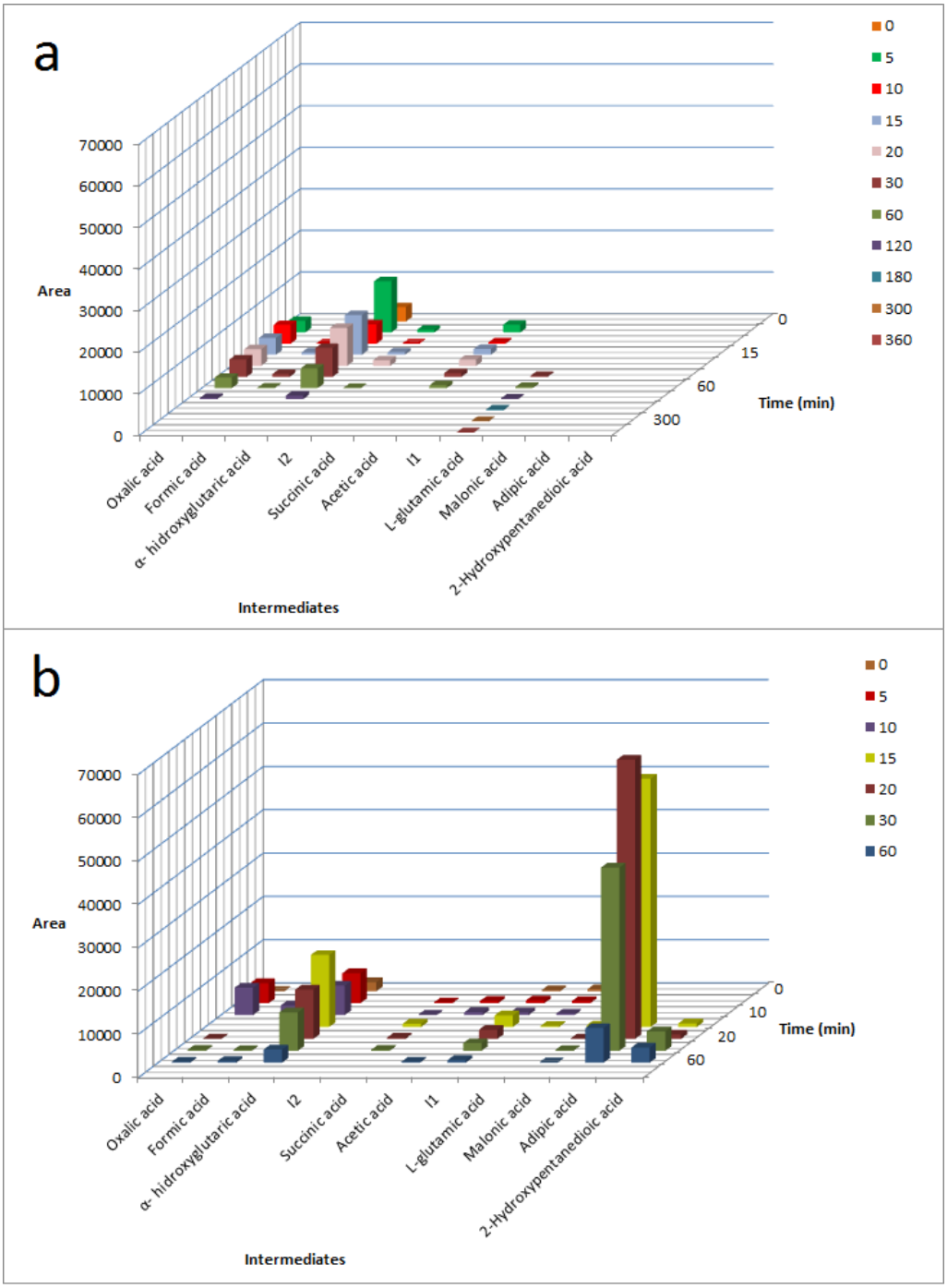
Figure 2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0
15
60
300
Time (min)
Oxalic acid
Formic acid
α- hidroxyglutaric acid
I2
Succinic acid
Acetic acid
I1
L-glutamic acid
Malonic acid
Adipic acid
2-Hydroxypentanedioic acid
Intermediates
b
Area
70000
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Time (min)
Oxalic acid
Formic acid
α- hidroxyglutaric acid
I2
Succinic acid
Acetic acid
I1
L-glutamic acid
Malonic acid
Adipic acid
2-Hydroxypentanedioic acid
Intermediates

Figure 3