

Production of value-added substances from the electrochemical oxidation of volatile organic compounds in methanol medium

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Abstract

In the search for a method that can remove pollutants from gases or enhance the efficiency of the treatment of liquid wastes, electrolysis of water and methanol solutions containing benzene, toluene, and xylene were carried out in this work. Using a filter-press flow electrochemical cell, the efficiency of two different anodes (diamond coatings and mixed metal oxides) were evaluated against the electrochemical oxidation of contaminants in the different solvents mentioned. Results demonstrate that these pollutants can be removed from both types of matrixes and that the nature of the electrode influences greatly on the efficiency. In aqueous medium both electrodes perform similarly but diamond overcomes metal oxide anodes in methanol. In addition to a higher mineralization rate in that case, several highly value-added products are obtained during the process. For instance, anisole, methyl anisole and dimethyl anisole were produced from electrochemical oxidation of benzene, toluene and xylene, respectively, in methanol medium. These results pointing out that a change in the paradigm of the treatment must be made in the next years, going from the destruction of the pollutants to their conversion into highly valuable products at the frame of the circular economy premises.

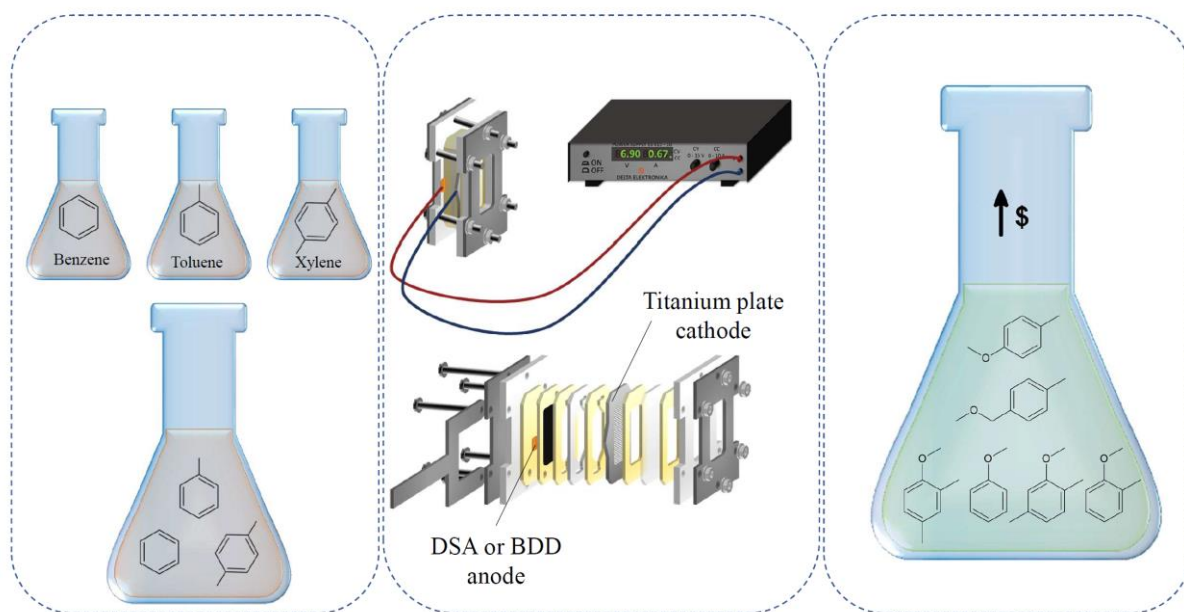
Keywords

electrochemical oxidation; volatile organic compound; methanol; value-added product; electro-refinery.

Highlights

- DSA[®] and BDD were very efficient in removing VOCs from aqueous medium.
- BDD shows a greater conversion of VOCs from methanol solutions than DSA[®].
- Added-value products were produced in methanol medium.
- The new concept of electro-refinery was explored.

Graphical Abstract



1. Introduction

Anodic oxidation of pollutants has been a topic of interest for researchers during the last fifty years, with special emphasis over the last two decades. Destruction of pollutants contained in wastewater, trying to discharge into the environment water free of anthropogenic pollutants, has been the main target and the search of efficient technologies in the mineralization of organics, that is, the conversion of the organic carbon contained in the pollutants into carbon dioxide has become the paradigm looked for [1–4]. Several electrodes have been used to reach this goal like metals, metal oxides, and carbonaceous materials [5–10]. The outstanding performance obtained in using anodes such as diamond has motivated that many research groups have centered their activity on the evaluation of the destruction of different pollutants [11–16]. The results obtained confirm that, except for very “special” molecules [17], complete mineralization of the anthropogenic pollutants is the rule.

The persistent increase in the emission of volatile organic compounds (VOCs) is a reflection of the increase in anthropogenic activities due to the accelerated urbanization and industrialization that occurred in the last decades. More than 40% of the VOCs emissions come from industrial activities that involve solvent use and production, petroleum refining and other petrochemical processing, coal combustion, use of fossil fuels, etc. [18,19]. About 37% of the total industrial VOCs emission is generated from the coal combustion and benzene, toluene and xylene are the main species emitted. These substances have been classified as hazardous air pollutants by the US EPA [20].

Recently, the interest in the application of the anodic oxidation has also been shifted to the treatment of gases by combining the exhaustively evaluated anodic oxidation with gas/liquid absorption processes into a technology, the electrochemically assisted absorption, which is becoming a very promising alternative [21–25].

One of the key conclusions in all these studies about the destruction of pollutants in liquid and gases is that electrolysis can be very efficient and, in using high-efficiency anodes, it is only controlled by mass transport limitations. In fact, for highly loaded wastes, faradaic efficiencies

reached can be nearly 100% and when the concentration of the organics in the waste decreases, a linear decay in the efficiency is always obtained from a value of the organic load within the range 1000-2000 mg L⁻¹ of COD (chemical oxygen demand), typically known as COD limit [26].

To overcome this limitation, many technologies have been proposed, such as the combination of the anodic oxidation with photolysis [27–32], sonolysis [33–36], the promotion in the production of oxidants, such as persulfates and hydrogen peroxide [37–41], and the combination of processes [42–46]. One of them, consists of the concentration of the pollutant by a granular activated carbon adsorption-desorption stage [47,48], that is, to retain the organics into activated carbon (removing pollutants from water) and then, to release these organics into methanol (because of the more unfavorable isotherm in this media). Although methanol is not as good as water as support for electrolysis, experimental results demonstrate that it can be successfully used for this purpose and the comparison of the electrolysis of the same species in the same concentration range in both media (water and methanol) is only slightly less efficient for methanol [49]. Therefore, the increase in log units in the concentration may allow a more efficient oxidation. In addition, this technique can be used not only for the concentration of organics contained in aqueous wastes, but also for the retention of pollutants contained in gas streams, which can be efficiently treated in this way.

An additional advantage of this technology, which is going to be proposed in this work, may be the formation of different intermediates in a cleaner solution (because methanol is not a waste but simply a collection media). This allows the change in the treatment paradigm from the current destruction of the pollutants by mineralization to a more environmentally friendly recovery of highly-value-added products, in agreement with the principles of the circular economy. Considering this background, in this paper it is aimed to compare the anodic oxidation of three volatile organic compounds (VOCs), benzene, toluene, and xylene, with two types of electrodes (coatings made with doped diamond or mixed metal oxides), in water and methanol as solvent. This comparison will confirm if it is worth further studies about the implementation of the electrochemically assisted adsorption for the treatment of these wastes and it will explore the first

steps in the use of electrochemical technology not for destruction of pollutants but for their recovery as valuable products.

2. Experimental

2.1. Chemical products

Reagents were of analytical grade and were used as received. Benzene (C_6H_6 , 99.7%) was supplied from OmniSolv, toluene anhydrous ($C_6H_5CH_3$, 99.8%) and p-xylene ($C_6H_4(CH_3)_2$, 99%) were supplied from Sigma-Aldrich. The solutions were prepared with deionized water (Millipore Milli-Q system, resistivity $18.2\text{ M}\Omega\text{ cm}$ at $25\text{ }^\circ\text{C}$) or methanol (HPLC grade, Scharlau, Spain) and sulfuric acid (95-98%, Scharlau, Spain) were used as supporting electrolyte. Hexane HPLC grade (98.5%, VWR Chemicals, Belgium) was used in the liquid-liquid extraction for analytics in gas chromatography (GC) were helium (Air Liquide, Spain) filtered by a hydrocarbon cartridge filter (Thermo Fisher Scientific) was used as carrier gas.

2.2. Experimental setup

The experimental setup is shown in Figure 1. As can be seen, a glass reaction tank (1) stored 1 L of solution of benzene, toluene, xylene, or ternary mixtures. The solution was pumped through a heating exchange column (3) and into the electrochemical cell with a peristaltic pump (2) and later it is recirculated to the reaction tank. A filter-press flow electrochemical cell (4) equipped with a dimensionally stable anode (DSA[®], nominal composition: $Ti/Ru_{0.3}Ti_{0.7}O_2$, purchased from DeNora do Brasil) or a boron-doped diamond (Si/BDD, purchased from NeoCoat/WaterDiam, France) as anode and titanium plate as cathode (with a geometrical area of 14.67 cm^2).

The liquid flow was 30 L h^{-1} and the supporting electrolyte was sulfuric acid (50 mmol L^{-1}). During the electrochemical oxidation, the power supply (5) provides a constant current density of 30 mA cm^{-2} . Solution concentrations were 300 mg L^{-1} of benzene or toluene, and 200 mg L^{-1} of xylene. The different amounts of each contaminant were used after considering their different solubility in water. For the ternary solutions were used 200 mg L^{-1} of each compound. Gaseous stream

produced by the electrolysis reactions is bubbled in hexane tank (6) to quantify if part of the organic compound is entrained by the gas flow.

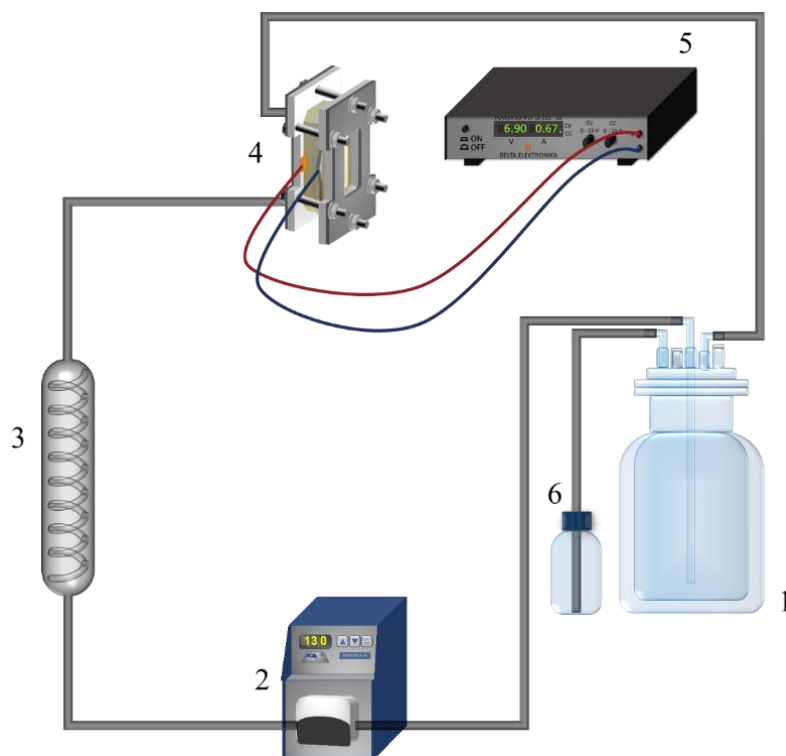


Figure 1. Electro-oxidation installation scheme. (1) reaction tank, (2) peristaltic pump, (3) heating exchanger column, (4) filter-press flow electrochemical cell with DSA[®] or BDD as anode and titanium plate as cathode, (5) current source, (6) liquid hexane tank.

2.3. Analytical techniques

Samples from both liquid and gas phases had an L-L extraction process with hexane before the analytical quantification. The samples (1.0 mL of liquid phase or 5 mL of gas phase **in normal conditions of pressure and temperature**) were mixed with 3.0 mL of hexane for 2 min using a vortex stirrer. After the separation of the phases, hexane was transferred to a GC vial. The pollutant concentration was measured by a Shimadzu Gas Chromatography (Nexis GC-2030) coupled to a Mass Spectrometer Detector (GCMS-QP2020 NX) using a capillary analytical column (SH-Rxi-5Ms 30 **m** x 0.25 mm x 0.25 **µm**) and a split/splitless injector working in the split mode with a split ratio of 20. The following temperature program were used: 38 °C (3 min), 40 °C min⁻¹ to 75

°C (0 min), 30 °C min⁻¹ to 200 °C (1.91 min). The injection temperature was 200 °C as well the detector temperature, and the total flow was 42.8 mL min⁻¹ (pressure 100.0 kPa) with a linear velocity of 48.3 cm s⁻¹. For instance (As an example or just deleted this), the results obtained using the patterns are represented in Figure 1S.

Liquid samples were also analyzed directly by HPLC (Jasco 2080Plus) with UV-vis detector and a Hi-Plex H column (Agilent Technologies) as stationary phase to identify carboxylic acids. Sulfuric acid 5 mmol L⁻¹ was the mobile phase with a flow of 0.8 mL min⁻¹. Wavelength applied was 210 nm.

Total organic carbon (TOC) was measured by using a Multi N/C 3100 analyzer (Analytik Jena).

3. Results and Discussion

3.1. Destruction of pollutants

Electrochemical oxidation treatment of benzene, toluene and xylene were carried out with the two models of anodes in water and methanol media. As already known, anodes consisting of coatings of mixed metal oxides are expected to perform a softer oxidation, while anodes consisting of coatings of conductive diamond typically lead to harder oxidation condition. In this work, commercial DSA[®] and BDD anodes were used as mixed metal oxide and diamond anodes, respectively. The concentration decay during the electrolysis of solutions containing only one of these pollutants is represented in the Figure 2.

As can be seen, when the degradation was carried out using BDD, the compound concentration decreased faster than when using DSA[®], regardless of the medium used as supporting electrolyte. It can be highlighted that the solvent has a remarkable effect on pollutant removal. Thus, for both electrodes used, the performance in terms of removal of the pollutant was worse in methanol media than during the treatment in water media, but it is important to note that the three compounds undergo transformation. Considering an arbitrarily selected applied electric charge of 1.32 Ah L⁻¹, more than 90% of each compound were transformed from water solutions, regardless the anode

used. Meanwhile, in methanol medium only a third of that percentage was achieved using DSA[®] and about 60% using BDD.

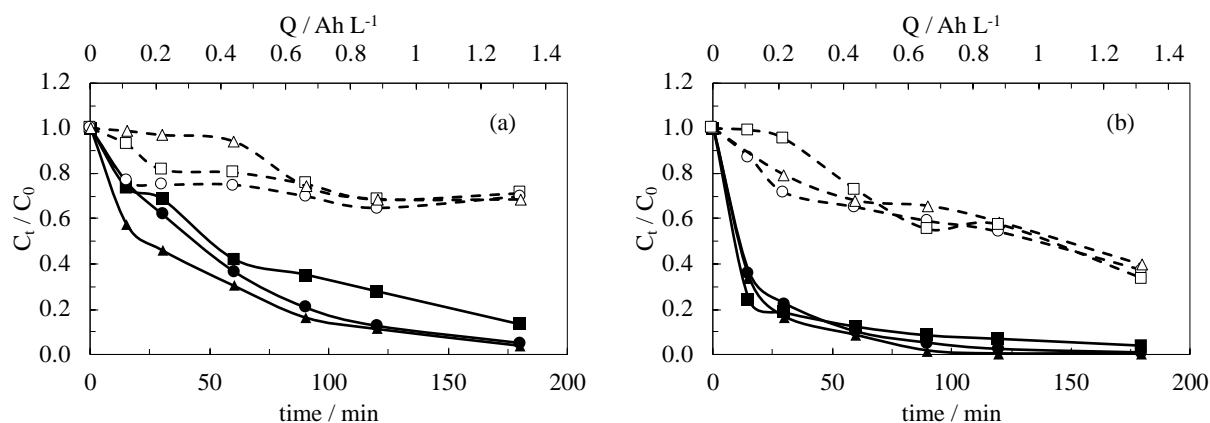


Figure 2. Concentration decay as function of the instant applied charge (upper axis) and time (lower axis) from single contaminant solutions in water (solid line) and methanol (dashed line) using (a) DSA[®] or (b) BDD electrodes. (■,□) benzene; (●,○) toluene; (▲,△) xylene. Supporting electrolyte: 50 mmol L⁻¹ H₂SO₄. Current density: 30 mA cm⁻².

Ternary contaminated solutions were also tested, and the results are shown in the Figure 3. In this case, the transformation of benzene, toluene and xylene from the ternary mixture was very similar for DSA[®] and BDD considering the aqueous medium. It is important to note that benzene had a lower conversion than toluene and xylene.

This can be explained by an increase in the electro-reactivity of toluene and xylene with the number of CH₃ substitutions in the benzenic ring, although the influence was low for the experiments carried out with each compound individually. In the experiment performed in methanol, the three compounds showed the same behavior, with nearly 42% of transformation for each compound at the end of the experiment. The methanol solution mixture was not tested with DSA[®] due the low anode efficiency in the single contaminant solutions.

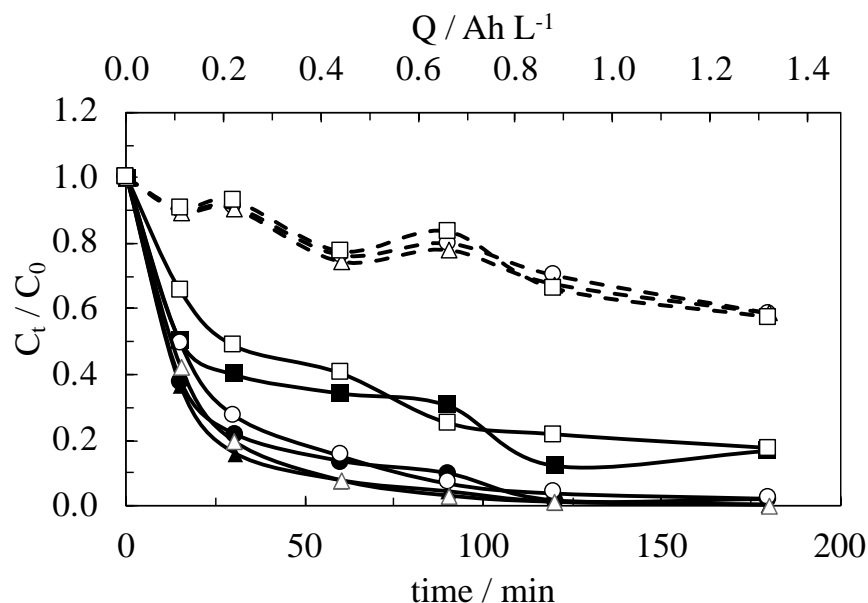


Figure 3. Concentration decay as function of the instant applied charge (upper axis) and time (lower axis) from ternary contaminant solutions in water (solid line) and methanol (dashed line). (■,□) benzene; (●,○) toluene; (▲,△) xylene. Anode: DSA[®] (full symbols) or BDD (empty symbols). Supporting electrolyte: 50 mmol L⁻¹ H₂SO₄. Current density: 30 mA cm⁻².

As expected, experimental degradation results fit well to a pseudo-first order kinetic model in both media. Although electrochemical processes are typically governed by zero order kinetics (I/nF), the electrochemical treatment of diluted solutions containing pollutants follows this first order model, because the degradation is not controlled by the exchange of electrons on the surface of the electrodes but by the transport of the pollutants to the electrode surface or by the action of oxidants produced on those surfaces. Table 1 summarizes the kinetic analysis for the transformation of benzene, toluene, and xylene using DSA[®] and BDD electrodes in water and methanol media. It is important to note that, as the Figure 2 and 3 previously indicated, the kinetic constant for each compound in **water** solutions increases in the order benzene < toluene < xylene, regardless the electrode used. These results agree with the statement that the number of substitutions on benzene ring turns it into more electro-reactive molecules and this facilitates the compound degradation by

electro oxidation. In addition, in methanol media, it is possible to note that BDD is more efficient than DSA[®] with values for kinetic constant up to three times higher.

Table 1. Kinetic constants* and removal percentage for the VOCs electrolysis.

		DSA [®]			BDD			
		k / min ⁻¹	R ²	Conversion	k / min ⁻¹	R ²	Conversion	
Single	Water	Benzene	0.0107	0.986	86.7%	0.0225	0.906	95.8%
		Toluene	0.0166	0.999	94.8%	0.0244	0.960	99.0%
		Xylene	0.0168	0.991	95.9%	0.0444	0.984	99.5%
	Methanol	Benzene	0.0030	0.992	28.6%	0.0062	0.962	66.3%
		Toluene	0.0034	0.976	30.3%	0.0050	0.960	71.6%
		Xylene	0.0037	0.969	31.6%	0.0047	0.966	60.1%
Ternary	Water	Benzene	0.0153	0.931	83.0%	0.0093	0.901	82.5%
		Toluene	0.0292	0.924	98.0%	0.0258	0.978	99.0%
		Xylene	0.0318	0.980	99.8%	0.0338	0.990	99.8%
	Methanol	Benzene				0.0030	0.920	42.6%
		Toluene				0.0028	0.944	41.4%
		Xylene				0.0028	0.937	41.1%

*The values of kinetic constants were calculated using the graphics represented in the Supplementary Material (Figure 2S).

When electrooxidation is carried out, one of the most important points to keep in mind during the treatment is the avoidance in the generation of more toxic products during the transformation of the pollutants underwent during the treatment. Traditionally, it has been considered that a treatment process is efficient if the complete compound mineralization is achieved. Figure 4 shows the initial and final TOC values normalized for better observation, as well as the percentage of

TOC removal in each test made in water solutions for an arbitrarily selected current charge passed. Considering the initial and the final values of TOC reached (these measured data are shown in the Supplementary Material, Figure 3S), there is a minimum of about 50% of mineralization after passing an electric charge of 1.32 Ah L^{-1} . It implies, as expected, that this mechanism is the main pathway for VOCs elimination in the electro-oxidation process. In general, both types of electrodes show similar percentage removal.

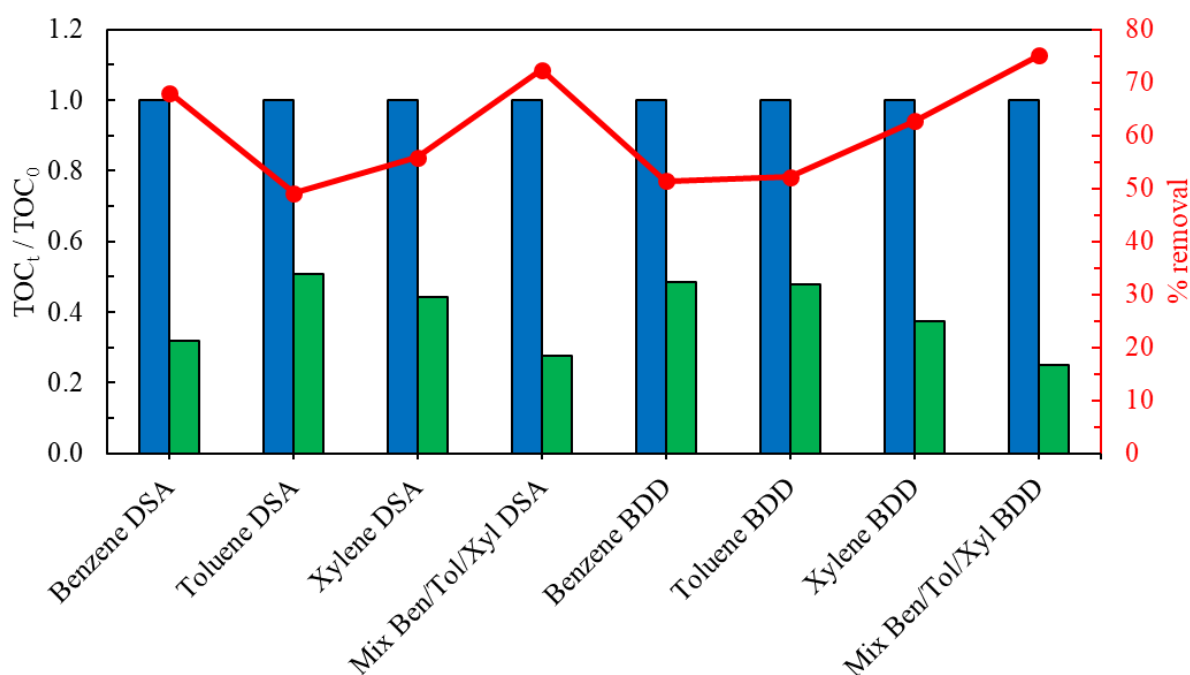


Figure 4. Normalized initial values (■), final values (■) and removal percentages (●, right axis) of total organic carbon (TOC) in electro-degradation of benzene, toluene, xylene, and their ternary mixtures with DSA[®] and BDD as anode for an electric charge passed of 1.32 Ah L^{-1} . Electrolyte: $50 \text{ mmol L}^{-1} \text{ H}_2\text{SO}_4$. Solvent: water.

Unfortunately, it is not possible to measure TOC from methanol solutions, because the extremely large concentration of carbon from methanol makes the measurement not accurate enough. Therefore, the theoretical TOC values were calculated based on quantification of the degradation products. The normalized values are represented in Figure 5. Additionally, the same (What is the same?) was done for water solutions and the results are represented in Figure 4S. As can be seen,

it is evident the better performance of BDD anode, once its efficiency in methanol media outperforms that of the DSA[®].

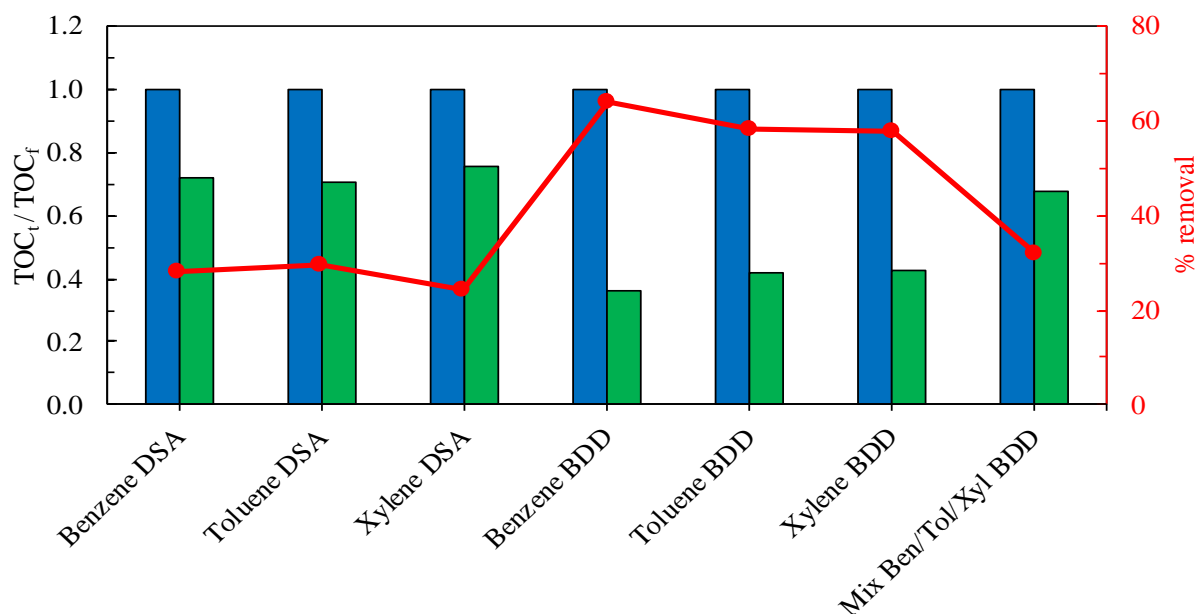


Figure 5. Theoretical initial values (■), final values (■) and removal percentages (●, right axis) of total organic carbon (TOC) in electro-degradation of benzene, toluene, xylene, and their ternary mixtures with DSA[®] and BDD as anode for an electric charge passed of 1.32 Ah L⁻¹. Electrolyte: 50 mmol L⁻¹ H₂SO₄. Solvent: methanol. Why the Y axis is different the one of figure 4? I think that it is the same but with theoretically values instead of experimental ones.

3.2. Changing the view: from destruction to conversion

So far, as we have seen, the degradation via electrochemical oxidation of VOCs is possible using both DSA[®] and BDD anodes in aqueous medium. Furthermore, the removal of these compounds is possible from methanol solutions too, and the obtained results are even better when BDD anodes were used. However, and unlike previous works in which degradation in methanol medium was evaluated and almost the same intermediates were found in methanol and water solutions [48,50], in the present case, an important difference should be highlighted, which may represent a turning point for the technology: the formation of highly value-added species. Thus, despite the

mineralization is lower in the electrolysis performed in methanol medium, an important observation is the formation of value-added substances as degradation products, as can be confirmed in the Figure 6, which shows the concentration of the different value-added substances that were measured during the electro oxidation of the different VOCs with both evaluated anodes in methanol media.

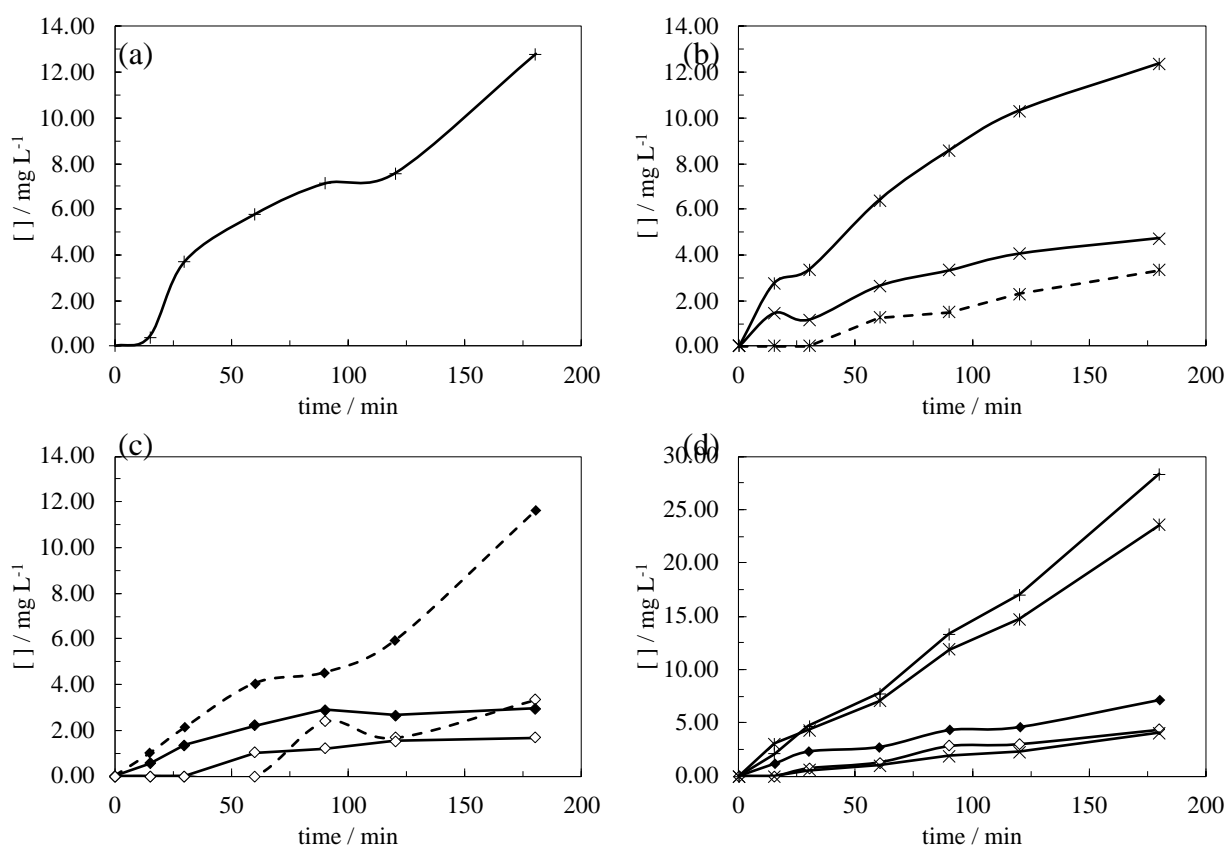


Figure 6. Concentration of value-added substances produced from methanol medium solutions during the electrochemical oxidation of (a) benzene, (b) toluene, (c) xylene and (d) the ternary solution. (+) anisole, (×) 2-methylanisole, (*) 4-methylanisole (◆) 1-(methoxymethyl)-3-methylbenzene, (◇) 2,4 and 2,5 dimethyl anisole. Anode: DSA[®] (dashed line) and BDD (full line). Supporting electrolyte: 50 mmol L⁻¹ H₂SO₄. Current density: 30 mA cm⁻².

Using BDD, a higher concentration of those substances was produced, in addition to the higher mineralization, meaning a higher electrochemical activity and a larger progress of the reaction

paths. Thus, a high concentration of anisole was produced from benzene (Figure 6.a). This substance is used as a precursor for perfumes and in the pharmaceutical and chemical industries and it is also considered as one of the greenest solvents [51,52] and can replace some hazardous ones, such as piperidine [53,54]. From toluene solutions, 2-methylanisole and 4-methylanisole are generated and, as can be seen both in the Figure 6.b. (single contaminant methanol solution) and 6.d. (ternary methanol solution), there is a preference for the formation of the second substance. Moreover, it is known that a substituting group linked in the aromatic ring affects both the reactivity and the orientation for the new entry group [55]. Alkyl groups guide the electrophile to ortho and para positions due its capacity to stabilize carbocations, leading to the formation of these substances as well. The larger concentration of the compound with the -OCH₃ group in the para position can be related to physical limitation by the adjacent group. These products are used as a precursor for fragrances and do not represent risk for the humans [56]. As well as toluene, xylene generates oriented degradation products: 2,4-dimethylanisole and 2,5-dimethylanisole as shown in the Figure 6.c and 6.d. Unfortunately, with the chromatographic method used in this work, it was not possible to separate the peak correspondent to each substance. So far, following the same idea for the predominance of 4-methylanisole during toluene electrolysis, it would be expected a higher amount of 2,5-dimethylanisole. Nevertheless, the primary product in this case was 1-(methoxymethyl)-3-methylbenzene. It was also detected the formation of tolualdehyde, but in a very low concentration (<1 mg L⁻¹ at the final of the experiment). It is important to note that in the experiments performed using DSA[®], anisole and 2-methylanisole were not detected.

Once, from methanol solution, both **processes** of removal and production of value-added **are** possible, it is important to know the amount of contaminant that is being valued. Table 2 represents the percentage of each product generated in relation to the amount of pollutant removed. As can be seen, apart from xylene electrolysis, BDD had a greater percentage of value-added products, and this indicates that the promotion in the generation of these species can become a paradigmatic change in the development of treatment technologies.

Table 2. Percentage of value-added products obtained from the electrochemical oxidation of benzene, toluene, and xylene **in relation to the amount of pollutant removed.**

	Single Solutions		Ternary Solution
	DSA [®]	BDD	BDD
Anisole (from benzene)	0.0%	1.0%	2.9%
2-methylanisole (from toluene)	0.0%	1.4%	3.0%
4-methylanisole (from toluene)	1.8%	3.6%	17.5%
2,4 and 2,5 dimethyl anisole (from xylene)	3.6%	0.7%	2.6%
1-(methoxymethyl)-3-methylbenzene (from xylene)	12.7%	1.3%	4.3%

Since this is an initial study, integrated in a larger study, which aims to carry out the pre-concentration of contaminants by adsorption and posterior treatment with methanol, which results in highly concentration solutions, it is interesting to understand if the production of those value-added products is affected. Thus, the production of these aromatic substances from solutions with different initial concentrations of contaminants was assessed and the results are shown in the Figure 7. The amount of each substance increases proportionally to the initial concentration of the contaminant, as expected, except for the formation of 4-methylanisole, which is three times greater for the solution with an initial concentration of 1000 mg L⁻¹ of toluene than for the solution with 500 mg L⁻¹ as initial concentration. For the lowest concentrated solutions, there is no production of value-added substances. This means a great advantage for carrying out the pre-concentration of the contaminant and subsequent electrochemical treatment.

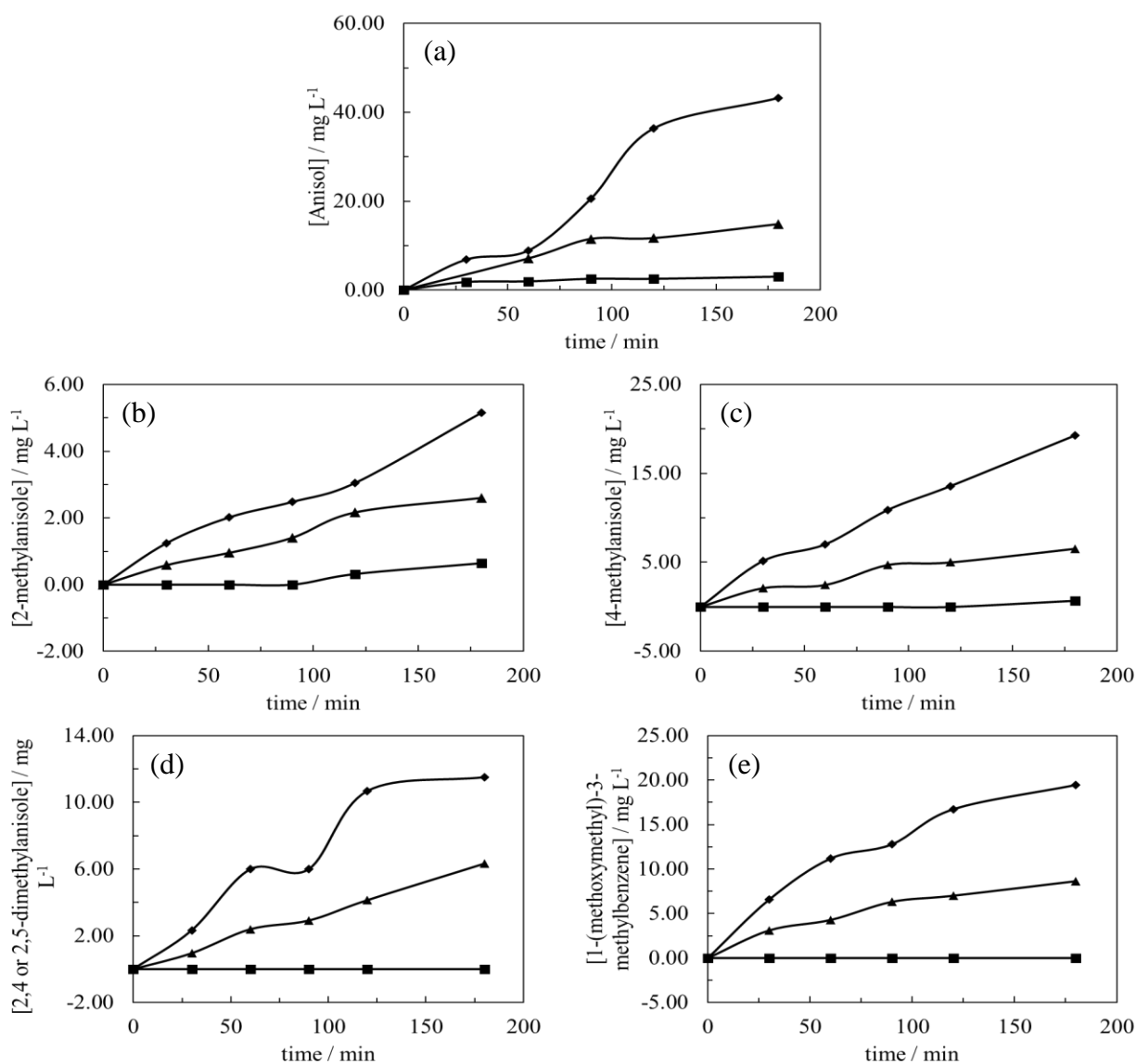


Figure 7. Concentration of value-added substances produced from methanol medium solutions during the electrochemical oxidation of (a) benzene, (b and c) toluene and (d and e) xylene in different initial concentrations: (■) 100 mg L⁻¹, (▲) 500 mg L⁻¹ and (◆) 1000 mg L⁻¹. Anode: BDD. Supporting electrolyte: 50 mmol L⁻¹ H₂SO₄. Current density: 30 mA cm⁻².

Based on these observations about the electrochemical oxidation of VOCs in methanol medium, a mechanism pathway has been proposed in Figure 8. Differently of aqueous media, which generates compounds by electrophilic attack of OH[•], such as phenol, benzoic acid, and benzaldehyde [24,57,58], the substances identified in this work come from methanol. It is an indication that

OCH_3 radicals are responsible for the formation of the value-added substances. As discussed before, in methanol media occurs simultaneously the destruction of the contaminant and production of value-added compounds and the detection of some acids, such as maleic, malonic, and oxalic, proves this statement. It was also detected the dimethyl maleate and methyl dimethoxy acetate, indicating that there is degradation of some value-added substance, despite the concentration of these compounds did not apparently decrease during the experiments.

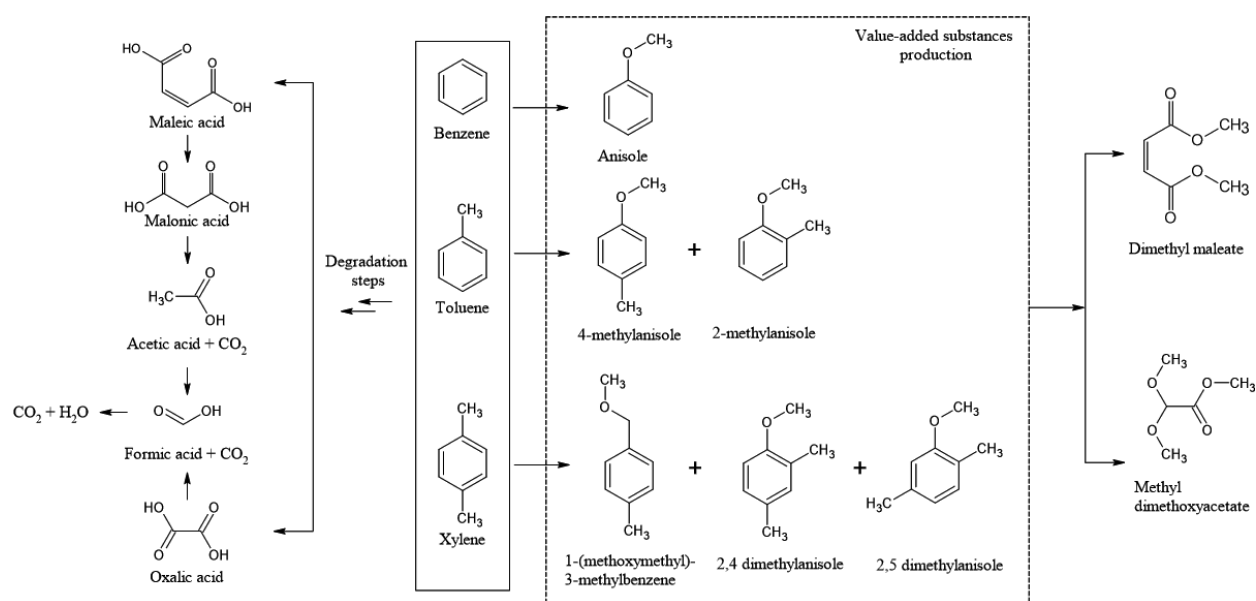


Figure 8. Pathways to production of value-added substances and to degradation of benzene, toluene, and xylene.

This means that it may be worth exploring the new concept of electro-refinery, which is a way to transform pollutants into valuable species by electrochemical technology, which may be intensified using the combined adsorption-desorption-electrolysis strategy, in which pollutants are concentrated in granular activated carbon, then released to a methanol solution and then electrolyzed. This strategy can be worth not only for the treatment of pollutants contained in liquids but also in gases.

4. Conclusions

This work highlighted the electrochemical oxidation of benzene, toluene, and xylene in water and in methanol media. The main obtained conclusions are the following:

- The removal of VOCs from water solutions is much more effective (regardless of the used anode) than from methanol solutions. Thus, more than 90% of the contaminant was destroyed from water solution whereas only 30% and 60% were achieved for DSA[®] and BDD electrodes, respectively, from single contaminant methanol solutions. From the ternary solution prepared in methanol medium, the removal was about 40% of each pollutant.
- The great advantage of the methanol medium is that value-added substances can be produced during the electrochemical oxidation of benzene, toluene, and xylene.
- The higher is the initial concentration of the contaminant, the larger will be the generation of value-added substances. This can be a great advantage in the system of pre-concentration of contaminants and posterior electrochemical treatment. This also may lead to a paradigmatic change in electrochemical wastewater treatment and can become a way to convert them into electro-refinery processes.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could influence the work reported in this paper.

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