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Electrochemical treatment of aqueous solutions of catechol by various electrochemical advanced oxidation processes: effect of the process and of operating parameters.

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Abstract

Catechol, one of the most abundant compounds in olive mills wastewaters, which is generated in the Fenton degradation of various aromatic compounds, is a toxic, possible carcinogen, persistent pollutant and it is not readily biodegradable. Hence, its degradation requires the utilization of advanced oxidation processes (AOPs). Here, the electrochemical treatment of aqueous solutions of catechol was investigated. The utilization of various electrochemical processes, such as electro-Fenton (EF), direct anodic oxidation (AO), indirect oxidation by electro-generated active chlorine and coupled processes was investigated. Furthermore, the effect of various operating conditions (including the nature of anode for AO, the initial pH and the current density) was widely studied in order to optimize the selected electrochemical processes. For EF process, the effect of the nature of the catalyst (homogeneous FeSO₄ and heterogeneous pyrite and chalcopyrite) was also analysed. It

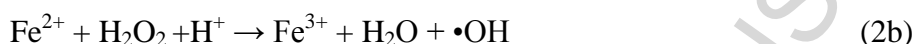
was shown that both EF and AO, under proper operating conditions, allow a very high removal of the TOC, while the indirect oxidation by electro-generated active chlorine is poorly effective. The utilization of a coupled EF-AO process allowed to enhance the abatement of both catechol and TOC with respect to single processes.

Keywords: Catechol; Advanced oxidation process, electro-Fenton, anodic oxidation; BDD

1. Introduction

Conservation of the environment, which requires a sustainable development to avoid compromising existing natural resources, is gradually becoming a major objective. As a result, a special research area of environmental electrochemistry has been developed, which is based on the utilization of electrochemical techniques to prevent or minimize environmental pollution. Traditional physical, chemical and biological techniques are widely used for the treatment of wastewater containing biodegradable organic pollutants. They are often inadequate for treating various kinds of industrial and agricultural effluents, as they are relatively expensive, inefficient, time consuming or a secondary cause of pollution. Consequently, over the past three decades, researchers have tried to develop new and more environmentally friendly technologies for the total elimination of persistent organic pollutants from wastewater and for the quantitative and rapid mineralization of non-biodegradable organics. In this context, the use of more innovative processes such as the advanced oxidation processes (AOPs) has acquired great relevance [1]. These processes have proved to have high efficiency with advantages such as versatility, high energy efficiency, amenability of automation, and safety because they operate at mild conditions with limited use of chemicals [2-4]. AOPs produce in situ hydroxyl radical ($\bullet\text{OH}$), the strongest oxidizing agent ($E^\circ = 2.80 \text{ V/SHE}$) after fluorine. These processes are especially efficient for aromatic molecules thanks to the non-selective electrophilic aromatic substitution of hydroxyl radical to aromatic moieties, leading finally to the ring opening reactions. Among them, electrochemical AOPs (EAOPs) such as anodic oxidation

(AO) and electro-Fenton (EF) processes have gained much interest for the removal of organic compounds. In AO, the destruction of pollutants is mediated by hydroxyl radicals generated on the surface of the anode by the oxidation of water and its efficiency depends strongly on the anode material. In EF process, H_2O_2 , produced at the cathode by oxygen reduction (eq. (1)), reacts with catalytic amounts of Fe^{2+} to generate the $\bullet\text{OH}$ radicals in the solution (eq. (2)) [5].



These formed $\bullet\text{OH}$ react rapidly on organics, leading to their oxidation / mineralization according to the following equations:



The advantages of this process with respect to conventional Fenton process is the continuous electro-generation of H_2O_2 inside the reactor and the cathodic regeneration of Fe^{2+} from cathodic reduction of Fe^{3+} .

Catechol is one of the most plentiful compounds in olive mills wastewaters (OMW) [6]. Furthermore, it is generated in the Fenton degradation of aromatic compounds [7] and it is the first intermediate produced by the degradation of tyrosol by electro-Fenton [8] (one of the most relevant compounds in OMW). It is a toxic, persistent pollutant and it is not readily biodegradable under environmental conditions because of its aromatic structure [9]. The International Agency for

Research on Cancer (IARC) has classified catechol as possibly carcinogenic to humans (Group 2B) [10]. For these reasons, several technologies have been investigated for the removal of catechol from wastewater and aqueous solutions, including biological methods [11, 12], adsorption [13, 14], ozonation process [15, 16], advanced photo-oxidation process [17] and Fenton and photo-Fenton [9, 18].

In this experimental work, an in-depth study on the electrochemical treatment of catechol is reported. The main aim of the work is to evaluate the potential utilization of various electrochemical processes (namely, AO, EF, oxidation by electro-generated active chlorine and coupled processes) for the degradation of such phenolic compound in aqueous solutions. Furthermore, the effect of various operating conditions (including the nature of anode for AO, the initial pH and the current density) was widely investigated in order to optimize the selected electrochemical processes. For EF process, the effect of the nature of the catalyst (FeSO_4 , pyrite and chalcopyrite) was also analysed. At the end of this work, the two more promising processes (AO and EF) were coupled to achieve a more effective degradation of catechol.

2. Experimental

2.1. Electrolysis system

Electrolyses were performed in a cylindrical, undivided tank glass cell under vigorous stirring performed by a magnetic stirrer with 50 mL of solution. Saturated calomel electrode (SCE) was used as reference electrode and all potentials reported in this study are referred to it. Different kinds of anode and cathode were used depending on the selected process:

- (i) Direct anodic oxidation (AO): Boron-doped diamond (BDD, wet surface area 1.53 cm^2 , from Condias, supported on Nb, 5,000–6,000 ppm boron) or $\text{Ti}/\text{IrO}_2\text{-Ta}_2\text{O}_5$ (Dimensionally

Stable Anodes, DSA, surface area 1.21 cm², from De Nora SpA) were used as anodes and Ni plate as counter electrode;

- (ii) Indirect anodic oxidation by electro-generated active chlorine: the above mentioned Ti/IrO₂-Ta₂O₅ (from De Nora SpA) was used as working electrode and Ni plate as cathode;
- (iii) Electro-Fenton (EF) process: the working electrodes used was Carbon Felt (surface area 1.97 cm², from Carbone Lorraine), while the counter electrode was the above-mentioned DSA electrode.
- (iv) For EF-AO coupled process, the BDD anode and the carbon felt cathode were used.

In all experiment the distance between the two electrodes were lower than 5 mm.

2.2 Chemicals

Electrolyses were usually performed at room temperature with an initial catechol concentration of 0.45 mM. The Catechol (C₆H₆O₂) used was of reagent grade, with purity > 98%, supplied by Fluka. The supporting electrolyte was in most cases composed by 0.1 M Na₂SO₄ (Sigma-Aldrich), while in some experiments 0.1 M NaCl (Sigma-Aldrich) was added to the system. Sulfuric acid from Sigma-Aldrich and Sodium hydroxide from Applichem were added in solution to adjust pH to the desired value. During Electro-Fenton experiment the catalysts used were of two types: synthetic and natural. As synthetic catalyst 0.5 mM of ferrous sulphate heptahydrate, (FeSO₄*7H₂O, in analytical grade from Fluka) was used. Pyrite (FeS₂) and chalcopyrite (CuFeS₂) used in this work were extracted from Jendouba (Tunisia). They were milled with a ceramic mortar and sieved (< 80 μm). To remove surface impurities, the resulting powder was ultrasonicated in 95% of ethanol for 5 min, washed with 1 M HNO₃, rinsed with deionized water and further with 95% of ethanol and finally dried at 30 °C. The working concentration was 1g/L. All solutions were prepared with distilled water. The use of the two catalysts pyrite and chalcopyrite required the addition of air or O₂ to facilitate the dissolution.

2.3. Instruments and analytical procedures

Galvanostatic mode electrolyses were performed with an AMEL 2055 potentiostat/galvanostat. The solution pH was measured with a Crison GLP 22 pH-meter. The removal of catechol was monitored from the decay of the absorbance (A) using Agilent Cary 60 UV Spectrophotometer. The concentration of catechol was determined at $\lambda = 270$ nm.

The mineralization of the starting pollutant during the electrochemical processes was assessed from the decay of the total organic carbon (TOC). This parameter was analysed by a TOC analyser Shimadzu VCSN ASI TOC-5000 A. The TOC value is given in milligrams of carbon per litre (mg/L), performing the average of three consecutive measurements with a precision of about 2%. The percentage of TOC removal was then calculated from:

$$\% X(\text{TOC}) = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} * 100 \quad (5)$$

Where TOC_t and TOC_0 are the experimental TOC values at time t and initial time, respectively.

The calibration of the equipment was made using potassium hydrogen phthalate standards in the range between 0 and 50 mg/L.

The presence of carboxylic acids (oxalic, maleic, malonic and lactic acids in analytical grade from Sigma–Aldrich) was identified by Prevail Organic 5 μ column under the following conditions: the mobile phase was a buffer solution containing KH_2PO_4 (Sigma Aldrich 99%) and H_3PO_4 at a pH of 2.5, prepared with water Sigma Aldrich G-chromasolv for gradient elution.

The current efficiency (CE) for the removal of TOC was defined as follows:

$$CE = nFVC^0X(\text{TOC})/(It) \quad (6)$$

where C^0 is the initial concentration of catechol in mol L^{-1} , n is the number of electrons exchanged during the mineralization of catechol according to eq. (7), V is the volume of the cathodic solution and F the Faraday constant (96487 C mol^{-1}).



3. Results and discussion

As previously mentioned, various electrochemical processes can be potentially used for the treatment of wastewater contaminated by organic pollutants resistant to conventional biological processes. Hence, in this work we have evaluated the utilization of various approaches including the direct anodic oxidation, the indirect oxidation by electro-generated active chlorine, the electro-Fenton and a coupled process (direct anodic oxidation and EF), with the main aim of selecting the most suitable processes for the treatment of catechol and to evaluate, for each of them, the effect of main operating parameters.

3.1 Direct anodic oxidation

The anodic oxidation of catechol was studied using two very different anodes: Ti/IrO₂-Ta₂O₅ (DSA) and boron doped diamond (BDD). The first is characterized by lower cost, higher surface due to internal porosity, but lower efficacy for the anodic abatement of many organics. Conversely, BDD presents a higher cost, but it is considered the most effective anode for the mineralization of organic pollutants [3, 19, 20]. A first series of electrolyses was carried out with the two electrodes at both 10 and 20 mA/cm², an initial pH close to 5.5 with an initial concentration of catechol of 0.45 mM. For both electrodes, as shown in Fig. 1, the electrolysis allowed a high removal of the catechol.

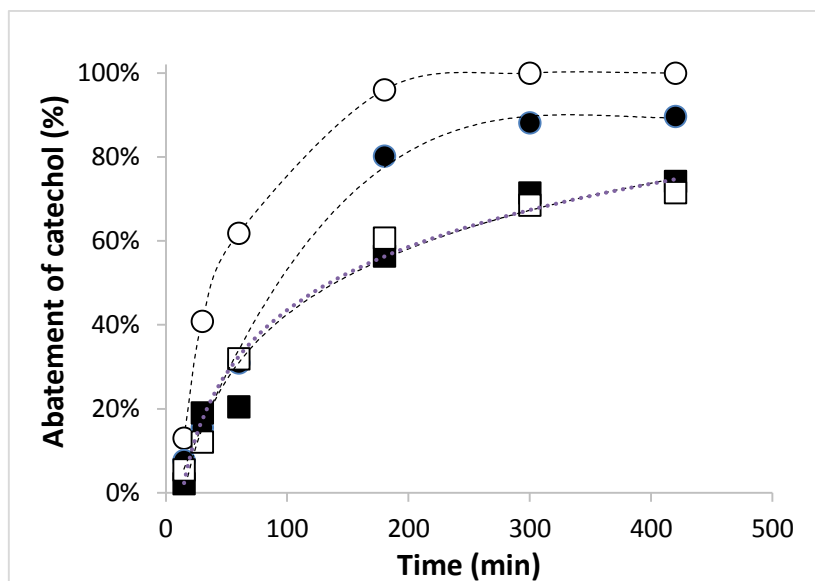


Figure 1. Abatement of catechol vs. time for experiments performed at 10 and 20 mA/cm² with aqueous solutions of catechol (0.45 mM) and Na₂SO₄ (0.1 M) using BDD (● 10 mA/cm², ○ 20 mA/cm²) or DSA (IrO₂-Ta₂O₅) (■ 10 mA/cm², □ 20 mA/cm²) as anodes and Ni as cathode at initial pH of 5.5. Lines are only guides for eyes.

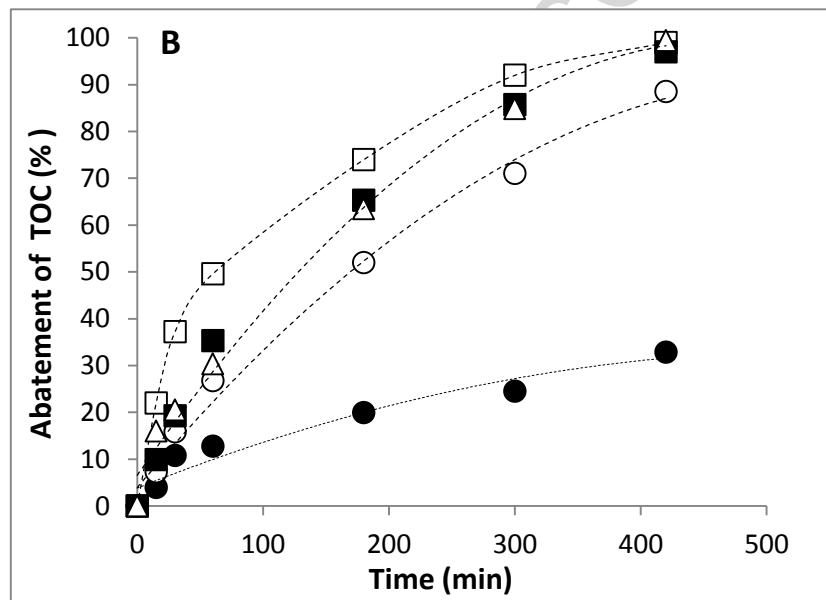
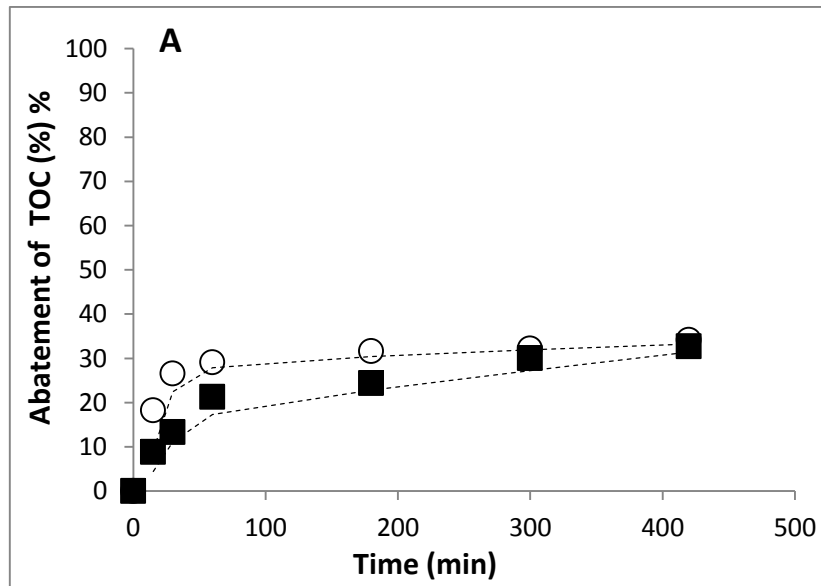
For the DSA anode, after 7 hours an abatement of catechol (estimated by uv-vis analyses) close to 70 % was obtained. For BDD, a higher abatement was obtained: after 7 h an abatement close to 90 and 100 % was achieved at 10 and 20 mA/cm², respectively.

To evaluate the applicative utilization of these processes, the abatement of catechol is an important but not exhaustive source of information. Indeed, it is also relevant to evaluate the ability of the process to mineralize the organic pollutant. At DSA anode, an abatement of the TOC slightly lower than 30 % was achieved after about one hour (Fig. 2A). For longer times, the further reduction of TOC was very low. As an example, at 10 mA/cm², after 1 and 7 hours an abatement of 27 and 33 % was achieved, respectively (Fig. 2A). These results indicate that the catechol is oxidized at DSA anode with the formation of some by-products that are rather resistant to further oxidation. When the current density was increased to 20 mA/cm², very similar final abatements of the TOC were achieved, in spite of the higher charge passed, because of the high resistance of by-products.

When the electrolyses were performed at BDD, a very high removal of the catechol was coupled with high abatements of the TOC. As shown in figure 2B, at 10 mA/cm² after 7 hours the abatement of the TOC was slightly lower than 90 %. To understand the different results achieved with the DSA anode and with BDD, one has to consider that in anodic oxidation process the removal of organics takes place by their reaction with heterogeneous hydroxyl radicals generated on the anode surface by oxidation of water (eq. (8)) [3]



The amount and reactivity of heterogeneous $\bullet OH$ are strongly related to the nature of anode materials. It is well known [3] that BDD($\bullet OH$) are physisorbed on the anode surface while on IrO₂-Ta₂O₅ anodes M($\bullet OH$) are chemisorbed. Consequently, the formers are more available and more reactive for oxidation of organics than the latter. Furthermore, in the case of BDD, sulphate ions from the supporting electrolyte can be oxidized to persulphate ions which can contribute to the oxidation of organics [19].



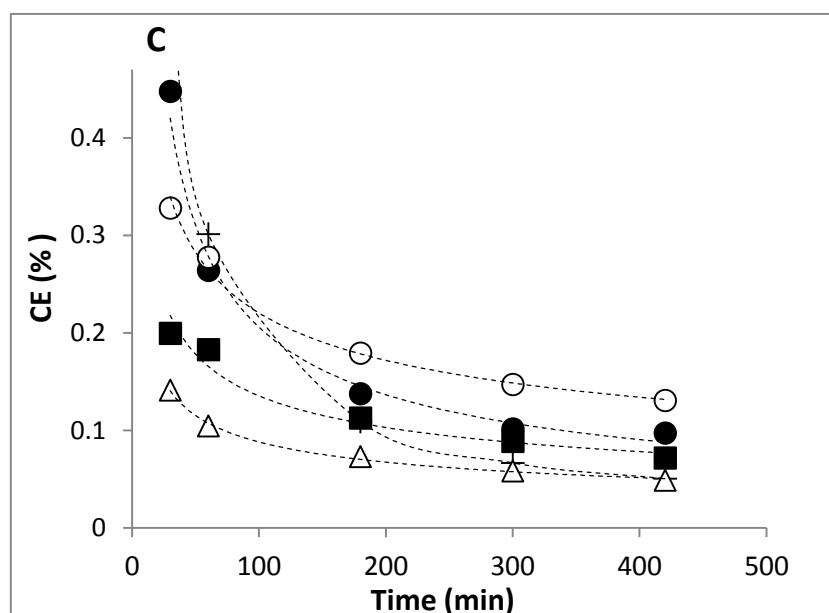
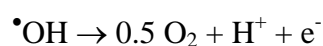


Figure 2. Removal of TOC by anodic oxidation at Ti/IrO₂-Ta₂O₅ (A) and BDD anode (B) of aqueous solutions of catechol (0.45 mM) and Na₂SO₄ (0.1 M) using Ni as cathode and various current densities (● 5, ○ 10, ■ 20, △ 30 mA/cm²). Fig. 2C reports the corresponding current efficiencies for experiments performed with natural pH at BDD (● 5, ○ 10, ■ 20, △ 30 mA/cm²) and Ti/IrO₂-Ta₂O₅ at 10 mA/cm² (+).

To evaluate the effect of current density on the oxidation of catechol at BDD, various experiments were performed at 5, 10, 20 and 30 mA/cm². As shown in fig. 2B, the abatement of TOC strongly increased upon an enhancement of the current density from 5 to 20 mA/cm². As an example, after 7 hours the abatement of TOC was about 32, 88 and 98 % at 5, 10 and 20 mA/cm², respectively. However, when the current density was further increased to 30 mA/cm², the trend of the abatement of the TOC vs. time was very similar to that observed for 20 mA/cm². This result is due to the fact that for high current densities the process is kinetically limited by the mass transfer of the organic to the anodic surface. Hence, in these conditions higher currents result just in a higher impact of parasitic processes such as the oxygen evolution (eq. (9)).



(9)

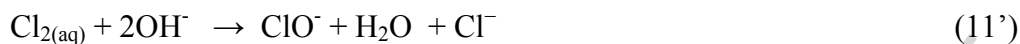
Fig. 2C reports the trend of the current efficiency (CE) vs. time for the experiments performed with BDD at various current densities. The current efficiency decreases with the time for all the experiments, because the reduction of the organic concentration, which decreases the rate of the mass transfer of the catechol to the electrode surface, thus making the anodic oxidation less favoured with respect to the oxygen evolution reaction. As shown in fig. 3C, the higher current efficiency for the mineralization CE was recorded for a value of current density of 10 mA/cm^2 , while the lower one for the higher adopted current density (30 mA/cm^2). For comparison, also the CE recorded at the DSA anode at 10 mA/cm^2 were reported. Lower CE were obtained with respect to that achieved at BDD, because of the lower abatements.

It has been shown [21] that the anodic oxidation can be affected by the pH of the media for some organic pollutants. Hence, some electrolyses were repeated at BDD with an initial pH of 3 and 20 mA/cm^2 . This value of pH was chosen also to assess the anodic oxidation at the pH of interest for electro-Fenton process, in the perspective of the evaluation of a coupled anodic oxidation-electro-Fenton process. It is worth mentioning that at pH 3 a faster degradation of TOC was achieved. As an example, after 3 hours the abatement of the TOC was about 65 and 74 % for experiments performed with an initial pH of 5-6 (natural pH) and 3, respectively. However, in both cases the electrolyses gave rise to very high final abatements of TOC (close to 99 %).

3.2 Indirect oxidation by electro-generated active chlorine

A widely adopted electrochemical route for the treatment of wastewater contaminated by organic pollutants is the indirect oxidation by active-chlorine electrogenerated by anodic oxidation of chlorides (eq. (10)). In this process, the anodic oxidation of chlorides at suitable anodes gives rise to the formation of chlorine, hypochlorous acid and/or hypochlorite, depending on pH (Eqs. 10 to 12),

which can oxidize the organics near the anode and/or in the bulk (see Eq. (13) in the case of alkaline medium) [21, 22] .



Here, this process was studied by a series of electrolyses of aqueous solutions of catechol (0.45 mM) and NaCl (0.1 M) performed at Ti/IrO₂-Ta₂O₅ anode. The addition of NaCl allowed to strongly increase the abatement of catechol. As shown in fig. 3, at 20 mA/cm² a total removal of catechol was obtained after 7 h (while in the absence of NaCl, in the same operating conditions, the removal of TOC was of about 70 %), thus demonstrating that catechol can be readily oxidized by electro-generated active chlorine.

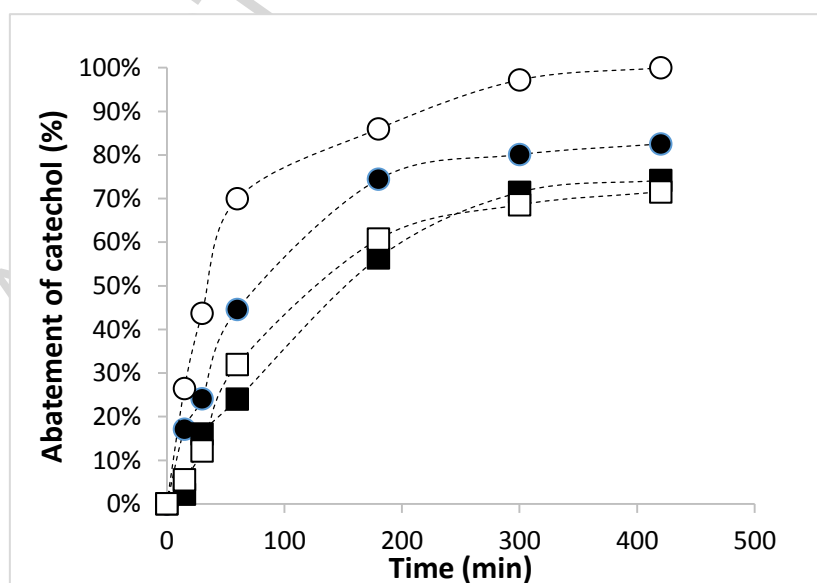


Figure 3. Abatement of catechol vs. time for experiments performed at 10 and 20 mA/cm² with aqueous solutions of catechol (0.45 mM) and NaCl (0.1 M) (• 10, ○ 20 mA/cm²) or Na₂SO₄ (0.1 M) using Ti/IrO₂-Ta₂O₅ anode and Ni cathode and various current densities (■ 10, □ 20 mA/cm²).

However, quite low abatements of TOC were obtained (Table 1) in this process. In particular, at 5 mA/cm², after 1 h an abatement of TOC of about 14 % was achieved (Table 1, entry 1). The abatement of TOC increased up to about 22-24 % after 2 h but it did not change significantly for the rest of the electrolysis. Hence, it seems reasonable to assume that the degradation of catechol by electro-generated active chlorine allows the effective oxidation of catechol, but it results in the formation of some by-products very resistant to further oxidation at least under adopted operating conditions. When the electrolyses were repeated at higher current densities (10 and 20 mA/cm²), the abatement of TOC achieved after 1 h increased with the current, because of the larger amount of charge passed (Table 1, entries 1-3). However, for all the experiments at the end of the electrolyses (7h) the abatement of TOC was always lower than 30 %. Furthermore, after 7 hours, very low *CE* were obtained in the range 2 – 7 % (table 1, entries 1-3).

Quite surprisingly, as shown in table 1 (table 1, entry 2), the addition of NaCl gave rise to lower abatements of the TOC for the same amount of charge passed with respect to the electrolyses performed at the same anode with an inert supporting electrolyte as Na₂SO₄ (table 1, entry 6). This result is probably due to the formation of very resistant organic chlorinated intermediates [21].

The effectivity of the oxidation by eletro-generated active chlorine is expected to depend on the pH for several reasons [21]: 1) lower pH favours the chlorine evolution reaction with respect to water oxidation; 2) chlorine is the predominant species up to pH near 3.0, HClO in the pH range 3 to 8 and ClO⁻ at pH > 8.0. Hence, the oxidation of organics is expected to be favoured in acidic media because of the higher E^0 of Cl_{2(aq)} ($E^0 = 1.36$ V vs. SHE) and HClO ($E^0 = 1.49$ V vs. SHE) compared with ClO⁻ ($E^0 = 0.89$ V vs. SHE). Furthermore, an intermediate pH favours the reaction

between hypochlorous acid and hypochlorite with the formation of chlorate, which is expected to reach the maximum rate at quasi-neutral pH; 3) the possibility to oxidize organics is also affected by pH, since their acid-base equilibria can yield structures with a different proneness to degradation. To evaluate the effect of the pH on the process, some electrolyses were repeated at 20 mA/cm^2 both in acidic (pH 3) and basic (pH 10) conditions. As shown in in Table 1, at pH 10 the abatement of the TOC was significantly lower (entry 5) with respect to that achieved at pH 3 or 6 (entries 3 and 4). Conversely, slightly higher abatements were achieved at pH 3 with respect to that recorded at natural pH, according to the literature (Table 1, entries 3 and 4) [21]. However, the final abatements of TOC were lower than 35 % also at the lower value of pH. Hence, it is possible to conclude that the oxidation of catechol by electro-generated active chlorine does not seem a feasible process from an applicative point of view.

Table 1. Electrochemical treatment of aqueous solutions of catechol by electro-generated active chlorine.^a

Entry	Current density (mA/cm ²)	Initial pH	Time (h)	Abatement of TOC (%)	Current efficiency (CE) (%)
1	5	Natural (5-6)	1	14	30
			7	23	7
2	10		1	17	18
			7	24	3
3	20		1	26	10
			7	29	2
4	20	3	1	25	13
			7	34	3
5	20	10	1	15	8
			7	18	1
6 ^b	10	Natural (5-6)	1	29	30
			7	34	5

^a Abatement of catechol vs. time for experiments performed with aqueous solutions of catechol (0.45 mM) and NaCl (0.1 M) using Ti/IrO₂-Ta₂O₅ anode and Ni cathode and various current densities.

^b Experiment performed with Na₂SO₄ (0.1 M) as supporting electrolyte without NaCl.

3.3 Electro-Fenton

The electro-Fenton process was first studied at carbon felt cathode with FeSO₄ (0.5 mM) as catalyst and Na₂SO₄ (0.1 M) as supporting electrolyte with an initial concentration of catechol of 0.45 mM at 5 and 10 mA/cm². An initial pH 3 was chosen (by addition of H₂SO₄) to optimize the process. Indeed, at pH 2.8 the concentration of Fe²⁺ in the solution is at its maximum, which gives rise to the highest rate of Fenton's reaction, while at higher pH Fe³⁺ species start precipitating as Fe(OH)₃, thereby decreasing the amount of catalyst in the solution [4]. As shown in Table 2 (entries 1 and 2), EF process allowed a very high removal of catechol and a slower but relevant removal of the TOC. In particular, an enhancement of the current density from 5 to 10 mA/cm² allowed higher removal of both catechol (from 83 to 93 %) and TOC (from 46 to 57 %), but a decrease of the final current

efficiency (from 16 to 8%), because at higher currents the process is more limited by the mass transfer of oxygen to the electrode surface, thus favouring the parasitic water reduction.

In order to go beyond one of the limitations of conventional EF process, i.e. the need of operating at an optimal pH of 3 adding a proper acid to the solution, as well as the loss of soluble iron catalyst by precipitation under ferric hydroxide for higher pH, some authors have reported the use of heterogeneous catalysts. In particular, heterogeneous Fenton-like systems utilizing iron supported catalyst, such as zero valent iron (FeO) [23], mineral iron oxides [24] and iron oxyhydroxide (FeOOH) [25], have been reported for the catalysis of Fenton processes. The utilization of pyrite (FeS₂), a common natural mineral found in the earth's crust, has been used as catalyst for both Fenton [26-28] and electro-Fenton [29-32] processes.

Table 2. Electrochemical treatment of aqueous solutions of catechol by electro-Fenton.^a

Entry	Current density (mA/cm ²)	Initial pH	Catalyst	Time (h)	Abatement of catechol (%)	Abatement of TOC (%)	Current efficiency (CE) (%)
1	5	3	FeSO ₄	1	45	25 - 27	54
				7	83	45 - 47	16
2	10	3	FeSO ₄	1	60	31 - 33	33
				7	93	55 - 58	8
3	5	Natural (5-6)	Pyrite	1	67	35 - 37	76
				7	84	85 - 87	26
4	10	Natural (5-6)	Pyrite	1	82	41 - 43	44
				7	84	84 - 86	13
5	20	Natural (5-6)	Pyrite	1	82	58 - 60	31
				7	96	89 - 91	7
6	30	Natural (5-6)	Pyrite	1	81	46 - 48	16
				7	96	76 - 78	4
7	5	3	Chalcopyrite	1	80	21 - 23	46
				7	69	75 - 77	24
8	10	3	Chalcopyrite	1	74	44 - 46	47
				7	70	68 - 70	10
9	5	Natural (5-6)	Chalcopyrite	1	60	26 - 28	56
				7	93	80 - 82	24
10	10	Natural (5-6)	Chalcopyrite	1	82	30 - 32	32
				7	98	79 - 81	12

^a Electrolyses performed at carbon felt anode and Ti/IrO₂-Ta₂O₅ cathode with aqueous solutions of catechol (0.45 mM), Na₂SO₄ (0.1 M) and FeSO₄ (0.5 mM) or pyrite or chalcopyrite (1g/L).

For EF, it was found that mineralization effectiveness was enhanced by the utilization of pyrite [30-32]. Chalcopyrite CuFeS₂ is an antiferromagnetic semiconductor with complex metal oxidation states, including Cu⁺, Cu²⁺, Fe²⁺, and Fe³⁺, which could contribute to the Fenton process [33].

Hence, some EF experiments were repeated replacing the conventional FeSO₄ catalyst with pyrite or chalcopyrite without changing the initial pH of the aqueous solution (which was between 5 and 6). In the case of chalcopyrite, some experiments were performed correcting the initial pH to 3 for the sake of comparison with experiments carried out with FeSO₄. As shown in Table 2, the utilization of both pyrite and chalcopyrite allowed a drastic enhancement of the abatement of the TOC with respect to that achieved with the homogeneous catalyst. As an example, for experiments performed with an initial pH 3 and 5 mA/cm², after 7 hours an abatement of the TOC of about 46 and 76% was achieved using FeSO₄ and chalcopyrite, respectively (Table 2, entries 1 and 7). It is worth mentioning that the utilization of a less initial acidic pH (close to 6) allowed to achieve high final abatement of TOC with chalcopyrite of about 81 % (table 2, entry 9). The utilization of pyrite as catalyst gave also rise to very high abatements of the TOC. As an example, at 5 mA/cm², after 7 hours an abatement of the TOC of about 85% was achieved using pyrite (Table 2, entry 3). It is important to observe that in all the experiments performed with pyrite or chalcopyrite with an initial pH of 5-6, the pH decreased to reach a value lower than 4. As shown in Table 2, for most of the experiments performed with pyrite and chalcopyrite, quite similar final abatements of the TOC were achieved operating at 5 or 10 mA/cm². In order to better assess the effect of the current density on the process, a series of electrolyses was carried out with pyrite with a larger range of current densities (5, 10, 20 and 30 mA/cm²). As shown in fig. 4 and in Table 2, an increase of the current density from 5 to 20 mA/cm² resulted in faster abatements of the TOC, but in lower *CE*. However, a

further increase of the current density to 30 mA/cm^2 resulted in lower final abatements of the TOC. Indeed, for too high current densities the generation of hydrogen peroxide is expected to be limited by the kinetic of the mass transfer of oxygen to the cathode surface. Under these conditions, a further increase of the current densities results in an enhancement of the cathode potential and in a larger involvement of parasitic processes, including the cathodic reduction of hydrogen peroxide to water, thus lowering the concentration of H_2O_2 and, as a consequence, the generation of hydroxyl radicals.

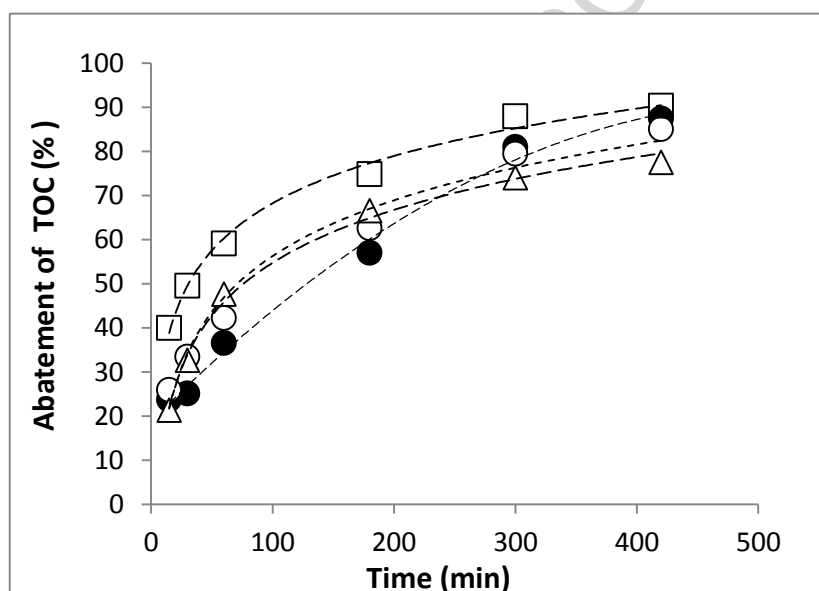


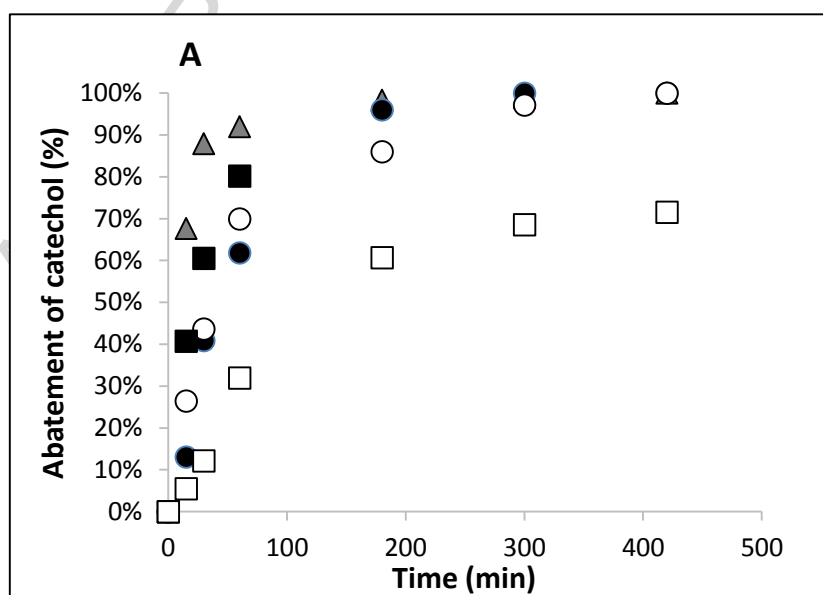
Figure 4. Effect of current density on the abatement of the TOC achieved by EF process with pyrite catalyst. The electrochemical oxidation of an aqueous solution of catechol (0.45 mM) and Na_2SO_4 (0.1 M) was performed at carbon felt cathode and BDD anode at various current densities (● 5, ○ 10, □ 20, △ 30 mA/cm^2) with an initial pH 5-6 with 1g/L of pyrite.

3.4 Comparison between the tested electrochemical processes

In order to compare the performances of all the investigated processes, the trends of the abatements of catechol and TOC and of the current efficiency CE with the time were reported in fig. 5 for

experiments performed at 20 mA/cm^2 and initial pH close to 6. In the case of EF, the experiment performed with pyrite was reported. As shown in fig. 5A, all the routes allowed a relevant removal of catechol. In particular, the highest removals of catechol were achieved by direct oxidation at BDD and indirect oxidation with electro-generated active chlorine, while the lower ones were recorded during direct oxidation at DSA. For EF, it was not possible to estimate the final values of the abatement of catechol, because the formation of a new peak in the *uv-vis* spectra very close to that of catechol did not allow to measure accurately the final concentrations of catechol. Quite relevant, this behaviour was observed for most of EF experiment, thus showing that the EF process gives rise to the formation of a rather resistant by-product.

As shown in fig. 5B, a slightly different picture was observed for the removal of the TOC with the time passed. The direct oxidation at BDD allowed the almost total removal of the TOC. Very high removals of the TOC were achieved also by EF performed with pyrite while both direct oxidation at DSA and indirect oxidation with active-chlorine gave rise to not high removal. As a consequence, AO at BDD and EF gave the highest current efficiencies.



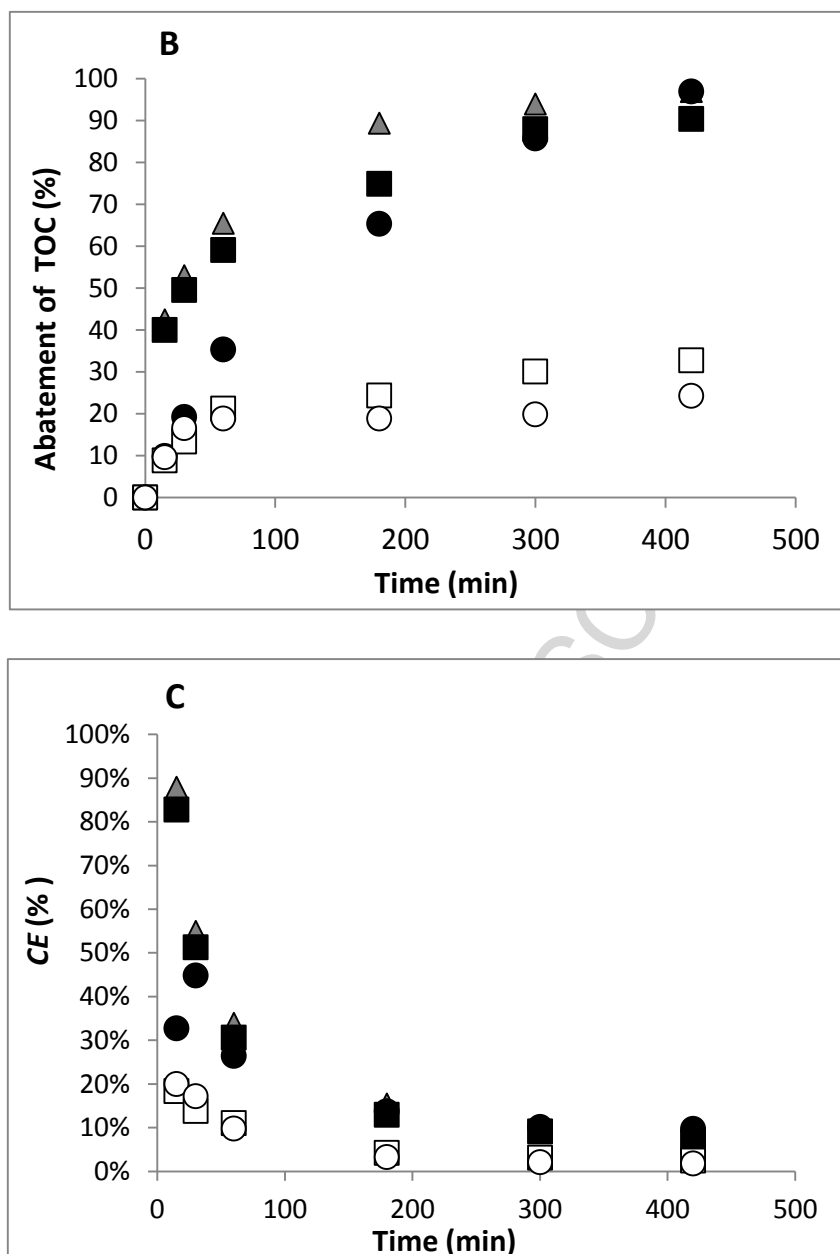


Figure 5. Comparison between direct oxidation at BDD (●) or DSA (□) anode, EF with pyrite (■) and indirect oxidation with NaCl (0.1 M) at DSA anode (○) and EF at BDD (▲) performed at 20 mA/cm² with an initial pH close to 5-6. Fig. 5A and 5B report the abatement of catechol and TOC, respectively, while fig. 5C reports the CE.

HPLC analyses have shown that the oxidation at BDD proceeds with the formation of some carboxylic acids including maleic and oxalic ones. However, their peaks strongly decreased in the

last part of the electrolyses, thus confirming the ability of BDD to mineralize also carboxylic acids [20, 34]. The formation of carboxylic acids (formic, maleic, oxalic and malonic acids) was observed also in the case of electro-Fenton process. Also in this case, the peaks decreased with the time, but presented higher areas with respect to the experiments performed at BDD, according to the literature [35].

3.5 Investigation of the coupled process EF - AO at BDD

In order to enhance the performances of the electrochemical treatment of aqueous solutions of catechol, some EF experiments were performed with pyrite as catalyst and BDD as anode with the aim to achieve the oxidation of catechol by means of $\text{HO}\bullet$ generated by both EF process and water oxidation at BDD anode. It is worth mentioning that the adoption of such coupled process allowed to still improve the high abatements of catechol (fig. 5A) and TOC (fig. 5B) achieved by single processes. Furthermore, in this case the *uv-vis* spectra did not show the occurrence of new peaks, thus showing that the by-product formed by EF was removed by hydroxyl radicals generated at BDD. Some experiments were repeated at 5, 10, 20 and 30 mA/cm^2 , in order to select the optimal current density. As shown in fig. 6A, an increase of the current density from 5 to 10 mA/cm^2 allowed a drastic enhancement of the TOC removal for the same amount of time passed, because the higher charge passed. However, further increases of the current density produce a slight increase of the abatement (fig. 6A) coupled with a strong decrease of the current efficiency (fig. 6B). Indeed, for high current densities the anodic process is kinetically limited by the mass transfer of organics to the anodic surface while EF is limited by the mass transfer of oxygen to the cathode surface. Hence, under these conditions higher current densities result only in a higher impact of parasitic processes and, as a consequence, in lower current efficiencies. Hence, the best current density among the adopted ones is 10 mA/cm^2 .

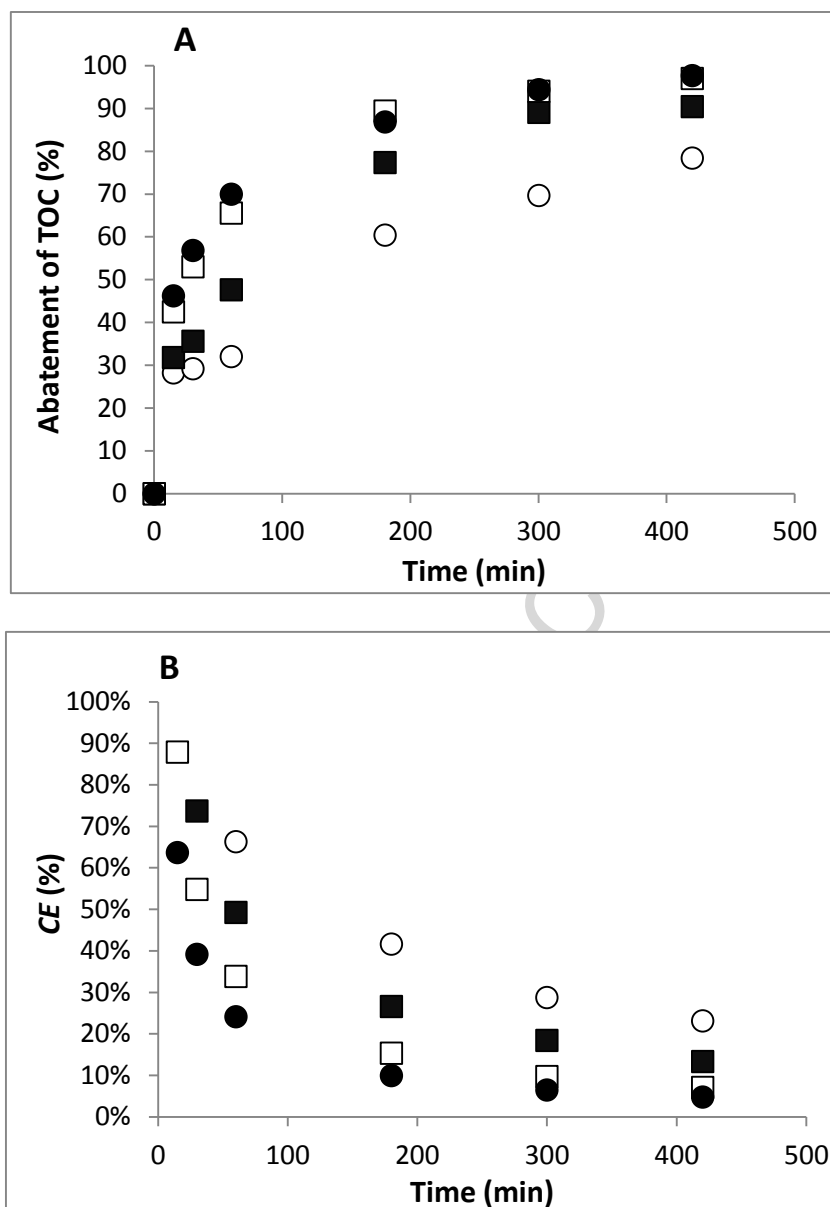


Figure 6. Effect of current density on the removal of TOC (6A) and *CE* (6B) achieved by EF at BDD anode performed at various current densities (○ 5, ■ 10, □ 20 and ● 30 mA/cm²) with an initial pH close to 5-6, 1g/L of pyrite, 0.45 mM of catechol and 0.1 M Na₂SO₄.

4. Conclusions

The treatment of aqueous solutions of catechol was performed by various electrochemical routes. It was found that the performances of the process, in terms of removal of catechol and TOC and of *CE*, dramatically depends on the adopted electrochemical route:

- quite high abatements of both catechol and TOC were achieved by electro-Fenton (EF) and further higher with direct anodic oxidation (AO) at BDD;
- lower abatements of catechol and TOC were obtained by AO at DSA anode;
- high abatements of catechol but very low abatements of TOC were achieved by indirect oxidation by electro-generated active chlorine at all adopted operating conditions;
- the highest abatement of both TOC and catechol were achieved by a coupled EF-AO at BDD process, which allows to use hydroxyl radicals generated by both water anodic oxidation and Fenton process.

The performances of both AO at BDD and EF depended on adopted operating parameters:

- For EF, heterogeneous catalysts such as pyrite and chalcopyrite gave higher removal of TOC and *CE* with respect to homogeneous FeSO_4 and they did not require the addition of an acid to correct the pH. The performances of the process were strongly affected by current density.
- AO at BDD works well at both acidic and natural pH. An increase of the current density up to 20 mA/cm^2 gave rise to an increase of the removal of the TOC for the same amount of time passed.

In conclusion, this work has shown that different electrochemical routes can be effectively used under optimized operating conditions to treat water solutions contaminated by the toxic and very resistant catechol.

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Research highlights

- The mineralization of catechol was performed by various electrochemical processes.
- The performances of direct anodic oxidation, electro-Fenton, oxidation by electro-generated active chlorine and coupled processes were evaluated.
- For electro-Fenton process, higher abatements were achieved with heterogeneous pyrite or chalcopyrite catalysts.
- Very high mineralizations were achieved by electro-Fenton and direct anodic oxidation.

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