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Electrochemical oxidation of paraquat in neutral medium

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ARTICLE INFO

Article history: Received 27 February 2015 Received in revised form 3 June 2015 Accepted 18 July 2015 Available online 26 July 2015

Keywords: paraquat anodic oxidation Co₂FeO₄ electrode electrochemical conversion mass spectrometry

ABSTRACT

Steel, Pt and pelleted Co₂FeO₄ electrodes were used for the electrochemical oxidation of paraquat in aqueous solutions at room temperature. The oxide electrodes were characterized by cyclic voltammetry. *Paraquat* electrochemical oxidation was carried out by electrolysis at constant current and monitored by UV–vis absorbance measurements. Different anode/cathode pairs were used. After 1.5 h of electrolysis the highest removal (\approx 79%), was obtained with the electrode pair Pt/steel followed by Co₂FeO₄/Pt (\approx 55%), corresponding to the *paraquat* oxidation by a conversion mechanism. Removals of \approx 64% were obtained with Co₂FeO₄ / Co₂FeO₄ after 3 h of electrolysis. Mass spectrometry analysis indicates that the main intermediate oxidation products were monopyridone and dipyridone derivatives.

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1. Introduction

Paraquat is one of the most toxic and widely used herbicides in the world. Although it is prohibited by European Union, it is still used in developing countries in other continents. As a nonselective contact herbicide, paraquat has been available to farmers for over 40 years and it is present as an environmental pollutant both in soil and in surface waters. It represents a threat to human health because even at very low doses, this herbicide can pass some treatment steps in a water treatment plant and reach the water distribution systems [1].

Paraquat [($C_{12}H_{14}N_2$)²⁺·2Cl⁻] is a bipyridinium herbicide very soluble in water (625 mg/L at 25 °C), and its IUPAC name is 1, 1'-dimethyl-4, 4'- bipyridinium dichloride, also known as methyl viologen dichloride hydrate (MV). Fig. 1 presents the chemical structure of the 1, 1-dimethyl-4, 4'- bipyridinium dication (MV²⁺). The MV²⁺/MV⁺ redox couple has the lowest reversible standard redox potential known for an organic species in aqueous solution: $E^{\theta} = -0.689$ V vs. SCE [2].

Advanced methods are in demand for effective treatment of herbicide-polluted ground and surface waters. Relevant results were obtained with advanced oxidation processes (AOPs) in which OH• radicals are produced by chemical, electrochemical,

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Electrochemical oxidation methods, which present environmental compatibility, are promising alternatives for the destruction of toxic organic waste [6]. They can be used as a pre-treatment technology in detoxifying ahead of bio-treatment, rather than mineralizing them completely. Due to its effectiveness and ease of operation, the application of electrochemical oxidation to treat effluents containing pesticides was studied with promising results [7]. The overall performance of electrochemical processes is determined by the complex interplay of different parameters, namely, electrode material and electrolysis conditions [8,9]. In the last decade there was a successful development of low cost mixed oxide electrodes with high stability and relevant activity to pollution abatement. During the past years our efforts have been devoted to study mixed valence oxides with spinel structures, with focus on the search of novel electrode materials, for oxygen reactions [10-12]. Recent work has used successfully Fe-Co₃O₄ thin film electrodes (Fe = 0%, 5% and 10%), for the electrooxidation of phenol in alkaline medium. An enhancement of the phenol removal was observed with the presence of Fe in the oxide. For the electrodes with 10% of Fe, around 30% of the initial phenol has been removed at ca. 3 h and the complete removal was achieved after 54 h of electrolysis [13]. The phenol oxidation was accomplished by a conversion mechanism giving rise to different species in solution and as final by-products organic acids. The use of iron-containing materials was also addressed through the so called heterogeneous Fenton like processes [14–16].





Fig. 1. Chemical structure of paraquat dication.

When using active mixed oxides, oxidation reactions occur through a higher oxidation state of the metal oxide surface sites, resulting in a partial oxidation of the organic compounds, due to the accumulation of intermediates, which are quite stable against further attack at these electrodes [8,17]. Accordingly, the metal cations in the oxide lattice may reach higher oxidation states under anodic polarization and a stabilization of adsorbed OH[•] radicals takes place, favoring the oxygen evolution at the expense of the electrochemical incineration reaction. As the best of our knowledge, only one study was published on the anodic oxidation of paraguat aqueous solutions. Pt cathodes and carbon felt anodes were used [18]. It was proposed the formation of demethylation products of the parent compound (4, 4'-bipyridine and monopvridone) and hydroxylation or oxidative ring cleavage products (4-carboxy-1-methyl-pyridinium ion, 4-picolinic acid and hydroxyl-4-picolinicacid), that subsequently undertake minor degradation, leading to incomplete mineralization of the herbicide.

The present work focuses on the electrochemical partial oxidation of *paraquat* in aqueous solution, using Pt, steel and a novel active spinel oxide Co₂FeO₄ as electrode materials. Cyclic voltammetric studies were undertaken to characterize the Co₂FeO₄/MV system. Subsequently several electrolysis operating factors were assessed. Attention was paid to simultaneous anodic and cathodic reactions. The *paraquat* removal and its oxidation intermediates were monitored by UV–vis absorbance measurements and identified by mass spectrometry analysis (MS).

The present study represents a continuing attempt in the search for more active electrode materials and we believe that the results can provide a direction guide for an exploratory study of other spinel oxides of interest for environmental applications.

2. Experimental

2.1. Electrode preparation

 Co_2FeO_4 powder samples were obtained by a previously described coprecipitation method, from the addition of aqueous solutions of FeCl₃·6H₂O and CoCl₂·6H₂O, both Merck pro-analysis, with molar ratio Co/Fe = 2/1, added to a KOH boiling solution under vigorous stirring. A black precipitate was formed and was subsequently filtered and dried on a sand bath at approximately 473 K [19,20]. The dry product was finally heated in a muffle furnace at 1173 K for 6 h.

The electrodes were prepared as parallelepiped pellets with dimensions $1.5 \text{ cm} \times 0.77 \text{ cm} \times 0.19 \text{ cm}$ by pressing the powders onto an inserted platinum mesh, which served as current collector and subsequently heated at 1173 K for 6 h. The electrical contact was made by welding the Pt mesh to a silver wire. The samples were then mounted in a glass tube with epoxy resin (Araldite[®]) so that the electrolyte could only make contact with the oxide.

Pt and steel were used as foils, with an immersed geometric area similar to the oxide electrode.

2.2. Structural and morphological characterization

The pellets were characterized by X-ray powder diffraction, using a Philips PW 1730 diffractometer with automatic data acquisition (APD Phillips v.3.6B) and the ICDD files for X-ray data indexation. All scans were recorded between 15° and 80° 2θ at a

scanning rate of 0.02° s⁻¹, using Cu K α radiation (λ = 1.5406 Å) as the incident radiation.

Morphological characterization was performed by scanning electron microscopy (SEM) using a JEOL (JSM-35C) unit.

2.3. Electrochemical studies

All voltammetric experiments were undertaken in a conventional three-compartment glass cell at room temperature. Before experiments, the solution was saturated with either air or N₂ or O₂, using vigorous bubbling for \approx 30 min. Platinum foil was used as counter electrode and Hg/Hg₂SO₄/K₂SO₄ sat. (+0.656 V vs. SHE) as reference (M.S.E.).

Bulk electrolysis preliminary studies were performed in a three-compartment glass cell, under various constant potentials and/or current intensities, from which the best conditions were selected. The subsequent bulk electrolysis were then accomplished in a one-compartment glass cell at constant current (0.1 A) and room temperature, under magnetic stirring with several duration times. The cell capacity was 100 mL. Co₂FeO₄ and Pt were used as anodes, Co₂FeO₄, Pt and steel as cathodes and M.S.E as reference electrode. The solutions were not deaerated.

Paraquat dichloride 10^{-4} M (Sigma[®]) in 0.05 M K₂SO₄ or KCl (Merck pro analysis) solutions, with pH \approx 7, were prepared using Millipore Milli-Q ultrapure water (18 M Ω cm).

The electrochemical measurements were carried out either using a low noise operational amplifier potentiostat programmed by a PPR1Hi-TEK Instruments wave generator, and a Kipp & Zonen Pro-1 recorder or a VoltaLabTM 32 System (RadiometerTM), consisting of a DEA-I Digital Electrochemical Analyzer, and comprising the IMT102 Electrochemical Interface and the DEA332 33 V/2A potentiostat with the VoltaMaster 2 software.

2.4. Analysis methods

The *paraquat* oxidation was followed by UV–vis absorbance measurements. At regular time intervals, small volume samples were withdrawn from the electrolytic cell and analyzed to follow the *paraquat* removal. Semi– micro quartz cells with 1.4 mL of capacity and 10 mm of optical length were used.

The UV–vis spectra of electrolyzed and non-electrolyzed solutions were acquired with a Jasco V 560 spectrophotometer.

In order to identify paraquat oxidation products, MS experiments were carried out on a LCQ Duo quadrupole ion trap mass spectrometer from ThermoFinnigan (San Jose, CA, USA) equipped with an electrospray ionization source (ESI). A positive potential of +4.5 kV was applied to the electrospray source (electrospray needle) working therefore in positive ion mode. A stream of nitrogen, carrier gas and a counter-flow gas, also nitrogen, 20-40 psi were applied, depending on the sample behavior under the ESI-MS operating conditions. The metallic capillary, located in the system interface, was maintained at 200 °C. The pressure in the region capillary/skimmer of the mass spectrometer recorded a value of 0.92 Torr, while the base pressure in the region of the analyzer and mass detector recorded a value of 1.12×10^{-5} Torr. The samples of analyte solutions were directly introduced into the electrospray source at a flow rate of 5 µL/min. Full scan mass spectra were recorded in the range mass/charge (m/z) ratio 80-285. The mass spectrometer was maintained in operation, registering three microscans with a maximum ion injection time of 50 ms (reference values), whereas the mass spectra obtained were based on a set of microscans equivalent to an operation time of the mass spectrometer of 1 minute. This procedure was adapted from the previously used on paraquat photodegradation studies performed in the same equipment [21].

3. Results and discussion

3.1. Electrode characterization

3.1.1. Structural and morphological characterization

The Co₂FeO₄ electrodes, fresh and after electrochemical tests, were characterized by X-ray powder diffraction. X-ray patterns show the formation of a single spinel phase indexed by comparison with the Powder Diffraction Files of Co₃O₄ (ICDD 9-418), CoFe₂O₄ (ICDD 3-0864) and Fe₃O₄ (ICDD 19-629). Comparing the diffractograms for fresh and used electrodes no structural changes were observed in the oxide after use, as Fig. 2 shows.

SEM images show a fairly homogeneous surface with small grain size and some porosity, which was expected considering the preparation method used. After the electrochemical tests no significant changes were observed on the electrodes surface morphology (Inset Fig. 2).

The electrodes roughness factor was estimated from double layer pseudo-capacitance measurements (SD-1). A roughness factor of ≈ 2 was obtained, indicative of fine and compact powders, which is in accordance with SEM results.

3.1.2. Voltametric studies

The voltammetric behavior of the Co₂FeO₄/0.05 M K₂SO₄ system was studied between 0 and -1.2 V vs. M.S.E. in air, N₂ and O₂ saturated solutions (Fig. 3). The negative potential limit has been established, according to the literature, in order to detect the MV² ⁺/MV^{+•} pair [2]. The recorded voltammograms (CV) present broad peaks, indicating a large heterogeneity in the surface sites and superposition of the redox processes regarding the metal oxide transitions [22]. When the solution is saturated with air or N_2 the CVs are guite similar, presenting a progressive increase of the cathodic intensity current between -0.7 and -1.0 V. On the anodic scan the development of peak A_1 followed by hump A_2 are observed between -0.9 and -0.6 V. Afterwards the current approaches zero and subsequently increases slowly up to the positive potential limit. In O₂-saturated solution, the voltammogram exhibits a different profile: on the cathodic sweep, peak C₄ goes with hump C_3 , between -0.5 and -0.7 V, followed by a current increase until the negative potential limit is reached. On the anodic scan two new peaks (A₃ and A₄) turn up at potentials greater than -0.5 V. These peaks are the anodic counterpart of peaks C₃ and C₄. Moreover an increase of current intensity is observed between -0.9 and -1.1 V. The voltammetric profiles contrast with those already reported by us for the same oxide electrode in alkaline medium. In that case the redox processes take





Fig. 2. X-ray powder diffractograms of (a) oxide electrode after being used in the electrochemical studies (b) Co₂FeO₄ powder. * peaks due to the sample holder.



Fig. 3. Co_2FeO_4 voltammograms in 0.05 M K₂SO₄ in solution under air, nitrogen and oxygen atmospheres, from 0 to -1.250 V vs. M.S.E. at 100 mV s⁻¹. Electrode geometric area: 3 cm².

place on two well-defined regions, separated by a large potential window (400 mV) where no Faradaic currents flow [12,20]. Using voltammetric and literature data [23-25] it was possible to find out the redox reactions occurring at the electrode surface by a method that has been used previously [12,20]. Table 1 presents values of peak potential, formal potential (E^{θ}) taken as the midpoint between the anodic and cathodic peaks and the calculated thermodynamic equilibrium potential (E_{eq}) for the redox couples of the oxide component species. Literature data on Fe₃O₄ and Co_3O_4 oxide electrodes were used for comparison. Peaks A₁ and A₂ occur in the potential region of the oxidation of Fe (II) to Fe (III) surface sites and are assigned to the oxidation of $Fe(OH)_2$ to Fe_3O_4 and Fe_3O_4 to Fe_2O_3 respectively [24,25]. The CVs obtained either in air or N2-saturated solutions indicate passivation of the electrodes surface, probably due to the formation of Fe₂O₃ film which presents low conductivity [23,25]. These results explain the low anodic current intensity in the less negative potentials as well as the absence of peaks on the cathodic scan [24]. On the other hand, the shape of the voltammogram recorded under O₂-saturated solutions suggests that the presence of high amount of oxygen dissolved in solution inhibits the electrode passivation. This fact could be due to the occurrence of reaction (1) that competes with the oxidation of Fe₃O₄ to Fe₂O₃, preventing the formation of Fe₂O₃

$$3Fe_3O_4 + \frac{3}{4}O_2 + \frac{9}{2}H_2O \to 9FeOOH$$
 (1)

The appearance of pairs of peaks A_3/C_3 and A_4/C_4 were assigned to the formation of cobalt oxides/hydroxides, due to the oxidation of weakly hydrated Co^{3+} species [24]. The negative current observed at the switching potential is due to oxide reduction although the occurrence of hydrogen evolution cannot be

Table 1 Peak potential (E_p), formal potential (E^{Θ}) and possible solid-state surface redox processes associated to the voltammetric peaks.

Peak	$E_{\rm p}/{\rm V}$	E/V	Solid-state surface redox process	$E_{\rm eq}/V$
A ₁	$-1.10{\pm}0.03$	-	$2Fe(OH)_2 \leftrightarrow Fe_2O_3 + H_2O + 2H^+ + 2e^-$	-1.127
			$3Fe(OH)_2 \leftrightarrow Fe_3O_4 + 2H_2O + 2H^+ + 2e^-$	-1.267
A_2	$-0.81{\pm}0.08$	-	$Fe(OH)_2 + H_2O \leftrightarrow Fe(OH)_3 + H^+ + e^-$	-0.799
			$2Fe_3O_4 + H_2O \leftrightarrow 3Fe_2O_3 + 2H^+ + 2e^-$	-0.850
A_3/C_3	-	-0.53	$3Co_2O_3 + H_2O + 2e^- \leftrightarrow 2Co_3O_4 + 2 OH^-$	-0.565
A_4/C_4	-	-0.31	$3CoO+H_2O\leftrightarrow Co_3O_4+2H^++2e^-$	-0.293

discarded, considering that for reaction (2) at pH = 7, E_{eq} = -1.070 V vs. M.S.E.

$$2H^+ + 2e^- \rightarrow H_2 \tag{2}$$

On the other hand the cathodic current between -1.1 and -0.9 V is due to the oxygen reduction.

CVs recorded in the presence of MV show a similar profile although with lower current densities, owing to the MV adsorption on the oxide surface, which slows down the redox processes. In order to confirm the presence of the $MV^{2+}/MV^{*\bullet}$ redox pair, the CV presented in Fig. 4, was recorded after polarization at -0.4 V vs. M. S.E for 1 h. Clearly the reduction and oxidation peaks are rather broad and asymmetrical, as expected for adsorbed species undergoing facile electron exchange with substrate [26]. The development of the (A/C) pair of peaks, centered at about -1.0 V vs. MMS, is attributed to $MV^{2+}/MV^{*\bullet}$ [2]. The higher cathodic peak current intensity is due to the reaction between $MV^{*\bullet}$ radical cation with oxygen present in solution, producing hydrogen peroxide, according to equations (3) and (4):

 $MV^{2+} + e^- \rightarrow MV^{+\bullet}$ (3)

 $2MV^{+\bullet} + O_2 + 2H^+ \rightarrow 2MV^{2+} + H_2O_2$ (4)

The reduction is coupled with a subsequent homogeneous chemical reaction and consequently the cathodic current of the first reaction is increased by the second reaction, while the anodic current is decreased by the loss of $MV^{+\bullet}$ [27].

The first reduction of the colorless viologen dication is highly reversible and leads to the formation of the intensely colored radical cation. However, the blue color was not detected in this assay. In order to ascertain the color absence, tests were performed under the same conditions replacing the Co₂FeO₄ oxide by a gold electrode. In this case a blue color was observed. For a direct comparison, the inset, in Fig. 4 presents the CV obtained with a gold electrode where the characteristic paraquat pair of peaks, appears in the same potential zone, confirming the assignment of the A/C peaks. The absence of color on the experiments with the oxide electrode indicates that the reduction occurs inside the oxide pores. This assumption is confirmed by a family of CVs recorded in regular time intervals of 10 min up to 2 h (not shown). The peak current associated with the MV²⁺/ MV^{+•} redox process increases initially and then tend towards constant value owing to the slow diffusion of electroactive species into the electrode pores. This



Fig. 4. Voltammogram for a Co_2FeO_4 electrode in 10^{-4} MMV+0.05 M K₂SO₄, recorded at 100 mV s⁻¹ after polarization at -0.400 V vs. M.S.E. for 1 h. Inset: voltammogram recorded under the same conditions with a gold electrode. Electrodes geometric area: 3 cm².

result shows that the interior of the porous electrodes makes an important contribution to the process.

3.2. Paraquat electrochemical oxidation

3.2.1. Preliminary tests

a)

Preliminary bulk electrolysis were performed to evaluate the influence of supporting electrolyte and type of cell. Electrolysis of 10^{-5} M MV + 0.05 M K₂SO₄ aqueous solutions were done in a three compartments glass cell using as anode materials Co₂FeO₄ or Pt and an applied constant current I = 1.5 A. The paraguat removal was monitored by UV-vis spectroscopy using as reference $\lambda \approx 257$ nm, the typical *paraquat* maximum absorption peak [28]. The electrolyzed solutions spectra did not show any significant differences to the initial spectrum. This could be due either to high ohmic drop or formation of an adherent film on the anode surface, which poisons the electrode surface [29]. The supporting electrolyte was then replaced by KCl in order to avoid film formation and to check the possibility of electrogenerated chloride/hypochlorite ions pair acting as mediator on the MV oxidation. Accordingly, at the anode the chloride ion is oxidized to hypochlorite ion, which could react with the MV and subsequently reduced back to chloride ion. On the other hand, at the cathode the dissolved oxygen is reduced, with the formation of hydrogen peroxide, which could also oxidize the MV [30]. In accordance an increase on the removal rate was expected. However, no significant changes were observed.

A more efficient removal was found by using a one-compartment cell. With these experimental conditions the *paraquat* oxidation could profit from the oxidative ability of both anodic and cathodic reactions [31]. In view of that, all subsequent electrolysis were carried out using a one-compartment cell with magnetic stirring. The MV concentration was also increased to 10^{-4} M.

3.2.2. UV-vis absorption spectroscopy

The effect of the electrode material (Co_2FeO_4 , Pt and steel) on the MV removal from aqueous solution was studied using Co_2FeO_4 as anode. Fig. 5a presents UV–vis spectra of 10^{-4} M MV + 0.05 M KCl electrolyzed solutions during 1.5 and 3 h at 0.1 A.

Spectra show similar variation with the maximum absorbance at $\lambda \approx 257$ nm characteristic of *paraquat* in aqueous solution. A clear decrease in the absorbance maximum is observed depending on the cathode used, indicating that the cathodic processes contribute for the *paraquat* disappearance. Probably at the cathode hydrogen peroxide is electrogenerated, by the reduction of O₂ produced at the anode, generating hydroxyl radicals. Considering the assays with the duration of 1.5 h, the Co₂FeO₄/steel pair exhibits the best performance (\approx 30%) followed by Co₂FeO₄/ Co₂FeO₄ (\approx 20%). When the electrolysis was performed during 3 h and using Co₂FeO₄ as both anode and cathode, the electrolyzed solution spectrum shows a reduction of \approx 65% on the absorbance maximum, more than twice the obtained after 1.5 h, indicating that the *paraquat* removal rate increases with the progress of the



Anode: Co FeO



Fig. 5. UV-vis spectra of 10^{-4} M MV + 0.05 M K₂SO₄ solution after 0, 1.5 and 3 h of electrolysis at 0.1 A, undertaken in a one-compartment cell, with magnetic stirring, using as anodes Co₂FeO₄ (a) and Pt (b) and different cathode materials. Relative absorbance for the different anodes/cathodes (c). * t=3 h.

electrolysis. The *paraquat* peak is still visible after 3 h, accompanied by a hump for $\lambda > 270$ nm, already noticeable for the spectrum recorded after 1.5 h. An increase of absorbance occurs between 220 and 240 nm for the spectra acquired at t = 1.5 h followed by a decrease, probably due to formation of intermediate species, which is in accordance with other authors [28,32]. The comparison of the bands for the *paraquat* electrolyzed solutions and those for possible by-products such as paraquat monopyridone: 225, 257, and 345 nm [33] or 222, 260, 347 nm [34], and paraquat dipyridone: 224 and 320 nm [33], indicates that these compounds are the main by-products of *paraquat* in neutral medium. This assumption is in accordance with published data [18,21,28,32].

Parallel experiments were carried out using Pt as anode. Fig. 5b presents UV-vis spectra of electrolyzed solutions, during 1.5 h. The spectra are symmetrical and show, as expected, the influence of the cathode material. The most striking feature is the shift of the absorption peak to higher values of λ , in the region of the hump observed when Co₂FeO₄ is used as anode. This indicates the formation of a new product, associated with the decrease on the amount of paraquat in solution, which reaches the maximum of absorbance when Co₂FeO₄ is used as cathode. According to other studies [21], the formation of *paraquat* iron complexes formed by ions leached from the oxide electrode into the solution bulk is possible. This assumption is supported by atomic absorption spectroscopic data that indicates the presence of Fe (2.64 ppm) and Co (2.33 ppm) in the electrolyzed solutions. After 1.5 h of electrolysis, the paraquat conversion is \approx 79% for Pt/steel and \approx 55% for the other electrodes (Fig. 5c).

A comparison between our results and selected studies on the *paraquat* degradation is presented in SD-2. The results obtained in this work are similar to those reported for *paraquat* anodic oxidation [18].

The above findings allow concluding that the conversion of *paraquat* on monopyridone, dipyridone and its derivatives takes place for all the tested electrodes. Further oxidation of the generated intermediates was not achieved after 3 h of electrolysis. In order to confirm this proposal, MS analysis was undertaken.

3.2.3. MS analysis

Fig. 6a presents MS with electrospray ionization for nonelectrolyzed and electrolyzed solutions, using Co_2FeO_4 as both anode and cathode.

The paraquat MS (t=0 h) shows two peaks at m/z=171 and m/z=186 with a relative intensity of $\approx 100\%$ and 60% respectively. The peak at m/z=171, corresponds to an ion fragment formed from the intact paraquat ion with loss of the methyl radical [MV^{+•}-CH₃•] ⁺ and the m/z=186 to the intact paraquat radical ion (MV^{+•}). It is also noted a low intensity peak at m/z=113 which, as explained ahead, corresponds to a fragment ion resulting from paraquat.

The appearance of new peaks (m/z = 93, 100, 197, 202 and 216) on the MS obtained for the electrolyzed *paraquat* solutions during 1.5 and 3 h indicates the formation of new ionic species. Table 2 presents an attempt to identify the ions corresponding to the most significant peaks observed on the MS of the electrolyzed solutions. The peaks at m/z = 93 and 186, both due to *paraquat* correspond to the (MV²⁺) dication and the (MV^{+•}) radical cation, respectively. To note that the peak at m/z = 93 is absent on the *paraquat* spectrum,



Fig. 6. Mass spectra with electrospray ionization of 10^{-4} M MV + 0.05 M K₂SO₄ solution after 0, 1.5 and 3 h of electrolysis at 0.1 A, undertaken in a one-compartment cell, with magnetic stirring, using Co₂FeO₄ as anode and cathode (a) and variation of the relative abundance of the peaks observed in the MS with electrolysis time (b).



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probably due to resonance stabilization of the cation radical. The peak at m/z = 113 with low intensity, corresponds to $[MV^{+}-CH_2NCH_3-CH_3NH^{\bullet}]^+$ ions.

Furthermore the peaks at m/z = 100 and 202 are assigned to ionic species associated to monopyridone, while the peaks at m/z = 197 and 216 correspond to ionic species related with dipyridone [21].

The variation of the relative intensity of each peak as a function of electrolysis time is presented in Fig. 6 b. The peak at m/z = 93, absent in the *paraquat* solution appears after 1.5 h of electrolysis with considerable relative intensity $\approx 30\%$, decreasing significantly after 3 h to $\approx 5\%$, which suggests that MV²⁺ species (m/z = 93) is an intermediate in the degradation process.

Regarding the peak m/z = 100, appearing after 1.5 h of electrolysis ($\approx 38\%$) and reaching $\approx 100\%$ after 3 h, indicates the formation of a new product, probably monopyridone or a derivative (Table 2). The appearance of this peak is accompanied by the decrease of the peak with m/z = 171, corresponding to an ion fragment obtained from the MV^{+•} ion, by loss of a methyl radical. The peaks at m/z = 197 and 216 follow a behavior similar to peaks with m/z = 100 and 202, therefore, these species are consistent with the formation of intermediates in the electrochemical oxidation process. It is important to note that, according to the International Programme on Chemical Safety (IPCS) (1991) [35], the resulting oxidation species are less toxic than *paraquat*.

4. Conclusions

These results led to conclude that using anodic oxidation, under the present experimental conditions, *paraquat* is partially oxidized by a conversion mechanism due to the fact that the Co_2FeO_4 electrode has an active behaviour and only permits the partial oxidation.

Voltammetric techniques allowed to identify the redox pair $MV^{2*}/MV^{+\bullet}$. UV-vis and MS spectroscopic data permitted to identify as main intermediate oxidation products monopyridone and dipyridone derivatives.

The paraquat higher conversion rate was obtained when using Pt/steel (\approx 79%) followed by Pt/Co₂FeO₄ (\approx 55%) after 1.5 h of electrolysis. Conversion of \approx 64% was obtained with Co₂FeO₄/Co₂FeO₄ after 3 h of electrolysis.

The use of Pt leads to high costs for practical applications. However a further way to improve *paraquat* oxidation and lower the process costs could be the use of Co_2FeO_4 and Pt nanoparticles composites.

Acknowledgement

The authors gratefully acknowledge financial support by Fundação para a Ciência e Tecnologia – FCT, under contracts UID/ MULTI/00612/2013. M.A.M. Cartaxo also thanks FCT for the grant SFRH/BD/30500.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2015.07.099.

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