Carbon nanotube modified glassy carbon electrode for electrochemical oxidation of alkylphenol ethoxylate

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ABSTRACT

Electrochemical oxidation of an emerging pollutant, 2-(4-methylphenoxy)ethanol (MPET), from water has been studied by cyclic voltammetry (CV). Multiwall carbon nanotubes glassy carbon electrodes (MWCNT-GCE) were used as working electrode due to their extraordinary properties. The oxidation process is irreversible, since no reduction peaks were observed in the reverse scan. The electrocatalytic effect of MWCNT was confirmed as the oxidation peak intensity increases in comparison to bare-GCE. The effect of functional groups on MWCNT was also studied by MWCNT functionalized with NH2 (MWCNT-NH2) and COOH (MWCNT-COOH) groups. The oxidation peak current decreases in the following order: MWCNT > MWCNT-NH2 > MWCNT-COOH. Taking into account the normalized peak current, MWCNT-NH2 exhibits the best results due to its strong interaction with MPET. Under optimal conditions (pH = 5.0 and volume of MWCNT = 10 μL), degradation was studied for MWCNT-GCE and MWCNT-NH2-GCE. A complete MPET removal was observed using MWCNT-GCE after four CV cycles, for a volume/area (V/A) ratio equal to 19. In the case of MWCNT-NH2-GCE, the maximum MPET removal was close to 90% for V/A = 37, higher than that obtained for MWCNT-GCE at the same conditions (~80%). In both cases, no organic by-products were detected.

Key words | advanced oxidation processes (AOPs), cyclic voltammetry, emerging pollutants, endocrine disruptors

INTRODUCTION

Alkylphenol ethoxylates (APEs) are the main components of non-ionic surfactants, which are used to formulate products such as detergents, paints, plastic antioxidants, pesticides, wetting products and petroleum recovery chemicals (Kuramitz et al. 2002; Esteban et al. 2014). APEs are considered an emerging organic pollutants group, mainly due to their endocrine disrupting activity (Murray et al. 2017). Their extensive use in industrial and commercial formulations has resulted in an increase of their presence in sewage sludge and sediments, wastewater, surface waters and even treated drinking water (Kim et al. 2005; Nagarnaik & Boulanger 2011). Furthermore, the degradation of this kind of pollutant in sewage treatment plants leads to the formation of even more toxic and resistant metabolites, responsible for feminization and carcinogenesis on different organisms (Shao et al. 2003).

The European legislation of the Water Framework Directive 2000/60/EC includes some APEs in its priority list (European Commission 2001). In addition, the European Directive No. 2003/53/EC (European Commission 2003) has forbidden the use of nonylphenol and its ethoxylates in the European Union. However, some industrial applications cannot replace them with alternative chemicals due to technical and economic reasons (Karci et al. 2014). Therefore, efficient methods for their removal must be developed.

Conventional treatments of water and effluents are poorly efficient for APEs degradation (Catapane et al. 2013), especially because of their low concentration in the wastewaters, μg·L⁻¹ to ng·L⁻¹ (Patiño et al. 2017a). Thus, new technologies have been proposed for this purpose, such as advanced oxidation processes (AOPs) and electrochemical degradation (Kuramitz et al. 2002; Kim et al. 2005). AOPs include techniques such as ozonation, photocatalysis, and Fenton, which needs greatly reactive oxidizing agents, highlighting hydroxyl radicals (HO·). In spite of AOPs’ widespread uses, they have several disadvantages: high operation
costs, need for additional chemicals and risk of production of harmful by-products.

Even though electrochemical degradation has been less studied than the abovementioned techniques, it presents several advantages, such as the easiness of operation and the mildest temperatures and pressures needed for accomplishing the process. At the same time, pollutant oxidation leads to a complete mineralization of the target compound (Kim et al. 2005). All these facts make this technique a good alternative for APEs degradation.

Although the degradation should be carried out at constant potential, the application of a sweep potential is important in order to characterize the reaction and determine the optimal operation conditions. At this point, cyclic voltammetry (CV) is commonly used to characterize redox systems, as well as to obtain information about the electrode transfer kinetics. Besides, CV has the advantage that with scanning the potential in both directions, it provides the chance to explore the electrochemical behaviour of the compounds generated at the electrode (Settle 1997).

Regarding the working electrode, electrochemical degradation can be improved with modified electrodes, which allow accelerating electron transfer for the electrochemical oxidation. Recently, multiwall carbon nanotubes (MWCNTs) have been proposed to modify electrodes due to their appropriate features – high surface area and porosity, enhanced electronic properties and rapid electrode kinetics (Moyo et al. 2015). Moreover, functionalized MWCNTs can improve dispersion and generate chemical modifications on the electrode surface that promotes the electrode activity. The electrochemical degradation of naldixic acid was studied in a previous work with non-functionalized and functionalized MWCNT modified glassy carbon electrodes (MWCNT-GCE) (MWCNT-NH2 and MWCNT-COOH) as working electrodes (Patino et al. 2017b). The naldixic acid was completely reduced to less toxic compounds using MWCNT-GCE, which demonstrates the effectiveness of this technique. However, it is necessary to extend the study to other compounds with different electrochemical functional groups to demonstrate the efficiency of electrochemical degradation.

For this reason, in this work, the electrochemical oxidation of 2-(4-methylphenoxy)ethanol (MPET) has been studied carrying out an extensive study of the process variables and the working electrode materials. MPET has been selected as representative compound of APEs due to its presence in both surface water and groundwater. In addition, to the best of our knowledge, the electrochemical degradation of MPET has not been reported yet.

MPET degradation has been studied by CV for MWCNT modified glassy carbon electrodes (MWCNT-GCE). Furthermore, the influence of different experimental parameters (pH, scan rate and volume of MWCNT) has been considered. In order to determine the effect of functional groups on MWCNT, the electrochemical behaviour under two functionalized MWCNT – MWCNT-NH2 and MWCNT-COOH – was compared with MWCNT, under optimal conditions.

MATERIALS AND METHODS

Chemicals and reactants

MPET was purchased from TCI Europe N.V., with a purity >98% and used in the experiments directly without any further purification.

The chemicals employed for the phosphate buffer (PBS) (NaCl, KCl, KH2PO4 and Na2HPO4), K4(Fe(CN)6) and K3(Fe(CN)6) were obtained from Sigma-Aldrich.

Three different commercial MWCNT manufactured by Dropsens (MWCNT, MWCNT-NH2 and MWCNT-COOH) were tested in this work.

Instrumentation

CV experiments, as well as the determination of the active surface area of the working electrode, were performed using a Zahner Xpot potentiostat and a µ-Autolab potentiostat/galvanostat PGSTAT20 respectively.

Batch oxidation was carried out in an undivided electrolytic cell with a conventional three electrodes arrangement: bare or modified glassy carbon (GCE) as working electrode, saturated calomel (SCE) as reference electrode and platinum (Pt) as auxiliary electrode. Before each measurement, the solution was deoxygenated by flowing purified nitrogen gas for 20 min, which prevents any interference from oxygen signals. Also, prior to each analysis a blank test was performed analysing the buffer without MPET, to ensure that once the compound was added, the obtained response was only due to MPET degradation.

MPET and the by-products obtained after electrochemical degradation were quantified by gas chromatography mass spectrometry (GC-MS) in a Shimadzu GC/MSQP2010 Plus instrument, using a 30 m long TRB-5MS capillary column. Samples were previously extracted with chloroform using a volume ratio (1:1), which allows determination of concentrations in the order of ppb. The calibration to calculate MPET concentration was obtained
from MPET aqueous solutions at different concentrations, prepared from the pure compound. Likewise, MPET degradation was confirmed by total organic carbon (TOC) measurements, which were carried out using a TOC analyser (Shimadzu TOC-VCSH).

**Preparation of the modified electrodes**

Suspensions of MWCNT were prepared by dispersing the material into dimethylformamide (0.25 g·L⁻¹) by ultrasonication until a well-dispersed suspension was obtained (García-González et al. 2013).

Bare-GCE was polished with 0.3 and 0.05 μm alumina slurry, and washed by ultrasonication in double distilled deionized water. After the electrode was dried in air, it 5, 10 or 15 μL of the MWCNT suspension was dropped onto it and then dried under room temperature before electrochemical measurements (Figure S1, available with the online version of this paper).

**RESULTS AND DISCUSSION**

*Active surface area of the electrodes*

Before starting the experiments, it is necessary to determine the active surface areas. They were determined by CV using 1 mM K₃(Fe(CN)₆) solution in PBS at different scan rates. According to the Randles–Sevcik equation, which correlates the peak current with scan rate potential at 20 °C for an electrochemically reversible process, the active surface area is calculated using Equation (1):

\[
I_p = 2.69 \times 10^5 n^{3/2} A C_0 D_R^{1/2} ν^{1/2}
\]

(1)

where \(I_p\) is the peak current, \(n\) is the number of electron transfer (\(n = 1\)), \(A\) is the surface area of the electrode, \(C_0\) is the concentration of species being oxidized, \(D_R\) is the diffusion coefficient (\(D_R = 7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\)) and \(ν\) is the scan rate. The electrochemically active area can be estimated from the slope of \(I_p\) versus \(ν^{1/2}\).

The electrode surface areas obtained follow the order: MWCNT (0.135 cm²) > MWCNT-NH₂ (0.054 cm²) > MWCNT-COOH (0.051 cm²) > bare (0.040 cm²).

The electrochemical active surface area increases after modification of the GCE with MWCNT, and to a lower extent for MWCNT-COOH and MWCNT-NH₂.

The active surface area of the electrode depends on the surface area of the materials, but also on their properties (specifically, conductivity) and the physical arrangement of the MWCNT layers on the electrode surface. Therefore, pristine MWCNT and COOH-functionalized MWCNT have almost the same surface area (277 and 273 m²·g⁻¹), whereas the surface area of the MWCNT-NH₂ is slightly higher (293 m²·g⁻¹). The highest active area of the modified MWCNT could be caused by a most favourable arrangement of the material (in good agreement with its more regular external surface) and/or their best electronic properties (also in agreement with their more pure aromatic character). Surface area of the MWCNT and the active surface area of the electrode are in good agreement with both functionalized MWCNT, with more similar morphology and electronic properties.

There is also agreement in the literature about the modification of the electrode surface area after the MWCNT deposition, in all cases the final area after modification being higher than for bare-GCE (Patil et al. 2011; Dogan-Topal et al. 2013).

**Electrochemical behaviour of MPET on GCE and MWCNT modified electrode**

The cyclic voltammogram of 1×10⁻⁵ M MPET on bare-GCE and MWCNT-GCE at pH 5 in PBS solution is shown in Figure 1. As is shown in this figure, the MPET oxidation is irreversible for both electrodes, since no peaks were detected on the reverse scan. Oxidation peaks were observed at 1.28 and 1.31 V for bare-GCE and MWCNT-GCE, respectively. It is also observed that the peak current increases at MWCNT-GCE, which clearly indicates the catalytic effect of MWCNT on the electrochemical oxidation of MPET (Jain & Rather 2011; Jain & Sharma 2002). This positive effect is attributed to the electronic properties of the nanotube (delocalized π electrons) and the highest effective area of the electrode. Considering the current density (peak current/electrode area), the maximum value is also obtained for MWCNT, which indicates that the effective surface area is not the only parameter that determines the electrochemical response (Figure 1(b)). The high electrical conductivity of carbon nanotubes accelerates the electron transfer reaction rate in the oxidation process (Gupta et al. 2013). Similar behaviour was also observed by other authors using MWCNT-GCE as working electrode (Fotouhi & Alahyari 2010; Gupta et al. 2013).

Once the influence of MWCNT on the MPET oxidation was demonstrated, it was important to determine the optimum MWCNT content on the electrode surface, since this loading influences the properties and functions of the
electrode surface. For accomplishing this purpose, different volumes – 5, 10 and 15 μL – of the MWCNT suspension were dropped, and the peak current obtained with this electrode was compared (Figure 2). The oxidation peak current shows a maximum at MWCNT suspension volume of 10 μL. The peak current variation is related to the thickness of the film. If it is too thin, the amount of MPET adsorbed on the electrode surface is small, which involves a small peak current. In contrast, when it is too thick, film conductivity is reduced, decreasing the film stability (Jain & Rather 2014; Patil et al. 2011). Moreover, the thick electrode hinders the conductivity through the whole film, reducing in this way the ability of the molecule to be adsorbed and subsequently degraded (Fotouhi & Alahyari 2010; Jain & Sharma 2012; Dogan-Topal et al. 2013). Therefore, 10 μL was selected as the optimum amount of MWCNT suspension and it was used from now on in all the reported experiments.

The effect of the MPET concentration is shown in Figure 3, where the peak current obtained using MWCNT-GCE increases with MPET concentration, following the regression equation:

\[ I_p (\mu A) = 115,254 (M) + 4.4343 \quad (r^2 = 0.9784) \]  

The measurements were carried out in triplicate with a standard deviation less than 1.3 × 10^{-7} in all cases.

**Optimization of operation parameters**

Cyclic voltammograms of 1 × 10^{-5} M MPET on MWCNT-GCE at different scan rates from 10 to 90 mV·s^{-1} were performed in order to investigate the effect of this parameter. By increasing the scan rate, the peak current rises up to 50 mV·s^{-1} and also peak potential shifted towards more positive values, an effect previously described (Fotouhi & Alahyari 2010; Patil et al. 2011; Dogan-Topal et al. 2013). Above 50 mV·s^{-1} the peak current remains constant with
The slope is close to the theoretical Nernstian value (0.059 V), indicating the participation of the same number of protons and electrons during the oxidation reaction (Luczak 2008).

Effect of functional groups of MWCNT

The effect of the functionalization of MWCNT on the electrochemical oxidation of MPET, has been studied by CV using three different modified MWCNT-GCEs as working electrodes: MWCNT, MWCNT-NH₂ and MWCNT-COOH. As is observed in Figure 5, the three materials present very different behaviour. The peak current increases in the following order: MWCNT (12.07 μA) > MWCNT-NH₂ (11.58 μA) > MWCNT-COOH (3.93 μA), coincident with the trend that follows the active surface area (Figure 5(a)). However, in the case of functionalized MWCNT (MWCNT-NH₂ and MWCNT-COOH), where the effective electrode area is very similar, there are large differences in the peak intensity obtained: it is almost three times higher for MWCNT-NH₂, suggesting that another factor influences the oxidation process. It was demonstrated that the process presents mixed control: diffusion-adsorption. During the electrochemical process, MPET is adsorbed on the electrode surface, where the electrochemical oxidation takes place; so the peak current trend may be influenced by the different strength of the adsorption due to the functionalization of MWCNT. The MPET adsorption onto MWCNT and functionalized MWCNT was studied in a previous work, by batch adsorption at three different temperatures (298, 303 and 308 K) (Patino et al. 2015). The strength of the interaction was measured in terms of standard enthalpy (ΔH°, kJ·mol⁻¹) and it follows the order MWCNT-NH₂ (101.7) > MWCNT (88.1) > MWCNT-COOH (67.4). Taking into account the differences in active area of the selected electrodes and trying to determine if the electrochemical oxidation could be influenced by adsorption, the current density has been calculated (Figure 5(b)). The current density decreases in the order: MWCNT-NH₂ > MWCNT > MWCNT-COOH, which is in a good agreement with the strength of the interaction (Patino et al. 2015) (Figure 6). As the strength of interaction increases, the stability of the adsorbed MPET increases, reducing the trend to leave the electrode surface. Thus, the highest is the adsorption strength, the highest is the normalized peak current.

Moreover, MWCNT-NH₂ presents the highest normalized peak current, as the nitrogen content in MWCNT could increase its affinity for MPET. In this case, the
electronic interactions play a key role: the nitrogen acts as electron donor and the MPET aromatic ring as electron acceptor, promoting the pollutant adsorption on the electrode surface (Fan et al. 2014; Patiño et al. 2018). In contrast, surface chemistry does not correlate to peak current. The electrode surface is negatively charged (pH = 5), since pH is, in all cases, higher than the pHPZC of the multiwall carbon nanotubes: pHPZC (MWCNT) = 4.19, pHPZC (MWCNT-NH₂) = 4.70 and pHPZC (MWCNT-COOH) = 0.64 (Patiño et al. 2015). On the other hand, MPET is expected to be in the protonated form (pK_a ≈ 14), acquiring positive charge. Therefore, MWCNT-COOH should present the best behaviour if the effect of the surface chemistry plays an important role, since it presents the most negative surface (pHPZC = 0.64), which is contrary to the results obtained (Patiño et al. 2015).

Removal of MPET using MWCNT-GCE and MWCNT-NH₂-GCE electrodes

MPET degradation has been studied by CV using two different working electrodes, and MPET concentration was analysed after each CV cycle by GC-MS. Although MWCNT-NH₂ presents the highest current density, its lower surface area can be a limiting factor. Therefore, both the effect of the area and the strength of interaction should be considered. For this reason, MWCNT and MWCNT-NH₂ modified GCE have been used as working electrodes.

Both working electrodes were tested by CV using a potential range from 0.9 to 1.7 V for an initial MPET concentration of 1 × 10⁻⁵ M. The final MPET concentration and possible intermediates were analysed by GC-MS to estimate the degradation percentage.

Firstly, the optimum volume/area (V/A) ratio was obtained. MPET oxidation was carried out initially in a total volume of 5 mL for both working electrodes: MWCNT (V/A = 37) and MWCNT-NH₂ (V/A = 98) modified GCE. After the first CV cycle, the MPET degradation was lower than 31% for both working electrodes. Trying to increase the degradation percentage, several CV cycles were successively repeated (Figure 7 empty symbols). The maximum degradation obtained was 79 and 58% for MWCNT and MWCNT-NH₂ respectively (between 2.6 and 2.8 times greater than for just one CV), remaining constant after four CV cycles.

Since it is not possible to increase the MPET degradation by more CV cycles, the next strategy proposed was to decrease the treated volume. In this way, the V/A ratio was modified in order to get higher MPET conversions (Figure 7 full symbols). For MWCNT modified GCE, the
degradation was carried out for a total volume of 2.5 mL (V/A = 19) and from one to five CV cycles. In this case, the conversion obtained after one cycle is more than twice that corresponding to a total volume of 5 mL, and a total degradation was achieved after four CV cycles. In the case of MWCNT-NH₂ modified GCE, the total volume was decreased to 1.9 mL (V/A = 37), because it is the smallest volume that supports the experimental device and it is coincident with the first V/A ratio employed for MWCNT. In this situation the maximum degradation is around 85–90% after three CV cycles. For this working electrode, it was no possible to achieve a total MPET degradation due to the experimental constraints.

When the V/A ratio is the same for both electrodes, MWCNT-NH₂-GCE performs slightly better than MWCNT-GCE, due to the highest interaction strength. The MPET adsorbed on the electrode surface is more stable in the case of MWCNT-NH₂-GCE, hindering its desorption during the degradation reaction. However, when the treated volume is the limiting factor, MWCNT-GCE shows better performance. These results suggest a new strategy for the electrochemical degradation of these kind of pollutants, and the degradation can be performed at constant potential (higher than the peak potential, 1.31 V). Kuramitz et al. (2002) studied the electrochemical removal of p-nonylphenol at constant potential with a carbon fibre electrode as working electrode with a removal efficiency of 100%. Also, the results obtained by electrochemical degradation can be compared with those achieved by other authors using AOPs. Nagarnaik & Boulanger (2011) studied the degradation of APEs by ultraviolet light coupled with hydrogen peroxide (UV/H₂O₂), Fenton’s reagent (Fe/H₂O₂) or photo-Fenton’s (Fe/UV/H₂O₂). The maximum removal efficiency follows the order: UH-UV/H₂O₂ (97.1%) > UFH-Fe/UV/H₂O₂ (85.8%) > FH-Fe/H₂O₂ (95.5%) with values lower or similar than those obtained in the present work. Karci et al. (2014) studied the oxidation of a non-ionic surfactant (NP-10) by three AOPs, where the oxidation efficiency decreased in the order: UV/H₂O₂ (100%) > photo-Fenton (100%) > Fenton (20%).

The final concentration of the reactant, as well as the formation of by-products, was analysed by GC-MS after each test, observing an important reduction of MPET after the electrochemical degradation, which confirms that oxidation takes place. Likewise, no other compounds were detected, which suggests that MPET is completely removed from the aqueous sample. In order to confirm the absence of MPET and other organic compounds in the final solution, Figure 8 shows the evolution of the total organic carbon (TOC) with each new cycle. The analysis was carried out for MWCNT and MWCNT-NH₂ under conditions where maximum degradation was reached. TOC removal values confirm the best behaviour for MWCNT in MPET degradation. TOC results are also consistent with the final MPET concentration, confirming the non-presence of other organic compounds in the final solution.

**CONCLUSIONS**

The obtained results demonstrate the feasibility of quantitatively removing MPET from water using electrochemical methods, as well as the catalytic effect of the addition of MWCNT in this electrochemical degradation.

MWCNT modified GCE exhibits an electrocatalytic effect on the electrochemical oxidation of MPET, with a peak intensity four times higher than bare-GCE.
Different parameters were optimized in order to obtain an improved oxidation: MWCNT volume dropped: 10 μL of MWCNT suspension, pH: 5.0 and scan rate: 50 mV·s⁻¹.

Functionalized MWCNT were checked to determine how the functional groups of MWCNT affect the electrochemical oxidation process. Peak current increases in the order: MWCNT > MWCNT-NH₂ > MWCNT-COOH, coincident with the electrode surface area. The order for the current density (I_p/A) changes in the order: MWCNT-NH₂ > MWCNT > MWCNT-COOH. This trend matches fairly well with the strength of adsorption on the electrode surface and with the nitrogen present on MWCNT-NH₂, which increases the affinity for MPET.

MPET was removed with MWCNT-GCE after four CV cycles under optimal conditions and V/A ratio equal to 19. In the case of MWCNT-NH₂ the maximum degradation obtained was around 90% for a V/A = 37. Degradation was confirmed by TOC measurements, reaching a reduction between 93 and 99% after the four CV cycles, as well as by GC-MS analysis of the treated samples, where no by-products were observed. Therefore, the MPET adsorbed on the electrode surface in each CV cycle is oxidized, allowing a new amount of compound to be deposited and oxidized. This way provides a green methodology without producing more toxic compounds.

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