Multiwalled carbon nanotube-glassy carbon electrodes (MWCNT-GCEs) were prepared and used to immobilize 5-nitroquinoline (5-NQ), 6-nitroquinoline (6-NQ) and 8-nitroquinoline (8-NQ). Cyclic voltammetry was used to study the conventional voltammetric behavior of these NQs dissolved in an aqueous alcoholic solution and compare them with the unconventional voltammetric behavior observed when the NQs were immobilized in a porous layer of MWCNTs. Increased currents and shift to lower overpotential can be explained by the change of the mass transport regime from semi-infinite diffusion to thin layer diffusion. Reduction peak potentials depended on the position of the nitro group (-NO2) in the quinoline structure and the test cell pH. Reduction peak potential of -NO2 was dependent on the mesomeric effect of the resonant structures and the inductive effect of the N heteroatom. ArNO/ArNHOH redox couple was electrogenerated in situ and immobilized on a nanstructured electrode network for all the studied NQs. The redox couple generated from 5-NQ was the most stable with 50% remaining at the 15th cycle. Even though the current intensity observed for 6-NQ was the largest, the stability of 6-NQ was 35% at the same voltammetric cycle. The lowest stability was observed for 8-NQ with only 25% remaining at the 15th cycle.

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Figure 1. Chemical structures of 5-NQ, 6-NQ and 8-NQ.

(For basic pH adjustments) and a WTW 537 pH microprocessor pH meter (for acidic pH adjustments). Electrochemical measurements (cyclic voltammetry, CV) were carried out with a voltammetric analyzer (BASI 100, BASI analytical Instruments, USA). A CHI 650C potentiostat (CH Instruments Inc., USA) and a multichannel potentiostat (MultiEmStat, PalmSense, The Netherlands) were also used. The measurements were performed with a conventional 3-electrode system: a GCE with a 3 mm diameter (model CHI1104, CH Instruments), Ag/AgCl/NaCl (BASI MF-2052) and a Pt wire were used as the working, reference and counter electrodes, respectively.

Preparation of the modified electrodes.—The GCEs were washed and polished with 0.3 and 0.05 μM alumina and thoroughly rinsed with water. The MWCNTs were dispersed following the procedure described in Ref. 9. Briefly, a dispersion (3 mg mL⁻¹) was prepared in 1,3-dioxolane by sonication the mixture three times for 5 min. Then, 5 μL of the MWCNT dispersion were deposited on the electrode surface, and the solvent was subsequently evaporated. The resulting modified electrode is designated as GCE-MWCNT.

Entrapment of NQ in the GCE-MWCNT network.—The GCE-MWCNT was immersed in a solution of 0.1 mM of the nitro compound in ethanol for a given time, i.e., the accumulation time (tac). After this, the electrode was washed with water to remove traces of solvent and any possible excess of nitro compound not trapped on the electrode. After washing, the electrode containing entrapped NQs was placed in an aqueous buffer for the voltammetric experiments.

Voltammetric measurements.—For unconventional voltammetry, the modified electrodes containing electroactive NQ were immersed in a cell containing only the aqueous buffer without a nitro compound. Conventional voltammetry was performed using a GCE immersed in an electrochemical cell containing electroactive NQ dissolved in an aqueous buffer-ethanol solution. All electrochemical measurements were performed after purging the cell solution with N₂ for 5 min. Experiments were carried out at room temperature.

Results and Discussion

Electrochemical behavior of substituted NQs entrapped in MWCNT-GCE.—First, the conventional cyclic voltammograms of NQs in solution were obtained using a GCE (Figure 2A). These NQs exhibited the typical electrochemical behavior of nitroaromatic compounds in buffer solutions;²¹ i.e., for a potential scan starting at −0.3 V and scanning in the negative direction, an irreversible reduction peak appears (peak N1) with a peak potential (Eₚ) that depends on the nitro-substituent position on the NQ. Thus, Eₚ values of −0.52, −0.58 and −0.47 V were observed for 5-, 6- and 8-NQ, respectively. This peak corresponds to ArNO₂ reduction, as shown in Equation 1, producing the reduced hydroxylamine derivative (ArNHOH).

\[
\text{ArNO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{ArNHOH} + \text{H}_2\text{O} \quad [1]
\]

In the reverse scan, oxidation of the hydroxylamine derivative is observed at approximately 0.0 V (peak N2a), resulting in the derivative ArNHOH + 2e⁻ + 2H⁺ → ArNO + 2H₂O [2]

As previously established by our research group, some nitroaromatic compounds can be entrapped in the three-dimensional network of MWCNTs, and unconventional voltammetry can be performed.¹⁰

ArNO. Finally, a second negative sweep reduces the ArNO derivative to ArNHOH (N2b peak). Thus, peaks N2a and N2b form a quasi-reversible redox couple, as described by the well-known Equation 2.

Figure 2. (A) CVs of 0.1 mM of 5-NQ, 6-NQ and 8-NQ in 0.1 M PBS pH 7.0 on GCE. Scan rate = 0.1 V s⁻¹. Inset: The dependence of the Ip values on (scan rate)¹/² for 6-NQ. (B) GCE-MWCNT with 5-, 6- and 8-NQ immobilized by dipping of the electrode in a NQ solution in ethanol. [NQ] = 0.1 mM, tac = 1 s. CVs registered in 0.1 M PBS pH 7.0 (without NQ compounds in solution). Scan rate = 0.1 V s⁻¹. Inset: The dependence of the Ip values on scan rate for 6-NQ.

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Consequently, voltammetric experiments were carried with on a MWCNT-coated GCE with NQ trapped in the MWCNT network instead of being dissolved in solution. The cyclic voltammograms were obtained in 0.1 M PBS at pH 7.0 without NQ in solution (Figure 2B). The same N1, N2a and N2b signals were observed with this unconventional method. A comparison of the conventional and unconventional mode voltammograms shows that they are relatively similar; however, large current intensities were observed for the three NQs in the unconventional mode. Furthermore, according to the results obtained from the Ip versus scan rate or (scan rate)1/2 (inset of Figure 3). The current intensity of both the anodic and cathodic signals decreased with the number of cycles (Figures 3A–3C). This result indicates the stability of the redox couple in the MWCNT network. Figure 3D shows the stability (expressed as percentage of gradual change in the current intensity) as a function of the number of cycles, and 5-NQ was the most stable with 50% remaining at the 15th cycle. Even though the current intensity observed for 6-NQ was the largest (Figure 3B), the stability of 6-NQ was 35% at the same voltammetric cycle. The lowest stability was observed for 8-NQ with only 25% remaining at the 15th cycle.

Influence of the accumulation time and the concentration of NQ on entrapment.—To study the effect of the accumulation time and NQ concentration on entrapment, the procedure described in Experimental sections of this manuscript was used. Voltammograms were recorded at 0.1 V/s after an accumulation time of 10 s. The results showed that in the studied concentration ranges, the current intensity of the nitro group (N1) increased as the concentration of NQ increased for all the studied NQs follow a similar behavior. The dependence of the peak current on the accumulation time was evaluated using solutions of NQ at different concentrations to modify the MWCNT network. As shown in the insert of Figure 4, for 6-NQ, adsorption was practically instantaneous and reached a virtually constant peak intensity value after 1 s, for concentration of 0.1 mM. In the case of the lowest concentrations the maximum was reached at somewhat higher times.

Stability of the ArNO/ArNHOH redox couple.—To estimate the stability or persistence of the ArNO/ArNHOH redox couple on the MWCNT-GCE, consecutive cycles were performed with shorter scans (Figure 3). The current intensity of both the anodic and cathodic couple R-NO/R-NHOH for 5-NQ (A), 6-NQ (B) and 8-NQ (C) encapsulated in MWCNT-GCE (PBS 0.1 M at pH 7.0; Scan rate = 0.1 V s−1). Evolution of the stability of the redox couple as a function of the number of voltammetric cycles (D).

Influence of pH.—The effect of the pH on the reduction peak N1 and the reversible couple (N2a/N2b) peaks was also studied by CV. Voltammograms of GCE-MWCNTs modified with NQs and immersed in a buffer with supporting electrolyte were recorded at pH 2–11. Figure 5 shows the voltammograms obtained at pH values of
Figure 4. Variation in the N1 peak current intensity (Ip N1) versus the concentration of NQ in the immersion solution. Inset: N1 peak current intensity as a function of accumulation time (tac) at different concentrations of 6-NQ.

Figure 5. CVs of the GCE-MWCNT with NQs at several pH values (Britton-Robinson buffer, 0.1 M). Scan rate = 0.1 V s\(^{-1}\).

Figure 6. \(E_p\) vs pH plots of the N1 peak of the GCE-MWCNT modified with 5-NQ (■), 6-NQ (○) and 8-NQ (▲). Figure 6 depicts the influence of the pH on the reduction peak N1 over the entire pH range. In general, all the peaks shifted toward more negative potentials as the pH of the supporting electrolyte buffer increased. Previous studies on the effect of pH on the reduction peak potential of nitroaromatic compounds have shown this effect.\(^{22}\) However, it is important to emphasize that in the present study, no nitroaromatic compounds were present in solution because they were completely immobilized in the MWCNT network.

Figure 6 shows that the dependence of \(E_p\) on pH is higher at an acidic pH than that at a basic pH. At pH 2, 5-NQ and 8-NQ showed nearly the same N1 peak potential, while at basic pH values (9 to 11), 5-NQ and 6-NQ had almost the same peak potential. At acidic pH values, the major species contains a protonated quinoline nitrogen. A change in the slope of \(E_p \) vs pH upon the reduction of the nitro group (N1 peak) was observed for all cases. The linear range was from pH 2.0 to pH 8.0 for 5-NQ and 6-NQ and pH 2.0 to pH 7.0 for 8-NQ. The slope values (\(m\)) are summarized in Table I.

The slopes for all observed voltammetric peaks (N1, N2a and N2b) were very close to the theoretical value of an \(e^-/H^+\) ratio of 1:1 (slopes near \(-0.059\) V, see Table I). These results are consistent with the stoichiometric ratio of transferred protons and electrons in Equations 1 and 2. However, changes in the slopes of the N1 peaks for the three compounds suggest a change in the reaction mechanism. Slopes values between \(-0.024\) and \(-0.034\) V were obtained in the pH range between 8.0 and 11.0, and these values correspond to an \(e^-/H^+\) ratio of 2:1 for the rate-determining step of this reaction.

Based on the possible effect of pH on the voltammetric signals of 5-NQ observed in previous work,\(^{16-19}\) the -NO2 group reduction of the 5-NQ peak (N1 signal) is split into two signals at basic pH values or in aprotic media; i.e., an initial 1-electron reduction step to form the ArNO2•− radical (Equation 3), followed by a 3-electron reduction step to form the hydroxylamine derivative (Equation 4).

\[
\text{ArNO}_2 + e^- \rightleftharpoons \text{ArNO}_2^{\cdot -} \quad [3]
\]

\[
\text{ArNO}_2^{\cdot -} + 3e^- + 4H^+ \rightleftharpoons \text{ArNHOH} + H_2O \quad [4]
\]

Table I. \(E_p \) vs pH slopes (\(m\)) calculated for GCE-MWCNTs modified with 5-, 6- and 8-NQ.

| Compound | N1     | N2a    | N2b    |
|----------|--------|--------|--------|
| 5-NQ     | -0.066 | -0.028 | -0.064 |
| 6-NQ     | -0.061 | -0.030 | -0.068 |
| 8-NQ     | -0.060 | -0.034 | -0.062 |
When GCE-MWCNTs is used, this split was not observed. Previous studies have shown that the formation of the species ArNO₂⁻ is favored on a solid electrode because the electron transfer rate is low. MWCNTs are nanomaterials with good conductive properties that facilitate electron transfer, which could be the reason why the main ArNO₂ reduction signal was not divided into two signals at alkaline pH values (Equations 3 and 4). Nevertheless, changes in the oxidation-reduction mechanism of the redox couple with pH when working with NQ derivatives trapped on this specific surface cannot be ruled out.

Effect of the nitro group position on the peak potential.—As shown in Figures 5 and 6, 8-NQ was clearly reduced at the lowest potential, while 6-NQ was reduced at the highest potential. The potential values of the N1 peak are directly related to the energy required to reduce the -NO₂ group. The experimentally obtained data can be interpreted by taking into account the position of this group on the molecule. Some effects can explain these results. First, consider the aromatic quinoline skeleton of these three compounds. Structures such as pyridine or quinoline are deficient-π systems, and the N heteroatom is a strong electron-withdrawing group. N has a nonbonding electron pair, but the pair is perpendicular to the electron π-cloud of the entire molecule. Thus, this pair of electrons does not participate in the aromaticity, resulting in this kind of molecule acting as a strong base. The resonance structures of a quinoline skeleton (Figure 7) show that the 5-position results in deficient electron density (structure IV, Figure 7). Since the N atom in the -NO₂ group also has a positive charge, the close proximity of both positive charges generates instability in the molecule, favoring the reduction of this group. This was observed for compound 5-NQ, in which the nitro group (N1 peak) was more easily reduced than that in 6-NQ.

However, these resonance structures do not explain the lower E_p of 8-NQ compared with that of the two other compounds. Since the distance between the 8-position of the quinoline skeleton and the electronegative N heteroatom is only two carbon bonds, the inductive effect of the heteroatom predominates over the mesomeric effect (resonance structures). Thus, the electronegative N atom attracts the electron density from adjacent atoms, resulting in the carbon atom in position 8 having a positive charge density. This effect, in addition to the positive charge of the N atom in the -NO₂ group, causes the molecule to be unstable, and reduction of the -NO₂ group is favored. Thus, a mesomeric effect of electron withdrawing from the N heteroatom at the 5-position in the quinoline skeleton is obtained, resulting in the nitro group reduction E_p of 5-NQ changing to a less negative potential close to the E_p of the 8-NQ nitro group reduction and separating the reduction peak potentials of 5-NQ and 6-NQ. Since the 8-NQ reduction is mainly affected by the inductive effect of the N heteroatom in the molecule, this signal appears at the lowest potential.

Another important factor is the nature of the quinoline moiety of the molecule, which is protonated or not depending on the pH. At acidic pH values, the N heteroatom in the molecule is protonated, increasing both mesomeric and inductive effects from this heteroatom. At a neutral pH, the protonated and deprotonated species are equal, and the mesomeric effect discussed above begins to decrease. Finally, at basic pH values, the N heteroatom is not likely to be protonated, and the mesomeric effect is almost completely eliminated. The N1 peak is almost the same for 5-NQ and 6-NQ, and the 8-NQ reduction E_p is a less negative potential than that of the other compounds. These results are consistent with the inductive and mesomeric effect discussions mentioned above.

Surprisingly, this behavior shows that the molecular electronic effects that manifest for species in solution in conventional voltammetry are equivalent to those that manifest for species trapped in the MWCNT network in unconventional voltammetric experiments.

Conclusions

All the NQs studied in this work can be immobilized or trapped in a porous layer of MWCNTs through weak interactions (e.g., hydrogen bonding, π–π stacking, electrostatic forces, Van der Waals forces and hydrophobic interactions) without the formation of covalent bonds. This form of immobilization is particularly attractive because it
allows chemical functionality to be attached while preserving the sp2 structure of the nanotubes, leaving the electronic structure unchanged.

Using the above approach, it is possible to trap NQ species in a porous network of MWCNTs on an electrode to perform unconventional voltammetry, which prioritizes thin-layer-type mass transport and results in larger peak currents and smaller concentration overpotentials. The same conclusion was reached by different authors under very different circumstances.28–33

We have shown that the position of the nitro group in an aromatic structure (quinoline) results in different voltammetric responses and adsorptive properties for 5-, 6- and 8-NQ trapped in a MWCNT-GCE network. The inductive effect of the N heteroatom in the molecule reduces the reduction potential of the nitro group in position 5 at acidic pH values and a neutral pH and decreases as the pH increases.

An ArNO/ArNHOH redox couple was electrogenerated in situ and immobilized on the nanostructured electrode network for all the studied NQS. The redox pair generated from the NQS promoters and their adequate stability represent an important result that can lead to the generation of interfaces with improved electrocatalytic characteristics, as has been demonstrated for other nitro compounds.1,9

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