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Electrochemical Study of 4-Nitrophenol at a Modified Carbon Paste Electrode

María del Mar Cordero-Rando, Manuel Barea-Zamora, Juan M. Barberá-Salvador, Ignacio Naranjo- Rodríguez, Juan A. Muñoz-Leyva, and **José L. Hidalgo-Hidalgo de Cisneros***

Department of Analytical Chemistry, Faculty of Sciences, University of Cádiz, 11510 Puerto Real, Cádiz, Spain

Abstract. A zeolite-modified carbon paste electrode (CPE) has been used for the determination of 4-nitrophenol by differential pulse voltammetry (DPV). The electrochemical reduction of 4-nitrophenol at $-1.0\,\mathrm{V}$ is carried out in a Britton-Robinson medium at pH 3.5. The cyclic voltammetric (CV) behaviour has been investigated to study the nature of the process. Studies on the effect of pH were carried out over the pH range 2–9 with the Britton-Robinson buffer solution, and the influence of pH on peak height and peak potential was analyzed. A linear relationship between peak intensity and concentration is obtained in the range 0.2–$10\,\mathrm{mg\,L^{-1}}$, with a detection limit of $0.04\,\mathrm{mg\,L^{-1}}$; a relative standard deviation of 1.5% for a $5\,\mathrm{mg\,L^{-1}}$ 4-nitrophenol concentration and a relative error of 2.6% were also obtained ($n = 11$).

Key words: 4-Nitrophenol; differential pulse voltammetry; zeolite-modified carbon paste electrode.

Phenols have received considerable attention in waste water analysis programs, and a wide variety of analytical techniques for their determination has been reported. Phenols are common in industrial effluents; the simple phenols are easily degraded and analysis must be done promptly. 4-Nitrophenol is one of the nitrophenols included in the U.S. Environmental Protection Agency List of Priority Pollutants [1, 2]. Phenolic compounds are released into the environment because they are products of many industrial processes; moreover they have been extensively applied as pesticides; the environmental concern of phenol pollution results from the high toxicity of many substituted phenolics to mammals, fish and other aquatic life [3].

Electrochemical techniques have been applied in flow systems to environmentally important reducible molecules, for example aromatic nitro compounds [4]. These methods compare favorably with the usual gas chromatographic methods. Electrochemical detection of 4-nitrophenol and other nitrophenols by a.c. and square wave voltammetry in HPLC has been described using mercury electrodes [5–7]. Differential pulse technique has been used in stripping voltammetry at a mercury electrode in a flow injection system. The use of different electroanalytical techniques has been described: d.c. polarography, a.c. polarography, cyclic voltammetry, adsorptive stripping voltammetry [8–15].

Voltammetric methods are particularly suited to the analysis of a wide variety of organic compounds. Carbon paste electrodes (CPE) are superior to the other solid electrodes in having a lower residual current and noise, and in being very cheap and easy to prepare and replace; these electrodes have a wide range of anodic and cathodic utility. To retain the advantages of CPE and remove most of their drawbacks, modified CPE have been studied, with incorporation of ion exchange resins and clays [13–17]. Zeolites have been used as modifiers for carbon pastes. Zeolites are mixed aluminosilicates containing $(\mathrm{Si,Al})_n\mathrm{O}_{2n}$ frameworks with cations added to maintain charge balance. These minerals contain cavities that are large enough for other molecules to enter. These materials are able to adsorb electroactive species for their direct determination. In this paper, the use of a zeolite-modified carbon paste rotating

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* To whom correspondence should be addressed

electrode (CPRE) for the electrochemical reduction of 4-nitrophenol is studied.

Experimental

Apparatus

A Metrohm E-506 Polarecord coupled to a 663 VA Stand was used for voltammetric experiments, with a rotating carbon paste working electrode (surface area 7 mm^2), a silver/silver chloride reference electrode and a platinum auxiliary electrode.

Reagents and Materials

The zeolite-modified carbon paste was prepared by mixing 5 g of graphite (spectroscopic grade, Ringsdorff-Werke GMBH) with 1.8 mL of mineral oil (light white oil, Sigma) and the necessary amount of zeolite (zeolite mixture, Aldrich) to obtain the required mass proportion. A small amount of this paste was used to fill up the hollow of the working electrode, with help of a small metallic shovel and the surface was smoothed. After each measurement the paste was removed and the cavity of the electrode was cleaned and dried with a tissue. This operation is easy and short (about 2–3 minutes).

Oxygen was removed from solutions by purging with nitrogen.

Artificial sea water was prepared by dissolving different salts in 1 L of twice-distilled water (10 g of $MgCl_2$, 1.5 g of $CaCl_2$, 0.7 g of KCl, 4 g of Na_2SO_4 and 23 g of NaCl, all from Merck, analytical reagent grade). The Britton-Robinson buffer solution was prepared with 2.3 mL of acetic acid, 2.7 mL of orthophosphoric acid and 2.5 g of boric acid in 1 L of twice-distilled water. The pH was adjusted using 1 M NaOH.

4-Nitrophenol stock solutions (5000 $mg\,L^{-1}$, Fluka, analytical reagent grade) were prepared in ethanol (Merck, analytical reagent grade); working solutions were prepared daily by dilution with ethanol.

Procedures

Voltammetric procedure for the study of variables. 40 mL of artificial sea water and 10 mL of Britton-Robinson buffer solution of pH 3.5 were placed in the electrochemical cell. After purging with nitrogen during 15 min, a voltammogram was recorded by differential pulse voltammetry at a zeolite-modified electrode and a potential range from 0 to -1.5 V. After addition of 50 μL of the 4-nitrophenol solution a new voltammogram was recorded. The paste was then removed from the electrode; the cleaning and packing procedures were repeated before new measurements. All the experiments were carried out by differential pulse voltammetry (DPV) except those in which the use of cyclic voltammetry (CV) is clearly specified.

In some cases ethanol can adsorb on the surface of the working electrode thus decreasing the height of the peak. However, the solubility of 4-nitrophenol in water is smaller than in ethanol and our stock solutions had a high concentration, 5 $g\,L^{-1}$ ($3.59 \cdot 10^{-2}$ M). Moreover, 4-nitrophenol samples were prepared by addition of 50 μL of 4-nitrophenol solution in 40 mL of artificial sea water and 10 mL of buffer solution; the percentage of ethanol was very small, 0.1%.

Preliminary studies were performed in stirred 5 $mg\,L^{-1}$ 4-nitrophenol solutions at a 5% modified electrode. For the accumulation studies, the zeolite-modified CPE was placed in the cell containing the stirred 4-nitrophenol solution and the study of the accumulation time and accumulation potential was carried out.

The CV behaviour of 4-nitrophenol was studied using the operating conditions described previously; for these studies, a stationary modified CPE was used.

Calibration graph and study of interferences were carried out by the operating conditions obtained through the study of variables: a 10% zeolite-modified carbon paste rotating electrode, a scan rate of 9 $mV\,s^{-1}$, a pulse amplitude of -100 mV, a rotation rate of 3000 rpm and a pulse repetition time of 0.4 s.

The procedure applied for the analysis of seawater samples is the same as described in the first paragraph of "Procedures" but using 40 mL of seawater samples spiked with different concentrations of 4-nitrophenol. The experimental conditions are the same as in calibration graph and study of interferences.

Results and Discussion

Preliminary Studies

When a zeolite-modified CPE was used an increase in peak height was observed over that obtained at an unmodified electrode: for 5 $mg\,L^{-1}$ 4-nitrophenol, the peak height was 7–8 times higher than that obtained at an unmodified electrode. A smaller increase was obtained when a bentonite-modified electrode was used, and the peak showed a better definition for the zeolite-modified electrode. Results are shown in Fig. 1.

The influence of accumulation time and accumulation potential at a 5% zeolite-modified electrode was

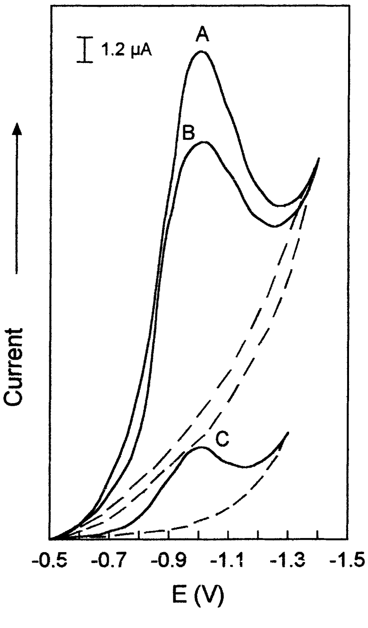

Fig. 1. Voltammograms of 4-nitrophenol (5 $mg\,L^{-1}$) for different modifiers and unmodified carbon paste: (*A*) zeolite 5%; (*B*) bentonite 5%; (*C*) unmodified; rotation rate 1500 rpm, pulse amplitude -40 mV, pulse repetition time 0.4 s

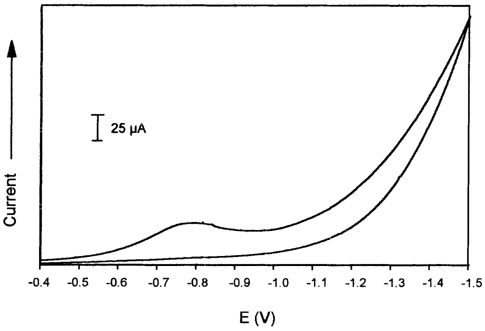

Fig. 2. Cyclic voltammogram for 4-nitrophenol at a scan rate of $25\,mV\,s^{-1}$ in unstirred solution

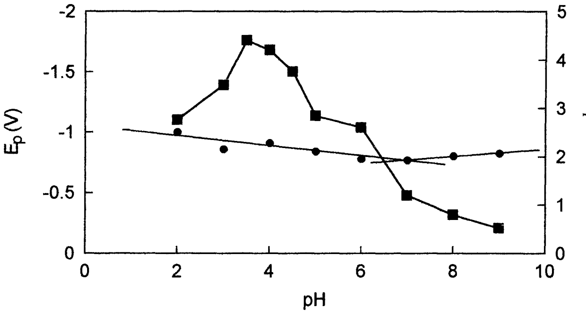

Fig. 3. Effect of pH on i_p (■) and E_p (●) for a $5\,mg\,L^{-1}$ 4-nitrophenol concentration at a 5% zeolite-modified CPE; rotation rate 3000 rpm, pulse repetition time 0.4 s, pulse amplitude −100 mV

studied; these parameters could influence the degree of adsorption of 4-nitrophenol at the electrode. Accumulation is due to the structure of zeolites, that improves the capacity of the electrode to adsorp. No significant increase in peak height was observed with increasing accumulation time. Accumulation potential values with a variation of 0.2 V could be investigated according to the limitations of the voltammetric device. Some dependence of peak height on the accumulation potential was observed. The 4-nitrophenol signals were therefore measured at a potential of 0 V.

The CV behaviour of the analyte was investigated to understand the rate-controlling step of the process. As can be observed in Fig. 2, the signal for 4-nitrophenol appears in the direct curve (reduction), while no peak can be detected in the reverse scan (oxidation); these results reveal an irreversible process. Scan rate studies were also carried out in the range of scan rates $0.01–0.1\,Vs^{-1}$. A linear relationship between peak height and square root of scan rate was found ($r = 0.99$), and the peak potential turns more negative when the scan rate increased. These two factors revealed an irreversible behaviour, in agreement with the absence of signal in the reverse scan. The influence of scan rate on i_p and E_p is also concordant with a phenomenon of adsorption of the analyte on the electrode surface [18].

Influence of pH and Buffer Solution

Studies on the effect of pH were carried out at a 4-nitrophenol concentration of $5\,mg\,L^{-1}$ over the pH range 2–9 with the Britton-Robinson buffer solution. The peak height versus pH plot showed a complex shape. In the range 2–3.5 the peak height increased with increasing pH; at pH 3.5 the peak height, i_p, reached its maximum value. A decrease in i_p was observed with increasing pH in the range 3.5–10; 4-nitrophenol signal disappeared above pH 10. Well-defined peaks were obtained for 4-nitrophenol in the pH range 2–6. The peak is probably due to the reduction of the nitro-group of 4-nitrophenol to an hydroxylamine-group. The peak potential, E_p, shows a dependence on pH with two linear regions with different slopes, and an intersection point at pH 7.0, which agrees with the pK_a value reported in the literature [19]. In Fig. 3, the variation of i_p and E_p with pH can be observed. The pH used for subsequent experiments was pH 3.5.

Artificial sea water: buffer solutions with several buffer solutions of pH 3.5 and at different ionic strength (I) were studied to investigate the effect of this parameter on the analyte response. The ionic strength of the medium (artificial sea water/buffer) can be modified only by variations of the ionic strength of the buffer since artificial sea water has constant ionic strength given by the salt quantities used in its preparation. The effect of a decrease of the ionic strength is an increase of the current intensity due to an increase of the diffusion current constant.

The results are shown in Table 1. There are significant differences in i_p; different peak heights are observed for a given buffer due to the effect of ionic strength. Similar variation was found in the dependence of E_p on ionic strength. The i_p maximum is obtained when the Britton-Robinson buffer solution is used. The less negative peak potential is obtained with the formic acid/sodium formate buffer of ionic strength 0.05, but the peak potential with the Britton-

Table 1. Influence of buffer solution and ionic strength (M) on i_p and E_p; 10% zeolite-modified CPRE, rotation rate 3000 rpm, pulse repetition time 0.4 s, pulse amplitude −100 mV

Buffer solution (pH 3.5)	i_p(μA)	E_p(V)
Acetic acid/sodium acetate I = 0.05	3.7	−1.1
Acetic acid/sodium acetate I = 0.1	1.9	−1.2
Formic acid/sodium formate I = 0.05	4.3	−0.9
Formic acid/sodium formate I = 0.1	2.9	−1.0
Britton-Robinson I = 0.01	4.4	−1.0

Robinson buffer solution is similar. In order to improve the sensitivity a Britton-Robinson buffer of pH 3.5 was used for further studies.

Effect of Percentage of Zeolite

The behaviour of the electrode is improved when zeolite is used in the preparation of the carbon paste. The proportion of zeolite mixed with the carbon paste is a control factor of great interest. As expected, an increase in the percentage gives a higher i_p (Table 2), at least up to 10% zeolite. The peak width did not increase with the percentage of zeolite. When percentages of zeolite above 10% were used, less compact pastes were obtained, which fell away with the rotation movement.

In view of these results, a zeolite percentage of 10% was chosen. This proportion gives the i_p maximum and eliminates the possibility of paste loss.

Effect of the Rotation Rate, Pulse Amplitude and Temperature

The use of a CPRE improves the sensitivity and the peak shape compared with a stationary electrode. The best result of peak height was obtained at 3000 rpm so this was the rotation rate chosen for further studies.

The measurements were always carried out at room temperature. The temperature variations (15–25 °C) lead to negligible differences in the intensity.

Table 2. Effect of the percentage of zeolite within the modified CPE on i_p and E_p; rotation rate 3000 rpm, pulse repetition time 0.4 s, pulse amplitude −100 mV

% Modifier	i_p (μA)	E_p(V)
2.5	3.20	−1.1
5	4.28	−1.0
7.5	4.40	−1.0
10	5.92	−1.0

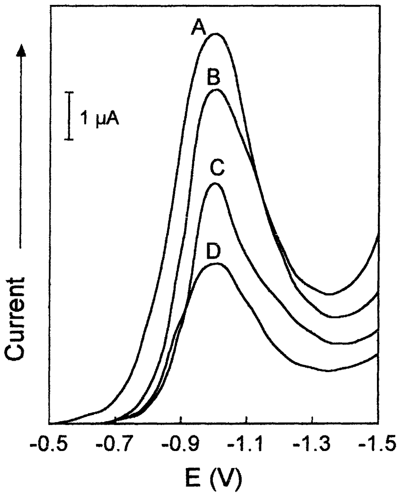

Fig. 4. Voltammograms for different pulse amplitudes at a zeolite-modified CPE for a concentration of 5 mg L^{-1}: (*A*) −100; (*B*) −80; (*C*) −50; and (*D*) −10 mV; rotation rate 3000 rpm, pulse repetition time 0.4 s

The relationship between i_p and the pulse amplitude, ΔE, was linear over the range 0 to −100 mV; this fact is concordant with an irreversible process [20]. Although the peak height increases with the pulse amplitude, the peak width also increases with increasing pulse amplitude and in practice only certain values of pulse amplitude are used. In this work, a pulse amplitude of −100 mV was chosen; in Fig. 4 can be observed that the increase of pulse amplitude leads to small variations of the peak width, whereas peak height increases with increasing pulse amplitude. Less negative peak potentials were obtained when ΔE increased. Thus a pulse amplitude of −100 mV was chosen as the optimum value.

Calibration Graph

A linear relationship exists between i_p and the concentration in the range 0.2–10 mg L^{-1} ($r^2 = 0.9986$) with a slope of 1.11 μA L mg^{-1} and an intercept of 0.03 μA. The detection limit [21] (calculated from $y_B + 3\sigma_B$) was 0.04 mg L^{-1}; a relative standard deviation of 1.5% for a 5 mg L^{-1} 4-nitrophenol concentration and a relative error of 2.6% were also obtained (n = 11).

Interferences

Several organic and inorganic species were tested to ascertain whether they interfered with 4-nitrophenol

Table 3. Effect of inorganic and organic species on the determination of 4-nitrophenol at a concentration of $1\,\mathrm{mg\,L^{-1}}$. Interferent: 4-nitrophenol mass ratio 1:1; 10% zeolite-modified CPRE, rotation rate 3000 rpm, pulse repetition time 0.4 s, pulse amplitude −100 mV

Interferent	Deviation (%)
Ni^{2+}	−6.6
Co^{2+}	−14.8
Zn^{2+}	−12.5
Mn^{2+}	−16.2
Al^{3+}	−21.1
Cr^{3+}	−16.2
Fe^{2+}	−14.8
Fe^{3+}	−5.4
Pb^{2+}	−2.5
Cu^{2+}	−32.5
NH_4^+	−13.3
SiO_3^{2-}	−6.6
NO_3^-	−6.6
CO_3^-	−16.6
PO_4^{3-}	−6.6
Picric acid	+16.4
2,4-Dinitrophenol	+62.0
2-Nitrophenol	–
2-Methyl-4,6-dinitrophenol	+41.9
2,4,6-Trichlorophenol	−15.5
Pentachlorophenol	−7.5
2,4-Dichlorophenol	−19.6
4-Chloro-3-methylphenol	−24.2

signals. Solutions contained an interferent: 4-nitrophenol mass ratio of 1:1 for $1\,\mathrm{mg\,L^{-1}}$ of 4-nitrophenol. Results are shown in Table 3.

Only six inorganic species showed deviations below 10%. The other species showed deviations in the range 12–32%. All the inorganic interferents studied caused negative deviations.

All nitrophenols interfered with the signal of 4-nitrophenol because all of them contain the same reducible group. Picric acid, 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol produced two peaks; the differences of the second peak potentials with respect to the peak potential for 4-nitrophenol were not enough to detect selectively the analyte, and high deviations were obtained. For 2-nitrophenol, the peak height was much higher than for 4-nitrophenol and the signal for the analyte appears as a shoulder which could not be adequately measured.

Except for pentachlorophenol, chlorophenols caused deviations above 10%. These compounds showed less cathodic activity than that observed for nitrophenols, probably due to the reductive dechlorination at the ortho and para positions but the influence on 4-nitrophenol signals was high and high deviations were obtained.

The method for the determination of 4-nitrophenol was applied to seawater samples taken in the Bay of Cádiz. No signal for 4-nitrophenol was observed when the samples were analyzed. Thus, the method was applied to samples spiked with 4-nitrophenol. Several sea water samples were spiked with 4-nitrophenol giving concentrations in the range $0.1–1\,\mathrm{mg\,L^{-1}}$. The results show excellent recoveries of 98.1% and 98.2% for 0.5 and $1\,\mathrm{mg\,L^{-1}}$ respectively. For a $0.1\,\mathrm{mg\,L^{-1}}$ 4-nitrophenol concentration a recovery of 98% was obtained.

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