Exhaustive oxidation/reduction of nitrite, nitrate and hydrazine using a square wave potential regime

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Abstract

Exhaustive oxidation–reduction of nitrite, nitrate and hydrazine was achieved by application of a square wave potential regime to a platinum electrode. The parameters of the square wave were chosen after investigation of the adsorption behaviour of the three compounds. The three compounds were found to adsorb and desorb at a platinum electrode in the potential window from -0.2 V to 1.3 V and hence the lower potential of the square wave was -0.2 V while the upper potential was 1.3 V. The square wave was applied to a solution containing the test compound for 10 h. The results of analysis indicated a decrease in the concentration of the tested compounds with respect to the control sample. The optimal frequencies for the conversion were 10, 50 and 10 for nitrite, nitrate and hydrazine, respectively. Analysis of solutions for possible products of the exhaustive oxidation gave negative tests for NO_2^-, NO_3^-, and NH_3 leaving the possibility of conversion to nitrogen as the end product.

1. Introduction

Elimination of hazardous chemicals and pollutants is receiving considerable attention in water treatment [1, 2]. Electrooxidation or reduction is one of the promising approaches to destruction of pollutants [3–5]. Electrochemical cleaning, by cycling the electrode potential between the hydrogen evolution limit and the oxygen evolution limit in aqueous media, has been used to clean electrode surfaces [6]. On the premise that the square wave comprises a complete potential cycle which may involve dissociative adsorption and desorption of some compounds, we have applied a square wave to a solution containing thiophene where the exhaustive oxidation–reduction of thiophene to water, carbon dioxide and SO_4^{2-} was demonstrated [7].

The present work aims at extending the applicability of well-designed potential regimes for exhaustive oxidation–reduction of some nitrogen-containing compounds; nitrite, nitrate and hydrazine. Thus, a potential regime based on adsorption–desorption data, is designed, such that adsorption and desorption of the compounds or their oxidation–reduction intermediates occur in a single potential cycle. Analysis of the solutions after application of the potential regime demonstrates the feasibility of the elimination process for the tested compounds.

2. Experimental details

2.1. *Cell, materials and electrodes*

A 362 potentiostat (Princeton Applied Research) with a Philips x–y recorder was used for electronic control and data acquisition. A conventional, H-shape, three-electrode cell equipped with a multiple inlet system for admission of the supporting electrolyte, purging and blanketing solution with oxygen-free nitrogen was used for voltammetric measurements. All the potentials reported in this paper are referenced to the Ag/AgCl/ [Cl⁻] (1.0 M) electrode. The working electrode used for voltammetric measurements of adsorptive behaviour of the compounds was a 1 mm diameter platinum rod (99.99% pure, Johnson Matthey). The real surface area of the electrode was estimated from hydrogen UPD data to be 0.5 cm². The purged supporting electrolytes were dispensed from bubblers into the electrochemical cell by gravity action. All the tubes used for purging with nitrogen or used for conveying solutions to the cell were made of PTFE (Cole Parmer).

Another three-electrode, 500 ml capacity, bulk-electrolysis cell was used for testing the feasibility of exhaustive oxidation–reduction of nitrite, nitrate and hydrazine. The working electrode was a platinum foil working electrode with a surface area of 3.22 cm². A platinum foil auxiliary electrode and a Ag/AgCl/[Cl⁻] (1.0 M) reference electrode were housed in an insert tube whose bottom was made of a fine-pore glass frit.

All the reagents used were highly pure certified analytical reagent grade (AR) chemicals and used as received without further purification. The electrode material was 99.99% platinum (Johnsen Matthey). All solutions were made from the aforementioned reagents dissolved in triply distilled water.

2.2. Experimental procedures

For the potentiostatic adsorption measurements of the three compounds, the electrode was initially cleaned with a freshly prepared chromic acid solution, and characterized by cyclic voltammetry. The working electrode was potentiostatically allowed to equilibrate with a 0.5 M H_2SO_4 solution which contained 1.0×10^{-3} M of the test compound for 5 min. After extensive rinsing, with plain 0.5 M H_2SO_4 solution the voltammogram of the dosed platinum electrode was recorded in plain 0.5 M H_2SO_4. This procedure was applied to nitrite, nitrate and hydrazine.

After investigation of the adsorptive behaviour of the test compound on platinum, a potential regime was designed for exhaustive oxidation–reduction. A square wave supplied from a function generator (Simpson 420) was fed into the external input of the potentiostat. The square-wave parameters were chosen such that adsorption and desorption of the test compound occurred within the potential limits of the square wave. The square wave was applied to the working electrode for 10 h. By the end of this period, the concentration of the test compound was determined photometrically [8]. A control experiment was performed by maintaining the same experimental conditions except for application of the square wave. The results were corrected by subtraction of the change observed, if any, in the control experiment.

3. Results

3.1. Potentiostatic adsorption of nitrite, nitrate and hydrazine

Figure 1(a) shows a representative voltammogram of a polycrystalline platinum electrode that was potentiostatically pretreated with nitrite at $+0.2$ V. The voltammetric features for reduction of adsorbed nitrite merge with those for hydrogen adsorption as indicated by the enhanced charge under the hydrogen adsorption peaks. The presence of hydrogen desorption peaks, on the other hand, indicates that the reduction of adsorbed nitrite insignificantly interferes with hydrogen adsorption at the platinum electrode. Hence, the difference between the charge due to hydrogen desorption and the adsorbed nitrite reduction/hydrogen adsorption peaks is taken as a measure for nitrite coverage on the platinum surface.

Figure 1(b) shows the positive-going potential scan for the platinum electrode pretreated with nitrite at $+0.2$ V. Nitrite oxidation is manifested by a hump in the oxidation region starting from $+0.7$ V, and peaking at
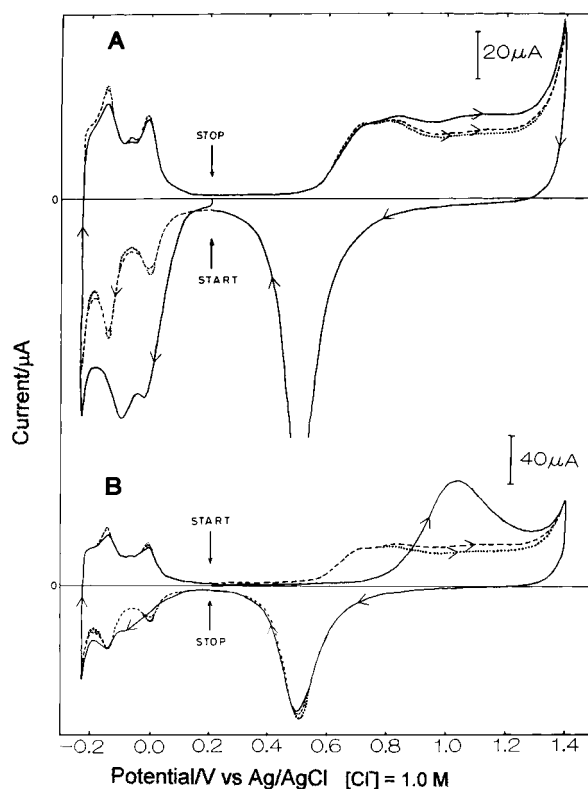

Fig. 1. Cyclic voltammogram of a Pt electrode pretreated potentiostatically with NO_2^- at $+0.2$ V in 0.5 M $H_2SO_4 + 1.0 \times 10^{-3}$ M NO_2^-. Cyclic voltammogram recorded in NO_2^--free 0.5 M H_2SO_4 at 50 mV s^{-1}. (a) Negative-going scan; (b) positive-going scan. Key: (——) first scan, (- - - -) second scan and ($\cdots\cdots$) third scan.

$+1.02$ V. The counter peak for oxygen desorption shows no significant difference between the first potential cycle and the subsequent ones. This indicates that nitrite oxidation occurs concurrently but with negligible interference with oxidation of the platinum surface. This allows calculation of the charge due to oxidation of adsorbed nitrite from the charge underneath the oxidation peak with correction for the charge of the oxidation of the nitrite-free platinum surface.

Figure 2 shows the charge due to oxidation of adsorbed nitrite and the charge due to reduction of the adsorbed nitrite as a function of adsorption potential relying on the above-mentioned criteria. This Figure illustrates that the nitrite coverage decreases in the potential range -0.2–0.2 V with decreasing potential but shows less dependence on potential in the range 0.2–0.6 V. The decrease in the coverage in the potential range -0.2–0.2 V can be attributed to the lower stability of nitrite at lower potentials.

A representative negative-going i/E curve for a platinum electrode pretreated with nitrate at $+0.2$ V is shown in Figure 3(a). The hydrogen adsorption region on the voltammogram is marked by a decrease in the areas under the hydrogen adsorption and desorption peaks. The decrease in the area under these peaks suggests that the electrode surface is partially covered with adsorbed nitrate. We have taken the difference in charge between the charge under the hydrogen
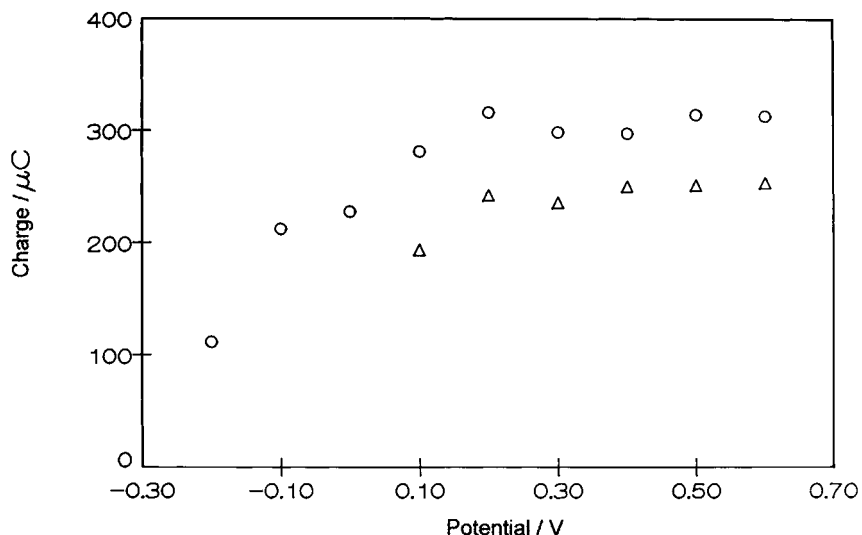
Fig. 2. Charge corresponding to NO_2^- adsorption at Pt electrode against potential at which the nitrite was adsorbed. NO_2^- was adsorbed potentiostatically from 0.5 M $H_2SO_4 + 1.0 \times 10^{-3}$ M NO_2^-. Key: ($\triangle$) charge due to reduction of adsorbed nitrite and ($\bigcirc$) charge due to oxidation of adsorbed nitrite.

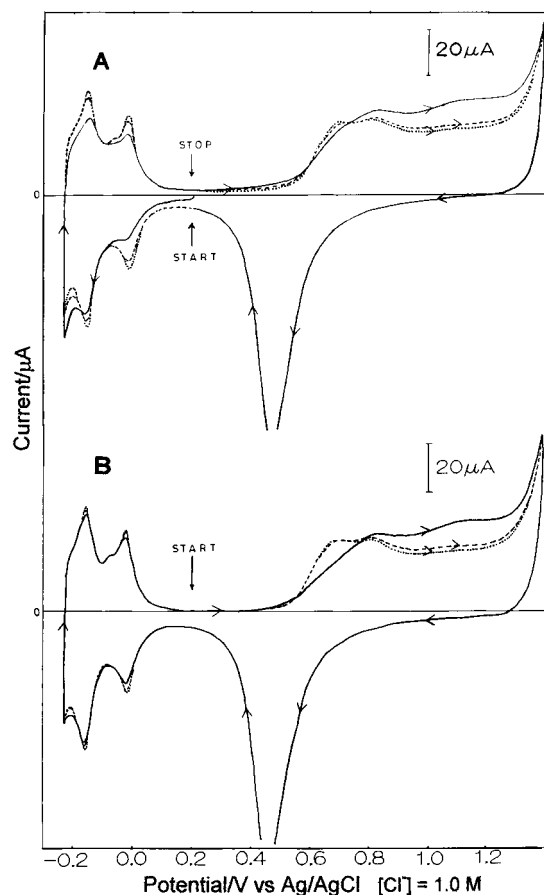adsorption peaks in the absence and in the presence of nitrate at the surface of the electrode to be proportional to the nitrate coverage at the surface (Figure 4).

Fig. 3. Cyclic voltammogram of a Pt electrode pretreated potentiostatically at $+0.2$ V with NO_3^- in 0.5 M $H_2SO_4 + 1.0 \times 10^{-3}$ M NO_3^-. Cyclic voltammogram recorded in NO_3^--free 0.5 M H_2SO_4 at 50 mV s^{-1}. (a) Negative-going scan; (b) positive-going scan. Key: (——) first scan, (- - - -) second scan and ($\cdots\cdots$) third scan.

Figure 3(b) shows the positive-going scan for the platinum electrode pretreated with nitrate at 0.2 V. For a similar argument to that discussed in the case of nitrite adsorption, the area between the oxidation peak for the nitrate-dosed electrode and the oxidation peak for the nitrate-free surface was taken as a measure for the nitrate coverage at the platinum surface. The charge due to nitrate oxidation as calculated from the charge underneath the oxidation peak after correction for the surface oxidation background as a function of electrode potential is depicted in Figure 4. The maximum adsorption occurs at -0.10 V where the surface is partially covered with hydrogen which may form some hydrogenated intermediates with the nitrate.

Figure 5 shows a representative voltammogram for a platinum electrode that was potentiostatically pretreated with hydrazine at $+0.20$ V. The voltammogram shows two fairly well resolved peaks centred at 0.03 V, 0.22 V in addition to a wave in the oxidation region. These peaks are attributed to stepwise oxidation of the adsorbed hydrazine. The fifth potential cycle produced a voltammogram very close to that of the clean platinum electrode.

Similarly, the difference in charge between that underneath the oxidation peak for the first potential cycle and that underneath the fifth potential cycle is taken as a measure for the amount of adsorbed hydrazine. Figure 6 shows the oxidation charge of the adsorbed hydrazine as a function of adsorption potential. The maximum adsorption of hydrazine occurs at -0.1 V similarly to the adsorptive behaviour of nitrate.

3.2. Exhaustive oxidation–reduction of nitrite, nitrate and hydrazine

3.2.1. Exhaustive oxidation–reduction of nitrite
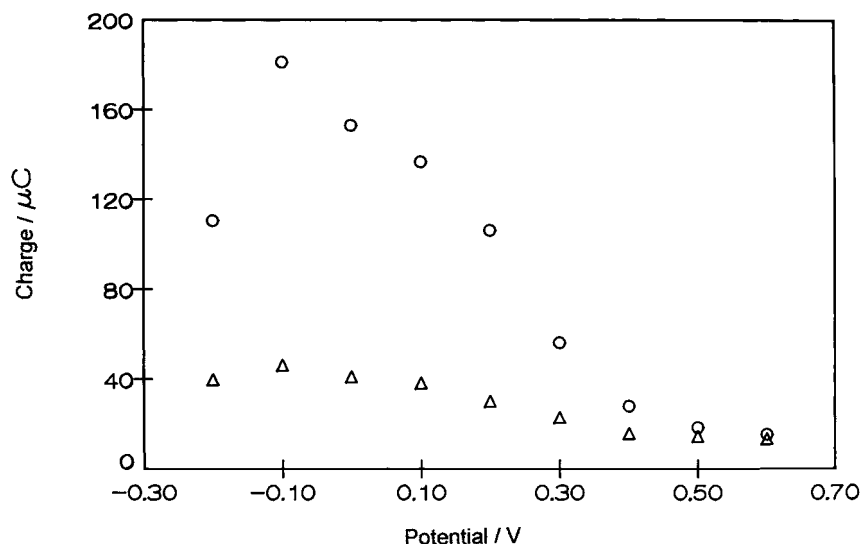A square wave with 1.3 V and -0.2 V potential limits was applied to the working electrode in a solution

Fig. 4. Charge corresponding to NO_3^- adsorption at Pt electrode against adsorption potential. NO_3^- was adsorbed potentiostatically from 0.5 M $H_2SO_4 + 1.0 \times 10^{-3}$ M NO_3^-. Key: ($\triangle$) charge due to suppression of hydrogen adsorption and ($\bigcirc$) charge due to oxidation of adsorbed NO_3^-.

containing 0.01 M nitrite solution without addition of supporting electrolyte to avoid interference with the subsequent analyses. The concentration of the nitrite was measured photometrically after ten hours from applying the square wave regime to the working electrode. The results were corrected by subtracting the change observed in the control experiment. The results are depicted in Figure 7(a) indicating that the optimal frequency for exhaustive oxidation–reduction of nitrite is 10 Hz. Since a finite time is needed for adsorption and desorption, a square wave with high frequency might be too fast to allow adsorption and desorption to occur and hence the exhaustive oxidation efficiency deteriorates. On the other hand, at very low frequencies, though the exhaustive oxidation of the

nitrite is efficient in a single potential cycle, the number of adsorption–desorption cycles per unit time is low and consequently the exhaustive oxidation–reduction efficiency is low. Thus, the optimum frequency compromises the suitable time scale for adsorption and desorption and the number of cycles per unit time.

The fate of the exhaustive oxidation/reduction of nitrite in the solution might be one of the species NH_3, NH_4^+, NO_3^-, one of the nitrogen oxides or elemental nitrogen. The solution was analyzed for NH_3, NH_4^+ where a negative test was indicated for NH_3 and NH_4^+ (Nessler's reagent). Nitrate ion was detected in the solution and its quantification amounted to a value of 18% conversion of the nitrite to nitrate. The fate of the other 82% of the converted NO_2^- was not amenable to
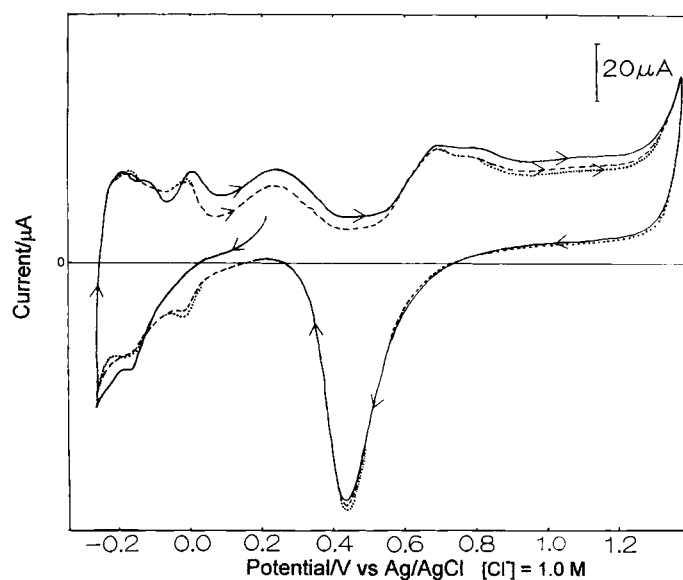

Fig. 5. Cyclic voltammogram of a polycrystalline Pt electrode pretreated potentiostatically at 0.2 V with hydrazine in 0.05 M $H_2SO_4 + 1.0 \times 10^{-3}$ M N_2H_4. Voltammogram was recorded in hydrazine-free 0.05 M H_2SO_4 at 50 mV s^{-1}. Key: (——) first scan, (- - - -) second scan and (······) third scan.
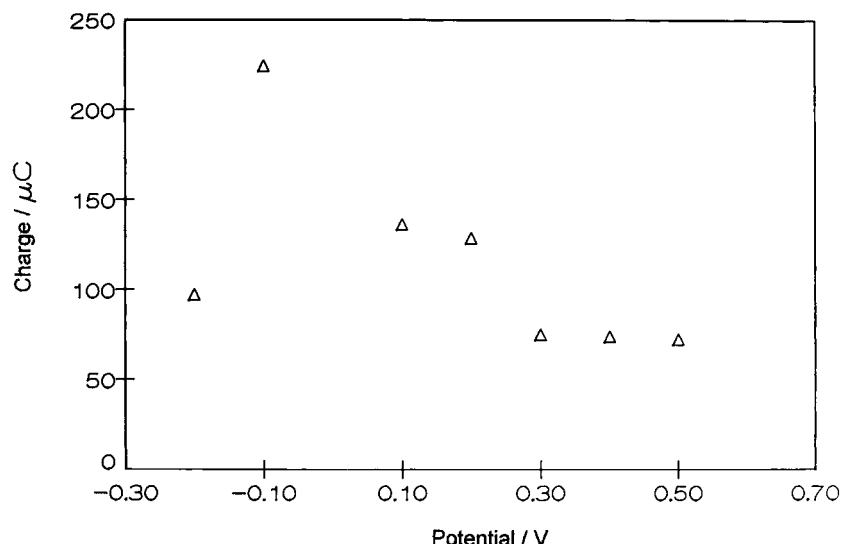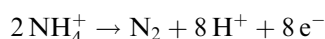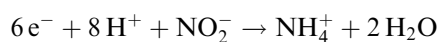
Fig. 6. Charge corresponding to hydrazine adsorption at a Pt electrode against adsorption potential. Hydrazine was potentiostatically adsorbed from 0.05 M $H_2SO_4 + 1.0 \times 10^{-3}$ M N_2H_4.

detection in the solution. This indicates that NO_2^- is converted to nitrogen. The following equations explain the fate of the nitrite in the solution [9–11]:

$$6\,e^- + 8\,H^+ + NO_2^- \rightarrow NH_4^+ + 2\,H_2O$$

$$2\,NH_4^+ \rightarrow N_2 + 8\,H^+ + 8\,e^-$$
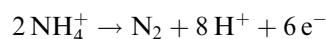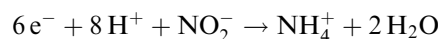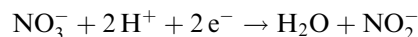
$$H_2O + NO_2^- \rightarrow NO_3^- + 2\,H^+ + 2\,e^-$$

3.2.2. *Exhaustive oxidation–reduction of nitrate*

A square wave with 1.3 V as the upper potential and -0.2 V as the lower potential was applied to a working electrode in 0.010 M NO_3^- without addition of supporting electrolyte to avoid interference with the subsequent analysis of the nitrate. Although a lower potential of 0.2 V seemed to be sufficient, the lower limit was extended to -0.2 V to avoid any potentiostatic limitations. After application of the square wave for 10 h the solution was analysed for the concentration of nitrate. The control experiment indicated that the concentration of nitrate in the solution showed no change. Figure 7(b) shows the concentration change as a function of the frequency of the applied square wave. The optimal frequency for the exhaustive oxidation–reduction of nitrate appears to be 50 Hz. As in the case of exhaustive oxidation of nitrite, this frequency compromises the efficiency of adsorption–desorption in a single cycle with the number of cycles per unit time.

Analysis for potential products of exhaustive oxidation/reduction of nitrate gave negative tests for nitrite, ammonia and ammonium ions. Thus, the most possible end product for the exhaustive oxidation for nitrate is molecular nitrogen.

The following equations describe the fate of NO_3^- in the solution [9–11]:

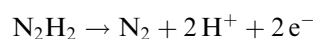$$NO_3^- + 2\,H^+ + 2\,e^- \rightarrow H_2O + NO_2^-$$

$$6\,e^- + 8\,H^+ + NO_2^- \rightarrow NH_4^+ + 2\,H_2O$$

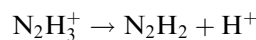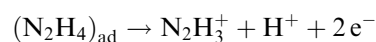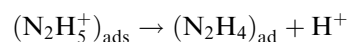$$2\,NH_4^+ \rightarrow N_2 + 8\,H^+ + 6\,e^-$$

3.2.3. *Exhaustive oxidation of hydrazine*

A square wave with $E_h = 1.3$ V and $E_l = -0.2$ V was applied to the working electrode in a solution containing 0.010 M hydrazine + 0.05 M H_2SO_4 solution. The parameters of the square wave were selected such that adsorption and desorption of hydrazine occurred in the same potential cycle. The concentration of the hydrazine was measured spectrophotometrically ten hours after applying the square wave regime to the working electrode. The results were corrected by subtraction the change observed in the control experiment. Figure 7(c) shows that the optimal frequency for exhaustive oxidation of hydrazine is 10 Hz. Again, the optimum frequency compromises the suitable time scale for adsorption and desorption and the number of potential cycles per unit time.

The fate of the exhaustive oxidation-reduction of hydrazine in the solution might be one of the species NH_3, NH_4^+, NO_3^-, NO_2^-, N_2, or one of the nitrogen oxides. The solution was analysed for NH_3, NH_4^+, NO_2^- and NO_3^- where a negative test was indicated.

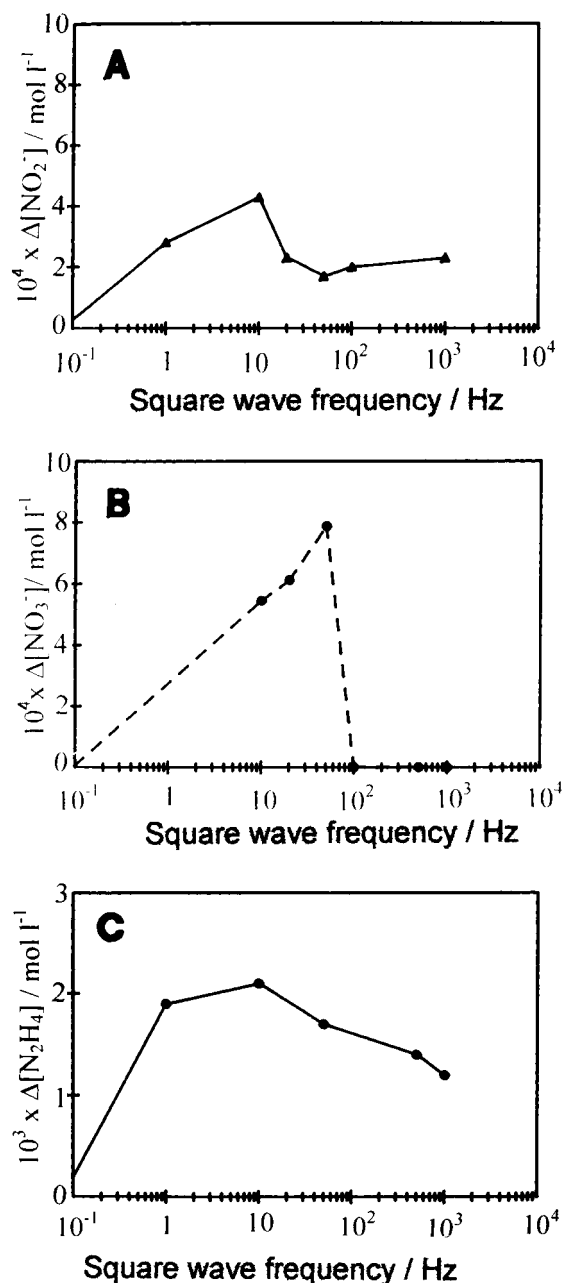The fate of hydrazine in the solution may be explained on the basis of the following equations [13–16]:

$$(N_2H_5^+)_{ads} \rightarrow (N_2H_4)_{ad} + H^+$$

$$(N_2H_4)_{ad} \rightarrow N_2H_3^+ + H^+ + 2\,e^-$$

$$N_2H_3^+ \rightarrow N_2H_2 + H^+$$

$$N_2H_2 \rightarrow N_2 + 2\,H^+ + 2\,e^-$$

Fig. 7. Change in compound concentration against frequency of the square wave. Square was applied to a 3.22 cm^2 Pt working electrode in a solution containing 1.0×10^{-3} M of the test compound. (a) Nitrite, (b) nitrate and (c) hydrazine.

4. Conclusions

We have shown that application of an electrochemical regime to a solution containing nitrite, nitrate and

hydrazine leads to exhaustive oxidation/reduction of these compounds. one advantage of the application of square wave potential regimes over constant potential oxidation or reduction is the continuous interaction of the electrode with the chemical species over the whole potential range, which leads to further oxidation or reduction of the produced intermediates.

The notion of applying a potential regime for elimination of pollutants by electrolysis using a well-designed potential regime is fulfilled. The efficiency of elimination of the tested compounds showed a dependence on frequency of the square wave. The optimum frequency for the tested compounds amounted to an intermediate value which compromises the efficiency of adsorption–desorption in a single cycle and the number of cycles per unit time.

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