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DETECTION OF ELECTROACTIVE PRODUCTS RESULTED FROM ELECTROCHEMICAL NITRATE REDUCTION IN ALKALINE MEDIA

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ABSTRACT. Nowadays, the damage of the environment quality has reached alarming levels requiring severe measures for stopping this process. In order to harmonise with the maximum admitted concentrations of nitrate in the discharged effluents, the electrochemical procedures represent a clean, flexible and efficient alternative of decontamination. Electrochemical reduction of nitrate/nitrite (ERNN) can be advantageously applied to the treatment of industrial waste water, whereby this species can be transformed into harmless products. In this context, the present paper describes the results of our researches concerning the design of an original technique for on-line detection of electroactive products resulted from ERNN in alkaline media. The obtained results shows that, using an adequate pH value, at least three electroactive species generated from the NO_3^- reduction (NO_2^-, NH_2-OH and NH_4^+) could be electrochemically detected at different applied potentials on the Pt-ring electrode.

Keywords: nitrate, nitrite, waste waters, electroactive products detection

INTRODUCTION

The interest for the nitrate/nitrite removal results from the high concentration of this ions in the surface and subterranean water streams and the need to reduce this dangerous pollution [1]. The main source of this pollution are industrial wastewater and, in some areas, the intensive agriculture. The problem of nuclear waste treatment represents another aspect of NO_3^- removal because this ion significantly increases the volume of waste and has a negative impact on the waste cohesion after solidification [2].

The maximum contaminant level (MCL) of nitrate in the potable water is 45 mg/L in the United States, while the European Union legislation admits a maximum level of 50 mg/L for drinking water [2, 3]. Various methods such as biological, physicochemical, etc. have been proposed for the removal of nitrate from potable water and wastewaters. Even the biological denitrification represent the most used method, it has several disadvantages e.g. it is slow,

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difficult to control, produces organic residues and requires intensive maintenance and a constant supply of the organic substrate [4]. The physicochemical processes such as ion exchange [5], reverse osmosis [6] and electrodialysis [7] produce secondary brine wastes, because the nitrates are merely separated but not destroyed. The reduction of the nitrate/nitrite is another mean for removing these ions from polluted waters.

The electrochemical reduction of nitrate/nitrite represents an attractive and promising solution due to its convenience, environmental friendliness, and low cost effectiveness [8]. Nitrate electroreduction leads to the coexistence of several more or less stable intermediate products like nitrite, hydrazine, hydroxylamine, ammonia, nitrogen and other oxygen-containing nitrogen species [9]. From a practical and an environmental point of view, it is highly desirable that the electrochemical process transform nitrate efficiently and selectively into the harmless N_2 gas.

Using the electrochemical reduction of nitrate/nitrite (ERNN), the final compounds composition depends mainly on the electrolyte pH, the applied potential and the used cathode material. On the other hand, electrochemistry provides promising solutions when it is combined with ion exchange, the last one being capable of NO_3^- selective removal from the treated water.

The nitrate reduction using a copper electrode, in alkaline media, represents an interesting option because this system is less liable to produce oxides of nitrogen as by-products [10, 11, 12, 13], but, in this case, ammonia represents the main product. The use of other electrode materials (Cu-Sn alloys [14], Rh [15], Sn [16], Pd-Cu alloys [17]) allows the selectively reduction of nitrate/nitrite ions into the harmless N_2 gas. Nevertheless, the ERNN process requires fast and easy monitoring method of generated species.

In this context, in our work, we evaluate the possibility of on-line detection of electroactive products resulted from ERNN in alkaline media: NH_3, NO_2^- and NH_2-OH.

The electrochemical measurements were carried out in unconventional conditions, combining the cyclic voltammetry at relative high scan rate (500 mV/s) with the controlled hydrodynamic mass transport using a Pt/Pt or Pt/Cu rotating ring-disk electrode (RRDE). This original technique will be named cyclic hydrodynamic voltammetry (CHV).

RESULTS AND DISCUSSION

Detection of electroactive species in mono-component solutions

In order to evaluate the possibility of electrochemical detection of electroactive products resulted from ERNN in alkaline media, we perform preliminary studies in mono-component solution.

The CHV measurements were completed using the Pt ring as working electrode, at a scan rate of 500 mV/s and a rotation speed of 1000 rpm. In order to assure the desorption of adsorbed species on the electrode surface, the electrode potential was scanned between – 1.5 and +2.0 V/RE. For each studied species, the electrochemical cell was firstly filled with 100 mL of 1 M Na_2SO_4 as supporting electrolyte after that different amounts of NO_2^-, NH_2-OH and NH_4^+ concentrated solutions were added successively (resulting concentration of 0.1, 0.5, 1.0, 2.0 g/L). Before each experiment, the pH value of the prepared solutions was adjusted at 11 using 1 M NaOH solution.

The details including the anodic and cathodic peaks corresponding to the voltammograms recorded in the presence of different concentrations of NO_2^- and NH_2-OH are presented in Figure 1 and Figure 2.

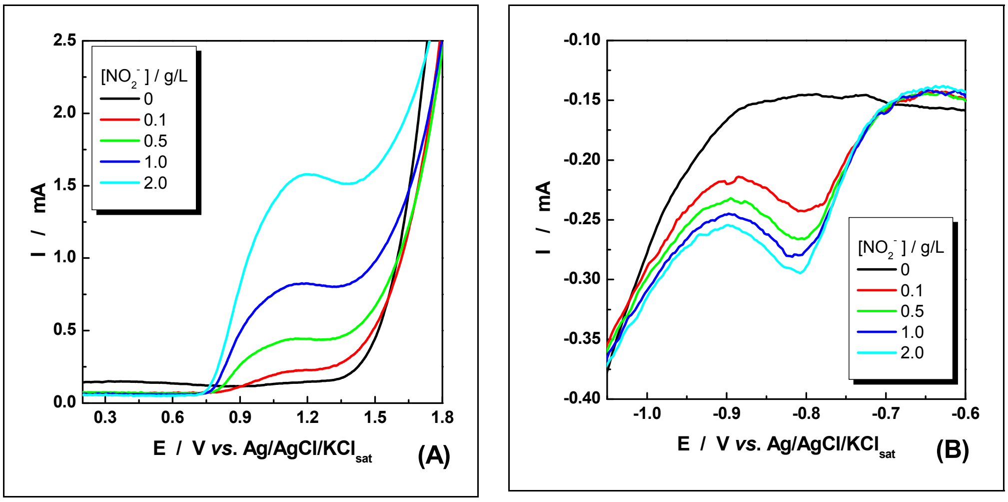

Figure 1. Influence of NO_2^- concentrations on the corresponding anodic (A) and cathodic (B) peak currents recorded by CHV. (Disk electrode disconnected).

As it can be seen from Figure 1, in monocomponent solutions, nitrite presents oxidation peaks close to + 1.2 V/RE and cathodic peaks at – 0.8 V/RE. The corresponding peak currents are proportional with the nitrite concentrations.

Similarly, hydroxylamine (see Figure 2), in monocomponent solutions, presents oxidation peaks near + 1.3 V/RE and cathodic peaks around – 0.9 V/RE. Also, the corresponding peak currents are proportional with the hydroxylamine concentrations.

Comparing Figure 1 and 2, it can be observed that both species present similar oxidation and reduction peaks' potentials, causing difficulties for individual ion detection. From another point of view, for the same concentration, the peak current values corresponding to the hydroxylamine oxidation and reduction are 4, respectively, 8 times higher than the corresponding peak currents recorded for nitrite.

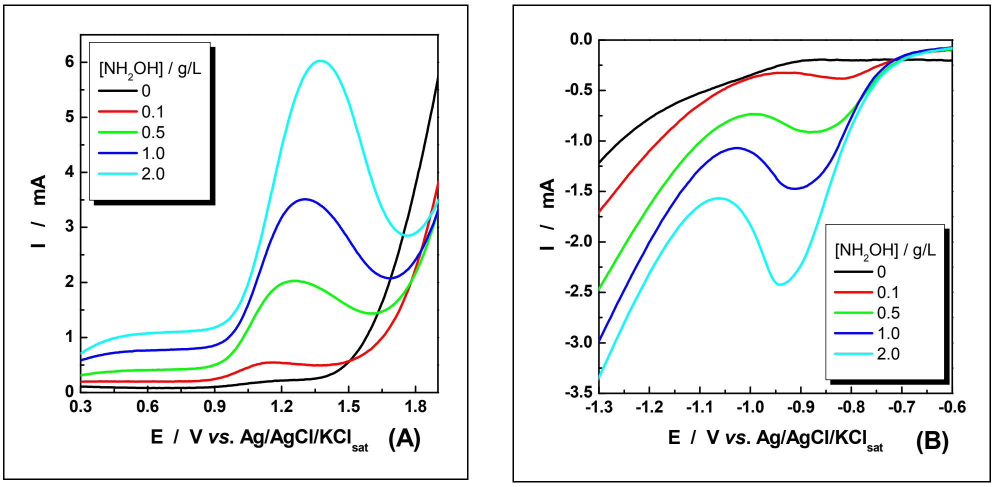

Figure 2. Influence of NH_2-OH concentrations on the corresponding anodic (A) and cathodic (B) peak currents recorded by CHV. (Disk electrode disconnected).

The details including the anodic peaks related to the voltammograms recorded in the presence of different concentrations of ammonium are presented in Figure 3.

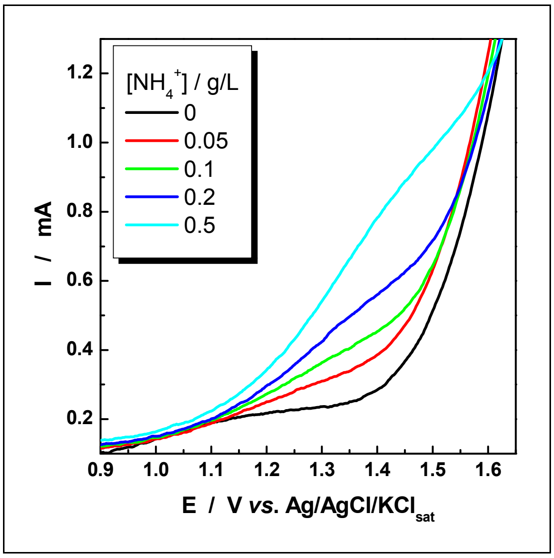

Figure 3. Influence of NH_4^+ concentrations on the anodic peak currents recorded by CHV. (Disk electrode disconnected).

As it can be seen from Figure 3, due to the fact that, at pH= 11, the ratio between NH_3:NH_4^+ is 40:1, ammonium can be electrochemically detected by ammonia oxidation at potentials over + 1.4 V/RE.

Starting from the presented results, we tray to perform similar measurements in mixed solutions, containing different concentrations of NO_2^-, NH_2-OH and NH_4^+. The obtained results (not shown in this paper) demonstrated that the invoked species interact among themselves, making very difficult their individual detection.

Detection of electroactive species generated by nitrate reduction

In order to evaluate the possibility of electrochemical detection of electroactive products resulted from ERNN in alkaline media by CHV, a consecrated working disk electrode of Cu was used. This choice was based on the fact that, on this material, depending on the applied potential, a wide variety of species can be generated. For a real and accurate comparison, before each set of CHV measurements, the surface of the Pt rotating disk electrode was covered with a thin layer (0.5 μm) of freshly electrodeposited cooper. A 45 g/L $CuSO_4$ solution in 177 g/L H_2SO_4 was used for Cu electrodeposition and also for the complete removing of the previous Cu layer by anodic dissolution. The amount of copper on the surface of the Pt rotating disk electrode was controlled by the charge quantity used for electrodeposition.

For each set of measurements, the working disk electrode (Pt covered with Cu) was polarised at a constant potential value, fixed between -0.7 and -1.8 V/RE, with 0.1 V increment. The potential applied to the Pt ring electrode was cycled between -1.5 and +2.0 V/RE at a scan rate of 500 mV/s, recording 8 successively cycles without Cu layer refreshing. The measurements were performed in a 2 g/L NO_3^- solution containing 1 M Na_2SO_4 as supporting electrolyte (pH = 11), at a rotation speed of 1000 rpm.

In order to evaluate the electrocatalytic stability of Cu layer towards ERNN, we compare the anodic currents recorded on the Pt ring electrode, corresponding to the oxidation of the disk generated species. For example, Figure 4 presents details of the currents recorded on the Pt ring electrode during the anodic scans, for 3 different disk polarisation potentials. In order to assure a better visibility, only the anodic portions from the 1st, 2nd, 4th and 8th cycles are presented. It can be observed that, for all presented potentials, every first cycle indicates a maximum electrocatalitic activity of the freshly copper disk electrode, which decreases rapidly for the following recorded voltamograms. The decrease of the copper electrode electroactivity upon the first seconds (one complete cyclic scan take 14 s) may be related to the adsorption of hydrogen and nitrate reduction products [18]. We can conclude that the Cu disk electrode surface can be rapidly poisoned by the reduced products and presents a poor stability, requiring a periodic surface refreshing.

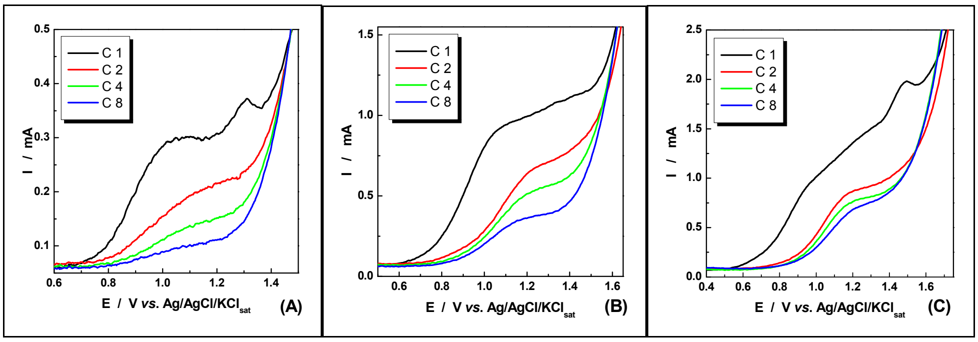

Figure 4. Influence of progressive poisoning of Cu disk surface on the oxidation currents recorded by repeated CHV on the Pt ring, at different disk polarisation potentials: (A) -0.9 V, (B) - 1.2 V. and (C) – 1.4 V.

Based on previous obtained information, we start a detailed study concerning the influence of the polarization potentials of the Cu disk electrode on the ERNN product composition. The anodic current of the voltamograms, corresponding for every first cycle recorded at different values of the applied potential on the Cu disk electrode, are presented in Figure 5.

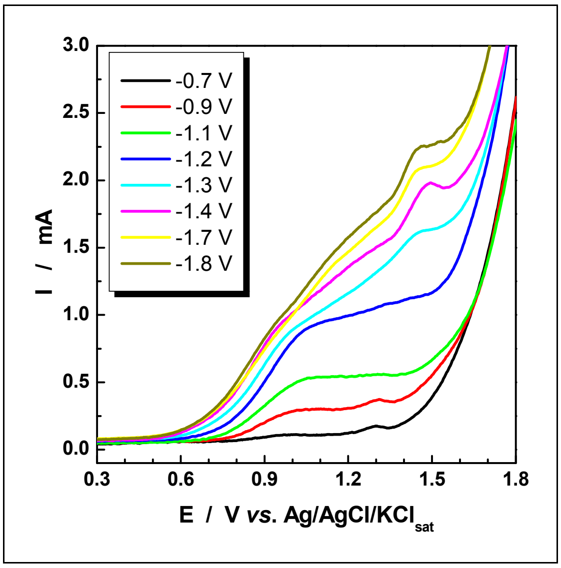

Figure 5. Influence of the polarization potential of Cu disk electrode on the oxidation currents recorded by CHV on the Pt ring electrode. The figure presents only the first anodic scan after the disk surface renewing by Cu electroplating

As expected, the nitrate reduction rate and the ratio between the amounts of the resulted species strongly depend of the applied potential. The decrease of disk applied potential to more negative values determines the increase of the ring currents corresponding to the detection of the generated species on the Cu electrode.

It is worth to note that, depending on the disk applied potential, different electroactive species can be detected at specific ring polarization potentials. For example, at potential values applied on the disk electrode more positive than -1.1 V/RE, two oxidation peaks can be observed, corresponding to nitrite and hydroxylamine oxidation. If the applied potential on the Cu electrode ranges among -1.1 and -1.3 V/RE, the interaction between the electrogenerated species makes complicated the detection of these compounds. For disk potentials more negative than -1.3 V/RE (corresponding to “hydrogen domain”), a net peak corresponding to ammonia oxidation can be observed at ring potentials around +1.5 V.

CONCLUSIONS

The results of our researches concerning the on-line detection of electroactive products resulted from ERNN in alkaline media allow us to formulate the following conclusions:

- The measurements performed in monocomponent solutions proved that, combining cyclic voltammetry at high scan rates with hydrodynamic techniques and using an adequate pH value, at least three electroactive species generated from the NO_3^- reduction (NO_2^-, NH_2-OH and NH_4^+) could be electrochemically detected at different applied potentials on the Pt-ring electrode.
- The designed technique was tested using a Cu disk electrode (one of the most used electrode material for ERNN), demonstrating the ability of *on-line* detection of the invoked species.
- The voltammograms, recorded successively without Cu layer refreshing, demonstrated that the electrocatalytic activity of this electrode material decreases very fast (in few seconds), requiring additional studies concerning the synthesis of new electrode materials with increased stability and/or the periodic reactivations of the electrode surface.

EXPERIMENTAL SECTION

Reagents

The solutions were prepared using analytical grade solid reagents ($NaNO_3$, $NaNO_2$, $(NH_3OH)_2SO_4$, $(NH_4)_2SO_4$ and Na_2SO_4) and double-distilled water. 1 M Na_2SO_4 was used as supporting electrolyte for all measurements.

Before each experiment, the pH value of the prepared solutions was adjusted at 11 using 1 M NaOH solution. All measurements were made at room temperature (298±1 K).

Experimental setups

Electrochemical measurements were carried out in controlled hydrodynamic conditions using a Pt/Pt and Pt/Cu rotating ring-disk electrode (Radiometer, France; ring: ID = 4.2 mm, OD = 4.8 mm; disk: ϕ = 4 mm). The CE was a Pt wire (ϕ = 0.8 mm, L = 15 mm) and an Ag/AgCl/KCl$_{sat}$ system was used as reference electrode (RE). A fully computer controlled home-made bipotentiostat and applications elaborated with the Labview 8.5 software were used for experimental parameter's control and data acquisition.

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