

Electrochemical determination of nitrate ion from fresh water on nanosphere polypyrrole modified electrode surface

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ABSTRACT

Electrochemical determination of ammonium nitrate is very important in now days. Nitrate has been widely used in industrial and agricultural production and is ubiquitous in food, water, biology and the environment. However, nitrate is also a toxic inorganic contaminant that is hazardous to the health of humans and other organisms. Electrochemical methods receive an electric signal from dissolved nitrate, with voltammetric, potentiometric and impedimetric methods included. Nitrates can also cause damage to aquaculture through its toxicity to aquatic animals, including fish and crustaceans. As nitrate can oxidize hemoglobin to methemoglobin, which is not capable of carrying oxygen, the latter can reach toxic concentrations in a high-density aquaculture system in contaminated waters. Present study focusing on determination of hazardous compound of ammonium nitrate and real samples on polymer modified electrode glassy electrode surface. The modified electrodes were studied in various pH from 1.0 to 13.0. After optimization of pH the compound best responds in pH 9.0 it is used for further studies of electrochemical behaviours. The condition parameters are optimized and calibration plot also derived on different concentration of ammonium nitrate. The stripping voltammetric behavior of ammonium nitrate exhibits very low limit of detection on coated electrode.

Keywords: Ammonium Nitrate, Voltammetric, polymer modified electrode, Hazardous

Introduction

Among the water pollution, ammonia contamination of water bodies is a widespread environment problem. Ammonia containing wastewaters will cause eutrophication and fish kills which disrupt aquatic ecosystems in a severe manner [1]. The need to monitor this ion in both environmental and physiological contexts is recognised by various regulatory bodies worldwide and, as such, legislation relating to maximum permissible concentrations in both drinking water and food produce is often levied [2]. Nitrate, a relatively non-toxic substance, represents a risk since it can be reduced to nitrite in the environment, in foods and in the digestive system causing serious human diseases. Ammonia also a common component of waste streams, can damage internal organ systems [3,4]. Heavy utilization of fertilizers has been known to cause penetration of large quantities of nitrates into ground and surface waters, resulting in a large distribution of nitrates on nature [5].

Because of the risks associated with nitrate for the human health and the environment, particular interest has recently been devoted to the detection of nitrate and nitrite [6, 7]. The quantitative determination of nitrite and nitrate concentration is of rapidly increasing interest, especially for drinking water quality, wastewater treatment, for the food industry and for the control of remediation procedures [8]. Besides the high-performance liquid chromatography [9, 10], many other methods for simultaneous determination of nitrite and nitrate are also designed such as flow injection analysis [11, 12], UV resonance Raman spectroscopic [13], ion chromatography [14, 15], and electrochemical methods [16, 17]. Ammonium nitrate (AN) and urea nitrate (UN) are commonly used materials in improvised explosive devices (IEDs). Detection by mass spectrometry (MS) and/or ion mobility spectrometry (IMS) is traditionally difficult [18].

The use of bare unmodified electrodes for direct nitrate analysis is undoubtedly the most attractive option but there are a number of problems. Low sensitivity and reproducibility associated with cumulative passivation effects have served to strengthen the interest in the use of immobilised electrocatalysts. These can offer marked improvements in selectivity and sensitivity however the complexities inherent in their fabrication and use have tended to limit their applicability. In addition, higher reagent expense and lifetimes which are not significantly better than those exhibited by their bare electrode counterparts have

contributed to the low acceptance of electrochemical techniques. The electrochemical methods represent useful alternatives for faster and low cost reduction of nitrates and offer at the same time a relatively simple technology [19].

The electrochemistry of nitrate has been studied for the best part of a century but it is only recently that significant effort has been expended in its quantitative determination [20]. An electronic tongue has been developed to monitor the presence of ammonium nitrate in water [21]. The fresh copper-modified electrode was formed in situ and the signals of nitrate were recorded in time, the whole experiment does not require sample preparation and oxygen removal from the solution degassed with nitrogen [22]. The determination of nitrate by square wave voltammetric method with a freshly copper plated glassy carbon electrode was described [23]. Voltammetric determination of nitrate in 0.1M Na₂SO₄ solution (pH 2.0) at copper modified bismuth bulk (BiB/Cu) electrode was presented in this article [24]. Nitrate monitoring biosensors also have been constructed and applied for the detection of nitrate in various matrixes [25].

The electrochemical detection of various explosives containing electrochemically active nitro group are reviewed [26, 27]. Attention is paid both to the use of traditional mercury electrodes and non-traditional, recently developed electrodes based on mercury amalgams, bismuth films, boron-doped diamond films and carbon films in voltammetric and amperometric mode. Screen-printed, chemically modified and/or biologically modified electrodes are discussed as well [28]. Zeolite-modified electrodes have been developed for the determination of various compounds and the use of a mixture of a zeolite and graphite in various forms has been proposed [29]. Zeolite-supported electrocatalysts can be exploited to improve the performance of the electrocatalytic responses with reduced overpotentials and increased voltammetric/amperometric signals allowing low detection limits and high sensitivities [30, 31]. Polypyrrole(PPy) nanowire modified electrodes were developed by template-free electrochemical method based on graphite electrode. The modified electrode was characterized by their amperometric response towards nitrate ions [32]. The electrochemical behavior and electro-catalytic activity of silver nanoparticles/PPy/GCE were characterized by cyclic voltammetry [33].

In this work, we report the development and testing of an electrochemical-based solution for the detection of explosives. The study was to develop electro-analytical strategies based on certain advanced voltammetric techniques for the sensitive detection of ammonium nitrate in aqueous solution using a specific PPy electrode. Direct oxidation of ammonium nitrate on this specific electrode and as consequence, their determination was investigated by cyclicvoltammetry (CV) and differential-pulsed voltammetry (DPV) techniques-based procedures were tested, developed and optimized for selective and detection of ammonium nitrate.

EXPERIMENTAL METHODS

Pyrrole and ammonium nitrate was purchased from e-Merck. The monomer was purified by distillation under nitrogen atmosphere before use, stored at low temperature and protected from light. All other reagents were of analytical grade and were used without further purification. All solutions used for electrochemical measurements were prepared using distilled water. All experiments were carried out at ambient temperature. The supporting electrolyte (pHs) solutions were also prepared by same water. The pH values of the buffer solutions were measured by Hanna HI 2211 pH/ORP meter.

All electrochemical measurements were carried out with an electrochemical workstation (CHI 650C). The electrochemical cell contains a three-electrode system, a glassy carbon electrode (GCE) as the working electrode, Ag/AgCl as the reference electrode, and a platinum (Pt) wire as the counter electrode. Atomic force microscope (AFM) was used to characterize the polymer and compound adsorbed surface.

Preparation of PPy modified electrodes

Before polymerization conducted, electrolyte solutions were desecrated thoroughly with pure nitrogen. Unless stated otherwise, all pyrrole polymerization were conducted at ambient temperature and potentiostatically 0.85 V vs. Ag/AgCl in aqueous solution containing 0.15 M pyrrole with 0.10 M LiClO₄ and 0.10 M carbonate. Freshly prepared PPy electrodes were usually conditioned in 0.10 M HClO₄ solution for 24 hrs to remove the carbonate ions.

RESULT AND DISCUSSION

Effect of pH

To determine the influence of the pH on the response of nitrate by cyclic voltammetric studies on the PPy modified electrode surface, the current of the analyte was analysis in the range of pH from 1.0 to 13.0 solution, varying the different pH media. The figure 1 exhibits the peak current responds against pH. The higher peak current behavior was observed in pH 9.0. The decreasing behavior was illustrate in peak

current at pH values lesser than pH 7.0 for nitrate, because the reduction step of nitrate to nitrite takes place in acidic media and consumes proton ion, the increase in pH causes lower reduction of nitrate to nitrite in accumulation step and therefore a decrease in peak current take place in basic pH media. The higher peak current pH 9.0 was selected for best and further studies.

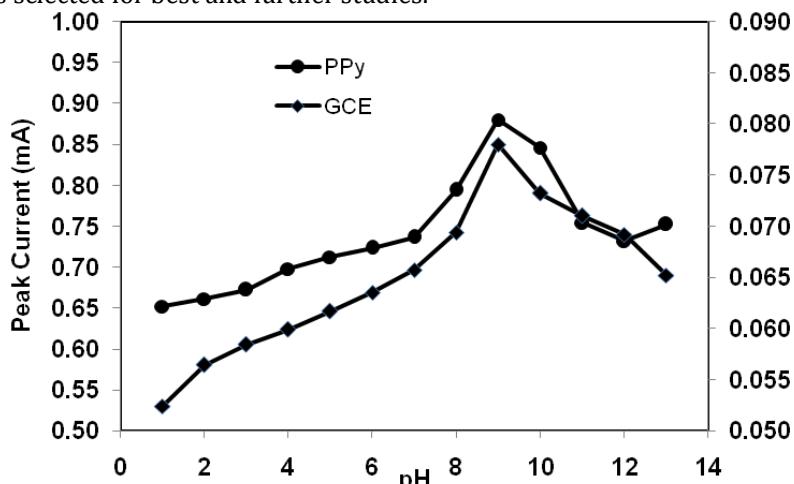


Figure 1. Curve of peak current vs. pH

Voltammetric studies

The cyclic voltammetric behaviour of ammonium nitrate in pH 9.0 was studied at GCE and PPy modified electrode surface. Figure 2 presents the respective cyclic voltammogram with one reduction peak was observed in the potential range from 1.2 to -2.0 V. The cathodic peak was observed around at the potential -1.7 V. As scan rate increases the peak current also increased on linearly. The double log plot of peak current vs scan rate was indicated that non-linear.

The electrochemical reduction of nitrate ions at a bare, freshly prepared PPy modified glassy carbon electrode was examined under identical conditions and the responses obtained to increasing nitrate additions. While there is very change in the voltammetric response at the bare electrode, a consistent peaked response was observed around -1.7 V using the PPy electrode. The peak increased in height with subsequent additions of nitrate with the linear range extending from 0.001 to 0.006 mM nitrate. The mechanism of nitrate reduction at solid electrodes remains unresolved and would appear to be dependent upon the experimental conditions employed. However, in most cases the final product of the electrochemical reduction reaction is usually ammonia.

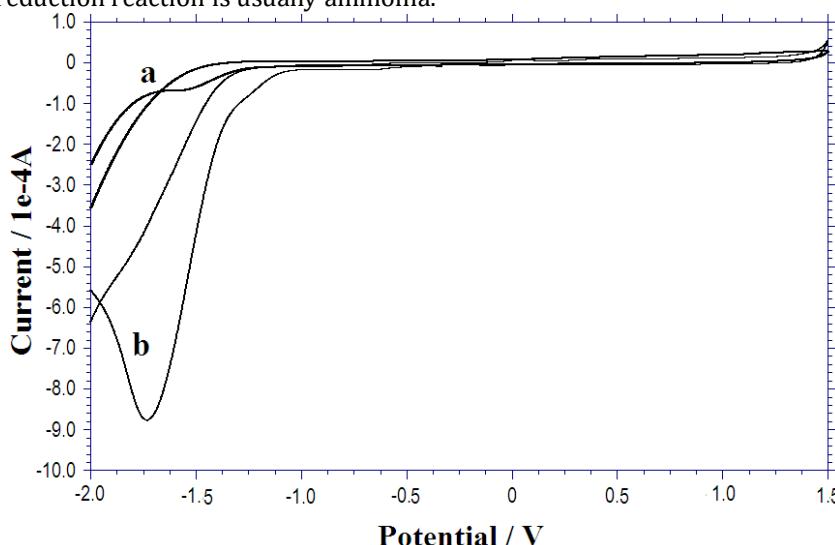


Fig.2. cyclic voltammogram of 0.005 mM ammonium nitrate on
a) GCE b) PPy/GCE at scan rate 50 mV/s.

Square Wave Stripping Voltammetry

Square wave stripping voltammetric experiments were carried out to ascertain the best conditions for the adsorption process. Many preconcentration-stripping experiments were performed for accumulation potentials (E_{acc}) varying from -2.0 to 1.2 V at an accumulation time (t_{acc}) of 15 seconds, to evaluate the electrostatic attraction/repulsion between electrode surface and analyte. Maximum peak current was found at -1.4 V (Fig 3) accumulation potential of ammonium nitrate. This might be due to the electrostatic interaction between the positive nature of electrode at this potential and the electron rich substrate. The accumulation time was optimized between 15 and 150 s led to the maximum peak current at 50 s. The maximum current signal condition was due to maximum electrode surface coverage under these conditions. The adsorption behavior of ammonium nitrate on PPy surface shows mixture like structure. The morphology behavior adsorbed compounds carried out through AFM and present in figure 4.

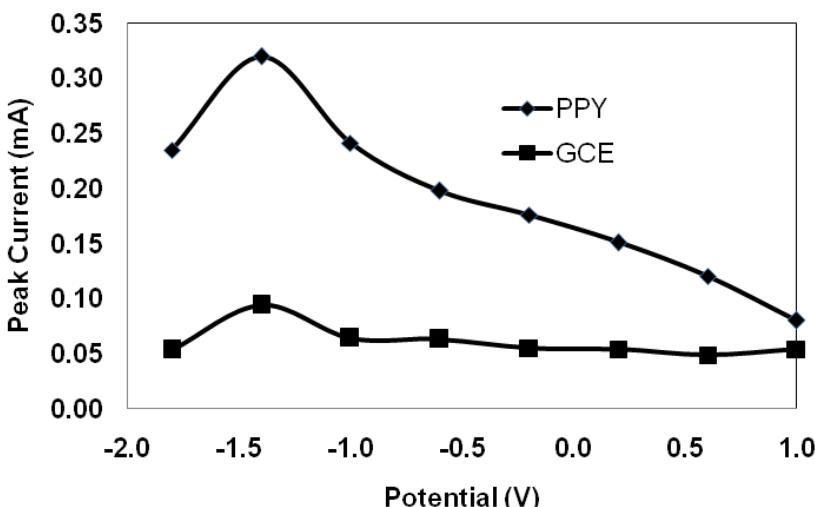


Fig 3. Curve of peak current vs Accumulation potential

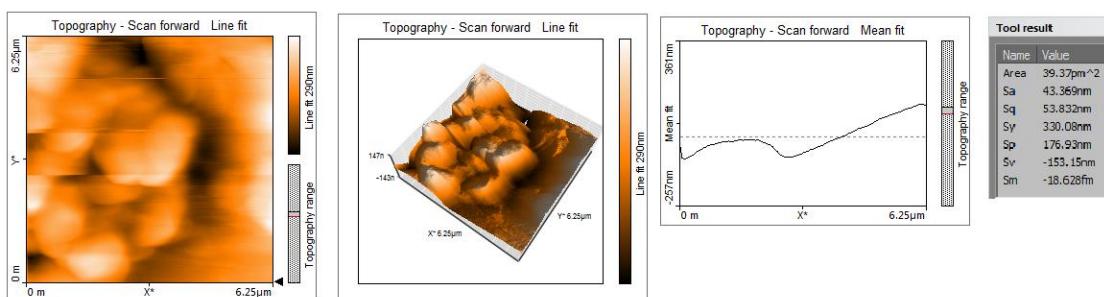


Fig.4. 2D, 3D AFM photographs, particle distribution graphs and roughness data of ammonium nitrate adsorbed on PPy modified surface

The initial scan potential, (E_{is}), is also an important parameter in controlling the peak characteristics. The initial potential was varied between 1.2 V to -1.0 V and an initial scan potential of 0.0 V was chosen for stripping voltammetric studies of the environmental sample of nitrate because of maximum current signals. The stripping peak current increased with an increase in square wave amplitude from 25 to 150 mV and decreased above 150 mV. However, amplitude of 100 mV was selected owing to maximum current peak response. The dependence of the peak current on the frequency was studied between 10 and 100 Hz. This experiment was carried out for a constant value of the step potential 4 mV and the results showed the maximum peak current at 100 Hz. When the step potential was varied between 2 and 10 mV, a decrease in peak current was observed above 5 mV. Hence, a frequency of 100 Hz and a step potential of 5 mV were used which provided sufficiently sensitive analytical signal at a reasonable scan rate of 350 mV s⁻¹. The effects of stirring rate (100 to 2000 rpm) and rest period (2 to 30 s) were studied. The optimum values were found to be 300 rpm and 5 seconds respectively. The experimental conditions for maximum signal

from square wave stripping voltammetry are arrived. A representative stripping voltammograms of the ammonium nitrate are given in figure 5. .

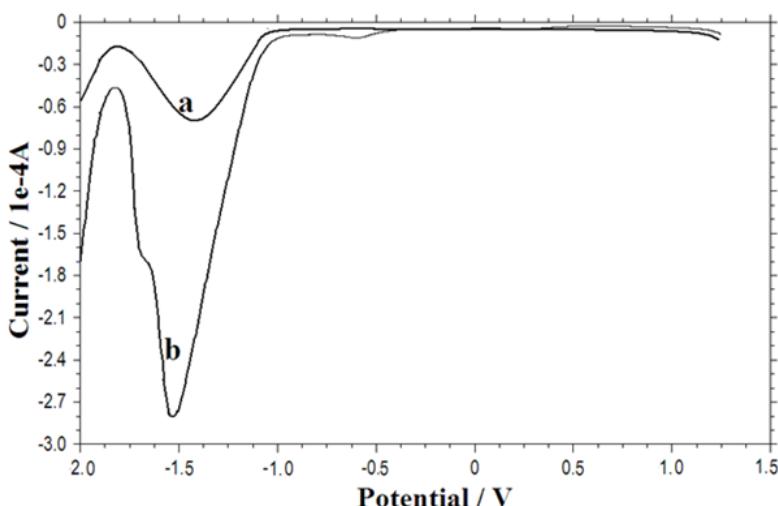


Fig.5. Stripping voltammogram of 0.005 M ammonium nitrate on
a) GCE b) PPy/GCE at scan rate 50 mV/s.

Analytical Characteristics

Square wave stripping voltammograms at different concentrations of ammonium nitrate was recorded using their maximum signal conditions. The peak current linearly increased with an increase in concentration. The calibration plots of i_p vs. Conc are presented good linear correlation and given in figure 6. The range of determination was from 0.001 M to 0.006 M and LOD was 0.0001 M. The relative standard deviation found for five identical measurements of the stripping current at 0.005 M analyte concentration was 2.81%.

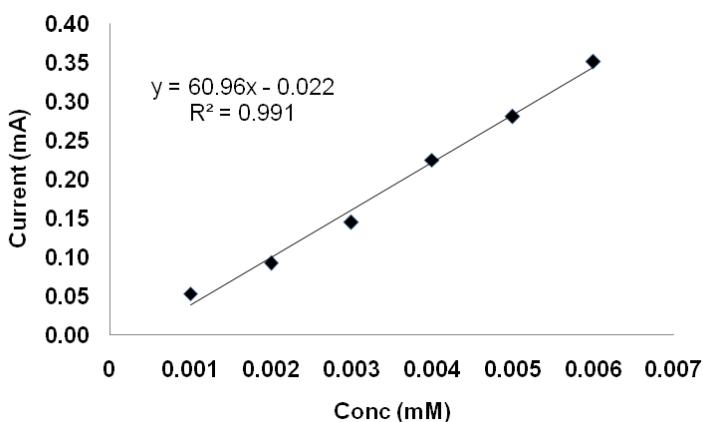


Figure 6. Calibration plot of ammonium nitrate

Determination of nitrate in Water Sample

The water sample was collected from five various places at Thanjavur, Tamilnadu, India. The nitrate ion was determined by square wave stripping voltammetric method. The amount of nitrate ion and relative standard deviations were found out. The amount of nitrate ion is 50 ppb - 85 ppb.

Conclusions

Voltammetric behavior of ammonium nitrate was carried out on nanosphere polypyrrole modified and glassy carbon electrode surface. The cyclic voltammogram was exhibits one good reduction peak with higher peak current responds on modified electrode surface at pH 9.0. The peak current correlated with scan rate it shows best adsorption behavior. The stripping behavior of nitrate ion observed on accumulation

potential on both electrode shows -1.4 V. the adsorption behavior clearly proved through AFM. The optimized experimental condition of stripping voltammetry is more favorable on determination of nitrate from fresh water.

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