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Voltermetric And Amperometric Behaviour Of Polyaniline Modified Carbon Paste Electrode For The Analysis Of Atrazine

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Abstract: *The modification of the surface of the electrode with polyaniline greatly detected atrazine on the electrode. In this study, two types of sensors, i.e. bare and PANI modified carbon paste electrodes (CPE) were prepared and compared for their voltermetric and amperometric response towards atrazine. A low detection limit (LOD) of 0.3μmolL^{-1} and a dynamic working linear range of 1–18 μmolL^{-1} concentration of atrazine using PANI modified carbon paste electrode were obtained in comparison with No detection at on carbon paste electrode. No significant differences were encountered in the repeatability analysis of the electrodes. The proposed method (electrochemical) features unbiased identification of negative (blank) and positive samples. Importantly, this method provided a promising electrochemical sensing platform for atrazine analysis and its detection for human safety.*

Keywords: *Voltermetric, Amperometric, Carbon Paste Electrode, Polyaniline and Atrazine*

I. INTRODUCTION

Environmental problems as a result of use of agro-chemical have received a great deal of interest. One class of agro-chemicals of interest is Atrazine used in agriculture and other applications. Although many advances have been made in recent years in developing reliable means for detecting these compounds, much is yet to be accomplished. Analytical chemistry plays a vital role in providing qualitative as well as quantitative characterization of Atrazine. It has been warned that some organic and inorganic compounds have harmful effects at substantially lower levels than previously suspected [1]. Thus, there is a great necessity for new analytical methods with better precision, accuracy, sensitivity and selectivity. These methods must not be prohibitively expensive and, ideally, could be adapted for measurement in the field. In this regard, electrochemical sensors are advantageous than other methods.

Because of the simple preparation and easy renewal of the surface, carbon has been used extensively as a working electrode for a variety of electrochemical applications. Among the carbon electrodes, the carbon paste electrode (CPE) is of particular importance. The ease and speed of preparation and of obtaining a new reproducible surface, the low residual current, porous surface and low cost are some advantages of CPEs over all other carbon electrodes. Therefore, the CPE can provide a suitable electrode substrate for preparation of modified electrodes [2].

More interestingly, some electroactive modifiers provide an excellent electrocatalytic property that makes the analyte electroactive at a lower potential enhancing the power of electrochemical detection. Electroactive modifiers, on the other hand, interact with analyte molecules and alter chemical reactions, or alternatively, they act as a new phase on the conducting phase of the electrode [3].

Advantages of polyaniline in the field of sensor are indicated by impressive signal amplification and elimination of electrode fouling, sensitivity and selectivity of analyte [3, 4]. This accounts for the large surface area for the analysis of Atrazine [3, 6] as such, developed a sensor for the analysis of atrazine based on polyaniline and gold particles modified carbon paste electrode.

Due to the drawback of carbon paste electrode in the electro analysis of atrazine, a sensitive electrochemical sensor to determine the level of atrazine in samples was developed by means of electrochemical deposition of polyaniline on the surface of carbon paste electrode.

II. EXPERIMENTAL

2.1 Material

Ammonium persulfate $(NH_4)_3S_2O_6$, 98% Sigma Aldrich), hydrochloric acid (HCl, 35%, Alpha), sulfuric acid (H_2SO_4, 98%, Fisher chemicals), ammonium hydroxide (NH_4OH, 35%, PSPark), cyclohexane (99%, Fisher Chemicals), acetone $(CH_3)_3CO$, 100%, Whitehouse Runcorn), ethyl actate $C_4H_8O_2$ (99%, Sigma Aldrich), potassium nitrite (KNO_3, 99%, Qualikems), aniline ($C_6H_5NH_2$, 100%, Sigma Aldrich) and atrazine ($C_8H_{14}ClN_5$, 95%, Sigma Aldrich) were used as received without any other treatment. Aqueous solutions were prepared with deionized water. In this study, the chemicals were used as received without further purification.

For the preparation of the carbon paste electrode, graphite powder (100%, Sigma Aldrich) was mixed with Mineral oil (paraffin, 95%, Finkem) and the paste filled into the tip of plastic syringe (2.3 mm internal diameter, Shan Chuan) and connected with copper wire (99.9%, Finkem).

2.2 Preparation of bare carbon paste electrode

Bare carbon paste electrode will be prepared by mixing (800 mg) graphite powder with (100 μL) of paraffin oil and thoroughly hand mixed in a mortar and pestle. The paste was packed into electrode assemblies made from 3mL plastic syringe of 2.4mm outer diameter using spatula and smoothened on a glass slide surface. Electrical contact will be made with a copper wire through the syringe [5].

2.3 Electrodeposition of Polyaniline

Electropolymerisation was carried out by mixing 2.5 ml of 0.25 M of ammonium persulfate aqueous solution with 2.5 ml of 1M aniline hydrochloride in a vial. Cyclic voltermmetry at potential between -0.2 and 1.0 V, on carbon paste electrode vs. Ag/AgCl electrode at a scan rate of 50 mV in 5 cycles was carried out, taking several successive scans [8]

2.4 Electrode modification strategy

A polyaniline film prepared on carbon paste electrode was employed as substrate for the detection of atrazine (analyte) as show in figure 1.

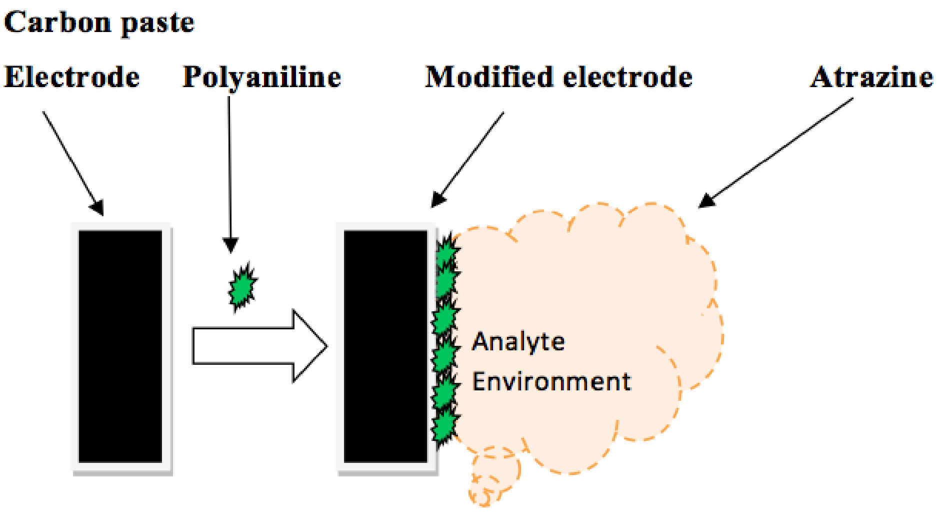

Figure.1: The schematic presentation of the sequential electrodepositing/protection of Polyaniline on Carbon paste electrode.

2.5 Electrochemical Measurements

The Epsilon (BASI) was used to carry out all electrochemical measurements. A conventional three-electrode setup was used with the CPE electrode as the working electrode and a platinum wire as a counter electrode ((1 mm) mw 4130, an Ag/AgCl (Thermo Scientific Orion Model Number: 900011) served as a reference electrode. All potentials were reported with respect to this reference electrode. All gold depositions were performed from solutions containing 10 µL of $KAuCl_4.3H_2O$ in 0.5 m/L H_2SO_4.

III. RESULTS AND DISCUSSION

3.1 Electrodeposition of PANI at CPE

Electrodeposition of polyaniline on the surface of CPE was carried out by running cyclic voltammetry in an acidic medium containing monomers. Aniline electro-polymerization started from 0.6 V in the first cycle. Successive cycles indicated the growth of polyaniline film as evidenced by the increase in the redox currents. The first redox processes located at 0. 4V and 0.1 V in the positive and negative scans respectively as shown on fig 2, corresponded to electron transfer from/to the electrodeposited polyaniline film. In order to compensate the charge of polyaniline film, anion transport from/to the electrolyte solution, i.e., anion doping and de-doping, occurred according to the literature [9].

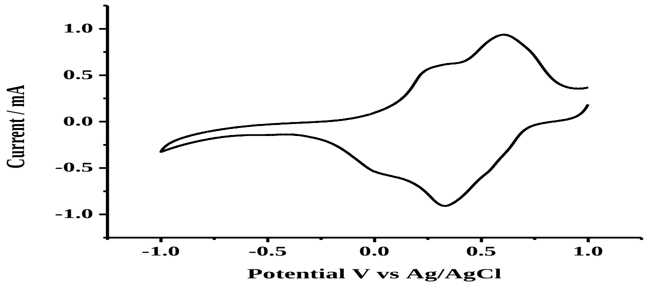

Figure 2: Cyclic voltermmetry for surface PANI modified electrode in 0.5 mM H_2SO_4 at scan rate 100 mVs^{-1} between potentials of -1.0 and 1.0 V (including atrazine potential range -0.5 V).

The following redox process, at 0.4 V, was due to polymer decomposition. Finally, the last process located at more positive potential (approximately at 0.9 V) was related with two steps: the first is the electron transfer that could be attributed to the oxidation of the PANI film and the second, is due to the monomer oxidation [8, 9]. Therefore, the number of deposition cycles on polymerization of aniline makes greater impact on deposition of the fibers. The CV polymerization was repeated in 5 cycles to obtain the best-coated surface to carry out the task. Cycles 2 (Fig: 3 and 4) shows higher current response but the coating appears thin which was worn out due to the catalytic reaction with organic compounds dissolved in solution leaving almost a bare electrode.

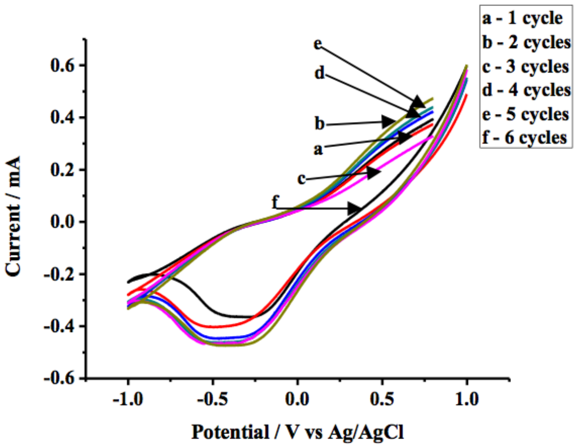

Figure 3: Cyclic Voltammogram of number of cycles of 1-6 cycles of aniline polymerization in 0.12 mM atrazine in acetate buffer (pH 3) supporting electrolyte at a scan rate 100 mVs^{-1}

The next cycle was cycles 4 and 5 which are of moderate coating so cycles 5 was used for the deposition of PANI at CPE for atrazine analysis because it appeared thicker than 4 cycles even though they are of same response. The surface PANI modified CPE further run in 0.5 mM H_2SO_4 including the potential range of atrazine confirming the reduction peak of PANI and interferes on the potential range of atrazine. No effect around the possible potential range of atrazine at -0.5 V, which is in accordance with [10].

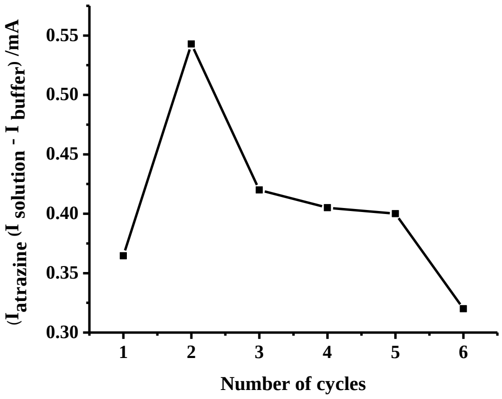

Figure 4: Effect of number of cycles of 1-6 cycles of aniline polymerization in 0.12 mM atrazine in acetate buffer (pH 3) supporting electrolyte at a scan rate 100 mVs^{-1}

3.2 Effect of pH at PANI and Au/ PANI modified CPEs

The effect of the pH of supporting electrolyte on the electrode response was tested in the range of 3.0 to 4.0 at PANI (Fig 5 and 6). The CV response of the PANI modified CPE increased reaching pH 3.3. The current response was found to be higher at pH 3.3. The optimum pH in this work is close to other reported pH values in literatures [10, 11].

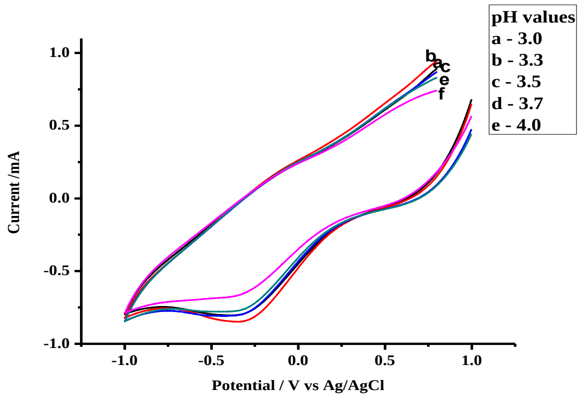

Figure 5: Cyclic voltammogram of pH on PANI modified CPE of 0.12 mM atrazine in 0.2 mM acetate buffer with different pH value at 3.0 – 4.0 ran at scan rate of 100 mVs^{-1}

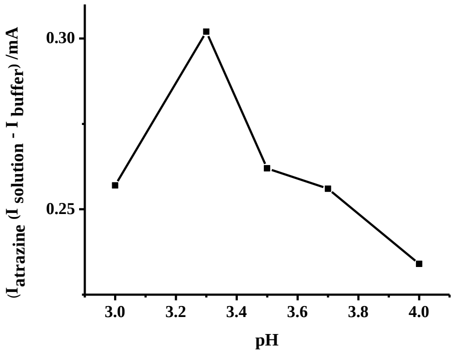

Figure 6: Effect of pH on PANI modified CPE of 0.12 mM atrazine in 0.2 mM acetate buffer with different pH value at 3.0 – 4.0 ran at scan rate of 100 mVs^{-1}

3.3 Detection of atrazine under optimized conditions

3.4 Detection of atrazine using PANI and Au/PANI modified CPEs by Cyclic Voltammetry

The cyclic voltammogram of atrazine at PANI modified CPE shows a reduction peak at around -0.5 V. The voltammogram show the response of atrazine at PANI (Fig 7) modified CPEs to addition of atrazine ranging from 0 (blank)

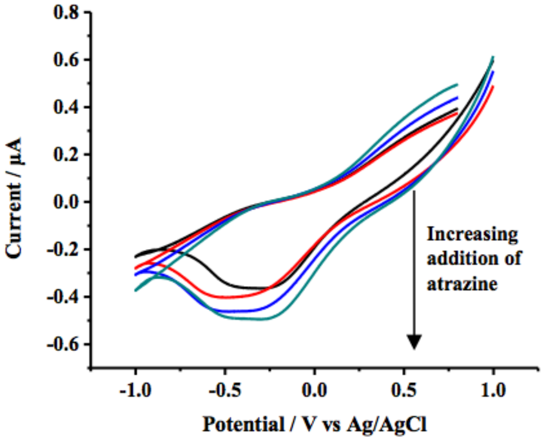

Figure 7. The voltammetric response of PANI modified CPE when atrazine (0, 3.2, 6.34, 9.32, 12.08 µM) was added to acetate buffer (0.2 mM, pH 3.3) and run at scan rate 100 mV/s

3.5 Amperometry Study of Atrazine at PANI and Au/PANI modified CPE

Since amperometry under stirred condition is much more sensitive than cyclic voltammetry and it is important for developed electrodes, this method was employed for determination of atrazine even at much lower concentrations. Fig 5 shows the current-time response of the modified CPE with successive injection of atrazine at an applied potential of -0.8 V vs Ag/AgCl. As shown in fig 8, the current-time response of the PANI modified CPE for successive additions of atrazine increases stepwise with each additions of atrazine.

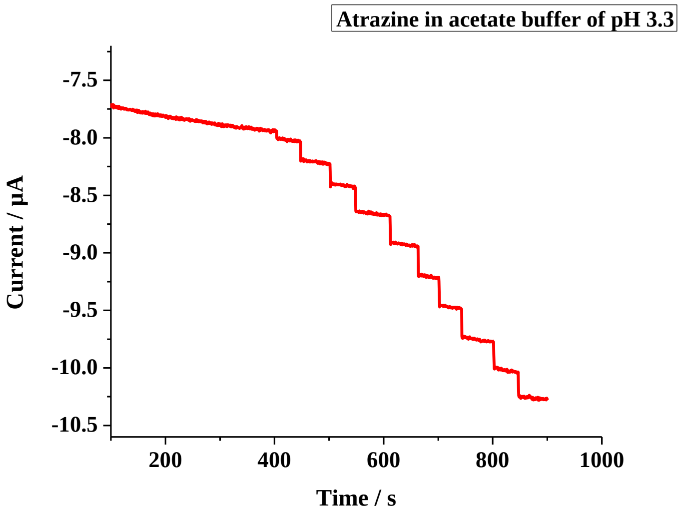

Figure 8: A- current –time response and Calibration curve of successive additions of atrazine at PANI modified CPE in 0.2 mM of acetate buffer at pH 3.3 with a LOD of 0.3 µM (3δ)

3.6 Real samples analysis at PANI CPE

To investigate the possible application of the electrochemical modified sensor for real sample, 5ml of the atrazine extracted from the sediment sample from atrazine used environment was analysed with UV – Vis spectroscopy and the proposed method. The concentration found with the proposed method is 0.03 ± 0.67 µM which were in accordance with the value 0.09 mM found with UV - Vis spectroscopy method Therefore, the proposed modified electrode is accepted and could be applied for less concentrated samples.

3.8 Electrodes Repeatability

The repeatability of the electrochemical modification of the three used electrodes (Bare and PANI modified electrodes) was evaluated by using several modified electrodes toward the detection of 0.12 mM atrazine for 5 times on different days (Fig 6). The experimental result was found to be 3.2±1.28. No significant differences at the 95% confidence level were encountered. Thus, the reproducibility of the three electrodes was acceptable

Table 1: Comparison of different modified electrodes for atrazine determination

S/№	Electrode	Detection limit (µM)	Ref.
1	Nano chemical receptor electrode	10.8	[9]
2	Amperometric separation-free immunosensor	0.13	[11]
3	Multiwalled carbon nanotubes	3	[12]
4	PANI modified CPE	0.3	This work.

IV. CONCLUSION

In this work, we introduced amperometric atrazine sensor by electrochemical deposition of PANI. The electrochemical sensor exhibited a linear range and acceptable repeatability. Remarkable electrocatalytic activity and significantly lower detection limit of this modified electrode. Furthermore, the modification procedure is less expensive and more convenient. The analytical performance of the modified electrode indicates that it can be used as sensitive amperometric detector for lower concentration detection of atrazine. The highlight of this study is simple to perform without the need of extensive sample preparation steps beyond extraction, filtration and dilution. In order to fully assess the application potential and added value of the developed sensors, future/or further research is required to improve the sensitivity of the electrochemical sensor and focus on other target analytes. Table: 1 shows that the detection limit for this work has no significant difference with that of the previous work.

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