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Quick and Easy Modification of Glassy Carbon Electrodes with Ionic Liquid and Tetraruthenated Porphyrins for the Electrochemical Determination of Atrazine in Water

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Abstract: Atrazine is a pesticide used to control broadleaf weeds, however its wide distribution and its high persistence in the soil and in surface waters has resulted in a public and environmental health problem. Present results shows the design, construction and characterization of glassy carbon electrodes modified with tetraruthenated metalloporphyrin (M=Ni (II) and Zn (II)) and 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide,

BMIMNTF₂. The modification was reproducible and sensitive for the electrochemical detection of atrazine in neutral media. The detection limit was 230 nM when using GC/BMIMNTF₂/ZnTRP and 540 nM with GC/BMIMNTF₂/NiTRP, meaning that his methodology can be a feasible and inexpensive way to detect atrazine in trace levels.

Keywords: Tetraruthenated porphyrins • Modified electrodes • Atrazine • Ionic Liquids

1 Introduction

Atrazine (6-chloro-N-ethyl-N-[1-methylethyl]-1,3,5-triazine-2,4-diamine; **ATZ**) is a widely used pesticide that constitutes an excellent model for the study of small organic pollutants [1]. ATZ can react with quinine-binding proteins, inhibiting electron transport and as a consequence blocking the photosynthetic process in weeds. When ATZ was first released in 1958, it was thought that animals would be immune to any effects of ATZ since photosynthesis is limited to plants [2]. More recent studies demonstrated that ATZ has carcinogenic and mutagenic activity, becoming a serious threat to environment and human health [3,4], hence, accumulation of ATZ in water and soil must be carefully controlled.

Long-term consumption of high levels of atrazine has caused adverse health effects in animals, including tremors, and damage to liver and heart. In 2010, Hayes et al. [5] have demonstrated that ATZ is a potent endocrine disruptor that turns male frogs into female at relatively low concentration (0.1 ppb). In humans, ATZ oral ingestion or inhalation may cause abdominal pain, vomiting, and irritation in mucous membranes and eyes. Several studies have found possible connections between ATZ exposure and higher rates of poor semen quality in men and also the manifestation of some birth defects [6,7].

Over the last decade, several instrumental methods for the determination of atrazine have been reported, including high performance liquid chromatography (HPLC) [8], gas chromatography (GC) [9], mass spectroscopy (MS) [10], and GC-MS [11] as well as HPLC-MS [12]. There is no doubt that instrumental methods are extremely sensitive and useful for laboratory measurements, however, this methodologies demands in many cases to

pretreat the sample, are very time consuming and requires qualified and experienced staff to be achieved, making this methods highly inconvenient for in-field detection. Electrochemical measurements are considered as an ideal candidate for detecting pollutants in field, due to their advantages such as selectivity, simplicity, sensitivity, operational feasibility, and easy miniaturization [13,19].

On the other hand, tetraruthenated porphyrin (TRP) consists of a Tetrapyridylporphyrin (TPyP) coordinated to four Ru (II) complexes in the periphery of the macrocycle. These kind of macrocycles are particularly attractive because they display unusual electrocatalytic [20,21] and photoelectrochemical properties [22,23]. In particular, these porphyrins have been used in the electroanalytical detection of S (IV) oxoanions [24–26] and electrocatalytic reduction of O₂ [27] and CO₂ [28]. In all cases, a

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multielectron transfer is essential to enhance the catalytic activity [24–26,28–32].

Ionic liquids (IL) are ionic salts formed from large and very asymmetric ions, whereby their cation-anion forces are weaker than inorganic salts, this phenomenon makes this salts liquid over a wide range of temperatures [33,34]. Ionic liquids present a wide variety of interesting properties, among them highlights their capacity to solvate hydrophobic molecules, their high viscosity, ionic structure, ionic conductivity, very low volatility and biocompatibility making them attractive for electrode modification [35].

In most cases, electrodes modified with IL droplets or film are prepared by direct deposition of IL or a drop of a diluted solution in volatile solvent on the electrode surface. These two procedures may provide different geometry of the deposit [35]. For some studies, unmodified electrode substrates like basal plane pyrolytic graphite (bpg) [36–38], glassy carbon [39,40], gold [41], indium tin oxide (ITO) [42] or edge plane pyrolytic graphite [43] were used. Other examples of ionic liquids modification describes focus in a more efficient IL wetting process, a good example of that procedure is the study of a pre-modification of a gold surface with self-assembled 2-aminoethanethiol [44] or the use of paraffin-impregnated graphite [45]. A typical solution to avoid the use of organic solvents is the use of a microliter amount of IL or an aqueous solution of IL deposited in the electroodic surface [36–40,42,45]. Also a system in which working, counter and reference electrodes are coated with an ionic liquid have been previously reported [46,47].

Due to its high conductivity, fast ion mobility and remarkable solvation properties, ionic liquids appear as a promising mediator and agglutinating agent in carbon paste electrodes, partially replacing paraffin oil, allowing the inclusion of a wide variety of catalyst to the electrode mixture. This kind of modified electrodes have been used as sensors for a series of analytes, going from sulphite [48] to dopamine [49]. Recently, Atar and collaborators have designed a wide variety of carbon based modified electrodes [50,53], one of the most important results was obtained with a carbon paste modified electrode, used as a Rutin sensor [51], authors have incorporate CoFe_2O_4 nanoparticles and *n*-ethyl-3-methylimidazolium hexafluorophosphate into a classic carbon paste electrode. This novel surface have been tested for determination of Rutin in real samples, with high selectivity and recovery percentage reaching a detection limit of 0.1 nM and percentages of recovery very close to 100% in orange juice.

Same authors have also developed a method to determine atrazine using a carbon paste electrode modified with CuO nanoparticles, reaching detection limits as low as 0.01 nM [50].

Herein, the design, construction and characterization of a glassy carbon modified electrode with tetra-ruthenated metalloporphyrin ($\text{M}=\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$) and 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

BMIMNTF_2 (see Figure 1). These modified electrodes will be evaluated as electrocatalysts toward the electrochemical detection of atrazine in neutral media. Differential pulse voltammetry (DPV) was used as the determination technique. The analytical application of the proposed electrode will be evaluated, and electroanalytical data such as limit of detection and quantification will be determined.

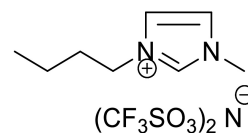


Fig. 1. 3-methylimidazolium bis(trifluoromethylsulfonyl)imide structure.

2 Materials and Methods

2.1 Reagents

All chemical reagents used were reagent grade or better.

The precursor complex cis dichloro (2,2'-bipyridine) ruthenium (II) dihydrate was prepared following the procedure previously described in the literature [54]. The supramolecular complexes of Zn (II) and Ni (II) μ -{*meso*-5,10,15,20-tetra(pyridyl)porphyrin}tetrakis bis (bipyridine)(chloride) ruthenium(II)} (PF_6)₄ were prepared by the method described by Toma et al. [54,55]. The purity of these compounds was checked by optical absorption spectroscopy, elemental analysis and ¹H-NMR. The ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($\geq 98\%$, Merck, Germany) was vacuum dried and used without any further purification.

2.2 Apparatus

For Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) were carried out using a CH Instruments 760 C. Working electrodes were glassy carbon discs purchased from CH Instrument ($r=1.5$ mm), as auxiliary electrode a Pt wire (CH Instruments) was used, and a Ag/AgCl_(aq) (CH Instruments) was used as reference electrode. All potentials are referred to this reference electrode. SECM images was registered using Carl Zeiss EVO MA10 microscope. Contact angle measurements were performed in a home-built apparatus equipped with a digital camera, connected to a computer. Sessile water and BMIMNTF_2 -MTRP mixtures drops of 8 μL was used for static contact angle [56,57].

2.3 Preparation of Modified Glassy Carbon Electrode

After each experiment, the GC electrode was cleaned by polishing with 0.3 μm and 0.05 μm alumina slurries. The electrode was rinsed with double distilled, deionized water and left in an ultrasonic bath for 30 s, to remove any

remaining alumina. Finally the electrodes were rinsed again with abundant deionized water.

The procedure for the preparation of the modified electrodes (ME) is described briefly below.

GC/BMIMNTF₂/MTRP-modified electrode. A 1:9 mixture of IL and 1 mM MTRP is prepared, the resulting mixture is immersed in an ultrasonic bath for 5 minutes to ensure total dissolution of MTRP. Eight microliters of this solution was placed on the surface of the GC electrode, and it was allowed to dry at room temperature (drop coating) [24,25,32].

2.4 Cyclic and Differential Pulse Voltammetry Measurements

The cyclic and differential pulse voltammetry experiments were performed using a 0.10 M NaClO₄ (pH 6) as supporting electrolyte. All the experiments were carried out at room temperature. Differential pulse voltammetry was then performed, applying the potential range of 0.5 to 0.9 V, step potential of 4 mV, modulation amplitude of 50 mV, modulation time of 0.05 s and interval time of 0.1 s.

3 Results and Discussion

3.1 Morphological Characterization of Modified Electrodes

3.1.1 Scanning Electron Microscopy

The modified electrodes were morphologically characterized by SEM. Figure 2 shows SEM images obtained for GC, GC/BMIMNTF₂ and GC/MTRP/BMIMNTF₂ electrode, using the same procedure described in Section 2.

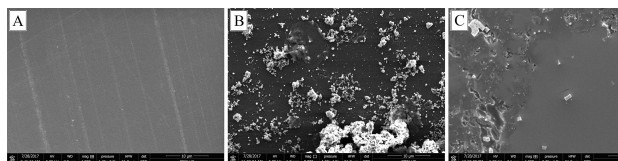


Fig. 2. SEM images of A) GC, B) GC/ ZnTRP and C) GC/ ZnTRP/BMIMNTF₂ (amplification 10 μm).

When ZnTRP is incorporated into the surface of the GC, it is covered by irregular nodules, as shown in Figure 2B.

However, the addition of BMIMNTF₂ (Figure 2C) drastically changes the morphology evidencing a kind of encapsulation of MTRP in the ionic liquid (this can be justified by means of π system and/or electrostatic interactions between both).

This phenomenon is common in carbonaceous surfaces modified with porphyrins in ionic liquid media [58], and can be interpreted as a change in morphology due to interactions between the ionic liquid and the extended π

ring of the macrocycle, giving rise to strong interactions that impede proper precipitation of MTRP on the electrodic surface. It is known that the bipyridine ligand can be considered as a π -extended system and sufficiently planar to facilitate interactions by stacking between adjacent molecules [58].

The modified surface is too soft and fragile to be characterized by atomic force microscope and/or Raman spectra.

3.1.2 Contact Angle

Figure 3 shows the contact angle formed between a glassy carbon plate and a) water, b) BMIMNTF₂, and c) the mixture ZnTRP/BMIMNTF₂. Using the contact angles between the glassy carbon plate and a polar reference solvent (water, 60°) and an apolar solvent (diiodomethane, 42.4°), surface free energy for the glassy carbon plate was estimated using the Wu equation, being 57.02 mNm⁻¹, where the dispersive part corresponds to 39.04 mNm⁻¹ and the polar component being (17.98 mNm⁻¹) [56]. According to these results, the glassy carbon surface behaves as a polar surface, hence, polar substances will interact strongly, and therefore, adhesive interactions will be predominant in the solvent/electrode surface system [56,57].

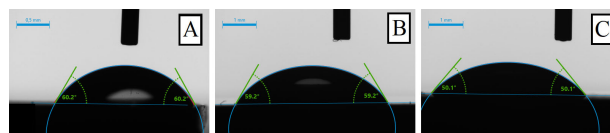


Fig. 3. Microscopic images of a drop of a) water, b) BMIMNTF₂ and c) ZnTRP/BMIMNTF₂ on glassy carbon. Contact angles are represented in each image and calculated according to the model.

Figure 4 shows the variation on contact angle between the surface and a droplet of ZnTRP/BMIMNTF₂. It is very clear that contact angle reaches a maximum in 0% of ZnTRP, and it start decreasing in a non-linear way while the percentage of ZnTRP increases, reaching a plateau at 50% ZnTRP.

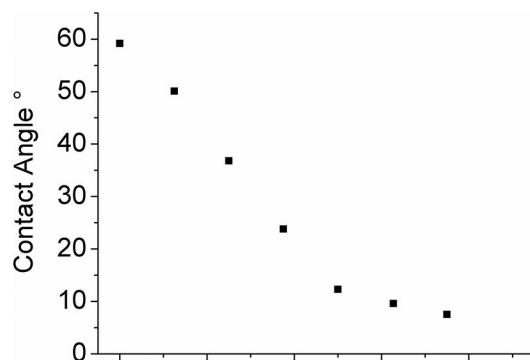


Fig. 4. Contact angle vs % de ZnTRP in the mixture.

The observed behavior fits well with the expected character of the surface. As it was previously calculated, glassy carbon behaves as a polar surface, hence, any increases in the relative polarity of the substance will result in an increase in the adhesive interaction between the surface and the drop. According to this observation we can assume that the electrode will interact intimately with the solution and that the affinity between the solution and the surface will be stronger when the ZnTRP concentration reaches its maximum, giving rise to a robust modification of the electrodic surface [56,57].

3.2 Voltammetric Studies of ATZ Oxidation

The electrocatalytic activity of GC, GC/BMIMNTF₂ and GC/BMIMNTF₂/MTRP (M=Zn (II) and Ni (II)) was evaluated by comparing voltammetric response obtained in absence and presence of 6.5 μM ATZ.

Voltamograms containing MTRP (See Figure 5C and D) exhibit characteristic redox process, associated with porphyrin is present at 0.8 V and corresponds to Ru(III)/Ru(II) redox couple.

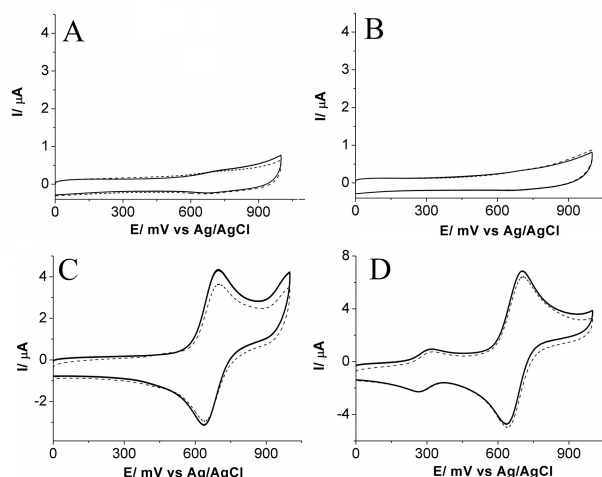


Fig. 5. Cyclic Voltammetry of A) GC, B) GC/BMIMNTF₂, C) GC/BMIMNTF₂/ZnTRP and D) GC/BMIMNTF₂/NiTRP in absence (dash line) and presence (thick line) of 6.5 μM of atrazine in 0.1 M NaClO₄.

In the absence of ATZ, none of the electrodes exhibit relevant voltammetric signals (except those mentioned in the previous paragraph). However, when ATZ is added there is a current increase possibly related to its oxidation. It should be noted that this increase only occurs in the electrodes modified with BMIMNTF₂ and MTRP, since the unmodified GC and the one modified with the ionic liquid do not present any variation.

Although the increase in current in cases C and D is small, it is significant in the use of a more sensitive technique and large compared to bare glass carbon and with ionic liquid. Additionally, the electrode is very stable

when exposed to air for 30 days, the reproducibility of the modification protocol was calculated from ten independent runs obtaining a RSD of 5 %.

On the other hand it is important to note that tests were performed with BMIMBF₄ and BMIMPF₆. However, the modification was not reproducible since this ionic liquids were not able to form a stable film on the surface of the electrode. When the electrodes modified with BMIMBF₄ and BMIMPF₆ are immersed in the solution, the formed film is either detached or dissolved. This fact can be explained by the polarity of BMIMBF₄ and by the size of each anion (See Figure 6), it is suggested that smaller anions will form weaker films.

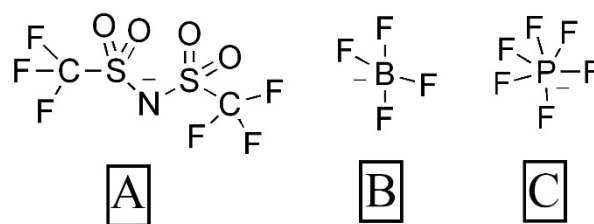


Fig. 6. Structure of A) NTF₂⁻, B) BF₄⁻ and C) PF₆⁻ anions.

3.3 Differential Pulse Voltammetry Study of Atrazine Oxidation at the GC/BMIMNTF₂/MTRP Modified Electrodes

Since ionic liquids are highly viscous, mass transport is limited between the electrode and the solution, leading to a high capacitive current that could affect the determination and quantification of the analyte. To solve this issue, differential pulse voltammetry (DPV) is used, it is evident that DPV is much more current sensitive than cyclic voltammetry, and that using this method the sensitivity to atrazine of the modified electrodes can be successfully determined. The Figure 7 depicts the corresponding calibration plots at 730 mV obtained after sequential additions of atrazine at modified electrodes.

There is a linear relation between the current response and atrazine concentration in the range 0 to 2.5 μM for GC/BMIMNTF₂/NiTRP and 0 to 3.5 μM for GC/BMIMNTF₂/ZnTRP (see Figure 7). Limit of detection (LOD) were calculated as three times the standard deviation of the blank over the sensitivity and in all cases the value was in the order of 10⁻⁹ M. The regression equations obtained were $y(\mu\text{A}) = 0,212 + 697,12 \times (\text{nM})$ and $y(\mu\text{A}) = 0,077 + 1368,1 \times (\text{nM})$ for the electrodes modified with NiTRP and ZnTRP respectively.

Results suggest that both modified electrodes can efficiently detect and quantify atrazine, being the electrode modified with ZnTRP the most sensitive. It is worth note that after a certain concentration the electrochemical signal becomes no longer linear with the concentration, suggesting a saturation of the modified surface, this fact

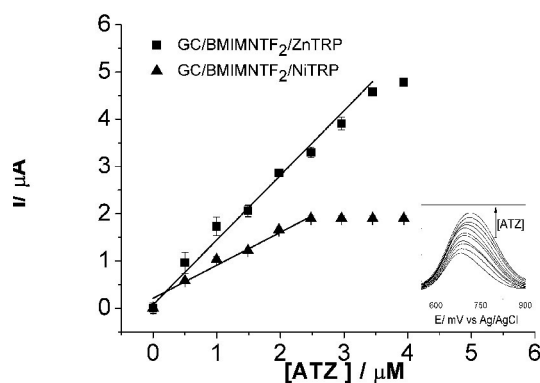


Fig. 7. Calibration curve for differential pulse voltammetric response of GC/BMIMNTF₂/ZnTRP and GC/BMIMNTF₂/NiTRP. **Insert:** Electrochemical response of GC/BMIMNTF₂/ZnTRP.

can be explained by a saturation of the active sites in the electrode [58].

At present there are several studies of atrazine oxidation, however the objective of these is to degrade this herbicide for the remediation of contaminated groundwater and not its quantification [59–63]. The results show that the main oxidation products are desethyl atrazine, desethyl desisopropyl atrazine and cyanuric acid (see Figure 8).

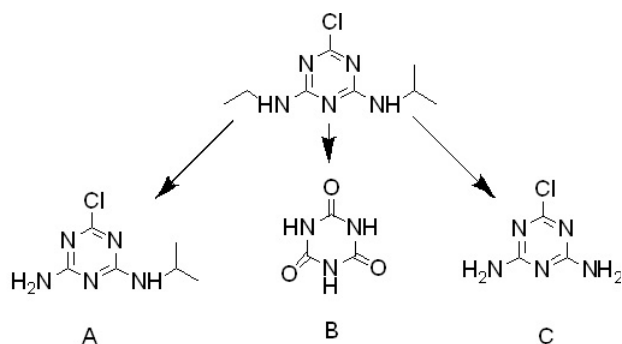


Fig. 8. Main atrazine oxidation products, a) desethyl desisopropyl atrazine, b) cyanuric acid and c) desethyl atrazine.

Recently several analytical methods have been developed for the determination of atrazine such as: gas chromatography coupled to mass spectrometry (GC/MS), liquid chromatography (LC), quartz crystal microbalance (QCM), carbon paste electrodes and electrode modified with molecularly printed polymers [8, 9, 50, 64, 65].

GC, LC and QCM methods have very low detection limits, however, they are very expensive and difficult to carry and harder to implement when compared to electrochemical methods. The electrochemical methods presented by Yolas and Kardas [50, 65], although they are sensitive and portable, the preparation of the modified electrodes is very long compared to the one presented in

this study. Although the LODs presented in this work are higher (see Table 1), herein the preparation of the electrodes are simpler and faster, resulting in a considerable gain of time. Although our electrodes are above the standard recommended by the EPA [66] regarding the maximum amount of atrazine in drinking water (13.9 nM) these can still be improved.

Table 1. Comparison of the prepared modified electrodes in this study with the others analytical methods.

Material or Method	Linear Range/ nM	LOD/ nM	Reference
Pt NPs/Carbon nitride nanotubes with MIP	0.001–0.1	0.00015	53
CuO nanoparticles	0.01–2	0.002	54
MIP	0.08–1.5	0.028	55
Graphene-coated magnetic NPs	0.46–232	0.116	8
Al wire with MIP layer	463–41728	199	9
GC/BMIMNTF ₂ /ZnTRP	212–2500	230	This work
GC/BMIMNTF ₂ /NiTRP	76.8–3500	540	This work

4 Conclusions

A simple procedure was used to modify glassy carbon electrodes using a tetra-ruthenated metalloporphyrin (M:Zn (II) and Ni (II)) and the ionic liquid BMIMNTF₂. The electrocatalytic activity of these modified electrodes were compared against oxidation of atrazine in neutral media (0.1 M NaClO₄).

Interactions between the electrodic surface and the porphyrin solution were studied with contact angle and SEM, finding that the porphyrin solution and the carbon surface interact intimately, forming robust films on the electrode.

These modified electrodes shows a good performance for the atrazine oxidation, this results translate into a low detection limit, high sensitivity, short response time, satisfactory linear concentration range, very good stability and reproducibility. The quick and easy preparation of modified electrode, production low cost in addition to its very good stability and catalytic effect, shown these modified electrodes can potentially be used for the determination of atrazine in water.

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