ELECTROANALYSIS OF ATRAZINE IN WATER AND BEVERAGES

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This article proposed a new electronalytical method for the assay of atrazine, which is a triazine herbicide widely used in the environment due to its water solubility and slow degradation. An electrochemical sensor constructed using the physical immobilization of 5,10,15,20-tetraphenyl-21H,23H-porphine in a nanographene paste was used for the determination of atrazine in water and in beverages. The working concentration range was between 1×10^{-8} and 1×10^{-4} mol L^{-1} with a sensitivity of 178.10 A $mol^{-1}L$. Recoveries higher than 97.00% were obtained, when the sensor was used for the assay of atrazine in water, apple flavored drink, and apple juice.

Keywords: atrazine, electrochemical sensor, 5,10,15,20-tetraphenyl-21H,23H-porphine, water, beverages

1. Introduction

Herbicides are used to help and regulate the growth of plants. They are used by farmers and the food industry in order to help manage the food production worldwide. It is important to provide a healthy and environmentally conscious food system with the right principles. Atrazine is an herbicide belonging to the triazine chloride class, known for its systemic properties. It is often employed in the management and suppression of weed and mold development. Pesticide mixes that incorporate atrazine have been officially approved for use on many agricultural crops, with the highest utilization observed in the cultivation of field corn, sweet corn, sorghum, and sugar cane. Because atrazine has a low absorptivity in soil and a long lifespan (about 231 days), it has a greater potential to create contamination in both ground water and surface water [1].

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Furthermore, atrazine products have been officially authorized for use on crops such as wheat, macadamia nuts, and guava, as well as for non-agricultural purposes like nursery/ornamental and turf applications. Although its utilization was limited or even prohibited in many cases, atrazine is still used by farmers. Therefore, one can find from small to bigger (far higher amounts than the limits established by specialized bodies) amounts in surface water, fruits, beverages, and vegetables. According to the Environmental Protection Agency of the United States, atrazine is a substance that is classified as a carcinogen and is also considered to be an endocrine disruptor. [2, 3].

By concentrating on environmental monitoring at low concentrations (mg/L–ng/L), analytical techniques are being developed with the goal of improving selectivity and specificity. It is still of utmost significance to regulate the presence of this substance in water and food samples, despite the fact that the consumption of atrazine has been prohibited in some countries. This is because of the negative impact that it has on the health of humans and the aquatic environment. To date, the methods proposed for the analysis of atrazine are based on utilization of chromatographic, optical and electroanalytical techniques. Chromatographic methods were extensively used in order to conduct the analysis of atrazine in biological materials, food and water [4,5]. In addition to being time-consuming, labor-intensive, and expensive, the detection of atrazine using standard chromatographic methods [6–10] necessitates the presence of significantly large quantities of reagents and individuals who have received the requisite level of training. In recent years, there has been a rise in research and development for electrochemical methods for pesticide detection, such as atrazine. This is due to the fact that the procedures stated above have their limitations [11,12]. Photoelectrochemical aptasensors [13,14], an optical fiber chemiluminescent biosensor [15], an electrochemical sensor [16], and a portable instrument based on a sensor constructed with ultrasonically dispersed graphene [17] are the latest sensors - based determination methods recently reported for the assay of atrazine.

Utilization of electrochemical sensors for on-site fast analysis of pollutants is the most cost-effective method that may be used for continuous monitoring of the quality of water and also for on-site assay of pollutants from beverages. The development of electrochemical sensors has been accomplished by employing a variety of carbonaceous materials. Because of the several remarkable features that they exhibit, these materials have attracted an enormous amount of interest thanks to their many advantages. A few examples of these qualities are the presence of exceptional chemical and physical characteristics, resistance to corrosion, great heat resistance, extremely high electrical conductivities, and enormous specific surface areas. Additionally, these elements are the functional materials that have become the subject of the greatest research in the field of sensor development. Therefore, this paper proposed a sensor based on 5,10,15,20-tetraphenyl-21H,23H-

porphine (TPP) physically immobilized in a paste formed by mixing graphene nanopowder and paraffin oil. The novelty of the paper is given by the electrochemical sensor's design, and its utilization for on-site monitoring of atrazine.

2. Experimental

2.1 Materials and reagents

Atrazine, 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TPP), copper sulfate, iron sulfate, simazine, potassium carbonate, sodium chloride were purchased from Sigma Aldrich. From Merck was purchased paraffin oil. Atrazine solutions were prepared daily, in Britton Robinson buffer (BRB, pH = 2). The nanographene was purchased from Nano Innova Technologies.

2.2. Apparatus

All measurements were conducted using a Mini Potentiostat "EmSTAT Pico" (software PsTrace 5.8 PalmSens, Houten, Netherlands), which was linked to a laptop. The investigation of atrazine was conducted using the differential pulse voltammetry (DPV) method.

The experiment involved introducing samples into an electrochemical cell equipped with the proposed electrochemical sensor, a counter electrode (platinum wire), and a reference electrode (Ag/AgCl, 0.1mol/L KCl).

2.3. Design of the electrochemical sensor

In order to get a uniform consistency, the nanographene powder was combined with paraffin oil, resulting in a homogenous paste. This paste was subsequently subjected to a further modification with 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TPP). 100µL of TPP were added to 100mg nanographene paste (nGR). A three-dimensional plastic tube had been filled with the nanographene paste after it had been modified. The electrical connection that linked the modified paste to the outside circuit was made with silver wire. Before using the sensor, its surface was cleaned with deionized water and polished with paper. The electrochemical sensor had been maintained under controlled conditions, specifically at ambient temperature and in a light-restricted environment, prior to its utilization.

2.4. Recommended procedure

Differential pulse voltammetry (DPV) (working parameters: scan rate 25 mV/s, scanning potential range -0.3 to 0.7 V) experimental measurements were conducted at a temperature of 25°C for every standard solution (10^{-2}–10^{-12} mol/L). The peak heights were quantified by measuring their intensities, and subsequently, a calibration equation was derived by the use of the linear regression approach. The

concentrations of unknown samples were determined using the calibration equation derived from statistical analysis.

2.5. Samples

The analytical applicability of the TPP/nGR sensor was tested by detecting atrazine in water samples, apple juice, and apple flavoured drink. Britton Robinson buffer (BRB) with a pH=2 containing 0.1 mol L^{-1} NaCl was used to buffer the samples.

2.6. Selectivity studies

The analysis regarding the selectivity of the electrochemical sensor was conducted by examining its response to several compounds, including simazine, Cu^{2+}, Fe^{2+}, and CO_3^{2-}. The purpose was to evaluate the selectivity of the designed electrochemical sensor. To estimate the selectivity coefficients, the amperometric technique was employed, utilizing mixed solutions. The selection of these substances was based on their common occurrence in water and beverage samples. In the combined solutions, the molar ratio among atrazine and the presumed interferent was 1:10.

3. Results and discussions

3.1. Characteristic response of the proposed electrochemical sensor

Differential pulse voltammetry (DPV) technique was used to determine the response characteristics of the electrochemical sensor. The voltammograms employed for calibrating the suggested sensor in the assessment of atrazine were depicted in Fig. 1. The concentration range within which the electrochemical sensor works is between 1×10^{-8}mol L^{-1} and 1×10^{-5}mol L^{-1}, the limit of determination was 1×10^{-8}mol L^{-1}, while the limit of detection was 3×10^{-9} mol L^{-1}.

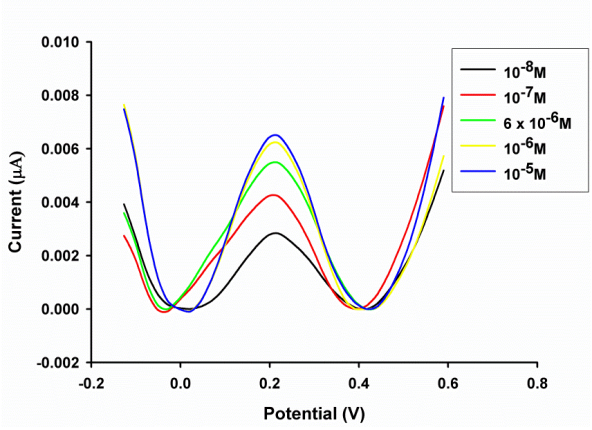

Fig. 1. Differential pulse voltammograms obtained for different concentrations of atrazine, when a scan rate of 25 m s^{-1}, and modulation amplitude of 25 mV were used.

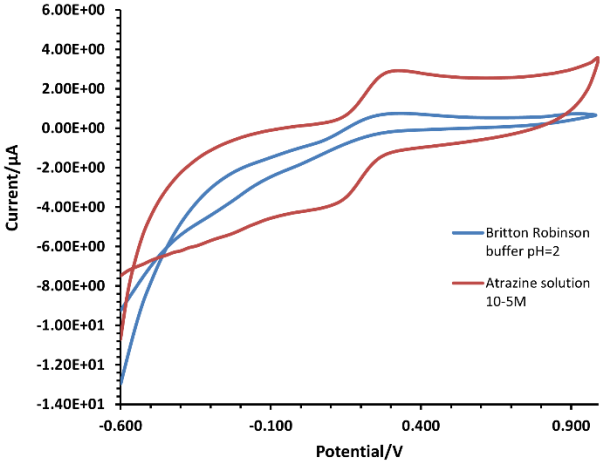

Fig. 2. Cyclic voltammograms obtained: a) in the absence of atrazine (blue line), and b) in the presence of atrazine (red line), when a scan rate of 25 m s^{-1}, and step potential of 25 mV were used.

The cyclic voltammograms presented in Fig. 2, show a clear difference between the results obtained using only Britton Robinson buffer (BRB) pH=2 (blue line), and a solution containing atrazine with a concentration of 10^{-5}M (red line).

Fig. 3 shows the calibration graph for atrazine. The equation of calibration is the following:

$$I = 0.01 + 178.10 \times C_{atrazine} \quad (1)$$

where I is the current recorded in A, $C_{atrazine}$ is the concentration of atrazine in mol L^{-1}.

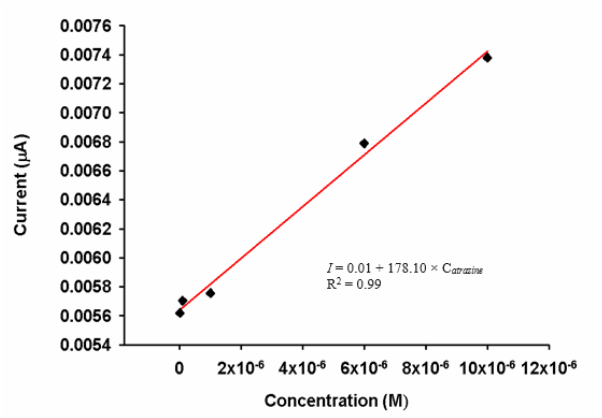

Fig. 3. The calibration graph for atrazine was obtained utilizing the proposed sensor based on the modified nanographene paste.

The correlation coefficient obtained for the equation of calibration is 0.9949. The sensitivity recorded (178.1 A mol^{-1} L) is very high allowing excellent concentration differentiation.

In order to determine atrazine, Švorc et al. [18] devised a new electrochemical approach that is sensitive, easy to use, and uses square-wave voltammetry on a boron-doped diamond electrode. With the improved square-wave voltammetric settings, we were able to obtain a linear concentration range of 0.05 to 40 μM (5.00×10^{-8} – 4.00×10^{-5} mol L^{-1}), high repeatability, and a detection limit of 10 nM (1.00×10^{-8} mol L^{-1}). The atrazine concentration in river water samples spiked with the chemical was accurately determined using the suggested methodology.

Atrazine detection was achieved by Helali et al. [19], by development and use of a disposable immunomagnetic electrochemical sensor utilizing magnetic particles. A streptavidin-coated magnetic monolayer was grown on a gold electrode using a magnetic field, and this structure served as the basis of the sensor. Atomic force microscopy (AFM), cyclic voltammetry, and faradaic impedance spectroscopy were used to analyze the magnetic monolayer. Atrazine can be detected sensitively with this method, and the linear response is good in the concentration range of 10-600 ng/ml (4.63×10^{-8} – 2.78×10^{-6} mol L^{-1}).

An atrazine biosensor based on tyrosine inhibition was introduced by Guan et al. [20]. After 15 minutes of incubation in a phosphate solution containing atrazine, they measured the signal of the biosensor that had been blocked to a phenol solution with a concentration of 5 mM. A limit-of-detection of 46.36 nM (4.63×10^{-8} mol L^{-1}) and a linear response from 231.82 to 13090 nM (2.31×10^{-7} – 1.30×10^{-5} mol L^{-1}) were achieved.

Table 1

Electrochemical detection methods for atrazine.

Sensor Material	Method	Linear range (mol L-1)	Limit of detection (mol L-1)	Reference
BDD	SWV	5.00×10^{-8} – 4.00×10^{-5}	1.00×10^{-8}	[18]
biotinyl–Fab fragment K47 antibody/magnetic beads/Au-electrode	CV	4.63×10^{-8} – 2.78×10^{-6}	-	[19]
poly(L-Dopa)-tyrosinase (PDM-Tyr)/Nafion/Au	Inhibition measurement	2.31×10^{-7} – 1.30×10^{-5}	4.63×10^{-8}	[20]
TPP/ nGR	DPV	1×10^{-8} – 1×10^{-5}	3×10^{-9}	(this work)

All of the results obtained in Table 1 are similar to the results obtained in this study.

3.2. Selectivity of the electrochemical sensor

The two most prevalent approaches to amperometric electrodes are the mixed solution technique and the separate solution method. Both of these techniques may be used to get the amperometric selectivity coefficients by employing any of these two methods. For the purpose of calculating the amperometric selectivity coefficients, it is recommended to make use of the mixed solution approach rather than the separate solution technique. This is due to the fact that the mixed solution approach accurately portrays the actual conditions under which the electrode is utilized.

Through the use of the aforementioned approach, we are able to derive the equation for finding the amperometric selectivity coefficient by using Wang's proposed equation [21]. When conducting an analysis of a solution, it is usual practice to compare the current that is measured for a solution that only contains the major species to the total current that is derived by the equation that was published by Wang [21] for a solution that contains both the main species and the species that interfere the main species.

The following equation was utilized in order to determine the amperometric selectivity coefficients [22]:

$$Ki,j(amp) = \left(\frac{\Delta It}{\Delta Ii} - 1\right) * \frac{ci}{cj} \qquad (2)$$

where $K_{i,j}^{(amp)}$ is the amperometric selectivity coefficient, $\Delta I_t = \Delta I_t - \Delta I_b$, ,$\Delta I_b$ = the current intensity recorded for the blank solution, ΔI_t =the total current intensity, $\Delta I_i = \Delta I_i - \Delta I_b$, ΔI_i= the current intensity recorded for the main ion, and c_i and c_j, concentrations of the main ion and the interfering ions.

The selectivity of the electrochemical sensors may be understood from the amperometric selectivity coefficients ($K_{i,j}^{amp}$) in the following ways:

(i) When it comes to magnitude orders that are more than 10^{-3}, the ion that was tested for interference does interfere;

(ii) For magnitude orders of 10^{-3}, the ion that was tested for interference does not constitute a substantial interferent;

(iii) There is no influence of the ion on a scale that is less than 10^{-3}.

The capability of the ion-selective electrode to distinguish between one ion and other ions, known as interference ions, is characterized by these coefficients.

In order to carry out an examination into the selectivity of the electrode that was recommended, the mixed solution approach was applied. In the process of preparing synthetic mixed solutions, a ratio of 1:10 (mol/mol) was utilized between the atrazine and the alleged interferent. Table 2 presents the results of calculations performed to determine the amperometric selectivity coefficients.

Table 2

Amperometric selectivity coefficients

Interferent	K_{sel}^{amp}
Cu^{2+}	-2.21×10^{-4}
Fe^{2+}	-8.04×10^{-4}
CO_3^{2-}	1.3×10^{-4}
Simazine	1.27×10^{-3}

The results show that Cu^{2+}, Fe^{2+}, CO_3^{2-}, and simazine did not interfere in the determination of atrazine.

3.3. Determination of atrazine in water and beverages samples

Differential pulse voltammetry was used for the determination of atrazine whole two water samples. The electrochemical cell containing the three electrodes was immersed in the cell which was filled with the sample (water, beverages). The results of the measurements are presented in Table 3. Atrazine was first determined from water samples/beverages and then known amounts of atrazine were added. The differences between the amounts of atrazine found after addition of known amounts and the initial value were compared with the added amount. The recovery test shows a high recovery of atrazine, and low RSD values.

Table 3

Determination of atrazine in water samples and beverages using the proposed electrochemical sensor and HPLC based methods [5] (N=10).

Samples	**Amount of atrazine added (mol L^{-1})**	**Amount of atrazine found using the electrochemical sensors (mol L^{-1})**	**%, Recovery obtained when the electrochemical sensor was used**	**Amount of atrazine found using the HPLC method [5] (mol L^{-1})**
Surface water	1×10^{-6}	9.89×10^{-7}	98.91±4.50	9.67×10^{-7}
Waste water		9.73×10^{-7}	97.27±3.99	1.02×10^{-6}
Apple flavoured drink		9.95×10^{-7}	99.48±1.86	9.78×10^{-7}
Apple juice		1.00×10^{-6}	100.20±5.31	1.04×10^{-6}
Student -t-test				1.79

A student paired-t-tests was used to compare the results obtained with the proposed electrochemical sensor, and the results obtained with the HPLC method

developed by Jacomini et al. [5]. The 99.00% level of confidence (tabulated theoretical t-value: 4.032) was considered for the t-test. There is no statistically significant difference between the findings obtained using the electrochemical sensor and the HPLC approach, as the values obtained (1.79) are lower than the calculated theoretical value. Accordingly, the atrazine can be determined in fruits, and beverages accurately using the proposed electrochemical sensor.

4. Conclusions

An electrochemical sensor constructed using the physical immobilization of 5,10,15,20-tetraphenyl-21H,23H-porphyrin (TPP) in nanographene powder has been proposed for the analysis of atrazine in water and beverages samples. The electrochemical sensor exhibited elevated levels of sensitivity and selectivity, in addition to low limits of determination and detection. The wide working concentration range obtained facilitated the determination of atrazine from very low to high concentrations in water samples and beverages. The features of the proposed electrochemical sensors are connected with its utilization as screening tool for the quality of water, as well as in supermarkets for food security checks.

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