Atrazine Voltammetric Determination in the Pesticide Industries Wastewater by Gold Nanoparticles at a Modified Glassy Carbon Electrode

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Abstract

In this study, gold nanoparticles (AuNPs) were synthesized using sodium borohydride ($NaBH_4$) as reductant. AuNPs size and shape were experimented by using various characterization techniques. The synthesized AuNPs performance capability for atrazine (ATR) detection, at a glassy carbon electrode (GCE), was verified using cyclic voltammetry (CV) as the determining mode. AuNPs impressive electrochemical performance and stability at the GCE led to further studies, without the need to apply nafion. ATR linear concentration plot ranged from 10 to 17 nM, with a lower limit of detection (LOD) of 0.17 nM, and a regression coefficient (R^2) of 0.9934, under optimized conditions. The proposed sensor was very reliable, with a relative standard deviation (RSD) of 1.1%, for $n = 20$, and it was quite sensitive for ATR, with no discernible interference from other ions. Consequently, AuNPs were effectively used to identify ATR in several pesticide industry wastewater samples.

Keywords: ATR, AuNPs, GCE, sensor and wastewater.

Introduction

Gold nanoparticles (AuNPs) diversity allow their application in a number of emerging fields, such as catalysis, electronics and sensors [1], due to their fascinating properties, such as high stability and size dependence. Moreover, AuNPs morphology and size can be easily controlled. Additionally, AuNPs optical and physical properties, and functionalization with surface molecules according to their charge, have enabled significant changes to them in recent years. Capping agents play a crucial role in NPs controlled synthesis, preventing their aggregation/agglomeration, reducing their toxicity, controlling their reactivity, and providing a better understanding of electron-transfer dynamics phenomena [2-4].

Over the last 20 years, organotin compounds have been widely used as pesticides [5]. However, their alarming physiological effects led to the study of synthetic routes. The physical and chemical properties of special compounds, such as ametryn, prometryn, simazine, simeton, cephradine [6] and ATR, along with their biochemical behavior, have been taken into great consideration.

Despite being a problematic pesticide, ATR is listed among the approved products for farming and growing use on a variety of crops, such as cocoa, coffee, pecans, groundnuts, hops, carrot, celeriac, celery, sugar beet and potatoes, in various parts of the world, to control fungal diseases.

The selective detection of compounds by various methods has been reviewed by Saleh IA et al. [7]. A study conducted on ATR (0.01 to 10 mg/L) biological treatment showed that submerged biological aerated filters (SBAFs), with a consortium of adapting bacteria, could remove it from wastewater, in a pilot-scale trial, up to 97.9%. Amounts higher than the guideline value of 3 μg/L in water were considered threatening [8]. This work aimed to study the possible use of AuNPs/GCE for ATR electrochemical measurement, in the pesticide industry wastewater, using CV. Electrochemical parameters, such as buffers, solution pH, CV, stirring rate, accumulation potential and time, were adjusted. The sensor analytical capabilities, such as sensitivity, selectivity and accuracy, were thoroughly investigated.

Experimental

Chemical reagents

In the current work, analytical reagents and chemicals that needed no further purification were utilized and purchased from BDH and Merck. The deionized water used in preparing most of the solutions was Milli-Q®, of low recommended conductivity. An ATR methanol standard solution was prepared.

Instrumentation

For recording spectra in the range from 400 to 1100 nm, a Lambda 2 model (Perkin-Elmer) UV-visible spectrometer was used. A Jeol (JSM 6380A) model device was employed for performing scanning electron microscopy (SEM). The CV recording was assisted by the 760 model potentiostat, of CH instruments (Texas, USA).

AuNPs growth

300 μL of 0.2% chloroauric acid ($HAuCl_4$) were used for AuNPs synthesis. The solution was further filled with 5mL deionized water. To this, 100 μL of 0.1 M sodium hydroxide (NaOH), with 4 mL of a $NaBH_4$ solution, were added. AuNPs growth was evident from the solution wine red color. To study AuNPs synthesis, a UV-vis spectrophotometer, in the range from 200 to 800 nm, was utilized. AuNPs absorbance was measured with a blank reagent, at a SPR wavelength of 518 nm.

Electrode fabrication with AuNPs

About 5 µL AuNPs were carefully dropped on the top of the GCE conductive surface, which was then dried at room temperature.

GCE modification by AuNPs

The GCE modification was done by adding a layer of AuNPs, soaking it in a 4 mL Britton–Robinson buffer (BRB) (pH 6) solution with ATR, at the desired concentration, for each 10 mL volumetric flask. Deionized water was added to the solution, which was put in an electrochemical cell. Under the optimized conditions, CV was employed for the solution analysis. The obtained CVs were compiled and recorded for use in various standard solutions, while ATR determination was being performed.

Applicability of the method for real samples

Approximately 4 mL of industrial wastewater samples were dissolved in a 4 mL BRB (pH 6) solution, and the volume was increased to 10 mL with deionized water. The AuNPs/GCE CVs obtained by the system proved to be accurate for a standard ATR solution. The sensor also analyzed ATR by simple calibration, to confirm the results with a standard addition method.

Results and discussion

UV-vis spectroscopic study

UV-vis spectroscopy is one of the most commonly used techniques for preliminary characterization. AuNPs synthesis was performed by using varied concentrations of reagents, such as $HAuCl_4$, NaOH and $NaBH_4$. When all the parameters were optimized, a blue shifted peak was obtained (Fig. 1).

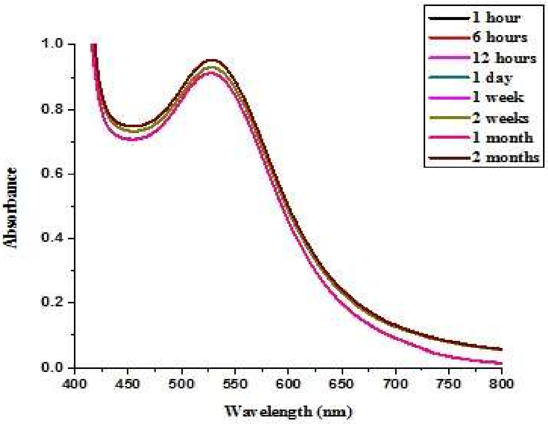


Figure 1. UV-vis spectra of derived AuNPs, with a time lapse study.

AuNPs absorption peak shows a surface plasmon on the absorption band at 508 nm, which exhibits a specific wine red color [9]. This phenomenon, called surface plasmon resonance (SPR), is produced by the electrons oscillation on AuNPs surface, resulting in their synthesized different shades and shapes that are size dependent [10]. Most importantly, AuNPs exhibited remarkable stability in aqueous solutions, even without stabilizing agents or surfactants, using red cabbage extracts under UV light and its catalytic activity.

AuNPs surface characterization by X-Ray Diffraction (XRD)

AuNPs crystalline surface is illustrated by the diffraction peaks (Fig. 2) of XRD data, at 2θ = 37.98° (1 1 1), 44.08° (2 0 0), 64.34° (2 2 0) and 77.36 ° (3 1 1), as reported by Yan et al. [11]. The strong signal attributed to the orientation was predominant at (1 1 1), indicating that these particles are nanoscale sized, with an affinity to similar particles, and that they adjust to a highly stable low energy surface.

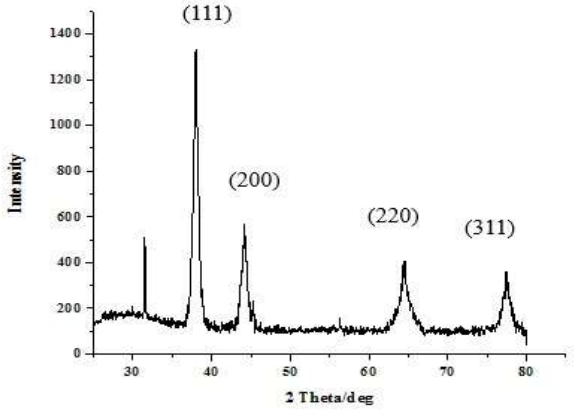


Figure 2. XRD pattern of AuNPs in powdered form.

ATR CV characterization by AuNPs/GCE

CV was used as the voltammetric mode for studying ATR electrochemical behavior, and it was recorded in a BRB (0.04 M, pH 7) solution with AuNPs/GCE. It clearly reveals a strong peak related to ATR reduction process (Fig. 3a).

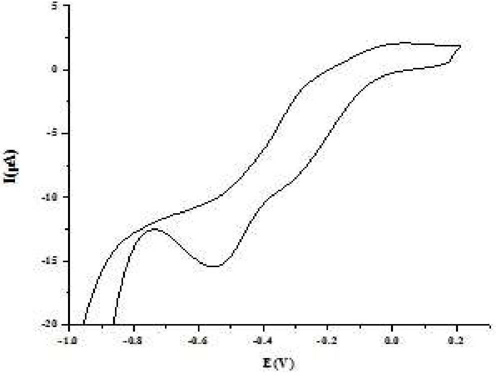
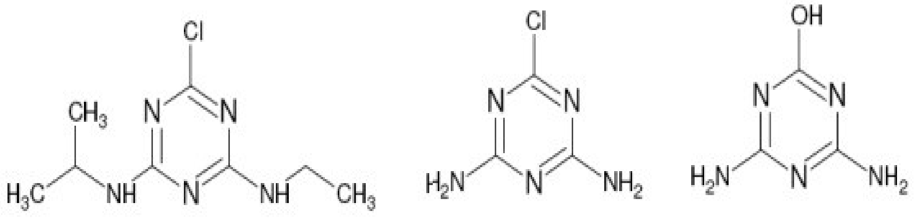


Figure 3a. Typical ATR CV.

According to this reduction peak, these signals contribute to the possible reaction route for ATR degradation, which was carried out by the electrochemical method [12]. Since full protonation influences the substitution at the ring, and creates one or more dealkylated products, the reaction medium acidity has a significant impact on ATR degradation (Fig. 3b). The carbon (C) atoms of the ring linked to amines will be susceptible to electrophilic assault in a similar way. The steric barrier should be greater for the C molecule adjacent to the ethylamine group, because the latter has no chain ramifications, and it has one C atom less than that of the isopropylamine group.



1 **2** **3**

Figure 3b. ATR degradation pathway.

Comparison between bare GCE and AuNPs/GCE

The modified GCE electrochemical sensing capability for ATR determination has been studied with three different phases of electrodes, using 2 mL of a slightly acidic medium. The BRB solution, with pH 5 and a molar concentration of 0.04 M (Fig. 4), produced ATR low determination, when the bare GCE was put to work. In comparison, AuNPs/GCE showed an elevated peak current (I_p) corresponding to the AuNPs electron transfer action that was affected by the synergistic catalytic behavior. It must be kept in mind that nafion [13], as binding reagent, had no noticeable effect on ATR reduction.

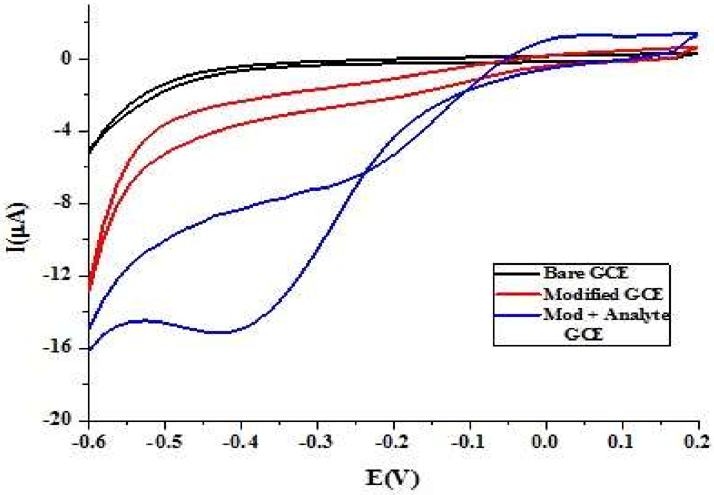


Figure 4. CVs of bare GCE, mod-GCE and mod-GCE with an analyte.

Voltammetric mode selection

Various voltammetric modes, such as CV, square-wave voltammetry (SWV) and differential pulse voltammetry (DPV), were investigated utilizing AuNPs/GCE. for ATR determination. ATR CV determination mode showed a higher peak potential (E_p) than that of other modes (Fig. 5).

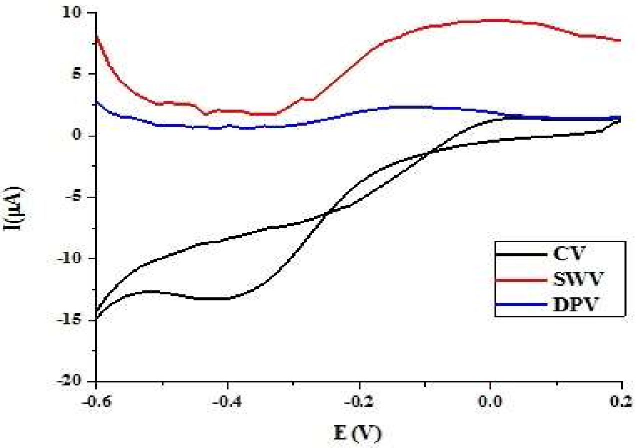


Figure. 5 Voltammetric mode study.

AuNPs amount impact on the GCE surface

The I_p value increased as AuNPs volume was raised at the GCE surface (Fig. 6).

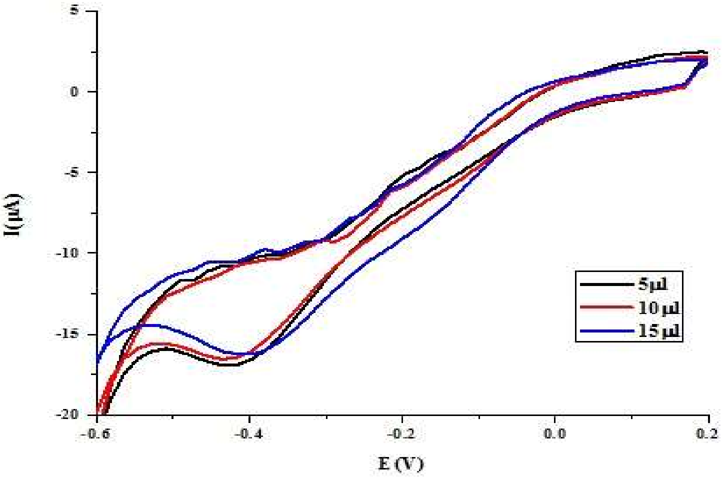


Figure 6. AuNPs coating amount (5 to 15 µl) impact on the GCE.

This indicated an efficient electrons transport network inside AuNPs. Although this layer was also responsible for giving a high surface area to the GCE, the excessive electrons transfer sites provided by AuNPs widened the peak shape. Thus, one 5 µl drop was found to be sufficient for GCE modification. The cations pre-concentration at the electrode/solution interface was greatly induced by the ion exchanging property, which improved ATR electrochemical response [13].

Electrolytes and Ph values effects

ATR was quantified using three different electrolytes (acetate, phosphate and BRB), aiming to achieve the finest peak shape and quality response. Fig. 7a clearly shows that the BRB had the best electrochemical results. Hence, it was finalized for further ATR determinations with AuNPs/GCE.

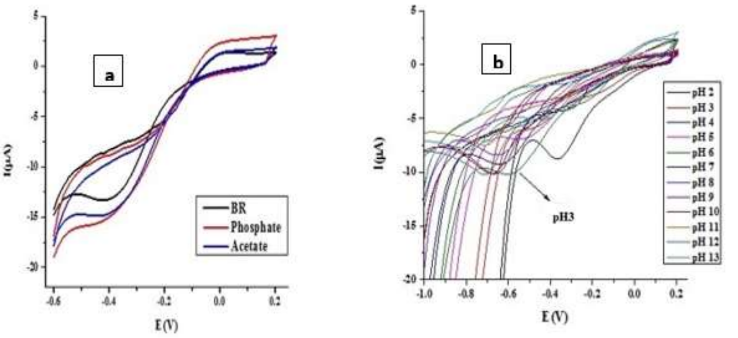


Figure 7. ATR CVs **(a)** with three different electrolytes; **(b)** with pH variations (2 to 13).

The recorded BRBs, with different Ph values (from 2 to 13), showed a slight I_p and E_p dependence on the supporting electrolyte (SE) pH. A shift towards higher current values with increasing pHs was examined, and this was confirmed by the change in the peak position, as well as in I_p, causing a disturbance in its shape (Fig. 7b).
Since a fine shaped peak was obtained with pH 3, additional CVs and calibration plots were recorded at this pH. ATR electrochemical nature has also been investigated, to study its reaction mechanism and structural changes with these variations in the pH. The cathodic peak was slightly dependent on the pH, rising to slightly higher values with an increase in the latter, but the peak shape was being compromised. Thus, CV, with a BRB electrolyte (pH 3) confirmed the reduction peak at -10.3 V.

Interference study

The study of the interference from other ions that are persistently found with ATR is an important key to understand the sensor selectivity. In this aspect, other pesticides were analyzed, and the response of the interfering species towards the signal of the electrode developed for ATR determination was also recorded. All the interfering ions were combined at the 1:1 ratio among the pesticides. Table 1 shows the results of the interference with other pesticides. A positive value reflects an increase in the real detection feedback, while a negative value indicates its 10 μM drop. These results reveal a considerable interference from the majority of the studied ions on ATR signals. Only few ions showed a minor positive or negative interference, but each case was within the tolerable RSD of ±5%. This study suggests that the fabricated sensor proved to be highly selective for ATR monitoring in real samples.

Table 1. Interference of co-existing ions on ATR determination.

Interfering species	Ratio	RSD (%)
Nitenpyram	1 : 1	4.03
Bispyribac sodium	1 : 1	3.98
Fipronil	1 : 1	-2.29
Bensulfuran methyl	1 : 1	4.88
Imidaclopride	1 : 1	-0.98
Azocyclotin	1 : 1	3.33
Haloxyfop	1 : 1	1.98

CV method analytical performance for ATR

The calibration curves for CV ATR determination, in a 0.04 M BRB (pH 7) solution, are displayed in Figs. 8a and b. I_ps were absolutely proportional to ATR concentrations ranging from 10 to 70 nM, with the identification and quantitation limits (LOQ) of 0.17 and 0.58 nM, respectively. Due to ATR high health risks, recently updated data base could be not found. Therefore, this work can serve as a reference for further studies in this research domain.

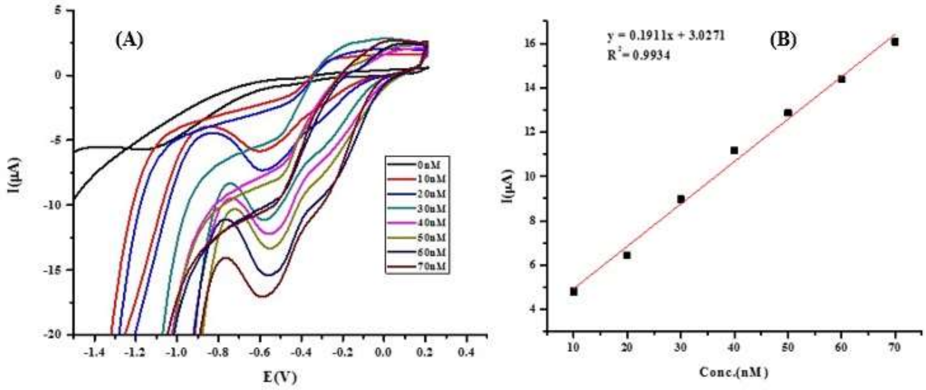


Figure 8. ATR CVs and calibration graph on the AuNPs/GCE electrode in a 0.04 mol/L BRB solution, at pH 3.0.

Applicability of the developed method for ATR determination in wastewater

For ATR determination, water samples were collected from the pesticide industry areas in the Sindh, near the Kotri barrage, and artificial samples were prepared. All the water samples filtration was performed using a 40 mm filter paper (Whattman). The linear relation has been used for ATR quantification. According to the results, ATR was determined in the range from 73.685 to 81.982 nM, in the real water sample, as shown in Table 2.

Table 2. ATR determination by AuNPs/GCE in the pesticide industry wastewater.

Industrial wastewater samples	Calibration method	Standard addition method
Sample 1	82.073 ± 6.61	81.982 ± 4.32
Sample 2	74.025 ± 3.05	73.685 ± 2.88
Sample 3	77.551 ± 5.18	77.456 ± 4.92
Sample 4	79.652 ± 6.81	78.618 ± 4.92

Conclusion

This work reports a ground-breaking AuNPs synthesis. The synthesized material proved to be one of its kind for ATR pesticide detection, which is currently being utilized in Pakistan. The proposed study highlights the degradation of ATR derivatives that are potentially more harmful, and serves to make the concerned authorities more aware of the need for the controlled use of the studied pesticide. The proposed sensor is relevant, under the economical point of view, while it keeps its high sensitivity and selectivity.

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Author's contributions

Safia Sanam Memon: collected the data; performed the analysis. **Muhammad Waris**: inserted the data and analysis tools; wrote the paper. **Ahmed Raza Sidhu**: conceived and designed the analysis. **Marriam Zaqa**: other contributions.

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