

Oxidized Glyphosate Detection by Polypyrrole Imprinted on Copper: A Step towards Impedimetric Affinity Sensors

Diana Jiménez-Rivas¹, José Herrera-Celis^{2,*}, F.M. Cuevas-Muñiz¹

¹ Centro de Investigación y Desarrollo Tecnológico en Electroquímica, México

² Universidad Industrial de Santander, Colombia

djimenez@cideteq.mx, jherrece@uis.edu.co

Abstract. Glyphosate is an aminophosphonate chemical compound part of most commercial herbicides. Due to its wide use in agriculture, it is found in water bodies as an emerging contaminant. This work uses a polypyrrole-based molecularly imprinted polymer as a recognition layer to detect glyphosate. A glyphosate oxidation study was carried out with a non-imprinted polymer (NIP) and a molecularly imprinted polymer (MIP) deposited on a planar Cu electrode using the cyclic voltammetry (CV) technique. Parameters such as scan rate and glyphosate concentration were varied. Glyphosate oxidation tests were performed using the linear voltammetry technique on NIP/Cu and MIP/Cu electrodes and at the highest glyphosate concentration used in the experiments. In conjunction, Raman spectroscopy measurements were performed before and after glyphosate oxidation. Then, impedance spectroscopy measurements were carried out before and after of the linear scan in the presence of glyphosate. Percentage changes were obtained from the impedance measurements. The maximum change in impedance for each glyphosate concentration was achieved around 1 Hz. According to these results, the printed MIP/Cu electrode sites reduce glyphosate oxidation potential due to their higher affinity for glyphosate. Furthermore, low detection limits (LODs) are obtained.

Keywords: Impedance, glyphosate, polypyrrole.

1 Introduction

Glyphosate (gly) is the world most widely used non-selective anionic herbicide (by volume and treated surface). The reported data reveal concentration in water bodies ranging between 10 µg/mL and 10 mg/mL [1–3]. Gly persists in the

environment due to the inert nature of the carbon-phosphorus bond, which causes strong enzymatic inhibition and hinders further degradation [4,5].

Currently, conventional devices, methods, and techniques are used for gly detection; however, they have several disadvantages, such as long response times, the need for specialized knowledge, and in some cases, a lack of selectivity. Therefore, it is important to investigate affinity-based detection platforms for gly.

The fabrication of copper structures and electrodes for applications in sensing devices is increasing. This is due to their easy manufacturing and integration into sensing devices and the possibility of large-scale production in less time compared to alternative materials [6,7]. Another significant advantage of Cu electrodes is the possibility of integrating them with molecularly imprinted polymers (MIPs), which gives them selectivity.

MIPs are synthetic materials designed to recognize and bind specific molecules with high selectivity [8, 9]. MIPs based on polypyrrole (ppy) are particularly notable for their high selectivity, resistance to pH variations, and ease of electrosynthesis, which enables the formation of thin, well-defined films on conductive surfaces [10–12].

2 Experimental Section

The MIP was synthesized using two processes: electropolymerization and overoxidation.

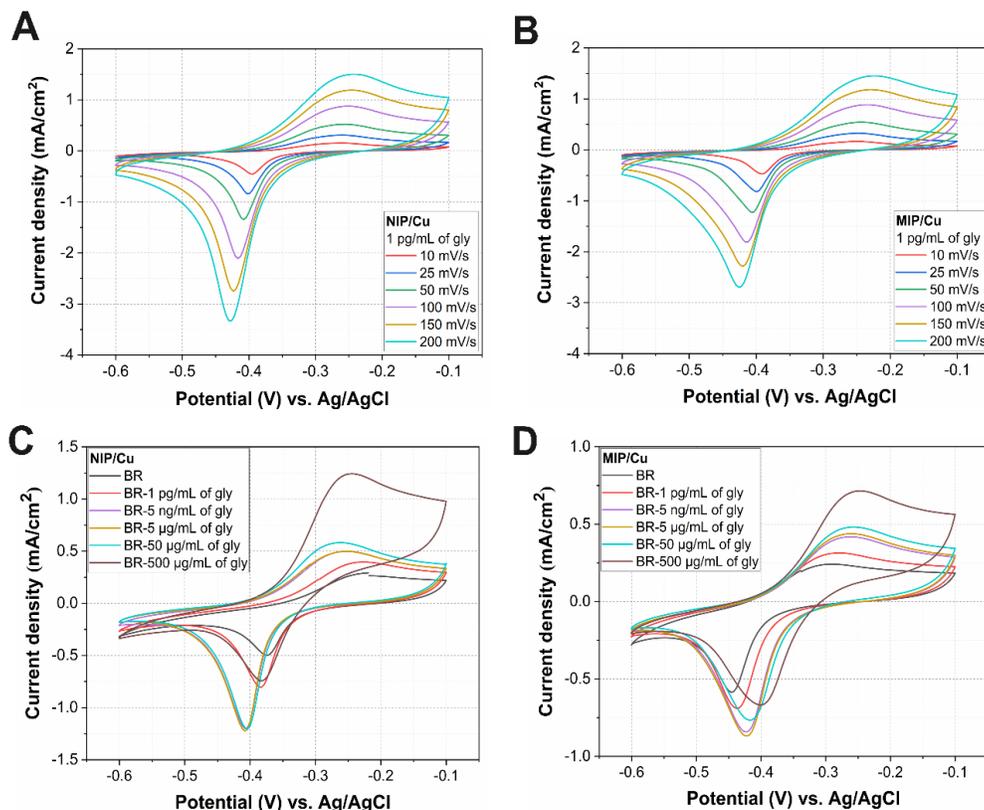


Fig. 1. Cyclic voltammograms of Britton Robinson solution (BRB) and glyphosate (gly) at 1 pg/mL on A) a non-imprinted polymer (NIP/Cu) and B) an imprinted polymer with scan rates of 10, 25, 50, 100, 150, and 200 mV/s. Cyclic voltammograms of gly on C) a non-imprinted polymer and D) an imprinted polymer with gly concentrations of 1 pg/mL, 5 ng/mL, and 5, 50, and 500 μg/mL

Electropolymerization involves the deposition of a polypyrrole film with gly molecules, while overoxidation is in charge of the removal of the glyphosate molecules from the polymer film, creating specific binding sites for glyphosate.

Cyclic voltammetry (CV) at scan rates from 10 to 200 mV/s was performed on non-imprinting polymer (NIP) and MIP on planar copper electrodes using Britton-Robinson buffer (BRB) as supporting electrolyte and gly concentrations ranging from 1 pg/mL to 500 μg/mL.

NIP/Cu and MIP/Cu electrodes before and after gly oxidation at the highest concentration were analyzed by Raman spectroscopy. The following procedure was then performed on the MIP/Cu electrodes to determine the percentage change in

impedance: first, an impedance spectroscopy measurement was performed in the range of 10 kHz to 100 mHz using Britton-Robinson (BR) as buffer solution; second, a linear scan was performed from open circuit potential to -0.1 V in BR in the presence of gly; third, BR washes were performed; and finally, a second impedance spectroscopy measurement was performed under the same parameters as the first.

3 Results

Scan rates on NIP/Cu (Figure 1A) and MIP/Cu (Figure 1B) electrodes with a concentration of 1 pg/mL of gly were studied. For both electrodes, two similar redox peaks were observed as the scan

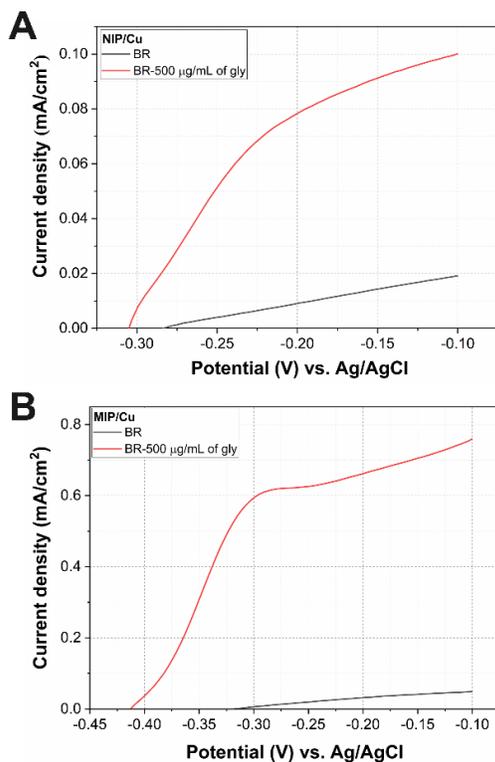


Fig. 2. Linear voltammograms of Britton Robinson solution (BRB) and BRB with glyphosate (gly) at 500 µg/mL on A) a non-imprinted polymer (NIP/Cu) and B) an imprinted polymer

rate increases; the peak at -0.24 V was associated with the oxidation of gly. The 50 mV/s scan rate is more suitable because it allows a better monitoring of the system, where metal complexes, in this case Cu-gly, could form. Furthermore, the modification of the Cu electrode with MIP increases the resistance to charge transfer, so lower scan rates yield sharper redox signals.

In the voltammograms of NIP/Cu and MIP/Cu electrodes (Figure 1C and Figure 1D, respectively), the oxidation peak shows a progressive increase in the peak current as the gly concentration increases in both electrodes; however, the oxidation peak of the NIP/Cu initially more positive (compared to that obtained with the MIP/Cu electrode, see Figure 1D) progressively shifted towards less positive potentials as the gly

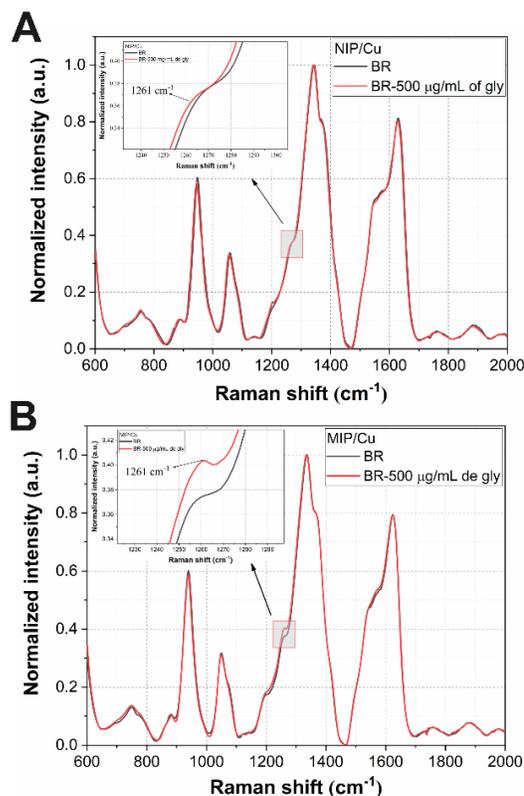


Fig. 3. Raman spectra of Britton Robinson solution (BRB) and BRB with glyphosate (gly) at 500 µg/mL on A) a non-imprinted polymer (NIP/Cu) and B) an imprinted polymer

concentration increased. An opposite behavior was observed with the MIP/Cu electrode.

To analyze the oxidation peak at -0.24 V, linear voltammetry was performed in the oxidation direction for both NIP/Cu and MIP/Cu electrodes. The voltammograms presented in Figure 2 show an increase in current density after each linear voltammetry with the gly-BRB solution. In Figure 2B, which shows the results obtained with the MIP/Cu electrode, a peak associated with gly oxidation is observed with a current density 8 times higher than that obtained with NIP/Cu (see Figure 2A). This increase is due to the imprinted sites on MIP/Cu, which favor the approximation of glyphosate molecules to the electrode surface.

As part of the linear voltammetry analysis, Raman spectroscopy measurements were carried

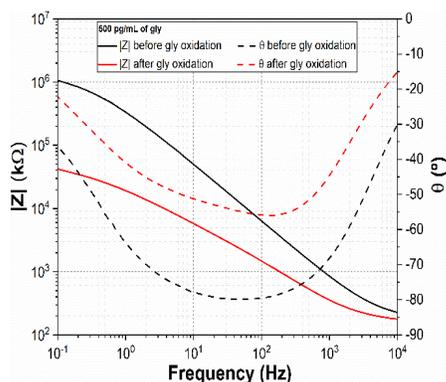


Fig. 4. Impedance spectra before and after of glyphosate (gly) oxidation with 500 µg/mL in a frequency range of 0.1 Hz to 10 kHz

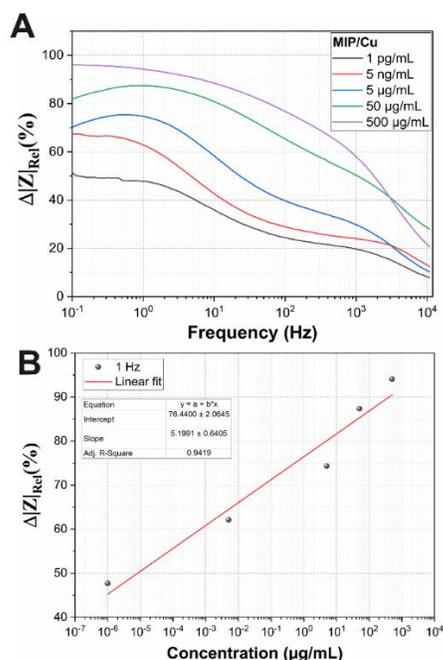


Fig. 5. Percentage changes in impedance ($\Delta|Z|_{\text{Rel}} (\%)$) of before and after glyphosate (gly) oxidation A) of 1 pg/mL, 5 ng/mL, and 5, 50, and, 500 µg/mL of gly in a frequency range of 0.1 Hz to 10 kHz, and B) of 1 pg/mL, 5 ng/mL, and 5, 50, and, 500 µg/mL of gly at 1 Hz

out after the oxidation processes, both with the BRB and gly-BRB solutions, and on the NIP/Cu and MIP/Cu electrodes. The results are presented in Figure 3. In Figure 3A, corresponding to the

NIP/Cu electrode, two similar voltammograms are observed before and after of the oxidation process.

In contrast, Figure 3B, corresponding to the MIP/Cu electrode, shows a peak at 1261 cm^{-1} associated with the P=O bonds characteristic of the glyphosate phosphate group [13,14]. These results suggest that glyphosate oxidation facilitated its integration into the MIP. Based on these findings, the impedance spectroscopy technique was used for characterization after each glyphosate oxidation process using linear voltammetry.

Figure 4 presents two impedance spectra corresponding to the MIP/Cu electrode before and after the gly oxidation at 500 µg/mL of gly concentration. The spectra show a decrease in the impedance magnitude after the oxidation process, which is attributed to the incorporation of gly in the MIP/Cu. This behavior is due to the presence of gly in the MIP/Cu, which increases the relative permittivity and capacitance of the system. Since capacitance and impedance are inversely proportional, an increase in capacitance leads to a decrease in impedance. Therefore, the decrement in impedance magnitude is attributed to these changes. In addition, the gly incorporation in the polymer film was confirmed by Raman spectroscopy. This same behavior of the impedance magnitude, with gly concentrations of 1 pg/mL, 5 ng/mL, and 5, and 50 µg/mL, was observed.

The percentage change in impedance ($\Delta|Z|_{\text{Rel}} (\%)$) for each concentration was calculated. The results are shown in Figure 5A. The highest $\Delta|Z|_{\text{Rel}} (\%)$ were obtained at low frequencies. The maximum $\Delta|Z|_{\text{Rel}} (\%)$ for each gly concentration was achieved around 1 Hz. This maximum change varied from 50% for BRB with gly at 1 pg/mL to 95% for BRB with gly at 500 µg/mL (see Figure 5B).

4 Conclusions

The study of glyphosate oxidation allows us to know its oxidation potential and at the same time corroborate its incorporation into the polymeric film. Based on the results obtained by voltammetry, the printed sites of the MIP/Cu electrode reduce the peak of oxidation potential (compared to

NIP/Cu), as a result of their greater affinity for glyphosate. This phenomenon is particularly relevant for those concentrations in which the number of printed sites is related to the number of molecules in solution. From the results of the percentage change in impedance, it was determined that it is possible to detect concentrations around 1 pg/mL. These results are outstanding since detection platforms with LODs and selectivity for glyphosate are required.

Acknowledgments

This work was supported by Consejo Nacional de Humanidades, Ciencias y Tecnologías (CONAHCYT), Laboratorio Nacional de Micro y Nanofluidica (LabMyN), and Laboratorio Nacional de Impedancia y Bioimpedancia (LNCIBi) through the Catedras CONAHCYT project No. 746. Diana Jiménez-Rivas thanks CONAHCYT for the awarded doctoral scholarship.

References

- Abdullah, H.S. (2012).** Electrochemical polymerization and Raman study of polypyrrole and polyaniline thin films. *International Journal of Physical Sciences*, Vol. 7, No. 38, pp. 5468–5476. DOI: 10.5897/IJPS12.529.
- Benbrook, C.M. (2016).** Trends in glyphosate herbicide use in the United States and globally. *Environmental Sciences Europe*, Vol. 28, No. 1, pp. 1–15. DOI: 10.1186/s12302-016-0070-0.
- Chen, L., Wang, X., Lu, W., Wu, X., Li, J. (2016).** Molecular imprinting: Perspectives and applications. *Chemical Society Reviews*, Vol. 45, No. 8, pp. 2137–2211. DOI: 10.1039/C6CS00061D.
- Costa, J.C.S., Ando, R.A., Sant'Ana, A.C., Corio, P. (2012).** Surface enhanced Raman spectroscopy studies of organophosphorous model molecules and pesticides. *Physical Chemistry Chemical Physics*, Vol. 14, No. 45, pp. 15645. DOI: 10.1039/c2cp42496g.
- Gkika, D.A., Tolkou, A.K., Lambropoulou, D.A., Bikiaris, D.N., Kokkinos, P., Kalavrouziotis, I.K., Kyzas, G.Z. (2024).** Application of molecularly imprinted polymers (MIPs) as environmental separation tools. *RSC Applied Polymers*, Vol. 2, No. 2, pp. 127–148. DOI: 10.1039/d3lp00203a.
- Ibau, C., Md-Arshad, M.K., Subash C.B., Nuzaihan, M., Fathil, M.F., Estrela, P. (2019).** Gold interdigitated triple-microelectrodes for label free prognostic aptasensing of prostate cancer biomarker in serum. *Biosensors and Bioelectronics*, Vol. 136, pp. 118–127. DOI: 10.1016/j.bios.2019.04.048.
- Lacroix, R., Kurrasch, D.M. (2023).** Glyphosate toxicity: In vivo, in vitro, and epidemiological evidence. *Toxicological Sciences*, Vol. 192, No. 2, pp. 131–140. DOI: 10.1093/toxsci/kfad018.
- Larkin, P. (2011).** IR and Raman spectroscopy. In *Infrared and Raman Spectroscopy*.
- Li, Y., Luo, L., Kong, Y., Li, Y., Wang, Q., Wang, M., Li, Y., Davenport, A., Li, B. (2024).** Recent advances in molecularly imprinted polymer based electrochemical sensors. *Biosensors and Bioelectronics*, Vol. 249. DOI: 10.1016/j.bios.2024.116018.
- Muñoz, J.P., Bleak, T.C., Calaf, G.M. (2021).** Glyphosate and the key characteristics of an endocrine disruptor: A review. *Chemosphere*, Vol. 270. DOI: 10.1016/j.chemosphere.2020.128619.
- Ogunbiyi, O.D., Akamo, D.O., Oluwasanmi, E.E., Adebajo, J., Isafiade, B.A., Ogunbiyi, T.J., Alli, Y.A., Ayodele, D.T., Oladoye, P.O. (2023).** Glyphosate based herbicide: Impacts, detection, and removal strategies in environmental samples. *Groundwater for Sustainable Development*, Vol. 22. DOI: 10.3390/microorganisms13030651.
- Soledad-Rodríguez, B. (2017).** Empleo de Polímeros de Impronta Molecular como pre Concentradores de muestras en el análisis químico de trazas. *Tekné*, Vol. 20, pp. 3–22. DOI: 10.62876/tekhn.v20i2.3449.

13. **Valavanidis, A. (2018).** Glyphosate: The World 's Most Widely Used Herbicide. University of Athens (Issue March).
14. **Zhang, C., She, Y., Li, T., Zhao, F., Jin, M., Guo, Y., Zheng, L., Wang, S., Jin, F., Shao, H., Liu, H., Wang, J. (2017).** A highly selective electrochemical sensor based on molecularly imprinted polypyrrole-modified gold electrode

for the determination of glyphosate in cucumber and tap water. *Analytical and Bioanalytical Chemistry*, Vol. 409, No. 30, pp. 7133–7144. DOI: 10.1007/ s00216-017-0671-5.

Article received on 19/09/2024; accepted on 13/01/2025.
**Corresponding author is José Herrera-Celis.*