An Electrochemical Sensor Based on Chitosan Molecularly Imprinted Polymers for the Selective Detection of Diphenylamine

Simona Sawan[1], Perla Nassif[1], Nicole Jaffrezic-Renault [2]*, Rita Maalouf [1]*

1 Department of Sciences, Faculty of Natural and Applied Sciences, Notre Dame University - Louaize, Zouk Mosbeh, Lebanon
2 Institut des Sciences Analytiques, Université de Lyon, 5, rue de la Doua, 69100 Villeurbanne, France.

** Corresponding authors: rita.maalouf@ndu.edu.lb , nicole.jaffrezic@univ-lyon1.fr*

Introduction

Diphenylamine (DPA) is a colorless derivative of aniline containing an amine with two phenyl groups. It has been employed as a rubber antioxidant, precursor in the synthesis of azo dyes, a solid fuel rocket propellent and an agrochemical product having strong antioxidant properties to treat superficial scalds in fruits such as apples and pears. Due to its limited ability to dissolve in water, it remains present in the fruit even after processing. As a result, DPA and its derivatives have the potential to be found in processed products as well as environmental water samples. Oral ingestion of DPA in certain levels has been known to cause several ailments including cancer. The European Union (EU) has placed DPA on its priority pollutant list, no longer authorizing its use. The maximum acceptable concentration range DPA is 5 to 10 $mg.kg^{-1}$ as suggested by the EU (91/414/EEC) committee.

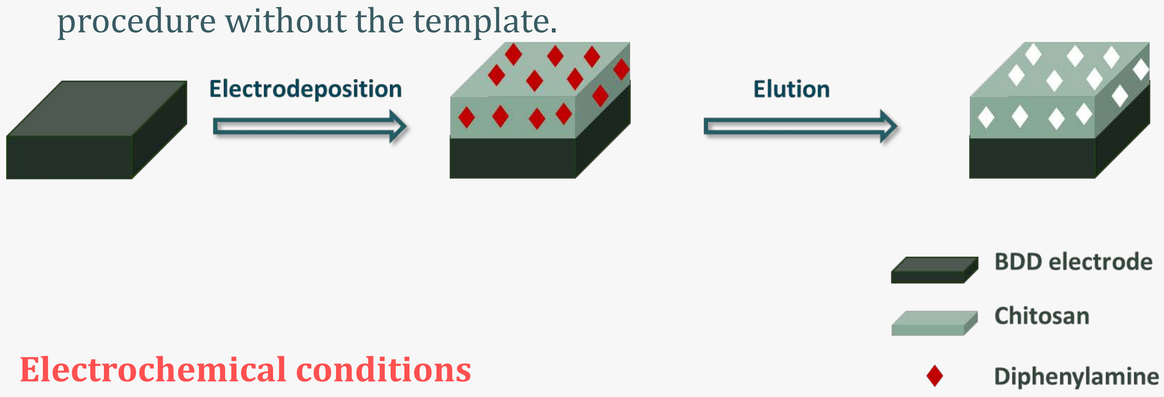
Objectives

- Synthesize molecularly imprinted polymers (MIPs) using chitosan for the detection of DPA
- Optimize synthesis conditions
- Characterize the synthesized MIP
- Assess the analytical performance of the sensor

Methodology

Assembly of the electrochemical sensor

- Electrodeposition was performed by mixing DPA and chitosan, using chronoamperometry at a potential of -1.1 V and a pH of 5.4.
- Elution was done using methanol/acetic acid (9:1) for 30 minutes under constant stirring.
- Non-imprinted polymers (NIP) were synthesized following the same procedure without the template.



Electrochemical conditions

All electrochemical measurements were performed using a PalmSens4 in PBS buffer medium of pH 7.4. A conventional three electrode system was utilized.

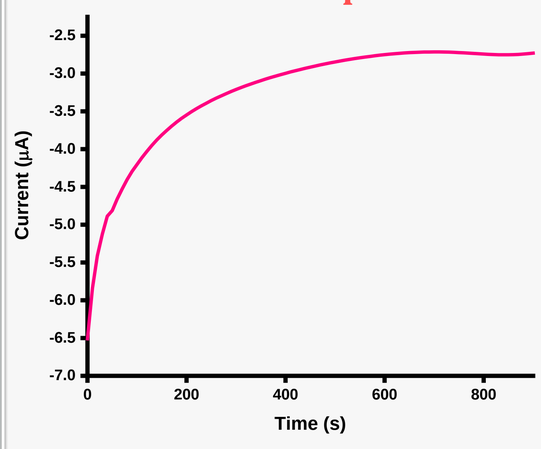
- **Working electrode**: boron doped diamond (BDD)
- **Counter electrode**: Platinum
- **Reference electrode**: Ag/AgCl

Differential Pulse Voltammetry

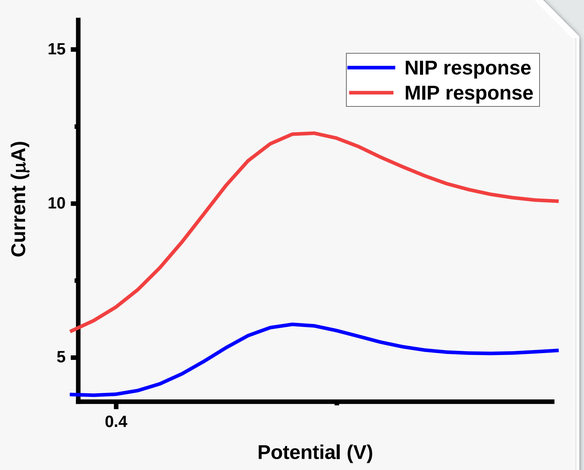
- E pulse 0.2 V
- t pulse 0.02 s
- Scan rate 0.1 v/s

Results

Electrochemical deposition



Chronoamperometry of electrodeposition of MIP on BDD electrode in PBS pH 7.4 at a potential of -1.1 V



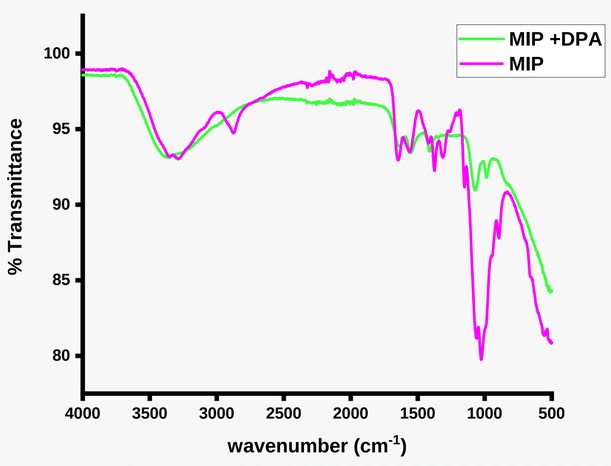
Voltametric responses of MIP and NIP modified electrodes in 25 µM DPA in PBS pH 7.4

Optimization

Variable	pH	$[DPA]_{added}$ (µM)	Optimum value
Deposition time	7.4	50	15 min
Incubation time	7.4	25	5 min
$[DPA]_{initial}$	7.4	25	20 mM

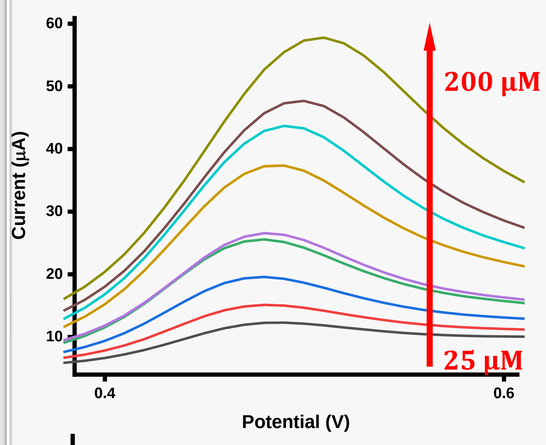
Results

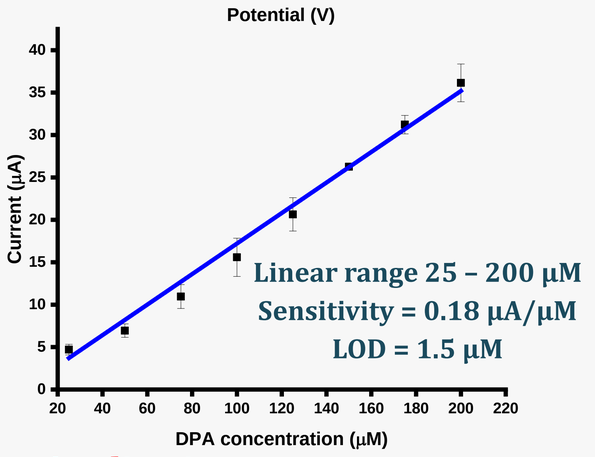
Characterization



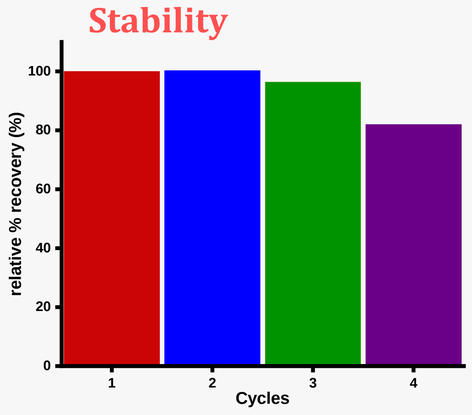
FTIR spectra of the synthesized MIP before and after the addition of DPA. The disappearance of the 2 peaks over 3000 cm^{-1} and formation of 1 broad peak prove the formation of hydrogen bonds between chitosan and DPA.

Analytical performance



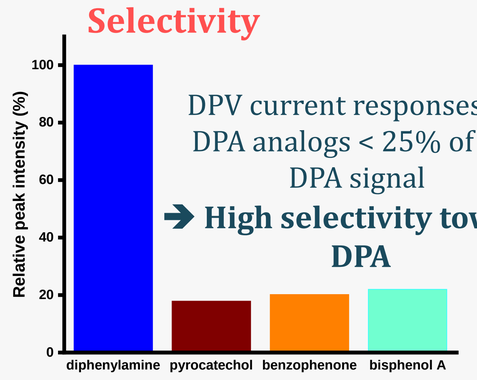


Stability



➔ Can be used up to 4 cycles with more than 82% efficiency

Selectivity



DPV current responses for DPA analogs < 25% of the DPA signal

➔ **High selectivity towards DPA**

Application

Applicability of the sensor was assessed using a spiked water sample. Results showed recoveries between 90 and 120%

Conclusions

- MIP was successfully electrodeposited on the BDD electrode
- Electrodeposition time, incubation time and DPA concentration were optimized
- The sensor showed a broad linear range and a good sensitivity and selectivity towards DPA with high stability

References

1. Liu, Lingyu, et al. "An electrochemical sensor for diphenylamine detection based on reduced graphene oxide/Fe3O4-molecularly imprinted polymer with 1, 4-Butanediyl-3, 3′-bis-l-vinylimidazolium dihexafluorophosphate ionic liquid as cross-linker." Polymers 10.12 (2018): 1329.
2. Granado, Vera LV, et al. "Thin-film electrochemical sensor for diphenylamine detection using molecularly imprinted polymers." Analytica Chimica Acta 809 (2014): 141-147.