

A Novel Electrochemical Sensor for Bisphenol A Detection Based on Molecularly Imprinted Polymer Coated Iron Oxide Nanoparticles

Rania Al Kaassamani¹, Simona Sawan¹, 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



Background

Bisphenol A (BPA) is predominantly employed as a primary building block in the synthesis of polycarbonates and epoxy resins. It has earned significant attention owing to its durability, high heat resistance, lightweight and high strength. These polycarbonates find application in an array of products including water containers, food storage containers and baby bottles, and as an inner coating of food cans. Conversely, research has unveiled the potent consequences of BPA. As an “endocrine disruptors”, this chemical has the potential to trigger hormonal imbalances disturbing reproductive health and curtail fertility, alongside possible effects on fetus development.

Aims

Synthesize molecularly imprinted polymers (MIPs) using iron oxide nanoparticles (NPs) for the detection of BPA

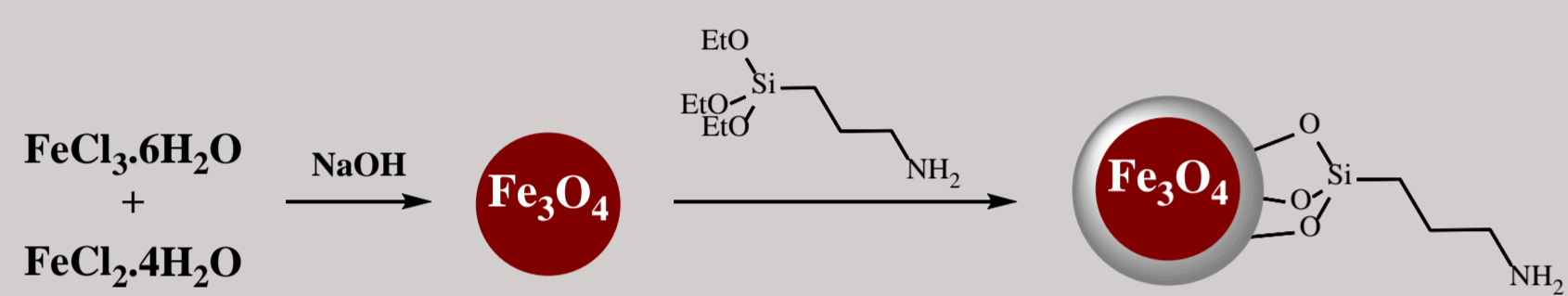
Characterize the synthesized MIP

Assess the analytical performance of the proposed sensor

Experimental methods

Iron oxide nanoparticles synthesis

The iron oxide NPs were synthesized using a modified Massart's method by mixing ferrous and ferric chloride in basic medium. The nanoparticles were then coated with (3-aminopropyl)triethoxysilane (APTES).



MIP/NIP synthesis

- 30 mg of BPA and 10 mg of NPs were dissolved in 30 mL of ethanol. The mixture was left under stirring for 1 hour at room temperature.
- 1 mL of TEOS and 5 mL of ammonium hydroxide solution were added. The mixture was left under stirring for 24 hours to obtain MIP.
- The template was eluted using methanol/acetic acid (9:1) for 15 min.
- NIP were prepared in the same way without BPA.

Electrochemical measurements

All electrochemical measurements were performed using a PalmSens4 in PBS buffered medium pH 7.4. A conventional three electrode system was employed:

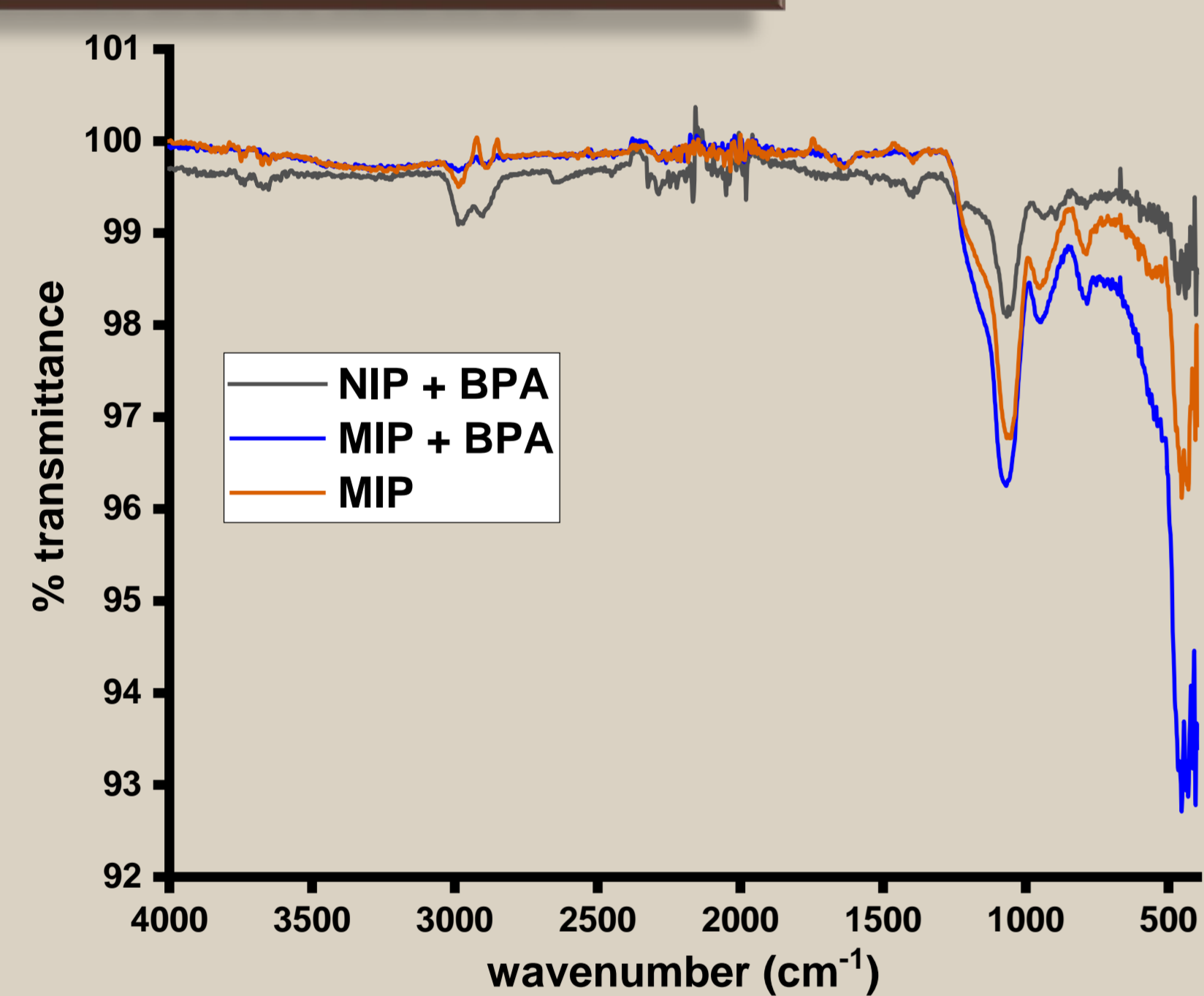
- Working electrode:** boron doped diamond modified with the magnetic nanoparticles coated with MIP
- Counter electrode:** Platinum
- Reference electrode:** Ag/AgCl

Differential Pulse Voltammetry

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

Results

Characterization



FTIR spectrum of MIP:

No peaks at 1395 cm⁻¹ and 1638 cm⁻¹, for O-H bending and C=C of the phenyl group respectively.

FTIR spectrum of MIP + BPA:

Peak at 2988 cm⁻¹ indicating a characteristic bond of C-H stretching of alkenes,

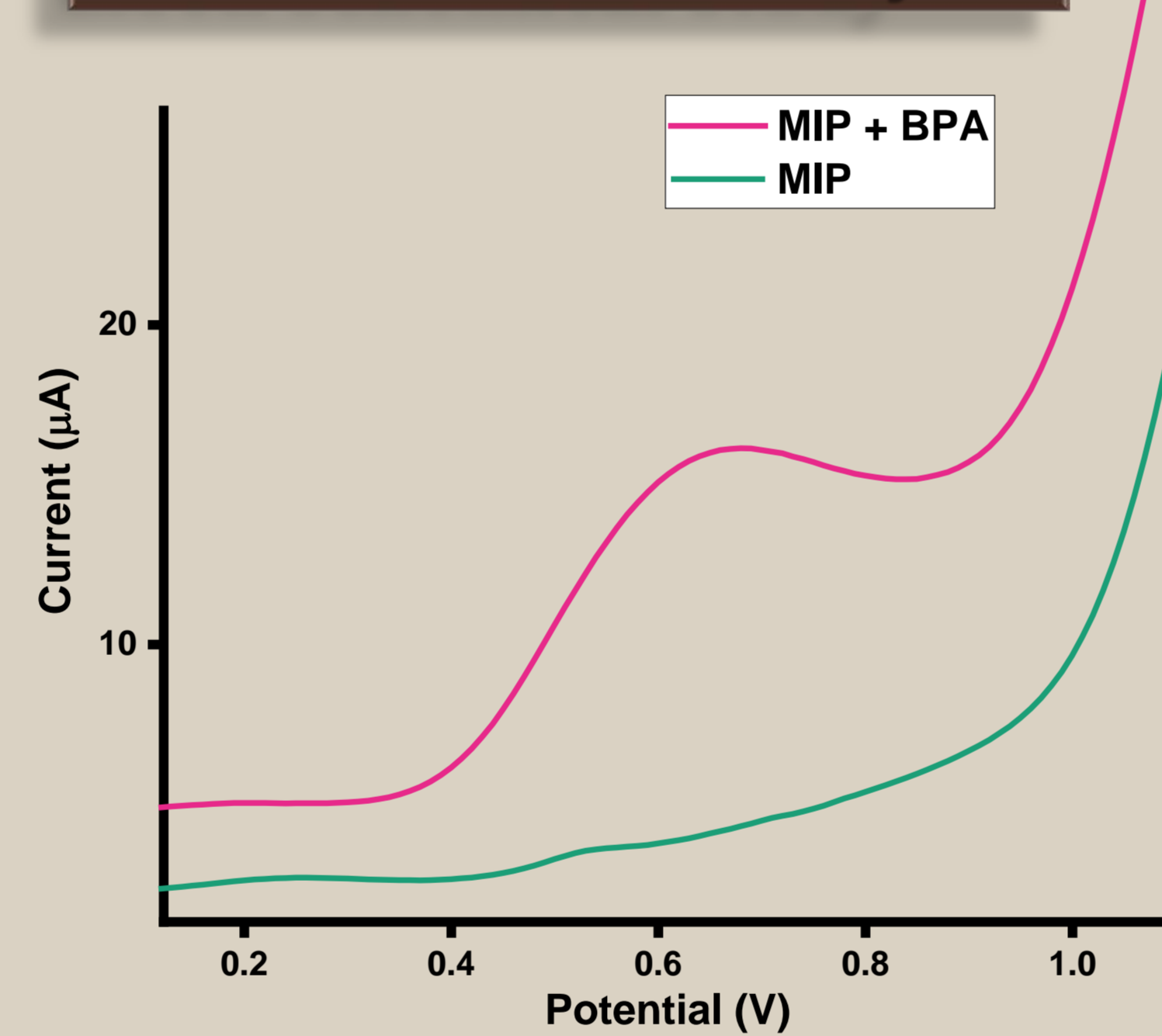
→ BPA is grafted on the surface of iron oxide NPs in MIP

FTIR spectrum of NIP after adding BPA:

The same peaks as MIP with BPA are shown with a smaller intensity

→ BPA is present but in smaller concentration compared to MIP

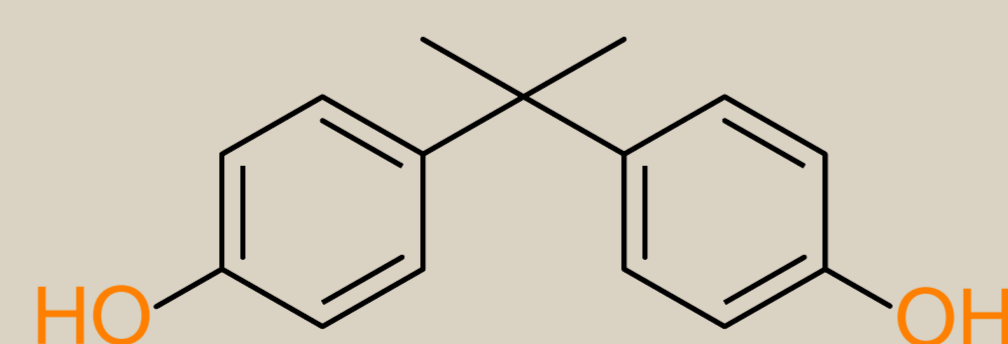
Electrochemical study



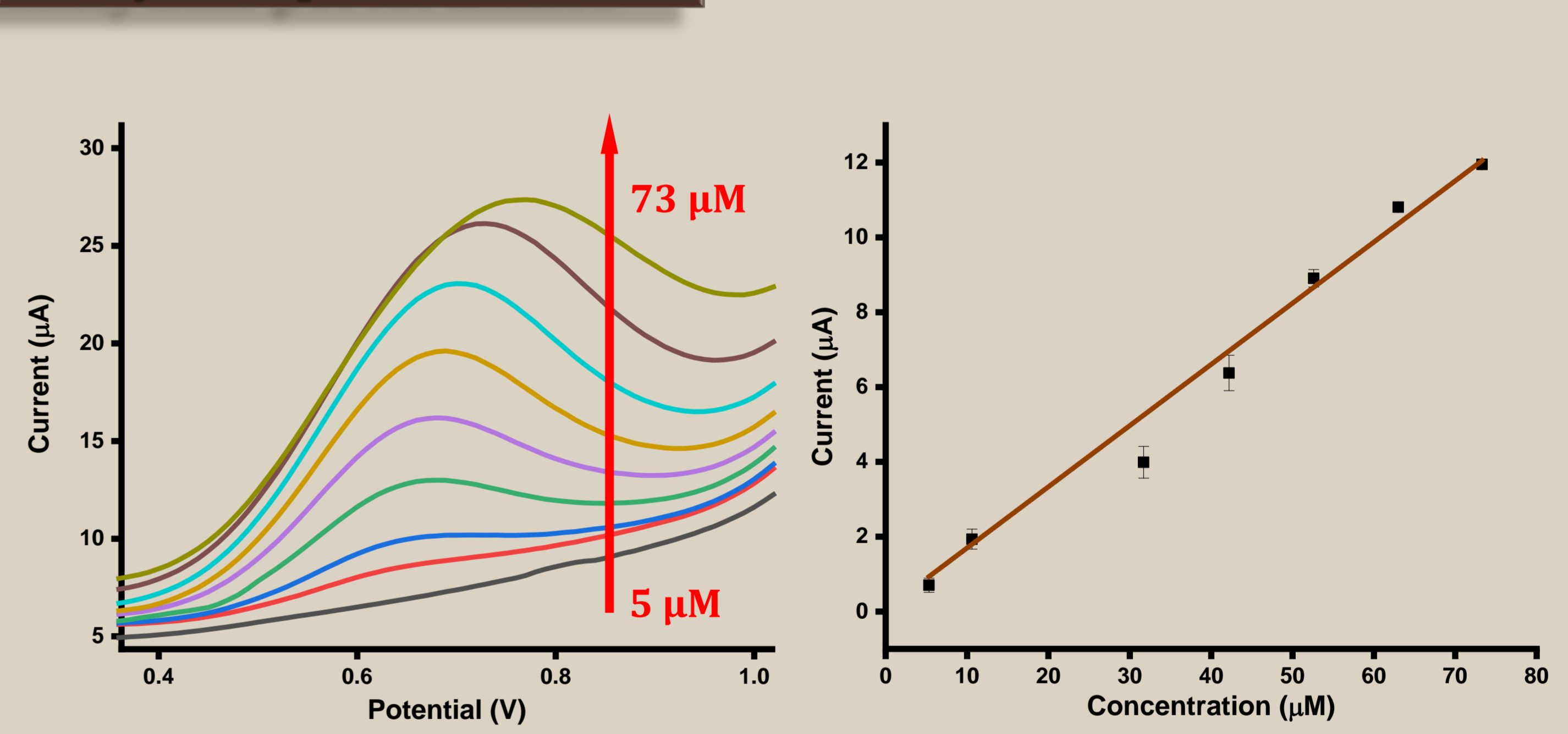
DPV of MIP-modified BDD electrode in PBS buffered medium at pH 7.4 showed no observable peaks.

DPV of MIP in PBS buffered medium at pH 7.4 in presence of bisphenol A showed a peak at 0.69 V.

This peak is characteristic of the oxidation of BPA shown below.



Analytical performance

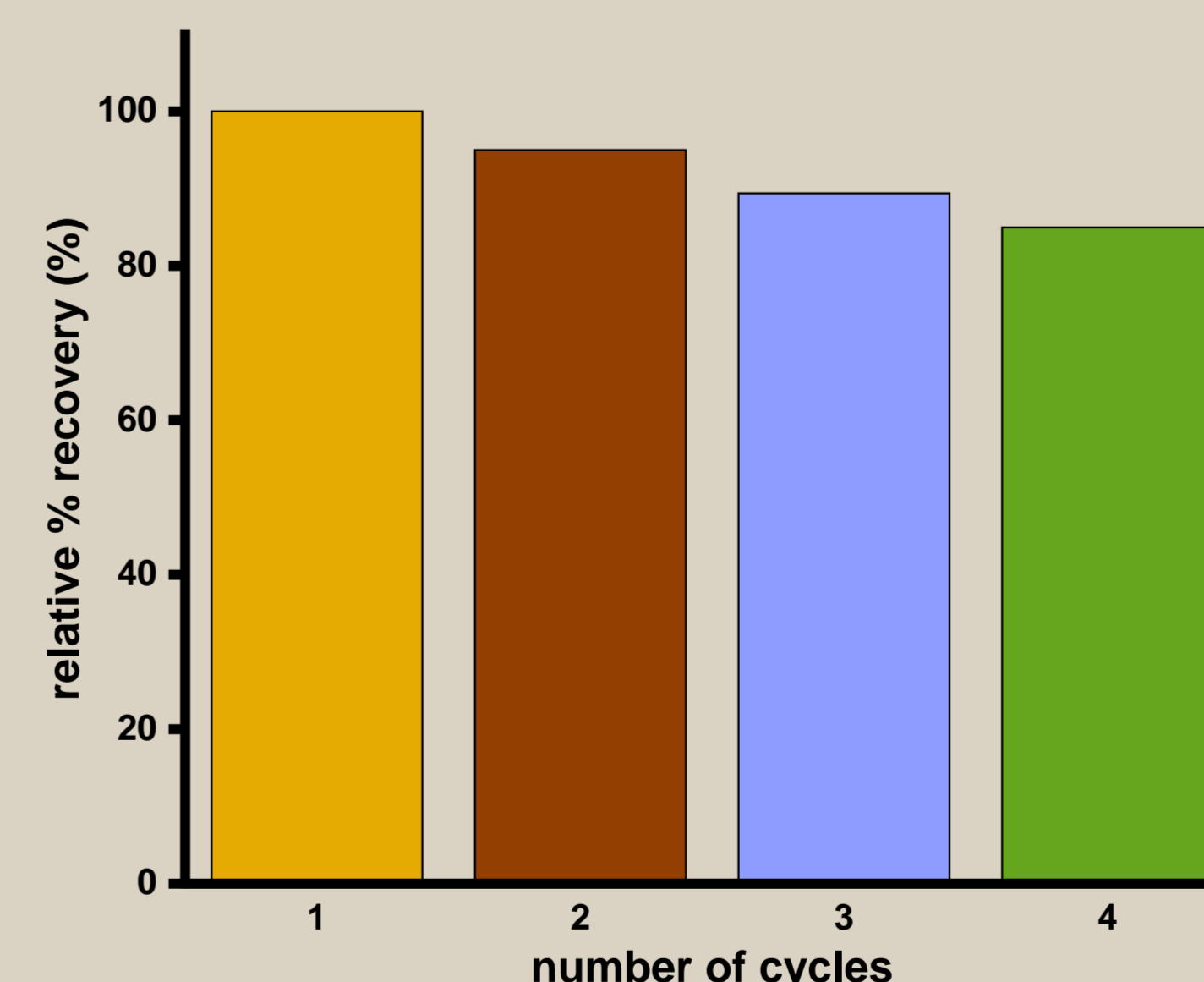


Upon increasing the concentration of BPA, DPV response increased to obtain:

Linear range: 5 – 73 µM

Sensitivity: 0.163 µA/µM

LOD: 0.38 µM



The stability of the sensor was also assessed by reusing the same electrode and adding 20 µM of BPA.

It was shown that the sensor can be reused up to 4 times with an 85% efficiency.

Conclusions

MIP was successfully synthesized and used to modify the BDD electrode

MIP showed a better response in presence of BPA as compared to NIP

The sensor showed a good linear range, sensitivity and selectivity towards BPA with a high stability and low LOD

Perspectives

Study the effect of the presence of interfering compounds on the BPA signal

Use the proposed sensor to detect BPA in water samples

References

- Dadkhah, Sahar, et al. "A glassy carbon electrode modified with amino-functionalized graphene oxide and molecularly imprinted polymer for electrochemical sensing of bisphenol A." *Microchimica Acta* 183 (2016): 1933-1941.
- Kim, Minsoo, et al. "Electrochemical detection and simultaneous removal of endocrine disruptor, bisphenol A using a carbon felt electrode." *Journal of Electroanalytical Chemistry* 880 (2021): 114907.