Voltammetric sensor based on electrodeposited molecularly imprinted chitosan film on BDD electrodes for catechol detection in buffer and in wine samples

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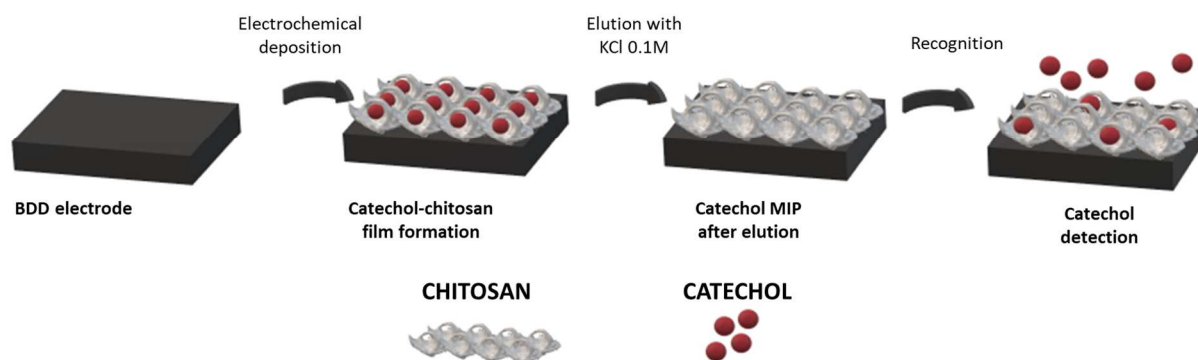
Abstract

Phenolic compounds such as catechol are present in a wide variety of foods and beverages; they are of great importance due to their antioxidant properties. Their consumption protects against the development of certain diseases such as cancer and cardiovascular diseases. A MIP chitosan (CS) film has been electrodeposited on a boron doped diamond (BDD) electrode, by chronoamperommetry in the presence of catechol, followed by elution with 0.1 M KCl. The morphology of the MIP and non-MIP (NIP) film has been studied by AFM. The electrochemical response of the sensor analyzed by cyclic voltammetry (CV) indicates that the sensor shows excellent reproducibility (RSD = 4.1%) and repeatability (RSD = 7.0%) for catechol detection in the range of 0 to 80 µM, with a detection limit of 6.9×10^{-7} M and high selectivity to catechol recognition versus different phenolic compounds. The results obtained in a red wine show that it can detect catechol in a complex matrix.

Keywords: molecular imprinted polymer, voltammetric sensor, catechol, chitosan, BDD electrode

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract

1. INTRODUCTION

Polyphenol content in a wide variety of foods and beverages is of great importance due to its antioxidant properties [1]. Their consumption protects against the development of certain diseases such as cancer and cardiovascular diseases. The classical analytical methods reported for the determination of phenolic compounds include gas chromatography [3], HPLC [4], spectrophotometry [5], capillary electrophoresis [6]. Developing electrochemical sensors and biosensors is worthwhile due to their simplicity, low cost and fast response time. Most of them are based on enzymatic reaction, laccase or tyrosinase being phenol oxidase. However, enzymatic stability limits the shelf lifetime of these enzymatic biosensors. For this reason there are an endless number of non-enzymatic methods for the electrochemical detection of phenolic compounds, such as catechol. These include phtalocyanines deposited by the layer by layer [7] or Langmuir Blodgett [8] methods, electropolymerized polyfurfural films [9] for the electrode modification. The detection of phenolic compounds such as catechol is also of particular interest in wines, in order to guarantee their organoleptic characteristics [2].

Molecular Imprinted Polymers (MIP) are based on imprinted cavities designed for the target template elements. The holes created in the polymeric matrix match the template molecule in shape and size; for these reasons, MIP are interesting elements for direct recognition in electrochemical sensors providing excellent properties of sensitivity and selectivity [10]. The selection of the polymer matrix is crucial in the preparation of MIP electrochemical sensors

[11], and a large variety of polymers has been employed for sensing and molecular imprinted applications [12]. Different types of electropolymerizable materials were used for designing MIPs: poly(o-phenylene diamine) [13] and, in association with nanomaterial-modified electrodes in order to increase the sensitivity of detection, polypyrrole [14] and polyphenol [15].

In order to obtain ideal biocompatible MIP electrochemical sensors, natural biopolymers should be used for the MIP design. Chitosan (CS) is a non-toxic and biocompatible amine rich linear polysaccharide, derived by deacetylation of chitin components extracted from the shells of crustaceans. This biopolymer has a pKa value of 6.3 which is related to its primary amino groups [16]. Chitosan is positively charged and water soluble in acidic conditions and uncharged and insoluble under basic conditions. This excellent layer-forming ability, produces films with high permeability and mechanical strength, good adhesion, low cost and susceptibility to chemical modification [17].

Moreover, CS can be electrodeposited, due to its insolubility at high values of pH. The value of pH at the electrode surface is increased by applying cathodic potential, through the production of hydroxyl ions, according to the following reaction: $2H_2O + 2e^- \rightarrow H_2 + 2 OH^-$. This procedure was used to obtain MIP layers from where the template molecule can be easily eluted [18]. Electrodeposition provides control of the thickness of the polymer layer and its strong anchoring on the electrode surface [16].

Few studies were performed on MIP-based electrochemical sensor using chitosan as polymeric material, for detection of phenolic compounds. An acetylene black paste electrode modified through drop-coating with a chitosan film [19] and modified with a chitosan-graphene composite film [20] was used for the voltammetric detection of bisphenol A. Detection limit were respectively 60 nM and 6 nM. 2,4,6-Tribromophenol was detected with a MIP based on a chitosan film electrodeposited through cyclic voltammetry on a gold electrode [16]. A limit of detection of 13.2 nM and a large dynamic range from 100 nM to 1 mM were obtained.

The selection of the conducting material is critical in electrochemical measurements; conducting boron doped diamond electrodes (BDD) are excellent candidates for MIP based sensors due to their exceptional properties such as low background current, chemical and mechanical stability, resistance to fouling, wide potential window and biocompatibility [21]. In addition, BDDs allow a greater variety of direct electrochemical modifications on the top of the electrode [22].

The main purpose of this work is to develop a novel type of sensor for the electrochemical detection of catechol using a biocompatible MIP based voltammetric sensor and a biocompatible electrode material, BDD. The MIP film was prepared by electrodeposition of chitosan through chronoamperometry, on the surface of a BDD electrode with catechol as template molecule, which was never performed until now. Catechol was directly detected by cyclic voltammetry using the MIP based electrode and the electrochemical signal was compared to that of the NIP based electrode. One of the advantage of this technique is that the template molecule can be directly monitored during the optimization of the MIP elaboration process and the catechol detection. Finally, the capability of the sensor to detect catechol in a real wine sample was tested.

2. MATERIALS AND METHODS

Chemicals

Chitosan (average MW=45 kDa with a degree of acetylation>75.0%), acetic acid (99.8%) and N-(2-Hydroxyethyl) piperazyne-N'-(2-ethanesulfonic acid) (HEPES) were purchased from Sigma Aldrich. Phosphate buffered saline (PBS; pH 7.4, 0.1M) was prepared with Na_2HPO_4, NaH_2PO_4 and NaCl salt also obtained from Sigma Aldrich. The acetone, ethanol, sulfuric acid (95%) and hydrogen peroxide (30.0% in water) were purchased from Fluka

Pyrocatechol, bisphenol-A (≥99.0%), 2-nitrophenol (98.0%), 4-aminothiophenol (97.0%), 4-terc-butylcatechol (≥99.0%) and 4-nitrophenol (≥99.5%) were purchased from Sigma Aldrich. Aqueous solutions were prepared using Milli Q water (resistivity 18.2 MΩ·cm).

Instruments

The electrochemical deposition of chitosan was performed by chronoamperommetry (CA) and the electrochemical measurements were recorded by cyclic voltammetry (CV) at room temperature using a Voltalab 80 model PGZ 402 analyzer instrument (Hach Lange, France) connected with Voltamaster 4.0 software. The three electrode system, composed of a 5 mL electrochemical cell, employed a platinum plate as an auxiliary electrode (0.19 cm^2 of active surface, determined by an O-ring seal), a saturated calomel electrode (SCE) as a reference electrode and a boron doped diamond electrode (BDD) as the working electrode (0.07 cm^2 of active surface, determined by an O-ring seal).

Electrochemical deposition was carried out at -1100 mV fixed potential for 1.5 min and voltammetric measurements were made between -800 to 1500 mV with a scan rate of 100 mV/s.

The AFM measurements were carried out using an Agilent 5500 AFM (Agilent Technologies, Palo Alto, CA, USA). Silicon tips with a nominal spring constant of 20 Nm^{-1} were used in tapping mode at a frequency of ~300 kHz.

Preparation of CS-MIP/BDD sensor

BDD electrodes (8000 ppm of boron, 10x10 mm square) were purchased from NeoCoat (La Chaux-de-Fonds, Switzerland). Their surfaces were cleaned for 10 min in acetone under ultrasonication and then in Milli Q water. Then, they were immersed in piranha solution ($H_2SO_4:H_2O_2$ =3:1 v/v), cleaned in Milli Q water and ethanol and dried under a nitrogen flow. The 1.5 mg/mL CS solution was prepared by dissolving 1.5 mg in 1 mL of a solution obtained by mixing 0.7 mL of HEPES buffer solution at pH 7.4 and 0.3mL of acetic acid.

MIP film was obtained by immersing the BDD electrode in a CS solution (CS concentration: 1.5 mg/mL) that contained catechol (0.1M). The mixture was stirred for 5 min. Polymerization was carried out using chronoamperometry under a potential of -1100 mV for 1.5 min. Finally, without removing the electrode from the cell, the solution was removed and the electrode was stored at 4 °C overnight.

The template catechol molecules were eluted in 0.1 M KCl solution under stirring for 20 min. The NIP film was prepared in the same conditions as the MIP film, without any catechol template during electrodeposition.

Measurements in real wine samples

In this work, a red wine sample was purchased from a supermarket. The sample was diluted at 10% in PBS solution 0.1M, pH 7.4 and catechol content was determined through the standard addition method.

3. RESULTS AND DISCUSSION

Surface morphology of the CS-MIP/BDD sensor

The AFM image of the CS-NIP BDD surface, shown in Figure 1.a, denotes a thickness of 66 nm with a rough surface (rms value: 14.7 nm). The AFM image of the CS-MIP surface, after the template elution, shows a thickness of 95 nm with a lower roughness (rms value: 12.5 nm) (Figure 1.b). These results can be compared with the values of ΔI obtained during the electrodeposition process: during the electrodepostion of the CS-NIP film, the ΔI value obtained for the stabilization current was 345 µA, whereas for CS-MIP the value was 2372

µA. The difference in the current intensity values could be due to the adsorption of catechol on BDD surface, as phenolate anion [23]. The presence of the adsorbed specie could improve the surface conductivity of the BDD electrode. The higher observed current intensity will lead to a higher rate of production of OH⁻ according to the following reaction: $2H_2O + 2e^- \rightarrow H_2 + 2 OH^-$ - the local pH value would then then higher. A thicker CS film is obtained, as shown on the AFM 3D images. A smoother surface of MIP film is observed. SEM images confirm the higher roughness of NIP and the lower roughness of MIP.
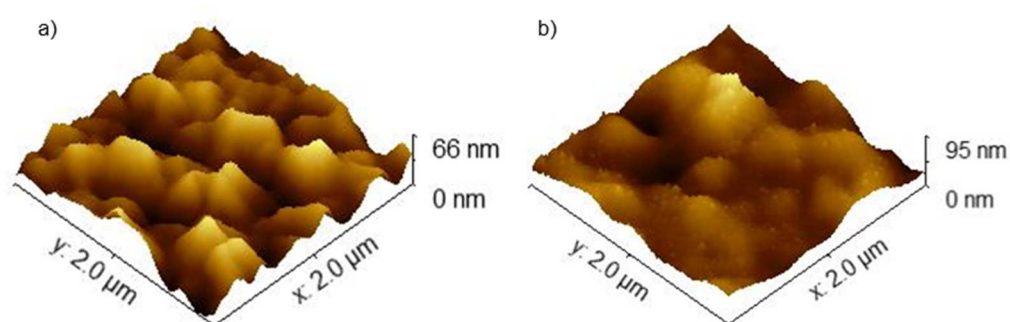

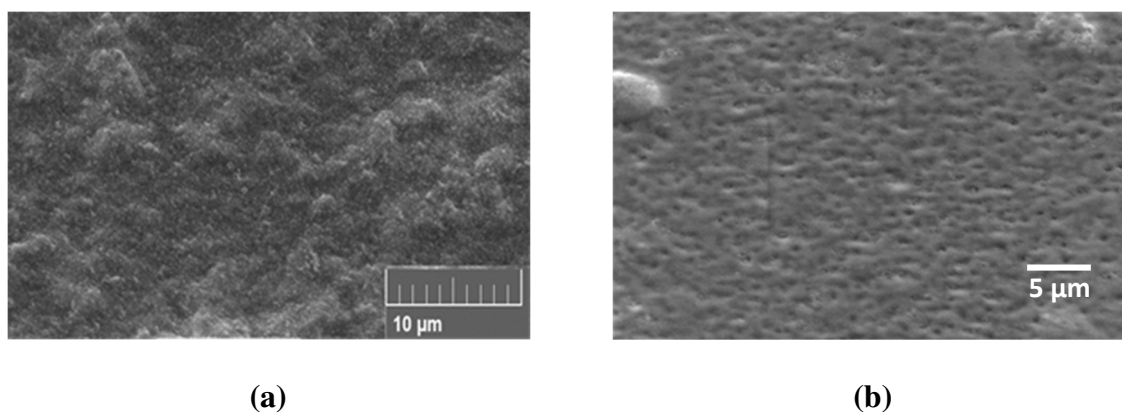Figure 1A: AFM images of a) the CS-NIP/BDD surface and b) the CS-MIP/BDD surface.

(a) **(b)**

Figure 1B: SEM images of a) the CS-NIP/BDD surface and b) the CS-MIP/BDD surface.

Optimization of electrodeposition conditions

The first step towards developing the optimized CS-MIP/BDD electrochemical sensor is to optimize the elution. After the formation of the MIP film, the presence of catechol was evident as shown by the high intensity of the reduction and oxidation peaks (Figure 2.a., red

6

curve). After the elution of the catechol with 0.1M KCl for 20 min, the signal of the peaks underwent an intense decrease confirming the release of the catechol and the creation of the imprinted cavities. Different concentrations (0.001M to 0.1M) of template molecule were tested for the formation of the CS MIP film. After the elution of catechol, the different MIP films were equilibrated in 10^{-4}M catechol in 0.1M PBS solution, pH 7.4. Figure 2.b shown that with the higher concentration of catechol employed as template in MIP fabrication, the peak intensities were higher, due to a larger number of generated cavities, improving the detection of catechol.
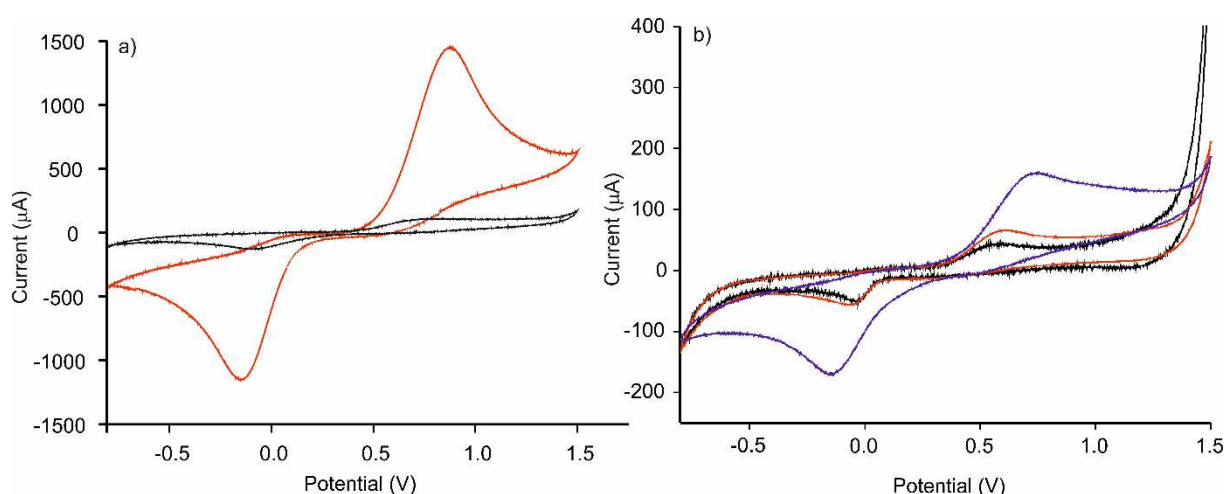

Figure 2: Voltammetric responses of a) CS-MIP/BDD sensor before elution in 0.1M KCl in red, CS-MIP/BDD sensor after elution in 0.1M KCl in black in 0.1M PBS solution, pH 7.4 and b) CS-MIP/BDD sensor in 10^{-4}M catechol in 0.1M PBS solution, pH 7.4 with increasing catechol template concentration, 0.001M in black, 0.01M in red and 0.1M in blue.

Electrochemical characterization of the CS-MIP/BDD sensors

Cyclic voltammetry was employed to determine the electrochemical behavior of the modified CS-MIP/BDD sensors. Figure 3.a shows the different voltammetric responses of the prepared sensor in the absence and presence of the template molecule during their elaboration and the bare electrode in 0.1M PBS solution, pH 7.4 containing 10^{-4} M catechol. In the absence of the template molecule during electrodeposition (CS-NIP/BDD sensor), the intensity of the cathodic and anodic signals are similar to those given by a bare electrode. When the CS-MIP film was deposited onto the BDD electrode surface, the intensity of the peaks increased by a factor of 3.2, showing an improvement in the electron transfer between the solution and the modified electrode. The responses of CS-MIP/BDD electrode towards increasing concentrations of catechol (0, 0.005, 0.01, 0.025, 0.05, 0.075 and 0.1 mM) are represented in

Figure 3.b. The signal intensity in the cathodic and anodic regions was shown to increase with increased catechol concentrations.
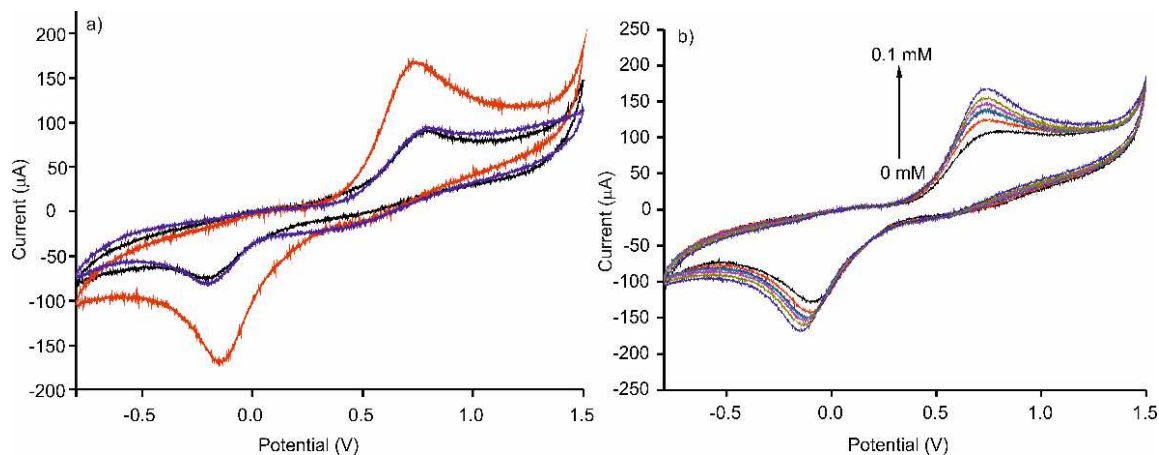

Figure 3: Voltammetric responses of a) CS-MIP/BDD sensor in red, CS-NIP/BDD sensor in blue and bare electrode in black in 0.1M PBS solution, pH 7.4 containing 10^{-4}M catechol and b) CS-MIP/BDD sensor in 0.1M PBS solution, pH 7.4 for increasing concentrations of catechol (0, 0.005, 0.01, 0.025, 0.05, 0.075 and 0.1 mM).

Sensitivity, Reproducibility, Stability, and Selectivity

The CV response of three different CS-MIP/BDD sensor, prepared under the same conditions, was obtained to determine the sensitivity and the reproducibility of the prepared sensors, Figure 4.a shows the current intensity response to increasing concentrations of detected molecule for the MIP and NIP sensor. The ΔI_{anodic} signals offered two linear calibration curve ranges for the CS-MIP/BDD sensor following the equations y=3972.00·x + 3.38 (R^2= 0.8401) in the 0-001 mM range and y=294.42·x + 37.52 (R^2= 0.9669) in the 0.01 mM – 0.08 mM range, respectively. In contrast, for CS-NIP/BDD only one linear range was detected with the y=526.01·x -2.27 (R^2= 0.9740) equation. From the sensitivities of MIP and NIP in the low range of detection, an imprinting factor of 13.5 is obtained, this value being very high, the values in the literature being not higher than 5. The LOD of the CS-MIP/BDD sensor was calculated in the first linear range, of catechol concentration in the oxidation range, using the 3·σ /m criterion where σ is the standard deviation of 3 different blanks and m is the slope of the calibration plot. The LOD value of 6.9×10^{-7}M indicates good sensitivity of the prepared sensor for catechol detection. Moreover, a relative standard deviation (RDS) value of 4.1% is obtained for the reproducibility of the sensors. The LOD of the CS-NIP/BDD sensor was calculated following the same criterion, the reached value of 1.1×10^{-5}M testifies to the improvements obtained when using the molecular imprinting polymers technique.

The stability of CS-MIP/BDD sensor to detect phenol was evaluated by CV. The repeatability was measured for catechol detection from 0 to 0.075mM with the same electrode for 3 different times. Each measurement was followed by 20 min of washing to remove the catechol adsorbed on the MIP and NIP electrodes surface. The RDS value was 7.0 % for the repeatability of the same sensor used three times.
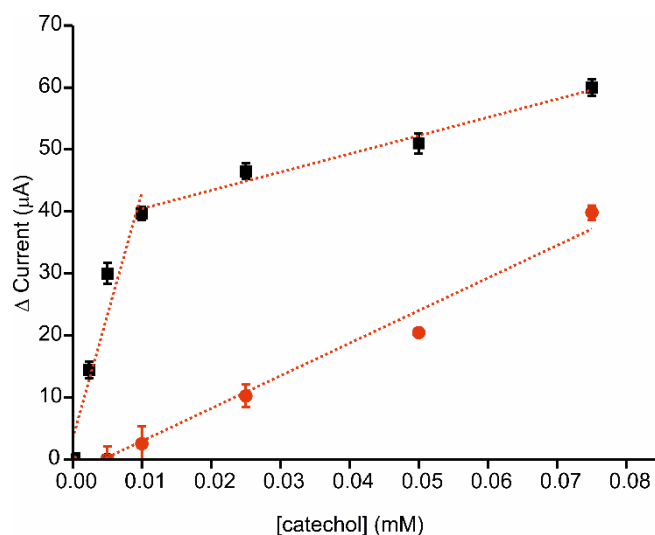

Figure 4: Calibration curves of CS-MIP/BDD sensor in black and CS-NIP/BDD sensor in red in 0.1 M PBS solution, pH 7.4 for increasing concentrations of catechol (0, 0.005, 0.01, 0.025, 0.05 and 0.075 mM) for 3 sensors prepared under the same conditions.

The influence of the presence of different interfering phenolic compounds in catechol detection was studied in order to determine the selectivity of the performed sensor. CS-MIP/BDD sensor was tested for the detection of 10^{-4} M catechol prepared in 0.1 M PBS solution, pH 7.4, in the presence of different phenolic compounds in 10^{-4}M concentration. Figure 5 shown the CV anodic peak maximum obtained for the detection of 10^{-4} M catechol in the presence of bisphenol-A, 4-aminothiophenol, 2-nitrophenol, 4-nitrophenol and 4-tert-butylcatechol. The results demonstrated the selectivity of the developed sensor to detect catechol. However, when the interferences were bisphenol A or 4-tert-butylcatechol (the biggest molecules selected in that study) the intensity of the current increased. Both these molecules adsorb on the MIP surface, leading to signal increase of 18%.

In the presence of 2-nitrophenol, 4-nitrophenol and 4-aminothiophenol, the variation of the catechol anodic peak is around 6%, which is in the range of reproducibility.
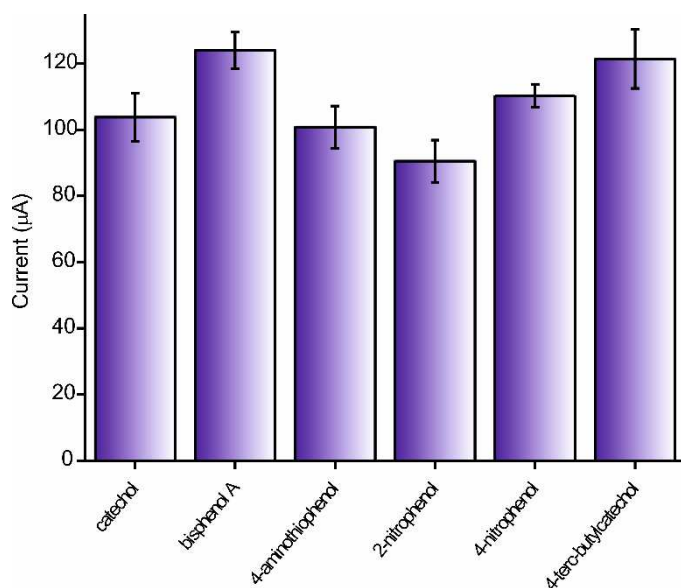
Figure 5: CV anodic peak maximum offered by CS-MIP/BDD electrode for the detection of 10^{-4} M catechol containing different interfering phenols10^{-4}M prepared in 0.1M PBS solution, pH 7.4.

The analytical parameters obtained with the CS-MIP/BDD sensor for catechol detection were compared to previous works reported in the bibliography based on catechol detection. Table 1 shown that the LOD reached with this novel sensor is lower than in the majority of the cases mentioned; moreover, the sensitivity reached was higher than those reported in the collected data.

Sensor description	Electrochemical technique	Sensitivity (μA mM^{-1})	LOD (M)	[Catechol] range (μM)	Ref.
Au/TiO2 BDD electrode	Voltammetry	51.58	$1.4 \cdot 10^{-6}$	5-200	[24]
Nanograss array BDD electrode	Voltammetry	719.71	$1.3 \cdot 10^{-6}$	5-100	[25]
CS-MIP/BDD sensor	Voltammetry	3972.00	$6.9 \cdot 10^{-7}$	0-80	This work

Table 1: Comparison of analytical parameters of different sensors for catechol detection based on electrochemical measurements.

Determination of catechol in real wine sample

In order to evaluate the applicability of CS-MIP/BDD sensor developed, CV was employed to measure catechol in a ten times diluted real sample of red wine using the standard addition method. Figure 6 presents the obtained values, fitted with the straight lines corresponding to the calibration curve obtained in buffer. The deduced concentration of catechol in the red

wine sample is 170 µM. Some other phenolic molecules such as ethylcatechol, ethylphenol are also detected in red wines.
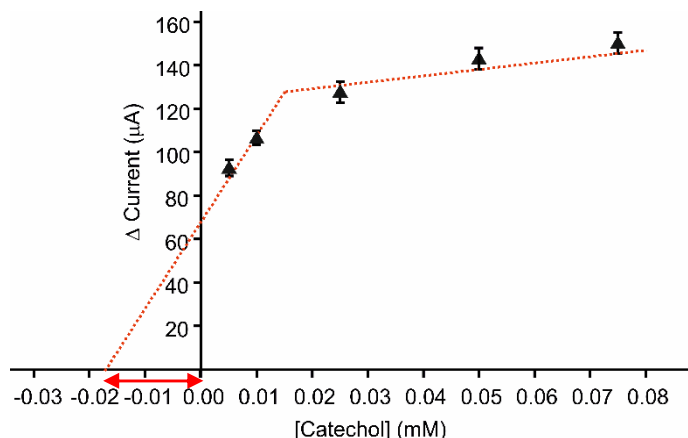

Figure 6: Calibration curves to increasing concentrations of catechol of the CS-MIP/BDD sensor in in a diluted wine sample (10% diluted in 0.1M PBS solution, pH 7.4). ⟷ Original concentration of catechol in diluted wine.

4. CONCLUSION

In this research, a simple, novel and biocompatible electrochemical sensor for catechol detection has been developed. The optimized performance is based on a MIP electrochemical sensor, where a chitosan film was deposited by electrodeposition onto a BDD electrode, thereby offering a sensitive and selective sensor with excellent reproducibility and repeatability. It has been demonstrated that the proposed sensor could be employed for quantitative detection of catechol in red wine samples. Furthermore, the developed sensor supplies an interesting line of research for imprinting electrochemical sensor for phenols detection based on biocompatible polymers.

5 ACKNOWLEDGMENTS

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