

2014 - 2020 Interreg V-A  
Italy - Croatia CBC Programme  
Call for proposal 2019 Strategic

## CoAStal and marine waters integrated monitoring systems for ecosystems proteCtion AnD managemEnt

**CASCADE**

Project ID: 10255941

Priority Axis: Environment and cultural heritage

Specific objective: Improve the environmental quality conditions of the sea and coastal area by  
use of sustainable and innovative technologies and approaches

### D2.2.9

Submission of at least 2 open-access peer-reviewed and/or  
conference papers.

Part 7

PP in charge: All PPs

Final version

Public document

June, 2023

Project acronym	<b>CASCADE</b>
Project ID number	<b>10255941</b>
Project title	<b>CoAStal and marine waters integrated monitoring systems for ecosystems protection AnD managemEnt</b>
Priority axis	<b>3 - Environment and cultural heritage</b>
Specific objective	<b>3.2 - Contribute to protect and restore biodiversity</b>
Strategic theme	<b>3.2.1 - Marine environment</b>
Word Package number	<b>WP2</b>
Word Package title	<b>Communication activities</b>
Activity number	<b>Activity 2.2</b>
Activity title	<b>Website, Social Media and dissemination material</b>
Partner in charge	<b>All PPs</b>
Partners involved	<b>PP9 - Unisalento</b>

Abstract

# Development of Electrochemical Sensors Based on Electrosynthesized Imprinted Polymers for Cobalt (Co<sup>2+</sup>) Ion Determination in Water †

Nelson Arturo Manrique-Rodriguez , Sabrina Di Masi \*  and Cosimino Malitesta 

Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, 73100 Lecce, Italy; nelsonarturo.manriqueroedrodriguez@studenti.unisalento.it (N.A.M.-R.); cosimino.malitesta@unisalento.it (C.M.)

\* Correspondence: sabrina.dimasi@unisalento.it

† Presented at the 2nd International Electronic Conference on Biosensors, 14–18 February 2022; Available Online: <https://sciforum.net/event/IECB2022>.

**Abstract:** Preliminary results on an electrosynthesized ion-imprinted polymeric (IIP) film for the development of a Co<sup>2+</sup> sensor are reported herein. The sensor was prepared by CV electropolymerization of 2-aminophenol (2-AP) monomer in the presence of Co<sup>2+</sup> ions, which acted as the template. The screen-printed carbon electrodes (SPCEs) were used as transducers during sensor development, whereas the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used for the electrochemical characterization of sensors and for Co<sup>2+</sup> ion sensing, respectively. The CV (potential range −0.2 and 1.2 V) and EIS measurements were performed in PBS (pH 7.8, 0.1 M) containing 0.1 mol L<sup>−1</sup> KCl solution and 5.0 mmol L<sup>−1</sup> of Fe(CN)<sub>6</sub><sup>3−/4−</sup> as the redox probe; for EIS an open circuit and data were settled through a sinusoidal potential perturbation of 0.01 V amplitude and 57 as frequency values that were logarithmically distributed over a range of frequencies between 0.01 Hz and 100 kHz. A not imprinted polymer (NIP) was prepared as a control under the same protocol, but without adding the template into the polymerization mixture. In these preliminary tests, the electropolymerization patterns of IIP polymers were found to be consistent with the findings previously reported. After electropolymerization, rinsed electrodes were incubated in different Co<sup>2+</sup> concentrations of ions to be tested through EIS showing a response in the range 1–8 μM. A multivariate optimization based on the design of experiment (DOE) was employed to study the effect of parameters on electrochemical performances of the sensor.

**Keywords:** ion-imprinted polymer; 2-AP; electrochemical sensor; Co<sup>2+</sup> ions; electropolymerization



**Citation:** Manrique-Rodriguez, N.A.; Di Masi, S.; Malitesta, C. Development of Electrochemical Sensors Based on Electrosynthesized Imprinted Polymers for Cobalt (Co<sup>2+</sup>) Ion Determination in Water. *Eng. Proc.* **2022**, *16*, 15. <https://doi.org/10.3390/IECB2022-12281>

Academic Editors: Giovanna Marrazza and Sara Tombelli

Published: 15 February 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/IECB2022-12281/s1>.

**Author Contributions:** Conceptualization, S.D.M. and C.M.; methodology, S.D.M. and C.M.; formal analysis, N.A.M.-R.; investigation, N.A.M.-R.; data curation, S.D.M., C.M. and N.A.M.-R.; writing—original draft preparation, S.D.M. and N.A.M.-R.; writing—review and editing, S.D.M. and C.M.; supervision, S.D.M. and C.M. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the project “CASCADE” (014-2020 Interreg V-A IT-HR CBC “strategic” project ID 10255941).

**Institutional Review Board Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

# Preliminary Study on Electrochemical Ion Imprinted Polymeric Film in Sensor Development for Cd(II) Ions Determination in Water <sup>†</sup>

Sabrina Di Masi <sup>1,\*</sup>, Antonio Pennetta <sup>2</sup> and Cosimino Malitesta <sup>1</sup>

<sup>1</sup> Laboratorio di Chimica Analitica, Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, 73100 Lecce, Italia; cosimino.malitesta@unisalento.it

<sup>2</sup> Laboratorio di Spettrometria di Massa Analitica e Isotopica, Dipartimento di Beni Culturali, Università del Salento, Via Monteroni, 73100 Lecce, Italia; antonio.pennetta@unisalento.it

\* Correspondence: sabrina.dimasi@unisalento.it; Tel.: +39-0832-299-457

† Presented at the 1st International Electronic Conference on Biosensors, 2–17 November 2020; Available online: <https://iecb2020.sciforum.net/>.

Published: 2 November 2020

**Abstract:** Preliminary results on an electrosynthesized ion imprinted polymeric film (IIP-film) for Cd(II) ions determination in sensor development are here reported. The sensor was prepared by electropolymerization of 4-aminophenylacetic acid (4-APA) monomer in presence of Cd(II) ions, which acts as the template. The screen-printed carbon electrodes (SPCE) were used as transducer during sensor development, whereas the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were selected as the electrochemical methods for the synthesis and Cd(II) ions sensing, respectively. The incubation of the developed sensor in NaOH 250 mM involved into remove the template and the formation of specific recognition cavities into the polymer. A multivariate optimization based on central composite design (CCD) was employed to study the effect of three independent parameters on electrochemical performances of the sensor. The electrochemical characterization of sensors was performed in ferrocyanide-ferricyanide redox couple and in KCl 0.1 M, the latter revealing redox properties from the polymeric film. The performances of sensors and the control (non-imprinted film, NIP) was observed in sodium acetate buffer (100 mM, pH = 5) over the Cd(II) concentration range 0.1–10  $\mu$ M.

**Keywords:** ion imprinted polymer; 4-APA; electrochemical sensor; Cd(II) ions; electropolymerisation

---

## 1. Introduction

Heavy metals pollution refers to a global issue, due to the high toxicity and dangerous effects on environment and human health. Among heavy metals, cadmium is one of the most toxic. Main sources of this ion in environment is industrial wastewater, fertilizers and so on. Currently, the most analytical method for cadmium detection is represented by atomic adsorption spectroscopy (AAS), inductively coupled plasma-mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Those techniques are sensitive, accurate but also expensive, and on-site determination of targets is not so suitable. Due to the complexity of those instrumentation, there is the need to point different methods to be available for on-site determination. Electrochemical methods can be used for that. Moreover, diverse electrochemical methods are explored today for the determination of heavy metals in water environment [1].

Imprinted polymers define robust and artificial materials able to mimic recognition processes of such analytes, such as proteins, small molecules, or ions [2]. The process results in the selective formation of ion-sized imprinted cavities, which are complementary to a specific template in terms of its functional groups. These materials can be easily applied to identify, monitor and remove the target ions in water environment [3]. In this view, the ion imprinted polymers (IIPs) can be described. Their synthesis can be carried out both chemically and electrochemically. The latter leads to the preparation of imprinted films, which are compatible in conjunction with transducers in sensor development [4,5]. Very few works report the electrochemical synthesis of ion imprinted polymers and their application as sensors for metal ion detection [6,7]. With this regard, we propose the synthesis, optimization, characterization and subsequent application of an electrosynthesized IIPs for the electrochemical detection of cadmium (II) in water. The proposed sensor was prepared by electropolymerization of 4-aminophenylacetic acid (4-APA) monomer in presence of Cd(II) ions, which acts as the template. The screen-printed carbon electrodes (SPCE) were used as transducer during sensor development, whereas the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were selected as the electrochemical methods for the synthesis and Cd(II) ions sensing, respectively. The incubation of the developed sensor in NaOH 250 mM involved the removal of the template and the formation of specific recognition cavities into the polymer. A multivariate optimization was employed for studying the effect of three independent parameters on electrochemical performances of the sensor. The electrochemical characterization of sensors was performed in ferrocyanide-ferricyanide redox couple and in KCl 0.1 M, the latter revealing redox properties from the polymeric film. The performances of sensors and the control (non-imprinted polymer, NIP) were observed in sodium acetate buffer (100 mM, pH = 5) over the Cd(II) concentration range of 0.1–10  $\mu$ M.

## 2. Materials and Methods

### 2.1. Materials

Acetic acid, 4-Aminophenylacetic acid (4-APA, 98%), sodium acetate trihydrate, cadmium nitrate tetrahydrate (98%), and ethylenediaminetetraacetic acid (99%) were purchased from Sigma-Aldrich (Italy). Sulphuric acid and sodium hydroxide solutions were commercially available as analytical reagent grade. All reagents were used without further purification. MilliQ water was used for washing the polymeric film after the preparation. Sodium acetate buffer (100 mM, pH = 5).

### 2.2. Apparatus

CV and DPV measurements were performed using a PalmSens potentiostat equipped with a cable connector (DropSens, Milano, Italy) for screen-printed electrodes. PSTrace was the software to control the instrument and data acquisition. The polymeric film was deposited on screen-printed carbon electrode (SPCE). The SPCEs were composed of three-electrode configuration on a planar ceramic support ( $3.3 \times 1$  cm) and they consisted of a carbon disk-shaped working electrode (4 mm diameter), a platinum electrode as counter electrode and a pseudo Ag/AgCl paste electrode as reference electrode. SPCE were commercially available (Metrohm, Milano, Italy).

### 2.3. Preparation of Electrosynthesized Ion Imprinted Polymer and Non-Imprinted Polymer

The preparation of ion imprinted polymer (IIP) based on poly-4-aminophenylacetic (poly-4-APA) films was performed by cyclic voltammetry (CV) in a potential range between  $-0.2$  and  $1.2$  V vs. pseudo Ag/AgCl, at a scan rate of  $50$   $\text{mV s}^{-1}$  for 40 cycles in a solution of  $\text{H}_2\text{SO}_4$   $0.5$  M containing  $1$  mM of  $\text{Cd}^{2+}$  ions. The porogen was chosen based on previous works about the electrosynthesis of poly-4-APA on SPE [8]. After the electropolymerization, the electrode was rinsed with MilliQ water and incubated in different solvent (EDTA  $100$  mM and  $250$  mM,  $\text{H}_2\text{SO}_4$   $500$  mM, NaOH  $100$  mM and  $250$  mM) to remove the target. The preparation of the control (non-imprinted polymer, NIP) was obtained with the same protocol, but without adding the template into the polymerization mixture.

The treatment in NaOH 250 mM was also performed on NIP. All prepared sensors were taken in air when not in use.

#### 2.4. Cd<sup>2+</sup> Ion Sensing

The electrochemical responses of IIP and NIP films towards Cd<sup>2+</sup> ions were recorded using DPV measurements in the potential range of -0.2 to + 0.4 V, modulation amplitude of 50 mV, step potential of 4.95 mV, and equilibration time of 2 s. Cd<sup>2+</sup> ions interacted with the imprinted film by drop-casting on the electrode surface an appropriate amount (100 µL) of a solution of sodium acetate buffer (100 mM, pH = 5) containing different concentration of Cd<sup>2+</sup> ions (0.1–10 µM), by leaving the drop on the electrode for 10 min. After each measurement, the electrode surface was gently washed with sodium acetate buffer for 2 min.

#### 2.5. Experimental Design in Optimization Studies

Multivariate optimization was conducted with the light to optimize the development of IIPs and NIP. The selected optimization model was the central composite design (CCD), which allowed the selection of main three factors affecting the development of the sensors, such as (i) the monomer concentration, (ii) the rate between template-monomer (mainly affecting the number of cavities on the polymeric network) and (iii) the number of CV cycles during the electrosynthesis. MODDE® Software (Umetrics, version 12, <https://www.sartorius.com/en/products/process-analytical-technology/data-analytics-software/doe-software/modde>) was used for design, mathematical modelling and optimization. The levels of studied independent variables are listed in Table 1.

**Table 1.** Levels of independent variables considered in this work.

Variable	Low	High
Monomer concentration (X <sub>1</sub> )	0.5	5
Rate Cd <sup>2+</sup> /monomer (X <sub>2</sub> )	1	3
Number of CV cycles (X <sub>3</sub> )	10	40

The response was the difference of current ( $\Delta i$ , µA) recorded in ferrocyanide-ferricyanide redox probe before and after the electropolymerization of the different imprinted sensors. Based on CCD principle, the design consisted of 2<sup>k</sup> fractional factorial points plus 2<sup>k</sup> axial points and 1 center point, where k defines the number of central points (in this case, k = 3). Eighteen experiment runs were conducted, and the second-order polynomial equation consisted of linear, quadratic, and first-order interaction terms is shown below (Equation (1)):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j(\neq i)}^k \beta_{ij} X_i X_j + \varepsilon, \tag{1}$$

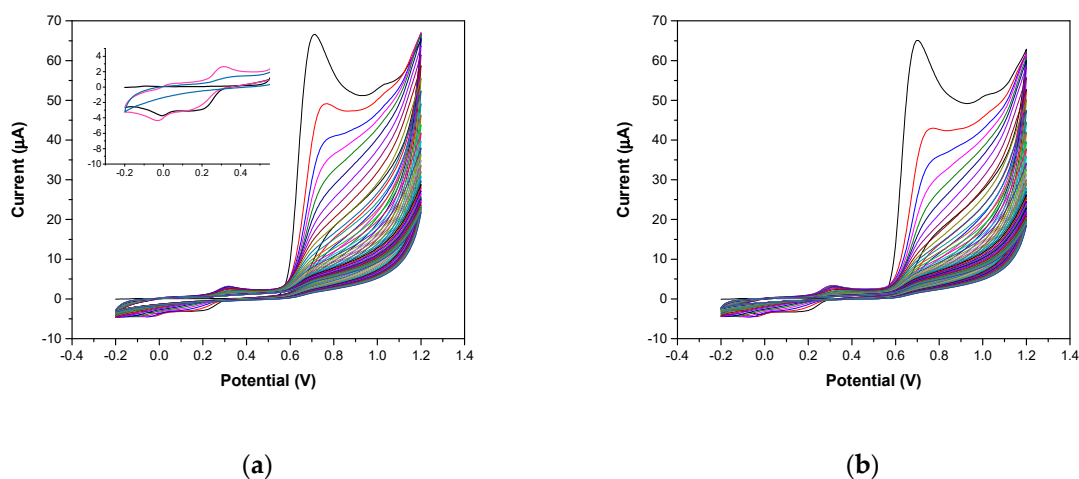
where Y is the response variables, X<sub>i</sub> represent the dependent variables, β<sub>0</sub>, β<sub>i</sub>, β<sub>ii</sub>, β<sub>ij</sub> were the regression coefficient for intercept, linear, quadratic and interaction terms, respectively.

### 3. Results and Discussions

The electropolymerization of 4-APA in presence of Cd<sup>2+</sup> produced a sensitive polymeric imprinted film for that template, showing superior characteristics against its control. The optimal condition of synthesis was established by employing a multivariate experimental design, and this approach has recently gained interest from scientists regarding optimized sensors and biomimetic sensors. The advantage of using the produced IIPs consisted of revealing a redox property of the polymer, which directly addresses the interaction between imprinted cavities and template. The interaction was visible, close to + 0 V (see related DPV measurements), of which potential is higher than normally observed for the electroactivity of Cd<sup>2+</sup> in solution.

### 3.1. Preparation of Electrosynthesized IIP and NIP Films

Figure 1a presented a typical cyclic voltammetry recorded during the electropolymerization of 2.1 mM 4-APA in the presence of 2.1 mM  $\text{Cd}^{2+}$  ions in 0.5 M  $\text{H}_2\text{SO}_4$  on a screen-printed carbon electrode. Figure 1b shows the electropolymerization of 4-APA on SPCE, without the template (NIP).



**Figure 1.** (a) The electropolymerization of 2.1 mM 4-APA in the presence of 2.1 mM  $\text{Cd}^{2+}$  in 0.5 M  $\text{H}_2\text{SO}_4$ . Inset: Focused cyclic voltammetry for (black) 1st, (pink) 2nd (blue), and 17th cycle; (b) the electropolymerization of 2.1 mM 4-APA in 0.5 M  $\text{H}_2\text{SO}_4$ . Voltammetric condition: (i) Potential range:  $-0.2$  to  $+1.2$  V; (ii) scan rate:  $50 \text{ mV s}^{-1}$ ; (iii) CV cycles: 40.

During the CV, the first peak at  $+0.70$  V indicated the formation of cation radicals that promoted the polymerization process, once to the oxidation of 4-APA. Further peaks at  $+0.19$  V and at  $-0.025$  V are related to the reduction of the polymer film on the SPCE surface. Following the second potential cycle, two oxidation waves appeared at the potentials of  $+0.040$  and  $+0.305$  V, corresponding to the oxidation of the formed polymeric film. After around 17 cycles of polymerization, a decrease in the anodic peaks current was notable, indicating the subsequent formation of the polymer film (see Inset of Figure 1a). Finally, the formation of the film produced a partial blockage of the electrode surface. The electropolymerization of NIP (Figure 1b) followed the same interpretation of the process, with differences in terms of current appeared along the second cycle of CV.

### 3.2. Optimization of Sensor Performances by Experimental Design

The optimization of performances was possible by a multivariate approach, that considered all factors together, including linear, quadratic and interaction terms in the model. All the selected factors were related to the electrosynthesis process. Among them, with the emphasis to develop imprinted materials, the relationship between all reagent should be described. Preliminary results have shown the factor's importance on responses were the initial concentration of functional monomer ( $X_1$ ) and the number of CV cycles during the electrosynthesis ( $X_3$ ). Figure 2 shows the significant coefficients related to factors.

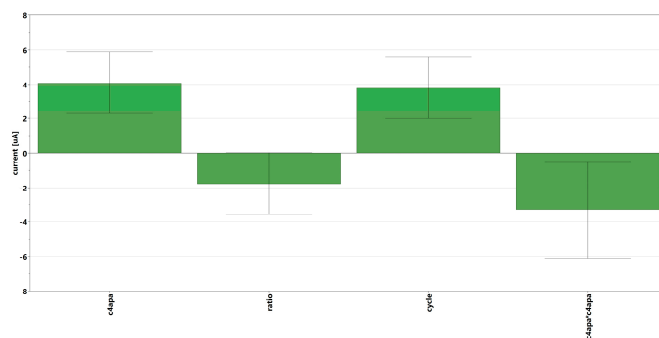


Figure 2. Plot of the significant coefficients obtained from model.

The regression equation for the achieved responses, including significant factors, is reported (Equation (2)).

$$Y = 14.86 + 4.08X_1 - 1.78X_2 + 3.80X_3 - 3.30X_1X_1, \tag{2}$$

After evaluation of Equation (2), it appears as though the monomer concentration is in strong correlation with the other factors. In particular the ratio of monomer/ $Cd^{2+}$  should be regulated to assume a correct orientation of cavities on the polymer network. The factor related to the growth of the electro synthesized imprinted film was also significant, confirming that the deposition of the film on electrode surface is involved in the difference of currents recorded by the electrochemical probe. In light of maximizing the responses, the experimental conditions used for further measurements were (i) 2.1 mM 4-APA, (ii) 2.1 mM  $Cd^{2+}$  (ratio 1:1), and (iii) 40 CV cycles during the electro synthesis.

### 3.3. Electrochemical Characterization of IIP and NIP Films

The prepared sensors were first subjected to electrochemical characterization in ferrocyanide-ferricyanide redox probe and in KCl 0.1 M, by applying a CV measurement for bare SPCE, IIP film and NIP film after the electrodeposition (Figure 3a,b).

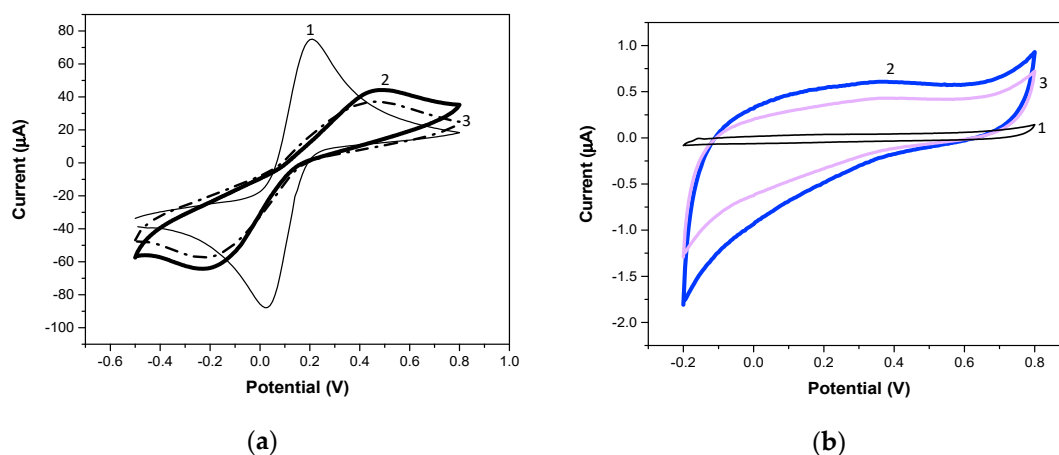


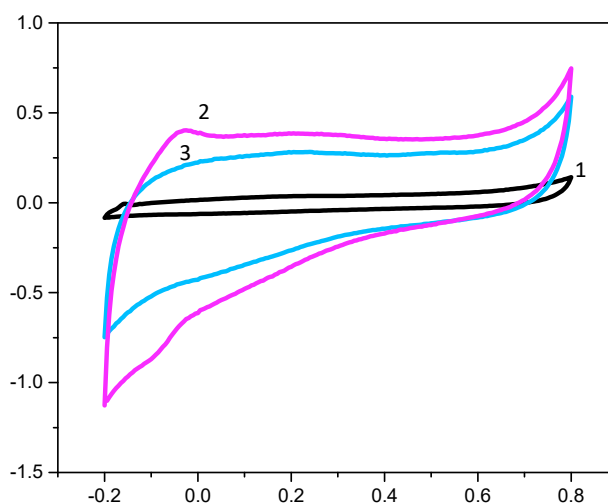
Figure 3. (a) Electrochemical characterization by CV (fifth cycle) in ferrocyanide-ferricyanide redox probe for (1) bare screen-printed carbon electrode; (2)  $Cd^{2+}$ -ion imprinted polymer film/screen-printed carbon electrode (SPCE) and (3) non-imprinted polymer (NIP) film/SPCE after polymerization. Voltammetric condition: (i) Potential range:  $-0.5$  to  $+0.8$  V; (ii) scan rate:  $50\text{ mV s}^{-1}$ ; (iii) CV cycles: 5; (b) electrochemical characterization by CV (fifth cycle) in 0.1 M KCl for (1) bare screen-printed carbon electrode; (2)  $Cd^{2+}$ -IIP film/SPCE; and (3) NIP film/SPCE after polymerization. Voltammetric condition: (i) Potential range:  $-0.2$  to  $+0.8$  V; (ii) scan rate:  $50\text{ mV s}^{-1}$ ; (iii) CV cycles: 5.

Both electrochemical characterizations revealed higher electroactivity of the imprinted polymer when compared to NIP film. In addition, as shown in Figure 2b, no signals were obtained for bare SPCE. The electroactivity of IIP film than NIP suggest the imprinting effect of the polymer, where



possibly  $\text{Cd}^{2+}$  ions are possibly able to enhance the overall electrochemical process during polymerization.

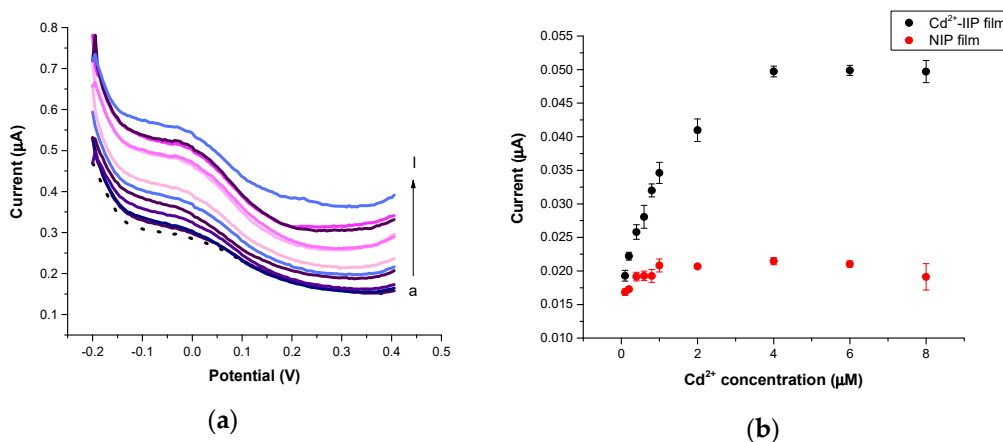
The removal of the template ion—to obtain the imprinted cavities—was carried out by exposure of the sensor to different solutions, such as EDTA 100 mM and 250 mM,  $\text{H}_2\text{SO}_4$  500 mM, NaOH 100 mM, and 250 mM. In all cases, different times of elution were tested, in a range between 1 and 15 min (1, 3, 5, 10, 15 min, respectively). As the most effective method, NaOH 250 mM incubated for 3 min was used. CV markable differences recorded in KCl 0.1 M for NIP and IIPs treated with NaOH 250 mM were visible (Figure 4), confirming the elution of  $\text{Cd}^{2+}$  ions from the imprinted cavities.

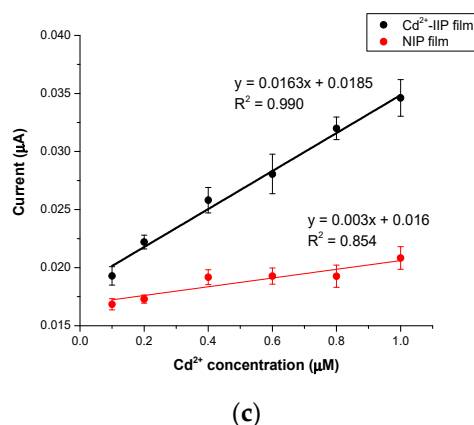


**Figure 4.** Electrochemical characterization by CV (fifth cycle) in 0.1 M KCl for (1) bare screen-printed carbon electrode; (2)  $\text{Cd}^{2+}$ -IIP film/SPCE; and (3) NIP film/SPCE after treatment in 250 mM NaOH for 3 min. Voltammetric condition: (i) Potential range:  $-0.2$  to  $+0.8$  V; (ii) scan rate:  $50 \text{ mV s}^{-1}$ ; (iii) CV cycles: 5.

### 3.4. Electrochemical Performances of IIP and NIP Film

The electrochemical sensing of  $\text{Cd}^{2+}$  ions was performed by DPV measurements on NIP and  $\text{Cd}^{2+}$ -IIP film: 100 mM sodium acetate buffer (pH = 5) was selected as the electrolyte solution for the determination of  $\text{Cu}^{2+}$  ions. DPV measurements recorded for  $\text{Cd}^{2+}$ -IIP film are shown in Figure 5, and related calibration curves are also reported (Figure 5b).





**Figure 5.** (a) Differential pulse voltammograms recorded for Cd<sup>2+</sup>-IIP film after the exposure to (a) blank (sodium acetate buffer), (b) 0.1, (c) 0.2, (d) 0.4, (e) 0.6, (f) 0.8, (g) 1.0, (h) 2.0, (i) 4.0, (j) 6.0, (k) 8.0, (l) 10 µM of Cd<sup>2+</sup> ions in the presence of sodium acetate buffer; (b) comparison of the electrochemical responses between Cd<sup>2+</sup>-IIP and NIP films along all tested Cd<sup>2+</sup> concentration; (c) comparison between responses from Cd<sup>2+</sup>-IIP and NIP film in the linear range revealed between 0.1 and 1 µM Cd<sup>2+</sup> ions.

As shown from Figure 5a, the current responses value increased within the tested Cd<sup>2+</sup> ion concentration. However, saturation reached value upper than 2 µM, due to the occupancy of cavities. Notably, the imprinted sensor shows high affinity and specificity towards Cd<sup>2+</sup> ions compared to that obtained for NIP films, confirming the imprinting effect on this polymer. The linear regression was established between 0.1 and 1 µM, with a sensitivity of 0.0163 µA µM<sup>-1</sup>. In addition, it was possible to evaluate the imprinted factor as 6.86, highly indicating the specific recognition of template from imprinted cavities on Cd<sup>2+</sup>-IIP films.

The proposed imprinted sensor shows high sensitivity and possesses superior specific properties towards Cd<sup>2+</sup> ions. These preliminary results are currently encouraging us to perform further experiments in regard to selectivity properties of the imprinted polymer against NIP and its application to real water matrices, of which discussion will be presented soon.

#### 4. Conclusions

Preliminary study on electrosynthesis of ion imprinted polymeric sensor on SPCE transducer for Cd<sup>2+</sup> ion determination in water is reported here. The electrosynthesis of the imprinted cavities revealed the newly approach to produce highly sensitive films towards environmental targets. In this light, the developed imprinted polymeric film shows greater sensitivity than NIP film, with an imprinting factor of 6.86. Those achieved preliminary results open the possibly to employ this sensor for quantitative determination of Cd<sup>2+</sup> ions in water. Further experiments to evaluate more properties of the sensor are currently under study.

**Funding:** This research was funded by the project “CASCADE” (014-2020 Interreg V-A IT-HR CBC “Strategic” project ID 10255941).

**Acknowledgments:** Authors would like to thank Marco Costa for his helping during experiments.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Wong, A.; A. Ferreira, P.; Santos, A.M.; Cincotto, F.H.; Silva, R.A.B.; Sotomayor, M.D.P.T. A new electrochemical sensor based on eco-friendly chemistry for the simultaneous determination of toxic trace elements. *Microchem. J.* **2020**, *158*, 105292, doi:10.1016/j.microc.2020.105292.
2. Li, N.; Yang, H. Construction of natural polymeric imprinted materials and their applications in water treatment: A review. *J. Hazard. Mater.* **2021**, *403*, doi:10.1016/j.jhazmat.2020.123643.

3. Jinadasa, K.K.; Peña-Vázquez, E.; Bermejo-Barrera, P.; Moreda-Piñeiro, A. New adsorbents based on imprinted polymers and composite nanomaterials for arsenic and mercury screening/speciation: A review. *Microchem. J.* **2020**, *156*, 104886, doi:10.1016/j.microc.2020.104886.
4. Crapnell, R.D.; Hudson, A.; Foster, C.W.; Eersels, K.; van Grinsven, B.; Cleij, T.J.; Banks, C.E.; Peeters, M. Recent advances in electrosynthesized molecularly imprinted polymer sensing platforms for bioanalyte detection. *Sensors* **2019**, *19*, 1204, doi:10.3390/s19051204.
5. Sharma, P.S.; Pietrzyk-Le, A.; D'Souza, F.; Kutner, W. Electrochemically synthesized polymers in molecular imprinting for chemical sensing. *Anal. Bioanal. Chem.* **2012**, *402*, 3177–3204, doi:10.1007/s00216-011-5696-6.
6. Sharma, G.; Kandasubramanian, B. Molecularly Imprinted Polymers for Selective Recognition and Extraction of Heavy Metal Ions and Toxic Dyes. *J. Chem. Eng. Data* **2020**, *65*, 396–418, doi:10.1021/acs.jced.9b00953.
7. Di Masi, S.; Pennetta, A.; Guerreiro, A.; Canfarotta, F.; Egidio, G.; Benedetto, D.; Malitesta, C. Sensor based on electrosynthesised imprinted polymeric film for rapid and trace detection of copper (II) ions. *Sensors Actuators B. Chem.* **2020**, *307*, 127648, doi:10.1016/j.snb.2019.127648.
8. Pimenta, T.C.; Santos, C.d.C.; Thomasini, R.L.; Ferreira, L.F. Impedimetric immunosensor for dengue diagnosis using graphite screen-printed electrodes coated with poly(4-aminophenylacetic acid). *Biomed. Microdevices* **2018**, *20*, 1–9, doi:10.1007/s10544-018-0324-2.

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).