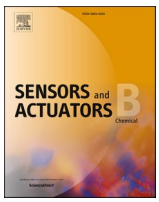
Sensors & Actuators: B. Chemical 383 (2023) 133559

Contents lists available at ScienceDirect

Sensors and Actuators: B. Chemical

journal homepage: www.elsevier.com/locate/snb



Disposable electrochemical sensor based on ion imprinted polymeric receptor for Cd(II) ion monitoring in waters

Marco Costa [a], Sabrina Di Masi [a,*], Alvaro Garcia-Cruz [b], Sergey A. Piletsky [b], Cosimino Malitesta [a]

[a] Laboratorio di Chimica Analitica, Edificio A6, DiSTeBA, Università del Salento, Via per Monteroni, 73100 Lecce, Italy
[b] Department of Chemistry, University of Leicester, University Rd, LE1 7RH Leicester, UK

ARTICLE INFO

Keywords:
Electropolymerisation
4-Aminophenylacetic acid
Ion imprinted polymer
Amperometric sensor
Cadmium
Water

ABSTRACT

Cadmium is a highly toxic heavy metal, even at low concentrations. Moreover, it bio-accumulates with a long biological half-life producing a wide variety of acute and chronic effects like cancer in humans. Therefore, there is significant interest in providing a portable and user-friendly sensor for heavy metal detection. A highly sensitive and selective electrochemical sensor for Cd(II) determination was developed as an alternative. The Cd (II) receptors were integrated into the sensor using an ion-imprinted polymer film (IIPs film). Accordingly, 4-aminophenylacetic acid (4-APA) was electropolymerised in the presence of Cd(II) ions as a template using cyclic voltammetry (CV) on screen-printed carbon electrodes (SPCEs). Imprinted cavities were obtained after the alkaline elution of ions. Sensor characterisation was performed using SEM, ATR-FTIR and electrochemical methods, such as cyclic voltammetry (CV) and electrochemical Impedance Spectroscopy (EIS), and compared to control experiments (not imprinted polymeric film, NIP film). Analytical performances of the IIP sensor revealed a sensitivity 5-order of magnitude higher than the NIP response in a concentration range from 10 to 1200 nM of Cd (II). This technology can potentially be applied for water quality control and monitoring of heavy metals.

1. Introduction

Industrial activities are the primary source of cadmium pollution causing a substantial threat to human and animal life [1]. A critical source is the industrial waste and water disposal contaminated by heavy metals generated in extractive industries of metals, batteries, iron and steel production, and effluents [2]. Intake of low cadmium concentrations in humans can severely affect cellular functions such as proliferation, apoptosis, cell signalling and gene expression[3]. Both short-term and long-term cadmium exposure harms human health and can lead to severe diseases and several cancers [4]. Cd(II) ions have been classified as carcinogenic to humans by the World Health Organization (WHO), even at low doses, with a maximum limit of 3 μg L^{-1} in drinking water [5].

Different analytical techniques have been developed for the detection of Cd(II), such as inductively coupled plasma mass spectrometry (ICP-MS) [6], atomic absorption/emission spectroscopy (AAS/AES) [7], ultraviolet–visible spectrometry [8], voltammetry [9–16], atomic fluorescence spectrometry (AFS) [14] In general, some of them require expensive equipment, complex and intensive sample pre-treatment, and the analyte pre-concentration steps. Regardless of their performance, most of them are often tedious and time-consuming and require significant amounts of reagents, trained personnel and sophisticated apparatuses. Consequently, there is a need for a cost-effective, rapid, simple, selective, and sensitive method that permits real-time detection of metal ions. In addition, minimal sample treatment is desirable due to the danger that heavy metal ions pose to operators.

As an alternative, electrochemical sensors for Cd(II) detection offer high sensitivity, simple operation, and allow miniaturisation, which is suitable for the mass production of sensors. Therefore, electrochemical sensors are considered up-and-coming tools for sensitive, rapid and low-cost monitoring of a wide range of analytes. In the field of sensors, biosensors have been primarily explored; however, they present several limitations. Biosensors are not suitable for on-field applications since the biological receptors can be easily deactivated in the presence of potential inhibitors, poisoned by sample contaminations and limited to specific working conditions [17].

To overcome these challenges, molecularly imprinted polymers

* Corresponding author.
E-mail address: sabrina.dimasi@unisalento.it (S. Di Masi).

https://doi.org/10.1016/j.snb.2023.133559
Received 20 December 2022; Received in revised form 16 February 2023; Accepted 20 February 2023
Available online 1 March 2023
0925-4005/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

(MIP) represent the versatile, scalable, and cost-effective approach to creating synthetic molecular receptors. MIPs are artificial receptors containing recognition cavities highly specific to a target. These cavities can be designed to bind to small ions and molecules specifically and large ones as proteins. These polymers are generally stable in various temperatures, pH, and pressure. They can also be applied in organic solvents and are much more robust than their biological counterparts (antibodies, enzymes etc.) [18,19]. In addition, ion-imprinting technology enables the formation of ion imprinted polymeric (IIP) films with recognition sites for heavy metal ions using specific chelating functional groups [20–24].

The IIPs can also be prepared by electropolymerization, which allows for controlling the deposition and polymer nature efficiently. Moreover, integrating IIP into screen-printed electrodes (SPE) results in portable devices, enabling fast monitoring at the point of care testing, with high performance and lower cost than lab-based analytical techniques. Recently, amperometric sensors based on electrochemically imprinted polymers have been developed in our group[25] for the monitoring of heavy metals, e.g. Cu(II). These IIP films contain chelating functional groups allowing metal complexation, such as amine (-NH2) and carboxyl (-COOH). Herein, 4-aminophenylacetic acid (4-APA) was used as a functional monomer for IIP preparation allowing selective determination of Cd (II) ions in water matrices. To our knowledge, this is the first demonstration-using poly (4-APA) as an ion-imprinted polymeric film employed as a sensor for heavy metal monitoring in water.

2. Materials and method

2.1. Chemicals

4-aminophenylacetic acid (4-APA), and cadmium nitrate tetrahydrate (98 %) were purchased from Merck (Milano, Italy). Glacial acetic acid, sulphuric acid, and sodium hydroxide solutions were commercially available as analytical reagent grade. Acetate buffer solution (0.05 mol L^{-1}, pH = 5) was prepared from glacial acetic acid brought to pH = 5 with NaOH. Elution processes were carried out in presence of 0.25 mol L^{-1} NaOH solution under stirring. Cd(II) ions stock solutions were prepared in acetate buffer and diluted with the same buffer to give the required concentration. MilliQ water was used for the polymeric film wash after the electrochemical preparation and after elution processes. All reagents were used without further purification.

2.2. Apparatus

Analytical experiments were carried out with a PalmSens potentiostat (Metrohm, Italy) controlled by PSTrace software. Disposable screen-printed carbon electrodes (SPCE, DRP-150, Metrohm, Italy) were used as transduction element for sensor development. They consisted in a carbon disk-shaped (12.6 mm^2) working electrode, platinum strip counter electrode, and a paste of silver reference electrode on a ceramic substrate (3.3 cm × 1.0 cm). A cable connector for SPEs has been connected to the potentiostat.

2.3. Optimisation of sensor development

To determine the optimal conditions in sensor development, the use of quadratic mathematical models in which several factors are considered with two or more levels has gained interest [26,27]. The experimental design was based on a face centred composite design (FCCD from Minitab software (version 18). Based on preliminary results, three independent variables with two levels were selected (Table S1): Cd(II) concentration (2.1, 10.5 mmol L^{-1}), number of CV scans (10, 40), elution time (10, 60 min). FCCD matrix was designed with 8 cube points, 6 axial points, and 3 centre points in cube, to finally obtain 17 experimental runs. Experimental runs were conducted randomly to minimise the effect of unexpected variability on the observed responses. Three experiments were performed at the centre points for the estimation of the variance. The response variable (Y) that was analysed was the sensitivity of Cd(II)-IIP film for Cd(II) ions (in the range of concentration between 10 and 640 nmol L^{-1}) obtained from the logarithmic linearised regression plots under the different experimental trials. The relationship between the achieved current and the logarithmic scale of concentration was evaluated by the Temkin isotherm adsorption (Section 3, Supplementary material), which has been already applied in the field of IIP sensors [28–31].

2.4. Sensor preparation

The procedure adopted for sensors preparation is described as shown in Scheme 1. First, a bare SPCE was subjected to electrochemical conditioning by cyclic voltammetry in redox probe solution of 10 mM ferrocyanide/ferricyanide in 0.1 M KCl, at number of cycles until reaching a steady state (at least 20 cycles). The electrode was then rinsed with MilliQ. The polymerisation mixture composed by the presence of 4-aminophenylacetic acid monomer and Cd(II) ions dissolved in sodium acetate buffer solution (50 mmol L^{-1}, pH= 5) was drop-casted on SPCE surface. The CV was performed in the potential range between from − 0.2 to + 1.2 V (vs Ag/AgCl), at scan rate of 50 V s^{-1}, potential step of 5 mV.

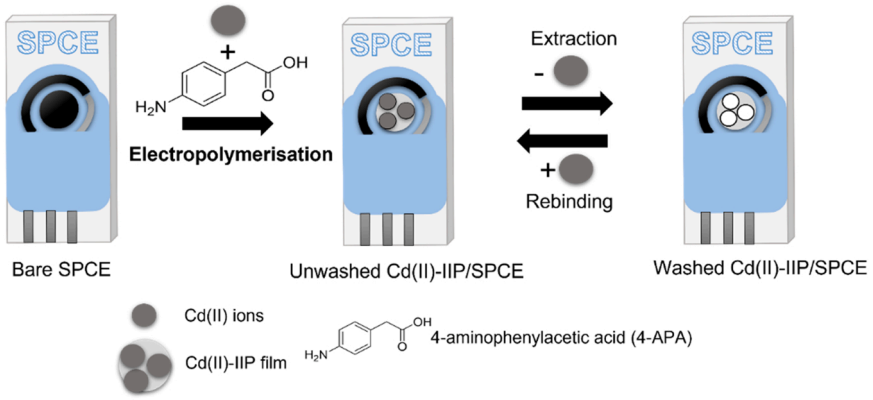
After the electropolymerisation, the modified electrode (unwashed Cd(II)-IIP film) was rinsed for few minutes with MilliQ to remove unreacted monomers from the electrode surface and then dipped in the template removal solution (NaOH 0.25 mol L^{-1}) for variable minutes (see Section 2.3 for further information). An alkaline media was chosen to avoid degradation of polymerised aniline films [32] and possibly permitted the elution of Cd(II) in solution. The same protocol was adopted for not imprinted polymer (NIP) preparation, without adding Cd(II) ions in the polymerisation mixture. All experiments were performed at room temperature. A schematic diagram of the electrosynthesis process and target interactions is also illustrated and discussed in SM (Scheme S1).

2.5. Characterisation of developed sensors

The optimised Cd(II)-IIPs film and NIP film were characterised by SEM, and ATR-FTIR. Spectra were acquired in the 800–4000 cm^{-1} range with a resolution of 4 cm^{-1} and by accumulating 64 scans. The morphology of the imprinted and not imprinted films vs bare electrodes was evaluated by SEM analysis. Samples were applied to carbon sticky tabs mounted on 12.5 mm aluminium SEM stubs (Agar Scientific Ltd) and coated with gold/palladium in a Quorum Q150 TES coating unit. The samples were viewed on a Hitachi S3000H Scanning Electron Microscope with an accelerating voltage of 10 kV. FT-IR analysis was performed using an Alpha platinum-ATR FTIR spectrometer (Bruker, UK).

2.5.1. Electrochemical characterisation

CV and Electrochemical impedance spectroscopy (EIS) analysis were used to characterise the polymeric films. CV measurements were recorded in a ferrocyanide solution (0.1 mol L^{-1} KCl, 0.01 mol L^{-1} $Fe(CN)_6^{3-/4-}$), and also in a solution of acetate buffer solutions (50 mmol L^{-1}, pH = 5). Voltammograms were also recorded in the potential range from – 0.5 to + 0.5 V (vs Ag/AgCl), the scan rate of 50 mV s^{-1}, and 20 cycles. EIS analysis were accomplished in the frequency range from 0.01 Hz to 100 KHz in 0.1 mol L^{-1} KCl solution containing 0.01 mol L^{-1} $Fe(CN)_6^{3-/4-}$ as the redox probe, at AC amplitude of 10 mV, E_{dc} of + 0.2 V. The impedance spectra were fitted and interpreted by Randle's equivalent circuit, as shown from Fig. S1. EIS and CV were applied to study differences between bare SPCE, after modification with ion imprinted polymeric film and not imprinted polymeric film, and after wash treatments. The facial properties of modified electrodes surface were measured by means of the electron transfer resistance (R_{et})



Scheme 1. Scheme of Cd(II)-IIP films preparation. The same protocol was adopted for NIP films preparation without adding Cd(II) ions in the polymerisation mixture.

and compared during EIS characterisation studies.

2.6. Cd(II) ion sensing and binding isotherms

The prepared Cd(II)-IIP film and NIP film was tested for determination of Cd(II) ions in sodium acetate buffer (50 mmol L^{-1}, pH = 5.0). CV was used to evaluate the analytical performances of sensors. For that, Cd (II) solutions were measured by drop casting for 10 min. Subsequently, electrodes were rinsed with MilliQ water, and 20 CV cycles were measured in 50 mM sodium acetate buffer solution (blank). After each tested concentration, sensors were incubated for 3 min with 0.25 M NaOH solution for metal removal. The protocol was followed, and different concentration of Cd(II) ions were measured. The experimental data for Cd(II)-IIP films and NIP films were fitted by Temkin isotherm model [33,34] to assess the adsorption dynamics and calibration curves (more information available in Section 3, SM). Calibration plots were thus obtained by plotting the Δi (μA) vs log[Cd(II)] ions (nmol L^{-1}), according to the following relationship:

$$\Delta i = B * \log K + B * \log[Cd(II)] \quad (1)$$

In Eq.1, "B" is constant, "Δi" is the CV current oxidation peak recorded at + 0.1 V after exposure to tested Cd(II) concentration. Therefore, a calibration plot can be obtained by plotting the current change "Δi"(μA) against the logarithmic of the Cd(II) concentration.

2.7. Sample analysis

In order to investigate the promised application of our sensor to selective monitor Cd(II) ions in real matrices, water sample analysis was conducted, including a commercial drinking water (pH = 7.7), tap water (pH= 7) and marine water (pH= 8). Prior to analysis, the water samples were buffered at pH 5 (1:10 sodium acetate buffer), this was used as a blank. The obtained solutions were allowed to rotate under stirring for 2 h. Therefore, water samples were spiked with (0.5 mmol L^{-1}) Cd(II) ions to obtain a series of dilutions from 10 to 640 nmol L^{-1}. Finally, 100 μL of spiked samples were drop casted on Cd(II)-IIP film sensor to obtain a calibration curve.

3. Results and discussion

3.1. Optimisation of sensor performances

Several factors are important effect on the ion recognition properties of IIPs: (i) ratio between monomer concentration and template concentration, (ii) number of CV scans during electropolymerisation, and (iii) elution time during cavities formation. To determine the best concentration ratio between the monomer and the ion template, the Cd(II)-IIP film was grown in solution of fixed concentration of 4-APA (2.1 mmol L^{-1}) and varying concentration of Cd(II) ions. The sensitivities of Cd(II)-IIP films were collected in the range of concentration between 10 and 640 nmol L^{-1}. The report of the experimental runs and the sensitivity for each developed sensor is shown in Table S2.

Subsequently, the response surface regression was calculated, considering the significant factors affecting the sensitivity. Thus, concentration of Cd(II) ions, CV cycles during electropolymerization and elution time were considered. Standardised effects on the sensitivity were presented in the Pareto Chart as shown Fig. S2**.** Pareto chart demonstrated that CV scan cycles and Cd(II) concentration are the remarkably significant factors affecting the sensitivities of Cd(II)-IIP films. Possibly, because the amount of the imprinted sites in polymeric films increases with the increase of the thickness. Nevertheless, thick imprinted films can lead to slow diffusion of ions, leading to inefficient communication with the transducer. The effect of concentration of Cd (II) ions, CV cycles and elution time in the sensor response was represented in Fig. S3. It is observed that increasing the concentration of Cd (II) into the polymerisation mixture had a positive effect on sensor sensitivities up to the Cd(II) concentration of 6.3 mM (ratio 1:3 monomer/template). Also, the increase in the number of the cycles led to a significant increase in sensor sensitivity up to 25 cycles, nonetheless a diminishing value was observed after 25 cycles. Additionally, it was observed a linear rise of the sensor response with increased elution time, due to the ability of the eluent to leach the Cd(II) ions from the polymer structure. The determination coefficient ($R^{2=}$91%) confirmed that the model was well fitted to the experimental data with high confidence (Table S3). Therefore, these optimised parameters were employed, with the goal to maximise the sensor sensitivities. The optimisation plot (Fig. S4) revealed the optimum conditions to be employed during sensor synthesis, which were 6.3 mM for Cd(II) concentration, 26 of CV scans during the electrosynthesis, and 60 min to elute Cd(II) ions from the imprinted network.

3.2. Sensor preparation

The electrochemical sensor was prepared by the electropolymerisation of 4-APA on SPCE in presence of Cd(II) ions by cyclic voltammetry, as shown in Fig. 1 A. An oxidation peak at 0.83 V can be observed during the first potential cycle, which is related to the oxidation of monomer to form cation radicals, which promote the polymerisation reaction. In the reverse scan, two peaks can be observed at + 0.08 V and + 0.263 V, respectively, indicating the reduction of the polymeric film. During the second cycle, oxidation peaks of deposited film on the electrode can be observed at + 0.137 V and + 0.434 V (vs Ag/AgCl). In the following scans, a current decrease of the oxidation peak of the monomer is observed, confirming the polymer film

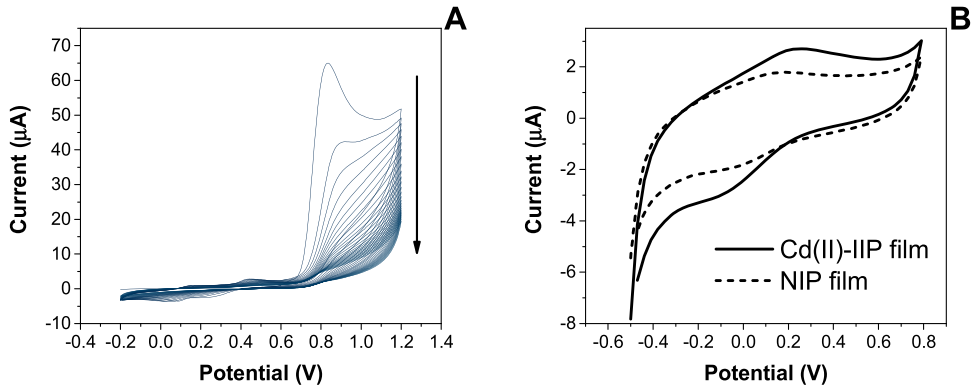


Fig. 1. (A) Cyclic voltammetry of growing of 4-APA monomer (2.1 mmol L^{-1}) in presence of Cd(II) ions (6.3 mmol L^{-1}) in H_2SO_4 solution (0.5 mol L^{-1}, pH = 5). Parameters: − 0.2–1.2 V potential range, 5 mV of potential step, scan rate of 50 mV s^{-1}, 26 CV scans number. (B) CV measurement performed in acetate buffer (50 mM, pH= 5) for NIP film and Cd(II)-IIP film after the wash treatment in 0.25 M NaOH.

deposition on the electrode. The electropolymerisation process of NIP films (data not shown) was quite similar. Therefore, the prepared Cd(II)-IIP and NIP films were exposed to 100 μL of NaOH for 60 min, to perform both elution of target from the imprinted polymer and to remove unreacted monomers. Fig. 1B shows the remained electroactivity of the polymeric films after the wash treatment, that might be arise from the own electroactive properties of the obtained polymers, which can be compared to that of electrically conducting polyanilines [35,36]. The adopted wash procedure was able in freeing specific binding sites with reduced damage.

The characterisation of bare SPCE, Cd(II)-IIP film/SPCE and NIP film/SPCE before and after washing treatments was performed by analysing the electrochemical response to the redox probe $Fe(CN)_6^{3-/4-}$ by using CV and EIS measurements. Fig. 2A shows the Cd(II)-IIP film deposited on the surface of bare SPCE. After electrode modification, the $Fe(CN)_6^{3-/4}$ electron transfer is hindered, revealing a significant decrease of peak currents. This can be attributed to the effect of a polymer film of low permeability on electrode surface. After treatment with an alkaline elution, Cd (II) were removed. As a consequence, the current response of washed Cd(II)-IIP film was increased, the removal of metal ions creates imprinted cavities on polymer network, which leads to increasing the permeability of the membrane. Therefore, the higher permeability of the film increases the diffusion of the redox probe in solution, and consequently the charge transfer increases; this is known as the gate effect. As expected, NIP films showed a lower recovery of the current after metal removal compared to Cd (II)-IIP film, since the polymer film permeability is not affected. Additionally, EIS measurements agreed with those of the CVs.

Fig. 2 B shows the Nyquist plot obtained for Cd(II)-IIP film and NIP film before and after washing with the alkaline elution, respectively. The EIS results were analysed using a fitted Randles equivalent circuit (Fig. S1).

Before the electropolymerization, the R_{et} value of bare SPCE was 3284 Ω. Afterwards, an increased resistance can be observed after the electrosynthesis of Cd(II)-IIP film (3.09×10^5 Ω) and NIP film (2.64×10^5 Ω), confirming the modification of electrodes. The increase of resistance was more significant in Cd(II)-IIP film, indicating the metal complexation in the polymer network. The removal of the metal leads to the creation of cavities, leading into a permeable membrane. After washing treatment, the R_{et} significantly decreased for Cd(II)-IIP film (9397 Ω) confirming the successfully removal of Cd(II), resulting in an increasing of the redox probe permeation. These changes are not observed for NIP films (2.98×10^4 Ω).

3.2.1. SEM analysis

The different topography of bare and modified SPCEs are shown in Fig. S5. The bare electrode displays relatively smooth surface when compared to the electrodes modified with the NIP film, keeping a similar roughness or appearing a little rougher upon the washing treatment. The Cd(II)-IIP film presents an irregular morphology with some flake-like structures and aggregates. After washing, the topography became rougher and flakes are more predominant, indicating an increase of surface presumably due to the template extraction leading to a more porous material.

3.2.2. ATR-FTIR characterisation of Cd(II)-IIP film and NIP film

Cd(II)-IIP film and NIP films were characterised by ATR-FTIR before and after metal removal (Fig. S6). The structure of the poly 4-APA is speculated to start at the amine group and disseminate at the para position [37]. The recognised mechanism was speculated to include first the formation of a radical cation from 4-APA, after the generation of a dimeric species by meta-coupling between the radical cation with either

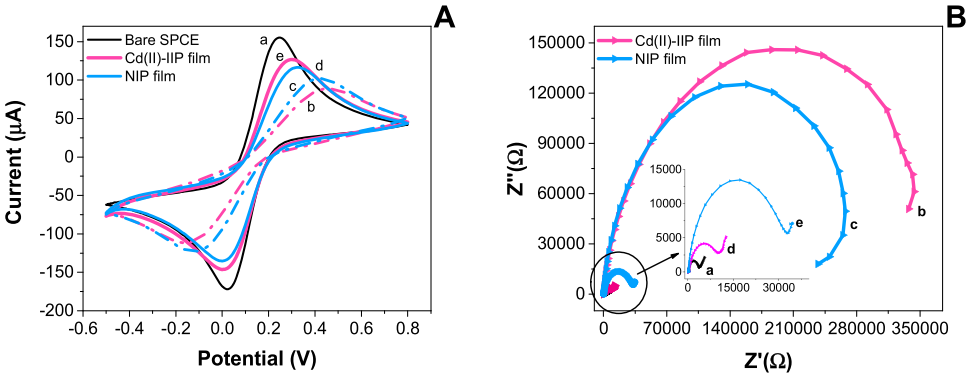


Fig. 2. (A) CV responses of (a) bare SPCE (black line), (b) unwashed Cd(IIP)-film/SPCE (dash dot lines), (c) unwashed NIP film/SPCE (dash dot lines), (d) washed NIP film/SPCE (solid line) and (e) washed Cd(IIP)-film/SPCE (solid line) in 0.1 mol L^{-1} KCl and 0.01 mol L^{-1} $Fe(CN)_6^{3-/4-}$ redox probe. (B) Nyquist plot of (a) bare SPCE, (b) unwashed Cd (II)-IIP film/SPCE, (c) washed Cd(II)-IIP film/SPCE, (d) unwashed NIP film/SPCE, (e) washed NIP film/SPCE. EIS and CV measurements were recorded in in 0.1 mol L^{-1} KCl and 10 mmol L^{-1} $Fe(CN)_6^{3-/4-}$ redox probe. NIP film and Cd(II)-IIP film were washed using 0.25 M NaOH.

a non-oxidised monomer or another radical cation, enabling the propagation of the polymerisation. The Cd(II)-IIP film and NIP film presented the same polymer structure characterised by the aromatic, amine and carboxyl bands. The C═O stretching appears as a strong band in the region between 1703 and 1650 cm^{-1}. The band between 1600 and 1450 cm^{-1} is related to C═C stretching from aromatic compounds [38]. Axial deformation of C═C from aromatic rings between 1550 and 1420 cm^{-1} can be seen in all spectra, indicating that the polymers aromaticity is preserved as previously reported [37,38]. N-H stretching in the region at 3500 cm^{-1} for the poly(4-APA), which is confirmed by absorptions related to the N-H angular deformations in the region between 1640 and 1540 cm^{-1}. The N-H stretching at 3461 and at 3357 cm^{-1} relative to the presence of amine, disappears in the poly (4-APA) spectra. The band at 1150–870 cm^{-1} is related to the C–N–C asymmetric axial deformation characteristic of secondary amines. The main changes between the NIP and Cd(II)-IIP (no washed films) appear in the C═O stretching from the carboxylic acid, which plays the role of ligand during the coordination reaction (Fig. S6A). Unwashed Cd(II)-IIP film presented higher intensity and a shift from 30 cm^{-1} to higher frequencies, that can be attributed to a C═O···Cd(II) bonding, indicating the presence of the metal into the polymer. The spectra of the Cd(II)-IIP after washing treatment changes at the carboxyl bands. This band decreases in terms of the intensity by 2 % and the band shift at 14 cm^{-1} to lower frequencies, indicating the successful removal of the metal coordinated (Fig. S6A). On the other hand, NIP film before and after wash treatment, do not present any changes in the spectra, as expected (Fig. S6B).

3.3. Analytical performances

The analytical performances of Cd(II)-IIP film and NIP film sensors were evaluated by the exposure to distinct Cd(II) ions concentrations ranging from 10 to 1200 nmol L^{-1} by CV measurements performed in 50 mM sodium acetate buffer solution. Fig. 3 depicts the CV measurements recorded on Cd(II)-IIP film and NIP film, respectively.

The current response for Cd(II)-IIP and NIP films can be explained as the redox activity of polymers in the presence of the target ion, which resulted in the presence of an anodic peak at + 0.1 V (vs Ag/AgCl), and a cathodic peak at − 0.02 V (vs Ag/AgCl), respectively. A slight electroactivity of the polymer is already evident before exposure, probably due to the redox properties of the polyaniline-like structures present into the polymer. It increases with Cd(II) concentration both for IIP and NIP, possibly due to an increased electrochemical reversibility of the polymer redox process at + 0.1 V (vs Ag/AgCl) [39]. The proper electroactivity of the IIPs films permitted the monitoring of the electrochemical currents flow from the polymer and the electrode, avoiding the use of external/internal redox probes. The comparison between NIP and IIP film also revealed the high sensitivity of Cd(II)-IIP film due to the presence of selective binding cavities which are also responsible to achieve the higher permeability for Cd(II)-IIP film than NIP film. However, NIP film weakly interacts with Cd(II) ions through no specific binding with the polymeric structure.

The experimental data for Cd(II)-IIP and NIP film sensors were quite well fitted by the Temkin isotherm model (Fig. 4 A). According to the Temkin isotherm, it is assumed that the adsorption energy of Cd(II) ions in the polymeric imprinted layer decreases linearly with the surface coverage. Therefore, it was possible to calculate the dissociation constants, Kd, of the Cd(II)-IIP film and NIP film, which were 1.212×10^{-8} mol L^{-1} and 3.554×10^{-8} mol L^{-1} respectively, reflecting a tighter binding (high affinity) of Cd(II)-IIP films for its template. The sensitivities of Cd(II)-IIP and NIP films sensors (Fig. 4B) were 1.280 ± 0.051 μA/log(nmol L^{-1}) and 0.255 ± 0.045 μA/log(nmol L^{-1}), respectively, that additionally confirm the high sensitivity properties of imprinted film. In fact, the imprinted factor of 5.01 confirmed the goodness of the imprinting process. The limit of detection, LOD, calculated as 3 s/*m* where s was the standard deviation of the intercept and *m* is the slope of the regression plot, was 1.71 nmol L^{-1}.

The analytical performances of Cd(II)-IIP films are compared (Table 1) with other reports including electrochemical sensors based on imprinted polymers as the sensitive receptor for Cd(II) ion sensing. The advantages in producing electropolymerised IIP directly onto electrode surface are here denoted in the higher sensitivities and the practical working range of concentration of our produced sensors. Moreover, the proposed sensor preparation does not need any additional functionalisation or activation of electrode surfaces. Finally, the electrosynthesis of IIPs can be more convenient than traditional methods, due to the ability to control the polymerisation process, in term of the thickness of films and the distribution of imprinted layers on electrode surfaces.

3.4. Selectivity, reproducibility, and stability tests

Selectivity, reproducibility, and stability are crucial properties for the successfully application of electrochemical sensors to real environmental matrices. In this work, interferences from other metal ions such as Pb(II), Zn(II), Cu(II), Co(II), Cr(III), Mn(II), Ni(II), and Ag(I) were investigated. (Fig. 4 C, Fig. S8). As can be seen, the Cd(II)-IIP film sensor exhibited a very selective response to its target (Cd(II) ions), being the response to interferent metal ions quite lower. Selectivity does not seems to be related to ion size as the current response of ions smaller than Cd (II) (ionic radius 95 pm) like Ni(II) (ionic radius 83 pm), Cu(II) (91 pm), Zn(II) (74 pm), Mn(II) (67 pm) Co(II) (79 pm), Cr(III) (61.5 pm) and larger Ag(I) (115 pm), Pb(II) (119 pm) is lower. Stability and reproducibility of Cd(II)-IIP sensors were investigated by the measurement of CV response to 320 nmol L^{-1} of Cd(II) ions dissolved into the acetate

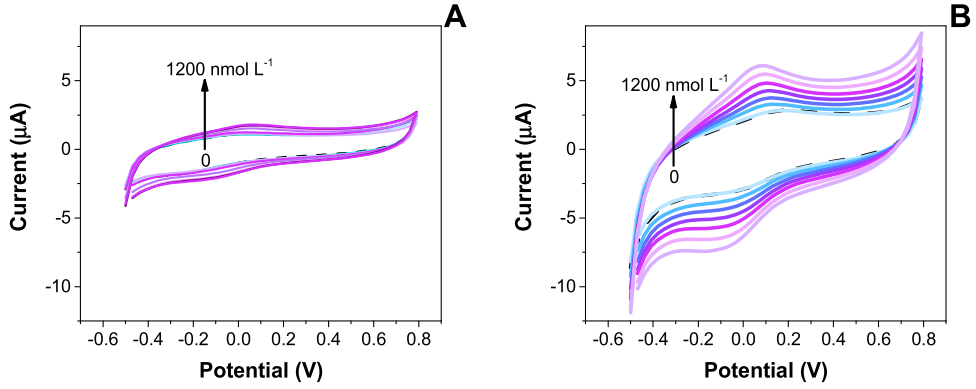


Fig. 3. CV performed for (A) NIP film and (B) Cd(II)-IIP film in sodium acetate buffer (blank, 0) and after exposure to 10, 20, 40, 80, 160, 320, 640, 1200 nmol L^{-1} of Cd(II) ions dissolved in 50 mM sodium acetate buffer. Parameters: CV scan for − 0.5 V to + 0.8 V, potential step of 30 mV, scan rate of 350 mV s^{-1}, 20 cycles per tested concentration.

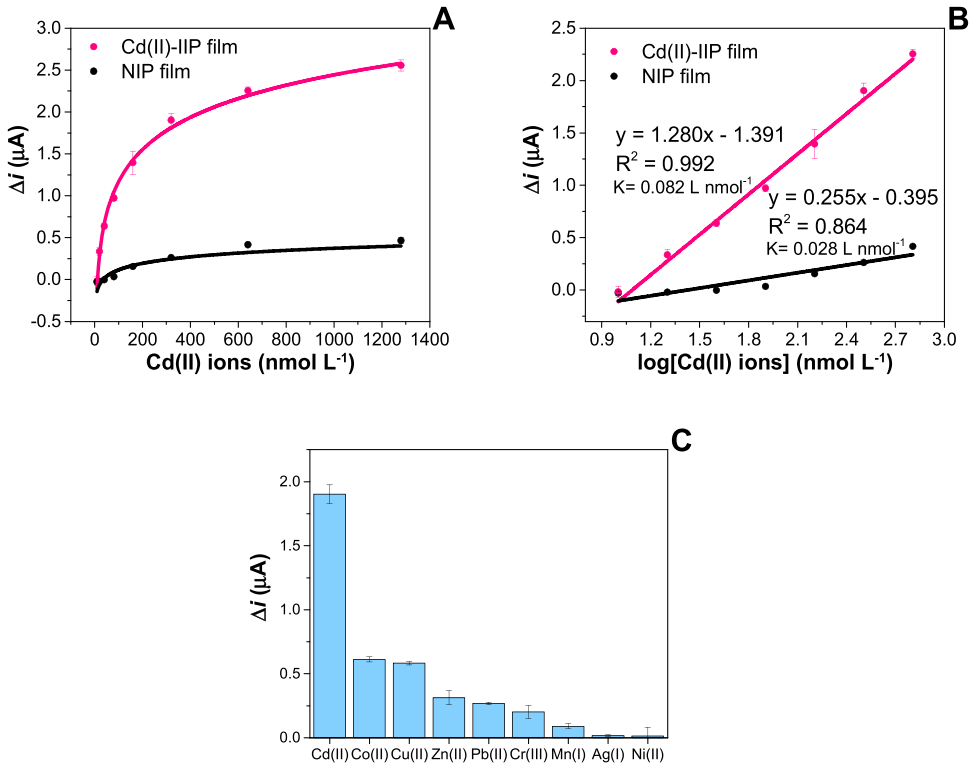


Fig. 4. (A) Temkin isotherm calibration curves and (B) related linear regression plots for NIP film and Cd(II)-IIP film exposed to increased concentration of Cd(II) ions dissolved in 50 mM sodium acetate buffer. (C) Selectivity studies on Cd(II)-IIP film towards potential interfering ions at the concentration of 320 nmol L^{-1} (n = 19).

Table 1
Recent reports on ion imprinted polymers for Cd(II) determination in water.

Sensor	Monomers in the polymerisation mixture	Method of synthesis	Working linear range (mol L^{-1})	Limit of detection (mol L^{-1})	Reference
CS-N-rGO/GCE	Chitosan, N-rGO Sodium tripolyphosphate	One-step deposition method (chronoamperometry)	1.0×10^{-8} – 1.0×10^{-7}	3.51×10^{-9}	[40]
IIP/rGO-CR	Polyethylenediamine; methylacrylic acid	UV light-initiated copolymerisation	8.68×10^{-9} – 8.68×10^{-7}	3.6×10^{-9}	[41]
CS/SiO_2/ AuNPs/CPE	VTEO EGDMA MAA	Precipitation polymerisation	1×10^{-9} – 1×10^{-5}	1.43×10^{-10}	[42]
IIP/CPE	Quinaldic acid, 4-vynil pyridine, 2,2′-azobisisobutyronitrile, EGDMA	Precipitation polymerisation	1.0×10^{-9}–5.0×10^{-7}	5.7×10^{-10}	[43]
IIP/CPE	4-vynil pyridine Organosilane 3-mercaptopropyltrimethoxylane AIBN TMSPM	Sol-gel polymerisation	9.0×10^{-11}–2.5×10^{-8} and 2.5×10^{-8}–6.0×10^{-8}	1.6×10^{-8}	[44]
Cd(II)-IIP film/ SPCE	4-aminophenylacetic acid	Electropolymerisation	1.0×10^{-8} – 1.2×10^{-6}	1.71×10^{-9}	This work

CPE: carbon paste electrode; CR: chemoresistor; CS: chitosan; EGDMA: ethylene glycol dimethacrylate; GCE: glassy carbon electrode; AuNPs: gold nanoparticles; rGO: reduced graphene oxide.

buffer solution (pH = 5). To explore the working life (stability) of the sensor, a fresh Cd(II)-IIP film was prepared and consecutive measurements were carried out over the time of 180 min. The relative standard deviation (RSD) was about 4.9 % for seven successive measurements, indicating an acceptable stability of the sensor for a daily measurement. The (interelectrode) reproducibility of the sensor was investigated by preparing five sensors and comparing the current response from each sensors after the exposure to 160 nmol L^{-1} of Cd(II) ions (Fig. S7). The RSD of the current response obtained for the electrodes was 5.6 %.

3.5. Validation tests on spiked water matrices

To investigate the practical application of Cd(II)-IIP film, detection of Cd(II) ions in spiked water matrices, such as marine water, tap water, and commercial drinking water was carried out. Table 2 indicate the recovery percentage of Cd(II) ion in those samples.

The recovery percentage of Cd(II) ion was found to be between 98 % and 106 %, indicating a promising application of the sensor from different complex real matrices monitoring, confirming the use of the proposed sensors for rapid and inexpensive point-of-use identification of

Table 2
Recovery studies on spiked water samples.

Sample	Added value (nM)	Found value (nM)	Recovery (%)
Drinking water	10	10.63 ± 0.05	106.3
	20	19.73 ± 0.01	98.6
Tap water	10	9.99 ± 0.008	99.9
Marine water*	10	10.51 ± 0.02	105

* Marine water sample did not contain Cd, as analysed by ICP-MS (LOD= 0.9 nM).

Cd(II) in complex matrices.

4. Conclusions

This study reported an electrochemical sensor for Cd(II) ions in water matrices based on ion-imprinted polymer film as a selective receptor. The imprinted process was carried out using an electrochemical technique, leading to the preparation of imprinted films on the transduction element. The optimisation performed by experimental design allowed the optimisation of sensitive, selective, reproducible and stable sensors for Cd(II) ions in water matrices. Successful determinations by developed sensors in real water matrix candidate them for environmental monitoring of Cd(II) ions in water with high sensitivity and selectivity.

CRediT authorship contribution statement

MC: Investigation, Data curation, Formal analysis. **SDM:** Conceptualization, Data curation, Investigation, Writing – original draft, Writing – review & editing. **AGC:** Data curation, Formal analysis, Writing – original draft, Writing – review & editing. **SAP:** Writing – original draft, Writing – review & editing. **CM:** Visualization, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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.

Data availability

Data will be made available on request.

Acknowledgements

Authors would like to thank the financial support of the project “CASCADE” (014-2020 Interreg V-A IT-HR CBC “strategic” project ID 10255941), the project “Sviluppo di sensori elettrochimici biomimetici a base di polimeri a stampo molecolare per la determinazione di metalli in matrici ambientali” (Department of Excellence of the University of Salento, CUP: F85D18000130001) and the Ph.D. programme entitled “Green Analytical Chemistry: Development of Molecularly Imprinted Polymers for Emerging Pollutants” (CUP:F85F21005750001) funded by “Dottorati su tematiche Green del PON R&I 2014–2020″. Authors would like to thank Dr. Antonio Pennetta for ICP-MS measurements.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2023.133559.

References

[1] P. Qi, J. Wang, X. Wang, Z. Wang, H. Xu, S. Di, Q. Wang, X. Wang, Sensitive and Selective Detection of the Highly Toxic Pesticide Carbofuran in Vegetable Samples by a Molecularly Imprinted Electrochemical Sensor with Signal Enhancement by AuNPs, RSC Adv. 8 (2018) 25334–25341, https://doi.org/10.1039/C8RA05022H.
[2] M.M.N. Ahmed, F.S. Bodowara, W. Zhou, J.F. Penteado, J.L. Smeltz, P. Pathirathna, Electrochemical Detection of Cd (ii) Ions in Complex Matrices with Nanopipets, RSC Adv 12 (2022) 1077–1083, https://doi.org/10.1039/D1RA07655H.
[3] J.-X. Han, Q. Shang, Y. Du, Effect of Environmental Cadmium Pollution on Human, Health 1 (2009) 159, https://doi.org/10.4236/health.2009.13026.
[4] A. Hartwig, Cadmium and cancer, Met Ions Life Sci (2013) 491–507, https://doi.org/10.1007/978-94-007-5179-8_15.
[5] S.P. Sreekanth, A. Alodhayb, A.K. Assaifan, K.E. Alzahrani, M. Muthuramamoorthy, H.I. Alkhammash, S. Pandiaraj, A.M. Alswieleh, Q.V. Le, R. Mangaiyarkarasi, A.N. Grace, V. Raghavan, Multi-walled Carbon Nanotube-based Nanobiosensor for the Detection of Cadmium in Water, Environ. Res. 197 (2021) 111148, https://doi.org/10.1016/j.envres.2021.111148.
[6] A.T. Townsend, K.A. Miller, S. McLean, S. Aldous, The Determination of Copper, Zinc, Cadmium and Lead in Urine by High Resolution ICP-MS, J. Anal. At. Spectrom.13 (1998) 1213–1219, https://doi.org/10.1039/A805021J.
[7] S. Zhao, H. Liang, H. Yan, Z. Yan, S. Chen, X. Zhu, M. Cheng, Online Preconcentration and Determination of Trace Levels Cadmium in Water Samples Using Flow Injection Systems Coupled with Flame AAS, Clean - Soil Air Water 38 (2010) 146–152, https://doi.org/10.1002/clen.200900228.
[8] X. Wen, Q. Yang, Z. Yan, Q. Deng, Determination of Cadmium and Copper in Water and Food Samples by Dispersive Liquid–liquid Microextraction Combined with UV–vis Spectrophotometry, Microchem. J. 97 (2011) 249–254, https://doi.org/10.1016/j.microc.2010.09.010.
[9] M.F.M. Noh, I.E. Tothill, Determination of Lead (II), Cadmium (II) and Copper (II) in Waste-water and Soil Extracts on Mercury Film Screen-printed Carbon Electrodes Sensor, Sains Malays 40 (2011) 1153–1163.
[10] L.C.S. Figueiredo-Filho, B.C. Janegitz, O. Fatibelilo-Filho, L.H. Marcolino-Junior, C. E. Banks, Inexpensive and Disposable Copper Mini-sensor Modified with Bismuth for Lead and Cadmium Determination Using Square-wave Anodic Stripping Voltammetry, Anal. Methods 5 (2013) 202–207, https://doi.org/10.1039/C2AY26078F.
[11] A. Nourbakhsh, M. Rahimnejad, M. Asghary, H. Younesi, Simultaneous Electro-determination of Trace Copper, Lead, and Cadmium in Tap Water by Using Silver Nanoparticles and Graphene Nanoplates as Nanocomposite Modified Graphite Electrode, Microchem. J. 175 (2022) 107137, https://doi.org/10.1016/j.microc.2021.107137.
[12] D.S. Rajawat, N. Kumar, S.P. Satsangee, Technology, Trace Determination of Cadmium in Water Using Anodic Stripping Voltammetry at a Carbon paste Electrode Modified with Coconut ShellPowder, J. Anal. Sci. Technol. 5 (2014) 1–8.
[13] S. Abbasi, A. Bahiraei, F. Abbasai, A Highly Sensitive Method for Simultaneous Determination of Ultra Trace Levels of Copper and Cadmium in Food and Water Samples with Luminol as a Chelating Agent by Adsorptive StrippingVoltammetry, Food Chem.129 (2011) 1274–1280, https://doi.org/10.1016/j.foodchem.2011.05.020.
[14] L. Ebdon, P. Goodall, S.J. Hill, P.B. Stockwell, K.C. Thompson, Ultra-trace Determination of Cadmium by Vapour Generation Atomic, Fluorescence Spectrometry, J. Anal. At. Spectrom. 8 (1993) 723–729, https://doi.org/10.1039/JA9930800723.
[15] J. Gardiner, M.J. Stiff, The Determination of Cadmium. Lead, Copper and Zinc in Ground Water, Estuarine Water, Sewage and Sewage Effluent by Anodic Stripping, Voltammetry, Water Res.9 (1975) 517–523, https://doi.org/10.1016/0043-1354(75)90077-9.
[16] A.A. Ensafi, K. Zarei, Simultaneous Determination of Trace Amounts of Cadmium, Nickel and Cobalt in Water Samples by Adsorptive Voltammetry Using Ammonium 2-amino-cyclopentene Dithiocarboxylate as a Chelating Agent, Talanta 52 (2000) 435–440, https://doi.org/10.1016/S0039-9140(00)00334-9.
[17] R. Attaallah, A. Amine, An Ultrasensitive and Selective Determination of Cadmium Ions at ppt Level Using an Enzymic Membrane with Colorimetric and Electrochemical Detection, Biosensors 12 (2022) 310, https://doi.org/10.3390/bios12050310.
[18] Y. Saylan, Ö. Erdem, F. Inci, A. Denizli, Advances in Biomimetic Systems for Molecular Recognition and Biosensing, Biomimetics 5 (2020) 20, https://doi.org/10.3390/biomimetics5020020.
[19] S.A. Piletsky, A.P. F. Turner, Electrochemical Sensors Based on Molecularly Imprinted Polymer, Electroanalysis14 (2002) 317–323. https://doi.org/10.1002/1521-4109(200203)14:5<317::AID-ELAN317>3.0.CO;2-5.
[20] S. Di Masi, A. Garcia Cruz, F. Canfarotta, T. Cowen, P. Marote, C. Malitesta, S. A. Piletsky, Synthesis and Application of Ion-Imprinted Nanoparticles in Electrochemical Sensors for Copper (II), Determination, ChemNanoMat 5 (2019) 754–760, https://doi.org/10.1002/cnma.201900056.
[21] T.P. Rao, R. Kala, S. Daniel, Metal Ion-imprinted Polymers—novel Materials for Selective Recognition ofInorganics, Anal. Chim. Acta 578 (2006) 105–116, https://doi.org/10.1016/j.aca.2006.06.065.
[22] C. Branger, W. Meouche, A. Margaillan, Recent Advances on Ion-imprinted Polymers, React. Funct. Polym 73 (2013) 859–875, https://doi.org/10.1016/j.reactfunctpolym.2013.03.021.
[23] P.E. Hande, A.B. Samui, P.S. Kulkarni, Highly Selective Monitoring of Metals by Using Ion-imprinted, Polymers, Environ. Sci. Pollut. Res. 22 (2015) 7375–7404.
[24] A. Sala, H. Brisset, A. Margaillan, J.U. Mullot, C. Branger, Electrochemical Sensors Modified with Ion-imprinted Polymers for Metal Ion Detection, TrAC, Trends Anal. Chem. 148 (2022) 116536, https://doi.org/10.1016/j.trac.2022.116536.
[25] S. Di Masi, A. Pennetta, A. Guerreiro, F. Canfarotta, G.E. De Benedetto, C. Malitesta, Sensor Based on Electrosynthesised Imprinted Polymeric Film for

Rapid and Trace Detection of Copper (II) Ions, Sens. Actuators B Chem. 307 (2020) 127648, https://doi.org/10.1016/j.snb.2019.127648.
[26] C.R.T. Tarley, G. Silveira, W.N.L. dos Santos, G.D. Matos, E.G.P. da Silva, M. A. Bezerra, M. Mirò, S.L. Costa Ferreira, Chemometric Tools in Electroanalytical Chemistry: Methods for optimization Based on Factorial Design and Response Surface Methodology, Microchem 92 (2009) 58–67, https://doi.org/10.1016/j.microc.2009.02.002.
[27] L. Uzun, A. Turner, Molecularly-imprinted Polymer Sensors: Realising Their Potential, Biosens. Bioelectron. 76 (2016) 131–144, https://doi.org/10.1016/j.bios.2015.07.013.
[28] F.D.L.M. López, S. Khan, M.A. da Silva, J.A.G. Neto, G. Picasso, M.D.P. T Sotomayor, Systematic Study on the Synthesis of Novel Ion-imprinted Polymers Based on Rhodizonate for the Highly Selective Removal of Pb(II), React. Funct. Polym. 159 (2021) 104805, https://doi.org/10.1016/j.reactfunctpolym.2020.104805.
[29] M. Sadani, T. Rasolevandi, H. Azarpira, A.H. Mahvi, M. Ghaderpoori, S. M. Mohseni, A. Atamaleki, Arsenic selective adsorption using a nanomagnetic ion imprinted polymer: Optimization, equilibrium, and regeneration studies, J. Mol. Liq. 317 (2020), 114246, https://doi.org/10.1016/j.molliq.2020.114246.
[30] H.-x Zhang, Q. Dou, X.-h Jin, J. Zhang, J. Yang, X. Han, D.-d. Wang, Magnetic Zn (II) Ion-imprinted Polymer Prepared by the Surface Imprinting Technique and Its Adsorption Properties, Environ. Technol. 36 (2015) 2702–2711, https://doi.org/10.1080/09593330.2015.1043748.
[31] E. Moniri, H.A. Panahi, K. Aghdam, A.A.M. Sharif, Selective Solid-phase Extraction of Zinc (II) from Environmental Water Samples Using Ion Imprinted Activated Carbon, J. AOAC Int. 98 (2015) 206–212, https://doi.org/10.5740/jaoacint.11-293.
[32] B.M. Kennedy, V.J. Cunnane, The Degradation of Pinhole Free Poly (1, 3-Dihydroxybenzene) Films in Sodium Hydroxide for the Production of Microelectrode Ensembles, J. Electroanal. Chem. 615 (2008) 197–204, https://doi.org/10.1016/j.jelechem.2007.12.008.
[33] X.-j Hu, J.-s Wang, Y.-g Liu, X. Li, G.-m Zeng, Z.-l Bao, X.-x Zeng, A.-w Chen, F. Long, Adsorption of Chromium (VI) by Ethylenediamine-modified Cross-linked Magnetic Chitosan Resin: Isotherms, Kinetics and Thermodynamics, J. Hazard. Mater.185 (2011) 306–314, https://doi.org/10.1016/j.jhazmat.2010.09.034.
[34] M.E.H. Ahamed, X.Y. Mbianda, A.F. Mulaba-Bafubiandi, L. Marjanovic, Selective Extraction of Gold (III) from Metal Chloride Mixtures Using Ethylenediamine N-(2-(1-imidazolyl) ethyl) Chitosan Ion-imprinted Polymer, Hydrometallurgy 140 (2013) 1–13, https://doi.org/10.1016/j.hydromet.2013.08.004.
[35] D. Runsewe, T. Betancourt, J.A. Irvin, Biomedical Application of Electroactive Polymers in electrochemical sensors: a Review, Materials 12 (2019) 2629, https://doi.org/10.3390/ma12162629.
[36] S. Ramanavicius, A. Jagminas, A. Ramanavicius, Advances in Molecularly Imprinted Polymers Based Affinity Sensors, Polymers 13 (2021) 974, https://doi.org/10.3390/polym13060974.
[37] C. da Cruz Santos, T.C. Pimenta, R.L. Thomasini, R.M. Verly, D.L. Franco, L. F. Ferreira, Electropolymerization of Phenol and Aniline Derivatives: Synthesis, Characterization and Application as Electrochemical Transducers, J. Electroanal. Chem. 846 (2019) 113163, https://doi.org/10.1016/j.jelechem.2019.05.045.
[38] A. Benyoucef, F. Huerta, J. Vázquez, E.J. Morallon, Synthesis and In Situ FTIRS Characterization of Conducting Polymers Obtained from Aminobenzoic Acid Isomers at Platinum Electrodes, Eur. Polym. J. 41 (2005) 843–852, https://doi.org/10.1016/j.eurpolymj.2004.10.047.
[39] A.J. Bard, L.R. Faulkner, H.S. White, Electrochemical Methods: Fundamentals and Applications, John Wiley & Sons, 2022.
[40] J. Chen, Y. Chen, Y. Liang, Application of Chitosan-N-doped Graphene Oxide Ion-imprinted Sensor in Cd (II) Ions Detection, Diam. Relat. Mater. 119 (2021) 108591, https://doi.org/10.1016/j.diamond.2021.108591.
[41] J. Hu, M. Sedki, Y. Shen, A. Mulchandani, G. Gao, Chemiresistor Sensor Based on Ion-imprinted Polymer (IIP)-Functionalized rGO for Cd (II) Ions in Water, Sens. Actuators B Chem. 346 (2021) 130474, https://doi.org/10.1016/j.snb.2021.130474.
[42] W. Huang, Y. Liu, N. Wang, G. Song, X. Yin, L. Zhang, X. Ni, W. Xu, A Sensitive Electrochemical Sensor Based on Ion Imprinted Polymers with Gold Nanoparticles for High Selective Detecting Cd (II) Ions in Real Samples, J. Inorg. Organomet. Polym. Mater. 31 (2021) 2043–2053.
[43] T. Alizadeh, M.R. Ganjali, P. Nourozi, M. Zare, M. Hoseini, A carbon paste electrode impregnated with Cd2+ imprinted polymer as a new and high selective electrochemical sensor for determination of ultra-trace Cd^{2+} in water samples, J. Electroanal. Chem. 657 (2011) 98–106, https://doi.org/10.1016/j.jelechem.2011.03.029.
[44] M.K.L. Coelho, H.L. De Oliveira, F.G. De Almeida, K.B. Borges, C.R.T. Tarley, A. C. Pereira, Development of carbon paste electrode modified with cadmium ion-imprinted polymer for selective voltammetric determination of Cd^{2+}, Int. J. Environ. Anal. Chem. 97 (2017) 1378–1392, https://doi.org/10.1080/03067319.2018.1424330.

Marco Costa received his M.S. degree (cum laude) in Environmental Science from the University of Salento (Lecce, Italy) in 2020. In 2021, he was a research fellow in the Laboratory of Analytical Chemistry at the University of Salento (Lecce, Italy). Currently, he is a Ph.D. student in the Laboratory of Analytical Chemistry at the University of Salento (Lecce, Italy). His research interest focuses on developing electrochemical sensors based on molecularly imprinted polymers to determine environmental compounds (e.g. heavy metal ions, perfluorooctanoic acids,) and targets of biological interest.

Sabrina Di Masi received her M.S. degree (cum laude) in Environmental Science from the University of Salento (Lecce, Italy) in 2016. She also got her European PhD in Biological and Environmental Sciences and Technologies, SSD: CHIM/01, in May 2020. Since 2016, Dr Di Masi has been working with Prof. Cosimino Malitesta. In 2018, she visited the Laboratory of Biotechnology in the group of Prof. Sergey A. Piletsky at the University of Leicester (U.K.). In 2019, Dr Di Masi has visited the University of Florence (Italy) under the supervision of the CEO of Ecobioservices and Researchers, S.r.l. Currently, she is a postdoc fellow in the Laboratory of Analytical Chemistry at the University of Salento (Lecce, Italy). Her research interest focuses on developing biosensors and electrochemical sensors to determine environmental compounds (e.g. heavy metal ions). Her research activities are also focused on the design, optimisation by multivariate approaches, preparation and application of chemical molecularly imprinted polymer, MIPs (and electrochemical imprinted polymeric films, eMIP films) for food and diagnostics purposes.

Alvaro Garcia Cruz received his BSc (Hons) in Chemistry from the University of Guanajuato (Mexico) in 2008 and his master's degree (Hons) in Catalysis and Physical Chemistry at the University Claude Bernard Lyon 1 (France) in 2010. He completed his PhD studies at the same University in 2015, focusing on Nanotechnology and Biotechnology. He worked as an assistant professor in the Institute of Physical Chemistry of the Polish Academy of Science in Warsaw (Poland), working in chemical sensors. Currently, he is working as a Senior scientist at the University of Leicester (UK) in the group of Prof Sergey A. Piletsky in assays and sensors based on molecularly imprinted polymers. In addition, he is a Co-Founder at Gamanity Health and Cosmetics Ltd (2019). Dr Garcia-Cruz's research interest focuses on bioelectronics, assays, drug delivery, polymer nanoparticles, microfabrication and microfluidics, bio-functionalization and nanobiotechnology applied to medical devices and diagnostics.

Sergey A. Piletsky is a Professor of Bioanalytical Chemistry and a leading expert on Molecular Imprinting and Biosensors. Also, Prof Piletsky is the Research Director for the School of Chemistry at the University of Leicester. Prof Piletsky graduated from Kiev University in 1985 with an M.Sc. in Bioorganic Chemistry. In 1991 he received PhD from the Institute of Bioorganic Chemistry. Since 1992 he has worked with world-leading experts in biosensors, such as Prof. Karube at Tokyo University, Prof. Wolfbeis at Regensburg University and Prof. Turner in Cranfield University. In 2002 Sergey became Professor of Polymer Chemistry and Head of Cranfield Biotechnology Centre. In 2013 Sergey moved his group to the University of Leicester, where he works as a Research Director and Head of Leicester Biotechnology Group. For his scientific achievements, Sergey received several awards such as JSPS, DFG and Leverhulme Fellowships, the recognition of the President of Ukraine, the Royal Society Wolfson Research Merit Award, and a DSc from Cranfield University. Sergey has published more than 390 papers and patent applications (H-index-82). Sergey's work has focused on molecularly imprinted polymers, driven by a practical need to find stable and generic alternatives to antibodies and natural receptors, as well as reduce the use of animals in antibody production. His research interests also include computational design and molecular modelling, developing sensors and assays for clinical and environmental diagnostics, and nanoparticles for diagnostics and therapeutic applications. 11 EU projects have supported this work, grants from MRC and EPSRC (JREI), grants from HPA, FSA and Home Office, Department of Health, Wellcome Trust, (UK), NOAA (USA), and numerous grants from industry.

Cosimino Malitesta received his MSc degree in Chemistry cum laude in 1983 and his PhD in Analytical Chemistry in 1989 from the University of Bari. Since then, he has been a lecturer and associate professor in Analytical Chemistry. In 2001 he was appointed as a full professor of Analytical Chemistry at the University of Salento. He is a member of the Italian Chemistry Society and served as Deputy President of the Analytical Chemistry Division and in the Board of Sensors Group. His main research interests include biosensors and biomimetic sensors based on electrosynthesized polymers, electrosynthesis of molecularly imprinted polymers, XPS development and application, and development and analytical application of nanostructures. He has published over 150 peer-reviewed articles in international journals.