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Enhanced Electrochemical Detection of Heavy Metal Ions Using TPyP-sPEEK Composite-Modified Electrodes

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Porphyrin/sulphonated polyetheretherketone (sPEEK) composites are successfully obtained at different dye/polymer weight/weight percentage taking advantage of electrostatic interactions among the protonable nitrogen atoms of 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphyrin porphyrin (TPyP) and anionic sulphonated groups of the polymer with 65% of sulfonation degree. These supramolecular adducts(TPyP-sPEEK) are drop-casted onto a commercial screen-printed carbon substrate (SPCE) to fabricate new modified TPyP-sPEEK /SPCE sensors for the detection of heavy metal ions such as Pb^{2+}, Cd^{2+}, and Hg^{2+}. Sample at different porphyrin loads has been analyzed by electrochemical techniques. sPEEK composite with 5% porphyrin/polymer w/w% is identified as the optimal one in terms of stability and high percentages of recovery of the tested heavy metal ions in seawater environment.

1. Introduction

Industrialization, urbanization, and agricultural practices are the primary sources of heavy metal pollution. Heavy metal ions are introduced into the environment through various anthropogenic activities, such as mining, smelting, manufacturing, and the improper disposal of waste products.[1] These are a significant concern in environmental research due to their toxicity, persistence, and widespread occurrence in various ecosystems.[2] The contamination of water by heavy metals is of great concern due to the potential adverse effects on aquatic life and human health.[3] Heavy metals can accumulate in living organisms and cause chronic health problems, such as cancer and neurological disorders.[4,5] Lead (Pb), cadmium (Cd), mercury (Hg), and copper (Cu), among others, are hazardous substances that can cause severe harm to human health and the environment.[6] In recent years, there has been growing interest in the development of effective methods for detecting and removing heavy metals from water. Several techniques, including electrochemical sensors, spectrophotometry, and atomic absorption spectroscopy, have been developed. Due to their structures and peculiar optical properties, tunable by metal ion coordination, porphyrins have been largely used as sensitive and selective optical probe. Typically, in the sensory field, porphyrins are absorbed, covalently or by electrostatic interactions, or simply encapsulated on a solid matrix. This approach leads to stability, reproducibility, and reversibility of the materials.[7–9] Water soluble porphyrins immobilized onto poly(vinyl chloride) (PVC), VA-Epoxy, and Nafion membranes have been reported as Cd(II), Hg(II), and Pb(II) ion sensors.[10,11] 5,10,15,20-Tetraphenylporphyrin (H_2TPP)[12] and meso-tetrakis(2-hydroxynaphthyl) porphyrin (MTHNP), respectively, dissolved in plasticized PVC membranes, showed selectivity for mercury detection.[13] Cd (II) ion sensors were obtained using meso-tetrakis cationic porphyrin (N-methyl-4-pyridyl)-porphyrin (TMPyP) supported by electrostatic interaction on poly(sodium 4-Stirensulfonate) (PNaSS) on a polysulfone microporous membrane (CMPSF)[14] or immobilized on membranes of chitosan and cellulose acetate[15] or on graphene quantum dots (GQDs).[16] Among the plethora of polymeric matrices,[17,18] poly-etheretherketone (PEEK) is a high-performance thermoplastic one with intriguing thermal, mechanical, and chemical features.[19,20] PEEK offers a wide range of uses due to its unique properties, including in automotive, medical, aerospace, engineering, and electronic areas.[21] However, PEEK's intrinsic hydrophobicity limits its use in various applications, especially in biological and environmental fields.[22] Therefore, various modification strategies have been developed to enhance its hydrophilicity and functionality.[19] Sulfonation, which involves the introduction of sulfonic acid groups onto the PEEK backbone, is one of the most commonly investigated modification approaches[23,24]

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to improve hydrophilicity and ion exchange capacity.[25] This modification makes sulfonated PEEK (sPEEK) suitable for applications in areas such as ion exchange membranes, water treatment, and in various industries.[23,26] sPEEK has also been employed as a biomaterial due to its biocompatibility, cyto-compatibility, and superior mechanical properties.[27,28] Sulfonated PEEK membranes are utilized in fuel cells as proton exchange membranes[29–31] while carbon fiber-reinforced PEEK composites are used in high-performance engineering applications.[32] In this contest, s-PEEK composite membranes with high stability have been reported by interaction between the sulfonated functional groups of the poly (ether-ether ketone) and peripheral substituent moieties of different porphyrin rings showed good performance in fuel cell applications. In particular, composite membranes functionalized by addition of the *meso*-tetrakis(4-pyridyl)porphyrin (TPyP) improved the s-PEEK mechanical stability preserving the structural and morphological properties of the pure polymer.[33] Furthermore, meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) induces a reorganization at the nanoscale of the polymeric ionic domains, improving the proton conductivity, achieving a more stable and organized structure with very interesting results in electrochemical degradation tests in a PEMFC single cell in portable and automotive applications operative conditions.[31,33,34] In this research, we examined the electrochemical properties of a sulfonated PEEK (sPEEK) composite membrane with a 65% degree of sulfonation, incorporating varying percentages of TPyP for application as a sensing material for heavy metal cations. A thorough characterization of the composite membranes was conducted, and their electrochemical behavior was evaluated for the simultaneous detection of heavy metal ions in seawater. The targeted cations included Hg^{2+}, Cd^{2+}, and Pb^{2+}.

2. Experimental Section

2.1. Materials

Stock solutions of heavy metal ions (Cd(II), Hg(II), and Pb(II)) were prepared by dissolving the corresponding nitrate and chloride salts in distilled water. All extra pure analytical grade chemicals used in this study were purchased from Sigma–Aldrich.

2.2. Synthesis of Composite Membranes

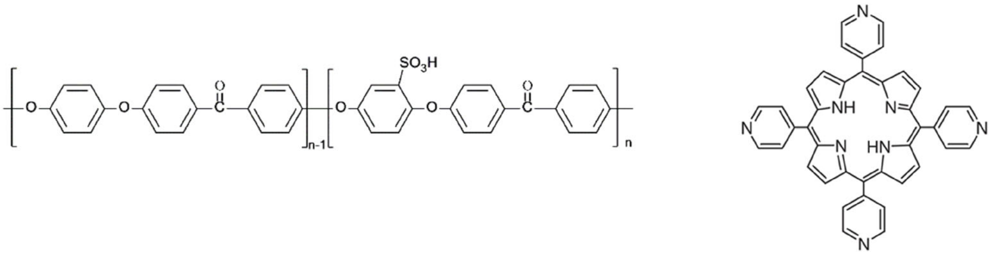
A polyetheretherketone (Victrex PF450) with sulfonation degrees (SD) of 65% was obtained according to a standardized procedure already reported by Carbone et al.[35] Composite membranes were prepared using the sulphonated polymer and 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) in different weight percentages sPEEK/TPyP (0.2, 0.77, 5, 8, and 12.8 w/w%) (**Scheme 1**) in DMAc solution by Doctor-Blade procedure.

2.3. Spectroscopic Characterization of TPyP-sPEEK Composites

UV/Vis extinction spectra were collected on an Agilent 8453 diode array spectrophotometer. Front-face fluorescence emission spectra were recorded on a Jobin Yvon-Spex Fluoromax 4 spectrofluorimeter.

2.4. Electrochemical Characterization

The electrochemical experiments were carried out using a commercial screen-printed carbon electrode (SPCE) model C110, manufactured by DropSens (Methrom). This SPCE features a ceramic substrate measuring ≈3.5 cm in length and 4.0 mm in diameter. It comprises three key components: the carbon-working electrode, the silver pseudo-reference electrode, and the carbon counter electrode, which collectively constitute the electrochemical cell. The electrochemical response of the modified sensors was investigated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. CV analysis was performed at different scan rates in a solution containing 5 mM $K_3Fe(CN)_6$. The EIS measurements were conducted by using a 5 mM $K_3Fe(CN)_6$ solution with a frequency range of 0.1–105 Hz and an amplitude of 5 mV. The electrochemical experiments were carried out using the DropSens μStat 400 Potentiostat, which was equipped with Dropview 8400 software for data acquisition, and a Galvanostat potentiostat by Metrohom autolab. The modified sensors were characterized by FTIR spectroscopy, performed directly on the sensor surface modified with 5% TPyP-sPEEK (TPyP-sPEEK-5), both before and after exposure to Cd^{2+} and Hg^{2+} ions. The FTIR spectra were recorded at room temperature in the 4000–700 cm^{-1} range, with a resolution of 4.0 cm^{-1}, a scan speed of 0.2 $cm\ s^{-1}$, and 20 scans, using a Spectrum Two spectrometer (PerkinElmer Inc.) equipped with a universal ATR accessory. This analysis aimed to assess whether the chemical modification and the sensor's spectral response were consistent with the proposed sensing mechanism (described in paragraph 3.5).



Scheme 1. Sulphonated polyetheretherketone (s-PEEK) (left) and 5,10,15,20-tetrakis(4-pyridyl)-21H,23H-porphine (TPyP) (right).

2.5. Fabrication of sPEEK-Modified Electrodes

To prepare the modified electrodes, the TPyP-sPEEK membranes were solubilized in DMAc to reach a concentration useful to be applied on the carbon electrode. In particular, the modified sensors were prepared by applying 6 μL of each TPyP-sPEEK sample directly onto the surface of the carbon working electrode through drop-casting. Then, the electrode was allowed to dry before adding the following deposition of other 6 μL of sample. Subsequently, the modified sensors were left to dry overnight at room temperature. The same procedure has been applied for TPyP-sPEEK membranes with different porphyrin loading (0.2/12.8%) and unfunctionalized sPEEK.

2.6. Electrochemical Detection of Heavy Metal Ions

Square Wave Anodic Stripping Voltammetry (SWASV) technique was employed to investigate the electrochemical detection of heavy metal ions. The measurements were conducted in 0.1 M acetate buffer (pH: 4.5) using a scan rate of 50 mV s^{-1}. The preconcentration step consists of the application of a potential of 0.6 V for 60 s, followed by a deposition potential of −1 V for 240 s and an equilibrium time of 15 s. Anodic oxidation was used to strip the metals by cycling within the potential window ranging from −1.2 to 0.6 V. To create calibration curves, the faradaic current was plotted against the concentration of the analyte. Sensitivity was determined as the slope of the calibration curve, and the limit of detection (LOD) was determined through the formula LOD = 3σ/*m*, where *m* represents the slope of the calibration curves, and σ denotes the standard deviation derived from five replicate measurements conducted using the proposed modified electrode in acetate buffer solution (0.1 M, pH 4.5).

3. Results and Discussion

3.1. Spectroscopic Characterization

Transparent colored membranes of homogeneous thickness ranging from 60 to 70 μm have been obtained at different porphyrin/sPEEK load by electrostatic interactions between the negatively charged sulphonate groups of the sPEEK polymer and the protonable pyridyl groups present in the periphery of the TPyP porphyrins. This allowed to stabilize the polymer/chromophore interactions both on sol, gel, and solid phase. The embedded dyes in the membranes exhibit good stability and chemical resistance to both thermal annealing and acid treatments typical of the treatments.[33] As a representative example, **Figure 1** reports the extinction spectrum of composite sPEEK-0.77% TPyP. This shows the presence of a Soret band centered around 455 nm not clearly detected due to high absorbance of the sample and two Q-bands centered at 595 and 645 nm, respectively. The spectroscopic behaviors are ascribable to the presence of porphyrin in its diacid form, due to protonation of the central core. Exposition of the membranes to ammonia vapors or immersion in sodium hydroxide aqueous solution 0.1 M induces a modification of the extinction spectrum where four Q-bands centered at 518, 552, 590, 645 nm respectively, are evident. The latter points out the occurrence of the porphyrin core deprotonation useful for further metal ion coordination.

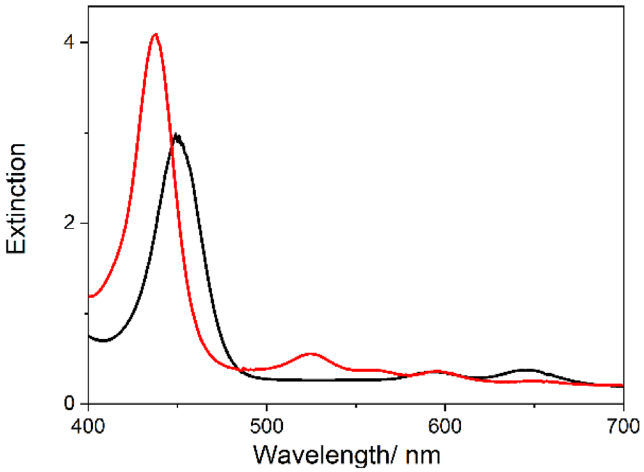


Figure 1. Extinction spectra of sPEEK-0.77% TPyP (black line) and after exposition to ammonia vapors (red line).

Due to the permeability of the composite membranes to metal ions, they are tested as spectroscopic sensor for heavy metals in aqueous solutions. Taking advantage of their emission properties, the fluorescence emission spectroscopy has been selected as higher sensitive technique with respect to the extinction one. In this framework, we tested 1 cm^2 samples for all tests. Salt solutions of heavy metals with chlorides and nitrates as counter-anions have been used for testing. In conventional arrangements, fluorescence quenching has been successfully used to detect the analyte, due to its heavy metal ion effect. According to the literature, the fluorescence emission spectrum of the deprotonated 0.77 w/w% sample (**Figure 2**, red line) shows two bands centered at 650 and 716 nm (A. Carbone et al. 2015). For example, the fluorescence quenching of TPyP in the presence of Pb^{2+} ions is reported (Figure 2, black line). Immersion of the metalated samples in 0.1 M H_2SO_4 aqueous induces the demetallation of the porphyrin core and successively immersion in 0.1 M NaOH aqueous solution allows to restore the

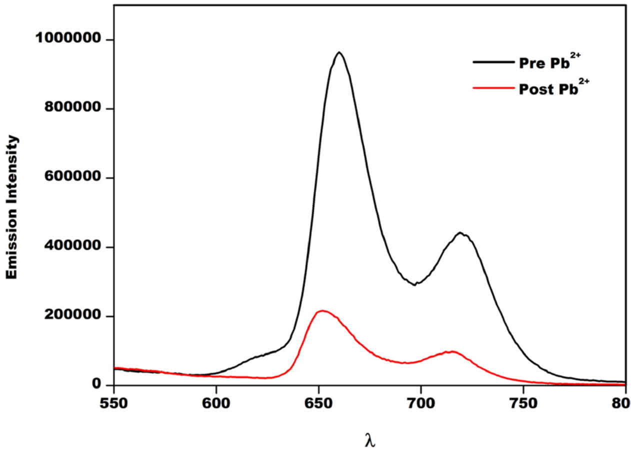


Figure 2. Fluorescence spectra of deprotonated sPEEK-0.77% TPyP (red line), after detection of Pb^{2+} ions (dark line) (λ_{ex}= 450 nm).

sensor, as confirmed by invariance of the spectroscopic features with respect to the untreated sample.

Figure 3 and **4** show the fluorescence quenching percentages for Hg^{2+}, Cd^{2+} and Ni^{2+} chlorides and Cd^{2+}, Ni^{2+}, and Pb^{2+} nitrates, respectively. Hg^{2+} and Ni^{2+} chlorides show a better response with respect to Cd^{2+}. Whereas in nitrates solutions, Cd^{2+} and Ni^{2+} gave a better response with respect to Hg^{2+}. The Pb^{2+} has also tested as nitrate salt, but it was detected only at concentration in solution higher than millimolar. For all the investigated samples we were not able to detect heavy metals by fluorescence emission at metal ion concentration lower than 100 μM.

3.2. Electrochemical Behavior

The electrochemical properties of the modified sensors (TPyP-sPEEK/SPCEs) were investigated using CV and EIS, and the results were compared with those of the unmodified bare sensor (SPCE). **Figure 5**a reports CV cycles registered in the presence of the ferro/ferricyanide redox specie ($Fe[(CN)_6]^{4-/3-}$). Bare SPCE exhibits a redox wave corresponding to the reversible redox reaction of ($Fe[(CN)_6]^{4-/3-}$). After the modification of SPCE with sPEEK, the $Fe[(CN)_6]^{4-/3-}$ peaks were no longer observed, suggesting that sPEEK inhibits the electrochemical process, which confirms that SPCE has been functionalized.[36]

Interestingly, the addition of porphyrin (TPyP) to the sPEEK membrane used to modify the sensor again shows the appearance of a redox wave. The intensity of the peak increased with TPyP loading, showing that porphyrin facilitates the redox process on the surface of the modified electrode. TPyP-sPEEK-12.8/SPCE exhibits the highest peak current among the modified sensors, while TPyP-sPEEK-5/SPCE had the lowest peak-to-peak separation (ΔEp) of 158 mV (Figure 7b), indicating the highest electron transfer rate.

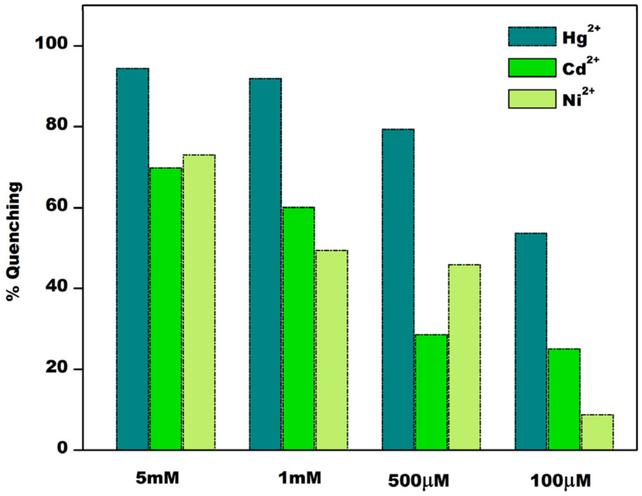


Figure 3. Histograms show TPyP fluorescence quenching (%) in sPEEK-0.77% TPyP membrane in contact with metal chloride solutions at different concentration values (5 mM, 1 mM, 500 μM, and 100 μM).

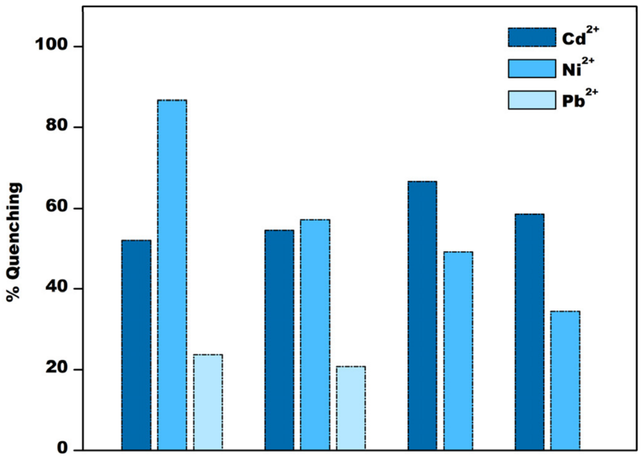


Figure 4. Histograms show TPyP fluorescence quenching (%) in sPEEK-0.77% TPyP membrane in contact with metal nitrate solutions at different concentration values (5 mM, 1 mM, 500 μM, and 100 μM).

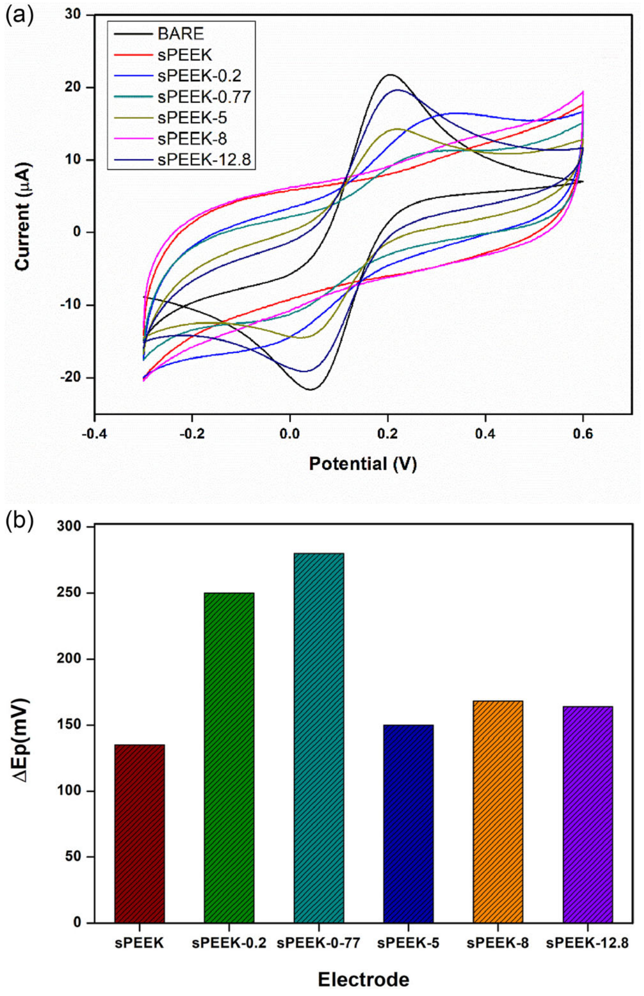


Figure 5. a) CV in $Fe[(CN)_6]^{4-/3-}$. b) ΔEp calculated from the CV in (a).

EIS analysis was conducted in 5 mM $K_3Fe(CN)_6$, with an applied potential of 0.25 V, and in the frequency range of 0.1 Hz to 105 Hz (amplitude 5 mV). **Figure 6** shows the plotted Nyquist data for all the modified and unmodified sensors and the relative Randles circuit model (inset). The data obtained from

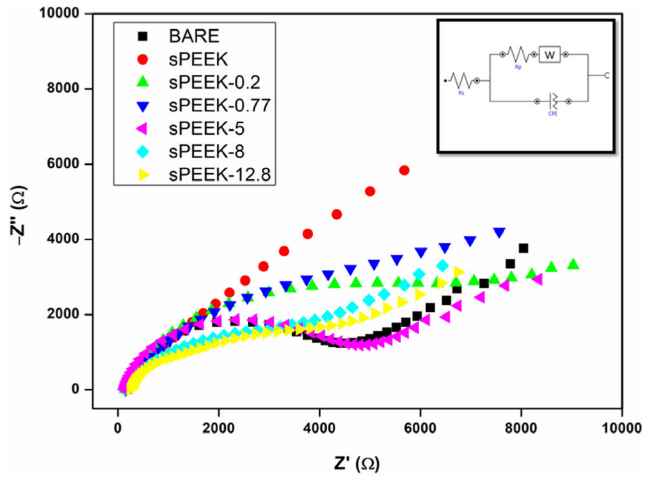


Figure 6. EIS of the bare SPCE and modified sensors in Fe[(CN)$_6$]$^{4-/3-}$ and (inset) the circuit model relative electrical equivalent circuit (Rs, solution resistance; Rp, charge-transfer resistance; W, Warburg; and CPE, capacitance).

the equivalent circuit study showed charge transfer resistance (Rp) values of 5.66, 16.8, 18.1, and 4.95 kΩ for SPCE, sPEEK-8/SPCE, sPEEK-12.8/SPCE, and sPEEK-5/SPCE, respectively. Knowing that the value of Rp is inversely proportional to the electron transfer rate, it can be deduced that the sPEEK-5/SPCE sensor exhibits better electrochemical behavior in promoting the redox reaction. In addition, the electrolyte resistance (Rs) for SPCE, sPEEK-8/SPCE, sPEEK-12.8/SPCE, and sPEEK-5/SPCE show values of 165, 161, 178, and 160 Ω, respectively, confirming a better electrical conductivity of the sPEEK-5 sensor in solution. The linear trend observed implies that a diffusion process is occurring on the electrode surface for all the sensors.

The electrochemical active surface area (ECSA) for the different modified electrodes in Fe[(CN)$_6$]$^{4-/3-}$ was calculated according to the CV outcomes. **Figure 7** displays the results, demonstrating that the active surface area increases proportionally with the percentage of porphyrin. Nevertheless, the sPEEK-5 sensor exhibited the best electrochemical results, further affirming that ΔEp is the optimal index for monitoring the performance of a modified sensor.

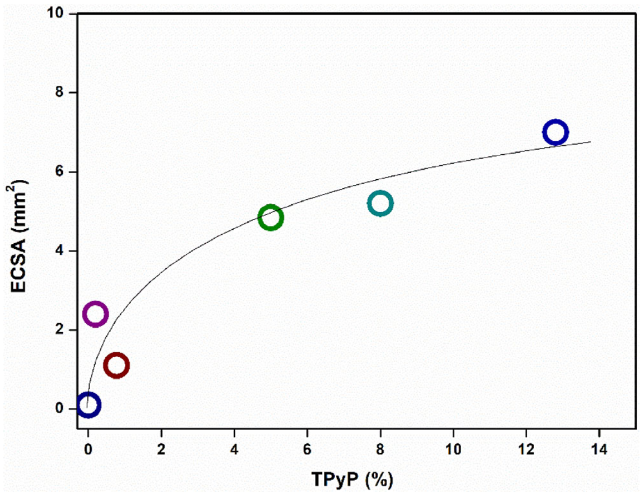


Figure 7. Electrochemical active surface area versus porphyrin loading.

3.3. Detection of Heavy Metal Ions in Water

The study employing the three-electrode screen printed sensor and the SWASV technique to evaluate the sensitivity of TPyP-sPEEK composites for the simultaneous detection of heavy metals, including Pb^{2+}, Cd^{2+}, and Hg^{2+}, is presented here. Among these parameters, pH was found to be one of the most critical parameters, affecting the preconcentration step, during which metals accumulate and deposit on the working electrode's surface. As shown in **Figure 8**, the sensitivity to mercury ions was not impacted by pH, whereas for lead and cadmium, the maximum peak current was observed in acidic medium. Furthermore, negligible contamination effects were observed between the metals at acidic pH, while a severe memory effect was noted at neutral and basic pH. The pH of 4.5 represents an optimal compromise that allows for high sensitivity to lead and cadmium, minimal interference between metals, and signal stability, while simultaneously reducing residual effects that could compromise the reliability of the analyses. As a result, the optimal working pH was determined to be 4.5, and all measurements were conducted in acidic media. All electrochemical measurements were performed in triplicate to ensure reproducibility and statistical consistency.

Figure 9 shows the sensitivity to heavy metals as a function of the porphyrin loading of the samples. The sensitivity to heavy metals in porphyrin-incorporated samples increases with the dye content up to 5%, then reaches a plateau or decreases slightly for the TPyP-sPEEK-12.8. These results indicate that the modified TPyP-sPEEK-5 sensor displays the best performance in terms of selectivity for all the analyzed ions.

The calibration curves of sPEEK-0.77, sPEEK-5, and sPEEK-12.8 composites for the sensing of the three analytes (Pb^{2+}, $Cd^{2+}$and Hg^{2+}) are shown in **Figure 10**. Noticeable variations in the peak currents can be detected, confirming the best response of TPyP-sPEEK-5 as sensor in comparison to the other composites. In all the cases, the response (peak current) follows a consistent trend of higher affinity for Pb^{2+} ions, followed by Cd^{2+} ions and Hg^{2+} ions.

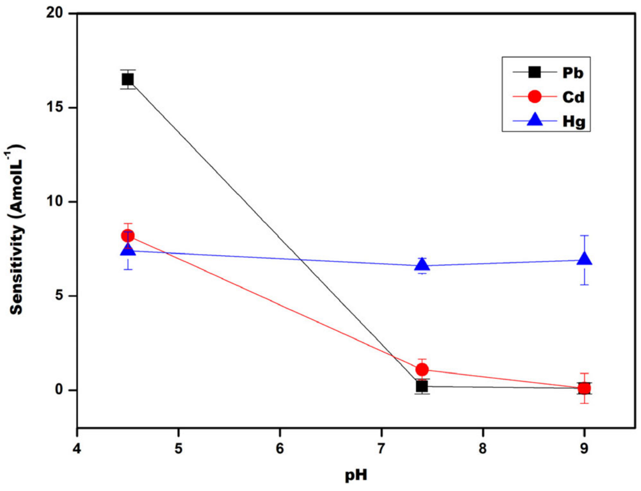


Figure 8. pH effect on the response to heavy metal ions.

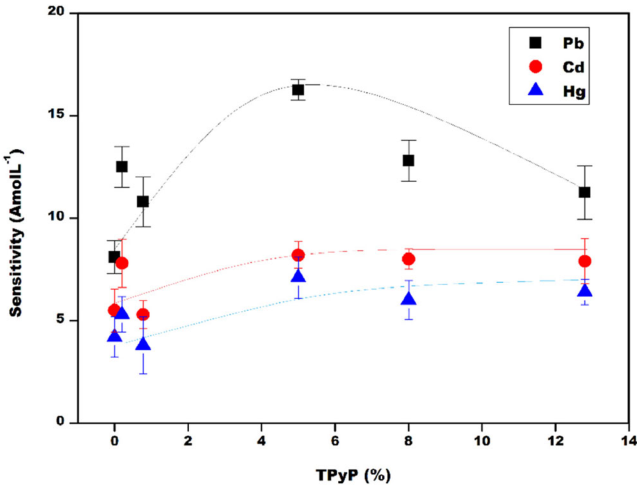


Figure 9. Response of sPEEK to heavy metal ions as a function of porphyrin contents.

Considering the best performance of TPyP-sPEEK-5, its response to metal ions in the concentration range 0.5–50 μM has been analyzed (**Figure 11**), as obtained from single cation SWV measurements.

The outcomes indicate a high affinity of the sensor toward lead and cadmium ions ($R^2 = 0.96$ and $R^2 = 0.99$, respectively), with a comparatively lower response toward mercury ions ($R^2 = 0.88$). This trend is also evident at lower concentration values (see inset). The calculated LOD (**Figure 12**) for each metal were 0.30, 0.17, and 0.29 μM, respectively for Hg^{2+}, Pb^{2+}, and Cd^{2+}.

3.4. Reproducibility, Repeatability, and Stability Tests

The reproducibility, repeatability, and stability of the modified electrodes in detecting heavy metal ions were evaluated through three replicated experiments conducted in acetate buffer solutions (pH 4.5), each containing 50 μM of the target metal ions. **Figure 13**a shows the reproducibility of the signal obtained using three independently prepared modified electrodes, along with the average standard deviations of the SWV oxidation peaks. The relative standard deviations (RSDs) were below 6% for all tests, confirming a high degree of consistency between different electrodes. The corresponding results regarding repeatability are presented in Figure 13b. The data demonstrate excellent intra-electrode repeatability for all the tested metal ions. Finally, the stability of the modified electrode was assessed over a period of up to 72 h (Figure 13c). The electrode maintained reliable performance, with RSD values remaining below 10%, indicating good temporal stability.

3.5. Mechanistic Insights into Heavy Metal Ion Detection in TPyP-SPEEK Composites

Figure 14 illustrates the explanation of the underlying mechanism responsible for the different responses of the modified sensor to the analyzed metal cations. The sPEEK, due to the sulfonic

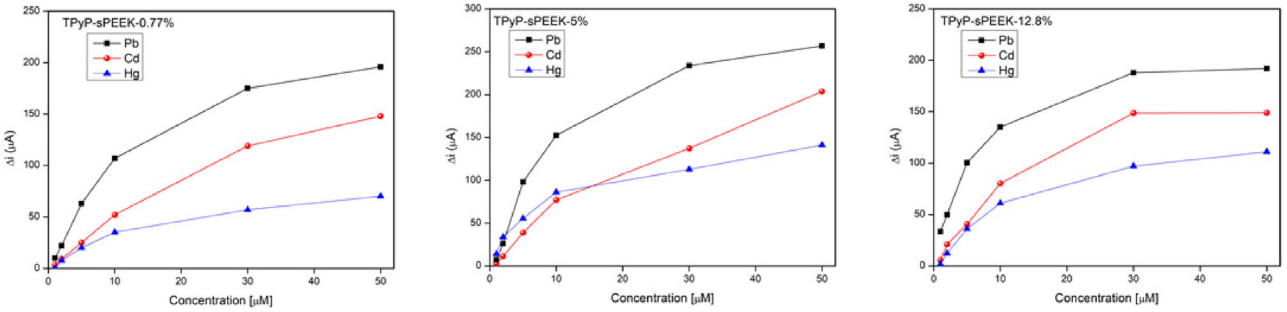


Figure 10. Concentration versus Δi curves of TPyP-sPEEK-0.77, TPyP-sPEEK-5, and TPyP-sPEEK-12.8 composites for the detection of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions.

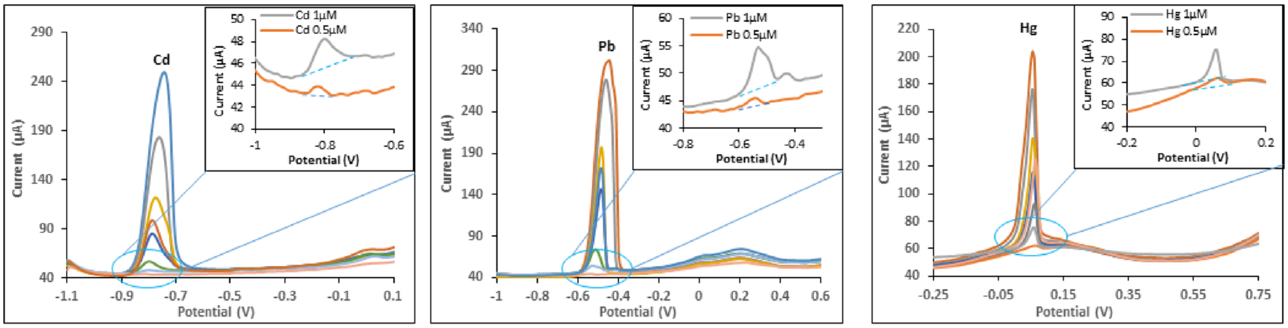


Figure 11. Response sensor sPEEK-5 to the heavy metal ions in the concentration range from 0.5 up to 50 μM in acetate buffer 0.1 M pH 4.5 + NaCl 0.5 M. Parameters: Econd 0.6 V, tcond 60 s, Edep 1, tdep 240 s, teq 15 s, Eamp 25 mV, Estep 5 mV, Freq 5 Hz.

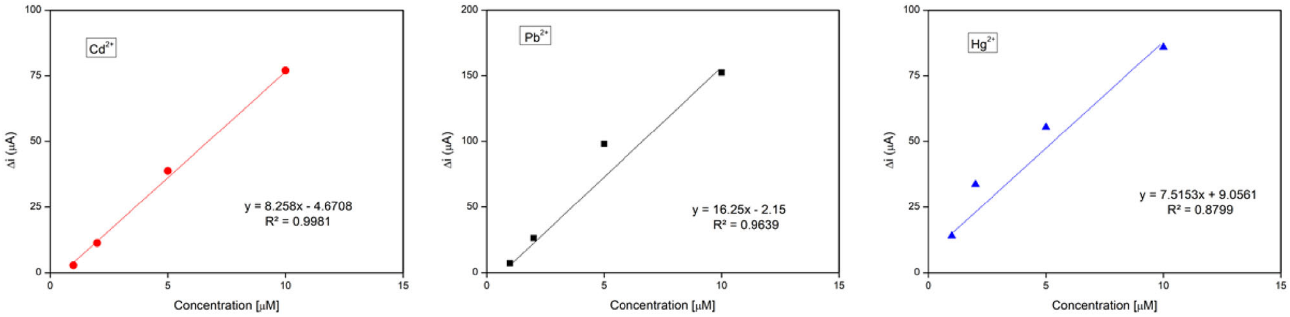


Figure 12. Calibration curves of the sPEEK-5 sensor toward heavy metal ions in the 0.5–10 μM concentration range.

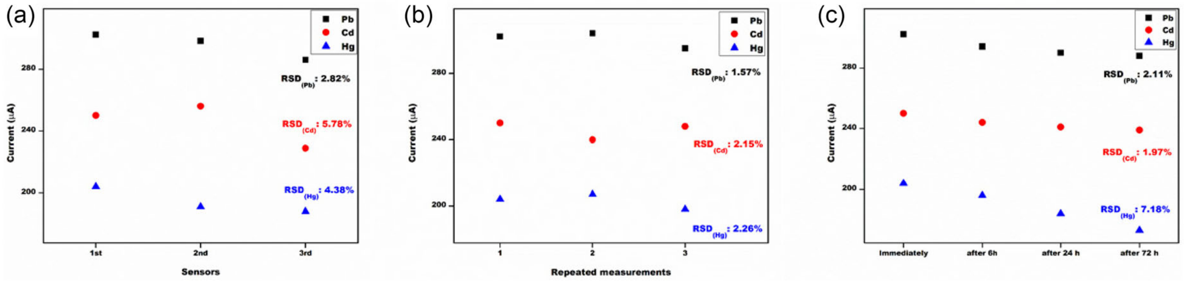


Figure 13. Repeatability tests of sensor sPEEK-5 obtained a) by using three modified sensors, b) after three repetition tests, and c) over time (immediately, after 6 h, after 24 h, after 72 h) to the heavy metal ions at 50 μM in acetate buffer 0.1 M pH 4.5 + NaCl 0.5 M.

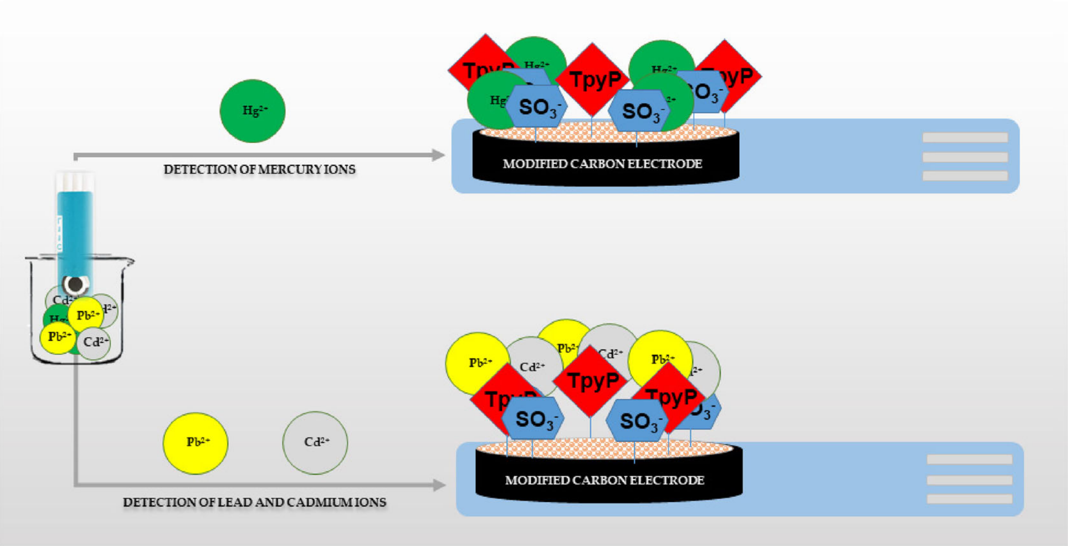


Figure 14. Schematic representation of the mechanism involved in heavy metal ion detection in TPyP-sPEEK-modified electrode.

groups in its structure, provides highly acidic binding sites that interact primarily with metal ions like mercury (Hg^{2+}), promoting its rapid adsorption and stabilization on the sensor. This effect leads to a significant response even at low Hg^{2+} concentrations; however, the overall sensitivity toward Hg^{2+} remains lower than that for the other analyzed ions, partly due to the high affinity of the sulfonic groups, which may slow down interaction kinetics at higher concentrations. Additionally, mercury's electrochemical redox behavior is known to be less reversible in aqueous media, which could also contribute to signal variability and, consequently, to a lower R^2 value in the calibration curve. Regarding lead (Pb^{2+}) and cadmium (Cd^{2+}), an enhanced response is observed for the porphyrin-modified sensor, particularly notable in the sample with 5% of TPyP. This porphyrin acts as a complexing ligand, creating preferential binding sites for Pb^{2+} and Cd^{2+} due to its ability to form stable complexes through coordination

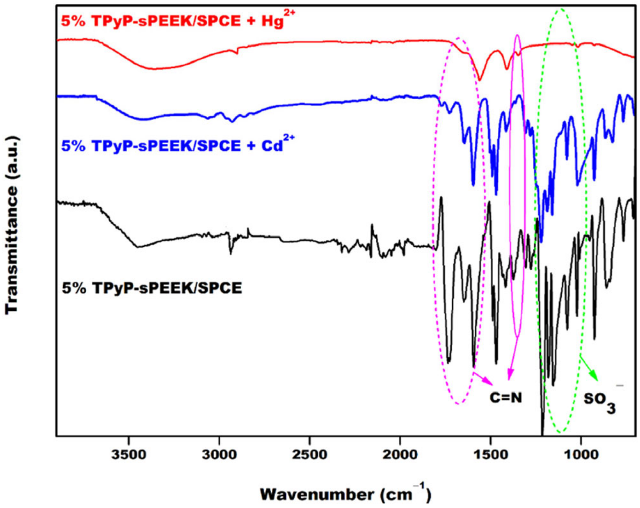


Figure 15. FTIR spectra of the sensor modified with 5% TPyP-sPEEK before (black line) and after exposure to Hg^{2+} (red line) and Cd^{2+} (blue line) ions.

interactions. The presence of porphyrin thus increases the charge density available for binding these cations, improving sensor sensitivity and showing a linear response to increasing concentrations up to a certain point, after which sensitivity levels off.

To confirm the validity of the proposed mechanism, FTIR analyses were performed directly on the sensor modified with 5% TPyP-sPEEK, both before and after exposure to Hg^{2+} and Cd^{2+} ions. The corresponding spectra are shown in **Figure 15**. The Hg^{2+} spectrum (red) displays notable changes in the 1200–1000 cm^{-1} region, which correspond to interactions between the SO_3^- groups and Hg^{2+} ions. In contrast, the spectrum after exposure to Cd^{2+} (blue) reveals more significant variations in the 1700–1400 cm^{-1} region, associated with porphyrinic groups vibrations (C=N and C=C), indicating a stronger interaction with the porphyrin core. The involvement of SO_3^- groups appears less prominent here, unlike the behavior observed with Hg^{2+}. These changes, though somewhat subtle, are likely due to the limited sensitivity of FTIR at low metal ion concentrations. Nevertheless, the overall sensing response supports the proposed interaction mechanism.

In summary, while probably the sulfonic groups in sPEEK provide a rapid and strong response for Hg^{2+}, the selective complexation offered by TPyP makes the composite more effective for detecting Pb^{2+} and Cd^{2+}, thereby confirming the sensor's preference for these latter cations.

3.6. Real Sample Analysis

To evaluate the possible use of TPyP/sPEEK membrane-modified sensor for the detection of contaminant ions in real samples, seawater samples have been analyzed.

Seawater samples were collected from Jonio sea (Siderno, Italy) and were diluted with an acetate buffer solution at a 1:1 ratio. This dilution was performed in a way to achieve a final acetate buffer concentration of 0.1 M and a pH of 4.5. Subsequently, these prepared samples were subjected to SWASV under the previously optimized conditions. However, the initial analysis yielded no detectable response signals for Cd(II), and Pb(II) in the analyzed seawater samples. To address this, we spiked the seawater samples with 1, 2, and 5 μM concentrations of Cd(II) and Pb(II). The recovery rates for these heavy metal ions were determined and are presented in **Table 1**.

Table 1. Results for Cd^{2+} and Pb^{2+} determination (μM) in seawater samples obtained under the optimum conditions ($n = 3$).

Sample	Analyte [μM]	Added [μM]	Found [μM]	Recovery [%]	RSD [%]
Seawater	Cd^{2+}	1	1.11	111.0	12.1
		2	2.34	117.0	8.4
		5	5.93	118.6	11.7
	Pb^{2+}	1	1.14	114.0	7.4
		2	2.11	105.5	5.9
		5	5.44	108.8	6.3

The results revealed that the recovery rates for these two common heavy metal ions fell within the range of 105.5–118.6%. Furthermore, the relative standard deviation (RSD) values ranged from 5.9 to 12.1%. These findings demonstrate the promising applications of TPyP/sPEEK composite for the detection of heavy metals in seawater samples.

4. Conclusions

In this study, composite membranes containing various percentages of TPyP porphyrin have been employed to develop an electrochemical sensor for the simultaneous detection of heavy metal ions in seawater. The electrochemical properties of TPyP-sPEEK composites allow the facile identification and quantification of the cations of interest, i.e., Pb^{2+}, Cd^{2+}, and Hg^{2+}. The outcomes showed amplification effect on the investigated anodic peak current due to the incorporation of porphyrin into the sPEEK membrane, which can be attributed to the complexation effect of the porphyrin. The modified electrode with 5% TPyP content exhibited the best performance, with a sensitivity of 16.25, 5.83, and 5.72 $AmolL^{-1}$ and a limit of detection of 0.17, 0.29, and 0.30 μM for Pb^{2+}, Cd^{2+}, and Hg^{2+}, respectively. This is the first instance where a composite membrane with different percentages of porphyrin is employed for developing an electrochemical sensor for heavy metal ion detection in seawater.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Keywords: electrochemical detection of heavy metals · modified screen-printed carbon electrode · sulphonated polyetheretherketone composites · TPyP-sPEEK-based sensors

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