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Tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium chloride (TPQPCL) ionomer chemically modified electrodes: An electroanalytical study towards sensing applications

Thomas R. Jones^a, Sandra Hernandez-Aldave^a, Robert B. Kaspar^b, Michael P. Letterio^b, Yushan Yan^b, Paolo Bertoncello^{a, c, *, 1}

^a Systems and Process Engineering Centre, College of Engineering, Swansea University, Bay Campus, Crymlyn Burrows, Swansea, SA1 8EN, United Kingdom

^b Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, DE, 19716, USA

^c Centre for NanoHealth, Swansea University, Singleton Park, Swansea, SA2 8PP, United Kingdom

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ABSTRACT

We report for the first time the redox properties of an anion-exchange ionomer membrane, tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium chloride (TPQPCL). TPQPCL was solubilized in ethanol/water solutions and films of TPQPCL at different concentrations were drop casted on glassy carbon electrodes. The thickness of TPQPCL films in dry conditions was evaluated using profilometer. The anion-exchange properties and charge transport properties of TPQPCL coated electrodes were investigated using $K_4Fe(CN)_6$ as anionic redox probe. The permselectivity properties of TPQPCL coated electrodes were assessed using hexaammine ruthenium(II) chloride. Cyclic voltammetry performed at low scan rate was utilized to determine the concentration of the redox mediator inside the films, with the apparent diffusion coefficient values of different TPQPCL coating estimated using both the Randles-Sevcik equation and the Anson's method. We found the concentration of the ferro/ferricyanide couple redox within the TPQPCL films in the order of 10^{-2} – 10^{-1} mol dm⁻³, with values of D_{app} in the order of 10^{-9} cm² s⁻¹. TPQPCL drop casted films evidenced good preconcentration capabilities towards incorporation of anions. To ascertain the suitability of the ionomer coated films towards the electroanalytical detection of anions, TPQPCL coated electrodes were utilized for the voltammetric detection of nitrites in tap and river waters. The results showed that TPQPCL coated electrodes are suitable to quantify nitrites in fresh waters with a limit of detection, LoD, of 1.07 μM, sensitivity as 0.267 μA μM⁻¹ cm⁻² and linear range between 1 μM and 500 μM.

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1. Introduction

Ionomers are an important class of ion-containing polymers. Specifically, ionomers can be defined as ionized copolymers constituted by a nonionic backbone with a small proportion (up to 15%) of ionized units with associated counterions [1]. As such, ionomers have found utilization in a variety of industrial applications, most significantly as membranes to separate the anode and cathode in fuel cells (proton exchange and alkaline fuel cells) [2–8] water electrolyzers [9–11] water purification [12,13] and electro-

membrane processes for desalination [14,15]. From the electrochemical point of view, ionomers are an interesting class of material because when they are used as coating of electrode surfaces, the ionized groups can be utilized to preconcentrate, and hence quantify, electroactive species of opposite charge (cationic or anionic) using voltammetric methods [16]. Modification of electrode surfaces with ion selective polymeric materials has led to the development of the ion exchange voltammetry (IEV) with a variety of electroanalytical applications [16–19]. Among ionomers, Nafion[®], a sulfonated tetrafluoroethylene based fluoropolymer-copolymer, has undoubtedly been the most utilized material, since pioneer works from the Bard's [20–23] and Anson's [24–27] groups in the early 80' until today. In these works, Nafion[®] coatings were deposited on electrode surfaces by evaporation from alcoholic solutions. The dissociable proton allowed the incorporation of redox cations via ion-exchange from contacting solutions. Typical

* Corresponding author. Systems and Process Engineering Centre, College of Engineering, Swansea University, Bay Campus, Crymlyn Burrows, Swansea, SA1 8EN, United Kingdom.

E-mail address: p.bertoncello@swansea.ac.uk (P. Bertoncello).

¹ ISE member.

redox mediators incorporated in Nafion[®] films include tris(2'-bipyridyl)ruthenium(II) and methylviologen for electrochromic [28–30] and electrochemiluminescence [20,21,31,32] applications. These studies provided also fundamental insights into the mechanisms (physical diffusion and “electron hopping”) of charge transport within ionomers containing redox mediators [22,23,33–38]. Other redox mediators incorporated in Nafion[®] films include positively charge ferrocene derivatives for biosensing applications [39–41]. For electroanalytical purposes, ionomers also possess additional advantages such as permselective properties: this means that not only they do preconcentrate cations (if the ionomer is negatively charged) or anions (if the ionomer is positively charged), but at the same time, they help on preventing potential interferences by repelling ions of same charge. While there is an extensive literature for Nafion and other cation-exchanger ionomers for electroanalytical applications, in the case of anion (alkaline)-exchange ionomers, their use as coating membranes for voltammetric detection is more limited and mainly based on quaternary ammonium functionalized membranes [16,19,42–52]. In 2009, Gu et al. reported for the first time the synthesis and characterization of tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium hydroxide (TPQPOH) with ion-exchange capability (IEC) values comparable to Nafion[®] towards use as a membrane in hydroxide fuel cells [53,54]. Recently, we demonstrated the possibility to use a TPQPOH derivative as composite material with graphite nanoplatelets for simultaneous detection of ascorbic acid and dopamine [55]. However, the evaluation of charge transport and diffusion properties of TPQPCI ionomer has not yet been reported. TPQPOH is the first example of quaternary phosphonium functionalized membrane that showed exceptional thermal stability as well as high solubility in methanol [53,54]. These properties led us to explore in this study whether the TPQP-based ionomer can effectively be utilized in electroanalytical sensing applications, for instance detection of anions such nitrites. Nitrite ions (NO₂⁻) are ubiquitous in nature, and extensively utilized as an additive in the food industry to prevent the formation of microorganisms that causes rancidity, and to maintain the color of red meat. However, nitrites in acidic environments as it is the stomach for example, combined with amines of food, lead to the formation of carcinogenic nitrosamines, which have been linked to various forms of cancer [56–58]. This has led the World Health Organisation (WHO) to set up a daily intake limit of nitrite as 0.07 mg NO₂⁻/kg body weight. Various electrochemical methods have been developed for the detection of nitrites and these involved either the oxidation or reduction of nitrites at bare or chemically modified electrodes [59–64]. Because the reduction of nitrites is affected by interferences such as oxygen and nitrate reduction, hence oxidation is usually preferred [59,65,66]. In this work, with a ligand exchange procedure, we exchanged the hydroxide counterion with the chloride one to obtain TPQPCI, to avoid potential interferences in the electrochemical characterization. Then, we fabricated TPQPCI coatings on glassy carbon electrodes and we investigated the charge transport properties using K₄Fe(CN)₆ as a model anionic redox probe. The electrochemical characterization allowed us the estimation of the concentration of the redox species inside TPQPCI coating as well as the apparent diffusion coefficients. Finally, we demonstrated the potentiality of TPQPCI coated electrodes for the detection of anions, such as nitrite ions in tap and river waters.

2. Experimental section

2.1. Materials

Potassium ferrocyanide K₄Fe(CN)₆, NaCl, NaNO₂ and all other

reagents were obtained from Sigma Aldrich and used as received. Hexaammineruthenium(III)chloride [Ru(NH₃)₆]Cl₃ was purchased from Strem Chemicals. All electrodes and polishing materials were purchased from IJ Cambria (UK). All aqueous solutions were made using Milli-Q Ultra-pure water (UWP with a resistivity of ≥18.2 MΩ cm @ 25 °C) from a Millipore Direct Q3 water purifier.

2.2. Synthesis of TPQPCI

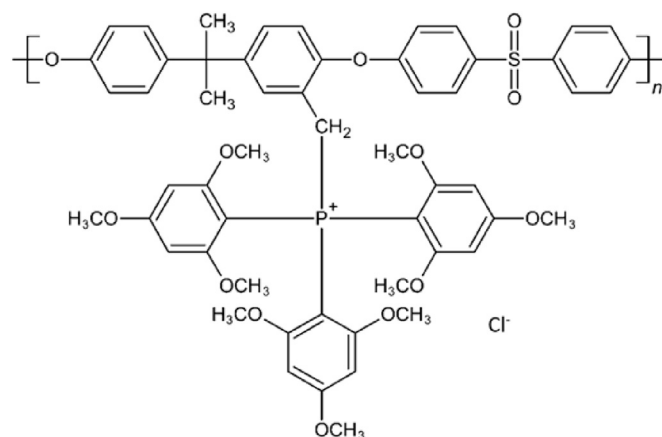
TPQPCI was synthesized using the procedure reported earlier by one of us: the quaternary phosphorization of chloromethylated polysulfone, CMPSf, with tris(2,4,6-trimethoxyphenyl)phosphine [53]. The CMPSf was determined by ¹HNMR to have a degree of chloromethylation (dc) of 165%, leading to the final TPQPCI product containing 1.65 quaternary phosphonium group ion exchange sites per polysulfone unit, or a degree of functionalization (df) of 165%. By knowing the average molecular weight of the Udel-3500 polysulfone precursor (80–86 KDa) [67], and the degree of functionalization of TPQPCI (165%) [53], the average molecular weight of TPQPCI has been calculated as 242–261 KDa. The structure of TPQPCI is reported in Scheme 1.

2.3. Apparatus and procedures

Cyclic voltammetry (CV), chronoamperometry (CA), and differential pulse voltammetry (DPV) measurements were performed using a bipotentiostat electrochemical analyzer (CH Instrument, Model CHI760). A conventional three electrode configuration was used, where the working electrode was a glassy carbon electrode (CH Instruments) of 3 mm diameter; a platinum wire as a counter electrode and a Ag/AgCl was used as a reference electrode. The experiments were carried out at room temperature. Glassy carbon electrodes (GCEs) were cleaned by successive polishing to gain a mirror-like appearance using 1 μm and 0.05 μm alumina slurry on micro cloth pads (Buehler), followed by sonication in acetone, ethanol and water, respectively, for 15 min. The cleaning procedure was carried out immediately prior to each use or polymer deposition. Film thicknesses were measured using a Taylor Hobson Taly-surf stylus profilometer, while pH measurements were recording using a Hanna instruments 2002 Edge pH meter.

2.4. TPQPCI coated electrodes

A 2.5% stock solution of TPQPCI was prepared by dissolving TPQPCI powder in a solvent mix that was 1:1 by weight ethanol and



Scheme 1. Structure of Tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium chloride (TPQPCI).

water using sonication. 50 mg of TPQPCI were dissolved in 1.23 ml ethanol and 0.975 ml of DI water to give a 2.5% TPQPCI solution. 1% and 0.5% TPQPCI concentrations were prepared by dilution of the 2.5% TPQPCI solution as appropriate in an ethanol/water mixture. Drop casted TPQPCI films were prepared by casting 10 μl aliquots of the polymer solutions (1% or 0.5%) on a polished GCE surface using an Eppendorf micropipette and then evaporating to dryness under ambient conditions. Typical drying times were 25 min. TPQPCI films were loaded in $\text{K}_4\text{Fe}(\text{CN})_6$ redox mediator solutions of varying concentrations with a 0.1 M NaCl supporting electrolyte. All TPQPCI coated electrodes were loaded for 60 min in the redox mediator solution to ensure complete saturation of the TPQPCI. The polymer-coated electrodes loaded with the redox mediator were rinsed briefly with distilled water and placed in the electrochemical cell containing only supporting electrolyte solution, where CVs were carried out at a different range of scan rates. The surface coverage values were experimentally calculated from the charge, Q , associated with the complete oxidation of the film-bound redox species. Q was extracted by graphical integration of the background corrected cyclic voltammograms at scan rate of 1 mV s^{-1} in 0.1 M NaCl supporting electrolyte. The concentration of redox mediator incorporated into TPQPCI films was calculated from thickness measurements and the calculated surface coverage.

2.5. Detection of nitrite ions

A 50 mM sodium nitrite stock solution was prepared using NaNO_2 (Sigma) and 0.1 M NaCl as supporting electrolyte. All other solutions were obtained by dilution of the 50 mM nitrite solution. For pH experiments the solution was adjusted as appropriate by addition of concentrated HCl or NaOH solutions with stirring. For the analysis of nitrite ions in tap and river waters, the samples were used as received without any pH adjustment. The pH values of these samples were in the range of pH 7–8.1. The investigation on potential interference were carried out by addition of various analytes to the 0.1 M solution of NaCl supporting electrolyte at 25 s time intervals, whilst running a chronoamperometry experiment with applied potential of 0.86 V under constant stirring (1000 rpm). Each interference analyte was dissolved in 0.1 M NaCl supporting electrolyte before addition to the electrochemical cell and the final concentration of each analyte in the solution was 5 μM . Tap water samples were taken from the mains water tap in our laboratory, while samples of water from the Llynfi River were collected near the Bridgend Paper Mills (Bridgend, Wales, UK) and used without any treatment. TPQPCI coated electrodes were conditioned in each nitrite sample for 20 min with stirring, whereas DPV scans were carried out under quiet conditions. DPV scans were carried out with increment 0.005 V, amplitude 0.05 V, pulse width 0.05 s, sampling width 0.0334 s, pulse period 0.5, E_{initial} 0.5 V; E_{final} 1.3 V.

3. Results and discussion

3.1. General electrochemical properties

In order to ascertain the dynamics of incorporation of the redox mediators, TPQPCI coated electrodes were exposed to a negatively charged redox mediator such as the $\text{K}_4\text{Fe}(\text{CN})_6$ redox couple, and several CVs were recorded during the loading procedure. S1 reports typical CVs (first 100 scans) performed at 1% TPQPCI coated electrode during loading in a solution containing 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$. The incorporation of the redox mediator occurs rapidly with peak currents that increase linearly with the time until CVs revealed time-invariant peak currents at higher loading times (up to 7200 s, see S2). The CVs recorded under loading conditions with the redox mediator in the electrolyte solution (Fig. 1, solid line) reveals the

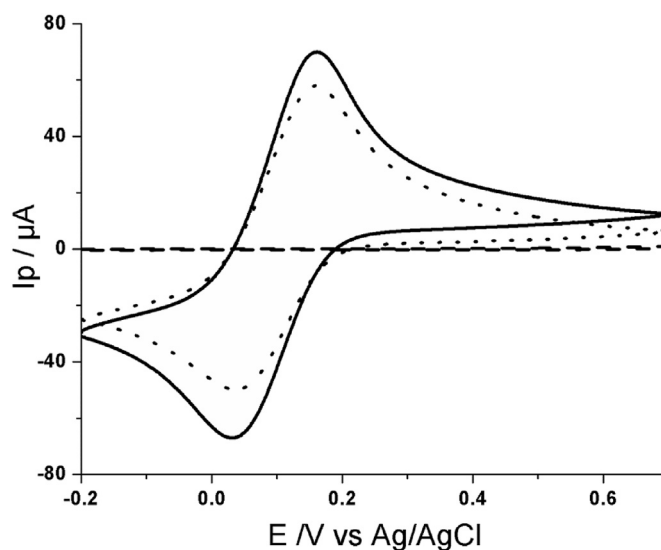


Fig. 1. CVs of 1% TPQPCI coated film loaded in 5 mM $\text{K}_4\text{Fe}(\text{CN})_6$ (solid line) and after transferring to 0.1 M NaCl supporting electrolyte (dotted line). Dashed line: background CV of 1% TPQPCI coated film in 0.1 M NaCl supporting electrolyte prior to loading. Scan rate of 100 mV s^{-1} .

typical redox behavior of the $\text{Fe}^{2+/3+}$ couple with peak currents that scale linearly with the square root of the scan rate as in indication of a process diffusion-controlled. When the electrode is transferred into the medium containing only supporting electrolyte (Fig. 1, dotted line), the peak currents for the TPQPCI coated electrodes decreased slightly to $70 \mu\text{A}$ from the initial value of $82 \mu\text{A}$ recorded in the loading solution, and with ΔE_p values slightly decreased compared to those obtained under loading conditions.

Note that the ΔE_p values were found to be larger at a higher scan rate (up to 150 mV at scan rate of 750 mV s^{-1}), whereas they decreased down to 23 mV at a lower scan rate (between 1 and 10 mV s^{-1}). In 0.1 M NaCl supporting electrolyte, the peak currents depended linearly on the scan rate at $v < 10 \text{ mV s}^{-1}$ as shown in Fig. 2(a). This indicates a thin-layer like behavior. However, at high scan rates (from 100 mV s^{-1} to 2000 mV s^{-1}), the current was found to scale linearly with the square root of the scan rate, as an indication of a diffusion-controlled process (Fig. 2(b)).

A similar behavior was observed also in the case of 0.5% TPQPCI coated electrode (see S3). Diffusion control is operative when the ionomer coating layer is thicker than the concentration gradient of the redox species in the films, hence the transition from thin-layer to diffusion-control is also thickness dependent. Note that the loss of the redox mediator in the time scale of the experiment (20 min) recorded at the beginning and the end of the experiments was typically around 15% (see S4). The surface coverage values (Γ , mol cm^{-2}) of the redox probe $\text{K}_4\text{Fe}(\text{CN})_6$ in the loaded TPQPCI coated electrodes were calculated from the CVs recorded in the electrolyte solution without redox species (Fig. 2 (a) and (b)), and displaying thin-layer characteristics using the relation [68].

$$\Gamma = \frac{Q}{nFA} \quad (1)$$

where Q (C) is the charge on the forward or reverse scan, n is the number of electrons transferred, A (cm^2) is the geometric area of the electrode, and F is the Faraday constant (96486 C mol^{-1}). These values can be expressed as concentrations, with the knowledge of the thickness of the TPQPCI coated film, ϕ (cm), and calculated using the profilometer. To estimate the apparent diffusion

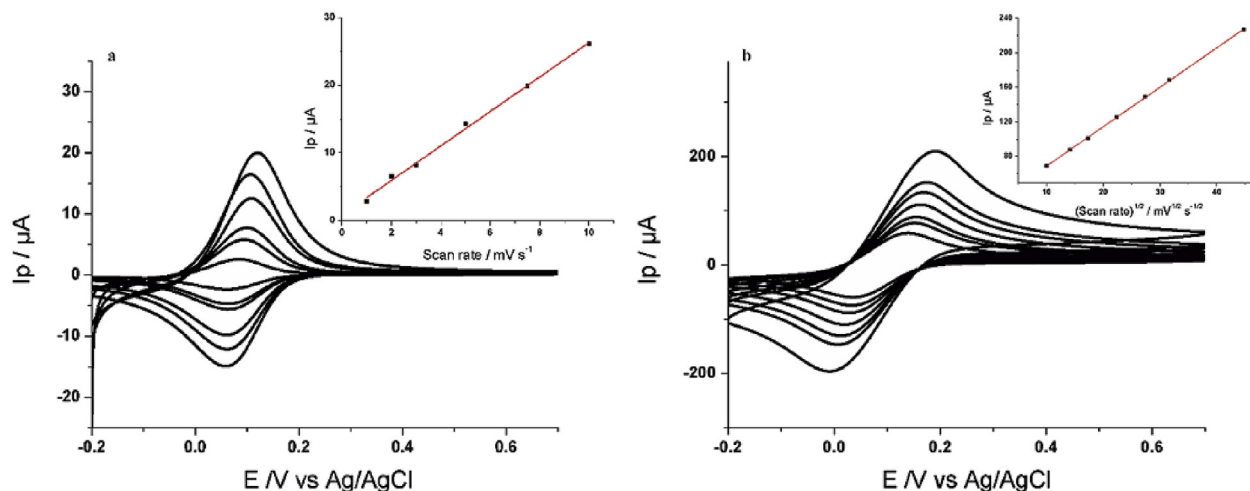


Fig. 2. CVs of 1% TPQPCI coated film loaded in 5 mM $K_4Fe(CN)_6$ after transferring to 0.1 M NaCl supporting electrolyte. Scan rate: from 1 $mV s^{-1}$ to 10 $mV s^{-1}$ (a) and from 100 $mV s^{-1}$ to 2000 $mV s^{-1}$ (b). The inset shows the plot of the anodic peak current vs the scan rate (a) and square root of the scan rate (b).

coefficients, we utilized two methods, e.g. (1) the Randles-Sevcik equation and (2) the Anson's plot method. For the former, we plotted the anodic peak currents, $I_{p,a}$ versus the square root of the scan rate, $v^{1/2}$, and applied the Randles-Sevcik equation [68], with the underlying assumption that the redox process is reversible. Note that the ΔE_p for each recorded CV increased monotonically with the scan rate which will tend to lead to an underestimation of D_{app} . The slope of these plots in the faster scan rate regime, combined with the polymer film thickness (calculated using the profilometer) and the number of electroactive species obtained by coulometric integration of the anodic peak current under thin layer conditions allowed the evaluation of the apparent diffusion coefficient values of TPQPCI coated electrodes. The calculated D_{app} for the $Fe^{2+/3+}$ redox couple using the Randles-Sevcik equation was found to be $7.1 \pm 0.9 \times 10^{-9} cm^2 s^{-1}$. For the latter method (Anson's plot), potential-step chronocoulometry was used to determine the values of D_{app} from the slope of the plots of the charge Q vs the square root of time, $t^{1/2}$, using the following relation:

$$D_{app} = \left[\frac{S\Phi\pi^{1/2}}{2FI} \right]^2 = \left[\frac{S\pi^{1/2}}{2FC} \right]^2 \quad (2)$$

where S is the chronocoulometric slope ($C cm^{-2} t^{-1/2}$), with I , Φ , and F with the conventional meaning as previously mentioned [33]. The value of D_{app} using the Anson's plot was estimated as $5.4 \pm 1.1 \times 10^{-9} cm^2 s^{-1}$ and in good agreement with that one calculated using the Randles-Sevcik equation. These values are consistent and of the same order of magnitude of D_{app} of ferrocyanide within cationic perfluoropolymer on basal plane pyrolytic graphite electrodes as reported by Oyama et al. [69]. To note that in using these methods to evaluate the apparent diffusion coefficients we made the tacit assumptions that ionomer films do not swell

when immersed in solution, as well as that it is uniformly distributed throughout the ionomer coated film. Analysis of topography using AFM (see Fig. S5) on TPQPCI recasted films (0.5% and 1%) evidenced the formation of a uniform film with root mean squared roughness (R_q) between 0.6 nm and 0.7 nm. These values are similar to those reported by Paul et al. for Nafion self-assembled films [70]. Measurements of the thickness of TPQPCI recasted films using profilometer before and after immersion in 0.1 M NaCl for 15 min did not show any variation due to swelling of the ionomer film. However, the values of D_{app} have to be taken as a general estimation, since TPQPCI may swell as a result of ingress and egress of ions during the voltammetric scans. Despite that, the values of D_{app} herein calculated are within the expected range for ionomer coated films, such as Nafion with redox mediators such as $Ru(bpy)_3^{2+}$ and $Ru(NH_3)_6^{3+}$ [22,24]. Table 1 reports the values of the surface coverage, concentration of redox probe, and apparent diffusion coefficient extracted using these methods for 0.5% and 1% TPQPCI coated electrodes. It is interesting to note that loaded TPQPCI coated films retains the redox species after been transferred in supporting electrolyte solution as evidenced by the concentration of the redox mediator inside the film in the order of magnitude of 10^{-2} – $10^{-1} mol dm^{-3}$.

The coated TPQPCI film retains a significant portion (ca. 70%) of the redox mediator after continuous cycling, and despite the peak current decreasing with the time, a voltammetric peak is still clearly visible even after 24 h of continuous cycling (see S4). An important characteristic of ionomer membranes is the permselectivity, e.g. the ability to incorporate ions of opposite charge, whilst repelling those of the same charge. Fig. 3 shows the CVs recorded at 1% TPQPCI coated electrodes fully loaded in 5 mM of $K_4Fe(CN)_6$ after transferring in supporting electrolyte containing different concentrations (from 0.1 mM to 50 mM) of a positively charge redox probe such as $Ru(NH_3)_6^{3+}$. The TPQPCI coated

Table 1

Parameters extracted using cyclic voltammetry and chronocoulometry relating to 0.5% and 1% TPQPCI coated electrodes loaded in 5 mM $K_4Fe(CN)_6$ after transferring to 0.1 M NaCl supporting electrolyte.; S = Anson slope of I_p vs. $t^{1/2}$, Φ = film thickness, C_p = concentration of $K_4Fe(CN)_6$ in TPQPCI, m = number of moles of $K_4Fe(CN)_6$ incorporated into the film.

[TPQPCI] %	$\Phi/(10^{-4})$ cm	$\Gamma/(10^{-8})$ mol cm^{-2}	$C_p/(10^{-4})$ mol cm^{-3}	$m/(10^{-9})$ moles	D_{app}/RS (10^{-9}) $cm^2 s^{-1}$	$S/(10^{-5})$ C $s^{-1/2}$	$D_{app}/Anson$ (10^{-9}) $cm^2 s^{-1}$
0.5	1.64 ± 0.28	1.47 ± 0.03	0.9 ± 0.023	1.09 ± 0.03	2.35 ± 0.29	3.88 ± 0.70	3.26 ± 0.90
1	2.57 ± 0.22	3.40 ± 0.14	1.33 ± 0.09	2.44 ± 0.11	7.1 ± 0.43	7.07 ± 0.90	5.40 ± 1.10

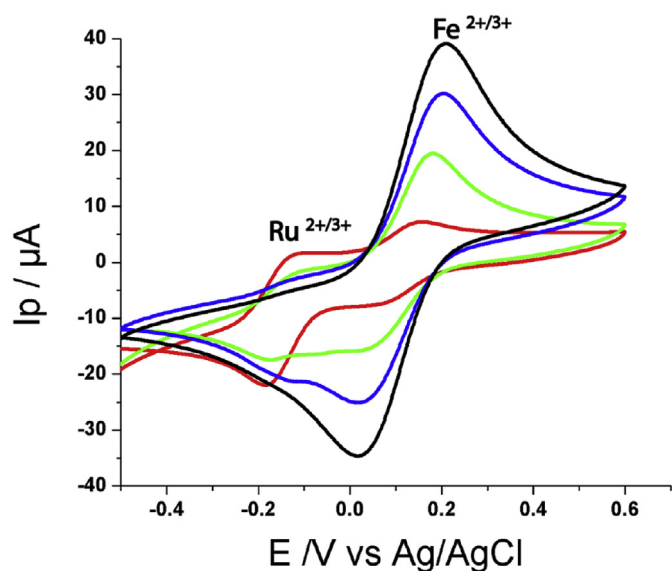


Fig. 3. CVs of 1% TPQPCI coated film loaded in 5 mM $K_4Fe(CN)_6$ after transferring to 0.1 M NaCl supporting electrolyte, and with addition of different concentration of $Ru(NH_3)_6^{3+/2+}$: 0.1 mM (black); 1 mM (blue), 10 mM (green), and 50 mM (red). Scan rate of 100 mV s^{-1} . (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

electrode does not show any voltammetric peak related to the redox behavior of the $Ru(NH_3)_6^{3+/2+}$ couple for concentration below 1 mM (see S6). At concentrations higher than 1 mM, the typical redox peak of the couple $Ru(NH_3)_6^{3+/2+}$ is noticeable at -0.15 V along with the redox peak current related to the $Fe(CN)_6^{4-/3-}$ at 0.2 V , which instead tends to decrease, as expected, as the concentration of $Ru(NH_3)_6^{3+/2+}$ increase. Note that in order to clearly detect the peak of $Ru(NH_3)_6^{3+/2+}$, a high concentration (up to 50 mM) has to be added to the solution.

3.2. Electrochemical behavior of nitrite at TPQPCI coated electrodes

The electrochemical behavior of TPQPCI coated electrodes in the presence of nitrite ions were investigated using cyclic voltammetry and differential pulse voltammetry. Fig. 4 shows the CV of bare GCE (left) and 1% TPQPCI (right) obtained at different concentration of

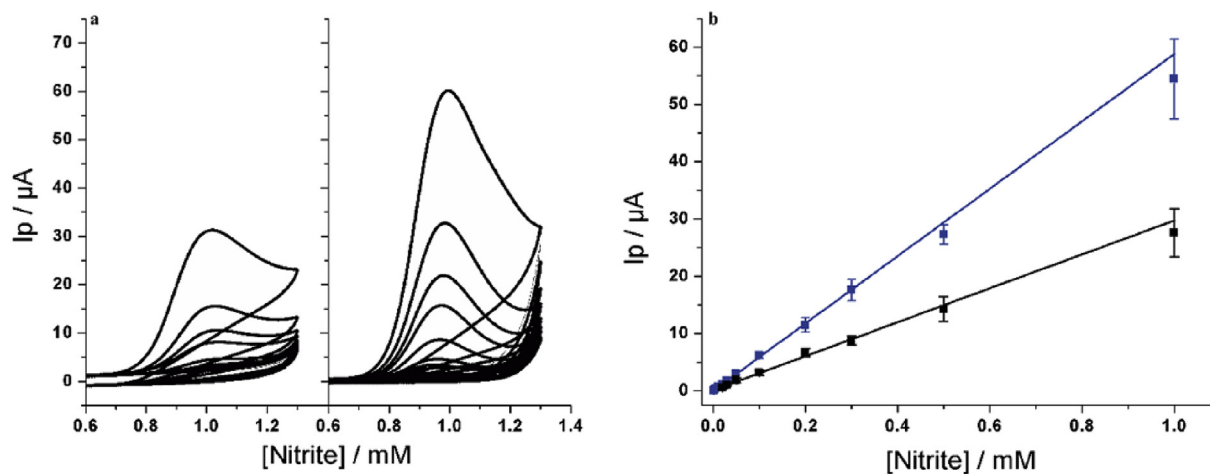


Fig. 4. (a) CVs of bare GCE (left) and 1% TPQPCI coated electrode (right) recorded in 0.1 M NaCl supporting electrolyte in the presence of various concentrations of NO_2^- , from 5 μM to 1 mM. Scan rate of 100 mV s^{-1} . (b) Inset: plot of peak currents vs concentration of NO_2^- : bare GCE (black line), TPQPCI coated electrode (blue line). Error bars calculated from 5 repeat measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

sodium nitrite from 5 μM to 1 mM. Both CVs depict the presence of an irreversible oxidation peak at 1.05 V and 0.97 V for bare GCE and TPQPCI coated electrode, respectively. Noticeably, the peak current at the TPQPCI coated electrode is ca. 3 times higher than the bare GCE. While for the TPQPCI coated electrode the addition of 2 μM of nitrite ions is sufficient to clearly visualize the related oxidation peak, for the bare GCE a voltammetric peak is only visible at concentrations higher than 20 μM . For the TPQPCI coated electrodes we observed a slight deviation from linearity at concentrations of nitrite higher than 0.5 mM as an indication that at such concentrations the TPQPCI coated films may have reached saturation. In fact, for concentration of nitrite ions higher than 20 mM, the peak current at the pristine GCE is larger than that one observed at TPQPCI coated electrode (see Fig. S7). We believe this is an indication that as such high concentrations the fully saturated ionomer film further prevent the diffusion of nitrite ions. We observed also that the background current at the bare GCE to be higher than that one observed for TPQPCI coated electrode (see Fig. S8). This fact, along with the ability of TPQPCI to accumulate nitrite ions, implies that lower concentrations of nitrite ions can be detected at TPQPCI coated electrodes. (Figs. S8(a–b)). Interestingly, while the full preconcentration of $K_4Fe(CN)_6$ within TPQPCI films requires a relatively long time (at least 20 min, see S2(b)), in the case of nitrite ions the preconcentration occurs in a matter of a couple of minutes as evidenced in Fig. S9. This is due to the fact that nitrite ions are smaller than ferrocyanide ions and therefore penetrate more easily into the ionomer film.

These data highlight as TPQPCI coated electrodes are able to accumulate the nitrite ions as a result of the exchange properties between the positively charged phosphonium groups of the ionomer and the negatively charged nitrite ions available in solution. The peak current scale linearly with the concentration of nitrite ions until 1 mM concentration, then it increases until 25 mM where it starts to plateau (See Fig. S7). It is worth mentioning that typically the nitrite content in water and food are in the order of sub-micromolar concentrations, and therefore it is at such range of concentrations that the sensor will have to operate. The sensitivity of TPQPCI coated electrode is even more pronounced when using DPV. Fig. 5 shows the DPV curves recorded at bare GCE and TPQPCI coated electrode at different concentrations of nitrite. In this case the oxidation peak of nitrite at TPQPCI coated electrode occurs at a potential ca. 0.2 V less positive than the bare GCE (0.77 V vs. 0.97 V). Also, the intensity of peak current at the ionomer coated electrode

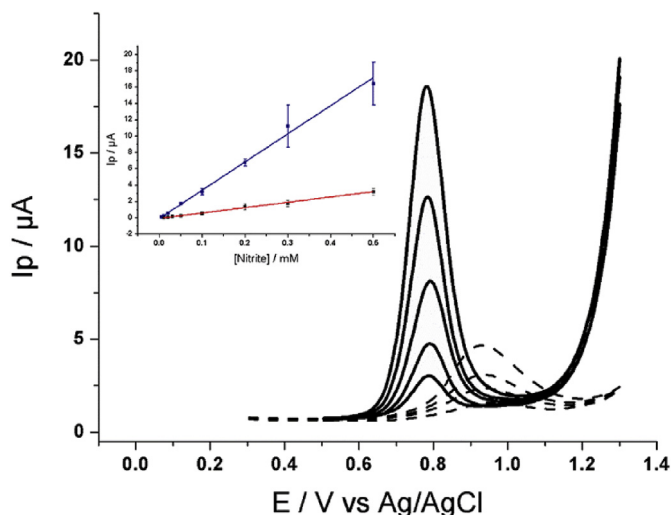
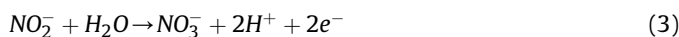


Fig. 5. DPVs of bare GCE (dashed line) and 1% TPQPCI coated electrode (solid line) recorded in 0.1 M NaCl supporting electrolyte in the presence of various concentrations of NO_2^- , from 5 μM to 0.5 mM. Scan rate of 10 mV s^{-1} . Inset: plot of peak currents vs concentration of NO_2^- : bare GCE (red line), TPQPCI coated electrode (blue line). Error bars calculated from 5 repeat measurements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

is ca. 5 times higher than that one recorded at the bare GCE.

The irreversible oxidation of nitrite to nitrate ions occurs through the following mechanism [71,72]:



Equation (3) shows that the oxidation of nitrite to nitrate occurs via a two-electron reaction with concomitant formation of protons. This relation suggests that the peak current is pH dependent. For this purpose, we performed several experiments using DPV at different pH values from 2 to 12. Fig. 6 depicts the plot of the oxidation peak currents obtained using DPV after addition of 1 mM of NO_2^- . The peak current shows a maximum for values of pH between 7 and 10, while outside this range (pH < 7 and pH > 10) the peak current values drop significantly. The fact the peak current

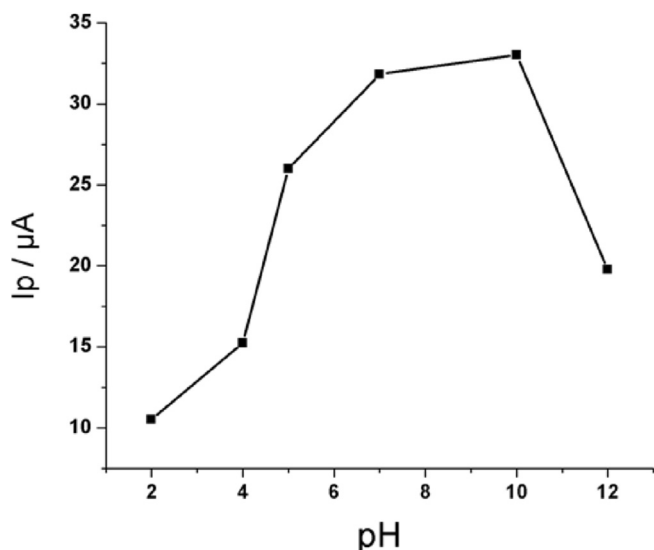
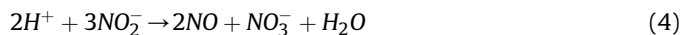


Fig. 6. Plot of anodic peak current vs pH for 1% TPQPCI coated electrode recorded in 1 mM NO_2^- and 0.1 M NaCl supporting electrolyte. Scan rate of 10 mV s^{-1} .

decreases at pH < 7 shows that nitrite ions are not stable in acidic conditions. It is well established that nitrite ions in acidic environment undergo the following chemical reactions:



In this case NO_2^- ions are converted into NO and NO_3^- ions, with the latter that, of course, can not be further oxidized. Also, the pK_a of HNO_2 is 3.3, hence, at very acidic pH, nitrite ions are protonated forming HNO_2 . Since TPQPCI is effective in exchanging anionic species, if NO_2^- ions are in protonated form they will not be incorporated by the phosphonium groups within TPQPCI. Instead, in the case of pH > 10, the decrease of the voltammetric signal can be attributed to the higher concentration of OH^- ions that at this pH range is well in excess and will compete with NO_2^- ions for the phosphonium sites. This is not surprising, taking into account that TPQPCI is originally derived from TPQPOH utilized as a membrane in alkaline fuel cells, hence its affinity for OH^- ions is very high [53]. Based on these results we performed all experiments involving nitrite ions at pH 7 which is also the measured pH of the supporting electrolyte solution.

We have also evaluated the response of the TPQPCI coated electrode using chronoamperometry. Fig. 7 (a) depicts the amperometric $i-t$ response obtained at 1% TPQPCI coated electrode recorded in 0.1 M NaCl as supporting electrolyte, at various concentration of sodium nitrite and by applying a potential of 0.86 V. The addition of sodium nitrite was performed at regular intervals time of ca. 30 s and under stirring conditions. The chronoamperometry (CA) $i-t$ curve shows that TPQPCI coated electrode responds rapidly to every addition of nitrite with an increase of the current, and reaching the steady-state after ca. 5 s. However, the currents measured are ca. 3 times smaller than those registered using cyclic voltammetry previously shown in Fig. 4. We explain this difference with the fact that in the CA experiment different concentrations of nitrites were added every 30 s, instead the CVs were recorded after 20 min elapsed time at each nitrite addition. We also observed (Figures not shown) that CVs recorded without elapsing times give consistently lower current than those registered after at least 5 min elapsing time, as an indication that TPQPCI coated electrodes needs few minutes of recovery time in order to be fully regenerated.

The corresponding plot of the current vs. nitrite concentrations exhibits a linear response in the range from 1 μM to 0.5 mM with a regression equation expressed as $I_p (\mu\text{A}) = 0.0189 [\text{nitrite}] (\mu\text{M}) + 0.125$ ($R^2 = 0.9971$). Moreover, the sensitivity of TPQPCI coated electrode is calculated as $0.267 \mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$, whereas the limit of detection, LoD, is 1.07 μM , and calculated from the slope of the linear regression plot, S , and the standard deviation, S_b , of 5 repeats of 0.5 μM nitrite addition, using the relation $\text{LoD} = 3S_b/S$. Similarly, the limit of quantification, LoQ, is calculated as 3.45 μM , from the slope of the linear regression plot, S , and the standard deviation, S_b , of 10 repeats of 0.5 μM nitrite addition, using the relation $\text{LoQ} = 10S_b/S$.

The as-prepared TPQPCI coated electrodes are also very stable up to two weeks when left in aqueous solutions. The performance of TPQPCI coated electrodes herein obtained shows that the as-prepared ionomer-coated electrode is competitive with other systems reported in literature in terms of linear range, sensitivity and limits of detection, despite not being the best, as summarized in Table 2. However, we want to emphasize the simplicity of the as-prepared ionomer coating herein presented compared to the other materials reported in Table 2.

An important property of chemically modified electrodes is the selectivity, e.g. the ability of the ionomer coated electrode to discriminate analytes that could interfere with the analytical

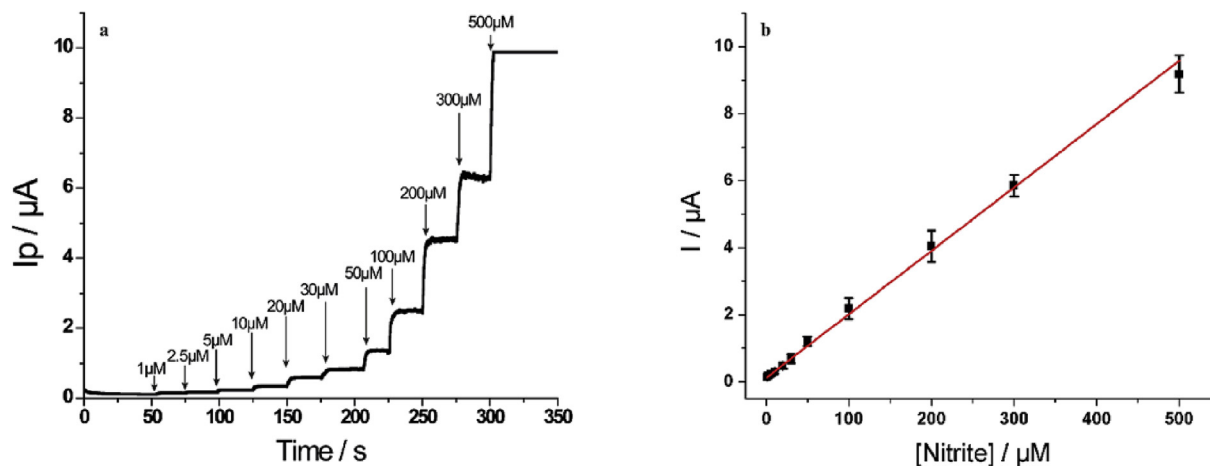


Fig. 7. (a) Chronoamperometric (*i-t*) response of 1% TPQPCL coated electrode obtained with successive concentration of nitrite from 0.001 mM to 0.5 mM recorded in 0.1 M NaCl supporting electrolyte (pH 7), applied potential 0.86 V. (b) Calibration plot as a function of nitrite concentration as in (a). Error bars calculated from 5 repeat measurements.

Table 2

Analytical performances of amperometric sensors for the detection of nitrite ions.

Electrode	Linear Range (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$)	Detection limit (μM)	Technique	Reference
Ag-Fe ₃ O ₄ -GO modified GCE	0.5–720	1.996	0.17	Amperometry	Li et al. (2015) [73]
GE/AEBA/DPAN/PtNPs	10–1000	–	5	Amperometry	Miao et al. (2011) [74]
Thionin modified ACNTs	3–500	0.396	1.12	DPV	Zhao et al. (2007) [75]
CaFe ₂ O ₄ modified SPCE	0.016–1928	0.3712	0.066	Amperometry	Balasubramanian et al. (2018) [72]
Cu/MWCNTs modified GCE	5–1260	0.4558	1.8	Amperometry	Manoj et al. (2018) [76]
NiHCF/PDAP hybrid on GCE	0.1–131	7.5	0.0151	Amperometry	Wang et al. (2018) [77]
AgNS/GCE	0.1–8	0.580	0.031	Amperometry	Shivakumar et al. (2017) [78]
Ag-RGO nanocomposite	10–1000	0.373	–	Amperometry	Shaikh et al. (2016) [79]
Pd/Fe ₃ O ₄ /polyDOPA/RGO	2.5–6470	0.01537	0.5	Amperometry	Zhao et al. (2017) [80]
TPQPCL Modified GCE	3–2000	0.488	1.18	DPV	This work
TPQPCL Modified GCE	1–500	0.267	1.07	Amperometry	This work

determination of the selected analyte, in our case nitrite ions. Fig. 8 illustrates the chronoamperometric response obtained in the presence of several interference species such as sodium sulfite, potassium chloride, glucose, sodium persulfate, and copper nitrate. The concentration of these interference species was as that of sodium nitrite, in our case 5 μM . The results showed that the voltammetric response of TPQPCL coated electrode is not affected by the presence of these interference species at least when their

concentration is of the same magnitude of nitrite ions (see Fig. 8 (a)). Instead, for the bare GCE, the addition of sodium sulfite is sufficient to generate a noticeable interference (Fig. 8 (a)).

This behavior can be explained with the fact that sulfite ions at pH 7 coexist in solutions as HSO_3^- and SO_3^{2-} and the hydronium ions produced as a result of the electrochemical oxidation of nitrite to nitrate (see Eq. (3)) will protonate HSO_3^- to H_2SO_3 and SO_3^{2-} to HSO_3^- . We performed an experiment by recording CVs at bare GCE

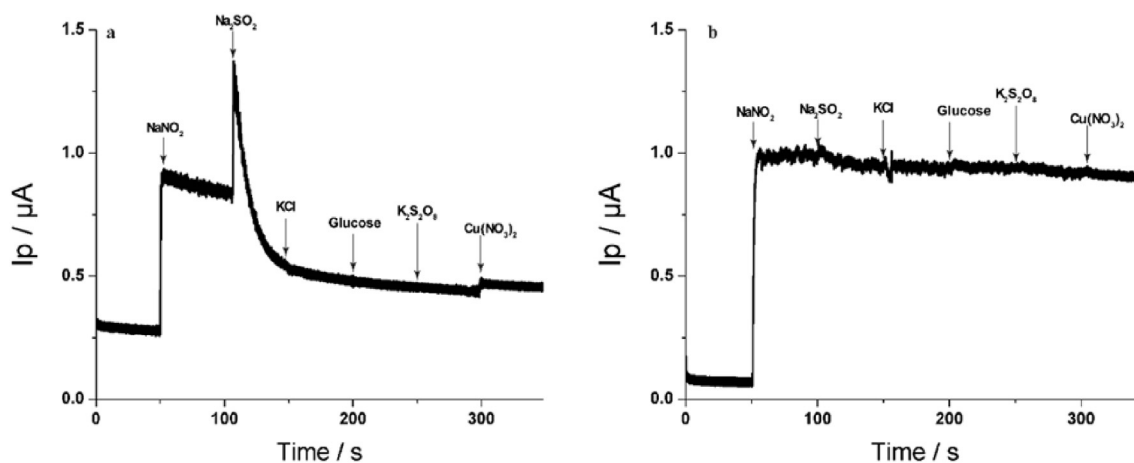


Fig. 8. Chronoamperometric (*i-t*) response of (a) bare GCE and (b) 1% TPQPCL coated electrode obtained with the addition of interference species as highlighted in the figure. The concentration of nitrite and of interference species is 5 μM , supporting electrolyte 0.1 M NaCl (pH 7), applied potential 0.86 V.

and 1% TPQPCI at different pH values (pH 7 and pH 10) in the presence of 10 mM sulfite ions where we observed higher oxidation current peaks at basic pH compared to neutral pH (see Fig. S10). At pH 10 sulfite ions are present as SO_3^{2-} suggesting that TPQPCI coated electrode have higher affinity for bivalent anions. In this range of pH we expect sulfite to become a potential serious interference species. Additional study of potential interference species was performed using dopamine and ascorbic acid (see Fig. S11). Dopamine, which is a positively charged is repelled by TPQPCI and as expected, does not show any interference in the detection of nitrite. In the case of ascorbic acid which is negatively charged, we observed a light interference, however further study using DPV showed that it may become significant at concentrations of ascorbic acid higher than 1 mM, even though the peak separation between the two species could allow the simultaneous detection (see Fig. S12). Before proceeding on testing TPQPCI coated electrodes with real samples we have investigated potential issues of memory effects, e.g. accumulation time upon the signal of nitrite. Fig. S13 reports the DPVs obtained after addition of 0.1 mM nitrite ions. Immediately after recording the DPV (black curve), we recorded a second DPV curve without recovery time. The DPV showed a substantial decrease in the peak current, however, a recovery time of 3 min was sufficient to restore the initial value of the peak current. Also (figure not shown), running a DPV in 0.1 M supporting electrolyte allowed to clean the TPQPCI coated electrode for further measurements.

In order to validate the as-prepared sensor, we tested the TPQPCI coated electrode towards the detection of nitrite in samples

of tap water and of water taken from the effluent outflow of a paper mill in the Llynfi Valley. The samples were spiked with 0.1 M NaCl supporting electrolyte before use and the pH measured before analysis was equal to 8 and 7.8 for the tap water and effluent river samples, respectively. A known concentration of nitrite was spiked in these samples and the chronoamperometric curves and I_p vs. [nitrite] curves are reported in Fig. 9.

The results obtained from the chronoamperometry experiment are summarized in Table 3. The values obtained for the nitrite concentration are 0.0507 mg NO_2^-/L and 0.0814 mg NO_2^-/L in tap and river water, respectively. The values found are well below the European standard limits for tap water of 0.5 mg NO_2^-/L , set up by the European commission [81]. The results showed good reproducibility and RSD values for the nitrite spiked water samples are around 3%. All the results point out as the as-prepared TPQPCI coated electrode as a competitive and simple system compared to other voltammetric systems for the determination of nitrite ions.

Table 3

Analytical performances of TPQPCI coated electrode for the detection of nitrite in tap water and river sample.

Sample	Added (μM)	Found (μM)	Recovery %
Tap water	–	1.10 ± 0.08	–
	20	22.05 ± 0.65	104.5%
Paper mill Effluent water	–	1.77 ± 0.19	–
	20	21.56 ± 0.72	99.1%

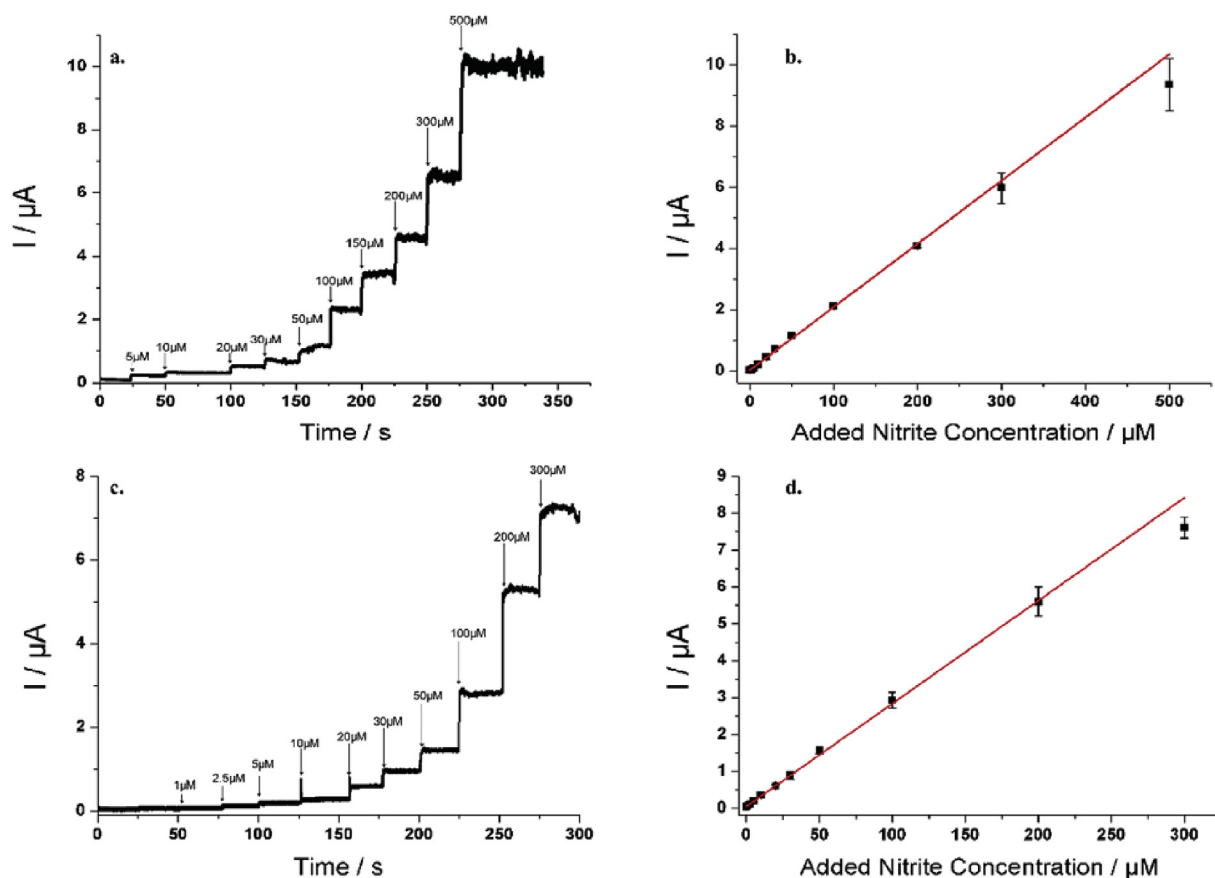


Fig. 9. (a) Chronoamperometric (i - t) response of 1% TPQPCI coated electrode obtained in tap water (pH 8.02) and water effluent from a paper mill (pH 7.81) (c), after addition of different concentration of nitrite. Calibration plot (b), (d) as a function of nitrite concentration as in (a), and (c), respectively; Applied potential 0.86 V. Error bars calculated from 3 repeat measurements.

4. Conclusions

We have demonstrated that TPQPCL ionomer can be effectively utilized in electroanalysis for detection of anions. The electrochemical characterization performed using cyclic voltammetry and chronocoulometry allowed the concentration of redox mediator within TPQPCL films, and the apparent diffusion coefficients to be determined. Also, through electrochemical experiments we were able to investigate the permselectivity properties of the ionomer. TPQPCL coated electrodes were tested for determination of anions such as nitrite ions in tap and river water samples. The results indicated that the as-prepared TPQPCL coated films can detect nitrite ions with a limit of detection (LoD) of 1.07 μM , sensitivity as 0.267 $\mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$, and linearity range between 1 μM –500 μM . The results herein point out that TPQPCL ionomer is an attractive material in electroanalysis for detection of nitrite ions.

Author contributions

T.R.J. performed all electrochemical experiments and analyzed the results. S.H.-A performed some of the electrochemical experiments and the evaluation of ionomer thickness using profilometer. R.B.K. and M.L. synthesized the ionomer membrane. P.B. and Y.Y. cowrote the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.electacta.2019.04.089>.

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