



Amperometric determination of sulfide based on its electrocatalytic oxidation at a pencil graphite electrode modified with quercetin

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ABSTRACT

This study describes a new approach for the investigation of electrocatalytic oxidation of sulfide using a pencil graphite electrode modified with quercetin (PGE/QH₂). Adsorption procedure was used for the preparation of the modified electrodes. It was observed that PGE/QH₂ showed a significant electrocatalytic activity toward sulfide oxidation. Cyclic voltammetric studies show that the peak potential of sulfide shifts from +450 mV at bare PGE to +280 mV at PGE/QH₂. The electrocatalytic currents obtained from amperometric measurements at +300 mV vs. Ag/AgCl/KCl_{sat} and at pH 8.0 BR buffer solution containing 0.1 M NH₄Cl were linearly related to the concentration of sulfide. The calibration graph consisted of two linear segments of 1–20 μM and 20–800 μM with a detection limit of 0.3 μM (based on 3s_b). The proposed method was successfully applied to the determination of sulfide in waste waters and was compared with the spectrophotometric method.

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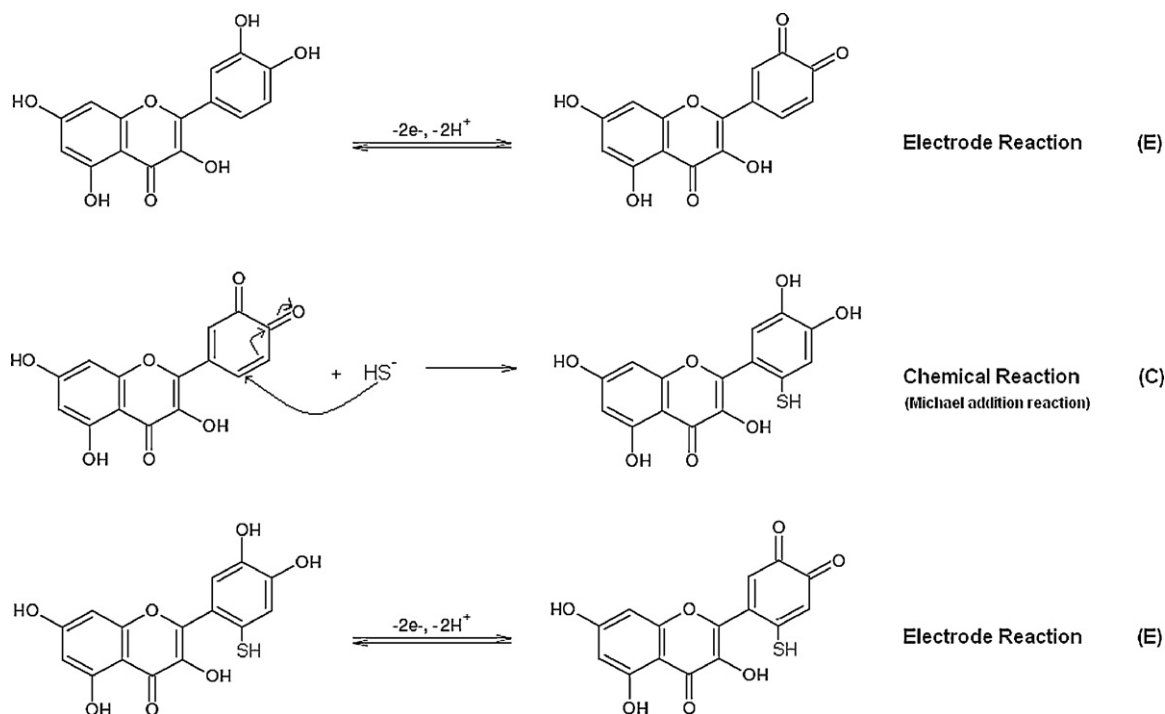
1. Introduction

Sulfide has an important role in the aquatic environments due to its toxic effect on many organisms. Sulfide is released into aquatic environments by the action of anaerobic bacteria on organic matters such as sulfur containing proteins, amino acids, etc. Sulfide salts are used in industrial waste streams in order to control the levels of several toxic metals (e.g. mercury, lead) discharged into environment, since many metal sulfides are insoluble and precipitate out in the waste stream. In aqueous media, total sulfide can be found as dissolved H₂S, bisulfide ion (HS⁻, pK_{a1} = 6.88) and sulfide ion (S²⁻, pK_{a2} = 14.15) depending on protolytic equilibria [1]. The level of total sulfide is very important as well as H₂S. Thus, the total level of sulfide in waste discharges has been limited because of its toxicity, capacity to remove dissolved oxygen and capability to produce H₂S. Sulfide acts as a cellular poison through the deactivation of aerobic respiration and causes asphyxiation. Clinical cases of sulfide poisoning typically occur at levels between 30 and 3000 μg L⁻¹ and its lethal doses depending on exposure of H₂S may vary in the range of 300–1000 ppm [2]. Therefore, the determination of sulfide species or total sulfide in samples such as industrial liquid wastes, domestic waste water, rivers and H₂S in air close to contaminated aquatic

sources has gained importance for analytical and environmental chemists.

Several methods describing the determination of sulfide and its species in aqueous media have been reported. A comprehensive review on the analytical methods related with the detection of sulfide was reported by Lawrence et al. [2]. Titrimetric [3,4], spectroscopic [1,5–9], chromatographic [10–15] and electrochemical [4,16–33] methods have been successfully applied to the sulfide determination. Among these methods, the electrochemical techniques have some advantages such as easy application, low cost, providing direct, sensitive and fast detection of H₂S. However, the direct electrochemical oxidation of sulfide is highly irreversible with a great overpotential at the bare electrodes. Additionally, the oxidized products of sulfide can be adsorbed on the electrode surface which may result in the fouling and passivation of the electrode surface leading to poor sensitivity, poor selectivity and unstable analytical signals. In order to overcome these problems, the modification of electrode surface with redox mediators has been extensively used. Approaches based on redox mediators such as ferricyanide [16–18], ferrocene carboxylate [19] ferrocenesulphonate [20,21], N,N'-diphenyl-p-phenylenediamine [22], cobaltpentacyanonitrosylferate [23], vanadium pentoxide [24], cinder/tetracyano nickelate [25], hexadecylpyridinium-bis(chloranilato)-antimonyl (V) [26], 2,6-dichlorophenolindophenol [27] and 2-(4-fluorophenyl)indole-modified xerogel [28] were employed as amperometric sensors for the determination of dissolved sulfide in aqueous media. Although

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Scheme 1. Redox behavior of QH₂ and electrocatalytic oxidation mechanism of sulfide at PGE/QH₂.

some of the redox mediators were used in aqueous media, the chemically modified electrodes (CMEs) prepared from the redox mediators were extensively preferred due to their enhanced sensitivity and reliability in the measurement of sulfide concentration.

When compared with other carbon based electrodes, PGEs have some advantages such as high electrochemical reactivity, commercial availability, good mechanical rigidity, disposable, low costs, low technology and easy modification [34–38]. Additionally it was reported that pencil leads electrodes offer a renewal surface which is simpler and faster than polishing procedures, common with solid electrodes, and results in good reproducibility for the individual surfaces [34]. Therefore PGEs have been increasingly utilized in many different electroanalytical applications recently [34–43]. For example, Özcan and Şahin [35] reported that electrochemically treated PGE was successfully used in the determination of low levels of dopamine in blood serum. Özcan and Şahin showed that electrochemically treated PGEs were very promising because they have high adsorption capacity for organic compounds.

Among the flavonoids, quercetin (3,3,4',5,7-pentahydroxyl-flavone, QH₂) (Scheme 1), has a great importance due to its strong anti-oxidant effect which can be attributed to the high numbers of hydroxyl substituent groups and to its conjugated π orbitals by which QH₂ is able to donate electrons or hydrogens [44]. Several studies on the electrochemical behavior and voltammetric determination of QH₂ have been reported using multi walled carbon nanotubes paste electrode [45] and glassy carbon electrode [46,47]. In the report of Zare et al. [46] the well-defined redox peaks (E_{pa} : 365 mV and E_{pc} : 315 mV) were obtained from cyclic voltammograms of QH₂ in 0.1 M phosphate buffer solution (pH 4.0) using a glassy carbon disk electrode. Moreover, some reports on the preparation of modified electrodes with QH₂ were described for the determination of some biologically important molecules. For example, the determination of dopamine in the presence of ascorbic acid was performed by using glassy carbon electrode modified with multi walled carbon nanotube, QH₂ and Nafion [48], and using QH₂-self assembled monolayer-modified gold electrode [49]. In another study, a QH₂ modified wax-impregnated graphite

electrode was prepared for the determination of uric acid in the presence of ascorbic acid [50].

Our literature research demonstrated that there was no report on the preparation of PGE modified with QH₂ and no investigation on the electrocatalytic oxidation of sulfide with this modified electrode. In this study, we describe the electrocatalytic determination of sulfide by using a new, simple and disposable electrode (PGE) modified with a new redox mediator (QH₂) for the first time.

2. Experimental

2.1. Chemicals

Sodium sulfide (Na₂S·9H₂O), quercetin dihydrate and all other chemicals were of analytical reagent grade (purchased from Merck). All of the solutions throughout this work were prepared by using deionized water from a Milli-Q (Millipore, Bedford, USA) device.

The stock solution of Na₂S (0.1 M) was prepared by dissolving Na₂S·9H₂O crystals in degassed 0.1 M NaOH solution and kept at +4 °C in a refrigerator for maximum one week. Na₂S solution was periodically standardized with the iodometric method.

The stock solution of QH₂ (1.0 mM) was freshly prepared with ethanol. Britton–Robinson (BR) buffer solutions with various pH values were prepared by proper mixture of stock standard solutions of H₃PO₄, H₃BO₃, and NaOH.

2.2. Apparatus

Cyclic voltammetric and amperometric experiments were performed in a traditional three electrode systems. A platinum wire as the counter electrode, an Ag/AgCl/KCl_{sat} as the reference electrode and a PGE as the working electrode were used. Pencil leads with a diameter of 0.5 mm and a total length of 60 mm (Tombo, Japan) and a mechanical pencil Model T 0.5 (Rotring, Germany), which was used as the holder for the pencil lead, were purchased

from a local bookstore. Electrical contact to the lead was obtained by wrapping a metallic wire to the metallic part of the holder. For each measurement, totally 10 mm of lead was immersed into the solutions.

All electrochemical experiments were carried out by using a Compactstat Electrochemical Interface (Ivium Technologies, Eindhoven, Netherlands). A HI 221 Hanna pH-meter with a combined glass electrode (Hanna HI 1332) was used to follow the pH values of the solutions.

2.3. Preparation of the modified electrodes

The modification of PGE was achieved by an adsorption procedure. Firstly the surface of PGE was pre-treated by applying a potential of +1.45 V for 60 s in the blank supporting electrolyte (0.1 M phosphate buffer solution containing 0.1 M KCl, pH 7.0). This pre-treatment procedure was applied in some electroanalytical studies by using PGE in order to clean the impurities from the electrode surface and to obtain more sensitive and stable analytical signals [34,38–41]. Since pre-treatment at the positive potentials increases the hydrophilic properties of the electrode surface through introduction of oxygenated functionalities, this procedure can provide a good adsorption property to PGE. After the pre-treatment, the pencil lead was immersed into the stock QH₂ solution (1.0 mM in ethanol) for 60 s. The same modification procedure was repeated for the untreated PGE. The obtained modified electrodes (PGE/QH₂) were used for the investigation of the electrocatalytic oxidation of sulfide after rinsing with ultrapure water.

2.4. Electrochemical procedure

The electrochemical behavior of PGE/QH₂ was investigated by recording the cyclic voltammogram in 0.1 M BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl at a scan rate of 50 mV s⁻¹. In order to investigate the effect of the scan rate on the peak potentials and peak currents, the cyclic voltammograms of the PGE/QH₂ were recorded at different scan rates, in the potential range between 0.0 and +0.50 V. Additionally the effect of pH between 2.0 and 10.0 on the peak potentials of the modified electrodes was also investigated at a scan rate of 50 mV s⁻¹.

The electrocatalytic oxidation of sulfide at the PGE/QH₂ was investigated through the addition of a freshly prepared sulfide solution to the supporting electrolyte solution. The cyclic voltammograms were recorded in the potential range of -0.25 to +0.6 V, in 0.1 M BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl at a scan rate of 50 mV s⁻¹. The amperometric detection of sulfide based on its electrocatalytic oxidation was also studied by using PGE/QH₂. After the background current reached to a steady state value of +300 mV, which was found as optimum value, aliquots of a stock solution of sulfide were added to the supporting electrolyte.

The supporting electrolytes were deaerated by allowing highly pure argon to pass through for 5 min before all electrochemical experiments. Samples were collected from Kepez municipal wastewater treatment plant and Biga organized tannery region in Canakkale, Turkey at July of 2011. All of the samples were filtered to remove particulate matter. Then, the sulfide level was determined according to the proposed and spectrophotometric methods [7].

3. Results and discussions

3.1. Preparation of modified electrode and its electrochemical behavior

The cyclic voltammograms of PGE/QH₂ showed that the peak currents of the modified electrodes decreased when the cycle

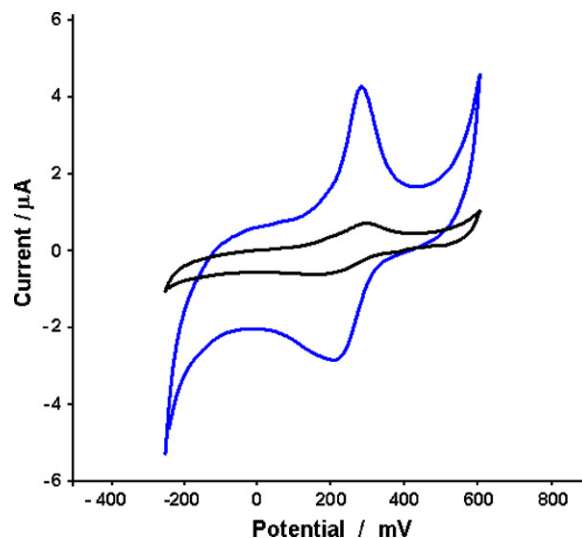


Fig. 1. Cyclic voltammograms of untreated (a) and pretreated (b) PGE/QH₂ in BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl at a scan rate of 50 mV s⁻¹.

numbers were increased due to the desorption of QH₂ to the supporting electrolyte and the peak currents were stable after the 10th scan (data not shown). The modified electrode was used only once time for electrocatalytic studies and a new PGE was modified with the same procedure. The cyclic voltammograms of the untreated and pre-treated PGE/QH₂ at the 10th scan are given in Fig. 1a and b, respectively. As it can be seen from Fig. 1, the peak currents of pre-treated-PGE/QH₂ were higher than that of untreated-PGE/QH₂. QH₂ displayed an anodic peak at +280 mV at 50 mV s⁻¹, indicating its oxidation to o-quinone form with two electrons and two protons (Q) (Scheme 1). During the reverse scan a cathodic peak also occurred at +220 mV, corresponding to the reduction of the quinone form to QH₂. These results indicate that the electrochemical behavior of QH₂ is quasi reversible. Similar results were also obtained in the cyclic voltammogram of QH₂ in supporting electrolyte media (0.1 M phosphate buffer, pH 4.0) using a glassy carbon disk electrode [46] and multi walled carbon nanotubes-paraffin oil paste electrodes [45].

The cyclic voltammograms of pre-treated-PGE/QH₂ in a 0.1 M BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl at various scan rates were recorded. The peak currents increased with a small shift of anodic and cathodic peaks potentials when the scan rate increased. While the shape of the anodic peak was not changed at sweep rates above 200 mV s⁻¹, the cathodic peak was broadened. Additionally the potentials of the anodic and cathodic peaks were shifted to more positive and negative values, respectively, indicating the limitation arising from the charge transfer kinetic. It was found that the anodic (I_{pa}) and cathodic (I_{pc}) peak currents of the modified electrode are linearly proportional to the scan rate (ν) between 10 and 200 mV s⁻¹ ($I_{pa} = 0.034\nu + 0.062$, $R^2 = 0.998$ and $I_{pc} = -0.013\nu + 0.354$, $R^2 = 0.996$). These results prove that the electrochemical process at the PGE/QH₂ is surface-controlled.

In order to determine the effect of pH on the formal standard potential ($E^{\circ} = (E_a + E_c)/2$) of the modified electrodes, the cyclic voltammograms of PGE/QH₂ were recorded in BR buffer solutions containing 0.1 M NH₄Cl of pH values between 2.0 and 10.0, at a scan rate of 50 mV s⁻¹. The formal potential of QH₂ was pH dependent with a slope of -60.83 mV per unit of pH which is very close to the anticipated Nernstian value of -59 mV. Therefore, it can be said that the numbers of transferred electrons and protons are equal in the electrochemical reaction of QH₂ at PGE surface. Our results are in accordance with the reported one in literature, in which the electron and proton numbers were found to be two for the

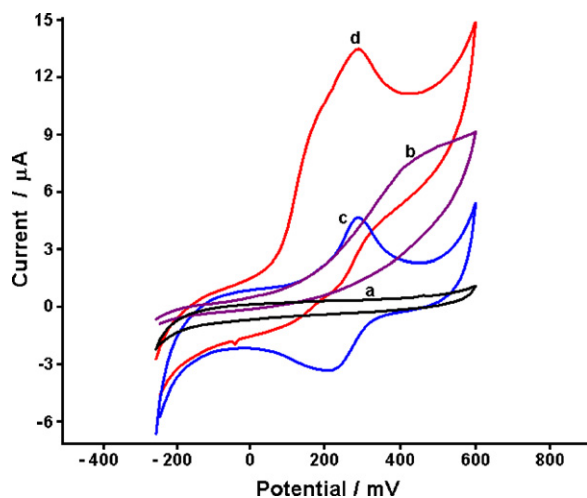


Fig. 2. Cyclic voltammograms of bare PGE (a and b) and PGE/QH₂ (c and d) in the absence (a and c) and in the presence (b and d) of 0.1 mM Na₂S. (Supporting electrolyte: BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl; scan rate: 50 mV s⁻¹.)

aqueous solutions of QH₂ at multi walled carbon paste electrode [45] and glassy carbon electrode [46].

3.2. Electrocatalytic oxidation of HS⁻ at PGE/QH₂

In order to test the electrocatalytic activity of PGE modified with QH₂ toward sulfide oxidation, cyclic voltammograms of PGE/QH₂ were recorded in both the absence and the presence of sulfide. Fig. 2c shows the cyclic voltammogram of PGE/QH₂ in BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl at 50 mV s⁻¹ in the absence of sulfide. An anodic peak and cathodic peak were observed at +280 mV and +220 mV, respectively. As it can be seen from Fig. 2d, the oxidation peak at +280 mV was increased significantly, while the cathodic peak current at +220 mV decreased in the presence of 0.1 mM sulfide. The electrochemical oxidation of sulfide was additionally investigated by using an unmodified PGE. If we compare the peak potential of sulfide at the unmodified and pretreated PGE (about +450 mV, Fig. 2b) with that of the PGE/QH₂ (about +280 mV, Fig. 2d), the overpotential for the electrochemical oxidation of sulfide was found to decrease by 170 mV. So, a decrease in the overpotential of ca. +170 mV and an enhancement of the peak current were achieved by using PGE/QH₂. These results indicate that PGE/QH₂ shows efficient electrocatalytic effect toward sulfide oxidation.

In order to see the effect of scan rate on the electrocatalytic oxidation, the cyclic voltammograms of 0.1 mM sulfide were recorded at various scan rates between 20 and 1000 mV s⁻¹ using the PGE/QH₂. It was observed that the oxidation peak potential was shifted to a more positive potential by increasing scan rates, indicating the kinetic limitation of the electrochemical reaction. Besides, the electrocatalytic peak current of sulfide increases linearly with the square root of the scan rate ($I_{\text{pec}} = 0.553v^{1/2} + 0.948$, $R^2 = 0.995$, I_{pec} : electrocatalytic peak current of sulfide). This result indicates that the electrocatalytic oxidation of sulfide is a diffusion-controlled process.

The electrocatalytic oxidation of sulfide on the mediator modified electrodes can be explained by ECE mechanism (Scheme 1). According this mechanism, firstly the oxidized form of QH₂ at electrode surface undergoes a chemical addition–reduction process (Michael addition) with HS⁻ as a nucleophilic agent to produce the reduced adduct compound [51–53]. The thiol moiety in the structure of product facilitates the re-oxidation of the additional product due to its electron donating property. Finally the anodic peak potential shifts to less positive potentials. This mechanism

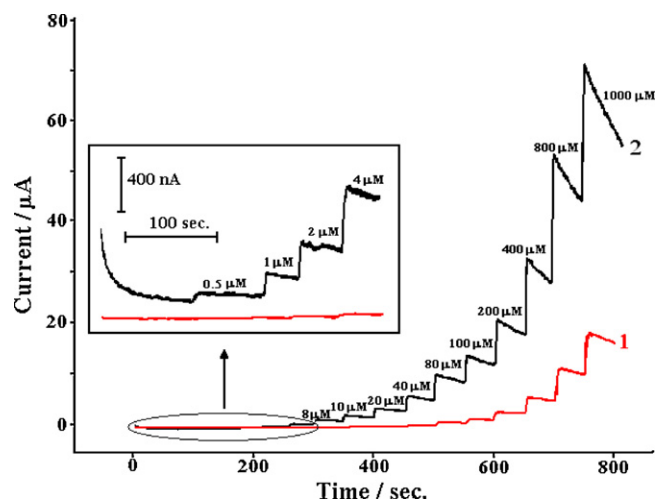


Fig. 3. Amperometric responses of pre-treated bare PGE (1) and PGE/QH₂ (2) to sulfide with different concentrations. (Supporting electrolyte: BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl; Applied potential: +300 mV.)

was also proposed for electrocatalytic oxidation of some thiolic compounds such as N-acetyl-L-cysteine [51], cysteamine [52] and pyrimidine-2-thiol [53] with catechol and catechol type compounds. In order to verify the possibility of this mechanism, the cyclic voltammograms of PGE/QH₂ were also recorded in the presence of cysteine and sulfite. While PGE/QH₂ exhibits slightly electrocatalytic activity toward the electro-oxidation of cysteine, it does not exhibit an electrocatalytic activity to sulfite at pH 8.0 buffer solution. This result showed that while bisulfite (HSO₃⁻) does not undergo Michael addition reaction, nucleophilic property of SH⁻ is better than cysteine.

3.3. Amperometric detection of sulfide

In order to obtain the best amperometric response of PGE/QH₂ toward sulfide, the effect of the applied potential on the electrocatalytic current of 20 μM sulfide was investigated by recording current–time curves. After a steady background current was obtained, 20 μM sulfide solution was added into the supporting electrolyte, BR buffer solution (pH 8.0) containing 0.1 M NH₄Cl, and the amperometric currents were measured from the current–time curves obtained at various applied potentials. The response currents for the electrocatalytic oxidation of sulfide became apparent at 0 mV and reached a maximum value at about +300 mV which was selected as the optimum potential. At this potential, the oxidation current of 20 μM sulfide was observed as a very small value when a bare PGE was used.

Fig. 3 presents the typical current–time curve for the successive addition of sulfide at different concentrations between 0.5 and 1000 μM. The current immediately changed after the addition of sulfide and reached another steady-state current within 5–10 s. PGE/QH₂ showed higher amperometric response to sulfide than PGE (Fig. 3). A relationship between the sulfide concentration and the peak current (I_p), which was obtained from the difference between the observed and the background currents, was investigated. Fig. 4 clearly shows that the calibration graph consists of two linear segments of 1–20 μM and 20–800 μM with slopes of 0.082 μA μM⁻¹ and 0.029 μA μM⁻¹, respectively. The calibration curve, in the range of 1–20 μM, was used to estimate the lower detection limit at the PGE/QH₂ surface. The limit of detection (LOD) was found to be 0.3 μM sulfide by using the equation $\text{LOD} = 3s_b/m$, where s_b is the standard deviation of the blank response and m is the slope of the calibration plot (0.082 μA μM⁻¹). The precision of the method was investigated by repeated measurement of the

Table 1
A comparison of analytical detection parameters obtained from PGE/QH₂ with different modified electrodes in the literature for electrocatalytic detection of sulfide.

Modified electrode	Medium	Met.	DP vs. Ag/AgCl	LR (μM)	LOD (μM)	Ref.
SPE modified with Tosflex anion exchange polymer including ferrocyanide mediator	PBS; pH 7.0	FIA Amp.	+300 mV	0.1–1000	0.0089	[17]
GCE modified cobalt pentacyanonitrosylferrate film	0.5 M KNO ₃	CV	Anodic potential of CV	75–770	46	[23]
GCE modified with vanadium pentoxide	0.1 M PBS; pH 10.28	CV	+600 mV	–	1.9	[24]
SP carbon electrode modified with industrially waste cinder/tetracyano nickel	0.1 M KCl/NaOH solution; pH 10	FIA Amp.	+700 mV	1–100	0.06	[25]
SP graphite electrode modified with hexadecylpyridinium-bis(chloranilate)-antimony (V)	0.25 M PBS in 1 M KCl; pH 6.5	Amp.	+80 mV	10–700	5	[26]
GCE modified with a cellulose acetate polymeric film bearing 2,6-dichlorophenolindophenol	0.25 M PBS in 0.5 M KCl; pH 7.25	FIA Amp.	+80 mV	20–1000	17	[27]
SP Pt electrode modified with 2-(4-fluorophenyl)indole-modified xerogel	0.05 M PBS in 0.05 M KCl; pH 5.5	FIA Amp.	+450 mV	10–2000	6	[28]
This work (PGE modified with QH ₂)	BRBS in 0.1 M NH ₄ Cl; pH 8.0	Amp.	+300 mV	1–20 and 20–800	0.3	

GCE: glassy carbon electrode; SP: screen printed; PBS: phosphate buffer solution; BRBS: Britton–Robinson buffer solution; Met.: methodology; FIA: flow injection analysis; CV: cyclic voltammetry; Amp.: amperometry; DP: detection potential of sulfide; LR: linearity range; LOD: limit of detection; Ref.: reference.

20 μM sulfide and the relative standard deviation (RSD) was found to be 2.8%.

The various analytical detection parameters such as detection potential of sulfide, linearity ranges and calculated LOD obtained from PGE/QH₂ were compared with other modified electrodes in the previously published reports for the electrocatalytic detection of sulfide. The results are illustrated in Table 1. As it can be seen from Table 1, the electrocatalytic detection potential (DP) of sulfide at PGE/QH₂ was better than the DP of the modified electrodes in the previous reports [23–25,28]. Although the DP results for the modified electrodes in Refs. [26,27] were better than PGE/QH₂, the proposed electrode had a better LOD and larger linearity range than the compared modified electrodes for the electrocatalytic determination of sulfide. As a result, it can be concluded that PGE/QH₂ had a significant LOD for the detection of sulfide.

Our literature search shows that many electrochemical methods have been described for the determination of sulfide with or without surface electrode modification with redox mediators [16–28]. In the present study, a new modified electrode using PGE/QH₂ behaves as a highly sensitive electrochemical sensor. Additionally when we consider the advantages of PGE such as disposability, low cost, easy modification, renewable surface, etc., it can be stated that the proposed method is very useful for the electrocatalytic oxidation and detection of sulfide. The advantages of the PGE/QH₂

can be written as: (i) usage of cheap pencil graphite as electrode, (ii) easy usage of electrochemical measurements, (iii) disposability, (iv) simple pretreatment with adsorption of quercetin, (v) higher sensitivity with a detection limit of 0.3 μM, (vi) compatibility at pH 8.0, (vii) allows sensitive amperometric detection at +300 mV, (viii) produces excellent calibration curve between 1–20 and 20–800 μM of linearity range, and ix) compatible with waste water measurements without interference.

The proposed method was applied for the determination of sulfide level in domestic and tannery waste water samples. The results for two kinds of samples are summarized in Table 2. The results were compared with those obtained with the methylene blue spectrophotometric method [7]. The accuracy of the method was also verified by the recovery studies implemented by adding standard sodium sulfide solutions to the samples. Recoveries of 95–115% were obtained in this study.

3.4. Interference study

The interference effect of various reductive species and common environmental matrix components on the signal of sulfide was investigated in the presence of 0.1 mM Na₂S. Interferents were added at concentrations 100 times higher than the sulfide concentration which is much higher than those normally exist in real samples. In the case of metal cations, 10 mM solutions of the corresponding nitrate or chloride salts were analyzed without sulfide present because it is known that metal ions form insoluble sulfides. The response for Co²⁺, Pb²⁺, Zn²⁺, Cu²⁺, Ni²⁺, Mn²⁺, Mg²⁺, Fe³⁺, Fe²⁺ and Ca²⁺ was not detectable. On the other hand, some of these metal ions were precipitated as their hydroxides in the supporting electrolyte medium (pH 8.0 BR buffer solution). In the case of anions, 10 mM solutions of the corresponding sodium or potassium salts were analyzed with sulfide. No interference effect was observed in the presence of SO₃²⁻, SO₄²⁻, S₂O₃²⁻, SCN⁻, NO₃⁻, NO₂⁻, CO₃²⁻, I⁻, Cl⁻ and F⁻. Only ascorbic acid, uric acid and dopamine exhibited significant positive interference. Since these compounds are rarely present in real sulfide samples, their interferences can be ignored.

Table 2

The sulfide levels in anaerobic waste water samples (n = 3).

Sample	Proposed method (mg L ⁻¹)	Reference method (mg L ⁻¹)
Domestic waste water	20 ± 2	21 ± 2
Tannery waste water	15 ± 1	17 ± 2

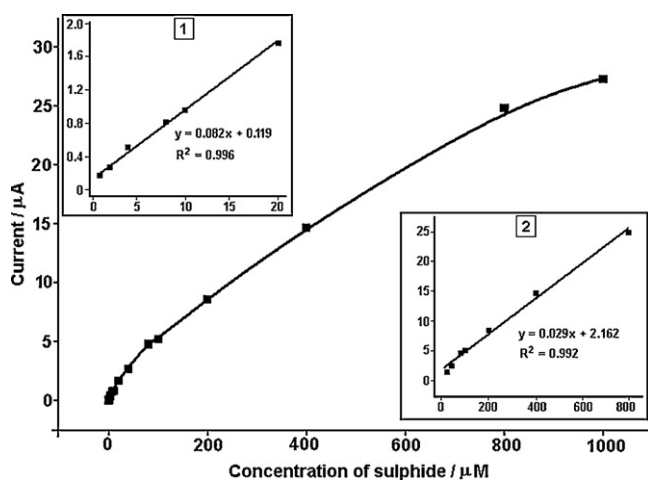


Fig. 4. Plot of electrocatalytic response current of PGE/QH₂ at 0.3 V (vs. Ag/AgCl) vs. sulfide concentration. Inset: the corresponding linear calibration curve (1) between 1 and 20 μM and (2) between 20 and 800 μM.

4. Conclusions

In this study, the development of a simple and highly sensitive electrochemical sensor for sulfide based on a new modified electrode, which was easily prepared by the adsorption of QH₂ on PGE surface, was described for the first time. PGE/QH₂ exhibited a good electrocatalytic response for the measurement of sulfide and two linear ranges were obtained between 1 and 20 μM and between 20 and 800 μM with a detection limit of 0.3 μM (based on 3σ_b). When we take into consideration the properties of PGE, PGE/QH₂ electrode is a robust, sensitive, lower-cost electrode which is suitable to construct an electrochemical sulfide sensor.

References

- [1] M. Shamsipur, J. Tashkhourian, H. Sharghi, *Instrum. Sci. Technol.* 33 (2005) 703–714.
- [2] N.S. Lawrence, J. Davis, R.G. Compton, *Talanta* 52 (2000) 771–784.
- [3] Z. Pawlak, A.S. Pawlak, *Talanta* 48 (1999) 347–353.
- [4] S. Balasubramanian, V. Pugalenthi, *Water Res.* 34 (2000) 4201–4206.
- [5] M.S.P. Silva, I.S. Da Silva, G. Abate, J.C. Masini, *Talanta* 53 (2001) 843–850.
- [6] Y.J. Yuan, H. Kuriyama, *Biotechnol. Lett.* 22 (2000) 795–799.
- [7] M.F. Mousavi, N. Sarlack, *Anal. Lett.* 30 (1997) 1567–1578.
- [8] M.A. Spaziani, J.L. Davis, M. Tinani, M.K. Carroll, *Analyst* 122 (1997) 1555–1557.
- [9] J.R. Fernández, J.M. Costa, R. Pereiro, A. Sanz-Medel, *Anal. Chim. Acta* 398 (1999) 23–31.
- [10] L.J.J. Catalan, V. Liang, C.Q. Jia, *J. Chromatogr. A* 1136 (2006) 89–98.
- [11] T. Ubuka, T. Abe, R. Kajikawa, K. Morino, *J. Chromatogr. B* 757 (2001) 31–37.
- [12] E. Bald, S. Sypniewski, *J. Chromatogr.* 641 (1993) 184–188.
- [13] D. Tang, P.H. Santschi, *J. Chromatogr. A* 883 (2000) 305–309.
- [14] M.L. Chen, M.L. Ye, X.L. Zeng, Y.C. Fan, Z. Yan, *Chin. Chem. Lett.* 20 (2009) 1241–1244.
- [15] J.M. Small, H. Hintelmann, *Anal. Bioanal. Chem.* 387 (2007) 2881–2886.
- [16] N.S. Lawrence, M. Thompson, C. Prado, L. Jiang, T.G.J. Jones, R.G. Compton, *Electroanalysis* 14 (2002) 499–504.
- [17] D.-M. Tsai, A.S. Kumar, J.-M. Zen, *Anal. Chim. Acta* 556 (2006) 145–150.
- [18] P. Jeroscheewski, C. Steuckart, M. Kuhl, *Anal. Chem.* 68 (1996) 4351–4357.
- [19] N.S. Lawrence, *Electroanalysis* 18 (2006) 1658–1663.
- [20] N.S. Lawrence, G.J. Tustin, M. Faulkner, T.G.J. Jones, *Electrochim. Acta* 52 (2006) 499–503.
- [21] C.E. Banks, A.S. Yashina, G.J. Tustin, V.G.H. Lafitte, T.G.J. Jones, N.S. Lawrence, *Electroanalysis* 19 (2007) 2518–2522.
- [22] M. Thompson, N.S. Lawrence, J. Davis, L. Jiang, T.G.J. Jones, R.G. Compton, *Sens. Actuators B* 87 (2002) 33–40.
- [23] L.L. Paim, N.R. Stradiotto, *Electrochim. Acta* 55 (2010) 4144–4147.
- [24] E.A. Khudaish, A.T. Al-Hinai, *J. Electroanal. Chem.* 587 (2006) 108–114.
- [25] J.-M. Zen, J.-L. Chang, P.-Y. Chen, R. Ohara, K.-C. Pan, *Electroanalysis* 17 (2005) 739–743.
- [26] M.I. Prodromidis, P.G. Veltsistas, M.I. Karayannis, *Anal. Chem.* 72 (2000) 3995–4002.
- [27] A.B. Florou, M.I. Prodromidis, M.I. Karayannis, S.M. Tzouwara-Karayanni, *Talanta* 52 (2000) 465–472.
- [28] G. Roman, A.C. Pappas, D.K. Demertzi, M.I. Prodromidis, *Anal. Chim. Acta* 523 (2004) 201–207.
- [29] N.S. Lawrence, J. Davis, L. Jiang, T.G.J. Jones, S.N. Davies, R.G. Compton, *Electroanalysis* 12 (2000) 1453–1460.
- [30] N.S. Lawrence, T. Jiang, T.G.J. Jones, R.G. Compton, *Anal. Chem.* 75 (2003) 2054–2059.
- [31] V. Stanic, T.H. Etsell, A.C. Pierre, R.J. Mikula, *Electrochim. Acta* 43 (1998) 2639–2647.
- [32] S.S.M. Hassan, S.A.M. Marzouk, H.E.M. Sayour, *Anal. Chim. Acta* 466 (2002) 47–55.
- [33] A. Manova, M. Strelec, F. Cacho, J. Lehotay, E. Beinrohr, *Anal. Chim. Acta* 588 (2007) 16–19.
- [34] J. Wang, A.-N. Kawde, E. Sahlin, *Analyst* 125 (2000) 5–7.
- [35] A. Özcan, Y. Şahin, *Electroanalysis* 21 (2009) 2363–2370.
- [36] A. Özcan, Y. Şahin, *Biosens. Bioelectron.* 25 (2010) 2497–2502.
- [37] A. Özcan, Y. Şahin, *Anal. Chim. Acta* 685 (2011) 9–14.
- [38] H. Karadeniz, B. Gülmez, F. Şahinci, A. Erdem, G.I. Kaya, N. Ünver, B. Kivcak, M. Özsöz, *J. Pharm. Biomed. Anal.* 33 (2003) 295–302.
- [39] E. Keskin, Y. Yardım, Z. Şentürk, *Electroanalysis* 22 (2010) 1191–1199.
- [40] A. Erdem, D.O. Arıksoysal, H. Karadeniz, P. Kara, A. Şengönlü, A.A. Sayiner, M. Özsöz, *Electrochem. Commun.* 7 (2005) 815–820.
- [41] Y. Yardım, E. Keskin, A. Levent, M. Özsöz, Z. Şentürk, *Talanta* 80 (2010) 1347–1355.
- [42] M. Özsöz, A. Erdem, K. Kerman, D. Özkan, B. Tuğrul, N. Topçuoğlu, H. Ekren, M. Taylan, *Anal. Chem.* 75 (2003) 2181–2187.
- [43] M.R. Majidi, K.A. Zeynali, B. Hafezi, *Microchim. Acta* 169 (2010) 283–288.
- [44] M. Biesaga, K. Pyrzynska, *Crit. Rev. Anal. Chem.* 39 (2009) 95–107.
- [45] P. Xiao, F. Zhao, B. Zeng, *Microchem. J.* 85 (2007) 244–249.
- [46] H.R. Zare, M. Namazian, N. Nasirizadeh, *J. Electroanal. Chem.* 584 (2005) 77–83.
- [47] D. Zielinska, B. Pierozynski, W. Wiczowski, *J. Electroanal. Chem.* 640 (2010) 23–34.
- [48] P.Y. Chen, R. Vittal, P.C. Nien, K.C. Ho, *Biosens. Bioelectron.* 24 (2009) 3504–3509.
- [49] J. Kang, L. Zhuo, X. Lu, X. Wang, *J. Solid State Electrochem.* 9 (2005) 114–120.
- [50] J.B. He, G.P. Jin, Q.Z. Chen, Y. Wang, *Anal. Chim. Acta* 585 (2007) 337–343.
- [51] J.B. Raoof, R. Ojani, M. Amiri-Aref, F. Chekin, *J. Appl. Electrochem.* 40 (2010) 1357–1363.
- [52] J.B. Raoof, R. Ojani, F. Chekin, *J. Mater. Sci.* 44 (2009) 2688–2693.
- [53] L. Fotouhi, L. Behrozi, M.M. Heravi, D. Nematollahi, *Phosphorus Sulfur Silicon Relat. Elem.* 184 (2009) 2749–2757.