Pyrocatechol Violet Modified Graphite Pencil Electrode for Flow Injection Amperometric Determination of Sulfide

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Abstract

In this study, pyrocatechol violet (Pcv) is proposed for the first time as an efficient electrocatalyst for oxidation of sulfide and flow injection analysis (FIA) of sulfide. A graphite pencil electrode (GPE) was modified with Pcv via immersion of the GPE into 0.01 M Pcv solution for 15 min. Cyclic voltammograms (CVs) demonstrated that Pcv/GPE exhibits a good electrocatalytic performance due to shift in the potential from +400 at bare GPE to +70 mV at Pcv/GPE and obtaining an enhancement in the peak current compared with the bare GPE. A linear range between 0.25 and 250 μM sulfide with a detection limit of 0.07 μM was obtained from the recorded current-time curves in Flow Injection Analysis (FIA) of sulfide. Sulfide in water samples was also successfully determined using the proposed FI amperometric methods.

Keywords : Graphite Pencil Electrode, Pyrocatechol Violet, Electrocatalytic Oxidation, Sulfide, Flow Injection Analysis

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1. Introduction

Sulfur (S^{2-}), the reduced form of sulfur compounds (such as HS^- and H_2S), is generally formed in waste water by anaerobic bacteria on organic matter [1]. It has been reported that over 50 ppm of sulfide concentration was declared as to be high toxicity which is harmful to the human health [2]. Beside toxic effects, the studies in the last decade approved that H_2S acts a significant role in extending of the postharvest shelf life of many herbal foods such as vegetables and fruits [2,3,4]. Also, sulfide salts have been commonly used to control the toxic metal levels in environment, because most of metal sulfides are insoluble and they are easily found as precipitated in waste waters [1]. Due to the mentioned reasons above, detection of sulfide has aroused significant interest on the analytical researchers [1]. Therefore, selective, rapid and sensitive determination of sulfide has aroused a massive significance and interest for scientists [2].

Pyrocatechol violet (Pcv), 1,2-Benzenediol, 4,4'-(3H-2,1-benzoxathiol-3-ylidene)bis-, S,S-dioxide; is an aromatic sulfonic acid dye synthesized from the condensation reaction between pyrocatechol and o-sulfobenzoic acid anhydride in the mole ratio of 2:1 [5]. Pcv has been widely used as a colorimetric and efficient complexometric reagent as well as an indicator in various analytical studies because it forms stable colored complexes with various metal ions [5-9]. Pcv can be strongly adsorbed onto inorganic materials due to containing catechol groups which have $-\text{OH}$ groups bonding to the adjacent carbon atoms of the aromatic ring; furthermore, it has conjugated $\pi-\pi$ bonds [9,10]. In addition, Pcv can be polymerized on electrode surfaces so that obtained polymeric films of Pcv possess a larger surface area, more active sites, better conductivity, etc. in comparison with a modified electrode prepared in its monomeric form [9-13]. Therefore, Pcv has been used as an efficient redox mediator for electrocatalytic oxidation of several biologically and environmentally important compounds and also for the sensitive and selective determination of metal ions [9-23]. For example, the electrocatalytic oxidation of NADH [9,13], hydrazine [10-12] and H_2O_2 [10,17-19], construction of ethanol biosensor [9], and the simultaneous determination of uric acid, xanthine and hypoxanthine [12] have been reported using Pcv-

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modified electrodes. Moreover, voltammetric determination of Cd and Pb [11], Cu species [20] and Al [21] was successfully achieved at various types of Pcv-modified electrodes.

Chemically-modified electrodes (CMEs) prepared with organic redox mediators have been extensively used in the determination of various compounds based on their electrocatalytic oxidation or reduction at CMEs. One of the applications of the CME is determination of sulfide based on the electrocatalytic oxidation of sulfide at the CME. Oxidation of sulfide at bare electrodes has some drawbacks, such as a highly-irreversible and broad oxidation peak with overpotential, poor selectivity and unstable and weak analytical signals resulting in low sensitivity due to adsorption of oxidation products of the sulfide onto the electrode surface. In order to overcome these problems, various organic redox mediators such as hematoxylin, quercetin, calmagite, methylene blue, alizarin, hemin, ferricyanide, etc. have been used for the electrocatalytic oxidation of sulfide [22-34]. It can be said that amperometric [23-31], voltammetric [32-34] and potentiometric methods [35] have been successfully developed for the electrochemical determination of sulfide. However, our search of the literature shows that Pcv used as an efficient electrocatalyst for many compounds has so far not been used for the electrocatalytic oxidation of sulfide.

In this study, Pcv was modified onto the GPE by the adsorption and flow injection analysis (FIA) of sulfide is proposed based on its electrocatalytic oxidation at the Pcv/GPE, for the first time. Recently, the GPE has attracted a great deal of attention as a working electrode in electroanalytical studies since it possesses important properties, such as high electrochemical reactivity, ease of surface modification, high stability, low cost, disposable electrode material, and avoidance of time-consuming polishing procedures [9,23-25,36-45]. Thus the combination of an advantageous electrode (GPE) and the electrocatalytic property of redox mediator (Pcv) offer a selective, sensitive and cheap FI amperometric sulfide sensor.

2. Experimental

2.1. Chemicals, Reagents and Apparatus

All the chemicals used in this study are in analytical grade. Pcv, sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and cysteamine hydrochloride were

purchased from Sigma-Aldrich. L-ascorbic acid, uric acid, citric acid, salicylic acid, L-glutamic acid, D-glucose, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, NaOH, CH_3COOH , H_3BO_3 , H_3PO_4 and KCl were supplied from Merck Company. Dopamine hydrochloride was bought from Alfa-Easer.

The stock solutions of 0.10 M sodium sulfide nonahydrate and 0.01 M Pcv were prepared in deoxygenated 10 mL of 0.10 M NaOH and in 5 mL of deoxygenated ultrapure water, respectively. The stock Na_2S solution was daily prepared and standardized by the iodometric method. Standard Na_2S solutions were prepared by dilution of standardized stock solution (0.10 M Na_2S) in deoxygenated pH 9.0 Britton Robinson buffer solution (BRBS). The BRBS was prepared by mixing the appropriate volumes of acid solution (including 0.040 M H_3PO_4 , 0.040 CH_3COOH , 0.040 H_3BO_3 , 0.10 or 1.0 M KCl) and alkaline solution (including 0.20 M NaOH, 0.10 M or 1.0 M KCl) and the pH (9.0) of buffer solution was arranged by a Hanna HI 221 pH-meter with combined glass electrode. Ultrapure water from Elga Option Q7B water purification system (18.2 $\text{M}\Omega \text{ cm}$) was used in preparation of the all solutions.

The traditional three-electrode system consisting of Pt wire, $\text{Ag}/\text{AgCl}_{(\text{sat. KCl})}$ and graphite pencil electrode (GPE) was used in the electrochemical experiments. GPEs supplied from Tombow 2B (diameter: 0.5 mm, length: 10 cm) was placed into holder and a geometric area of 0.159 cm^2 (total length: 1.0 cm) was used in all electrochemical experiments. Electrochemical measurements were carried out using devices reported in our previous study [14].

2.2. Experiments on Electrocatalytic Oxidation at Modified Electrode

A procedure in a previously published article was partially modified and used for the modification of Pcv onto GPE surface in this study [14]. Differently from this published procedure, GPE was immersed in the solution of 0.01 M Pcv stock solution for 15 min, washed with ultra-pure water and dried at room temperature before use. To show the electrocatalytic oxidation of sulfide at the Pcv/GPE, CVs of bare GPE and Pcv/GPE were recorded in the absence and presence of 0.20 mM sulfide at the pH 9.0 BRBS with 0.10 M KCl in the potential range between -0.30 V and +0.60 V at a scan rate of 50 mV s^{-1} .

2.3. Flow Injection Analysis of Sulfide at Pcv/GPE

A home-made electrochemical flow cell proposed in our previous studies [40-42] was also used for the FIA of sulfide at the Pcv/GPE. The FIA of sulfide was performed by recording current time curves at a constant potential using a carrier solution of pH 9.0 BRBS with 1.0 M KCl. In this context, the optimum working potential and flow rate values were determined by injection of 1.0×10^{-4} M sulfide into the FIA system. To determine the analytical performance parameters (linearity range, limit of detection, reproducibility, selectivity) of the FI amperometric sulfide sensor, sulfide solutions prepared at different concentrations, carrier solution as a blank, a sulfide solution with a known concentration and sulfide solutions including possible interference compounds were individually injected into the FIA system. For each experiment, FI amperometric current time curves (Figures) were recorded under optimized conditions.

In the final step, the proposed sensor was applied to determine sulfide in the water samples. For this, two water samples (sea water from the Dardanelles Straits and tap water obtained from the municipality of Çanakkale, Turkey) were used. FI amperometric responses of the Pcv/GPE were monitored by injection of these water samples into the FIA system under optimized conditions after the water samples had been spiked with sulfide in BRBS including 1.0 M KCl.

3. Results and Discussion

3.1. Electrochemical Characterization and Behavior of Pcv/GPE

In our previous report [14] studies on the electrochemical characterization with electrochemical impedance spectra (EIS) and electrochemical behavior of Pcv modified GPE with CVs was performed as detail. The reported EIS showed that transfer resistance (R_{ct}) values of 200 Ω for obtained the bare GPE increased to 250 Ω by adsorption of GPE with Pcv. The rather high R_{ct} value of the modified electrode explained by formation of negatively charged sulfonic acid group in the Pcv which repel the anionic redox probes ($[\text{Fe}(\text{CN})_6]^{3-/4-}$) diffused to electrode surface. This electrostatic repulsion obstructs electron transfer between redox probe and electrode and therefore R_{ct} values of the bare GPE slightly increased by adsorp-

tion of Pcv onto the electrode surface. These results indicate that the modification of Pcv on the GPE was achieved via adsorption procedure. In addition, reported CVs showed that the anodic and cathodic peak currents of Pcv/GPE increased linearly based on scan rate indicates an adsorption-controlled process taking place in the solution [14]. Moreover, it was reported that the all peak potentials of Pcv changed depending on pH between pH 2 and 10 [14].

3.2. Electrocatalytic Oxidation of Sulfide at Pcv/GPE

Fig. 1 shows CVs of 0.2 mM sulfide in pH 9.0 BRBS with 0.1 M KCl at the bare GPE and Pcv/GPE. While bare GPE has not any peak in its baseline CV (Fig. 1a), oxidation of sulfide at bare GPE started at +100 mV and turned into a broad and irreversible oxidation peak located at +400 mV (Fig. 1b). On the other hand, two redox couples located at anodic (-20 mV and +100 mV) and cathodic (-60 mV and +75 mV) directions attributed to reversible oxidation of the catechol groups to quinone were obtained from the CVs of the Pcv/GPE in the absence of sulfide (Fig. 1c). Upon the addition of 0.20 mM Na_2S , a sharp enhancement in current at these anodic peaks was observed at the potential of +70 mV. Simultaneously, the cathodic peak that located at +75 mV disappeared and the current of the other cathodic peak located at -60 mV decreased (Fig. 1d). In general, decrease in overpotential and enhance-

Fig. 1. CVs of bare GPE (a and b) and Pcv/GPE (c and d) in absence (a and c) and presence (b and d) of 0.20 mM Na_2S in pH 9.0 BRBS with 0.10 M KCl at 50 mV s^{-1} .

Scheme 1. Schematic representation of preparation of modified electrodes and proposed mechanism for electrocatalytic oxidation of sulfide at Pcv/GPE.

ment in catalytic current are both significant parameters in consideration of electro catalytic effect. The obtained results showed that Pcv/GPE exhibits a favorable electro catalytic effect towards the oxidation of sulfide. Similar electrocatalytic activity of Pcv-modified electrodes was also reported for other compounds such as NADH [9,13], hydrazine [14-16] and H_2O_2 [10,17-19].

An Electrochemical-Chemical-Electrochemical (ECE) mechanism proposed for electrocatalytic oxidation of sulfide at organic redox mediators with modified electrodes in previous studies can also be proposed for the Pcv/GPE [23-25]. Scheme 1 shows the electrocatalytic oxidation mechanism of sulfide at the Pcv/GPE. In the first step, Pcv on the GPE surface is oxidized by reversible redox reaction of the catechol groups, which convert to quinone in the structure of Pcv. A large part of the sulfide exists in HS^- form in the pH 9.0 BRBS and the HS^- acts as a nucleophilic agent for a Michael addition-reduction reaction. Thus, this reaction takes place between the oxidized form of Pcv and HS^- and a reduced adduct compound forms at the end of this reaction in the second step. In the last step, thiol moiety in the structure of the product facilitates re-oxidation of the additional product due to its electron-donating property

and the formed reduced compound (catechol groups) is further electrochemically reoxidized to quinone groups, so the anodic peak current of the mediator increases in the presence of sulfide. After formation of the adduct compound, the electrocatalysis proceeds through a chemical reaction between the oxidized form of the adduct compound (Pcv-SH(ox)) and sulfide. Pcv-SH(ox) is reduced to Pcv-SH(red), while the sulfide is oxidized to SO_3^{2-} (Scheme 1). In the final step, Pcv-SH(red) is reoxidized by giving its electrons to the electrode.

3.3. Amperometric Determination of Sulfide at Pcv/GPE in FIA system

Before starting to the FIA of sulfide using proposed electrode, two parameters (working potential and flow rate) which affect the peak current were optimized. The diagrams of 1.0×10^{-4} M sulfide were recorded at bare GPE and the Pcv/GPE at various working potentials. The plot of peak currents versus working potential for both electrodes shown in Fig. 2A illustrates that the response of the Pcv/GPE toward sulfide is better than the bare GPE and that the sulfide oxidized at a more negative working potential due to electrocatalytic activity of the Pcv/GPE. For the following studies, a working potential of +100 mV was selected as optimum working potential because, electrocatalytic currents of 1.0×10^{-4} M sulfide at +100 mV at the Pcv/GPE were fifty times higher than its oxidation current at the GPE. The diagrams of 1.0×10^{-4} M sulfide at the Pcv/GPE at +100 mV were recorded at various flow rates. It can be seen that the peak currents heightened by increasing the flow rate until 2.0 mL min^{-1} then decreased after this point. As can be seen inset in Fig. 2B, the maximum current was obtained at a flow rate of 2.0 mL min^{-1} . Therefore, this value was used as optimum flow rate for the following studies.

Fig. 3A and 3B show diagrams of various concentrations of sulfide recorded at the bare GPE and Pcv/GPE, respectively, in the carrier stream of the pH 9.0 BRBS including 1.0 M KCl under optimized conditions (working potential of +100 mV and a flow rate of 2.0 mL min^{-1}). Peak currents increased in accordance with an increase of sulfide concentration for both electrodes; however, peak currents obtained from the Pcv/GPE were found to be significantly higher compared with the bare GPE for all concentrations. The plots of peak current versus sulfide con-

Fig. 2. A) Graph of electrocatalytic current of sulfide (0.10 mM) versus working potential for bare GPE (a) and Pcv/GPE (b) and B) Graph of electrocatalytic current of sulfide (0.10 mM) versus flow rate.

Fig. 3. Diagrams of A) bare GPE and B) Pcv/GPE according to increased sulfide concentration in Ar-saturated pH 9.0 BRBS with 1.0 M KCl at 100 mV and 2.0 mL min⁻¹.

centration and obtained calibration curves are shown in Figs. 4A and 4B for the bare GPE and Pcv/GPE, respectively. As displayed in the inset of Fig. 4A,

peak currents of sulfide at the bare GPE increased linearly depending on sulfide concentration ranging from 1.0 to 250 μM with a linear equation of $I (\mu\text{A}) =$

Fig. 4. Graph of current versus sulfide concentration for A) bare GPE and B) Pcv/GPE (Inset: Calibration curves between current and concentration of Na₂S for each electrode).

Table 1. Comparison of merits of the Pcv/GPE with other modified electrodes prepared using redox mediators in previous studies.

Modified Electrode	Detection Potential (mV)	Linearity range (μM)	LOD (μM)
Hematoxylin modified GPE [23]	+200 vs. Ag/AgCl	1-200	0.4
Quercetin modified GPE [24]	+300 vs. Ag/AgCl	1-20 & 20-800	0.3
Poly-calmagite modified GPE [25]	+300 vs. Ag/AgCl	0.1-500	0.03
Hematoxylin-MWCNT modified Carbon paste electrode [26]	+150 mV vs. Ag/AgCl	0.5-150	0.2
Poly-methylene blue modified GCE [28]	+150 vs. Ag/AgCl	0.5-500	0.27 0.15
GCE modified with a cellulose acetate polymeric film bearing 2,6-dichlorophenolindophenol [27]	+80 vs. Ag/AgCl/	20-1000	17
Hemin functionalized reduced graphene oxide modified GCE [28]	+50 vs. Ag/AgCl	2-212	1.3
Ferricyanide polymeric ionic liquid modified Screen printed carbon paste electrode [29]	0.0 vs. Ag/AgCl	1-3000	0.0129
Screen printed Pt electrode modified with 2-(4-fluorophenyl) indole-modified xerogel [31]	+450 vs. Ag/AgCl	10-2000	6
Alizarin and reduced graphene oxide nanosheets modified GCE [33]	+465 vs. Ag/AgCl	6-3280	1
Pcv modified GPE (This work)	+100 vs. Ag/AgCl	0.25-250	0.07

$0.0009C(\mu\text{M}) + 0.002$ ($R^2 = 0.9982$). However, peak currents of sulfide obtained from diagrams of the Pcv/GPE increased linearly between 0.25 and 250 μM sulfide concentration, with a linear equation of $I(\mu\text{A}) = 0.0446C(\mu\text{M}) + 0.0528$ ($R^2 = 0.9993$), as shown in Fig. 4B inset. In addition, the limit of detection (LOD) was found to be 0.07 μM based on $3 \times S_{\text{blank}}/\text{slope}$. Slope of calibration curves for both electrodes show that the FI amperometric response of the Pcv/GPE is about 50 times higher than the

bare GPE due to the higher sensitivity and efficient electrocatalytic activity of the Pcv/GPE toward oxidation of sulfide.

To discuss the advantages of the proposed method for electrocatalytic determination of sulfide, results of the Pcv/GPE experiment were compared with previous studies in which various organic redox mediator-modified electrodes were used. As seen in Table 1, the LOD of the Pcv/GPE is lower than that of other organic redox mediator-modified electrodes, indicat-

Fig. 5. The diagrams of Pcv/PGE recorded by injections of solutions 1:10 ratios including sulfide and interfering molecules. (Carrier solution: Ar-saturated pH 9.0 BRBS with 1.0 M KCl at 100 mV and 2.0 mL min⁻¹)

ing that the proposed electrode has good sensitivity. Moreover, FI amperometric detection of sulfide at the Pcv/GPE was carried out at +100 mV, which is a more negative value than the detection potential of some modified electrodes given in Table 1. On the other hand, those redox mediators were generally modified on expensive electrodes with low reproducibility and involving time-consuming polishing steps compared to the GPE. Although hematoxylin [23] quercetin [24] and calmagite [25] modified GPEs were used for electrocatalytic oxidation of sulfide in our previous studies, FI amperometric determination of sulfide was studied only at a calmagite-modified GPE. It is generally known that interference effects of some biologically important molecules (such as dopamine, ascorbic acid and uric acid etc.) are intensive at high potentials. However, the Pcv/GPE exhibits significant sensitivity for the detection of sulfide at lower detection potential (+100 mV) compared to the calmagite-modified GPE (+250 mV). As a result, (i) Pcv, (ii) GPE and (iii) FIA system were firstly combined for sensitive FI amperometric determination of sulfide.

3.4. Interference Effect of Compounds on FI Amperometric Detection of Sulfide

Diagrams of sulfide at the Pcv/GPE were recorded in the presence of some anions (SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- , NO_2^- , NO_3^- , CO_3^{2-} , Cl^- , F^- , Br^- , I^- , ClO_3^- , BrO_3^- , IO_3^-) and these result shows that in Fig. 5. The FI amperometric curve recorded by injections of solutions including varying ratios of sulfide:interfering molecules which are 1:1, 1:2, 1:5 1:10. Also some compounds such as hydrazine, hydrogen peroxide, ascorbic acid (AA), uric acid (UA) and dopamine

(DA), which are usually found in environmental and biological samples were used for interference studies. An error rate of less than 10% was taken into consideration for the interference effect of substances on the determination of 1.0×10^{-4} M sulfide at different interference ratios (1:1, 1:2, 1:5 and 1:10). Results of these interference experiments demonstrated that all studied anions except for IO_3^- do not exhibit any interference effect on sulfide. However, some compounds such as hydrazine, AA, UA and DA had a considerable impact, whereby the peak current of the sulfide increased significantly in the presence of these compounds. However, their interference cannot be considered as significant due to the rare presence of these compounds in environmental samples.

3.5. Determination of Sulfide in Water Samples with Proposed Electrode

Two water samples were used for investigation of the applicability of the proposed method in real samples; sea water from the Dardanelles Straits and tap water obtained from the municipality of Çanakkale, Turkey. FI amperometric responses of the Pcv/GPE were monitored by injection of the water samples into the FIA system under optimized conditions after the water samples had been spiked with sulfide in BRBS including 1.0 M KCl. The obtained results (Table 3) demonstrated that the proposed electrode has good recovery in the range of 98.4 to 104.4% for determination of sulfide. It can be concluded that a practical, fast and cheap FI amperometric method for sulfide detection in water samples was successfully developed using an efficient redox mediator (Pcv) modified GPE.

Table 2. Recovery values of sulfide added to real water samples (n=5).

Sample	Added (mol L ⁻¹)	Found (mol L ⁻¹)	Recovery (%)
Tap water	1.0×10 ⁻⁶	9.89×10 ⁻⁷ ±4.5×10 ⁻⁸	98.9
	1.0×10 ⁻⁵	1.02×10 ⁻⁵ ±2.3×10 ⁻⁷	102.0
	7.5×10 ⁻⁵	7.58×10 ⁻⁵ ±9.3×10 ⁻⁷	101.2
	1.0×10 ⁻⁴	9.99×10 ⁻⁵ ±2.8×10 ⁻⁶	99.9
	2.5×10 ⁻⁴	2.58×10 ⁻⁴ ±4.1×10 ⁻⁶	103.0
Sea water	1.0×10 ⁻⁶	1.02×10 ⁻⁶ ±5.8×10 ⁻⁸	102.0
	1.0×10 ⁻⁵	1.04×10 ⁻⁵ ±5.7×10 ⁻⁷	104.0
	7.5×10 ⁻⁵	7.38×10 ⁻⁵ ±2.8×10 ⁻⁷	98.5
	1.0×10 ⁻⁴	9.85×10 ⁻⁵ ±4.9×10 ⁻⁷	98.5
	2.5×10 ⁻⁴	2.55×10 ⁻⁴ ±2.6×10 ⁻⁶	104.4

4. Conclusions

In this study, a Pcv-modified GPE was used for electrocatalytic oxidation and FIA of sulfide for the first time. Comparison of the CVs of the Pcv/GPE with bare GPE show that the oxidation potential of sulfide shifted to more negative direction and peak current increased 2.5 fold in the case of CVs of the Pcv/GPE. These results have been showed that Pcv/GPE exhibits the typical electrocatalytic properties of a modified electrode. Although Pcv has been used an efficient organic redox mediator for electrocatalytic oxidation of various compounds, it has not been used for electrocatalytic determination of sulfide in a FIA system. The proposed FI amperometric sensor has a wide linear range between 0.25 and 250 µM with a detection limit of 0.07 µM. In addition, the applicability of proposed sensor to detection of sulfide in water samples was tested with a good accuracy. It can be concluded that the use of a Pcv/GPE in a FIA system exhibits a cheap, disposable, sensitive and rapid electrochemical approach for sulfide detection.

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