

A Electrochemical Sensor based on Poly (Sulfosalicylic Acid) Film Modified Electrode and Application to Phenol Detection in Oilfield Wastewater

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Abstract

In this paper, a highly sensitive and selective method based on the poly (sulfosalicylic acid) modified electrode (PSA /CPE) to detect phenol was established. The morphologies and interface properties of PSA film were characterized by scanning electron microscopy and electrochemical impedance spectroscopy. It was illustrated that the PSA/CPE had an excellent electrocatalytic ability towards the oxidation of phenol. Meanwhile the influence of parameters such as pH and scan rate effect on the analytical performance of the sensor was evaluated. Moreover, the interference from o-nitrophenol can be neglected. By using differential pulse voltammetry (DPV), linear calibration curves were obtained as 5–175 and 220–555 $\mu\text{mol L}^{-1}$ for phenol. The detection limits are 2.2 $\mu\text{mol L}^{-1}$ for phenol. With favorable selectivity and sensitivity, the present method has been applied to the determination of phenol in oilfield wastewater.

Keywords: Electrochemical sensor, Oilfield wastewater, Phenol detection, Sulfosalicylic acid, Surface modification.

1. Introduction

Oil and gas production often accompany the production of large quantities of wastewater¹. The wastewater usually contains a number of toxic contaminants, including petroleum hydrocarbons, heavy metals, radionuclides, and treatment process chemicals². Generally, most of produced wastewater was reused and reinjected into the underground to enhance oil recovery after certain treatment. But there are also large amounts of produced wastewater were directly discharged into the environment³. If released into the environment without treatment and determination, the wastewater may have adverse effects on both environment and human beings.

Phenol and a considerable number of its derivatives are important but toxic compounds which extensively exist in the oilfield wastewater^{4,5}. It is well-known that phenol is carcinogenic and toxic even at low concentrations, is potentially fatal if ingested, inhaled and absorbed by skin and that may cause severe burns and affect central nervous system, liver and kidney⁶. Owing to its toxicity, the US Environmental Protection Agency (EPA) and the European Union (EU) have now listed phenol as a priority toxic pollutant and set a standard permeable total limit of 0.5 ppb in drinking water⁷. Therefore, it is very important to develop the effective

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methods to quantitatively determine phenol not only for oilfield environment and the research of the wastewater treatment but also for diagnostic and pathological purpose.

There have been many analytical techniques reported to detect phenol sensitively and selectively, such as gas chromatography/mass spectrometry, liquid chromatography, capillary electrophoresis, ultraviolet spectrophotometry and electrochemistry⁸⁻¹². Particularly, electrochemical methods are very convenient to the analysis of this kind of organic compounds¹³⁻¹⁵. Moreover, to improve the sensitivity and selectivity of the detection method, the bare electrode surface were modified with various polymeric materials, including layered double hydroxide¹⁶, gold nanoparticles¹⁷, multiwall carbon nanotubes¹⁸ bacteria¹⁹ and HDTMA-bentonite²⁰. However, it should not be neglected that the fabrication of the electrodes was so complex that the reproducibility and stability of the method are not very favorable, thus leading to many limitations in practical applications.

Polymer film, which can be easily deposited onto the surface of the electrode by electropolymerization, has significant advantages including easier fabrication process, more excellent electrochemical catalytic ability, better physical stability over composites as modifier. In recent years, many researches which use polymer film modified electrodes to determination of phenol have been reported, such as poly(vinyl alcohol) film coated carbon paste electrode(CPE)²¹, poly(3,3'-diaminobenzidine) modified glassy carbon electrode(GCE)²², poly(zincon) film coated CPE²³, and so on. As we all know, there have been very few reports about poly (sulfosalicylic acid) film-modified carbon paste electrode.

Herein we developed a new analytical method based on the poly (sulfosalicylic acid) modified electrode (PSA /CPE) to detect phenol, and the electrochemical behaviors of phenol at the resulting electrode were carefully studied. At the same time, the interferences of o-nitrophenol on the determination of phenol were removed. Because of high electron density of carbonyl and sulfonic groups in sulfosalicylic acid molecule (COO^- and SO_3^-), the PSA film has high concentrations of negatively charged surface-functional groups. The modified electrode showed excellent electrocatalytic properties with obvious reduction of overpotential and enhancement of oxidation current. Moreover, the modified electrode showed good sensitivity, selectivity and reproducibility, making it suitable to determine the content of phenol at trace level in oilfield wastewater.

2. Experimental

2.1 Reagents and Chemicals

Sulfosalicylic acid(SA) was purchased from Shanghai Chemical Reagents Company (China). Phenol, o-nitrophenol, catechol was obtained from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). All the reagents were of analytical grade and used without any further purification. Phosphate buffer solutions (PBS) were prepared with $0.1 \text{ mol L}^{-1} \text{ K}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$ and $0.1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ or KOH were used to adjust the value of pH. Double distilled water was used throughout the experiments, and all the experiments were conducted at room temperature.

2.2 Apparatus

Electrochemical measurements were performed on a Reference 600 electrochemical Workstation (Gamry Instruments in Philadelphia, USA) with a conventional three-electrode system, where a modified and bare CPE (carbon paste electrode) as the working electrode, a platinum wire and SCE (saturated calomel

electrode) as the counter electrode and the reference electrode, respectively. All the value of pH was adjusted by a pH meter (FE20K, Mettler Toledo, China) and the surface morphology of the resultant electrodes were observed with scanning electron microscope (JSM-6700F, Japan).

2.3 Preparation of the Modified Electrode

CPE was prepared according to our prior report²³. First, mix graphite powder and mineral oil at the ratio of 5:0.7 (w/w) carefully, and then pack the mixture into a plastic tube (3 mm diameter; 3 cm depth). The electrical contact was provided by a copper wire connected to the paste in the inner hole of the tube. Importantly, a well prepared CPE must be polished successively with sulfate paper to obtain a mirror surface, rinsed with double distilled water, and subsequently treated in pH 7.0 PBS by repetitive scanning in the potential range of -2.0 V and 2.0 V at a scan rate of 100 mV s^{-1} to remove contaminations, activate electrode, until a stable background was obtained before modification.

Cyclic voltammetry (CV) method was used to form polymerization film. The polymertic film was deposited on the surface of CPE by cyclic sweeping from -1.0 to 2.0 V at 100 mV s^{-1} for 8 cycles in 0.1 mol L^{-1} PBS (pH 5.0) containing 10 mmol L^{-1} SA. Prior to use, the modified electrode was rinsed with double distilled water, and then treated in pH 7.0 PBS by repetitive scanning in the potential range from 0.4 V to 1.0 V at a scan rate of 100 mV s^{-1} until a stable blank background was obtained.

3. Results and Discussion

3.1 Characterization

Fig. 1A displays the continuous CVs for the electrochemical polymerization of SA over the range of -1.0 to 2.0 V at 100 mV s^{-1} for 8 cycles. In the first cycle, one anodic peak at 1.27 V was observed. From the second cycle on, a new oxidation peak appeared with potential at 0.59 V, and the largest peaks were observed upon continuous scanning in the subsequent cycles. It is clear that the anodic peak at 0.59 V corresponding to the oxidation of SA increased gradually with cyclic time increasing and trended to be stable after 6 scans. This phenomenon implies the formation of poly-SA membrane on the surface of CPE. Fig. 1B shows the typical morphology of PSA film by SEM, indicating that the film has a fine cluster-like structure. This confirms that the PSA film was formed and successfully deposited on the surface of carbon paste electrode²⁴.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to monitor the features of the modified electrode surface. The electron transfer resistance (R_{et}) at the electrode surface is equal to the diameter of the semicircle obtained in EIS and can be used to describe the interface properties of the electrode. Fig. 2A depicts the Nyquist diagrams of the bare CPE and PSA/CPE measured in the presence of $5.0 \text{ mmol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6](1:1)$ with $0.1 \text{ mol L}^{-1} \text{ KCl}$ at the formal potential of $\text{Fe}(\text{CN})_6^{4-/3-}$. A large semicircle diameter ($R_{\text{et}}=10.7 \text{ k}\Omega$) with an almost straight tail line is observed by the bare CPE (curve a). The large semicircle demonstrates the high electron transfer resistance of the CPE to the redox probe dissolved in the electrolyte solution. In case of PSA/CPE (curve b), it can be seen that a much smaller semicircle diameter ($R_{\text{et}}=0.8 \text{ k}\Omega$) appeared. This suggests that the resistance to the redox reaction was lower at PSA/CPE than that at the bare CPE. Cyclic voltammetry (CV) experiments (Fig. 2B) were also studied in $5.0 \text{ mmol L}^{-1} [\text{Fe}(\text{CN})_6]^{3-/4-}$ solution dissolved in $0.1 \text{ mol L}^{-1} \text{ KCl}$ with a potential range of -0.4 to 0.8 V. It can be seen that the redox peaks at the PSA/CPE are well-shaped while the

peak shape was deteriorated at the bare CCE. According to EIS, the results of CV indicated that the PSA film had good conductivity and the resulting PSA/CPE composite can accelerate electron transfer between the objective molecules and electrode surface.

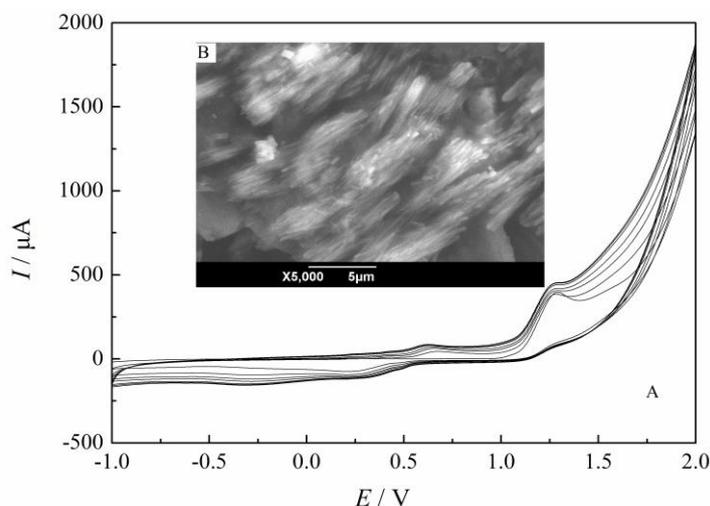


Figure 1 - (A) Continuous CVs for the Electrochemical Polymerization of Sulfosalicylic Acid Over the Range of -1.0 to 2.0 V at 100 mV s⁻¹ for 10 Cycles; Inset (B) Shows the SEM Image of PSA/ CPE

3.2 CV Curves for Phenol at PSA/CPE

The typical cyclic voltammograms (CVs) of phenol at bare CPE and PSA/CPE were recorded as Figure 2C. A small and broad oxidation peak at 0.758V was observed at bare CPE (curve a), which indicated a slow electron transfer rate and irreversible electrochemical process. In contrast, a sharp oxidation peak at 0.662 V was obtained at PSA/CPE (curve b). A negatively shifted anodic peak potentials and greatly enhanced peak currents strongly indicated excellent catalytic ability of the polymer on the oxidation of phenol as well as the faster electron transfer between phenol and the electrode²⁴. The possible reason was that phenol was formed o-quinine while poly (sulfosalicylic acid) was nonprotonated in pH 7.0 PBS. Therefore, the accelerated electron transfer may on the one hand ascribe to that the reduction of o-quinone was liberated from the PSA catalyzed reaction of phenol at the electrode surface^{7,23}, on the other hand attribute to the hydrogen bond between the two compounds, both of which would lead to a higher concentration of phenol around the electrode surface and make the electron transfer become easier and faster.

3.3 Effects of Scan Rates on the Electrochemical Response of Phenol at PSA/CPE

Electrochemical mechanism usually can be obtained from the relationship between the oxidation current and scan rate. Hence, the electrochemical response of phenol in pH 7.0 PBS with different scan rates were processed by CV. As Figure 3 illustrated, the anodic peak current (I_{pa}) increased with the increase of scan rate. Figure 3a shows that the logarithm of the peak current of phenol is proportional to that of scan rate within the range of 50–2500 mV s⁻¹, with the linear regression equations of $\log I_{pa} (\mu A) = 2.383 + 0.864 \log v (V s^{-1})$ ($r=0.9982$). It can be inferred from the slopes of the equations that the oxidation process of phenol was controlled by diffusion accompanied with absorption²⁵. Furthermore, the anodic peak potential (E_{pa}) shifted positively with the increase in scan rate, indicating the quasi-reversible

nature of the electrode reaction. According to Figure 3b, the E_{pa} was proportional to the natural logarithm of scan rate ($\ln v$) in the range of 50–2500 mV s^{-1} with the linear regression equation of $E_{pa} = 0.0564 \ln v + 0.689$ ($r = 0.9938$). Based on the equation²⁶, $\Delta E_p = 0.059/n$, the number of electrons transferred n can be calculated to be 1.

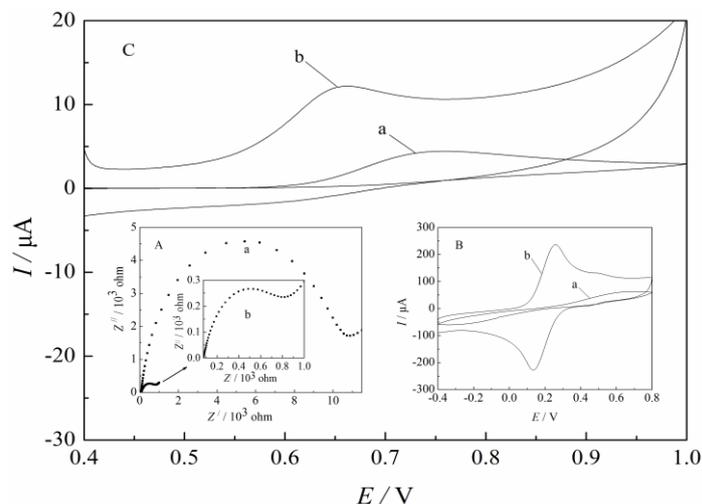


Figure 2 - EIS (A) and CVs curves (B) in 5.0 mmol L⁻¹ K₃Fe(CN)₆/K₄Fe(CN)₆ (1:1) with 0.1 mol L⁻¹ KCl in potential range of -0.4 to 0.8 V at bare CPE (a) and PSA/CPE (b), respectively; CVs curves (C) of 0.1 mmol L⁻¹ phenol at different electrodes in 0.1 mol L⁻¹ pH 7.0 PBS at the scan rate of 100 mV s^{-1} (a)CPE and (b) PSA/CPE.

3.4 Effects of pH on the Electrochemical Responses of Phenol at PSA/CPE

The electrochemical response of phenol was generally pH dependent²³, so the CVs of phenol were studied over the pH range from 5.0 to 9.0, and the results are shown in Figure 4. The experimental results of CV confirmed that the phenol has only one oxidation peak, with the pH of the solution varying from 5.0 to 9.0, the peak potential ranges from 0.4 to 1.0V. As shown in Figure 4A, the peak current of phenol increased with increasing pH from 5.0 to 7.0, and then it decreased when pH increased further. Because pH 7.0 was the physiological condition and the response current of phenol was the highest at this pH, it was chosen as the experiment pH value in the electrochemical detection of phenol. In addition, it can be seen from Figure 4B that E_{pa} of phenol linearly shifted to negative potentials with regression equations of $E_{pa} = 1.094 - 0.061 \text{ pH}$ ($r=0.9983$). The slopes value of -61 mV pH^{-1} was very close to the theoretical value of -57.6 mV pH^{-1} , indicating that the participated protons are equal to the transferred electrons through the PSA film²⁷.

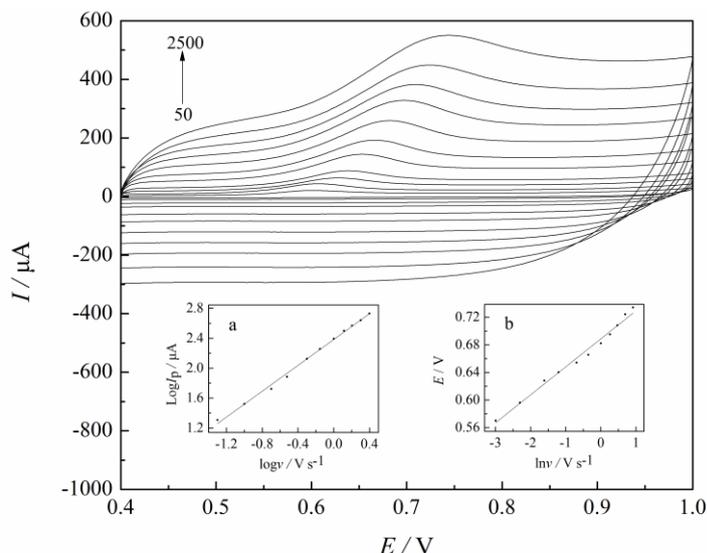


Figure 3 - CVs of PSA/ CPE in the presence of 0.1 mmol L-1 phenol with varying scan rate. CVs were measured in 0.1 mol L-1 pH 7.0 PBS. Scan rate (mV s-1): 50, 100, 200, 300, 500, 700, 1000, 1300, 1600, 2000, 2500; inset (a) shows a linear relationship between log I_{pa} versus log v ; (b) shows a linear relationship between E_{pa} versus $\ln v$.

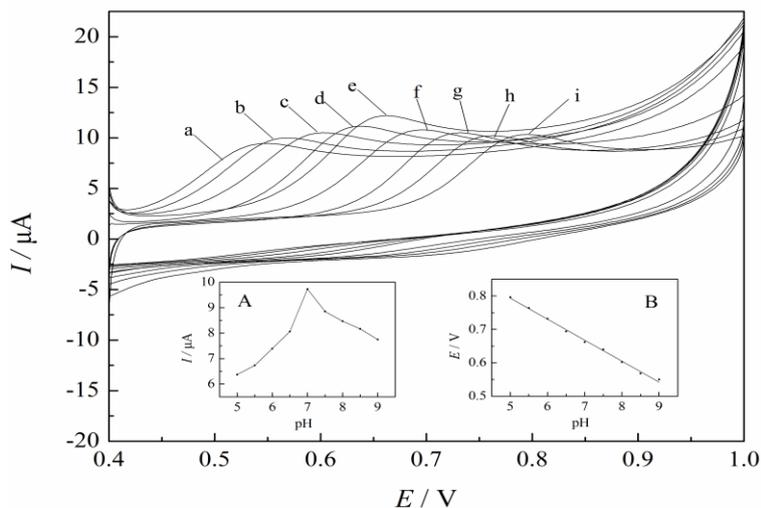


Figure 4 - CVs of PSA/ CPE in the presence of 0.1 mmol L-1 phenol at different pH: a) 9.0 b)8.5 c)8.0 d)7.5 e)7.0 f)6.5 g)6.0 h) 5.5 i) 5.0; inset (A) shows plots of the anodic peak current versus pH; (B) shows a linear relationship between E_{pa} versus pH.

3.5 Calibration Curve and Interferences

The determination of phenol concentration was performed at the PSA/CPE by using the DPV mode because of its higher current sensitivity and better resolution than CV. As shown in Figure 5A, The anodic peak current was linear to phenol concentration in the ranges of 5 to 175 $\mu\text{mol L}^{-1}$ and 220 to 555 $\mu\text{mol L}^{-1}$. The linear regression equations were $I_{pa} (\mu\text{A}) = 0.1661 + 0.0128c (\mu\text{mol L}^{-1})$ ($n=9, r=0.9952$) and $I_{pa} (\mu\text{A}) = 1.9233 + 0.0031c (\mu\text{mol L}^{-1})$ ($n=5, r=0.9921$), respectively (Figure 5B). The detection limit was calculated as $2.2 \times 10^{-6} \text{ mol L}^{-1}$ ($S/N = 3$), which

was lower than some previous reports. Table 1 summarizes the analytical performance of PSA/CPE and some previously reported modified electrodes in terms of linearity and detection limit. Improved or comparable performance for the determination of phenol can be achieved by using the PSA/CPE compared with other modified electrodes.

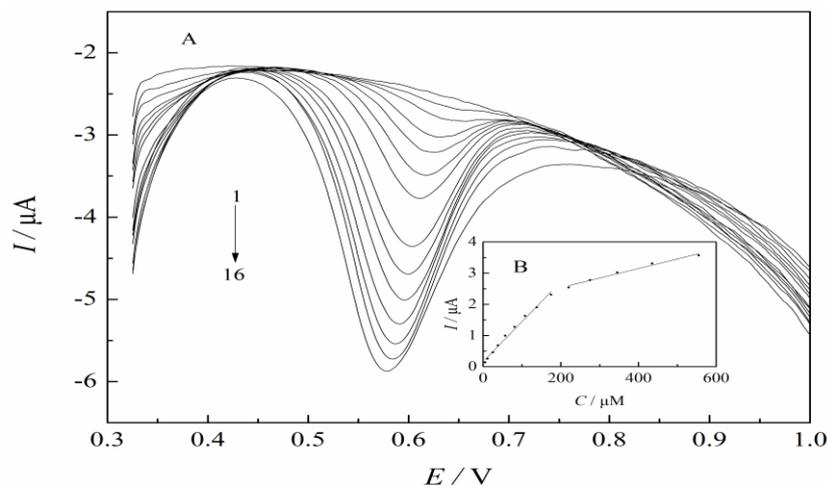


Figure 5. - (A) DPVs of PSA/ CPE in pH 7.0 PBS containing different concentrations of phenol. The numbers 1-14 correspond to: 0, 5, 11, 25, 38, 57, 81, 138, 175, 220, 275, 345, 435, 555 $\mu\text{mol L}^{-1}$; inset (B) shows the calibration curve of phenol concentrations from 5 $\mu\text{mol L}^{-1}$ to 175 $\mu\text{mol L}^{-1}$ and 220 $\mu\text{mol L}^{-1}$ to 555 $\mu\text{mol L}^{-1}$.

Tyr-AuNPs/BDD: biosensor based on immobilizing Tyr on AuNPs electrodeposited on a boron-doped diamond (BDD) electrode

PZn/CPE: poly (zincon) modified carbon paste electrodes

Pt/PTy/G: platinum–polytyramine composite graphite electrode

CNT/PPy/HRP: multiwalled carbon nanotube-poly (pyrrole)-horseradish peroxidase nano-biocomposite film

Tyrosinase/ZnO/BDND: biosensor based on the covalent immobilization of tyrosinase on biofunctional ZnO nanorod microarrays on the boron-doped nanocrystal line diamond electrode

In oil field wastewater samples, there are some potential interference substances like o-nitrophenol which often coexists with phenol, so the influences of various foreign species on the determination of phenol were investigated. Fig. 6 describes the DPVs of different concentrations of o-nitrophenol at PSA/CPE in the presence of 0.05 mmol L^{-1} phenol. It can be seen that two well-separated peaks present at the detached potentials and the peak current of phenol had no obvious changes, indicating that the o-nitrophenol toward response of phenol is negligible when the concentration is more than 4-times. Furthermore, the interference tests were also investigated in the presence of 100-fold concentration of bisphenol, p-chlorophenol, pyrocatechol, hydroquinone, hydroxyphenol, K^+ , Cu^{2+} , Fe^{3+} , Pb^{2+} , Mg^{2+} , Ca^{2+} , Al^{3+} , NO_3^- , SO_4^{2-} , Br^- , and the results showed the substances above had no obvious interference with phenol detection.

Table 1. Performance Comparison of the Proposal Sensor for Phenol Detection with other Electrodes

Electrodes	Linear range ($\mu\text{mol L}^{-1}$)	Detection limit ($\mu\text{mol L}^{-1}$)	References
Tyr-AuNPs/BDD ^a	0.1-11	0.07	17
PZn/CPE ^b	21-292,357-922	9	23
Pt/PTy/G ^c	30-10000	-	28
CNT/PPy/HRP ^d	16-44	3.52	29
Tyrosinase/ZnO/BDND ^e	1-175	0.1	30
PSA/CPE	5-175,225-555	2.2	This work

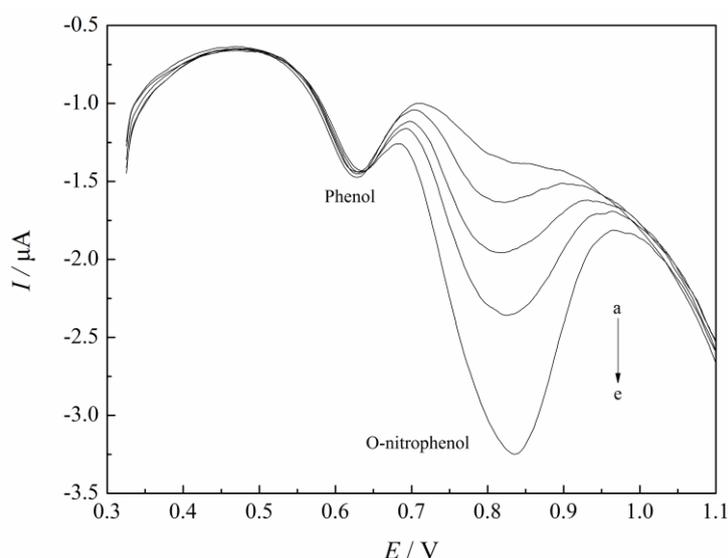


Figure 6 - DPVs of Different Concentrations of o-nitrophenol (a: 0.01 mmol L⁻¹, b: 0.03 mmol L⁻¹, c: 0.06 mmol L⁻¹, d: 0.1 mmol L⁻¹, e: 0.2 mmol L⁻¹) at PSA/CPE in the presence of 0.05 mmol L⁻¹ Phenol

3.6 Reproducibility and Stability

The stability of PSA/CPE was examined by using the same modified electrode for six repetitive measurements of 0.1 mmol L⁻¹ phenol. The relative standard deviation (RSD) was 3.3%, indicating that the modified electrode for phenol sensing was stable. In addition, for ten electrodes prepared in the same way, an acceptable reproducibility with a RSD of 4.2% was obtained for the determination of 0.1 mmol L⁻¹ phenol, indicating a good reproducibility of the fabrication method.

The long-term stability of PSA/CPE was also investigated. After the modified electrode was stored in pH 7.0 PBS for three weeks, the result shows that the catalytic current response maintains 96.7%, illustrating a good stability of the modified electrode.

3.7 Analytical Applications

The practical analytical utility of the modified electrode was illustrated by determination of phenol in real samples. The wastewater samples were collected from the sewage treatment station of Changqing Oilfield No.2 Oil Production Plant, which were treated according to our prior report²³. The standard addition technique was used to detect phenol by the proposed DPV method. The obtained results were summarized in Table 2. It can be seen that all spike recoveries were accurate and precise, which indicated the good applicability of the modified electrode to determination of phenol in the real oil field wastewater samples.

Table 2. Determination of Phenol in Real Samples(n=5).

Samples	Measured ($\mu\text{mol L}^{-1}$)	Added ($\mu\text{mol L}^{-1}$)	Found ($\mu\text{mol L}^{-1}$)	Recovery(%)
1	3.72	10.00	13.95	101.7
2	3.45	10.00	13.42	99.8
3	3.36	10.00	13.25	99.2

4. Conclusions

In conclusion, PSA/CPE had an excellent catalytic ability on electrochemical oxidation of phenol and an efficient method for the detection of phenol was established. The PSA/CPE enhanced the oxidation peak current of phenol obviously and the peak potential was shifted negatively. The results showed wide liner concentration range, low detection limit and high selectivity. In addition, this proposed method can be applied to the determination of phenol in real oil field wastewater samples with satisfactory results.

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