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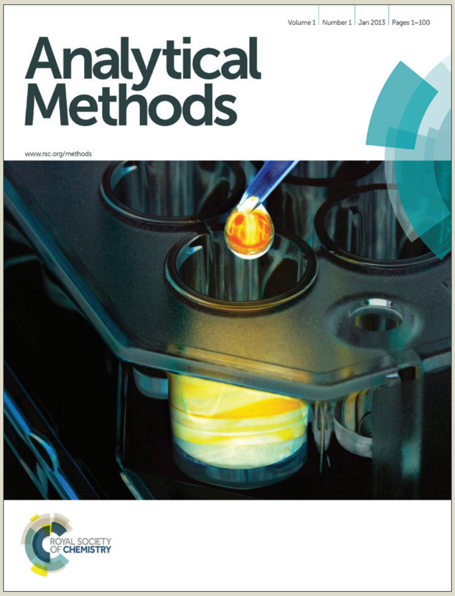

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Amperometric sensors for detection of phenol in oilfield wastewater using electrochemical polymerization of zincon film

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Abstract: Phenol and its derivatives are common organic contaminants, which are known to give adverse impact on human, thus the detection of phenol is very important. Herein, an amperometric sensor was fabricated based on electrochemical polymerization of zincon onto carbon paste electrode (CPE) surface. The cyclic voltammogram of phenol on the sensor exhibited a well-defined anodic peak at 0.640 V in 0.1 mol L^{-1} phosphate buffer solutions (PBS, pH 7.0). The sensor was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). Meanwhile, the influence of measuring parameters such as pH and scan rate on the analytical performance of the sensor was evaluated. Under the optimized conditions, the oxidation peak current was proportional to phenol concentration change in the range from 21 μmol L^{-1} to 292 μmol L^{-1} and 357 μmol L^{-1} to 922 μmol L^{-1} with the correlation coefficient of 0.9911 and 0.9966, respectively. The limit of detection was estimated to be 9×10^{-6} mol L^{-1} (S/N = 3). Furthermore, the fabricated sensor was successfully applied to determine phenol in oilfield wastewater.

Keywords: Amperometric; Sensors phenol; Zincon; Oilfield wastewater.

1. Introduction

Oil exploration activity is usually accompanied by the production of water [1]. The wastewater existing in oil mainly composed n-alkane (TNA), and also contains high concentration of minerals, radioactive substances, benzenes, phenols, humus and polycyclic aromatic hydrocarbons (PAHs) [2]. Before been released into the environment, such wastewater must be treated and determined. Otherwise its mineral and organic contents may severely pollute coastal waters, rivers, seashore, soil, and even the farmland [3]. For this reason, constituents analysis and contaminants determination of oilfield water are very important. Nevertheless, due to the complexity of components in wastewater, oilfield water analysis is difficult for a long time.

As the crucial components of oilfield wastewater, phenol and its derivatives are common organic contaminants. They are known to give adverse effects, such as reduced growth, reduced resistance against diseases and taste effects. In recent years, study has already proved that approximately 150 kinds of phenolic compounds have medical or toxic effects on animals and plants [4]. Phenol is easily absorbed through ingestion, inhalation and skin, and prolonged oral or subcutaneous exposure causes damage to lungs, liver, kidney and genito-urinary tract [5]. From the other point of view, phenol and its derivatives are important compounds that are extensively used in the manufacturing of a wide variety of products, such as paints, insecticides, fertilizers, antiseptics, adhesives, herbicides, disinfectants and so on [6]. Consequently, different kinds of phenols are included in the US EPA list of priority pollutants. Because of their toxicity, the concentration of phenol existing in the environment is strictly limited [4]. Thus, the research of detection methods for phenol is very important in environmental sciences.

Many determination methods for phenol have been proposed, such as the Gibbs method [7], aqueous liquid chromatography [8-9], spectrophotometry [10-11], flow injection spectrophotometry [12], synchronous fluorescence [13], pervaporation–flow injection analysis [14], solid-phase extraction method [15], flow-injection with chemiluminescence detection [6], absorptiometric determination [16] and electrochemical methods [17-19]. Among them, electrochemical sensor should be a promising technique with the advantage of reliability, fast response, cheap instrument, low cost, simple operation, time saving, high sensitivity, good selectivity and real-time detection in situ condition [20]. Electrochemical determination of phenol may be accomplished by its oxidation on solid electrodes. However, if the oxidation reaction carried out directly on the electrode surface, the surface gradually becomes bluntness due to the formation of phenol polymer. This problem is usually avoided through the modification of electrode surface [21]. So far, the electrochemical behaviors of phenol at various modified electrodes have been reported. Zhang et al. [22] have demonstrated a glass carbon electrode modified with horseradish peroxidase immobilized on partially reduced graphene oxide, which were used for detecting phenolic compounds. Klink et al. [23] reported a thermodynamical growth control concept of ZnO and RhO_2 nano-structured metal oxides on a titanium substrate for electro-catalytic oxidation of phenol. Mülazmolu et al. [24] have developed procaine modified carbon paste electrode (CPE) to detect phenol in natural decayed leaves.

Zincon (2-carboxy-20-hydroxy-50-sulfoformazylbenzene, Scheme 1), an excellent chromophoric reagent for the detection of zinc and copper ions in aqueous solution [25]. It has been also used as a chelator in the determination of metal contents in metalloproteins [26], but it has not attracted much attention for determination of contaminants in electrochemical analysis.

To the best of our knowledge, the electropolymerization of zincon as sensor to determination of phenol has not been reported previously. In this paper, a simple and high sensitive amperometric sensor for detection of phenol using electrochemical polymerization of zincon film was presented, and the electrochemical behaviors of phenol at proposed electrode were carefully studied. In addition, the sensor was used to determine the content of phenol at trace level in oilfield wastewater.

Scheme 1

2. Experimental

2.1. Chemicals

Graphite powder and paraffin were purchased from Sinopharm Chemical Reagent Company (China). Phenol was obtained from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Zincon was purchased from Shanghai Chemical Reagents Company (China). $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl, K_2HPO_4, KH_2PO_4, H_3PO_4, NaOH were obtained from China National Medicine Corporation. All reagents were of analytical grade and used without any further purification. Phosphate buffer solutions (PBS) (0.1 mol L^{-1}) with various pHs were prepared by mixing stock standard solutions of $K_2HPO_4$and $KH_2PO_4$and adjusting the pH with 0.1 mol L^{-1} H_3PO_4 or KOH. All solutions were prepared with doubly distilled water.

2.2. Apparatus and measurements

Cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) measurements and Differential pulse voltammetry (DPV) experiments were performed on a CHI 660d electrochemical Workstation (Chenhua Instruments in Shanghai, China) 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 experiments were performed at room temperature (25°C). The surface morphology of sensor was analyzed by scanning electron microscope (SEM, Quanta 200).

2.3 Preparation of poly (zincon)/CPE modified electrode

The CPE was prepared via mix graphite powder and mineral oil at the ratio of 7:3 (w/w) in a mortar and then pack the mixture into an insulating tube (3 mm diameter; 3.5 cm depth) carefully. Electrical contact was established with a copper wire. The CPE surface was mechanically polished with alumina powder (Al_2O_3, 0.05 μm) up to a mirror and rinsed with double distilled water. Then, the poly-zincon was electrochemically deposited on the surface of CPE by cyclic sweeping from -1.0 to 2.2 V at scan rate of 100 mV s^{-1} for 14 cyclic times in 0.1 mol L^{-1} PBS (pH 6.0) containing 0.2 mmol L^{-1} zincon. After electrochemical polymerization of zincon and each measurement, the modified electrode was rinsed with doubly distilled water, and then treated in pH 7.0 PBS by repetitive scanning in the potential range from -0.4 V to 0.8 V at a scan rate of 80 mV s^{-1} until a stable blank background was obtained. The electrode was then stored at room temperature.

3. Results and discussion

3.1 Electrochemical polymerization of zincon

Fig. 1 displays the continuous CVs for the electrochemical polymerization of zincon over the range of -1.0 to 2.2 V at 100 mV s^{-1} for 14 cycles. During the polymerized process, it is clear that the cathodic peak at 0.25 V corresponding to the oxidation of zincon increased gradually with cyclic time increasing and trended to stable after 8 scans. The peak location moved at the last circle, this phenomenon implies the formation of poly-zincon membrane on the surface of CPE. After electropolymerization, the modified electrode carefully rinsed with doubly distilled water.

Fig. 1

3.2. Electrochemical characterization of poly (zincon) electrode

Firstly, electrochemical behavior of poly (zincon) electrode was investigated by cyclic voltammetry using $Fe(CN)_6^{4-/3-}$ as a redox probe. Fig. 2A shows the CVs of 5.0 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) dissolved in 0.1 mol L^{-1} KCl with potential range of -0.4 to 0.8 V at different electrodes. Curve a is CV of bare CPE, which has a pair of inconspicuous voltammetric peaks with cathodic peak potential (Epc) of -0.288 V and anodic peak potential (Epa) of 0.716 V. The peak-to-peak separation (□Ep) is 1004 mV. Curve b is cyclic voltammogram of poly (zincon) electrode with Epc of 0.082 V, Epa of 0.313 V, and □Ep of 231 mV. Compared with bare CPE, the peak currents on poly (zincon) electrode increased dramatically and the peak-to-peak separation decreased obviously. These results demonstrate that the poly (zincon) film is conductive and does not block electron transfer, which indicated that zincon modified CPE could greatly increase the electron transfer rate of $[Fe(CN)_6]^{3-/4-}$.

For further characterization of the modified electrode and clarify the differences among the electrochemical performance of bare CPE, and poly (zincon) modified electrode, electrochemical impedance spectroscopy (EIS) was carry out. Fig. 2B shows impedance plots for (a) bare CPE, (b) poly (zincon) electrode in 5.0 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) with 0.1 mol L^{-1} KCl. The semicircular elements correspond to the charge transfer resistances (R_{et}) at the electrode surface, a large diameter was observed for the bar CPE in 45 kΩ as curve a showed. However, the diameter of the semicircle diminished when poly (zincon) electrode were employed. Curve b showed an arc, the diameter of which displayed Ret = 1 kΩ, which was really less than that for CPE. The charge transfer resistance

(Ret) values obtained from this observation implied that the charge transfer resistance of the electrode surface decreased and the charge transfer rate increased using zincon modified CPE. The experimental results of EIS confirmed that the zincon modified CPE could effectively increase the electron transfer rate of $[Fe(CN)_6]^{3-/4-}$.

Fig. 2

3.3 Characterization of the electrode surface

SEM analysis was performed to determine the microscopic surface morphology of electrode. Fig. 3 displays the surface morphology of bare carbon paste electrode and poly (zincon) modified CPE using scanning electron microscopy. The surface of bare CPE was irregularly shaped by micrometer sized flakes of graphite. However, the poly (zincon) film coated CPE has typical uniform arrangement of poly (zincon) molecules on the surface of carbon paste electrode. This confirms that the CPE was coated by poly (zincon) film.

Fig. 3

3.4 Cyclic voltammetric behaviors of phenol

Fig. 4 showed the electrochemical behaviors of 0.5 mmol L^{-1} phenol dissolved in 0.1 mol L^{-1} PBS (pH 7.0) at different electrodes with the scan rate of 100 mV s^{-1}. On bare CPE, a small oxidation peak was observed (curve a) with the oxidation potential of 0.640 V and the oxidation peak current of 0.379 μA. While on the poly (zincon) electrode (curve b), the oxidation peak increased obviously (I_{pa}=21.19 μA) accompanied with the oxidation peak potential negatively shifted to 0.636 V. It can be seen that the oxidation peak potential was negatively shift for 4 mV with the oxidation peak current increased for about 55 times, which can be attributed to the excellent electro-catalytic activity of zincon on the electrode surface. It is obvious that the modified electrodes show high background currents compared with bare CPE. The enhanced anodic peak at poly (zincon) electrode is attributed to the efficient catalytic reactions of phenol to form o-quinine. The electrochemical oxidation of phenol is a complex process and the reaction pathway may be affected by many factors. The mechanism was proposed by several researchers [27-29]. As shown in Schemes 2. First a phenoxy radical (b) is formed when phenol is oxidized. In the presence of water, the radical can be further oxidized to quinol or catechol (c). The quinol can be oxidized again to produce hydroxyl quinone radical (d). It is well known that radical is extremely actived. So the radical is finally oxidized by lost one electron and one proton and oxidized to quinone (e).So zincon acted as an effective mediator in the electrocatalytic oxidation of phenol.

Fig. 4

Schemes 2

3.5 pH effect

The effects of pH on the catalytic responses of phenol at the modified electrode were studied by cyclic voltammetry over the pH ranging from 2.0 to 9.0, and the results shown in Fig. 5A. 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 range from 1.0 to 0.4 V. However, the results became different when phenol in acidic medium. From Fig.5A curve a) pH 2.0 and curve b) pH 3.0, we can see two oxidation peaks in 0.88 V, 0.55 V and 0.84 V, 0.5 V, which were similar with the peak at curve g) pH 8.0 and curve h) pH 9.0 in 0.57 V and 0.5 V, respectively. Moreover, the anodic peak currents increased with the pH rising to 7.0, and then decreased with the pH rising to 9.0. In order to facilitate the analysis, pH 7.0 was selected as the optimal experimental condition.

The oxidation peak potential shifted negatively with the increase of pH value (Fig. 5B), indicating that protons involved in the electrode reaction. A good linear relationship between E_{pa} and pH was constructed with linear regression equation as E_{pa} = 1.002 - 0.051 pH (r=0.9967). The slope value of -51 mV/pH was very close to the theoretical value of -57.6 mV/pH, indicating that an equal number of protons and electrons involved in electrode reaction [30].

Fig. 5

3.6 Scan rate effect

The effect of scan rate on the oxidation of phenol in pH 7.0 PBS was also investigated by cyclic voltammetry with the results shown in Fig. 6. It can be seen that the oxidation peak currents increased gradually with the increase of scan rate. In order to explore that the process was controlled by diffusion or adsorption, the relationship of logarithm of peak current (log I_{pa}) versus logarithm of scan rate (logυ) was discussed. According to the literature [31], a slope of 0.5 and 1.0 indicate that the electrode reaction is simultaneously controlled by the diffusion and the adsorption process, respectively. A linear relationship between the oxidation peak currents and scan rate was constructed in the range of 40-2600 mV s^{-1} with the linear regression equation as $log\ I_{pa}$ (μA) = 1.959 + 0.674 $log\ \upsilon$ (V s^{-1}) (r=0.9973) (shown in Fig. 6a). The result indicated that the oxidation of phenol on poly (zincon) electrode was controlled by diffusion accompanied with absorption.

In addition, with increasing scan rate, the anodic peak potential (E_{pa}) shifted positively. The relationship between E_{pa} and the natural logarithm of scan rate (lnυ) was shown in Fig. 6b. It can be seen that E_{pa} changed linearly versus lnυ with a linear regression equation of $E_{pa} = 0.039\ ln\ v + 0.704$ (r = 0.9949) in the range from 40 to 2600 mV s^{-1}. For a totally irreversible electrode process, the relationship between the potential (E_{pa}) and scan rate (υ) could be expressed as follows by Laviron (1974) [32]:

$$E_{\mathrm{pa}} = E^{\theta} + \left(\frac{RT}{\alpha nF}\right)\ln\left(\frac{RTk^{\theta}}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right)\ln \nu \quad (1)$$

where α is transfer coefficient, k^{θ} is standard rate constant of the reaction, n is electron transfer number involved in rate determining step, E^{θ} is formal redox potential, R is the gas constant, T is the absolute temperature, and F is the Faraday constant. Generally, α is assumed to be 0.5 in a totally irreversible electrode process. So, the number of transfer electron (n) in the electrooxidation of phenol is calculated to be 1.31 ≈ 1. The pH effect on Epa demonstrated that the number of electrons and protons involved in the phenol oxidation process is equal (see Section 3.5). Therefore, the electrooxidation of phenol on poly (zincon) electrode is a one-electron and one-proton process.

Fig. 6

3.7 Calibration curve, linear range and detection limit

By using the differential pulse voltammetry (DPV) as the detection method, the poly (zincon) electrode was further used for the phenol detection. Under the optimal conditions, the oxidation peak current of phenol increased with its concentration increasing in the range from 21 μmol L^{-1} to 922 μmol L^{-1} with typical DPVs shown in Fig. 7A. Two calibration curves could be obtained in the phenol concentration ranges from 21 μmol L^{-1} to 292 μmol L^{-1} and 357 μmol L^{-1} to 922 μmol L^{-1} with the linear regression equations as I_{pa} (μA) = -0.3112 + 0.0245c (μmol L^{-1}) (n=8, r=0.9911) and I_{pa} (μA) = 4.1824 + 0.0106c (μmol L^{-1}) (n=6, r=0.9966), respectively (Fig. 7B). The detection limit was calculated as 9.0×10^{-6} mol L^{-1} (S/N = 3), which was lower than some previous reports. Table 1 showed the analytical performances of different methods for phenol detection. It can be seen that this method exhibited relatively broader detection range and lower detection limit. Although the sensitivity was not good as some analytical methods such as FI-CL or solid-phase extraction method, electrochemical methods have the advantages of simple and easy to do, rapid detection, low cost of the apparatus and wide dynamic ranges. In addition, have compared with other electrochemical methods and shown in Table 2. The results inditate the proposed method has low detection limit and wide linear range, which are superior to the other electrochemical methods. Therefore, the poly (zincon) electrode was an excellent sensor for the electrochemical detection of phenol.

Fig. 7

Table 1

3.6 Repeatability and interference

In order to test and verify the precision and practicability of the proposed method, the reproducibility of the poly (zincon) electrode for phenol detection were also established. The reproducibility for ten poly (zincon) electrodes was carried out by comparing the oxidation peak current of 0.5 mmol L^{-1} phenol, the relative standard deviation (RSD) was 4.3%. The results illustrate that the poly (zincon) electrode has good reusability as a phenol sensor. Moreover, we studied the stability of poly (zincon) electrode stored at vacuum. For electrolyte solution containing 0.5 mmol L^{-1} phenol, the reduction peak current of phenol on poly (zincon) electrode stored at vacuum for 4 and 8 days decreased by 4.2% and 6.0% compared to the data obtained on poly (zincon) electrode applied immediately after been prepared. Therefore, the better reusability and stability make this electrode as a promise biosensor. The interference test was performed in the presence of 100-fold concentration of bisphenol, hydroquinone, pyrocatechol, hydroxyphenol, p-chlorophenol, K^+, Cu^{2+}, Ca^{2+}, Fe^{3+}, Pb^{2+}, Mg^{2+}, Al^{3+}, Br^-, NO^{3-}, SO_4^{2-}, and the result showed the substances above have no interference for the detection of phenol.

3.7 Voltammetric response to phenol in real samples

In order to confirm the applicability of the proposed method, the sensor was used to detect phenol in real samples, which collected from the sewage treatment station of Changqing Oilfield No.1 Oil Production Plant. We random take three samples in different days from the station and numbered it as S1, S2, S3. The collected water samples were filtered through filter membrane before analysis. After that, 5.00 mL water sample was diluted for 5 times by pH 7.0 PBS, and a certain amount of phenol standard solution was added into it. Then modified poly (zincon) electrode was used for the quantitative determination by DPV method. Each sample solution undergoes five parallel determinations. The data given in Table 3 indicated that our approach could provide satisfactory results for the determination of phenol. The final value of the oilfield wastewater is 36.72 μmol L^{-1}.

Table 3

4. Conclusions

The simple and effective preparation method of a sensor based on poly (zincon) modified for phenol was developed here. We demonstrated that the modification of CPE with zincon is effective for the highly sensitive determination of phenol. The poly-zincon film could remarkably enhance the response of phenol and decrease its oxidation overpotential. The electrochemical behavior of phenol at the modified elector surface is controlled by diffusion accompanied with absorption and involving in equal numbers of electrons and protons. The responses of poly (zincon) electrode toward the concentration change of phenol were studied. Under optimized conditions, the poly (zincon) electrode showed wide linear behaviors in the range of 21 μmol L^{-1} to 292 μmol L^{-1} and 357 μmol L^{-1} to 922 μmol L^{-1} for phenol with the detection limits 9.0×10^{-6} mol L^{-1}, and the result showed that this modified electrode was superior to some other reported electrode. Ultimately, the proposed method was successful applied to phenol detection in the real oil field wastewater samples and its average value is

36.72 μmol L^{-1}.The result show the poly (zincon) electrode could be used in environment science as a sensor for phenol determination.

Acknowledgments

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References

[1] S.F. Jerez Vegueria, J.M. Godoya, N. Miekeley, *J. Environ. Radioact.* 2002, **62**, 29-38.

[2] X. Zhao, Y.M. Wang, Z.F. Ye, Alistair G.L. Borthwick, J.R. Ni, *Process Biochem.* 2006, **41**, 1475-1483.

[3] H.Z. Ma, B. Wang, J. Hazard.Mater. 2006, **132**, 237-243.

[4] P. Önnerfjord, J. Emnéus, G. Marko-Varga, L. Gorton, F. Ortega, E. Dominguez, *Biosens. Bioelectron*. 1995, **10**, 607-619.

[5] Z. Mojović, N. Jović-Jovičić, A. Milutinović-Nikolić,P. Banković, A. Abu Rabi-Stanković, D. Jovanović, *J. Hazard. Mater.* 2011, **194**, 178-184.

[6] W.W Liu, W. Cao , W.H Liu, K. Du, P.X Gong, *Spectrochim. Acta. A*. 2012, **85**, 283-287.

[7] AI. R. Ettingek, C. C. Kuchhoit, *Anal. Chem.* 1948, **20**, 1191-1196.

[8] K. Kuwata, M. Uebori, Y. Yamazaki, *Anal. Chem.* 1980, **52**, 857-860.

[9] K. Bhatia, *Anal. Chem.* 1973, **45**, 1344-1347.

[10] S. Amlathe, S. Upadhyay and V. K. Gupta, *Anal. Chem.* 1987, **112**, 1463-1465.

[11] C.L. Kang, Y. Wang, R.B Li, Y.G Du, J. Li, B.W Zhang, L.M Zhou, Y.Z. Du, *Microchem. J.* 2000, **64**, 161-171.

[12] M. C. B. Quaresma, R. J. Cassella, M. de Fatima B. Carvalho, R. E. Santelli, *Microchem. J.* 2004, **78**, 35-40.

[13] M. F. Pistonesi, M. S. Di Nezio, M. E. Centurión, M. E. Palomeque, A. G. Lista, B. S. Fernández Band, *Talanta* 2006, **69**, 1265-1268.

[14] S. Y. Sheikheldin, T. J. Cardwell, R. W. Cattrall, M. D. Luque de Castro, S. D. Kolev, *Anal. Chim. Acta*. 2000, **419**, 9-16.

[15] M.A. Crespín, M. Gallego, M. Valcarcel, *J. Chromatogr. B*. 2002, **773**, 89-96.

[16] F. W. Ochynsi, *Analyst* 1960, **85**, 278-281.

[17] P. Skládal, N. O. Morozova, A. N. Reshetilov, *Biosens. Bioelectron.* 2002, **17**, 867-873.

[18] A. Lindgren, J. Emnéus, T. Ruzgas, L. Gorton, G. Marko-Varga, *Anal. Chim. Acta*. 1997, **347**, 51-62.

[19] Z. Mojović, N. Jović-Jovičić, A. Milutinović-Nikolić, P. Banković, A. Abu Rabi-Stanković, D. Jovanović, *J. Hazard. Mater.* 2011,**194**, 178-184.

[20] H.S. Yin, L. Cui, S.Y. Ai, H. Fan, L.S. Zhu, *Electrochim. Acta.* 2010, **55**, 603-610.

[21] A. Abu Rabi-Stanković, Z. Mojović, A. Milutinović-Nikolić, N. Jović-Jovičić, P. Banković, M. Žunić, D. Jovanović, *Appl. Clay. Sci.* 2013, **77**, 61-67.

[22] Y. Zhang, J.L. Zhang, H.X. Wu, S.W. Guo, J.Y. Zhang, *J. Electroanal. Chem.* 2012, **681**, 49-55.

[23] M. J. Klink, A. M. Crouch, *Mikrochim Acta* 2009, **66**, 27-33.

[24] I.E. Mülazımoğlu, E. Yılmaz, *Desalination* 2010, **256**, 64-69.

[25] R.M. Rush, J.H. Yoe, *Anal. Chem.* 1954, **26**, 1345-1347.

[26] Crystal E. Säbel, Joseph M. Neureuther, Stefan Siemann, *Anal. Biochem.* 2010, **397**, 218-226.

[27] Serdar Abaci, Ugur Tamer, Kadir Pekmez, Attila Yildiz, *Electrochimica Acta* 2005, **50**, 3655-3659.

[28] Z.H. Dai, X.X. Xu, L.N. Wu, H.X. Ju, *Electroanalysis* 2005, **17**, 1571-1577.

[29] Marystela Ferreira, Hamilton Varela, Roberto M. Torresi, Germano Tremiliosi-Filho, *Electrochimica Acta* 2006, **52**, 434-442

[30] H.S. Yin, L. Cui, Q.P. Chen, W.J. Shi, S.Y. Ai, L.S. Zhu, L.N. Lu, *Food. Chem.* 2011, **125**, 1097-1103.

[31] J. A. Rather, K. D. Wael, *Sens. Actuators, B* 2013, **176**, 110-117.

[32] E. Laviron, *Electroanalytical Chemistry and Interracial Electrochemistry*, 1974, **52**, 355-393.

[33] Seyda Korkut, Bulent Keskinler, Elif Erhan, *Talanta* 2008, **76**, 1147-1152.

[34] Jutta Metzger, Monika Reiss, Winfried Hartmeier, *Biosens. Bioelectron.* 1998, **13**, 1077-1082.

[35] Lida Fotouhi, Mahsa Ganjavi, Davood Nematollahi, *Sensors* 2004, **4**, 170-180.

[36] Amarjeet S. Bassi, Cynthia McGrath, J. Agric. *Food. Chem.* 1999, **47**, 322-326.

Figure captions:

Fig. 1 displays the continuous CVs for the electrochemical polymerization of zincon over the range of -1.0 to 2.2 V at 100 mV s^{-1} for 14 cycles.

Fig. 2 CVs (A) and EIS curves (B) in 5.0 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) with 0.1 mol L^{-1} KNO_3 in potential range of -0.4 to 0.8 V at bare CPE (a) and poly (zincon) modified CPE (b), respectively.

Fig. 3 SEM image of (A) bare CPE and (B) poly (zincon) modified CPE.

Fig. 4 CVs of 0.5 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) poly (zincon) modified CPE.

Fig. 5 (A) CVs of the poly (zincon) modified CPE in the presence of 0.5 mmol L^{-1} phenol in different pH: a) 2.0 b)3.0 c)4.0 d)5.0 e)6.0 f)7.0 g)8.0 h) 9.0; (B) inset A shows plots of the anodic peak potential versus pH.

Fig. 6 CVs of the poly (zincon) modified CPE in the presence of 0.5 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}): 40, 100, 220, 300, 350, 450, 550, 650, 800, 1100, 1400, 1700, 1900, 2200, 2600, 3000, 3800, 4400; inset a) shows a linear relationship between log I_{pa} versus logυ; b) shows a linear relationship between E_{pa} versus lnυ.

Fig. 7 (A) DPVs of the poly (zincon) modified CPE in 0.1 mol L^{-1} pH 7.0 PBS containing different concentrations of phenol. The numbers 1-15 correspond to: 21, 45, 82, 101, 125, 155, 192, 237, 292, 357, 435, 525, 632, 762, 922μmol L^{-1}; (B) inset A shows the calibration curve of phenol concentrations from 21 μmol L^{-1} to 292μmol L^{-1} and 357 μmol L^{-1} to 922μmol L^{-1}.

Table1 Performance comparison of the proposal sensor for phenol detection with other methods.

Methods	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	References
HDTMA-B/GCE [a]	100-5000	18	[5]
FI-CL [b]	0.021-4.25	0.0043	[6]
Aqueous liquid chromatography	2.6-12000	1.4	[9]
Flow injection analysis	0.11-0.35	0.11	[12]
SF-PLS [c]	0.53-4.25	-	[13]
Spectrophotometric method	0.53-53.13	-	[11]
Solid-phase extraction method	0.021-5.63	0.032	[15]
P-FI analysis [d]	10.13-531.29	9.56	[14]
poly (zincon) electrode	21-292,357-922	9	This work

[a] HDTMA-B/GCE: Hexadecyl trimethylammonium bromide (HDTMABr) modified glassy carbon electrode.

[b] FI-CL: Flow injection (FI) methodology based on luminol chemiluminescence (CL) detection.

[c] SF-PLS: synchronous fluorescence (SF) using partial least-squares (PLS)

[d] P-FI: Pervaporation–flow injection

Table2 Performance comparison of the proposal sensor for phenol detection with other electrodes.

Electrodes	Linear range (μmol L^{-1})	Detection limit (μmol L^{-1})	References
Tyrosinase-HRP/MCM-41/GCE[a]	0.2-230	0.0041	[28]
CNT/PPy/HRP[b]	16-44	3.52	[33]
NADH-PHY[c]	2.5-400	-	[34]
GC electrode[d]	1-100, 200-1000	11	[35]
SBP/CPE[e]	0-700	50	[36]
poly (zincon) electrode	21-292,357-922	9	This work

[a] Tyrosinase-HRP/MCM-41/GCE: tyrosinase-horseradish peroxidase-mesoporous silica glassy carbon electrode

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

[c] NADH-PHY: biosensor based on reduced form of nicotinamide-adenine dinucleotid (NADH)- phenol hydroxylase(PHY)

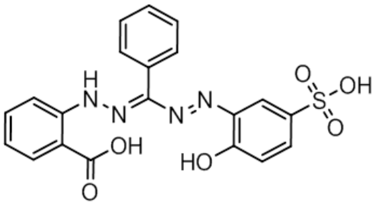
[d] GC electrode: glassy carbon electrode.

[e] SBP/CPE: soybean peroxidase modified carbon paste electrodes

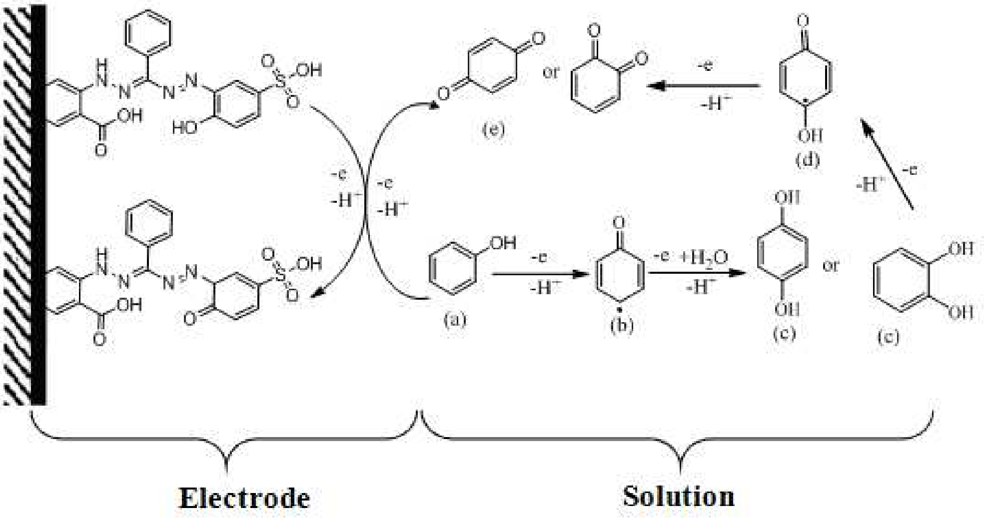
Table 3 Determination of phenol in real samples.

Samples	Measured [a] (μmol L^{-1})	Added (μmol L^{-1})	Found (μmol L^{-1})	Recovery (%)
S1	7.43	10.00	17.35	99.4
S2	7.32	10.00	17.41	100.8
S3	7.28	10.00	17.13	98.8

[a] Mean of five measurements.



Scheme. 1. The molecular structure of zincon



Scheme. 2. The mechanism of phenol oxidation at poly (zincon)/CPE

Fig. 1.

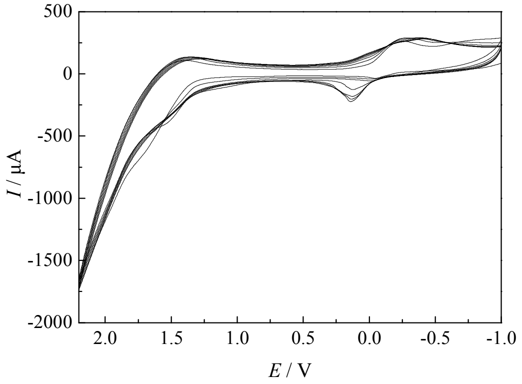


Fig. 2.A

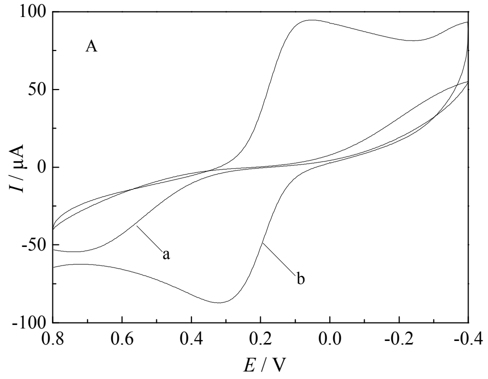


Fig. 2.B

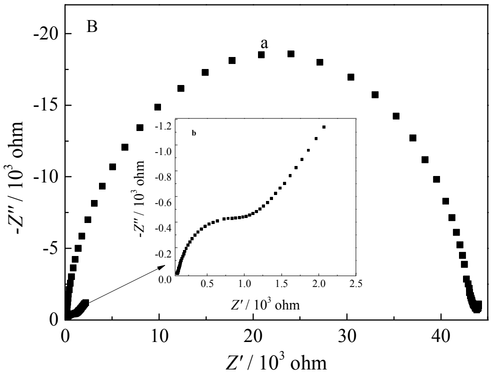


Fig. 3.A

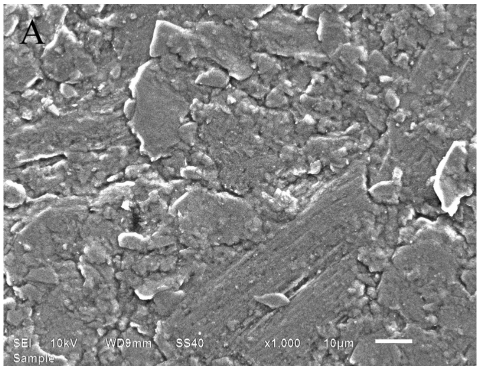


Fig. 3.B

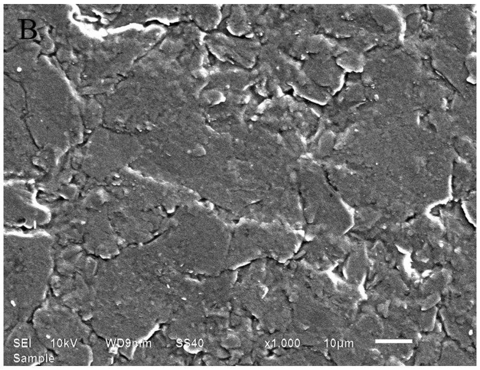


Fig. 4.

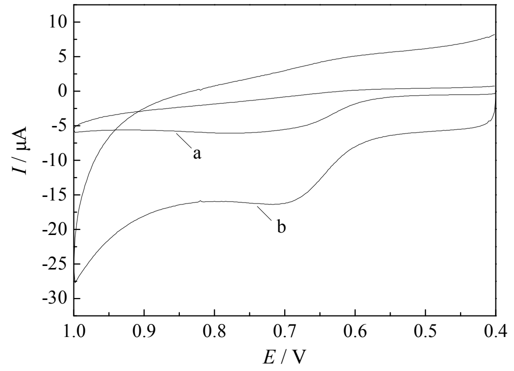


Fig. 5.

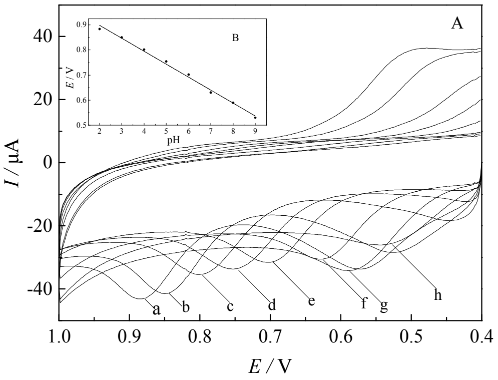


Fig. 6.

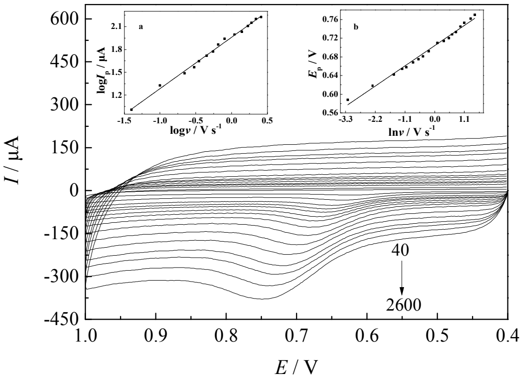


Fig. 7.