A New Electrochemical Sensor Based on TiO2 Nanoparticles Modified Carbon Paste Electrode for Voltammetric Determination of Phenol

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Abstract: ***A new nanostructure modified electrode was established for the voltammetric determination of the pollutant compound phenol. The mechanism of the oxidation process was studied using Cyclic voltammetric technique. A well-defined oxidation peak was obtained. linear sweep voltammetry (LSV) was used for the quantitative determination of the pollutant compound phenol. The parameters may affect the peak current responses such as pH, scan rate, and buffer type were examined to select the optimum conditions for determination of phenol at low concentrations as possible as. The collected results indicated a linear relationship on plotting concentration versus peak current from $1x10^{-7}$ to $1x10^{-6}$ M with correlation coefficient of 0.997, from other hand a detection limit of 1×10^{-9} M was obtained. The designed electrode showed a good performance for the voltammetric measurements of the phenol compounds comparing to the unmodified one. The modified electrode was used for the quantification of phenol in water samples.***

Keywords: Carbon Paste Electrode, Cyclic Voltammetry, Nano-Particles, Phenol, Modified electrode.

1. Introduction

Among the organic pollutants encountered in water, phenol and its derivatives are important and a number of industrial processes contribute to it. The US EPA has listed some of the phenols as priority pollutants [1] .Phenol and its derivatives are important industrial products for a variety of organic wastewater contaminants discharged from many industries like paper, resin, textile, plastic, coking, tanning, rubber, pharmaceutical, herbicides, fungicides and petroleum[2-4].The primary use of phenol is in the production of phenolic resins, which are used in the plywood, construction, automotive, and appliance industries. Phenol is also used in the production of caprolactam and bisphenol A, which are intermediates in the manufacture of nylon and epoxy resins, respectively. Other uses of phenol are as a disinfectant [5] and in medicinal products, such as ear and nose drops, throat lozenges and mouthwashes [3]. Phenol consider very important toxic compound [5-7], showing harmful effects on plants, animals, and human health [3,8-10]. Inhalation and dermal exposure to phenol is highly irritating to the skin, eyes, the respiratory tract and mucous membranes in humans [3, 7, 11].

Therefore, Phenol is one of the organic compounds that should be monitored, so it is urgent that reliable analytical methods must be developed to detect their presence and quantify their concentrations in aqueous solution. Determination of this compound is very important. Although most of these compounds are present at low concentrations, many of them raise considerable toxicological concerns. Assessing the impact of pollutants in aquatic systems requires improved analytical methods and tools [12]. Several methods have been proposed for the determination of PhenoL, including high-performance liquid chromatography capillary electrophoresis, spectrophotometry [4, 9-11,13]. These methods are time-consuming, complex, have low precision and the equipment are expensive [9], Compared to these methods, electrochemical sensors methods, which have the impressive advantages for environmental analysis attracted more attention due to their sensitivity, accuracy, lower cost, high dynamic range and simplicity [2,9,11-13]. Different electrodes including modified carbon paste were used before to determine phenol derivatives and different organic compounds, [14-17]

In this work it is aimed to determine phenol by electrochemical oxidation using carbon paste electrode modified by TiO_2 nanoparticles. And to create an electrode with desirable electrochemical/physical and economical characteristics, which include: enhanced sensitivity, high stability, physically rigid, with low detection limits, selectivity, wide linear response range, and low production cost with simple hand-made electrode design. Modification of the electrode surface can grants and improve some remarkable advantages in the electrochemical responses. Some special properties can be considered in modification of the electrodes using nano materials, e.g., catalysis, the large specific surface area and more adsorption sites comparing to unmodified carbon paste electrode[8,13] as shown in Fig (1). Phenol determination by electrochemical means is done by an oxidation process on modified electrodes using linear sweep voltammetry(LSV) and cyclic voltammetry(CV), but it is known that if oxidation takes place directly over the electrode surface, this surface gradually passive due to polymer formation during the oxidation process. These polymers are severely adsorbed and their elimination requires mechanical treatment of the electrode surface, for example by polishing [4].

2. Experimental

2.1Reagents

0.01M Phenol (Sigma-Alderish) was prepared by dissolving 94 mg in absolute alcohol. Solutions of different concentrations were prepared by suitable dilution from the stock solution. 0.1 M of B.R buffer was prepared and sodium hydroxide (BDH) 1:1 solution (50 gm / 50 ml H2O) was prepared and well stored to adjust the pH value from 3.00 to 11.00

2.2Apparatus

A potentiostat model 263 (EG& G PARC) Princeton applied corporation (made in USA), was used in this work. The characteristic of modern stripping analyzer potentiostat control the working electrode, which minimize errors from the cell resistance This is accomplished with a three-electrode system, The used working electrode was a carbon paste modified by TiO_2 nanoparticles, the reference electrode was (Ag / AgCl) and a Pt wire was used as a counter one.

2.3 Preparation of carbon paste electrode modified by TiO_2 electrode

This electrode is prepared by mixing 60% of pure graphite (99.9%) with 15% of TiO_2 nanoparticles in presence of 25% from paraffin wax as a binder. The mixer is heated and then packing in Teflon tube with 3mm diameter. Finally a copper wire is immersed in paste to contact with the cell. This construction give a good response for electrode as shown in picture(1).

3. Results and Discussions

The hydroxyl group of phenol was easy to be oxidized under appropriate conditions [4]. Fig. (1) shows the linear sweep voltammograms of $1x10^{-4}$ M of phenol in B.R as supporting electrolyte pH=7.00 at a scan rate of 50 mV/s., (a)-modified CPE by $TiO_{2,}$ (b)-unmodified CPE. Which suggested that the peak was attributed to the oxidation of phenol. Fig. (2) illustrates the difference between SEM image of unmodified CPE , b– SEM image of a modified CPE by TiO_2 and c- SEM image of a modified CPE by TiO_2 with adsorption particles of phenol molecules.

3.1 Cyclic Voltammetric measurments

The recorded CV voltammograms indicated that, the studied compound undergos oxidation process and convert to phenoxy radical according to Eq.1 (1)

$$C_6H_5OH \rightarrow C_6H_5O^{\bullet} + H^{+} + e^{-} \qquad \ldots(1)$$

Figure (3) represents the oxidation process of $3x10^{-5}$ M phenol in B.R buffer, pH=3.00 at a scan rate 50 mV/s. An anodic peask was observed at -836.3 mV. During the reverse scan no reduction peak was observed [1, 10]. This may attributed to the rabid polymerization reaction of the oxidation product formed during forward reaction [1].

Repetitive cyclic voltammograms for $3x10^{-5}$ M showed that the second cycle decreases comparing to the first one. This behavior arises due to the blocking of the electrode surface with the phenolic oxidation products. Phenol undergoes electro-oxidation possibly leading to the formation of phenoxy radical, which then undergoes polymerization with other phenol molecules. This polymeric product tends to stick to the electrode surface as a film. The polymeric film, thus formed on the electrode surface, hinders/prevents diffusion of further phenoxide ions to the electrode surface for oxidation, thereby causing a significant decrease in the anodic peak current[1,15]. Since the polymeric film is not chemically bound to the electrode surface (i.e. physically stuck), its removal can be achieved by merely physically rubbing against a tissue paper [1]

Different parameters were examined to choose the optimum conditions to determine and detect phenol compound.

3.2 Effect of the Supporting Electrolyte

The effect of supporting electrolyte were examined on the oxidation peak of phenol at the same conditions such as : sodium phosphate, sodium nitrate, Britton-Robison buffer, sodium sulphate, sodium chloride, potassium chloride, sodium acetate buffer. Britton-Robison buffer, sodium phosphate and sodium acetate buffer have a response toward electrooxidation peak of phenol. The shape and the height of the oxidation peak of phenol were taken into consideration on choosing the suitable supporting electrolyte. The results showed that the suitable oxidation peak (shape and height) of phenol in Britton-Robison buffer. .

3.3 Effect of Scan rate

The electrooxidation peak of $6x10^{-6}$M phenol in B.R buffer (pH=3.0) using CPE modified by TiO_2 nanoparticles was studied at different scan rates varying from 5 to 300 mV/s. By increasing scan rate the oxidation peak current increased [1,4] and shifted slightly to the positive side[1,3,5,6,8] as shown in Figure (3). But at scan rate more than 100 mV/s the peak shape was distorted specially at high concentration of phenol so the scan rate of 50 mV/s was selected for further work to avoid the distortion of the peak at higher concentrations of the phenol. The plots of peak currents against the square root of the scan rates exhibited linear relationship with correlation coefficients of 0.99. Showing that the electrocatlytic oxiadition of those phenol compounds was diffusion control [1, 5, 6, 11] .

3.4 Effect of pH

The effect of pH value is an important factor affecting the electrooxidation of phenol compound in aqueous solution [1,6,8,]. The pH values of B.R buffer was examined over the rang from acidic, neutral and basic medium on the oxidation peak of phenol (pH=3 to pH= 11). The results showed that, the peak potentials shifted to more negative values with increasing the solution and agreeing the published ones [1,4,6] and the best peak shape and highest current was obtained at pH value equal 7 neutral medium [8]. In basic medium the peak current of oxidation peak decrease due to the rate of formation of polymerization process which lead to decrease the oxidation peak of phenol. Moreover, the peak of oxidation current of phenol decrease in acidic medium that is may be due to the hydrogen bond which lead to decrease the peak current of oxidation peak. The effect of varying of pH on ($7x10^{-4}$M) of phenol with scan rate 50mV/s at CPE modified by TiO_2. by increasing pH values, the oxidation shifted to more negative value agreeing the reported works [1,2,10] .

3.5 Effect of concentration

Influence of phenol compound concentration on the oxidation peak current was studied over the range ($1x10^{-9}$ – $1x10^{-4}$ M) in B.R (pH= 7.0). The oxidation peak current of phenol increase rabidly by addition more concentration from phenol compound. But after 20 addition of phenol the surface of modified electrode blocking. Where phenol undergoes electro-oxidation possibly leading to the formation of phenoxy radical, which then undergoes polymerization with other phenol molecules. This polymeric product tends to stick to the electrode surface as a film[1]. And the removal of this blocking illustrated above. Fig. (4) shows a typical linear sweep voltammograms for different concentrations of phenol from ($1x10^{-9}$ to $8x10^{-8}$ M) and ($1x10^{-7}$ to $1x10^{-6}$M) in B.R buffer. On plotting concentration versus peak current a linear dependence of the peak current on the concentration of phenol was observed with correlation coefficient of 0.997 and standard deviation of 0.20.

3.6 Reproducibility

The reproducibility of the results was examined by six successive measurements of $6x10^{-6}$ M phenol under the optimum conditions. The relative standard deviation (RSD) was calculated and it was found to be 0.65%. Fig.(5) illustrates six typical voltammograms for the repeated measurements of $6x10^{-6}$ M phenol.

4. Analytical Application

The proposed method was applied to determine phenol in water samples such as tab water. Under the optimum conditions selected before, phenol has been determined in tap water sample. The concentration of phenol was determined using the method of standard additions and the recovery of the results ranged from 96-100% with a good response as shown in Table [1].

The collected results are compared with the previously published data as illustrates in Table(2)

5. Conclusion

In this work a new handmade Nano modified carbon paste electrode with special properties such as catalysis, the large specific surface area and more adsorption sites comparing to unmodified electrode was prepared. The obtained results showed that the optimum conditions to detect and determine phenol in lower concentration are: B.R buffer (pH=7.00) and scan rate of 50mV/s.

The suggested procedures can be used to detect the studied compounds with accurate, easily, rabidly, simple, cheap good reproducibility and low detection limit.

Picture 1: Handmade CPE modified by TiO_2 nanoparticles

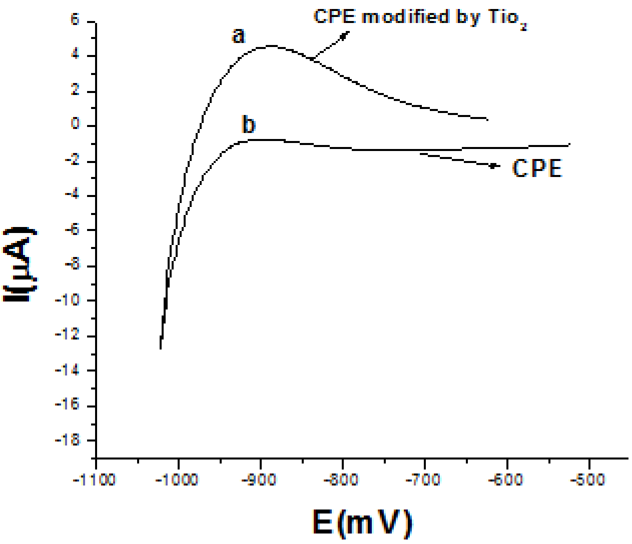

Figure 1: peak current of $1x10^{-4}$ mole of phenol in the presence of B.R buffer (pH=7.00) and scan rate of 50mV/s. a- at carbon paste electrode, b- at modified carbon paste electrode

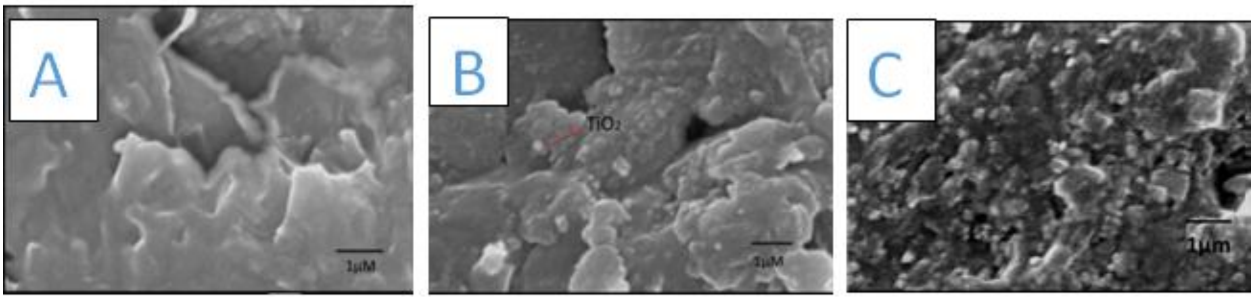

Figure 2: A- SEM image of unmodified CPE , B– SEM image of A + TiO_2, C- SEM image of B + phenol molecules

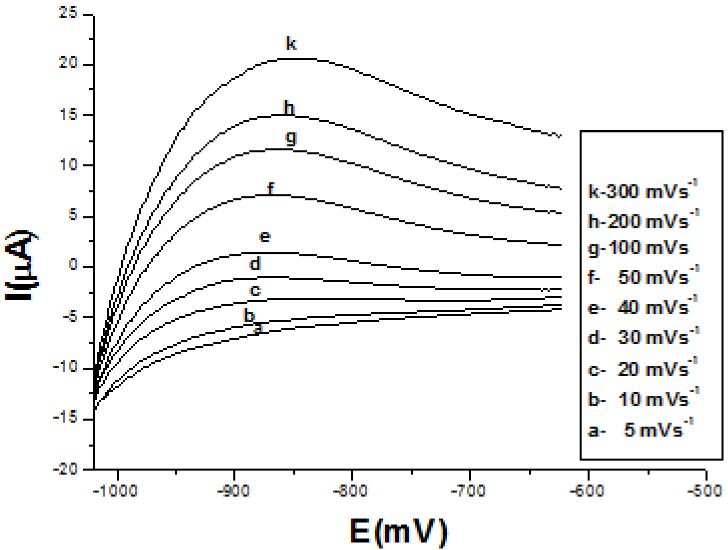

Figure 3: The effect of scan rate on the peak current of 6×10^{-6}M phenol in the presence of B.R buffer (pH = 3.0) and CPE modified by TiO_2 nanoparticles as a working electrode

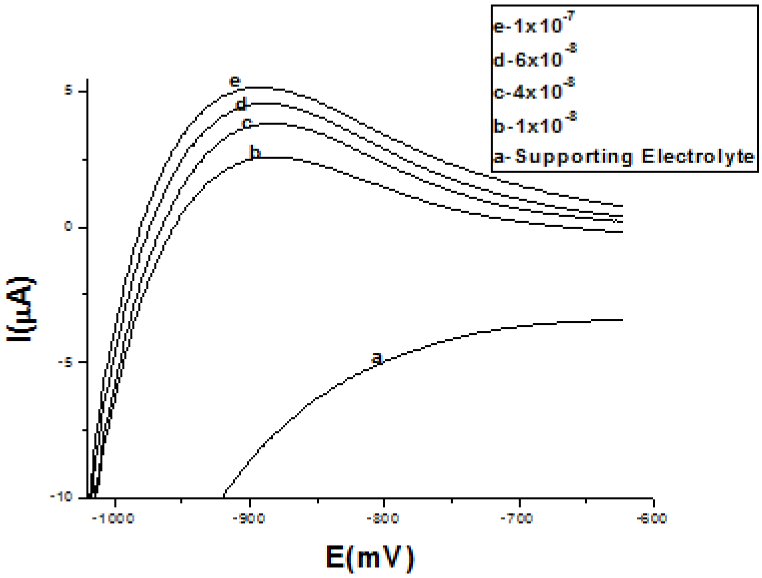

Figure 4: Linear sweep Voltammograms for different concentrations of phenol using CPE modified by TiO_2 nanoparticles in the presence of B. R. buffer pH = 7.0) at scan rate of 50 mV/s

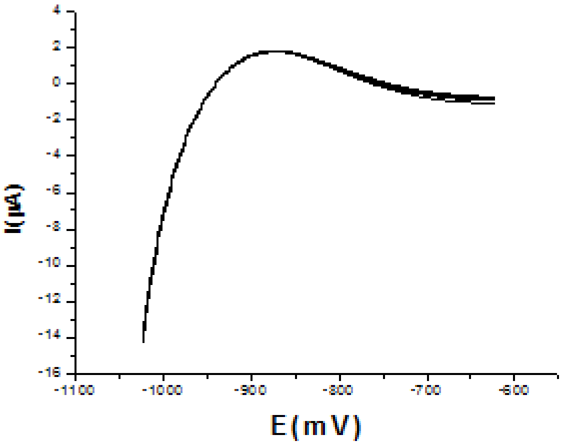

Figure 5: The reproducibility of the results was examined by successive measurements of 6×10^{-6} M of phenolin B.R buffer (pH=7.0) using CPE modified by TiO_2 nanoparticles at scan rate of 50 mV/s.

Table 1: Determination of the content of phenol in the tap water sample

Tap Water	Added $\times10^{-5}$ M	Found $\times10^{-5}$ M	Recovery%
	1×10^{-5}M	1.008 M	100%
	3×10^{-5}M	2.88 M	96%
	Added $\times10^{-4}$ M	**Found $\times10^{-4}$ M**	**Recovery%**
	1×10^{-4} M	0.99 M	99%
	3×10^{-4}M	2.98 M	99.3%

Table 2: Comparison between the DOL in this work and in other published ones .

	Working Electrode	Detection limit	Reference
Voltammetric Technique	Modified glassy carbon by Walled carbon nanotube electrode.	$2.3\text{x}10^{-9}$ M	5
	Single Wall Carbon Nanotube/Poly (3,4-ethylenedioxythiophene) modified Screen-Printed Carbon Electrode.	$3.8\text{x}10^{-7}$ M	6
	PLATINUM Electrode modified with Polypyrrole doped with Ferricyanide.	$5\text{x}10^{-6}$ M	12
	Composite film of multiwall carbon nanotube/surfactant/tyrosinase on a carbon paste electrode.	$1.1\text{x}10^{-6}$ M	8
	A Novel Sol-Gel TiO_2 Carbon Paste Electrode.	$1\text{x}10^{-6}$ M	10
	Glassy carbon electrodemodified by an acetylene soot–dihexadecyl hydrogenphosphate composite in the presence of cetyltrimeth_ ylammonium bromide	1×10^{-7} M	18
	Carbon paste electrode modified with pchloraniland carbon nanotubes.	$2\text{x}10^{-6}$ M	11
	Carbon Paste Electrode modified with TiO_2 nanoparticles.	$1\text{x}10^{-9}$ M	Present Work

References

[1] J. Mathiyarasu, J. Joseph, K. Phani and V .Yegnaraman,Indian Journal of Chemical Technology, 11: 797- 803, (2004).
[2] Z.Sun, H. Zhang, X. Wei, X. Ma and X. Hu,J Solid State Electrochem, 19: 2445–2456, (2015).
[3] L. Hernández, P. Hernández, V. Velasco and Anal BioanalChem, 377 : 262–266, (2003).
[4] Y, Peng, J.Xu, J. Zhao, B. Huand S, Hu,Russian in Elektrokhimiya, 44 (2) 222–229, (2008).
[5] M.Govindhan, T,Lafleur, B. Adhikari, and A. Chen,Electroanalysis, 27, 902– 909 , (2015).
[6] N. Negash,H.Alemu, and M. Tessema, International Scholarly Research Notices, Volume Article ID 459246, 11 pages, (2015).
[7] H.Maleh, M. Moazampour, A. Ensafi, S. Mallakpour and M.Hatami, Environ SciPollut Res, 21:5879–5888, (2014).
[8] S. Hashemnia, Sh. Khayatzadeh and M. Hashemnia,J Solid State Electrochem, 16:473–479, (2012).
[9] H.Moghaddam, H.Beitollahi, S.Tajik,M.Malakootian and H.Maleh, Environ Monit Assess, 186, 7431–7441, (2014).
[10] M. Hughes, P. Nguyen1, S.Lunsford, C.Han and D. Dionysiou,JSM Chem, 1: 1001, (2013).
[11] R.Sadeghi, H.Maleh, M. Khalilzadeh, H. Beitollahi,Z.Ranjbarha, M. ZanousiS.Z. Ranjbarha, M.Bagher, and P.Zanousi, Environ SciPollut Res, 20:6584–6593, (2013).
[12] S. LUPU, I. ION and A. ION.Revue Roumaine de Chimie, 54(5), 351–357, (2009).
[13] H. Beitollahi, S. Tajik and P. Biparva,Measurement, 56, 170–177, (2014).
[14] M. Khodari, Electroanalysis, 5(5-6), 521-523, (1993).
[15] M Khodari, AA El-Rady, E Rabee, N Nabil, Journal of Chemistry and Chemical Engineering 8 (7), 654-661 (2014)
[16] M Khodari, JM Kauffmann, GJ Patriarche, MA Ghandour
[17] Journal of pharmaceutical and biomedical analysis 7 (12), 1491-1497 (1989)
[18] M Khodari, U Bilitewski, AAH Basry, Electroanalysis 27 (2), 281- 284, (2014)
[19] N.Tahar, R. Abdelhedi and A.Savall,J ApplElectrochem, 39, 663–669, (2009).