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Pd-1%Ni Composite Electrodes for Electrooxidation of Phenol in Acid Solution

R.N. Singh[*], *D. Mishra, Anindita*

Chemistry Department, Science Faculty, Banaras Hindu University, Varanasi-221005, India
[*]E-mail: rnsbhu@rediffmail.com

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Binary Pd and 1% Ni composite has been prepared by borohydride reduction method and produced in the thin film forms on Ti by an ink painting method. The catalyst electrode was investigated as electrocatalyst for the oxidation of phenol in acid medium at 25°C, using cyclic voltammetry (CV), chronoamperometry and HPLC. The CV study showed that with the increase in phenol concentration from 0.5 to 5mM, the oxidation peak current (I_p) initially increases and attends a constancy thereafter. The I_P value, however, varies linearly with (scan rate) $^{1/2}$. The peak potential (E_p) corresponding to I_p was found to be practically unchanged with phenol concentration. The rate for phenol oxidation, as measured in terms of I_p, at the surface of the electrocatalyst is found to be independent of pH of the reaction mixture. Further, the electrode does not seem to undergo deactivation due to intermediates and products formed during the phenol oxidation. Oxalic acid has been identified as the end product of the reaction.

Keywords: Phenol oxidation, electrocatalysts, borohydride reduction, cyclic voltammetry, chronoamperometry

1. INTRODUCTION

Widespread contamination of water by phenol and its chloro-derivatives has been considered as a matter of great concern throughout the world during recent years. Phenol is a potential known carcinogen and is of considerable health concern, even at low concentration [1]. The toxicity of chlorophenol increases with number of chloro-substituents but is lowered by the presence of chloro-substituent in the ortho position [2]. An increase in number of chloro-substituent can also promote the accumulation of such chemical compound in fish and other living organisms [3] and, thereby, increase their hazardous properties. It is reported that phenolic compounds concentrations above 2 mg per liter are toxic to fish and that their concentrations between 10 and 100mg l^{-1} result death in aquatic life within 96 hours [4].

Most widely used methods, at present, for removing phenol and phenolic compounds from wastewaters are: biological treatment, activated carbon adsorption, solvent extraction, chemical oxidation and electrochemical methods [5]. The transformation of toxic organic compounds into non toxic ones using electrochemical methods has attracted great attention during recent years [6,7,8-9,10] and recognized to be advantageous due to versatility, high efficiency, easy to control, amenability to automation, environment compatibility and cost effectiveness. Though, the electro-oxidation of most organic compounds, including phenol is possible theoretically in the potential region before oxygen evolution, the oxidation reactions are sluggish practically and their rate are limited more by kinetic than by thermodynamic factors [11]. It is, therefore, desired to search for low cost, efficient and thermodynamically stable anodes so as to improve the oxidation kinetics.

Most probably, Comninellis studied [12], for the first time, the electrochemical oxidation of phenol at Pt and DSA anodes and demonstrated that traditional electrode materials (Pt, Ti/IrO_2, Ti/RuO_2, Ti/PbO_2) give relatively low current efficiency. Contrary to this, the SnO_2 anodes which do not only give high current efficiencies but allow quasi complete total organic carbon (TOC) elimination. The unexpected behaviour of the SnO_2 anode has been ascribed to the change of chemical structure of the electrode surface during anodic polarization [13]. Subsequently, the electrochemical oxidation of benzoquinone on Ti/IrO_2 and Ti/SnO_2 in water [14] and on Fe-doped PbO_2 on Ti in 0.1M H_2SO_4 [15] and 2-chlorophenol on a composite PbO_2/polypyrrole electrode in 0.1M H_2SO_4 [16] have also been reported.

In recent years, the study on the electrochemical detoxification of organic pollutants, particularly phenol and its chloro-derivatives in wastewater has become an important and burning research area of electrochemistry. In order to increase the efficiency vis-à-vis to reduce the cost of the process, a variety of electrode materials have been examined in the process of phenol oxidation. Some of the important electrode materials made of noble metals and based on metal oxides recently reported are Pt and Au [17-19], PbO_2 [20-23], SnO_2 [24-26], Ti/IrO_2, Ti/RuO_2, Ti/PbO_2, and Ti/SnO_2 [27], Bi/PbO_2 [28], Ti/SnO_2-PbO_2 [29], Ti/ Sb-Sn-RuO_2-Gd, Ti/Sb-Sn-RuO_2 [10], RuO_2-TiO_2 [30], Pt coated with quaternary metal oxide film containing Ti, Ru, Sn, and Sb oxides [31], and synthetic diamond electrodes [32-35,6,7].

We have obtained thin films of Pd-1%Ni composite on Ti through $NaBH_4$ reduction method and investigated, for the first time, as electrocatalysts for oxidation of phenol in 0.5M H_2SO_4. Preliminary results of the investigation were very encouraging as very negligible or no inhibition effect of phenol oxidation intermediates/products, particularly at low concentration (< 3 mM) was observed on the electrocatalyst. Details of results obtained are described in the present paper.

2. EXPERIMENTAL PART

2.1. Preparation of Pd-1%Ni/Ti electrodes

Pd-1%Ni composite in powder form was obtained by dissolving required amounts of $PdCl_2$ (anhydrous Merck) and $NiCl_2$ (Merck 97%) in 5 ml acidified double distilled water and subsequent reduction of metal ions by adding excess of $NaBH_4$ (Sigma-Aldrich, 98%) solution under stirred conditions as described elsewhere [36]. The catalyst obtained in powder form was mixed together with few ml of ethanol (Merck)-water mixture and then ultrasonicated for 15 min so as to obtain an ink. To obtain the electrode, 2-3 drops of ink were dropped onto a pretreated Ti plate through a syringe, dried and then one drop of 1% Nafion solution (Alfa Aesar) was dropped over the dried catalyst layer to cover it. The catalyst electrodes, thus obtained, were finally irradiated with microwave (800 watt) for one minute. Prior to use, the Ti-support was treated with concentrated HCl for 10 min, degreased with acetone by ultrasonication, washed with distilled water and dried. Electrical contact with the catalyst over layer and electrode mounting were carried out as described elsewhere [37].

2..2 Material characterization

X-ray diffraction pattern (XRD) of Pd-1%Ni composite was recorded on an X-ray diffractometer (Thermo-electron) using $CuK_{\propto}$ as the radiation source (λ = 1.541841Å). Morphology of the composite was studied by a transmission electron microscope (TECNAIG FEI Neederland). For TEM examination, the sample was prepared by dispersing the catalyst in redistilled water, transferring a drop of the suspension onto a colloidal coated copper grid and subsequent drying in air.

2.3. Electrochemical studies

A conventional three-electrode single compartment Pyrex glass cell was used to carry out electrochemical studies. Pt-foil (~8 cm^2) and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammetry (CV) and chronoamperometry studies were performed using an EG & G PAR model 273A galvanostat / potentiostat. The CV study was performed in the potential region, - 0.20 – 1.30 V, in 0.5M H_2SO_4 and in 0.5M H_2SO_4 + x mM Phenol ($0.5 \leq x \leq 5.0$) at 25°C. Prior to carry out the actual CV experiment, each electrode was cycled 10 times at a scan rate of 50mV s^{-1} in 0.5M H_2SO_4. All electrochemical experiments were performed with triplicate electrodes in an Ar-deoxygenated electrolyte at 25°C.

2.4. Identification of oxidation intermediates / products

The oxidation products formed during the anodic oxidation of phenol were analyzed by HPLC on a Younglin Acme 9000, using a C18 column and the mobile phase: 65%water-33%methanol-2%acetic acid. The flow rate was 1.0ml min^{-1}. Before each analysis, the sample and solvent were filtered.

3. RESULTS AND DISCUSSION

3.1. XRD/TEM

The XRD pattern of Pd-1%Ni shown in Fig. 1 displays the three characteristic diffraction peaks corresponding to planes, (111) (200) and (220), for the face centered cubic (fcc) structure of Pd

(JCPDS file No. 05-0681). Also, this figure indicates the formation of PdO (d = 1.99756 Å, JCPDS file No. 06-9515) and NiO (d = 2.0866 Å: JCPDS file No. 04-0835) as impurity phases.

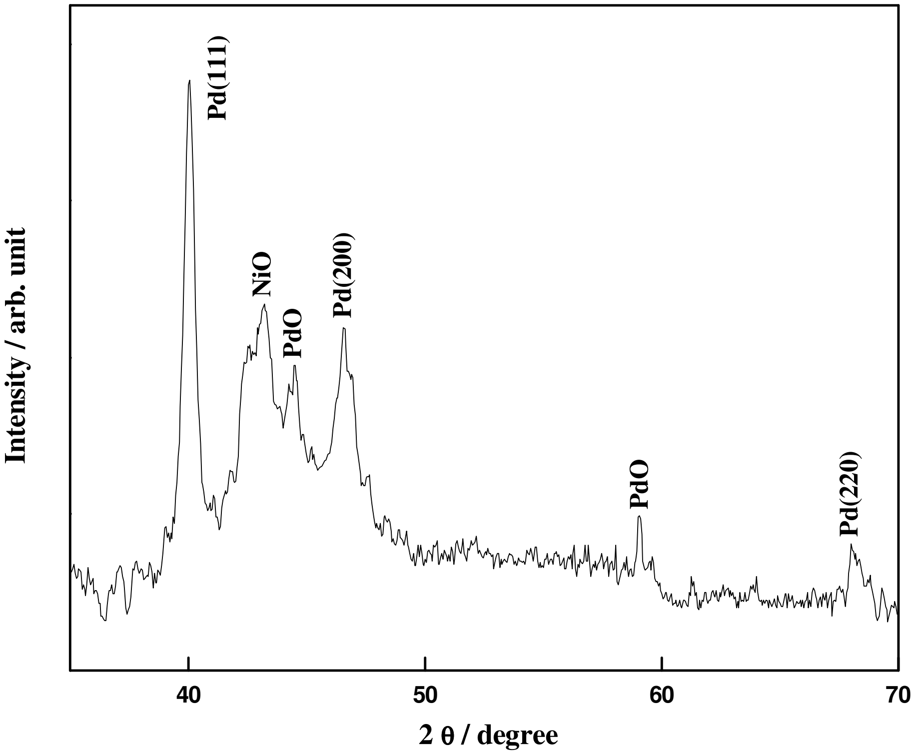

Figure 1. XRD pattern of Pd-1%Ni composite.

TEM pictures of Pd-1%Ni are shown in Fig. 2. This figure shows that particles agglomerate to produce a network of clusters.

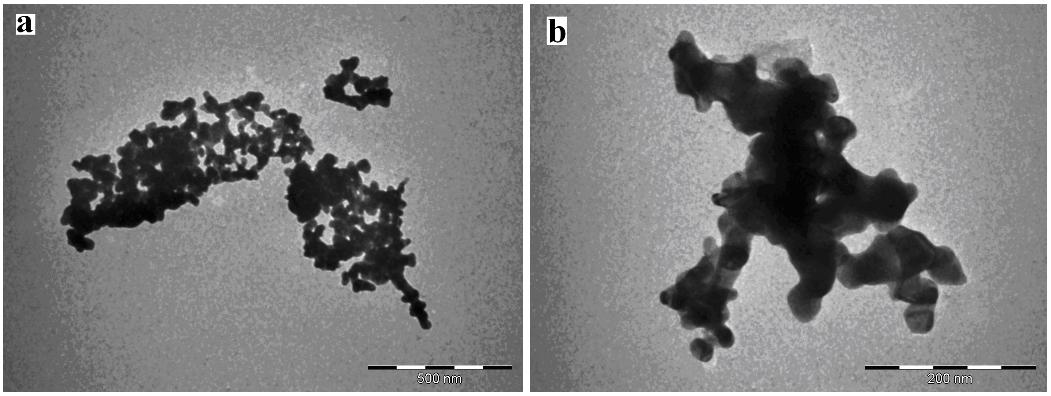

Figure 2. TEM pictures for Pd-1%Ni composite: (a) 500 nm and (b) 200 nm.

3.2. Cyclic Voltammetry (CV)

CV of Pd-1%Ni/Ti electrode in 0.5M H_2SO_4 with and without containing phenol has been recorded at a scan rate of 50mV s^{-1} between E = -0.20 and E = 1.3 V and curves, so obtained, are reproduced in Fig. 3. In Fig. 3, cathodic and anodic curves produced in the potential region, - 0.20 V and 0 V are due to the adsorption and desorption of hydrogen. The strong cathodic peak appeared at E = 0.30-0.313 V corresponds to the reduction of palladium (II) oxide, formed due to transformation of Pd into palladium (II) oxide in the potential region ~ 0.5-1.0 V under anodic conditions. At E > 1.25 V, the oxygen evolution reaction takes place. The comparison of CV of the electrode obtained in presence and absence of phenol shows that oxidation of phenol takes place in the potential region which corresponds to the Pd (II) oxide formation.

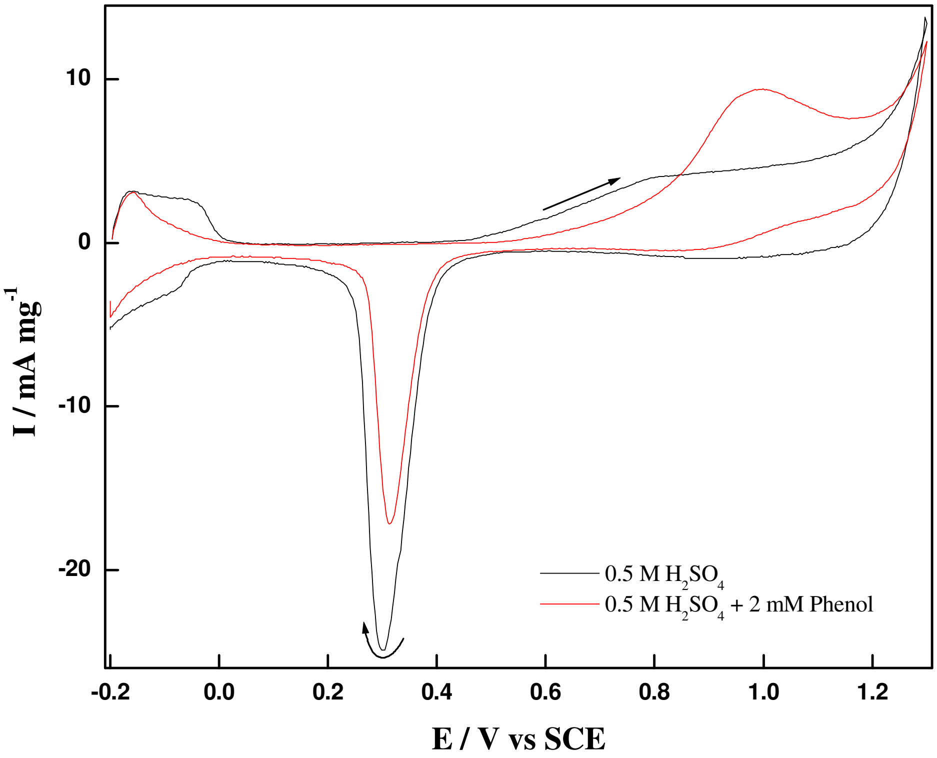

Figure 3. Cyclic voltammogram of the Pd-1%Ni/Ti electrode at 50mV s^{-1} in 0.5M H_2SO_4 and in 0.5M H_2SO_4 + 2.0mM Phenol at 25°C.

As reported elsewhere [36], the total charge(Q) involved in the complete reduction of palladium oxide into Pd metal has been used to determine the electrochemical active surface area (EASA) of the catalyst electrode, using the relation, EASA = Q/Sl, where 'S' is the proportionality constant used to relate charge with area and 'l' is the catalyst loading in mg. A charge value of 405μC cm^{-2} is assumed for the reduction of PdO monolayer [38]. Q-value was estimated by integrating the cathodic peak observed at E ≈ 0.30 V.

To examine the stability, a set of 10 consecutive cyclic runs at 50mV s^{-1} were recorded at the catalyst electrode in 0.5M H_2SO_4 and 0.5M H_2SO_4 + 2.0mM Phenol at 25°C. The total charge involved in the complete reduction of PdO into Pd metal in each cycle was determined by integrating the cathodic peak for the reduction of PdO. Values, so obtained, are shown in Tables 1 and 2. CV curves determined at varying scans on the electrode are given in Fig. 4 and 5.

Table 1. Effect of No. of cycles on electrochemically active surface area of Pd-1%Ni/Ti electrode in 0.5M H_2SO_4 at 50mV s^{-1}.

Cycles	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Q / mC	5.32	5.43	5.66	5.70	5.64	5.61	5.64	5.72	5.76	5.79
EASA / $cm^2 mg^{-1}$	~ 88	~ 90	~ 94	~ 95	~ 94	~ 93	~ 94	~ 95	~ 96	~ 96

Table 2. Effect of phenol concentration on electrochemically active surface area of electrocatalyst in 0.5M H_2SO_4 at 50mV s^{-1}.

[Phenol] / mM	0	0.5	1.0	2.0	3.0	4.0	5.0
Q / mC	3.78	3.42	3.32	3.17	3.16	3.36	2.71
EASA/$cm^2 mg^{-1}$	~67	~60	~58	~56	~56	~59	~ 48

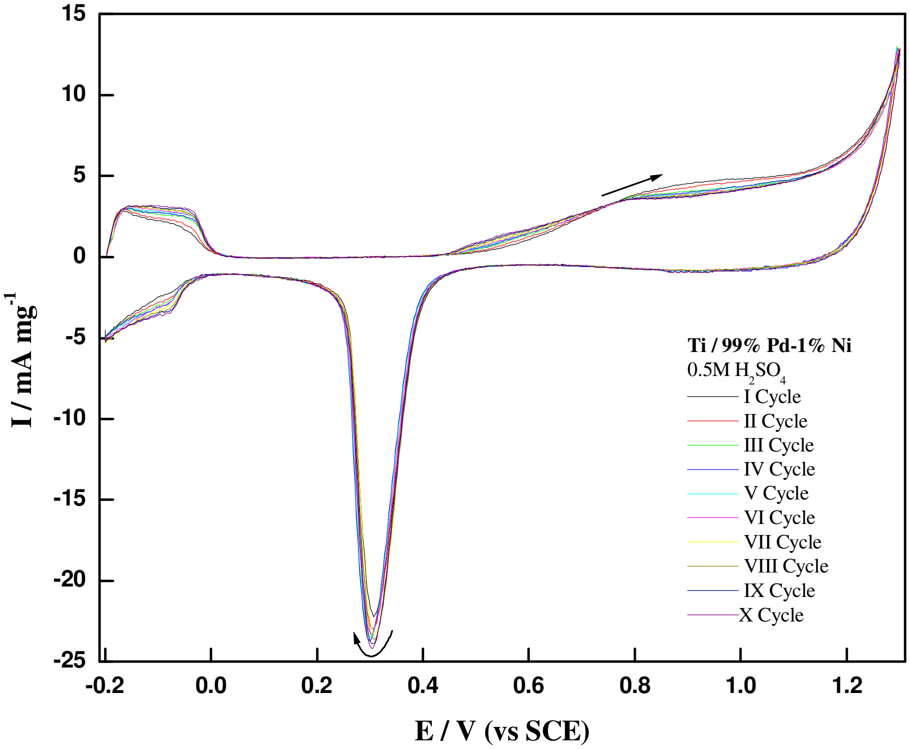

Figure 4. Cyclic voltammogram of Pd-1%Ni/Ti electrode at 50mV s^{-1} in 0.5M H_2SO_4 at varying scans.

Results, shown in Table 1, show that the EASA values of electrodes in 0.5M H_2SO_4 are constant, particularly after the second cycle, regardless of the number of scans. Thus, the catalyst eletctrode seems to be quite stable in 0.5M H_2SO_4 under potential cycling condition. The average values of EASA were found to be ~ 94 cm^2 mg^{-1}in case of Pd-1%Ni/Ti electrode. In estimation of average, all the values of EASA obtained after the second cycle were considered.

Results shown in Table 2 show that the EASA values for Pd-1%Ni/Ti are practically constant regardless of concentration of phenol/intermediate oxidation products during cyclic run, however, these values are lower than that obtained for the same electrode in 0.5M H_2SO_4 in absence of phenol. This indicates that nearly small and a constant fraction of the Pd active sites are covered by phenol oxidation intermediates/products.

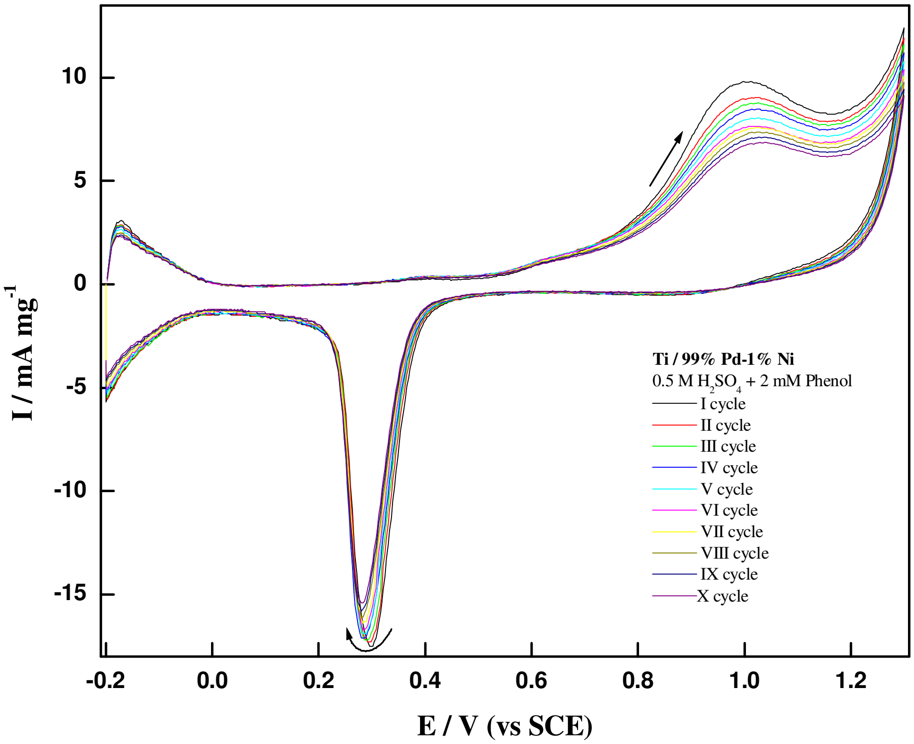

Figure 5. Cyclic voltammogram of Pd-1%Ni electrode at 50mV s^{-1} in 0.5M H_2SO_4 + 2.0 mM Phenol at varying scans at 25°C.

3.2.1. Electro-oxidation of phenol

Fig. 5 shows CV curves for the Pd-1%Ni/Ti electrode at scan rate of 50mV s^{-1} and at varying scans in 0.5M H_2SO_4 + 2.0mM Phenol. Curves shown in Fig. 5 exhibit that the Phenol oxidation peak current (I_p) observed in the first cycle declines in the second cycle and it becomes more or less constant in the subsequent cycles (3rd to 10th). The observed decrease in the I_p values from first to second cycle were observed to be 8% with the use of 2.0mM Phenol concentration in the electrolyte

(0.5M H_2SO_4). However, the peak potential (E_p) value corresponding to the oxidation peak does not change with the number of cycle as well as phenol concentration. Small decrease in the peak current may be due to small coverage of the electrode surface by phenol or its oxidation intermediates / products. So, in subsequent studies, the oxidation peak current (I_p) of the first anodic cycle was considered for analysis of results.

3.2.2. Effect of scan rate

The effect of scan rate has been observed on the cyclic voltammogram of the electrode, Pd-1%Ni/Ti, in 0.5M H_2SO_4 + 2.0mM C_6H_5OH and the results, so obtained demonstrate that the I_p value increases with the scan rate following constancy (Fig. 6). Plot, I_p vs (scan rate)$^{1/2}$ was found to be linear, particularly at higher scan rates (Fig. 7), indicating thereby that the oxidation of phenol at the Pd-1%Ni/Ti is diffusion controlled under the applied experimental conditions [39]. With the increase in scan rate from 10 to 200mV s^{-1}, the peak potential also increased showing constancy at higher scan rates (Fig. 8). The phenol oxidation peak current (I_p) corresponding to each scan rate was corrected for the background current measured at that scan rate.

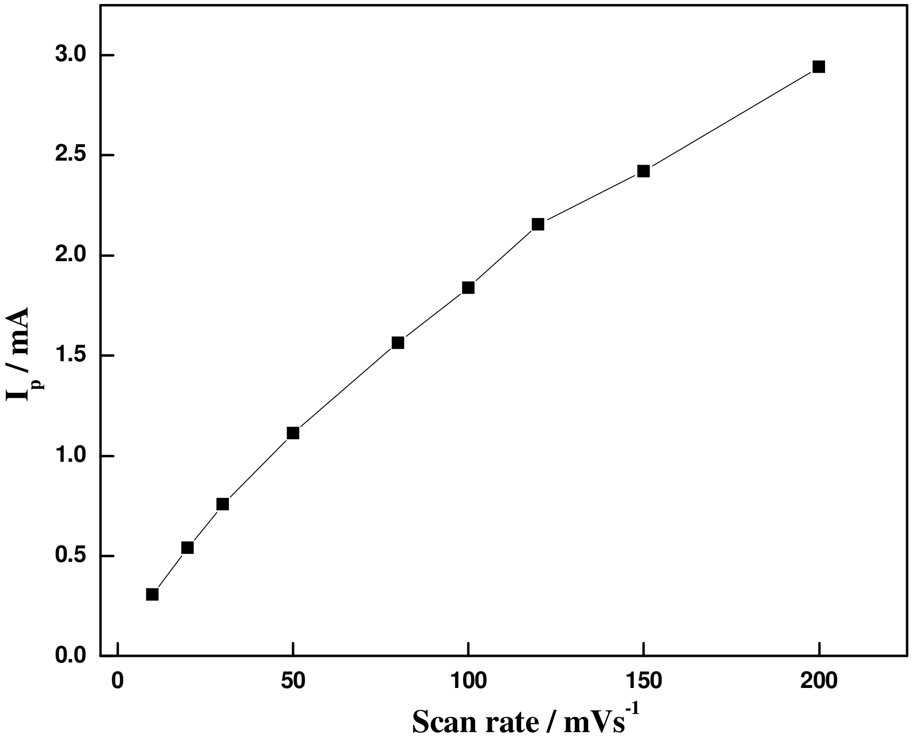

Figure 6. Plot, I_p versus Scan rate on the Pd-1%Ni/Ti electrode in 0.5 M H_2SO_4 + 2.0 mM Phenol at 25°C.

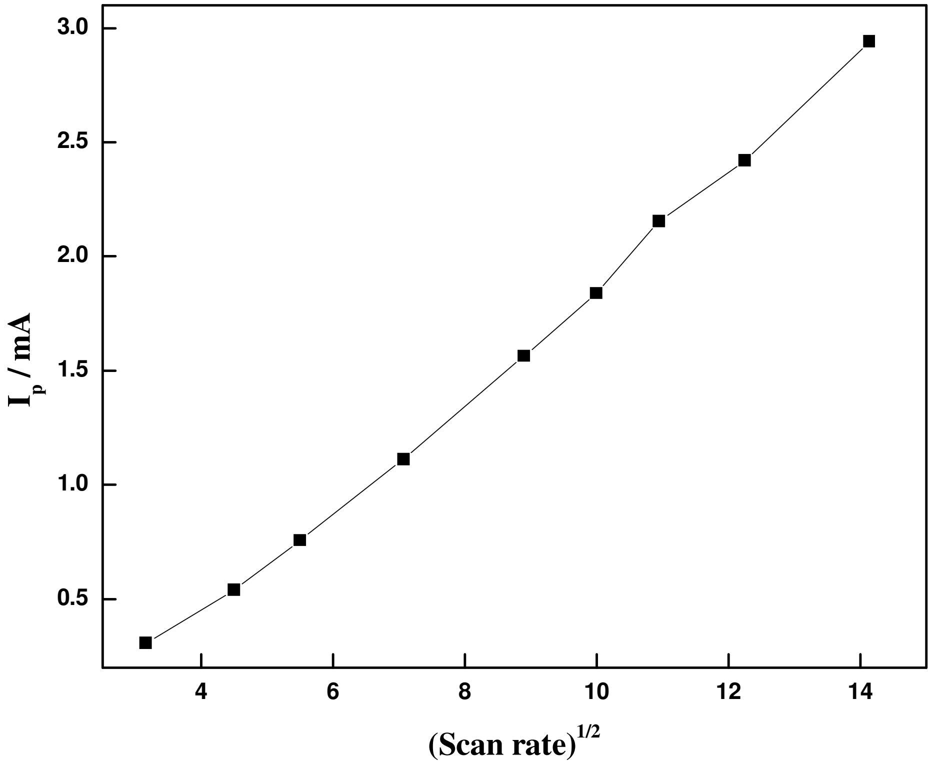

Figure 7. Plot, I_p versus (Scan rate)$^{1/2}$ on the Pd-1%Ni/Ti electrode in 0.5M H_2SO_4 + 2.0 mM Phenol at 25°C.

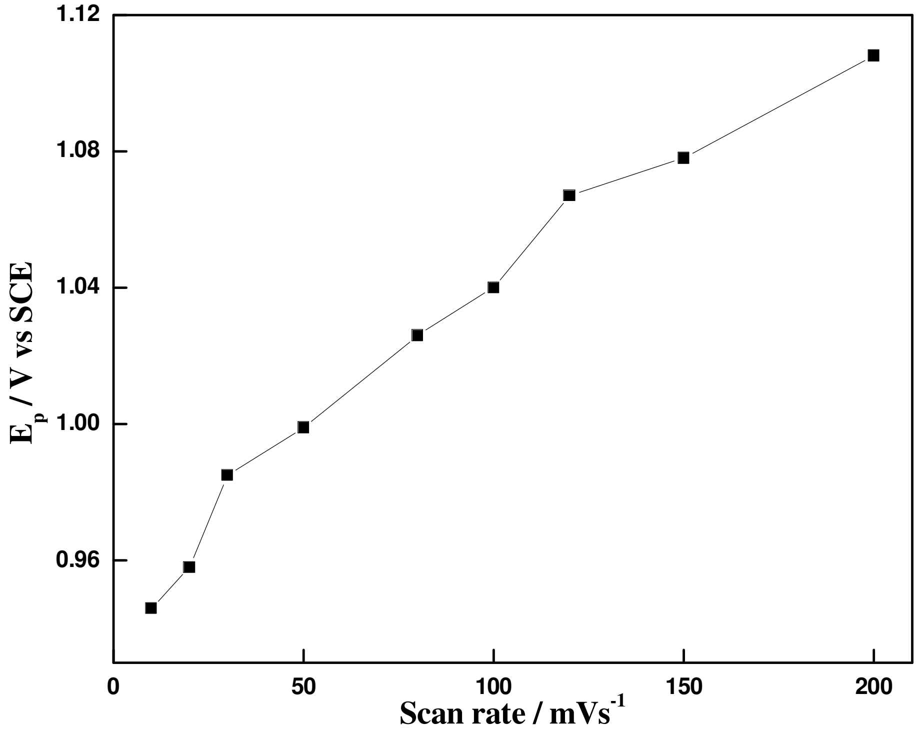

Figure 8. Plot, E_p versus Scan rate on the Pd-1%Ni/Ti electrode in 0.5M H_2SO_4 + 2.0mM Phenol at 25°C.

3.2.3. Effect of Phenol Concentration

To investigate the effect of the phenol concentration on the rate of electrochemical oxidation, the CV of the Pd-1%Ni/Ti electrode has been recorded at 50mV s^{-1} in 0.5M H_2SO_4 containing varying concentrations of Phenol from 0.5mM to 5.0mM and results, so obtained, are shown in Fig. 9. This figure shows that with the increase in phenol concentration from 0.5 to 5.0mM, the I_p value initially increases and attains nearly constancy thereafter. Moreover, the E_{pa} value is found to be practically unchanged with the phenol concentration. However, in the case of phenol oxidation at Pt electrode in 0.5M H_2SO_4, Arslan et al. [40] found that with the increase in phenol concentration the peak current initially increases, attends a maximum and decreases thereafter.

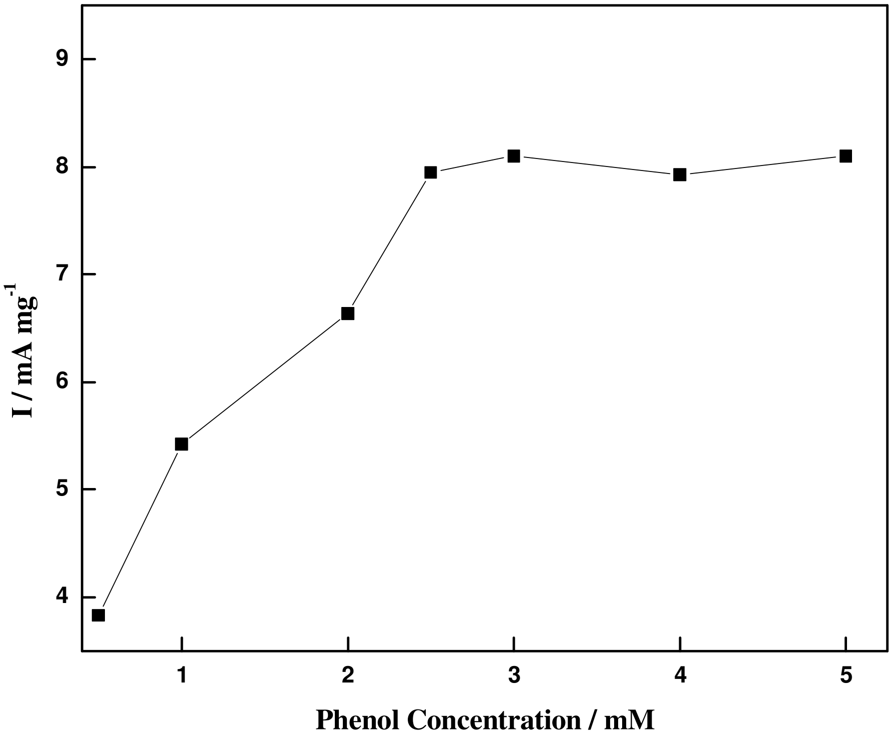

Figure 9. Effect of phenol concentration on the rate of phenol oxidation at the Pd-1%Ni/Ti electrode in 0.5M H_2SO_4 at 25°C; scan rate = 50mV s^{-1}.

3.2.4. Effect of pH

Results have shown that the I_p values are practically constant with the change in pH of the solution from pH 1 to pH 0.0.

Table 3. Effect of pH on peak current of electrocatalyst in 0.5M H_2SO_4 at 50mV s^{-1}.

pH	0	0.2	0.4	0.6	0.8	1
I_p(mA mg^{-1})	6.4	4.5	5.9	5.8	5.4	5.4

3.3. Product analysis

For identification of phenol oxidation products, chronoamperometry of the electrocatalyst in 0.5M H_2SO_4 + 2mM Phenol at a constant current density of 5mA cm^{-2} at 25°C has been carried out. Small volumes of the reaction mixture were withdrawn at different times and analyzed by running HPLC program. Four chromatographic peaks were found, which were identified as phenol (most intense), hydroquinone, catechol and oxalic acid. Further, CV of the electrocatalyst in 0.5M H_2SO_4 with and without containing oxalic acid did not change practically. On the other hand, CV and HPLC measurements showed that the oxidation product of the hydroquinone and catechol in 0.5M H_2SO_4 is oxalic acid. Therefore, this confirms that the end product of the phenol oxidation is oxalic acid.

The working solvent and mobile phase used were water and a mixture of water, methanol and acetic acid in 65:33:2 ratios, respectively.

4. CONCLUSION

The study indicates that Pd-1%Ni/Ti electrode is quite stable and does not undergo deactivation by the phenol oxidation intermediates and products under the employed experimental conditions. Thus, the results show that Pd electrode with improved electrocatalytic properties by suitable means can be a potential anode for detoxification of phenol at low concentration (≤ 3 mM). The rate of phenol oxidation is observed to be independent of pH of the reaction mixture. The investigation of mechanism is continued.

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