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Adsorptive Stripping Voltammetric Determination of Hydroquinone using an Electrochemically Pretreated Glassy Carbon Electrode

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Abstract

A simple and efficient adsorptive stripping voltammetric (AdSV) method was developed for the determination of hydroquinone at an electrochemically pretreated glassy carbon (GC) electrode in waste water. Various parameters such as solvent system, accumulation potential, accumulation time and scan rate were optimized. The electrochemically pretreated GC electrode showed good response towards hydroquinone determination by using AdSV. Under the optimized conditions the peak current showed good linear relationship with the hydroquinone concentration in the range of 0.5-4.0mg L^{-1} and 5-30mg L^{-1}. The 60/40 methanol/water composition was found to be the best solvent system and 0.05mol L^{-1} H_2SO_4 was found as useful supporting electrolyte concentration. The accumulation time was 60 s and the detection limit was 50µg L^{-1}. The developed method was successfully applied for the determination of hydroquinone in polymeric industrial discharge samples waste photographic developer solution and cream sample without any significant effect of surface fouling.

Keywords: Hydroquinone**,** Electrochemically pretreated GC electrode, AdSV, polymeric discharge samples, photographic developer samples.

Introduction

Hydroquinone is an important phenolic compound used in a wide variety of biological [1] and industrial processes [2]. It is used principally as inhibitor in polymer industries to stop polymerization of acrylic acid, methyl methacrylate during storage and shipping processes. Hydroquinone is used as an intermediate in the manufacturing of antioxidants for rubber, dyestuffs and food products. The major use of hydroquinone is as a reducing agent in photographic developing solution which reduces silver halides to elemental silver in black-and-white photography and lithography [3]. Hydroquinone mostly discharges from the effluents of photographic developing processes and from the gasification condensate water [3, 4]. Besides its importance it is also very much toxic and creates serious water pollution problems in many localities. Exposure to hydroquinone produces health hazard effects to humans and animals [3-5]. There are varieties of method available in the literature for the determination of hydroquinone using colorimetry [6], titrimetry [8, 9], spectrofluorimetry [9, 10], spectrophotometry [11, 12, 13], high-performance liquid chromatography (HPLC) with different detectors [14, 15] and gas chromatography-mass spectrometry (GC-MS) [16, 17].

Due to easy instrumentation, low equipments and running cost, high selectivity and sensitivity, better reproducibility, broad linear dynamic range and easy sample preparation, the electrochemical technique such as differential pulse voltammetry has clear edge over the other techniques for the quantitative determination of environmentally toxic organic compounds in complicated matrices [18]. The determination of hydroquinone in different samples have been reported by voltammetry using various chemically or biologically modified electrode which act as an intermediary in its oxidation process [19-25], but the maintenance and the procedures for the construction of such type of electrodes is cumbersome and time

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consuming. Due to high rate of electrode processes, broad anodic potential window, the glassy carbon electrode is considered to be the most suitable sensor for the oxidation of various substances and extensively being used in electrochemistry for the analysis of various important electroactive substances and as a template for the modification of electrodes [26].The organic compounds such as nitro substituted phenols have been successfully adsorbed at carbon paste electrode and exploited for sensitive adsorptive stripping voltammetric detection [27, 28]. The sensitivity of the glassy carbon can be improved by activating the electrode surface by pretreatment. Various types of pretreatment procedures have been proposed to activate the electrode surface, such as cleaning by ultrasonication [29], polishing with alumina [30], chemical pretreatment [31], vacuum heating [32], electric arc treatment [33], laser irradiation [34] and electrochemical pretreatment [35-41]. The electrochemical pretreatment procedure is useful due to its easy handling with no additional requirements and its importance in vivo electroanalysis. The electrochemical pretreatment (anodization) may be performed at a fixed high anodic potential (usually at +1.8 V or more) for a specific time or successive cycling between wide range of potentials [35]. It has been studied extensively that electrochemical pretreatment of the carbon electrode leads to the formation of an oxide film on the surface which include carbonyl, carboxyl, quinones and hydroxyl groups [29, 34, 35- 41]. These groups at the surface of pretreated carbon electrode represent catalytic behavior which has been exploited to improve the sensitivity for the determination of many important organic and inorganic substances in various biological and industrial samples [42-48].

Another advantage of the electrochemically pretreated glassy carbon electrodes is that it makes the surface highly porous thereby increasing the surface area which greatly improves the adsorption processes [36]. The phenolic compounds having the surface active properties can be readily adsorb at this pretreated surface [49-52] and therefore has been exploited for the adsorptive stripping voltammetric determination of environmentally toxic phenols at trace level [53].

Up to the best of our knowledge there is no method reported for the sensitive determination of hydroquinone using adsorptive stripping voltammetry at an electrochemically pretreated glassy carbon electrode. Therefore the aim of this study was to develop a new simple sensitive adsorptive stripping voltammetric method for the determination of hydroquinone in waste water effluents and cream sample.

Experimental

Apparatus

A PAR Model 303 SMDE was used in conjunction with a PAR Mode 174A EG&G Polarographic Analyzer USA and an X-Y Recorder Model RE0089 to record all the DP voltammograms. Cyclic voltammetric experiments were performed by Metrohm polarographic analyzer (Switzerland) model 797 version 1.1 with a personal computer. GC electrode was used as a working electrode. An Ag/AgCl/ saturated KCl reference electrode and a pt-wire as an auxiliary electrode completed the three electrodes set-up. Lambda 2 UV/ Visible Spectrometer of Perkin-Elmer was used for comparative analysis of the samples.

Chemicals and reagents

Hydroquinone, methanol and H_2SO_4 were of analytical grade from E. Merck. Germany. Stock solution of 100 mg L^{-1} hydroquinone was prepared by dissolving 0.01g/100 ml in 60/40 methanol/water mixtures. The supporting electrolyte 1M H_2SO_4 was also prepared in 60/40 methanol/water separately. Appropriate amount of these solutions were diluted to 10 ml and putted into polarographic cell for voltammetric studies. Double distilled water was used throughout in experiment. Polymeric industrial sample was obtained from the discharges of various industries of Karachi. The photographic developer solution was obtained from Kodak laboratory, Hyderabad and the Hyderoquin cream was obtained from the local drug store.

Cleaning and preparation of GC electrode by electrochemical pretreatment

First of all, the GC electrode was vigorously polished with emery paper followed by 0.3 mm alumina powder on cloth surface and then thoroughly washed with double-distilled water. To remove residue from the surface, the electrode was cleaned in an ultrasonic bath for 2 min in distilled water and then for 2 min in ethanol. The electrochemical pretreatment of glassy carbon electrode was carried out by employing a constant anodic potential of +1.8 V for 300 s in 0.1 M H_2SO_4. Then the electrode was scanned between potential of 0.0 V and +1.2 V at a scan rate of 100 mV/s. After scanning for about 25 cycles, a stable voltammetric peak was obtained.

Voltammetric procedure

A 10ml solution containing 5mg L^{-1} hydroquinone and 0.05 M H_2SO_4 in 60/40 methanol/water mixture was placed in a polarographic

cell and then the voltammetric measurement was performed by employing first electrodeposition for 60 s at a potential of +0.0 V followed by pushing the scan button to initiate the adsorptive stripping voltammetric scan in the anodic direction. After each experiment the electrode was cleaned by employing regeneration potential in the same solution containing 0.05 M H_2SO_4 at a potential of +1.2 V for 60 s. The study was performed at a scan rate of 10 mV/s, modulation amplitude of 25 mV, accumulation potential of 0.0 V for definite period of time. All experiments were carried out at room temperature.

Sample analysis:

A 10 ml solution containing 4 ml clarified waste water of polymer industry or 0.1 ml of photo graphic developer solution or 0.1 ml cream sample containing 0.05 M H_2SO_4 in 60/40 methanol/ water mixtures was placed in polarographic cell. Standard addition method was used for the determination in sample by spiking appropriate amount in this solution. Then the adsorptive stripping voltammogram was recorded after accumulation time of 60 s at an accumulation potential of + 0.0 V and then the peak current was noted.

Results and discussion

Choice of solvent system

First of all fifteen successive voltammtric measurements were performed in pure aqueous medium in order to study the reproducibility of hydroquinone signal by using adsorptive stripping voltammetry. The results showed that the peak current value decreased gradually up to about 80% of the original value which indicated that the surface of the electrode has been passivated in pure aqueous medium. The passivation of the electrode in pure aqueous medium was due to a deposit formation on the electrode during successive voltammetric scanning, ascribed to insoluble polymerization products [54, 55]. This deteriorates the surface of electrode by making strong interactions with the surface and hence cannot be removed completely from the surface during stripping. This deposit formation limits the performance of the analytical procedure. After this, fifteen successive voltammetric measurements were performed in 60/40 methanol/ water mixture containing 0.05 M H_2SO_4. The peak current value decreased to 10 of the original value. This indicated that the adsorptive product was almost dissolved in this medium. In pure non aqueous medium the electrode is less prone to surface fouling because the polymerization products do not form on the surface due to the solubility of the reaction product during scanning. After thorough study in various methanol to water ratio, the 60/40% methanol/water ratio was chosen, because in this medium the analyte, (1) is less prone to surface fouling, (2) can be deposited and removed easily from the surface during measurements. However, in order to get more reproducible results the surface of the electrode should be clean by employing a constant regeneration potential at +1.2 V for 60 s in the same solution after each experiment or after passivation.

Choice of voltammetry

The voltammetric study was carried out by using differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV) at an electrochemically pretreated electrode in 60/40 methanol/water mixture containing 0.05 M H_2SO_4 in order to compare the voltammetric peak of hydroquinone, depicted in Fig. 1. This figure shows that the peak current obtained by using AdSV (Fig. 1B) is higher than that obtained by using DPV (Fig. 1A). This indicates that hydroquinone is adsorbed at the surface of pretreated GC electrode resulting into increased peak current by using AdSV.

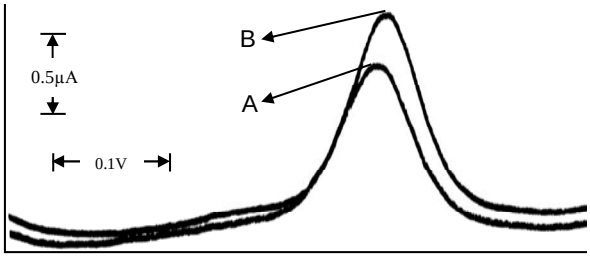

***Figure-1*- Voltammetric peaks of 5 mg/L hydroquinone at electrochemically pretreated GC electrode in 60/40 methanol/ water mixture containing 0.05 M H_2SO_4 obtained by using differential pulse voltammetry (DPV) (A) and Adsorptive stripping voltammetry (AdSV) (B) at (E_{acc}) of +0.0 V and (t_{acc}) of 30 s (B).**

Cyclic voltammetry

To check the reversibility or the electrode reaction mechanism, cyclic voltammetry of hydroquinone was carried out in 0.05 M H_2SO_4 at an accumulation potential of 0.0 V and accumulation time of 60 s. The peak appeared at about + 0.45 V in the anodic direction and the subsequent peak appeared in the cathodic direction, depicted in Fig. 2. This showed that the process is reversible. The peak current of the anodic peak was relatively higher than the cathodic peak which means that the electrochemically deposition rate is much less than the stripping rate [53]. The anodic peak increased further with the increase of accumulation

time while the cathodic peak almost remain the same, which hints for the adsorption of analyte at the surface of pretreated electrode [56].

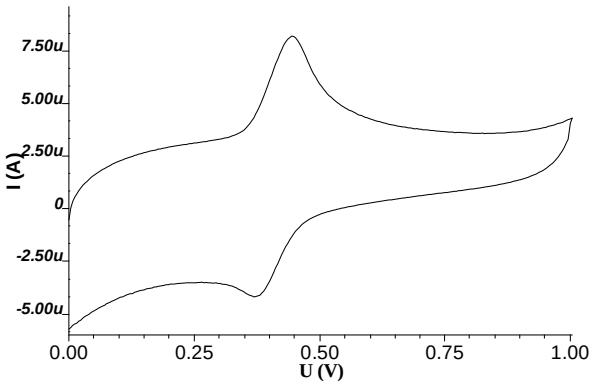

Figure-2. **Cyclic voltammogram of hydroquinone in 60:40 methanol/ water mixture containing 0.05 M H_2SO_4, c (hydroquinone) = 5 mg/L, (E_{acc}) = +0.0 V and (t_{acc}) = 30 s, sweep rate 100 mV/s.**

Influence of accumulation time (t_{acc})

The effect of accumulation time (t_{acc}) on the peak current of hydroquinone was carried out as shown in Fig. 3. After increasing the accumulation time (t_{acc}) from 60 s onwards.

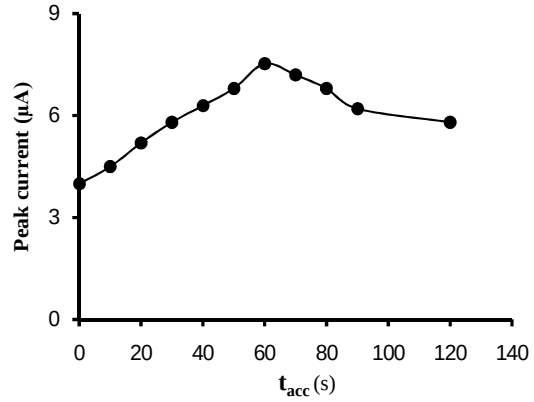

Figure-3. **Influence of accumulation time (tacc) on peak current of 5mg L^{-1} hydroquinone using AdSV in 60/40 methanol/ water mixture containing 0.05 M H2SO4, accumulation potential (Eacc) = +0.0 V.**

The variation of adsorption time between 0 and 120 s at an adsorption potential of 0.0 V, showed that the peak current increased with the increase of accumulation time (t_{acc}) up to 60 s and then decreased The increase of peak current with increase of accumulation time (t_{acc}) indicated that hydroquinone can be accumulated at the surface of GC electrode due to its increase surface activity by electrochemical pretreatment. The decrease in peak current after 60 s shows that the surface of the electrode has been completely saturated by the substance [57], so accumulation potential of 60 s was selected as an optimum accumulation time (t_{acc}) for further experiment. These results showed that the limiting current of hydroquinone is controlled by the adsorption of analyte at an electrochemically pretreated GC electrode.

Influence of accumulation potential (E_{acc})

The effect of accumulation potential (E_{acc}) on the AdSV peak current was studied at various accumulation potentials between -0.2 V and 0.15 V. The maximum peak current was obtained at an accumulation potential (E_{acc}) of + 0.0 V as shown in Fig. 4. Therefore the accumulation potential (E_{acc}) of + 0.0 V was chosen as an optimum potential.

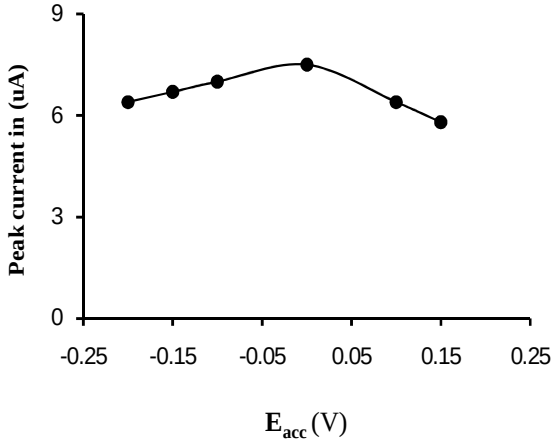

Figure-4. **Influence of accumulation potential (E_{acc}) on the peak current of 5mg L^{-1} hydroquinone using AdSV in 60/40 methanol/ water mixture containing 0.05 M H_2SO_4, accumulation time (t_{acc}) = 60 s.**

Effect of scan rate

The effect of potential scan rate on the AdSV peak of hydroquinone was observed in the range from 2 - 50 mV/s. The peak current increased linearly with the scan rate, as shown in Fig. 5. And at the same time it was observed that with increase of scan rate the peak potential also slightly shifted towards more positive values i.e. from 0.45 V to 0.52 V but not in the linear fashion which is the characteristics of the pure adsorptive controlled. The linear increase of peak current with scan rate and the shift of peak potential towards higher values are the indication of the adsorption of analyte on the electrode. These results and

the cyclic voltammetric results suggested that the process may be partly controlled by the adsorption and partly by the diffusion of analyte i.e. diffusion - adsorption type of electrochemical behavior. Further more; the 10 mV scan rate and 25 mV modulation amplitude was optimized for the experiment because it gave better results in term of peak height and peak shape.

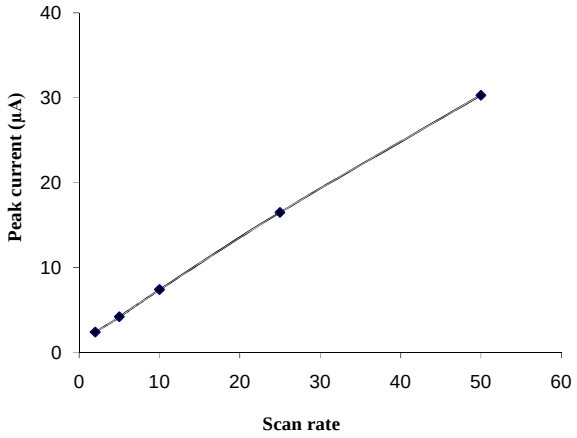

Figure-5. **Effect of scan rate on the peak current of hydroquinone using AdSV. The peak current linearly increased with scan rate in the range from 2 – 50 mV/s in 60/40 methanol/ water mixture containing 0.05 M H_2SO_4, (t_{acc}) = 60 s and (E_{acc}) = +0.0 V.**

Analytical performance of the method:

The optimum conditions for the determination of hydroquinone using adsorptive stripping voltammetry were: modulation amplitude 25 mV, scan rate 10 mV/s, accumulation time 60 s, and accumulation potential + 0.0 V. Under these optimum conditions linear calibration plots were recorded in both low and high concentrations in the range from 0.5 – 4.0mg L^{-1} and 5 – 30mg L^{-1} of hydroquinone, respectively in 60/40% methanol/water mixture containing 0.05 M H_2SO_4.The values of the coefficient of determination R^2 were 0.9967 and 0.9984 for lower and higher ranges as shown in Fig. 6 and Fig. 7, respectively. This indicated that the method is suitable for the determination of hydroquinone in the broad range of concentrations. The limit of detection of hydroquinone was 50µg L^{-1} and calculated by using the equation for (LOD) = 3s/S [58]. The LOD reflects that the method is very sensitive for hydroquinone determination by the currently developed method.

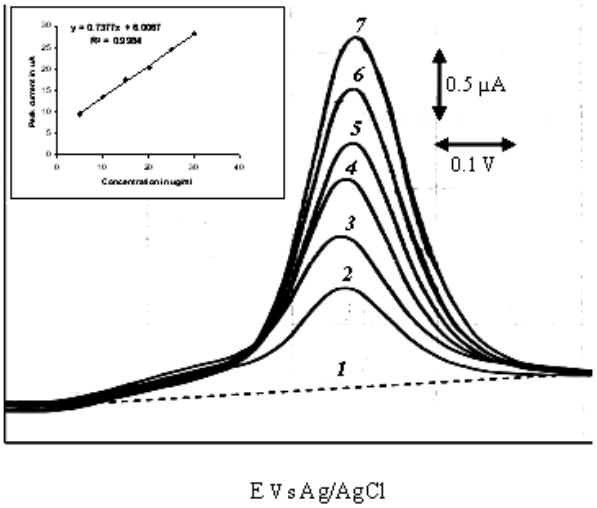

Figure-6. **Calibration curves of hydroquinone at electrochemically pretreated GC electrode in 60/40 methanol/water containing 0.05 M H_2SO_4 in the range of (1) 0, (2) 5, (3) 10, (4) 15, (5) 20, (6) 25, (7) 30mg L^{-1}, tacc = 60 s, (E_{acc}) = +0.0 V, scan rate 10 mV/s, modulation amplitude 25 mV.**

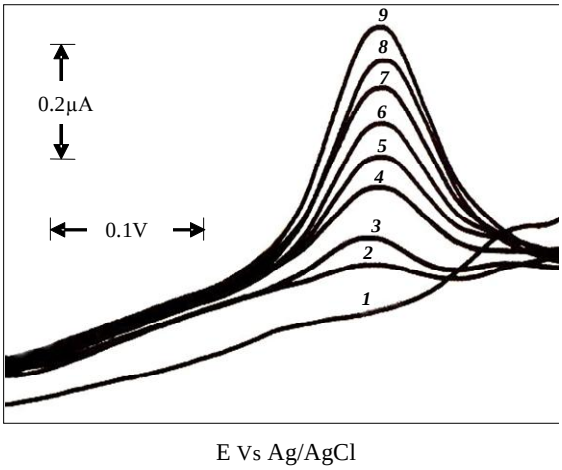

Figure-7. **Calibration curves of hydroquinone at electrochemically pretreated GC electrode in 60/40 methanol/water containing 0.05 M H_2SO_4 in the range of (1) 0, (2) 0.5, (3) 1.0, (4) 1.5, (5) 2.0, (6) 2.5, (7) 3.0, (8) 3.5, (9) 4.0mg L^{-1}, tacc = 60 s, (E_{acc}) = +0.0 V, scan rate 10 mV/s, mod: Amp 25 mV.**

Interference study

The influence of various likely interferences present in polymeric industrial wastes and photographic developer solution such as phenol, catechol, nitrophenols, chlorophenol and metol were studied in the solution containing 5mg L^{-1} hydroquinone. The amount of the foreign species tolerated is that concentration (equal to or greater than 5mg L^{-1} hydroquinone) which causes a change in the signal of ± 5%. All the interference substances studied at various

concentrations (equal to or greater than 5mg L^{-1} hydroquinone) were within the limit of ± 5% except catechol which interfered on the peak current of hydroquinone, because it oxidized nearly at the same potential as that of hydroquinone. The various inorganic ions did not showed any interference effect due to their very limited solubility in the proposed medium.

Sample analysis

The proposed method was applied to determine hydroquinone in model polymeric industrial samples and the results are compared to those obtained by UV/ Visible spectroscopy [11] given in Table 1.

Table-1. **Comparative analysis of polymeric industrial discharge samples containing hydroquinone by our proposed method and UV/ visible Spectrophotometry.**

Sample	Hydroquinone$^{N=3}$	
	proposed method[a] (mg/L)	UV/ Vis. Spec.[a] (mg/L)
1	0.48 ± 0.05	0.49 ± 0.06
2	0.98 ± 0.04	1.09 ± 0.07
3	5.10 ± 0.09	5.13 ± 0.10
4	9.70 ± 0.20	9.60 ± 0.26
5	20.4 ± 0.30	20.7 ± 0.35

N= no. of replications; [a], average of 3 values ±, standard deviation

For the analysis of hydroquinone in photographic developer solution a sample amount of 0.1 ml was taken from the waste photographic solution and was diluted to 10 ml polarographic cell with 0.05 M H_2SO_4. The AdS voltammograms were recorded by using standard addition method under optimized conditions depicted in Fig. 8. From this 19mg L^{-1} hydroquinone was calculated in 0.1 ml waste sample. This showed that waste photographic developer solution contained very high amount of hydroquinone and thus the suitability of the proposed method was evident. We have also applied the method to determine hydroquinone in hyderquin cream (ATCO laboratory, Ltd. Karachi Pakistan). 1 g cream was dissolved in 25 ml methanol and from this solution 0.1 ml was added into 10 ml cell containing 60/40 methanol/water and 0.05 M H_2SO_4. A quantitative recovery of 92.4% was obtained using the standard addition procedure.

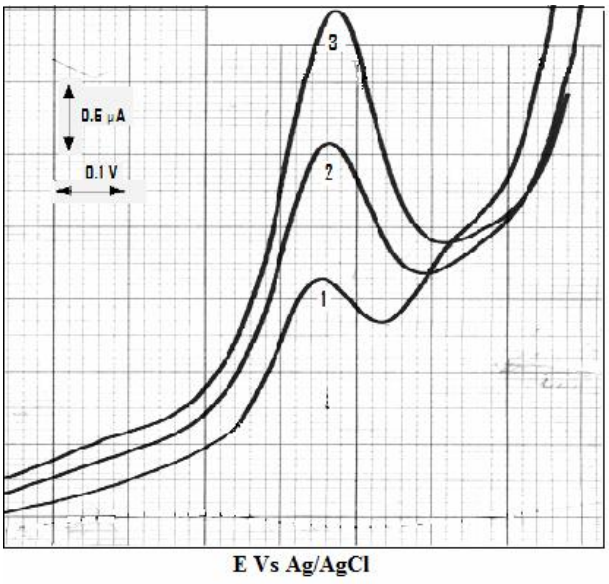

Figure-8. **Determination of hydroquinone in waste photographic developer sample using standard addition method. Peak (1) corresponds to solution containing 0.1 ml sample, (2) first addition of 10mg L^{-1} hydroquinone from the standard solution and (3) 2nd addition of 10mg L^{-1} hydroquinone from the standard solution.**

Conclusion

It was concluded from this study that electrochemically pretreated GC electrode is suitable sensor for the determination of hydroquinone in micro gram level. The electrode showed sensitive response by using AdSV than DPV which indicated that hydroquinone showed adsorptive electrochemical behavior at an electrochemically pretreated GC electrode. From this study it is proposed that the developed method will be useful for the quantitative determination of hydroquinone at trace level without any significant effect of electrode fouling.

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