



Simultaneous Electrochemical Determination of Dihydroxybenzene Isomers at 1-Butyl-3-Methylimidazolium Hexafluorophosphate Modified Pencil Graphite Electrode

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Received 06 Sept 2020,
Revised 12 March 2020,
Accepted 17 March 2020

Keywords

- ✓ Dihydroxybenzene isomers,
- ✓ 1-Butyl-3-Methylimidazolium hexafluorophosphate,
- ✓ Pencil graphite electrode,
- ✓ Cyclic voltammetry,
- ✓ Differential pulse voltammetry.

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Abstract

A simplistic and inexpensive electrochemical platform has been fabricated for the simultaneous detection of Dihydroxybenzene Isomers; named- Hydroquinone (HQ), Catechol (CC) and Resorcinol (RS); in aqueous system. Cyclic Voltammetry and Differential Pulse Voltammetry were adopted for the detection technique. 2B pencil (Faber Castell) collected from the resident stationary shop was used for fabricating Pencil Graphite Electrode (PGE) used as working electrode. PGE was characterized by SEM and EDX. It was modified electrochemically by ionic liquid, 1-Butyl-3-Methylimidazolium hexafluorophosphate (BIHP). Total analyses were performed in phosphate buffer solution at pH 7.0. BIHP-PGE showed good selectivity and robust anti-interference for detection of HQ, CC and RS simultaneously in aqueous media. For HQ, CC and RS, the limit of detection is $9.09 \mu\text{M L}^{-1}$, $8.15 \mu\text{M L}^{-1}$ and $26.78 \mu\text{M L}^{-1}$, respectively and sensitivity is $525.21 \mu\text{A/mM/cm}^2$, $585.68 \mu\text{A/mM/cm}^2$ and $178.00 \mu\text{A/mM/cm}^2$, respectively at BIHP-PGE in simultaneous detection.

1. Introduction

Phenolic compounds extensively survive in nature since they are formed during biological degradation processes [1]. Hydroquinone (1,4-dihydroxybenzene, HQ), catechol (1,2-dihydroxybenzene, CC) and resorcinol (1,3-dihydroxybenzene, RC) are commonly called dihydroxybenzene isomers (DHBI) [2]. They are widely used in cosmetics, tanning, pesticides, flavoring agents, medicines, antioxidant, dye and photography chemicals [3]. Due to high toxicity to both environment and human even at very low concentrations, and low degradability in the ecological environment, they have classified as a periodic environmental pollutant and Group 2B human carcinogen [4]. Therefore, various methods have been developed for the simultaneous assay of DHBIs with high selectivity is of high significance including chromatography [5] spectrophotometry [6], HPLC [7] synchronous fluorescence [8], spectrophotometry [9], chemiluminescence [10], electrochemistry [11] etc. Among them, the electrochemical methods are more efficient due to their fast response, cheap instrument, low cost, simple operation, time saving, and free of complicated sample pre-treatments [1].

Although DHBIs are electrochemically active, it was found that the oxidation potentials of CC and HQ on bare electrode were close to each other [12]. Recently, a few reports for electrochemical detection of

DHBIS has been developed. Rahman *et al.* (2015) investigated DHBIs in KCl, acetate buffer and phosphate buffer at glassy carbon electrode (GCE) using cyclic voltammetry (CV). His results show that, in all cases the redox process is quasireversible, RS behaves almost irreversibly in all three electrolytic media. Good linear relationships were obtained between the peak currents and the concentrations of DHBIs. The electrochemical process in all the isomers was controlled by diffusion process [13]. Hossain *et al.* (2015) modified GCE with polyglutamic acid. From his experiment, DHBIs exhibited voltammograms with highly overlapped redox peaks that impeded their simultaneous detection in binary and ternary mixtures at bare electrode. On the contrary, at polyglutamic acid modified GCE binary and ternary mixtures of the DHBIs showed well-resolved redox peaks in both CV and differential pulse voltammetry (DPV) experiments. This resolving ability of polyglutamic acid modified GCE proves its potential to be exploited as an electrochemical sensor for the simultaneous detection of DHBIs [14]. Yang *et al.* (2014), synthesized hexadecyl trimethyl ammonium bromide (CTAB) functionalized graphene oxide (CTAB-GO). The composite of CTAB-GO and multi-wall carbon nanotubes (MWNT) was used to modify GCE. The calibration curves for CC, HQ and RS were obtained in the range of 1×10^{-7} to 4×10^{-4} , 1×10^{-7} to 2×10^{-4} and 1×10^{-6} to 1×10^{-4} mol L⁻¹, respectively. The detection limits were 1×10^{-8} , 3×10^{-8} and 2×10^{-7} mol L⁻¹ for CC, HQ and RS, respectively (S/N=3) [15]. Liu *et al.* (2014), prepared nitrogen doped porous carbon nanopolyhedrons (N-PCNPs)-multi-walled carbon nanotubes (MWCNTs) hybrid materials and deposited on GCE. The linear response ranges for HQ, CC and RS were 0.2-455 μ M, 0.7- 440 μ M and 3.0-365 μ M, respectively, and the detection limits (S/N = 3) are 0.03 μ M, 0.11 μ M and 0.38 μ M, respectively [16].

The unmodified electrodes displayed a poor selectivity and sensitivity along fouling of signals towards the detection of HQ and CC [17]. Therefore modification is necessary for simultaneous detection of DHBIs. Graphite has both metallic and nonmetallic character being thus supportive as electrode material [18]. Graphite is used to produce pencils consisting of fine graphite powder in an inorganic (resin) or organic matrix (clay or a high polymer). The pencil graphite leads are composite materials containing graphite (~65%), clay (~30%), and a binder (wax, resins, or high polymer) [19]. According to the European Letter Scale, graphite pencils are labeled with letters H (hardness) and B (blackness) and numbers indicating the degree of hardness or blackness from 9H (the hardest) to 8B (the softest). B type leads contain more graphite and are softer, and the harder H type leads have more clay [20]. The use of solid materials, such as composite electrodes, as detectors for electrochemical analysis is commonly known [21]. Over the past five decades, carbon paste electrode composed by a mixture of carbon powder and a binder has become one of the most popular electrodes used as the sensors and detectors [22]. In the past years, ionic liquid (IL) has been proved to be an efficient binders and/or modifiers in the preparation of carbon composite electrodes [23].

In the field of electrochemical sensor, researchers are trying to develop the method of higher selectivity as well as lower detection limit in a cost effective way. Speaking of cost effective methods PGE holds a non-replacing position and it has been highly appreciated if we go through a couple of articles published in recent times. Oghli *et al.* (2021) modified PGE with nitrogen-doped graphene and molecular imprinted polyacrylamide for determination of fexofenadine in biological media. The detection limit of this sensor has been calculated equal to 1.5×10^{-10} M; represents a superior detection limit as reported when compared to the other electrochemical sensor [24]. Devani *et al.* (2021) fabricated silver nanoparticles/poly(L-cytine) nanocomposite modified PGE for electrochemical quantitative detection of guaifenesin in real samples. This modified electrode showed a linear relationship between the concentrations of guaifenesin and peak current in the range of 3.0×10^{-8} to 3.0×10^{-4} M with detection limit 6.1×10^{-9} M [25]. Wong *et al.* (2021) developed a PGE using palladium nanoparticles in the

electrochemical modification process for simultaneous detection of direct yellow 50, tryptofan, carbendazime and caffeine in environmental biological fluid samples. Under optimum condition, for direct yellow 50, tryptofan, carbendazime and caffeine, the linear range concentration was 0.99-9.9 $\mu\text{mol L}^{-1}$, 1.2-12 $\mu\text{mol L}^{-1}$, 0.20-1.6 $\mu\text{mol L}^{-1}$ and 25-190 $\mu\text{mol L}^{-1}$ respectively. This sensor showed good sensitivity, repeatability and stability [26]. Arabali *et al.* (2020) made a PGE modified using CuO nanoparticle and polypyrrole nanocomposite for the detection of tramadol. In this experiment, square wave voltammetric technique was used. This electrode showed acceptable data for the determination of tramadol in the concentration range 5.0 nM to 380 μM with detection limit 1.0 nM [27]. Rouhani *et al.* (2020) modified the surface of PGE by Dawson heteropolyacid-embedded silver nanoparticles and graphene oxide for sensing levodopa. This experiment reveals that, in phosphate buffer solution at pH 6.0, this modified electrode was able to measure trace amount of levodopa in the concentration ranges from 3.0×10^{-9} to 1.0×10^{-7} M and 1.0×10^{-7} to 1.0×10^{-5} M and the detection limit was 7.6×10^{-10} M, which was much better than previously reported electrochemical sensor [28]. Ghanbary *et al.* (2020) invented a PGE modified with 5-ethyl-5-phenyl barbituric acid on polyvinylpyrrolidone for quantitative estimation of gibberellic acid. Under optimized condition, the linear range concentration was 15 to 225 nmol L^{-1} and the limit of detection was 4.97 nmol L^{-1} ; recommended for determination of gibberellic acid in real samples with convincing analytical results [29]. Yarali *et al.* (2020) prepared an electrochemical PGE sensor modified with ionic liquid (1-Butyl-3-methylimidazolium hexafluorophosphate) for detection of protein (globulin). Using differential pulse voltammetric technique, the linear range was found to be 20 to 100 nM with detection limit 7.64 nM. Selectivity of globulin was also tested individually as well as in the mixture of nearly similar characteristic compounds, results acceptable analytical values [30].

In this study, an attempt has been made for the fabrication of 1-butyl 3-methylimidazolium hexafluorophosphate (BIHP) (an ionic liquid) modified PGE. CV and DPV were used for the simultaneous detection of DHBIs.

2. Materials and Methods

2.1. Reagents and Apparatus

Chemicals used in this experiment are (i) hydroquinone (BDH); (ii) catechol (BDH); resorcinol (BDH); (iv) sodium dihydrogen phosphate (Sigma-Aldrich); (v) disodium hydrogen phosphate (Sigma-Aldrich); (vi) acetic acid (Sigma-Aldrich); (vii) sodium acetate (Sigma-Aldrich); (viii) sodium bicarbonate (Sigma-Aldrich); (ix) sodium hydroxide pellets (Sigma-Aldrich); (x) 1-Butyl-3-Methylimidazolium hexafluorophosphate (TCI, Japan). Double distilled water used for the preparation of solutions and for the cleaning of apparatus. The solutions were purged with 99.99% dry nitrogen (BOC, Bangladesh) to remove oxygen and the atmosphere was maintained to be inert prior to investigation. All reagents were obtained as AR grade and were used without further refinement. The whole experiment was carried out using potentiostat (μ -stat 8000, DropSens, Spain). A wooden pencil graphite electrode (PGE) was used as bare working electrode while Ag/AgCl and spiral Platinum (Pt) wire performed as reference and counter electrode respectively. The pH of the solution was measured using pH meter (Hanna Instruments).

2.2. Preparation of BIHP-PGE

0.2 M PBS (pH=7.0) was prepared. 0.1 g of BIHP was taken in 30 ml PBS. Then the solution was sonicated and stirred until BIHP was mixed with PBS resulting BIHP -PBS solution.

A pencil (Faber Castell, Grade 2B) was cut; wooden part of the two sides was removed. Then it was painted and the end tip of the rod was unpainted for using as circular electrodes surface (2mm diameter). The side portion of graphite rod was painted, so that only uncovered portion can take part as working surface. Then the working surface was polished by rubbing it on a smooth offset white paper. The resultant working surface would look like a shiny black mirror. The unpainted part was used to make the connection with the potentiostat.

The bare PGE was rinsed with distilled water. Then it was placed in BIHP-PBS solution, which was previously purged with highly pure nitrogen for 10 minutes. The PGE was treated with 10 cycles of CV between -1.5 and +1.5 V at a scan rate of 200 mV. Then the modified electrode was rinse with double distilled water for further experiments. This type of electrodeposition is very popular and have widespread use for modification of PGE [31] as well as conventional disc electrode [14].

2.3. Morphological Characterization of BIHP-PGE

Figure 1(a) shows the surface morphologies of bare PG electrode. Greyish-black color corresponds to graphite on the surface. Surface is uneven as well. A lot of grooves and pits present at surface of the PGE. It indicates that the graphite rod of the pencil is not pure crystalline. A lot of defects and few foreign materials may be present there. Figure 1(b) is the SEM images of modified BIHP-PGE. The images of the surface of modified electrodes are different from the bare PGE. The surface of BIHP-PGE is covered by many different sizes of white spots and fiber like lines. It looks like shining stars in the sky. White spots and the fibrous lines may be thin films of BIHP spread over the surfaces of PGE. This modified PGE could be expected to be an attractive platform for the detection and separation of DHBIs.

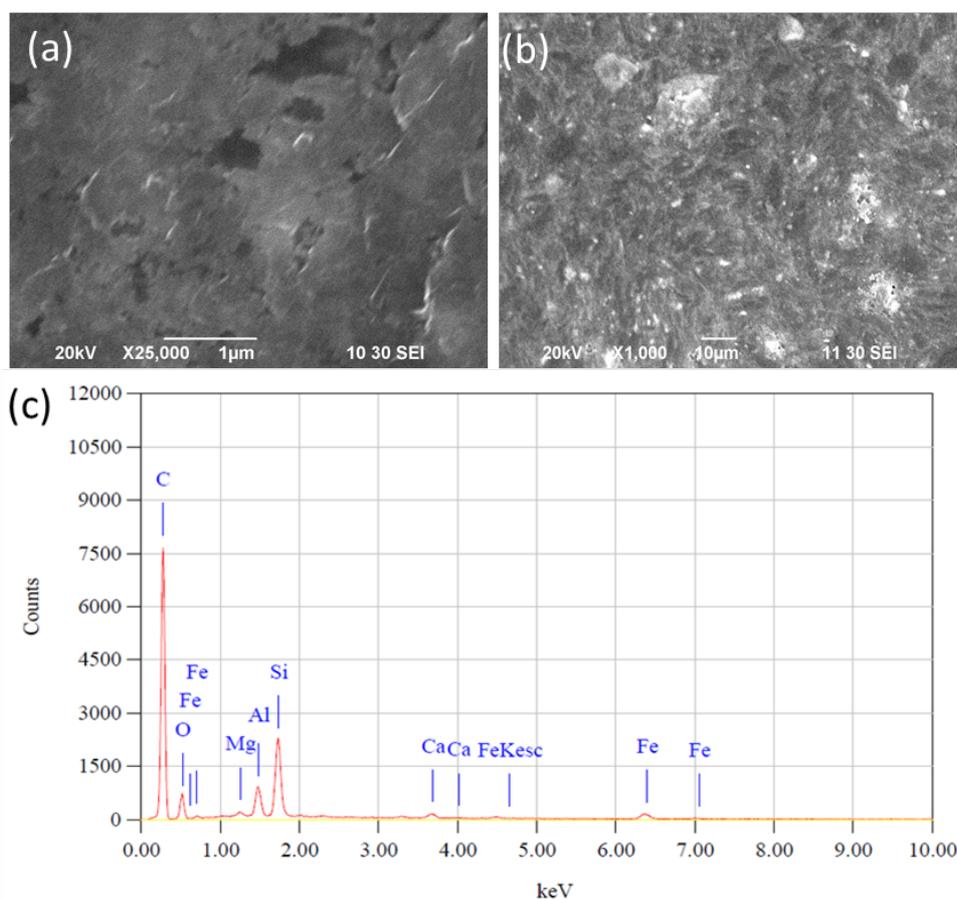


Figure 1 : SEM image of (a) Bare PGE, (b) BIHP-PGE; (c) EDX of bare PGE

Figure 1(c) shows the EDX results of bare surface of PGE. The PGE surface is impure as guessed by SEM. Instead it is composed of about 79% of carbon with a little amount of Si, O₂, Al, Fe, Mg and Ca. In bare GCE and pure graphite electrode, there is 100% carbon without impurities. So it may be concluded that PGE is mainly carbon composite material. In spite of impurities present in the graphite of PGE has been modified by BIHP successfully and exhibits gallant response for the simultaneous detection of DHBIs.

3. Results and Discussion

3.1. Behavior of DHBIs at Bare and BIHP-PGE

At 50 mV/s scan rate the CVs of CC, HQ and RS was taken in PBS (pH=7) both at bare PGE and BIHP-PGE. Figure 2 shows the CVs of 5mM HQ, CC and RS at bare PGE. Here, HQ shows one broad anodic peak and one broad cathodic peak, CC shows one broad anodic peak and two broad cathodic peaks and RS shows a broad anodic peak indicating confusion on the detection of HQ and CC but RS shows an irreversible character. Figure 3 shows the CVs of 5mM HQ, CC and RS at BIHP-PGE.

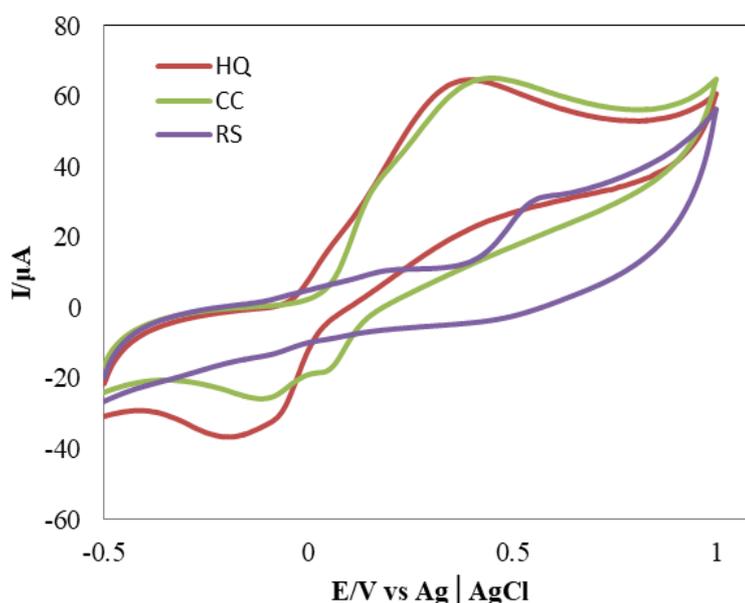


Figure 2 : CVs of 5mM HQ, CC and RS at Bare-PGE in PBS at scan rate 50 mV/s

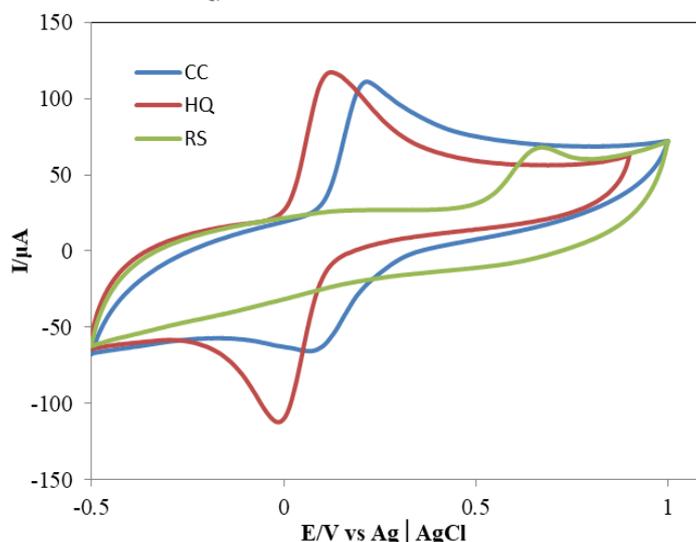


Figure 3 : CVs of 5mM HQ, CC and RS at BIHP-PGE in PBS at scan rate 50 mV/s

Here, HQ shows one anodic and one cathodic sharp peak with nearly same values of anodic peak current and cathodic peak current, indicating the reversible behavior of HQ [31] and the peak potential separation indicates two electron transfer reaction. CC shows one anodic and one cathodic sharp peak with considerable high value of anodic peak current compared to cathodic peak current [32], indicating quasi-reversible behavior of CC and peak potential separation indicates two electron transfer reaction. RS shows one sharp anodic peak indicating irreversible behavior [33]. Possible electrochemical behavior of HQ, CC and RS can be shown by Figure 4.

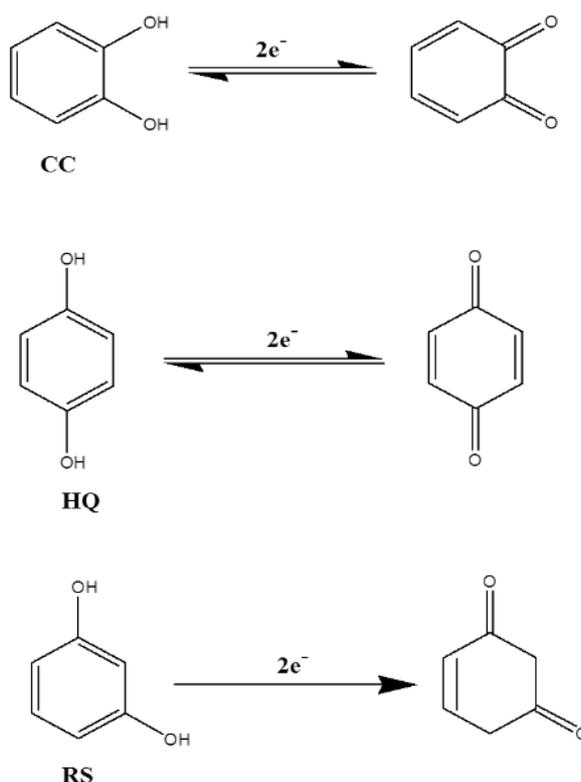


Figure 4 : Electrochemical behavior of DHBIs

3.2. Effect of pH

The activity of HQ, CC and RS at BIHP-PGE was examined by taking the three experiments in acetate buffer, phosphate buffer and bicarbonate buffer. pH was taken from 3 to 11. HQ, CC and RS gave sharp peaks at pH 7. So, for this research, pH 7 was taken, has also been reported by Li *et al.*, found the optimum pH at 7 for maximum DHBIs performance at [34].

3.3. Effect of Scan rate

CVs of 5mM of CC, HQ and RS were taken separately at different scan rates at BIHP-PGE [Figure 5(a), 5(c) and 5(e)]. The anodic peak currents were calculated and those were plotted against square root of scan rates [Figure 5(b), 5(d) and 5(f)]. A straight line was obtained for each system that passed through the origin, which indicated that the system of CC, HQ and RS were diffusion controlled. Similar work has been reported by Rahman *et al.*, found the redox behavior of HQ, CC and RS in PBS at glassy carbon electrode diffusion controlled [13].

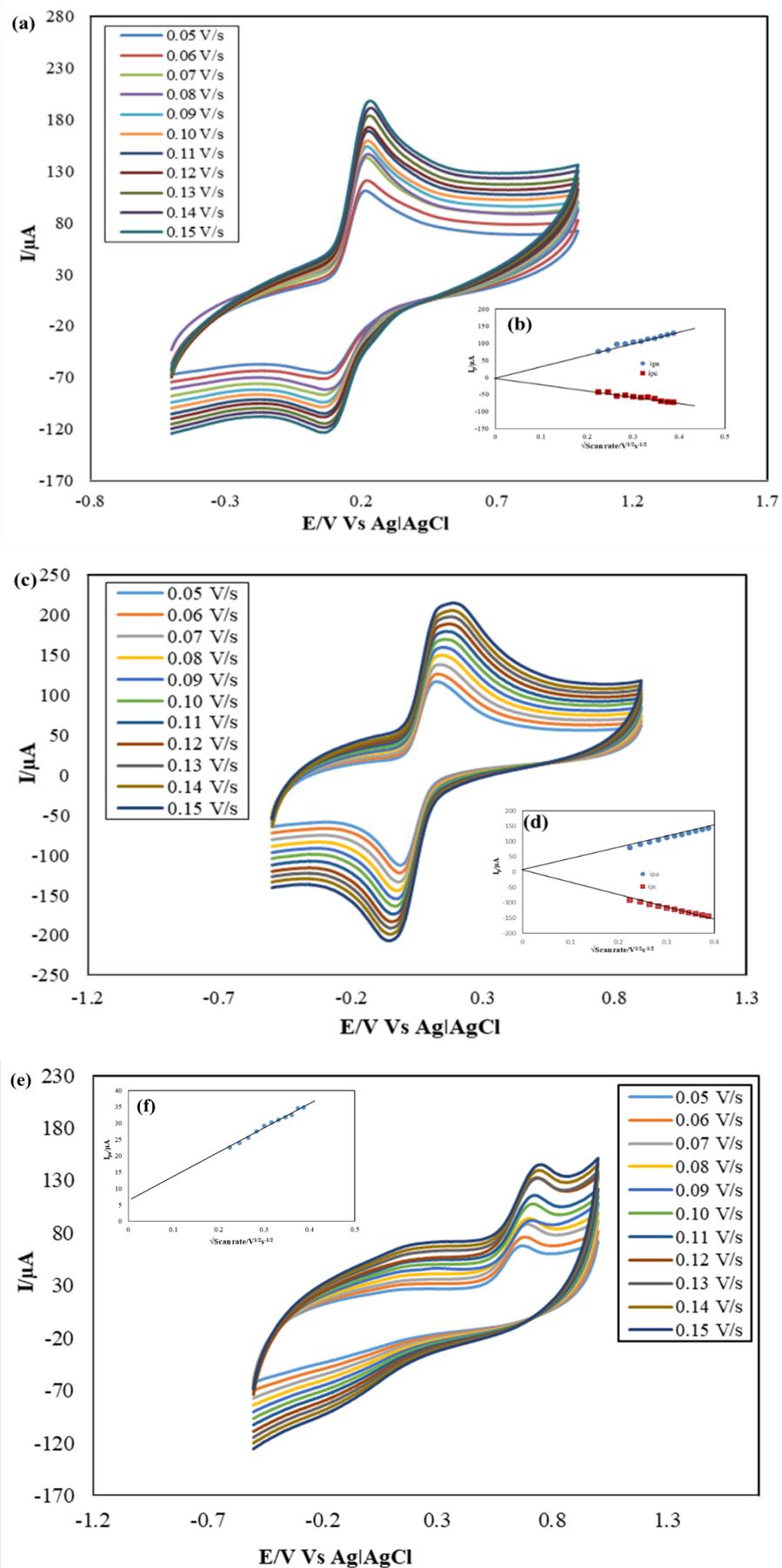
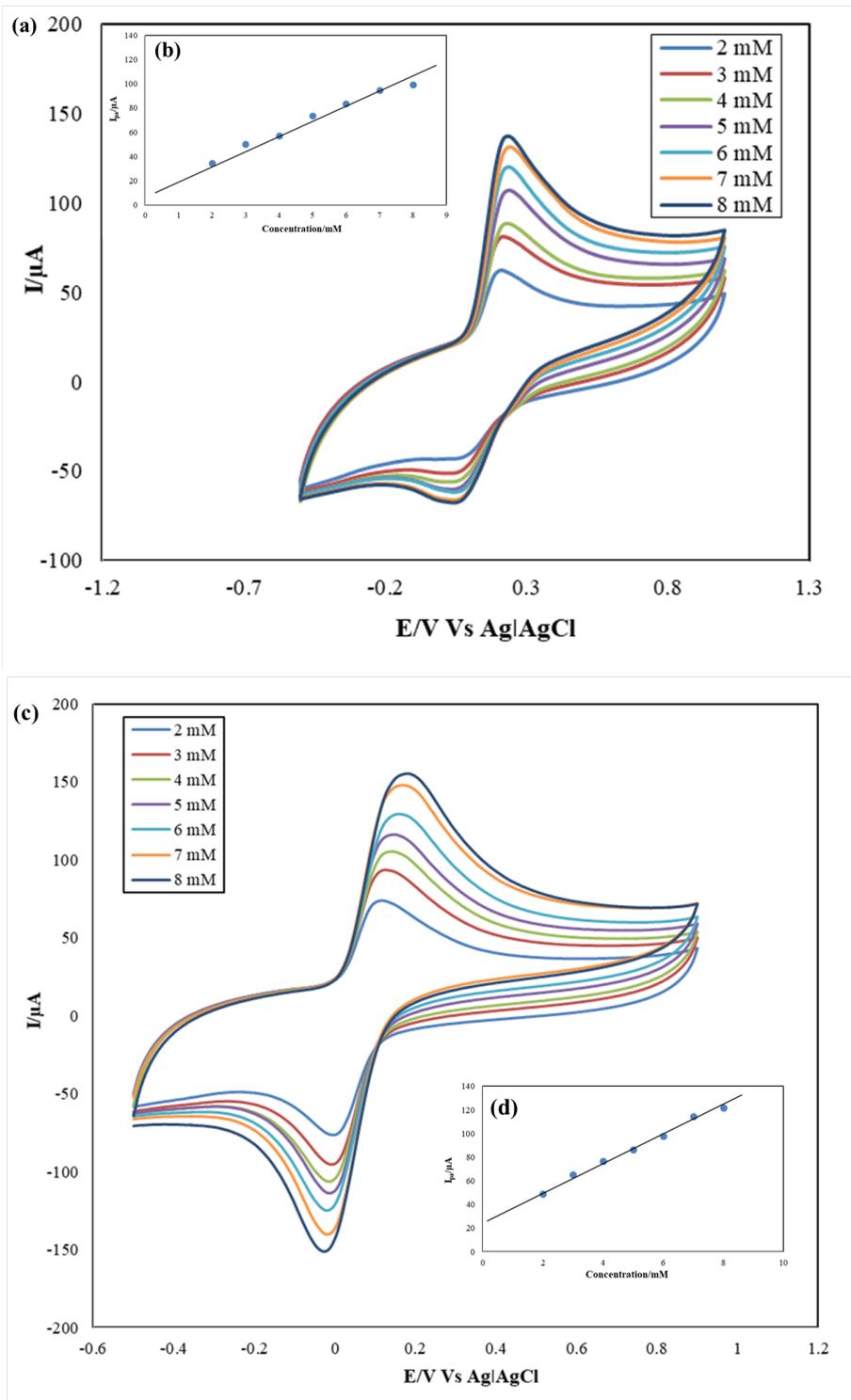


Figure 5 : CVs of 5mM (a) CC, (c) HQ, (e) RS in PBS at different scan rates at BIHP-PGE; Variation of peak currents of 5mM (b) CC, (d) HQ, (f) RS with square root of scan rate

3.4. Effect of concentration

CVs were taken for CC, HQ and RS at different concentrations (2mM to 8mM) at BIHP-PGE [Figure 6(a), 6(c) and 6(e)]. The anodic peak currents were calculated and it was seen that the peak currents were increased linearly [Figure 6(b), 6(d) and 6(f)]. This results can also be supported by Rahman *et al.*, found the peak current caused by HQ, CC and RS in PBS is linear with their concentration at glassy carbon electrode [13].



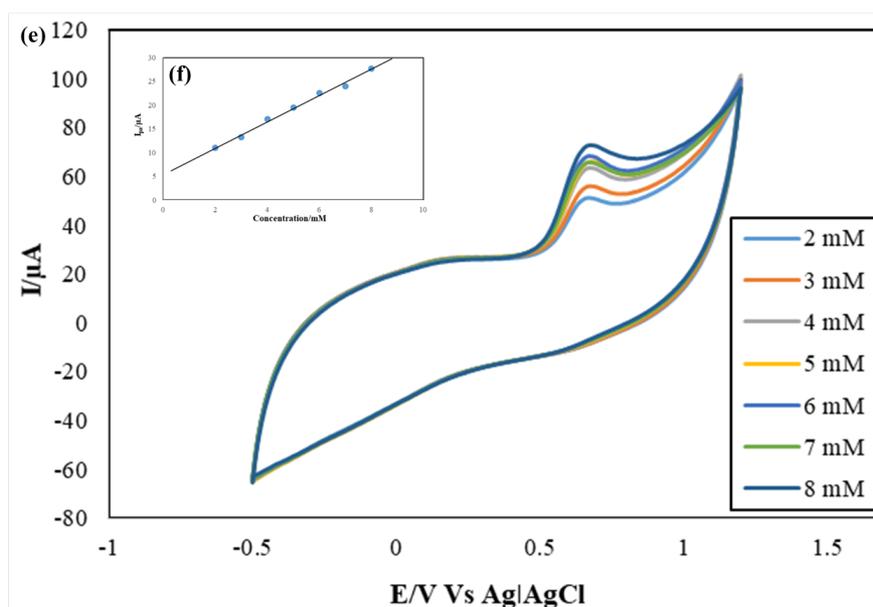


Figure 6 : CVs of (a) CC, (c) HQ, (e) RS at different concentration in PBS at 50 mV/s at BIHP-PGE; Variation of anodic peak currents of (b) CC, (d) HQ, (c) RS with the concentration

3.5. CVs and DPVs of HQ, CC and RS in their mixture

Figure 7 shows the CVs of 5mM HQ, CC and RS in their ternary mixture (1:1:1) in PBS at BIHP-PGE at scan rate 50 mV/s. At BIHP-PGE, the CV of the mixture of three isomers shows two well defined anodic peaks at +0.32 V and +0.71 V respectively and a very small peak at 0.15 V, one big cathodic peak at 0.11 V and two very small peaks at 0.325 V and -0.207 V. From the positions of the anodic and cathodic peaks it can be inferred that the peak of RS was found but the peaks of HQ and CC were overlap in such a way that they are far away from detection. The BIHP-PGE could not separate the anodic and cathodic peaks of CC, HQ and RS when they are present in a mixture. This separating ability of the BIHP-PGE cannot be used to detect CC, HQ and RS in presence of other qualitatively by CVs in contrast with the results reported by Ahammad *et al.*, found overlapped peak of HQ and CC at bare PGE but well defined individual peaks of at carbon nanotube modified PGE [32].

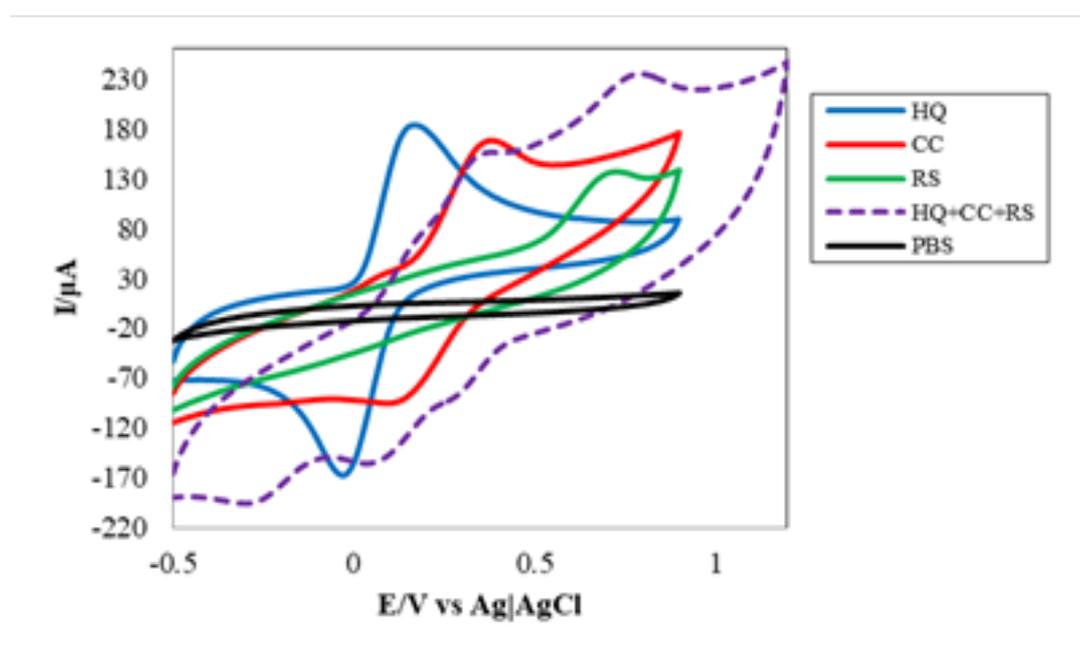


Figure 7 : CVs of 5mM HQ, CC and RS in PBS at BIHP-PGE at scan rate 50 mV/s

The DPV of HQ, CC, RS and the ternary mixture (5mM) of HQ, CC and RS in PBS at BIHP-PGE is shown in Figure 8. In BIHP-PGE, HQ, CC and RS gave three peaks at +0.01 V, +0.125 V and +0.46 V with peak currents 48.7 μA , 49.85 μA and 20.8 μA respectively and for the ternary mixture of HQ, CC and RS, there three peaks were seen at +0.005 V, +0.125 V and +0.515 V with peak currents 20.45 μA , 24.7 μA and 13.4 μA . The BIHP-PGE could separate the peaks of CC and HQ when they are present in a mixture by DPVs reinforced the investigation of Ahammad *et al.*, found well defined individual peaks of HQ and CC with appreciable peak potential separation value at carbon nanotube modified PGE [32].

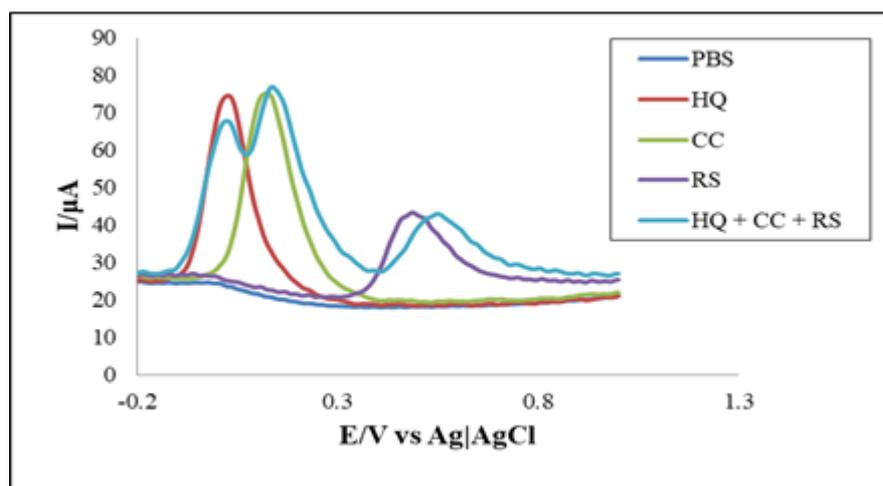


Figure 8 : DPVs of 5mM HQ, CC and RS in PBS at BIHP-PGE at scanrate 50 mV/s

3.6. Quantitative Estimation of HQ in Presence of CC and RS

DPV was performed on the ternary mixture of HQ, CC and RS at BIHP-PGE within the potential range -0.2 V to +1.0V. A ternary solution was prepared where CC and RS were kept constant concentration of 3mM and the concentration of HQ was increased by adding successive amount of HQ in the ternary solution every time. The resulting DPVs are shown in Figure 9(a). A calibration curve [Figure 9(b)] was drawn for different concentrations of HQ in presence of CC and RS in a ternary mixture. The detection limit of HQ in presence of CC and RS was found in micromolar range ($9.09 \mu\text{M L}^{-1}$) using signal-to-noise ratio ($S/N=3$) rule and the sensitivity was found to be $525.21 \mu\text{A/mM/cm}^2$.

3.7. Quantitative Estimation of CC in Presence of HQ and RS

DPV was performed on the ternary mixture of HQ, CC and RS at BIHP-PGE within the potential range -0.2 V to +1.0V. A ternary solution was prepared where HQ and RS were kept constant concentration of 3mM and the concentration of CC was increased by adding successive amount of CC in the ternary solution every time. The resulting DPVs are shown in Figure 9(c). A calibration curve [Figure 9(d)] was drawn for different concentrations of CC in presence of HQ and RS in a ternary mixture. The detection limit ($S/N=3$) of CC in presence of HQ and RS was found in micro molar range ($8.15 \mu\text{M L}^{-1}$) and sensitivity was found to be $585.68 \mu\text{A/mM/cm}^2$.

3.8. Quantitative Estimation of RS in Presence of HQ and CC

DPV was performed on the ternary mixture of HQ, CC and RS at BIHP-PGE within the potential range -0.2 V to +1.0V. A ternary solution was prepared where HQ and CC were kept constant concentration of 3mM and the concentration of RS was increased by adding successive amount of RS in the ternary solution every time. The resulting DPVs are shown in Figure 9(e). A calibration curve [Figure 9(f)] was

drawn for different concentrations of RS in presence of HQ and CC in a ternary mixture. The detection limit ($S/N=3$) of RS in presence of HQ and CC was found in micromolar range ($26.78 \mu\text{M L}^{-1}$) and sensitivity was found to be $178.00 \mu\text{A}/\text{mM}/\text{cm}^2$.

Above results indicate that this separating ability of BIHP-PGE can be used to detect HQ, CC and RS qualitatively in presence of others.

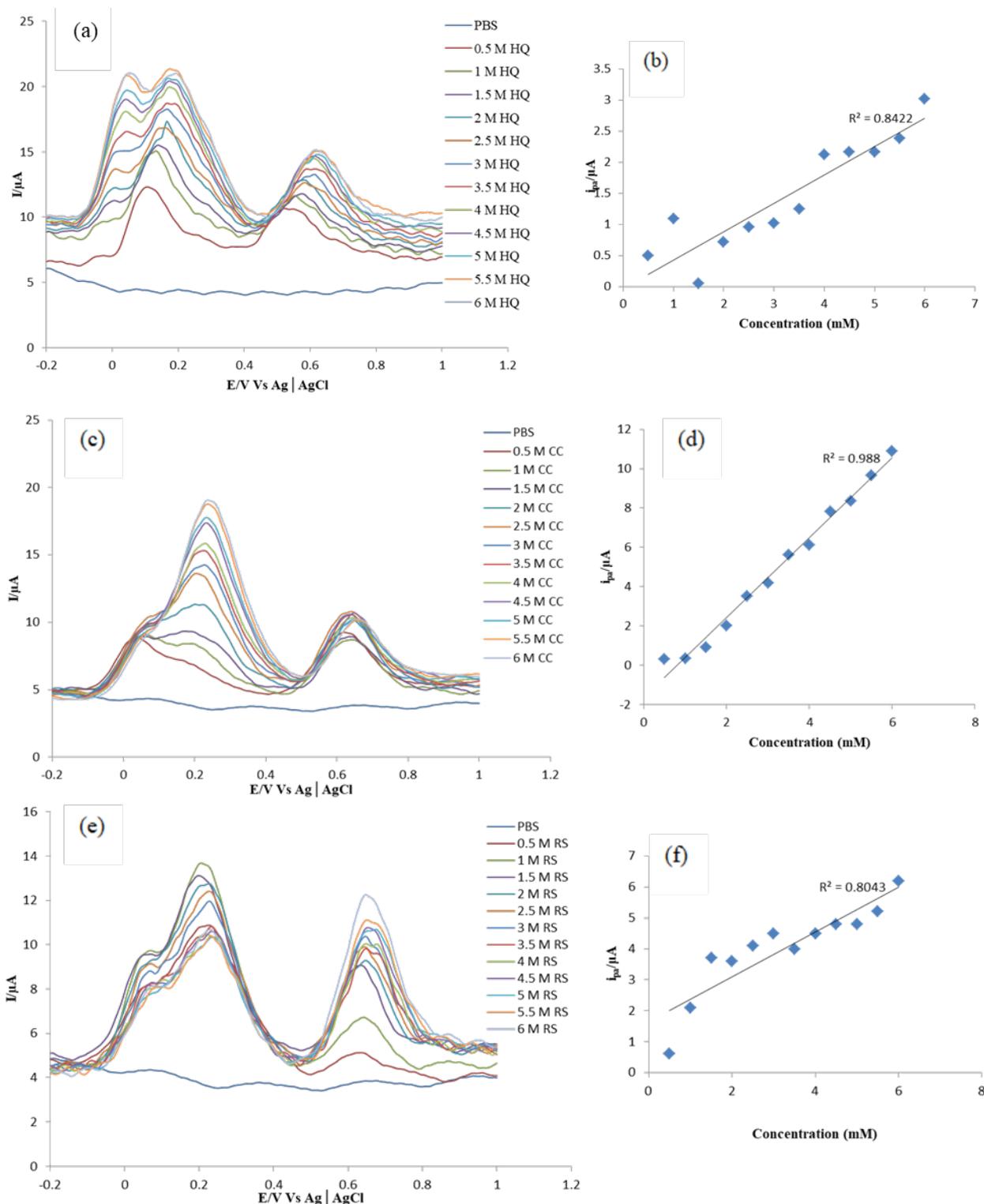


Figure 9 : DPVs of (a) HQ in presence of CC and RS, (c) CC in presence of HQ and RS and (e) RS in presence of HQ and CC at BIHP-PGE in PBS; Calibration curve for the quantitative determination of (b) HQ in ternary mixture with CC and RS, (d) CC in ternary mixture with HQ and RS and (f) RS in ternary mixture with HQ and CC

3.9. Feasibility of use

It is desirable that a sensor be suitable for repeated use in a highly reproducible manner. One of the electrodes used in the experiments described above was stored in an empty beaker for a period of 2 months without any deterioration in performance during use.

Conclusion

In this work, a cost-effective sensor was prepared by using simple yet effective method for simultaneous detection and estimation of HQ, CC and RS using electrochemical techniques. BIHP-PGE electrode is very effective for simultaneous detection of DHBIs and it was prepared by using BIHP-PBS solution and the thin film of BIHP was deposited on PGE surface by using CV. HQ, CC and RS have been detected from binary and ternary mixtures with high sensitivity and selectivity in PBS at BIHP-PGE. For HQ, CC and RS, the limit of detection is $9.09 \mu\text{M L}^{-1}$, $8.15 \mu\text{M L}^{-1}$ and $26.78 \mu\text{M L}^{-1}$ respectively and sensitivity is $525.21 \mu\text{A/mM/cm}^2$, $585.68 \mu\text{A/mM/cm}^2$ and $178.00 \mu\text{A/mM/cm}^2$ respectively at BIHP-PGE in simultaneous detection. This method could be used to detect DHBIs qualitatively in real samples.

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