

## Synthesis of Poly(Vinylferrocene) Perchlorate/Poly(3,3'-Diaminobenzidine) Modified Electrode in Dichloromethane for Electroanalysis of Hydroquinone

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Poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) (PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB) composite film was synthesized electrochemically for the first time on Pt disc electrode in a dichloromethane solution containing poly(vinylferrocene) (PVF) polymer, 3,3'-diaminobenzidine (DAB) monomer and tetrabutylammonium perchlorate as supporting electrolyte. This modified electrode was characterized using cyclic voltammetry, Fourier transform infrared spectroscopy (FTIR), UV-Vis spectrophotometry, atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) methods and it was used for amperometric determination of hydroquinone (HQ) at potential ranges of 0.40 and 0.60 V. The best analytical results for HQ was obtained at 0.45 V in NaHSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> solution (pH 2.0) and limit of detection, limit of quantification and linear response range were found as 7.469 × 10<sup>-5</sup>, 2.489 × 10<sup>-4</sup> and 2.489 × 10<sup>-4</sup>-65.0 mmol L<sup>-1</sup> (R<sup>2</sup> = 0.996), respectively. These results were compared to poly(3,3'-diaminobenzidine) (PDAB) coated and uncoated Pt electrodes. The best analytical results were obtained with composite film because of behavior as electron transfer mediator of PVF.

**Keywords:** poly(vinylferrocene), poly(3,3'-diaminobenzidine), hydroquinone, amperometric determination, composite film

### Introduction

Phenols are natural products resulting from the decomposition of some plants and animal organisms. Also, phenols as a class of organic materials have similar structure with pesticides resistant to biodegradation. Phenols widely used in chemical, petroleum and pharmaceutical industries can be found at ecosystem as human-induced. Hydroquinone (HQ), a phenolic compound derivative, is harmful ecotoxin. The toxic effects of this compound are associated with occurrence organic radicals.<sup>1</sup>

HQ is an important phenolic compound commonly used in pharmaceuticals, dyes, pesticides, medicines, petrochemical products, photo and cosmetic industries.<sup>2-4</sup> Products containing HQ are used as cosmetic cream for decolorization of skin. Over exposure to HQ causes skin irritation and sensitivity also color change at nails.<sup>5</sup> In the meantime, HQ is known as environmental pollutant due to low degradability and high toxicity like other phenolic compounds. For these reasons, determination of HQ is important. Because of oxidation of hydroxyl groups to

quinone form by electrochemical oxidation, it can be analyzed using electrochemical methods with lower cost, easier and faster than other techniques such as ultraviolet spectrophotometric analyses, gas chromatography and liquid chromatography.<sup>5,6</sup> Modified electrodes, especially coated with conductive polymers, are widely used for determination of phenolic compounds.

Conductive polymers are interesting materials for sensing elements due to their unique electrochemical, electrical and optical properties.<sup>7</sup> As 3,3'-diaminobenzidine (DAB), organic compounds containing polyamine groups are utilized in the preparation of modified electrode by electrochemical polymerization on electrode surface. Poly(3,3'-diaminobenzidine) (PDAB) coated modified electrode was synthesized in aqueous acidic solution<sup>8</sup> and some organic solvent.<sup>9,10</sup> Cai and Khoo<sup>8</sup> reported electropolymerization of DAB on several electrode surfaces (platinum, gold and glassy carbon) for determination of Se<sup>IV</sup> by differential pulse anodic stripping voltammetry. Nateghi *et al.*<sup>9</sup> studied polymerization of DAB in aqueous solution and propylene carbonate, acetonitrile, and ethanol solvents. It was reported that the prepared modified electrode in ethanol solvent was used in determination of Se<sup>IV</sup>. Also,

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there are some sensors, biosensors and immunoassay studies based on PDAB modified electrodes. Phenol determination over modified PDAB glassy carbon electrode in acetonitrile was carried out using electrochemical method.<sup>10</sup> Zhang *et al.*<sup>11</sup> reported PDAB-hydrogen peroxide-horseradish peroxidase system for determination of carcionembryonic antigen in human serum.

Poly(vinylferrocene) (PVF) is obtained by chemical polymerization of vinylferrocene monomer.<sup>12</sup> This redox polymer may be attached on the electrode surfaces as PVF<sup>13</sup> or PVF<sup>+</sup>X<sup>-</sup>.<sup>14</sup> This electroactive film plays an important role as electron transfer mediator between the substrate and the reactant. PVF<sup>+</sup> coated modified electrode was successfully used for electroreduction and oxidation of some substrates for catalytic studies. Obtained PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup> modified electrode using polymerization solution containing PVF and tetrabutylammonium perchlorate (TBAP) as supporting electrolyte showed catalytic effect for electroreduction and oxidation of anthracene and derivatives,<sup>15,16</sup> and electrooxidation of methanol.<sup>17</sup> In other study, electrochemical response of I<sup>-</sup>, SCN<sup>-</sup> and CN<sup>-</sup> ions with this modified electrode was investigated.<sup>18</sup> Also, some biosensor studies were reported based on immobilized enzyme to PVF<sup>+</sup> electrode for amperometric determination of alcohols,<sup>14</sup> choline and acetylcholine<sup>19</sup> and galactose.<sup>20</sup>

In this study, PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film was potentiodynamically synthesized for the first time on Pt disc electrode in the dichloromethane solvent containing 100 mmol L<sup>-1</sup> TBAP/1.0 mg mL<sup>-1</sup> PVF/1.0 mmol L<sup>-1</sup> DAB. Characterization of this film was performed by cyclic voltammetry, UV-Vis spectrophotometry, Fourier transform infrared spectroscopy (FTIR), atomic absorption spectroscopy (AAS), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Optimum conditions for determination with amperometric I-t method of HQ using prepared PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film were provided in solution consisting of NaHSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> buffer solution (SBS) (pH 2.0) and results were compared with PDAB coated and uncoated Pt disc electrodes.

## Experimental

### Reagents

DAB monomer was supplied Sigma-Aldrich. Ammonium iron(II) sulfate hexahydrate ((NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O) (Merck), hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) (Sigma-Aldrich), 1,10-phenanthroline (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>) (Merck), and sodium acetate (CH<sub>3</sub>COONa) (Merck) were used for

UV-Vis measurements. Iron-free nitric acid (HNO<sub>3</sub>) (Merck 1.01518.0250) was used to shred PDAB and PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite films. PVF was synthesized by chemical polymerization of vinylferrocene (C<sub>12</sub>H<sub>12</sub>Fe) (Aldrich).<sup>12</sup> For non-aqueous studies, supporting electrolyte TBAP (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N(ClO<sub>4</sub>) was chemically synthesized by the reaction of tetrabutylammonium hydroxide (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N(OH) (40% aqueous solution, Sigma-Aldrich) with perchloric acid (HClO<sub>4</sub>) (BDH) and recrystallization in 1:9 (v:v) water and ethylalcohol, drying at 120 °C under vacuum for 12 h, according to the literature.<sup>21</sup> Anhydrous dichloromethane, ≥ 99.8% (CH<sub>2</sub>Cl<sub>2</sub>) (Sigma-Aldrich), solvent was used for non-aqueous medium without further purification. Sodium hydrogen sulfate (NaHSO<sub>4</sub>) (Merck) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) (Merck) were used for preparation of SBS (pH 2.0-6.5) for amperometric experiments in aqueous media. Before the electrochemical experiments, dissolved oxygen in optimum circumstances SBS prepared solutions both free and containing HQ was removed using nitrogen gas (Linde).

### Apparatus

Electrochemical experiments were performed with CH Instruments system, model 1140B. Three electrode systems were used for electrochemical studies. Pt disc (A = 7.85 × 10<sup>-3</sup> cm<sup>2</sup>) and Pt wire (A = 1.0 cm<sup>2</sup>) electrode were used as working and counter electrode, respectively. Pt macroelectrode was used for characterization studies. Silver/silver chloride (Ag/AgCl) and saturated calomel electrode (SCE) were used as reference electrode for non-aqueous and aqueous medium, respectively. Before each experiment, the working electrode (Pt disc) was polished with slurry of Cr<sub>2</sub>O<sub>3</sub> with ultrapure water, rinsed with ultrapure water, cleaned in the ultrasonic bath, washed with CH<sub>2</sub>Cl<sub>2</sub> solution and dried. Pt foil used as working electrode for UV-Vis, FTIR, AAS, SEM and EDX measurements was cleaned by holding it in flame for a few minutes. For determination of iron in composite film, UV-Vis measurement based on absorption of Fe<sup>2+</sup>-1,10-phenanthroline complex was performed using a Molecular Devices equipment (model SpectraMax M5) in the 400-700 nm range with slits of 10 nm. Deposited films were scraped from Pt foil electrode and KBr pellets were prepared. FTIR spectra of these films were taken using Perkin Elmer Spectrum 100 spectrometer (resolution: 4 cm<sup>-1</sup> and scan number: 4). AAS experiment was performed on a GBC Avanta B. Images of SEM (Rigaku Jeol JSM-6610) and EDX measurements (Oxford Instruments 51-Add0013) were directly taken using deposited polymer films on Pt foil electrode.

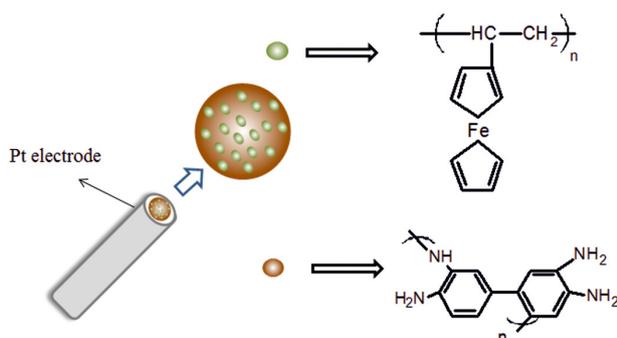
## Results and Discussion

### Preparation and characterization of composite film

In our previous work,  $\text{PVF}^+\text{ClO}_4^-$  redox polymer was synthesized by both potentiodynamic and potentiostatic methods on Pt electrode in non-aqueous  $\text{CH}_2\text{Cl}_2$  medium containing  $100 \text{ mmol L}^{-1}$  TBAP/ $1.0 \text{ mg mL}^{-1}$  of PVF. Electroprecipitation of  $\text{PVF}^+\text{ClO}_4^-$  on the Pt electrode surface by using potentiostatic method (such as  $0.70 \text{ V}$ ) is easy. However, for potentiodynamic method the potential window must be established. Potentiostatically deposited  $\text{PVF}^+\text{ClO}_4^-$  films were scanned at various potentials (from  $0.0 \text{ V}$  and  $-0.20$  to  $1.80 \text{ V}$ ) in  $\text{CH}_2\text{Cl}_2$  blank solution. The currents of both reduction and oxidation peaks decrease with increasing number of cycles, after the third cycle the value of peak current approaches the blank solution, at the last cycle, green-colored  $\text{PVF}^+\text{ClO}_4^-$  film was not observed on Pt electrode. It can be concluded that all  $\text{PVF}^+$  moieties were reduced to PVF and resulting film was stripped from the surface by dissolution in  $\text{CH}_2\text{Cl}_2$  solution. As cathodic potential shifted to more positive values, the peak current did not decrease more rapidly on successive scans. In the case of  $0.20 \text{ V}$ , cathodic potential was limited to a value in order not to reduce the film. It was recognized that the green film was observed not to strip from Pt electrode even if potentiodynamic scan was performed. Consequently, the optimum lower potential value was chosen as  $0.20 \text{ V}$  not to remove  $\text{PVF}^+\text{ClO}_4^-$  polymer from the electrode surface.<sup>22</sup> Because of all these reasons, the most suitable potential range for potentiodynamic synthesis of  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film was selected between  $0.20$  and  $1.80 \text{ V vs. Ag/AgCl}$  in  $\text{CH}_2\text{Cl}_2$  medium.

Structure of  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film deposited potentiodynamically on Pt disc electrode surface is shown in Figure 1.

Figure 2 shows the growth voltammograms between  $0.20$  and  $1.80 \text{ V}$  potentials (20 cycles) of green colored  $\text{PVF}^+\text{ClO}_4^-$  (Figure 2a), brown colored PDAB (Figure 2b)

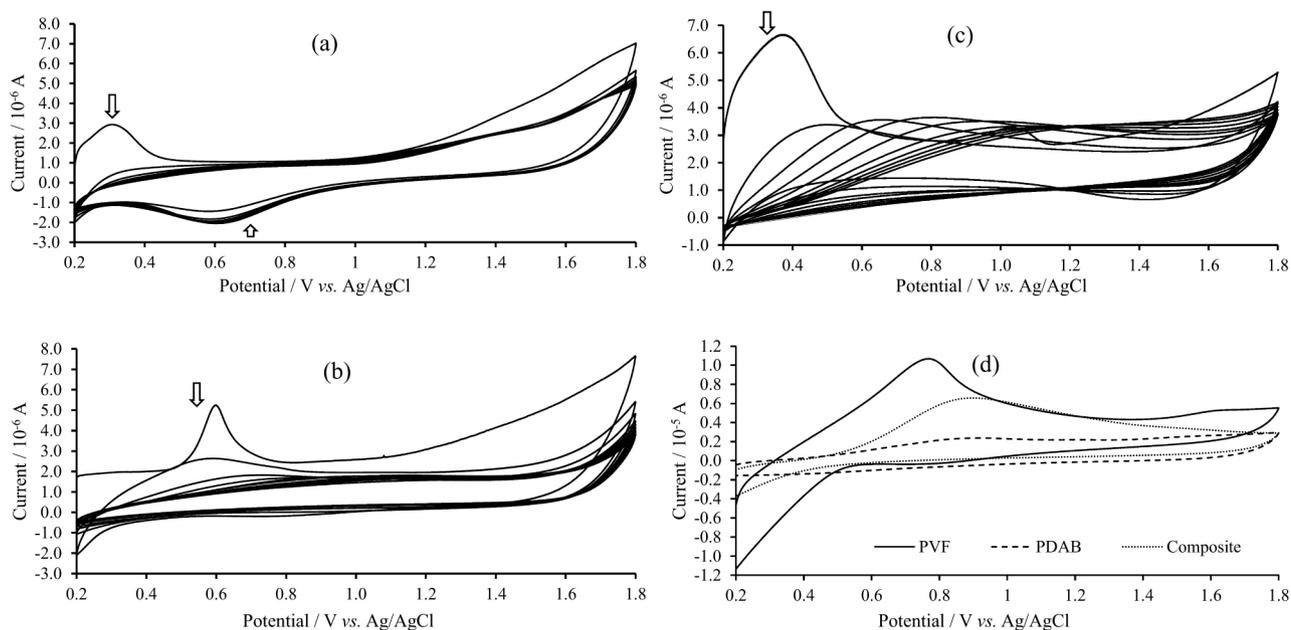


**Figure 1.** Schematic representation of  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film structure.

and green-black colored  $\text{PVF}^+\text{ClO}_4^-$ -PDAB films (Figure 2c) on Pt disc electrode in  $\text{CH}_2\text{Cl}_2$  polymerization solutions containing  $100 \text{ mmol L}^{-1}$  TBAP/ $1.0 \text{ mg mL}^{-1}$  PVF;  $100 \text{ mmol L}^{-1}$  TBAP/ $1.0 \text{ mmol L}^{-1}$  DAB and  $100 \text{ mmol L}^{-1}$  TBAP/ $1.0 \text{ mmol L}^{-1}$  DAB/ $1.0 \text{ mg mL}^{-1}$  PVF, respectively. As can be seen in Figure 2, when oxidation peak potentials of homopolymer films obtained using polymerization solutions containing only PVF and DAB appear at about  $0.30 \text{ V}$  (Figure 2a) and  $0.60 \text{ V}$  (Figure 2b), oxidation peak potential of the composite film deposited in the solution polymerization containing both monomers was observed as a broader peak at about  $0.40 \text{ V}$  (Figure 2c). Figure 2d shows the cyclic voltammograms of these films between  $0.20$  and  $1.80 \text{ V}$  in the  $\text{CH}_2\text{Cl}_2$  solution containing  $0.10 \text{ mmol L}^{-1}$  TBAP (blank solution). According to Figure 2d, it can be said that the composite film contains both  $\text{PVF}^+\text{ClO}_4^-$  and PDAB because of its oxidation peak current value was between homopolymers oxidation peak current values.

UV-Vis and AAS methods were used for determination of iron in the PDAB and  $\text{PVF}^+\text{ClO}_4^-$ -PDAB films. Before the measurements, these films deposited on Pt foil electrode were scraped from electrode surface, weighed on analytical balances, and were shred until dryness on hot plate with  $2.0 \text{ mL}$  of iron-free  $\text{HNO}_3$  in porcelain crucibles which contained only iron with the disintegration of the films washed with ultra pure water and were diluted to  $100 \text{ mL}$ . These solutions were directly used for determination of iron in the PDAB and  $\text{PVF}^+\text{ClO}_4^-$ -PDAB films with AAS (Table 1). For determination of  $\text{Fe}^{2+}$  with UV-Vis method,  $\text{Fe}^{2+}$ -1,10-phenanthroline complex was generated in the same solutions.  $\text{Fe}^{2+}$ -1,10-phenanthroline complex formed by the same method using ammonium iron(II) sulfate hexahydrate was used as standard containing  $0.1$ ;  $0.5$ ;  $1.0$ ;  $3.0$  and  $5.0 \text{ ppm Fe}^{2+}$  solutions. Table 1 shows the iron amount as ppm and percentage of films using characteristic absorption band at  $510 \text{ nm}$  due to charge transfer. As seen Table 1, while PDAB film does not contain iron,  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film contains  $2.98\%$  iron. So, it was shown that synthesized composite film contains PVF structure. Figures 3a and 3b show spectra of complexes with 1,10-phenanthroline of standard  $\text{Fe}^{2+}$  and  $\text{Fe}^{2+}$  solutions obtained by decomposition in nitric acid of composite film and calibration graph obtained with read absorbance values against standard  $\text{Fe}^{2+}$  concentration at  $510 \text{ nm}$ , respectively.

Iron proportion in composite structures using calibration graph was found as  $2.62\%$ . Thus, the presence of PVF in both spheres and on the surfaces of PDAB film in the composite was proven with iron determination using two instrumental methods as AAS and UV-Vis.



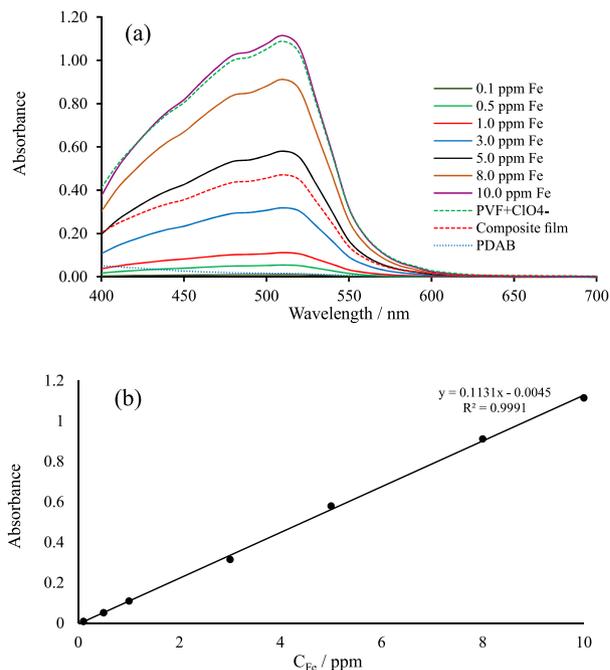
**Figure 2.** Cyclic voltammograms recorded during potentiodynamic growth of (a) poly(vinylferrocenium) perchlorate; (b) poly(3,3'-diaminobenzidine) and (c) poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) films using solutions containing 100 mmol L<sup>-1</sup> tetrabutylammonium perchlorate/1.0 mg mL<sup>-1</sup> polyvinylferrocene; 100 mmol L<sup>-1</sup> tetrabutylammonium perchlorate/1.0 mmol L<sup>-1</sup> 3,3'-diaminobenzidine and 100 mmol L<sup>-1</sup> tetrabutylammonium perchlorate/1.0 mmol L<sup>-1</sup> 3,3'-diaminobenzidine/1.0 mg mL<sup>-1</sup> polyvinylferrocene, respectively. (d) Their cyclic voltammetric behavior in 100 mmol L<sup>-1</sup> tetrabutylammonium perchlorate CH<sub>2</sub>Cl<sub>2</sub> blank solution (vs. Ag /AgCl,  $v = 100$  mV s<sup>-1</sup>).

**Table 1.** Fe amounts in poly(3,3'-diaminobenzidine) and poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) films

Sample	C <sub>Fe</sub> / ppm		Fe / %	
	UV-Vis	AAS	UV-Vis	AAS
PDAB	0.10	–	0.05	–
PVF <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> -PDAB	4.63	5.25	2.63	2.98

PDAB: poly(3,3'-diaminobenzidine); PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB: poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine); AAS: atomic absorption spectroscopy.

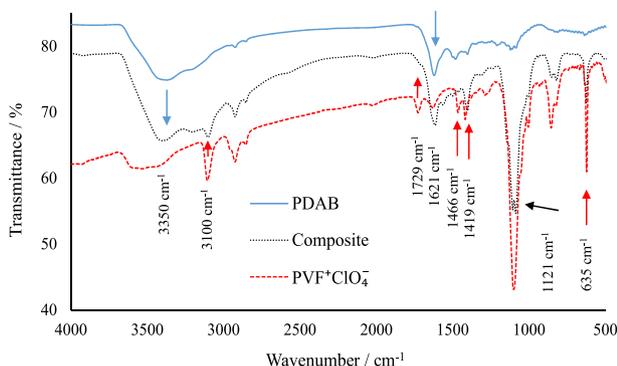
FTIR spectra of PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite and its homopolymer films are given in Figure 4. Peaks located in the infrared spectrum of PDAB film at 2950, 2920, 1621, 1501, 815, and 635 cm<sup>-1</sup> correspond to the presence of C–H and C–C vibrational bands in aromatic nucleus. The peaks at 3350 and 1121 cm<sup>-1</sup> are attributed to the N–H stretching and the Cl–O stretching arisen from the monomer and perchlorate ions supplied by supporting electrolyte, respectively.<sup>9,23</sup> In the spectrum of PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>, –C=C skeleton stretching of aromatic structure at 1419, 1466, and 1632 cm<sup>-1</sup>; aromatic –C–H outside of plane bending at 1729 cm<sup>-1</sup>; aliphatic –C–H stretching at 2851 and 2923 cm<sup>-1</sup> and –C–H stretching in aromatic pentadienyl cycle at 3100 cm<sup>-1</sup> appeared.<sup>21,24</sup> When the FTIR spectrum of the composite film was compared with its homopolymers, the 3100 and 3350 cm<sup>-1</sup> peaks in the FTIR spectrum of composite film were attributed to both



**Figure 3.** (a) UV-Vis spectra of standard Fe<sup>2+</sup> solution (lines), Fe<sup>2+</sup> in poly(vinylferrocenium) perchlorate (green dashes), poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) composite film (red dashes) and poly(3,3'-diaminobenzidine) film (dot); (b) calibration curve of standard Fe<sup>2+</sup> solution.

–C–H stretching of aromatic pentadienyl cycle of PVF and N–H stretching in structure of PDAB, respectively. As a result, these peaks located in the FTIR spectrum of the

composite film prove that  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film includes both PDAB and  $\text{PVF}^+\text{ClO}_4^-$  homopolymer films in its structure.

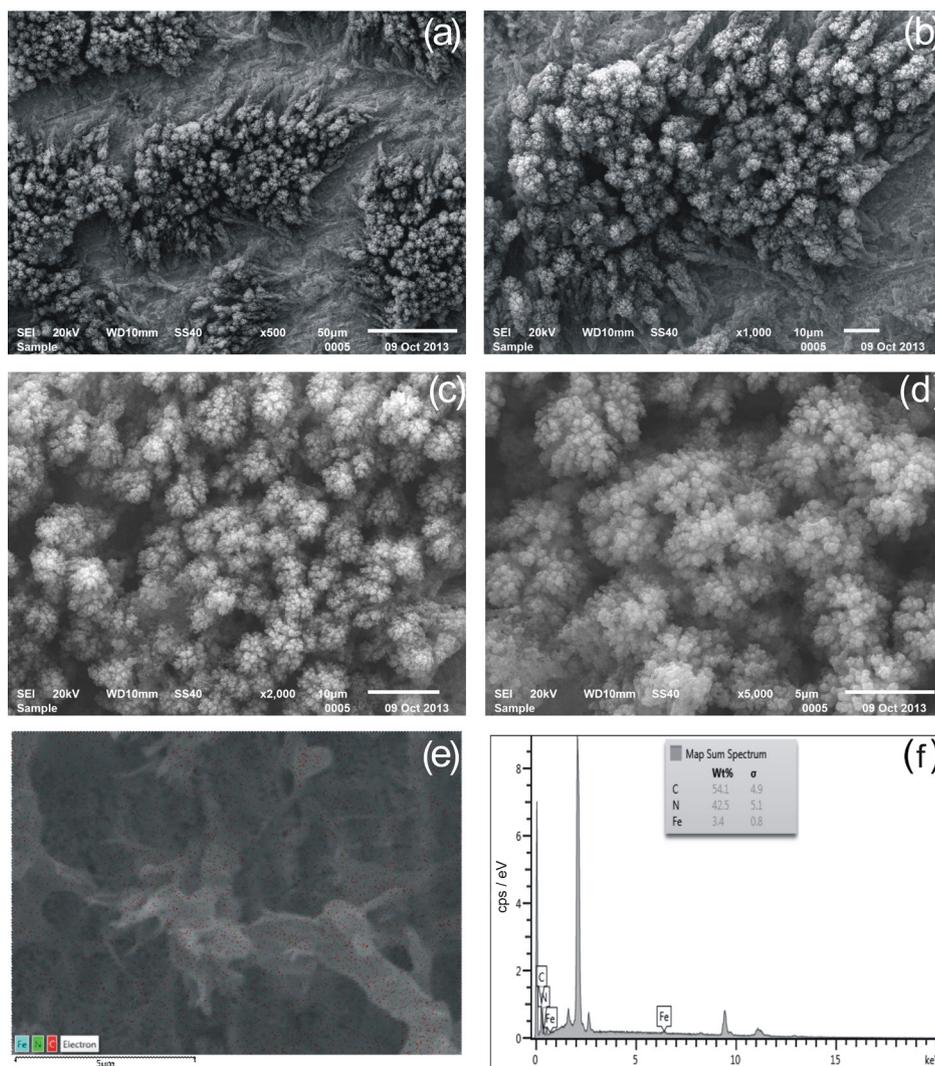


**Figure 4.** FTIR spectrum of poly(3,3'-diaminobenzidine), poly(vinylferrocenium) perchlorate homopolymers and poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) composite film.

Surface image of  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film deposited on Pt foil electrode in  $\text{CH}_2\text{Cl}_2$  solution was taken by SEM in different magnifications (500-5000 $\times$ ). Figures 5a-5d show SEM images of this film. Surface morphology of composite film was stated as a coral-like structure by comparing with similar SEM images in the literature.<sup>25,26</sup> EDX spectrum of composite film was recorded using the mapping method to determine the chemical composition of composite film (Figures 5e and 5f). According to Figure 5f, EDX results verified presence of both  $\text{PVF}^+$  and PDAB in the composite film (Fe (3.4%) at about 0.7 and 6.3 keV and N (42.5%) at about 0.39 keV).

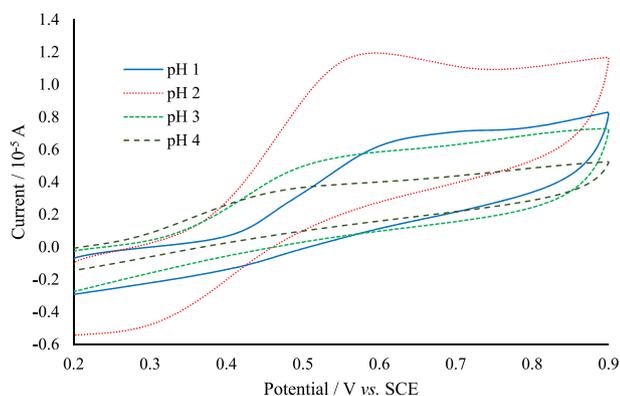
Effect of pH on the composite film and interaction of HQ with homopolymers and composite film

pH behavior of composite film was investigated in different SBS solutions (pH 1.0-4.0) vs. SCE. As seen



**Figure 5.** SEM images of composite film at (a) 500 $\times$ , (b) 1000 $\times$ , (c) 2000 $\times$  and (d) 5000 $\times$ ; (e) EDX-layered mapping image; and (f) EDX spectrum of composite film.

in Figure 6, the composite film is considered as most electroactive at pH 2.0 values. So, pH 2.0 solution was used in aqueous medium in subsequent studies.

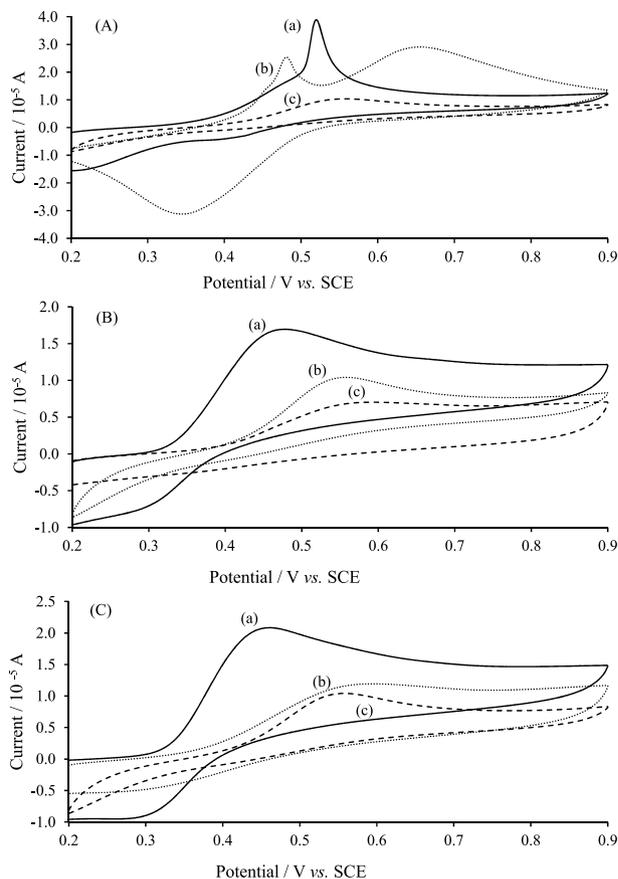


**Figure 6.** Effect of pH on electrochemical behavior in different SBS solutions (pH 1.0-4.0) of PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film deposited between 0.20 and 1.80 V ( $v = 100 \text{ mV s}^{-1}$ , vs. SCE).

Electrochemical behaviors of PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (Figure 7A, curve a), PDAB (Figure 7B, curve a) and PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB (Figure 7C, curve a) coated and uncoated Pt (Figures 7A-7C, curve c) disc electrode in pH 2.0 solution containing 5.0 mmol L<sup>-1</sup> HQ were determined. To compare the results, cyclic voltammograms of coated electrodes were taken in HQ-free pH 2.0 solution (Figures 7A-7C, curve b). According to Figure 7A, two oxidation peaks belonging to PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup> coated Pt electrode were observed in pH 2.0 solution not including HQ at about 0.48 and 0.65 V, respectively (Figure 7A, curve b). These peaks were observed as a single peak at about 0.52 V in the presence of HQ and its current value increases (Figure 7A, curve a). For the PDAB film (Figure 7B), oxidation peak potential at about 0.56 V was shifted at about 0.48 V in the presence of HQ and this peak current was increased (Figure 7B, curve a). While HQ was oxidized at about 0.55 V potential over bare Pt electrode, oxidation peak in presence of HQ was shifted to more cathodic values at about 0.44 V using composite film (Figure 7C, curve a).

Determination of HQ over PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film by amperometric I-t method

The response of PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film coated electrode to HQ was investigated using amperometric I-t method in SBS at pH 2.0 and the results were compared with PDAB coated and uncoated Pt electrodes. Due to dropping of the PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup> film from the electrode surface during amperometric I-t measurements, this modified electrode could not be used for determination of HQ by this method. PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB modified electrode was



**Figure 7.** Cyclic voltammograms of (A) poly(vinylferrocenium) perchlorate, (B) poly(3,3'-diaminobenzidine), and (C) poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) composite-coated electrodes in (a) SBS containing 5.00 mmol L<sup>-1</sup> hydroquinone and (b) SBS. (c) Cyclic voltammogram of 5.00 mmol L<sup>-1</sup> hydroquinone solution on bare Pt electrode ( $v = 100 \text{ mV s}^{-1}$ , vs. SCE).

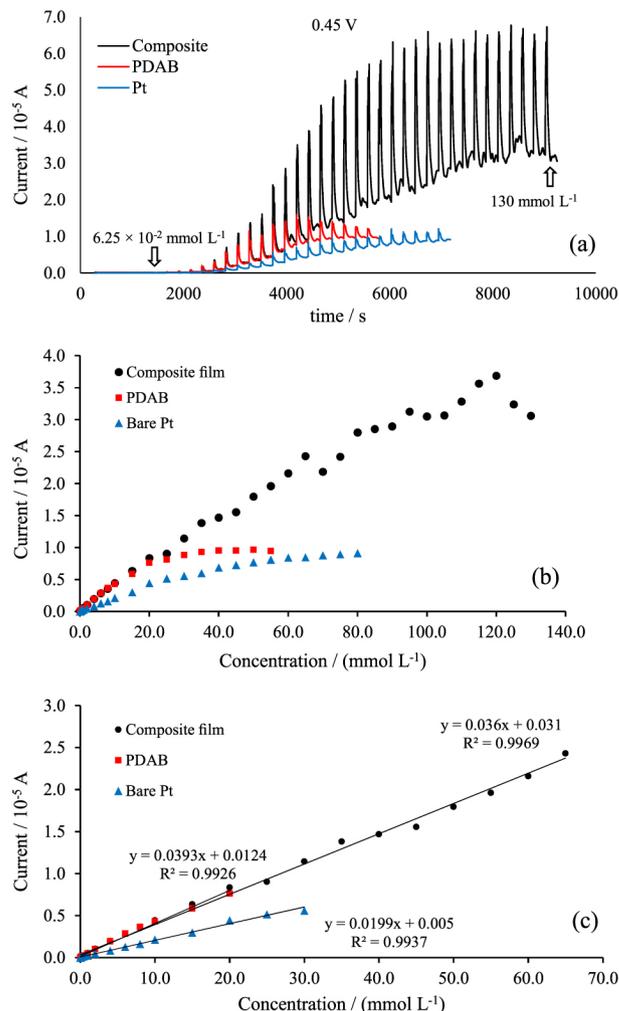
synthesized in CH<sub>2</sub>Cl<sub>2</sub> solution containing 100 mmol L<sup>-1</sup> TBAP/1.0 mmol L<sup>-1</sup> DAB/1.0 mg mL<sup>-1</sup> PVF between 0.20 and 1.80 V potentials vs. Ag/AgCl. Amperometric determination for HQ over the PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film coated electrode was carried out between potentials 0.40 and 0.60 V with periodically adding of various HQ concentrations vs. SCE, respectively. Before the measurements, coated and uncoated electrodes were ensured to reach steady-state current values at applied potentials with electrolysis about 1000 s. After this, calculated volume was added from stock solution to obtain final  $9.77 \times 10^{-4}$  mmol L<sup>-1</sup> HQ concentration and mixed for 30 s to make homogeneous solution. Steady-state current values were measured at the end of the 200 s vs. increasing HQ concentration and were recorded over coated and uncoated Pt electrodes (Figure 8a). A plot of the steady-state current values measured vs. the HQ concentration (Figure 8b) and calibration curves for linearity range of HQ concentration (Figure 8c) over coated and uncoated Pt electrodes were plotted. When compared with uncoated Pt,

PDAB and  $\text{PVF}^+\text{ClO}_4^-$ -PDAB coated electrodes, the highest current values were obtained for HQ at 0.45 V potential over the  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film coated electrode. Limit of detection (LOD), limit of quantification (LOQ), linear response ranges and regression coefficient for HQ were found as  $7.469 \times 10^{-5} \text{ mmol L}^{-1}$ ,  $2.489 \times 10^{-4} \text{ mmol L}^{-1}$ ,  $2.489 \times 10^{-4} - 65.0 \text{ mmol L}^{-1}$  and 0.996, respectively. Results for coated and uncoated Pt electrodes are given in Table 2. LOD and LOQ were calculated from the equations  $3s/m$  and  $10s/m$ , respectively.<sup>27</sup> As seen in Table 2, lowest LOD values and wide linear response were obtained using composite film coated electrode.

Finally, obtained results were compared with previous studies in Table 3. According to Table 3, developed method is usable for determination of HQ and it was found to be simpler, rapid, convenient, selective and highly sensitive than any reported methods.

## Conclusions

The redox polymer such as  $\text{PVF}^+\text{ClO}_4^-$  gives rise to some interesting electrochemical results when coated as a layer on Pt surfaces. To combine the electrocatalytic properties of intrinsically conducting polymer (PDAB) and redox polymer ( $\text{PVF}^+$ ) they were co-deposited electrochemically for the first time on Pt disc electrode in  $\text{CH}_2\text{Cl}_2$  containing PVF polymer, DAB monomer and TBAP as supporting electrolyte and  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film-coated electrode was fabricated. This composite film was characterized electrochemically and spectroscopically.  $\text{PVF}^+$  was not stripped from  $\text{PVF}^+\text{ClO}_4^-$ -PDAB structure due to encapsulation, even if this polymer was in the reduced form. Some phenolic compounds are capable of forming chelates with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions.<sup>33</sup> PVF in deposited composite film acted as an electron transfer mediator in the electrochemical oxidation of HQ due to its perfectly reversible redox properties.  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite film-coated electrode was examined to determine HQ. When the interaction between  $\text{PVF}^+\text{ClO}_4^-$ -PDAB and HQ was investigated, it was determined that HQ was



**Figure 8.** (a) Amperometric I-t curve recorded at 0.45 V vs. SCE with the successive additions of various hydroquinone concentrations. (b) Plot of the steady-state current values measured from amperometric I-t curve vs. hydroquinone concentrations. (c) Calibration curves for linearity range of hydroquinone concentrations over uncoated Pt, poly(3,3'-diaminobenzidine) and poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) coated electrodes.

immobilized into this composite.  $\text{PVF}^+\text{ClO}_4^-$ -PDAB composite-coated electrode has lower working potential, larger linearity range, and lower LOD when compared with PDAB-coated electrode and uncoated Pt electrode. As a

**Table 2.** Analytical parameters for amperometric determination of hydroquinone over uncoated Pt, poly(3,3'-diaminobenzidine) and poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine) coated modified electrodes

	Uncoated Pt	PDAB coated	$\text{PVF}^+\text{ClO}_4^-$ -PDAB coated
Applied potential / V	0.45	0.45	0.45
Linearity range / (mmol L <sup>-1</sup> )	$1.601 \times 10^{-2}$ -30.0 (R <sup>2</sup> : 0.993)	$6.310 \times 10^{-4}$ -20.0 (R <sup>2</sup> : 0.992)	$2.489 \times 10^{-4}$ -65.0 (R <sup>2</sup> : 0.996)
LOD / (mmol L <sup>-1</sup> )	$4.810 \times 10^{-3}$	$1.890 \times 10^{-4}$	$7.469 \times 10^{-5}$
LOQ / (mmol L <sup>-1</sup> )	$1.601 \times 10^{-2}$	$6.310 \times 10^{-4}$	$2.489 \times 10^{-4}$
Linear equation	$y = 0.019x + 0.005$	$y = 0.039x + 0.012$	$y = 0.036x + 0.031$

PDAB: poly(3,3'-diaminobenzidine);  $\text{PVF}^+\text{ClO}_4^-$ -PDAB: poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine).

**Table 3.** Comparison of electrochemical methods for the determination of hydroquinone

Electrochemical methods	Using modified electrode	LOD / (mmol L <sup>-1</sup> )	Linear response range / (mmol L <sup>-1</sup> )	Reference
Cyclic voltammetry	poly(phenylalanine) modified GCE	7.0 × 10 <sup>-4</sup>	0.010-0.14	28
Differential pulse voltammetry	poly(glutamic acid) modified GCE	1.0 × 10 <sup>-3</sup>	5.0 × 10 <sup>-3</sup> -0.08	29
Differential pulse voltammetry	poly( <i>p</i> -aminobenzoic acid) coated GCE	4.0 × 10 <sup>-4</sup>	1.2 × 10 <sup>-3</sup> -0.60	30
Differential pulse voltammetry	PEDOT/CNT/CPE	3.0 × 10 <sup>-4</sup>	1.10 × 10 <sup>-3</sup> -0.13	31
Square wave voltammetry	chitosan and gilo ( <i>Solanum gilo</i> )	2.0 × 10 <sup>-3</sup>	0.250-5.50	32
Amperometric	PVF <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> -PDAB coated Pt electrode	7.47 × 10 <sup>-5</sup>	2.49 × 10 <sup>-4</sup> -65.00	This work

LOD: limit of detection; GCE: glassy carbon electrode; PEDOT: poly(3,4-ethylenedioxythiophene); CNT: carbon nanotube; CPE: carbon paste electrode; PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB: poly(vinylferrocenium) perchlorate-poly(3,3'-diaminobenzidine).

result, the catalytic activity of PDAB film was improved by the addition of PVF<sup>+</sup> as an electron transfer mediator. Synthesized PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film is expected to exhibit promising electrocatalytic effects toward HQ. As compared with the analytical results obtained by using composite film, PVF<sup>+</sup>ClO<sub>4</sub><sup>-</sup>-PDAB composite film is better than PDAB coated and uncoated Pt electrode because PVF behaves as electron transfer mediator.

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