

# Poly(vinylferrocenium) perchlorate–polyaniline composite film-coated electrode for amperometric determination of hydroquinone

Muammer Kavanoz · Nuran Özçiçek Pekmez

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**Abstract** Poly(vinylferrocenium) perchlorate–polyaniline (PVF<sup>+</sup>–PANI) composite film was synthesized electrochemically on Pt electrode in a methylene chloride solution containing a mixture of poly(vinylferrocene) (PVF) polymer and aniline monomer. PVF<sup>+</sup> polymer in the composite film was used as an electron transfer mediator. The composite coating showed significant electrochemical activity towards hydroquinone (HQ) at pH 4, with high sensitivity and a wide linearity range. The interaction of HQ with PVF<sup>+</sup> and PANI homopolymer films was investigated electrochemically and spectroscopically. HQ molecules are accumulated on the electrode surface due to trapping by both polymers in the composite film and then oxidized catalytically by PANI. The most significant contribution of PVF<sup>+</sup> polymer is that it facilitates electron transfer in the composite film. The linear response range was found to be between  $1.60 \times 10^{-4}$  mM and 115 mM ( $R^2=0.999$ ) at 0.45 V vs saturated calomel electrode. The limit of detection (LOD) was  $4.94 \times 10^{-5}$  mM.

**Keywords** Conducting polymer · Composite · Coating · Polyaniline · Poly(vinylferrocene) · Hydroquinone

## Introduction

Phenolic compounds are released into the environment by a large number of industries, such as coal mining, oil refinery,

paint, photographic chemicals, pesticides, polymer and pharmaceuticals, and organic-reducing agents (e.g., in cosmetic creams as depigmenters). These compounds are harmful to humans and animals [1]. Among phenolic compounds, hydroquinone (HQ) can cause irritation and sensitization in the eyes and irritation in the nose and throat. In addition, it has been shown to be mutagenic in animals [2]. Indeed, it has been included in the lists of priority pollutants to be monitored in the aquatic environment by international bodies, such as the US Environmental Protection Agency and the European Union [3].

Nowadays, several analytical techniques, including high performance liquid chromatography, capillary electrochromatography, micellar chromatography, and kinetic spectrophotometry are being replaced by inexpensive, rapid, and reliable methods [4]. Electrochemical determination of HQ is to make use of chemically modified electrode [5] and chemically modified electrode containing immobilized bacteria [6]. Biosensors based on immobilized peroxidase, such as horseradish peroxidase [7], laccase [8], polyphenol oxidase, or tyrosinase [9], bienzyme electrode with horseradish peroxidase/glucose oxidase, and tyrosinase/laccase bienzyme [10] have been used for phenol detection. Of all these methods, electrochemical method is the most advantageous one because of its simplicity, rapidness, and sensitivity. In addition, electrochemical sensors can be fabricated to extremely small dimensions, and thus, they become ideal for direct placement into biological samples with minimal damage to tissues.

Polyaniline (PANI) is one of the most promising conductive polymers due to its high conductivity, good redox reversibility, and environmental stability. One of the most striking properties of PANI is its ability to catalyze the electrochemical redox reactions of some inorganic ions and organic compounds [11, 12]. Polyaniline exists in three well-defined oxidation states: leucoemeraldine, emeraldine, and pernigraniline [13]. Poly-

M. Kavanoz  
Department of Chemistry, Rize University,  
53100 Rize, Turkey

N. Ö. Pekmez (✉)  
Department of Chemistry, Hacettepe University,  
Beytepe, 06800 Ankara, Turkey  
e-mail: npekmez@hacettepe.edu.tr

aniline can be oxidized and reduced reversibly at a given pH range, which is accompanied by electron transfer. Therefore, polyaniline and its derivatives can be used as a mediator in electrocatalytic fields such as  $\text{Fe}^{2+/3+}$ ,  $\text{Fe}[(\text{CN})_6]^{4-/3-}$ , and hydroquinone/benzoquinone [11, 14]. Mu et al. showed that polyaniline synthesized in the presence of ferrocenesulfonic acid can catalyze the oxidation of ascorbic acid, gallic acid, and hydrogen peroxide [15].

The redox polymer polyvinylferrocenium perchlorate ( $\text{PVF}^+$ ) gives rise to some interesting electrochemical results when used as a layer on Pt surfaces [16, 17]. The  $\text{PVF}^+$  modified platinum electrode can be prepared by electrooxidation of polyvinylferrocene (PVF) on platinum electrode in a methylene chloride solution containing tetra-*n*-butyl ammonium perchlorate as a supporting electrolyte. Perchlorate ions ( $\text{ClO}_4^-$ ) in the structure of tetra-*n*-butyl ammonium perchlorate (TBAP) are incorporated into the polymeric structure as a counter ion. The PVF solution is yellow, and the  $\text{PVF}^+$  film is green [18]. It is known that the reduced form of this redox polymer film, PVF, is a homogeneous compact film, whereas the oxidized form,  $\text{PVF}^+$ , is an inhomogeneous film [19]. Pores or pinholes exist in  $\text{PVF}^+$  film, through which dissolved reactants could diffuse to the underlying metal surface [16]. This electroactive film can act as a modified surface through which an electron transfer between a substrate and a reactant can take place. Gülce and coworkers reported that  $\text{PVF}^+$ -coated electrode catalyzed the electrooxidation and electroreduction of some organic species such as anthracenes in acetonitrile and the electrooxidation of  $\text{H}_2\text{O}_2$  in aqueous solution. Furthermore, they showed that this matrix could be used as a preconcentration agent for the analysis of some anions in aqueous medium [17].

In the present study, to combine the electrocatalytic properties of intrinsically conducting polymer and redox polymer, PANI and  $\text{PVF}^+$  were codeposited electrochemically on Pt electrode in a methylene chloride solution containing PVF polymer and aniline monomer, and  $\text{PVF}^+$ -PANI composite film-coated electrode was fabricated. PVF in deposited composite film was used as an electron transfer mediator in the electrochemical oxidation of HQ due to its perfect reversible redox properties. This composite film was characterized electrochemically and spectroscopically.  $\text{PVF}^+$ -PANI composite film-coated electrode was examined to determine HQ.

## Experimental

Aniline (Riedel de Haen) was distilled under vacuum before use. Poly(vinylferrocene) (PVF) was synthesized using a method of chemical polymerization of vinylferrocene (Aldrich) [20]. Methylene chloride (Riedel de Haen), which

was used to prepare polymerization solutions, was kept under the nitrogen atmosphere (BOS). TBAP (Sigma-Aldrich) was used as the supporting electrolyte in methylene chloride solution. The solutions with different pH (2–6.5) were prepared using  $\text{NaHSO}_4$  (Merck) and  $\text{Na}_2\text{SO}_4$  (Merck). Hydroquinone (HQ) solution was prepared in a  $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$  solution (SBS) at pH 4 under nitrogen atmosphere. All solutions were deoxygenated by bubbling pure nitrogen gas prior to use in the electrochemical experiments.

The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl (sat)) and counter electrode (Pt spiral). In aqueous medium, a saturated calomel electrode (SCE) was used as the reference electrode. Pt disk electrode ( $7.85 \times 10^{-3} \text{ cm}^2$ ) was used as the working electrode. Before each experiment, the working electrode was polished with a slurry of  $\text{Cr}_2\text{O}_3$  with water, rinsed with triple distilled water, cleaned in the ultrasonic bath, washed with methylene chloride, and dried, respectively. For Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and conductivity measurements, Pt foil ( $1.0 \text{ cm}^2$ ) was used as the working electrode. This electrode was cleaned by holding it in flame for a few minutes. The polymers deposited on Pt or indium tin oxide (ITO) electrodes were immersed in methylene chloride to remove adsorbed electrolyte, monomer, and the soluble oligomers formed during the electropreparation of the films and then dried at room temperature before measurements. PVF coating was prepared by immersing the ITO electrode into a solution of  $1.0 \text{ mg mL}^{-1}$  PVF in methylene chloride and following solvent evaporation [21]. ITO electrode was cleaned with immersing in methylene chloride and/or DMSO using ultrasonic bath and then wiped out. FTIR spectra were obtained using KBr pellets. The dry conductivity values of polymers were measured using the four-probe measuring technique at room temperature. The ohmic contact to the films was made with Au-plated four-probe tips, and at least ten different current values were used in the measurement of potential drops. Electrochemical studies were carried out with CH Instruments System, Model 660B. The characterization of electrochemically obtained polymers were performed by UV–visible (UV–vis) spectrophotometry, SEM, and FTIR by using Double Beam PC8 Scanning Auto Cell UVD-3200 spectrometer (and Perkin Elmer Spectrum UV–vis spectrometer), Carl Zeiss EVO-50 scanning electron microscopy, and Perkin Elmer Spectrum One B FTIR spectrometer, respectively.

Theoretical calculations were performed using ab initio (Minimal (STO-3G)) and semi-empirical Austin Model 1 (AM1) in the Hyperchem 7.5 program package with a Pentium III 600 MHz computer [22, 23]. The hydrogen bond lengths were computed after AM1 geometrical optimization.

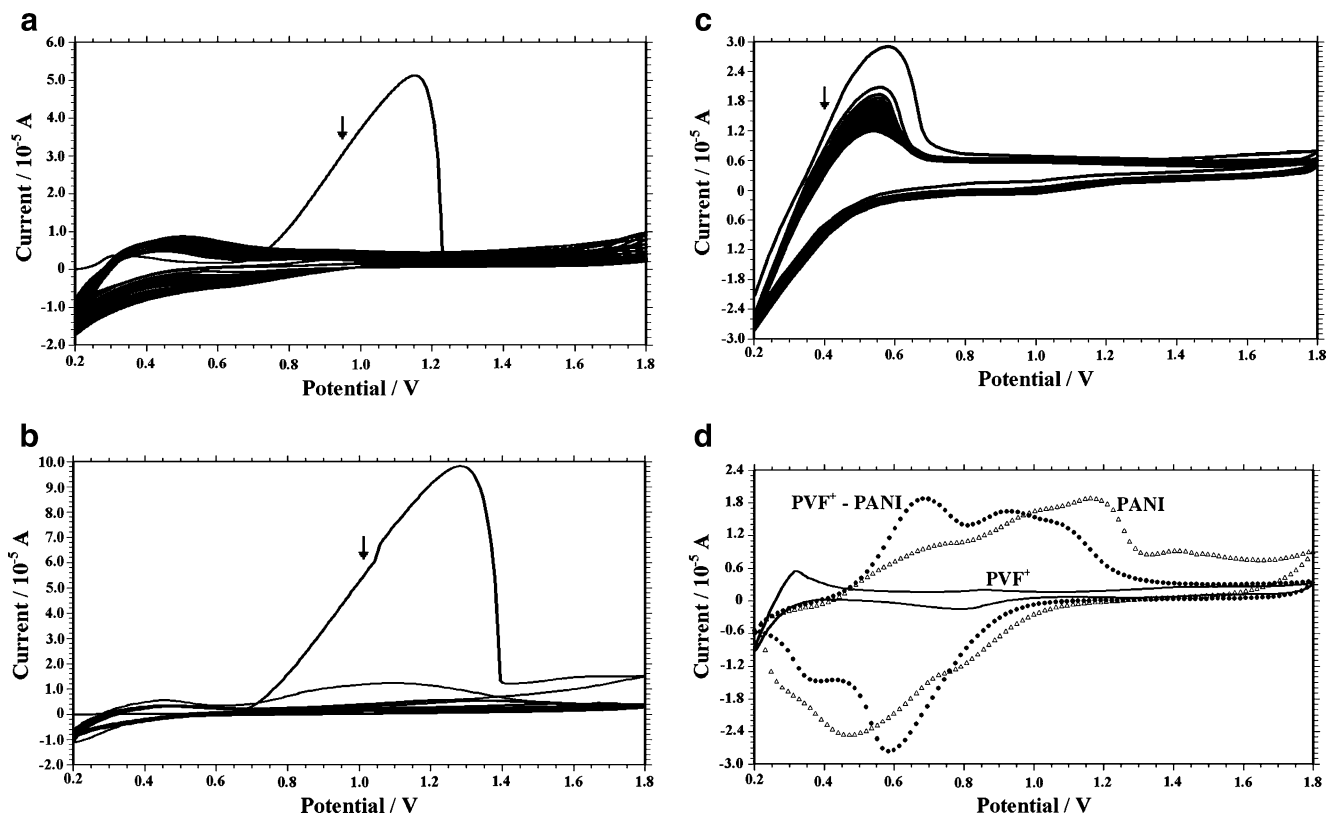
## Results and discussion

### Preparation and characterization of PVF<sup>+</sup>-PANI composite film

Deposition of the composite film containing PVF<sup>+</sup> and PANI polymers was achieved electrochemically on Pt electrode in a non-aqueous methylene chloride/0.1 M TBAP solution containing PVF polymer, aniline monomer, and HClO<sub>4</sub>. Figure 1a shows the cyclic voltammograms (20 cycles) taken during the deposition in the potential region between 0.20 and 1.80 V vs Ag/AgCl in this solution. Aniline monomer and PVF polymer are oxidized at about 1.3 and 0.5 V vs Ag/AgCl in this medium, respectively (Fig. 1b, c). Therefore, PANI and PVF<sup>+</sup> polymers must be deposited simultaneously as a mixture during scanning between 0.20 and 1.80 V in the methylene chloride solution containing both PVF polymer and aniline monomer. For comparison, PANI and PVF<sup>+</sup> homopolymer films were synthesized from individual polymerization solutions under the same condition. The cyclic voltammograms (20 cycles) taken during the deposition are given in the same figure (Fig. 1b, c). PVF<sup>+</sup> here denoted the

polymer film which was electrochemically deposited on Pt electrode. This film consists of PVF and PVF<sup>+</sup> moieties, and ClO<sub>4</sub><sup>-</sup> was incorporated into the polymeric structure as a counter ion. Figure 1d shows the cyclic voltammogram behavior of the composite and homopolymer films in the methylene chloride/0.1 M TBAP solution containing 10.0 mM HClO<sub>4</sub> (blank solution). From a comparison of both the peak currents and potentials, it was clear that the properties of composite film were different than those of homopolymers. As seen in Fig. 1d, while the main anodic and cathodic peaks of PANI film are at about 1.2 and 0.5 V, these peaks shift to more cathodic and anodic values (0.7 and 0.6 V) for the composite film, respectively. The oxidation and reduction peaks of composite film are more reversible than that of PANI film. This indicates that PVF polymer accelerates the electron transfer in the composite film.

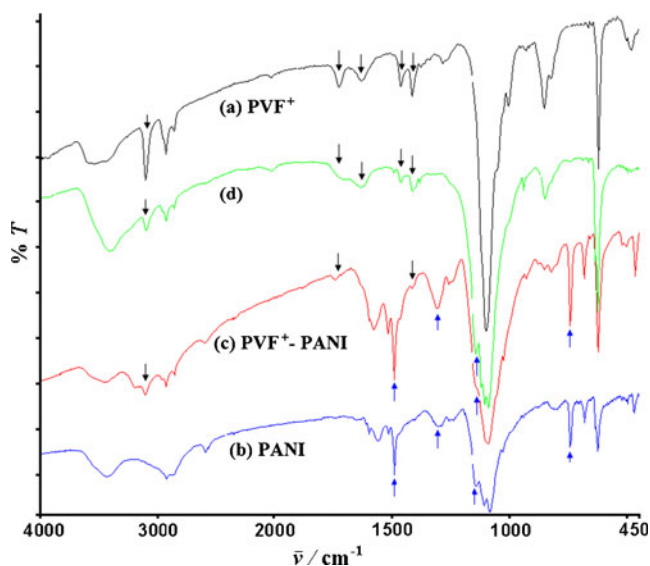
In order to confirm whether the composite film consists of each polymer or not, FTIR spectrum of PVF<sup>+</sup>-PANI composite film was taken and compared with those of their homopolymer films. Firstly, FTIR spectra of homopolymers were recorded (Fig. 2a, b) and then they were characterized. In the spectrum of PVF<sup>+</sup> film, these characteristic peaks appear; -C=C- skeleton stretching in aromatic structure at



**Fig. 1** Cyclic voltammograms recorded during potentiodynamic growth of **a** PVF<sup>+</sup>-PANI composite film obtained using 100 mM aniline/1.00 mg/mL PVF/33.0 mM HClO<sub>4</sub>, **b** PANI obtained using 100 mM aniline/33.0 mM HClO<sub>4</sub>, **c** PVF<sup>+</sup> obtained using

1.00 mg mL<sup>-1</sup> PVF/33.0 mM HClO<sub>4</sub> on Pt electrode (20 cycle), and **d** their cyclic voltammogram behavior in acidic blank solution,  $v=100 \text{ mV s}^{-1}$

1,419, 1,466, and 1,632  $\text{cm}^{-1}$ ; aromatic  $\text{C-H}$  outside of plane bending at 1,729  $\text{cm}^{-1}$ ; aliphatic  $\text{C-H}$  stretching at 2,851 and 2,923  $\text{cm}^{-1}$ ;  $\text{C-H}$  stretching in aromatic pentadienyl cycle at 3,100  $\text{cm}^{-1}$  [16]. The FTIR spectrum of PANI shows similar characteristics to the literature reports [24–26], with vibration bands of a doped polyaniline structure (Fig. 2b). The absorption peaks at 742 and 1,142  $\text{cm}^{-1}$  are assigned to  $\text{C-H}$  bending outside and inside of plane, respectively. If the sample was PANI base, the spectrum would exhibit the main peaks at about 1,593 and 1,492  $\text{cm}^{-1}$ , corresponding to quinone and benzene ring-stretching deformations, respectively. In this spectrum (Fig. 2b), the peaks are observed at 1,561 and 1,492  $\text{cm}^{-1}$ . One of these modes shows a red shift from 1,593  $\text{cm}^{-1}$  to 1,561  $\text{cm}^{-1}$  as is the case in the study carried out by Stejskal et al. [24]. This shift is indicated that the quinoid structures in PANI are protonated. The absorption band at 1,312  $\text{cm}^{-1}$  corresponds to p-electron delocalization induced in the polymer by protonation [24]. The band characteristic of the conducting protonated form is observed at 1,243  $\text{cm}^{-1}$  and is interpreted as a  $\text{C-N}^+$  stretching vibration in the polaron structure. Out-of-plane deformations of  $\text{C-H}$  on 1,4-disubstituted rings are located in the region of 800–880  $\text{cm}^{-1}$ . The broad band at 1,083  $\text{cm}^{-1}$  shows the presence of positive charges in PANI and PVF<sup>+</sup> chains [13]. The peak at 625  $\text{cm}^{-1}$  is also assigned to  $\text{Cl-O}$  stretching due to  $\text{ClO}_4^-$ . As shown by a comparison of the spectra of the composite film and homopolymers, the presence of the bands located at 1,492, 1,561, 1,312, 1,142, 742  $\text{cm}^{-1}$  and 3,100, 1,729, and 1419  $\text{cm}^{-1}$  indicated that both PVF<sup>+</sup> and PANI could be deposited as composite film on Pt electrode (Fig. 2c).

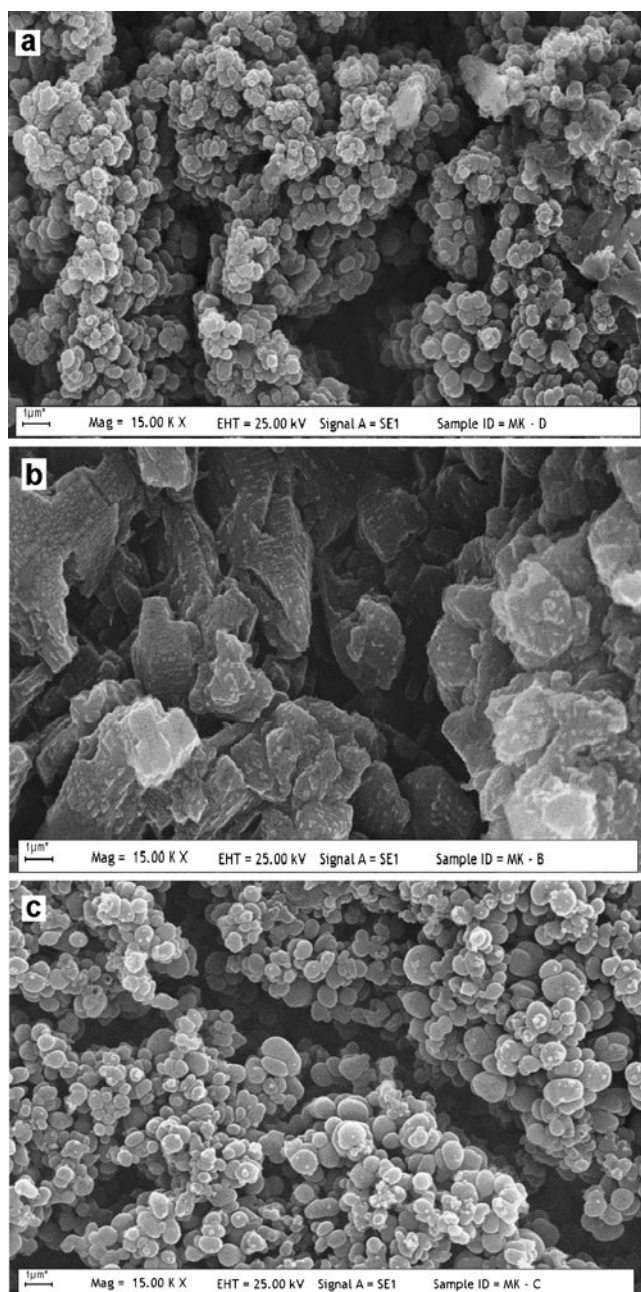


**Fig. 2** FTIR spectra of: **a** PVF<sup>+</sup>, **b** PANI, **c** PVF<sup>+</sup>-PANI composite film, and **d** same composite film after electrolysis at  $-0.20$  V in blank solution

Dry conductivity values of the composite and its homopolymer films deposited under the same conditions were measured by using the four-probe measuring technique at room temperature. Conductivity values of PVF<sup>+</sup>, PANI homopolymers, and PVF<sup>+</sup>-PANI composite films were  $6.00 \times 10^{-4}$ ,  $5.73 \times 10^{-1}$ , and  $2.50 \times 10^{-1}$   $\text{S cm}^{-1}$ , respectively. The conductivity value of the composite film was smaller than that of the PANI film. It is clear from a comparison of conductivity values that PVF<sup>+</sup> polymer was present along with PANI in the composite film.

The morphologies of the composite and homopolymer coatings were investigated by SEM. The PVF<sup>+</sup>-PANI composite film was deposited on Pt electrode from methylene chloride/0.1 M TBAP solution containing 1.00 mg/mL PVF, 100 mM aniline, and 33.0 mM  $\text{HClO}_4$ . The PVF<sup>+</sup> and PANI homopolymer films were performed in a methylene chloride/0.1 M TBAP/33.0 mM  $\text{HClO}_4$  solutions containing 1 mg PVF/mL and 100 mM aniline, respectively. Figure 3 shows the image of PVF<sup>+</sup>, PANI, and PVF<sup>+</sup>-PANI composite coatings deposited in the methylene chloride medium. Morphology of PVF<sup>+</sup> exhibits a globular structure (Fig. 3a). PANI synthesized in the acidic methylene chloride medium shows a crystalline structure in contrast to other media (Fig. 3b) [27–30]. Chao et al. showed that PANI synthesized in aqueous solution had honeycombed clews which were tenuous, interconnected fibrillar network [27]. Pandey et al. revealed that the PANI polymer growth in acetonitrile medium had aggregate rod-shaped structure with smooth surface and least porosity [29]. The image of PVF<sup>+</sup>-PANI composite film is similar to that of PVF<sup>+</sup> (Fig. 3c). The difference of these two images is the dimensions of particle size. The diameters of globulars vary between 40 and 400 nm and between 40–700 nm for PVF<sup>+</sup> homopolymer and PVF<sup>+</sup>-PANI composite film, respectively. Energy dispersive X-ray spectroscopy study confirmed the presence of iron in the composite film structure.

When PVF<sup>+</sup> homopolymer-coated electrode was electrolyzed at  $-0.20$  V for 10 min in blank solution, it was observed that this film was stripped entirely from the electrode surface. In other words, PVF<sup>+</sup> moieties in the polymer are reduced to PVF and then the film dissolve in methylene chloride. The same experiment was performed with composite coating to confirm whether this adhesive film consisted of PVF<sup>+</sup> polymer or not, and its FTIR spectrum was taken (Fig. 2d). As seen in this figure, the peak at 3,100  $\text{cm}^{-1}$  belonging to the pentadienyl ring of PVF<sup>+</sup> still exists in the spectrum after electrolysis. This means that PVF formed during the electrolyzing was not stripped from the composite film. It could be concluded that PVF<sup>+</sup> and PANI polymers encapsulated within each other as a mixture during the deposition of composite film. The encapsulation of PVF<sup>+</sup> polymer inside the growing PANI polymer provides the retainment of PVF<sup>+</sup> on the electrode



**Fig. 3** SEM images of **a** PVF<sup>+</sup>, **b** PANI, and **c** PVF<sup>+</sup>-PANI composite films

surface even if the polymer is in the reduced form (PVF). Consequently, the film deposited in the solution mixture of both PVF and aniline by scanning the potential between 0.20 and 1.80 V is suitable for electroanalytical applications, especially in the cathodic region.

#### Effect of pH in aqueous medium

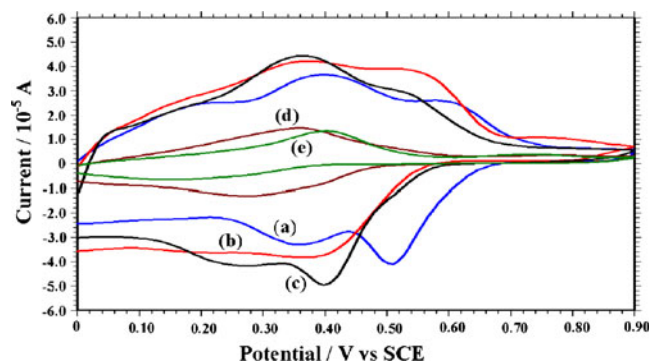
In general, electroactivity of PANI decreases with increasing pH value of aqueous solution and at pH values greater than 5; electroactivity is very limited and does not show

any electrocatalytic effect for some species [15, 31]. The effect of pH on the electrochemical behavior of PANI film synthesized in the acidic methylene chloride medium was investigated in aqueous medium. Figure 4 shows the cyclic voltammograms of PANI coatings recorded at different pH values in NaHSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub> solution (SBS). As it is clear from this figure, PANI film has the highest electroactivity at a pH value of 4.0. PANI gradually loses its electroactivity as pH decreases and also increases. At more basic regions than the pH value of 4, leucoemeraldine and emeraldine radical cations are very unstable and easily converted to pernigraniline species. At more acidic regions, PANI is protonated and is converted to another form that includes much more leucoemeraldine species which are nonconducting [13]. Therefore, the studies were carried out at pH 4.

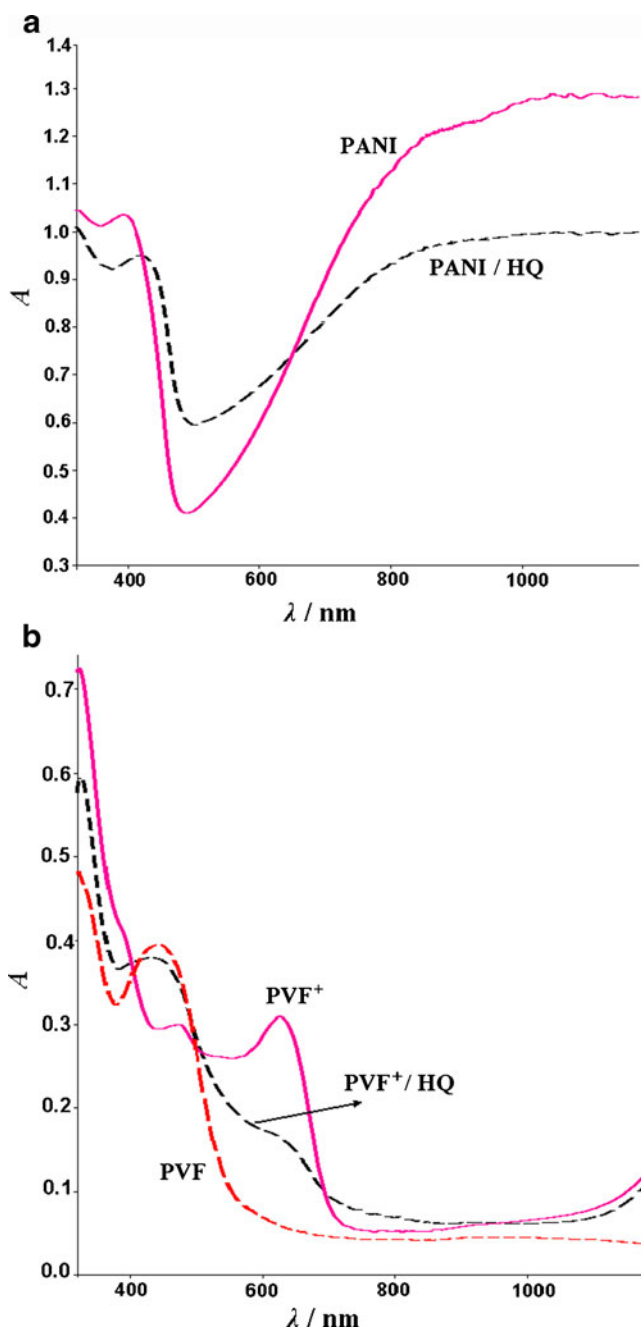
#### Interaction of HQ with homopolymer films

The interaction of HQ with homopolymer films were investigated by FTIR and UV-vis measurements. Firstly, PVF<sup>+</sup> and PANI films deposited on Pt and ITO electrodes were immersed in SBS at pH 4 containing 500 mM HQ under nitrogen atmosphere for 30 min and then immersed in the hydroquinone-free solution to clean this compound adsorbed on electrode surfaces. This cleaning procedure was repeated for three times to remove residual HQ molecules. Figures 5 and 6 show UV-vis spectra of the films and HQ solutions before and after these treatments. FTIR spectra of the films are also given in Fig. 7.

As seen in Fig. 5, the polaron band at about 410 nm and bipolaron band [32] after 800 nm were clearly observed in the UV-vis spectrum of PANI. The ratio peak intensity observed at 800 to 410 nm decreases after interaction with HQ. In addition, a new peak was observed at about 400 nm in the UV-vis spectrum of its HQ solution, when compared to that of freshly prepared clear HQ solution as seen in Fig. 6. This might be due to the oxidation of HQ to benzoquinone (Q). To prove this property, UV-vis spectrum of HQ solution that was left to open atmosphere and



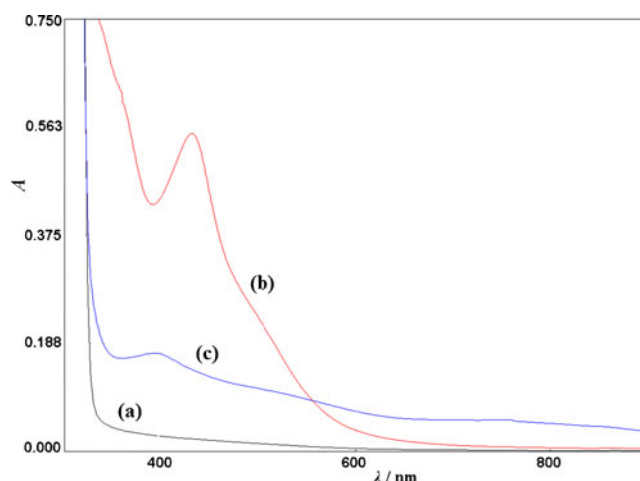
**Fig. 4** Cyclic voltammograms of PANI films in SBS at pH values of **a** 2.0, **b** 3.0, **c** 4.0, **d** 4.5, and **e** 6.5,  $v=100 \text{ mV s}^{-1}$



**Fig. 5** UV-vis spectra of **a** PANI-coated and **b** PVF<sup>+</sup>-coated ITO electrodes before and after immersion in 500 mM HQ solution in nitrogen atmosphere at pH 4. (UV-vis spectra of PVF was also given in **b**)

oxidized by oxygen in atmosphere to Q was recorded and is given in the same figure (Fig. 6b). It can be concluded that HQ is oxidized chemically to Q by quinoid structure of PANI film [33]. This reaction provides oxidation of HQ catalytically during the amperometric measurements and also hinders the over-oxidation of PANI (and hence fluctuation in conductivity) in aqueous solution.

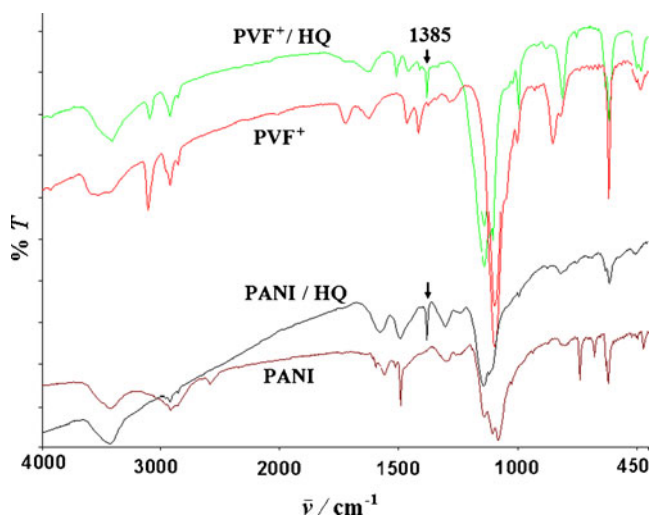
When FTIR spectra of PANI films are compared (Fig. 7), the additional peak to the absorbance peaks of films is observed at



**Fig. 6** UV-vis. spectra of HQ solution at pH 4 **a** freshly prepared in nitrogen atmosphere, **b** left to open atmosphere, and **c** after immersion of PANI film for 30 min in nitrogen atmosphere.  $c_{\text{HQ}}=500$  mM

1,385  $\text{cm}^{-1}$  after being immersed in HQ solution. This peak belongs to in-plane O–H bending in HQ molecule. This means that HQ molecules do not remove the polymer structure after cleaning. It is possible to consider the formation of H-bonding between HQ and lone-pair electrons of nitrogen of PANI polymer as is the case with water molecule [34].

In order to explain the H-bonding between H atoms of HQ and lone-pair electrons of N atoms of PANI polymer, theoretical calculations were performed using ab initio (Minimal (STO-3 G)) and semi-empirical Austin Model 1 (AM1). Table 1 shows the heats of formation, total energies, and hydrogen bond lengths of the hydrogen-bonded PANI polymer. The hydrogen bond length values support the feasibility of the formation of hydrogen bonds [22, 23, 35]. The calculated results show that the hydrogen bonds form from both imine and amine centers of PANI. If the

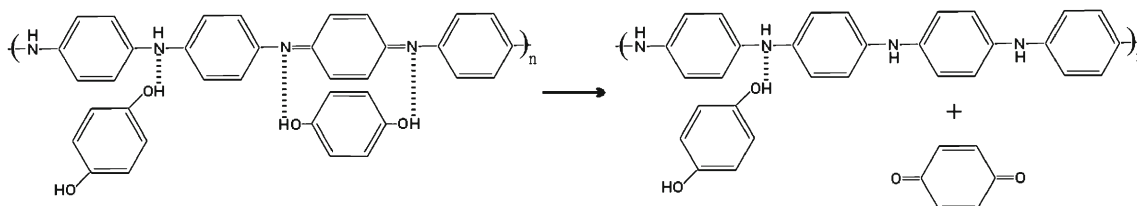


**Fig. 7** FTIR spectra of PVF<sup>+</sup> and PANI films before and after immersion in 500 mM HQ solution at pH 4 in nitrogen atmosphere

calculated  $E_{\text{tot}}$  and  $H_f$  values for the hydrogen-bonded species are compared, it will be seen that the hydrogen bonding occurs preferably on imine atoms.

As a result, HQ molecules are immobilized into both imine and amine centers of the PANI or the PANI in the

composite film as seen in Table 1. Here, HQ is not encapsulated in the polymer coatings. The immobilization results from hydrogen bonding. Also, HQ immobilized imine center is oxidized chemically to Q due to quinoid structure:



Consequently, HQ molecules not only immobilized on the electrode surface but also cause reduction of PANI film.

As seen in Fig. 5, one can speak of two major absorption bands that can be singled out in the UV–vis spectrum of  $\text{PVF}^+$  polymer. For comparison, the spectrum of  $\text{PVF}^+$  coated ITO electrode was recorded and given in the same figure. In the UV–vis spectrum of  $\text{PVF}^+$ , the first band with a pronounced maximum about 450 nm corresponds to  $\pi$ – $\pi^*$  electronic transitions and the other absorption band corresponds to the oxidized film fragments in deposited film as  $\text{PVF}^+$  about 650 nm. The dark green color of  $\text{PVF}^+$  film was converted into yellow after being immersed in HQ solution;

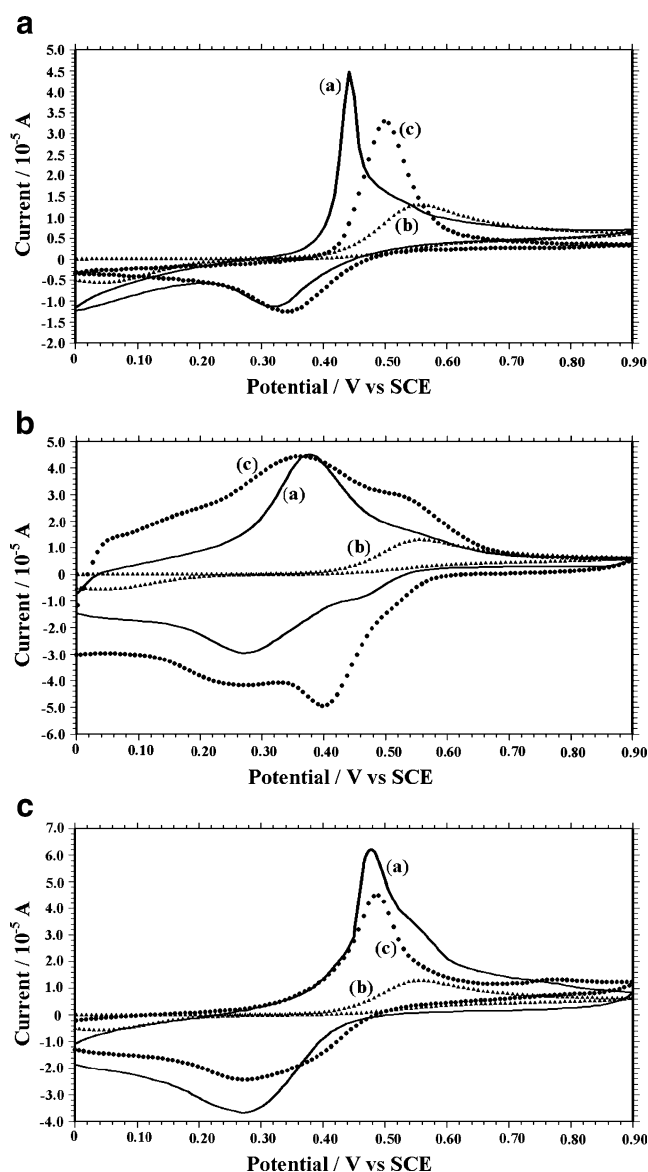
in other words, the ratio peak intensity observed at 650 to 450 nm decreases after interaction as shown in Fig. 5b. On the other hand, it was observed that the color (and also the UV–vis spectrum) of its HQ solution did not change after treatment. This means that HQ is not oxidized by  $\text{PVF}^+$  in contrast to the case in PANI polymer. Furthermore, an analysis of the FTIR spectrum of  $\text{PVF}^+$  (Fig. 7) showed that the same additional peak to the absorbance peak of film was observed at  $1,385\text{ cm}^{-1}$  after immersion in the HQ solution, as is the case in PANI polymer. To put it differently, HQ molecules were also immobilized into  $\text{PVF}^+$  film or this polymer in the composite film. This may arise from the complexation between iron ions in ferrocene moieties and

**Table 1** Heats of formation and hydrogen bond lengths calculated using AM1 method and total energy (TE) values calculated using ab initio (STO-3G) method for PANI and its hydrogen-bonded species

	$H_f / (\text{kcal mol}^{-1})$	Hydrogen Bond length / (Å)	$TE / (\text{kcal mol}^{-1})$
<b>PANI</b> 	167.7554	----	–101,317.57
<b>PANI(amine)----HQ</b> 	100.9262	2.767	–135,714.28
<b>PANI(imine)----HQ</b> 	99.73732	2.671	–135,715.47

OH group in the HQ molecule. In the literature, it was demonstrated that some phenolic species make chelate ions with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions [36].

Figure 8 shows the electrochemical behavior of HQ on  $\text{PVF}^+$ -coated (Fig. 8a (a)), PANI-coated (Fig. 8b (a)),  $\text{PVF}^+$ -PANI-coated (Fig. 8c (a)), and bare Pt electrode (Fig. 8a–c (c)) in SBS at pH 4. For comparison, the cyclic voltammograms of coated electrodes recorded in SBS at pH 4 are given in the same figure (b). It is clear from the comparison of these cyclic voltammograms that the electrochemical behavior of films was influenced by the presence of HQ. As seen in Fig. 8a, PVF is oxidized to



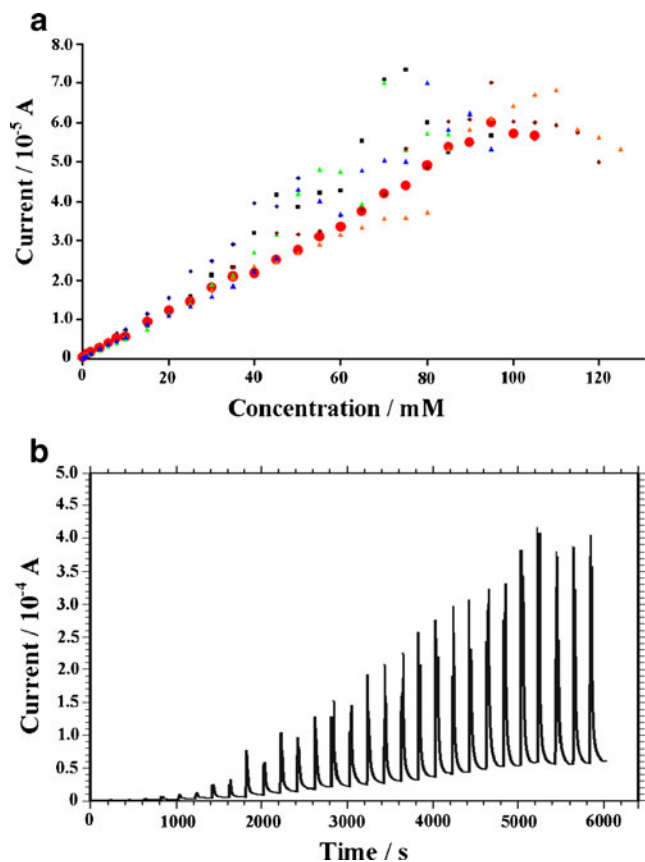
**Fig. 8** Cyclic voltammograms of **a**  $\text{PVF}^+$ , **b** PANI, **c**  $\text{PVF}^+$ -PANI composite-coated electrodes (a) in SBS containing 5.00 mM HQ and (b) in SBS. (c) Cyclic voltammogram of 5.00 mM HQ solution on bare Pt electrode,  $\nu=100 \text{ mV s}^{-1}$

$\text{PVF}^+$  at about 0.50 V vs SCE in the hydroquinone-free SBS. This peak shifts to lower potential (about 0.45 V) in the presence of HQ. In addition, its intensity increases. These results support formation of the complex structure, like the results of the UV-vis and FTIR spectra indicated above. In the case of PANI, the intensities of broad oxidation and reduction peaks belonging to the protonated polymer [13] at about 0.55 and 0.40 V vs SCE decreased, respectively (Fig. 8b). This could be due to the formation of hydrogen bond between HQ and PANI. For  $\text{PVF}^+$ -PANI composite film (Fig. 8c), the intensity of oxidation peak (about 0.48 V) increased in the presence of HQ, as is the case in  $\text{PVF}^+$  polymer. On the other hand, the oxidation and reduction peaks are broader and more intense than that of  $\text{PVF}^+$  polymer. Also, the oxidation peak of composite does not shift to lower potential in the presence of HQ.

#### Determination of HQ

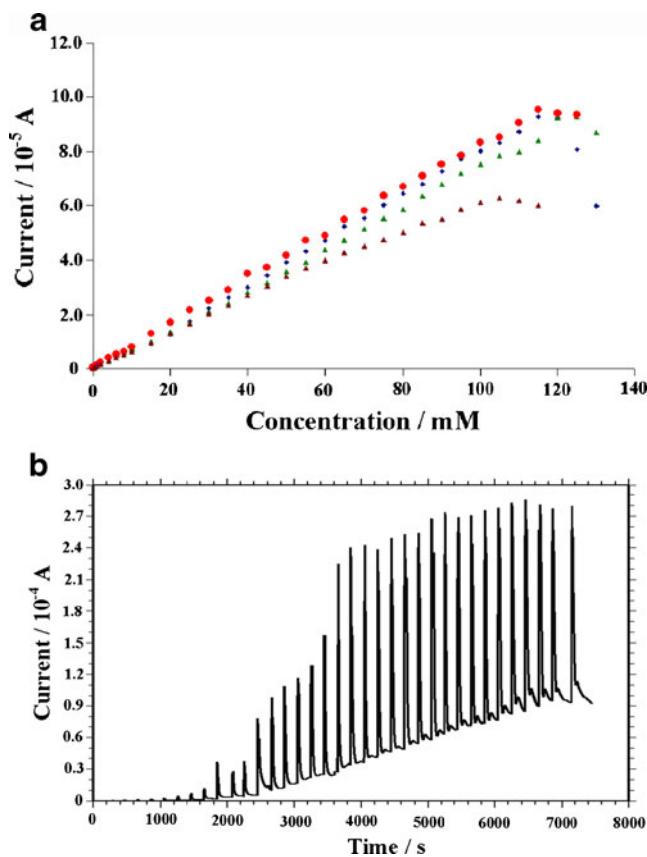
The response of  $\text{PVF}^+$ -PANI composite film-coated electrode to HQ was investigated by using amperometric  $I-t$  method in SBS at pH 4 and evaluated by comparing it to those of PANI-coated and uncoated Pt electrodes.  $\text{PVF}^+$ -coated electrode could not be used because of partial stripping of film from the electrode surface during amperometric measurements. PANI coatings were performed in a methylene chloride/0.1 M TBAP solution containing 33.0 mM  $\text{HClO}_4$  and various concentrations of aniline (50.0, 100, and 150 mM) by scanning the potential between 0.20 and 1.80 V vs Ag/AgCl. The amperometric responses of the PANI-coated electrodes were obtained at potentials varying between 0.50 and 0.60 V vs SCE on successive additions of various HQ concentrations in an unstirred solution. The steady-state current values measured on these amperometric curves were plotted against HQ concentration (Fig. 9a). As it is clear from these graphs, there are relatively high deviations in the data especially when HQ concentration is high. The reason for these deviations might be the chemical reaction between the quinoid structure of PANI and HQ. The oxidized form of PANI is chemically reduced due to HQ; on the other hand, the reduced form of PANI is oxidized electrochemically during an application of potential (i.e., 0.55 V). When the analytical parameters of calibration curves obtained from these amperometric curves were compared, the calibration curve with the best regression coefficient and larger linearity range of concentration was achieved at 0.55 V for the polymerization solution containing 100 mM aniline. Under these conditions, the response of PANI-coated electrode to HQ could be steadied by controlling the two competitive reactions (chemical and electrochemical). The amperometric curve and its calibration curve plotted in the linear concentration range are given in Figs. 9b and 11 for the emphasized film, respectively.





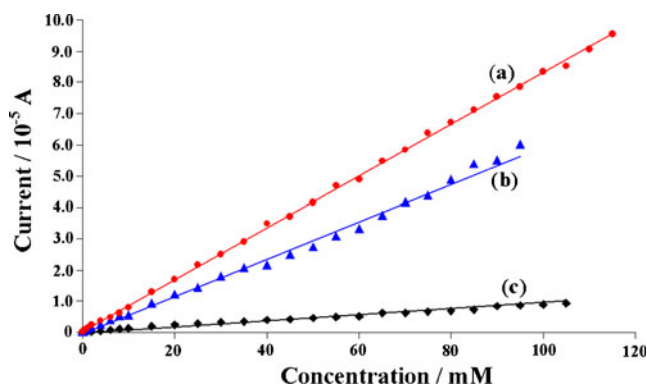
**Fig. 9** **a** A plot of the steady-state current values measured from amperometric *I*-*t* curve over PANI films synthesized from polymerization solutions containing various aniline concentration by applying various potentials (◆ 50 mM aniline/0.55 V; ■ 100 mM aniline/0.60 V; ● 100 mM aniline/0.55 V; ▲ 100 mM aniline/0.50 V, ◆ 150 mM aniline/0.60 V; ▲ 150 mM aniline/0.55 V; ▲ 150 mM aniline/0.50 V) vs. the HQ concentration. **b** Amperometric *I*-*t* curve recorded at 0.55 V vs SCE on the successive additions of various HQ concentrations over PANI coating obtained from the polymerization solution containing 100 mM aniline and 33.0 mM HClO<sub>4</sub>

The PVF<sup>+</sup>-PANI composite film was deposited on Pt electrode from methylene chloride/0.1 M TBAP solution containing 1.00 mg/mL PVF, 100 mM aniline, and 33.0 mM HClO<sub>4</sub> by scanning the potential between 0.20 and 1.80 V vs Ag/AgCl. Amperometric curves were recorded at different potentials varying between 0.40 and 0.55 V vs SCE, and the calibration curve was constructed (Fig. 10a). In contrast to PANI, there are no high deviations in current values as seen in this figure. It must be due to the coexisting PVF/PVF<sup>+</sup> in the composite film as an electron transfer mediator. Thus, current values are not influenced by the conductivity change of PANI in the composite film, which caused the chemical reaction between PANI and HQ. When the analytical parameters of calibration curves were compared, the maximum sensitivity was obtained at 0.45 V vs SCE. Figures 10b and 11 show this amperometric response and



**Fig. 10** **a** A plot of the steady-state current values measured from amperometric *I*-*t* curve over PVF<sup>+</sup>-PANI composite films synthesized from polymerization solutions containing 1.00 mg/mL PVF, 100 mM aniline, 33.0 mM HClO<sub>4</sub> by applying various potentials (▲ 0.40 V; ● 0.45 V; ◆ 0.50 V; ▲ 0.55 V) vs. the HQ concentration. **b** Amperometric *I*-*t* curve recorded at 0.45 V vs SCE on the successive additions of various HQ concentrations over PVF<sup>+</sup>-PANI composite coating

its calibration curve plotted in linear concentration range, respectively. The nearly equal steady-state current steps for each addition of HQ (Fig. 10b) indicated the stable and



**Fig. 11** Calibration curves for linearity range of HQ concentration over **a** PVF<sup>+</sup>-PANI composite-coated (at 0.45 V), **b** PANI-coated (at 0.55 V), and **c** uncoated Pt (at 0.55 V) electrodes obtained under their optimum conditions

**Table 2** Analytical parameters of calibration curves by using uncoated, PANI-coated and PVF<sup>+</sup>-PANI composite film-coated Pt electrodes for determination of HQ

	Uncoated Pt	PANI-coated Pt	PVF <sup>+</sup> -PANI-coated Pt
Applied potential (V)	0.55	0.55	0.45
Sensitivity ( $\mu\text{A mM}^{-1}$ )	0.089	0.60	0.83
$R^2$	0.994	0.996	0.999
Linearity range (mM)	$1.60 \times 10^{-4}$ –105.0	$1.14 \times 10^{-3}$ –95.0	$1.60 \times 10^{-4}$ –115.0
Limit of quantification (LOQ) (mM)	$1.60 \times 10^{-4}$	$1.14 \times 10^{-3}$	$1.60 \times 10^{-4}$
Limit of detection (LOD) (mM)	$6.60 \times 10^{-5}$	$3.40 \times 10^{-4}$	$4.94 \times 10^{-5}$

efficient catalytic properties of the PVF<sup>+</sup>-PANI composite film-coated electrode. The measured current is proportional to HQ concentration in the range of  $1.60 \times 10^{-4}$  to 115 mM. This is a significantly wide range when compared to those reported in the literature:  $\beta$ -cyclodextrin poly(*N*-acetylaniline)/carbon nanotube composite modified glassy carbon electrode (1–5,000  $\mu\text{M}$ ) [37], mesoporous platinum electrode (50–2,000  $\mu\text{M}$ ) [38], modified core shell magnetic nanoparticles supported on carbon paste electrode (0.1–137.5  $\mu\text{M}$ ) [39], covalent modification of a glassy carbon electrode with penicillamine (15–115  $\mu\text{M}$ ) [40], and La (OH)<sub>3</sub> nanoparticles self-assembled film modified electrode (0.27–6,500  $\mu\text{M}$ ) [41].

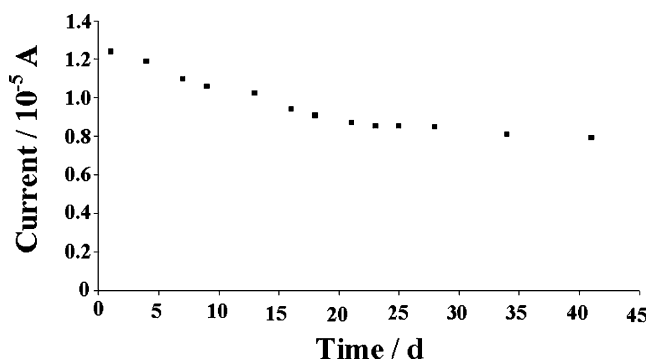
To compare the performance characteristics of PANI homopolymer and PVF<sup>+</sup>-PANI composite film with bare Pt electrodes, the amperometric curve over bare Pt electrode was recorded at 0.55 V vs SCE. The calibration curve obtained from these responses was compared to those of PANI- and composite-coated electrodes (Fig. 11). Performance parameters for this comparison are shown in Table 2. Limit of detection (LOD) and limit of quantification of (LOQ) were calculated from the equations  $3s/m$  and  $10s/m$ , respectively [42].  $s$  was calculated from the current responses of the lowest concentration that generate a measurable current in five replicate measurements. As it is clear from this table, both coated electrodes have higher sensitivity than bare Pt electrode. It might be due to the immobilization of HQ molecules into both PANI and PVF<sup>+</sup> polymers and also to the oxidation of HQ catalytically on PANI polymer. A comparison between the coated electrodes revealed that PVF<sup>+</sup>-PANI composite film-coated electrode has lower analysis potential, higher sensitivity, lower LOD, larger linearity range, and better correlation coefficient than PANI-coated electrode. The presence of PVF<sup>+</sup> polymer in composite film not only enhanced but also steadied the amperometric response of HQ. The most significant contribution of PVF<sup>+</sup> to the composite film is its facilitation of electron transfer without being affected by fluctuation in the conductivity of PANI polymer. This effect has a key role in decreasing the deviation of the measured data. Consequently, the composite film has the most significant catalytic effect on the amperometric response of HQ.

#### Reusability of composite film-coated electrode

The reusability of PVF<sup>+</sup>-PANI composite film-coated electrode was investigated over a 6-week period. During this period, the prepared electrodes were stored in nitrogen atmosphere. Before measurement, the composite film-coated electrode was reduced at 0.20 V vs Ag/AgCl in blank solution for 10 min. Current values were measured at 0.45 V vs SCE for 5.00 mM HQ solution over a period of 40 days. As seen from Fig. 12, the current values obtained for HQ gradually decreased in time. After 20 days, the electrode response nearly reached at a steady state. This electrode preserved 65% of its initial responses over 40 days. This might be due to the chemical reaction between HQ and PANI and also encapsulation of PVF<sup>+</sup>. Chemical reaction hinders the over-oxidation of polymer by causing the continuous reduction of PANI. The encapsulation of PVF<sup>+</sup> inside the growing PANI polymer provides that it could be retained on the electrode surface even if the polymer is in the reduced form.

#### Conclusions

A PVF<sup>+</sup>-PANI composite film-coated Pt electrode was performed electrochemically in a methylene chloride solution containing a mixture of PVF polymer and aniline monomer. PVF<sup>+</sup> was not stripped from the composite film due to encapsulation, even if this polymer was in the



**Fig. 12** Long-term stability of PVF<sup>+</sup>-PANI coating at pH 4 by using amperometric  $I-t$  method.  $c_{\text{HQ}}=5.00$  mM

reduced form. When the interaction between homopolymers and HQ was investigated, it was determined that HQ molecules were immobilized into both polymers. Also, HQ molecules ensured that PANI was retained in the reduced form. The composite-coated electrode has lower working potential, larger linearity range, and lower LOD when compared to PANI-coated electrode. Also, this electrode shows higher reproducibility as well as higher sensitivity and can be used for HQ determination with satisfactory results. As a result, the catalytic activity of PANI-coated electrode was improved by the addition of PVF<sup>+</sup> as an electron transfer mediator. Also, it steadied the amperometric response of composite film to HQ. Consequently, PVF<sup>+</sup>–PANI composite film is expected to exhibit promising electrocatalytic effects toward the phenolic compounds.

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