Detection and Determination of Cr^{VI} in Solution Using Polyaniline Modified Quartz Crystal Electrode

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ABSTRACT: Conducting polymers such as polyaniline and polypyrrole exhibit novel sensoric properties and are able to interact chemically or electrochemically with the species of interest for detection. In the current investigation, construction of a sensor based on an electrochemical reaction between Cr^{VI} and a thin layer of polyaniline, coated at the surface of quartz crystal electrode, is reported. Polyaniline was synthesized, electrochemically, at the surface of quartz crystal electrode. It was then reduced at -0.1 V versus Ag/AgCl. The modified electrode was exposed to various concentrations of Cr^{VI} solutions ranging from 10^{-7} to $10^{-1} M$. Mass changes of the polymer-modified electrode due to the reaction between Cr^{VI} and polyaniline was found to be linear, corresponding to the concentration of Cr^{VI}. The experiments in both acidic and nonacidic conditions were performed. In both conditions, linear double-logarithmic calibration curves of mass change of the polymer film versus Cr^{VI} concentration were obtained. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2772–2780, 2002

Key words: conducting polymers; polyaniline; quartz crystal microbalance; heavy metals; chromium (Cr^{VI})

INTRODUCTION

Various polymeric materials have gained wide theoretical interest and practical applications in the sensing area over the last two decades.[1,2] Inherently conducting polymers such as polypyrrole and polyaniline, as a new group of polymeric materials, have unique sensoric properties.[3–6] Electroactivity and conductivity of conducting polymers provide a unique basis for the signal generation steps. A number of electronic signals relating to some chemical or electrochemical change within the polymer can be measured. Because of the mass change of the polymer during the reaction with interest analyte, the frequency shifts of a quartz crystal microbalance (QCM) can also be used as signal in a conducting polymer-modified QCM sensor. QCM is one of the techniques that was used recently to study the structure and electrochemical behavior of conducting polymers.[7,8] This is a low-cost piezoelectric technique where small changes in mass (Δm) can be monitored by measuring the oscillation frequency (ΔF) of a quartz crystal according to the well-known Sauerbrey equation[9]:

$$\Delta F = -2f_0^2 \Delta m / A(\mu_g d_g)^{1/2}$$

where f_0 is the frequency of a quartz crystal, μ_g is the shear modules of the quartz, d_g is the density of the quartz, A is the surface area of the quartz

plate undergoing oscillation, and Δm is the mass change corresponding to the frequency change (ΔF).

Recent studies,[10–13] including our previous works,[14,15] indicated that QCM-modified electrodes can be used as effective sensors for detection of environmental pollutants.

Heavy metals are major pollutants of the environment. Because of their ability to accumulate in livestock, they present major hazards to ecosystems and are a serious danger to human populations.[16] Pollution due to toxic hexavalent chromium (Cr^{VI})[17] has reached dangerous levels in some parts of the world, especially in third-world countries. Therefore, the analysis of Cr^{VI} is of considerable environmental and health importance. Several analytical methods and techniques have been used to detect Cr^{VI}, ranging from amprometric titration[18] to coulometric and flame photometric methods,[19] visible-light spectrophotometry,[20] ion-exchange chromatography,[21] adsorptive stripping voltammetry,[22] and electrothermal vaporization–inductively coupled plasma–mass spectrometry (ICP-MS).[23] Although these techniques are precise, all of them require sophisticated instruments and time-consuming stages.

Although there are a number of reports on the application of conducting polymer-modified electrodes for detection of heavy metals,[24,25] detection of Cr^{VI} had not been yet investigated by this method, until the recent report of Desimoni and Bassani.[26] Desimoni and Bassani have designed a polypyrrole-modified quartz crystal electrode for the detection of Cr^{VI}. Ionic transfer during the oxidation of polypyrrole by Cr^{VI} produced frequency shifts proportional to the concentration of Cr^{VI}. The observed responses depend on several experimental parameters such as thickness of the polymer film, the mode of the reduction of the polymer (chemical or electrochemical), pH, and temperature. However, factors were not optimized and reported in detail.

In this article, construction of a sensor, based on polyaniline modified quartz crystal electrode, for the detection and determination of Cr^{VI} in acidic and nonacidic media is reported.

EXPERIMENTAL

Reagents and Materials

Hydrochloric acid, sulfuric acid, potassium dichromate, and aniline were all purchased from Merck Chemicals (Germany) and were of analytical grade. All chemicals were used as received, and aniline was distilled prior to use.

Instrumentation

Commercially available 10-MHz AT-Cut quartz crystals with gold electrodes on both sides were supplied by International Crystal Manufacturer (ICM, OK). For EQCM experiments, a homemade apparatus was used, which was described in our previous work.[7] A galvanostate/potentiostate Wenking TG 97 from Bank (Germany) and a pH
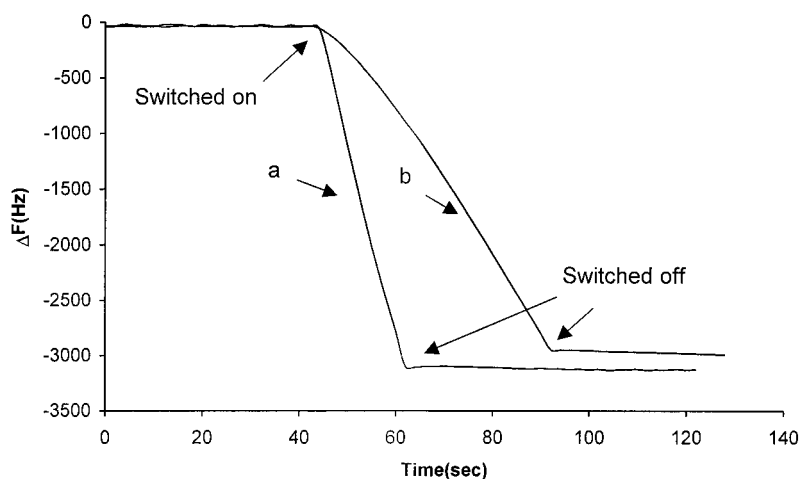

Figure 1 Frequency changes of quartz crystal electrode during the electropolymerization of aniline at the surface of quartz electrode by: (a) constant potential of +0.8V versus Ag/AgCl; (b) constant current density of 1 mA/cm².
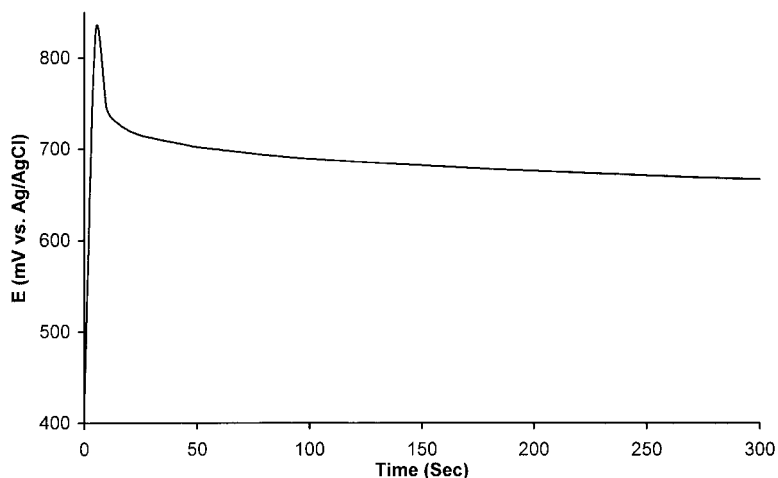
Figure 2 Chronopotentiogram for the galvanostatic electropolymerization of aniline at the surface of quartz electrode by constant current density of 1 mA/cm^2 in an aqueous solution of 1M aniline and 2M HCl.

meter 654 from Metrohm (CH 9101-Herisau, Switzerland) were used for the synthesis and oxidation/reduction of the polymer. A three-electrode system consisting of a gold working electrode on quartz crystal, a platinum gauze as auxiliary electrode, and Ag/AgCl as reference electrode was used for polymer synthesis and electrochemical experiments.

Polymer Synthesis

Polyaniline was synthesized electrochemically as previously reported.[27] A solution containing 1M aniline and 2M HCl was used for electropolymerization. For galvanostatic polymerization, a con-

stant current density of 1 mA/cm^2, and for potentiostatic polymerization, a constant potential of 0.8V versus Ag/AgCl were applied to working gold quartz crystal electrode.[28] During electropolymerization, frequency shift of quartz crystal electrode was recorded. Also during galvanostatic polymerization, the potential of working electrode was recorded against time.

RESULTS AND DISCUSSION

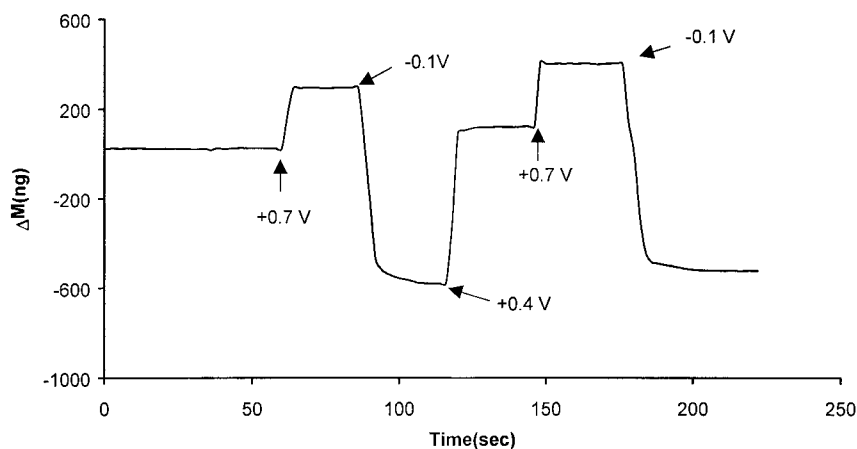Two electrochemical modes were employed to prepare polyaniline films. In both galvanostatic (con-

Figure 3 Mass changes of polyaniline, coated at the surface of quartz electrode, under potentiostatic oxidation and reduction at 0.7, 0.4, and −0.1 V (versus Ag/AgCl) in 0.1M H$_2$SO$_4$ solution.
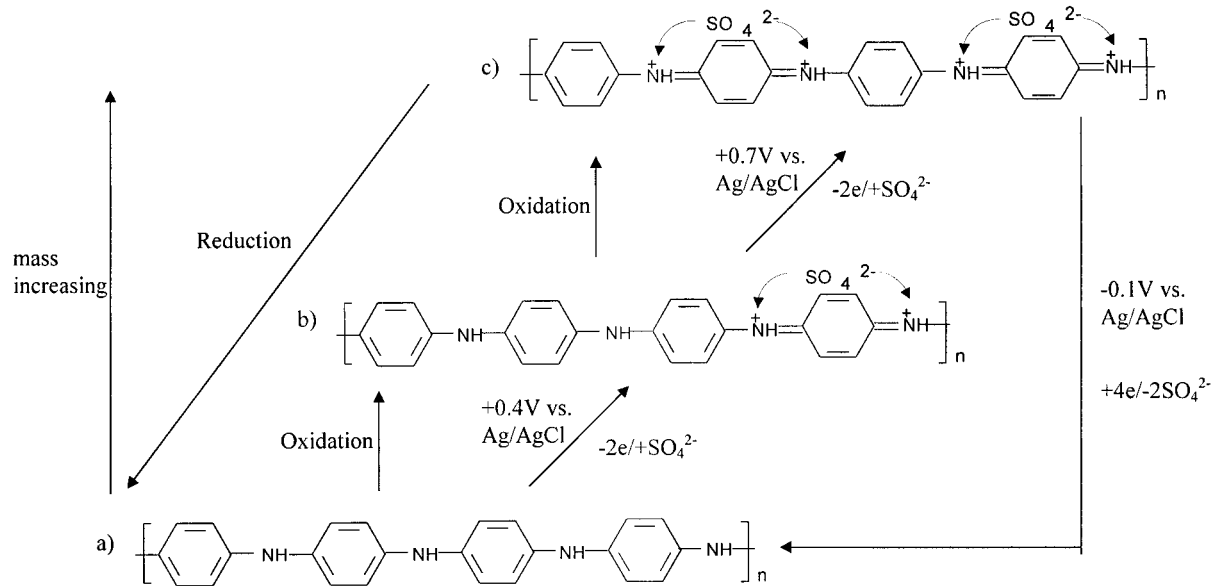
Figure 4 Different redox states of polyaniline: (a) leucoemeraldine (fully reduced form); (b) emeraldine; (c) pernigraniline (fully oxidized form).

stant current) and potentiostatic (constant potential) methods, the frequency change as a function of time were recorded during electropolymerization (Fig. 1). To apply Sauerbrey's equation,[9] the assumption was made that the acoustic properties of the foreign layer were identical to those of the quartz. This assumption is valid only if a rigid material is deposited. It was shown that the polymer films can be treated as rigid and free from elastomeric effects if a linear response of frequency with time (or charge) is observed during electrodeposition.[29] In our case, a linear relationship between the time of electrodeposition and frequency change was observed in both methods employed for the electrodeposition (Fig. 1). This indicates that the polymer could be treated as rigid and free of viscoelastic effects and validates the use of the Saurebrey equation to convert frequency data to mass change. Therefore, mass changes calculated from the data in Figure 1 were
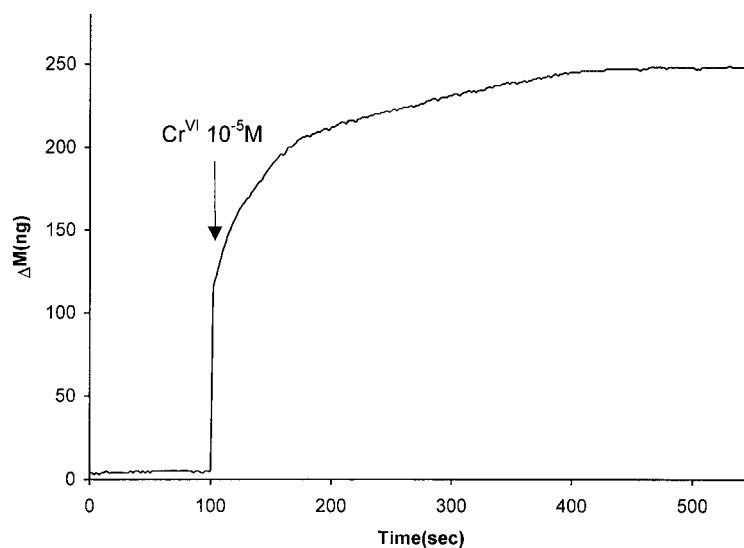

Figure 5 Mass changes of polyaniline coated on quartz crystal, in contact with a solution of Cr^{VI} ($10^{-5}M$) in $0.1M$ H$_2$SO$_4$.

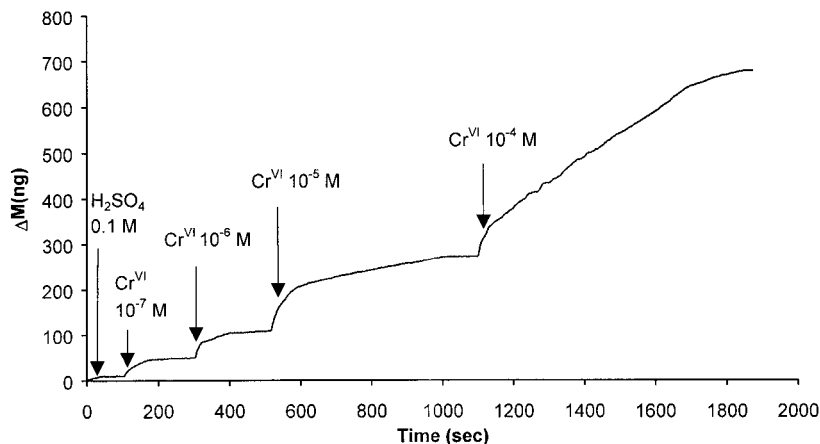**Figure 6**   Mass changes of polyaniline in contact with solutions containing different concentrations of Cr^{VI} in $0.1M$ H_2SO_4 solution.

2850 and 3030 ng, respectively, for galvanostatic and potentiostatic polymerization methods.

Chronopotentiometric response of the galvanostatic oxidation of aniline was also recorded (Fig. 2). The decrease in potential indicates the deposition of a conductive layer of the polymer.

Polyaniline was prepared either galvanostatically or potentiostatically; there was no difference in terms of the mode of synthesis regarding the sensoric responses. Therefore, in the case of this work, the results obtained by galvanostatic-prepared polymer are represented.

The galvanostatically synthesized polyaniline was oxidized (at 0.7 and 0.4 V versus Ag/AgCl reference electrode) and reduced (at -0.1 V) in $0.1M$ H_2SO_4 solution. The mass changes of the polymer during oxidation/reduction were re-

corded (Fig. 3). The polymer mass increased upon oxidation and decreased upon reduction. This behavior is a reproducible process, as shown in Figure 3. The increase in mass upon oxidation and decrease upon reduction may be accounted for on the basis of incorporation and expulsion of anions during oxidation and reduction, respectively (Fig. 4).

Reduced polyaniline (coated on quartz electrode) was exposed to a solution of $10^{-5}M$ of Cr^{VI} ($K_2Cr_2O_7$) in $0.1M$ H_2SO_4. As a typical response, the polymer mass increased until a constant value was reached (Fig. 5). This is presumably due to the oxidation of polymer by Cr^{VI}, according to the following equations:
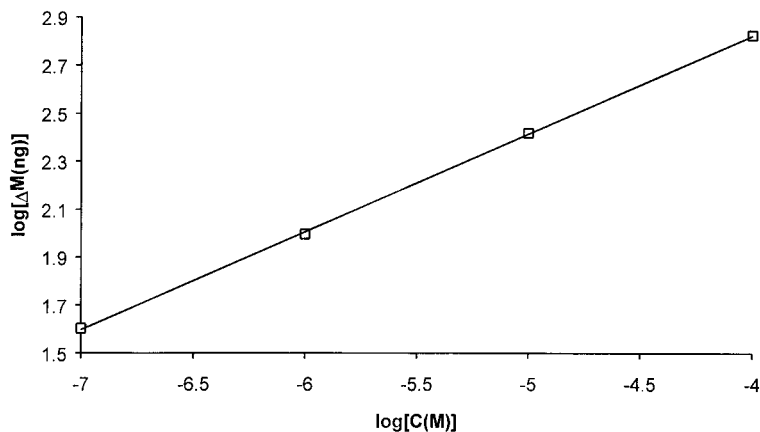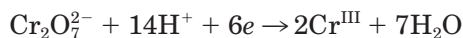
$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{III} + 7H_2O$$

Figure 7   Calibration curve for the detection of Cr^{VI} in $0.1M$ H_2SO_4 solution, obtained by reduced polyaniline coated on quartz crystal electrode.
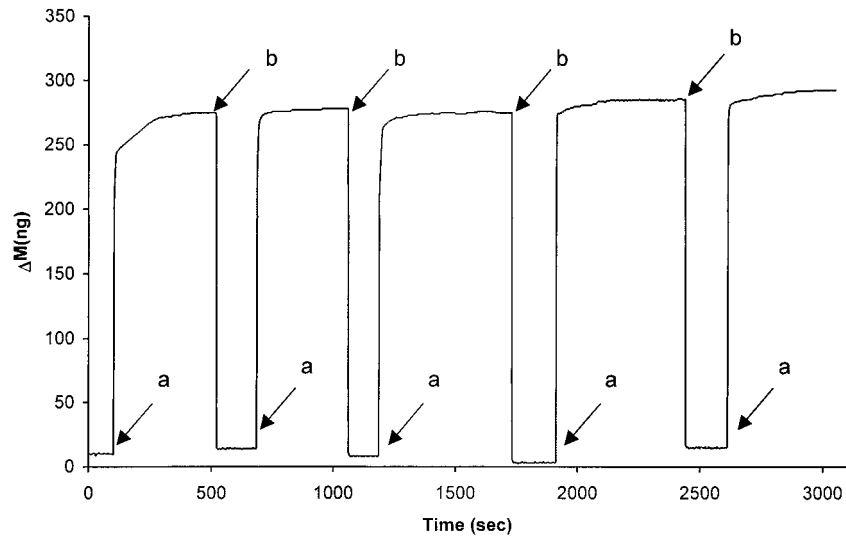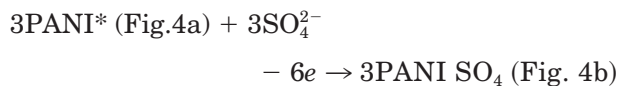
Figure 8 Mass changes of reduced polyaniline coated on quartz crystal electrode: (a) in contact with $10^{-5}M$ Cr^{VI} solution in $0.1M$ H$_2$SO$_4$; (b) under potentiostatic reduction at constant potential of -0.1 V versus Ag/AgCl in $0.1M$ H$_2$SO$_4$ solution.

3PANI* (Fig.4a) + 3SO$_4^{2-}$

$$- 6e \rightarrow 3\text{PANI SO}_4 \text{ (Fig. 4b)}$$

where PANI represents one tetramer. The polymer was exposed to various concentrations of Cr^{VI} (10^{-7}-$10^{-4}M$) in $0.1M$ H$_2$SO$_4$ solution. The mass changes in each solution were recorded (Fig. 6). The polymer mass further increased as it was exposed to more concentrated chromium solution.

Mass changes of the polymer were sampled after reaching a constant value in each concentration and plotted versus concentration of Cr^{VI} in solution. The relation between chromium concentration and mass change was quite linear ($R^2 = 0.9998$) in the range between 10^{-7} and $10^{-4}M$ (Fig. 7).

One of the most important characteristics of a sensor is ability to be regenerated. It is also important to get reproducible responses. To investi-
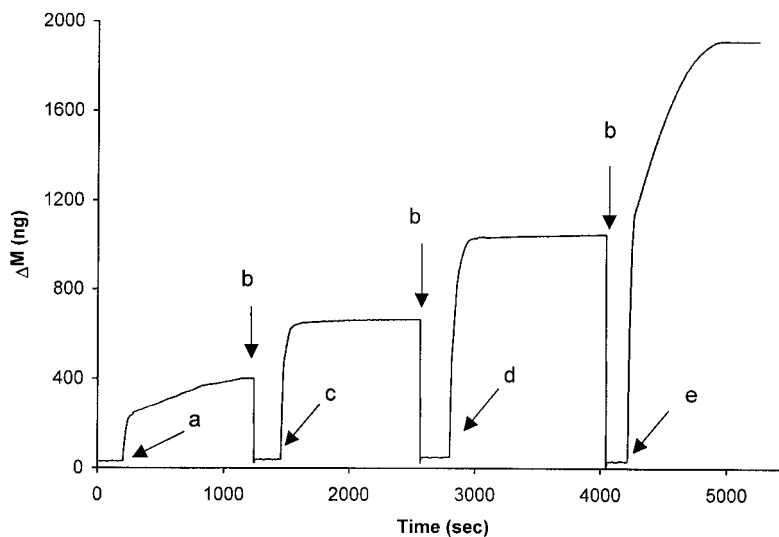

Figure 9 Mass changes of reduced polyaniline in contact with solutions containing different concentrations of Cr^{VI} in $0.1M$ H$_2$SO$_4$ solution: (a) $10^{-7}M$ Cr^{VI}; (b) reduction of the polymer at -0.1 V versus Ag/AgCl in $0.1M$ H$_2$SO$_4$ solution; (c) $10^{-6}M$ Cr^{VI}; (d) $10^{-5}M$ Cr^{VI}; and (e) $10^{-4}M$ Cr^{VI}.
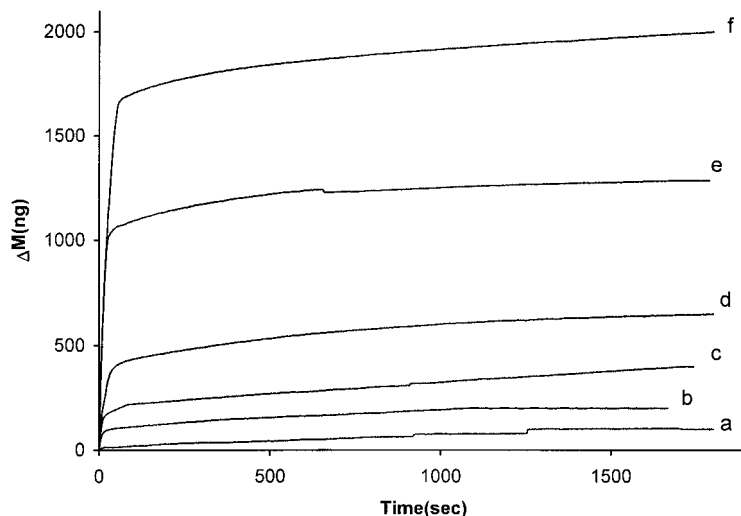
Figure 10 Mass changes of reduced polyaniline in contact with solutions containing different concentrations of Cr^{VI} in distilled water (nonacidic conditions): (a) $10^{-6}M$; (b) $10^{-5}M$; (c) $10^{-4}M$; (d) $10^{-3}M$; (e) $10^{-2}M$; and (f) $10^{-1}M$.

gate this, further experiments were carried out. The polyaniline electrode was exposed to a solution of Cr^{VI} ($10^{-5}M$), in H_2SO_4($0.1M$); then it was reduced at a constant potential of -0.1 V versus Ag/AgCl in $0.1M$ H_2SO_4 solution. The polymer mass decreased upon reduction, as expected, to reach its original state (before exposing to Cr^{VI} solution). The experiment was repeated five times (Fig. 8). The results showed reproducible responses with relative standard deviation of 2.75% for five experiments. Similar results were obtained for different concentrations of Cr^{VI} (Fig. 9).

These results indicate that the electrode performance is quite regenerable and reversible.

The response of the sensor was further investigated in nonacidic media (Fig. 10). The mass changes of polyaniline electrode in contact with solutions containing different concentrations of Cr^{VI} in distilled water were recorded. As acidic media, the polymer mass increased upon exposure to a solution of Cr^{VI}. The relation between mass changes and Cr^{VI} concentrations was linear ($R^2 = 0.9954$), in the range of 10^{-6}-$10^{-1}M$ (Fig. 11).
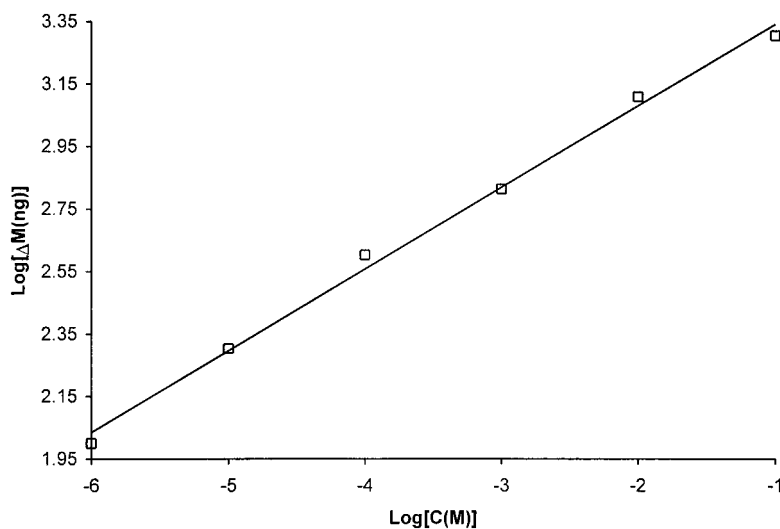

Figure 11 Calibration curve for the detection of Cr^{VI} in distilled water obtained by reduced polyaniline coated on quartz crystal electrode.
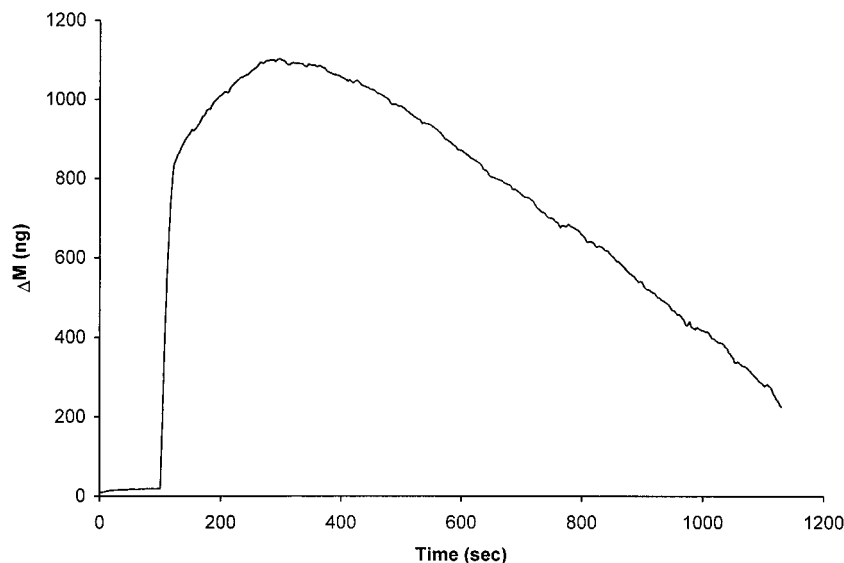
Figure 12 Mass changes of reduced polyaniline coated on quartz crystal electrode in contact with Cr^{VI} solution ($10^{-3}M$) in $0.1M$ H$_2$SO$_4$ solution.

Further investigations revealed that the mass change signal of polyaniline-modified quartz electrode deteriorated when more concentrated solution of Cr^{VI} in acidic media was used. A typical mass change response of polyaniline-modified quartz electrode, exposed to the solution of Cr^{VI} ($10^{-3}M$) in $0.1M$ H$_2$SO$_4$, is shown in Figure 12. Apart from the signal deterioration, the electrode surface was also deformed, indicating degradation of polyaniline.

The fact that the polyaniline undergoes a degradation process in contact with concentrated acidic solutions of chromium may be due to the high oxidation power of Cr^{VI} in acidic media that promotes overoxidation and degradation process in polyaniline film. However, in nonacidic conditions, the electrode can be exposed to higher concentrations of Cr^{VI} without any degradation in polymer backbone (Fig. 10). The measuring range can be further expanded even to $10^{-1}M$. However, in nonacidic media, the signal obtained for diluted solution of Cr^{VI} ($10^{-7}M$) was not considerable. It may be accounted due to the fact that the oxidative power of Cr^{VI} in nonacidic media is low. The measuring range in nonacidic media was obtained between 10^{-6} and $10^{-1}M$.

CONCLUSION

The unique sensing properties of conducting polymers can be studied by the technique of quartz crystal microbalance. A polyaniline-coated quartz crystal microbalance was employed for detection of toxic Cr^{VI} in solution. Oxidation of the polymer by Cr^{VI} resulted in frequency shifts, which linearly corresponded to Cr^{VI} concentration in solution. In acidic media, the Cr^{VI} was determined in the range between 10^{-7} and $10^{-4}M$. Degradation of the polymer occurs in higher concentrations of Cr^{VI}. However, in nonacidic conditions, the measuring range of 10^{-6}-$10^{-1}M$ was obtained. Galvanostatic and potentiostatic methods were used for the synthesis of polyaniline; however, very similar results regarding sensing performance were obtained for both methods.

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