

Nano Structured Potentiometric Sensors Based on Polyaniline Conducting Polymer for Determination of Cr (VI)

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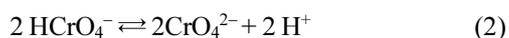
In this paper, a potentiometric sensor based on polyaniline conducting polymer for potentiometric determination of Cr (VI) ions is reported. Polyaniline was synthesized electrochemically (cyclic voltammetry method) onto a micro pencil graphite electrode (0.7 mm diameter) in the presence of HCl and diphenylcarbazide (termed as PGE/PAni/DPC). Some initial experiments were performed in order to find out the optimized conditions for preparation of the introduced Cr (VI) sensor electrode. The plot of E vs. log [Cr (VI)], showed a linear response in the range from 1.0×10^{-6} to 1.0×10^{-1} M. High repeatability with the detection limit of 8.0×10^{-7} M was obtained.

Key Words : Chromium (VI), Potentiometric sensor, Polyaniline, Diphenylcarbazide

Introduction

Chromium is an element widely used in industrial activities such as chrome plating and electroplating, metal smelting and metallurgy to manufacture alloys, dye stuff industries, leather tanning and wood treatment.^{1,2} It exists in the environment as Cr (III) and Cr (VI) oxidation states, which present different chemical properties. Cr (III) is a stable and slightly soluble cation considered an essential microelement, while Cr (VI) is a soluble and mobile anion, known as a highly toxic pollutant, with mutagenic and carcinogenic effects.^{3,4} While chromium in its Cr (III) form is not considered a toxic element and is a required diet nutrient. In humans, Cr (VI) exposure caused marked irritation of the respiratory tract and ulceration and perforation of the nasal septum in workers in the chromate producing and using industries.

Due to the high toxicity of Cr (VI), it is essential to determine Cr (VI) rather than the total chromium concentration using a rapid and simple method that can be applied in industrial and environmental fields.^{4,5} The chemistry of Cr (VI) is very dependent on the pH of solution. Under acidic conditions (pH=2-4) chromium ion is predominantly exist as HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ and under neutral or alkaline media it exist predominantly as chromate ion (Eqs. 1, 2).



Several analytical techniques have been developed to detect chromium, ranging from visible-light spectrophotometry to ion chromatography, atomic absorption spectrometry, GC-MS, electron probe microanalysis, flow injection analysis-ICP, synchrotron X-ray microprobe, isotope dilution mass spectrometry and *etc.* Most of them, however, do not distinguish the oxidation state of chromium, and only

total concentrations are measured. When the discrimination of the chromium species is necessary, for example in environmental and biochemical studies, chemical sensors can be a good choice.⁵⁻⁷

Potentiometry is an analytical technique very used for monitoring because it presents a number of advantages, such as simplicity, low cost, short measurement time, selectivity, adequate precision and accuracy, as well as ability to determine the analytes in coloured and turbid samples.⁸ Also, it is possible to determine and differentiate between chemical species of one metal depending on the used compound as the sensing component of the sensor. Potentiometric sensors for chromium (VI) analysis containing as modifiers nickel tris (1,10-bathophenanthroline), bis(acetylacetonato) cadmium (II), cyclic amines, diaza crown ethers, Rhodamine-B or calyxarene have been reported, but they are based on liquid membranes or PVC membranes.⁹⁻¹⁶

Conducting electroactive polymers (CEPs) such as polypyrrole, polyaniline and polythiophene have been the focus of numerous theoretical and experimental investigations in the last two decades due to their interesting and unique electrical conductivity and electroactivity.¹⁷ Their structural versatility is attracting researchers for their multiple applications such as in rechargeable batteries, light emitting diodes, super capacitors, sensors, solar cells, actuators, separation and *etc.*¹⁸⁻²²

The ion-exchange properties of conducting polymers are of special interest for potentiometric sensor development. Conducting polymers are ideally suited matrix for sensor applications because of their good conductivity and high environmental stability.²³ Among the electrically conductive polymers, polyaniline (PAni) is considered as one of the most interesting materials. PAni is a conducting polymer, which is easy to deposit from aqueous acidic solutions and has been applied in various analytical systems.²⁴⁻²⁶

Conventional polyaniline synthesis is known to produce

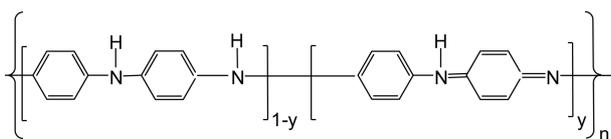


Figure 1. General structure of polyaniline (PAni) in various oxidation states.

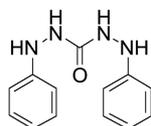


Figure 2. Chemical structure of diphenyl carbazide (DPC).

particulate products with irregular shapes. Therefore, many methods have been developed to make nanostructures of polyaniline by introducing “structural directing agents” during the chemical polymerizing reaction.²⁷⁻²⁹ Some recent work indicates that uniform polyaniline nanofibers can be obtained without the need for any template simply by controlling the electrochemical polymerization kinetics.³⁰ Polyaniline can exist in various oxidation states characterized by the ratio of imine to amine nitrogen (Figure 1).³¹⁻³³ The value of y can be varied between 0 (fully reduced state) to 1 (fully oxidized state).

The purpose of this research is to prepare a solid state Cr (VI) sensor electrode using PAni conducting polymer as thin film on the surface of pencil graphite micro electrode. DPC was employed during electropolymerisation because of its high sensitivity to Cr (VI) ion. Also as shown by Figure 2, DPC should have strong interactions (*e.g.* H-bonding) with PAni because of the $-\text{NH}-\text{NH}-$ groups in its structure.

Experimental

Chemicals. Twice-distilled water was used for preparing all aqueous solutions. Aniline was obtained from Merck and distilled before use. NaOH, nitric acid, sulfuric acid, diphenylcarbazine (DPC), ammonium chloride, ferric chloride and nitrates of the interferent cations were of analytical reagent grade (Merck), and were used as received. 1.0 M stock solutions of Cr (VI) were prepared by dissolving an appropriate amount of potassium dichromate. Standard solutions prepared in the concentration range 1.0×10^{-1} – 1.0×10^{-7} M were prepared by successive dilutions of the 1.0 M stock solution with water. The pH adjustments were made with dilute hydrochloric acid and sodium hydroxide solutions as required.

Apparatus. A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for showing pH values. All potentiometric measurements were carried out at ambient temperature with a cell of the following type: SCE||Cr (VI) (a_A) | PGE/PAni/DPC, using a digital multimeter (model DT9208A). A double junction saturated calomel electrode was used as reference electrode. Electrochemical polymerisation was carried out using a

SAMA 500 (Iran). The surface morphology of polyaniline was examined by the scanning electron microscopy (SEM) using Philips XL30 scanning electron microscope at an accelerating voltage of 17.0 kV. A UV-vis spectrophotometer (Perkin-Elmer 35) with a 1 cm cell was used for measuring all of absorption data in analytical application section.

Measurement of Cr (VI). The measurements of Cr (VI) ions in real sample (tap water) were carried out using both spectrophotometry and potentiometry *via* spike and standard-addition methods. The employed spectrophotometric method is based on the formation of an intense red-violet color complex between Cr (III) [the reduced form of chromium (VI)] and diphenylcarbazone (DPCO, the oxidized species of DPC) is formed in acidic media ($\lambda_{\text{max}} = 540$ nm at pH 1.5).³⁴

In this procedure, a solution of DPC (%0.25) was first prepared in acetone. Aliquot of a tap water samples were spiked with standard solutions of Cr (VI) ion (1.00×10^{-3} , 5.00×10^{-4} and 1.00×10^{-4} M) after addition of 1 mL of DPC at adjusted pH value of 1.5 (using H_2SO_4 6 M). Analysis of Cr (VI) with standard addition method was then performed using the following equation:

$$C_X = \frac{A_1 \times C_S \times V_S}{(A_2 - A_1) \times V_X} \quad (3)$$

Where C_X and C_S are the concentrations of Cr (VI) ion in tap water and standard solution. V_X and V_S are the volumes of test and added standard solutions respectively. A_1 and A_2 are the absorption of the sample before and after standard addition. The accuracy and validity of Cr (VI) analysis using fabricated electrode (PGE/PAni/DPC) *via* potentiometric method was performed using the same spiked procedure as used for spectrophotometric method. The following equation was used for potentiometric analysis of Cr (VI) in test solution:

$$C_X = \frac{C_S \times V_S}{(V_X + V_S) \times 10^{\frac{\Delta E}{S}} - V_X} \quad (4)$$

Where, ΔE ($E_X - E_S$) is the difference in measured potentials before and after standard addition. Subsequently, S is the slope of electrode response obtained from calibration curve.

Results and Discussion

Preparation of Sensor Electrode for Cr (VI). Electrochemical studies were carried out in a single compartment three-electrode cell. A platinum electrode was used as counter-electrode. All potentials were measured versus a saturated calomel electrode (SCE) with a salt bridge containing the supporting electrolyte. The working electrode was pencil graphite electrode (diameter 0.7 mm). The electrodes were soaked in HNO_3 (2 M) and rinsed with distilled water in order to remove any possible impurities. For further purification the electrodes were also treated with 0.20 M H_2SO_4 at + 0.10 V for 3 min followed by the potential

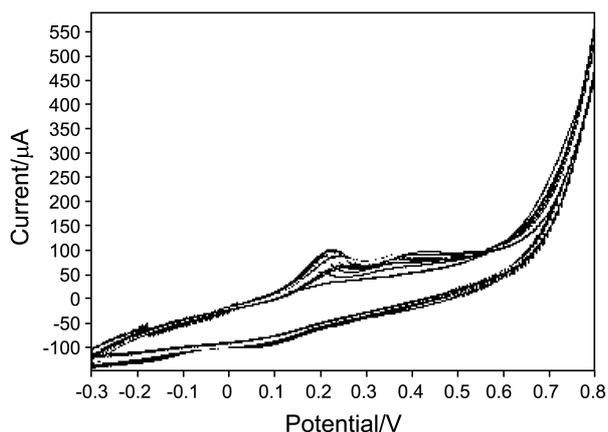


Figure 3. CV of PGE electrode in an aqueous solution of aniline (0.5 M), diphenylcarbazide (0.02 M) and HCl (0.5 M). No. of cycles = 20, Scan rate = 50 mVs^{-1} Potential ranges = -0.30 and $+0.80 \text{ V}$.

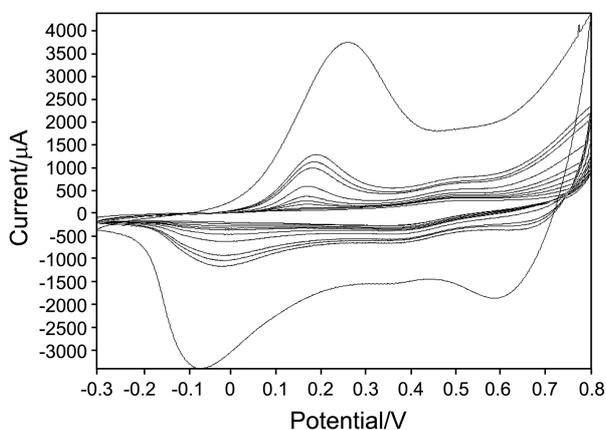


Figure 4. CV of PGE electrode in aqueous solution of aniline (0.5 M) and HCl (0.5 M). No. of cycles = 20, Scan rate = 50 mVs^{-1} Potential ranges = -0.30 and $+0.80 \text{ V}$.

cycling between -0.5 and $+1.0 \text{ V}$ at 50 mVs^{-1} for 3 minutes.

After cleaning, the electrode was placed into the solution of 0.5 M aniline in 0.50 M HCl and a 0.02 M solution of DPC and then the potential was scanned between -0.30 and $+0.80 \text{ V}$ at 50 mVs^{-1} . DPC was first dissolved in acetone and then diluted with distilled water to desired volume. A stream of nitrogen gas deaerated the solutions before scanning. 20 cycles of potential were used to obtain a dense continuous polymer film. The cyclic voltammograms (CV) recorded during synthesis is illustrated in Figure 3.

Electrodeposition of polyaniline using HCl as dopant electrolyte is also shown in Figure 4. Comparison of the CVs recorded from the polymer coated electrode, prepared in the

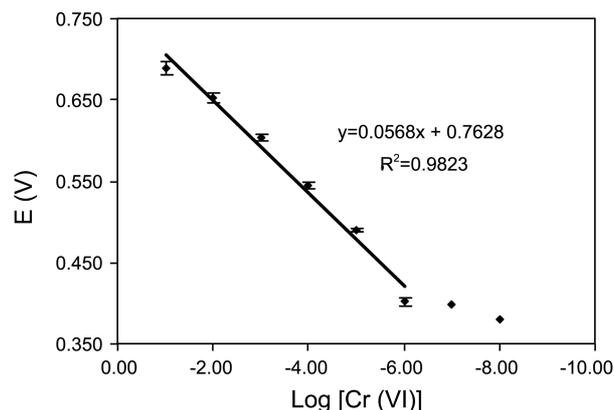


Figure 5. Calibration curve obtained for Cr (VI) by PGE/PAni/DPC.

presence and absence of DPC clearly indicate that the electroactivity of the PAni has greatly been affected by the presence of DPC which indicate the incorporation of DPC with the polymer.

Potential Measurements. The potential measurements were carried out at room temperature with a digital voltmeter, saturated calomel electrode (SCE) as reference electrode, PGE/PAni/DPC as working electrode and salt bridge filled with potassium nitrate for connection between solution and working electrode. Before potential measurements, the fabricated electrode conditioned in a Cr (VI) solution with concentration of $1.0 \times 10^{-4} \text{ M}$ for 5 hours. The potential readings were recorded when they reached steady-state values. The data were plotted as observed potential versus the logarithm of the Cr (VI) concentration (Figure 5). As the results indicate PGE/PAni/DPC electrode exhibited a linear response over a concentration range of 1.0×10^{-6} to $1.0 \times 10^{-1} \text{ M}$ of Cr (VI) at $\text{pH} = 2$. The limit of detection (LOD) estimated from the obtained calibration curve (Figure 5) by extrapolating the linear region of the plot to the base-line was $8.0 \times 10^{-7} \text{ M}$. The high regression coefficient obtained ($R^2 = 0.982$) implies the linearity of the response. The maximum relative standard deviation (RSD) obtained was less than 2%.

As the results show (Table 1), the Nernstian response, dynamic range and limit of detection obtained with the introduced Cr (VI) sensor electrode in the current research seems to be superior to those which have previously been reported for Cr (VI) sensor electrode.

Characterization. The micrographs obtained for polyaniline used in this investigation are shown in Figures 6(a) and 6(b). As the SEM pictures show, the PAni is electro-

Table 1. Comparison of characteristics of the prepared electrode with the previously reported Cr (VI) electrode

References	Detection limit (ppm)	Slope (mV decade^{-1} of activity)	Linearity range	Response time (s)
Singh <i>et al.</i> [12]	0.3	29.6	5.0×10^{-6} to $1.0 \times 10^{-1} \text{ M}$	10
Hassan <i>et al.</i> [13]	0.2	30.8	5.0×10^{-6} to $1.0 \times 10^{-1} \text{ M}$	10-20
Choi <i>et al.</i> [15]	1.052	53.7	2.0×10^{-5} to $1.0 \times 10^{-1} \text{ M}$	1
This work	0.042	56.8	1.0×10^{-6} to $1.0 \times 10^{-1} \text{ M}$	45

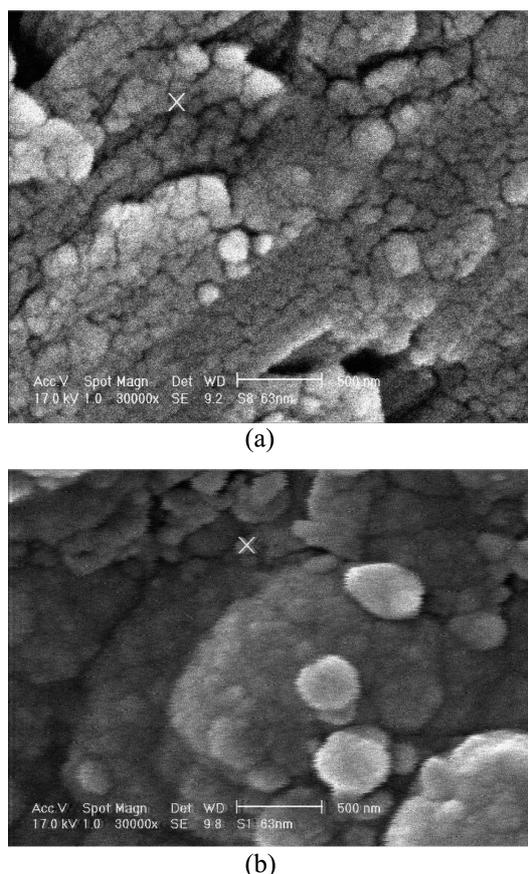


Figure 6. (a) SEM image of PGE/PAni (acid doped) (b) SEM image of PGE/PAni/DPC (acid doped).

deposited onto pencil graphite electrode as a nanostructure layer and shows a mass of clews, which are nonuniformly distributed. These images also demonstrate that a bulk quantity of nanoparticle size of DPC on the PAni exists. The small difference observed in the SEM graph obtained from PGE/PAni/DPC electrode (Figure 6(b)) can be due to the presence of DPC in the polymer structure.

Effect of pH. The pH dependence of the PGE/PAni/DPC electrode potentials for 1.0×10^{-4} M of Cr (VI) ion was tested over a pH range of 1-12 and the results obtained are depicted in Figure 7. As it can be seen, the electrode prepared is also sensitive to the pH of solution. All of the potentiometric analysis was carried out at pH value of 2 since DPC is a very sensitive reagent for Cr (VI) at this pH.³⁴ The pH adjustment was performed using dilute HCl solution. It might be useful to mention that the polyaniline film is changed into a nonconductive material at alkaline conditions. On the other hand, polyaniline film used as solid state sensor electrode should be used under neutral or slightly acidic conditions

Suggested Mechanism. Polyaniline film was selected for fabrication of the introduced sensor electrode for chromium (VI) because of its simple electrodeposition and electrical conductivity. DPC was employed for preparation of the polyaniline film because of its high sensitivity to the very low concentration of the Cr (VI) ion (0.1 mg L^{-1}). So it

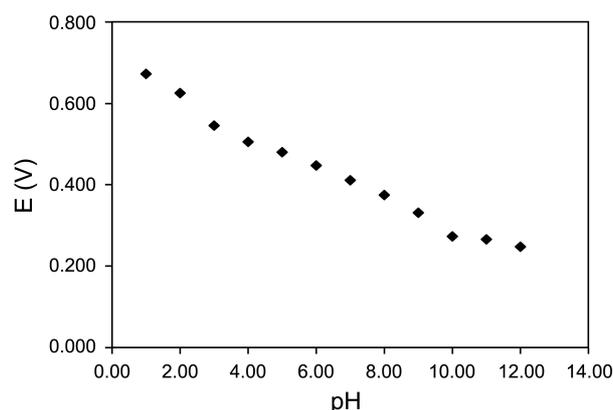


Figure 7. Effect of pH on the potential of PGE/PAni/DPC electrode in 1.0×10^{-4} M of Cr (VI) ion.

could be utilized as an ionophore or chelator for Cr (VI). DPC is incorporated with the polymer matrix due to its chemical structure *via* strong intermolecular interactions such as hydrogen bonding.

When the PGE/PAni/DPC electrode is conditioned in a solution of Cr (VI), a complex between Cr (III) [the reduced form of chromium (VI)] and diphenylcarbazone, DPCO (the oxidized species of DPC) is formed on the electrode surface (Eq. 3). According to this literature data, a mixed potential could be established assuming the following reaction is involved on the electrode surface of the developed sensors:³⁵



When polyaniline coated electrode in the absence of DPC was used for detection of Cr (VI), the electrode response was not reversible. Also when the electrode was used at high concentration of Cr (VI), the electrode response was neither repeatable and nor stable. The instability of the response might be due to the polymer overoxidation which is occurred at strong oxidative conditions. Overoxidation is accompanied by losing of the electrical conductivity and electroactivity because of destruction of the polymer conjugated system. So, the PAni sensor electrode is not recommended to be used at high concentration of Cr (VI) at strong acidic media.

Response Time. For analytical applications, the response time of a sensor is of critical importance. The response time of the electrodes was tested by measuring the time required to achieve a 90% of the steady potential when the concentration of Cr (VI) solution changed by from 1.0×10^{-6} to 1.0×10^{-1} M. The results showed that, the PGE/PAni/DPC electrode has a fast response time of ~ 45 s.

Lifetime. The lifetimes of potentiometric sensor was determined by reading the potentials of standard solutions after 1 month. After this time, the slope values of PGE/PAni/DPC electrode don't show significant changes (about 3.0%) and are very close to the initial responses.

Selectivity of Sensor. The selectivity is clearly one of the most important characteristics of a potentiometric sensor, which represents the preference of a sensor for the response

Table 2. Effect of lifetime on PGE/PAni/DPC electrode response

Lifetime (day)	Slope of calibration curve for PGE/PAni/DPC (mV)
1	56.8
3	56.7
5	56.4
10	56.3
15	55.9
20	55.6
24	55.1
28	54.8
30	54.6

to primary or target ion over other (interfering) ions that are present in the solution. Selectivity coefficient ($K_{A,M}^{Pot}$) values for a range of common interferent cations were calculated by separated solution method (SSM):³⁶

$$\log K_{A,M}^{Pot} = \frac{(E_M - E_A)Z_A F}{RT \ln 10} + \left(1 - \frac{Z_A}{Z_M}\right) \log a_A \quad (6)$$

Where a_A is the activity of the primary ion (Cr (VI)) and a_M the activity of an interfering ion producing the same potential. E_A and E_M are the potential of the solution of target and interfering ions, Z_A and Z_M are the charges of the analyte and interfering ion respectively. The concentration of interfering ions used in the present studies was 1.0×10^{-2} M. For preparing of calibration curve, standard solutions of Cr (VI) (1.0×10^{-6} to 1.0×10^{-1} M) were prepared and the potentials were recorded after 45 s or less until the readings were stable to within ± 0.1 mV. The results of potentiometric selectivity coefficients for sensor PGE/PAni/DPC are summarized in Table 3.

The selectivity coefficients clearly indicate that the fabricated electrode is very sensitive and selective to Cr (VI) ions over all the examined interfering ions listed in Table 3. From the dynamic range and Nernstian slope (~ 57 mV per decade) of calibration curve obtained by PGE/PAni/DPC, it can be concluded that the prepared electrode can be successfully used for measurement or analysis of Cr (VI) in real samples at very low concentrations. In the study of selectivity, various anions such as SO_4^{2-} , Cl^- , PO_4^{3-} , I^- , NO_3^- and CH_3COO^- were also examined. Not any measurable interference in the potentiometric response of the sensor electrode was observed. Among the investigated metal ions,

Table 3. Selectivity coefficients of the PGE/PAni/DPC electrode

Interfering ion	$K_{Cr,M}$	Interfering ion	$K_{Cr,M}$
K ⁺	10 ^{-4.57}	Pb ²⁺	10 ^{-3.18}
Na ⁺	10 ^{-4.99}	Hg ²⁺	10 ^{-2.53}
Ag ⁺	10 ^{-4.55}	Fe ³⁺	10 ^{-1.98}
Ca ²⁺	10 ^{-3.86}	Al ³⁺	10 ^{-3.25}
Mg ²⁺	10 ^{-3.75}	Zn ²⁺	10 ^{-3.99}
Co ²⁺	10 ^{-3.75}	Mn ²⁺	10 ^{-3.87}
Cu ²⁺	10 ^{-3.15}	NH ₄ ⁺	10 ^{-4.87}
As ³⁺	10 ^{-2.15}	Cr ³⁺	10 ^{-3.31}

Table 4. Analytical application of PGE/PAni/DPC electrode

Added Cr (VI) (M)	Expected conc. (M)	Potentiometric method	Spectrophotometric method
1.0×10^{-4}	1.96×10^{-6}	$2.17 \times 10^{-6} \pm 1.9\%$	$2.05 \times 10^{-6} \pm 0.8\%$
5.0×10^{-4}	9.80×10^{-6}	$9.31 \times 10^{-6} \pm 2.3\%$	$9.77 \times 10^{-6} \pm 0.6\%$
1.0×10^{-3}	1.96×10^{-5}	$2.20 \times 10^{-5} \pm 2.1\%$	$1.98 \times 10^{-5} \pm 0.5\%$

only As (III) and Fe (III) ions showed some serious interference, if presented at high concentration.

Analytical Application. To assess the applicability of the PGE/PAni/DPC electrode to real samples, an attempt was made to determine Cr (VI) in spiked solutions by standard addition method. In this experiment aliquot volumes (1.0 mL) of standard Cr (VI) solutions with different concentrations (10^{-4} , 5.0×10^{-4} , 10^{-3} M) were added to 50 mL of tap water (as real sample) and the potential of the potentiometric cell were recorded. The prepared samples were also analyzed using another standard method (spectrophotometric) and the data obtained were compared with the results of PGE/PAni/DPC electrode (Table 4).

As the data indicate the measurements observed were in good agreement with those obtained by the spectrophotometric method. Therefore, the accuracy and validity of Cr (VI) analysis using fabricated electrode (PGE/PAni/DPC) are interestingly ascertained by performing recovery studies *via* spike or standard addition methods. It could be concluded that the PGE/PAni/DPC electrode may have successful applications in monitoring of Cr (VI) ions in real samples.

Conclusions

The introduced Cr (VI) sensor electrode exhibited wide dynamic response ranges, high selectivity responses, low detection limits, suitable lifetime and good response times. Furthermore the preparation of the sensor electrode is very simple, reproducible and cost effective. Nernstian slope of 56.8 mV/decade was observed in the range from 1.0×10^{-6} to 1.0×10^{-1} M for the electrode at pH value of 2. The proposed sensor can be used in determination of Cr (VI) in real samples with high accuracy and precision.

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