Research Article

Modification of Nanoclinoptilolite Zeolite with Hexadecyltrimethylammonium Surfactant as an Active Ingredient of Chromate-Selective Membrane Electrode

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A novel chromate selective PVC membrane electrode was constructed using a hexadecyltrimethylammonium-surfactant modified zeolite (SMZ) . Nano particles of an Iranian clinoptilolite zeolite were prepared by a ball-mill mechanical method and characterized by FT-IR, SEM and XRD. Best performance was exhibited at the membrane composition of SMZ : PVC : dioctyl phthalate (DOP) in the ratio of $4:32:64$. This membrane worked well over a wide concentration range from 5×10^{-6} to 1.0×10^{-2} mol L^{-1} of CrO$_4{}^{2-}$ with a Nernstian slope of -29.38 ± 0.29 mv per decade of CrO$_4{}^{2-}$ concentration with detection limit of 2×10^{-6} mol L^{-1} in a wide pH range of 6.8–10.7. The response time of the sensor is 5–10 s over a period of 2 months with good reproducibility. The selectivity coefficients of the proposed electrode towards various interfering ions were determined by FIM and SSM methods. The sensor was successfully used as indicator electrode in the potentiometric titration of CrO$_4{}^{2-}$ against Pb(II) and determination of chromium in an electroplating wastewater sample.

1. Introduction

Ion-selective electrodes (ISEs), because of their great interests regarding to their advantages, are used in a wide range of applications for the determination of ions and pharmaceuticals in aqueous environments. Comparing with other analytical methodologies, ion selective electrodes have some advantages such as: ease of preparation, relatively inexpensive, robust, durable, rapid response time, continuous monitoring, measure activity rather than concentration, do not affected by turbidity or color of sample and ideal for their use in the environmental studies [1]. As an important advantage, ISEs are known to be one of the few techniques that can measure both positive and negative ions depending on the nature of the ionophore.

Chromium is an element widely used in industrial activities such as chrome plating and electroplating, metal smelting and metallurgy to manufacture alloys, dyestuff industries, leather tanning, and wood treatment [2, 3]. It exists as two major species, Cr (VI) and Cr (III) in natural waters and soils. Cr (III) is a stable and slightly soluble cation considered as an essential microelement [4], while Cr (VI) (as chromate) is highly water soluble and mobile anion, known as a toxic pollutant, with mutagenic and carcinogenic effects [5]. Due to the different toxicities of these two species, it is essential to determine hexavalent chromium rather than the total chromium concentration using a rapid and simple method that can be applied in industrial and environmental fields.

Potentiometric sensors for Cr (VI) analysis containing modifiers as nickel tris(1,10-bathophenantroline) [6], bis(acetylacetonato) cadmium (II) [7], cyclic amines [8], diaza crown ethers [9], rhodamine-B [10], or calix[4]arene [11] have been reported.

Zeolites, clinoptilolite is the most abundant of their natural category, are crystalline microporous aluminosilicates with very well-defined structures that consist of a framework

formed by tetrahedra of SiO_4 and AlO_4. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedra results in a negative charge on the zeolite framework that can be balanced by exchangeable cations. Hence, zeolites can exchange cations but not anions. It has been demonstrated that the cationic surfactants have a great affinity to this negative charge. This property has been used to modify the external surface of the zeolites by adsorbing a cationic surfactant to improve its anion exchange capacity. The cationic surfactants that are most commonly used to modify zeolites are usually long alkyl chains with a quaternary ammonium group at one end of the chain such as hexadecyltrimethylammonium (HDTMA) bromide [12]. The sorption of a cationic surfactant on the external surface of a zeolite can be governed mainly by cationic exchange and hydrophobic interactions [13]. At a low surfactant loading, the surfactant cations are exchanged with the exchangeable cations of the zeolite until a monolayer of surfactant cations is formed at the external surface. At concentrations above the critical micelle concentration, a bilayer of surfactant molecules (admicelle) is attached to the external surface, where the outer layer of surfactant molecules is bound by hydrophobic interactions [14]. In this case a surfactant modified zeolite (SMZ) has produced whit changing the external surface charge of the zeolite from negative into positive which now displays anion exchange capacity.

Different properties were observed when immobilizing HDTMA on different substrate. Li et al. immobilized HDTMA onto the clinoptilolite for sorption of oxyanions [15]. Natural mordenite (NM) was used for adsorption of As (V) by Chutia et al. [16], and also zeolite NaY was used as substrate for ethylene adsorption by Patdhanagul et al. [17]. Zeolites have different cation exchange capacities (CECs) and external cation exchange capacities (ECECs) depending on their structures and Si/Al ratio, where the latter case affects on the properties of the obtained SMZ. In addition, presence of bilayer on SMZ acts as an organic medium which affects in the hydrophilicity of obtained SMZ. Hence, we believe that the support on different SMZs has a major role in their adsorption behavior. Regarding different behaviors of HDTMA on different supports, we have constructed different selective electrodes based on SMZ modifier towards potentiometric determination of anions [18–21].

In this work, an Iranian natural clinoptilolite as an abundant zeolitic material in Iran was pretreated and changed to nanoparticles by mechanical ball milling process. After purification of the solid by reflux method, the purified nanoparticles were ion exchanged in HDTMA solution to yield SMZ. Then, the obtained SMZ was used as an active ingredient to modify PVC membrane. Constructing the electrode by this membrane shows better Nernstian behavior towards chromate anions rather than the other investigated anions. After the investigation of some experimental factors which affect the behavior of the proposed electrode, the electrode was used as indicator electrode in the potentiometric determination of chromate in a precipitation titration by Pb (II) solution. The statistical "t" and "g" tests were used to prove the validity of the results.

2. Experimental

2.1. Reagents. The natural zeolite used in this study originated from Semnan Province, in the north east of Iran. For membrane preparation, poly(vinyl chloride), dioctyl phthalate (DOP), tetrahydrofuran (THF), and hexadecyltrimethylammonium bromide (HDTMABr) were purchased from Aldrich chemicals and were used without further purification. All salts were purchased from Merck and used as received. Double-distilled deionized water was used throughout the experiments. The pH of the solutions was appropriately adjusted with NaOH or HCl solution as appropriate.

2.2. Preparation of the Nanozeolite and the SMZ. Natural clinoptilolite zeolite was mechanically pretreated, by crushing in an agate mortar and sieving in analytical sieves for the separation of <100 μm particle-size fractions. Nanoclinoptilolite was prepared using a planetary ball mill (PM100; Retsch Corporation). The milling can be down in two states including dry milling and wet milling. The milling conditions including the dry milling speed, the dry milling time, the ball-to-powder ratio for dry milling and the wet milling speed, the wet milling time, the balls-to-powders ratio, and the water-to-powder ratio for wet milling should be optimized to reach size reduction and crystallinity retention. In this study, dry milling was applied. The milling speed, milling duration, and balls-to-powder ratio were 600 rpm, 6 h, and 4.0, respectively.

In order to remove the water-soluble impurities and also paramagnetic impurities especially, one entered during the ball milling step, the obtained nanoparticles were refluxed at 70°C for 8 h in distilled water while the suspension was stirred by a magnetic stirrer continuously. This was repeated five times to reach complete purification by observing the elimination of the adsorbed magnetic particles on magnet. In order to reach fixed water content, after filtration, washing, and drying of the powder, the purified material was stored in a desiccator over saturated sodium chloride solution for 2 weeks.
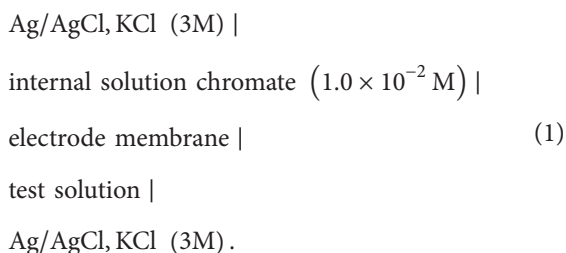
Surfactant modification of the zeolite was carried out using the surfactant, hexadecyltrimethylammonium bromide (HDTMABr), a cationic surfactant. A preweighed quantity of nanoclinoptilolite sample was mixed with HDTMABr solution in a 125 mL polyethylene bottles in a 1 : 100 (solid : liquid) ratio. The concentrations of HDTMABr solutions used for preparation of SMZ-1, SMZ-2, and SMZ-3 were 50, 100, and 200 mM, respectively. The solution was agitated for 24 h at 150 rpm on an orbital shaker and a temperature of 25°C, a period shown sufficient to obtain sorption equilibrium. The mixture was then centrifuged at 3000 rpm for 15 min. The solution was then filtered, and the solid residue was washed with double-distilled water and air-dried for 24 h. The synthesized SMZ was then mechanically ground with a mortar and pestle to a fine particle size.

2.3. Characterization. Nano-particles of clinoptilolite were prepared using a planetary ball mill (PM100; Retsch Corporation). The zeolites were characterized by X-ray diffraction (XRD) by using a diffractometer Bruker, D8ADVANCE,

X-ray tube anode: Cu, wavelength: 1.5406 Å (Cu Kα radiation), Filter: Ni. The Fourier transform infrared (FT-IR) spectra of the samples were recorded at room temperature in KBr pellets using a Perkin Elmer FT-IR (Spectrum 65) spectrometer between 4000 and 400 cm^{-1} wavenumbers. To study probable changes of morphology for ground powders after ball milling, samples were subjected to SEM investigation (Seron technology, model: AIS2100).

2.4. Preparation of Electrodes.

2.4. Preparation of Electrodes. The general procedure to prepare the SMZ-PVC membrane was mixing of various amounts of the ionophore (SMZ) together with appropriate quantities of DOP (as plasticizer) and PVC to give a total mass of 100 mg in 1.5 mL of THF. The optimum composition of the membrane was 32 mg of powdered PVC, 64 mg of DOP plasticizer, and 4 mg of SMZ. These compounds were dissolved in 1.5 mL of THF. The resulting mixture was poured into a glass dish of 2 cm diameter. The solvent was slowly evaporated until an oily concentrated mixture was obtained. A Pyrex tube of 4 mm i. d. was dipped into the mixture for about 5 s, so that a nontransparent membrane of 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for 24 h. Then it was filled with internal filling solution 1.0×10^{-2} M $Na_2CrO_4 \cdot 4H_2O$. The prepared electrodes were finally conditioned for 2 h by soaking in a 1.0×10^{-2} M $Na_2CrO_4 \cdot 4H_2O$ solution. A silver-silver chloride wire was used as the internal reference electrode.

2.5. Potential Measurements. The potential measurements were carried out at $25 \pm 1^\circ$C with a Metrohm pH meter 691. To prevent any transfer of ions to the measuring solution, the external reference electrode used was an Ag/AgCl electrode shielded by an intermediate salt bridge compartment containing the background electrolyte. The cells for potential (mV) measurement were of the following configuration:

$$
\begin{aligned}
&\text{Ag/AgCl, KCl (3M)} \,| \\
&\text{internal solution chromate} \left(1.0 \times 10^{-2}\,\text{M}\right) | \\
&\text{electrode membrane} \,| \\
&\text{test solution} \,| \\
&\text{Ag/AgCl, KCl (3M)} \,.
\end{aligned}
\tag{1}
$$

A small magnetic stirring bar and 20 mL of chromate solution were placed in a 50 mL beaker. The test solutions were constantly stirred by a magnetic stirrer. The electrodes were conditioned with chromate and thoroughly rinsed with double-distilled deionized water, and the surface of the ISE was washed between measurements to minimize electrode fouling. The chromate selective electrode and reference electrode were then inserted into the solution, and the potential difference was measured.
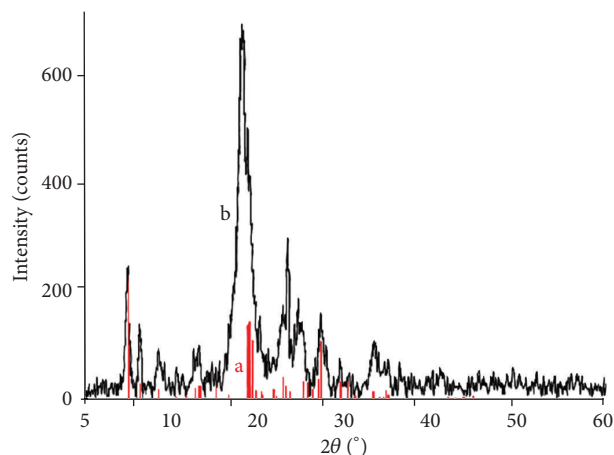

FIGURE 1: XRD patterns of (a) the reference pattern of clinoptilolite and (b) prepared zeolite nanoclinoptilolite.

3. Results and Discussion

3.1. Characterization of Prepared Nanoclinoptilolite and SMZ

3.1.1. X-Ray Diffraction Studies. The X-ray diffraction (XRD) patterns of reference clinoptilolite and prepared nanoclinoptilolite are shown in Figures 1(a) and 1(b), respectively. The XRD pattern of the reference clinoptilolite sample was selected from the manual library of the instrument which is in accordance with the JCPDS no. 39-1383. The lines and position remained intact that show a good agreement with the data of clinoptilolite in the literature [22]. Good agreement between the results shows that the original natural zeolite includes clinoptilolite structure as major component. XRD pattern also showed that the used zeolite tuffs include slight amounts of quartz (3.5%) and cristobalite (7.8%) phases as impurities. Presence of the broad lines in the XRD pattern of the prepared sample agrees with the formation of nanoparticles during the ball-milling process. So, we determined the average size of this sample using β, the excess of width line of the diffraction peak in radians, and θ, the Bragg angle in degrees, and using the Debye-Scherrer formula:

$$
d = \frac{k\lambda}{\beta_{1/2}} \cos\theta,
\tag{2}
$$

where d is the mean crystallite diameter, λ is the X-ray wavelength, K is the Scherer's constant (0.89), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the diffraction peaks and θ is the diffraction angle. The average particle sizes of prepared nanoclinoptilolite lays between 20 and 28 nm.

3.1.2. FT-IR Studies. The FT-IR spectra of natural and modified zeolite samples covering the range from 400 to 4000 cm^{-1} were taken. FT-IR spectra obtained using KBr pellets of the unmodified clinoptilolite zeolite, the HDTMA surfactant, and the SMZ are presented in Figures 2(a), 2(b), and 2(c), respectively. Comparing the IR spectrum of the SMZ sample with others (Figure 2(c)) shows characteristic peaks at wavenumbers of 3016, 2919, 2849, and 1483 cm^{-1}
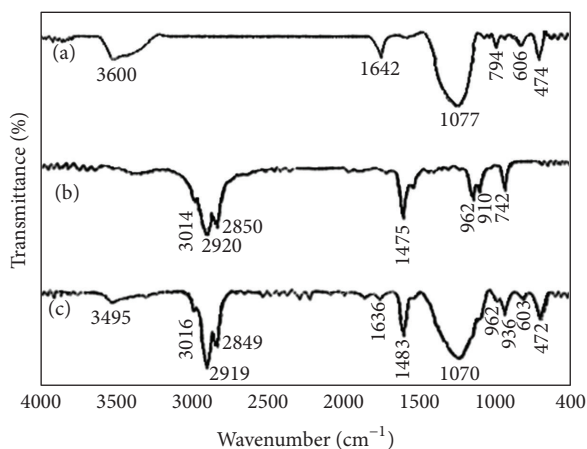
Figure 2: FT-IR patterns for (a) the prepared zeolite nanoclinoptilolite, (b) HDTMA and (c) SMZ.

which indicate the incorporation of HDTMA onto the zeolite surface. Although there are some slight shifts in the peaks position at each wavenumber in spectra of (a) and (c) in Figure 2, both of the patterns are nearly the same, showing unchanging of the zeolite structure during the HDTMA loading. Particularly, the presence of peaks at 3016, 2919, 2849 and 1483 cm^{-1} in the SMZ spectrum (related to C–H, C–C and N–C vibrations in the surfactants, resp.), that are absent in the clinoptilolite spectrum, confirms the loading of HDTMA onto the zeolite surface.

3.1.3. Surface Morphology Studies.

Some of the SEM images of nanoclinoptilolite and the obtained SMZ are shown in Figure 3. SEM images indicated that almost in all samples, zeolite powder with particles size less than 100 nm can be recognized as a separated particle or in the form of larger agglomerates. Moreover most particles have lost their initial layered shape and converted into spherical, elliptical, or irregular shapes. By careful considerations of SEM images, some crystals with sharp edges and clean surfaces were observed; which are about 100–200 nm in size. Therefore, it can be concluded that careful selection of milling conditions may result in production of nanoclinoptilolite zeolite with desirable crystalline structure. Nevertheless, mechanical production of zeolitic nanoparticles by means of planetary ball mills may also reduce the zeolite crystallinity.

3.2. Potentiometric Experiments

3.2.1. Theoretical and Membrane Composition Investigations.

Anionic properties can easily be imparted on the zeolitic surface using the surface modification by surfactants. When the initial concentration of the sorbed surfactant molecules is less than its critical micelle concentration (CMC), a monolayer of surfactant molecules forms on the zeolite surface. At concentration greater than the CMC and when enough surfactant exists in the system, the sorbed surfactant molecules form bilayers which induces positively charged

functional groups to orient toward the solution; thus creating sorption sites for anions was performed [23–28]. The surfactant molecules form bilayers on zeolite external surfaces with the lower layer held by electrostatic interaction between the negatively charged zeolite surface and the positively charged surfactant head groups while the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers [29]. Sorption of inorganic anions on cationic surfactant modified zeolite has been attributed to the formation of a surface-anion complex [30]. The positively charged head groups are balanced by counter ions, and the sorption or exchange of other anionic constituents involves the replacement of weakly held counter ions by more strongly held counter ions.

Preliminary experiments showed that when SMZ was mixed with a solution containing chromate anion, the concentration of chromate in the remaining solution was decreased. These investigations confirm that the double layers of surfactant on the surface of zeolite have been formed and SMZ can adsorb anions. Adsorption of colored anions such as chromate, dichromate, and permanganate onto the surface of the SMZ causes colored surfaces and this color is stable even by rinsing the surface for several times while if the raw zeolite was added to this colored anions solution, the anion adsorption separated with rinse easily and color intensity on surface of zeolite decreases extremely. This method was reported as the easiest and fastest way to confirmation for produce of SMZ in previous works [21, 31].

In this work, we were interested in investigating the possibility of the use of surfactant modified zeolite, formulated as SMZ, as an ionophore in PVC-based membranes for chromate ion. Thus, in preliminary studies, SMZ was used as an ionophore to prepare PVC membrane ion-selective electrodes for a wide variety of anions. The potential responses of various anion-selective electrodes based on SMZ used are shown in Figure 4 and Table 1. As seen, with the exception of chromate ion, all anions tested show negligible responses in the concentration range of 1.0×10^{-7}–1.0×10^{-1} mol L^{-1}. Noteworthy, among these anions, chromate shows a higher potential response at higher concentrations. Hence, the modified nanoclinoptilolite with HDTMA was used as an ionophore for construction of a potentiometric sensor for this anion. Since CrO_4^{2-} is the predominant form of chromium species at the conditions used in this work, the sorption mechanism can be shown by the following reaction:

$$2\left(R_4N^+ \text{ in SMZ}\right) + CrO_4^{2-} \longleftrightarrow \left(R_4N\right)_2CrO_4, \quad (3)$$
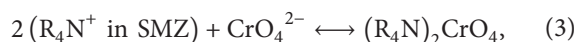
where, R_4N^+ represents the anion-exchange sites of HDTMA surfactant on SMZ. Thus, when the SMZ-PVC membrane electrode is immersed in the chromate solutions, an anion exchange reaction occurs between the anion on the electrode surface (Br$^-$) and CrO_4^{2-} in the solution.

So, the electrode was investigated in further detail. Secondly, the amount of SMZ modifier was optimized. The responses of the electrodes to several SMZ compositions are presented in Table 2. It is clear that only the electrode containing 4% SMZ prepared from clinoptilolite at 100 mM HDTMA solution shows Nernstian behavior. This electrode

TABLE 1: Potentiometric response of the SMZ-PVC electrode toward different anions ($n = 5$) with each electrode conditioned in a 0.01 M solution of the corresponding anion for 2 h at 25 (membrane includes 4% SMZ).

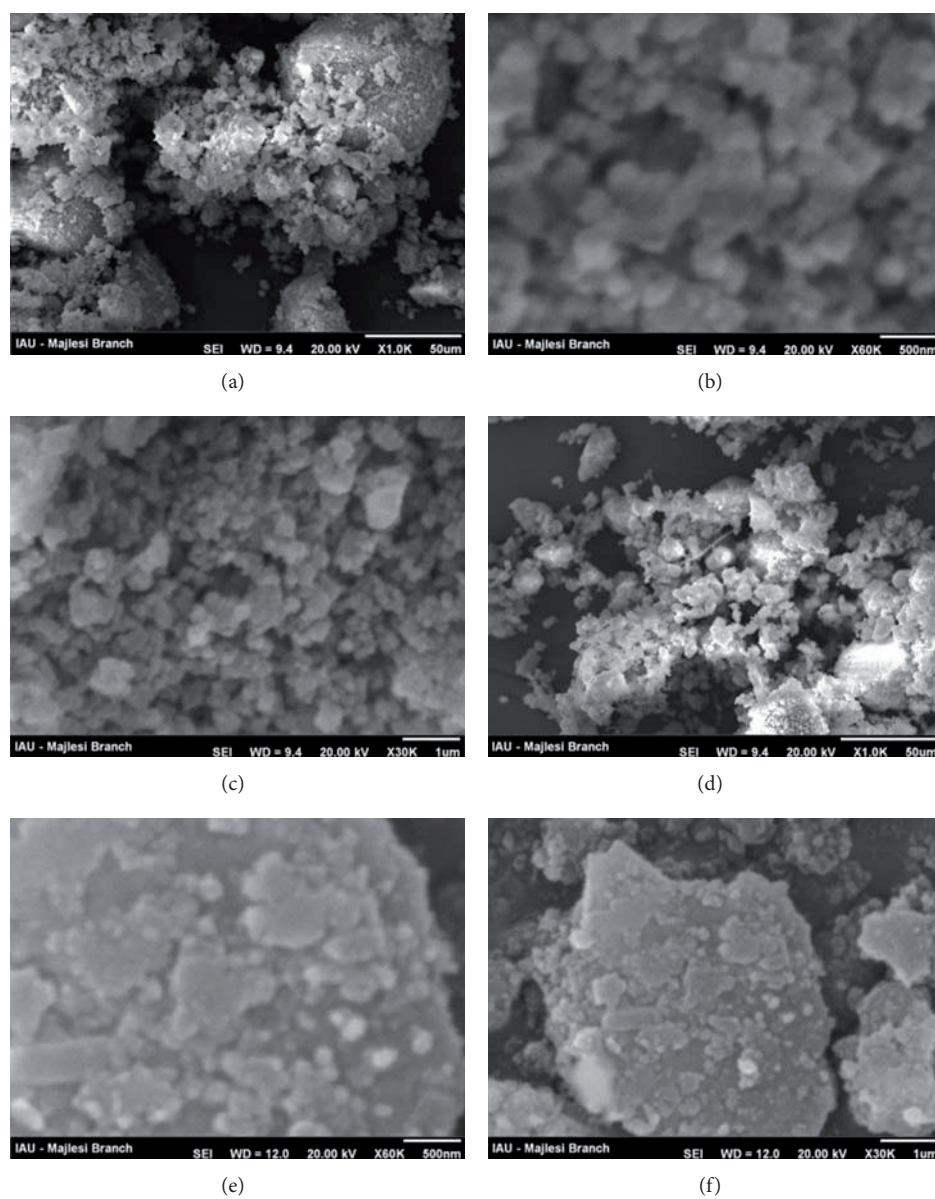| Anion	Slope (mV·decade^{-1})	r^2	Linear range ($-\log C$)
Benzoate	-35.0 ± 1.1	0.9705 ± 0.0137	2–4
ClO_3^-	-36.3 ± 1.3	0.9975 ± 0.0018	1–4
CN^-	-46.4 ± 1.4	0.9936 ± 0.0113	3–5
I^-	-40.0 ± 0.9	0.9980 ± 0.0005	1–5
NO_3^-	-19.9 ± 0.5	0.9896 ± 0.0136	1–4
$C_2O_4^{2-}$	-43.5 ± 0.6	0.9811 ± 0.0072	2–4
ClO_4^-	-41.8 ± 1.7	0.9910 ± 0.0053	1–4
CrO_4^{2-}	-29.0 ± 0.6	0.9965 ± 0.0061	2–5

(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 3: SEM images of nano-clinoptilolite (a–c) and SMZ (d–f).

TABLE 2: Optimization of the modifier percentage in chromate-selective electrode based on SMZ at 25°C ($n = 5$).

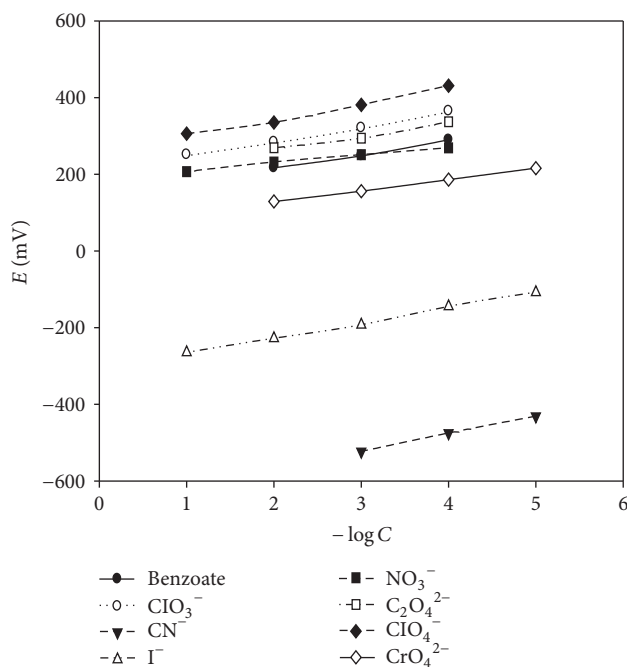| Electrode	Modifier percentage	Slope (mV·decade^{-1}) ($n = 5$)
A	4% (nanoclinoptilolite +50 mM HDTMA)	-47.7 ± 1.3
B	4% (nanoclinoptilolite +100 mM HDTMA)	-29.2 ± 1.4
C	4% (nanoclinoptilolite +200 mM HDTMA)	-38.9 ± 0.6

FIGURE 4: A schematic diagram of the electrode response to various anions.

FIGURE 5: Various orientations of surfactant molecules on zeolite surface zeolite surface (a) lower coverage monolayer, (b) midcoverage monolayer, and (c) higher coverage monolayer.

also showed good linear response within the concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} chromate. In the 50 mmol L^{-1} HDTMA solution, a bilayer may be formed partially at the zeolite surface, and the obtained SMZ is not suitable for CrO$_4^{2-}$ adsorption (Table 2A). The electrode C in Table 2, prepared in a 200 mmol L^{-1} HDTMA solution, does not exhibit Nernstian behavior. In this case, a partial bilayer may be loaded on the zeolite surface. Consequently, the obtained SMZ does not respond appropriately to CrO$_4^{2-}$. These observations are in accordance with our previous works [18–21] and also with results for antimonate sorption [32]. Wingenfelder et al. found when the external CEC was almost twofold, the zeolite absorbed >98% of the initial HDTMA in solution. When the applied HDTMA concentrations were more than twice the concentration of the external CEC, the zeolite absorbed 84% of the initial HDTMA concentration. Sullivan et al. upon the FT-Raman spectroscopy and batch sorption methods showed the orientation of surfactant depends on the surfactant's amount that was adsorbed onto surface of zeolites (Figure 5). For example, if concentration of surfactant is lower than the certain value, interaction between surfactant and zeolite will be horizontal; it means that, at lower loadings, the sorbed HDTMA tail groups tended to have more disorder, similar to solution monomers shown in
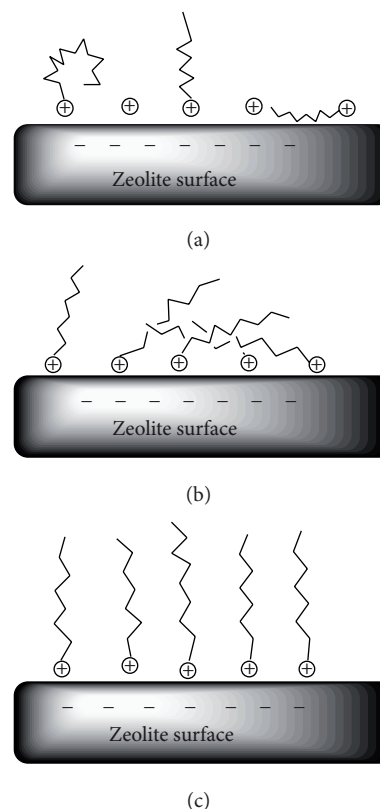
Figures 5(a) and 5(b), but if concentration of surfactant is appropriate, interaction of them will be vertical, and in this situation we have the highest order, shown in Figure 5(c) [33].

The response properties of ion-selective electrodes based on ionophore are strongly influenced by the membrane composition, especially ionic sites [34, 35]. In the case of ISEs based on neutral carriers, ionic sites with a charge sign opposite to that of the primary ions are necessary for obtaining a Nernstian response, to decrease the membrane resistance, reduce the counter-ion interferences, and improve the detection limit and optimization of selectivity. In ISEs based on the electrically charged carriers, on the other hand, the use of ionic sites with the same charge sign as the primary ions can significantly improve the response properties and selectivity of the sensor. Thus, the influence of the membrane composition and amount of SMZ as an ionophore on the potential response of the chromate sensor was investigated.
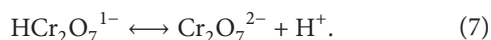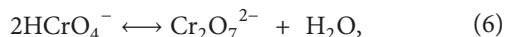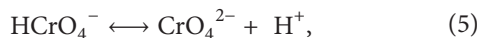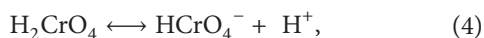
TABLE 3: Effect of SMZ-PVC membrane composition on the potentiometric behavior of the chromate-selective electrode ($n = 5$) at 25˚C.

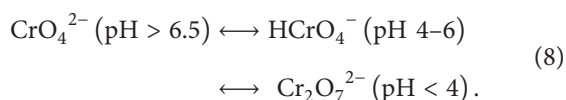| No.	PVC%	SMZ%	DOP%	Slope (mV·decad^{-1})	r^2	Linear range ($-\log C$)
1	32.7	2	65.3	40.1 ± 0.7	0.9822 ± 0.0010	2–5
2	32	4	64	29.9 ± 0.9	0.9944 ± 0.0035	2–5
3	31.3	6	62.7	16.4 ± 1.3	0.9865 ± 0.0019	2–4
4	30	10	60	20.3 ± 0.6	0.9901 ± 0.0058	2–4

The effect of the membrane composition on the potentiometric response of the electrodes was investigated by varying the proportions of the ionophore (SMZ), plasticizer (DOP), and PVC. Table 3 presents the compositions of several typical membranes, along with their potentiometric response characteristics. The potential response of all the SMZ-PVC electrodes was studied in the concentration covering the range of 1×10^{-7}–$1 \times 10^{-1}\,\mathrm{mol\,L^{-1}}$ chromate. The results indicate that the electrode comprised of 4% SMZ, 32% PVC, and 64% DOP is suitable and the electrode exhibited a Nernstian response with a small standard deviation (membrane no. 2, Table 3). Thus, this membrane composition (optimized electrode) was used in the next experiments.

The performance characteristics of the investigated electrodes were studied as a function of conditioning times. For this purpose, the electrode was soaked in $1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ chromate solution for different intervals, and then the effect of soaking on the calibration graph slope was measured. Table 4 presents the results of investigating conditioning times. The results show that the best Nernstian response, combined with a dynamic range, was obtained at 2 h. Hence, this time was employed as the conditioning time in later studies.

3.2.2. Effect of pH.

In the aqueous phase, chromate exists in different ionic forms ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCr_2O_7^-$). The distribution of Cr (VI) species is dependent on both the total concentration of Cr (VI) and pH of the equilibrium solution. The following equations describe the distribution of chromium species in aqueous solution [36]:

$$H_2CrO_4 \longleftrightarrow HCrO_4^- + H^+, \tag{4}$$

$$HCrO_4^- \longleftrightarrow CrO_4^{2-} + H^+, \tag{5}$$

$$2HCrO_4^- \longleftrightarrow Cr_2O_7^{2-} + H_2O, \tag{6}$$

$$HCr_2O_7^{1-} \longleftrightarrow Cr_2O_7^{2-} + H^+. \tag{7}$$

The CrO_4^{2-} anion prevails in basic or slightly acidic solution while the $Cr_2O_7^{2-}$ anion is dominant in acidic Cr (VI) aqueous solution [37]:

$$CrO_4^{2-}\,(\mathrm{pH} > 6.5) \longleftrightarrow HCrO_4^-\,(\mathrm{pH}\,4\text{–}6)$$
$$\longleftrightarrow Cr_2O_7^{2-}\,(\mathrm{pH} < 4). \tag{8}$$

The pH of aqueous $10^{-4}\,\mathrm{mol\,L^{-1}}$ CrO_4^{2-} solution was altered by dilute NaOH or HCl solutions, and the potential of the solutions was monitored. The pH dependence of the

TABLE 4: Conditioning time for the SMZ-PVC membrane electrode based on 4% SMZ ($-\log C = 5$–2; $n = 5$) at 25˚C.

t (h)	Slope (mV·decade^{-1})	r^2
2	29.4 ± 1.5	0.9927 ± 0.0069
4	20.6 ± 1.2	0.9682 ± 0.0258
7	45.4 ± 0.74	0.9790 ± 0.0022
10	21.3 ± 1.0	0.9841 ± 0.0071
12	16.7 ± 1.4	0.9746 ± 0.0135
16	22.3 ± 0.84	0.9768 ± 0.0110
24	32.1 ± 2.2	0.9530 ± 0.0110
48	14.4 ± 0.63	0.9748 ± 0.0160

potential response of the proposed electrode in the pH range of 1–12 was tested, and the results are shown in Figure 6. As can be seen, the potential response remains almost constant over the pH range of 6.8–10.7. pH values decrease in the measurable concentration of chromate and formation of dichromate and polychromate [38], to which the sensor does not appear to respond in Nernstian manner. For studying the effect of pH, another method was used as follows: different series of solutions covering the concentration range from 1×10^{-5} to $1 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ were made, and the pH of each set was kept constant value. Results which are shown in Table 5 show the good Nernstian behavior for pH = 8. Subsequently, in our investigations, the solution pH values were adjusted to 8 when required. More acidic pH values affected the potential response probably due to partial destruction of the zeolite lattice, which occurs in acidic media [39], and interference from Cl$^-$. Zeolite minerals decompose in acids and form gels or insoluble silica depending on the structure of the zeolite and Si/Al ratio [21]. Conversely, in high pH media, the interference by a high concentration of OH$^-$ ions induces an increased electrode response [21]. In addition to the dealumination of zeolites in acidic media, many of the zeolites, although stable under the particular conditions of their synthesis, may undergo conversion to different species with time [21]. In these conditions, SMZ may decompose due to the different external CEC values of clinoptilolite and the converted materials. In highly acidic and basic media, the electrode may respond to monovalent Cl$^-$ and OH$^-$ anion additions to the chromate, and due to the their different charges and hence different slopes (according to Nernst equation for monovalent Cl$^-$ and OH$^-$ anions) with chromate, a potential change occurs. In addition to these problems, chromate protonation that occurs with a decrease in pH must be taken into consideration. Therefore, a pH of 8 was selected as the optimal value.

TABLE 5: Effect of pH on Nernstian behavior of the chromate-selective electrode ($-\log C = 5$–2; $n = 5$) at $25°C$.

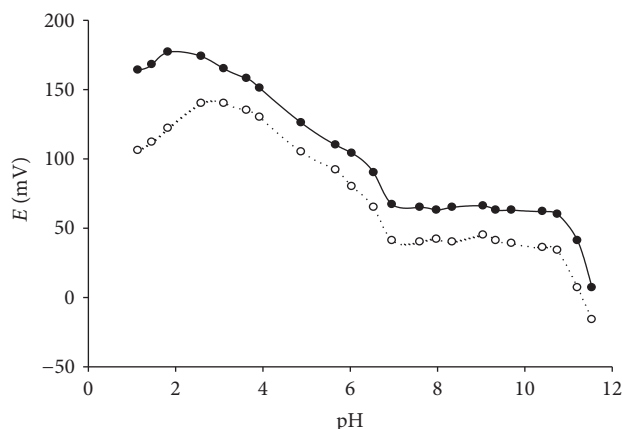| pH	Slope (mV·decad^{-1})	r^2
2	33.9 ± 1.0	0.9880 ± 0.0171
4	41.4 ± 1.3	0.9811 ± 0.0116
6	43.7 ± 0.8	0.9955 ± 0.0073
7	29.8 ± 0.6	0.9905 ± 0.0054
8	29.3 ± 0.4	0.9940 ± 0.0041
9	28.6 ± 0.9	0.9900 ± 0.0057
10	29.5 ± 0.3	0.9926 ± 0.0049
11	19.3 ± 1.6	0.9854 ± 0.0123

FIGURE 6: Influence of pH on the potential response of the chromate-selective electrode to 1.0×10^{-4} mol L^{-1} chromate.

3.2.3. Effect of Temperature.
To study the thermal stability of the sensors, they constructed at different test solution temperatures of 25, 30, 35, 40, 45, 50, and $60°C$. The results which are shown in Table 6 show the electrode exhibited good Nernstian behavior in the range of 25–$40°C$. The Nernstian and experimental slope values at each temperature were compared statistically by t-test [40], showing conformity of the slopes for 5 replicates. On the other hand, the smaller experimental t-values than its critical value in the 25–$40°C$ temperature range show systematic errors affect the response the proposed electrode. The results prove the validation of the obtained results with the expected values in the temperature range of 25–$40°C$. However, at temperatures higher than $40°C$ the slopes show a significant deviation from the theoretical values, because of the presence of the systematic errors in the responses. The main factors for this deviation can be considered as the phase boundary equilibrium at the gel layer test solution interface which is disturbed by the thermal agitation of the solution [21] and may also be related to surfactant desorption from the SMZ and destruction of the electrode surface at higher temperatures.

3.2.4. Response Time.
Generally, dynamic response time is an important factor for any sensor. The critical EMF response of the electrode was assessed according to IUPAC recommendations [42]. The average time required for the mentioned
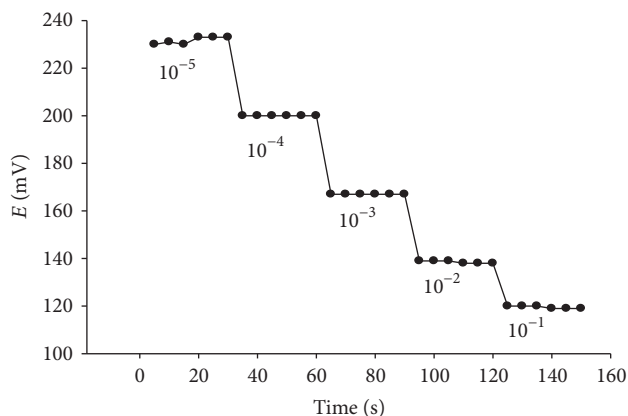

FIGURE 7: Response time of the SMZ-PVC to different concentration of chromate (pH = 8) in the range of 1×10^{-5} to 1×10^{-1} mol L^{-1}.

electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of chromate ion solutions, each having a 10-fold difference in concentration, was investigated. The measurements of potential versus time were carried out with chromate solutions from lower 1.0×10^{-5} mol L^{-1} to higher 1.0×10^{-1} mol L^{-1} concentrations (Figure 7). The electrode yielded steady potentials within 5–10 s. The potentials remained constant for about 150 s. The response time increased to 10 s when the concentration was lowered to 1.0×10^{-5} mol L^{-1} because of the longer equilibration time, whereas higher concentrations have response times of less than 5 s.

3.2.5. Potentiometric Selectivity.
Interfering of concomitants on the response of the analytical methods is the most limiting factor of these methods. The most important characteristic of any ion-selective electrode is its response for the primary ion in the presence of other anions in solution, which is expressed in terms of the potentiometric selectivity coefficient ($k_{A,B}^{pot}$). Potentiometric selectivity coefficients were determined by the fixed interference method (FIM) at fixed concentration of interfering ions and varying amounts of the primary ion [43]. This method measured the potential of the electrode in a series of solutions containing a fixed activity of the interfering anion a_B (0.1 mol L^{-1}) and varied concentrations of chromate in the range of 5×10^{-6} to 1×10^{-2} mol L^{-1}. The potential values obtained are plotted versus the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the value of a_A which is to be used to calculate $k_{A,B}^{pot}$ from the equation (Figure 8):

$$\log k_{A,B}^{pot} = E_2 - \frac{E_1}{2.303RT/Z_A F} + \left(1 - \frac{Z_A}{Z_B}\right)\log \alpha_A, \tag{9}$$

where both Z_A and Z_B have the same signs, positive or negative, and are the valence of primary and interfering ions, respectively.

TABLE 6: Effect of temperature on the optimized SMZ-PVC electrode behavior ($n = 5$).

Temperature (°C)	Nernstian slope (mV·decade^{-1})	Mean of exp. slope ($n = 5$) (mV·decade^{-1})	t_{exp} [a]
25	29.6	29.7 ± 0.4	0.59
30	30.1	30.3 ± 0.7	0.69
35	30.6	30.4 ± 1.3	0.34
40	31.1	31.4 ± 0.9	0.71
45	31.6	15.6 ± 2.6	13.63
50	32.1	12.9 ± 0.5	93.50
60	33.1	18.2 ± 2.0	16.88

[a] $t_{0.05,4}$ = 2.78 [40].

The selectivities of electrodes were also investigated by the separate solution method [43] ($a_A = a_B = 10^{-2}$ mol L^{-1}) in the way that the potential of a cell comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing the ion A at the activity a_A (but no B) and the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are E_1 and E_2, respectively, the value of $k_{A,B}^{pot}$ can be calculated from the equation:

$$\log \ k_{A,B}^{pot} = \frac{\alpha_A}{\alpha_B^{(Z_a/Z_b)}}. \tag{10}$$

In Table 7, the selectivity coefficients and response characteristics of the SMZ-PVC electrode are compared with the other chromate selective electrodes. According to the results, selectivity shows deviation from Hofmeister series. The reason the selectivity coefficients of this electrode do not comply with the Hofmeister series, and show an anti-Hofmeister behavior, is thought to be due to the possible interaction of the anions with HDTMA [44]. Depending on the mode of interaction with cationic surfactants, anions are classified into four classes [44]. Most "Hofmeister" anions do not bind strongly on the head groups and behave as typical counter ions (OH$^-$, CH$_3$COO$^-$, and HCOO$^-$). Class II ions are usually large complex ions with large polarizabilities, which form water-insoluble ion pairs with the amine-based surfactants (I$^-$, SCN$^-$, and ClO$_4^-$). Class III consists of complex anions containing transition metal ions, which form covalent bonds with the amine-head groups and also between themselves through oxygen bridges. Finally, class IV consists of a number of hydrophobic organic anions (benzoate, salicylate, tosylate), which partly dissolve in the palisade layer of the surfactant. Hofmeister anions also affect the size and shape of micelles of cationic surfactants and their phase diagrams regarding their hydrated sizes [44]. It often happens that several different anions compete for a cationic micellar surface.

According to the previous discussion, different anions have different interactions with head group and the chain of HDTMA surfactant, which in turn cause a deviation from Hofmeister series.

3.2.6. Life-Time Study.
Lifetime or durability of ISEs is one of the important factors in deciding the applicability of ISE. The lifetime of electrodes based on ionophores in
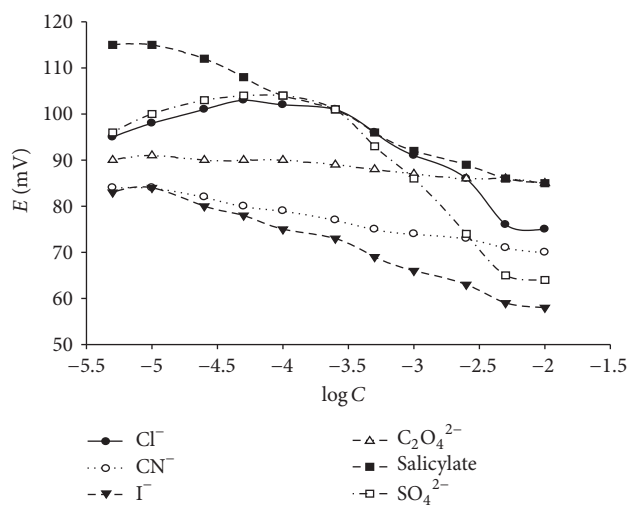

FIGURE 8: A schematic diagram of the electrode response to various interferences with FIM method.

solvent polymeric membranes depends on the distribution coefficient of the ionophore and the plasticizer between the aqueous and membrane phases [43]. Hence, the lifetime of electrodes must depend on the components of the solution and the measured specimens with electrodes. Durability of the membrane was tested by monitoring the change in the slope and linear response range with time. The lifetime of the electrode was determined by reading its potentials and plotting the calibration curves for a period of 2 months. The results of the studies revealed a very slight gradual decrease in the slope of the electrode after 2 months. This negative effect of soaking is attributed to the leaching of the ionophore and plasticizer to the bathing solution which is related to the distribution equilibria and diffusion rates. Another explanation can be related to the penetration of the water molecules from the bathing solution to the membrane and consequently slow solvation of the lipophilic salts in situ, so they are slowly leached out and limit the electrode life [45].

3.2.7. Response Characteristics of the Electrode.
Using the optimized membrane composition and conditions described previously, the critical response characteristics of the electrode were evaluated according to IUPAC recommendations [42].

TABLE 7: Comparison of some potentiometric characteristics of the chromate ISE described in this paper with previously published reports.

Interference ions	Log k values in the references		This paper	
	[41]	[7]	SSM	FIM
CN⁻	—	—	0.2	−3.2
Cl⁻	−1.4	−2.9	2.5	−1.8
I⁻	—	−1.8	1.6	−3
SO_4^{2-}	−1.5	−4.0	−2.8	−2.9
$C_2O_4^{2-}$	−1.4	−2.1	−0.2	−3.2
CO_3^{2-}	−1.6	−2.6	−1.3	−3.1
ClO_4^-	−1.9	−1.8	−1.5	−3.0
NO_3^-	−1.6	−2.4	−1.2	−1.9
Sal[a]	—	−2.3	−1.5	−3.0
OAc⁻	—	−3.2	1.8	−2.3
D.L. (p Chromate)	5.9	6	5.7	
D.R. (p Chromate)	1–5.3	1–5.6	2–5.3	
Response time (s)	13	20–25	5–10	
Stability (day)	300	60	60	
pH range[b]	6.5–10.0	8.0–12.0	6.8–10.7	
Slope (mV·decade⁻¹)	−29.0	−28.8	−29.4	
Conditioning time (h)	—	—	2	
Standard deviation	0.2	0.5	0.29	

[a]Salicylate.
[b]The pH range of the electrode response is independent of pH.

The EMF response of the electrode to different concentrations of chromate samples demonstrated a linear range from 5.0×10^{-6} to 1.0×10^{-2} ($r^2 = 0.9954$) (Figure 9). Inset of Figure 8 shows the linear segment of the response of the electrode. The slope of calibration curve was 29.4 ± 0.3 mV per decade of CrO_4^{2-} concentration.

To study the effect of modification and also the effect of nanoparticles on the potentiometric behavior of the proposed electrode, the potentiometric responses of some different membranes containing PVC alone, PVC + nanoclinoptilolite (NCP), PVC + surfactant, PVC + SMZ-clinoptilolite (SMZ-CP), and the proposed modified electrode (SMZ-NCP), were studied and the obtained results are shown in Figure 10. As results show, the membranes containing the raw PVC, nanozeolite alone, and also surfactant alone do not show a Nernstian response towards chromate. Comparing the results confirms the active component in the membranes is SMZ. According to the results, both prepared SMZs using micro- and nano-sized clinoptilolite show a Nernstian response towards chromate. But the obtained linear rang decreased when surfactant modified micro-sized clinoptilolite was used (2.0×10^{-5} to 5.0×10^{-3}, $r^2 = 0.9918$, slope = 30.36 mV per decade).

The lower and higher detection limits were 2.0×10^{-7} and 2.0×10^{-2} mol L⁻¹, respectively. The relative standard deviation (RSD) of a single electrode (within electrode variation) was also funded out ($n = 10$). The RSD was small (1.01%); the good electrode repeatability indicates that the membrane is homogeneous.

The reproducibility of the potentiometric response of the optimized electrode was also investigated by measuring
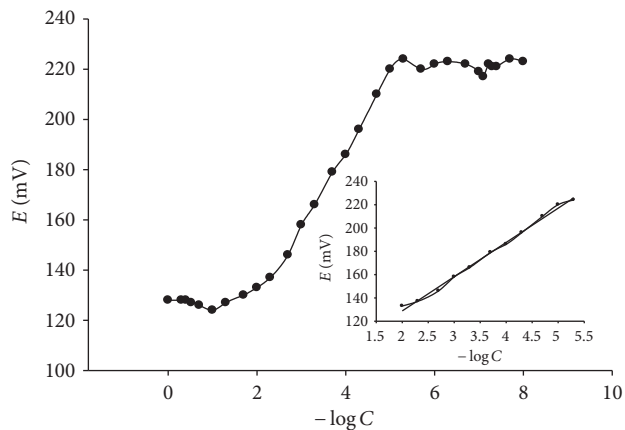
FIGURE 9: Potentiometric response of the proposed electrodes towards chromate ion (inset: linear segment (calibration curve) of the electrode response).

the response of five independent electrodes with the same composition. These measurements were also carried out in 4 replicates. The RSD (between electrode variations) was less than 2.5 % (Table 8). The validity of the results was examined by "g" value statistical testing, or a g-test [40], using the following equation:

$$g = \text{largest} \frac{s^2}{(s_1^2 + s_2^2 + s_3^2 + s_4^2)}, \tag{11}$$

where s_i^2 is the variance of each class of determinations. The calculated g value was 0.4261, which is less than the critical

TABLE 8: Potentiometric response of four independent optimized SMZ-PVC membrane electrodes.

Electrode	Slope $= \bar{x}$ ($n = 5$) (mV·decade^{-1})	r^2	RSD%	g_{exp} [a]
1	-29.9 ± 0.5	0.9903	1.7	
2	-29.3 ± 0.4	0.9841	1.4	0.4261
3	-29.3 ± 0.7	0.9900	2.4	
4	-29.3 ± 0.5	0.9883	1.7	

[a] $g_{0.05,5,4} = 0.6287$ [40].

TABLE 9: Results of analysis of determination of chromate in electroplating waste water.

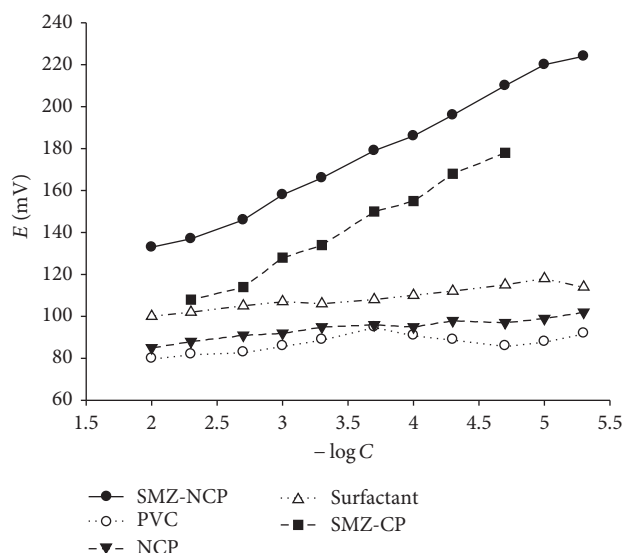| No.	Method	Cr(VI) in molar determined ($n = 6$)	t_{exp} [a]
1	Potentiometric method	0.090 ± 0.0006	1.56
2	AAS method	0.092 ± 0.0008	

[a] $t_{0.05,10} = 2.23$ [40].

FIGURE 10: Potentiometric responses of some different membranes containing PVC, NCP, HDTMA surfactant, SMZ-CP, and SMZ-NCP towards chromate.

g value at a 95% confidence interval ($g_{0.05,5,4} = 0.6287$, 5 replicates per 4 classes) [40].

As shown in Table 7, the selectivity coefficient and dynamic linear range obtained for the proposed electrode are superior in some cases and comparable to those reported previously for other chromate-selective membrane electrodes based on a variety of different ionophores. Notably, in all cases in Table 7, response time, conditioning time, Nernstian behavior (slope values), and electrode response of the independent pH range for the proposed SMZ-PVC electrode are improved compared with other reported electrodes. Additionally, the short conditioning period of the proposed electrode saves time. The RSD values obtained from analyzing the reproducibility and repeatability of the SMZ-PVC electrode confirmed that the SMZ-PVC electrode has good precision.

4. Analytical Application

4.1. Analysis of Electroplating Waste. The proposed chromate sensor was also used for determining chromium (as chromate) in wastes discharged from electroplating industry. Sample from a local electroplating unit was collected, filtered, and stored without any further pretreatment. Suitable aliquots of sample solution were analyzed, after neutralizing with NaOH within pH range 7.0–8.0. The analyses were performed by direct potentiometry using calibration plot, and the results showed the chromate content in the wastewater obtained from measurement with the sensor was found to be in agreement with that determined by atomic absorption spectrometry (AAS) (Table 9).

4.2. Potentiometric Titration. The analytical applicability of the proposed sensor has been tested by using it as an indicator electrode to find out the end point in potentiometric titration of CrO_4^{2-} with Pb^{2+}. 10 mL of 1.0×10^{-2} mol L^{-1} CrO_4^{2-} solution was brought to pH 8.0 with NaOH and then titrated with 1.0×10^{-2} mol L^{-1} Pb^{2+} solutions. Addition of Pb^{2+} to the solution precipitates Pb–CrO_4 which causes an increase in potentials as a result of decrease in the concentration of CrO_4^{2-} in the solution. The end point obtained from the potentiometric curve is sharp and corresponds to the 1 : 1 stoichiometry of $Pb^{2+} : CrO_4^{2-}$ (Figure 11). Inset of Figure 11 shows the first-derivation titration curve of electrode. Therefore, the sensor assembly can be successfully used as an indicator electrode.

5. Conclusions

The results of this work showed that the surfactant-modified zeolite when incorporated in polymeric matrix membrane preserved the anions adsorption manner. The amount of the modifier used in the membrane affected hydrophilicity and hydrophobicity properties definitely and this behavior will affect membrane response to different anions. According to this information the electrode with a composition
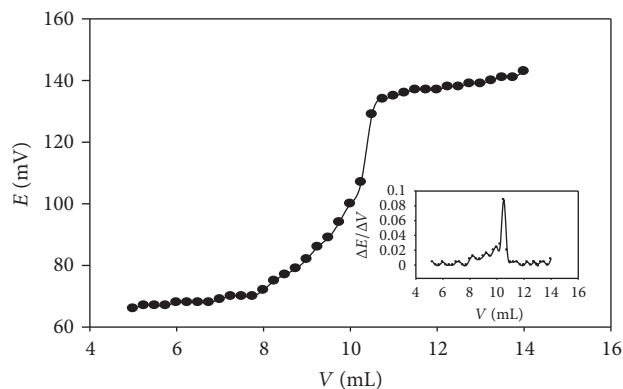
Figure 11: A potentiometric titration curve for 10 mL of a 0.01 mol L^{-1} CrO$_4$$^{2-}$ solution with 0.01 mol L^{-1} Pb(NO$_3$)$_2$ using the proposed sensor as an indicator electrode at 25°C (inset: first-derivative curve, $\Delta E/\Delta V$ versus titrant volume).

SMZ : PVC : DOP in the ratio 4 : 32 : 64 made useful quali-fication for chromate potentiometric determination among anions such as benzoate, perchlorate, chlorate, oxalate, nitrate, iodide, and cyanide. The main advantage of the potentiometric sensor is its simplicity of preparation, short conditioning time, fast response time, Nernstian behavior, and improved good selectivity. The practical utility of mem-brane sensor was demonstrated by its use as an indicator electrode in the potentiometric titration of CrO$_4$$^{2-}$ with Pb^{2+} and was successfully applied to the determination of chro-mate in real samples.

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