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A novel chromium selective electrode based on surfactant-modified Iranian clinoptilolite nanoparticles

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ABSTRACT

A novel modified hexadecyltrimethyl ammonium surfactant-modified nanoclinoptilolite electrode was constructed for the potentiometric determination of dichromate and showed a Nernstian response in the concentration range of $7.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M. A Nernstian slope of 29.7 ± 0.9 m V per decade of dichromate concentration and a detection limit of 3.1×10^{-7} M dichromate were obtained for the proposed electrode. The proposed electrode exhibited a rapid response about 10 s over a period of 2 months with good reproducibility and also without any considerable divergence in potential response. It was also applied as an indicator electrode in the potentiometric titration of dichromate.

Keywords: Ion-selective electrode; Dichromate; Surfactant-modified zeolite; Nanoparticles; Clinoptilolite

1. Introduction

Potentiometric measurements using ion-selective electrodes (ISE) for determination of various metal ions have been widely used due to their simple design, low cost, adequate selectivity, good accuracy, wide concentration range, applicability to colored and turbid solutions, and no requirement for the sample pretreatment [1–19]. In recent decades, there has been considerable growing of attention in initializing nanozeolites due to their advantages over conventional micron-sized materials, because the reduction of the particle size of zeolites causes larger external surface areas available for interaction, shorter diffusion path lengths, reducing mass and heat transfer resistances in the catalytic and sorption applications, decreasing of side reactions, enhancing selectivity, as well as lowering tendencies to coke formation in some catalytic reactions [20]. Hence, using of nanoparticles of clinoptilolite as cheap and abundant zeolite in nature [21] was subjected in this work. Although natural zeolites have been widely used to remove cationic heavy metals from aqueous solutions, they are not useful for removing different toxic inorganic oxyanions such as chromate [22]. However, by modification of the external surface of zeolites with cationic surfactants such as hexadecyltrimethyl ammonium (HDTMA), they can be suitable materials to adsorb different oxyanions. At surfactant concentrations greater than the critical micelle concentration, a bilayer or admicell can be formed on the external surface of zeolites. This causes a charge reversal on the external zeolite surface, pro-

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viding sites where anions can be retained and cations repelled [23].

Chromium can be regarded as a long-standing environmental contaminant which can release in the environment by industrial activities such as chrome plating and electroplating, pigment, metal smelting and metal lurgies to manufacture alloys, dyestuff industries, leather tanning and wood treatment [24], and also by natural processes such as: volcanic activity and weathering of rocks [25]. It exists in the environment as Cr(III) and Cr(VI) oxidation states which display different chemical properties. Cr(III) is a stable and slightly soluble cation and is considered as an essential microelement [26], while Cr(VI) is a soluble and mobile anion, known as a toxic pollutant. So, Cr (VI) causes lung cancer, nasal cavity, and par nasals sinus, and also is suspected of causing stomach cancer and larynx effects [27]. 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 the industrial and environmental fields [28,29].

As far as we know, zeolites have used in the potentiometric determination of different cationic species [30] and use of them in determination of anionic species has limited to our published works [22,23,31–35]. In this work, clinoptilolite–zeolite was pretreated and crushed by mechanical method to obtain micro-sized particles. The nanoparticles of zeolite were obtained during ball-milling process of the obtained micro-sized powder. The obtained nanoparticles were modified with HDTMA to obtain surfactant-modified zeolite (SMZ). The resulting SMZ was used to modify PVC membrane for constructing the proposed selective electrode (SMZ-PVC). The obtained electrode was used for potentiometric determination of some anionic substances. According to obtained results, the sensor showed a better response toward dichromate compared to the other anions. Finally, effect of some key experimental parameters affecting the electrode response was studied and the validity of the obtained results was proved by statistical “*t*” and “*g*” tests.

2. Experimental

2.1. Reagents

The zeolite tuffs used in this work, belong to a mineral deposit located in the Semnan region in the east–north of Iran, were purchased from Afrand Tuska Company (Isfahan, Iran). Double-distilled deionized water was prepared in our laboratory and used throughout the experiments. The polymeric matrix was prepared from high-relative molecular weight polyvinyl chloride. Reagent grade dioctylphthalate, tetrahydrofuran, and hexadecyltrimethyl ammonium bromide (HDTMABr) and all other salts (all obtained from Merck) were purchased from Normal Labo Company (Isfahan, Iran) and used without further purification. The pH of the solutions was appropriately adjusted with NaOH or HCl solution.

2.2. Preparation and modification of clinoptilolite nanoparticles.

Clinoptilolite–zeolite was crushed by mechanical method to obtain micro-sized particles. The nanoparticles of zeolite were obtained by ball-milling of the obtained micro-sized powder. To remove any water soluble impurities as well as entered magnetic impurities during the ball-milling step, the nanopowder was refluxed at 70˚C for 8 h on a magnetic stirrer ($n = 8$). The suspension was centrifuged (3,000 rpm, $2.291 \times g$, Sigma 2-16 p for 15 min), dried at 80˚C for 3 h. For preparation of SMZ, the nanoclinoptilolite powder (2 g) was mixed with 50 mL of 50, 100, and 200 mM HDTMA solutions and stirred for 24 h on a magnetic stirrer. The suspensions were then centrifuged and the resulting SMZs were air-dried and used for constructing the modified electrodes (SMZ-PVC).

2.3. Electrode preparation

The proposed membrane was fabricated by dissolving 33 mg of powdered PVC, 63 mg of DOP plasticizer, and 4 mg of SMZ in 1.5 mL THF. The resulting mixture was transferred into a glass dish to slowly evaporate THF until an oily, concentrated mixture was obtained. A Pyrex tube (1 mm o.d.) was dipped into the mixture for approximately 10 s, so that a membrane with approximately 0.5 mm thickness was formed. The tube was then withdrawn from the mixture and maintained at room temperature for approximately 2 h. A 1.0×10^{-2} M dichromate ion solution was used as the internal reference solution in the electrode.

2.4. Procedure

The SMZ–PVC membrane electrode was conditioned by soaking it in a 1.0×10^{-2} M dichromate solution for 2 h. The electrode was then rinsed with water and immersed into a measuring cell containing the dichromate solution (adjusted the pH to 4.0 by adding HCl or NaOH as appropriate) until the response of the potentiometer with respect to the Ag/AgCl reference electrode became stable (20 s). The following cell assembly was used for the potentiometric measurements at room temperature:

$$\mathrm{Ag/AgCl\ ref.\ elec.}|\ \mathrm{analyte\ solution}|\mathrm{membrane}\ |1.0\times10^{-2}\mathrm{M\ K_2Cr_2O_7,\ Ag_2Cr_2O_7}|\mathrm{Ag}$$

The ion activities were calculated according to the Debye–Huckel equation. A potentiometric titration was conducted manually under the convective mass transport provided by magnetic stirring. The data were plotted as the observed Cell-EMF vs. the logarithm of the dichromate concentration.

2.5. Characterization and apparatus

Potentiometric experiments were carried out using a 691 potentiometer (Metrohm, Switzerland). The XRD pattern of the used zeolite nanoparticles was recorded with a Bruker diffractometer, (D8 Advance, Germany) with Ni-filtered Cu Kα radiation ($\lambda = 1.5406$) in a 2θ range of 10–60°. The thermogravimetric analysis of the natural zeolite and the SMZ was carried out using a thermogravimetric analyzer (TG-DTG, Model Setaram STA, Australia). The FTIR spectra of samples were recorded in KBr pellets using a Nicolet 6700 FTIR (USA) spectrophotometer. The TEM images of samples were recorded using a transmission electron microscope S-3500N with an absorbed electron detector S-6542 (Hitachi Science System Ltd, Japan).

2.6. Dichromate measurement in real samples

Liquid sample of dichromate wastewater was prepared from an electroplating factory (Isfahan) and diluted more than 200 times, so it was located in the linear range of the electrode response. The dichromate content of the diluted sample was determined by suggested method as well as atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. Characterization of the zeolite and SMZ

Fig. 1 shows the FT-IR spectra of HDTMA and SMZ. The first group of bands in FT-IR spectra of zeolitic materials (600–1,200 cm^{-1}) comes from stretching vibrations of $\mathrm{SiO_4^{4-}}$ and $\mathrm{AlO_4^{5-}}$, while the second (1,400–1,650 cm^{-1}) and third groups (3,000–4,000 cm^{-1}) appear as a consequence of deformation and stretching vibrations in water molecules, respectively [36]. Comparison of the spectra of nanoparticles of clinoptilolite (NCP) and SMZ shows the presence of new bands at 2,849, 2,919, and 1,483 cm^{-1} in spectrum of SMZ. These bands correspond to C–C, C–H, and C–N vibrations of HDTMA and confirm the loading of HDTMA onto the zeolite surface.

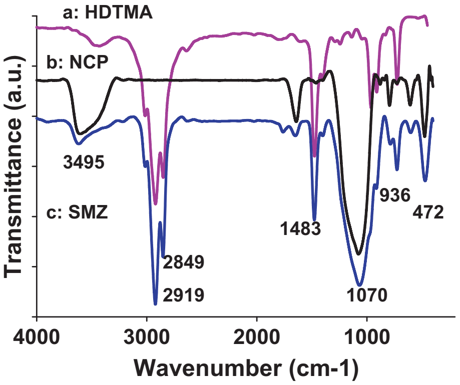

Fig. 1. FT-IR spectra of (a) clinoptilolite, (b) HDTMA, and (c) SMZ.

Fig. 2 shows the XRD pattern of nanozeolite particles. Characteristic peaks at 2θ values of 10.0°, 22.7°, and 30.0° are in good agreement with the characteristics lines of the reference clinoptilolite in the library of the instrument (JCPDS No. 39-1383). XRD pattern also showed that the used zeolite tuff includes slight amounts of quartz (3.2%) and cristobalite (7.1%) phases as impurities. The average crystallite size of sample was determined in the range of 25–40 nm using Scherrer equation [23] as follows:

$$d = k\lambda/\beta\cos\theta \tag{1}$$

where d is the relative crystallite diameter of units in nm, β is the excess of width line of the diffraction peak in radians, K is the fixed digit between 0.6 and 1.2, λ is the wavelength of X-ray in nm and the Bragg angle in degrees.

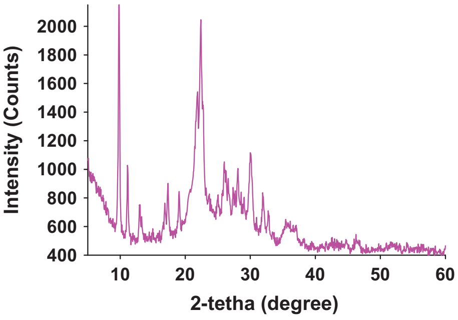

Fig. 2. XRD pattern of the nanozeolite clinoptilolite (pattern "a": reference pattern of clinoptilolite in the instrument).

On the basis of TG/DTG thermograms, in Fig. 3 it can be observed that the mass–loss curve was continuously decreased until it leveled off at a temperature near 600°C for used nanoclinoptilolite. The DTG curve of the zeolite showed two maximum at temperatures before 150°C due to the loss of physically adsorbed water and also water between particles. The water found within the zeolite structure is known as zeolitic water and its peak appears at a temperature close to 200°C. Gottardi and Galli [37] have reported the TG/DTG curves for different clinoptilolite samples from different deposits. Our results are in good agreement with their results. In TG/DTG curve of SMZ, in addition of water removal peaks, there is also another weight loss peak at 250°C which confirms the removal of HDTMA molecules from the SMZ surface. The weak peaks at 440 and 540°C correspond due to the further decomposition of the surfactant. This analysis confirms loading of HDTMA and formation of double layer on the zeolite surface. According to the TG/DTG results, the total mass–losses of 10.3 and 14.5% were obtained for the raw nanoclinoptilolite and the related SMZ, respectively. These results are in accordance with the FTIR results confirming the loading of HDTMA on the zeolite surface.

The surface morphology of the natural zeolite and SMZ particles were studied by SEM. This analysis revealed information about the details of the surface and morphology of the particles. Fig. 4(a) presents the corresponding image of natural zeolite that displays partially developed crystalline laminar habits and conglomerates of compact crystals different from those of the zeolite crystals that correspond to certain impurities such as quartz. In addition, crystals with a tabular habit which is typical of clinoptilolite are observed as well as the presence of a large variety of crystal and particle sizes. Fig. 4(b) shows the corresponding image of the SMZ, but the observed crystals in Fig. 4(a) cannot be seen clearly, because of the adsorption of the surfactant molecules on the external surface of the zeolite crystals. The average particle size of SMZ was estimated to be less than 100 nm as shown in the corresponding TEM image in Fig. 4(c). As shown by loading the surfactant onto zeolite surface, the dimensions of original clinoptilolite remained below 100 nm.

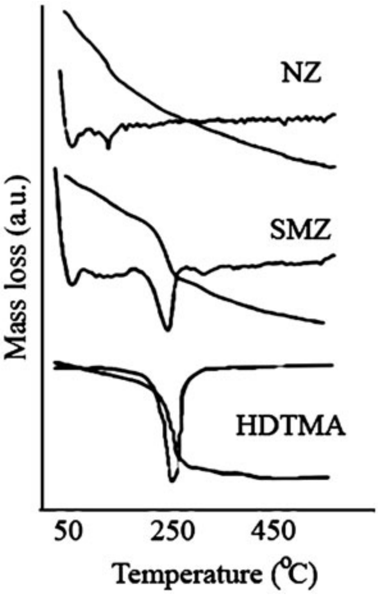

Fig. 3. Thermogravimetric analysis curves for NZ, HDTMA, and SMZ.

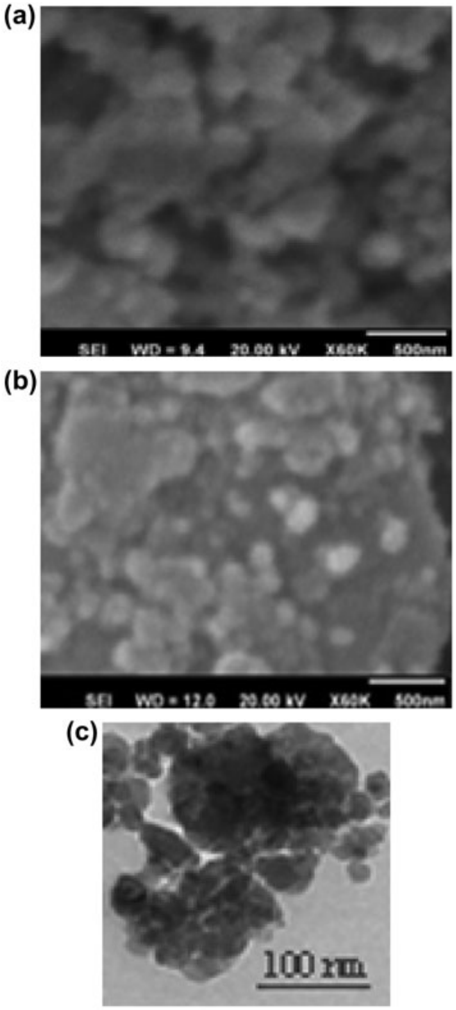

Fig. 4. SEM photographs: (a) NZ, (b) SMZ, and TEM image of (c) SMZ.

Table 1
Optimization of the concentration of HDTMA and electrode ingredient on the response of the electrode

Optimization of the concentration of HDTMA for dichromate-selective electrode based on SMZ = 10%

Electrode	C_{HDTMA} (mM)	Slope (mVdecade^{-1}) ($n = 5$)	t_{exp}
A	50	47.1 ± 1.8	25.4
B	100	29.0 ± 1.1	0.9
C	200	39.0 ± 0.7	16.1

Effect of SMZ–PVC membrane composition on the potentiometric behavior of the dichromate-selective electrode, SMZ = 10%, at 25˚C. ($n = 5$)

No.	PVC %	SMZ %	DOP %	Slope (mV decade^{-1})	t_{exp}
1	32.7	2.0	65.3	16.3 ± 1.5	16.8
2	32.0	4.0	64.0	41.7 ± 0.1	7.2
3	31.3	6.0	62.7	39.2 ± 0.6	5.4
4	30.0	10.0	60.0	30.0 ± 4.0	1.8

Note: $t_{0.05,4} = 2.78$ (Ref. [39]).

3.2. Optimization of the electrode composition

Based on the potentiometric results, the best response, E_{cell} vs. log concentration, was obtained for dichromate among the investigated mono and divalent anions (Fig. 5). Since dichromate is the predominant form of Cr(VI) at the used conditions, the sorption mechanism can be shown by the exchanging of dichromate anions in the test solution with bromide anions in the exchange sites of the SMZ in the membrane ($R_4N^+Br^-$ in SMZ). In the next step, the concentration of the surfactant on the electrode response was studied (Table 1). As shown, only the modified electrode, containing the SMZ prepared in 150 mM HDTMA solution (SMZ-150), showed the best Nernstian behavior. In 50 mM HDTMA solution, a bilayer may be formed partially at the zeolite surface and the obtained SMZ is not suitable for $Cr_2O_7^{2-}$ adsorption (case A in Table 1). Non-Nernstian behavior of electrode C shown in Table 1 (SMZ prepared at 200 mM HDTMA solution) can be related to formation of a partially bilayer on the zeolite surface. On the other hand, at high HDTMA concentrations, more micelles form in the solution instead of zeolite surface and hence an incomplete double layer will form onto the zeolite surface. Consequently, the obtained SMZ does not respond appropriately to $Cr_2O_7^{2-}$. This completely agrees with the results which were obtained by Wingenfelder et al. [38] for antimonite sorption. The validity of the obtained results was statistically performed by "t-test." Comparing the t_{exp} and its critical value at 95% confidence interval ($t_{0.05,4} = 2.78$) showed that the electrode response was limited by random errors when the (SMZ-150) was used for constructing the electrodes [39].

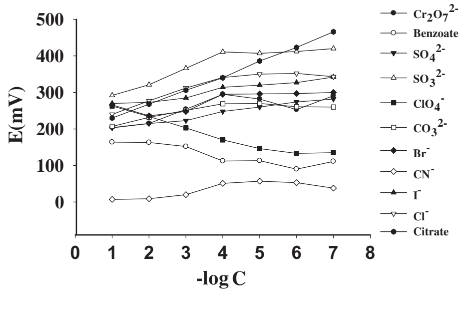

Fig. 5. The electrode response to various anions, SMZ = 10%, ($n = 10$), at 25˚C.

The sensitivity and selectivity of ISEs for a species depend not only on the ionophore but also on the type and percentage of the membrane ingredients [40,41]. Thus, the influence of the membrane composition on the potential response of the electrode was investigated. For this goal, several membranes were prepared with different compositions and corresponding results are summarized in Table 1. As shown, the best response was observed with the membrane composed of the following ingredients (optimized electrode): 30% PVC, 60% DOP, and 10% SMZ confirm that the potentiometric response of the electrode towards dichromate anion depends on SMZ content of the membrane. By changing the amount of the SMZ from 10%, a non-Nernstian behavior in the electrode response was observed. Further addition of the SMZ worsened the electrode response, most probably due to saturation of the membrane or due to some non-uniformity of the membrane. Statistical comparison of the Nernstian and experimental slopes at 95% confidence interval also showed that random errors affect the electrode behavior for the membrane containing 10% SMZ and other cases were limited by systematic errors.

At the next step, the effect of internal reference solution was investigated. The concentration of the internal solution ($K_2Cr_2O_7$) in the electrode was changed from 1.0×10^{-5} to 1.0×10^{-2} M and the EMF–$pCr_2O_7^{2-}$ plots were obtained. The results found that the variation of the concentration of the internal $K_2Cr_2O_7$ solution did not cause any significant difference in the Nernstian behavior of the electrode except an expected change in the intercept of the resulting plots. Hence, a 1.0×10^{-2} M $K_2Cr_2O_7$ was used for the next studies. Different conditioning times covering the range from 2 to 48 h were also studied on the potentiometric behavior of the proposed electrode. The best Nernstian response was observed at conditioning time of 2 h which counts a short time and a good characteristic for the proposed electrode. On the other hand, the electrodes can be kept in open air when not in use and it will rapidly re-condition in adequate dichromate solution. This makes comfortable the preservation condition of the electrode when it not in use.

3.3. Effect of pH

The pH of the test solution plays an important role on equilibrium concentration. On the other hand, the type of dichromate ($Cr_2O_7^{2-}$)/ bichromate ($HCrO_4^-$)/chromate ($CrO_4^{2-}CrO_4{}^{2-}$)/chromic acid (H_2CrO_4) species present in aqueous solution as predominant species significantly depend on pH. Hence, it is desirable that pH affects the potentiometric response of the proposed electrode in determination of dichromate. In this point of view, effect of the pH of test solution on the response of the electrode was studied by two different ways. First, the effect of pH on the potential response of the electrode was studied. The potential of the system as a function of solution pH was recorded in solutions of 1.0×10^{-2} and 1.0×10^{-4} M of dichromate (Fig. 6). As shown, the potential response remained almost constant over a pH range of 3.0–9.0 in 1.0×10^{-4} and 1.0×10^{-2} M dichromate solutions. Inset of Fig. 6 shows the distribution of different forms of dichromate/chromate as a function of pH [42]. Although, $HCrO_4^-$ is greater than $Cr_2O_7^{2-}$ ions at $pH \leq 6$, but, according to our results, the proposed electrode has much tendency to $Cr_2O_7^{2-}$ due to higher charge density of $Cr_2O_7^{2-}$. On the other hand, $Cr_2O_7^{2-}$ has better interaction with SMZ in the membrane. In severe acidic and basic pHs, sharp deviations appear from the plateau region, because of the presence of another species of Cr (VI) in these conditions which have different behaviors on the SMZ. Partial destruction of the zeolite lattice and interference from Cl^- in sever acidic media [23], and also interference from OH^- in severe basic pHs are another reasons for these deviations.

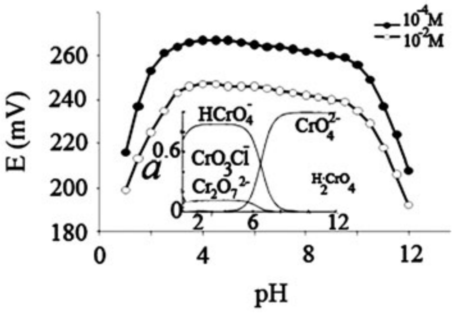

Fig. 6. The influence of pH on the potential response of the optimized PVC-SMZ electrode for a 1.0×10^{-2} and 1.0×10^{-4} M dichromate solution at 25˚C, SMZ = 10%.

The solution pH affects also the surface charge of the SMZ and the correspond membrane. The point of zero charge for the similar SMZ has reported 8 [43]. On the other hand, the SMZ surface has negatively charged at $pH > 8$ and hence the anionic Cr(VI) species can be repelled by the SMZ surface. In contrast, the SMZ surface has positively charged at $pH < 8$ and the anionic Cr (VI) species in solution can be attracted by the SMZ surface. Due to stronger interaction between $Cr_2O_7^{2-}$ and SMZ, in rather acidic pHs (4–6), the electrode has more tendency to this anionic species of Cr(VI).

In the second method, the effect of pH was studied on the experimental potentiometric slopes. The results are summarized in Table 2 which shows the best responses in the pH range of 3–5. The results also show that the electrode responses affected by random errors in this range while systematic errors can limit the electrode response out of this range. In the previous work [22], Cr(VI) as chromate species was determined by the SMZ-modified electrode. The electrode showed Nerstian behavior in the pH range of 7–10 because in this pH range, Cr(VI) is present as chromate in aqueous solution.

3.4. Effect of temperature

According to Nernst equation, temperature of the used media can affect the potential response of ISEs. To investigate the thermal stability of the electrode, calibration curves (E_{cell} vs. log [$Cr_2O_7^{2-}$]) were constructed at different temperatures covering the range from 20 to 60˚C. As shown in Table 2, the electrode exhibited good Nernstian behavior in the range of 20–

Table 2
Effect of pH and temperature on the response of the electrode, SMZ = 10%, at 25˚C

Effect of pH

pH	Slope (mV decade^{-1})	R^2	t_{exp}
2	18.0 ± 1.9	0.9921 ± 0.0213	11.3
3	28.9 ± 0.9	0.9895 ± 0.0214	1.7
4	29.1 ± 1.1	0.9976 ± 0.0112	0.3
5	30.1 ± 1.3	0.9891 ± 0.0141	0.9
6	21.2 ± 2.2	0.9862 ± 0.0011	4.9
8	23.2 ± 0.8	0.9942 ± 0.0009	3.7

Effect of temperature

Temperature (˚C)	Nernstian slope (mV decade^{-1})	Exp. slope (mV decade^{-1})	t_{exp}
20	29.0	29.1 ± 0.9	0.93
25	29.2	30.1 ± 1.1	1.21
30	30.0	30.3 ± 1.5	0.11
35	30.5	30.6 ± 0.8	0.46
40	31.5	31.8 ± 0.5	2.32
50	32.0	33.1 ± 1.9	3.65
60	35.3	35.5 ± 2.0	9.45

Note: $t_{0.05,4} = 2.78$ (Ref. [39]).

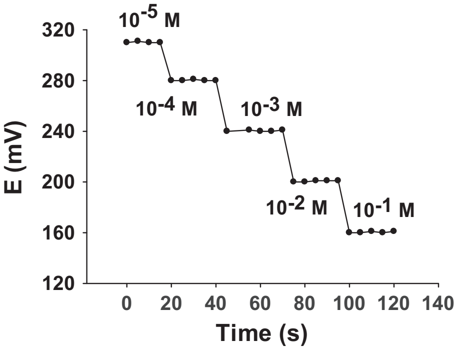

Fig. 7. The response times of the optimized PVC-SMZ electrode for stepwise changes in the concentration of dichromate ranging from 1.0×10^{-5} to 1.0×10^{-1} M at 25˚C (low to high investigation and high to low studies), SMZ = 10%, (n = 10), at 25˚C, pH = 4.

40˚C. The Nernstian and experimental slope values were compared statistically, showing conformity of the slopes for five replicates. The results show that the electrode responses can be affected by random errors in temperature range of 20–40˚C. However, at temperatures higher than 40˚C, the slopes significantly deviate from the theoretical values which may be related to desorption of the surfactant from SMZ and destruction of the electrode surface.

3.5. Response time

The static response time for any sensor is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential, upon successive immersion of a series of interested ions, each having a 10 fold difference in concentration. The response time of any sensor is affected by experimental parameters including [44]. Fig. 7 shows the response time of the proposed ion selective electrode when the concentration of dichromate was changed from 1.0×10^{-5} to 1.0×10^{-1} M. As the results show, the response of the electrode reaches to equilibrium before 10 s which is a fast response time.

3.6. Selectivity of the electrode

Selectivity of any ion selective electrode is its ability to distinguish a particular ion from any other interfering ions [31]. The selectivity coefficients, $K^{pot}_{A,B}$, were determined by fixed interference method (FIM) and SSM methods [45]. The obtained results are shown in Table 3. The selectivity coefficients by SSM were calculated using the following equation:

$$\log K^{pot}_{Cr} = n \cdot F\,(E_j - E_i)/2.303\ \mathrm{RT} + \log\,(a_i/a_j^{n/m}) \qquad (2)$$

Table 3
Comparison of some potentiometric characteristics of the dichromate ISE described in this work with previously published reports [5,26–29]

	log k values in the references:					This work	
Interfere anions	5	46	47	48	49	SSM	FIM
ClO_4^-		−2.15	−3.0	−1.2		−1.38	−2.61
CN^-				−3.0	−1.2	−3.91	−3.84
Cl^-Cl^-	−2.25		−3.6	−4.3	−1.9	−2.8	−3.7
HPO_4^{2-}			−3.8			−3.91	−3.67
SO_4^{2-}	−3.70	−4.5	−3.3	−4.0	−3.1	−2.46	−3.52
CO_3^{2-}				−3.3	−1.7	−2.26	−4.29
$S_2O_3^{2-}$				−3.6	−2.8	−1.92	−3.38
NO_3^-	−.57	−3.0	−3.9	−1.2	−1.8	3.0	−3.50
AsO_3^{3-}						−2.1	−3.61
D.L. (M)	1.2×10^{-6}	4.3×10^{-8}	1.0×10^{-6}	3.0×10^{-6}	2.5×10^{-6}	3.1×10^{-7}	
L.R. (M)	1.0×10^{-6} -2.16×10^{-6}	1.0×10^{-1} $- 1.0 \times 10^{-7}$	1.0×10^{-1} -1.0×10^{-6}	1.0×10^{-1} $- 3.0 \times 10^{-6}$	1.0×10^{-1} $- 5.2 \times 10^{-6}$	7.0×10^{-6} -1.0×10^{-1}	
Response time (s)		15–20s	23s	5–10s	>30s	10s	
Stability (months)	6	14	6	2	2	2	
pH range	3.5–5	3–5	4		6.5–10.5	4–6	
Slope (mV decade^{-1})	51.6	41.5	52.6	28.6	28.8	29.7	

where K_{cr}^{pot} is the potentiometric selectivity coefficient, E_i is the measured cell potential at primary ion activity ($Cr_2O_7^{2-}$), E_j is the measured cell potential at interference ion activity a_i, n and m are the charges of the primary and interference ions, respectively, and R, T, and F are the gas constant, temperature, and Faraday's constant, respectively. Cell potentials at a 0.01 M concentration were used to calculate the selectivity coefficients. The interfering effect of the ions is in the following order:

$$ClO_4^- > S_2O_3^{2-} > NO_3^- > SO_4^{2-} > ASO_3^{3-} > -HPO_4^{2-} > Cl^- > CN^- > CO_3^{2-}$$

The selectivity of the electrode toward many inorganic anions was also determined by the FIM. This method measures the potential of the electrode in a series of solutions containing a fixed activity of the interfering anion (0.1 M) and varied concentrations of analyte (in this work dichromate in the range of 1.0×10^{-6}–1.0×10^{-1} M). The calibration curve, E_{cell} vs. logarithm of the activity of dichromate, log a_j, was constructed. The intersection of the extrapolated linear segments of this plot indicated the value of a_i that can to be used to calculate selectivity coefficients by the following equation:

$$\log K_{Cr}^{pot} = a_i / a_j^{(zi/zj)} \quad (3)$$

where z_i and z_j are the charges of measuring and interfering anions, respectively. In Table 3, the selectivity coefficients and response characteristics of the SMZ-PVC electrode are compared with other dichromate selective electrodes [5,46–49]. Selectivity coefficients indicate that interfering ions could not significantly interfere in the determination of $Cr_2O_7^{2-}$ by proposed electrode. Interestingly, the observed selectivity pattern differs from the Hofmeister selectivity sequence [50]. The following sequence was obtained in FIM studies:

$$ClO_4^- > S_2O_3^{2-} > HA_sO_3^{-2} > CO_3^{2-} > SO_4^{2-} > Cl^- > NO_3^- > CN^- > HPO_4^{2-}$$

3.7. Life time

The life time is one of the most important factors for any sensors. The average life time of different ion-selective sensors has been reported in the range of 4–10 weeks and after this period the slope and detection limit of the sensor will drastically change (decreasing in the slope and increasing in the detection limit) [51]. The life time of the proposed dichromate PVC-membrane electrodes was tested for 70 d and the results are given in Table 4. Statistical comparison of the results by t-test shows that significant changes in the slopes were happened after 60 d. Thus, the proposed PVC membranes can be used for at least 8 weeks.

Table 4
Effect of lifetime and real sample analysis

The life time of the proposed dichromate-selective electrode, SMZ = 10%, ($n = 5$), at 25˚C, pH = 4

Time	Linear range (−log C)	Slope (mV decade^{-1})	R^2	t_{exp}
2 h	2–6	29.2 ± 0.1	0.9862 ± 0.0036	0.592
3 h	2–6	29.8 ± 0.0	0.9866 ± 0.0042	0.698
10 h	2–6	30.0 ± 0.1	0.9824 ± 0.0057	0.074
16 h	2–6	30.1 ± 0.2	0.9945 ± 0.0023	0.637
1 d	2–6	29.7 ± 0.1	0.9934 ± 0.0047	0.446
7 d	2–6	29.9 ± 0.4	0.9972 ± 0.0025	0.223
30 d	2–6	29.2 ± 0.3	0.9951 ± 0.0039	0.415
60 d	2–6	28.6 ± 0.2	0.9582 ± 0.0036	0.658
70 d	2–5	24.3 ± 0.7	0.9238 ± 0.0085	3.345

Results of dichromate analysis in an electrolysis wastewater sample ($n = 3$), SMZ = 10%, at 25˚C

ISE (M)	AAS (M)	t_{exp}
4.74 (±0.9) × 10^{-4}	4.63 (± 0.3) × 10^{-4}	2.35

Note: $t_{0.05,4} = 2.78$ (Ref. [39]).

During this time, a slight gradual decrease in the slopes was observed (from 29.2 to 24.3 mV per decade). It is well known that the loss of plasticizer, carrier, or ionic site from the polymeric film, due to leaching into the solution, is a primary reason for the limited lifetimes of the sensors [46].

3.8. Analytical applications

To apply the proposed electrode for determination of dichromate in real samples, an attempt was made to determine dichromate in an industrial wastewater sample, using the standard addition method. The concentration of dichromate in the resulting solution was determined by AAS, as the reference technique. The results indicated a close agreement between the concentration of dichromate determined by the proposed potentiometric and reference methods (Table 4). The results indicate that $\bar{x}_2 - \bar{x}_1 < ts_{\text{pooled}}\ \sqrt{(N_1 + N_2)}/(N_1 \times N_2)$, which means that there is no significant difference between the obtained averages by two methods at 95% confidence level. The small difference between the two methods arises from random errors; therefore, the proposed electrode can be successfully applied to determine the dichromate at concentrations normally present in some water samples.

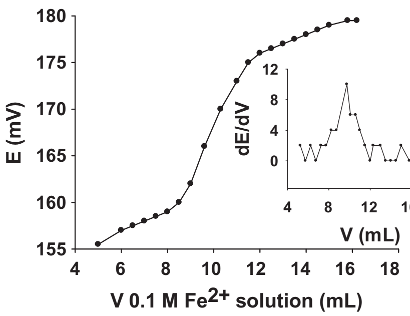

Fig. 8. A typical potentiometric titration curve for 20 mL of a 0.01 M $Cr_2O_7^{2-}$ solution with 0. 1 M Fe^{2+} using the proposed sensor as an indicator electrode at 25˚C, SMZ = 10%.

In addition, the sensor was used for the potentiometric titration of $Cr_2O_7^{2-}$ with Fe^{2+} in a oxidation–reduction titration. Typical results for titration of a 20 mL aliquot of 0.01 M (0.05 N) dichromate solution with 0.1 M Fe^{2+} solution had a very good inflection point, showing perfect stoichiometry as observed in the titration plot (Fig. 8). Inset of Fig. 8 shows differential titration curve to obtain an accurate and precise end point.

Some characteristics of the proposed electrode have compared to other Cr(VI) electrodes in Table 3. As shown, in some cases, selectivity coefficient, response time, stability, electrode response-independent pH range, dynamic linear range, and detection limit that were obtained for the proposed electrode are superior and comparable to those reported previously for other Cr(VI) selective membrane electrodes based on variety of different ionophores. Also, using natural zeolite and ball-mill production of clinoptilolite nanoparticles are cost effective and in agreeing to the goal of green chemistry with respective to synthetic one because of eliminating the synthesis method.

4. Conclusion

The incorporation of cationic surfactants onto the zeolite surfaces changes the charge of the zeolite surface, thus creating suitable anionic exchangers. Combining these SMZs with PVC-based membranes yields a suitable membrane electrode for the determination of anions such as dichromate. The obtained electrode exhibited response characteristics (i.e. Nernstian sensitivity, broad linear range, low detection limit, fast response, and good selectivity) that are in most cases comparable or even superior to those reported for other dichromate ISE in literature. The proposed assembly was employed as an indicator electrode in the potentiometric titration of dichromate ions.

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