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Modification of carbon paste electrode by surfactant-modified ZSM-5 nanozeolite for potentiometric determination of sulfate

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ABSTRACT

Carbon paste electrode (CPE) was modified by cetyltrimethyl ammonium bromide (CTAB) surfactant-modified ZSM-5 nanozeolite (SMNZ). The Fourier transform infrared and SEM techniques indicated that the fabricated electrode was successfully modified by CTAB surfactant and ZSM-5 nanozeolite. The electrochemical behavior of the modified electrode was considered for determination of sulfate using potentiometric technique. The influence of some parameters, such as different mass ratio of ZSM-5 nanozeolite and graphite, surfactant concentration, ionic strength, pH, and temperature, was investigated on the potentiometric response of modified electrode (SMNZ/CPE), which was demonstrated to be independent of the solution pH in the range 4.0–9.0 and remained constant in presence of 1.0×10^{-4}–1.0×10^{-3} M $NaNO_3$. In additon, the best Nernstian response occurred at room temperature (25°C) and with SMNZ containing 15% ZSM-5 nanozeolite, which was prepared at 80 mM CTAB. Under optimal conditions, in a buffer solution, the voltage decreased linearly with the concentration of sulfate ion and discovered Nernstian behavior over wide SO_4^{2-} ion concentration range (1.00×10^{-6}–1.00×10^{-2} M) with slopes of 29.2 mV per decade and low detection limits of 4.1×10^{-7} M. This fabricated electrode has advantages of low resistance, very fast response, and good selectivity relative to a wide variety of other anions. Such an electrode was used as an indicator in determination of sulfate in two kinds of mineral water and a ferrous sulfate tablet.

Keywords: CTAB-modified ZSM-5 nanozeolite; CPE-modified electrodes; Potentiometric technique; Sulfate determination

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1. Introduction

The determination of trace quantities of anionic species by simple methods is of critical importance in chemical, clinical, and environmental analyses. Potentiometric sensors prepared by coating polymeric films containing electroactive species on metallic or graphite conductors with no internal electrolyte solution are known to be very effective in determination of a variety of cations and anions [1]. Sulfate is a highly widespread anion, and its determination has been a significant task in environmental, such as sweet and mineral water, atmospheric precipitation (in particular acid rain) in various products, and raw materials of chemical and pharmaceutical industry. Shamsipur et al. [2] applied a Schiff base complex of Zn(II) as a neutral carrier for highly selective PVC membrane sensors for the determination of sulfate ion. They reported that this electrode has a Nernstian slope of 29.3 mV per decade and a detection limit (DL) of 8.5×10^{-8} M. Also, Soleymanpour et al. [3] reported a chemically modified carbon paste electrode (CPE) based on chromium(III) Schiff base complex for this goal. Application of surfactant-modified zeolite (SMZ) (13X) CPE towards potentiometric determination of sulfate ion was reported by Nezamzadeh et al. [4]. They were stated that this electrode has a Nernstian slope of 29.8 mV per decade and a DL of 2.0×10^{-6} M.

The CPE and chemically modified carbon paste electrodes (CMCPEs) are extensively used in various fields of electrochemistry [5–7]. In comparison with ion-selective electrodes based on polymeric membranes, CMCPEs own advantages such as ease of preparation and regeneration, stable response and very low Ohmic resistance [8]. Although, considerable attention has been given to the preparation of CMCPEs, the applications of these electrodes have been focused on the voltammetric techniques [9–13] and only a few of these electrodes have been used as potentiometric sensors [3,6,14–18]. Moreover, most of the reported potentiometric CPEs were cation-selective electrodes and only few papers have reported about anion-selective electrodes [19,20]. Rolison [21] and Walcarius [22] have reviewed the zeolite-modified electrodes. Moreover, applications of surfactant-modified zeolites to environmental remediation were reviewed by Bowman [23].

Zeolites and related nanoporous materials are characterized by high specific surface areas and high cation exchange capacities. Their rigid three-dimensional structures make them free of the shrink/swell behavior associated with smectite clays [23,24]. Zeolites have been particularly useful in removing cationic species, such as ammonium and some heavy metals, from water. The negative charge of zeolites is appropriate for surface modification of nanozeolites using cationic surfactants, namely the quaternary amine cetyltrimethyl ammonium bromide (CTAB). When surfactant concentration is greater than the critical micelle concentration, the adsorbed surfactant molecules primarily form a bilayer on the zeolite external surfaces [25]. This bilayer formation results in a charge reversal on the external zeolite surface, providing sites where anions will be retained and cations repelled, meanwhile neutral species can partition into the hydrophobic cores [4,23,26]. The resultant SMZ is stable in water and aggressive chemical solutions, and is capable of simultaneous sorption of anions, cations, and non-polar organic molecules from water [23]. Its relatively low cost makes it a viable alternative to other reactive media, such as activated carbon and ion exchange resins [27].

In respect of literature survey, no ZSM-5 nanozeolites were employed hitherto for modification of CPE for potentiometric determination of sulfate anion. In this study, ZSM-5 nanozeolite was modified with CTAB surfactant and the resulting surfactant-modified nanozeolite (SMNZ) was used for modification of CPE to produce SMNZ/CPE, which was then used as a new potentiometric sensor for determination of sulfate anion.

2. Materials and methods

2.1. Reagents and materials

Sodium sulfate, sodium nitrate, sodium nitrite, sodium hydroxide, potassium chloride, potassium iodide, disodium monohydrogen phosphate, monosodium dihydrogen phosphate, and phosphoric acid were analytical reagent grade and obtained from Merck Company (Darmstadt, Germany) and used without further purification. The CTAB was purchased from Fluka Company. Double distilled water was used throughout. Graphite powder and paraffin oil (density 0.88 $\mathrm{g\,cm^{-3}}$), as the binding agent (both from Dayjung company), were used for preparing the pastes. The ZSM-5 nanozeolite was synthesized in our laboratory and was reported in our previous work [28]. This synthesized nanozeolite has spherical nanosized particle with average diameter of 97 nm. Some data for characterization of synthesized ZSM-5 nanozeolite are presented in Table 1. To prepare SMNZ, the 0.1 g of ZSM-5 nanozeolite was mixed with 5 mL of 10, 40 and 80 mM CTAB solutions in separate flasks, and stirred for 24 h on a magnetic stirrer. Then, the mixture was centrifuged at 10,000 rpm for 20 min and the resulting SMNZ was dried in air.

Table 1
Data extracted from XRD pattern, IR spectrum, and SEM image of ZSM-5 nanozeolite

Peak position in XRD pattern	Absorption frequency in IR spectrum	Crystal shape	Size	Ref.
2θ = 7.9°, 8.9°, 23.2°, and 24.5°	3,470, 1,219, 1,200, 1,080, 833, 790 and 542 cm^{-1}	Spherical	97 nm	[4]

A stock solution of sulfate anion (0.1 M) was prepared by dissolving 1.4204 g of sodium sulfate in water and the solution was diluted to mark with double distilled water in a 100-mL volumetric flask. Working solutions were prepared in the cell by addition of appropriate amounts of stock solution to the appropriate amount of phosphate buffer solution. Phosphate buffer solutions, PBS, (orthophosphoric acid, disodium monohydrogen phosphate, sodium dihydrogen phosphate, and sodium hydroxide 0.1 M) with different pH values were used in the pH range of 1.0–12.0.

2.2. Apparatus

Scanning electron microscopy (SEM, model MIRA-TESCAN) was employed to study morphology and shape of the electrodes. The Bruker Fourier transform infrared (FT-IR) spectrometer (Vector 22) was used for recording FT-IR spectrum at room temperature. Potentiometric experiments were performed at room temperature using a 691 potentiometer (Metrohm, Switzerland) in a two-electrode configuration. The CPE, modified carbon paste electrodes with ZSM-5 nanozeolite (NZM/CPE), and surfactant-modified ZSM-5 nanozeolite (SMNZ/CPE) were used as working electrodes. The Ag|AgCl|KCl (3 M) electrode was used as a reference one. The Microprocessor pH meter, (pH 211, Romania) model glass electrode was employed for measuring pH values of the aqueous phase.

2.3. Preparation of modified electrode

For preparation of (SMNZ/CPE), an appropriate amount of the obtained SMNZ (10, 15, and 20% wt. with respect to graphite) was mixed with 200 mg of graphite powder, and then paraffin oil (35% wt.) was blended with the mixture in a mortar by hand mixing for 30 min until a uniformly wetted paste was obtained. This paste was packed into the end of a glass tube (*ca*. 3.5 mm i.d. and 10 cm long) with a copper wire as electrical contact. This proportion was used because a better response was obtained in a preliminary test; however, a more detailed study about the paste composition should be made. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing with a weighing paper. For comparison, ZSM-5 nanozeolite-modified CPE electrode (ZSM-5/CPE) in the absence of CTAB and unmodified CPE in the absence of ZSM-5 and CTAB were also prepared in the same way.

2.4. Procedure

The SMNZ/CPE electrode was polished on a soft paper and rinsed with water. This electrode was immersed into the measuring cell containing sulfate at desired pH (adjusted by addition of HCl or NaOH solution) and the equilibrium potential was recorded after 30 s. All potentiometric measurements were conducted at room temperature. The electrode was kept in open air when was not in use. The activities of ions were calculated according to Debye–Huckel theory [29]. Potentiometric titration was conducted manually under convective mass transport provided by magnetic stirring. The end point was calculated by differentiation of the titration curve.

2.5. Determination of sulfate in two kinds of mineral water and a pharmaceutical ferrous sulfate tablet

The SMNZ/CPE was utilized for the determination of sulfate anion in Damavand and Nava mineral waters and a pharmaceutical ferrous sulfate tablet. Preparation of ferrous sulfate tablet solution was carried out according to the following procedure: 10 tablets of ferrous sulfate (from Daropakhsh Pharmaceutical Company, Tehran, Iran) were powdered in a mortar and a weight equivalent of one tablet was dissolved in 50 mL of distilled water. After 30 min of stirring and 15 min of standing in the dark, the solutions were filtered for removing of any probably undissolved species and diluted to mark in a 50-mL volumetric flask. The sulfate content of this solution was then determined by proposed method.

3. Results and discussion

3.1. Characterization of the SMNZ

FT-IR spectra of CTAB surfactant, ZSM-5 nanozeolite, and SMNZ were recorded using KBr pellets, as can be seen in Fig. 1. The IR spectrum of SMNZ displays characteristic peaks at 2,922, 2,845, and 1,525 cm^{-1} suggesting the incorporation of CTAB into the nanozeolite structure. Comparison of CTAB and ZSM-5 spectra shows a slight shift in peaks at each wavenumber; however, both of the patterns are nearly the same. Particularly, the presence of peaks at 2,922, 2,845, and 1,525 cm^{-1} in SMNZ spectrum (related to C–H, C–C, and N–C vibrations in the surfactants, respectively), that are not observed in the ZSM-5 nanozeolite spectrum [28,30], can confirm successful loading of CTAB on ZSM-5 nanozeolite.

Fig. 2 displays SEM images of CPE, ZSM-5/CPE, and SMNZ/CPE (2a–2c, respectively). As can be seen in Fig 2(a), the layer of irregular flakes of graphite powder was present on the surface of CPE, which are isolated from each other [31]. After addition of ZSM-5 nanozeolite or SMNZ to the carbon paste, it can be seen that the ZSM-5 nanozeolite and/or SMNZ were distributed on the surface of the electrode with a special three-dimensional structure (Fig. 2(b) and (c)), indicating that the ZSM-5 nanozeolite or SMNZ were successfully modified at the surface of ZSM-5/CPE and SMNZ/CPE.

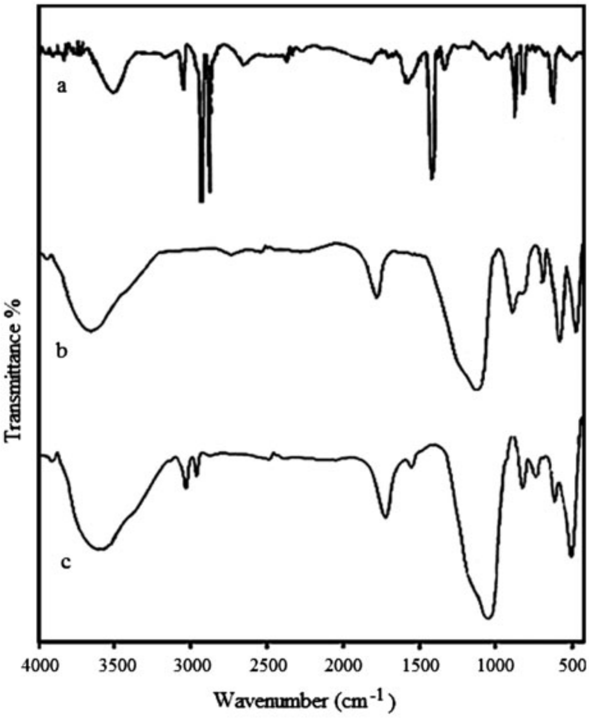

Fig. 1. FT-IR spectra of (a) SMNZ, (b) ZSM-5 nanozeolite, and (c) CTAB.

3.2. Theoretical considerations of SMNZ

As previously mentioned [23–26], the SMNZ can be used for sorption of anionic species. This is based on the following theoretical model. At low concentrations, CTAB can form a monolayer on the nanozeolite surface with the hydrophobic ends of the molecules turned toward the solution. With increasing coverage, a second CTAB layer is also made. This bilayer structure causes arrangement of positively charged functional groups toward the solution, which can serve as sorption sites for anions [22,23]. Complete formation of the second layer means that adsorbed CTAB concentration is twice the external cation exchange capacity. Some experiments showed that when SMNZ is mixed with a solution containing sulfate anion, the concentration of sulfate in the remaining solution is decreased. Therefore, we decided to use the SMNZ as

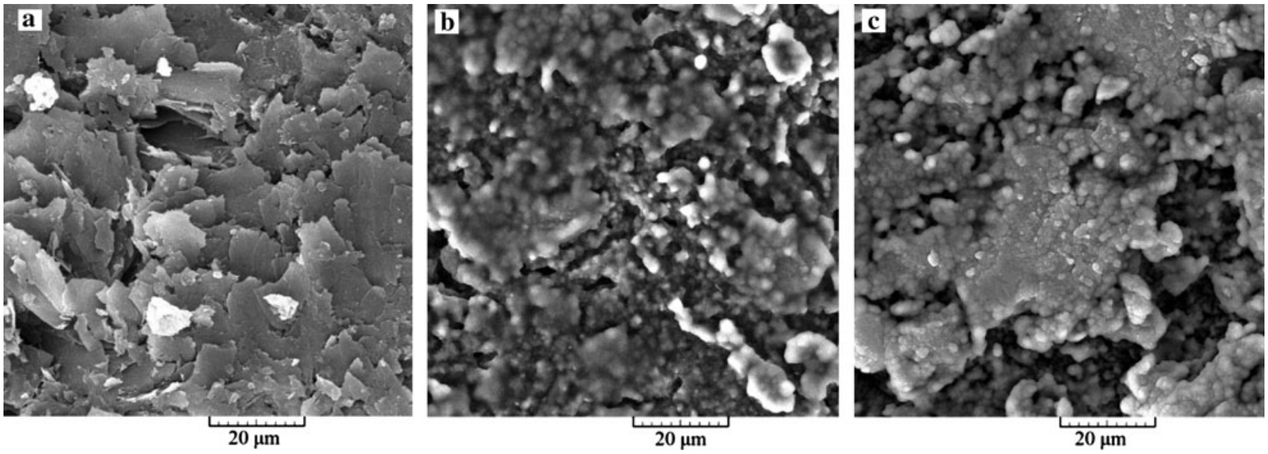

Fig. 2. SEM images of (a) bare CPE, (b) ZSM-5/CPE, and (c) SMNZ/CPE.

an active ingredient for construction of a potentiometric sensor for this anion. The sorption mechanism can be shown by the following reaction:

$$2(R_4N^+ \text{ in SMNZ}) + SO_4^{2-} \rightleftarrows (R_4N)_2SO_4$$

where R_4N^+ represents the anion exchange sites of CTAB surfactant on SMNZ. According to the above discussions, when SMNZ/CPE is immersed in sulfate solutions, anion exchange reaction takes place between anions on the electrode surface and SO_4^{2-} in solution.

3.3. Optimization of the amount of modifier in the electrode

Optimization of CTAB concentration and amount of SMNZ for preparation of modified electrode is an important issue. Some experiments were performed for determination of the optimum amount of modifier in order to obtain the best regression line in the several sulfate concentrations. The best potentiometric response was obtained by plotting E_{cell} vs. log concentration of sulfate anion. Firstly, the amount of SMNZ modifier was optimized. The responses of the electrodes with various SMNZ compositions are represented in Table 2. As can be seen in Table 2, only the electrode D (containing 15% SMNZ and prepared at 80 mM CTAB) was displayed Nernstian behavior (slope = 29.2 mV decade^{-1}). Furthermore, this electrode showed good linear response within the concentration range of 1.0×10^{-6}–1.0×10^{-2} M of sulfate anion.

3.4. Effect of pH

It is well known that the potentiometric behavior of sulfate is dependent on pH value of the solution. The effect of pH on the response of the SMNZ/CPE electrode was tested in 1×10^{-3} M of sulfate ion in the pH range of 1.0–12.0 (see Fig. 3). The pH was regulated by adding small volumes of 0.1–1 M hydrochloric acid or sodium hydroxide to the test solutions. As can be seen in Fig. 3, the potential response remains almost constant in the pH over range of 4.0–9.0 and shows sharp variations out of this range. At the pH values more than 9, the increase in potential is due to the interference of OH$^-$ anion.

Table 2
Optimization of CTAB concentration and SMNZ in the preparation of modified electrodes

Electrode	Percentage of modifier	Slope (mV decade^{-1}) (n = 5)
A	10% (10 mM CTAB)	16.5 ± 0.4
B	10% (40 mM CATB)	25.6 ± 0.4
C	15% (40 mM CTAB)	26.4 ± 0.3
D	15% (80 mM CTAB)	29.2 ± 0.5
E	20% (40 mM CTAB)	30.1 ± 0.6
F	20% (80 mM CTAB)	27.6 ± 0.7

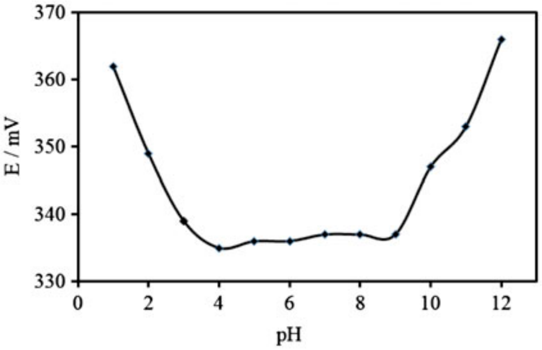

Fig. 3. Effect of solution pH on the potential response of the SMNZ/CPE.

3.5. Effect of ionic strength

The effect of ionic strength was investigated on the calibration curve of sulfate anion at the surface of SMNZ/CPE in the 1.0×10^{-4}–5.0×10^{-3} M of $NaNO_3$. The electrode response has Nernstian slopes with linear range (LR) of 1.0×10^{-6}–1.0×10^{-2} M of sulfate species within the 1.0×10^{-4}–5.0×10^{-3} M of $NaNO_3$ (see Table 3). The constant Nernsian behavior and the same linearity range were obtained at different ionic strength values. Although in 1.0×10^{-3} M of $NaNO_3$, a Nernstian response detected but the linearity of response decreased to 1.0×10^{-6}–1.0×10^{-2} M of sulfate anion Nevertheless, the Nernstian slopes are not obtained at concentration of more than 1.0×10^{-3} M of $NaNO_3$ suggesting the possibility of the occupation of ion exchange sites in SMNZ by NO_3^- anions. Consequently, it causes a decrease in electrode response comparing to the higher concentrations of the sulfate species. According to Table 3, the difference in the intercept values at nitrate concentrations lower than 1.0×10^{-3} M is not significant. The small differences can represent that the sensor is free from nitrate interference at concentrations lower than 1.0×10^{-3} M. On the other hand, the intercept values vary greatly at nitrate concentrations higher than 1.0×10^{-3} M showing more interference of the anion. The validity of obtained results was performed by statistical methods. By comparing calculated "t" value (t_{exp}) and critical t at 95% confidence interval, $t_{0.05,5} = 2.78$, it is concluded that there is a random error in the concentration range of 1.0×10^{-4}–1.0×10^{-3} M of $NaNO_3$ [32].

Table 3
Effect of ionic strength on the potentiometric response of SMNZ/CPE for determination of sulfate

$NaNO_3$ (M)	Slope ($n = 6$) (mV $decade^{-1}$)	t_{exp} [a]	Intercept (mV)	LR of sulfate anion
1×10^{-4}	29.91	1.50	317.87	1.0×10^{-6}–1.0×10^{-2}
4×10^{-4}	29.95	1.64	326.71	1.0×10^{-6}–1.0×10^{-2}
7×10^{-4}	30.1	1.75	327.47	1.0×10^{-6}–1.0×10^{-2}
1×10^{-3}	30.17	1.96	323.61	1.0×10^{-6}–4.27×10^{-4}
2×10^{-3}	28.71	5.16	338.72	4.5×10^{-6}–3.74×10^{-4}
5×10^{-3}	26.5	8.77	345.4	6.4×10^{-6}–3.12×10^{-4}

[a] $t_{0.05,5}$ = 2.57 (Ref. [32]).

3.6. Effect of temperature

It must be noted that the potential of a cell has a direct dependence to the temperature. Therefore, to investigate the thermal stability of the proposed electrode, calibration curves (E_{cell} vs. log $a_{SO4}{}^{2-}$) were obtained at different temperatures covering the range of 25−55˚C (Table 4). This table indicated that the best Nernstian response occurs when the temperature is 25˚C. The Nernstian and experimental slope values at each temperature were compared statistically [32]. The results indicated that the expected values were validated in the temperature range of 25–45˚C. However, at temperatures higher than 45˚C, the slopes show a significant deviation from the theoretical Nernstian values. This deviation may be ascribed to desorption of the surfactant from SMNZ and destruction of the electrode surface [33].

3.7. Selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode that is relative electrode response for the primary anion (i) over other anions present in solution (j), which is usually expressed in terms of potentiometric selectivity coefficient ($K^{pot}_{SO_4,j}$) The ($K^{pot}_{SO_4,j}$) were determined by the separation solution method in 0.01 M solutions of the corresponding sulfate anion and interfering anions with the following equation [34]:

$$\log\left(K^{pot}_{SO_4,j}\right) = \frac{nF(E_j - E_i)}{2.303\,RT} + \log\left(a_i/a_j^{n/m}\right)$$

where($K^{pot}_{SO_4,j}$)is the Nicolski or potentiometric selectivity coefficient, E_i and E_j are the values of electrode potential at primary ion activity a_i (SO_4^{2-}) and interfering ion activity a_j, respectively, terms n and m are the charges of the primary and interference ion, respectively, R is the gas constant (8.314510 J mol^{-1} K^{-1}), T is the absolute temperature in Kelvin, and F is the Faraday constant (96485.309 C mol^{-1}).

The resulting values for selectivity coefficients and response characteristics of the SMNZ/CPE are compared with the other sulfate selective electrodes and present in Table 5. From the data given in Table 5, it is immediately obvious that the proposed modified CPE (SMNZ/CPE) is highly selective to sulfate anion with respect to other interfering anions, such as chloride, bromide, iodide, nitrite, nitrate, monohydrogen phosphate, and dichromate. The analytical performance and selectivity coefficients of SMNZ/CPE electrode are compared with the corresponding values previously reported for the sulfate-selective electrodes [3,4,19,35–39]. As can be seen in Table 5, the proposed

Table 4
Effect of temperature on the potentiometric behavior of SMNZ/CPE for determination of sulfate

Temperature (˚C)	Nernstian slope (mV $decade^{-1}$)	Mean of exp. slope ($n = 8$) (mV $decade^{-1}$)	Standard deviation	t_{exp} [a]
25	29.57	29.20	0.85	1.23
30	30.07	29.63	0.86	1.45
35	30.56	29.91	0.85	2.16
40	31.06	30.52	0.82	1.86
45	31.55	31.81	0.72	1.02
50	32.05	34.85	2.1	3.77
55	32.55	34.20	1.1	4.24

[a] $t_{0.05,7}$ = 2.36 (Ref. [32]).

Table 5
The comparison of selectivity coefficients (log $K_{A,B}^{pot}$), response time, stability, pH rang, slope, DL, and LR for determination of sulfate described in this work with previously published work

Interference ions	[35]	[36]	[37]	[38]	[19]	[3]	[39]	[4]	[40]	[41]	This work
Cl^-	−0.1	−3.0	−0.2	1.3	−2.3	−3.1	−2.3	−2.4	–	–	−1.5
Br^-	1.1	−2.2	2.4	3.2	−2.1	−2.5	−2.2	−2.5	–	–	−1.6
I^-	–	−2.2	7.4	–	−2.1	−1.8	−2.1	−2.5	–	–	−1.8
No_2^-	–	–	–	–	−3.0	−2.8	–	–	–	–	−2.7
No_3^-	1.6	−2.4	4.3	1.6	−2.3	−3.1	−2.3	−2.4	–	–	−2.7
HPO_4^-	–	–	–	–	−1.5	–	–	–	–	–	−2.8
$Cr_2O_7^{2-}$	–	–	–	–	–	–	−3.7	0.7	–	–	−3.2
Response time (s)	–	60	–	–	45	15	15	10	–	–	30
Stability (day)	28	–	30	–	–	–	–	180	–	–	120
pH range	–	4–7	–		–	4–9	–	4–10	–	–	4–9
Slope (mVdecade^{-1})	28.1 ± 1.8	29.6 ± 0.8	–	–	28.8	28.9	28.8 ± 0.2	29.8 ± 0.8	–	–	29.2 ± 0.7
DL (μM)	1.5	–	1	21.0	2.5	0.9	7.0	2.0	10	14.8	0.41
LDR (M)	1.0×10^{-5}–1.0×10^{-2}	4×10^{-5}–4×10^{-2}	3×10^{-6}–0.2	3.2×10^{-5}–0.5	–	1.5×10^{-6}–4.8×10^{-2}	9×10^{-6}–0.1	2.0×10^{-6}–3.1×10^{-3}	24.7×10^{-6}–3.1×10^{-3}	0–1.56×10^{-4}	1.00×10^{-6}–1.00×10^{-2}

[a] The pH range in this range electrode response is independent of pH.

SMNZ/CPE showed somewhat similar, in most cases, or superior, in some cases, selectivity behavior to the sulfate sensors reported previously. However, low DL and response time, ease of preparation, and low cost are most advantages of our fabricated electrode over the previously reported electrodes or works [3,4,19,35–41]. To be very useful, an analytical method should have a linear dynamic range (LDR) of at least two orders of magnitude [42]. LDR was obtained four orders of magnitude (1.0×10^{-6}–1.0×10^{-2} M) for determination of SO_4^{2-} by fabricated SMNZ/CPE. In some cases, the obtained LDR is much better than previously reported works [4,35–37,40]. Also, the DL of proposed method is lower than previous works [3,4,19,35–41].

3.8. Response characteristics of the electrode

Using the optimized paste composition and conditions described above, the critical response characteristics of the electrode were assessed according to IUPAC recommendations [34]. The emf response of the electrode to varying concentrations of sulfate species indicates a LR from 1.0×10^{-6}–1×10^{-2} M (R^2 = 0.9919) (see Fig. 4(a)). The slope of calibration curve was 29.2 ± 0.5 mV per decade of SO_4^{2-} concentration. As can be seen in Fig. 4, the calibration curve with CPE (Fig. 4(c)) and ZSM-5/CPE (Fig. 4(b)) were not suitable for determination of SO_4^{2-} anion.

The stability and reproducibility of any sensor are two important parameters. Long-term stability of the electrode was investigated by taking the response of the optimized electrode in a period of four months. Potentiometric measurements were performed every four days during the first month and then every seven days for the rest of the period. The electrode retained its full activity during this period. The relative standard deviations (RSD) of a single electrode (within electrode variation) were determined every 30 s during a period of 0–150 s without renewing the electrode surface, with repeated times of 10 (n = 5). The RSD values were obtained to be between 1.2 and 2.3%. These measurements also were achieved with renewing the electrode surface. The small RSD and good repeatability of the SMNZ/CPE electrode indicates that the paste is homogeneous. Another advantage of this electrode is ease of renewing the electrode surface that is advantage of CPEs, rather than other electrodes. High stability of the electrode is another advantage of proposed electrode that in turn causes an increasing of precision. In investigation of reproducibility and repeatability, the RSD values for proposed SMNZ/CPE (1.2–2.3%) are small, which indicated our proposed electrode has a good precision.

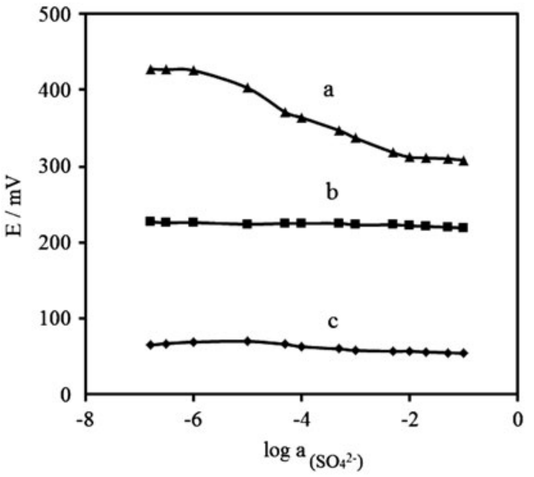

Fig. 4. Potentiometric response of different fabricated electrodes towards sulfate anion: (a) SMNZ/CPE, (b) ZSM-5/CPE, and (c) bare CPE.

3.9. Analytical application of the SMNZ/CPE electrode

The proposed electrode was found to work well under laboratory conditions. The SMNZ/CPE electrode was also applied as an indicator electrode in the successful potentiometric titration of a sulfate ion solution (10 cc, 0.01 M) with the 0.01 M of Ba^{2+} solution [43]. The result of titration is shown in Fig. 5, indicating that the amount of SO_4^{2-} ion can be accurately determined with this electrode.

In order to evaluate the applicability of the proposed method for the determination of sulfate in real samples, its utility was performed to the determination of sulfate in Damavand and Nava mineral waters and a pharmaceutical ferrous sulfate tablet according to the procedure described in the experimental section. The results are shown in Table 6, which indicate that the determination of sulfate using the SMNZ/CPE is effective and can be applied for detection of sulfate in real samples with satisfactory results.

Analysis of variance (ANOVA) is a useful technique for comparing three treatment means. We used this technique for characterization of obtained result of three treatments in Damavand and Nava mineral waters and a ferrous sulfate tablet, separately, and the results are presented in Table 7. It can be noted that four experiments were performed in each treatment. From the F-tables [32], the critical value of F at p = 0.05 for 2° and 9° of freedom is 4.25. Since the experimental F value (F_{exp}) is smaller than 4.25 in all cases (F_{exp} = 2.73, 3.82 ,and 4.03 for Damavand mineral water, Nava

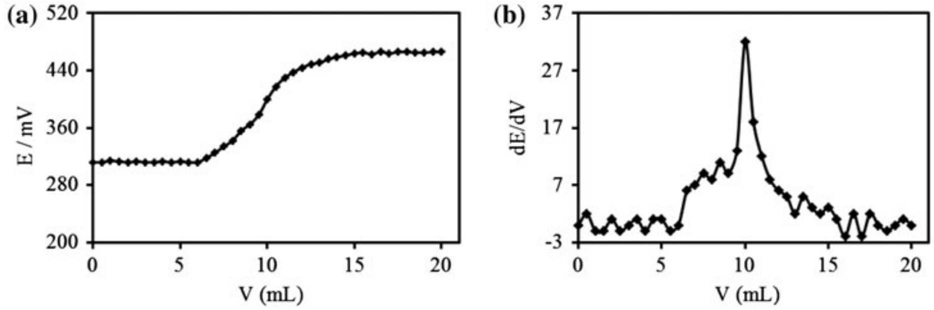

Fig. 5. (a) Typical potentiometric titration curves of 0.01 M of sodium sulfate solution (10 cc) with 0.01 M $BaCl_2$ solution using SMNZ/CPE and (b) first-derivative curve, dE/dV, vs. titrante volume.

Table 6
Determination of sulfate in two mineral waters and pharmaceutical ferrous sulfate tablet by potentiometric method in the surface of SMNZ/CPE

Sample	Expected value (*n* = 4)	Found by this method	Recovery (%)
Damavand mineral water	20.00	21.52 ± 1.06 ppm	107.60
Nava mineral water	9.00	9.76 ± 1.72 ppm	108.44
Ferrous sulfate tablet	50.00	48.60 ± 1.45 mg per tablet	97.20

Table 7
ANOVA table for determination of sulfate in two mineral waters and pharmaceutical ferrous sulfate tablet

Sample	Source of variation	Degrees of freedom	Sum of squares (SS)	Mean squares (MS)	F_{exp}[a]
Damavand	Between treatments	2	1.644	1.644/2 = 0.822	0.822/0.301 = 2.73
Mineral	Residual error	9	2.710	2.710/9 = 0.301	–
Water	Total	11	4.354	–	–
Nava	Between treatments	2	1.736	1.736/2 = 0.868	0.868/0.227 = 3.82
Mineral	Residual error	9	2.046	2.046/9 = 0.227	–
Water	Total	11	3.782	–	–
Ferrous	Between treatments	2	26.118	26.118/2 = 13.059	13.059/3.243 = 4.03
Sulfate	Residual error	9	29.185	29.185/9 = 3.243	–
	Total	11	55.303	–	–

[a] The critical value of *F* at *P* = 0.05 for 2° and 9° of freedom is 4.25 [32].

mineral water, and a ferrous sulfate tablet, respectively), it may be concluded that the null hypothesis will be confirmed and there is no significant difference between the sulfate content in each treatment.

4. Conclusions

In this study, the CPEs were modified with SMNZ and were used for the determination of sulfate anion using potentiometric method. The success of CTAB incorporation in ZSM-5 nanozeolite was proved with FT-IR analysis. This new modified electrode (SMNZ/CPE) has some advantages, such as low cost and stability, low background current, ease of preparation and regeneration, stable response, reasonable selectivity, fast response time, low DL, long-term stability, good potential reproducibility, and applicability over a wide pH range. Moreover, the electrode surface can be renewed with a simple polishing. Finally, the modified electrode was successfully used for the determination of sulfate in two kinds of mineral water and a ferrous sulfate tablet without prior separation steps.

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