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Surfactant Modified ZSM-5 Nanozeolite in the Modification of Carbon Paste Electrode for Voltammetric Determination of Sulfide

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Abstract- Carbon paste electrode was modified by surfactant modified ZSM-5 nanozeolite and the electrochemical behavior of this modified electrode was studied using cyclic voltammetry. This electrode showed enhanced electrochemical response and strong analytical activity towards the direct electrochemical oxidation of sulfide. The influence of some parameters such as different mass ratio of ZSM-5 nanozeolite and graphite, surfactant concentration, pH and scan rate of potential was investigated on the anodic peak height of the sulfide oxidation. Under optimal conditions in a buffer solution, pH 8.0, the anodic peak currents increased linearly with the concentration of sulfide and discovered two linear dynamic ranges with slopes of 0.6896 µA/µM and 5423.5 µA/M in the concentration ranges of 5×10^{-6} to 1×10^{-4} M and 3×10^{-4} to 0.1 M, respectively. The detection limit was achieved 1.32×10^{-6} mol L^{-1} (3σ). Also, the electron transfer coefficient (α) and diffusion coefficient (D) of sulfide at the surface of modified electrode were calculated. The proposed electrode was successfully used for the determination of sulfide in tap water and mineral water.

Keywords- Surfactant modified ZSM-5 nanozeolite, CPE modified electrodes, Cyclic Voltammetry, Sulfide determination

1. INTRODUCTION

Aluminosilicate zeolites and related nanoporous materials are widely used in the domains of ion-exchange, separation and shape-selective catalysis [1−4]. They are inorganic solids with large surface areas and well-defined internal structures of uniform cages, cavities or channels of monodisperse dimensions due to the crystallization of aluminosilicates in the presence of cation-directing agents [5]. Zeolites and nanozeolites attract interest for this application because they offer selectivity based on the size and shape of the reactants, together with a tridimensional lattice made of interconnected cages of molecular dimension coming in a variety of support sites for various catalysts [6,7]. Nanostructure materials have generated intense scientific and technological interest over the last few years because of their unique properties and potential applications in areas as diverse as electronics, optics, information storage, bio-medicine, sensors and product labeling[6]. Recently, nanozeolites have attracted significant attention to researchers [6–8].

The carbon-paste electrode (CPE) was introduced by Adams in 1958 [9]. CPE and chemically modified carbon-paste electrodes (CMCPEs) are extensively used in various fields of electrochemistry [10,11]. 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 [12]. Rolison and Walcarius have been reviewed the zeolite modified electrodes (ZMEs) [13,14]. Also, applications of surfactant-modified zeolites to environmental remediation were reviewed by Bowman [15]. Design of modified electrodes for electroanalysis has been extensively developed because it provides an excellent way to facilitate (accelerate) charge transfer processes [16–21].This contributes to decrease the overpotentials which often required to perform electrochemical transformations, as well as to increase the intensity of the corresponding voltammetric responses [14,22–24].

The negative charge of zeolites is appropriate for surface modification of nanozeolites using cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB). At surfactant concentrations greater than the critical micelle concentration (CMC) and when sufficient surfactant is present, 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 [15,26,27]. The surfactant modified zeolite (SMZ) is stable in water and aggressive chemical solutions. Its relatively low cost makes it a viable alternative to other reactive media such as activated carbon and ion exchange resins [28].

The detection of sulfide has gained significant importance within the analytical community as a consequence of the toxicity of hydrogen sulfide [29,30]. Sulfide analysis is well represented in most branches of analytical science emerging from the more classical

procedures to spectroscopy, electrochemistry, chromatography and combinations of them [31,32]. Lawrence et al. [30] has been reviewed some methods for determination of sulfide species. Also, determination of sulfide at a multi-walled carbon nanotube-dihexadecyl hydrogen phosphate composite film coated glassy carbon electrode was reported by Xiang and co-worker [33]. Also, Roman et. al. was prepared a 2-(4-fluorophenyl) indole-modified xerogel for the fabrication of screen printed electrodes for the electrocatalytic determination of sulfide in synthetic and real samples [34]. The quantitative determination of hydrogen sulfide on a solid polymer electrolyte-based was reported [35]. A modified PVC membrane with surfactant modified natural clinoptilolite zeolite as an ionophore along with dibutyl phthalate as a solvent mediator was applied for determination of sulfide ion [27].

In respect of literature survey, no zeolites and nanozeolites were utilized for modification of carbon paste electrode for electroanalytic determination of sulfide. In this article, ZSM-5 nanozeolite was modified with CTAB surfactant and the resulting surfactant modified nanozeolite (SMNZ) was used for modification of carbon paste electrode (CPE). The obtained electrode was used as a new voltammetric sensor for determination of sulfide.

2. MATERIALS AND METHODS

2.1. Materials

Sodium sulfide, sodium hydroxide, potassium chloride, potassium ferrocyanide, dipotassium monohydrogen phosphate, monopotassium dihydrogen phosphate and phosphoric acid were analytical reagent grade and were obtained from Merck Company (Darmstadt, Germany) and used without further purification. The cetyltrimethyl ammonium bromide (CTAB) was purchased from Fluka Company. All solutions were prepared using analytical grade reagents and double distilled water was used throughout. Graphite powder and paraffin oil (density 0.88 gcm^{-3}) as the binding agent (both from Day Jung company) were used for preparing the pastes.

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.
$2\theta = 7.9°, 8.9°, 23.2°,$ and 24.5°	3470, 1219, 1200, 1080, 833, 790 and 542 cm^{-1}	Spherical	97 nm	[4]

The ZSM-5 nanozeolite was synthesized in our laboratory and reported in our previous work [4]. This synthesized nanozeolite has spherical nanosized particle with average diameter of 97 nm. Some data for characterization of synthesized ZSM-5 nanozeolite listed in Table 1 (Nejad-Darzi et al.). For preparation of SMNZ, the ZSM-5 nanozeolite (0.1 g) was mixed with 5 mL of 10, 30 and 50 mM CTAB solutions in separate flasks, and stirred for 24 h on a magnetic stirrer. Then, the mixture was centrifuged at 10000 rpm for 20 min and the resulting SMNZ was dried in air.

A stock solution of sulfide anion (0.1 mol L^{-1}) was prepared by dissolving 0.7804 g of sodium sulfide in water and the solution was diluted to 100 mL with deionized water in a 100 mL volumetric flask. Working solutions were prepared in 25 mL volumetric flasks by addition of appropriate amounts of stock solution and diluted by deionized water to the mark. A 0.1 M potassium chloride (KCl) solution was used as supporting electrolyte. Phosphate buffer solutions (orthophosphoric acid, disodium monohydrogen phosphate and sodium dihydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1}), PBS, with different pH values were used in the pH range of 3.0–9.0.

2.2. Apparatus

The electrochemical experiments such as cyclic voltammetry and chronoamperometry were performed at room temperature using potentiostat/galvanostat electrochemical analysis systemIvium (Netherlands, V11100) with a voltammetry cell in a three electrodes configuration. A platinum wire and Ag|AgCl|KCl (3 M) were used as auxiliary and reference electrodes, respectively. The carbon-paste electrode (CPE), modified carbon paste electrodes with ZSM-5 nanozeolite (NZM/CPE) and surfactant modified ZSM-5 nanozeolite (SMNZ-CPE) were used as working electrode. 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 (10–20 wt% with respect to graphite) was mixed with 200 mg of graphite powder and then paraffin oil (20 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 7 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 outof the tube and polishing with a weighing paper. For comparison, ZSM-5 nanozeolite modified CPE electrode (NZM/CPE) and unmodified CPE (bare CPE) in the absence of both ZSM-5and CTAB were also prepared in the same way.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the SMNZ

FT-IR spectra of CTAB surfactant, ZSM-5 nanozeolite and SMNZ using KBr pellets were recorded and are illustrated in Fig. 1. The IR pattern of SMNZ shows characteristic peaks at 2922, 2845, and 1525 cm^{-1}, which indicate the incorporation of CTAB into the nanozeolite structure. There is a slight shift in peaks at each wavenumber; however, both of the patterns are nearly the same. Particularly, the presence of peaks at 2922, 2845 and 1525 cm^{-1} in SMNZ spectrum (related to C–H, C–C and N–C vibrations in the surfactants, respectively), that are absent in the ZSM-5 nanozeolite spectrum [4,36], confirm loading of CTAB onZSM-5 nanozeolite.
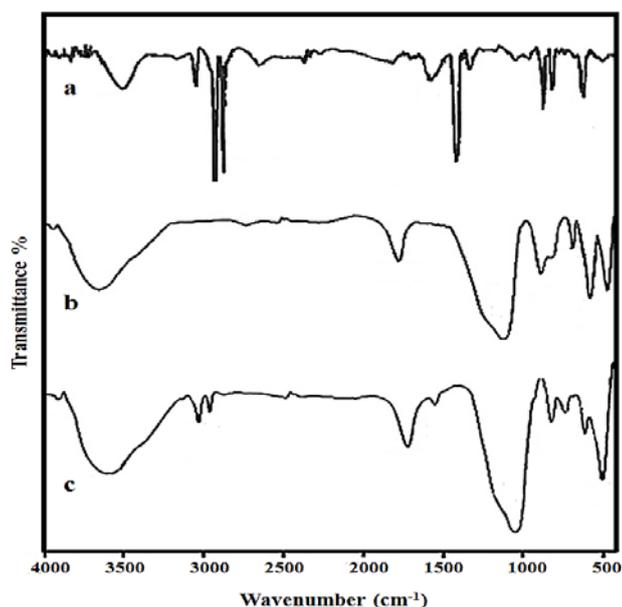

Fig. 1. The FT-IR spectra of (a) CTAB, (b) ZSM-5 nanozeolite and (c) Surfactant modified nanozeolite

As previously mentioned, the SMZ can be used for sorption of anionic species. This is based on the following theoretical model and illustrated graphically in Fig. 2. At low concentrations, CTAB forms 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 formed. This bilayer structure causes arrangement of positively charged functional groups toward the solution, which can serve as sorption sites for anions [15]. Complete formation of the second layer, means that sorbed CTAB concentration is twice of the external cation exchange capacity (ECEC). Some experiments showed that when SMNZ is mixed with a solution containing sulfide anion, the concentration of sulfide in the

remaining solution is decreased. Therefore, we were prompted to use the SMNZ as an active ingredient for construction of a voltammetric sensor for this anion. The sorption mechanism can be shown by the following reaction:

$$2(R_4N^+ \text{ in SMNZ}) + S^{2-} \rightleftarrows (R_4N)_2S$$

Where R_4N^+ represents the anion-exchange sites of CTAB surfactant on SMNZ. According to the above discussions, when SMNZ/CPE is immersed in sulfide solutions, anion exchange reaction takes place between anions on the electrode surface and S^{2-} in solution.
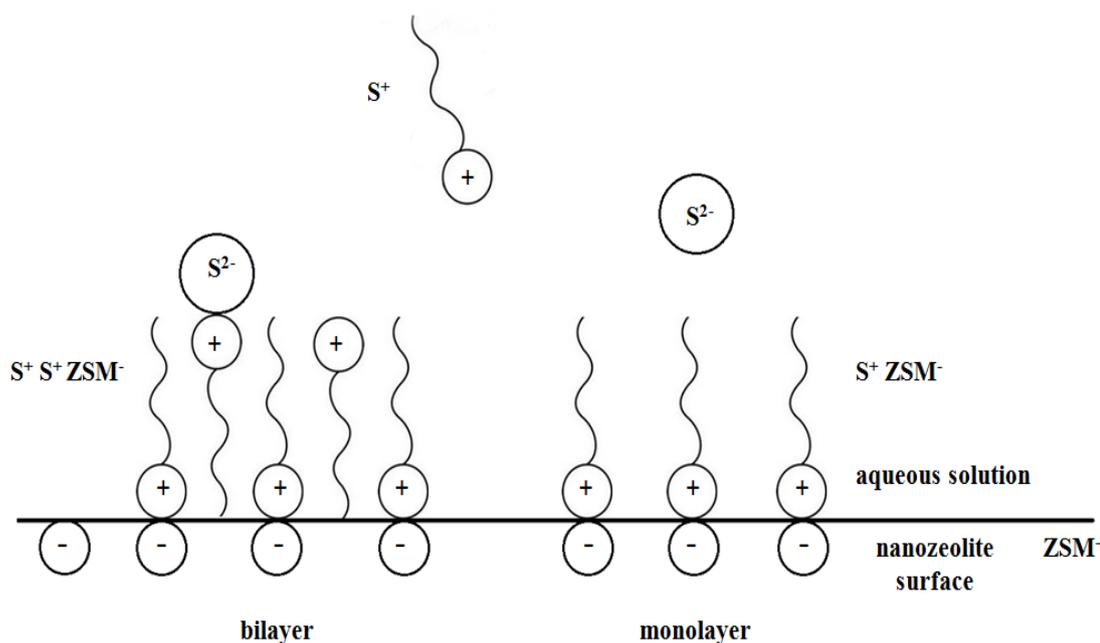
Fig. 2. Typically Model for the sorption of CTAB onto the ZSM-5 nanozeolite surface. S^{2-}: anion, S^+: free surfactant molecule, S^+ZSM^-: surfactant sorbed in monolayer, $S^+S^+ZSM^-$: surfactant sorbed in bilayer

3.2. Electrochemistry of the modified electrodes

Cyclic voltammetry was employed for the investigation of electrochemical properties of the unmodified and modified electrodes in potassium ferrocyanide ($K_4Fe(CN)_6$) solution. This solution was prepared by making the 10 mM of $K_4Fe(CN)_6$ and diluting aliquots of this solution with 0.10 M KCl. Fig. 3 illustrates the cyclic voltammetric responses from the electrochemical oxidation of $K_4Fe(CN)_6$ at bare CPE, NZM/CPE and SMNZ/CPE. As can be seen in this Fig., the anodic peak current for SMNZ/CPE is more than two others. The experimental results show well-defined and reproducible anodic and cathodic peaks related to ferrocene/ferricenium redox couple with quasi-reversible behavior with a peak separation

potential of $\Delta Ep = 170$ mV($E_{pa} - E_{pc}$) because the peak separation potential, ΔE_p, is greater than that of $59/n$ mV expected for a reversible system. The obtained result from cyclic voltammetry of the electrodes in various buffered solutions with different pH value does not show any shift in the anodic peak potentials for oxidation of $K_4Fe(CN)_6$. It means that the electrochemical behavior of the redox process of ferrocene/ferricenium redox couple in the NZM/CPE and SMNZ/CPE electrodes is not dependent on the pH of the solution.

The active surface areas of unmodified and modified electrodes were estimated according to the slope of the I_{pa} versus $\upsilon^{1/2}$ plot for a known concentration of $K_4Fe(CN)_6$, based on the Randles–Sevcik equation [20]:

$$I_{pa} = 269000 \, n^{3/2} \, A \, D_R^{1/2} \upsilon^{1/2} \, C_o \tag{1}$$
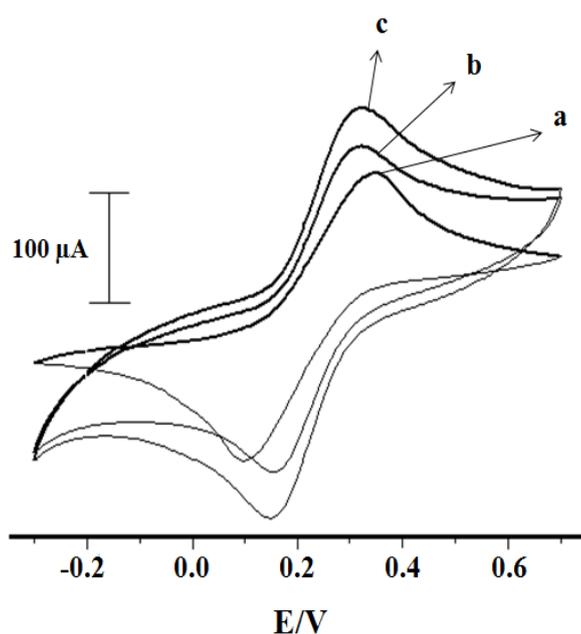
Fig. 3. The CVs of (a) bare CPE, (b) NZM/CPE and (c) SMNZ/CPE in the presence of 10 mM $K_4Fe(CN)_6$ solution plus 0.1 M of KCl at a scan rate of 100 mV s^{-1} and pH 8.0

where I_{pa} states to the anodic peak current, n the electron transfer number, A the surface area of the electrode, D_R the diffusion coefficient, υ the scan rate and C_o is the concentration of $K_4Fe(CN)_6$. For 1.0 mmol L^{-1} $K_4Fe(CN)_6$ in 0.1 mol L^{-1}KCl as supporting electrolyte the amount of n and D_R is 1 and 7.6×10^{-6} cm^2 s^{-1}, respectively. From the slope of the I_{pa} *vs.* $\upsilon^{1/2}$ and according to Randles-Sevcik equation, the active surface areas of electrodes were calculated. They were obtained 1.137×10^{-3}, 0.98×10^{-3} and 0.7×10^{-3} cm^2 for SMNZ/CPE, NZM/CPE and bare CPE, respectively. The results show that the presence of ZSM-5 nanozeolite and CTAB causes to increase the active surface of the electrode. Fig. 4 depicts

Plot of I_{pa} versus $\upsilon^{1/2}$ and cyclic voltammogram for the oxidation of $K_4Fe(CN)_6$ at the surface of SMNZ/CPE (R^2=0.999).

Fig. 5 demonstrates the cyclic voltammogram for the electrochemical oxidation of 0.01 M sulfide anion at the surface of CPE, NZM/CPE and SMNZ/CPE. The direct electrooxidation of S^{2-} requires a large overpotential at unmodified electrode surfaces (bare CPE; Fig. 5, curve a) and thus there is not any specific anodic peak current at this electrode. There is a weak anodic peak at the surface of nanozeolite modified CPE (NZM/CPE; see Fig. 5, curve b). As can be seen in Fig. 5c, a dramatic change in the voltammogram with a large enhancement of the anodic current (about 270 μA) is observed at a surface of SMNZ/CPE. Thus, a decrease in overpotential and enhancement in the peak current is achieved with the SMNZ/CPE.
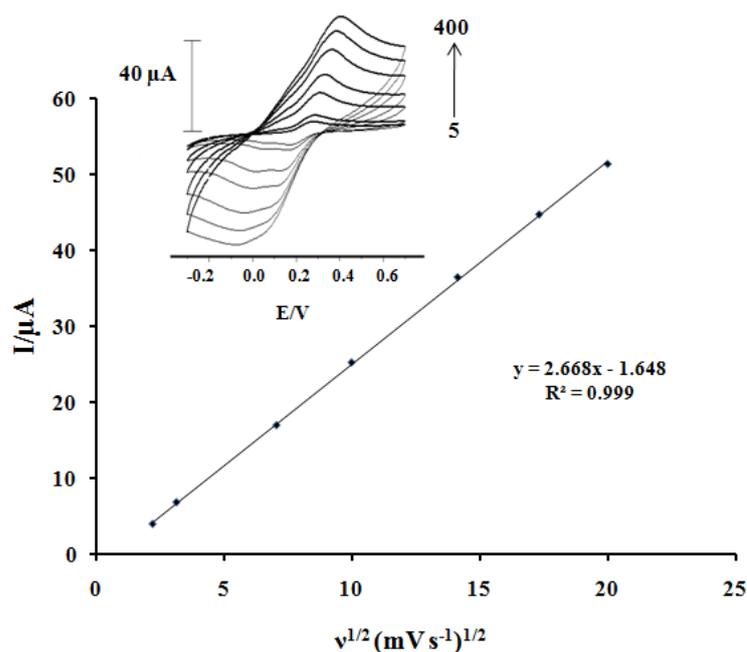
Fig. 4. The plot of I_{pa} versus $v^{1/2}$ for the oxidation of $K_4Fe(CN)_6$ at the surface of SMNZ/CPE. Inset shows CVs of SMNZ/CPE at various scan rates of 5, 10, 50, 100, 200, 300 and 400 mV s^{-1}. Electrolyte is 0.1 mol L^{-1} KCl

The obtained data clearly shows that the combination of ZSM-5 nanozeolite and CTAB definitely improved the characteristics of sulfide oxidation. It can be deduced that sulfide anions were adsorbed on the surfactant that present in the nanozeolite sites and therefore this peak can be attributed to the oxidation of sulfide to sulfur. The electrocatalytic oxidation of sulfide at low potentials (−0.1 V *vs.* Ag|AgCl|KCl (3 M)) is also very useful for practical applications, since there is less risk for interfering of electrochemical reactants to take place.
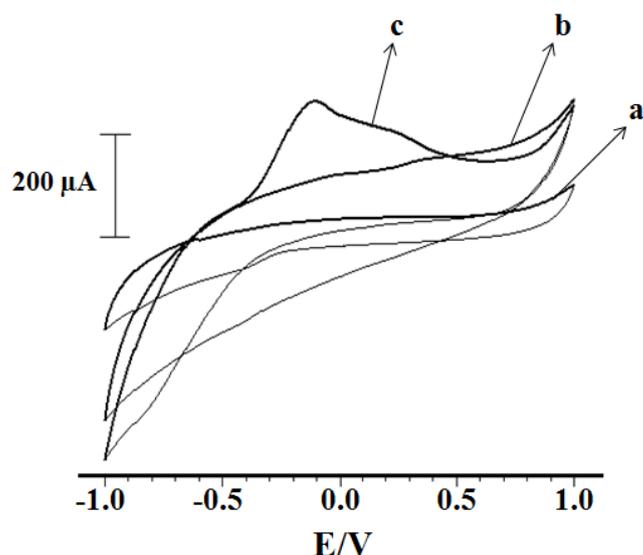
Fig. 5. The CVs of (a) bare CPE, (b) NZM/CPE and (c) SMNZ/CPE in the presence of 0.01 M sulfide solution plus 0.1 M of KCl at a scan rate of 100 mV s^{-1} and pH 8.0

3.3. Effect of pH

It is well known that the electrochemical behavior of sulfide is dependent on pH value of the solution. In order to evaluation of this, the voltammetric response of sulfide was obtained in solutions with varying pHs from 3.0 to 10.0 in 0.1 M PBS at the surface of SMNZ/CPE (Fig. 6). The results exposed that the anodic peak current for electrooxidation of sulfide reached to a maximum value at pH 8.0.
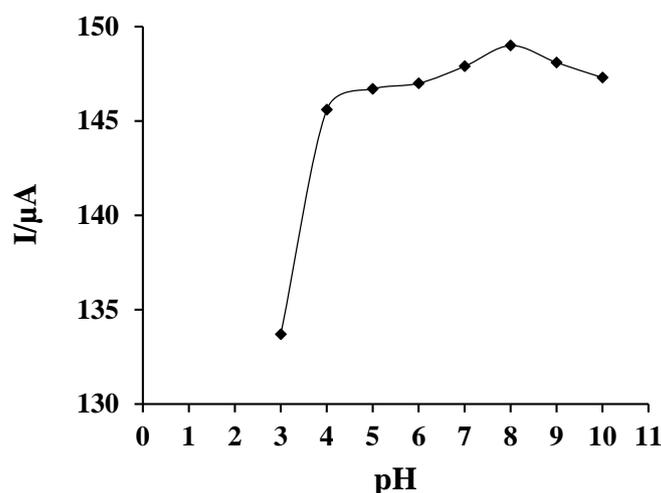
Fig. 6. The current-pH curve for electrooxidattion of 0.003 M sulfide in 0.1 M phosphate buffer solution, PBS, at pH values 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 at the surface of SMNZ/CPE at a scan rate of 50 mV s^{-1}

The decreasing of the oxidation peak current of S^{2-} at modified electrode in acidic media is due to the increasing of proton concentration. It can be deduced that S^{2-} is converted to the HS^- and H_2S in the lower pH and thus, the oxidation peak current is decreased. On the other hand, the decreasing in current at pH value more than 8 is due to increasing of hydroxide concentration that can be affected on the electrocatalytic activity of the modified electrode.

### 3.4. Optimization of the electrode composition

Optimization of CTAB concentration and amount of SMNZ for preparation of modified electrode is an important issue. Therefore, the electrode was investigated in more details. Table 2 is presented the responses of the electrodes to several CTAB and SMNZ compositions.

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

Electrode	CTAB (mM)	SMNZ (%)
A	10	10
B	30	10
C	30	15
D	50	15
E	30	20
F	50	20

These six electrodes were examined in different sulfide concentrations and electrodes performance in terms of anodic peak current was plotted respect to sulfide concentration. The electrode containing 15% SMNZ which its SMNZ was prepared with 30 mM CTAB (Electrode c) showed the best efficiency. This electrode also showed good linear response within the concentration range of 5×10^{-6}-0.1 M of sulfide. Because, the extent of ion exchange were decreased in the low amounts of the CTAB modifier, meanwhile high amounts of the modifier were increased the resistance of the electrode; both of which decrease the sensitivity of the electrode response [23]. In controlling experiments, the behavior of the carbon paste electrode containing 15% CTAB (free from zeolite) was investigated for determination of sulfide. There is no anodic peak for oxidation of S^{2-} at the surface of this electrode.

The influence of scan rate (ν) on anodic peak current (I_{pa}) of 0.003 M sulfide at the SMNZ/CPE was examined by cyclic voltammetry at various sweep rates. As shown in Fig.7, the anodic peak currents for oxidation of sulfide grow with the increasing of scan rates. The results confirmed that there is a linear relationship between the peak current (i_p) and the square root of the scan rate ($\nu^{1/2}$) in the scan rates of 20–150 mV s^{-1}, indicates that the oxidation of sulfide at the surface of SMNZ/CPE is a diffusion-controlled process [37,38]. On the other hand with increasing in the scan rate, the peak potential shifts in positive direction, meaning that the shift may be due to the Ohmic drop which generated at high current density.
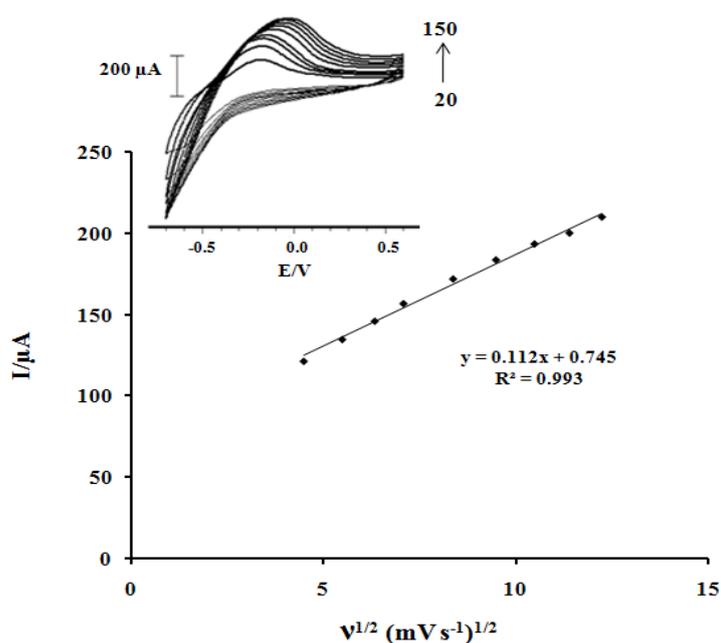
Fig. 7. The plot of I_{pa} versus $\nu^{½}$ for the oxidation of sulfide at the surface of SMNZ/CPE. Inset shows CVs of 0.003 M sulfide at the surface of SMNZ/CPE at different scan rates of 20, 30, 40, 50, 70, 90, 110, 130 and 150 mV s^{-1} in 0.1 M phosphate buffer, pH 8.0

To obtain more information about the rate of electrochemical reaction, a Tafel plot was developed for oxidation of sulfide at the surface of SMNZ/CPE using the data derived from the raising part of the current–voltage curve (see Fig. 8).The slope of the Tafel plot is equal to $n(1-\alpha)F/2.3\ RT$ which indicates that transfer coefficient (α) is approximately 0.93 for the irreversible electrode process.

3.5. Chronoamperometric measurements

The oxidation of sulfide at the surface of modified electrode was also studied using chronoamperometry method. Chronoamperometric measurement of different concentrations

of sulfide at the surface of the SMNZ/CPE was performed by setting the working electrode potential at +0.1 V *vs.* Ag|AgCl|KCl (3 M). From the chronoamperometric study, the diffusion coefficient, D, of sulfide was determined in aqueous solution by using Cottrell equation [39,40]:

$$I = nFACD^{1/2}\pi^{-1/2}t^{-1/2} \tag{2}$$

Where C is the known concentration of compound, F is the faraday number, D is the apparent diffusion coefficient and A is the area of the electrode. Fig. 9 demonstrates experimental plots of I *vs.* $t^{-1/2}$ for different concentrations of sulfide at the surface of SMNZ/CPE. The slopes of the resulting straight lines were then plotted *vs.* the sulfide concentration. From the slope of the resulting plots and using the Cottrell equation, we calculated the mean value of the D was found to be 6.614×10^{-6} cm^2 s^{-1} (with n=2, F=96485 C mol^{-1}, and A=0.0962 cm^2).
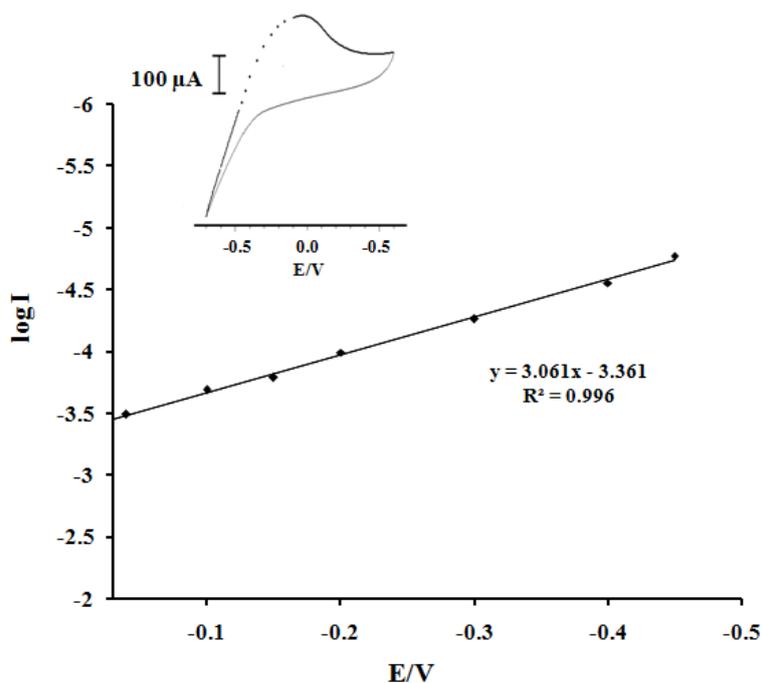


Fig. 8. The Tafel plot for SMNZ/CPE in 0.1 M PBS (pH 8.0) with a scan rate of 100 mV s^{-1} in the presence of 0.003 M sulfide

3.6. Stability and reproducibility of modified electrode

The stability and reproducibility of any sensor are two important parameters. We investigated these parameters for measurements of 0.003 M sulfide at the surface of SMNZ/CPE using cyclic voltammetric. The relative standard deviation (RSD) for six sequential assays was 1.5% and RSD for six measurements using six different SMNZ/CPEs

was 1.8%. The modified electrode was stored in the laboratory and it retained 97% and 94% of its initial response after 10 and 50 days, respectively. These results indicate that SMNZ/CPE has both a good stability and a satisfactory reproducibility so that it can be used for determination of sulfide.
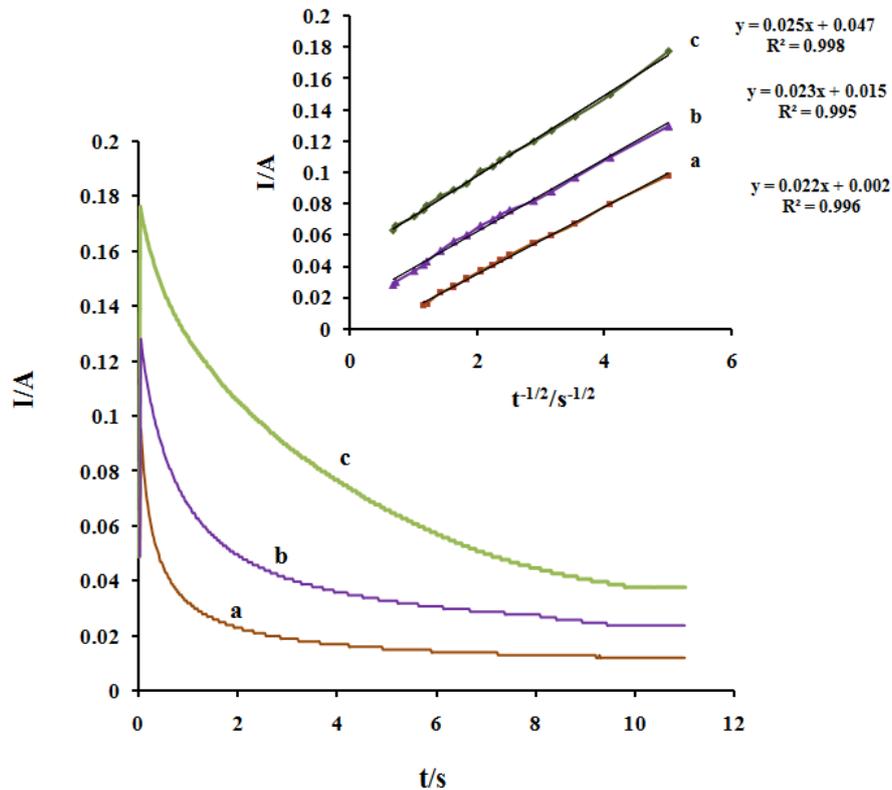
Fig. 9. The chronoamperograms obtained at SMNZ/CPE in the presence of (a) 0.01; (b) 0.02 and (c) 0.03 M sulfide in the buffer solution (pH 8.0). Inset shows Cottrell's plot for the data from the chronoamperograms

3.7. Calibration plot and limit of detection

Cyclic voltammetry was used to prepare calibration plot for determination of sulfide. The plot of the peak current *vs.* sulfide concentration is depicted in Fig. 10 that consisted of two linear segments with slopes of 0.6896 µA/µM and 5423.5 µA/M in the concentration ranges of 5×10^{-6} to 1×10^{-4} M and 3×10^{-4} to 0.1 M, respectively. The regression equation was I_{pa} (µA)=0.6896 $C_{sulfide}$+180.9 (R^2=0.9934, n=5) (Fig. 10, inset A) for 5–100 µM sulfide, where $C_{sulfide}$ is concentration of sulfide (µM). Also, The regression equation was I_{pa} (µA)=5423.5 $C_{sulfide}$+177.5 (R^2=0.9975, n=5) (Fig. 10, inset B) for 0.0003–0.1 M of sulfide, where $C_{sulfide}$ is concentration of sulfide (M). For a signal-to-noise ratio of 3, the limit of detection (LOD) of the method was found 1.32×10^{-6} M.
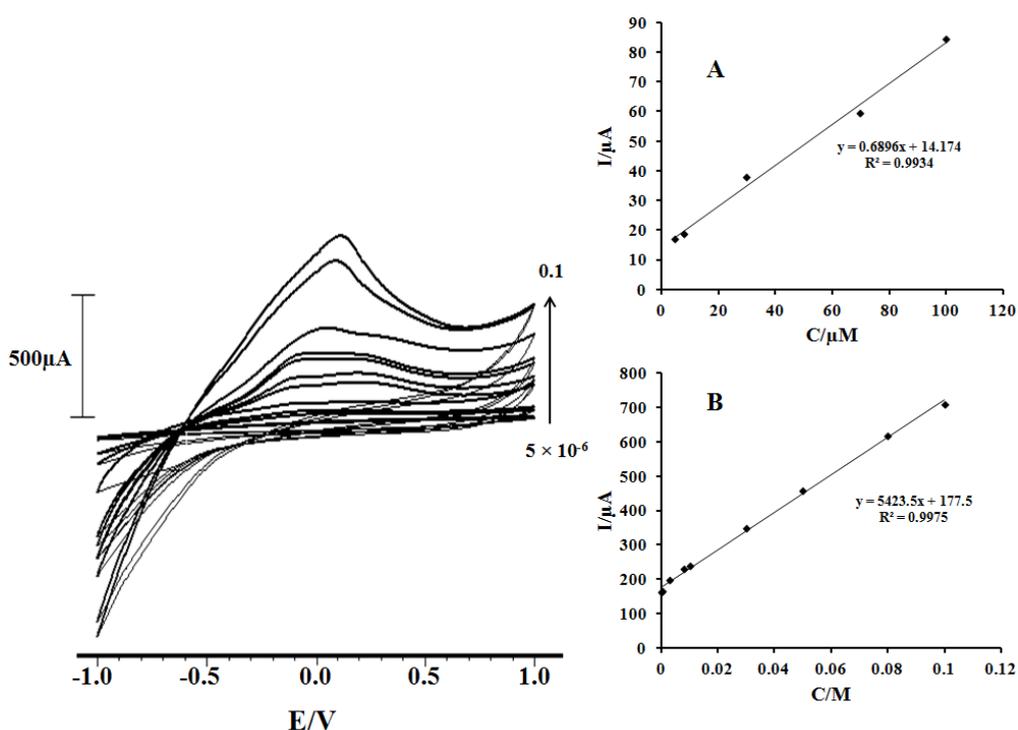
Fig. 10. The CVs of SMNZ/CPE in the buffer solution (pH 8.0) containing different concentrations of sulfide, from inner to outer: 5×10^{-6}, 8×10^{-6}, 3×10^{-5}, 7×10^{-5}, 10^{-4}, 3×10^{-4}, 0.003, 0.008, 0.01, 0.03, 0.08 and 0.1 M. Inset A and B, Plot of anodic peak current as a function of sulfide concentration at two ranges

3.8. Interference studies

To evaluate the selectivity of the modified electrode for the determination of sulfide in real samples, two types of samples were checked as potential interfering compounds. So, the interference effect of some compounds in mineral water and used wastewater in microbial fuel cell in the determination of sulfide has been investigated. Result indicated that these kinds of materials have no interference in the determination of sulfide in real samples. Also, the result of interfering studies showed that substances such as calcium, manganese, sodium, potassium and etcdid not show any interferences for electroctalytic determination of sulfide using surfactant modified ZSM-5 nanozeolite.

3.9. Real sample analysis

In order to evaluate the applicability of the proposed method for the determination of sulfide in real samples, its utility was performed to the determination of sulfide in tap water and mineral water using cyclic voltammetry method. The accuracy of this method was compared with a recognized published method for sulfide determination [41]. The results are

shown in Table 3, which indicate that the determination of sulfide using the modified electrode is effective and can be applied for detection of sulfide in real samples with satisfactory results.

Table 3. Determination of sulfide in real samples

Sample	Sulfide added ($\times10^{-4}$ M)	Proposed method ($\times 10^{-4}$ M)[a]	Recovery (%)	Published method ($\times 10^{-4}$ M) [41]
Tap water	-	<Limit of detection	-	-
	2.46	2.65 ±0.05	107	2.61 ±0.03
	2.65	2.7 ±0.07	101	2.56 ±0.03
	7.01	7.00 ±0.04	99	7.6 ±0.05
Mineral water	-	<Limit of detection	-	-
	1.12	1.25 ±0.10	111	1.17 ±0.02
	2.65	2.8 ±0.08	105	2.56 ±0.03
	7.01	7.5 ±0.05	106	7.6 ±0.05

(a) Average of five runs ± S.D.

4. CONCLUSIONS

In this study, the carbon paste electrodes were modified with ZSM-5 nanozeolite and surfactant modified ZSM-5 nanozeolite and was used for the determination of sulfide. The electrochemical behavior of sulfide at the surface of modified electrode was investigated in pH 8.0 phosphate buffer solution. The cyclic voltammetry method displayed effective electrocatalytic activity in lowering the anodic overpotential for sulfide at surfactant modified ZSM-5 nanozeolite carbon past electrode (SMNZ/CPE). This new modified electrode has some advantages such as low cost and stability, low background current, ease of preparation and regeneration, stable response and very low Ohmic resistance. The electron transfer coefficient (α) of sulfide at the surface of SMNZ/CPE was calculated 0.93 using Tafel plot and diffusion coefficient (D) was obtained 6.614×10^{-6} cm^2 s^{-1} using chronoamperometric methods. The relative standard deviation (RSD) for six sequential assays for six measurements using six different SMNZ/CPEs was less than 2%. Finally, the modified electrode (SMNZ/CPE) was successfully used for the determination of sulfide in tap water and mineral water samples.

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