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Article

Electrocatalytic oxidation of hydrazine on magnetic bar carbon paste electrode modified with benzothiazole and iron oxide nanoparticles: Simultaneous determination of hydrazine and phenol

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ABSTRACT

A magnetic bar carbon paste electrode (MBCPE) modified with Fe₃O₄ magnetic nanoparticles (Fe₃O₄NPs) and 2-(3,4-dihydroxyphenyl) benzothiazole (DPB) for the electrochemical determination of hydrazine was developed. The DPB was firstly self-assembled on the Fe₃O₄NPs, and the resulting Fe₃O₄NPs/DPB composite was then absorbed on the designed MBCPE. The MBCPE was used to attract the magnetic nanoparticles to the electrode surface. Owing to its high conductivity and large effective surface area, the novel electrode had a very large current response for the electrocatalytic oxidation of hydrazine. The modified electrode was characterized by voltammetry, scanning electron microscopy, electrochemical impedance spectroscopy, infrared spectroscopy, and UV-visible spectroscopy. Voltammetric methods were used to study the electrochemical behaviour of hydrazine on MBCPE/Fe₃O₄NPs/DPB in phosphate buffer solution (pH = 7.0). The MBCPE/Fe₃O₄NPs/DPB, acting as an electrochemical sensor, exhibited very high electrocatalytic activity for the oxidation of hydrazine. The presence of DPB was found to reduce the oxidation potential of hydrazine and increase the catalytic current. The dependence of the electrocatalytic current on the hydrazine concentration exhibited two linear ranges, 0.1–0.4 μmol/L and 0.7–12.0 μmol/L, with a detection limit of 18.0 nmol/L. Additionally, the simultaneous determination of hydrazine and phenol was investigated using the MBCPE/Fe₃O₄NPs/DPB electrode. Voltammetric experiments showed a linear range of 100–470 μmol/L and a detection limit of 24.3 μmol/L for phenol, and the proposed electrode was applied to the determination of hydrazine and phenol in water samples.

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1. Introduction

Although hydrazine is used in some fields, especially in industry, and plays an important role in human life, it is dangerous for the environment and hazardous to health [1,2]. Hydrazine is volatile, toxic and easily absorbed by oral, dermal, or inhalation routes [3]. Because of this, the measurement of hydrazine in the environment is important. Hydrazine can be measured using several methods, including spectrophotome-

try, chemiluminescence, ion-exclusion chromatography, high-performance liquid chromatography, amperometry and voltammetry [4–11]. Electrochemical methods are very simple, sensitive, and effective for detecting different species. However, many species have high oxidation potential and low current on the surface of unmodified electrodes. Chemically modified electrodes increase the rate of electron transfer by reducing the overvoltage for the reaction [12,13]. The oxidation of hydrazine at carbon paste electrodes (CPE) has a high overpotential and

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an extremely low oxidation current. Although the oxidation of hydrazine can be easily carried out on gold and platinum electrodes, these two metals are very expensive [14].

It is well known that phenol is highly dangerous to the skin, eyes, and mucous membranes in humans after short inhalation or dermal exposure, and is quite toxic via oral exposure. Prolonged exposure to phenol can have several serious effects on human health such as anorexia, progressive weight loss, diarrhea, vertigo, excessive salivation, darkening of the urine, and blood [15]. Therefore, the detection of phenol and phenol derivatives is also very important. Phenol and phenol derivatives have been measured using various methods, including spectrophotometry, high-performance liquid chromatography, amperometry, enzyme sensing, and voltammetry [16–20]. Although, there are numerous reports on the individual determination of hydrazine and phenol using voltammetric methods, but few researchers have reported the simultaneous determination of hydrazine and phenol [21].

Great attention has been paid to the use of magnetic beads (MBs) in electrochemistry in recent years [22–24]. Magnetic nanoparticles are usually used owing to their super strong paramagnetic properties, low toxicity, and easy preparation. Iron oxide nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) are one of the most important components for fabricating magnetic beads possessing high surface area. Owing to their good properties, magnetic nanoparticles have been used to modify the surface of electrodes [25]. At the same time, Fe_3O_4 nanoparticles have been applied as catalysts in electrochemical methods because they increase the electrode surface area, electrical conductivity, and electron transfer kinetics for many species [26,27].

Self-assembly procedures are useful for modifying surfaces, and have been recently applied in various fields such as surface protection, molecular electronics, and fabrication of sensors and biosensors [28,29]. Self-assembled monolayers (SAM) are an elegant way to modify an electrode surface, and can be formed by spontaneous adsorption of self-assembling molecules on solid metals such as gold, silver, iron, nickel, and platinum [29–32]. Until now only a few studies have been reported on the self-assembly of $\text{Fe}_3\text{O}_4\text{NPs}$ as a modification for the determination of chemical species. Herein, we report for the first time a novel electrochemical sensor for hydrazine determination based on self-assembled $\text{Fe}_3\text{O}_4\text{NPs}$ as modifier and carbon paste electrode as the platform.

The exploitation of electrocatalytic processes at the surface of modified electrodes has been investigated to increase the oxidation current and minimize the oxidation overvoltage of target species. In our previous work in electrocatalysis, a modified electrode (MBCPE/DPSPP/RGO/ $\text{Fe}_3\text{O}_4\text{NPs}$) was designed for the determination of hydrazine and simultaneous determination of hydrazine and hydroxylamine [33]. In this work, 2-(3,4-dihydroxyphenyl) benzothiazole (DPB), an organo-sulfur compound, was used as a modifier. The main aim was to achieve electrocatalytic oxidation of hydrazine and simultaneous determination of hydrazine and phenol using a self-assembling modifier (DPB) applied to the surface of Fe_3O_4 nanoparticles. Firstly, a magnet bar carbon paste electrode (MBCPE) was fabricated [34] and $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ was adsorbed onto the

electrode surface to prepare a MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ electrochemical sensor. A schematic representation of the MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ based electrochemical hydrazine sensor is shown in Scheme 1. As mentioned above, the magnetic bar was inserted into the CPE to attract the magnetic material to the electrode surface, a method that can lead to a great enhancement of effective surface area with a good stability and without any loss of magnetic nanoparticles from the electrode surface during electrochemical tests. The obtained results revealed that the anodic peak current for the MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ sensor was proportional to the hydrazine concentration in two ranges (0.1–0.4 and 0.7–12.0 $\mu\text{mol/L}$), and the obtained detection limit was 18.0 nmol/L. Under optimum conditions, some kinetic parameters for hydrazine oxidation, such as the diffusion coefficient and electron transfer coefficient, were determined using electrochemical methods.

The oxidation potentials of hydrazine and phenol on a bare carbon paste electrode are close to each other and their differential pulse voltammograms (DPV) overlap. The DPV of a mixture of these analytes at the proposed electrode (MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$) showed a peak potential difference (380.0 mV). This is sufficient to perform simultaneous determination of hydrazine and phenol, as conducted in this research. Additionally, the fabricated electrochemical sensor (MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DBP}$) was applied to the determination of hydrazine in tablet samples, and the simultaneous determination of hydrazine and phenol in water samples.

2. Experimental

2.1. Chemicals and apparatus

The DPB was synthesized according to a previously reported method [35]. The chemical structure of DPB is shown in the Scheme 1. Other materials and chemicals were purchased from Merck and used as received. The electrochemical measurements were performed with an Autolab potentiostat/galvanostat (PGSTAT-302 N, Eco Chemie, Netherlands). The experimental conditions were controlled with Nova 1.7 software on a PC. The working, counter, and reference electrodes were the magnetic bar carbon paste/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ electrode, a platinum electrode, and an Ag/AgCl (sat.), KCl (3 mol/L) electrode, respectively. All potentials in this research are reported

Scheme 1. Schematic representation of the electrochemical detection of hydrazine based on the MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ electrode.

with respect to this reference electrode. Metrohm model 691 pH/mV meters were used for pH measurements. FT-IR experiments were performed using a spectrometer (VERTEX 70, Bruker Optics, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector. Scanning electron microscopy (SEM) was performed with a TESCAN VEGA3 instrument. The absorption spectra of the samples were obtained using an Analytik Jena SPECORD-205 spectrophotometer in the range of 190–1000 nm and at 1 nm resolution.

2.2. Synthesis of $\text{Fe}_3\text{O}_4\text{NPs}$

Fe_3O_4 nanoparticles were synthesized in accordance with the method described in Ref. [36]. Briefly, 5.17 g FeCl_3 and 2.02 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 1 L deionized water under ultrasonication. Subsequently, a NaOH solution (1 mol/L) was added dropwise into the mixture over 50 min under ultrasonication and nitrogen atmosphere, using a burette. The colour of the resulting mixture changed from yellow to black [36]. The formed precipitate was collected with a permanent magnet and washed five times with distilled water.

2.3. Preparation of the electrode

Carbon paste was prepared by hand mixing 0.5 g graphite powder and three drops of paraffin (Dc 350, Merck) using a mortar and pestle. This paste was then packed into the end of a glass tube (ca. 6 mm i.d. and 10 cm long). A magnetic bar was inserted into the tube to be coated with the carbon paste to provide a magnetic field. An electrical contact was made by pushing a conductive copper wire through the glass tube to connect with the magnetic bar [34]. For the attraction of $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ onto the MBCPE electrode surface, a dispersion of $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ (1 mg/mL) was dropped onto the MBCPE electrode. After washing the electrode surface with deionized water, the fabrication of the electrochemical sensor (MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$) was complete.

3. Results and discussion

3.1. Modification of the $\text{Fe}_3\text{O}_4\text{NPs}$ by DPB

A self-assembled monolayer of DPB was formed on the Fe_3O_4 nanoparticles by mixing 5 mmol DPB and 1 mg $\text{Fe}_3\text{O}_4\text{NPs}$ in 1 mL ethanol solution for 5 h at room temperature. The mixture was placed onto the magnet bar electrode and then rinsed several times with distilled water until all unadsorbed modifier had been washed away. The FT-IR spectrum of the $\text{Fe}_3\text{O}_4\text{NPs}$ (Fig. 1(a), curve (1)) showed a weak peak at 3500–3300 cm^{-1} , corresponding to the O–H stretch of water molecules accompanying the $\text{Fe}_3\text{O}_4\text{NPs}$ [37]. Also shown in Fig. 1(a) curve (2), the FT-IR spectrum of DPB exhibited $\nu = 3478$ (OH), 1623 (C=N), 1589 and 1470 (C=C, aromatic), 1364, 1264 (C=S), 1200 (C–O), 1175, 1071, 1055, 765, 721 (=C–H) cm^{-1} [35]. The FT-IR spectrum of $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ (curve (3)) was similar to that of DPB, demonstrating that DPB molecules were successfully adsorbed on the nanoparticles. All of the DPB FT-IR peaks were

Fig. 1. (a) FT-IR spectra and (b) UV-Vis spectra of (1) $\text{Fe}_3\text{O}_4\text{NPs}$, (2) DPB and (3) $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$.

seen in the $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ spectrum except $\nu = 1264$ (C=S) cm^{-1} , which indicated that the DPB molecules were connected to the $\text{Fe}_3\text{O}_4\text{NPs}$ via the benzothiazole group. A peak (O–H, $\nu = 3300$ cm^{-1}) indicating the presence of free OH groups was also observed, meaning that the hydroxyl groups of DPB in $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ were free for an electrocatalytic role.

Fig. 1(b) reveals the UV-Vis absorbance spectra of the bare $\text{Fe}_3\text{O}_4\text{NPs}$, DPB, and $\text{Fe}_3\text{O}_4\text{NPs}$ with self-assembled DPB. The $\text{Fe}_3\text{O}_4\text{NPs}$ displayed a weak absorption band at 300 nm (curve (1)) [38]. DPB displayed an absorption band at 360 nm (curve (2)) [39], while a sharp peak at 420 nm was observed in the spectrum of $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ which was related to presence of DPB on the $\text{Fe}_3\text{O}_4\text{NPs}$ surface. Moreover, the red shift of the spectrum confirmed that the DPB molecules were self-assembled on the $\text{Fe}_3\text{O}_4\text{NPs}$.

3.2. Characterization of the electrode surface

The surface of the MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ electrode was studied by SEM, cyclic voltammetry, and electrochemical impedance spectroscopy. The morphology of bare MBCPE, MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ and MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ was studied by SEM (Fig. 2). As shown in Fig. 2(a), the bare MBCPE had an amorphous and flat structure. Fig. 2(b) shows that the $\text{Fe}_3\text{O}_4\text{NPs}$ -modified electrode had a higher surface area than the bare electrode because of the large amount of spherical

Fig. 2. SEM images of (a) MBCPE, (b) MBCPE/Fe₃O₄NPs, and (c) MBCPE/Fe₃O₄NPs/DPB electrodes.

shapes on its surface. Fig. 2(c) reveals that the Fe₃O₄NPs/DPB surface was not rougher than that of the Fe₃O₄NPs. In addition, the conjoined spherical-like shapes observable in Fig. 2(c) are probably indicative of the self-assembly of the DPB molecules on the surface of the Fe₃O₄NPs.

The surface of different electrodes was investigated by cyclic voltammetry in a solution containing the redox couple K₄Fe(CN)₆ (0.5 mmol/L)/K₃Fe(CN)₆ (0.5 mmol/L) and KCl (0.1 mol/L). Fig. 3(a) shows the cyclic voltammograms of the three prepared electrodes, MBCPE, MBCPE/Fe₃O₄NPs, and MBCPE/Fe₃O₄NPs/DPB in the solution. Curve (1) in Fig. 3(a)

reveals the peak current oxidation of [Fe(CN)₆]^{3-/4-} at the bare MBCPE. Placing Fe₃O₄NPs on the surface of the electrode (curve (2)) led to an increase in the peak current of the [Fe(CN)₆]^{3-/4-} redox couple, owing to the greatly increased electrode surface area. After adsorption of DPB on the MBCPE/Fe₃O₄NPs electrode surface (curve (3)), the [Fe(CN)₆]^{3-/4-} peak current decreased owing to reductions in the effective area and number of active sites for electron transfer. The surface area of the MBCPE/Fe₃O₄NPs electrode was estimated to be 0.52 cm² from cyclic voltammograms of K₃[Fe(CN)₆] (1.0 mmol/L) at various scan rates using the Randles-Sevcik equation [40].

Fig. 3. (a) Cyclic voltammograms of (1) MBCPE, (2) MBCPE/Fe₃O₄NPs, and (3) MBCPE/Fe₃O₄NPs/DPB electrode in KCl solution (0.1 mol/L) containing the redox couples of K₄Fe(CN)₆ (0.5 mmol/L) and K₃Fe(CN)₆ (0.5 mmol/L), scan rate 100 mV/s. (b) Nyquist plots of (1) MBCPE, (2) MBCPE/Fe₃O₄NPs, and (3) MBCPE/Fe₃O₄NPs/DPB. EIS conditions: ac potential amplitude of 5 mV, frequency range of 10 kHz to 0.1 Hz. Inset: The applied equivalent circuit to model impedance data in the presence of redox couples [Fe(CN)₆]^{3-/4-}. (c) Variation of anodic peak current versus concentration of Fe₃O₄NPs in KCl solution (0.1 mol/L) containing the redox couples of K₄Fe(CN)₆ (0.5 mmol/L) and K₃Fe(CN)₆ (0.5 mmol/L). (d) Variation of anodic peak current versus distance of magnetic bar of electrode surface in KCl solution (0.1 mol/L) containing the redox couples of K₄Fe(CN)₆ (0.5 mmol/L) and K₃Fe(CN)₆ (0.5 mmol/L).

The electrode fabrication process was also characterized by EIS. Fig. 3(b) shows a comparison of the EIS signals of the MBCPE, MBCPE/Fe₃O₄NPs, and MBCPE/Fe₃O₄NPs/DPB electrodes in KCl solution (0.1 mol/L) containing the [Fe(CN)₆]^{3-/4-} redox couple. The charge transfer resistance of the bare MBCPE was $R_{ct} = 1.64$ k Ω . When the Fe₃O₄ nanoparticles were added to the surface of the electrode the conductance surface increased, which decreased its charge transfer resistance ($R_{ct} = 0.42$ k Ω ; curve (2)). In contrast, when the electrode surface was covered by DPB, its electron transfer resistance increased ($R_{ct} = 1.76$ k Ω , curve (3)). Thus, there was a good agreement between the results of the CV and EIS characterizations of the electrode fabrication. The inset of Fig. 3(b) shows the Randles equivalent circuit applied for analyzing the Nyquist plots. In this equivalent circuit, R1 is the electrolyte resistance (for [Fe(CN)₆]^{3-/4-} (0.5 mmol/L) and KCl (0.1 mol/L)), W is the Warburg impedance resulting from the diffusion of ions, CPE is the constant phase element, and R2 (R_{ct}) is the electron transfer resistance.

The optimization of the concentration of Fe₃O₄NPs suspension applied to the electrode surface was performed (Fig. 3(c)). As shown in Fig. 3(c), ΔI ($\Delta I = I_{final} - I_{initial}$, where I_{final} and $I_{initial}$ are the [Fe(CN)₆]^{3-/4-} peak current in the presence and absence of Fe₃O₄NPs on the surface of the MBCPE, respectively, in 0.1 mol/L KCl) was enhanced by increasing the concentration of the Fe₃O₄NPs suspension from 0.2 to 1.0 mg/mL, beyond which it leveled off. These results indicated that increasing the concentration of the Fe₃O₄NPs suspension to 1.0 mg/mL allowed the total surface of the MBCPE electrode to become saturated with the NPs, and that increases beyond this value this had no effective influence on the surface of the designed electrode. According to these observations, 1.0 mg/mL was chosen as the optimum concentration of Fe₃O₄NPs for application to the electrode surface.

Another parameter which must be optimized in this work is the distance of the magnet bar from the surface of the prepared electrode, because of its significant effect on the attraction of the magnetic nanoparticles onto the surface of electrode. As Fig. 3(d) indicates, with increasing distance of the magnetic bar from the electrode surface (from 0.2 to 0.5 cm), ΔI ($\Delta I = I_{MBCPE} - I_{CPE}$, where I_{MBCPE} and I_{CPE} are the peak current measured at CPE and MBCPE, respectively, in a solution containing [Fe(CN)₆]^{3-/4-} (0.5 mmol/L) and KCl (0.1 mol/L)) was approximately constant until a certain point, and then decreased. This result can be explained by a decreasing amount of Fe₃O₄NPs attracted to the electrode surface when the distance was increased to more than 0.5 cm, so 0.5 cm was selected as the optimum distance of the magnetic bar from the electrode surface.

3.3. Electrocatalysis of hydrazine oxidation

Cyclic voltammetry was used to evaluate the electrocatalytic oxidation of hydrazine in the presence of the DPB modifier. The electrochemical parameters of DPB are reported in Ref. [35]. Cyclic voltammograms were recorded at the MBCPE, MBCPE/Fe₃O₄NPs, and MBCPE/Fe₃O₄NPs/DPB electrodes in a phosphate buffer solution (pH = 7.0). The typical processes associated with the electrochemical oxidation of hydrazine are

Fig. 4. Cyclic voltammograms of phosphate buffer solution (0.1 mol/L; pH = 7.0) at scan rate 20 mV/s. (1) MBCPE in absence of hydrazine; (2) MBCPE in presence of hydrazine (10 μ mol/L); (3) MBCPE/Fe₃O₄NPs in presence of hydrazine; (4) MBCPE/Fe₃O₄NPs/DPB in absence of hydrazine; (5) MBCPE/Fe₃O₄NPs/DPB in present of hydrazine.

illustrated in Fig. 4. Curves (1) and (2) in Fig. 4 show cyclic voltammograms of a phosphate buffer solution (0.1 mol/L; pH = 7.0) at the MBCPE in the absence and presence of hydrazine (10 μ mol/L), respectively. Curve (3) shows the cyclic voltammogram at MBCPE/Fe₃O₄NPs in presence of hydrazine. Curves (4) and (5) exhibit the cyclic voltammograms at MBCPE/Fe₃O₄NPs/DPB in the absence and presence of hydrazine, respectively. Comparison of curves (1) and (2) reveals that hydrazine was oxidized at 0.70 V on the MBCPE electrode in the absence of modifier. The oxidation current of hydrazine was enhanced in the presence of Fe₃O₄ nanoparticles. In the presence of DPB, the hydrazine was oxidized at 0.15 V; a potential about 550 mV more negative than that observed in absence of DPB. As this figure shows, hydrazine was more easily oxidized in the presence of DPB, and the current at MBCPE/Fe₃O₄NPs/DPB was enhanced by almost two times in the presence of hydrazine. These results confirm that electrocatalytic behavior was obtained for the oxidation of hydrazine in the presence of DPB as a heterogeneous modifier on the surface of MBCPE/Fe₃O₄NPs.

3.4. Influence of specific variables

The influence of variables including pH, DPB concentration, and time for self-assembly was studied. As previously explained, a self-assembled monolayer of DPB was formed on the Fe₃O₄ nanoparticles when different amounts of DPB and 1.0 mg of Fe₃O₄NPs were mixed in 1.0 mL ethanol solution for 5 h at room temperature. The influence of the concentration of DPB in the Fe₃O₄NP suspension (1.0 mg/mL) on the oxidation peak current of hydrazine was studied for mass ratios of 1:1 to 7:1 for DPB/Fe₃O₄NPs at a scan rate of 20 mV/s. This experiment was carried out for three different concentrations of hydrazine (0.1, 0.2, and 0.3 μ mol/L). The results showed that increasing the concentration of DPB in the Fe₃O₄NPs suspension up to a mass ratio of 3:1 increased the measured peak current. Further

Fig. 5. (a) Variation of anodic peak current of DPB versus time of self-assemblies in phosphate buffer solution (pH = 7.0); (b) Variation of anodic peak current of DPB versus pH in presence of hydrazine at phosphate buffer solution.

increases in the ratio of DPB had no effect on the magnitude of the hydrazine peak current. This result revealed that the total surface of the Fe_3O_4 NPs was saturated with DPB at a DPB/ Fe_3O_4 NPs mass ratio of 3:1. Therefore, mass ratio of 3:1 for DPB: Fe_3O_4 NPs was selected as the optimal mass ratio.

The optimum time for the self-assembly of DPB on the Fe_3O_4 NPs was also examined. As shown in Fig. 5(a), as the time allowed for the self-assembly of DPB on the Fe_3O_4 NPs was increased up to 5 h, ΔI ($\Delta I = I_{\text{final}} - I_{\text{initial}}$, where I_{final} and I_{initial} are the DPB peak current with and without hydrazine, respectively, in a buffer solution (0.1 mol/L)) first increased and then slightly decreased. Thus, the total surface of the Fe_3O_4 NPs appeared to be saturated with DPB within 5 h, and additional time did not influence the amount of DPB self-assembled on the Fe_3O_4 NPs. Therefore, 5 h was selected as the optimal period for the self-assembly of DPB on the Fe_3O_4 NPs.

The effect of pH on the oxidation peak of hydrazine at the MBCPE/ Fe_3O_4 NPs/DPB electrode was investigated by cyclic voltammetry in buffer solution (0.1 mol/L) at various pH from 2.0 to 12.0. The pH was found to affect electrocatalytic oxidation of DPB in the presence of hydrazine. It can be seen in Fig. 5(b) that ΔI increased from pH = 2.0 to 7.0, and then decreased after pH = 7.0 (7.0–12.0). Therefore, pH = 7.0 was selected as the optimum pH for the following experiments.

3.5. Effect of scan rate and Tafel plot

The effect of scan rate on the electrocatalytic oxidation of hydrazine at MBCPE/ Fe_3O_4 NPs/DPB was investigated by cyclic voltammetry. Fig. 6(a) shows the cyclic voltammograms of MBCPE/ Fe_3O_4 NPs/DPB at various scan rates obtained in a phosphate buffer solution (0.1 mol/L; pH = 7.0) containing hydrazine (4 $\mu\text{mol/L}$). Fig. 6(b) shows a selected region of the Tafel plot for the cyclic voltammogram obtained at a scan rate of 20 mV/s. The hydrazine oxidation current was found to increase linearly with the square root of scan rate (Fig. 6(c)), indicating that the reaction was mass transfer controlled. Also, a plot of normalized current ($I_p/\nu^{1/2}$) versus sweep rate (Fig. 6(d)) revealed that increasing ν caused the normalized currents ($I_p/\nu^{1/2}$) to decrease until a certain level was reached.

This confirms that the oxidation of hydrazine at MBCPE/ Fe_3O_4 NPs/DPB had an EC' catalytic mechanism. Fig. 6(e) reveals the Tafel plot drawn from the data of the rising part of the plotted current-voltage curve obtained at a scan rate of 20 mV/s. The slope of the Tafel plot was calculated to be 0.204 V/decade. The charge transfer coefficient between hydrazine and MBCPE/ Fe_3O_4 NPs/DPB was calculated to be $\alpha = 0.69$ using the slope of Tafel plot, the equation $2.3RT/n\alpha(1-\alpha)F$, and assuming $n\alpha = 1$.

3.6. Chronoamperometric measurements

The chronoamperometric behavior of MBCPE/ Fe_3O_4 NPs in a phosphate buffer solution containing DPB was examined in the absence and presence of hydrazine. Chronoamperometric measurements of various concentrations of hydrazine solutions were carried out by setting the potential of working electrode at 250 mV versus the Ag/AgCl electrode [41]. The obtained chronoamperograms are depicted in Fig. 7(a). The diffusion coefficient of hydrazine was determined from the results. In the presence of hydrazine at an experimental time of 0–20 s, the modifier was oxidized and the rate of electrocatalyzed hydrazine oxidation increased with the diffusion of hydrazine from the bulk to the modifier on the electrode surface, thus increasing oxidation current. The diffusion coefficient (D) of hydrazine can be evaluated using the Cottrell equation, which describes relationship between diffusion coefficient and the hydrazine bulk concentration [42,43].

$$I = nFAC(D/\pi t)^{1/2} \quad \text{Eq. (1)}$$

where D and C are the diffusion coefficient (cm^2/s) and the bulk concentration (mol/cm^3) of hydrazine, respectively. A is the effective electrode area ($A = 0.52 \text{ cm}^2$) and n is the number of electrons transferred ($n = 4$) in the oxidation reaction. Fig. 7(a) shows that the level of Cottrell current increased with the hydrazine concentration. Fig. 7(b) shows the plot of I vs. $t^{-1/2}$. The slopes of the straight lines from the Fig. 7(b) are plotted versus hydrazine concentration in Fig. 7(c). From the slope of this line, the diffusion coefficient of hydrazine was calculated to be $7.19 \times 10^{-6} \text{ cm}^2/\text{s}$, comparable with the previously reported values of $8.2 \times 10^{-6} \text{ cm}^2/\text{s}$ [14] and $4.5 \times 10^{-6} \text{ cm}^2/\text{s}$ [12].

Fig. 6. (a) Cyclic voltammograms of MBCPE/Fe₃O₄NPs/DPB in phosphate buffer (0.1 mol/L; pH = 7.0) containing hydrazine (4.0 μmol/L) at different scan rates. The curves from down to up correspond to 20, 40, 60, 80, 100, 150, 200 and 300 mV/s scan rates, respectively. (b) The selected region for plotting Tafel diagram in scan rate 20 mV/s for electrocatalytic oxidation of hydrazine at MBCPE/Fe₃O₄NPs/DPB. (c) Variation of the electrocatalytic peak currents vs. $\nu^{1/2}$. (d) Variation of the scan rate-normalized peak current ($I_p/\nu^{1/2}$) versus scan rate (ν). (e) Tafel plot derived from the rising part of current potential curve recorded at scan rate of 20 mV/s.

Fig. 7. (a) Chronoamperograms of MBCPE/Fe₃O₄NPs/DPB in phosphate buffer solution (0.1 mol/L) containing 0, 1, 2, 3 and 4 μmol/L of hydrazine (from down to up). (b) Plot of I vs. $t^{-1/2}$ obtained from chronoamperometric experiments. (c) The slopes of the resulting straight line of (b) vs. hydrazine concentration.

The chronoamperometric method was also applied to evaluate the catalytic rate constant, k (L/(mol·s)), of the reaction between hydrazine and DPB using the Galus method [44].

$$I_c/I_l = \gamma^{1/2} [\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \quad \text{Eq. (2)}$$

where I_c is the catalytic current of DPB in the presence of hydrazine at MBCPE/Fe₃O₄NPs, I_l is the limited current in the absence of hydrazine, and $\gamma = kCt$ (where C is the bulk concentration of hydrazine) is the argument of the error function. In

cases where γ is more than 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_c/I_l = \pi^{1/2}(kCt)^{1/2} \quad \text{Eq. (3)}$$

where k , C , and t are the catalytic rate constant (L/(mol·s)), catalyst concentration (mol/L), and time elapsed, respectively. I_c and I_l are the currents of MBCPE/Fe₃O₄NPs/DPB in a buffer solution (pH = 7.0) in the presence and absence of hydrazine, respectively. The values of I_c/I_l versus $t^{1/2}$ were plotted, and

from the slope of this plot, the average value of k was calculated to be $5.1 \times 10^3 \text{ L}/(\text{mol}\cdot\text{s})$.

3.7. Investigation of reaction mechanism

The following processes are suggested for the mechanism of the electrocatalyzed hydrazine oxidation reaction. (1) Firstly, DPB is oxidized on the surface of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$. (2) Electrocatalytic reaction between the oxidized form of DPB and hydrazine takes place on the surface of the electrode, increasing the anodic peak current. Fig. 8(a) shows cyclic voltammograms of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ /DPB in the presence of different concentrations of hydrazine. With increasing hydrazine concentration, the oxidation peak current increased while the cathodic peak current decreased. These results confirm an electrocatalytic behavior for hydrazine oxidation on the surface of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ /DPB via an EC' mechanism. This mechanism is shown in Fig. 8(b). Hydrazine is oxidized in the catalytic chemical reaction (C') by the oxidized form of DPB, which is produced via an electrochemical reaction (E). Hydrazine in aqueous solutions can be oxidized with the loss of four electrons and the production of nitrogen gas [45,46].

3.8. Differential pulse voltammetry investigations

Differential pulse voltammetry (DPV) is the most widely applicable technique in electrochemistry owing to its high sensitivity and low charging current contribution to the background current, so this technique was used to determine the limit and the linear range of hydrazine detection at the present electrodes. The effect of hydrazine concentration on the DPV at the electrodes is presented in Fig. 9(a). As Figs. 9(b) and (c) show, the plot of peak current vs. hydrazine concentration exhibited

Fig. 8. (a) CVs of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ /DPB in phosphate buffer solution (0.1 mol/L; pH = 7.0) at scan rate 10 mV/s in 0, 0.2, 0.4, 0.6 and 0.8 $\mu\text{mol/L}$ hydrazine from bottom to top, respectively. (b) The electrocatalytic reaction mechanism for hydrazine on the surface of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ /DPB.

two linear ranges, the first 0.1–0.4 $\mu\text{mol/L}$ with a correlation coefficient of 0.9995 and the second 0.7–12.0 $\mu\text{mol/L}$ with a correlation coefficient of 0.9705. Based on $3s_b/m$ (where s_b is the standard deviation of a blank solution and m is the slope of the calibration curve (Fig. 9(b)), the detection limit was deter-

Fig. 9. (a) Differential pulse voltammograms of MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}$ /DPB in phosphate buffer solution (0.1 mol/L; pH = 7.0) containing different concentrations of hydrazine. (b) Calibration curve in the range of 0.1 to 0.4 $\mu\text{mol/L}$. (c) Calibration curve in the range of 0.7 to 12.0 $\mu\text{mol/L}$.

mined to be 18.0 nmol/L. The limit of detection, linear range, optimal pH for the catalytic effect, and peak potential shift of a number of previously reported modified electrodes against that of the proposed electrode for the determination of hydrazine are listed in Table 1 [8,31,32,47–50]. According to Table 1, the detection limit of the proposed electrode sensor was lower than that of all other methods except for that of Ref. 48. The very low detection limit for determination of hydrazine obtained in this work arose from the presence of the magnetic bar in the CPE electrode, which caused the electrode surface to adsorb a large amount of Fe₃O₄NPs/DPB and thereby greatly increased the effective area of the electrode.

3.9. Effect of chemical interferences

Several cations and anions including Na⁺, Cs⁺, NH₄⁺, Mg²⁺, Ca²⁺, Ba²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Mn²⁺, Cu²⁺, C₂O₄²⁻, NO₃⁻, CH₃COO⁻, Br⁻, F⁻, I⁻ were checked for interference with the hydrazine oxidation reaction. To investigate the effect of these interferences, the concentration of hydrazine was set to 1.0 μmol/L under optimum conditions. Up to a molar ratio of 1000, none of the investigated anions and cations had any interference effect on the hydrazine oxidation peak current. The checking of compounds such as hydroxylamine that may be present in water matrix was also carried out, and it was found that hydroxylamine had a serious interference effect.

3.10. Simultaneous determination of hydrazine and phenol

Hydrazine and phenol are two important hazardous compounds that exist together in water samples. Owing to small difference between the oxidation potentials of hydrazine and phenol, the simultaneous determination of these two components using electrochemical methods is difficult but vital. In this work, the simultaneous determination of hydrazine and phenol was successfully achieved using the proposed chemically modified (Fe₃O₄NPs/DPB) electrochemical sensors.

DPV was used for the simultaneous determination of hydrazine and phenol at MBCPE/Fe₃O₄NPs/DPB, because of the better selectivity and lower detection limit of this technique compared with those of other electrochemical methods. At first, the intermolecular interaction between the two compounds was investigated at MBCPE/Fe₃O₄NPs/DPB and then the concentra-

tion of phenol was varied while the hydrazine concentration was kept constant. A hydrazine concentration of 0.3 μmol/L, the peak current of phenol oxidation was proportional to its concentration from 100–470.0 μmol/L (ΔI (μA) = 0.0061 C_{phenol} (μmol/L) + 0.655 and R^2 = 0.98) and there was no change in the peak current of hydrazine. Therefore, increasing the concentration of phenol did not affect the hydrazine peak current (Figure not shown). Similar experiments showed that increasing the concentration of hydrazine (ΔI (μA) = 4.38 $C_{\text{hydrazine}}$ (μmol/L) + 11.44 and R^2 = 0.975) did not affect the peak current of phenol at the MBCPE/Fe₃O₄NPs/DPB electrode. Thus, the two analytes did not exhibit any intermolecular interaction and simultaneous determination of these two analytes without interference was possible at MBCPE/Fe₃O₄NPs/DPB sensor. Differential pulse voltammograms obtained for different concentrations of hydrazine and phenol are plotted in Fig. 10(a). The oxidation peak currents of hydrazine and phenol increased with their respective concentrations. Figs. 10(b) and (c) exhibit the dependence of the peak current on the concentration of hydrazine (ΔI (μA) = 4.407 $C_{\text{hydrazine}}$ (μmol/L) + 12.45, R^2 = 0.972 and ΔI (μA) = 16.5 $C_{\text{hydrazine}}$ (μmol/L) – 1.55, R^2 = 0.985) and phenol (ΔI (μA) = 0.0062 C_{phenol} (μmol/L) + 8.74, R^2 = 0.991), respectively. It is notable that the sensitivity of the modified electrode to hydrazine was approximately the same in the absence and presence of phenol, which indicates that the oxidation of hydrazine and phenol at MBCPE/Fe₃O₄NPs/DPB were independent processes. From the calibration graph (Fig. 10), the lower detection limit of phenol (3 S_b /m) was found to be 24.3 μmol/L.

3.11. Repeatability and stability of the sensor

For repeatability investigations of the fabricated hydrazine sensor, three parallel MBCPE/Fe₃O₄NPs/DPB sensors were constructed and then examined using hydrazine (4 μmol/L). The three independent hydrazine sensors were produced on the same day and all solutions used, such as the Fe₃O₄NPs and DPB suspensions, were identical. An acceptable relative standard deviation of 3.8% (n = 3) was obtained for ΔI (where ΔI = I_{final} – I_{initial} and I_{final} and I_{initial} are DPB peak currents in buffer solution (0.1 mol/L) at pH = 7.0 with and without hydrazine, respectively), indicating that this electrochemical sensor (MBCPE/Fe₃O₄NPs/DPB) had a satisfactory repeatability. The stability of the proposed modified electrode was also investi-

Table 1

Comparison of the efficiency of some modified electrodes used for determination of hydrazine.

Method	Electrode	Peak potential shift (mV)	pH	Dynamic range (μmol/L)	Detection limit (μmol/L)	Ref.
Amp	WO ₃	700	7.0	100–1000	144	[8]
CV	PANI/Pd ₀	—	7.0	0.3–12000	0.05	[31]
CV	PEDOP/MWCNT-Pd	—	7.4	0.1–5000	0.04	[32]
DPV	<i>p</i> -APMWCNTPE	600	7.0	0.5–175	0.3	[47]
Amp	AG/Au-NPs	400	7.0	0.002–936	0.00057	[48]
DPV	BFT-CNT-GCE	170	8.0	0.5–700.0	0.033	[49]
DPV	Co(II)BBAEDI-MWCNT-CPE	500	7.0	0.3–70	0.1	[50]
DPV	MBCPE/Fe ₃ O ₄ /DPB	550	7.0	0.1–12	0.018	This work

CV = Cyclic voltammetry; DPV = Differential pulse voltammetry; Amp = Amperometry; *p*-APMWCNTPE = *p*-Aminophenol-multiwall carbon nanotube-paste electrode; BFT = 1-Benzyl-4-ferrocenyl-1H-[1,2,3]-triazole; PEDOP = Poly-ethylendioxy pyrrole; CNT = Carbon Nano tube; CPE = Carbon paste electrode; AG = Activated graphite.

Fig. 10. (a) Differential pulse voltammograms of MBCPE/Fe₃O₄NPs/DPB in phosphate buffer solution (0.1 mol/L; pH = 7.0) containing different concentrations of hydrazine and phenol. (1)–(9) Mixed solutions of 0.2+100, 0.3+130, 0.4+160, 0.7+210, 1+290, 2+340, 3+390, and 5+420 respectively, in which the values are the concentrations of hydrazine and phenol in μmol/L. (b) Plot of the peak currents as a function of hydrazine concentration (in the linear range of 0.2–5 μmol/L of hydrazine). (c) Plot of the peak currents as a function of phenol concentration of 100–470 μmol/L.

gated. After storage of the modified electrode in phosphate buffer solution (0.1 mol/L; pH = 7.0) at 25 °C for 4 d, the response of electrode retained about 94% of its primary response, a suitable stability.

3.12. Application of the hydrazine sensor

As explained, hydrazine in the environment poses some risks to human life. Although the determination of hydrazine with the designed MBCPE/Fe₃O₄NPs/DPB sensor was found to be applicable under laboratory conditions, an attempt was made to assess the practical analytical performance of the method with water samples. Five solutions containing appropriate amounts of hydrazine were prepared and analyzed by the proposed method. According to Table 2, an average recovery of 99% was obtained, which indicates that the typical constituents of water did not significantly interfere with the determination of hydrazine.

To ensure the accuracy of this method for the practical measurement of hydrazine, the hydrazine concentration of auxiliary cooling water from Yazd Power Generation Company

was analyzed by the proposed method, and the results were compared with those obtained using a spectrophotometric method. The hydrazine concentration of the water sample was found to be 150.2 (±3.8) ppb ($n = 4$) using the proposed method and 146.8 (±3.1) ppb ($n = 4$) using the selected spectrophotometric method [51], respectively. A t -test [52] was carried out and t_{exp} was found to be 1.42, which is less than the critical t (2.45) within a 95% confidence level. The t -test data show that there was no systematic error between the results obtained by the two methods. Therefore, the present electrochemical method seems to be promising for the determination of hydrazine in water samples. The standard addition method was also used to determine hydrazine and phenol concentrations in water samples by DPV. The obtained results are provided in Table 3. The recovery percentages in this table show that the proposed sensor (MBCPE/Fe₃O₄NPs/DPB) is applicable for the simultaneous determination of hydrazine and phenol in real water samples.

Table 3

Determination of hydrazine and phenol in water sample using proposed sensor ($n = 5$).

Sample	Added (μmol/L)	Found (μmol/L)	Recovery (%)
Hydrazine	0.00	—	—
	0.20	0.19	95
	0.30	0.31	103
	0.40	0.41	102
	0.70	0.69	98
	1.00	1.05	105
	0.00	—	—
Phenol	100	103	103
	130	129	99
	160	162	101
	210	208	99
	290	294	101

Table 2

Determination of hydrazine in water samples using proposed sensor ($n = 5$).

Sample	Hydrazine added (μmol/L)	Hydrazine found (μmol/L)	Recovery (%)
Drinking water	—	<Detection limit	—
Drinking water	1	1.03 (±0.08)	101
Drinking water	3	3.0 (±0.2)	100
Drinking water	6	6.1 (±0.5)	101
River water*	9	8.9 (±0.2)	98
River water*	10	10.5 (±0.1)	104
River water*	12	12 (±0.2)	100

*Zayandeh-Rood in Isfahan city.

4. Conclusions

In the present study, robust new magnetic bar carbon paste electrode modified with $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ was constructed as an electrochemical sensor for determination of hydrazine. The electrochemical oxidation of hydrazine at the proposed electrode was studied by cyclic voltammetry, differential pulse voltammetry, and chronoamperometry. Compared with the response observed for unmodified MBCPE, the electrochemical sensitivity of hydrazine at the modified electrode MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ was dramatically improved. Therefore, and owing to its unique structure, the fabricated sensor (MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$) has a number of advantages over the non-modified electrode (MBCPE), including as high conductivity and fast electron transfer. Briefly, kinetic parameters such as the diffusion coefficient and the electron transfer coefficient of hydrazine were determined by electrochemical methods under optimum conditions. The results obtained were comparable with those reported in the literature for similar approaches. The method was also successfully used for the determination of hydrazine in water samples. The fabricated sensor was very rapid, reproducible, stable, selective, and sensitive for determination of hydrazine. Generally, this electrochemical sensor is capable of simultaneous determination of hydrazine and phenol in water samples. The present work may lead to the fabrication of new electrochemical sensors based on the application of nano-materials and modifiers to various electrode surfaces for the determination of different compounds, especially toxic species.

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Graphical Abstract

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Electrocatalytic oxidation of hydrazine on magnetic bar carbon paste electrode modified with benzothiazole and iron oxide nanoparticles: Simultaneous determination of hydrazine and phenol

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To prepare MBCPE/ $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ sensor, a MBCPE was fabricated and then $\text{Fe}_3\text{O}_4\text{NPs}/\text{DPB}$ absorbed at the electrode surface for simultaneous determination of hydrazine and phenol.

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苯并噻唑和铁氧化物纳米粒子修饰的磁性棒碳糊电极上肼的电催化氧化反应：同时检测肼和苯酚

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摘要: 开发了一种磁性 Fe_3O_4 纳米粒子和2-(3,4-二羟基苯基)苯并噻唑(DPB)修饰的磁性棒碳糊电极(MBCPE)用于电化学检测肼。首先将DPB自组装在 Fe_3O_4 纳米粒子上,然后将此复合物吸附于设计的MBCPE上。MBCPE电极将磁性纳米粒子吸引到电极表面。所得新型电极具有高的导电性和大的有效比表面积,因而对肼的电催化氧化反应有非常大的电流响应。采用伏安法、扫描电镜、电化学阻抗谱、红外光谱和紫外-可见光谱对修饰电极进行了表征。采用伏安法研究了在磷酸盐缓冲溶液($\text{pH} = 7.0$)中MBCPE/ Fe_3O_4 NPs/DPB电极上肼的电化学行为。作为电化学传感器, MBCPE/ Fe_3O_4 NPs/DPB电极对肼氧化反应表现出极高的电催化活性。在DPB存在下,肼的氧化电势下降,但其催化电流增加。电催化电流与肼浓度在0.1–0.4和0.7–12.0 $\mu\text{mol/L}$ 二个区间内表现出线性关系,检测限为18.0 nmol/L。另外,研究了MBCPE/ Fe_3O_4 NPs/DPB电极同时检测肼和苯酚的性能。伏安实验结果显示,苯酚的线性区域为100–470 $\mu\text{mol/L}$,检测限为24.3 $\mu\text{mol/L}$ 。采用此电极检测了水样品中的肼和苯酚。

关键词: 修饰电极; 电催化氧化; 肼; 苯酚; 磁性棒修饰碳糊电极; 四氧化三铁纳米粒子

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