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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

Ali Benvidi *, Shahriar Jahanbani, Bibi-Fatemeh Mirjalili, Reza Zare

Chemistry Department, Yazd University, Yazd, Iran

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A magnetic bar carbon paste electrode (MBCPE) modified with Fe_3O_4 magnetic nanoparticles (Fe_3O_4NPs) and 2-(3,4-dihydroxyphenyl) benzothiazole (DPB) for the electrochemical determination of hydrazine was developed. The DPB was firstly self-assembled on the Fe_3O_4NPs, and the resulting Fe_3O_4NPs/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/Fe_3O_4NPs/DPB in phosphate buffer solution (pH = 7.0). The MBCPE/Fe_3O_4NPs/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/Fe_3O_4NPs/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.

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 spectrophotometry, 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

* Corresponding author. Tel: +98-353-8122645; Fax: +98-353-8210644; E-mail: abenvidi@yazd.ac.ir, benvidi89@gmail.com
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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 (Fe_3O_4NPs) 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 Fe_3O_4NPs 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 Fe_3O_4NPs as modifier and carbon paste electrode as the platform.

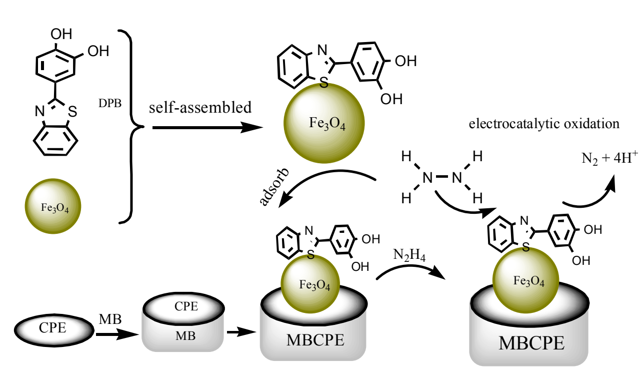
The exploitation of electrocatalytic processes at the surface of modified electrodes has been investigated to increase the oxidation current and minimize the oxidation overvoltage of target species. In our previous work in electrocatalysis, a modified electrode (MBCPE/DPSPP/RGO/Fe_3O_4NPs) was designed 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 Fe_3O_4NPs/DPB was adsorbed onto the electrode surface to prepare a MBCPE/Fe_3O_4NPs/DPB electrochemical sensor. A schematic representation of the MBCPE/Fe_3O_4NPs/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/Fe_3O_4NPs/DPB sensor was proportional to the hydrazine concentration in two ranges (0.1–0.4 and 0.7–12.0 μmol/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/Fe_3O_4NPs/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/Fe_3O_4NPs/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/Fe_3O_4NPs/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/Fe_3O_4NPs/DPB electrode.