A zeolite modified carbon paste electrode as useful sensor for voltammetric determination of acetaminophen

Leila Ahmadpour-Mobarakeh, Alireza Nezamzadeh-Ejhieh *

Department of Chemistry, Shahreza Branch, Islamic Azad University, P.O. Box 311-86145, Shahreza, Isfahan, Iran

A B S T R A C T

The voltammetric behavior of a carbon paste electrode modified with Co(II)-exchanged zeolite A (Co(II)-A/ZMCPE) for determination of acetaminophen was studied. The proposed electrode showed a diffusion controlled reaction with the electron transfer rate constant (K_s) of 0.44 s^{-1} and charge transfer coefficient of 0.73 in the absence of acetaminophen. A linear voltammetric response was obtained in the range of 0.1 to 190 $\mu mol \, L^{-1}$ of acetaminophen [$r^2 = 0.9979$, $r = 0.9989$ ($n = 10$)] with a detection limit of 0.04 $\mu mol \, L^{-1}$. The method was successfully applied to the analysis of acetaminophen in some drugs.

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1. Introduction

Acetaminophen, N-acetyl-p-aminophenol, or paracetamol is an analgesic compound that is regularly used to relieve headache, backache, arthritis and post-operative pain. This compound reduces fever associated with bacterial and viral infections [1]. Acetaminophen is a popular analgesic and antipyretic medication which has few side effects and little toxicity if it is used in its recommended doses [2], while overdose of acetaminophen may be toxic and results in sever side effects [3]. Its ready access has resulted in its increased use in attempted suicide [4]. Consequently, in recent years different techniques have been used for the determination of acetaminophen in a variety of matrices including: titrimetry [5], UV–Vis spectrophotometry [6], Fourier transformation infrared spectrophotometry [7], chromatographic methods [8,9], mass spectrometry [10,11], fluorimetry [12] and the amperometric method [2]. However, most of these methods are either time-consuming or need sophisticated instruments. Compared with other options, electrochemical techniques have inherent advantages including: simplicity, ease of miniaturization, high sensitivity and relatively low cost. Hence, modified electrodes have been widely used for electrochemical determination of different compounds because modification of the electrode surfaces significantly increases the sensitivity along with considerable decrease in detection limit and interfering effects [4,13–31].

For catalytic purposes, modification of zeolites was, therefore, carried out with some metals. Zeolites are crystalline microporous solids that contain many channel-networks proving molecular-sized cages and passageways for excellent steric control of reaction paths. The pore geometry is considered as the main reason for the different activities of zeolite-based catalysts. Transition metal-containing zeolites were found to exhibit a high catalytic activity [32–36]. Zeolite modified electrodes (ZMEs) display good sensitivity, reproducibility, selectivity, durability, ion-exchange capacity, high thermal, long lifetime, low detection limit and high chemical stability [37–46]. As far as we know, electrochemical detection of acetaminophen using zeolite modified electrode (ZME) has not been reported. This article reports the electrochemical behavior of Cobalt (II)-exchanged zeolite A incorporated in a zeolite-modified carbon paste electrode for the electrochemical investigation of acetaminophen in a 0.4 mol L^{-1} KCl solution. A simple electrode was designed with a reservoir for holding the carbon-paste. The electrode surface can be renewed very easily for a large number of times over a long period. The influences of several alkali ion electrolytes, pH, modifier percentage and instrumental parameters on the response characteristics of the electrodes were studied and the optimum operating conditions established. The modified electrode was used for the electrocatalytic oxidation of acetaminophen using cyclic voltammetry. The use of carbon-paste matrix, besides renewability by a simple polishing, offers several other advantages including easy preparation, uniform distribution of the catalyst into the paste, better reproducibility and stability, very low Ohmic resistance and adequate robustness in aqueous solutions [34].

2. Experimental

2.1. Apparatus and chemicals

Zeolite A was synthesized from waste porcelain (Esfahan glass factory, Isfahan, Iran). The porcelain was ball-mill grounded, and the particles ≤1 mm in size were sorted and washed with distilled water. Characterization of the waste porcelain used and the method of the synthesis of zeolite A were extensively described in our previous work [45]. Graphite powder, Nujol oil, cobalt nitrate and other used salts with analytical grade were obtained from Merck (Purchased from Normal Labo Co., Isfahan, Iran). Pure acetaminophen (99.99%, Aldrich) was obtained from Kimia Gostar Pooyesh Co. (Iran). Acetaminophen tablet (325 mg), acetaminophen–codeine table (325 mg) and pediatric oral drops were obtained from Hakim pharmaceutical company (Tehran, Iran). Adult cold tablet was purchased from Abidi pharmaceutical company (Tehran, Iran). Deionized distilled water was used throughout the experiments. Electrochemical experiments were carried out using an EG&G Model 273 potentiostat/galvanostat (PerkinElmer, USA) with powersuite electrochemical software. An Ag|AgCl|KCl (3 mol L^{-1}) electrode (Metrohm, Switzerland) as reference electrode, a platinum wire as the auxiliary electrode and Co(II)-A/ZMCPE as the working electrode were used. A JENWAY 3505 pH meter (UK) was used for pH adjustments. Square wave voltammograms were recorded using a Model PGSTAT101 potentiostat/galvanostat (Metrohm, Autolab B.V., Switzerland) equipped with Nova 1.8 software.

2.2. Preparation of the modified electrode

For ion exchange experiments, about 1 g of zeolite Na–A was lightly grounded and added to 25 mL of 0.01 mol L^{-1} Co(NO$_3$)$_2$·6H$_2$O solution and the obtained suspension was stirred for 24 h. In order to ensure full exchange of Co(II) with zeolitic Na$^+$, this process was repeated another time using a fresh Co(II) solution. Finally, the obtained suspension was centrifuged and the remaining solid was dispersed in dilute HCl (0.01 mol L^{-1}) for the removal of the surface adherent salts. The suspension was centrifuged and the solid was again dispersed in water and finally centrifuged. The solid Co(II)-zeolite A was air-dried and finally it was used for the preparation of zeolite modified carbon paste electrodes (ZMCPEs) as follows: an appropriate amount of the Co(II)-exchanged zeolite (5–15 wt.% with respect to graphite) was mixed with 100 mg graphite powder and then Nujol was added. After thorough hand mixing in a mortar (20 min) to obtain a fine paste (provides reproducible responses if solid particles are homogeneously dispersed into the paste), a portion of the composite mixture was packed into the end of a polyethylene tube. Electrical contact was made by forcing a copper wire of ~1 mm diameter, positioned into a glass tube with 2 mm diameter, down the polyethylene tube and into back of the paste. Unmodified electrode was prepared in a similar way, using a carbon-paste with unmodified zeolite (Na-A). For comparison, an unmodified raw carbon paste electrode (CPE) was also prepared in a similar method. A typical schematic diagram for the prepared electrodes was shown in our previous work [40]. The electrode surface was polished using a soft paper and then rinsed with ethanol and distilled water, respectively. All the electrochemical experiments were carried out under pure nitrogen atmosphere at room temperature.

2.3. Real sample preparation

Some commercial pharmaceutical samples including acetaminophen tablet (325 mg), acetaminophen–codeine table (325 mg), pediatric oral drops and adult cold tablet were used for the determination of their acetaminophen contents. An adequate amount of each tablet was finely powdered in a mortar with pestle. Calculated amounts of the tablets required for a suitable concentration were separately transferred into a 100 mL volumetric flask and dissolved in 0.4 mol L^{-1} KCl solution

(pH 3.0). The content of the flask was sonicated for 5 min to complete dissolution. Finally, the solutions were filtered and the cleared solutions stored in refrigerator for further uses.

2.4. Procedure

For cyclic voltammetric experiments, 25 mL supporting electrolyte solution was pipetted into the electrochemical cell and deaerated by purging with high purity nitrogen gas for 5 min. The inert gas was passed over the solution during all the voltammetric measurements. The modified electrode together with the reference and the counter electrodes were immersed into the solution and after several preliminary scans; the potential was scanned from + 1.4 to − 0.5 V vs. Ag/AgCl reference electrode using cyclic voltammetry. Then different volumes of acetaminophen solution were added to the voltammetric cell and the potential was scanned from + 1.4 to − 0.5 V vs. Ag/AgCl. All electrochemical measurements were conducted at room temperature (25 °C). The modified electrode was kept in open air when not in use. In all studies, after renewing the electrode surface by simple polishing and reusing the electrode, the response of the electrode was improved with increasing the repetitive scans and the best response was obtained at the 10th scan. Hence, in all experiments this was recorded as the best voltammogram.

3. Results and discussion

3.1. Electrochemical behavior of Co(II)-A/ZMCPE (in the absence of acetaminophen)

In preliminary studies, the effect of the modifier on the voltammetric behavior of the electrode was investigated because voltammetric response of ZMEs extremely relates to the nature of electroactive components incorporated in zeolite structure. Hence, it would be expected that Na-A/CPE electrode does not show a voltammetric response in supporting electrolyte solution. To confirm this postulate, voltammetric behavior of the raw carbon paste (CPE), unmodified Na-A carbon paste (UCPE) and the zeolite Co(II)-A modified carbon paste electrode (Co(II)-A/ZMCPE) was investigated in 0.1 mol L^{-1} KCl solution at a potential scan rate of 50 mV s^{-1}. Fig. 1A shows the resulting voltammograms, recorded after several preliminary scans. As shown, no voltammetric response was observed for CPE (Fig. 1A-a) and UCPE (Fig. 1A-b). This shows that when ion exchange process takes place between non-electroactive Na$^+$ zeolite framework and solution K$^+$ cations, Na$^+$ cannot produce any voltammetric response at the electrode surface. These observations have good agreement with the literature which shows that ZMEs containing alkaline and alkaline earth cations do not produce any voltammetric responses in an electrolyte solution [40].

From Fig. 1, it is obvious that a well-defined peak was observed only for the Co(II)-A-modified electrode (Fig. 1A–d). It can be described on the basis of possible mechanisms for the electrochemical processes at zeolite-modified electrodes. The electrochemical techniques are useful methods to study the diffusion of cations in zeolites. On the other hand, the electrochemistry involves heterogeneous chemical phenomena which occur heterogeneously on the electrode at the electrode–solution interface [46].

In general, three possible mechanisms including: extra-zeolite electron transfer, intra-zeolite electron transfer and boundary associated species or 'topological redox isomers' have been described for ZMEs [38,47]. In a typical extra-zeolite electron transfer mechanism (the mechanism describes the behavior of the electrode in this work), the redox species were first ion-exchanged by the supporting electrolyte cations and then diffuse to a conducting part of the electrode surface to undergo charge transfer. To investigate reaction mechanism, the effect of supporting electrolyte on voltammetric response of the electrode was studied.