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A Simple and an Effective Catalyst for Determination of Cefixime in Real Samples Using of Modified Carbon Paste Electrode with Cobalt Impregnated Zeolite

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Abstract

Carbon paste electrode modified with cobalt impregnated zeolite was prepared by mixing of cobalt-zeolite (Co-Z) and graphite powder with different percent. The electrochemical oxidation of cefixime at such electrodes was investigated using the cyclic voltammetric and amperometric techniques. It is not electrochemically active towards cefixime oxidation in 0.1 M phosphate buffer solution (pH=7) on a carbon paste electrode modified with zeolite. The presence of cobalt ions in the zeolite matrix, by soaking the electrode in an aqueous $Co(NO_3)_2$ solution, markedly enhances the electrocatalytic activity which was found to depend on the cobalt content. However, the electrocatalytic activity depends on different percent of Co-Z. Under the selected conditions, the anodic peak current was linearly dependent on the concentration of cefixime in the range 0.003–8 mM with the cyclic voltammetric method. The detection limit (S/N=3) was also estimated to be 2.98 µM. Finally, this method was applied for the determination of cefixime in tablet samples.

Keywords: *Cefixime, Cobalt, Electrocatalytic oxidation, Modified electrode, Zeolite.*

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Introduction

Zeolites are crystalline, microporous, aluminosilicate materials with the well-defined structures. Generally, they contain silicon, aluminum, and oxygen in their framework and cations, water, and/or other molecules within their pores. Zeolites have the capacity to be completely hydrated and dehydrated without damage to the crystalline lattice [1]. Zeolite–modified electrodes (ZMEs) are one of the kinds of the chemically modified electrodes, which are the results of a design of the surface of conventional electrodes in order to improve their response [2]. ZMEs became popular in the mid–1980s, and in the recent decades, numerous studies have been devoted to understanding their properties. Their main advantage consists of combining in a single device; the specificity of charge–transfer reactions with the molecular sieving and ion-exchange properties of the aluminosilicates. On the other hand, the hydrophilic character of zeolites makes them materials suited to the co–immobilization of enzymes and mediators in the preparation of biosensors [3].

Several methods have been used for incorporation of the zeolite particles into electrodes. These include the use of a pressed zeolite pellets [4], a polymer layer containing zeolite [5, 6], zeolite-carbon composites [7], and co-deposition of zeolite with organic salts [8]. One of the most flexible ways to obtain chemically modified electrodes with the zeolites is their incorporation in the carbon paste. Mixtures made of spectroscopic graphite powders (as a carbon moiety) and paraffin, mineral oils or silicone fluids were employed in the bare configuration or as the chemically modified carbon paste electrodes (CPEs), for the different analytical purposes [9, 10]. The CPE is popular because it is easily obtainable at minimal cost. The low background current, wide potential window, and versatility are the other advantages of it.

The preparation of coatings of transition metals such as Fe, Ni, Cu, Co, etc. has attracted considerable attention in view of their potential applications in the scientific and technological fields. Cobalt oxide–based materials, in particular, are used for the production of electrochromic thin films [11, 12], energy storage systems [13, 14], magneto-resistive devices [15], and heterogeneous catalysts [16-19]. Generally, the cobalt oxide films are prepared at high temperatures, namely by spray pyrolysis [20, 21], sol–gel [22-25], or sputtering [26, 27] methods, whose main drawback is the formation of defects by thermally induced stress, impairing the catalytic activity of the films. Choosing an electro-deposition technique for the preparation of thin oxide films or their alloys offers a number of unique advantages in comparison to other procedures. For instance, very thin and homogeneous films with specific morphological and chemical properties can be prepared. Electrochemical methods are interesting tools for the deposition of such materials at room temperature, but the low solubility of the cobalt hydroxide should be overcome. The physical properties of the relevant deposits can be easily modulated by means of the various experimental parameters affecting the electrodeposition process such as pH, electrolyte composition, the electrode substrate, time of polarizations, and applied potentials.

On the other hand, cefixime is a third generation cephalosporin. It is a useful antibiotic for the treatment of a number of bacterial infections such as otitis, sinusitis, tonsillitis, and bronchitis. It is also used to treat typhoid fever [28]. Up to now, several analytical methods have been reported for the determination of cefixime including high performance liquid chromatography (HPLC) [29, 30], high performance capillary electrophoresis[31], high performance thin layer chromatography (TLC) [32], liquid chromatography (LC)–tandem mass spectrometric [33] and various spectrophotometry methods [34]. In comparison with the above methods, using of the voltammetric methods has advantages such as simplicity, cheapness and increasing in sensitivity and selectivity by the modifying electrodes.

In the present work, we have attempted to improve the response characteristics of the Co–Z by incorporating the modifier in the carbon-paste matrix. A simple electrode was designed that it can be renewed very easily for a large number of times over a long period. The electrochemical response characteristics of the modified electrode were investigated. The influences of pH and different percents of Co–Z to graphite on the response characteristics of the electrodes were studied and the optimum operating conditions were established. Finally, these modified electrodes were used for the electrocatalytic oxidation of cefixime using voltammetry.

Experimental

Reagents and materials

The solvent used in this work was twice distilled water. The electrolyte solutions were 0.1 M phosphate buffer and sodium hydroxide in pHs of 2, 5, 7, 9, 11, and 13 respectively. The buffer solution (0.1 M, pH 2) was prepared by using 0.057 M phosphoric acid and 0.043 M sodium dihydrogen phosphate. The preparation of the buffer solution (0.1 M, pH 5) has been done by mixing of 0.099 M sodium dihydrogen phosphate and 0.001 M disodium hydrogen phosphate. The buffer solution (0.1 M, pH 7) was obtained by mixing of 0.062 M sodium dihydrogen phosphate and 0.038 M disodium hydrogen phosphate. Mixing of 0.001 M sodium dihydrogen phosphate and 0.099 M disodium hydrogen phosphate was used for the preparation of 0.1 M buffer solution with pH 9. Mixing of 0.097 M disodium hydrogen phosphate and 0.003 M tri-sodium phosphate was used for preparation of 0.1 M buffer solution with pH 11. We also used of 0.1 M sodium hydroxide for preparation of 0.1 M buffer solution with pH 13. The accurate adjustment of pH was made by adding hydrochloric acid and sodium hydroxide, and it has been controlled with a pH meter. All of the above buffer solutions contain 0.1 M KCl as a carrier electrolyte.

Cobalt nitrate used in this work was the analytical grade of Fluka (Sydney, Australia) origin and used without further purification. High viscosity paraffin (density = 0.88 g cm^{-3}) from Fluka (Sydney, Australia) was used as the pasting liquid for CPE. Graphite powder (particle diameter = 0.10 mm) from Merck (New Jersey, US) was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Apparatus

Electrochemical experiments were performed with a computer–controlled potentiostat/galvanostat μ-Auto lab type III modular electrochemical system (Eco Chemie BV, Netherlands), driven with general purpose electrochemical system (GPES) software (Nova). Voltammetry was done in a three-electrode cell using the modified CPE (MCPE) as working electrode, a Ag | AgCl | KCl (3 M) from Azar electrode (Urmia, Iran) as the reference electrode and a platinum rod from Azar electrode (Urmia, Iran) as counter-electrode. All experiments were carried out at ambient temperature. No action was taken to remove oxygen from solutions.

Experimental Procedure of Synthesis of zeolite

The zeolite used as a substrate is of A-type zeolite structure [35], it has been synthesized in Islamic Azad University, Qaemshahr Branch, Iran. Micro silica was first extracted from *Equisetum arvense* plant in North of Iran. It was calcined to 1300° C for 4 h, which is beyond the dehydroxylation range. The requirement of silica was met from *Equisetum arvense* itself, and no other source was used for the same. Based on SEM image, the particle size of micro silica was about 1-4 μm.Sodium silicate was prepared by mixing of 10 g micro silica and 20 g sodium hydroxide and charged into an electrical furnace at 700 C for 2 h. Zeolite A was prepared by adding sodium alumina to the reaction mixture and the reaction was maintainedat 80C for 48h. Finally, the product was washed thoroughly with the distilled water and dried at 150 C. Based on SEM image, the particle size of synthesized zeolite is about 300-500 nm [36].

Results and discussion

Electrochemical behavior of Co-ZMCPE

Figure 1 shows the cyclic voltammograms of CPE, ZMCPE, and Co-ZMCPE in 0.1 M phosphate buffer solution (pH=7) at 20 mV s^{-1}. In Fig. 1, it can be seen that, whereas both neither oxidation nor reduction peak is seen on CPE nor ZMCPE, a well-developed redox wave was observed on the Co-ZMCPE. It was attributed to the oxidation of Co (II) to Co(III) with a peak potential of 0.98 V and the reduction of Co(III) to Co(II) with a peak potential of 0.85 V [37-40]. The effect of scan rate on electrochemistry of Co-ZMCPE was discussed (not shown). With an increasing scan rate, the peak current value of Co-ZMCPE increased linearly with the increasing scan rate in the range of 20–100 mV s^{-1}, indicating a surface-controlled process. From the slope of this line (I_p vs. v), the electrode surface coverage (Γ^*) can be calculated using the following equation, which is for the reversible process with the adsorbed species [41]:

$$I_p = n^2F^2Av\Gamma^* / (4RT) \qquad (1)$$

where I_p, A, and Γ^* stand for peak current, electrode surface area, and the surface coverage of the redox species, respectively. The total surface coverage of the immobilized active species was calculated as 1.2×10^{-9} mol Co cm^{-2}.

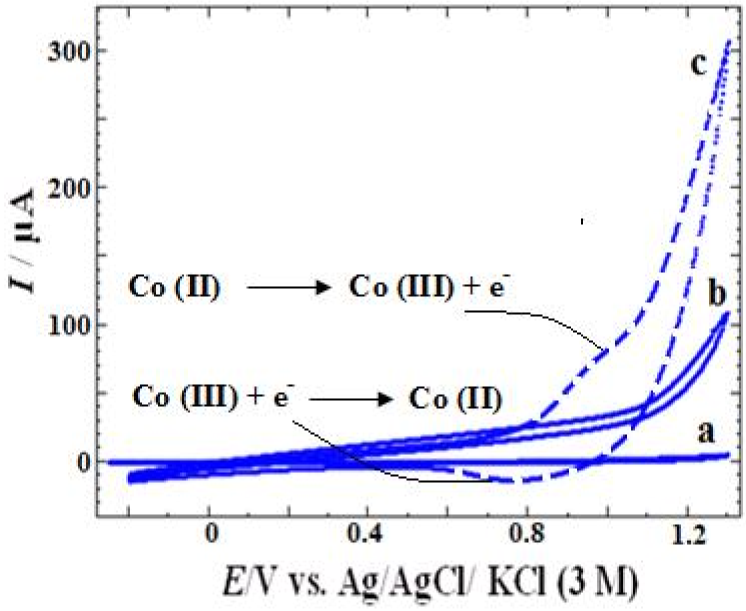

Figure 1. Cyclic voltammograms of (a) CPE, (b) ZMCPE, and (c) Co-ZMCPE in 0.1 M phosphate buffer solution (pH=7), scan rate 20 mV s^{-1}.

The cyclic voltammetric response of CPE, ZMCPE, and Co-ZMCPE is also investigated in the absence and presence of 1 mM cefixime inphosphate buffer of pH=7 at a scan rate of 20 mV s^{-1} (Figure 2). No cathodic and anodic peaks were observed in the investigated potential range on CPE and ZMCPE. However, by use of Co-ZMCPE, upon addition of cefixime to the solution, the shape of the cyclic voltammogram of modified electrodes change dramatically with an increase of the oxidation current in the potential of 0.98 V and a little decrease of the cathodic peak current. This phenomenon is attributed to the production of Co (II) and consumption of Co (III), respectively. These results showed that the modified electrode as a high ability for cefixime oxidation and the followingmechanism (electrocatalytic oxidation or EC') can be proposed for the mediated electrooxidationof cefixime at the surface of this modified electrode:

Co (II) Co (III)+ e$^-$ $\rightleftharpoons$ E (2)

Co (III) + cefixime Co (II) + products $\longrightarrow$ C' (3)

However, the Co sites at the electrode surface acts as a catalyst for cefixime oxidation.

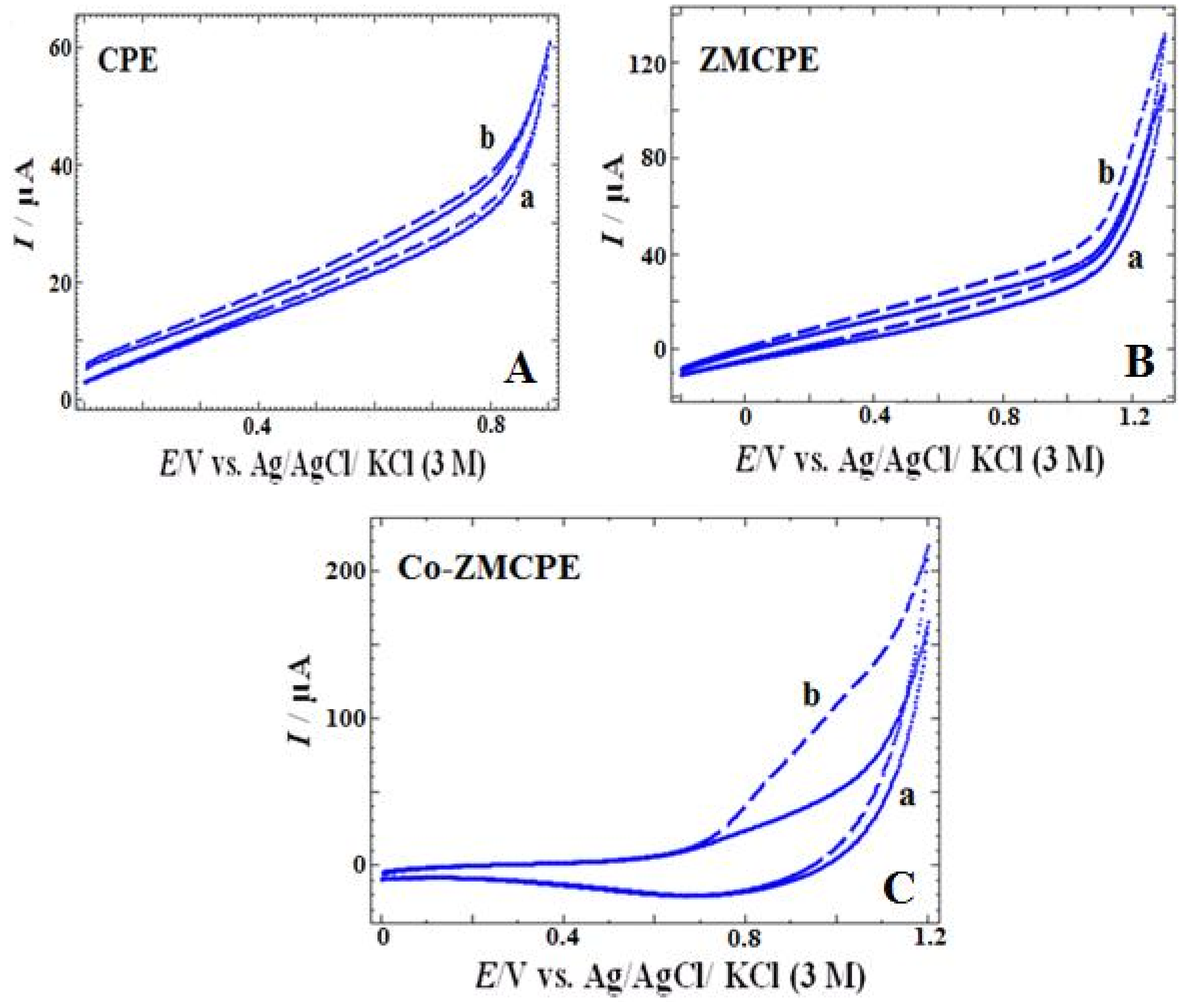

Figure 2. Cyclic voltammograms of (A) CPE, (B) ZMCPE, and (C) Co–ZMCPE in 0.1 M phosphate buffer solution (pH=7), in the absence (*a*) and presence of 1 mM cefixime (*b*), Scan rate = 20 mV s^{-1}.

Optimization of electrode variables for efficient performance of Co–ZMCPE towards cefixime oxidation

Effect of different percents of Co–Z to graphite

Figure 3 shows the effect of the paste composition on the resulting voltammetric response. Co–ZMCPE with different percents of Co–Z to graphite (0.3, 0.5, 1, 3, 5 and 10 %) was studied in the presence and the absence of cefixime. The results showed that the optimum ratio of Co–Z to graphite in the modified electrode was 1%. Larger and smaller amounts of the modifier reduced the sensitivity of the electrode response. Larger amounts of the modifier increased the resistance of the electrode and at smaller amounts of the modifier; the number of available cobalt active site was decreased. This is in agreement with the literature [42, 43].

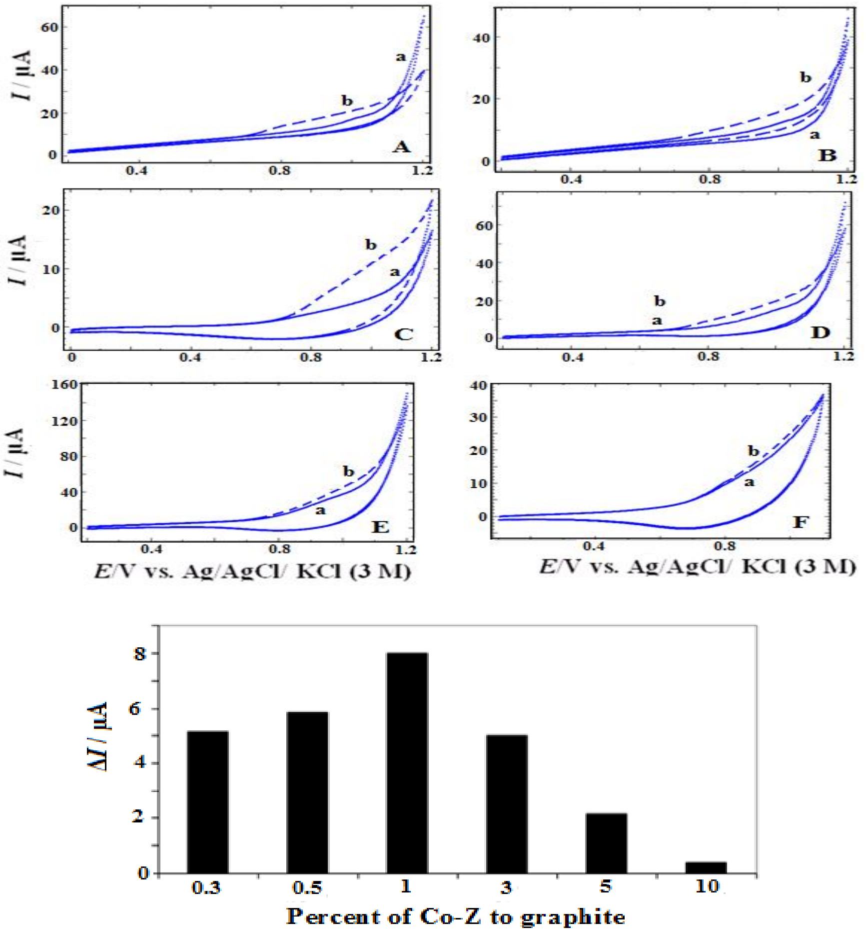

Figure 3. Cyclic voltammograms of different percents of Co–Z to graphite (A) 0.3%, (B) 0.5%, (C) 1%, (D) 3%, (E) 5% and (F) 10% at the Co-modified zeolite electrodes in (*a*) absence and (*b*) in presence of 1 mM cefixime and in 0.1 M phosphate buffer solution (pH=7) at a scan of 20 mV s^{-1}, Inset: Comparison of electrocatalytic currents (ΔI) for the oxidation of cefixime observed on Co–ZMCPE.

Effect of pH

We have tested the electrocatalytic activity of Co–ZMCPE against cefixime electrooxidation in the buffered solutions with various pHs in the range of 2–13 (Figure 4). For all of them, the modified electrode shows electrocatalytic activity. However, higher electrocatalysis peak currents are observed at pH=7 (the value of ΔI is the most of the others). Based on such investigations, a buffered solution of pH=7 was chosen as an optimum condition in order to obtain the best sensitivity in all voltammetric measurements.

Effect of cefixime Concentration

Figure 5 shows the effect of cefixime concentration on the cyclic voltammograms of the Co-ZMCPE. As can be seen from this figure, the height of the anodic peak increases with increasing in cefixime concentration. The characteristic shape of CV in this potential region indicates that the signal is due to the oxidation of cefixime. The catalytic peak current is proportional to the concentration of cefixime in the range of 0.003 to 8 mM. The linear regression equation is I (µA) = 3.865 C_{cefixime} (mM) + 9.287 (R^2 = 0.994). The detection limit calculated from the calibration graph was 0.00298 mM when the signal to noise ratio was 3.

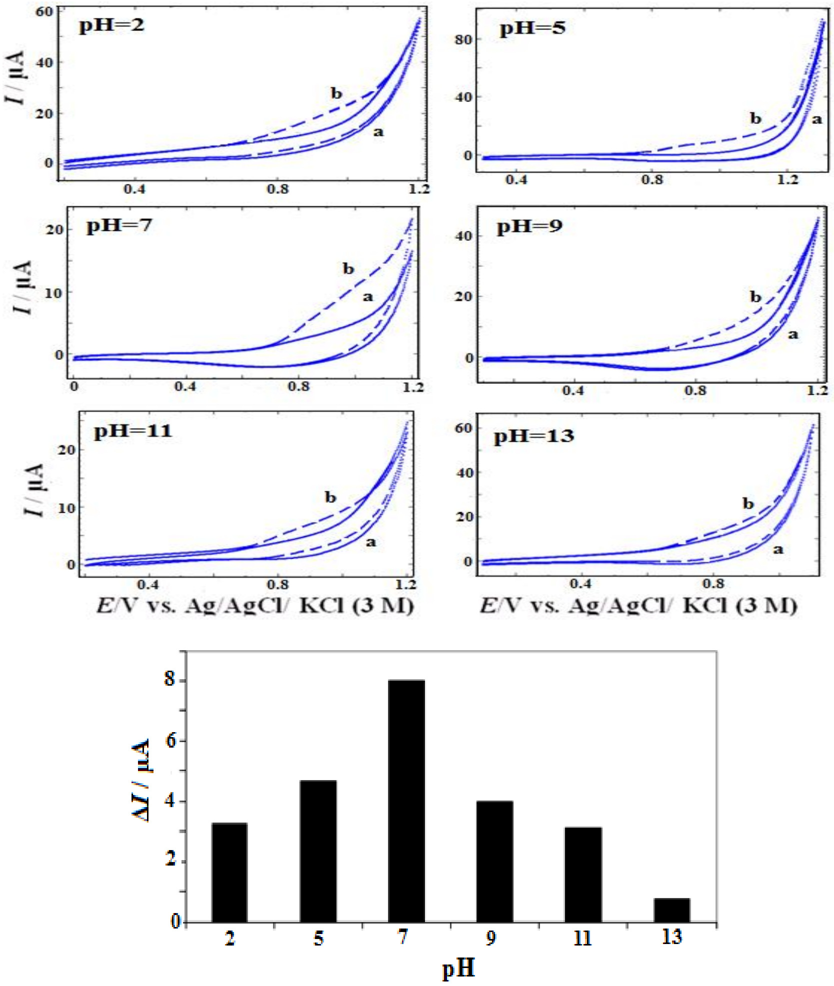

Figure 4. (A) Cyclic voltammograms of Co-ZMCPE in different pH solutions, in the absence (*a*) and the presence of 1 mM of cefixime (*b*) at scan rate of 20 mVs^{-1} (B) Plot of catalytic current *vs*pH.

Real sample analysis

In order to examine the applicability of the proposed method, we tested the determination of cefixime in commercial tablet sample using the standard addition method for prevention of any matrix effect under the optimized conditions. All samples were diluted with phosphate buffer solution (pH=7) and then appropriate amounts of cefixime standard samples were transferred to the electrochemical cell for the determination of it. There is a linear relationship between the I_{pa} versus cefixime concentration. It was found that the drug concentration determined using this method is in good agreement with the reported values. The value of the experimentally determined drug and the declared value in the tablet are tabulated in Table 1.

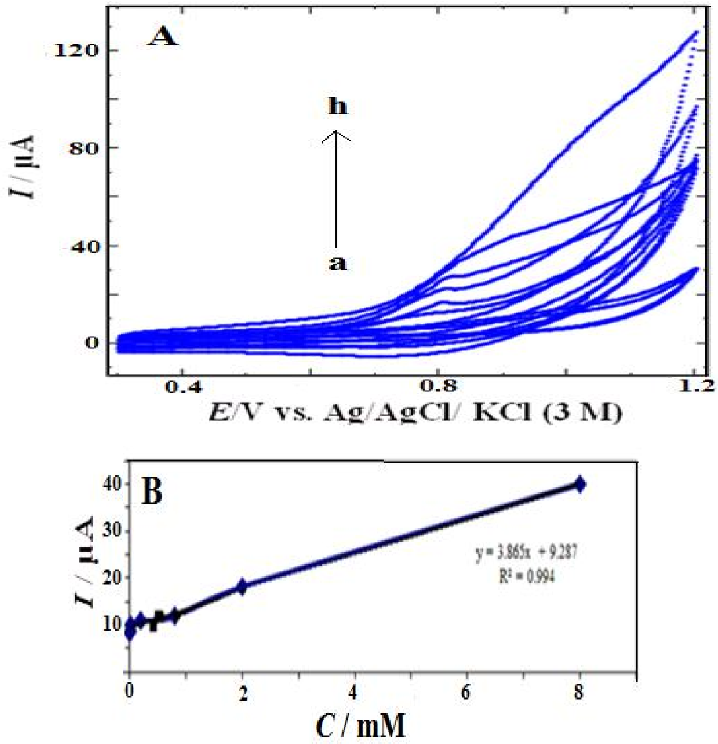

Figure 5. (A) Cyclic voltammograms of Co-ZMCPE in 0.1 M phosphate buffer solution (pH=7) containing 0, 0.003, 0.005, 0.01, 0.2, 0.8, 2 and 8 mM of cefixime from *a* to *h* at 20 mV s^{-1} (B) Plot of catalytic current *vs* cefixime concentration.

Table 1. Determination of cefixime in pharmaceutical sample using Co-ZMCPE.

Sample	**Amount Labeled / g**	**Amount Founded / g**	**Recovery %**	**RSD %, n=5**
Cefixime tablet	0.20	0.21	105	4

Effect of scan rate

The dependence of the anodic peak current response on the potential scan rate during the electrocatalytic oxidation of cefixime was examined employing CV by varying the scan rate from

10 to 1000 mV s^{-1} (not shown). Results indicated that there is a linear relationship between the anodic peak current (I_{pa}) and the square root of the scan rate ($v^{1/2}$) in the scan rates of 10–1000 mV s^{-1} for cefixime (I_{pa}=0.343 $v^{1/2}$+1.366, R^2=0.99). This indicates that the oxidation of cefixime at Co–ZMCPE is a diffusion-controlled process.

Chronoamperometric studies

We employed a chronoamperometric method for the investigation of electrochemical processes at Co-ZMCPE. Fig. 6 represents the current–time profiles obtained by setting the working electrode potential at 850 mV for various concentrations of cefixime. Plotting of the net current as a function of the inverse square root of time, gives a linear relationship (Fig. 6B), resulting in a diffusion controlled process. The diffusion coefficient of cefixime can be obtained by using the slope of this straight line, according to Cottrell equation [41]:

$$I = nFAD^{1/2}C^{*}\pi^{-1/2}t^{-1/2} \qquad (4)$$

where D is diffusion coefficient and C^* is the bulk concentration of cefixime. The value of diffusion coefficient of cefixime was found to be 3.12 × 10^{-5} cm^2 s^{-1}.

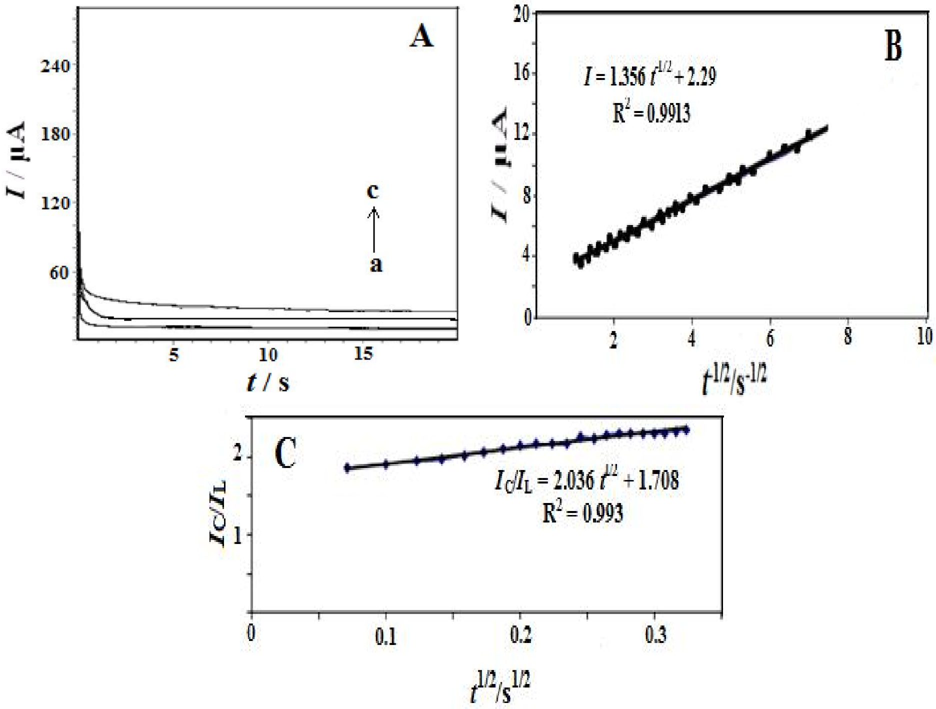

Figure 6. (A) Chronoamperograms of Co–ZMCPE in 0.1 M phosphate buffer solution (pH=7) with different concentrations of cefixime: (a) 0, (b) 0.5 and (c) 1 mM (B) Plot of I vs. $t^{-1/2}$ (C) Plot of I_C/I_L vs. $t^{1/2}$.

The rate constant for the chemical reaction between the cefixime and redox sites (cobalt ions) of Co–ZMCPE can be evaluated by chronoamperometry according to the method described in the literature [41].

$$I_C/I_L = \lambda^{1/2}\ [\pi^{1/2}\ \mathrm{erf}\ (\lambda^{1/2}) + \exp\ (-\lambda)\ /\ \lambda^{1/2}] \qquad (5)$$

where I_C is the catalytic current of the Co–ZMCPE in the presence of cefixime, I_L is the limiting current in the absence of cefixime and $\lambda = kc_ot$ (c_o is the bulk concentration of cefixime) is the argument of the error function. In the cases where λ exceeds 1.5, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_C/I_L = \pi^{1/2}\lambda^{1/2} = \pi^{1/2}(kc_ot)^{1/2} \qquad (6)$$

where k, c_o, and t are the catalytic rate constant (cm^3 mol^{-1} s^{-1}), cefixime concentration (mol cm^{-3}) and time elapsed (s), respectively. From the slope of the I_C/I_L versus $t^{1/2}$ plot, we can simply calculate the value of k for a given concentration of substrate. Fig. 6Cshows one such plot, constructed from the chronoamperogram of the Co-ZMCPE in the absence and presence of 1 mM cefixime. The mean value for (k) was found to be 3.18×10^4 cm^3 mol^{-1} s^{-1}.

The Electrode Stability, Repeatability, and Reproducibility

The long-term stability of Co–ZMCPEwas also studied by storing the electrode for 2 weeks at room temperature. The current response was not shown any changes after two weeks. It confirms the stability of modified electrode. To investigate the repeatability of the electrode, the Co-ZMCPE was applied to the six parallel determinations of 0.05 mM and the relative standard deviation (RSD) was calculated as 4.3 %. Further, under the same and independent conditions, it was found that the electro-catalytic oxidation currents of 0.05 mM cefixime almost remained the same by five Co-ZMCPE with a R.S.D. of 3.7 %, indicating a high reproducibility.

Conclusion

The study has described successfully the modification of CPE with Co–Z. This modified electrode acts as an active suitable catalyst for the oxidation of cefixime. The electrode showed high stability in repetitive experiments. The proposed electrode showed a low detection limit with the very easy preparation, surface regeneration and the reproducibility of the voltammetric response. The proposed system is very useful as a simple device for the determination of cefixime in the clinical samples, especially without the necessity for sample pretreatment or any time-consuming extraction or evaporation steps prior to the analysis, with satisfactory recovery. Table 2 compared the proposed electrode for cefixime determination with electrodes reported in literature. As shown, the proposed electrode is comparable with other electrodes.

Table 2. Comparison of performance for some electrodes in determination ofcefixime.

Electrode	Modifier	pH	LDR /µM	µM/ LOD	Reference
CPE	GN[a]	3	1.2-200	1	[44]
GC	Polymer/MWCNT	4	0.01-600	0.001	[45]
GC	MWCNT/$NiFe_2O_4$	8	1.8-600	1.74	[46]
SPGE[b]	GN/Cysteine	7	10-1×10^3	————	[47]
HMDE[b]	————	2.6	9.85-50.4	9.62	[48]
CPE	Co-Z	7	3-8×10^3	2.98	This work

[a] Gold nanoparticle
[b] Screen printed gold electrode
[c] Hanging mercury dropping electrode

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