

Preconcentration and Electroanalysis of Copper at Zeolite Modified Carbon Paste Electrode

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Received: 29 October 2008 / Accepted: 10 January 2009 / Published: 9 February 2009

A carbon paste electrode modified with zeolite was employed for quantities of copper from aqueous solutions. Copper (II) was chemically deposited on the zeolite modified carbon paste electrode (ZMCPE), and the electrode was transferred to an electrochemical cell for cyclic and square wave voltammetry. The response depends on the concentration of copper in the bulk solution as well as parameters involved in both the preconcentration and the measurement steps. The calibration graph is linear related to the concentrations of Cu^{2+} in the range from 0.064-64.0 mg l^{-1} with very good correlation coefficient. The detection limit (DL, 3σ) was about 0.05 mg l^{-1} and the response could be reproduced with a 4.3% relative standard deviation at the concentration level of 3 mg l^{-1} .

Keywords: Carbon paste; Copper; Voltammetry; Zeolite modified electrodes

1. INTRODUCTION

Zeolite-modified carbon paste electrodes (ZMCPEs) have attracted considerable attention of electrochemists during the recent years [1-10]. The main advantages of zeolite-modified electrodes (ZMEs), compared to other chemically-modified electrodes, arise from the unique size, shape and charge selectivity offered by zeolite-molecular sieves, concomitantly with a high ion-exchange capacity [11].

The direct detection of electroactive species was achieved either by exchanging charge transfer mediators within the zeolite or by using the microporous solid as a support for the electrode itself. The voltammetric detection after accumulation mainly called for the ion exchange capacity of the zeolite, while the indirect amperometric detection of nonelectroactive species combined this property with the molecular sieving properties of this solid. Other groups have characterized zeolite-modified electrodes for their response to Cu(II) and Fe(III) / Fe(II) [12-13]. However, while several reports on mechanistic

studies of zeolite-modified electrodes have been published; only a few workers have investigated the analytical possibilities of such electrodes. Walcarius et al.[14] have constructed an Cu(II)-sensitive electrode based on Na-A, Na-X and Na-Y zeolites by cyclic voltammetry with a concentration range 5×10^{-5} - 1×10^{-4} M Cu (II). Bing et al. [15] have reported determination of Cu^{2+} , Cd^{2+} , Zn^{2+} by square wave voltammetry with detection limit 300 mM [Cu^{2+}], 87 mM [Cd^{2+}] and 145 mM [Zn^{2+}] respectively.

Copper is one of the most widely distributed elements in the environment of industrialized countries. It is present in all organisms, land and marine. It has been shown that copper is an essential element for many biological processes such as blood formation and function of many important enzymes [16-20]. This element plays a vital role as a catalytic cofactor for several enzymes including cytochromecoxidase, superoxide-dismutase and other multi copper oxidations [21]. Several manifestations of copper deficiency in animals appear to be related to decreased tissue concentration of copper containing enzymes. However, high intake levels of copper result in certain disease states in man. Toxic signs of copper intake have been known for centuries. Its radical-forming characteristics, especially with molecular oxygen, make it toxic as it can cause damage to various biomolecules such as proteins and nucleic acids [22]. Elevated copper levels in humans are manifest in certain disease processes, for example, infections, Menkes' syndrome and Wilson' s disease [23, 24]. The development of a highly selective copper sensor, would enable the fast, easy and low-cost detection of this element in different samples.

This article reports on studies of the electrochemical behavior of copper(II) incorporated in ZMCPE using cyclic voltammetry and square wave voltammetry. Furthermore, the possible accumulation of the analyte onto the electrode was investigated. The aim of this paper was to study the voltammetric behavior of copper ion within a zeolite-modified carbon paste electrode [ZMCPE] (X-type) in a larger linear range between the peak current and the concentration of Cu(II).

2. EXPERIMENTAL PART

2.1. Apparatus

Electrochemical experiments were carried out using the μ Autolab potentiostat/galvanostat. A three-electrode cell was employed, which had a saturated calomel electrode (SCE) as reference electrode, a platinum wire as auxiliary electrode and a zeolite-modified carbon paste electrode (ZMCPE) or graphite-modified electrode (CME) as working electrode (home-made). All potentials were measured and reported vs. SCE. The pH of the sample solutions was monitored with a Metrohm 691 pH / mV meter. A magnetic stirrer (500 rpm) and a stirring bar provided convective mass transport when needed. X- ray diffraction (XRD) model pw 130/90 and X-ray fluorescence (XRF) model pw 1480 instruments both from Philips company have been used. All containers were soaked in a solution of 6 M HNO_3 for at least 24 h and then rinsed with deionized water before use. All experiments were performed at room temperature.

Each measuring involved four steps: (a) preparation of electrode, (b) immersion of the electrode in an acid solution such as HNO_3 solution for certain time, (c) immersion of the electrode

into a buffer solution containing Cu(II) for a required time to allow entry of copper ions in zeolite's pores in electrode (preconcentration step), and (d) immersing the electrode in cell containing ammonia buffer and record voltammogram for measuring copper ions at electrode (measuring step). After all the thoroughly above steps, the electrode was rinsed with deionized water.

2.2. Chemical and reagents

A synthetic zeolite molecular sieve type-X was obtained from Aldrich. Extra pure graphite fine powder and silicon oil Dc 350 were used for the graphite pastes purchased from Merck. Ammonia buffers were prepared by adjusting 0.2 M HNO₃ to the required pH with 30 % NH₄OH. Acetate buffer solution was prepared by mixing CH₃COONa and CH₃COOH to the required pH. Phosphate buffer solution was prepared through adjusting 0.05 M solution Na₂HPO₄ with NaH₂PO₄ to the required pH. All other chemicals were of the highest purity available from Merck, and were used without further purification. Ultra filtered deionized water was used for all solutions of electrolytes. All containers were soaked in a solution of 6 M HNO₃ for at least 24 h and then rinsed with deionized water before use. All experiments were performed at room temperature, with eliminating the dissolved oxygen.

2.3. Preparation of electrodes

Zeolite-modified carbon paste electrode was prepared by mixing 0.1 g zeolite molecular sieve and carbon graphite powder in a ratio 1:6 and 1:2 and 1:1 and grinding into micrograins as small as possible in a mortar. 0.2 g of the silicon oil was added to the 0.6 g mixture and mixing together until a uniformly wetted paste obtained. The paste was then packed into end of a glass tube (e.d. = 8 mm, i.d. = 6 mm) and the surface was smoothed. When necessary, a new surface was obtained by pushing an excess of paste out of the tube and polishing it on paper. The CME, used for comparison, was prepared in the same way without adding zeolite to the mixture.

2.4. Chemical preconcentration

The modified electrode was immersed in an acid solution such as 0.1 M HNO₃ solution for the definite range of time before chemical preconcentration. Preconcentration of Cu(II) on the electrodes was performed by immersing the electrodes into a phosphate buffer solution containing Cu(II) for the definite range of time with magnetic bar at a rate of 500 rpm.

2.5. Electrochemical pretreatment

Voltammetric measurements (cyclic voltammetry and square wave) were made at room temperature. The zeolite-modified carbon paste electrode was immersed in the cell containing the stirred copper solution and the effect of accumulation time was studied. The preconcentration proceeded at open circuit. The electrode was then removed from the preconcentration cell and

immersed for 2 min in deionized water (washing cell), then electrode transferred to the measurement cell containing 40 ml of the buffer solution that were purged with nitrogen gas for at least 10 min before starting measurements. Square wave and cyclic voltammetry were performed by scanning the potential in -0.3 to +0.4 V range.

3. RESULTS AND DISCUSSION

Synthetic zeolites are preferred for quantitative work because they are much more homogenous and purer than natural zeolites. The ion-exchange reaction used for the preconcentration process is represented by:

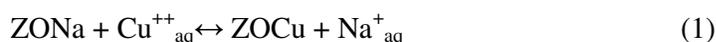


Table1 shows the effect of the paste composition on the preconcentration and the resulting voltammetric response. Carbon-paste electrodes with ratios 1:1, 1:2 and 1:6 (w/w) of zeolite and graphite yielded peak currents of 17, 15.9 and 0.065 μA , respectively. Thus, as expected from the increased ion-exchange capacity of the electrode, the amount of copper ion accumulated and the corresponding peak current are proportional to the amount of zeolite in the paste. A similar response was obtained at carbon paste electrodes containing another synthetic zeolite (the potassium-based Linde 3A and sodium-based Linde 4A). The peak height (i_p) and peak potential (E_p) using unmodified carbon paste, zeolite modified carbon paste electrode with 1:1, 1:2 and 1:6 (w/w) of zeolite and graphite were studied by cyclic voltammetry (under identical conditions). In all cases, ratios 1:1 and 1:2 have shown a higher peak at -0.15V. Ratio 1:2 was applied in other experiments. The i_p values are shown in Table1.

Table1. The effect ratio of graphite: zeolite on current peak of ZMCPE.

Graphite: zeolite	$i_p / \mu\text{A}$
1:1	17.0
1:2	15.9
1:6	6.45×10^{-2}

An electrochemical study of the Cu(II) behavior at ZMCPE revealed that an enhanced sensitivity was obtained when ZMCPE before preconcentration of Cu(II) step was immersed in an acidic solution such as 0.1 M HNO_3 . Because first cations in zeolite frameworks (Na^+ or NH_4^+) were exchanged by H^+ ions in acidic solution (eq 2), thus, in preconcentration step (step c) that the cathodic reduction of Cu(II) ions was only allowed after ion exchange, Cu^{2+} ions in solution were exchanged

better with H^+ ions in zeolite than Na^+ or NH_4^+ [14] (Fig.1). As a consequence, the reduction of Cu(II) species was fully controlled by the ion exchange reaction between the H^+ in zeolite and Cu^{2+} in solution (eq 3), thus immersing the electrode in acidic solution before preconcentration step has increased the sensitivity, sharply:



where subscripts s and z refer to solution and zeolite, respectively.

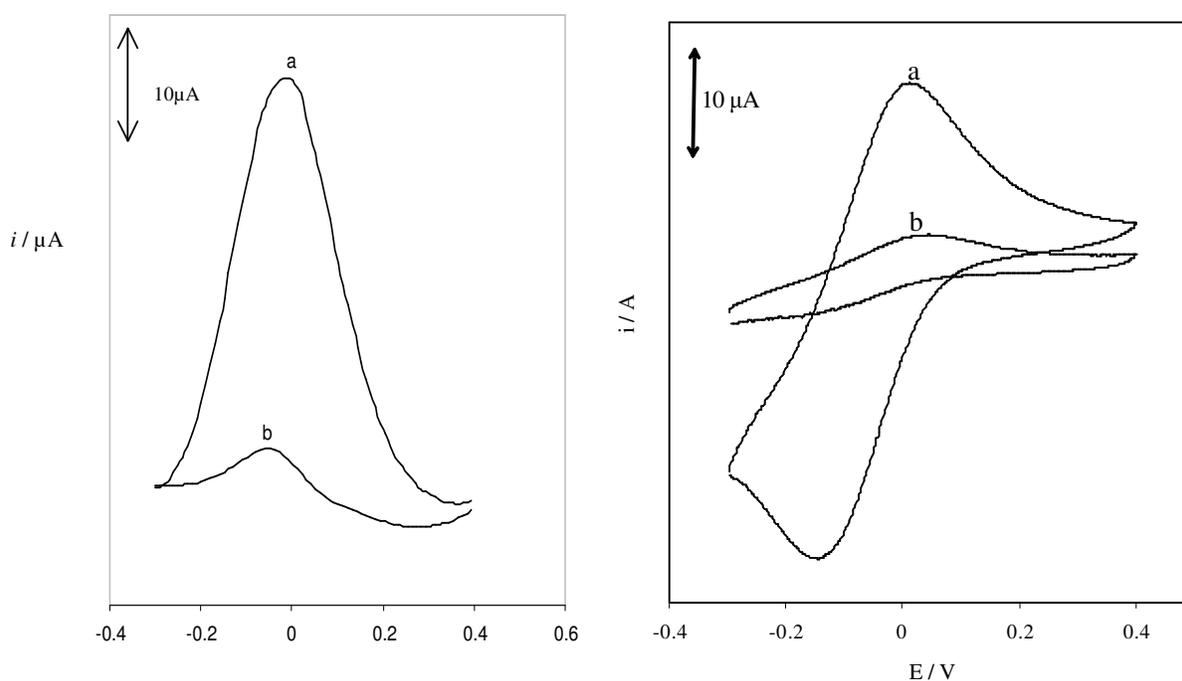


Figure 1. Square wave and cyclic voltammogram obtained in ammonia buffer for the acidified and non-acidified ZMCPEs after 15 min chemical preconcentration in the Na_2HPO_4 - NaH_2PO_4 buffer containing Cu(II) 3 mg l^{-1} with scan rate 50 mVs^{-1} and sweep range from -0.3 to 0.4 V : (a) for ZMCP; (b) for plain carbon paste electrode (PCPE).

Figure 2(A) shows cyclic voltammetry using a plain carbon paste electrode (PCPE) in ammonia buffer after 20 min chemical preconcentration in a phosphate buffer containing 3 mg l^{-1} Cu(II) and no voltammetric response was observed while Figure 2(B) shows the cyclic voltammogram obtained using ZMCPE at identical experimental condition as in figure 2(A) with scan rate 50 mVs^{-1} and sweep range from -0.3 to $+0.4 \text{ V}$. As a consequence, the reduction of Cu(II) species was fully controlled by the ion exchange reaction between the H^+ or NH_4^+ and Cu(II) species.

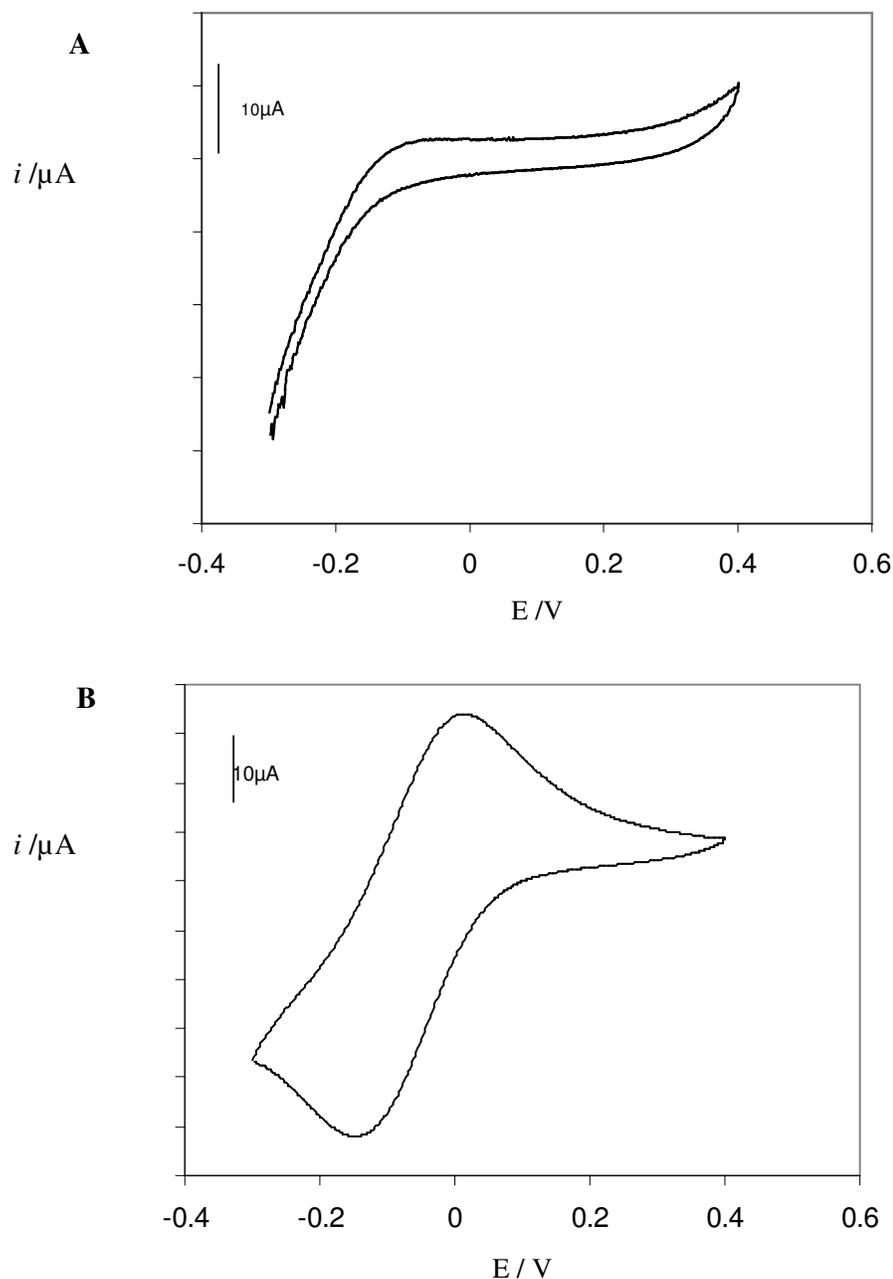


Figure 2. Cyclic voltammograms in ammonia buffer for both ZMCPE and PCPE after 15 min chemical preconcentration in the Na_2HPO_4 - NaH_2PO_4 buffer containing $\text{Cu}(\text{II})$ 3 mg l^{-1} with scan rate 50 mVs^{-1} and sweep range from -0.3 to $+0.4\text{ V}$: (A) for PCPE; (B) for ZMCPE.

The variation of the peak intensity and the peak potential with the scan rate was studied. Figure 3 shows cyclic voltammograms of $\text{Cu}(\text{II})$ 3 mg l^{-1} with different scan rate in ammonia buffer. An approximately linear relationship was found between the peak current, i_p and the square root of the scan rate, v_b ($i_p = 1.0698 + 0.1365 v_b^{1/2}$, $r^2 = 0.9901$). Thus i_p is proportional to the square root of the scan rate which indicates diffusion-controlled reaction.

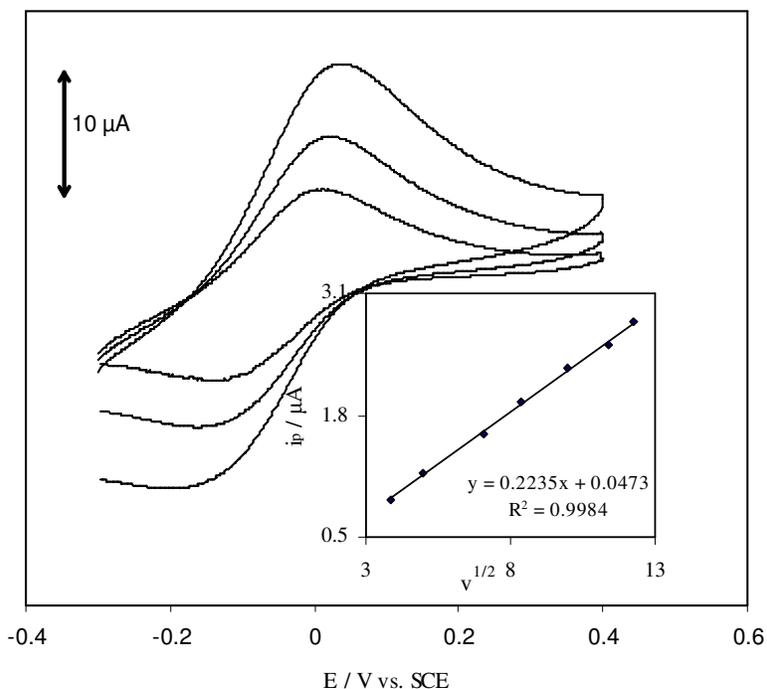


Figure 3. Cyclic voltammograms obtained in ammonia buffer for ZMCPE after 15 min chemical preconcentration in the phosphate buffer containing Cu(II) 3 mg l^{-1} sweep range from -0.3 to +0.4 in different scan rate (from outer to inner) 25, 50, 100 mVs $^{-1}$. Insert represents the peak current i_p vs. $v^{1/2}$.

Table 2. Dependence of dynamic linear range ZMCPE to pH of preconcentration.

pH	Linearity range / M
1	$1.0 \times 10^{-3} - 1.0 \times 10^{-5}$
2	$1.0 \times 10^{-2} - 1.0 \times 10^{-4}$
4	$5.0 \times 10^{-2} - 1.0 \times 10^{-7}$
5	$1.0 \times 10^{-2} - 5.0 \times 10^{-5}$
7	$5.0 \times 10^{-2} - 1.0 \times 10^{-5}$
9	$1.0 \times 10^{-3} - 5.0 \times 10^{-5}$
10	$1.0 \times 10^{-3} - 1.0 \times 10^{-4}$

Studies on the effect of pH were carried out at a Cu(II) concentration of a 3 mg l^{-1} at pH 1.0-10.0 with buffer solutions. The peak potential, E_p , shows a clear dependence on pH; with linear regions (Table 2). The peak heights reach their maximum value in acidic media. At a higher pH of 8 for preconcentration step solution containing ammonia buffer, the presence of ammonia would complex with the copper ions and result in a decrease in free copper ion concentration. It seemed to suggest that only free copper ions rather than copper-ammonia complexes were involved in the cation-exchange interactions with ZMCPEs. Similar observation was reported by Bowers and co-workers [25] and Shiu

and co-workers [26]. Fig. 4 shows the influence of pH on E_p and i_p for the peak potential in the range 1.0-10.0 where well-defined peaks were obtained. The highest peak was obtained for pH 3.7.

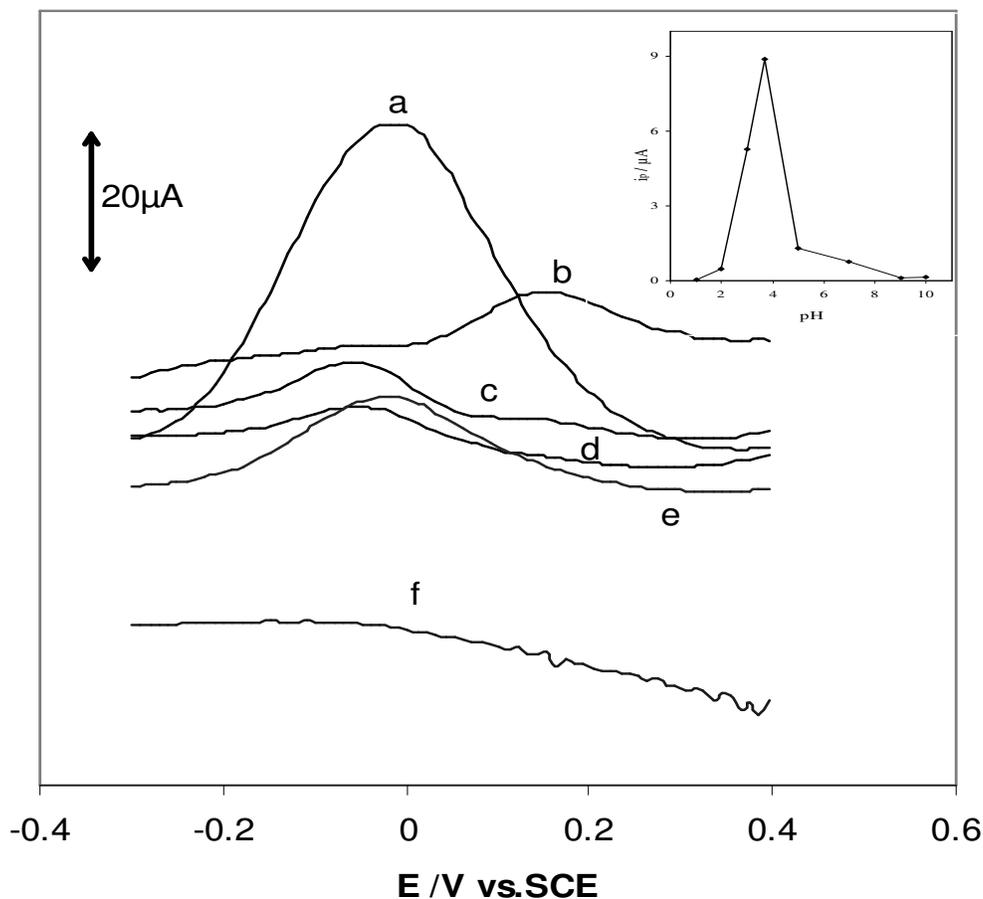


Figure 4. Square wave voltammograms obtained in ammonia buffer for ZMCPE in different pH of the preconcentration after 15 min chemical preconcentration in the different buffer containing Cu(II) 3mg l^{-1} with frequency 25 Hz, cathodic scan range from -0.3 to +0.4 V: a) pH = 3.7, b) pH = 2.0, c) pH = 7.0, d) pH = 9 e) pH = 5.0, f) pH = 10.0. Insert represents the peak currents against pH of the chemical preconcentration solution. The data was obtained in ammonia buffer after 15 min chemical preconcentration in different buffer containing Cu (II) 3mg l^{-1} with frequency 25 Hz, sweep range from -0.3 to +0.4 V.

The effect of the pH of the preconcentration solution on the voltammetric response of ZMCPE was investigated. The voltammetric response obtained in buffer for ZMCPE in different pH of the preconcentration solution after 15 min chemical preconcentration in the acetate buffer for $\text{pH} < 3$ and phosphate buffer for $3 < \text{pH} < 8$ and ammonia buffer for $\text{pH} > 8$ that all solutions containing Cu(II) 3mg l^{-1} with scan rate 50mVs^{-1} and sweep range from -0.3 to +0.4 V presented in Figure 4. The most efficient accumulation of Cu(II) was achieved for $3 < \text{pH} < 8$ with a maximum at pH 3.7.

As a consequence of these observation, the remaining part of the study was carried out with chemical deposition from $\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$ buffer (pH=3.7).

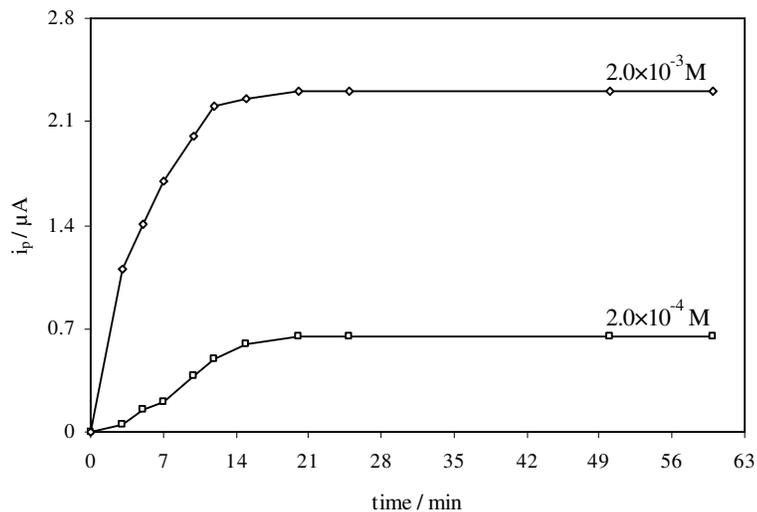


Figure 5. Plot of peak currents against different chemical preconcentration time. The data were obtained in ammonia buffer after different chemical preconcentration in the phosphate buffer containing Cu (II) with scan rate 100 mVs^{-1} and sweep range from -0.3 to $+0.4 \text{ V}$.

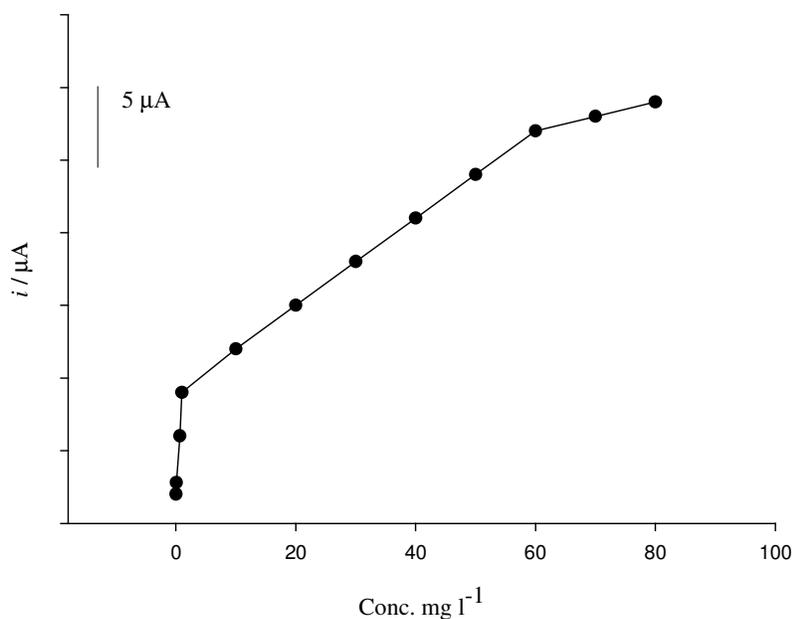
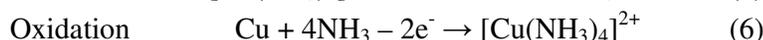
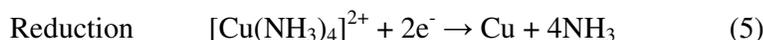


Figure 6. Dependence of the peak current on the copper concentration.

The influence of the buffer concentration in phosphate buffer of pH 3.7 is studied. An increase of peak current was observed. To obtain a maximum peak current, preconcentration in phosphate buffer was chosen for further work.

The influence of the preconcentration time on the peak current is illustrated in Fig. 5. The experiment is performed with 0.3 and 3.0 mg l⁻¹ Cu(II) solutions. A range of 0-60 min was studied and the measurements were carried out under the previously optimized conditions. Results are shown in Fig. 5. The observed dependence can be explained by a saturation of the electrode surface with the analyte after a long accumulation time. A period of 15 min has been chosen as an optimum to be applied in further experiments with accumulation. For short preconcentration times a linear dependence of the stripping peak current on preconcentration time can be observed; it levels off at a limiting value which is different for different concentrations. This is of course due to the fact that the maximum amount of the Cu(II) that can be accumulated is determined by the equilibrium constant for the preconcentration process. Thus for each concentration there is a certain amount which can be accumulated [17-19]. Such concentration-dependent rates have been reported for the ion-exchange process at various zeolites [27].

The influence of the pH in the measurement cell was studied. The best responses were obtained for pH 9. This is probably due to the formation of complexes of Cu(II) with NH₃ in ammonia buffer, while redox occurred in one step reaction during cyclic scanning. However, only single oxidation and reduction peaks were observed in this study (see fig. 2(B)).



A stable peak was obtained for the pH ranges from 4.5-9.0. Such pH effects are attributed to the formation of zeolite-bound copper hydroxide precipitate that enhances the reduction process. The copper hydroxide solubility product ($K_{sp} = 2.2 \times 10^{-20}$) strongly support this hypothesis.

The reproducible accumulation and effective cleaning was illustrated by the precision obtained for a series of ten repetitions, with 3 mg l⁻¹ copper. Such series yielded a mean 9.5 μA with a range of 9.2- 9.8 μA and a relative standard deviation of 4.3%. The initial preconditioning scheme (described in the Experimental section) is essential for achieving such good precision.

The dependence of the voltammetric peak height on the copper concentration is shown in Fig.6. The decreased slope at higher concentrations may reflect the extent of the copper binding, with exchange sites being saturated at higher concentrations [28, 29]. The nonlinearity is attributed also to the ion-sieve effect, i.e., entering ions cannot reach all the sites occupied by ions initially in the zeolites [30]. This behavior requires the use of calibration plots. A linear relationship between i_p and the concentration in the range 0.064-64.0 mg l⁻¹ has been found ($r^2=0.9991$) and detection limit (DL, 3σ) was 0.05 mg l⁻¹. The linear range obtained for the ZMCPE is superior to some of other reported zeolite modified electrodes (ZME) [12, 14].

3.1. Interferences and analysis of real samples

The possible influence of several ions on the reduction signal of copper was considered. An initial interferent: copper mass ratio of 5:1 was tested, which was decreased when interference was

observed. Interference studies were done using 3 mg l^{-1} copper. Voltammetric responses resulting from the presence of interfering ions were then compared with that obtained for pure copper incorporation. Experimental results are shown in table 3. Ni^{2+} and Zn^{2+} yielded a depression of the copper voltammetric response. The selective response in the presence of silver is significant because conventional voltammetric measurements of copper commonly suffer from an overlapping silver response. The accumulation step might be useful in the case of the existence of an interferent, because if it does not collect onto the modified carbon paste, the signal of the analyte will be less or not affected at all by the interferent, because they do not accumulate on carbon paste under the experimental conditions used. Consequently, although the accumulation step does not improve the detection limit, it can be used to avoid the effect of some interferents. In various instances, it was possible to eliminate interferences via a simple treatment. The interference study suggests the possibility of measuring other metal ions by using the zeolite-preconcentration / voltammetric approach.

The method for the determination of copper was applied to river water, sea water and alloy samples. The result for river water showed very good recovery of 104%. For sea water, value of 107% and for alloy sample 97% was obtained.

Table 3. Interference data for determination of copper with zeolite-modified carbon paste electrode

Interfering ions	Interferent:analyte mass ratio	Concentration / ppm	Percentage change in i_p
Pb^{2+}	5:1	10.4	-18.74
Pb^{2+}	1:1	2.1	-3.27
Mn^{2+}	5:1	2.8	-4.38
Zn^{2+}	5:1	3.3	-23.1
Zn^{2+}	1:1	0.7	-4.84
Cd^{2+}	5:1	5.6	-5.61
Co^{2+}	5:1	3.0	-12.45
Co^{2+}	1:1	0.6	-2.76
Fe^{2+}	5:1	2.8	-5.33
Ag^+	5:1	5.4	-2.49
Ni^{2+}	5:1	3	-30.27
Ni^{2+}	1:1	0.5	-5.32

4. CONCLUSIONS

By using a zeolite-modified carbon paste electrode, it has been shown that cyclic voltammetry is a good tool for the determination Cu(II) in real samples. This study shows that acidification of the ZMCPE, before preconcentration step, can increase electrochemical sensitivity to copper and does not affect work of the ZMCPE, although it is likely that severe loss in crystallinity of zeolite will occur under the acidification treatment. A variety of parameters related to voltammetric response of the ZMCPE was tested. Preconcentration processes at ZMCPE have been found to be affected by several

parameters, such as pH of copper solution, the presence or not of interferent species for the ion exchanging sites and finally the preconcentration time. As a general rule, the longer the preconcentration time has the better the sensitivity of the ZMCPE.

ACKNOWLEDGEMENTS

The authors wish to thank the Yazd University Research Council, IUT Research Council and Excellence in Sensors for financial support of this research.

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