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CARBON PASTE ELECTRODE MODIFIED WITH CLAY FOR ELECTROCHEMICAL DETECTION OF COPPER (II) USING CYCLIC VOLTAMMETRY

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Abstract: *This paper reports on the use of carbon paste electrode modified with clay (Clay-CPE) and cyclic voltammetry (CV) for analytical detection of trace copper (II) in Na₂SO₄ 0.1M. The electroanalytical procedure for determination of the Cu(II) comprises two steps: the chemical accumulation of the analyze under open-circuit conditions followed by the electrochemical detection of the preconcentrated species using cyclic voltammetry. The electrochemical responses obtained by CV at Clay-CPE were found to be analytically suitable to develop a method for the determination of copper at low concentration levels.*

Keywords: *Modified electrodes; Cyclic voltammetry; Clay; Cu(II).*

INTRODUCTION

Recently, rapid industrialization and urbanization led to the contamination of air, soil and water. The determination of pollution by heavy metals such as copper, mercury, lead, zinc and cadmium is of special concern because of the formation of complexes with proteins [1] and their high toxicity [2-4]. The heavy metal ions are hazardous to ecosystems and can cause serious danger to human population because of their accumulation in organs including liver, heart, brain etc. [5]. For this reason, up to now, several methods including atomic absorption spectrometry, UV-Vis spectroscopy, colorimetric analysis, ion chromatography, inductively coupled plasma mass spectrometry and electroanalytical techniques have been proposed for the determination of heavy metals [6,7]. Among these techniques, electrochemical sensors have great potential for environmental and biological monitoring of toxic metal ions in drinking or waste water and biological samples as blood, urine etc. due to their portability and field-applicability, excellent sensitivity, automation, rapid analysis, low power consumptions and inexpensive equipment [8-11].

Electrochemical determination of copper has been performed with mercury-coated platinum microelectrodes [12], glassy carbon electrode modified with glyoxime [13], polyphenols [14], phenanthroline [15,16] derivatives and poly-4-nitroaniline [17]. In addition to this, the design of electrodes with controllable surface properties can be achieved using self-assembled monolayers (SAMs), which become popular in the formation of well defined functional surfaces [18-20]. The advantages of SAMs include simplicity of preparation, versatility, stability, reproducibility and possibility to introduce different chemical functionalities [21, 22]. As an alternative to environmentally unfriendly mercury- [12] and bismuth- [23] based

electrodes several papers related to the detection of metal ions [4, 7, 24, 25,30-31] including Cu(II) ions [26-29] using SAM-modified electrodes have been published recently.

To enhance the preconcentration of metal ions, in this paper, a promising approach to the monitoring of Cu(II) ions was proposed. It was based on clay modified carbon paste electrode. The peak currents of Cu(II) ions were evaluated by cyclic voltammetry within a wide concentration range, with high selectivity, stability and sensitivity suitable for investigation of real samples. It was shown that the proposed sensor has great implications in the determination of Cu(II) ions in tap water even in the presence of some interfering ions.

EXPERIMENTAL

Apparatus and software

Voltammetric experiments were performed using a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) run under windows 2007. The three electrode system consisted of a chemically modified carbon paste electrode as the working electrode a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrodes

Modified electrodes were prepared by mixing a carbon powder and the desired weight of clay. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256cm². Electrical contact was made at the back by means of a bare carbon.

Procedure

The initial working procedure consisted of measuring the electrochemical response at

Clay-CPE at a fixed concentration of Copper ion Cu(II). Standard solution of Copper was added into the electrochemical cell containing 100 mL of supporting electrolyte.

The mixture solution was kept for 20 s at open circuit and deoxygenated by bubbling pure nitrogen gas prior to each electrochemical measurement. The cyclic voltammetry was recorded in the range from -0.8 V to 0.7 V. Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature. In order to insure the inert effect of Clay electrode during the experiment, the potential of 0mV was chosen in presence or in absence of accumulated copper. All other conditions were as described in the Voltammetric part.

RESULTS AND DISCUSSION

Cyclic voltammetry of Cu(II)

Cyclic voltammogram in 0.1 mol L⁻¹ Na₂SO₄ (at the pH 7) (Fig. 1) shows cathodic and anodic peaks, which makes it possible to determine this cation. The cyclic voltammograms were obtained for the Clay-CPE in the presence of Cu(II) and without Cu(II). There were no redox peaks in the CV of the Clay-CPE without Cu(II) (Fig. 1a). The Clay-CPE interacting with of Cu(II) showed an anodic peak at -0.05 V and cathodic peak at -0.3V versus calomel reference electrode (Fig. 1b).

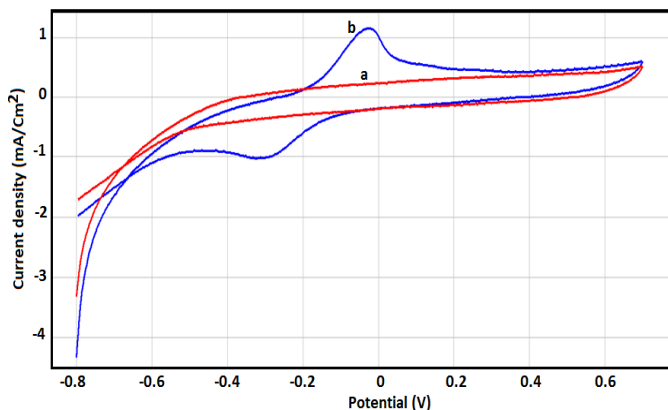


Figure 1: CV recorded for 0.31 mM Cu(II) at pH 7 at bare Clay-CPE (a) and Clay-CPE/Cu(II) (b), scan rate 100 mV/s, preconcentration time (t_p)=5min.

Influence of accumulation time

The effect of the accumulation time is investigated (Figure 2), this significantly affects the oxidation peak current of Cu(II). The peak current of 0.31 mmol L⁻¹ Cu(II) increases greatly within the first 5min. Further increase in accumulation time does not increase the amount of Cu(II) at the electrode surface owing to surface saturation, and the peak current remains constant. This phenomenon is due to the cavity structure of clay-CPE that improves the ability of the electrode to adsorb electroactive Cu(II). Maybe this is attributed to the saturated adsorption of Cu(II) on the Clay-CPE surface. Taking account of sensitivity and efficiency, accumulation time was 5 min in the following experiments.

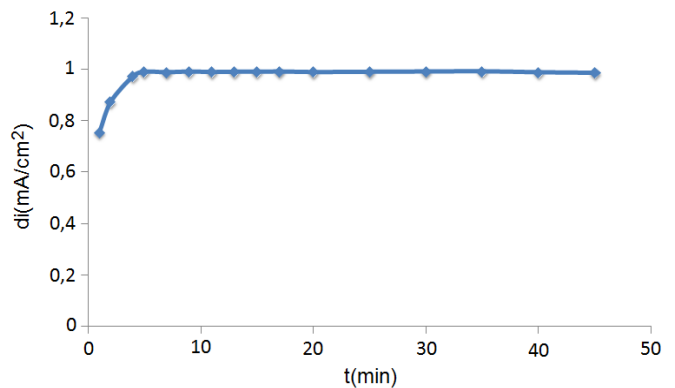
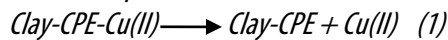


Figure 2: Effects of accumulation time on oxidation peak currents of 0.31 mmol L⁻¹ Cu(II) (pH 7) at Clay-CPE, supporting electrolyte is Na₂SO₄ 0.1M.

Voltammetric analysis of electrodeposit

As shown in Fig. 1, a voltammetric curve of the Clay-CPE preconcentrated for 5 min in Na₂SO₄ (0.1 M) with a scan rate of 100 mV s⁻¹. It may be noted the presence of a cathodic peak and anodic peak, the peak potentials were attributed to Cu(II) behaviour in Na₂SO₄ 0.1 M. An tampon medium was selected as suitable for relegate of Cu(II) according to Eq. (1). Cu(II) species leached out from the clay at the electrode/solution interface can be detected directly by reduction Eq. (2).



Effect of scan rate

The influences of scan rate on the oxidation peak potential (E_p) and peak current (I_p) and the reduction peak potential (E_c) and peak current (I_c) of copper, (0.1M Na₂SO₄, pH=7) were studied by cyclic voltammetry. The figure 3 shows both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 40 to 120 mVs⁻¹, suggesting that the electrons transfers for copper at the clay modified CPE is adsorption controlled reaction. The cathodic peak shifted towards negative potential with increased in scan rate, the anodic peak shifted towards positive potential with increased in scan rate. The figure 4 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of copper at Clay-CPE.

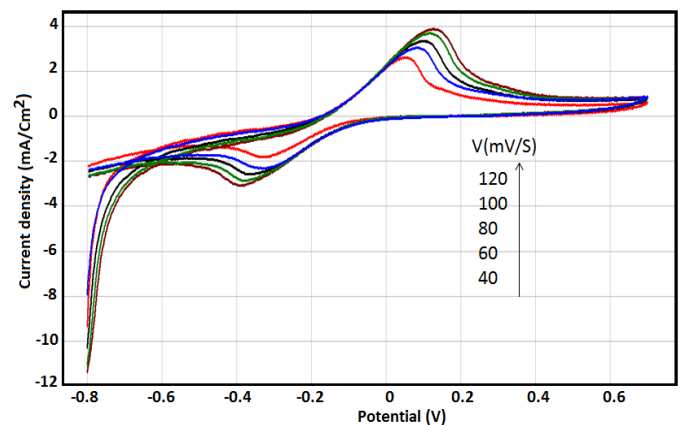


Figure 3: CV acquired on Clay-CPE with 1.86 mM Cu(II) in the buffer solution at different scan rates from 40 to 120 mV.s⁻¹.

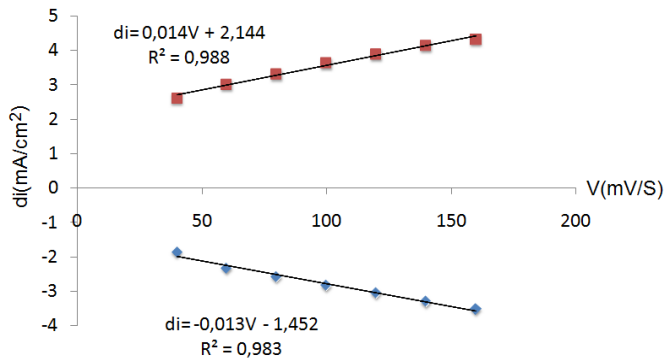


Figure 4: Plot of peaks area versus scan rate

Calibration graph

In order to obtain an analytical curve for the developed sensor, we carried out cyclic voltammograms for oxidation and reduction of Cu(II) at different concentrations in 0.1mol L⁻¹ Na₂SO₄ (pH=7) at a sweep rate of 100 mVs⁻¹.

Figure 5 shows the CV curves of different concentration of Cu(II) at Clay/CPE was increased from 0.31 mM to 1.55 mM. Both the anodic and cathodic peak current increases linearly with the concentration of Cu(II). It was also observed that the cathodic peak potential shift towards negative values and anodic peak potential shift towards positive side. This kind of shift in E_p in the cathodic and anodic direction with increasing concentration of the Cu(II) indicates that the product of Cu(II) are adsorbed over the electrode surface.

The figure 6 shows the linear relationship between the concentration anodic peak and cathodic peak currents of copper at Clay-CPE.

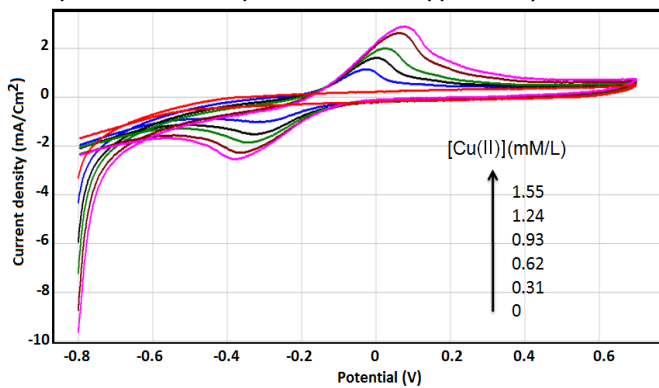


Figure 5: Cyclic Voltammograms of different concentration of Cu(II) (0.31mM to 1.55mM) at Clay-CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s.

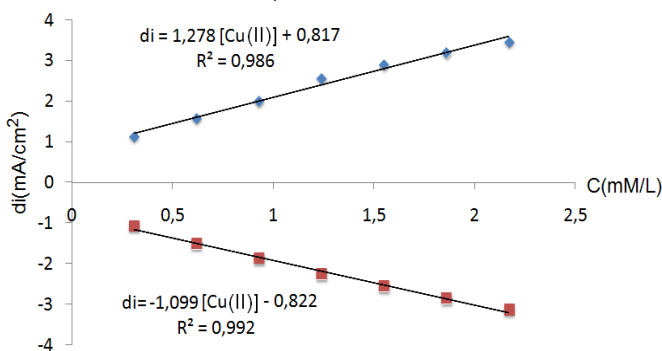


Figure 6: Plot of peaks area versus added concentration of Cu(II).

Influences of pH

In a first step, the effect of pH on electrode response was investigated. In most cases, the solution pH is important to the

electrochemical reaction. The Figure 7 a shows the cyclic voltammograms of the Cu(II) at different PH. The current of the peak depend on the solution PH. The anodic peak potential shifted towards negative side and cathodic peak potential E_{pc} shifted towards more positive potential. The figure 8 shows the graph of different pH versus peak current, it could be confirmed that the current density decreases with increased pH.

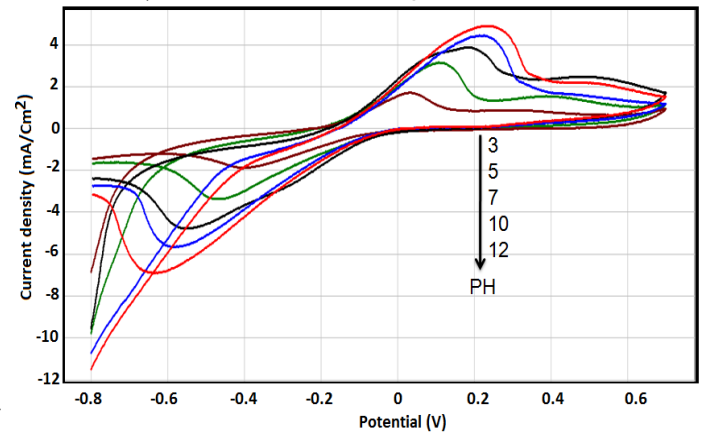


Figure 7: Effect of pH on the oxidation and the reduction of Cu(II) at the Clay modified CPE

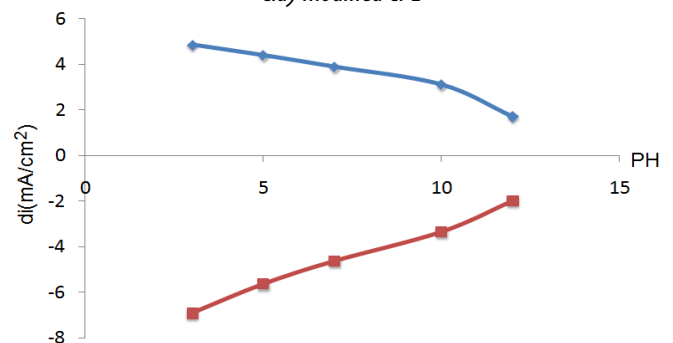


Figure 8: Plot of the relationship between solution pH and the oxidation and reduction peak Current

PRACTICAL APPLICATION

In order to evaluate the performance of Clay-modified carbon paste electrode by practical analytical applications, the determination of Cu(II) was carried out in tap water without any pretreatment. The analytical curves were obtained by CV experiments in supporting electrode (Figure 9). It was founded that the peaks currents increase linearly versus Cu(II) added into the tap water (Figure 10).

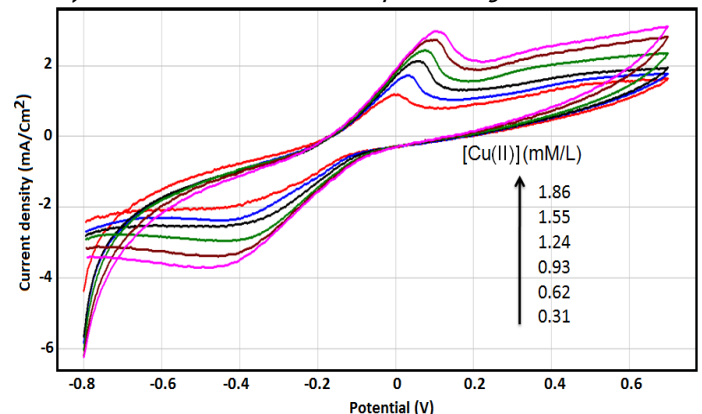


Figure 9: Cyclic Voltammograms of different concentration of Cu(II) at Clay/CPE in 100ml tap water, Scan rate 100 mV/s

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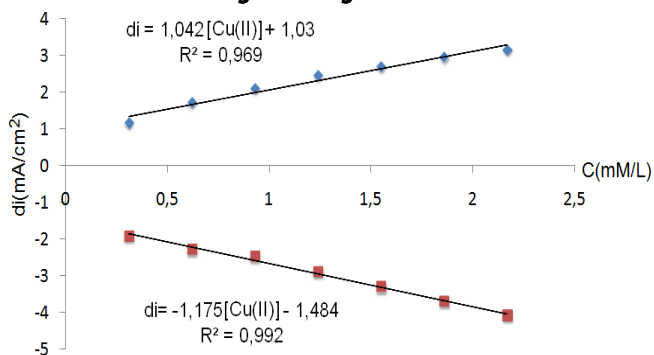


Figure 10: Plot of peaks area versus added concentration of Cu(II)

CONCLUSION

Cyclic voltammetry analysis utilizing the clay modified carbon paste electrode for the determination of copper dissolved in aqueous solutions has been demonstrated.

The use of CV is faster and more sensitive than other, conventional, techniques.

Besides, the use of clay modified carbon paste electrode enables direct analysis of tap water sample without treatment of the sample. This extra advantage could reduce the cost of the analysis and the time taken, hence resulting in improvements in analytical sensitivity.

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ACTA Technica CORVINIENSIS
BULLETIN OF ENGINEERING

ISSN:2067-3809

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