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Clay modified carbon paste electrode using cyclic voltammetry: Application to Hg(II) trace analysis

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ABSTRACT

A sensitive voltammetric method for detection of mercury ions is described which is made by modifying a carbon paste electrode with clay. A linear working range for concentration of mercury between 0.18mM to 0.91mM. The electrochemical responses obtained by cyclic voltammetry (CV) at clay modified carbon paste electrode (Clay-CPE) were found to be analytically suitable to develop a method for the determination of mercury at low concentration levels. The developed method was applied for the detection of Hg(II) in tap water.

KEYWORDS

Modified electrodes;
Cyclic voltammetry;
Clay;
Hg(II) detection.

INTRODUCTION

Mercury is the most neurotoxic element known to humans[1] that can exists in metallic, inorganic, and organic forms. Inorganic mercury compounds take the form of mercury salts and excessive exposure can cause a number of severe health problems such as brain damage, kidney failure, and various cognitive and motion disorders[2]. Methylation of inorganic mercury has been shown to occur in fresh water and in seawater, although almost all mercury in uncontaminated drinking-water is thought to be in the form of Hg2+[3]. Several techniques for the determination of the total mercury content have been reported, including cold vapor atomic fluorescence spectrometry[4], cold vapor atomic absorption spectrometry[5], inductively coupled plasma atomic emission spectrometry[6], and inductively coupled plasma mass spectrometry[7]. The high toxicity of mercury has prompted the development of various analytical methods for its determination towards the creation of a sufficiently stable detection system which is simple to operate, inexpensive and does not require mechanical or chemical treatment before analysis or for regeneration. Electrochemical sensors with recognition elements of biological origin have received particular attention due to which include a very broad range of electrode materials and measurement methodologies that can be selected. It also offers high sensitivity and selectivity, and impressive cost effectiveness and miniaturization[8]. A group of researchers have been investigating the development of electrochemical biosensors based on peptides for detecting heavy metals[9-14]. Some of them identify a peptide which is capable of binding cadmium ions specifically for the measurement of low concentrations with minimal interference from other metal ions. Amino acid in peptide can be arranged in any particular order or length and present an almost infinite number of ligands for binding metal[15]. The polar side chains of peptide might act as ligands for metal ions based on the theory of hard and soft acids and bases[16]. Amino acid bearing N donor ligands in their side chains (his, lys, arg) and S donor ligand (cys) have strong binding preferences for class B metals (Ag^+, Hg^{2+}, Cd^{2+}, and Au^+)[15-17]. In this work, we focus on determination of trace mercury in solution by clay modified electrode using cyclic voltammetry within a wide concentration range, with high selectivity, stability and sensitivity suitable for investigation of real samples.

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 $0.1256 cm^2$. 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 mercury ion Hg(II). Standard solution of mercury 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 -1 V to 1 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 mercury. All other conditions were as described in the Voltammetric part.

RESULTS AND DISCUSSION

Cyclic voltammetry of Hg(II)

The Figure 1 show the cyclic voltammograms in 0.1 mol L^{-1} Na_2SO_4 (at the PH=7) were obtained for the Clay-CPE in the presence of Hg(II) and without Hg(II). There were no redox peaks in the CV of the Clay-CPE without Hg(II) (Figure 1a). The Clay-CPE interacting with of Hg(II) showed an anodic peak at

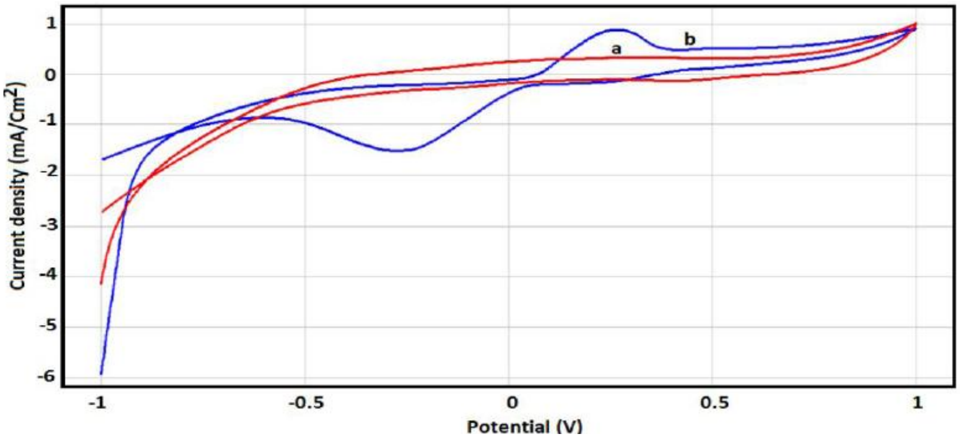

Figure 1 : CV recorded for 0.18 mM Hg(II) at pH 7 at bare Clay-CPE (a) and Clay-CPE/Hg(II) (b), scan rate was 100 mV/s, preconcentration time = 6min

0.25 V and cathodic peak at -0.25V versus calomel reference electrode (Figure 1b).

Influence of accumulation time

The Figure 2 shows the effect of the accumulation time. The peak current of 0.18 mmol L^{-1} Hg(II) increases greatly within the first 6min. Further increase in accumulation time does not increase the amount of Hg(II) at the electrode surface owing to surface saturation, and the peak current remains constant. Taking account of sensitivity and efficiency, accumulation time was 6 min in the following experiments.

Voltammetric analysis of electrodeposit

The presence of a cathodic and anodic peak, the peak potentials were attributed to Hg(II) behavior in Na_2SO_4 0.1 M. An tampon medium was selected as suitable for relegate of Hg(II) according to Eq. (1). Hg(II) species leached out from the clay at the electrode/solution interface can be detected directly by reduction Eq. (2).

$$\text{Clay-CPE-Hg(II)} \rightarrow \text{Clay-CPE} + \text{Hg(II)} \tag{1}$$

$$\text{Hg(II)} + 2\,e^{-} \rightarrow \text{Hg(0)} \tag{2}$$

Effect of scan rate

The influences of scan rate on the oxidation peak potential and, peak current and the reduction peak potential and, peak current of mercury, (0.1M Na_2SO_4, 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 mercury at the clay modified CPE is adsorption controlled reaction. The Figure 4 shows the linear relationship between the scan rate anodic peak and ca-

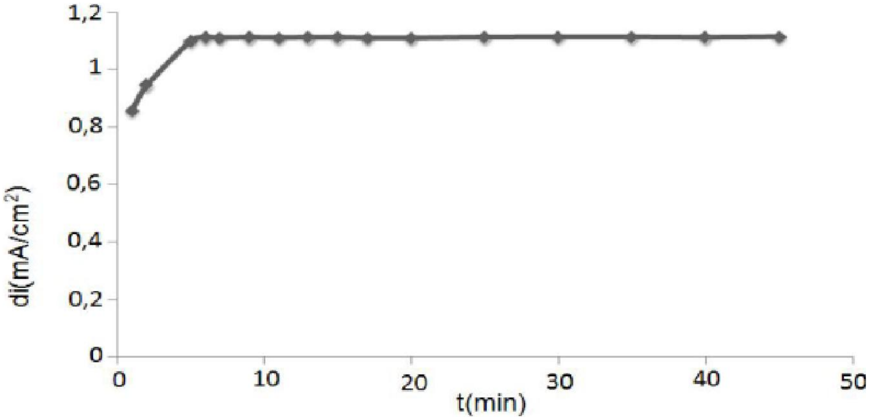

Figure 2 : Effects of accumulation time on oxidation peak currents of 0.18 mmol L^{-1} Hg(II) (pH 7) at Clay-CPE, supporting electrolyte is Na_2SO_4 0.1M

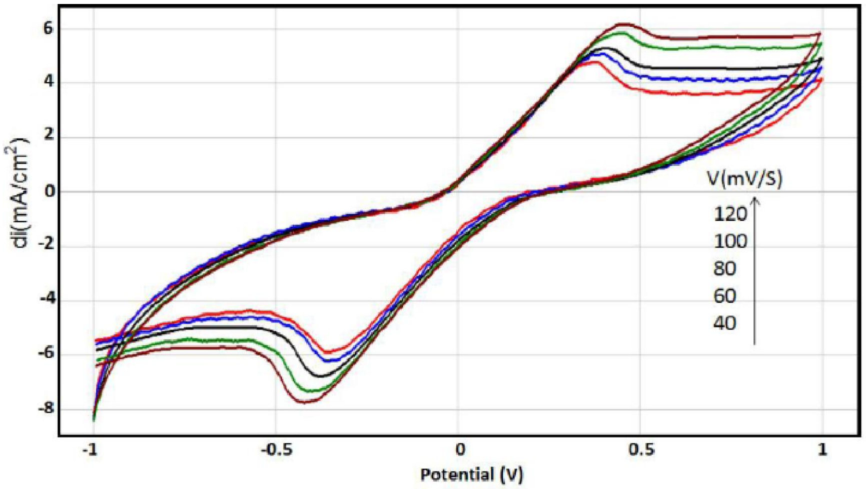

Figure 3 : CV acquired on Clay-CPE with 3.81 mM Hg(II) in the buffer solution at different scan rates variants from 40 to 120 $mV.s^{-1}$

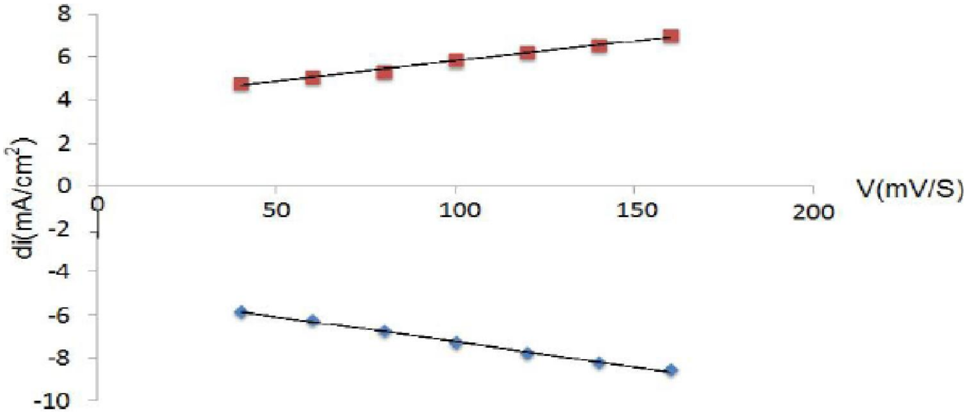

Figure 4 : Plot of peaks area versus scan rate

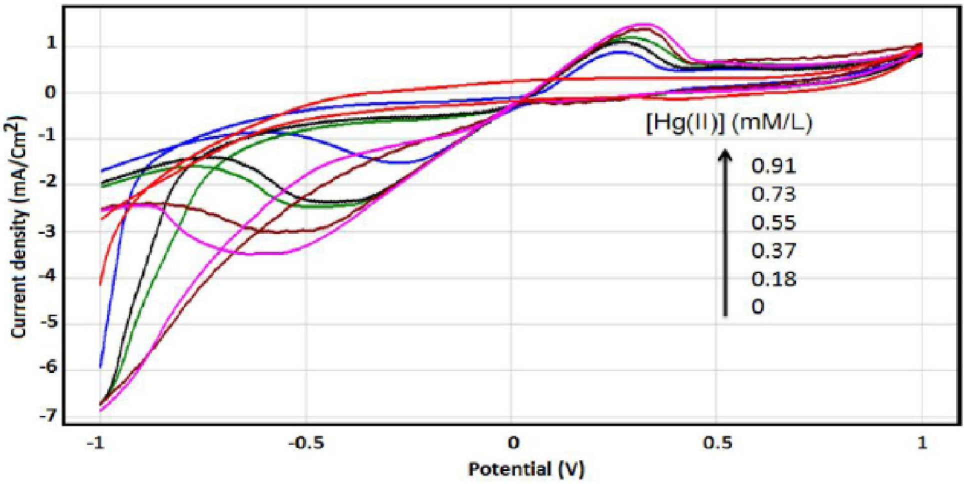

Figure 5 : Cyclic voltammograms of different concentration of Hg(II) at Clay-CPE in 0.1 M Na_2SO_4, Scan rate 100 mV/s

thodic peak currents of mercury at Clay-CPE. The linear regression equations:

I_{pa}=0.018V+3.962 **R^2=0,992**

I_{pc}=-0.023V-4.908 **R^2=0,996**

Calibration graph

Figure 5 shows the CV curves of different concentration of Hg(II) at Clay/CPE was increased from 0.18 mM to 0.91 mM. Both the anodic and cathodic peak current increases linearly with the concentration of Hg(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 Ep in the cathodic and anodic direction with increasing concentration of the Hg(II) indicates that the product of Hg(II) are adsorbed over the electrode surface.

The Figure 6 shows the linear relationship between the concentration anodic peak and cathodic peak currents of Hg(II) at Clay-CPE. The linear regression equations:

I_{pa}=0.830 [Hg(II)] + 0.739 **R^2=0.997**

I_{pc}=-2.413 [Hg(II)] -1.232 **R^2=0.986**

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 Hg(II) at different pH. The current of the peak depend on the solution pH. The anodic and cathodic peak potential shifted towards negative side.

The Figure 8 shows the graph of different pH versus peak current, it could be confirmed that the current density decreases when the pH increased.

PRACTICAL APPLICATION

The developed method was applied for detection of Hg(II) in tap water sample in order to evaluate the

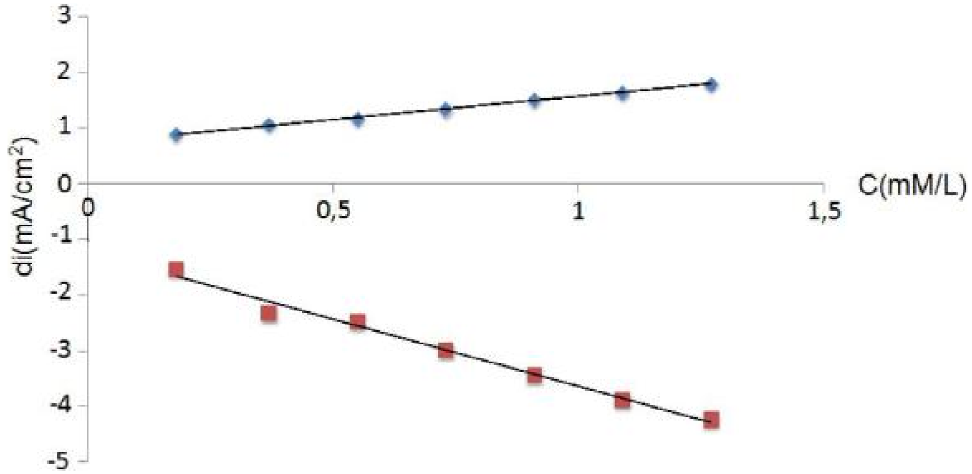

Figure 6 : Plot of peaks area versus added concentration of Hg(II)

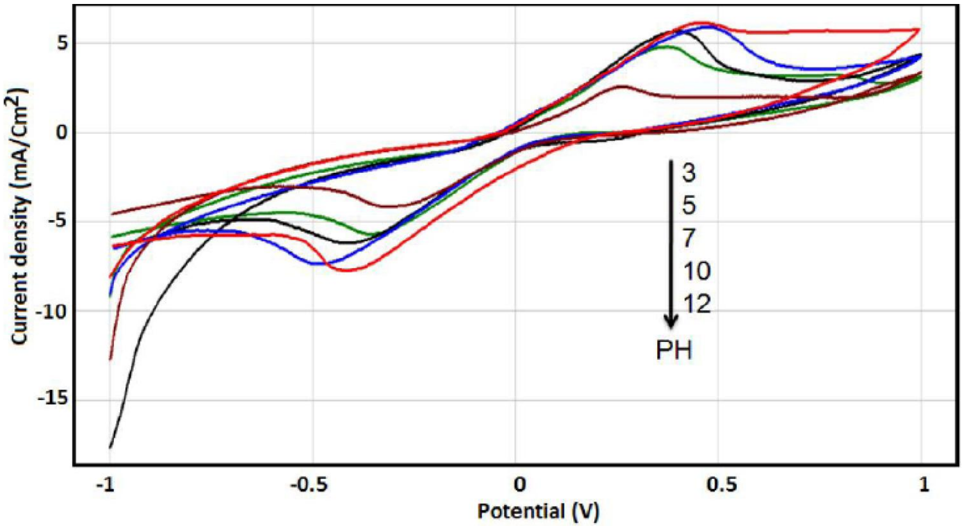

Figure 7 : Effect of pH on the redox of Hg(II) at the Clay modified CPE

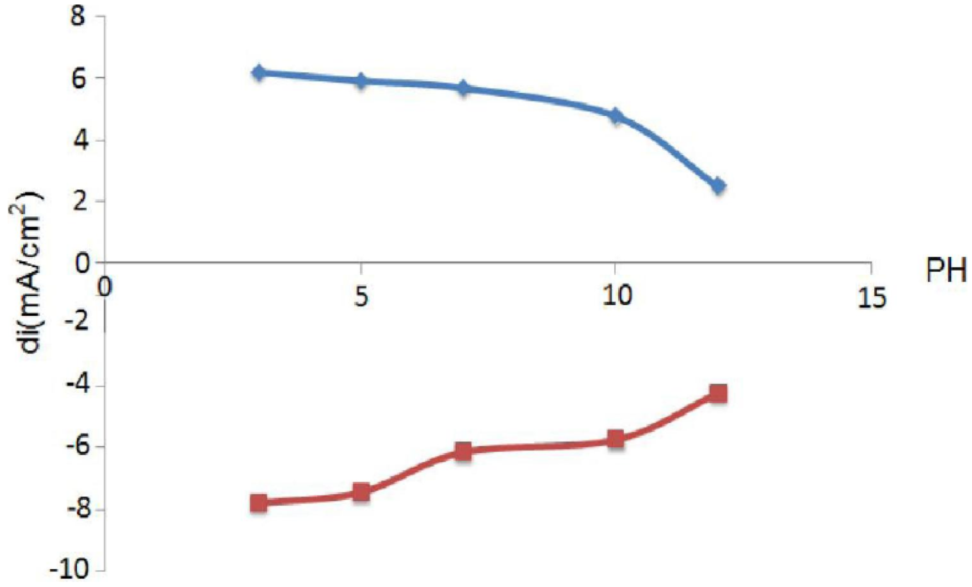

Figure 8 : Plot of the relationship between solution pH and the redox peak Current

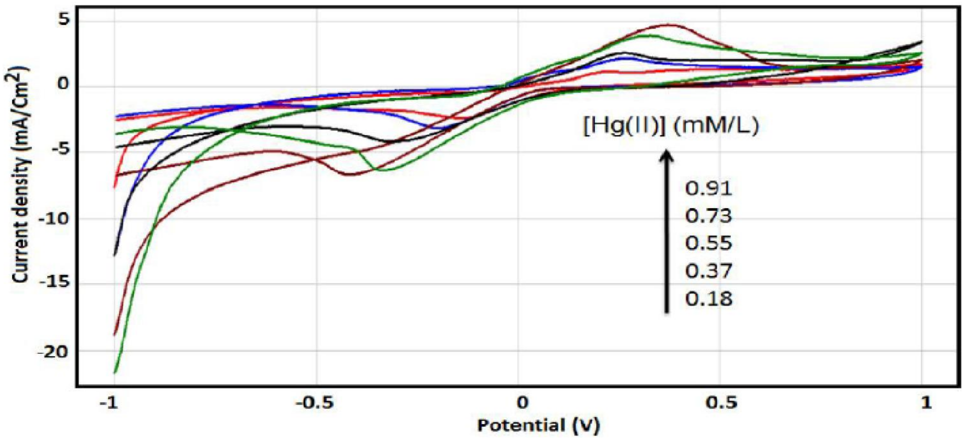

Figure 9 : Cyclic voltammograms of different concentration of Hg(II) at Clay-CPE in 100ml tap water, Scan rate 100 mV/s

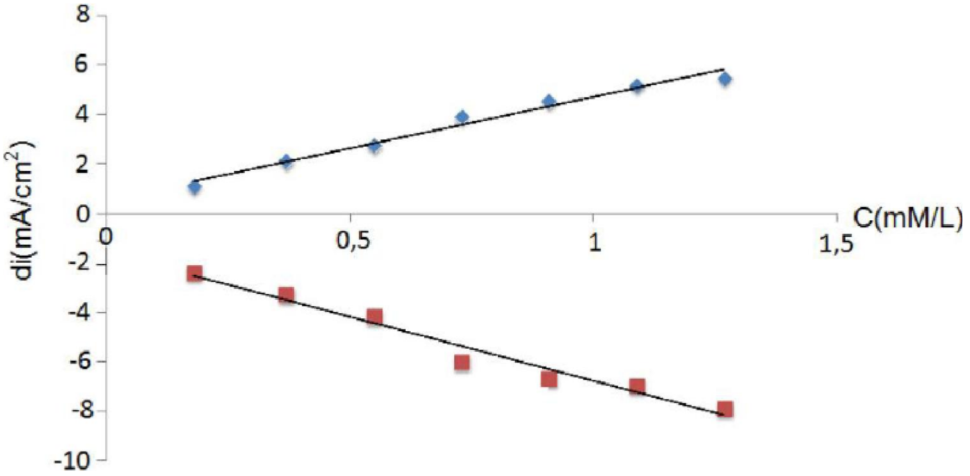

Figure 10 : Plot of peaks area versus added concentration of Hg(II)

applicability of clay modified carbon paste electrode in real sample application. Tap water was analyzed using the developed method.

The analytical curves were obtained by CV experiments in supporting electrode (Figure 9). It was founded that the peaks currents increase linearly versus Hg(II) added into the tap water (Figure 10). The linear regression equations:

Ipa=4.152 [Hg(II)] + 0.530 **R^2=0.980**
Ipc=-5.170 [Hg(II)] -1.578 **R^2=0.967**

CONCLUSION

The Clay-CPE, have been fabricated to study Hg2+ detection by voltammetry analysis.

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

This extra advantage could reduce the cost of the analysis and the time taken, hence resulting in improvements in analytical sensitivity. The Clay-CPE exhibits an improved performance for Hg^{2+} analysis. The application studies of Hg^{2+} detection by Clay-CPE give a very good sensitivity with high correlation coefficient with wider linear range.

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