

ORIGINAL ARTICLE

Voltammetric Characterization of Modification of the Glassy Carbon Electrode With Clay to Study Its Applications in Blood Medium

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ABSTRACT

Introduction: The clay molecules act as a discharge of free radicals as does the earth; it's always good property losing the excess of free radicals from the human body to avoid cancer disease. This study aimed to detect the conductivity of modified working electrodes with clay to use in the applications in blood medium by cyclic voltammetry. **Methods:** The study included to determine the electrochemical conductivity of clay by studying different concentrations, pH, scan rates, reliability, and stability. Also, the study included applications such as using a blood medium to determine the electro-conductivity of the clay. **Results:** The voltammetric behavior of different working electrodes such as GCE and modified electrode Clay/GCE were studied, cyclic voltammograms at potential range of - 2 Volts to +2 Volts were used, GCE and modified clay/GCE at 0.1 Vsec⁻¹. 0.15 mM K₄[Fe(CN)₆] exhibits the redox current peaks on the Clay/GCE with Epa (oxidation voltage) is 0.3V and Epc (reduction voltage) is 0.18V. Different concentration of Fe ions increasing from 0.1 mM to 0.2 mM at pH=6 on Clay/GCE which was enhancing the current peaks with dual folds. Our studied using blood media found that increasing of the Fe concentration was produced more amount of anti-oxidative complex. **Conclusion:** The current study shown the clay/GC electrode had a stable and reproducible response to iron ions. The novel electrode clay/GCE has good electrochemical properties in diffusion coefficient values and reversible electrode.

Keywords: Clay, Blood medium, Cyclic voltammetry, GCE, K₄[Fe(CN)₆], K₂SO₄

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INTRODUCTION

The earth provides an electrically neutral object, due to the virtually unlimited state of the earth; it is immune to electricity virtually. However, it should be noted that "the fact that the earth is immune to electric virtually" is actually a generalized phenomenon. In fact, the earth is a very complex subject given all the variables and materials that make up the earth. Some scientists were studied in the electrochemical field of blood as an electrolyte (1-5). It can be found some applications

which is useful in healthy life to avoid some danger diseases such as cancer (6).

The main difficulty to overlapping ascorbic acid oxidation potential can overcome by typical capability of the uric acid to co-ordinate with electrodes modified with electroplated clay(7). Stable films of mud and hemoglobin (Hb) layer by layer were assembled on different solid substrates by alternative adsorption of negatively charged clay plates from their water dispersants and positively charged Hb from pH 4.5 stores. Cyclic voltammetry, UV spectroscopy and quartz crystal microbalance used for screen film progress(8). A method for building biosensors with cytochrome P450 membrane congeners was developed based on mixed films of clay / detergent / protein. Thin membranes of

sodium montmorillonite colloids were prepared with cytochrome P450 2B4 (CYP2B4) with ionic detergent on glassy carbon electrodes. The modified electrodes were marked, and bio-stimulation reactions were followed (9) (10).

The hemoglobin films in clay revealed a distinct and reversible pair of annular voltameter (CV) peaks at about - 0.36 V versus SCE in pH 7.0 buffers, distinctive of Hb heme redox of Fe (III) / Fe (II). Hemoglobin was adsorbed onto the clay modified electrode(8, 10). Cyclic voltammetry (CV) measurement method is proposed to determine trace quantities of paracetamol in a modified carbon paste electrode with clay (Clay/CPE). The results showed that Clay/CPE showed excellent electrical catalytic activity of paracetamol. A quasi-reversible oxidation-reduction process was obtained from the modified electrode paracetamol. The concentration of paracetamol was investigated and the pH solution measured. This electrochemical sensor offers excellent detection performance for paracetamol. The sensor was effectively useful for identification of paracetamol of real sample tablets with acceptable results (11).

In this study clay was used electrochemical analysis and characterized by Fe ions in each of K_2SO_4 and blood media.

MATERIALS AND METHODS

Materials

Clay compounds from Iraqi soil (Karbala city, Iraq), potassium ferrous cyanide $K_4[Fe(CN)_6]$, and potassium sulfate (K_2SO_4) from Sinopharm Chemical Reagent Co Ltd. (SCRC), China. The healthy Blood samples selected from Baghdad City Drug Center. Analyses were done after serum separation from whole blood by type 8-1 electronic centrifugation (3000 r / min). Deionized water was used to prepare solutions. All serum samples were diluted with deionized water by 1: 9 (serum: deionized water).

Devices

NuVant Systems EZstat (Potentiostat / Glvanostat) series from USA is used. The voltametric cell was linked to a voltage state monitor and controlled by software installed on PC performing the cyclic voltammetry (CV) measurement. The Ag electrode contains Ag / AgCl in 3 Molar of KCl as reference electrode, using a 1 mm diameter of platinum wire as an assisting electrode. It was used GCE as a working electrode after performing by polishing and cleaning the surface of the electrode as show in Figure (1).

Prepare the modification electrode

Modify cleaned GC electrodes with clay molecules were done by a mechanical attachment method(12). The GCE surface was tapped about thirty times onto dry clay powder placed on a filter paper as shown in Figure

(2). In this work, the modified GCE with clay would be used as a working electrode and termed clay/GCE.

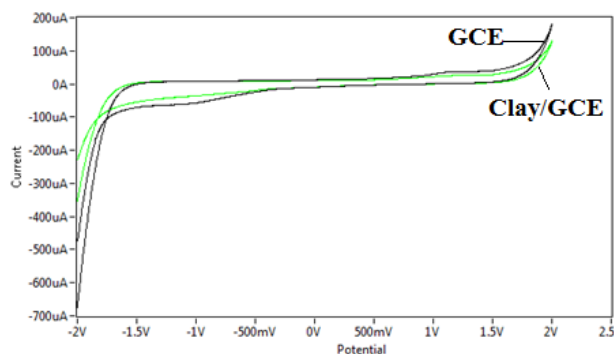


Figure 1: GCE as a working electrode after performing by polishing and cleaning the surface of the electrode

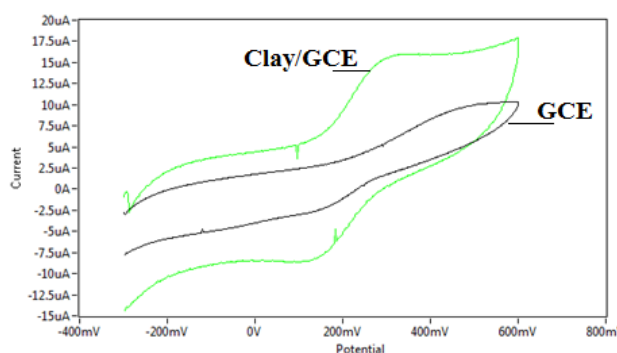


Figure 2: The GCE surface was tapped about thirty times onto dry clay powder placed on a filter paper

RESULTS

Study different electrodes

The voltammetric behavior of different working electrodes such as GCE and modified electrode Clay/GCE is studied, cyclic voltammograms at potential range of - 2 Volts to +2 Volts shows in Figure (1), GCE and modified clay/GCE at 0.1 Vsec^{-1} . Figure (2) shows that $0.15 \text{ mM } K_4[Fe(CN)_6]$ exhibits the redox current peaks on the Clay/GCE with E_{pa} (oxidation voltage) is 0.3V and E_{pc} (reduction voltage) is 0.18V with enhancement the redox peaks about three times than in the bar of GCE.

Experimental study

The optimal studies for the electrochemical response were determined by calculating the redox current peaks at dependence on all parameters.

Calibration graph

Figures (3-a) shows cyclic voltammogram of different concentration of Fe ions increasing from 0.1 mM to 0.2 mM at pH=6 on Clay/GCE which was enhancing the redox current peaks about two folds. Oxidation-reduction current peaks were elevated with the cumulative of the concentration of Fe ions was revealed in Figures (3-B) and Figures (3-a), respectively.

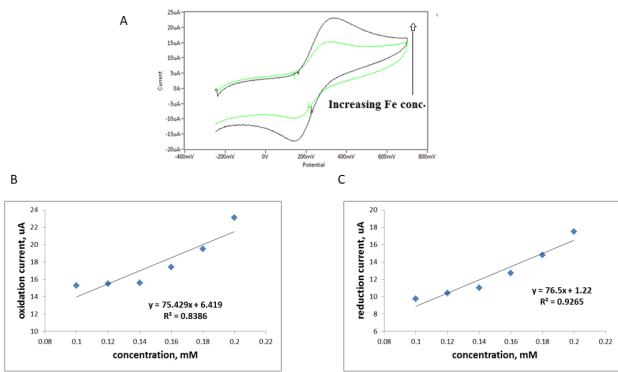


Figure 3: The cyclic voltammogram of different concentration of Fe ions

Effect of Acidity and Alkaline pH

We studied the effect of different pH (3-12) on the redox of iron (FeII/FeIII) in 0.2 mM Potassium ferrocyanide and 0.1M KCl which shows in Figure (4). The pH solution has a substantial effect on current top and oxidation reduction peaks of Fe II / Fe III.

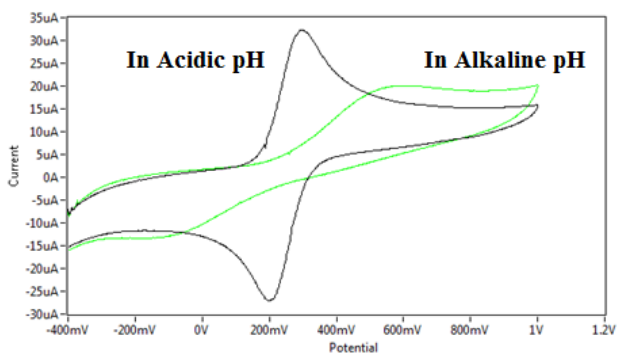


Figure 4: The effect of different pH (3-12) on the redox of iron

Reliability (stability) of the new clay/GC Electrode

The stability of modified clay/GCE was studied for ten times showing oxidation reduction peaks of Iron ions in Potassium sulfate electrolyte as shown in Figure (5) which explained the overlapping of redox peaks (13).

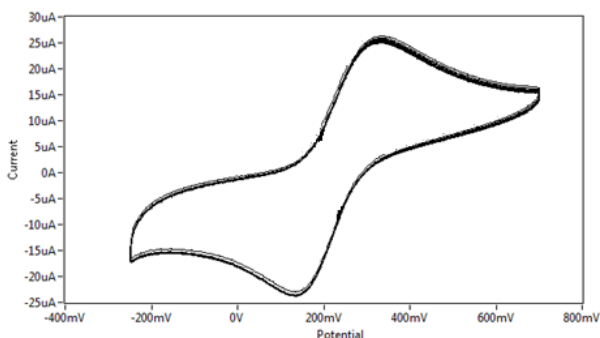


Figure 5: Oxidation reduction peaks of Iron ions in Potassium sulfate electrolyte

Influence of scan rate (SR)

Different scan rates were affected on the electrochemical reaction of FeII/FeIII on the clay/GC electrode was studied by CV which revealed in Figure 6-A. the linear relationship between the different scan rates and anodic-cathodic current peaks of FeII/FeIII at clay/GC electrode as shown in Figure 6-B.

Hence, the new modified electrode acted as electro-catalyst with the presence of clay on the surface of GCE. (1).

Using the Randles-Seveik equation, the diffusion coefficient value, which is described as the reversible oxidation – reduction current peaks, was found (14, 15):

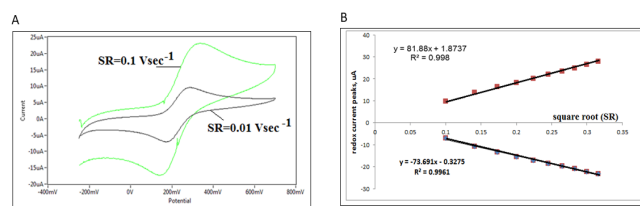


Figure 6: The electrochemical reaction

Studying the modified electrode (clay/GCE) in blood medium

One of the applications for using the preparation of modified electrode (clay/GCE) is studied in blood medium to find the consequence of different concentration of iron ions on the components of the blood as shown in Figure (7).

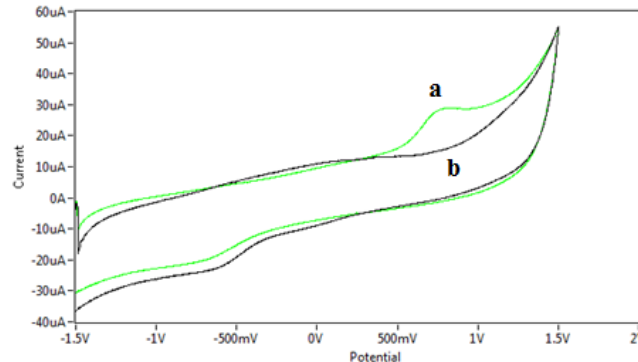


Figure 7: The consequence of different concentration of iron ions on the components of the blood

DISCUSSION

It was observed that no current peaks when used modified Clay/GC electrode. It was recognized that the surface of GCE has been effectively modified by clay particles. We shown that $K_4[Fe(CN)_6]$ exhibits the redox current peaks on the Clay/GCE with enhancement the redox peaks about three times than in the bar of GCE. It means that clay molecules act as an electro-catalyst in K_2SO_4 electrolyte this result coincides with Muhammed et al., 2010 (16).

Good lines of the relationships between iron ions anodic and cathodic current peaks in the electrolyte and the different concentrations (0.1 - 0.2 mM). It seems that a little detection limit was detected from the modified working electrode clay/GCE in electrolyte, so that the new modified electrode can be considered as a high sensitive sensor to be used in different electrochemical analyses (17, 18).

It was studied cathodic and anodic current peaks of the iron ions in alkaline pH have low current peaks and shifted to the higher potential, while in different properties the redox peaks of the iron ions in acidic pH enhanced the peaks with shift to lower potential. The discussion of this property, it is concluded that clay compound has a good electro-conductivity in acidic medium and acts as electro-catalyst (19). The redox peaks enhanced with the increasing of scan rate from -0.4 to 0.8 Vsec⁻¹ indicating that iron ions is reacted onto clay/GC electrode surface.

The coefficient of diffusion values for anodic-cathodic reaction for Fe ions in K₂SO₄ solution on clay/GC electrode was determined as anodic and cathodic diffusion coefficient D_{fa} = 1.05 × 10⁻⁶ cm² sec⁻¹ and D_{fc} = 5.66 × 10⁻⁶ cm² sec⁻¹, respectively. Figure 10 shows the relationship of anodic and cathodic current peaks of Fe(II)/Fe(III) sensor clay/GCE with the different scan rates in the voltammetric technique (20).

It was found that increasing of the Fe concentration was produced more amount of anti-oxidative complex, which discussed by the disappearing of the anodic current of Fe ions and enhanced the cathodic current peak (21). So, it was explained the new working electrode which acted as a high sensitive sensor to detection at low concentration of metal ions in blood medium (22).

CONCLUSION

The electrochemical performance of iron ions on the adapted working electrode clay/GCE was assessed using the voltammetric measurements. Clay/GC electrode showed a stable and reproducible response to iron ions. The modified electrode is insoluble in aqueous solution, and nontoxic. Also, the redox reaction of the FeII/FeIII with modified working electrode clay/GCE produces an electro-catalyst reaction by enhancing the peaks with increasing the concentration and scan rates. In other words the different pH was affecting the redox peaks which decreased at alkaline pH and enhanced at acidic pH. The novel electrode clay/GCE has good electrochemical properties in diffusion coefficient values and reversible electrode. A new method for characterization the iron ions was described as simple, fast and sensitive at low cost of analysis. The method has been satisfactorily applied to determine the pharmaceutical medicines in blood medium.

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