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ELECTROCATALYTIC OXIDATION OF DOPAMINE ON GLASSY CARBON ELECTRODE MODIFIED BY ETHYLCELLULOSE/CLAYS

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ABSTRACT

The aim of this study is the synthesis of ethylcellulose/clays nanocomposites by a very simple approach for an application as an electrocatalytic support of the oxidation of Dopamine. This electrochemical sensor was characterized by X-ray diffraction (XRD), Thermal analysis (TGA/DTA), scanning electron microscopy (SEM) and Transmission Electronic Microscopy (TEM). The results indicates that the proposed sensor has good electrocatalytic activity towards the oxidation of dopamine and exhibits a low detection limit of $1.15x10^{-6}$M, a wide linear range of $2,5x10^{-7}$–$7,65x10^{-7}$M and fast response.

Keywords: Detection limit, electrocatalytic, electrochemical sensor, ethylcellulose/clays.

INTRODUCTION

Research in the field of nanotechnology has shown that the combination of organic and inorganic material particles in the nanoscale range to manufacture the so-called organic-inorganic composites could give rise to new characteristics in or enhance the properties of the nanocomposites such as mechanical performance, optical properties, electrochemical characteristics, thermal stability, gas barrier capability, high permeability, solvent resistance, fire retardancy and flammability reduction as compared to the raw precursors (Michael Alexandre, 2000; Supratim Suin, 2012; Yoshitsugu Kojima, 1993; Jing He, 2008). Amongst the materials that have commonly been used as organic and inorganic precursors in the production of nanocomposites are various types of polymers and clays. Polymers are chosen due to their widespread use in connection with aerospace, automobile, construction, packaging, appliances, food, and pharmaceutical industries whereas clays have been selected because they are readily available and of low cost. Some results reported in the literature include: poly(ethylene oxide) and poly(ethylene glycol)and with montmorillonite, saponite and hectorite (Chaiko, 2003), polypropylene-*graft*-maleic anhydride and polystyrene with montmorillonite and fluorohectorite (Gilman, 2000), polystyrene with Na-montmorillonite, hectorite, laponite and Li-fluorohectorite (Henrik Mauroy, 2013), Nylon-6 with montmorillonite and saponite (Yoshitsugu Kojima, 1993), poly(lactic acid) with montmorillonite, smectite and mica (Pralay Maiti, 2002), polystyrene with Na-montmorillonite (MMT) and modified MMT (Ranya Simons, 2011), Bisphenol-A polycarbonate with Na montmorillonite (Supratim Suin, 2012). In order to take advantage of the exceptional properties exhibited by organoclay nanocomposites several studies today are focused towards the manufacture of novel composites via various synthetic techniques namely exfoliation-adsorption, in situ intercalative polymerization, melt intercalation and template synthesis and based on various precursors with a view to extend their applications. During the preparation of the polymer/clay composite materials, depending on the synthetic route and the nature of the precursors, several cases of interaction can be envisaged between the layers of the clay and the polymer: intercalation, exfoliation, and delamination, each leading to nanocomposites with specific morphology, responsible for their characteristic observed properties (Michael Alexandre, 2000; Chaiko, 2003; Gilman, 2000; Supratim Suin, 2012). In recent years, the outstanding properties of nanocomposites have been exploited in pharmaceutical and medical fields, especially in the electrochemical

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detection of traces of substances by electrodes rendered more sensitive and more selective by nanocomposite modification (Yang-Rae Kim, 2010; Yan Mao, 2011; Teo Peik-See, 2014).

Ethylcellulose (EC) due to its versatility, organosolubility, and its thermoplastic behavior appears to be a good polymer candidate for the fabrication of biologically-friendly nanocomposite electrochemical sensor. In addition to industrial applications, premium grades are approved for use in regulated markets such as food and pharmaceuticals. In the pharmaceutical industry, ethylcellulose is used in the formulation of acetaminophen (Ruiz NR, 1997). In combination with clays, it is environmentally friendly, naturally occurring, and readily available in large quantities.

Dopamine (3,4-dihydroxyphenyl ethylamine, DA) is one of the most important neurotransmitters which are produced in the adrenal glands and several areas of the mammalian central nervous system. As an inhibitory neurotransmitter, DA plays an essential role in the normal function of the human central nervous, renal, hormonal and cardiovascular systems metabolism. In neuropharmacology and neurophysiology, detection and quantification of dopamine constitute challenging tasks and are crucial steps in diagnosis, prevention, monitoring, and treatment of certain neurological disorders such as Schizophrenia, Parkinson's disease, and drug addiction which are caused by deficiency or abnormalities in the dopamine concentration (Wightman RM, 1988; Yan Mao, 2011; Teo Peik-See, 2014; Yang-Rae Kim, 2010; Damier, 1999).

Several techniques have been used for the detection of Dopamine including HPLC, GC-MS, fluorescence, fluorimetry, chemiluminescence, UV visible spectrometry and capillary electrophoresis (CE-luminescence) (Hitoshi Nohta, 1997; Li Jiango, 1997; Ruohua Zhu, 1997). However, these analytical techniques, though effective for the detection of dopamine, are time-consuming, of low sensitivity and expensive. Electrochemical techniques have attracted great interest in many cases since through the use of surface-modified electrodes, the detection employing these techniques has been made fast, low-cost, with higher sensitivity and better selectivity coupled with the advantages of low detection limit and high accuracy (Teo Peik-See, 2014; Wu Ying, 1996; Yan Mao, 2011).

In this work, purified clay was dispersed in ethylcellulose and then solvent-free polymerization was carried out to synthesize ethylcellulose/organoclays nanocomposites. Some analysis techniques, namely XRD, TGA-DTA, SEM and TEM, were applied. The ethyl cellulose/clays prepared were used to manufacture electrochemical sensor for detection of Dopamine (DA).

MATERIALS AND METHODS

Chemicals and Reagents

Dopamine has purchased from Sigma-Aldrich. Ethylcellulose has got from Fine-Chem Limited (India). (≥99.0%). Potassium phosphate monobasic (99%) and sodium hydroxide are purchased from Sisco Research Laboratories pvt. Ltd, India.

Characterization Techniques

The X-ray powder diffraction spectra were measured in the interval $2°<2\theta < 60°$ by using a Panalytical, Netherlands (Model: PW3040/60 X'pert PRO) equipped with a Cu anode (kα radiation, $\lambda = 1.54056$ Å) using a voltage of 40 KV and a current of 30 mA.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were recorded using a SDT Q600 V8.3 Build 101simultaneous DSC-TGA instrument.

The SEM micrographs of the polymer/Clays and unmodified clays were taken in Hitachi (Japan) S-3000H electron microscope with an accelerating voltage of 15kV.

Transmission electron micrographs of the nanocomposites and unmodified clays were taken with a Tecnai F20 (FEI) transmission electron microscope with an accelerating voltage of 200 kV.

Cyclic voltammetry (CV) on all prepared GCE/ethylcellulose/Clays as well as on an unmodified GCE has been performed on CHI 6084C electrochemical analyzer (USA). A three electrodes measurement cell equipped with an Ethylcellulose/Clays/GCE (working), an Ag/AgCl (saturated KCl) reference electrode and a Pt wire auxiliary electrode was used for all measurement. Phosphate Buffer Solution 0.1M (pH=7.4) is used as electrolyte solution.

Preparation of Ethylcellulose/Clays Nanocomposites

Makabaye Natural Clay (Ma) was purified according to a method reported elsewhere (Tributh, 1986). A 30 g sample of ethylcellulose was dissolved in 100 mL of millipore water at room temperature. 10 g of purified clay was dispersed in a 200 mL beaker containing 70 mL of hexane. The mixture was allowed to ultrasonicate at room temperature. After 1 h of sonication, the ethylcellulose/hexane solution was gradually (in 10min) added into the clay/hexane suspension under constant sonication. The sonication of the ethylcellulose/clay mixture was continued for 30 min. Finally, the mixture was stirred for 15 min at 70 rpm with a magnetic stirrer at room temperature, and the mixture was transferred in a Petri-dish to evaporate the solvent. The

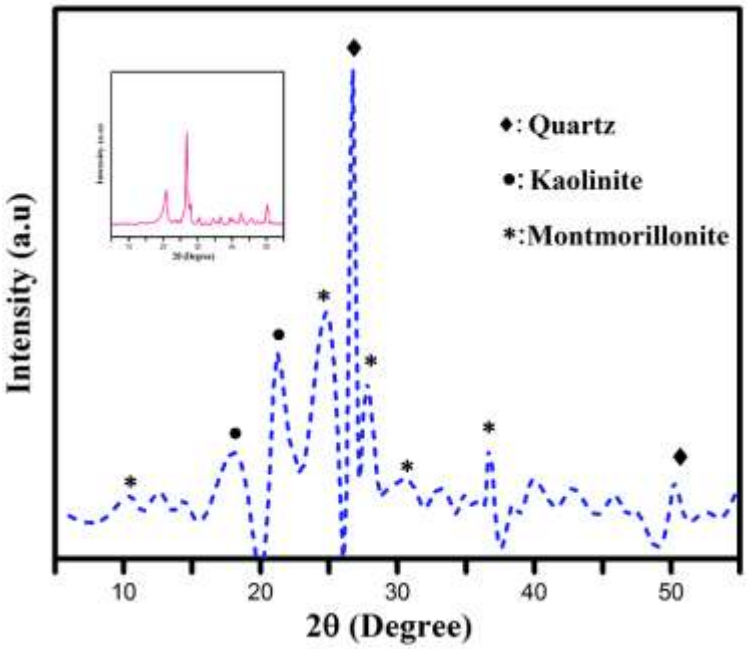

Fig. 1. XRD patterns for purified Makabaye Clays (Inserted XRD patterns for modified Makabaye Clays with Ethylcellulose).

ethylcellulose/clay composites were first air dried for 12 h and finally, kept in an air oven at 80°C for 12 h for complete removal of the solvent.

Preparation of working electrode

During the present work glassy carbon electrodes (GCE) were already polished with alumina slurries of different size (1, then 0.05 µm) on billiard cloth. They were then placed in an acetone solution and properly cleaned in a sonicator for 10 min to eliminate any remaining alumina particles. The thin Polymer/Clays film working electrode was prepared by" drop coating" 10 µL of the aqueous dispersion of Ethyl Cellulose/Ma on the active surface (3 mm in diameter) of the GCE. The clay mineral modified electrodes, denoted GCE/Ethyl Cellulose/Ma were stored at room temperature for about 3 h to ensure their complete drying before use.

RESULTS AND DISCUSSION

XRD Characterization

Figure 1 shows the XRD patterns of purified clay and the modified clay after modification with Ethylcellulose (inserted figure). Purified Clays shows the characteristic peak of the clay at 2θ of 9.02°, corresponding to the gallery height of ~97 nm. The d001 peak for the modified clay was shifted to a lower region and disappearand this is observable for all peaks, indicating the exfoliation of clay.

Thermal Analysis of Ethylcellulose/Organoclays

TGA and DTA curves obtained are showed in Figure 2. A slight loss mass in composites material occur around 245.06°C due to moisture. Ethylcellulose/Ma has hydrophobic nature and does not retain absorbed water. After this temperature, the plot of the TGA curve decreases downwards, which means that the heat flow increases, and the heat capacity of our composite increases, and this assumes that at the temperature of 346.62°C the phase of glass transition is observable, this is confirmed by a peak on the DTA curve at 367.02°C. At 644.33°C, it is beyond the glass transition, and the composite Ethylcellulose / Ma is mobile, it has gained enough energy to enter into very ordered arrangements that we call crystals.

Scanning Electronic Microscopy Analysis

The micrograph show the layers silicates is exfoliated into single layers for modified clay. The polymer is adsorbed onto the delaminated sheets (Fig. 3).

Transmission Electronic Microscopy Analysis

The macromolecular chain of the ethylcellulose of spherical shape joined together is well observable on the surface of the clay (Fig. 4).

Applications

Electrocatalytic response of dopamine at GCE/ EthylCellulose/Ma

The Figure 5 shows the cyclic voltammograms (CVs) at 50mV in the absence (a) and presence (b) $2.5x10^{-7}$M of dopamine in the pH = 7.4 solution of phosphate buffer solution (PBS). These curves shows the oxidation peaks at 206.62mV corresponding to an intensity at 9.79 µA and a reduction peak at 45mV corresponding to an intensity of -2.57µA, Oxidation of the dopamine to the modified

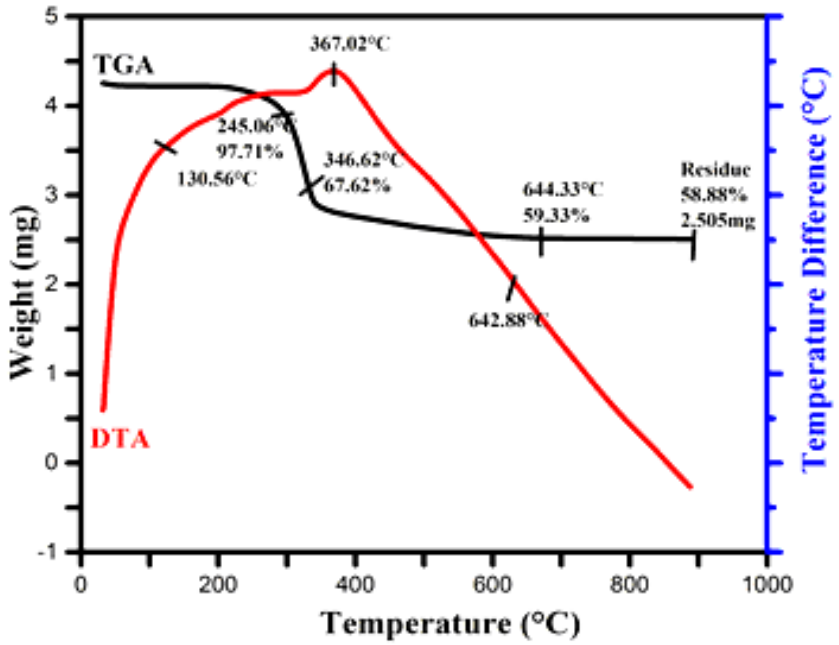

Fig. 2. TGA/DTA of modified Makabaye Clays with Ethylcellulose.

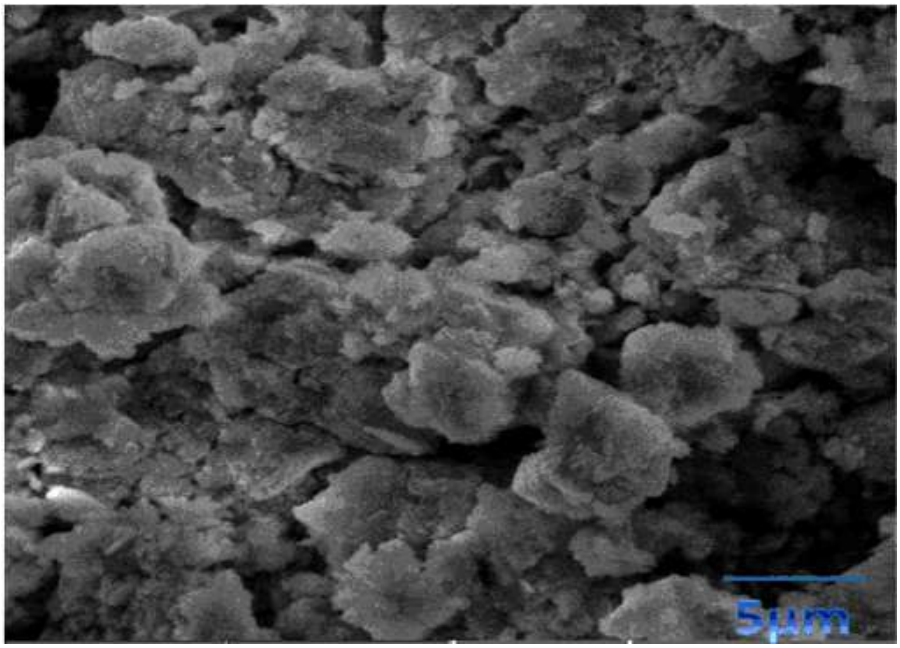

Fig. 3. Scanning Electronic Micrograph of modified Makabaye Clay with Ethylcellulose.

electrode, this shows the electrocatalytic activity of the modified glassy carbon electrode in the presence of dopamine.

In a PBS solution, the dopamine is cationic form (pKa 8.9) (Protiva Rani Roy, 2003). The oxidation of DA is therefore due to the electrostatic attraction between cationic dopamine and the high electron density of oxygen on ethylcellulose. This is justified by this very noticeable difference in oxidation and reduction potential. The value of the ratio of the intensity of oxidation current to that of reduction is equal to four what allows us to suggest the following mechanism, DA first diffuses onto the working electrode and releases electrons which are

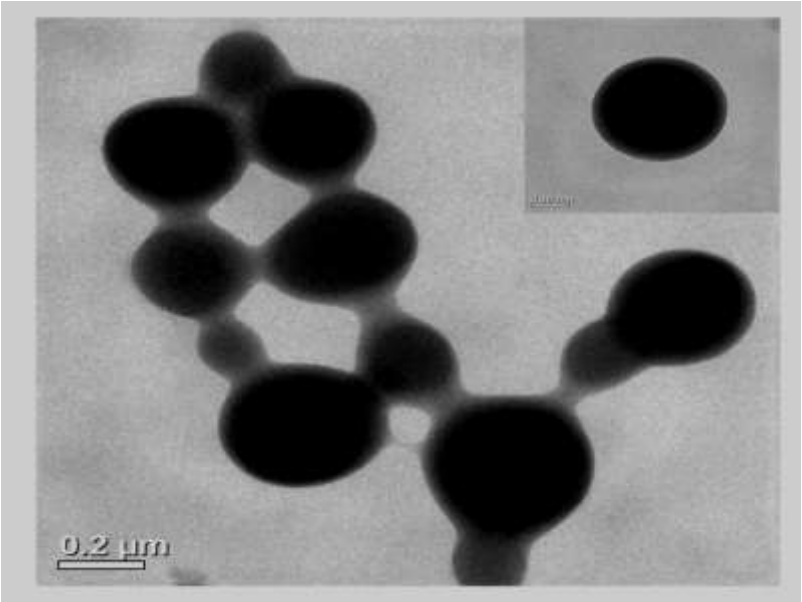

Fig. 4. Transmission Electronic Microscopy image of Ethylcellulose onto Makabaye clays.

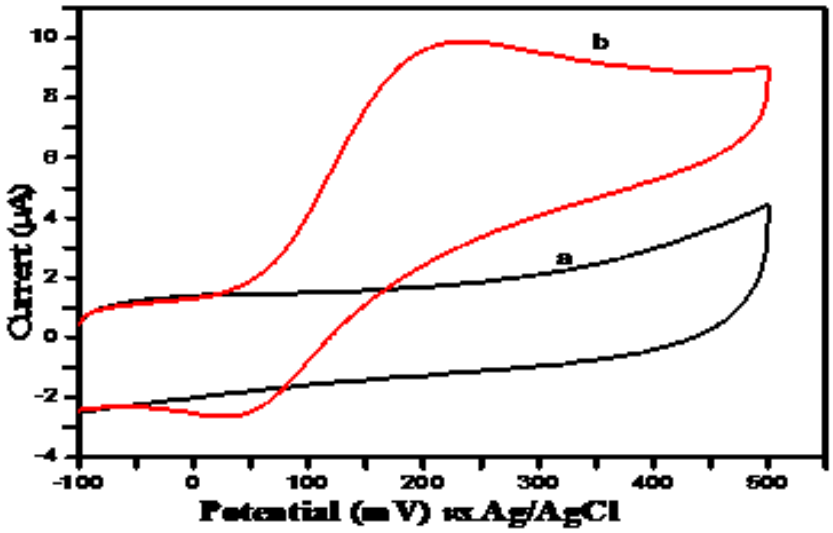

Fig. 5. Cyclic voltammograms of bare GCE in absence of Dopamine (a), GCE/Ethylcellulose/Ma in presence of $2.5x10^{-7}$M in 1M PBS (pH=7.4). Scan rate: $50mVs^{-1}$

accepted by the working electrode, while forming dopamine-O-quinone (DAQ). In the reverse scan o-quinone captures electrons from the electrode to form dopamine. However, as per the following mechanism DAQ may undergo chemical reaction to form leucodopaminechrome (LDAC) via intramolecular 1.4 dipolar addition and this could further get oxidized to dopaminechrome (DAC) through a two electron transfer reaction.

Effect of scan rate

The influence of the scan rate effect is studied; it was found that the intensities peaks of oxidation and reduction increase with scan rate (Fig. 6). In the range of 20 mV/s to 100 mV/s, the oxidation current intensities increase proportionally with the scan rate with a correlation coefficient of 0.9856 and the reduction current intensity also decreases with the scanning speed with a correlation coefficient of 0.9832. This justifies that the electron transfer phenomenon is controlled by the diffusion process (Li Zhang, 2016).

Effect of Concentration

Figure 7 shows the electrochemical response of dopamine at different concentration, the redox peak current increased with increasing the concentration of analyte.

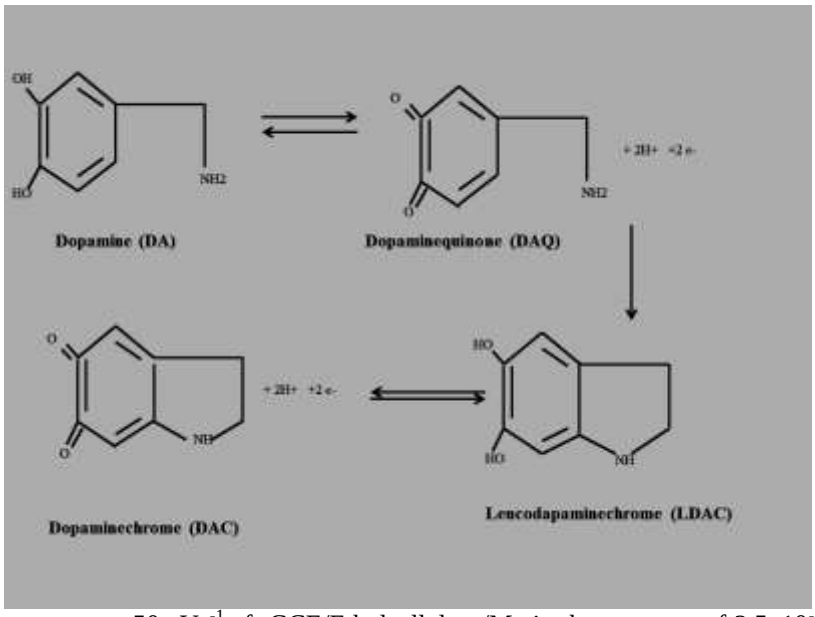

Fig. 6. Cyclic voltammograms at $50mVs^{-1}$ of GCE/Ethylcellulose/Ma in the presence of $2.5x10^{-7}$ M of Dopamine at different scan rates (a). Plot (b) is the Intensity peak of oxidation and reduction *vs.* scan rate.

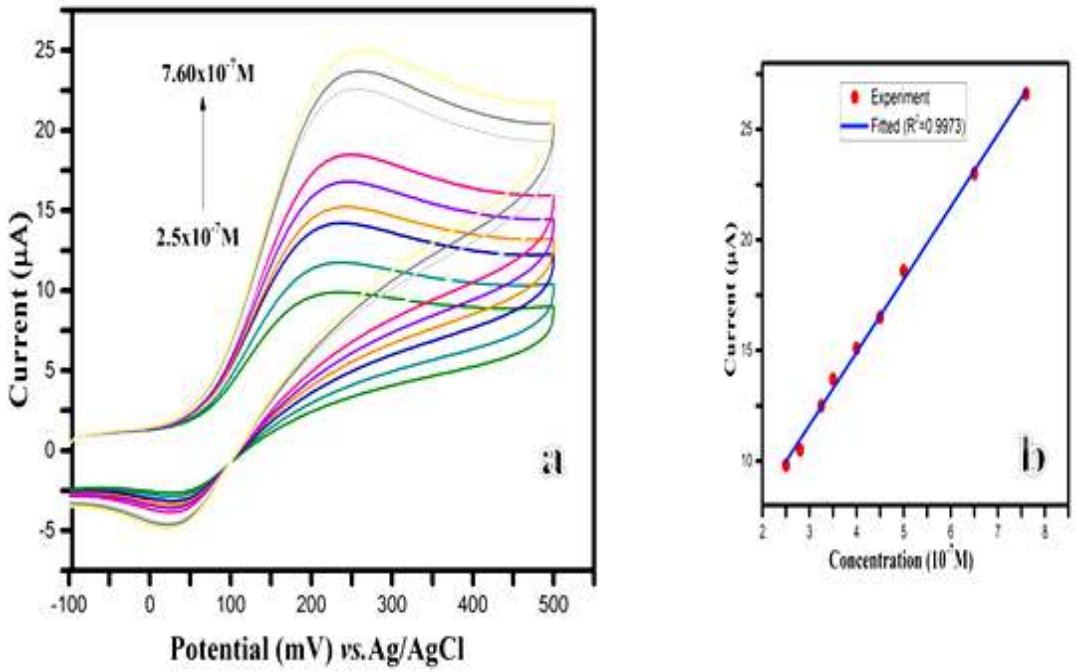

Fig. 7. Cyclic Voltammetry response at $50mVs^{-1}$ of GCE/Ethylcellulose/Ma at different added concentration of Pb^{2+} in the electrolytic medium (a), and plot (b) is oxidation peak versus Dopamine (DA) concentration.

Concentration of dopamine was increased from $2.5x10^{-7}$M a $7.60x10^{-7}$M. The plot of the oxidation peak of the concentration function gives a linear relationship between the oxidation current intensity and the concentration with the correlation coefficient 0.9973 and the limit of detection is $1.51x10^{-6}$ M (Huanshun Yin, 2011; Yang-Rae Kim, 2010).

CONCLUSION

In this study a composite was prepared from clay and ethylcellulose. The physicochemical analyzes performed on the composite led to the evaluation of the intrinsic properties of the material. The electrocatalytic activity of the composite material was investigated by modifying the

glassy carbon electrode obtained from the composite. It appeared to be capable to give a rapid response for the electrochemical detection of the Dopamine (DA) with a limit of detection of $1.15x10^{-6}$ M. This made it possible to consider the modified electrode of glassy carbon by ethylcellulose/clay a good candidate as an electrochemical sensor.

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