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ELECTROXIDATION OF PHENOL USING CARBON PASTE MODIFIED ELECTRODES: CHELATING EFFECT OF *MORINGA OLEIFERA*

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ABSTRACT

This work report a Cyclic Voltammetry (CV) and square wave (SQW) methods for the determination of chelating phenol by *Moringa oleifera* based on carbon paste electrode (CPE) modified with clay. The results showed that the CPE-clay has excellent electrocatalytic activity with *Moringa oleifera* acting as a chelating agent for phenol. The oxidation peak of phenol was observed around 1.00 V (vs.SCE). After Moringa treatment, the oxidation current density decreases and this is due to a sharp drop in phenol concentrations, suggesting that *Moringa oleifera* has a high phenol chelating capacity. This electrochemical sensor showed an excellent performance for detecting chelate phenol. The sensor has been successfully applied for the determination of phenol in a real chelation.

Keywords: *Moringa oleifera* , cyclic voltammetry, square wave, clay, phenol.

INTRODUCTION

Phenols are classified as the most toxic industrial pollutants even at low concentrations problems (Raghu and Hsieh, 1987). Effluents from chemical industries such as refineries, pesticides producing industries, agro-food industries contain mostly phenolic compounds (Saravanan *et al*., 2009). Several techniques have been used for the detection or degradation of phenols (Trasatti, 1992; Liu *et al*., 2008) . Among these techniques, there is the method by the degradation of microbubbles (Li *et al*., 2009), anodic polymerization (Thar et Saval, 2009; Hur *et al*., 2007; Mengoli and Musiani, 1986), oxidation by photocatalysis or by hydrogen peroxide (Tryba *et al*., 2006; Alnaizy and Akgerman, 2000; Kawaguchi, 1992; Czaplicka, 2006), as well as electrooxidation with various electrode materials (Alves *et al*., 2004; Scialdone *et al*., 2009; Ureta-Zanartu *et al*., 2003; Yavuz and Koparal, 2006).

Several authors have tried in the electrochemical oxidation of organic compounds as a method of treatment of organic effluents and in this thematic, others used the electrooxidation of phenols as a method of treatment (Comminellis and Pulgarim, 1991; Arslan *et al*., 2005; Kennedy *et al*., 2007; Pacheco *et al*., 2007; Li *et al*., 2005) Optimization of parameters such as concentration and pH was studied by Comminellis and Pulgarim (1991) by the method of anodic oxidation of phenol on the platinum electrode. They did not observe a blocking effect on the electrode surface . Arslan *et al*. (2005) studied the electrooxidation of phenol on the platinum electrode and parameters such as temperature and concentration were taken into account. The authors reported the blocking of the electrode surface for high concentrations of phenol in alkaline medium and a phenol polymerization on the electrode surface explained this process. Kennedy *et al*. (2007) investigated the oxidation and polymerization of amino-phenolic compounds in neutral solutions and they proposed a mechanism of substitution reaction, followed by oxidation and polymerization. Pacheco *et al*. (2007) was interested in the degradation of phenol, catechol and cresol on boron-doped diamond electrodes and concluded that the degradation process increases with increasing current densities. The effect of the solute concentration was also investigated; the results have shown that under conditions of diffusive control the degradation is independent of the concentration. Research on the electro-oxidation of

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phenol cannot fade because this technique makes it possible to obtain good destruction rates compared to other methods used. This technique allows the production of the phenoxy radical that can be reacted with other species present in the reaction medium. This radical can be oxidized in two different ways: the formation of polymers or quinones, depending on the conditions used. For high concentrations of phenol and the base medium, polymerization is favored, whereas for low concentrations of phenol and the acidic medium, the formation of quinones is favored (Mengoli *et al*., 1980; Busca *et al*., 2008; Jahn, 1981; Keer and Silva, 1999). From the oxidation reaction of quinone, carboxylic acids (maleic and oxalic) are obtained. These products are difficult to oxidize, but are biodegradable compounds, and therefore the electrooxidation process can be associated to a biological process.

Moringa oleifera is the best known species of the Moringaceae family. *Moringa oleifera* belongs to the Moringaceae family. It is a shrub that grows rapidly, reaching 12 meters in height. These leaves are edible and are widely used in the traditional pharmacopoeia in view of its therapeutic properties (Chen, 2004).

This work studies the electro-oxidation of phenol and evaluates the chelating capacity of *Moringa oleifera* on clay-modified carbon paste electrodes using cyclic voltammetry and square wave techniques.

MATERIALS AND METHODS

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 and a saturated calomel electrode (SCE) serving as reference electrode, and platinum as an auxiliary electrode.

Electrodes Preparation

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 0.1256cm^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 phenol. Standard solution of phenol was added into the electrochemical cell containing 100 mL of supporting electrolyte.

The 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 -1.5 V to 1.5V.

Optimum conditions were established by measuring the peak currents in dependence on all parameters. All experiments were carried out under ambient temperature.
The *Moringa oleifera* was prepared according to the procedure reported by El Mhammed *et al*., 2009). *Moringa oleifera* seeds were collected, pilled and sun-dried to maintain constant weight. The sun-dried seeds were grinded into powdered form using machine. The powder was added to the solutions containing phenol. After 15 minutes of contact with *Moringa Oleifera*, the solutions were purified and analyzed.

RESULTS AND DISCUSSION

Surface characteristics

The morphology of the electrode surface of Clay was observed by scanning electron microscopy (Fig. 1). This image shows compact particles with variable dimensions of the order of 1 and 15 μm. Treated Clay has the following chemical composition given by Energy dispersive spectroscopy (EDS): O (22%), Mg (5.4%), Al (22.4%), K (2.7%), Ca (1%), Ti (1.8%) Fe (17.1%), Si (27.8%) and more metals order ppm (Fig. 2). An examination of clay modified carbon paste electrode indicates some kind of agglomeration.

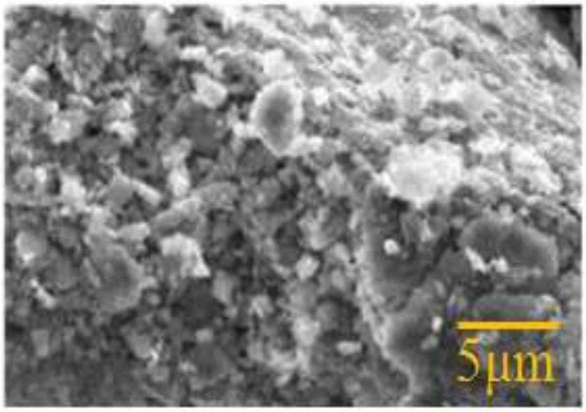


Fig. 1. Scanning electron micrograph of Clay paste electrode.

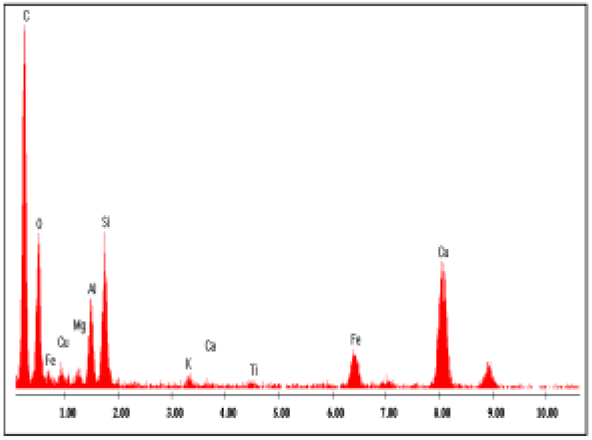


Fig. 2. Energy Dispersive Analysis of Treated clay.

Phenol oxidation

Phenol was studied at Clay/CPE by cyclic voltammetry study (CVS) and by Square Wave Voltammetry (SWV). The cyclic voltammogram of Figure 3 illustrates the electroxidation of the phenol shows a well defined anodic peak at 1V.

This sensitivity can be explained by the electrostatic interaction between positive charged phenol and clay / CPE. This figure shows that the phenol lost an electron. The presence of a anodic oxidation peak demonstrates that the electrochemical process is irreversible (See scheme 1). This result is confirmed by Figure 4 which shows, after a preconcentration time of 3 minutes, an anode current peak illustrating the electrooxidation of phenol.

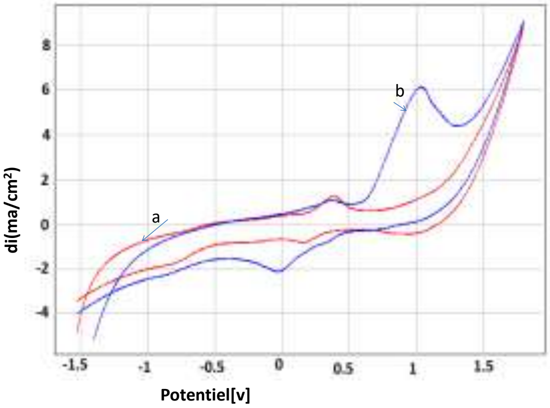


Fig. 3. CVs records of (a) 1 mM phenol at pH=5 at bare Clay-CPE and (b) ClayCPE/phenol, scan rate 100 mV/s, pre concentration time (tp)= 3min.

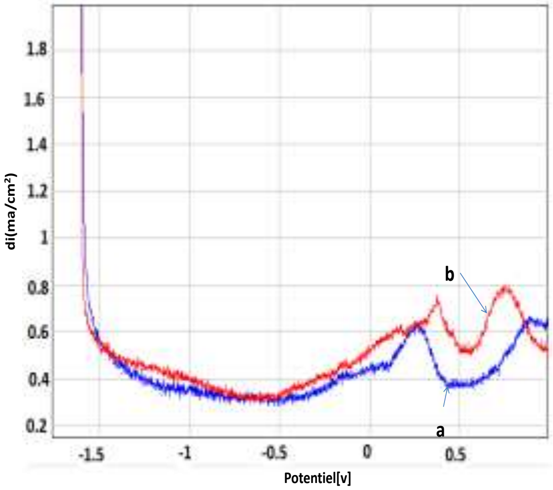
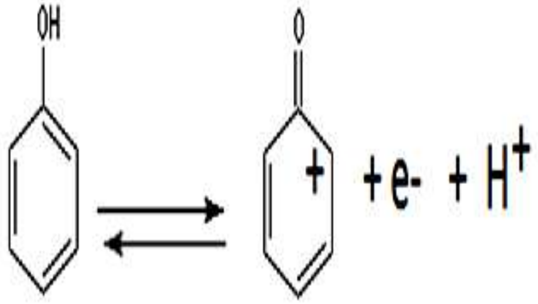


Fig. 4. SQW records of (a) 1 mM phenol at pH=5 at bare Clay-CPE and (b) Clay-CPE/phenol (b), preconcentration time (tp)= 3min.



Scheme 1. Mechanism of electrochemical oxidation-reduction reaction of phenol at Clay/CPE.

Chelating effect of *Moringa oleifera*

SQW and CV were recorded on a clay film-modified carbon paste electrode in a carrier solution containing phenol (curve a) and after addition of moringa oleifera (curve b) which are respectively shown in Figures 5 and 6. The peak of the current decreased considerably after the moringa treatment. This current density reduction is due to a sharp drop in phenol concentrations, suggesting that moringa has a high complexing capacity for phenol (Fig. 5 and 6). It was observed that the pH of the solution changed from 7.2 to 6.5 after moringa treatment, which can be explained by the fact that moringa exchanged two protons against the metal ion.

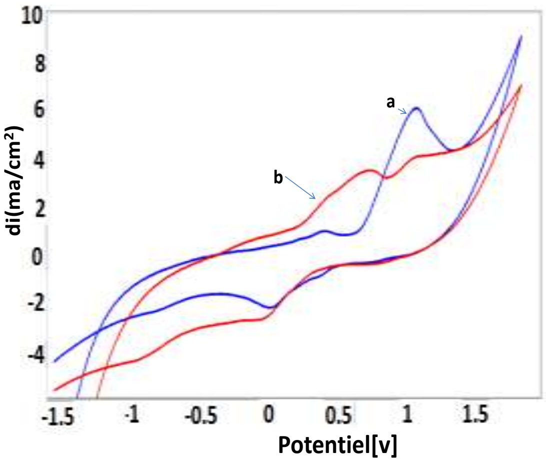


Fig. 5. Cyclic voltammograms for clay-CPE (a) in supporting solution after exposing electrode to 11Mm/l phenol contaminated solution before (b) after *moringa* treatment.

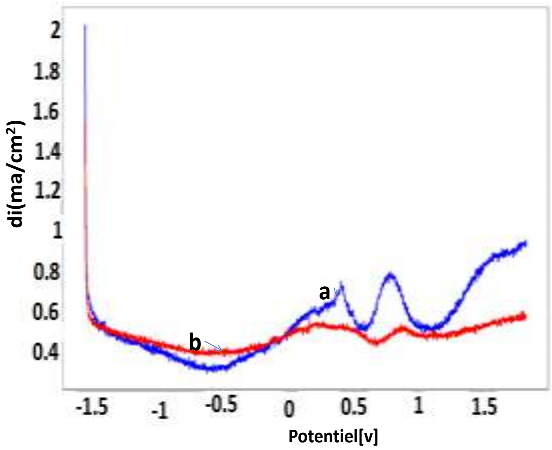


Fig. 6. Square wave voltammograms for clay-CPE in supporting solution (a) after exposing electrode to 1mM/L phenol contaminated solution before *moringa* treatment and (b) after *moringa* treatment.

Optimization Study

Parameters such as peak current versus *Moringa oleifera* concentration were evaluated under optimal conditions.

Calibration graph

Figure 7 and 8 show that the oxidation current density of the phenol decreases after the addition of *Moringa oleifera*, which shows that the *Moringa oleifera* has a chelating effect on the phenol.

Influence of *Moringa oleifera*

Concentration

The result shows that the oxidation peak current of 1 mmol.L^{-1} phenol was greatly reduced with the addition of *Moringa oleifera* concentration (0 mL to13 mL) and this suggest that *Moringa oleifera* has chelation action onto phenol. It was established that the current peaks of phenol decreases linearly relative to *Moringa oleifera* addition in solution (Fig. 9) and the zero waiting *moringa* were 60% for 1mM / l phenol (Fig. 10).

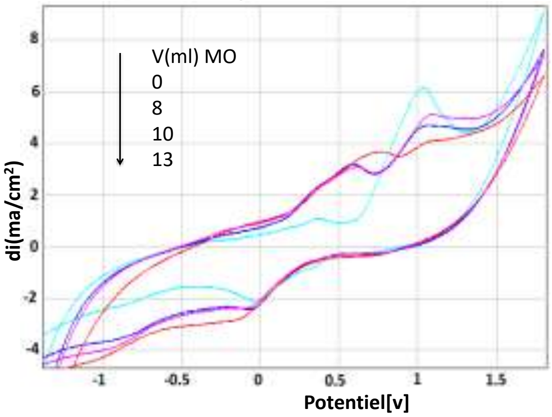


Fig.7. Cyclic Voltammograms of different concentration of MO (0 to 13 mL) on 1 mM/L phenol at Clay-CPE in 100mL tap water, Scan rate 100 mV/s.

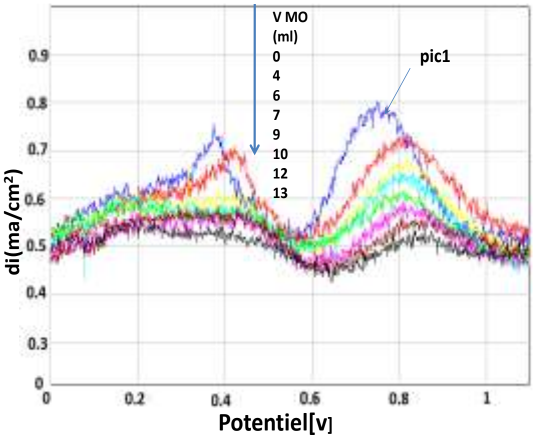


Fig. 8. Square wave voltammograms obtained of different concentration of MO (0mL to13mL) on 1 mM/L phenol at Clay-CPE in 100ml tap water, Scan rate 100 mV/s.

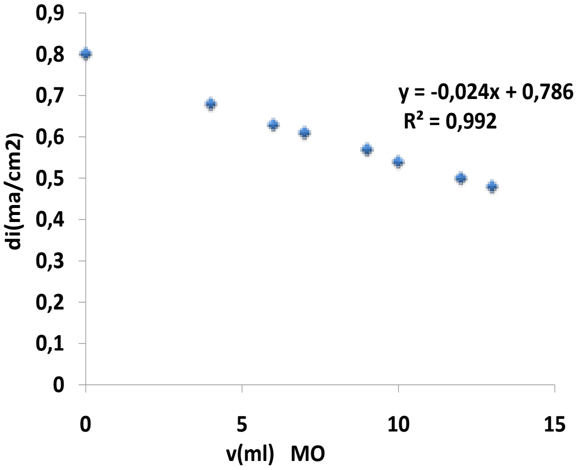


Fig. 9. *Moringa oleifera* concentration effect (peak 1) of oxidation of phenol as a function of density of run. (pic1).

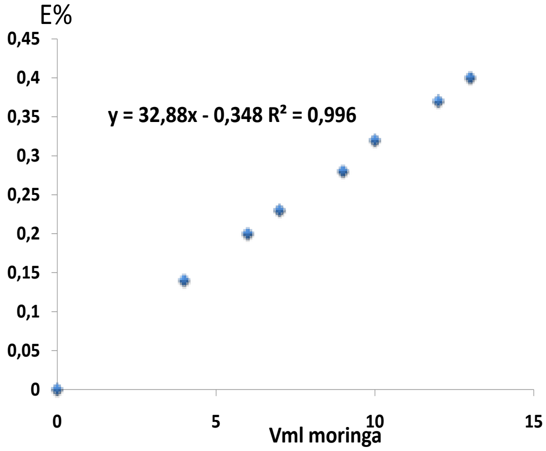


Fig. 10. *Moringa oleifera* efficiency of 1 mM / L phenol (pic1) versus volume.

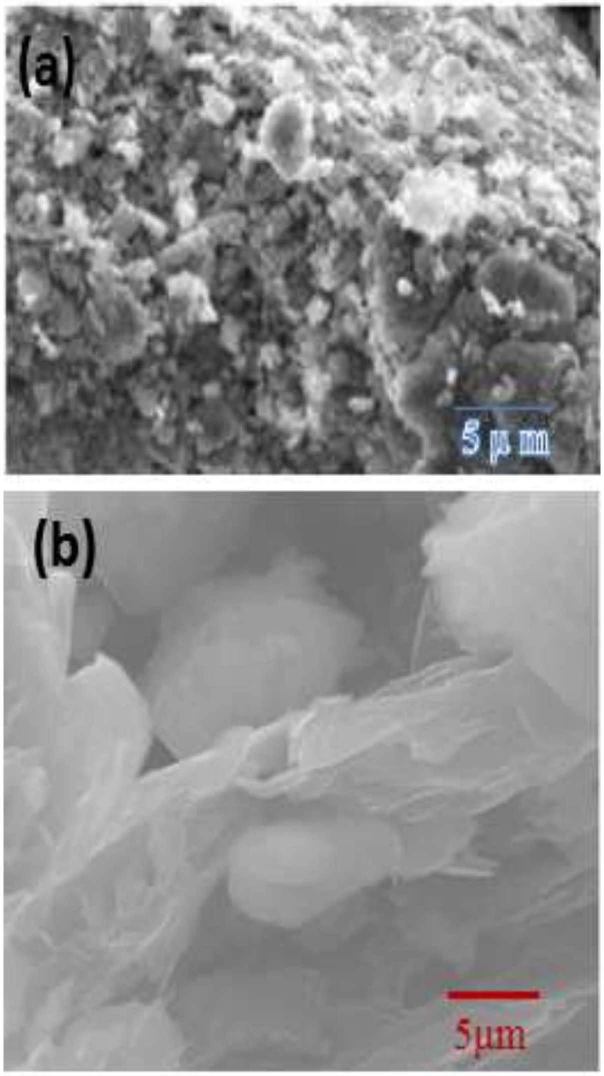


Fig. 11. SEM images of (a) natural phosphate MEB without *moringa* and (b) *Moringa* + p-chloroaniline.

SEM images clearly show the surface texture and morphololgy of the adsorbent (Fig. 11). The morphology of the surface of the first clay (a) is different from that of (MO + clay +Phenol) (see Fig. b) has a rough surface and pores are not seen, but after coagulation and activation (MO + clay +phenol), the surface becomes more porous with homogeneous in respect to clay, and thus has a greater surface area. The micrographs (MO + clay +Phenol) revealed clearly the presence of different diameters structures which could result in chelating phenol.

CONCLUSION

This work made it possible to highlight the chelating power of *moringa oleifera*. The electrochemical sensor set up in this work has a high sensitivity to phenol which is known to be very toxic to the environment. This composite material, designed at low cost and easy to implement, is therefore timely to contribute to the valorization of local materials for environmental detection and decontamination.

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