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Electrochemical Analysis of Hydroquinone using glassy carbon electrode coated with a clay film amended by L-cysteine

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Abstract

In this study, an amino acid namely L-cystein was used to modify a smectite type clay. The modified smectite was characterized by X-rays diffraction and thermal analysis. The results obtained showed that L-cysteine was successfully absorbed on the smectite external layers. Due to its organophilic character, the modified-clay was evaluated as electrode modifier for the accumulation of hydroquinone. The modified electrode was obtained by drop coating of previously modified clay on glassy carbon electrode. The cyclic voltammetry curves of hydroquinone exhibited one well-defined anodic peak around 0.4 V and one reduction peak around 0.2V. The peak current obtained on glassy carbon electrode coated by thin film of modified clay was two times higher than that obtained on bare glassy carbon electrode and three times higher than that exhibited by the same substrate covered by a film of the pristine clay. Many parameters that can affect the differential pulse voltammetric (DPV) response of hydroquinone (pH of the detection medium, pre-concentration medium, accumulating time, electrolysis potential) were systematically investigated to optimize the sensitivity of organoclay-modified electrode. After optimization, a linear curve was obtained in the concentration range of 2.10^{-6} mol $L^{-1}$to 10^{-5} mol L^{-1}leading to a detection limit of 8.10^{-7} mol L^{-1}.

Keywords:

Clay, L-cysteine, Hydroquinone, Cyclic voltammetry, Differential pulse voltammetry

1. Introduction

Hydroquinone is used for various purposes: first and foremost, this substance has long been the main depigmentation agent used against body spots and skin bleaching [1-3]. The reasons for its use vary from one continent to another depending on the skin color. The Caucasian population for example with clear skin and hair are more easily subject to skin spots. On the contrary, Asian women and above all, black women are more concerned with pigmentation phenomena and as such use hydroquinone as a skin bleaching agent. Unfortunately, imitation has brought into the market of cosmetic products, products in which hydroquinone is not of good quality and is at times overdosed [3, 4]. It should be noted that when highly concentrated, that is between 4 and 8.7%, frequent and prolonged usage of cosmetic products containing hydroquinone cause irritating dermatitis and burning or biting sensations [5-6]. Detailed literature exists examining the potential genotoxic effects of

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hydroquinone in a variety of *in vitro* and *in vivo* systems [7-10]. Decaprio[11] , Westerhof and Kooyers [12] have reported its nephrotoxicity, carcinogenesis, myelotoxicity, immunotoxicity, reproductive and developmental effects on animals and *in Vitro*. In Canada, this substance is forbidden in cosmetic products applied on the skin or mucous membrane especially in skin bleaching products [13]. To prevent its cancerous effects**,** the European Union that used to tolerate a maximum concentration of 2% forbade it in 2002 and rather proposed substitute products [14, 15].

Also worthy of note is the fact that hydroquinone and its derivatives are the most commonly used agents of picture development and revealing. They are amongst toxic wastes in dispersed quantities. Occasional reports of leukoderma and/or contact dermatoses are also encountered primarily associated with use of photographic developers [16-18]. It is therefore clear that hydroquinone used excessively in cosmetics or in effluents can be harmful to human and his environment. Its quantitative and qualitative detection should be a point of concern; the need for low costing techniques for its detection cannot be overemphasized. Recently, numeral works have been devoted to the development of new chemically modified electrodes for monitoring hydroquinone [19-25]. Materials with absorbent properties are often used among others such as activated carbon, resins, zeolites, silica, and clay. Natural clays are available, cheap and have interesting properties. For this reason sensors based on modified clays have attracted the attention of many researchers [26]. Most works have thus been focused on solid electrodes modified by natural clays or clays intercalated by substances [27-31]. Recently, Yong et al [32] have developed an amperometric sensor based on intercalated montmorillonite modified carbon paste electrode for hydroquinone determination. This work aims at developing a sensor of hydroquinone using glassy carbon electrode coated with a smectite clay film amended by L-cysteine.

2. Experimental

2.1. Apparatus

Voltametric curves were performed with an autolab potentiostat with potentiometer with a GPES software (General purpose electrochemical system), piloted by a computer. The GPES software realises the programation, the acquisition and the treatment of the results. For this work, measurements were carried out in an electrochemical cell using a conventional 3 electrodes assembly: working electrode (glassy carbon electrode), reference electrode (silver chloride saturated, Ag/AgCl/KCl) and an auxiliary electrode (stainless steel wire). The supporting electrolyte chosen is an acetate buffer solution (CH_3COOH/ CH_3COONa, pH 4.5; 0.1 mol L^{-1}) similar to a study carried out by Liang Wang *et al.* [24] and Shengfu *et al* [33].

2.2. Reagents.

L-cysteine purchased from Fisher Scientific was used without purification. The solution of NaCl is obtained through the dilution of that salt in distilled water; and the acetate buffer solution obtained by mixing equal concentrations of acetic acid and sodium acetate. Other reagents were used without purification.

2.3. Clay based material

The white clay used is a smectite from the Baba 1 locality in the North West Region of Cameroon. It is mostly made up of montmorillonite. It has a cation exchange capacity (CEC) of 88.9 meq/100 g and surface area of 154.67 m^2 g^{-1} [34]. It will be hereafter denoted as Ba1.

2.4. Homoionic saturation

Homoionic saturation consists of replacing each cation of clay by sodium ions. The Ba1 clay is converted to this form through mechanical dispersion for 8 hours: 5 g of clay is added to 200 mL of NaCl (1 mol L^{-1}) and after stirring, the suspension is centrifuged. The residue is re-introduced into 200 mL of NaCl (1 mol L^{-1}) and after 14 hours of stirring, the suspension is once more centrifuged. This operation is followed by several washings with distilled water until the nitrate agent is tested negative, with the aim of eliminating excess sodium chloride. Finally, sodium clay was obtained and named Ba1-Na.

2.5. Modification of clay by L-cysteine

Clays are generally negatively charged. Some as smectites have cations between their sheets; thus, cations and positively charged molecules are attracted and can bind to both the surface of the clay, and between its sheets by replacing the internal cations. For these reasons, the preparation of the cysteine is done in acidic medium (pH = 2) in order to increase its reactivity with clay. This high acidification is not without risk knowing that hydroquinone binds to cysteine through the hydrogen bond established between the nitrogen lone pair of the latter and the hydrogen atom of the hydroxyl group of the hydroquinone (N---H-O). Thus, in highly acidic medium, the NH_2 groups of cysteine exist in the forms NH_3^+. In these forms hydroquinone and cysteine repel one another. Our preliminary test showed a very low affinity between the clay and L-cysteine in weakly acidic medium.

The preparation of the clay-modified by L-cysteine is done from the suspension of Ba1-Na: the sodic clay is thus introduced in a tube containing 2.5 mL of distilled water and stirred for 48 hours to obtain suspension ready for usage. In another hand a quantity of of L-cysteine (0.077 g) is dissolved in a tube containing 2.5 mL of hydrochloric acid (pH 2); 0.5 g of Ba1-Na clay is then added and the mixture is stirred for 48 hours. The quantity of L-Cysteine in solution is in accordance with the cationic exchange capacity which is 88.90 meq/100g for the Ba1 clay sample [34]. The following identifications enable a distinction of natural clay from modified clay: Ba1 for natural clay, Ba1-Na for its sodic form and Ba1-Na/L-cys for modified clay.

2.6 Characterization techniques of the clay before and after modification

Differential Thermal Analysis (DTA), Thermo Gravimetric Analysis (TGA) and Differential Thermal Gravimetry (DTG)) and X-Ray diffraction (XRD) were used to characterize the clay materials. Cyclic voltammetry (CV) and Differential Pulse Voltammetry (DPV) were used as electrochemical techniques.

3. Results and discussion

3.1 Physicochemical characterization of raw and modified clay

3.1.1 XRD analysis of raw clay and sodium saturated clay

Fig. 1 presents the powdered X-ray diffractograms of the natural clay Ba1 and for its sodic form (Ba1-Na).

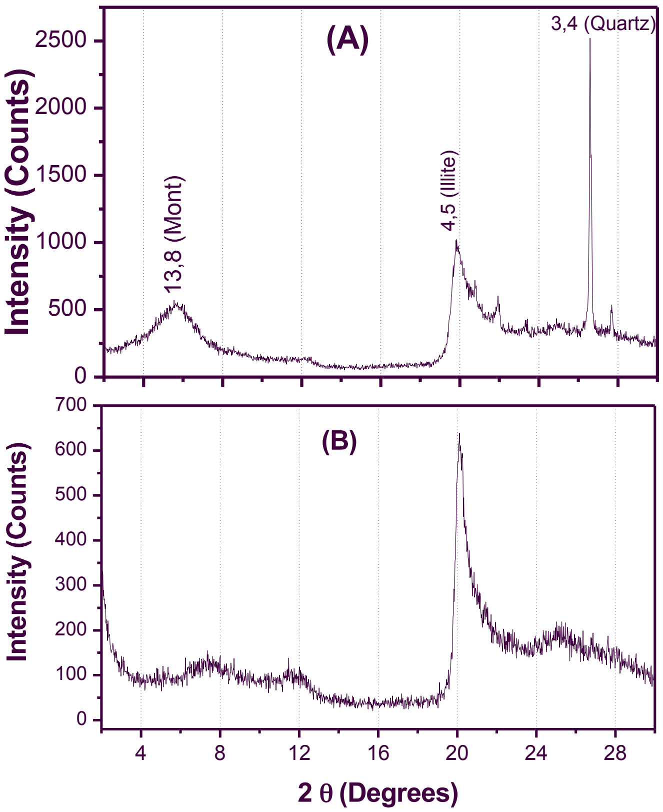

Fig. 1: XRD plot of (A) natural clay (Ba1); (B) homoionic clay (Ba1-Na)

By comparing the two diffractograms there is a slight difference for the d_{001} line characteristic of montmorillonite: 13.8 Å for Ba1 (2θ = 6.42 °) and 12.17 Å for Ba1-Na (2θ = 7.25 °); this is in agreement with literature data showing that the studied clay is a smectite [34]. This difference in interlamellar space between the sample of raw clay and sodium clay is explained by the fact that the interlamellar space of the natural clay is occupied by hydrated cations of various sizes. When the homoionic saturation is done, these cations are replaced by hydrated sodium ions which have smaller radii. The peak corresponding to 2θ = 21° is characteristic of illite. Moreover, on the diffractogram of the raw clay, we noticed the presence of the characteristic line of quartz (d = 3.4 Å) with great intensity, which explains that the raw material contains much impurity of this mineral. On the contrary, on the curve of the sodium clay (Ba1-Na), the reflection characteristic of quartz is absent since it was removed during the sedimentation process [34].

3.1.2. Comparative X-ray diffractogram of Ba1-Na and Ba1-Na/L-Cys

Powdered XRD analysis was not only performed on the natural Ba1-Na sample but also on Ba1-Na amended by L-cysteine and the results are given in Fig. 2. On examining this figure, we see that the XRD curves are similar; d_{001} line of the smectite is present in all samples and its intensity remains constant despite the increase in the concentration of L-cysteine. Whatever, the position of the peaks remains unchanged. Therefore, this clay does not retain the molecules of L-cysteine between its layers. The literature abounds in this direction and shows that the intercalation of L-cysteine between the layers of a homoionique smectite depends on the type of cation with which it has processed [36, 37].

When the homoionique treatment is carried out on the basis of alkali metal ions (Na^+) or alkaline earth metal ions (Ca^{2+}), there is no intercalation of L-cysteine between the layers of the smectite. Instead, there is a modification of the smectite clay by L-cysteine which is fixed to the outer layers of the smectite of negative charges. On the contrary when it is made from a transition metal cation (Cu^{2+}), the intercalation is effective [37].

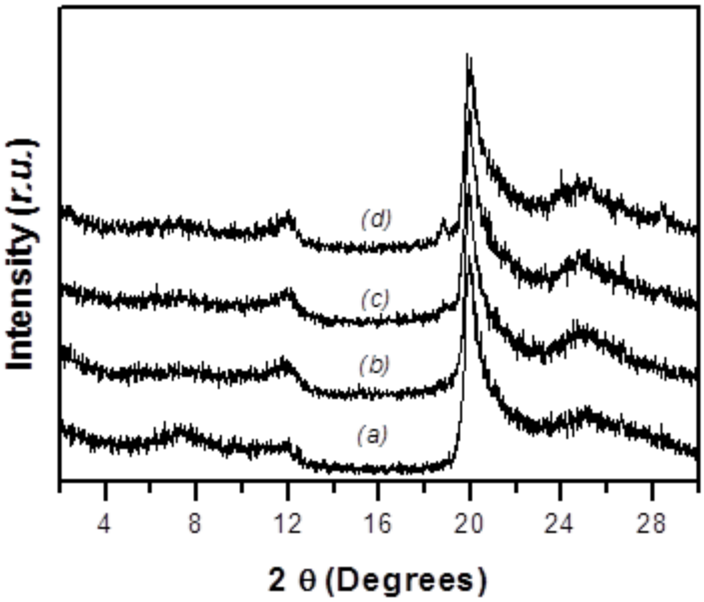

Fig. 2: Powder diffractograms of natural clay (a) (Ba1-Na) and clay modified by L-cysteine (Na-Ba1/L-cys) in equivalent concentration of L-cysteine: 0.5 CEC (b), 1.0 CEC (c) and 1.5 CEC (d).

3.2. Thermal Analysis

Thermal analysis of a material can provide information on its composition. Figure 3A contains the curves of Differential Thermal Analysis (DTA), Thermo Gravimetric Analysis (TGA) and Differential Thermal Gravimetry (DTG) of clay Ba1-Na. It appears from the examination of this figure that by heating, this material is subjected to two mass losses, both related to endothermic reactions: the first mass loss of about 11% which occurs around 65°C corresponds to the departure of physisorbed water from the clay. The second mass loss of about 5% that occurs around 470°C is characteristic of phyllitic clay minerals and is due to dehydroxylation of the clay layers, ie their collapse as a result of heating. In order to verify the effective modification of sodium clay by L-cysteine, characterization by thermal analysis of Ba1-Na/L-Cys was performed and the results are presented in Figure 3B. In this figure, we observed that once the modified smectite was done, there are three characteristic temperatures corresponding to three mass losses. The first at 67°C is that due to adsorbed water, which is released by heating with a loss of mass of 4%. The second, about 225°C, which was absent on the natural curves of Ba1-Na, is related to the destruction of L-cysteine whose melting point is exactly 225°C, proving that there is a connection between the L-cysteine and the outer layers of the smectite. The presence of organic modifiers have the effect of lowering the dehydroxylation temperature of the layers to 460°C which was 470°C on unmodified clay with a mass loss of 10% now.

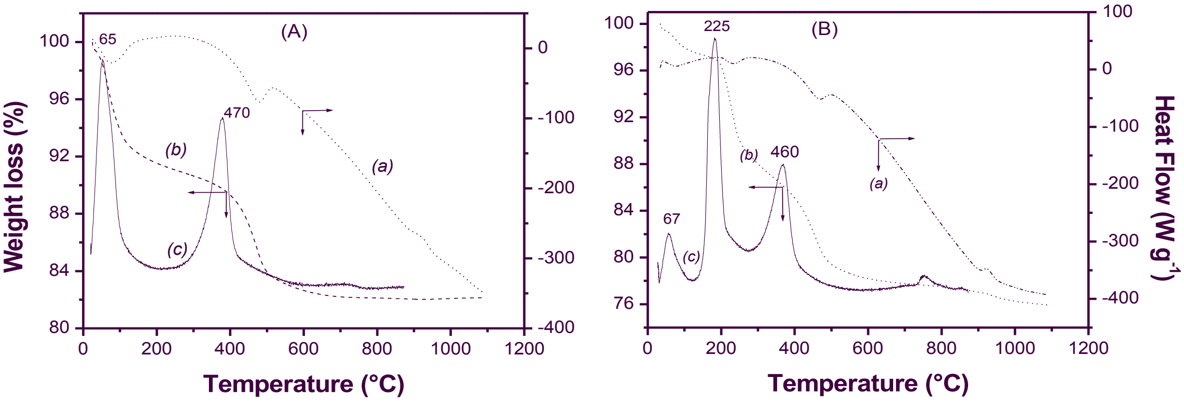

Fig. 3: (a) Derivative weight (solid line), (b) thermogravimetric (dashed line) and (c) differential thermal (dotted line) curves performed under N_2 atmosphere of (A): Ba1-Na and (B): Ba1-Na/L-cys materials.

3.3 Application to the electroanalysis of hydroquinone

3.3.1 Effect of modification of the glassy carbon electrode on the current response

The cyclic voltammograms of 10^{-4} mol L^{-1} hydroquinone solution in 0.1 mol L^{-1} acetate buffer solution pH 4.5 on bare glassy carbon electrode on one hand and the modified electrode on the other hand are shown in figure 4(b) and (c) above. From this figure, the process of accumulation of hydroquinone on the glassy carbon electrode takes place in a potential range from -0.2 V to 0.8 V. This potential range is in agreement with previous work carried out by Shengfu and Dan [33]. It was also noted that with the bare glassy carbon electrode, the process is almost irreversible because the oxidation potential of hydroquinone is 0.44 V and the reduction potential is 0.10 V, the difference, ΔEp between the anodic peak potential and cathodic peak potential (Epa-Epc) being 0.34 V. However with the glassy carbon electrode coated with a film of smectite clay modified by L-cysteine, the reversibility of the process of accumulation of hydroquinone is significant because the anodic peak potential is 0.35 V and cathodic peak potential is 0.17 V and ΔEp = 0.18 V. The peak current obtained with the modified electrode is twice greater than that obtained with the unmodified carbon electrode. Therefore, Cysteine attracts more molecules of hydroquinone at the electrode. To confirm this, we performed the electrochemical analysis of hydroquinone with a glassy carbon electrode modified by natural clay in order to see if the clay favors the adsorption of hydroquinone. The figure 4(a) shows the voltammograms registered. It appears that the signal obtained on a glassy carbon electrode modified by Ba1-Na is smaller than that obtained on bare glassy carbon electrode (b) even less than that obtained on glassy carbon electrode modified by Ba1-Na/L-Cys. (c).

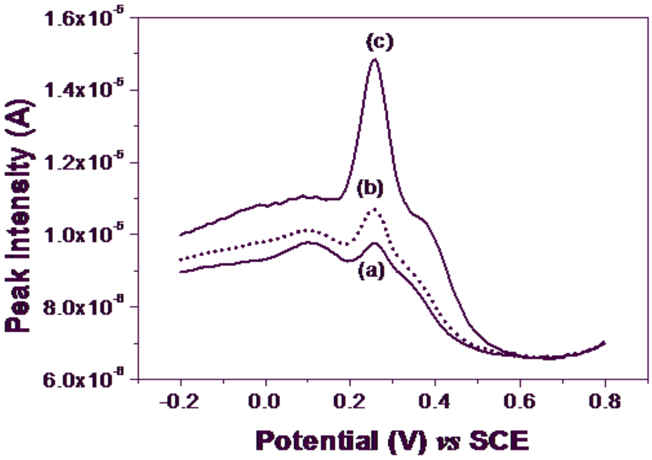

Fig. 4: Cyclic voltammograms obtained for 10^{-4} mol L^{-1} hydroquinone in acetate buffer solution (pH 4.5 (a) on the glassy carbon electrode modified by Ba1-Na, (b) on the bare glassy carbon and (c) on the glassy carbon electrode modified by Ba1-Na/L-Cyst.

Differential pulse voltammetry gives the same results and the peak current obtained with the modified electrode Ba1-Na/L-Cys is 3.5 times greater than that obtained with the unmodified carbon electrode (figure 5). This allows us to conclude that the natural clay does not adsorb hydroquinone, but hampers its detection. Contrary, with the glassy carbon electrode modified by Ba1-Na/L-Cys the signal is important, confirming that L-cysteine is a promoter in the adsorption of hydroquinone.

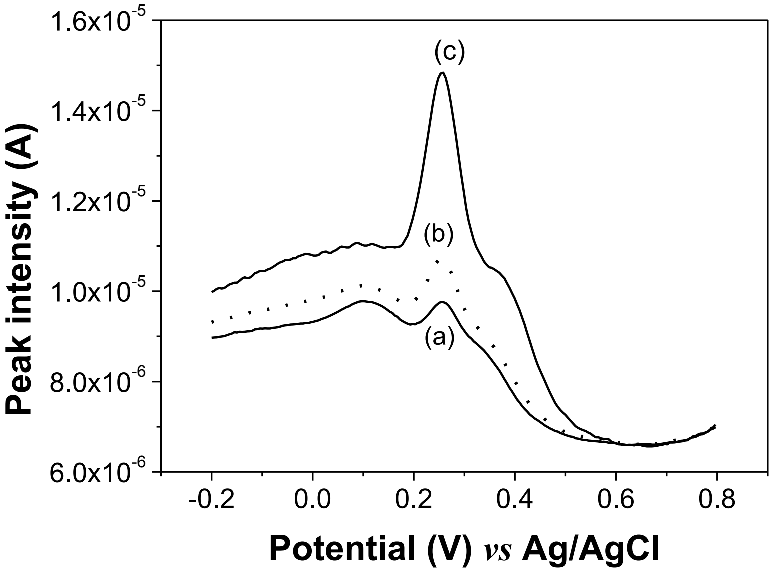

Fig. 5: Differential pulse voltammetry curves recorded using (a) the glassy carbon electrode modified by Ba1-Na (b) the bare glassy carbon electrode and (c) the glassy carbon electrode modified by Ba1-Na/L-cyst.

3.3.2. Optimization of the electrochemical response of the glassy carbon electrode modified by Ba1-Na/L-Cyst.

By varying the pH of the detection, we found that the current increases from pH 3 until reaching a maximum at pH 4.5 and then decreases and tends to disappear from pH 6 (figure 6). Thus the pH indicated for a good current response was pH = 4.5. Similarly we varied the accumulation time of hydroquinone. As might be expected, the peak intensity increases with the preconcentration time (figure 7). It is found that even without preconcentration, there is already a current response which increases from 0 minute to 9 minutes and becomes constant thereafter, meaning that the electrode is saturated 9 minutes later. When studying the effect of variation of the deposition potential, it appears that the current increases from -1.0 V to reach a maximum at -0.5 V (figure 8); after this maximum, the signal begins to decrease and tends to disappear around 0.0 V.

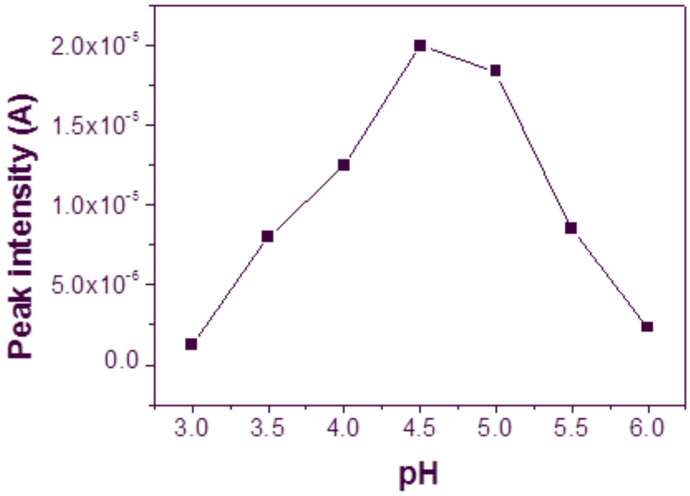

Fig. 6: Peak current as a function of pH pH obtained for 10^{-4} mol L^{-1} hydroquinone in acetate buffer solution on the glassy carbon electrode modified by Ba1-Na/L-cyst

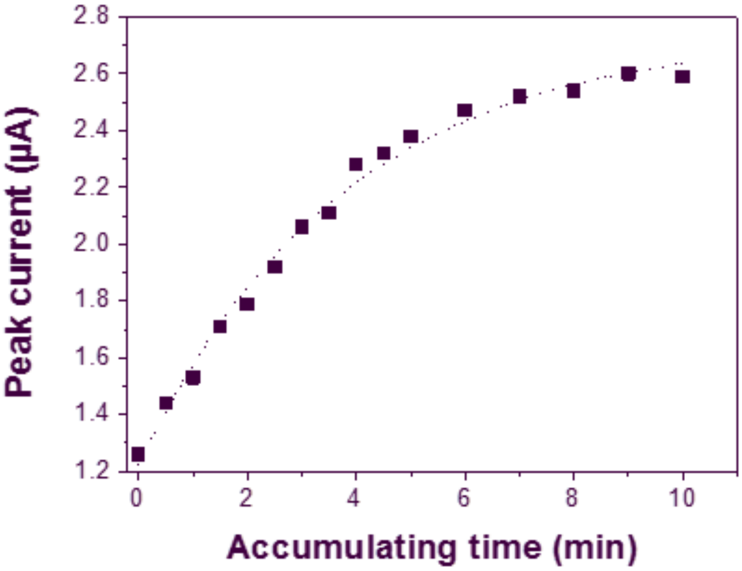

Fig. 7: Influence of the accumulating time on the peak current for 10^{-4} M hydroquinone in acetate buffer solution (pH 4.5) on the glassy carbon electrode modified by Ba1-Na/L-cyst

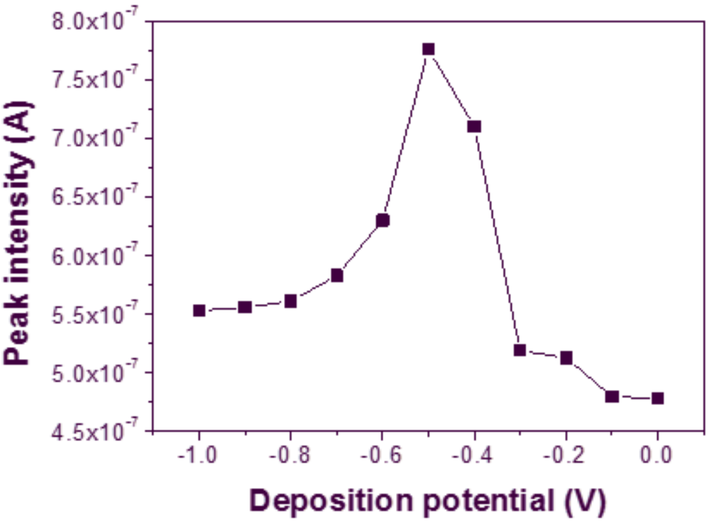

Fig. 8: Peak current Vs deposition potential obtained for 10^{-4} mol L^{-1} hydroquinone in acetate buffer solution (pH 4.5) on the glassy carbon electrode modified by Ba1-Na/L-cyst.

After considering the parameters such as the effect of pH medium, the accumulation time and deposition potential, we set these parameters each at its optimum value in order to study the influence of the concentration of hydroquinone in the detection medium. Figure 9 allowed us to see that the peak current changes as a function of the concentration of hydroquinone in the detection medium. In addition, it is possible with the glassy carbon electrode amended by L-Cysteine to detect very small amounts of hydroquinone in solution. Finally smectite modified by L-cysteine is shown to be sensitive sensor for hydroquinone in aqueous solutions. Indeed, the calibration curve allowed us to obtain a linear relationship (with a high correlation coefficient, R^2 = 0, 9963) linking the electrode response and the concentration of Hydroquinone in the range from 2.10^{-6} mol L^{-1} to 10^{-5} mol L^{-1}. This result suggests that the glassy carbon electrode modified by Ba1-Na/L-Cys can be used for electroanalysis of hydroquinone to the concentration limit of 8.10^{-7} mol L^{-1}. This detection limit is practically the same as that obtained by Yong et al., using intercalated montmorillonite modified carbon paste electrode [32].

3.3.3. Comparative study with the recent literature

Table I contains the data of some authors who have recently developed hydroquinone sensors. Parameters that we have chosen and that assess the performance of the sensors are: detection medium, potential scan, electrolysis voltage (anodic and cathodic potential), preconcentration time and detection limit. The supporting electrolyte is the same for almost all authors (HAc –NaAc buffer solution pH = 4.5). This is also the case of potential scan (-0.2 to 0.8 V). The hydroquinone/quinone system is irreversible on bare glassy carbon electrode while on modified glassy carbon electrode, the reversibility of the system is improved (Liang Wang et al [23]; Kamgaing et al., this study).We ignore the reversibility of the system on gold electrode as Shengfu et Dan[33] said nothing about. The best oxidation potential was obtained by shengfu et Dan with gold modified electrode (330 mV gained), followed by Kamgaing et al (90 mV) and Liang and Wang (39 mV). Yong et al (2012) [32] with intercalated monmorillonite modified carbon paste electrode obtained almost the same limite detection (5.7 $x10^{-7}$ mol L^{-1}) as Shengfu and Dan , 2002 [33] with cysteine modified gold electrode (4,0 x 10^{-7} mol L^{-1}). Our detection limit ($8x10^{-7}$ mol L^{-1}) is relatively better than that obtained by Liang et al. [23] but of the same order of magnitude ($1x10^{-6}$ mol L^{-1}). The best time of preconcentration is that we obtained in this study (9 mn) against 40 mn obtained by Shengfu et Dan [33].

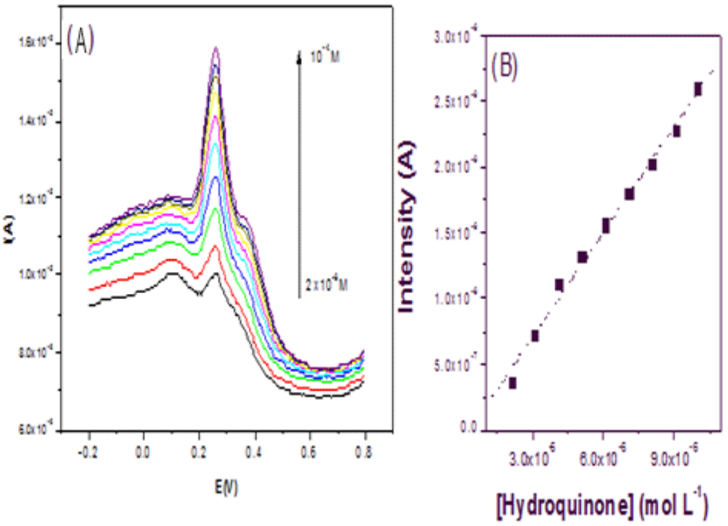

Fig. 9: (A) Differential Pulse voltammograms of hydroquinone in acetate buffer solution (pH 4.5) on the glassy carbon electrode modified by Ba1-Na/L-cyst, in the concentration range from 2.10^{-6} mol L^{-1} to 10^{-5} mol L^{-1}. Experimental conditions: preconcentration time: 9 minutes; deposition potential: -0.5 V; pH = 4,5 (B) corresponding calibration plot.

Conclusion

This work was to develop a sensor using a smectite clay modified by L-cysteine to detect hydroquinone. The raw clay of the Baba I region (Ba1) has been modified by L-cysteine (L-cys). This was used to change the active part of the glassy carbon electrode and then used for the analysis of hydroquinone at different concentrations in a solution of acetate buffer (0.1 M CH_3COOH/CH_3COONa) used as supporting electrolyte. The results obtained showed that the accumulation of hydroquinone is two times large on the electrode covered by a film of clay modified by L-cysteine than on the bare glassy carbon electrode. Some parameters that influence the current response were studied. It appears from this study that this sensor may be suitable for the analysis of hydroquinone for a detection limit of 8.10^{-7} M obtained in the following conditions of electrolysis: -0.5 V, 9 minutes, in 0.1 M acetate buffer medium at pH 4.5.

Acknowledgments

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Table 1: Recent literature data of hydroquinone

Authors	Electrode type	Techniques (1)	Detection medium	Potential scan (V/SCE)	ε_a and ε_c (mV) (2)	time (mn) (3)	limite (mol/L) (4)
Shengfu et Dan (2002) [33]	Cysteine modified gold electrode	ATR-FTIR, SEM, CV , impedance	Hydroq. 0.5M HAC-NaAc buffer solution (pH 4.8)	-0.8 to 0.2 at 100 mV/s	$\varepsilon_{a\,(BE)} = 657$ (5) $\varepsilon_{a\,(ME)} = 329$ $\boldsymbol{\Delta\varepsilon_a = 330}$	**40**	4.0×10^{-7}
Liang Wang et al. (2007) [23]	Glutamic acid modified glassy carbon electrode		Hydroquinone/Catechol, 0.1M HAC-NaAc buffer solution (pH 4.5)	-0.8 to 0.2 at 100 mV/s	$\varepsilon_{a\,(BE)} = 272$ $\varepsilon_{a\,(ME)} = 233$ $\boldsymbol{\Delta\varepsilon_a = 39}$ $\varepsilon_{c\,(BE)} = 91$ $\varepsilon_{c\,(ME)} = 164$	-	1×10^{-6}
Yong et al. (2012) [32]	MMCPE (6)	-	-	-	-	-	5.7×10^{-7}
Kamgaing et al. (this study)	CSMGCE (7)	DTA-TGA-DTG, XRD, CV.	Hydroquinone, 0.1M HAC-NaAc buffer solution (pH 4.5)	-0.8 to 0.2 at 100 mV/s	$\varepsilon_{a\,(BE)} = 440$ $\varepsilon_{a\,(ME)} = 350$ $\boldsymbol{\Delta\varepsilon_a = 90}$ $\varepsilon_{c\,(BE)} = 100$ $\varepsilon_{c\,(ME)} = 170$	**9**	8.0×10^{-7}

(1) Film characterization techniques ; (2) Anodic (εa) and Cathodic (εc) potential; (3) preconcentration time; (4) Detection limit; (5) BE: bare electrode, ME: modified electrode; (6) Intercalated monmorillonite modified carbon paste electrode; (7) cysteine/smectite modified glassy carbon electrode.

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