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Amperometric sensors based on sawdust film modified electrodes: Application to the electroanalysis of paraquat

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ABSTRACT

Natural or sodium hydroxide treated *Ayous* sawdusts were used to prepare thin film electrodes (denoted respectively as PSTFE and SSTFE). The sensors obtained exhibit good mechanical stability and a wide electrochemical potential range. Their electrochemical characterization revealed that they present a good capacity to accumulate cations, but are not useful for the electroanalysis of anions. In all cases, the signals were more intense and well defined on SSTFE compared to PSTFE. When applied to the electroanalysis of paraquat, a significant improvement of the current intensities was obtained on these electrodes compared to the bare glassy carbon electrode. The diffusion of this compound through the film which is the main process governing the electrochemical reaction at the electrode surface, is 2.2 times more important with SSTFE compared to PSTFE. After the optimization of the detection parameters, calibration curves were obtained in the concentration range 0.1–0.725 μmol L^{-1} for PSTFE and 0.05–0.6 μmol L^{-1} for SSTFE. The detection limits determined for a signal/noise ratio=3 are 5.49×10^{-9} mol L^{-1} for PSTFE and 3.02×10^{-9} mol L^{-1} for SSTFE.

1. Introduction

Electrochemical methods, due to their easy implementation, the simple apparatus used and their good performance for a wide variety of chemical compounds, are increasingly attractive [1,2]. Major improvements are constantly achieved in this research domain to increase the accuracy of the measurements and to reduce their cost. Most of these research efforts are devoted to the development of new electrodes, the interest of which can be expressed as follow:

(i) The surface of classical electrodes are usually altered after only a few number of scans, in such a way that they need to be polished for new analysis. This of course increases considerably the analysis time and introduces differences between consecutive measurements;
(ii) During the electroanalysis of organic compounds, the intermediates or substrates generally undergo irreversible adsorption on the electrode surfaces and reduce the accuracy of the measurements [3–5];
(iii) The detection limits obtained with conventional electrodes are limited by the flux of electroactive species on their surfaces.

The use of mercury drop working electrode, because of the constant renewal of the mercury drop, avoids most of these drawbacks. For this reason they are still used nowadays in electroanalysis [6–9], despite the pollutant character of mercury that requires an additional procedure for mercury recovery and recycling [9].

Researches have therefore been resolutely focused on new materials that can be used for the modification of the electrodes. They can be deposited as thin films on the electrode surface (thin film electrodes) [10] or can be intimately mixed with powdered carbon to obtain modified carbon paste electrodes [11]. The resulting sensors can be used repeatedly, are selective, and provide very low detection limits [11].

Clays, zeolites or synthetic silicates are the most widely used materials for electrode modification, especially because of their interesting cation exchange properties. Another important advantage is their ability to integrate (through intercalation or grafting) in their structure organic compounds with convenient functions that may increase their electrochemical properties [1,12–17]. Synthetic polymers have also been widely explored [18,19]; unlike clay materials, they can be synthesized directly on the electrode surface by electropolymerization, the quantity of the functional groups and their orientation being duly controlled. Organic polymers like cellulose or chitosan have also been successfully used [20].

Lignocellulosic materials derived from plants appear to be good adsorbents for a wide variety of chemical compounds. Indeed, they

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have been successfully used for the adsorption of heavy metals and organic compounds (dyes, pesticides, hydrocarbons…) [21–23], a fact that suggests their potential use as electrode material especially when there is a need to increase the concentration of the electroactive compound at the electrode. Along these lines the successful use of algae for the preparation of carbon paste electrode applied for the detection of some heavy metals has been published [24–27].

In this paper, we report, for the first time, the use of sawdust as modifier for thin film electrodes. The sensors obtained then were fully characterized and subsequently used for the electroanalysis of paraquat, a widely used cationic herbicide with harmful environmental effects [18].

2. Materials and methods

2.1. Materials and chemicals

Ayous (*Triplochiton Schleroxylon*) sawdust is the lignocellulosic material used in this work. *Ayous* is a tree which provides a wood extensively used in Cameroon and in the Central African subregion in light carpentry. The waste (sawdust) produced is used for cooking or dumped in landfills or in the nature. The sawdust used in the present work was collected from a sawmill with special caution to avoid its contamination with sawdusts from a different wood. The fraction with diameter less than 5 μm was collected by gravimetric method and used for all the experiments. Part of this material was treated with sodium hydroxide, consisting of stirring about 0.15 g of sawdust in 3 mL of a 2 mol L^{-1} sodium hydroxide solution for 2 h. The resulting material was washed several times with distilled water, dried in the open air and then in an oven at 105 °C. It is important to note that, the concentration of sodium hydroxide used for the treatment of the fine fraction of the pristine sawdust was the optimum value that we determined in preliminary experiment (not presented here).

Paraquat dichloride (98%) was purchased from Aldrich. All the other chemicals ($K_3[Fe(CN)_6]$, $Cl_3[Ru(NH_3)_6]$, KCl, NaOH, $CaCl_2$, $MgSO_4$ and NaCl) were of analytical grade.

2.2. Electrode preparation and analytical procedures

The pristine sawdust thin film electrode (PSTFE) and that issued from sodium hydroxide treated sawdust (SSTFE) were prepared by depositing 10 μL of an aqueous suspension of sawdust 2 g L^{-1} (natural or treated) at the surface of a glassy carbon electrode. The surface of the glassy carbon electrode was previously polished using an alumina powder, rinsed with distilled water and sonicated for about fifteen minutes. The thin film electrode was then dried in open air for about two hours and used without further treatment.

To record the cyclic voltammograms, the electrode was directly immersed in an electrochemical cell containing paraquat dissolved in the electrolytic solution. A platinum wire was used as counter electrode and a saturated calomel electrode as reference. All the experiments concerning the quantification of paraquat were carried out following three steps:

(i) An accumulation step at open circuit, during which the modified electrode was immersed in an aqueous solution of paraquat to let the analyte accumulated on the film;
(ii) A detection step, for which the electrode was freshly removed from the accumulation solution, rinsed with distilled water and transferred to the detection medium consisting of the electrochemical cell containing the supporting electrolyte. The signal of the paraquat accumulated during the previous step was immediately recorded using square wave voltammetry.
(iii) A desorption step during which the residual paraquat in the thin film was removed; a voltammogram was then recorded in order to confirm the complete removal of paraquat.

2.3. Apparatus

The sawdust samples used for the electrode modification were characterized by IR spectroscopy (ATR method (Attenuated Total Reflectance)) using a spectrophotometer alpha-P of Bruker. The voltammograms were recorded using a μ-Autolab potentiostat, controlled by the GPES software. The pH measurements were carried out with a Multi 340i/SET Weight Watchers International (WTW) pH-meter.

3. Results and discussions

3.1. Characterization

The lignocellulosic materials used were characterized by IR spectroscopy. As they were applied as electrode modifier, the electrochemical potential range and electrode stability were also determined. Finally, the ability of these sensors to be used for the electroanalysis of ionic compounds was study.

3.1.1. Infrared spectroscopy

Both materials: pristine and treated sawdust presented similar spectra: the main bands due to the functional groups encountered in lignocellulosic materials were observed: ν(O–H) of lignin and polysaccharides at 3330 cm^{-1}; ν_{as}(C–H) of CH and CH_2 at 2850 cm^{-1}; ν(C=O) of aldehydes, esters and carboxylic acids at 1730 cm^{-1}; ν(C=O) of carboxylates functions at 1645 cm^{-1}; aromatic rings of lignin at 1592 cm^{-1}; ν (C–O) of ethers and alcohols at 1030 cm^{-1} [28,29].

On comparing the spectra due to pristine (Fig. 1(a)) and treated sawdust (Fig. 1(b)), it was found that the treatment with sodium hydroxide solution results in the disappearance of the peak corresponding to the carbonyl of ether and carboxylic functions (1730 cm^{-1}). On the other hand, the peak of the carbonyl of carboxylate functions (1645 cm^{-1}) increases. This is not surprising, the treatment with sodium hydroxide tends to hydrolyze the esters functions and convert the carboxylic

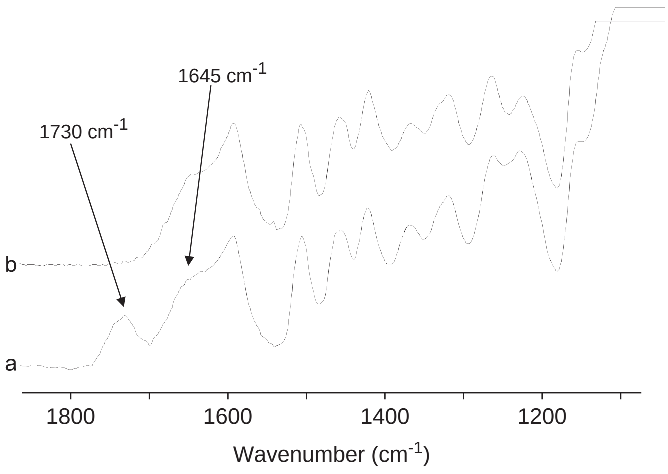

Fig. 1. IR spectra of (a) natural and (b) sodium hydroxide treated *Ayous* sawdust.

functions to carboxylates. Similar results were already pointed out by Min et al. during the alkaline treatment of juniper fiber [29].

3.1.2. Electrochemistry

3.1.2.1. Electroactivity domain and stability of the thin films electrodes. A suitable working electrode should provide a large potential window, in such a way that it may be used for the electroanalysis of compounds that exhibit electrochemical properties either at extreme anodic or cathodic potentials. The electroactivity domain was determined by recording cyclic voltammograms in a 0.1 mol L^{-1} NaCl solution. The signals obtained with the bare glassy carbon (BGC) and the modified electrodes are presented in Fig. 2.

The voltammograms of the pristine modified sawdust electrodes (PSTFE) is made of a reduction peak centered at -1.65 V. This peak is more important and broaden on PSTFE than on SSTFE; this may be due to the presence of extracts in the sawdust. The alkaline treatment reduces the quantity of these compounds in the lignocellulosic material structure. The electroactivity of the extracts was fully confirmed by a blank voltammogramm recorded under the same conditions on an electrode modified by a thin film of methanol treated sawdust (curve not shown), since the peak current at -1.6 V disappeared then: so, the electroactivity domain is wide as that of the bare glassy carbon electrode. However, in practice, we would recommend not to use these modified electrodes at potentials below -1.6 V to avoid that peak.

To assess the stability of these films, similar voltammograms were recorded after the modified electrodes have spent 24 h in the electrolyte solution. The blanks obtained so far remained constant and reproducible.

3.1.2.2. Electrochemical behavior of ruthenium ions. Hexaammine ruthenium complex ($[Ru(NH_3)_6]^{3+}$) cation is widely used for electrochemical characterization purposes [13,30]. In the present work we observe that on a glassy carbon electrode, this probe displays a well defined one-electron reversible and rapid system (Eq. (1)) (see Fig. 3(a)).

$$[Ru(NH_3)_6]^{3+} + e^- \rightleftarrows [Ru(NH_3)_6]^{2+} \quad (1)$$

A series of 50 cycles was recorded using PSTFE or SSTFE immersed in a solution containing ruthenium ions at 2×10^{-4} mol L^{-1}.

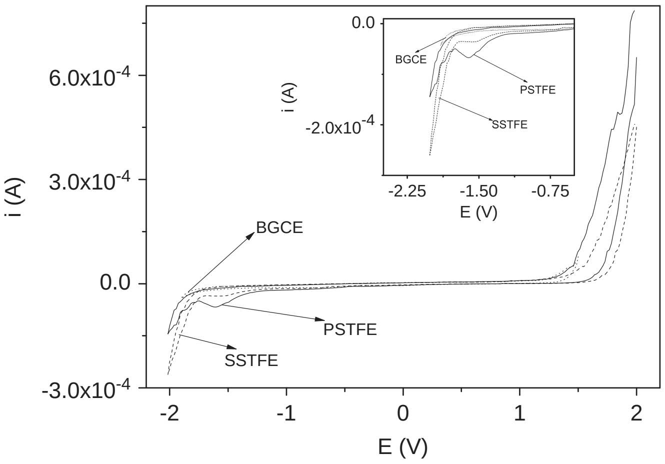

Fig. 2. Electroactivity domains of different electrodes recorded in 0.1 mol L^{-1} NaCl at a scan rate of 100 mV s^{-1}.

With PSTFE (Fig. 3(b)) one can observe that the peak intensities increase rapidly with the number of cycles, until the 30th scan is reached. This increase reflects the gradual accumulation of cations in the sawdust. Similar results were obtained by Tonle et al. during their work on a glassy carbon electrode, modified with a film of smectite clay [13]. These authors noticed that during the first scan, the presence of the material at the surface prevents the access of the analyte at the electrode. The gradual saturation of the film is reflected by the steady increase in peak intensities of the voltammograms with the number of cycles so that the saturation appears after more than 50 cycles. In our case, the saturation appeared very quickly (after 30 cycles) indicating high affinity between the sawdust and the ruthenium ions. For SSTFE (Fig. 3(c)), the first scan shows an intense and well defined signal. There is only a very low increase in peak intensities between the first and 50th scan. This result tends to show that the diffusion of the analyte to the electrode seems not to encounter any barrier due to the presence of the film. The NaOH treatment probably increases the affinity of the sawdust with the ruthenium ion. The macroporosity of the sawdust also seems to play an important role in this phenomenon: as a matter of fact, the mass diffusion within a material is facilitated by the large size of its pores [23].

On comparing the voltammograms at equilibrium with that obtained on BGC, there is an important improves of the peak intensities of the signals with the modified electrodes. However, this improvement was more pronounced on SSTFE compared to PSTFE. This confirmed once again the ability of these materials to accumulate cations.

Another noticeable fact was the displacement of the voltammograms to more cathodic potentials (approximately 100 mV) and this irrespective of the nature of the film material. This suggests that for the two lignocellulosic materials, adsorption sites of similar nature are responsible of the accumulation of ruthenium ions in the films. The NaOH treatment simply made these sites more abundant and easily available.

3.1.2.3. Electrochemical behavior of ferricyanide ions. The modified electrodes were subsequently used for the electroanalysis of ferricyanide ion ($[Fe(CN)_6]^{3-}$), a probe commonly used in electrochemistry for the characterization of electrodes [13,30]. The electrochemical behavior of this anion is well known: it is a mono electronic (Eq. (2)) and reversible system at a bare glassy carbon electrode.

$$[Fe(CN)_6]^{3-} + e^- \rightleftarrows [Fe(CN)_6]^{4-} \quad (2)$$

Like what is encountered in literature, the oxidation and reduction peaks on this electrode (Fig. 4(a)) are well defined and the difference between their potentials is close to 60 mV as one might expect for a fast one electron electrochemical system.

The sawdust thin film electrodes were then used to record a series of 50 voltammograms under the same conditions as those in Fig. 4(a). These voltammograms are plotted in Fig. 4(b) and (c).

With the modified electrodes the voltammograms were rather broad, and a displacement of the peaks towards more anodic potentials for the oxidation one and towards more cathodic potentials for the reduction one was observed. The films seem to oppose a resistance to the diffusion of the ferricyanide ions from the solution to the surface of the glassy carbon electrode, which was not the case with the ruthenium ions.

It was observed that the peak intensities increase with the number of cycles for the two electrodes; however, this increase was more pronounced for SSTFE compared to PSTFE. The increase in intensity was also accompanied by a shift of the peak potential (again more pronounced on SSTFE) to more favorable potentials.

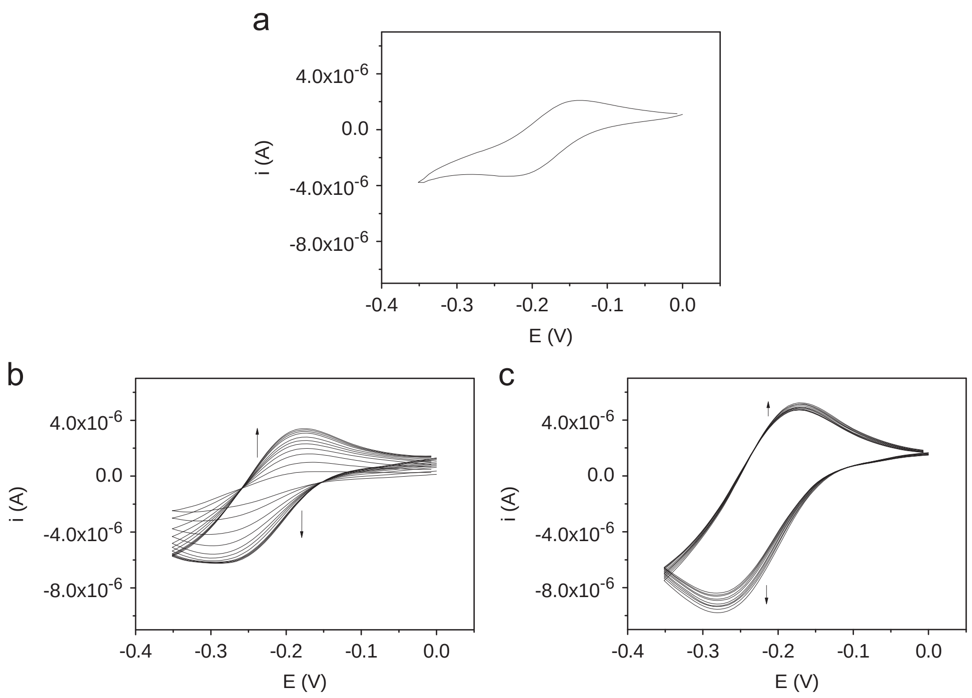

Fig. 3. Cyclic voltammograms of 2×10^{-4} mol L^{-1} [Ru(NH$_3$)$_6$]$^{3+}$ recorded in 0.1 mol L^{-1} KCl at 100 mV s^{-1} on (a) BGC, (b) PSTFE and (c) SSTFE.

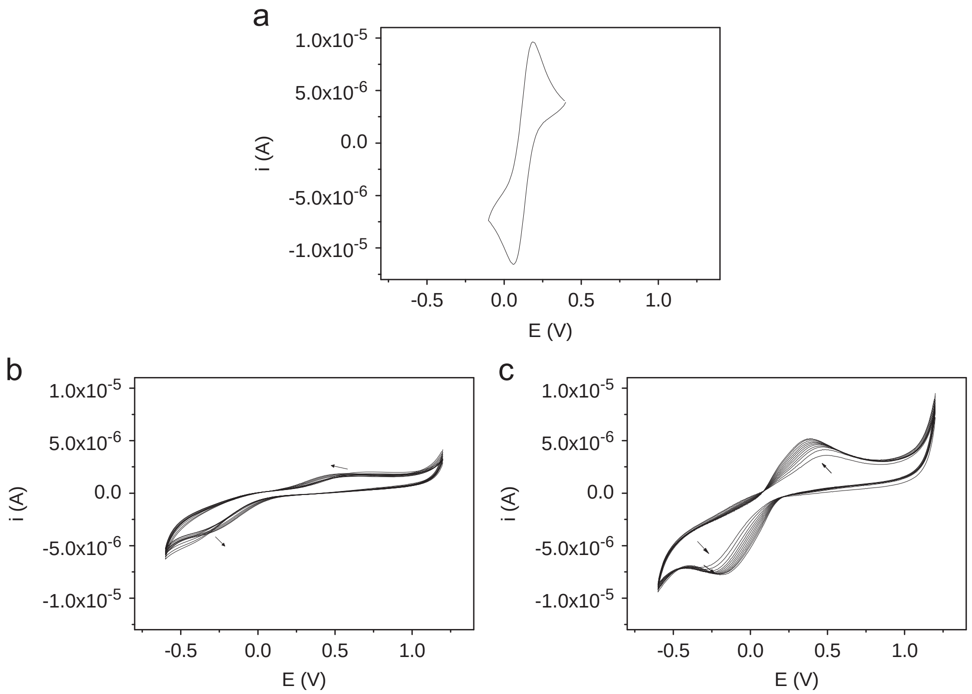

Fig. 4. Cyclic voltammograms of 10^{-3} mol L^{-1} [Fe(CN)$_6$]$^{3-}$ recorded in 0.1 mol L^{-1} NaCl at 100 mV s^{-1} on (a) BGC, (b) PSTFE and (c) SSTFE.

These observations tend to show that although these electrodes do not have a good affinity with ferricyanide ions, they can develop an accumulation capacity towards this species. Some works in the literature also reveal that lignocellulosic materials weakly accumulate anionic compounds in batch mode [31,32]. The NaOH treatment seems to increase this capacity as shown in Fig. 4(c). By contrast, on natural smectite clay modified electrodes, there is no signal with this anion [13]. However, with a modified clay bearing amine functions, one obtains in acidic solution, a well define signal with an intensity more important compared to the one on unmodified electrode [13].

From these electrochemical characterization studies, it appears clearly that the sawdust modified electrodes can quantitatively accumulate cations. We shall now evaluate to what extent this is true with paraquat, which is also a cationic compound.

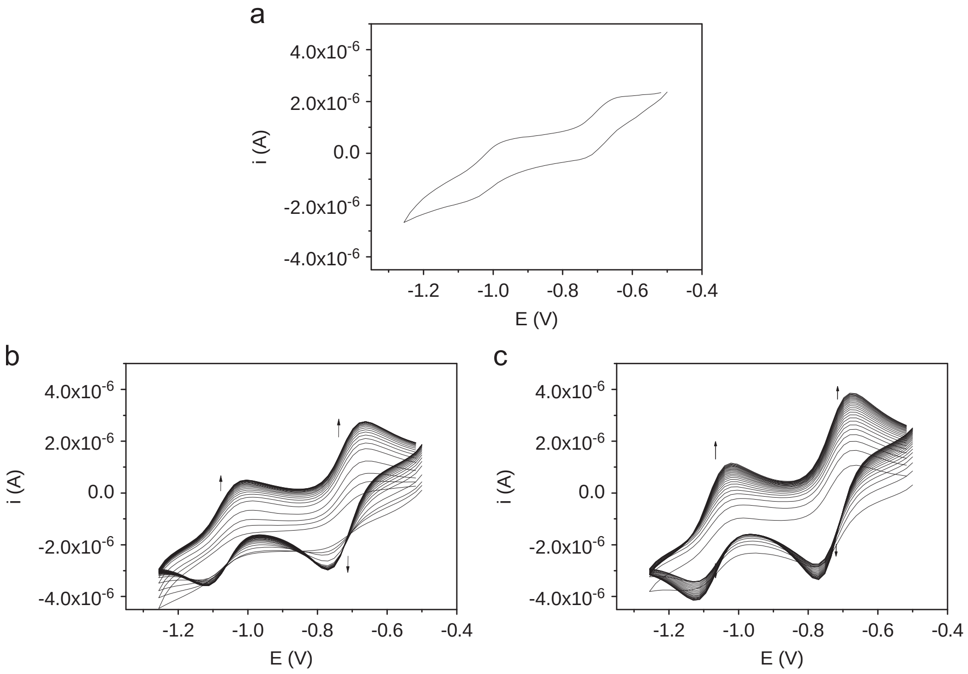

Fig. 5. Cyclic voltammograms of 5×10^{-5} mol L^{-1} paraquat recorded in 0.1 mol L^{-1} NaCl at 100 mv s^{-1} on (a) BGC (b) PSTFE and (c) SSTFE.

3.2. *Paraquat electroanalysis*

3.2.1. *Interactions between paraquat and the film of sawdust*

3.2.1.1. Accumulation of paraquat. A series of 50 voltammograms were recorded with different electrodes in an electrolytic solution containing paraquat at a concentration of 5×10^{-5} mol L^{-1}. The signals obtained are plotted in Fig. 5.

The modified electrodes PSTFE and SSTFE exhibit signals reflecting a gradual accumulation of paraquat as it is the case when the BGC electrode is modified with various other adsorbents found in the literature [33–38]. Paraquat is reduced according to the well described mechanisms given below [34–36].

$$PQ^{2+}_{sol} + e^{-} \overset{0,7\ V}{\rightleftarrows} PQ^{\bullet+}_{sol} \tag{3}$$

$$PQ^{\bullet+}_{sol} + e^{-} \overset{-1,1\ V}{\rightleftarrows} PQ^{0}_{sol} \tag{4}$$

$$PQ^{2+}_{sol} + PQ^{0}_{sol} \rightleftarrows 2PQ^{\bullet+}_{sol} \tag{5}$$

The second step is less reversible than the first one, because of the coproportionation reaction of the third step.

By comparing the signals obtained at equilibrium on the modified electrode (Fig. 5(b and c)) to that obtained on BGC electrode (Fig. 5(a)), it was noted that the presence of sawdust significantly improved the signal of paraquat. This improvement was more important on SSTFE. The treatment with sodium hydroxide increased the capacity of the natural *Ayous* sawdust to adsorb paraquat and cationic compounds generally. This observation also confirms the results obtained with the ruthenium ions. However, by contrast to what was noted with ruthenium, the progressive accumulation of paraquat was observed for the two modified electrodes, indicating that the diffusion of this analyte through the materials is more difficult than that of the ruthenium ions. However, saturation is achieved very quickly, after about 20 cycles. This result coupled with the fact that the first scan shows clearly the current peaks of the paraquat systems, confirms the affinity of paraquat for natural or treated *Ayous* sawdust in comparison with various other adsorbent materials reported in the literature [38]. During our previous work on the biosorption of paraquat on *Ayous* sawdust, we noticed that the diffusion of this pesticide in this material is very fast: an equilibrium time less than ten minutes was indeed obtained for kinetic studies [23].

We subsequently got interested in the diffusion of paraquat through the film to the electrode surface in order to facilitate electrochemical reactions.

3.2.1.2. Diffusion of paraquat in the film, influence of scanning the potential. On varying the scanning rate of the potential, the intensities of the signals change according to the Randles–Sevcick relationship expressed in Eq. (6).

$$I_P = kn^{3/2}Av^{1/2}C_fD^{1/2} \tag{6}$$

where v (V s^{-1}) is the scan rate, k a constant, n the number of moles of electrons exchanged per mole of substance, A (cm^2) the surface area of the electrode, C_f (mol cm^{-3}) the concentration of electroactive compound in the film and D (cm^2 s^{-1}) the diffusion coefficient of the compound in the film.

Accordingly, the peak intensity is proportional to the square root of the scan rate. Indeed, increasing the scanning rate turned to increase the number of reactive species at the electrode during the forward scan.

From Eq. (6), when the electrochemical reaction at the surface of the electrode is diffusion controlled, plotting the current peak intensities versus square root of scan rates should result in a straight line whose slope is directly proportional to the diffusion coefficient. This parameter indicates how ease is the diffusion of an electroactive compound to the electrode surface. By so doing, we were able to compare the diffusion coefficients of various materials.

Fig. 6(a) shows the voltammograms obtained at equilibrium on SSTFE for scanning rates ranging between 10 and 300 mV s^{-1}. It can be seen that the peak intensities increased with the scan rate. In Fig. 6(b) are plotted the peak intensities of the reduction

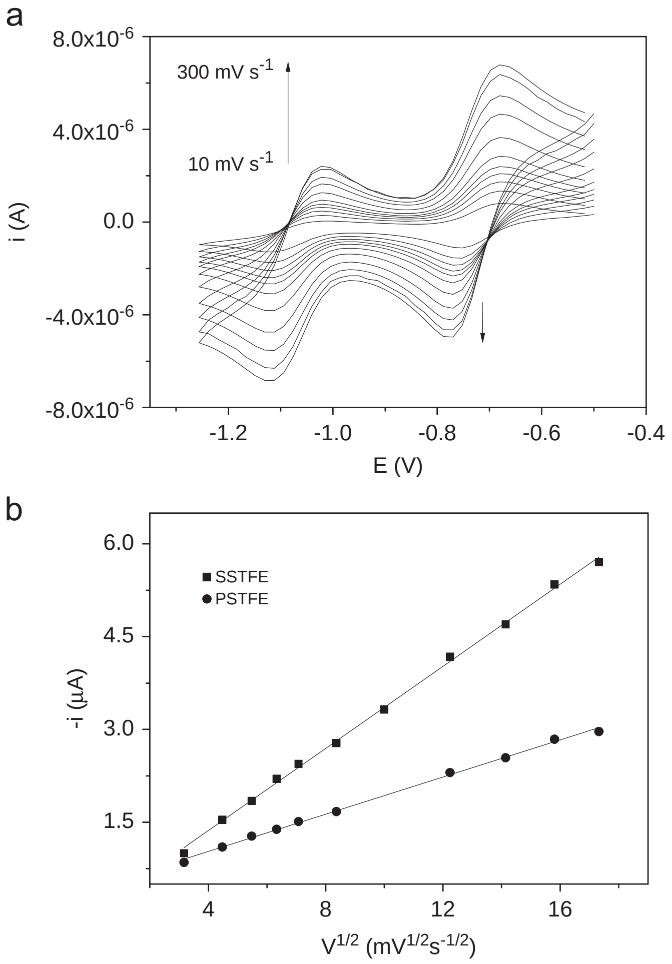

Fig. 6. Influence of the scan rate. (a) Cyclic voltammograms of 5×10^{-5} mol L^{-1} paraquat recorded in 0.1 mol L^{-1} NaCl, scan rate varied from 10 to 300 mV s^{-1}; (b) variation of the peak intensities of the first reduction (at −0.7 V) as a function of the square root of the scan rate.

peak at −0.7 V obtained with PSTFE and SSTFE as a function of the square root of the scan rate. These curve are straight lines with correlation coefficients close to unity (R^2 of 0.997 and 0.998 for PSTFE and SSTFE respectively), are evidence that the electron transfer at the electrode surface is controlled by the diffusion of paraquat. Identical plots derived from the reduction currents at −1.1 V (results not shown) gave correlation coefficients of the same order of magnitude indicating thus that in this case, diffusion also controls the process. This is not always the case: a survey of the literature, reveals that although, in general, the first reduction is diffusion controlled, the second one is not, because of the coproportionation reaction or the strong adsorption of paraquat (0) that occurs on the electrode or even the dimerization of the radical cation ($PQ^{\circ+}$) [6,39–42]. In our case the microenvironment produced by the sawdust film seems to prevent these chemical reactions.

The slopes associated with these plots (0.33 and 0.15 for SSTFE and PSTFE respectively) show that the diffusion of paraquat is easier through the film of sawdust treated with sodium hydroxide compared to the natural sawdust. More, the ratio of these slopes indicates that the diffusion is 2.2 times more important for SSTFE compared to PSTFE. This trend can be explained by the increase in porosity due to the alkaline treatment. Indeed, NaOH reduce the amount of lignin in lignocellulosic materials and contributes to increase their porosity [29].

3.2.1.3. Desorption of paraquat. In order to evaluate the strength of the interactions between paraquat and the electrode modifiers, we first performed the accumulation of this compound at open-circuit. After 3 min of accumulation in a solution of paraquat 5×10^{-5} mol L^{-1}, the electrode was transferred into the electrolytic solution (NaCl 0.1 mol L^{-1}) and a series of 50 cycles was recorded (results not presented here).

For the two electrodes, there was a rapid decrease of the currents (about 50% after the first scan, 80% after 5 scans and 90% after 10 scans), indicating that paraquat desorbed quantitatively from the film to the electrolytic solution. A cation exchange mechanism (Eq. (7)) between the sodium ions present in the electrolytic solution and paraquat in the film, promoted by the effect of the concentration gradient can explain this phenomenon.

$$PQ^{2+}_{film}+2Na^{+}_{sol}\rightarrow PQ^{2+}_{sol}+2Na^{+}_{film} \qquad (7)$$

After 50 cycles, the signal of paraquat had almost disappeared. So, the interactions between paraquat and the electrode material are essentially physical and therefore easy to break. However, some residual currents are observed, probably due to the paraquat which is adsorbed on the sawdust by stronger interactions. We reported similar observations previously, during our study of desorption of paraquat adsorbed on *Ayous* sawdust [23]. However, a gentle agitation of the electrochemical cell completely removed this residual signal. Walcarius et al. also obtained similar trend with a zeolite modified electrode, but with more slow release of adsorbed paraquat [38].

This result reinforces the idea that these two electrodes can be used for quantitative analysis of paraquat since the electrode can be completely regenerated after a measurement.

3.2.2. Quantitative analysis of paraquat

Square wave voltammetry, because of its greater sensitivity compared to cyclic voltammetry was used in this section. The results obtain on BGC electrode present some limitations in terms of signal intensity and reproductivity of the measurements. Fig. 7 shows in fact that an important improvement in current intensity is obtained with SSTFE and PSTFE (by a factor of 15 and 13 respectively in comparison with BGC) after prior accumulation in a solution containing only paraquat.

Our films do satisfy the conditions required for quantitative applications because the signals obtained so far are both intense and reproducible. However, prior to quantification experiments, it is useful to determine the optimal conditions for the detection of

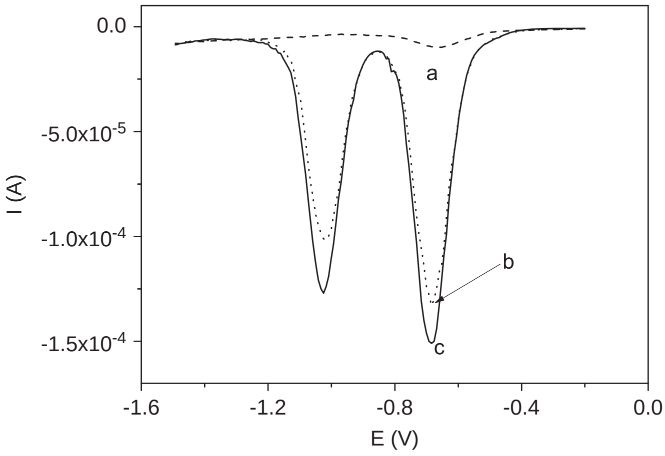

Fig. 7. Square wave voltammograms recorded in 0.1 mol L^{-1} NaCl of 5×10^{-5} mol L^{-1} paraquat on (a) BGC, (b) PSTFE and (c) SSTFE after a preconcentration step of 180 s in a 5×10^{-5} mol L^{-1} paraquat solution at pH 5.36.

paraquat in the solution through the investigation of the different parameters that can affect the signals.

3.2.2.1. Influence of the accumulation time. Our previous study on the biosorption of paraquat [23] revealed that during its accumulation in the *Ayous* sawdust, the saturation did not occur immediately. In this section, we intend to determine the time required for the saturation of the films by recording voltammograms for different accumulation time. Fig. 8 shows the variation of the intensity of the first reduction peak (at −0.7 V) versus accumulation time.

For the two electrodes, the peak intensities increased sharply with accumulation time during the first 30 s. This growth becomes less important as the accumulation time increases until the formation of a plateau at 180 s. Similar results were reported in the literature with films or carbon paste electrodes applied to the electroanalysis of paraquat [43–45]. However, with these electrodes, the optimum equilibrium time was more important in comparison with the one obtained in this work. These results confirm what we observed in our previous publication on the adsorbtion of paraquat onto *Ayous* sawdust; as a matter of fact, in batch mode, less than 10 min were sufficient to achieve the equilibrium [23]. For further manipulations, the accumulation time was maintained at 180 s.

3.2.2.2. Influence of the pH of the accumulation solution. It is well known that the efficiency of the accumulation of paraquat on a substrate which can exhibit acid–base properties varied very significantly with the pH of the solution [23,46,47]. We have thus varied the pH of the accumulation solution between 2 and 11.50. The corresponding peak intensities at −0.7 V plotted as functions of pH are gathered in Fig. 9.

For both electrodes, we observed similar trends. The peak intensities increased with pH, reaching a maximum at pH 10.50 before decreasing slightly. The very low current intensities noted between pH 2 and 3 are due to electrostatic repulsion between the protonated sawdust and paraquat. Between pH 5.36 and 9, the intensities decreases slightly, due to the fact that, the electrostatic effects (repulsion or attraction) are minimized; the quantity of protons involved in the acid–base reaction between the sawdust and the solution are not so important. At pH 10.50, the electrostatic attraction between the anionic sawdust and paraquat is very intense as evidenced by the high value of the peaks. The small decrease observed at pH 11.50 could be explained by the important retention of the adsorbed paraquat which is no longer fully available to diffuse to the electrode surface to permit the electrochemical reaction. We also observed that for pH value between 10.5 and 11.5, desorption of paraquat was rather difficult after the recording of the signal. For this reason, despite the more intense current at pH 10.5, the accumulation solution pH for further manipulation was taken equal to 5.36.

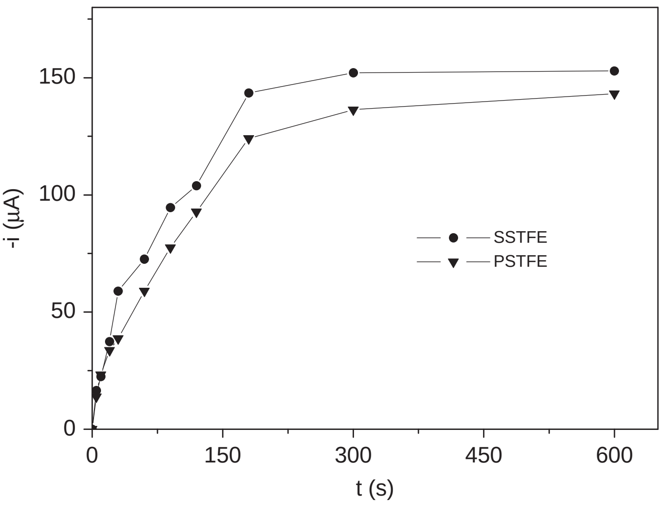

Fig. 8. Influence of the accumulation time on the intensity of the first reduction peak (−0.7 V) of paraquat on PSTFE and SSTFE. The preconcentration time is varied from 5 to 600 s. Paraquat solution 5×10^{-5} mol L^{-1}; pH: 5.36; electrolyte: 0.1 M NaCl.

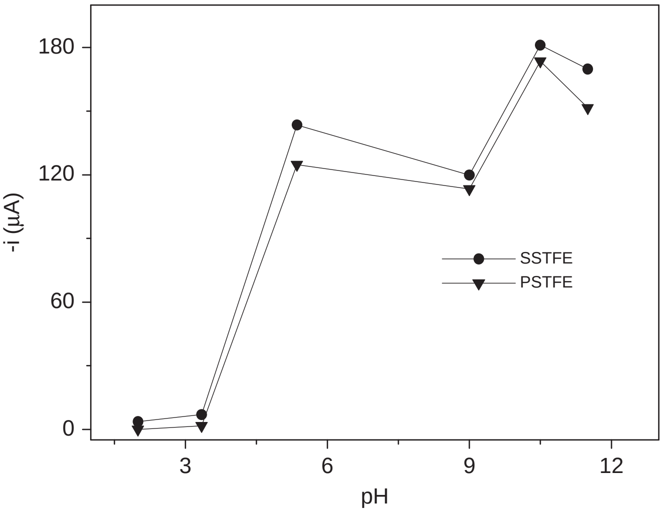

Fig. 9. Influence of the pH of the accumulation solution on the intensity of the first reduction peak (−0.7 V) on PSTFE and SSTFE. Electrolyte: NaCl 0.1 mol L^{-1}; preconcentration step: 180 s; paraquat concentration: 5×10^{-5} mol L^{-1}; pH range: 2–11.50.

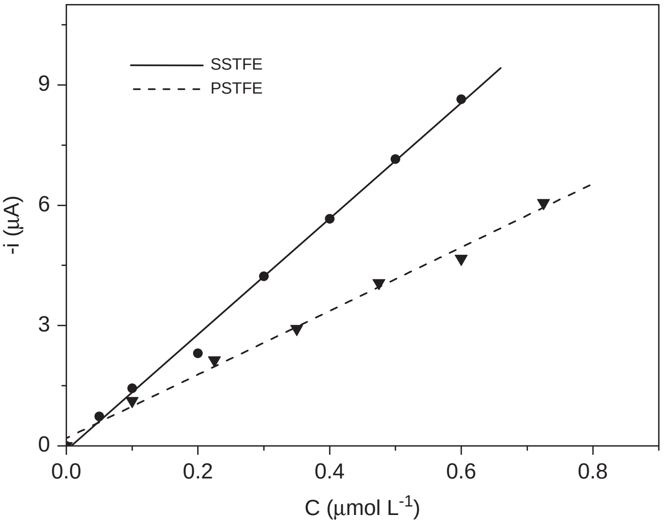

Fig. 10. Calibration plots of paraquat on PSTFE and SSTFE. Preconcentration step: 180 s; pH: 5.36; electrolyte: NaCl 0.1 mol L^{-1}.

3.2.2.3. Calibration curves and interference study. Taking into account the results obtained during the optimization of the experimental parameters, we plotted (Fig. 10) the calibration curves using the two electrodes, in the concentration range from 0.1 to 0.725 μmol L^{-1} for PSTFE, and 0.05 to 0.6 μmol L^{-1} for SSTFE. There was a good linearity for the two electrodes as evidenced by the correlation coefficients of 0.996 and 0.998 obtained respectively for PSTFE and SSTFE.

Table 1
Detection of paraquat in aqueous solution on various electrode materials.

Electrode	Modifier	Detection limit (mol L^{-1})	Ref.
Mercury drop	–	1.5×10^{-8}	[6]
Bare glassy carbon	Ion exchange resin	2.00×10^{-9}	[18]
Platinum ultramicroelectrode	–	1.51×10^{-8} (3.9 ppb)	[48]
Gold ultramicroelectrode	–	2.41×10^{-8} (6.2 ppb)	[48]
Carbon fiber ultramicroelectrode	–	7.89×10^{-8} (20.3 ppb)	[48]
Gold microelectrode	–	1.75×10^{-8} (4.51 μg L^{-1})	[41]
Bare glassy carbon	Nafion	1.94×10^{-9} (0.5 ppb)	[44]
Bare glassy carbon	Pristine *Ayous* sawdust	5.49×10^{-9}	This work
Bare glassy carbon	Sodium hydroxide treated *Ayous* sawdust	3.02×10^{-9}	This work

Table 2
Interference study of some metal (K^+, Na^+, Ca^{2+} and Mg^{2+}). Paraquat concentration: 5×10^{-6} mol L^{-1}; preconcentration step: 180 s; pH: 5.36; electrolyte: NaCl 0.1 mol L^{-1}.

C (μmol L^{-1})	NaCl		KCl		$CaCl_2$		$MgSO_4$	
	PSTFE	SSTFE	PSTFE	SSTFE	PSTFE	SSTFE	PSTFE	SSTFE
0	100	100	100	100	100	100	100	100
10	100.03	104.02	97.93	98.27	66.70	73.67	86.44	87.28
500	86.66	88.87	83.03	90.03	25.24	24.54	28.00	32.05
5000	52.59	58.14	47.63	48.44	14.32	12.46	13.27	15.12

The detection limits determined for a signal/noise ratio of 3 are 5.49×10^{-9} mol L^{-1} for PSTFE and 3.02×10^{-9} mol L^{-1} for SSTFE. The limits of quantification (defined for a signal/noise ratio of 10) are 1.83×10^{-8} mol L^{-1} PSTFE and 1.01×10^{-8} mol L^{-1} for SSTFE. These results were compared with some other reported in literature (Table 1).

The detection limit obtained with PSTFE is about 10 times lower than that obtained with a gold ultramicroelectrode, a carbon fiber electrode or a mercury drop electrode. This performance is however better than what is obtained with a glassy carbon electrode coated with an ion exchange resin. With SSTFE, the detection limit is even improved; the sensitivity is close to that of a glassy carbon electrode coated with Nafion.

The interference of some metal cations (i.e. Na^+, K^+, Ca^{2+} and Mg^{2+}) during the detection of paraquat was studied. A known amount of these cations were added directly into the preconcentration solution containing paraquat at a concentration of 5 μmol L^{-1}. The sensors performances (P) were then evaluated for different concentrations of interfering cation by comparing the current obtained to that was recorded after preconcentration in a solution without interfering cations (Eq. (8)).

$$P = \frac{I_C}{I} \times 100 \tag{8}$$

where I and I_C represent respectively the current measured when the preconcentration step was performed without or with an interfering cation.

The results in Table 2 show that concentrations of Na^+ or K^+ 100 times greater than that of paraquat have no significant effect on the detection of this pesticide, while for concentrations 1000 times greater, the currents were reduced for about 50%. However, with Ca^{2+} and Mg^{2+}, there is a low reduction of current for concentrations 2 times higher than paraquat and that becomes very significant for concentrations 100 times greater (P between 30% and 20%). It is however important to note that despite these interference effects, the sensors remain effective for the detection of paraquat but with a reduced sensitivity.

4. Conclusion

We report here the first study of sawdust used as a modifier for thin film electrode. Natural and sodium hydroxide modified *Ayous* sawdust were used for these purposes and allow us to obtain two electrodes, (PSTFE) and (SSTFE) respectively. The characterization of these sensors shows that they have a wide electroactivity domain and present a charge recognition property since they can quantitatively accumulate cationic compounds but not anions. Applied to the electroanalysis of paraquat it appears that the diffusion of this compound through the film is easier with SSTFE; the electrochemical reaction at the electrode surface is diffusion controlled. These electrodes exhibit a good behavior when the paraquat concentration is varied and the detection limits obtained are 5.49×10^{-9} mol L^{-1} for PSTFE and 3.02×10^{-9} mol L^{-1} for SSTFE. These promising results show that lignocellulosic materials applied as electrode modifiers can significantly improve the selective detection of some electroactive compounds.

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