

Detecting cadmium(II) by using coal extracted from argan oilcake waste (Argania spinosa) as modifier of carbon paste electrode.

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Abstract

The detection of Cd²⁺ ions was studied by cyclic voltammetry (CV) and Square Wave Voltammetry (SWV). This method is mainly based on the accumulation of Cd²⁺ ions on the surface of a carbon paste electrode modified by coal extract from argan oilcake waste (AC-CPE). To evaluate the detection performance of AC-CPE against Cd²⁺ ions, an optimization study was carried out to determine the following optimal conditions, pH=5, preconcentration time of 120s, and deposition potential of 1.2V. Under these optimal conditions, a linear relationship between current peak intensity and concentration has been defined over a concentration range from 5.10⁻⁴ to 5.10⁻⁷M; with detection limit (DL, 3 σ) of 3, 04.10⁻⁶M. An analytical application of the electrode in a real matrix, tap water, was performed and revealed good detection performance of AC-CPE. These results show that the AC-CPE can be used as an excellent detector of Cd²⁺ ions in aqueous solution.

Keywords: Cadmuim (II), coal , argan oilcake waste , square wave voltammetry, Tape water

1. Introduction

Mineral pollutants, essentially heavy metals, are major environmental contaminants that causes serious ecological problems [1,2]. Among these metal cations, cadmium is the most toxic cumulative poison. It inhibits cellular respiration and a number of fundamental enzyme mechanisms [3,4]. The maximum allowable cadmium levels in drinking water are 0.003 mg/L according to European, American and World Health Organization standards [5]. Cadmium detection is becoming a major concern for various researchers. To limit cadmium aggression on ecosystems and humans [6], it is necessary to develop early detection tools capable of detecting Cd^{2+} ions quickly, and which have a relatively low cost. [7, 11] For this purpose, several electrochemical techniques have been developed for the detection of cadmium in the aqueous phase [9], including AAS, ICP-AES or ICP-MS and square wave voltammetry (SWV) as an electrochemical technique using electrochemical sensors, which is one of the most favorable techniques for the determination of trace concentrations of heavy metals in liquid matrices due to its high sensitivity, ease of use and low cost compared to the other techniques mentioned above [13, 17]. In addition, the essential requirement to ensure selectivity of the electrochemical procedure is to use selective modifiers that show a high affinity for the target ion [12]. For this, in voltammetry, the choice of a suitable material for the modification of the electrode is very important. The desired properties of electrode materials include high selectivity, sensitivity, reproducibility, and long-term stability. In addition, the material must be environmentally friendly, inexpensive and easy to produce [18, 19].

In this work, a new electrochemical sensor has been developed by incorporating coal from argan waste into a carbon paste electrode (AC-CPE), in order to recycle this organic waste and at the same time, remedy to the problem of detecting cadmium traces in aqueous medium. The AC-CPE electrode can detect Cd^{2+} ions from aqueous solution, forming complexes with these ions and significantly increasing the sensitivity of its detection, the experimental data shows that AC-CPE represents a very high sensitivity, selectivity and reproducibility to Cd^{2+} ion detection. On the basis of the conducted research, the use of a carbon paste electrode (CPE) modified with coal from argan waste has not been reported for the detection of Cd^{2+} ions until now. Therefore, first, a modified CPE with coal from argan oilcake waste (AC/CPE) was made, and all parameters that can have an effect on the intensity detection of Cd^{2+} (including instrumental and chemical parameters) were optimized.

2. Experimental

2.1. Materials

Acetic acid and sodium acetate from Merck, cadmium sulphate, NaOH was from Sordalab brand, graphite powder was purchase from Lorraine (99% purity). The raw biomass of argan oilcake waste was collected from Sous Massa region (Agadir Region - Morocco). All solutions were prepared with distilled water

2.2 Methods

The raw biomass of argan oilcake waste was carbonized in a furnace by ISUNI SP95h. The Purity of coal extracted from raw argan oilcake waste bio-mass and the percentage of active groups are determined by FTIR analysis using the BRUKER-TENSOR 27 infrared spectrophotometer. A SIEMENS D500 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) was used for X-ray powder diffraction (XRD). The morphology of the product was carried out by the FEI ESEM Quanta200 environmental scanning microscope. The electrochemical investigations were performed with VMP3 Biologic potentiostats monitored by the EC-lab software. The Electrochemical system consists of three electrodes, a platinum electrode as counter electrode (CE), a saturated calomel electrode as reference electrode (RE)

and a modified carbon paste electrode as working electrode (WE). The pH values of the electrolyte solution have been adjusted by a pH meter of the brand HANNA 210.

2.3. Preparation of coal from argan oilcake

The raw biomass of argan oilcake waste was manually chosen, cleaned with deionized water and dried at 60 °C. The coal was prepared from argan oilcake waste by carbonization under air at 600 °C for 2h. The experiment was firstly started at 25 °C until 600 °C [15], with a yield that reached 81,9 % it was calculated by the following equation :

$$R\% = (M_i - M_f) / M_i \times 100$$

M_i : initial mass(g).

M_f : final mass(g).

2.4. Preparation of the modified AC-CPE electrode.

The modified carbon paste electrode was prepared by mixing proportionally 25% (w/w) paraffin oil and 75% (w/w) coal/graphite in an agate mortar until a homogeneous and smooth paste was obtained. The obtained homogeneous paste was compacted into an insulin syringe with a cross-section of 1.34 mm. Electrical contact is made with copper wire. Before use, the electrode surface was polished with abrasive paper (E320) and thoroughly rinsed with distilled water. An unmodified electrode was also prepared following the same protocol with the proportions of 25% (w/w) paraffin oil and 75% (w/w) of pure graphite.

2.5. Procedure

An Argan oilcake waste coal electrode is introduced into an electrochemical cell containing 40 mL of acetate buffer (0,2M) and a fixed concentration of cadmium(II) at (pH=3.45). Before each electrochemical measurement, the electrode was removed rinsed and dried with adsorbent paper. All experiments were repeated three times and performed at room temperature. The choice of electrolyte is made after testing several buffer solutions (Robinson, acetate, HCl, phosphate). The Electrochemical behavior of cadmium (II) ions adsorbed on Argan oilcake waste coal electrode surface was firstly studied by cyclic voltammetry and SWV. Optimal conditions were obtained by measuring peak currents in accordance with all following parameters (scanning speed, frequency, amplitude, deposition potential, buffer solution, mass percentage, presentation time, pH and electrolytic medium). These conditions will be applied to evaluate the performance and efficiency of our electrode to detect Cd^{2+} in different media such as: tap water from our laboratory.

3. Results and discussions

3.1. FTIR Characterization.

FTIR spectroscopy was performed to characterize the coal from argan oilcake waste (**Figure1**), this spectrum shows the presence of numerous functional groups on the surface of the prepared coal. The peaks observed, at 2970 cm^{-1} , 2920 cm^{-1} and 2848 cm^{-1} correspond to the symmetric and asymmetric C–H stretching vibration of $-\text{CH}_2$ and $-\text{CH}_3$ groups [16]. The Peaks at 1393 cm^{-1} and 1320 cm^{-1} correspond to O–H strong deformation in the plane and the peaks from $1300-1050\text{ cm}^{-1}$ correspond to C–O elongation. [9]

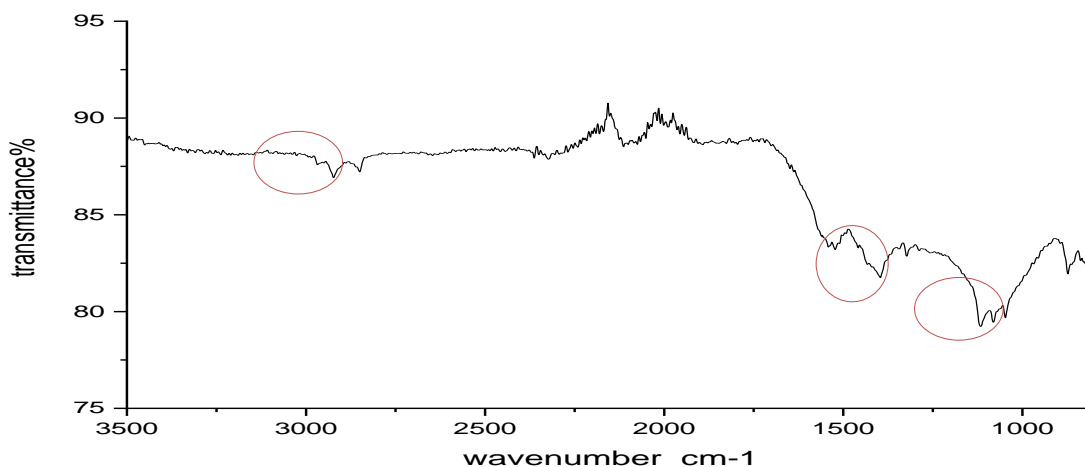


Figure 1: Infrared spectroscopy of argan oilcake waste.

3.2. XRD characterization.

According to the structure of the spectrum (**Figure2**) the structure of the coal is an amorphous but incomplete structure, i.e. some particles have semi-amorphous phases, peak is present in about $2\theta = 20^\circ$ which is rewarded to the turbostratic carbon phase.[17]

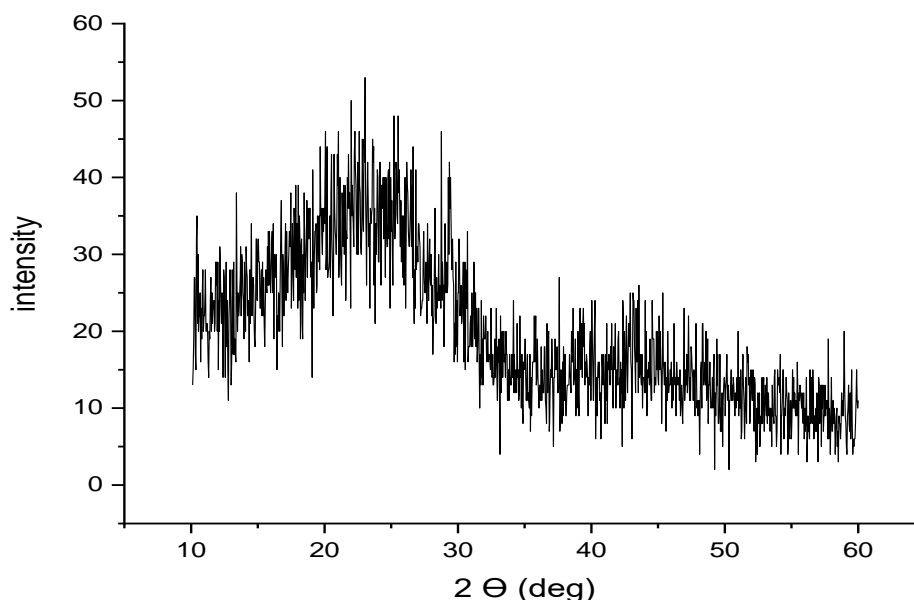


Figure2: XRD of argan oilcake waste

3.3. SEM Characterization.

Images obtained after scanning electron microscope (SEM) characterization are shown in (**Figure 3**). The observation of these images shows a difference in morphology on the surface of the prepared electrodes. The surface of the CPE shows uniformly distributed leaves. whereas after the modification of the electrode with argan coal, the morphology of the surface changed and became uneven. [9].

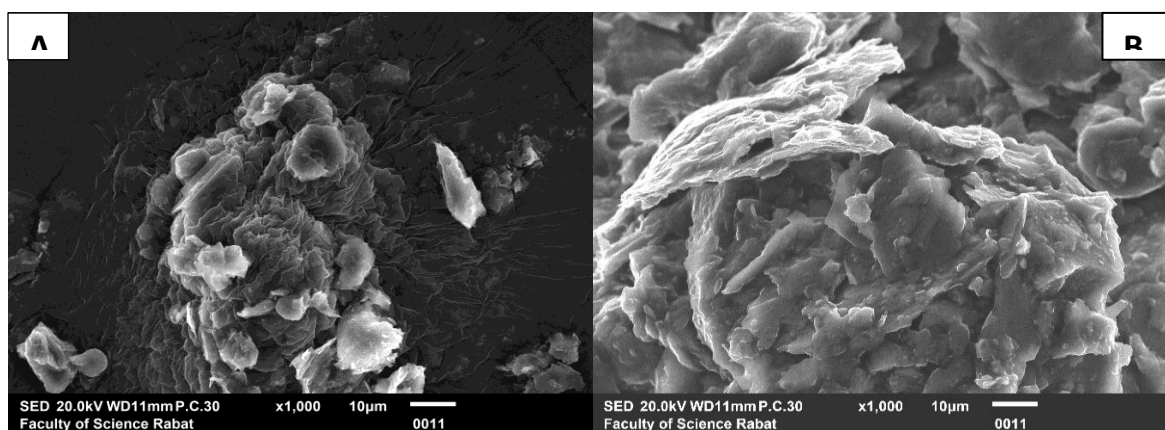


Figure 3: SEM images of (A) Graphite only, (B) Graphite modified by coal from argan oilcake waste.

4. Preliminary electrochemical study

4.1. Study by cyclic voltammetry (CV) and Square wave voltammetry (SWV)

The detection of (10^{-3} M) Cd^{2+} ions in acetate buffer solution at ($\text{pHi} = 3.45$), has been investigated on a carbon paste electrode (CPE) and another one modified by coal from argan oilcake waste (50% AC-CPE), by cyclic voltammetry (CV) and square wave voltammetry (SWV) at a potential range from -1V to 0V and then reversed to the initial potential at a sweep rate of 20mV/s. On the unmodified carbone paste electrode (CPE) surface, cadmium undergoes a reaction of oxidation /reduction, at anodic peak awarded to cadmium oxidation nearby -0.68V and cathodic peak is awarded to cadmium reduction proximity -0.84V (**Figure 4**). the incorporation of argan oilcake coal into the carbon paste electrode (AC-CPE) the result shows an anodic peak attributed to cadmium (II) oxidation at -0.63V and a cathodic peak attributed to cadmium (II) reduction at a potential of nearby -0.87V. The cyclic voltammograms obtained before and after modification represent a reversible system. This behavior is due to the high adsorbency properties of coal from argan oilcake waste[18]. The scan rate effect has been studied on the anodic and cathodic peak current. the peak currents increase linearly with the increase of scan rate from 10 mV/s to 100 mV/s. The linear relationship between the peak current and the scan rate was obtained with the linear regression equation as below: $I_a = 0,0604v + 0,5198$ and $I_c = -0,0645v - 0,1456$, ($R=0.993$) respectively. This result indicates that the electrochemical reaction of cadmium on the surface of AC-CPE undergoes a controlled diffusion process as (**Figure5**) shows.

(**Figure 6**) combines the results of square wave voltammetry, obtained for the responses of unmodified and modified carbon paste electrodes (CPE and AC-CPE), the voltammogram obtained shows an increase in the intensity of the current on AC- CPE against CPE up to 2600 μA , this result is explained by the strong electrocatalytic properties of AC-CPE.

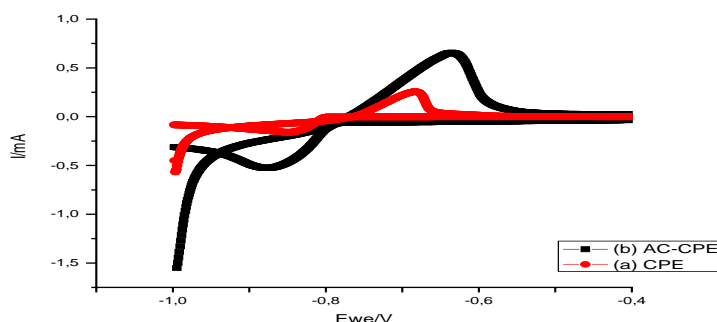


Figure 4: Cyclic voltammograms at acetate buffer solution (0,2M), (pHi=3.45) containing 1×10^{-3} mol.l⁻¹ of Cd²⁺, scanning rate 20mv/s on electrodes (a) CPE (b) AC-CPE.

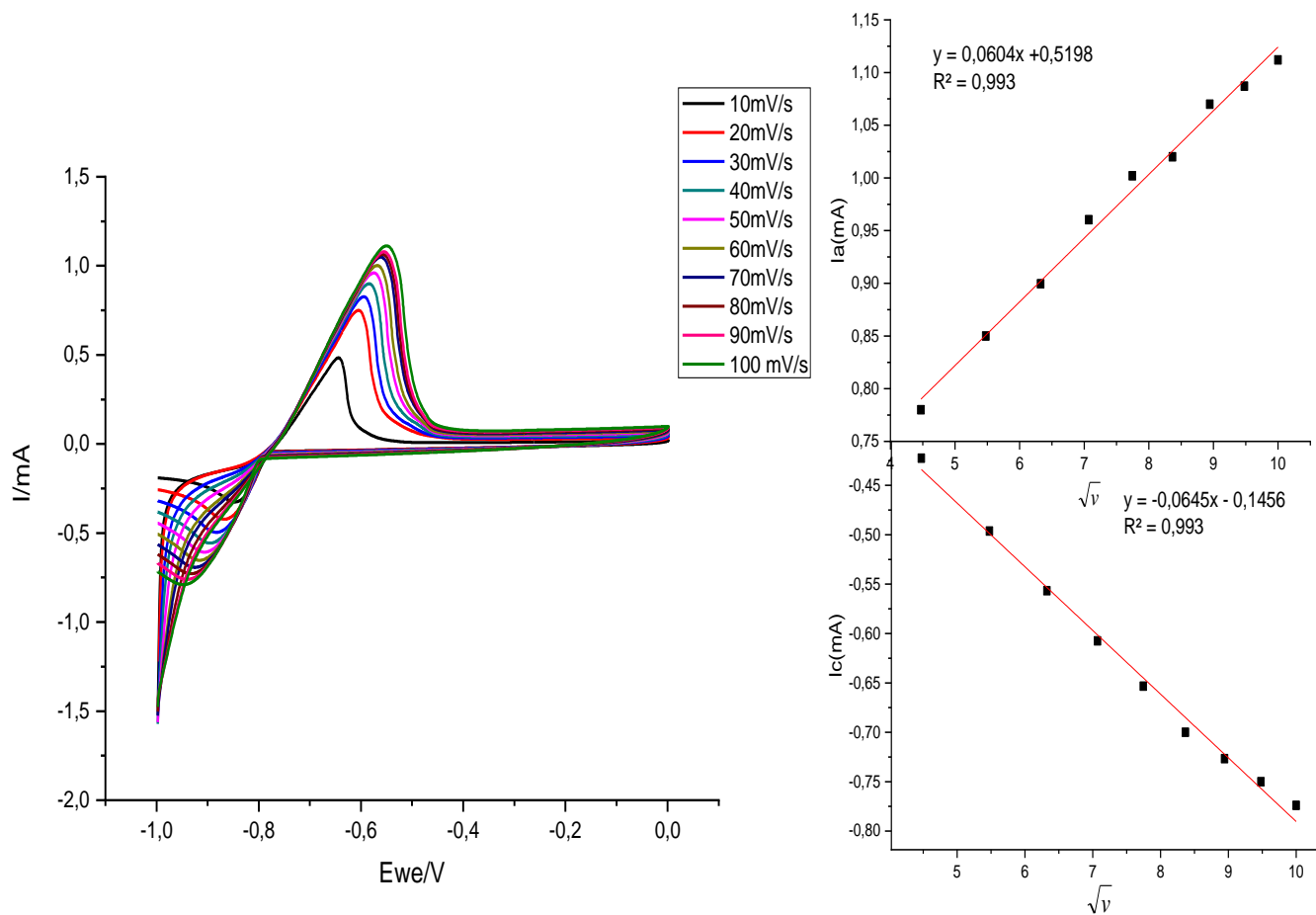


Figure 5: Effect of scanning rate on Cd²⁺ ion peak intensities (10^{-3} M), in a buffered acetate solution (0.2M)

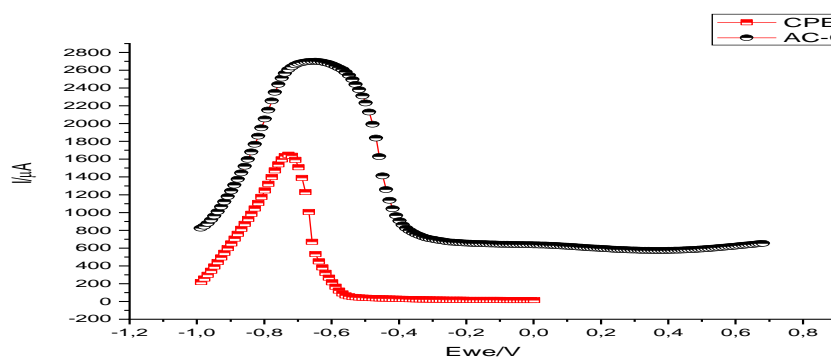


Figure 6: SWV response of Cd^{2+} (10^{-3}M), in 0.2 M acetate electrolyte solution, $\text{pH}=3.5$, preconcentration time =20s, deposition potential =-1V, frequency =50hz . (a) electrode before modification(b) electrode after modification with coal from argan oilcake waste.

4.2. Optimisation of experimental conditions

For obtaining the best conditions for the SWV determination of the target metal Cd^{2+} ions on argan coal electrode (AC-CPE) all measurements were performed in an electrolytic solution containing $1.0 \times 10^{-3} \text{ mol.L}^{-1}$ of Cd^{2+} ions. Different experimental conditions, such as, buffer solutions, deposition time, deposition potential, amplitude, frequency, pH, percentage modifier, Cd^{2+} ions concentration, were studied. First (**Figure 7 A**) shows the influence of the nature of buffer solutions on the current response using different electrolytic solutions, including hydrochloric acid (0.2M), phosphate (0.2M), acetate (0.2M) and Robinson (0.2M) buffer solutions. The highest current intensity was recorded in the acetate buffer solution. It was chosen as the optimal electrolyte medium for the rest of the work. Thus, the effect of deposition time on the current intensity has been studied on the AC-CPE electrode (**Figure 7 B**) in a range from 20s to 160s. It is clear that a variation of deposition time causes a variation in current intensity. up to 120 s the peak current were instable and not clear, this is due to saturation of electrode active sites by Cd^{2+} ions. Therefore, 120s is selected as the optimal deposition time for the rest of the work [19]. Then, the impact of deposition potential on signal strength was investigated by varying the deposition potential from -2000 mV to 0 mV (**Figure 7 C**). When the potential has been lowered to -1200 mV, there was an increase in Cd^{2+} ions detection at the electrode surface resulting an increase in current intensity. After the potential of -1200mV a strong decrease of the current intensity was been noticed. This is mainly due to the reduction of hydrogen to such high potential. Hydrogen bubbles can interfere with metal deposition on the electrode surface[20]. So -1200mV is selected as the optimal deposition potential for the rest of the work. Indeed, In order to maximize current intensity with good resolution and minimum peak width, amplitude and frequency have been optimized. The amplitude was optimized by varying amplitude from 50mV to 350mV (**Figure 7 D**), while the frequency varied from 10 Hz to 100 Hz. (**Figure 7 E**). According to the results obtained, shows an increase in current intensity with increasing amplitude until reaching a value of 350mV after this value the voltamograms become poorly resolved and less representative, For that an amplitude of 350mV was selected as optimal. Similarly, when the frequency varies, an increase in current intensity was observed. When the frequency reaches 40Hz, the current intensity is at its maximum. After this value, the current intensity starts to decrease. So 40 Hz was selected as an optimal frequency for this study.

Under variation of pH, the AC-CPE electrode was tested in an acetate buffer (0,2M) solution with different pH values ranging from (4 to 8) at a constant stirring speed. The result shows a maximum response at pH 5.0 (**Figure 7 F**). Selecting a pH value below 5.0 would attenuate the electrode signal due to a decrease in the amount of Cd^{2+} extracted by the electrode. Its can be attributed to the protonation of nitrogen fractions at selective sites of AC-CPE, which would weaken the interaction of Cd^{2+} ions with nitrogen fractions. On the other hand, higher pH values (above 5.0) can significantly decrease the electrode signal, as Cd^{2+} ions would precipitate as hydroxide sediments at higher pH levels. The optimum pH value for the devised approach was found to be 5 [20] Finally, It is clear that using an electrode with a different amount of argan coal can obviously influence the current intensity of Cd^{2+} ions detection. (**Figure 7 G**) illustrates the results obtained by varying the percentage of the modifier (argan coal /graphite, w/w) the electrode response is modified according to the percentage of coal used, a better detection was observed at a percentage of 10% of argan coal, The peak currents decreased significantly when a quantite more than 10 % of (coal argan, w/w) is used in the electrode preparation, this probably due to the electron transfer blockage by the modifier,

which reduces the conductive area of the electrode surface .Therefore the percentage of 10% of argan coal was chosen as the optimal value for the rest of the work.

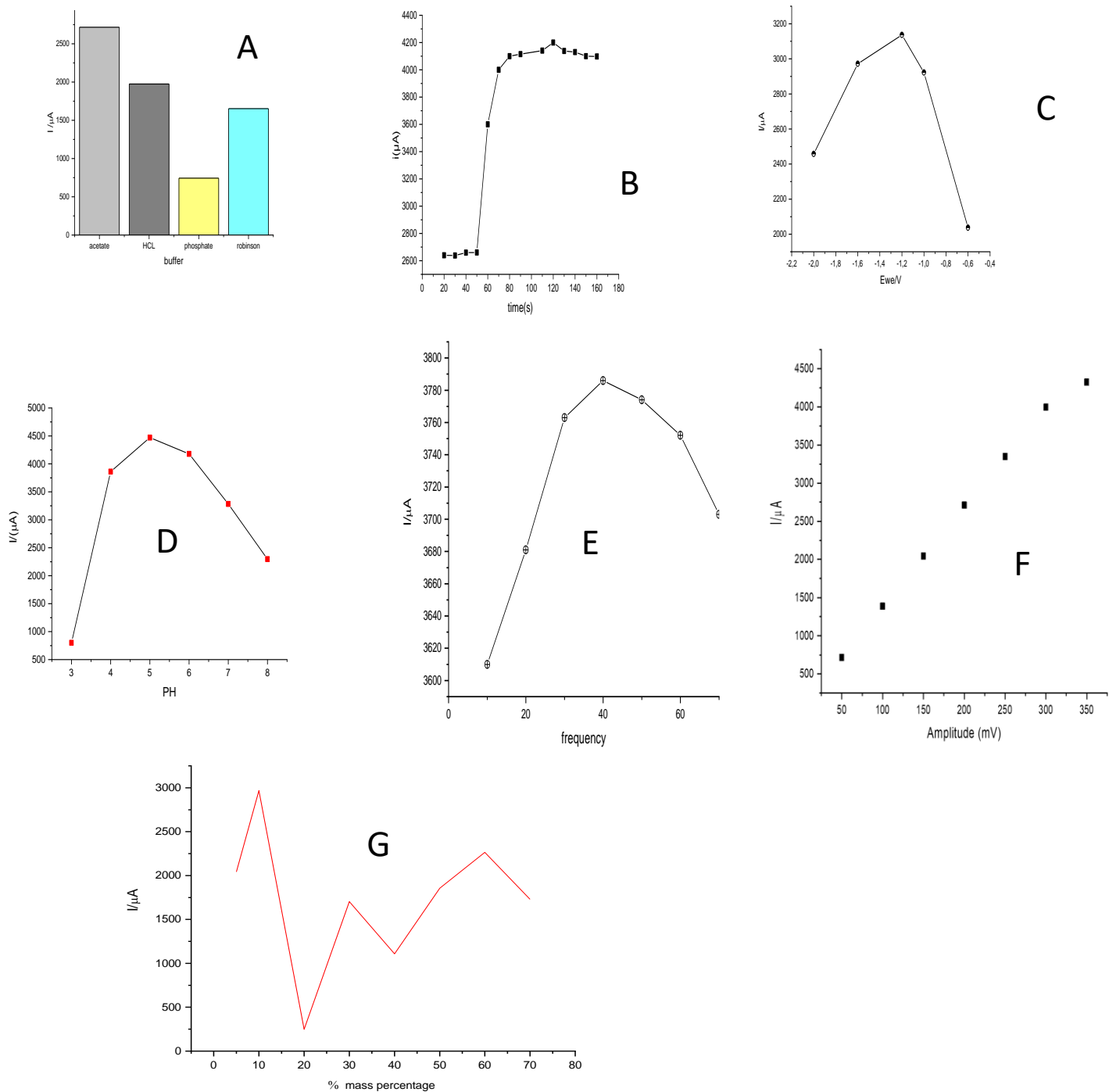


Figure 7: effect of experimental variables (buffer solution (A),deposition time (B),deposition potential(C),pH value (D),frequency (E), Amplitude (F),mass percentage (G)), on the response of (AC-CPE) in the presence of $1.10^{-3}M Cd^{2+}$.

4.3. Calibration curve

To determine the analytical performance of the AC-CPE electrode, its detection was evaluated in the presence of several Cd^{2+} ions concentrations from $5.10^{-4}M$ to $5.10^{-7}M$ (**Fig 8**) under the optimal conditions previously described above: electrolyte solution (acetate buffer), deposition time of 120s , deposition potential -1,2V , amplitude 350 mV , frequency 40Hz, pH 5, mass percentage(10%). It can be seen that calibration plots of peak current vs. concentration show a linear dynamic range and the current intensity increases linearly with variation of concentration following The linear regression equation below

$$I = 21.335[Cd^{2+}] + 185.98$$

With a correlation coefficient in order of 0.97. The detection limits are calculated from the standard deviation, equation, for the analytical blank of $5.10^{-5}M$ after three repeat measurements ($n=3$), or the $LOD = 3.04.10^{-6}M$ and $LOQ = 5.15.10^{-7}M$

By comparing these values with the literature (**table 1**), it can be seen that using coal from argan oilcake as a modifier increases the sensitivity and repeatability of the electrode. It is a safe and inexpensive alternative for Cd^{2+} ions detection, even in trace values. The standard deviation (σ) of the analytical blank is measured at the oxidation potential of Cd^{2+} ions for three repeats according to equation 1 [21]:

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=0}^n (I_i - I_m)^2}$$

or:

n : Number of repetitions.

I_i : Experimental value of each measurement.

I_m : Arithmetic mean calculated at the same concentration.

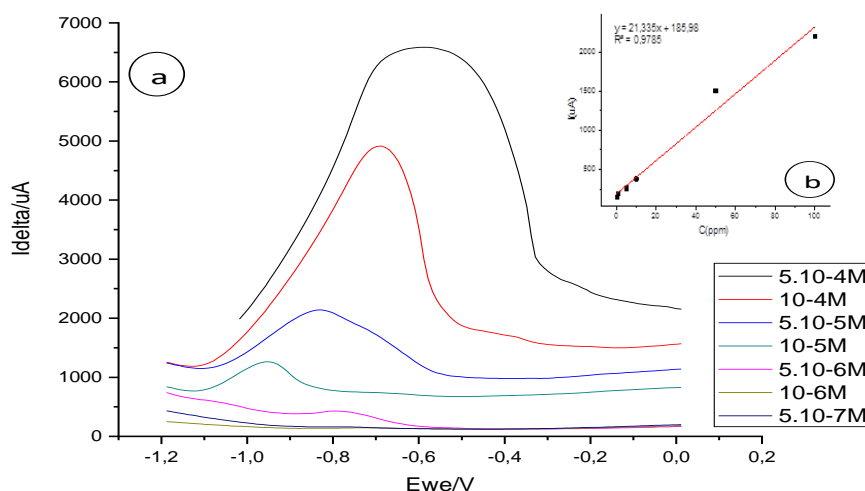


Figure 8: (a)SWV voltammograms of Cd^{2+} detection on AC-CPE for different concentration recorded at optimal condition (b)calibration curves of the stripping peak currents vs different concentrations of Cd^{2+} in acetate buffer.

Table 1: Comparison of the performances of some cadmium(II) electrochemical sensors.

Electrode	Detection limit	reference
SWCNTs/Biomass	0,1 μM	[8]
MPc	347.06 nM	[11]
Polyvinylchloride	8×10^{-7} M	[12]
AC-CPE	3.06 μM	This work

5. Interference study

(Figure 9) shows the effect of other metal ions present in solution on the anodic current peaks of Cd (II) ions, assuming that the variation in current response is less than 10% as (Table 2) shows. No effect on the detection of Cd (II) was observed for 10 fold of Cu (II), Ni (II), and Mn (II). The results of the interference study can be justified by the hard-soft acid base theory. The main binding sites in coal from argan oilcake waste are the COOH and OH groups, which are hard bases, while the metals Cu (II) are intermediate; Ni (II), and Mn (II) are soft acids. According to the theory of hard-soft acid bases, hard acids tend to form complexes with hard bases, and soft acids tend to form complexes with soft bases. Because copper is strongly bonded to the electrode surface, it is the metal that interferes the most with Cd (II)ions [22]

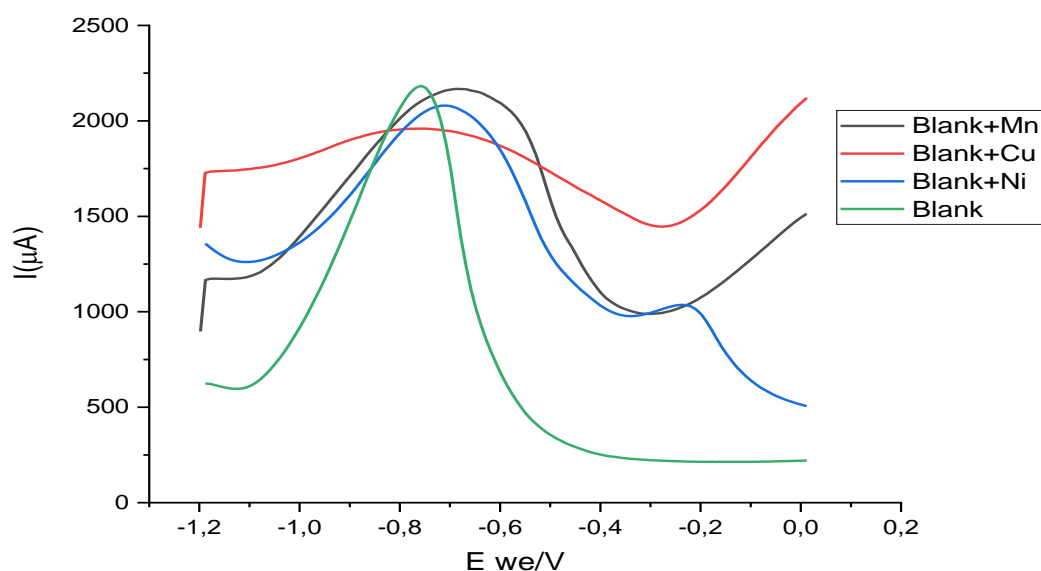


Figure 9: SWV response relative to 0,1mM of Cd^{2+} on AC-CPE in 0.2 M acetate buffer, (pH=5) with 10 fold of interfering ions (Mn^{2+} , Cu^{2+} , Ni^{2+}).

Table 2: current peak deviation of Cd^{2+} ions in the presence of interfering ions

Interfering ions	Current peak deviation % $(I_{\text{blank}} - I_{\text{blank+interfering}} \times 100) / I_{\text{blank}}$
Cu^{2+}	7.4%

Ni^{2+}	5.45%
Mn^{2+}	0.64%

6. Analytical application of the prepared electrode

6.1. Application in tap water

Under the optimum conditions already studied, the analytical performance of the AC-CPE was evaluated by the standard addition protocol of Cd (II) to acetate buffer. The support electrolytes were prepared by the addition of (0.2 mol.L^{-1}) acetate buffer to fresh water. The electroanalytical curves were obtained by using square wave voltammetry (Figure 10). A linear relationship was observed between the analytical signal and the cadmium concentration ranging from $8 \cdot 10^{-6}$ to 10^{-7} . The result equation is: $I = 31.21 [\text{Cd}^{2+}] - 1.154$ with an effective correlation of 0.99. The detection limit is estimated at about 10^{-7} M . ($S/N=3$) after 120 s of accumulation.

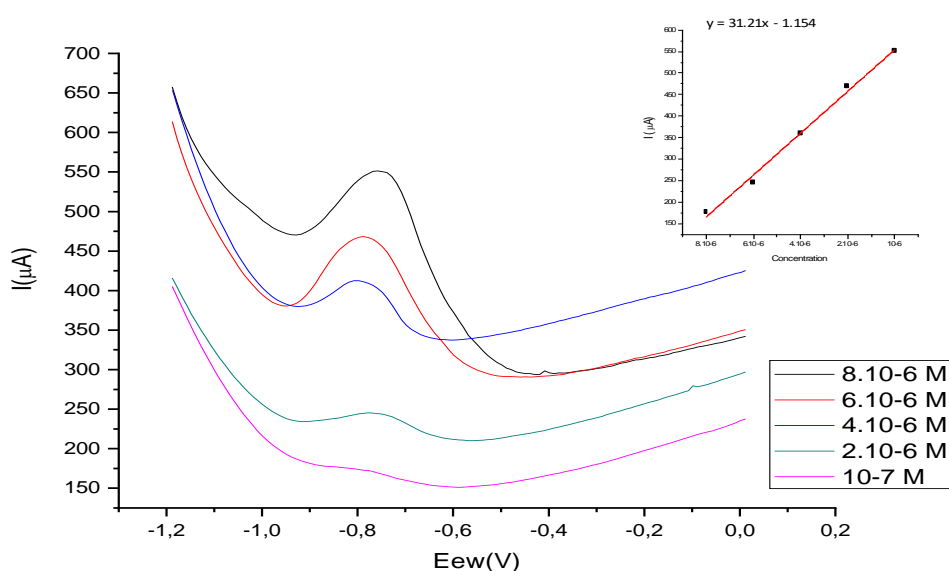


Figure 10: SWV voltammograms and calibration curves of Cd^{2+} detection on AC-CPE in 0.2 M acetate buffer, ($\text{pH}=5$) for different concentration under optimal condition, application in tap water

7. Conclusion

Square wave voltammetry was performed for the determination of cadmium (II) on an Argan Coal modified carbon paste electrode. The sensitivity of this electrode for determination of cadmium ions opens the possibility to consider the argan coal modified carbon paste electrode as a good alternative electrode. This electrode is characterized by good sensitivity associated with satisfying reproducibility. Moreover, coal presents the advantage of being more 'environmentally-friendly' than mercury, the toxicity of which will probably lead to progressive use of this electrode material for on-site monitoring of trace pollutants. The proposed methodology has a wider linear range and lower detection limit and is not interfered with significantly by other metal ions. The modified electrode was successfully applied to water samples. The electrode construction was extremely simple and low cost.

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