

A Sensitive Electrochemical Sensor Using a Dolomite-Graphite Composite for the Simultaneous Detection of Pb²⁺ and Cd²⁺

Manni, Ahmed**

Laboratory of Physical Chemistry, Materials and Catalysis (LCPMC), Geomaterials and Materials for Energy Team, Faculty of Sciences Ben M'Sick, Hassan II University of Casablanca, MOROCCO.

Maallah, Raja

Team of Molecular Electrochemistry and Inorganic Materials, Faculty of Sciences and Technology, Sultan Moulay Slimane University of Beni Mellal, MOROCCO

El Haddar, Abdelilah

Laboratory of Applied Geosciences, Faculty of Sciences, University of Mohammed I, Oujda, MOROCCO

Chtaini, Abdelilah

Team of Molecular Electrochemistry and Inorganic Materials, Faculty of Sciences and Technology, Sultan Moulay Slimane University of Beni Mellal, MOROCCO

Harrati, Achraf

Laboratory of Physical Chemistry, Materials and Catalysis (LCPMC), Geomaterials and Materials for Energy Team, Faculty of Sciences Ben M'Sick, Hassan II University of Casablanca, MOROCCO

Sair, Said

MAScIR Foundation, VARENA Center, Rabat Design, Rue Mohamed El Jazouli, Madinat Al Irfane, Rabat 10100, MOROCCO

El Bouari, Abdeslam

Laboratory of Physical Chemistry, Materials and Catalysis (LCPMC), Geomaterials and Materials for Energy Team, Faculty of Sciences Ben M'Sick, Hassan II University of Casablanca, MOROCCO

El Amrani El Hassani, Iz-Eddine

Department of Earth Sciences, Scientific Institute, University Mohammed V, Rabat, MOROCCO

Sadik, Chaouki

Laboratory of Physical Chemistry, Materials and Catalysis (LCPMC), Geomaterials and Materials for Energy Team, Faculty of Sciences Ben M'Sick, Hassan II University of Casablanca, MOROCCO

*To whom correspondence should be addressed.

+ E-mail: ahmedmannii@gmail.com

1021-9986/2023/10/3422-3434

13/\$/6.03

ABSTRACT: A sensitive electrochemical method for the detection of trace heavy metal ions such as lead Pb (II) and cadmium Cd (II) using a Carbon Graphite Electrode (CPE) chemically modified by a dolomite powder was applied. Firstly, local Moroccan dolomite was deeply characterized in order to understand its chemical composition and morphological structure. The performance of this sensor is revealed by three electrochemical methods: Square Wave Voltammetry (SWV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The effect of preconcentration time, concentration effect, media pH, and interference ionic response to the electrochemical response of the working electrode were all investigated under various experimental settings. The SWV determination coefficient (R^2 (Pb (II)) = 0.8385 and R^2 (Cd (II)) = 0.9307) is lower than the cyclic voltammetry result (R^2 (Pb (II)) = 0.989 and R^2 (Cd (II)) = 0.977), showing the latter's superior predicting ability. Even in the presence of interfering ions, the suggested electrochemical sensor exhibits good repeatability and selectivity, with detection limits of 0.10113 μM and 0.22227 μM for Pb^{2+} and Cd^{2+} , respectively. These values obtained from the calibration curves of the substances studied reveal that the developed sensor showed excellent electroanalytical performances for the detection of heavy metal ions. According to Atomic Absorption Spectroscopy (AAS), the prepared electrode from CPE-dolomite showed a highly sensitive capacity toward cadmium detection with a content of 178.43 mM was detected after mineralization of the electrode immersed in CdSO_4 solution. The same electrode has been used to reduce the lead in which the resulting solution was analyzed involving a value of 125.23 mM.

KEYWORDS: Electrochemical sensor; Carbon graphite (CPE); Dolomite; Lead (Pb); Cadmium (Cd).

INTRODUCTION

Heavy metals such as cadmium (Cd) and lead (Pb) exist naturally in varying concentrations in the earth's crust. Thus, they are omnipresent in the environment where they are found in ionic forms, in compounds or complexes, which are generally inoffensive to living organisms. However, an insufficient or too high concentration of a given metal in its bioavailable can harm ecosystems and the health of living beings, particularly the central nervous system, the kidneys or liver, skin, and bones [1-10]. Therefore, there is an urgent need to develop sensitive, rapid, and simple analytical methods for the simultaneous determination of Cd^{2+} and Pb^{2+} . In comparison to the widely used Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), electrochemical detection offers a number of advantages, including easy handling, low cost, suitability for on-site monitoring, and readily available equipment. Numerous electrodes have been developed as of late for the simultaneous measurement of Cd^{2+} and Pb^{2+} [11-14].

On the other hand, the dolomite of the chemical formula $\text{MgCa}(\text{CO}_2)_2$ has very interesting properties that will influence the performances of the measurement like the mechanical thermal properties and the chemical inertia. Furthermore, the advantageous properties of dolomite ($\text{MgCa}(\text{CO}_2)_2$) are attributed to its ability to form "complexes" with heavy metals [18-20]. A common approach is to integrate carbon materials, such as graphite. Moreover, graphite has a wide variety of properties and uses. This mineral is sought after for its electrical and thermal conductivity, softness, chemical inertness, heat resistance and lubricity. This combination of physical properties enables graphite applications in a wide range of technological fields such as nanoelectronic devices, capacitors, and sensors [21-26].

In this context, chemical sensors have gained increasing interest in heavy metal detection due to their advantages of fast analysis speed, simple instrumentation, low costs, and high sensitivity. Many studies have been carried out on chemical sensors using a combination of materials-carbon composite [27-34]. In this work, we developed a new electrochemical sensor based on Carbon Graphite Paste (CPE) functionalized with dolomite for the electroanalysis of Pb^{2+} and Cd^{2+} in solution by cyclic

voltammetry, square wave voltammetry and EIS. The search for optimal parameters, such as the best CPE/dolomite ratio (mass for mass), the best preconcentration time, the best scan speed, the ideal solution pH value, and the ionic concentration giving the best running response, was carried out. In addition, the interference effect and the performance and stability of the modified CPE-dolomite electrode were also studied. To evaluate the performance of the proposed analytical methodology the detection of heavy metals by the prepared electrode was tested in a real sample, such as tap water, without any pretreatment and under the optimal conditions.

EXPERIMENTAL SECTION

Raw materials

The dolomite material used in this work was the subject of previous work, which this substance was selected from the Boudkek deposit, which is located on the left side of the Oued Bouhya in the Rif of Morocco [20] in which, The raw sample taken in the carrier are crushed and dried in the open air, then steamed at 110°C for 24 hours. The dry materials are introduced into jars into which balls of various diameters are added. The whole is crushed for 30 min. The obtained powder is homogenized and then sieved to recuperate the size fraction $< 63\mu\text{m}$. The substance used in this study are analytically trustworthy, therefore they haven't been previously purified. Moreover, the binder used (paraffin oil) and Carbon paste electrode was supplied by (carbon, Lorraine, ref. 9900, French). $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2$ are obtained from Merck chemicals. Deionized water was used to prepare all solutions. Finally, the ultrapure sodium sulfate Na_2SO_4 used comes from Scharlau Chemie.

Characterizations

Chemical composition was determined by XRF using Bruker S8 Tiger X-ray spectrometer with wavelength dispersive detector (WD-XRF) equipped with an anticathode. The electrochemical experiments were carried out by a voltalab potentiostat (PGSTAT 100 model, Eco Chemie B.V., Utrecht, The Netherlands) controlled by the voltalab master 4 software. The dolomite-modified carbon paste electrode was used as working electrode, the saturated calomel electrode as reference electrode and a platinum plate was used

as a counter electrode. The pH meter (Copenhagen, PHM210, Tacussel, French) was used to adjust the pH values.

Preparation of chemical sensor

The Electrode was prepared by thoroughly mixing the dolomite powder (50%) with the carbon graphite powder (50%) using 0.36 mL paraffin oil, and thoroughly hand-mixing in a mortar and pestle. Subsequently, the resulting composite material was manually inserted into the cylindrical cavity of the electrode body (geometric surface of about 0.1256 cm^2). Electrical contact is established with a carbon rod. By dissolving 0.1598 g of lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in deionized water and then diluting to 1000 mL, a solution of Pb ions was obtained. Similar steps were taken to produce the cadmium solution, which was obtained by dissolving 0.16 g of $\text{Cd}(\text{NO}_3)_2$ in ultrapure water and then diluting to 1000 mL which on the one hand $0.242 \times 10^{-6}\ \mu\text{mol/L}$ of lead (II) and on the other hand $0.259 \times 10^{-6}\ \mu\text{mol/L}$ of cadmium (II).

RESULTS AND DISCUSSION

Characterization of raw dolomite

The chemical composition obtained by XRF (Table 1) showed a variable composition with the presence of several major chemical elements of the dolomite. This raw material generally consists of 28.73% CaO, 26.63% MgO and 40.34% fire loss due to the high carbonate content. The main undesirable impurities in the carbonate rocks are silica, K_2O , Na_2O , Fe_2O_3 and alumina. These types of impurities combine with calcium oxide at elevated temperatures to form a slag, which reduces the pore volume and the amount of available active lime [35]. Such impurities are either present in the matrix or are derived from material in crevices and other strata excavated with the limestone. Sample was selected from a career in which these impurities were low.

Fig. 1 shows the SEM micrographs on dolomite powder in which the results reveal a clearer and more apparent automorphic crystalline form. Noted that the rhombohedral aspect structure of the crystals of dolomite, as well as the edges of these crystals that are sharp ($100\ \mu\text{m}$). It can be also observed the micro porosity, which appears on the images as dark gray areas in different fractions of $10\ \mu\text{m}$, $50\ \mu\text{m}$ and $100\ \mu\text{m}$ (Fig. (2.a, 2.b, 2.c)). At the texture level, there is color homogeneity, indicating that the dolomite matrix shows a higher calcium and magnesium content in the gray areas. In addition, we can draw that the $10\ \mu\text{m}$

Table 1: Chemical composition of dolomite in oxides (% Wt)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	MnO	LOI (*)
Dolomite	3.06	2.96	0.13	26.63	28.73	0.06	0.19	0.02	0.01	38.34

LOI (*): Loss on ignition at 1000 °C

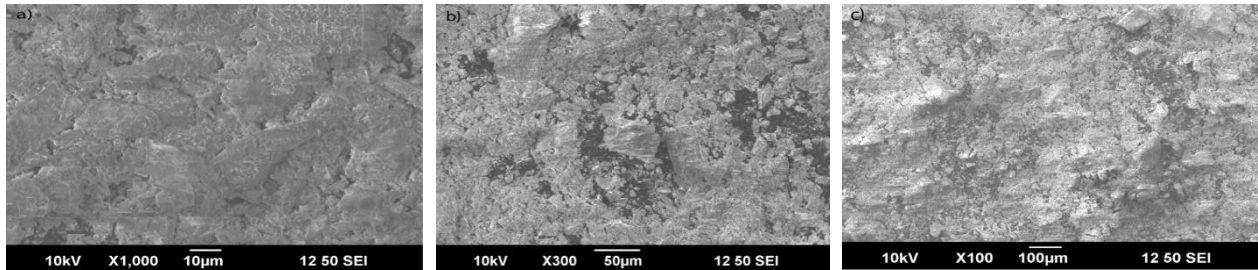


Fig. 1: SEM images of the raw dolomite powder of different scales of the 100 µm granular fraction

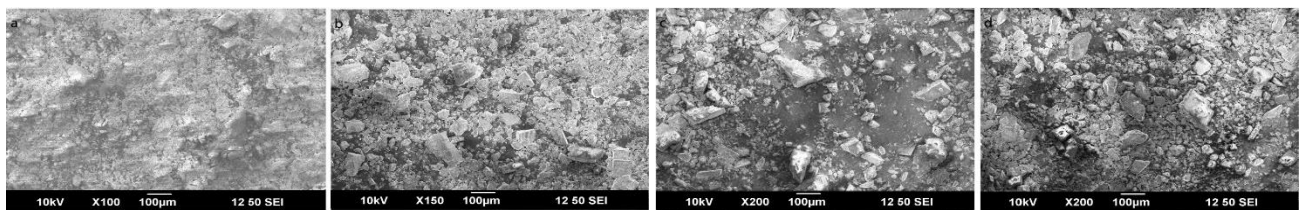


Fig. 2: SEM images of raw dolomite powder. (a): fraction of 10 µm, (b): fraction of 50 µm, (c): fraction of 100 µm

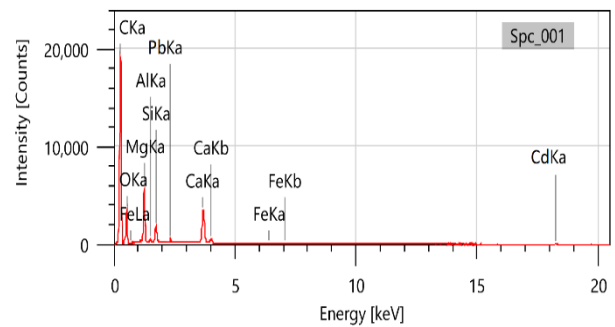
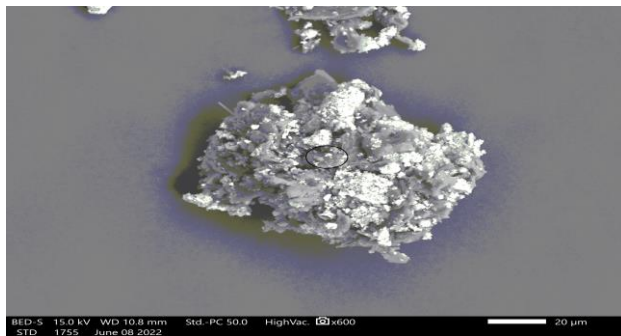


Fig. 3: SEM micrographs of CPE-dolomite electrode coupled with EDS analysis

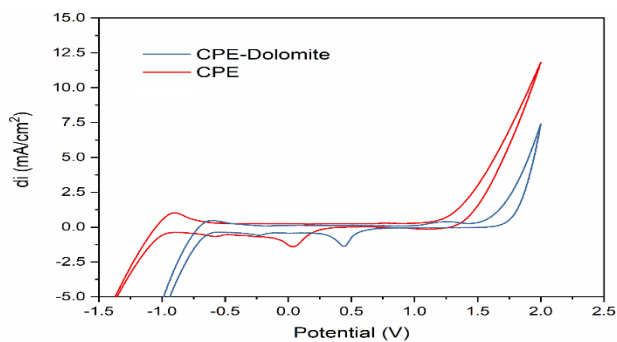


Fig. 4: Behavior of electrodes CPE and CPE-dolomite by cyclic voltammetry

granular fractions of dolomite have very fine small grains with great compactness (Fig.2-a). Fig. 3 shows the scanning

electron microscopy image of the CPE-Dolomite in the presence of Pb (II) and Cd (II). Carbon paste modified with the dolomite ($\text{CaMg}(\text{CO}_3)_2$), shown a uniform surface with homogenous dispersion, also, the particles shows non-uniform and irregular grey grains appear surrounded by a black graphite flakes. In addition, the EDS data confirmed and justified the good results obtained which we found small traces of lead (Pb) and Cadmium (Cd).

Electrochemical behavior of CPE-dolomite

Fig. 4 represents the cyclic voltammograms recorded, in electrolytic medium (Na_2SO_4 ; 0.05 M; $\text{pH} = 7.2$) in the potential range between -1.5 V and 2 V, respectively by carbon paste electrode, and the dolomite modified carbon

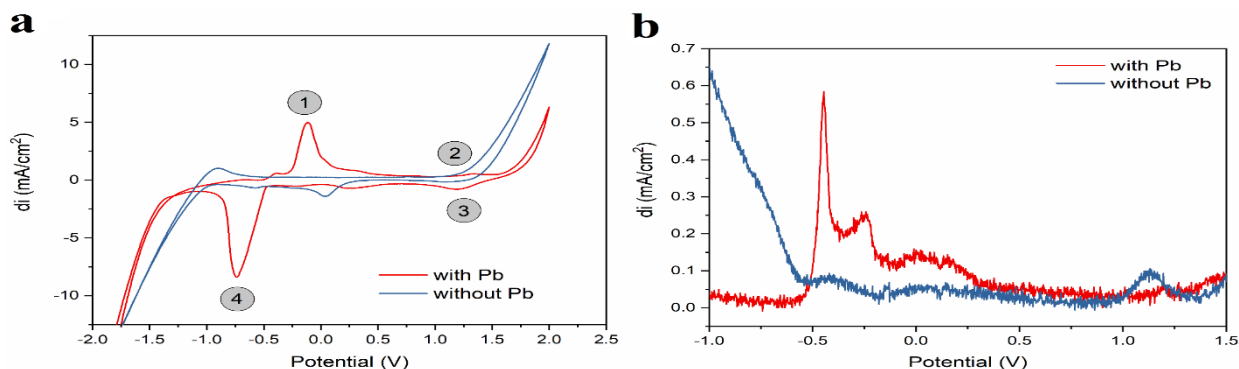


Fig. 5: Sensitivity of electrodes with Pb^{2+} by (a) cyclic voltammetry and (b) Square wave voltammetry

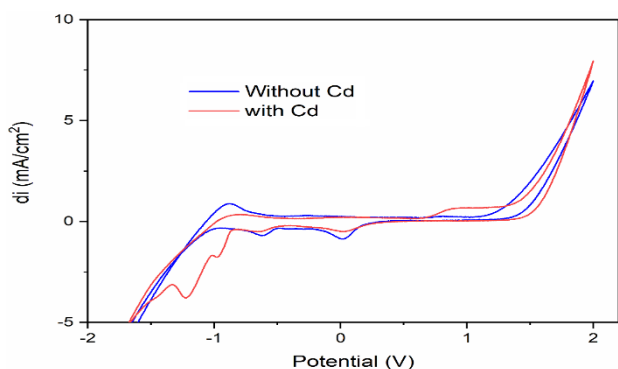


Fig. 6: Sensitivity of electrodes with Cd^{2+} by cyclic voltammetry

paste electrode at $100 \text{ mV}\cdot\text{s}^{-1}$. The voltammograms shows that the reduction peak, which appeared in 0.0 V (red voltammogram) transferred to 0.5 V (blue one) in modified electrode, which indicate that the CPE-dolomite shows more electrocatalytic effect compared with CPE, suggesting that the carbon paste electrode is well modified by dolomite.

Behavior of CPE-dolomite with Pb

Fig. 5 shows the voltammograms obtained in the absence and presence of $Pb(II)$ (0.52 mM) in the electrolyte medium. The anodic peak clearly corresponded to the oxidation of lead taken up chemically from the preconcentrating solution with the CPE-dolomite and the cathodic peak corresponded to the reduction of lead in which the voltammogram (b) shows two Red-Ox systems: the first one concerns the oxidation-reduction of lead ions in the interface (peaks 1 and 4 respectively $d_i = -11.5 \text{ mA/cm}^2$ at -0.77 V , $d_i = 7.352 \text{ mA/cm}^2$) and the second one concerns the oxidation-reduction of lead in the electrode matrix (peaks 3 and 2 respectively $d_i = -1.024 \text{ mA/cm}^2$ at -1.275 V , $d_i = 0.79 \text{ mA/cm}^2$ at -0.70 V).

The difference between the values of the anodic and cathodic peaks reveals that the system is quasi fast.

Behavior of CPE-dolomite with Cd

The electrochemical behavior of CPE-dolomite was studied as shown in Fig. 6. Cyclic voltammograms were recorded in 0.1 M of Na_2SO_4 in the potential range -2 V to 2 V . After 3 minutes of pre-concentration, the voltammograms show cathodic current peaks around -0.75 V and -1.18 V indicating the presence of cadmium and an anodic peak of 1.2 V potential very far from Cd reduction peaks (suggesting that Cd is trapped in the electrode matrix due to its interactions with other compounds). These relatively low peak currents compared to those obtained in the presence of lead can be explained by low energy interactions (which may suggest physisorption) between cadmium and the CPE-dolomite composite. Comparing the peak currents of the CPE-dolomite electrode against the metal ions Pb^{2+} and Cd^{2+} under the conditions of the experiment, this electrode is found to be more reactive and sensitive to lead. Similar results have been reported in previous work [36].

Influence of the preconcentration time

The final factor of critical relevance is the length of time permitted for the $Pb(II)$ and $Cd(II)$ to accumulate from the preconcentration solution at the electrode surface. The influence of the preconcentration time on the current intensities of the anodic peak of lead and the cathodic peak of cadmium is shown in Fig. 7. The intensity increases with the preconcentration time, between 0 and 25 min. Normally, the response increases until a maximum signal level is reached, which is expected to be equivalent to either a saturation or an equilibrium surface coverage.

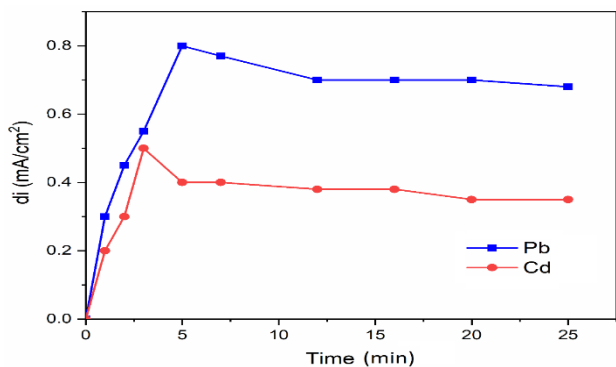


Fig. 7: Effect of accumulation time by SWV ($\text{Hg}/\text{Hg}_2\text{Cl}_2$; $\text{pH} = 7$; 0.1 M of Na_2SO_4)

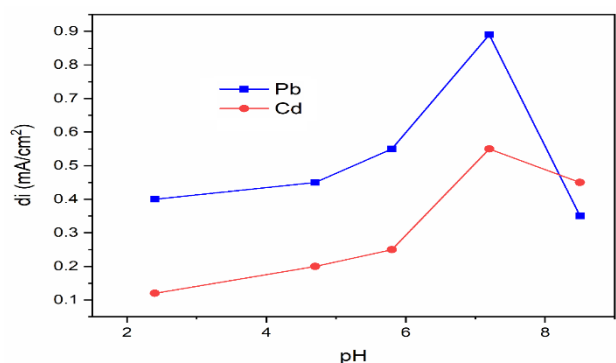


Fig. 8: Effect of pH by SWV ($\text{Hg}/\text{Hg}_2\text{Cl}_2$; $\text{pH} = 7$; 0.1 M of Na_2SO_4)

The results showed that exposure periods of 5 min for 0.57 M $\text{Pb}(\text{II})$ and 3 min for 0.51 M Cd were necessary to achieve higher accumulation levels of $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ at the electrode surface. In principle, it was discovered that the peak current is briefly dependent on the preconcentration time. However, a steady change in the peak current was seen as the preconcentration time increased. This observation is consistent with the outcomes of other adsorptive accumulation-based stripping techniques [37-40]. Beyond 12 and 5 min respectively for lead and cadmium, it becomes almost constant due to the probable saturation of the surface of the CPE-dolomite.

Influence of the pH of the medium

The electrode response with respect to variation in pH of the medium was investigated, with the objective of achieving the maximum peak current during practical experiments. In a solution with 0.57 M of $\text{Pb}(\text{II})$ and 0.51 M of $\text{Cd}(\text{II})$, the influence of pH on the voltammetric response of the dolomite modified carbon paste electrode

was investigated in the pH range of 2 to 9. The square wave voltammograms clearly displayed the current peak responses for the ions in the electrolytes at various pHs. The effect of the electrolyte's pH on the reaction of the CPE-dolomite is shown in Fig. 8, which shows that the peak current increases with pH in the range of 6.5–7.5, where the peak achieves a maximum, and then declines from $\text{pH} = 7.5$ to 9. This is caused by the completion of complex formation at higher pH and the increased complex formation of $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ with CPE-dolomite at the electrode surface. This wasn't observed in this study, though, since the $\text{Pb}(\text{II})$ solution was added to the preconcentration cell just before the electrode was inserted, and because a stable CPE-dolomite- $\text{Pb}(\text{II})$ and CPE-dolomite- $\text{Cd}(\text{II})$ complexes subsequently formed on the surface of the electrode [41-43]. As a result, $\text{pH} = 7.2$ was chosen as the ideal pH for the medium for the next experiments.

Study of the effect of ionic concentration

In order to assess the effect of ionic strength on the electrochemical behaviour of the proposed working electrode, electrochemical measurements were performed with $\text{Pb}(\text{II})$. The variation of the anodic peak intensity with lead concentration was followed by cyclic voltammetry (Fig. 9a), square wave voltammetry (Fig. 9b). Based on these Figs, it can be seen that the peak currents increase linearly with the concentration of Pb^{2+} in solution with a correlation coefficient of the order of 0.9986, indicating that the new electrode surface has a large number of active sites. The impedance diagrams confirm this result, which show curves in the form of semicircles at high frequencies attributed to electron transfer (R_t), the diameter of these semicircles corresponds to the electron transfer resistance. The increase of the lead concentration decreases the value of R_t (Fig. 9c).

Cyclic voltammograms recorded by the dolomite-modified electrode in Na_2SO_4 (0.1 M) electrolyte medium, containing different concentrations of Cd^{2+} . We note that the voltammograms show two peaks at about -0.5 V and 0.5 V . These peaks are associated with the reduction of Cd^{2+} ions adsorbed on the electrode surface. It also appears that the peaks grow linearly with the concentration of Cd^{2+} (Fig. 10). From this figure, the finding is that the peak currents increase linearly with the concentration of metal ions in solution with correlation coefficient of the order of 0.9955.

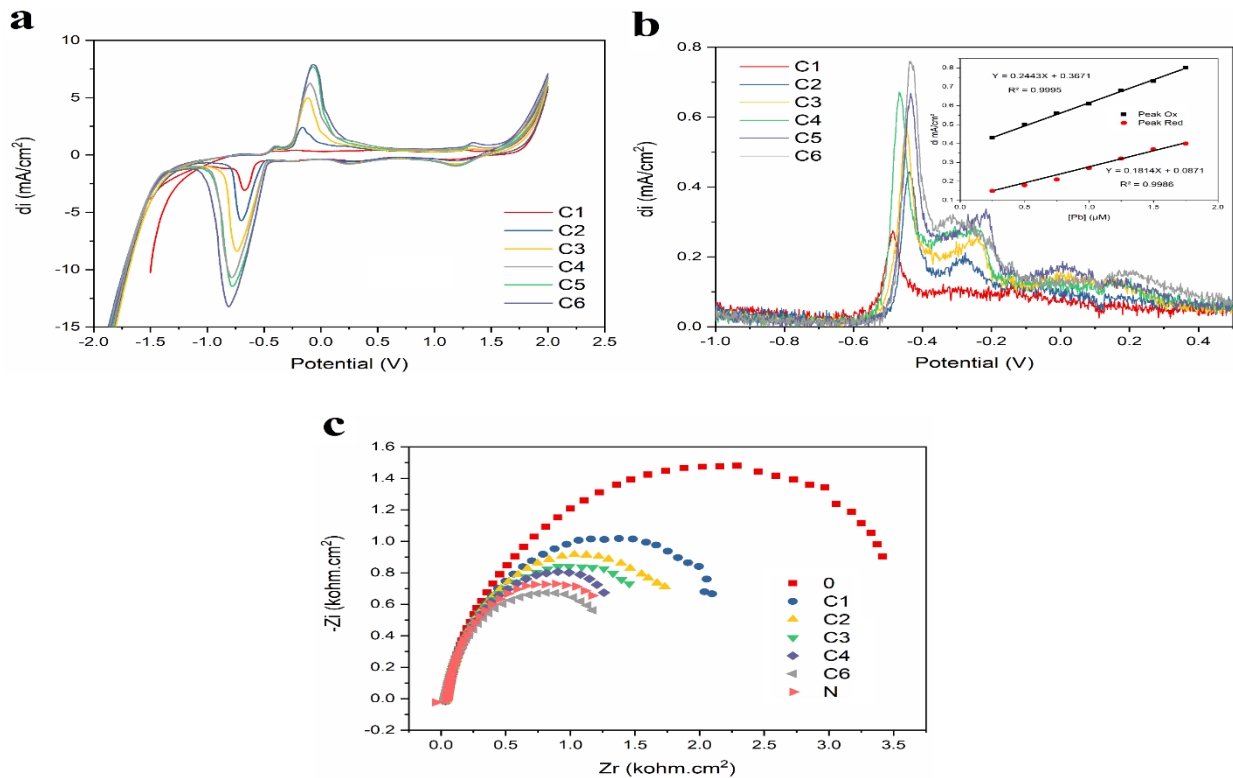


Fig. 9: Effect of concentration of Pb^{2+} (Hg/Hg_2Cl_2 ; $pH = 7$; $0.1 M$ of Na_2SO_4). (a) CV, (b) SWV and (c) EIS

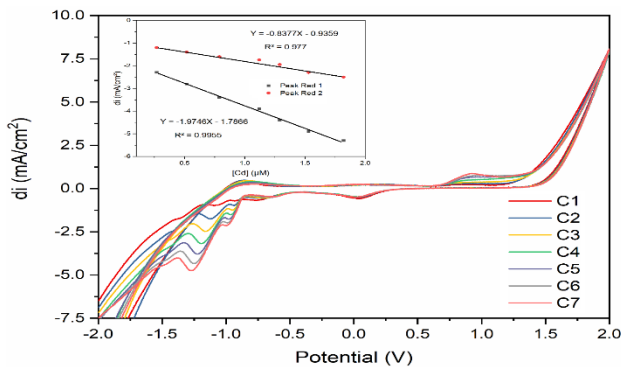


Fig. 10: Effect of concentration (Hg/Hg_2Cl_2 ; $pH = 7$; $0.1 M$ of Na_2SO_4) of Cd^{2+}

This increase is more pronounced with Pb^{2+} (Fig. 9a) than with Cd^{2+} (Fig. 10). This criterion the fact that the CPE-dolomite electrode is more reactive to Pb^{2+} than to Cd^{2+} . Furthermore, the detection limits were $0.10113 \mu M$ and $0.22227 \mu M$, respectively, for Pb^{2+} (anodic peak) and Cd^{2+} .

Study of the effect of the scan rate

The intensity of the oxidation peak varies linearly with the scan rate ($V^{1/2}$) in the potential range between 20 and 120 mV/s (Fig. 11a and Fig. 11b). The linear increase of the anode peak

currents with the square ratio of the scan rate (coefficient of correlation equal to 0.9847; 0.9806 for Cd^{2+} and 0.8385; 0.9307 for Pb^{2+} , respectively) shows some diffusion of the analyte on the electrode surface. This linearity reflects a surface phenomenon, and $Pb(II)$ and $Cd(II)$ ions have probably been scattered to the active sites of the CPE-dolomite [44].

Interference of Cd^{2+} and Pb^{2+} ions

At sites on CPE-dolomite, we evaluated elements that might exhibit some competition, and these tests were conducted under ideal circumstances. The voltammogram was plotted after preconcentration of CPE-dolomite in aqueous solutions of lead nitrate $Pb(NO_3)_2$ and cadmium nitrate $Cd(NO_3)_2$. The cathodic reduction of cadmium occurs at $-0.7 V/ECS$, lower than that of lead $-0.45 V/ECS$. The oxidation peak of metallic lead occurs at about $+0.1 V/ECS$. The clear separation of the three peaks offers us the possibility to determine both metals simultaneously (Fig. 12).

Application of the electrodes to tap water analysis

The CPE-dolomite electrode was subjected to tap water for application in a real-world environment. The study was performed by cyclic voltametry and square wave

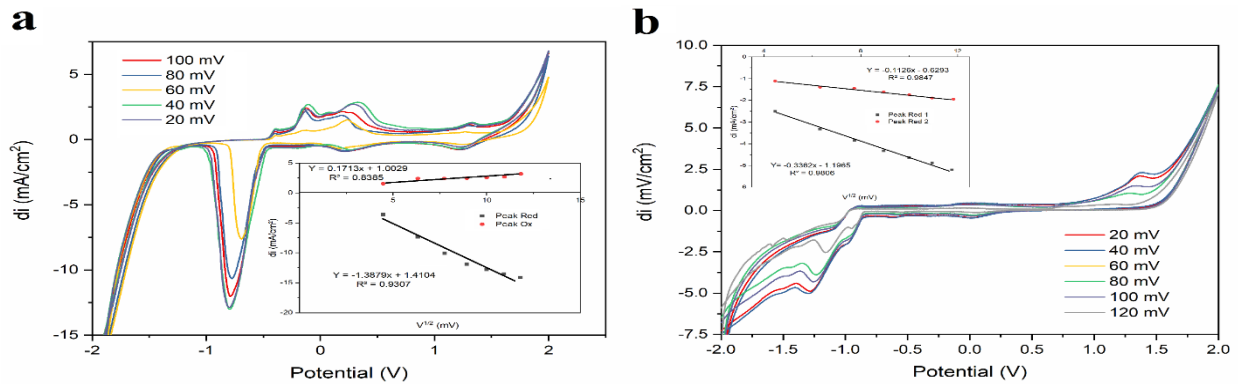


Fig. 11: Scan rate effect (Hg/Hg_2Cl_2 ; pH = 7; 0.1 M of Na_2SO_4 ; V: 100 mV/s). (a): Pb^{2+} , (b): Cd^{2+}

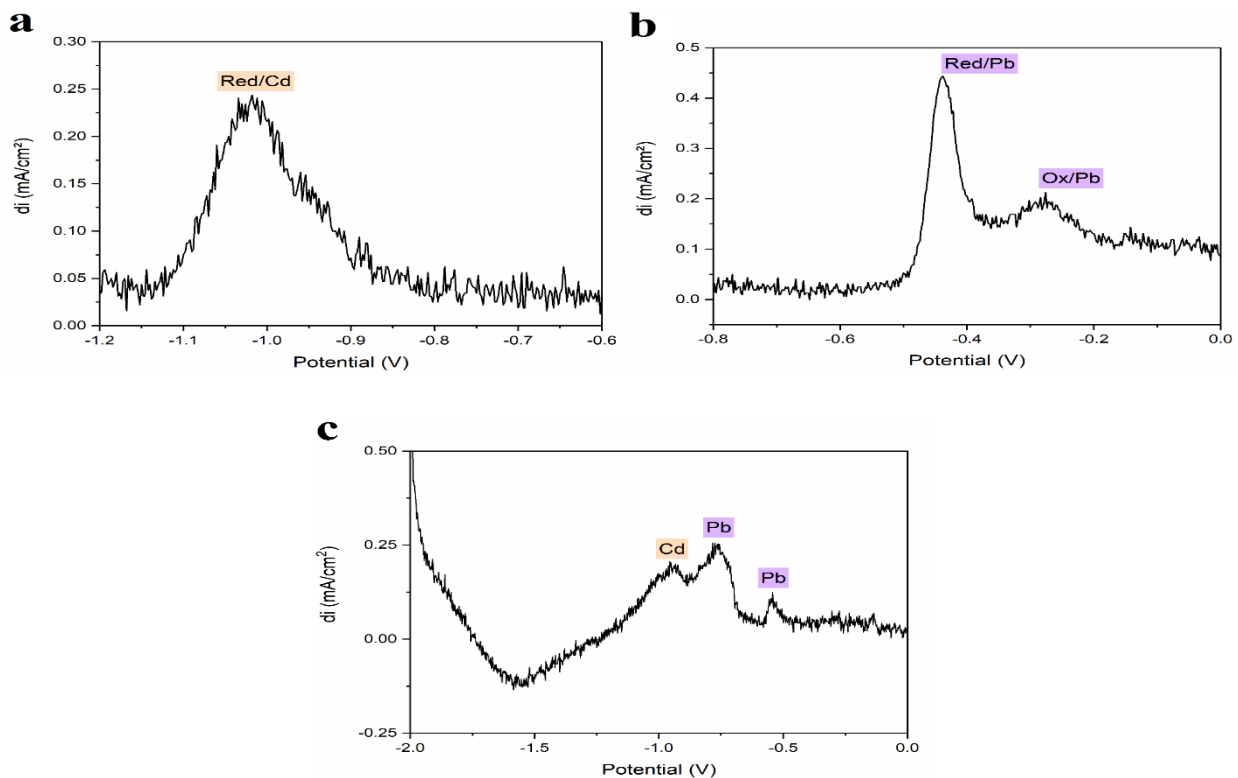


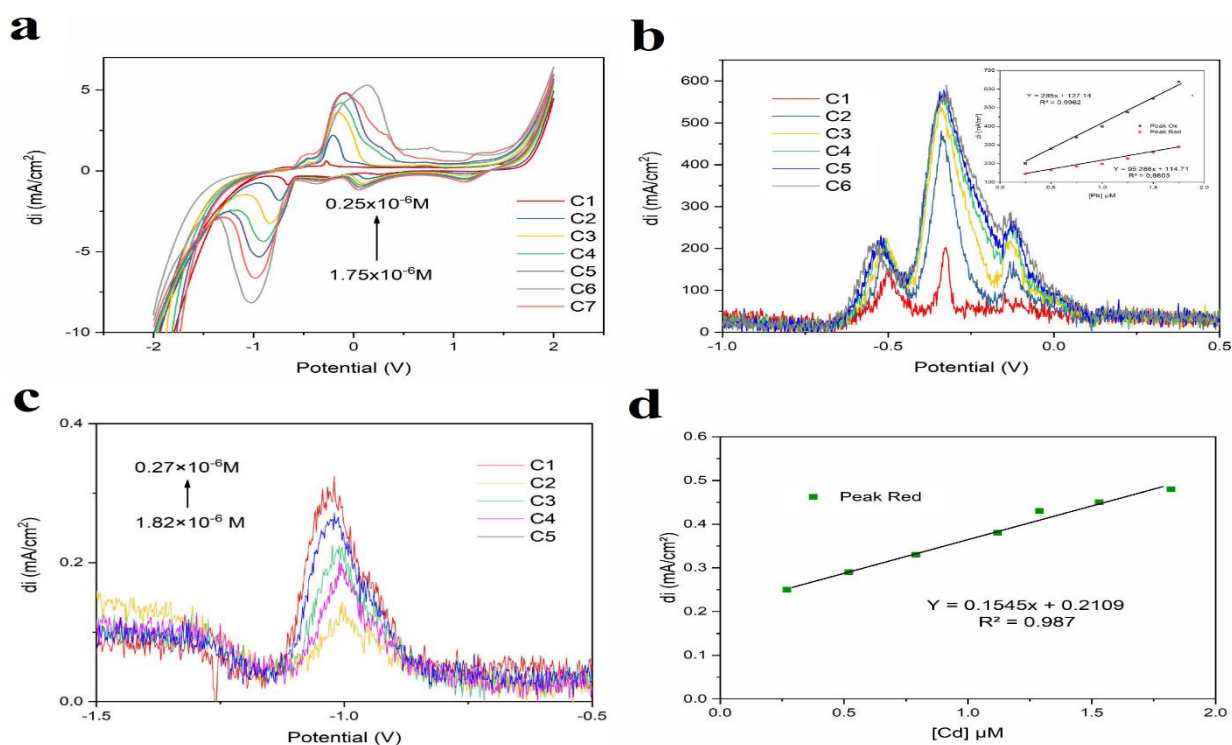
Fig. 12: Ionic interference effect by SWV (Hg/Hg_2Cl_2 ; pH = 7; 0.1 M of Na_2SO_4)

voltameter in 0.1 M Na_2SO_4 solution. The concentration of Pb (II) varied from 0.25×10^{-6} M to 1.75×10^{-6} M as shown in Fig. 13a. For Cd (II), the electrochemical responses were recorded in the concentration range of 0.27×10^{-6} M to 1.82×10^{-6} M as shown in Fig. 13c. From the above, it is clear that the anodic peak currents increase linearly with the concentration of Pb (II) in the solution with a strong correlation ($R^2 = 0.9962$, Fig. 13b) for a qualified detection limit of anodic peak at $0.06468 \mu\text{M}$. Furthermore, the electroanalysis of Cd (II) also shows that the peak currents that evolve with the concentration of Cd (II)

in the reaction medium. The correlation between peak current density and concentration is also high ($R^2 = 0.987$, Fig. 13d) but not as high as that of the concentration detection limit for the case of cadmium was $0.54502 \mu\text{M}$. These results show that the fabricated sensor detects Pb (II) more reliably in tap water than in distilled water. With Cd^{2+} on the other hand, this sensor is more reliable in distilled water than in tap water during electrochemical detection. Table 2 allows to evaluate the reliability of the sensor according to the study environment and to compare it with other works.

Table 2: Comparison of the performance of some electrodes with other analytical methods for lead and cadmium

Electrode material	Technique used	Solvent	Limit of detection		References
			Pb	Cd	
CPE-EDTA	SQW	Distilled water	0.0087 μM	-	[45]
RGO-GNPs	SWASV	Distilled water	0.00058 μM	0.00071 μM	[46]
ZnFe ₂ O ₄ -GCE	DPASV	Distilled water	0.00541 μM	0.02224 μM	[47]
BiPs-CNFs/[EMIM][NTf ₂]/CP	SWASV	Distilled water	0.00058 μM	0.00222 μM	[48]
CPE-ACC	SQW	Distilled water	0.15513 μM	0.24227 μM	[44]
CPE-ACC	SQW	Tap water	0.08438 μM	0.4652 μM	[44]
CPE-dolomite	SQW	Distilled water	0.10113 μM	0.22227 μM	This work
CPE-dolomite	SQW	Tap water	0.06468 μM	0.54502 μM	This work

**Fig. 13: Effect of the concentration and calibration curve of the Pb^{2+} ions (a, b) and Cd^{2+} (c, d) in tap water**

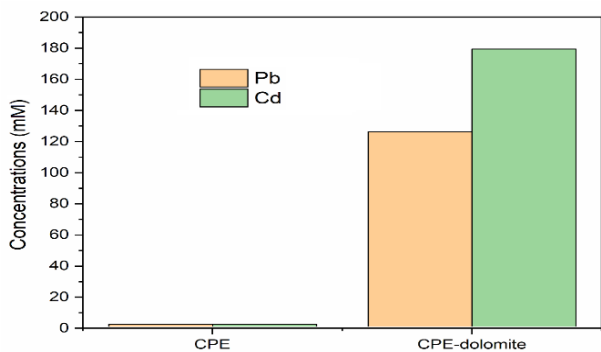
Determination of Pb and Cd by Atomic Absorption Spectroscopy (AAS)

In order to confirm the membrane's effectiveness to store metal cations in the anode compartment, as well as to verify the natural non-adsorption of heavy metals on the cell's materials (cell body, electrode, etc.), and to detect any other process that results in metal cation losses. Electrode material samples were processed in digestion tubes for 3 h in the presence of a mixture (3:1 hydrochloric acid: nitric acid) at a temperature of 100 °C. The resulting solutions were analyzed by atomic absorption spectroscopy technique to determine the content of cadmium and lead in the samples.

The AAS measurement of the cadmium and lead contents in the mineralized samples reveals that the digested solution of the graphite carbon electrode has no traces of cadmium or lead, suggesting that the graphite electrode is not sensitive to any form of ion reduction. However, the prepared electrode from CPE-dolomite showed a highly sensitive capacity toward cadmium detection. A content of 178.43 mM was detected after mineralization of CPE-dolomite electrode immersed previously in a solution of CdSO₄. The same electrode has been used to reduce the lead contained in an electrolyte charged with Pb²⁺, and consequently to detect its presence

Table 3: Determination of Pb and Cd by atomic absorption spectroscopy (AAS)

Sample	Digested mass (mg)	Concentration (mg/l)	Dilution factor	Average concentration (mM)
C1	0.071	<0.01	300	--
CPE-dolomite-Cd (II)	0.068	0.1311	300	578.434
CPE-dolomite-Pb (II)	0.1007	0.1183	300	352.432969

**Fig. 14: Cadmium (a) and lead (b) concentrations in electrode after digestion**

after an electrochemical cyclic voltameter. The recovered electrode after cyclic voltammetry was mineralized and the resulted solution was analyzed involving a value of 125.23 mM (Table 3 and Fig. 14). The high detected concentrations of cadmium and lead ions as well as the difference between these values and those calculated from the electrochemical results could be attributed to the sorption, intercalation and ions exchange phenomena which could be occurred simultaneously with the electrochemical reduction [49-50].

CONCLUSIONS

A simple and efficient system for the detection of heavy metals such as Pb²⁺ and Cd²⁺ was developed in this work. Measurements of these pollutants were carried out with a dolomite-based electrode, using mainly cyclic and square wave voltammetry. Optimized experimental conditions were determined by the variation of preconcentration time, the pH of the preconcentration solution. The intensity of the peak corresponding to the electroactivity of the analyzed element increases with the accumulation time until a limit is reached at which the peak profile changes. It becomes broader and the intensity of its maximum remains constant. The limit detection values obtained from the calibration curves of the investigated substances show that the dolomite modified electrodes are very sensitive to the detection of

the investigated metals. The proposed method for the detection of these metals is characterized by simplicity of invention. The modifiers are not soluble in water, non-toxic and non-polluting.

Acknowledgments

The authors would like to thank Team of Molecular Electrochemistry and Inorganic at Faculty of Sciences and Technologies of Beni Mellal, Sultan Moulay Slimane University of Beni Mellal, Morocco and Moroccan Foundation for Advanced Science, innovation and research for their technical assistance and their contribution in conducting some experiments.

Received : Jul.29, 2022 ; Accepted : Nov. 07, 2022

REFERENCES

- [1] Hayat M.T., Nauman M., Nazir N., Ali S., Bangash N., "Environmental Hazards of Cadmium: Past, Present, and Future", in: Cadmium Toxic Toler. Plants, Elsevier, 163–183 (2019).
- [2] Rice K.M., Walker E.M., Wu M., Gillette C., Blough E.R., *Environmental Mercury and Its Toxic Effects*, *J. Prev. Med. Pub. Health*, **47**(2): 74–83 (2014).
- [3] Lee S., Oh J., Kim D., Piao Y., *A Sensitive Electrochemical Sensor Using an Iron Oxide/Graphene Composite for the Simultaneous Detection of Heavy Metal Ions*, *Talanta*, **160**: 528–536 (2016).
- [4] Loh N., Loh H.-P., Wang L.K., Wang M.-H.S., "Health Effects and Control of Toxic Lead in the Environment", In: L.K. Wang, M.-H.S. Wang, Y.-T. Hung, N.K. Shamma, *Nat. Resour. Control Process.*, Springer International Publishing, Cham, 233-284 (2016).
- [5] Singh R., Gautam N., Mishra A., Gupta R., *Heavy Metals and Living Systems: An Overview*, *Indian J. Pharmacol*, **43**(3): 246 (2011).

- [6] Mitra S., Chakraborty A.J., Tareq A.M., Emran T.B., Nainu F., Khusro A., Idris A.M., Khandaker M.U., Osman H., Alhumaydhi F.A., Simal-Gandara J., [Impact of Heavy Metals on the Environment and Human Health: Novel Therapeutic Insights to Counter the Toxicity](#), *J. King Saud Univ. – Sci.*, **34(3)**: 101865 (2022).
- [7] Gworek B., Dmuchowski W., Baczevska-Dąbrowska A.H., [Mercury In The Terrestrial Environment: A Review](#), *Environ. Sci. Eur.*, **32(1)**: 128 (2020).
- [8] Esteban-Vasallo M.D., Aragonés N., Pollan M., López-Abente G., Perez-Gomez B., [Mercury, Cadmium, and Lead Levels in Human Placenta: A Systematic Review](#), *Environ. Health Perspect.*, **120(10)**: 1369–1377 (2012).
- [9] Sun H., Brocato J., Costa M., [Oral Chromium Exposure and Toxicity](#), *Curr. Environ. Health Rep.*, **2(3)**: 295–303 (2015).
- [10] Karbowska B., [Presence of Thallium in the Environment: Sources of Contaminations, Distribution and Monitoring Methods](#), *Environ. Monit. Assess.*, **188(11)**: 640 (2016).
- [11] Koike Y., Hagiwara K., Nakamura T., [Enhancement of the Atomic Absorbance of Cr, Zn, Cd, and Pb in Metal Furnace Atomic Absorption Spectrometry Using Absorption Tubes](#), *Anal. Chem. Res.*, **11**: 9–12 (2017).
- [12] Sani A., Abdullahi I.L., [Evaluation of Some Heavy Metals Concentration in Body Fluids of Metal Workers in Kano Metropolis, Nigeria](#), *Toxicol. Rep.*, **4**: 72–76 (2017).
- [13] Zheng Y., Huang X., Ling Y., Huang W., Wang J., Zheng Z., Wang X., Wang H., [Ultrasonic-Enhanced Preconcentration of Trace Pb\(II\) Using Hydrophobic, Lighter-than-Water Ionic Liquid Microextraction Combined with Solidification of the Aqueous Solution Prior to Detection by Graphite Furnace Atomic Absorption Spectrometry in Human Fluids](#), *Spectrochim. Acta Part B At. Spectrosc. (SAPB)*, **157**: 27–36 (2019).
- [14] Amani V., Ahmadi R., Naseh M., Ebadi A., [Synthesis, Spectroscopic Characterization, Crystal Structure and Thermal Analyses of Two Zinc\(II\) Complexes with Methanolysis of 2-Pyridinecarbonitrile as a Chelating Ligand](#), *J. Iran. Chem. Soc. (JICS)*, **14(3)**: 635–642 (2017).
- [15] Aragay G., Merkoçi A., [Nanomaterials Application in Electrochemical Detection of Heavy Metals](#), *Electrochimica Acta*, **84**: 49–61 (2012).
- [16] Zhao Q., Gan Z., Zhuang Q., [Electrochemical Sensors Based on Carbon Nanotubes](#), *Electroanalysis*, **14(23)**: 1609–1613 (2002).
- [17] Privett B.J., Shin J.H., Schoenfish M.H., [Electrochemical Sensors](#), *Anal. Chem.*, **80(12)**: 4499–4517 (2008).
- [18] Lin W., Zhou F., Luo W., Song T., Li H., [Alkali-Activated Dolomite and its Outstanding Mechanical Strength](#), *Mater. Lett.*, **270**: 127682 (2020).
- [19] Hanane B., Jihad R., Naima B., Soukaina T., Nadia B., Naima B.T., [Characterisation and Valorisation of the Moroccan Diatomite](#), *J. Geosci. Environ. Prot. (JGEP)*, **10(02)**: 109–134 (2022).
- [20] Manni A., Matadi Boumbimba R., Mikdam A., El Bouari A., Addiego F., Meziani J., Wary M., [Magnesite and Dolomite Micro-Particles: Preparation, Physical Properties and Application in Bio-Based Polymer Composite](#), *Polym. Bull.*, **79(4)**: 2149–2171 (2022).
- [21] Stozhko N.Yu., Khamzina E.I., Bukharinova M.A., Tarasov A.V., [An Electrochemical Sensor Based on Carbon Paper Modified with Graphite Powder for Sensitive Determination of Sunset Yellow and Tartrazine in Drinks](#), *Sensors*, **22(11)**: 4092 (2022).
- [22] Li Q., Sun S., Smith A.D., Lundgren P., Fu Y., Su P., Xu T., Ye L., Sun L., Liu J., Enoksson P., [Compact and Low Loss Electrochemical Capacitors Using a Graphite/ Carbon Nanotube Hybrid Material for Miniaturized Systems](#), *J. Power Sources*, **412**: 374–383 (2019).
- [23] Wang H., Yoshio M., [Graphite, a Suitable Positive Electrode Material for High-Energy Electrochemical Capacitors](#), *Electrochem. Commun.*, **8(9)**: 1481–1486 (2006).
- [24] Monteiro M.K.S., Paiva S.S.M., da Silva D.R., Vilar V.J.P., Martínez-Huitle C.A., dos Santos E.V., [Novel Cork-Graphite Electrochemical Sensor for Voltammetric Determination of Caffeine](#), *J. Electroanal. Chem.*, **839**: 283–289 (2019).
- [25] Purushothama H.T., Nayaka Y.A., Vinay M.M., Manjunatha P., Yathisha R.O., Basavarajappa K.V., [Pencil Graphite Electrode as an Electrochemical Sensor for the Voltammetric Determination of Chlorpromazine](#), *J. Sci. Adv. Mater. Devices*, **3(2)**: 161–166 (2018).

- [26] Song Y., Liu T.-Y., Xu G.-L., Feng D.-Y., Yao B., Kou T.-Y., Liu X.-X., Li Y., **Tri-Layered Graphite Foil for Electrochemical Capacitors**, *J. Mater. Chem. A*, **4(20)**: 7683–7688 (2016)..
- [27] Emir G., Dilgin Y., Ramanaviciene A., Ramanavicius A., **Amperometric Nonenzymatic Glucose Biosensor Based on Graphite Rod Electrode Modified by Ni-Nanoparticle/Polypyrrole Composite**, *Microchem. J.*, **161**:105751 (2021).
- [28] Salavagione H.J., Díez-Pascual A.M., Lázaro E., Vera S., Gómez-Fatou M.A., **Chemical Sensors Based on Polymer Composites with carbon Nanotubes and Graphene: The Role of the Polymer**, *J. Mater. Chem. A*, **2(35)**: 14289–14328 (2014).
- [29] Shoja Y., Kermanpur A., Karimzadeh F., **Diagnosis of EGFR Exon21 L858R Point Mutation as Lung Cancer Biomarker By Electrochemical DNA Biosensor Based on Reduced Graphene Oxide /Functionalized Ordered Mesoporous Carbon/Ni-Oxytetracycline Metallopolymer Nanoparticles Modified Pencil Graphite Electrode**, *Biosens. Bioelectron.*, **113**: 108–115 (2018).
- [30] Azadbakht A., Abbasi A.R., Derikvand Z., Karimi Z., **Fabrication of an Ultrasensitive Impedimetric Electrochemical Sensor Based on Graphene Nanosheet/Polyethyleneimine/Gold Nanoparticle Composite**, *J. Electroanal. Chem.*, **757**: 277–287 (2015).
- [31] Kokkinos C., Prodromidis M., Economou A., Petrou P., Kakabakos S., **Quantum Dot-Based Electrochemical DNA Biosensor Using a Screen-Printed Graphite Surface with Embedded Bismuth Precursor**, *Electrochem. Commun.*, **60**: 47–51 (2015).
- [32] Lei H., Pitt W.G., McGrath L.K., Ho C.K., **Resistivity Measurements of Carbon–Polymer Composites in Chemical Sensors: Impact of Carbon Concentration and Geometry**, *Sens. Actuators B Chem.*, **101(1-2)**:122–132 (2004).
- [33] Salajegheh, M., Ansari, M., Foroghi, M.M., Kazemipour, M. **Computational Design as a Green Approach for Facile Preparation of Molecularly Imprinted Polyarginine-Sodium Alginate-Multiwalled Carbon Nanotubes Composite Film on Glassy Carbon Electrode for Theophylline Sensing**, *Journal of Pharmaceutical and Biomedical Analysis*, **162**: (2019). 215-224.
- [34] Foroughi, M. M., & Jahani, S. **Investigation of a High-Sensitive Electrochemical DNA Biosensor for Determination of Idarubicin and Studies of DNA-Binding Properties**. *Microchemical Journal*, **179**: 107546 (2022).
- [35] Chan R.K., Murthi K.S., Harrison D., **Thermogravimetric analysis of Ontario limestones and dolomites I. Calcination, Surface Area, and Porosity**, *Can. J. Chem.*, **48(19)**: 2972–2978 (1970).
- [36] Maallah R., Moutcine A., Laghlimi C., Smaini M.A., Chtaini A., **Electrochemical Bio-Sensor for Degradation of Phenol in the Environment**, *Sens. Bio-Sens. Res.*, **24**: 100279 (2019).
- [37] Prabhu S.V., Baldwin R.P., Kryger L., **Preconcentration and Determination of Lead(II) at Crown Ether and Cryptand Containing Chemically Modified Electrodes**, *Electroanalysis*, **1(1)**: 13–21(1989).
- [38] Ramos J.A., Bermejo E., Zapardiel A., Pérez J.A., Hernández L., **Direct Determination of Lead by Bioaccumulation at a Moss-Modified Carbon Paste Electrode**, *Anal. Chim. Acta*, **273(1-2)**: 219–227 (1993).
- [39] Tuzhi P., Zhe T., Guoshun W., Baoen S., **Differential Pulse Voltammetric Determination of lead(II) with Benzoin Oxime-Modified Carbon Paste Electrodes**, *Electroanalysis*, **6(7)**: 597–603 (1994).
- [40] Hu Z., Seliskar C.J., Heineman W.R., **PAN-Incorporated Nafion-Modified Spectroscopic Graphite Electrodes for Voltammetric Stripping Determination of Lead**, *Anal. Chim. Acta*, **369(1-2)**: 93–101 (1998).
- [41] Pandey S.K., Sachan S., Singh S.K., **Ultra-Trace Sensing of Cadmium and Lead by Square Wave Anodic Stripping Voltammetry Using Ionic Liquid Modified Graphene Oxide**, *Mater. Sci. Energy Technol*, **2(3)**: 667–675 (2019).
- [42] Korolkov I.V., Zhumanazar N., Gorin Y.G., Yeszhanov A.B., Zdorovets, M.V., **Enhancement of Electrochemical Detection of Pb²⁺ by Sensor Based on Track-Etched Membranes Modified with Interpolyelectrolyte Complexes**, *J. Mater. Sci. Mater. Electron.*, **31(22)**: 20368–20377 (2020).
- [43] Alshawi J.M.S., Mohammed M.Q., Alesary H.F., Ismail H.K., Barton S., **Voltammetric Determination of Hg²⁺, Zn²⁺, and Pb²⁺ Ions Using a PEDOT/NTA-Modified Electrode**, *ACS Omega*, **7(23)**: 20405–20419 (2022).

- [44] Blaise N., Gomdje Valéry H., Maallah R., Oubaouz M., Tigana Djonse Justin B., Andrew Ofudje E., Chtaini A., [Simultaneous Electrochemical Detection of Pb and Cd by Carbon Paste Electrodes Modified by Activated Clay](#), *J. Anal. Methods Chem*, **2022**:1-9 (2022).
- [45] Laghlimi C., Ziat Y., Moutcine A., Hammi M., Zarhri Z., Maallah R., Ifguis O., Chtaini A., [Analysis of Pb\(II\), Cu\(II\) and Co\(II\) in Drinking Water by a New Carbon Paste Electrode Modified with an Organic Molecule](#), *Chem. Data Collect*, **29**: 100496 (2020).
- [46] Oularbi L., Turmine M., Salih F.E., El Rhazi M., [Ionic Liquid/Carbon Nanofibers/Bismuth Particles Novel Hybrid Nanocomposite for Voltammetric Sensing of Heavy Metals](#), *J. Environ. Chem. Eng*, **8(3)**: 103774 (2020).
- [47] Ns A.K., S A., Malingappa P., [Nano Zinc Ferrite Modified Electrode as a Novel Electrochemical Sensing Platform in Simultaneous Measurement of Trace Level Lead and Cadmium](#), *J. Environ. Chem. Eng*, **6(6)**: 6939–6946 (2018).
- [48] Zhao G., Wang H., Liu G., Wang Z., Cheng J., [Simultaneous Determination of trace Cd \(II\) and Pb \(II\) Based on Bi/Nafion/Reduced Graphene Oxide-Gold Nanoparticle Nanocomposite Film-Modified Glassy Carbon Electrode by One-Step Electrodeposition](#), *Ionics*, **23(3)**: 767–777 (2017).
- [49] Bashir A., Manzoor T., Malik L.A., Qureashi A., Pandith A.H., [Enhanced and Selective Adsorption of Zn\(II\), Pb\(II\), Cd\(II\), and Hg\(II\) Ions by a Dumbbell- and Flower-Shaped Potato Starch Phosphate Polymer: A Combined Experimental and DFT Calculation Study](#), *ACS Omega*, **5(10)**: 4853–4867 (2020).
- [50] Maslova M.V., Ivanenko V.I., Yanicheva N.Yu., Mudruk N.V., [Comparison of The Sorption Kinetics of Lead\(II\) and Zinc\(II\) on Titanium Phosphate Ion-Exchanger](#), *Int. J. Mol. Sci.(IJMS)*, **21(2)**: 447 (2020).