

Synthesis of Polyvinylpyrrolidone-Natural Swelling Clay Composites: Application for Complexation of Pb^{2+}

Valery H. Gomodje,^{*a} Guillaume P. Kofa^a, Abdoul Wahabou^b, Benoît Loura,^a Abdelilah Chtaini,^c
Bala Subramanian^d

^aNational Advanced Engineering School of Maroua, University of Maroua (Cameroon)

^bThe Higher Teachers Training School of Maroua, University of Maroua (Cameroon)

^cTeam of Molecular Electrochemistry and Inorganic Materials, Faculty of Sciences and Technology of Beni Mellal, University of Sultan Moulay Slimane (Morocco)

^dCentral Electrochemical Research Institute, Karaikudi, 630003, Tamil Nadu, (India).

Email*: valeryhambate@gmail.com

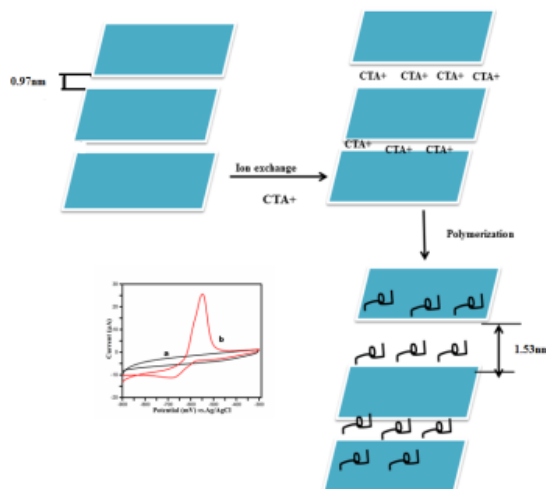
Permanent address: Senior Lecturer at the Higher Institute of the Sahel, University of Maroua (Cameroon), P.O.Box:46 Maroua (Cameroon)

Received 20th February 2017; Accepted 15th October 2017

• Novelty and Highlights:

- 1- Polyvinylpyrrolidone-Natural swelling clay film properties were determined and used for electrochemical detection of Lead ions.
- 2- It demonstrates a good electrocatalytic activity towards the electrochemical detection of lead ions.
- 3- The electrochemical sensor shows a good and high sensitivity of lead ions complexation.

• Graphical Abstract:





Synthesis of Polyvinylpyrrolidone-Natural Swelling Clay Composites: Application for Complexation of Pb²⁺

Valery H. Gombje,^{*a} Guillaume P. Kofa,^a Abdoul Wahabou,^b Benoît Loura,^a Abdelilah Chtaini,^c
Bala Subramanian^d

^aNational Advanced Engineering School of Maroua, University of Maroua (Cameroon)

^bThe Higher Teachers Training School of Maroua, University of Maroua (Cameroon)

^cTeam of Molecular Electrochemistry and Inorganic Materials, Faculty of Sciences and Technology of Beni Mellal, University of Sultan Moulay Slimane (Morocco)

^dCentral Electrochemical Research Institute, Karaikudi, 630003, Tamil nadu, (India).

Email*: valeryhambate@gmail.com

Permanent address: Senior Lecturer at the Higher Institute of the Sahel, University of Maroua, P.O.Box:46 Maroua (Cameroon)

Abstract: The aim of this work is to synthesize Polyvinylpyrrolidone-Natural Swelling Clay composite using chemical exchange reactions and intercalation method. The composite film was used to modify the Glassy glass electrodes to study the effect of the complexation of the lead ions by the electrochemical route and showed the good electrocatalytic activity toward lead ions. X-ray Diffraction, specific surface areas and pore volumes, Thermal analysis, Transmission Electronic Microscopy and X-ray Photoelectron Spectroscopy are used. The parameters such as pH of the electrolyte and preconcentration time were investigated to show the optimum conditions for chelation of lead in the electrolytic solution (1M KCl). A Voltammetric method for electrochemical chelation of Pb²⁺ shows the good response over the concentration range from 10⁻⁷ to 12x10⁻⁷M (R²=0.996), with a limit of detection is 1.815x10⁻⁷M. These values show that the modified glassy carbon electrode with polyvinylpyrrolidone-Natural Swelling clay film composite can be used as an electrochemical sensor for the detection of Lead (Pb²⁺) in solution.

Keywords: Polyvinylpyrrolidone-Natural Swelling Clay; Electrochemical detection; Glassy Carbon electrode; Voltammetry; electrochemical sensor.

Introduction

Composites with polymer and Clay have developed significantly in engineering domain. These materials have fairly improved properties due to their physicochemical properties [1-8]. They are classified according to the polymer layout in the interfoliaceous layers of the clays: intercalated which results in the insertion of the polymer in the interfoliaceous layer thus causing the increase of this distance and the exfoliated clays of which the silicate layer are separated and dispersed in the homogeneous mixture. [9].

The Clays are hydrophilic and this property allowed them to be compatible with a polar polymer, but to make them hydrophobic in order to facilitate compatibility with another compound, the necessity of modifying with surfactants such as phosphonium alkylammonium salts and

imidazolium [10-13] is essential. The method of complexation is also used [14-15], the silanes reaction are commonly used [16-18]. The montmorillonite is used via sol-gel reaction to prepare delaminated clay structures [19]. Swelling Clays are most often used to prepare polymer-Clay composite because the interlayer are filled with sodium ions and the cationic exchanges are easier with the polymer in the hydrophobic environment [20-21].

Some scientific studies have shown the adverse effects of heavy metals on human health and the environment [22-24]. The problem of lead determination has been addressed by several researchers [25-29], but all these techniques seem to show limits. Electrochemical technique specially modified electrodes have the advantage of being less expensive, easy to implement and their performance is improved by the modification of their surface [30].

In this work, polyvinylpyrrolidone and Natural swelling clay of Maroua (Cameroon) which they call in local language “Karal” was used to synthesize composite. The structural and physicochemical characterization, the morphology of composites using x-ray diffraction), The determination of the specific surface area by the BET method, Thermal gravimetric analysis, Transmission Electronic Microscopy and X-ray photoelectron spectroscopy were made. The PVP-Natural Swelling clay composite is used to modify Glassy Carbon Electrode (GCE) and sensing application for electrochemical detection of Lead (II) in aqueous solution have been studied.

Experimental

Chemical Reagents and clay mineral Pre-treatments

Cetyl trimethyl ammonium bromide (CTAB) Assay: was purchased from Himedia Laboratories Pvt.Ltd, India (99%). Polyvinylpyrrolidone K₃₀ (C₆H₉NO)_x, MW/ 40000, was purchased from central drug house, LTD, Dehli India. Lead nitrate Pb(NO₃)₂ was purchased from Avantor Performance Materials India Limited (99.0%). Potassium Chloride (KCl), Hydrochloric acid and sodium hydroxide were purchased from Merck specialities Privates Limited Mumbai, India.

The clay samples were collected in Maroua (Far-North region of Cameroon, Central Africa). Nya *et al* did the structural analysis of this clay in their work [31]. The method described in the literature was used for the purification of natural clay [32]. After purification, the cation exchange capacity is calculated and it is 63meq / 100.

Preparation of working electrode Synthesis of PVP-Swelling Clay 0.25 x CEC of CTAB equivalent to the corresponding amount of clay is added to 500ml of Flask and the mixture is stirred 2h. The mixture is thus put to rest for 10h at temperature room to make the surface clay hydrophobic. After 10 h the mixture of clay and CTAB gives an organoclay which is separated from the mixture by centrifugation for 1 hour at a speed of 5000 rpm then the residue is washed repeatedly with Millipore water. The organoclay complex is then dried in an oven at 50 ° C for 48 hours and crushed in a mortar in order to obtain a powder. Polyvinylpyrrolidone K₃₀ (PVP) was used as received. In order to insert the polymer into the interfoliaceous layer of organoclay, the method described in the literature was used [34-35]. In an Erlenmeyer flask, 20 mg of PVP and 75 mg of organo-clay prepared previously are mixed and agitated vigorously for 4 hours in order to homogenize the mixture, the mixture is allowed to

settle for 72h. The contents are heated to a temperature of 70 ° C. for a period of 2 hours bubbled by a stream of inert nitrogen. The polymer organoclays complex synthesized, the whole is brought to 180 ° C for 5 hours in an oven. At the end, the composite is collected for further analysis.

The glassy carbon electrode was polished with alumina slurries of different size (1, then 0.05µm) on billiard cloth. They were placed in an acetone solution and properly cleaned in a sonicator for 10min. The thin PVP-Natural Swelling clay composites film working electrode was prepared by “drop coating” 10µl of the aqueous dispersion of PVP-Natural Swelling clay on the active surface of the GCE. The modified electrode is placed at room temperature for 4 h in order to dry the layer of the composite present on the surface.

Characterization Techniques the X-ray diffraction of the modified and unmodified clay was applied by an experimental Panaltical device with the following characteristics: PW3040/60 X’pert PRO) equipped with a Cu anode (kλ radiation, λ = 1.54056 Å) using a voltage of 40 KV and a current of 30 mA. Specific surface areas and pore volumes were evaluated by the B.E.T. method from N₂ adsorption-desorption experiments performed at 77.35 K in the relative pressure range from 10⁻⁵ to 0.99, using an AutosorbiQ Station 2 (model Quantachrome Instruments). Prior to each measurement, the sample was outgassed at 105 °C under vacuum for 16 h. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were recorded using an SDT Q600 V8.3 Build 101 simultaneous DSC-TGA instrument. Transmission electron micrographs of the composites and Natural swelling clays were taken with a Tecnai F20 (FEI) transmission electron microscope with an accelerating voltage of 200 kV. The nature of surface functional groups on filler particles was determined by X-ray photoelectron spectroscopy (XPS) method. The XPS spectra were obtained using a Thermo Scientific; (Model: MULTILAB 2000 Base system with X-Ray, Auger and ISS attachments) under high vacuum conditions with a pressure of 10⁻⁸ Torr, an aluminium anode, and a resolution of 1 eV.

Cyclic voltammetry (CV) and Linear Stripping Voltammetry (LSV) on all prepared GCE/PVPCTAMa as well as on an unmodified GCE were performed on BAS 100W Electrochemical Analyzer. A three electrodes measurement cell equipped with a GCE/PVPCTAMa (working), an Ag/AgCl (saturated KCl) reference electrode and a Pt wire auxiliary electrode was used for all measurement. KCl 1M was used as an electrolyte solution.

Results and discussion

X-Ray diffraction analysis Figure 1 shows the X-ray diffraction of purified Natural swelling clays (Ma) before and after its modification with PVP/CTA+. To verify the success of surface modification of the clays, their interlayers were measured before and after modification using Bragg's equation [36]. The peak in X-ray diffraction patterns correspond to (001) plane reflection peaks of layered silicates is 0.969nm for purified Natural swelling clays, this value corresponds to the basal spacing of anhydrous montmorillonite [37-38]. After modifying the surface of the clay by PVP/CTA+ this value increased to 1.528 nm. The Changes in basal spacings are often an indication that organic compound has been incorporated within the interlayers during clay crystallization [39]. There is an interlayer expansion of 0.559nm due mainly to the partial insertion of the polymer [40] and the method of preparation of organoclays complex is not allowed to obtain the insertion of CTA⁺. The intercalation of PVP can be retained in this work for the expansion of the interlayer of the clay.

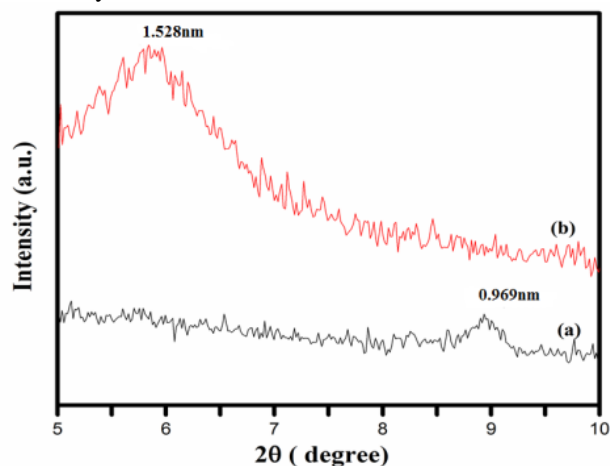


Figure 1 XRD patterns of a) Natural swelling Clay b) PVP-Natural Swelling clay.

Surface area and Pores volumes experiments the Surface area and pores volumes experiments of natural swelling clay and the PVP-Natural Swelling Clay prepared in this work were recorded, and is shown in Figure 2 the curves of the swelling clay are characterized by a rising curve reflecting the adsorption and a downward curve reflecting the desorption characterizing this type of clay marked by the presence of the mesopores. [41-44]. The pore volumes of these materials are $1.958 \times 10^{-02} \text{ cm}^3/\text{g}$ for Natural Swelling Clay and $1.485 \times 10^{-03} \text{ cm}^3/\text{g}$ for PVP-Natural

Swelling Clay, the BET surface area values are $65.790 \text{ m}^2/\text{g}$ for Natural swelling clay. The surface area of PVP-Natural Swelling Clay is $0.812 \text{ m}^2/\text{g}$. This reflects a change in the structural properties of the clay after modification which can be explained by the fact that part of the polymer layer covered the surface of the clay and thus prevent the passage of nitrogen gas through pores.

The disappearance of the hysteresis on the curve of the modified clay may be justified by a kind of coverage of the surface of the clay by the polymer causing the loss of its mesoporosity thus blocking the pores and preventing the passage of nitrogen [42].

Thermal Analysis the effect of temperature shown by TGA and DTA. The figure 3 (a) indicates that the DTA of Natural swelling clay shows an endothermic peak at 83.76°C which corresponds to dehydration within the interlayer of Natural swelling clay. A second endothermic peak located at 281.22°C indicates dehydroxylation. At 518.79°C , two phenomenon is observed, the first corresponding to the dehydroxylation and the second due to recrystallization specifically to the structural changes in the sample. This result confirms the high content of montmorillonite in the sample studied. The TGA curve of Natural Swelling Clay (See figure 3 (a)) confirms a first mass loss at 83.37°C which indicates the high content of the sample surface water.

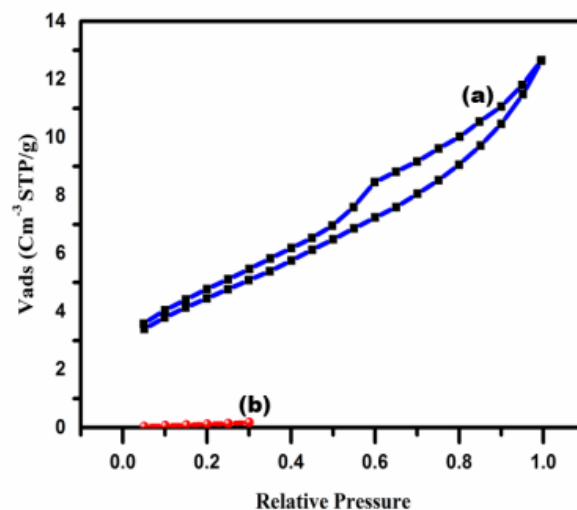


Figure 2 Surface area and volumes of pore curves at 77°K for a) Natural Swelling clay b) PVP-Natural Swelling clay.

A second loss is then observed between 214.45°C and 532.15°C which can be explained by the loss of bound

water and crystal clear water. DTA of the modified clay shown in figure 3(b) PVP-Natural Swelling Clay shows an endothermic peak at 144.99 °C corresponding to the dehydration of the water to the surface of the organoclay, a second peak at 526.83 °C which indicates the glass transition temperature of organic matter, representing the temperature range through which the organic material passes from a rubbery state to a vitreous state, solid (rigid). The peak at 637.4° C corresponds to the dehydroxylation of the organoclay.

These results were confirmed by the TGA of PVP- Natural Swelling Clay (Figure 3(b)), shows a weight loss at 81.98 °C in the range of 7.11% second loss observed at 241.37 °C in the range of 10.99% and a loss of mass at 522.46 °C. These can be translated as intercalated water loss, two-stage degradation of PVP / CTA + and finally degradation of the structure of the clay sheet to release H₂O.

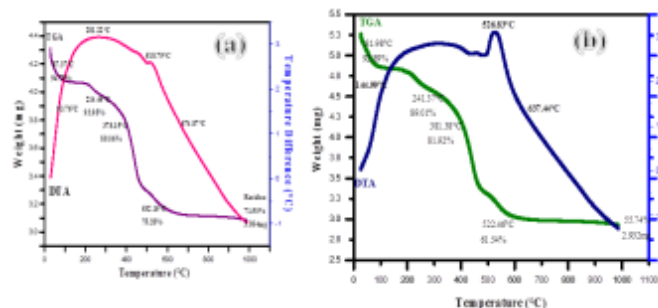


Figure 3 Thermal analysis data (TGA and DTA) of a) Natural Swelling Clay and b) PVP-Natural Swelling Clay.

Transmission Electronic Microscopy and particles size distribution analysis Figure 4a,b shows the representative bright field TEM images of modified and purified clay respectively. Fringes with oscillating contrast indicate the occurrence of a layered structure in the Natural swelling clay. The modified clay shows a uniform grey contrast indicating that the surface of the clay which has been completely covered by the polymer due to the compatibility between PVP and Natural swelling clay and their enhanced properties may be explained by hydrogen bonding interactions. At some regions in the periphery of the modified clay, some fringes are visible where the layered clay structure has been exposed.

X-ray Photoelectron Spectrometer the X-ray analysis photoelectron spectroscopy (Figure 6 and 7) shows the existence of atoms such as carbon, oxygen, nitrogen aluminium, silicon, in the modified clays and purified clays. The C 1s spectrum of PVP-Natural Swelling clay is characterized by two photo emissions centred at 285.7 and 287.2eV, corresponding to the C-C bond in the long chain and C-N, respectively. The slight widening in the

binding energy observable on the C1S spectrum may be due to the interaction between the polymer and the organoclay.

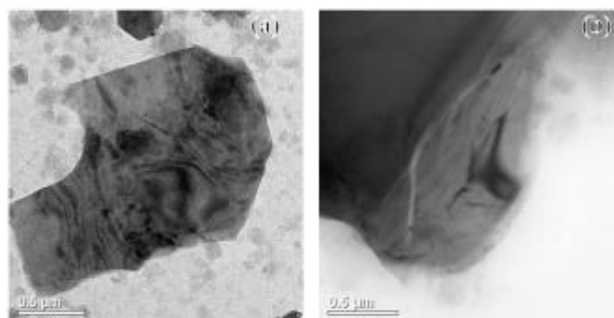


Figure 4 TEM images of (a) Natural Swelling Clay (b) PVP-Natural Swelling Clay at low Magnification.

The corresponding higher magnification image (Figure 5) shows the existence of layered nanoclay structure.



Figure 5 TEM image of PVP-Natural Swelling Clay at High Magnification.

A double 1s transition of Nitrogen is observed with a binding energy at 399 eV, which corresponds to the nitrogen linked to the long alkyl chain of CTAB and at 402 eV for nitrogen PVP [45].

The values of Si 2P binding energy shown in two different states justify the different environments silicon in purified and modified clay which is in the tetrahedral and octahedral coordination appearing 103.30 to 103 eV for Natural Swelling clay and 103.29 and 102 eV to modified clay.

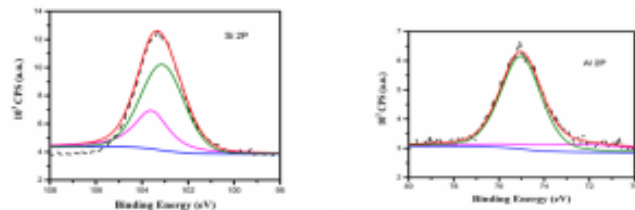


Figure 6 X-ray Photoelectron spectroscopy spectra of Si 2P and Al 2P high resolution of Natural Swelling Clay.

The results obtained by the solid-state NMR studies of organo-clays show a measurable shielding of the silicon nuclei 29 in the clays [46].

The energy transitions of Al 2P show two energy transitions to 75eV for the unmodified clay and 74.9eV for the modified clay; it is observed that too much change at this level this may occur due to the phenomenon described in a previous work [47].

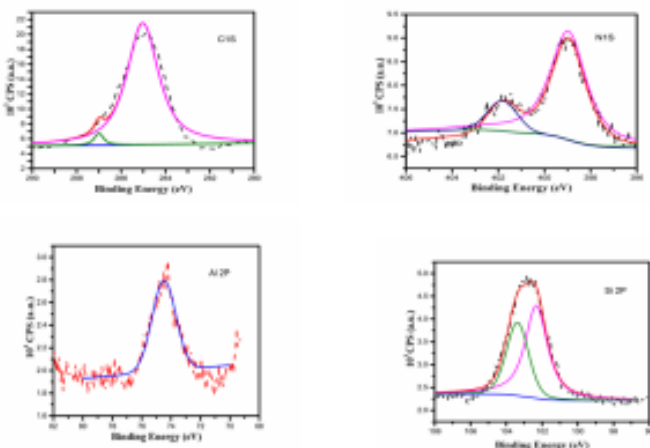


Figure 7 High-resolution XPS spectra of PVP-Natural Swelling Clay C1s, N1s, Al 2P, Si 2P.

Application for Electrochemical detection of Pb²⁺
Electrochemical response of Pb²⁺ the typical voltammetric behavior of 3x10⁻⁷M Pb²⁺ at the GCE/PVP/CTAMa is shown in Figure 8 Compared with the cyclic voltammogram of the modified GCE in to white electrolyte, a defined anodic peak at -550 mV corresponds to oxidation of metallic lead can be obtained after 5 min for accumulation of lead ions from the sample solution to the electrode membrane surface and cathodic peak was observed at -670 mV. The oxidation current is much larger than the reduction current.

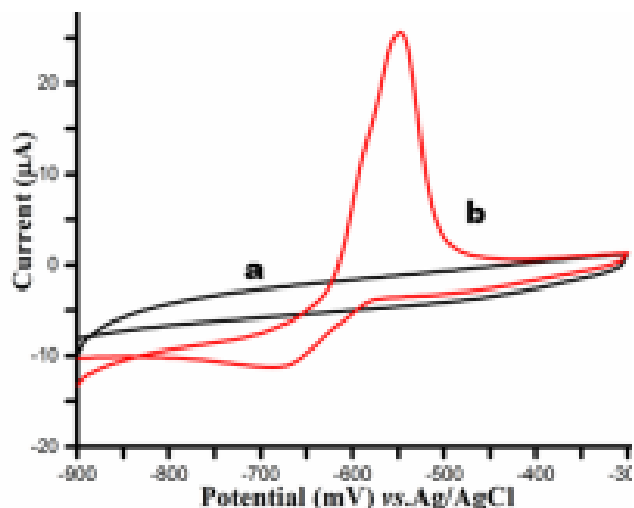


Figure 8 Cyclic voltammograms of bare GCE in absence of Pb²⁺ (a), GCE/PVPCTAMa in presence of 3x10⁻⁷M in 1MKCl. Scan rate: 50mVs⁻¹.

These results confirm that lead (II) cations are indeed complexed into anionic forms in the pre-concentration step [48]. The lead ions are accumulated on the surface of the modified electrode due to the complexation of the metal ion by the polymer which has polar groups such as carbonyl and then this ion is reduced after applying a voltage of -1.1v. FIG. 9 illustrates well an adsorption of pb²⁺ on the surface of the modified electrode.

The following mechanism can, therefore, be proposed [49-51].

1. Accumulation/Complexing Step
 $(Pb^{2+})_{\text{Solution}} + (\text{PVP/CTAMa})_{\text{Surface}} \rightarrow (Pb^{2+}-\text{PVP/CTAMa})_{\text{Adsorbed}}$
2. Reduction Step
 $(Pb^{2+}-\text{PVP/CTAMa})_{\text{Adsorbed}} + 2e^- \rightarrow (Pb^0-\text{PVP/CTAMa})_{\text{Adsorbed}}$
3. Stripping Step
 $(Pb^0-\text{PVP/CTAMa})_{\text{Adsorbed}} \rightarrow (Pb^{2+})_{\text{Solution}} + (\text{PVP/CTAMa})_{\text{Surface}} + 2e^-$

Optimization of the detection step chemical parameters such as pH, accumulation time, and analyte concentration were studied during the open-circuit pre-concentration time. The variation of the accumulation time was examined for the solution containing 10⁻⁷M of Pb²⁺ in the interval of time between 0 and 10 min and 5 min is chosen as an accumulation time.

As the accumulation time increases, the peak of oxidation current increases to a maximum which results in the time of the adsorption equilibrium due to the maximum site accumulation by the metal ions (figure 10,(a)).

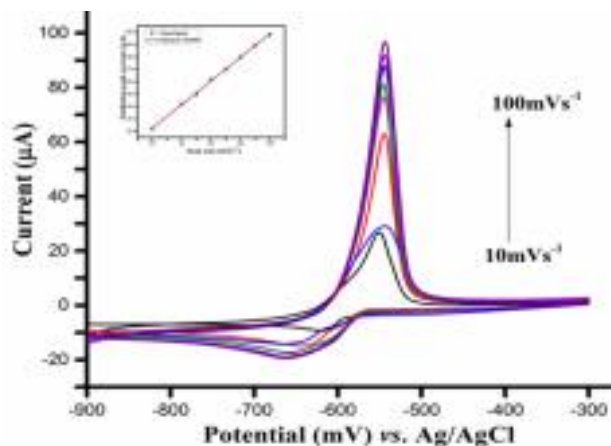


Figure 9 Cyclic voltammograms GCE/PVPCTAMa in the presence of 3×10^{-7} M of Pb^{2+} at different scan rates. The inset is the i_{peak} vs. scan rate.

The effect of pH is studied in the range of 2 to 11 in a solution containing Pb^{2+} at 10^{-7} M after a time of 5 min. The solutions of hydrochloric acid and 0.1M sodium hydroxide are used to adjust the pH. We observe a maximum peak at 3.99 which can be explained by the fact that there is a favourable and maximum adsorption at this pH (figure 10, (b)). Previous work has shown that around this pH there is complexation of lead ions by chloride ions [52]. The acid medium is therefore chosen as a suitable medium for the complexation of the lead ions [53].

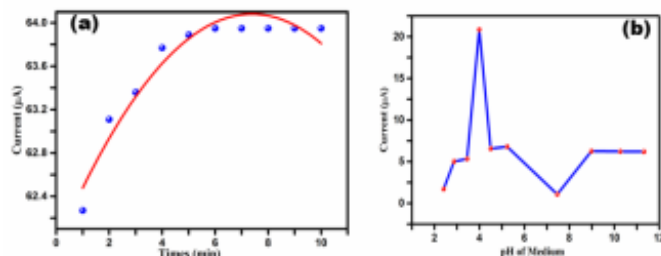


Figure 10 (a): accumulation time at GCE/PVPCTAMa, (b): Evolution of peak intensities at GCE/PVPCTAMa, as a function of the pH of the accumulating medium (1 MKCl) in solutions containing Pb^{2+} at 10^{-7} M.

The calibration graph of peak current versus lead ion concentration in the range 10^{-7} to 12×10^{-7} M is shown in Figure 11. The calibration graph is linear.

Conclusion

The synthesis of polyvinylpyrrolidone-Natural Swelling clay composite through cation-exchange and intercalation solution process provides compounds with interesting structural and functional properties.

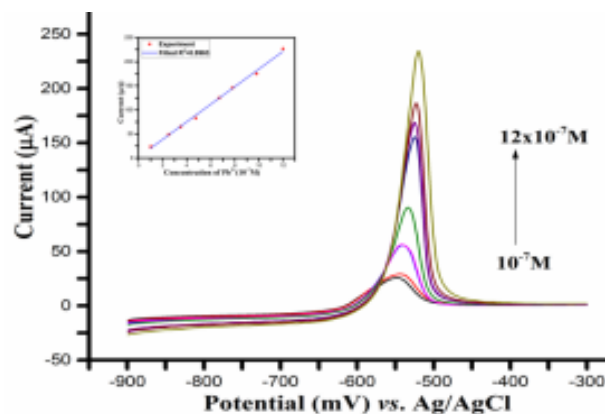


Figure 11: Linear Stripping Voltammetry of GCE/PVPCTAMa at a different added concentration of Pb^{2+} in the electrolytic medium, (at insert plot of oxidation peak versus Pb^{2+} concentration).

The characterization techniques have oriented this research to understand the structural and morphological differences of Natural Swelling clay and the change. The application of the glassy carbon electrode modified with polyvinylpyrrolidone-Natural Swelling clay film composites has to find the limit of detection 1.815×10^{-7} M, and a calibration curve with a linear regression 0.996. The present work is an example of the importance of composite materials from local materials such as the Maroua swelling clay commonly called "Karal". This work is, therefore, part of the promotion and the valorization of this clay which until then remains underexploited and this opens up new perspectives for an exploitation of this clay material.

Acknowledgements

This work was financially supported by The World Academy of Sciences for the Advancement of Science in developing countries (TWAS) and the Council of Scientific and Industrial Research (CSIR). We thank also Dr. Vijayamohan K Pillai, Director of Central Electrochemical Research Institute (CECRI) of Karaikudi, Tamilnadu (India) who gave us all the facilities to carry out our research.

Notes and references

1. D. Schmidt, D. Shah and E. P. Giannelis, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 212.
2. J. L. Suter, D. Groen, and P. V. Coveney, *Nano Lett.*, 2015, **15**, 8113.
3. S. Metz, R. L. Anderson, D. L. Geatches, J. L. Suter, R. Lines and H.C.Greenwell, *J. Phys. Chem. C.*, 2015, **119**, 12642.
4. J.Ahn, W.J.Chung, I.Pinnau, J. Song, N. Du, G. P. Robertson and M.D Guiver, *J. Membr. Sci.*, 2010, **346**, 287.

5. H. Mauroy, T. S. Plivelic, E.L.Hansen, J.O. Fossum, G. Helgesen, K. D. Knudsen, *J. Chem. C*, 2013, **117**, 19663.
6. P. J. Wallis, A. L. Chaffee, W. P. Gates, A. F. Patti, J. L. Scott, *Langmuir*, 2010, **26**, 4265.
7. W. Qin and J. F. Kadla, *Ind Eng Chem Res.*, 2011, **50**, 12555.
8. N. K. Singh, B. D. Purkayastha, J. K. Roy, R. M. Banik, M. Yashpal, G. Singh, S.Malik, P. Maiti, *Appl Mat and Interf.*, 2010, **2**, 81.
9. J. U. Park, Y. S. Choi, K. S. Cho, D. H. Kim, K.H. Ahn, S. J. Lee, *J. Polymer*, 2006, **47**, 5153.
10. R. A. Vaia, R. K. Teukolsky, E. P. Giannelis, *Chem Mater.*, 1994, **6**, 1017.
11. W. Xie, Z. Gao, W. P. Pan, D. Hunter, A. Singh, R.Vaia, *Chem Mater.*, 2001, **13**, 2990.
12. W. Xie, R. Xie, W. Pan, D. Hunter, B. Koene, L. S. Tan, R.Vaia, *Chem. Mater.*, 2002, **14**, 4845.
13. J.W.Gilman, W.H. Awad, R.D. Davis, J.Shields, R.H.Harris Jr, C. Davis, A.B. Morgan, T.E.Sutto, J. Callahan, P.C. Trulove and H.C.DeLong, *Chem. Mater.*, 2002, **14**, 3785.
14. W. H. Awad, J.W. Gilman, M. Nyden, R.H. Harris, T.E. Sutto, J. Callahan, P.C. Trulove, H.C. DeLong and D.Fox, *Thermochim Acta*, 2004, **3**, 409.
15. E.Loizou, P. Butler, L. Porcar, E. Kesselman, Y. Talmon, A. Dundigalla. and G.Schmidt, *Macromolecules*, 2005, **38**, 2049.
16. B.Shemper, J.F. Morizur, M. Alirol, A. Domenech, V. Hulin, and L.J. Mathias, *J. Appl. Polym. Sci.*, 2004, **93**, 1252.
17. K.A.Carrado, L.Q.Xu, R. Csencsits and J.V.Muntean, *Chem Mater.*, 2001, **13**, 3773.
18. J.Minet, S. Abramson, B. Bresson, C. Sanchez, V. Montouillout and N.Lequeux, *Chem Mater*, 2004, **16**, 3962.
19. S. Letaïef and E. Ruiz-Hitzky, *Chem. Commun.*, 2003, **24**, 2997.
20. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, *Macromolecules*, 1997, **30**, 6338.
21. P. C. LeBaron, Z. Wang, T. J. Pinnavaia, *Appl. Clay Sci.*, 1999, **15**, 29.
22. T. Kemper, S. Sommer, *Environ. Sci. Technol.*, 2002, **36**, 2747.
23. I. A. Darwish, D. A.Blake, *Anal Chem.*, 2002, **74**, 58.
24. K. Leopold, M. Foulkes, P. J. Worsfold, *TRAC-Trend Anal Chem*, 2009, **28**, 435.
25. H. Bagheri, A. Afkhami, H. Khoshsafar, M. Rezaei, A. Shirzadmehr, *Sensors and Actuators B: Chemical*, 2009, **86**, 460.
26. H. Bagheri, A. Afkhami, M. Saber-Tehrani and H. Khoshsafar, *Talanta*, 2012, **97**, 95.
27. A. Afkhami, M. Saber-Tehrani, H. Bagheri, *J. Hazard. Mater.*, 2010, **181**, 844.
28. Y. Li, Y. Jiang and X.P.Yan, Z.M.Ni, *Environ. Sci. Technol.*, 2002, **36**, 4891.
29. J. L. Mas, M. Villa, S. Hurtado, R.García-Tenorio, *J. Hazard. Mater.*, 2012, **205**, 207.
30. I. K. Tonle, E. Ngameni, F. M. M. Tchieno, A. Walcarius, *J. Solid State Electrochem.*, 2015, **19**, 1973.
31. F. T. Nya, E. N. Haulin, E. Yanne, C. Kabe, B. T. Touolak and J. M. Ndjaka, *Inter. J. of Basic and Applied Sci.*, 2015, **4**, 115.
32. H.Tributh G. Lagaly, *GIT Fachz. Lab.*, 1986, **30**, 529.
33. E.I.Unuabonah, O. Kayode Adebowale and F.Dawodu, *J. Hazard. Mater.*, 2008, **157**, 409.
34. W.B.Xu, S.P. Bao and P.S.He, *J. Appl. Polym. Sci.*, 2002, **84**, 849.
35. K.E.Strawhecker and E.Manias, *Chem Mater.*, 2000, **12**, 2949.
36. S.Y.Lee, W.J. Cho, K.J. Kim, J.H. Ahn, M. Lee, *J. Colloid Interf. Sci.*, 2005, **284**, 673.
37. J.L.Ahlrichs, C.J.Serna and J.M.Serratos, *Clays and Clay Miner.*, 1975, **23**, 119-124.
38. J.K.Wagheu, C.Forano, P. Besse-Hoggan, I.K.Tonle, E. Ngameni and C.Mousty, *Talanta*, 2013, **103**, 343.
39. S.Ramesh, A. Sivasamy, M.Alagar, F.Chandrasekar, *J.Composite Mater.*, 2011, **45**, 1489.
40. L.B.De Paiva, A.R. Morales, F.R. Valenzuela Diaz, *Appl. Clay.Sci.*, 2008, **42**, 24.
41. C. C.Wang, L. C. Juang, C.K. Lee, T. C. Hsu, J.F. Lee, H.P. Chao, *J. Colloid Interf. Sci.*, 2004, **280**, 35.
42. P. Stathi, K. Litina, D. Gournis, T. S. Giannopoulos and Y. Deligiannakis, *J.Colloid and Interf. Sci.*, 2007, **316**, 309.
43. Z. Mojovic, N. Jovic-Jovici, A. Milutinovic-Nikolic, P. Bankovic, A. A. Rabi-Stankovic, D. Jovanovic, *J. Hazard Mater.*, 2011, **194**, 184.
44. F. Kooli., *J. Chemistry*, 2015, 8.
45. M. Templin, U. Wiesner, H. W. Spiess, *Adv. Mater.*, 1997, **10**, 817.
46. G. Lagaly, S. Ziesmer, *Adv Colloid Interf.*, 2003, **100**, 128.
47. T. Takahashi, T. Ohkubo, K.Suzuki, Y. Ikeda, *Microporous Mesoporous Mater.* 2007, **106**, 297.
48. I. K. Breakwell, J.Homer, M.A.M. Lawrence and W.R.. Mcwhinnie, *Polyhedron*, 1995, **14**, 2518.
49. H. G. Valery, T. R. Ngono, H. Saâdane, M. Ennachete, M. Khouili, A. Hafid, L. Benoît, A. Chtaini, *Pharmaceut. Anal. Acta*, 2013, **4**, 271.
50. Y. Wang, H. Ge, Y. Wu, G. Ye, H. Chen, X.Hu, *Talanta*, 2014, **129**, 105.
51. M. Salarian, A. Ghanbarpour, M. Behbahani, S. Bagheri, A. Bagheri, *Microchim. Acta*, 2014, **181**, 1007.
52. I. Cesarino, E. T. G. Cavalheiro and M. A. B. Christopher, *Brett. Electroanalysis*, 2010, **22**, 68.
53. S. Tagashira, S. Kimoto, K. Nozaki, Y. Murakami, *Anal Sci.*, 2009, **25**, 726.