

## **ELECTROCHEMICAL PERFORMANCE OF COMPOST EXTRACTS CONTAINING N,N,N',N'-TETRAMETHYLPHENYLENEDIAMINE (TMPD)**

**S.E. Elaigwu\*<sup>1</sup>, A.U. Awode<sup>2</sup>, B.W. Tukura<sup>3</sup>**

<sup>1</sup>Department of Chemistry, University of Ilorin, Nigeria

<sup>2</sup>Department of Chemistry, University of Jos, Nigeria

<sup>3</sup>Department of Chemistry, Nasarawa State University, Keffi, Nigeria

Corresponding author: Tel. +2348036611634; [elaigwu.se@unilorin.edu.ng](mailto:elaigwu.se@unilorin.edu.ng);  
[sunnietrinex@hotmail.com](mailto:sunnietrinex@hotmail.com)

### **ABSTRACT**

Composting is a well-known practice for valorizing organic waste materials into useful product. Its use in the management of soils, which are contaminated with organic compounds has been widely studied and reported. Nevertheless, the present approach of analysing the organic compounds and its degradation products using GC-MS is costly. Hence, the need for an alternative analytical screening technique which is less expensive and fast, when compared with the GC-MS analysis. As a probable alternative approach, the cyclic voltammetry of compost extracts containing N,N,N',N'-Tetramethylphenylenediamine (TMPD) is described in this study. The result of the study, however revealed that cyclic voltammetry could neither detect the presence of the TMPD nor its degradation products in any of the compost extract. This might have resulted from the strong and complex matrix of the compost which prevented the oxidation of the TMPD in the compost extract.

### **INTRODUCTION**

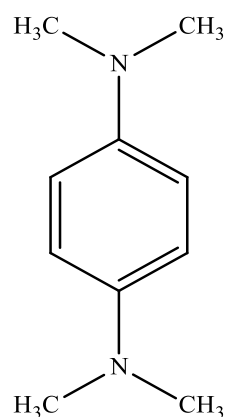
Composting technology serves as a waste management strategy as it provides a platform for the sustainable reuse of the biodegradable fraction of the organic waste materials, which is both microbial and nutrient rich. It has been used to improve soil properties, suppress pathogenic organisms, contribute to the partial disappearance of organic pollutants by decreasing their concentration, reducing heavy metals bioavailability, and balancing the organic material in the final compost before it can be applied to soils [1-3]. Composting technology signifies a cheap and low technology in contrast to other waste management practices.

Bioavailability of pollutants is a crucial factor that affects their degradation by microorganisms in soil and sediments, as the microorganisms are capable of attacking the pollutants of interest only when they are dissolved within the systems [4]. In order for the composting process to be effective and properly used for the bioremediation of contaminated soils and sites, there are numbers of physical, chemical, and biological factors which determine the microbial availability to the target molecules that are very essential [5,6]. The nature and content of the waste or soil organic matter that is basically made

up of humic acids (HAs) are believed to have the most significant role to play [7,8].

Bioremediation through composting has been revealed as a key environmental process which affects the fate of organic pollutant in aquatic and terrestrial biotas [9]. As a bioremediation process, co-composting approaches under certain conditions are known as a credible industrial process for the removal of pollutants [6,10]. Interest in this research area has increased in recent times due to the rapid progress in molecular ecological processes, and the influence of organic matter seems to significantly improve the removal of organic contaminants [11]. However, the precise mechanisms for the removal of organic pollutants are still not very clear. The mechanisms could either be via complete or incomplete mineralisation, or their fixation as non-extractable residues (NER) to organic matter [1,12]. Thus, the success of such composting bioremediation processes is inconclusive and contradictory. Joyce et al [13] revealed that organic pollutants were mostly removed during the active phases of composting with meagre removal taking place during the curing phases. However, Sayara et al. [14] proposed the use of mature compost in contrast to immature compost for the removal of organic contaminants. Consequently, conclusions amongst studies may differ depending on the experimental or analytical processes applied.

This study therefore aimed to develop a rapid screening method for studying the presence or the degradation of an organic compound during composting process. In order to achieve this, a model compound had to be identified that could preferably be analysed by an inexpensive rapid screening method as opposed to full analysis by GC-MS. Electrochemical analysis was identified as such promising technique, and the organic compound to be studied was the electroactive N,N,N',N'-Tetramethylphenylenediamine (TMPD) shown in Figure 1. It is a dye, which in the oxidized form (Wurster's Blue) is a redox mediator that is well-known and has been used greatly as an electron acceptor from ascorbic acid during the study of biological electron transfer processes, and also known to partition between organic and aqueous phases [15]. These properties meant that it would have an environmental impact, and the redox properties show that it could be studied by cyclic voltammetry.



**Figure 1:** N,N,N',N'-Tetramethylphenylenediamine (TMPD)

## MATERIALS AND METHODS

All chemicals used in this study were of analytical grade and were used subsequently without further purification. N,N,N',N'-Tetramethylphenylenediamine (TMPD) and anthracene (97% purity) were purchased from Sigma-Aldrich, UK. Hexane, dichloromethane, acetone and methanol were purchased from Fisher Scientific, UK. Stock solutions of TMPD were prepared, and diluted to the required concentration before use. Composts used were prepared from *Prosopis africana* shell. All experiments were performed in triplicate.

### *Composting Of Prosopis Africana Shell*

50 g each of the ground *Prosopis africana* shell were weighed into four different flasks of known weight. 50 ml of water was added and the whole content in each flask was weighed and placed in an incubator whose temperature was set at 30 °C. After four days a flask was taken out of the incubator and weighed, after which the content was dried in an oven at 105 °C for 72 hours. The dried compost was taken out from the oven, allowed to cool down to room temperature and weighed to obtain the weight lost (loss in dry matter). The same procedure was repeated for the remaining three flasks on a weekly basis after the first measurement.

### *Cyclic Voltammetry Of TMPD*

Electrochemical measurements were conducted with a  $\mu$ Autolab Type III potentiostat. A glassy carbon electrode was used as the working electrode, while a silver/silver chloride electrode was used as the reference electrode, and a nickel spiral as the counter electrode at a scan rate of 50 mVs<sup>-1</sup> and scan range of -0.2 to +0.4V. 0.1–1 mM solution of TMPD were prepared in 0.1 M KCl solution in water. The cyclic voltammetry of the different solution concentrations was studied, and used to determine the limit of detection for the TMPD.

### *Composting Of TMPD*

100 g each of the composts were weighed into eight different flasks and 10 ml each of 1 mM TMPD solution was added to four of the flasks, while 10 ml each of distilled water was added to the four remaining flasks (controls). One flask each containing 10 ml of TMPD and 10 ml of distilled water were sampled on the first day of the experiment and extracted successively with hexane, dichloromethane, acetone and methanol (in order of increasing polarity). Subsequent samplings were performed on the 5th, 16th and 22nd day. The extracts were concentrated by removing the solvents using a rotary evaporator. The concentrated extracts were then subjected to cyclic voltammetry. Before this experiment, the compost extracts from the different solvents were spiked with the TMPD and the CV measured.

### Extraction Of TMPD

12 g each of the dried samples were extracted sequentially with hexane, dichloromethane, acetone and methanol via a pressurized fluid extraction (PFE) on an Accelerated Solvent Extractor (Dionex, ASE 200) using a pre-programmed method in the instrument. The method is programmed to carry out multiple extractions in a run. It uses about 60 ml of the solvent, at 100 °C, 2000 psi pressure

and takes about 25 min to carry out the extraction. After the extraction, the extracts were allowed to settle, concentrated, and analysed using cyclic voltammetry. The control samples were also extracted by performing the same extraction procedures.

## RESULTS AND DISCUSSION

### Composting Of *Prosopis Africana* Shell Loss In Dry Matter

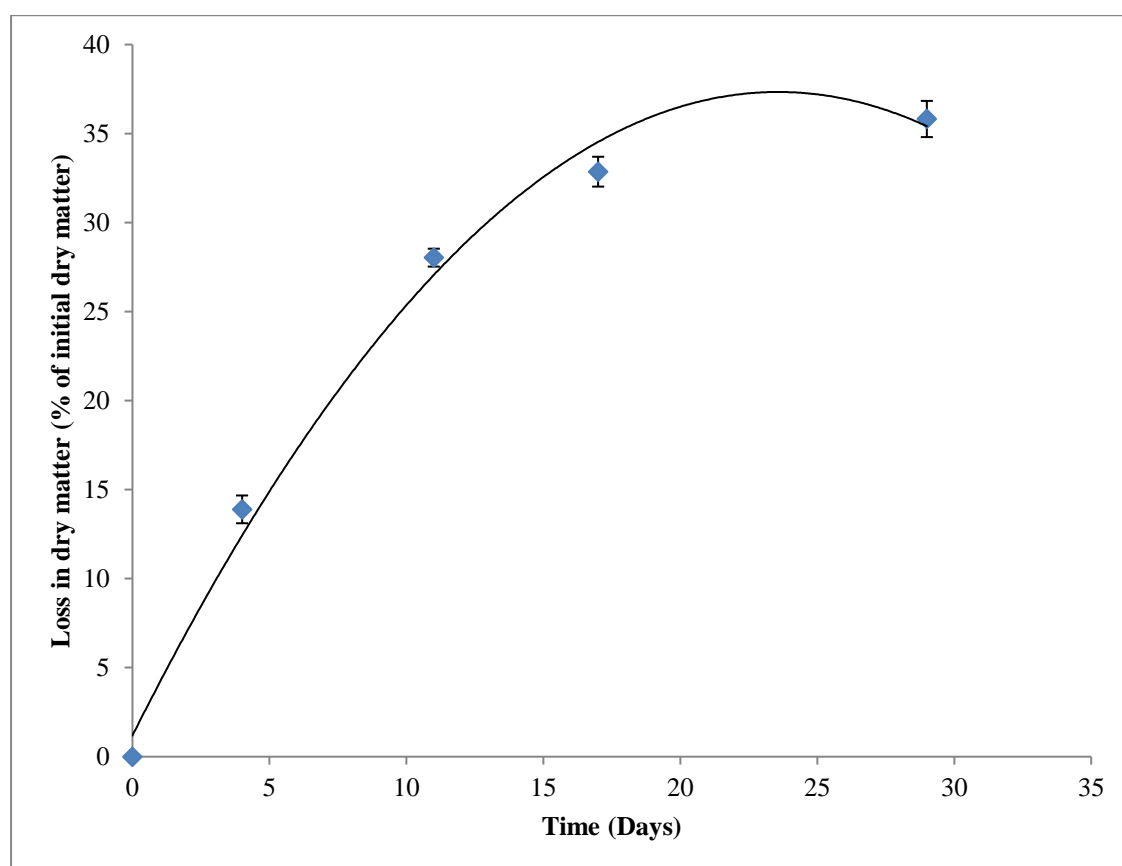


Figure 2: Loss in dry matter for the *Prosopis africana* shell

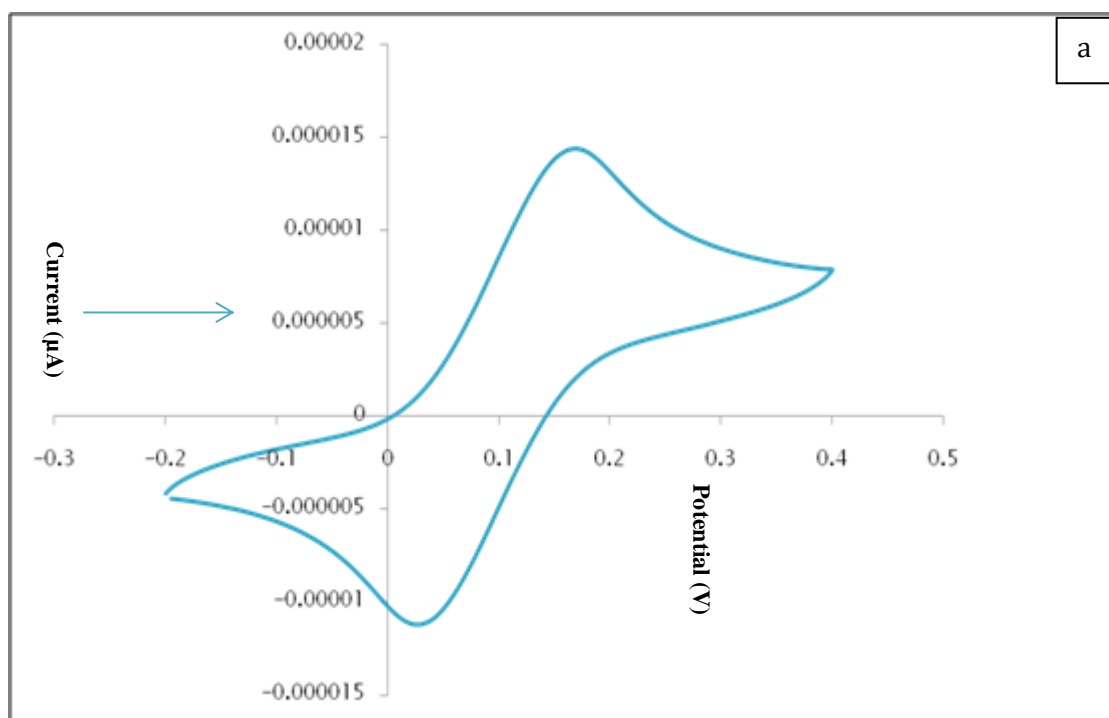
The result for the loss in total dry matter for the *Prosopis africana* shell is shown in Figure 2. The loss in dry matter during the bio-oxidative stage was 35.8%, which

happened swiftly at the start of the composting process. This decline in dry matter corresponds to the active phase of the composting process, with the highest

loss in dry matter in most cases taking place within this period [16]. The observed trend for the loss in dry matter in this study is consistent with previous reports in literature [16-18]. The maximum value for the loss in dry matter for the *Prosopis*

*africana* shell in this study is close to the 40% found for the composting of olive mill wastewater with olive leaves [18], indicating that the *Prosopis africana* shell composted well.

### Cyclic Voltammetry Of TMPD

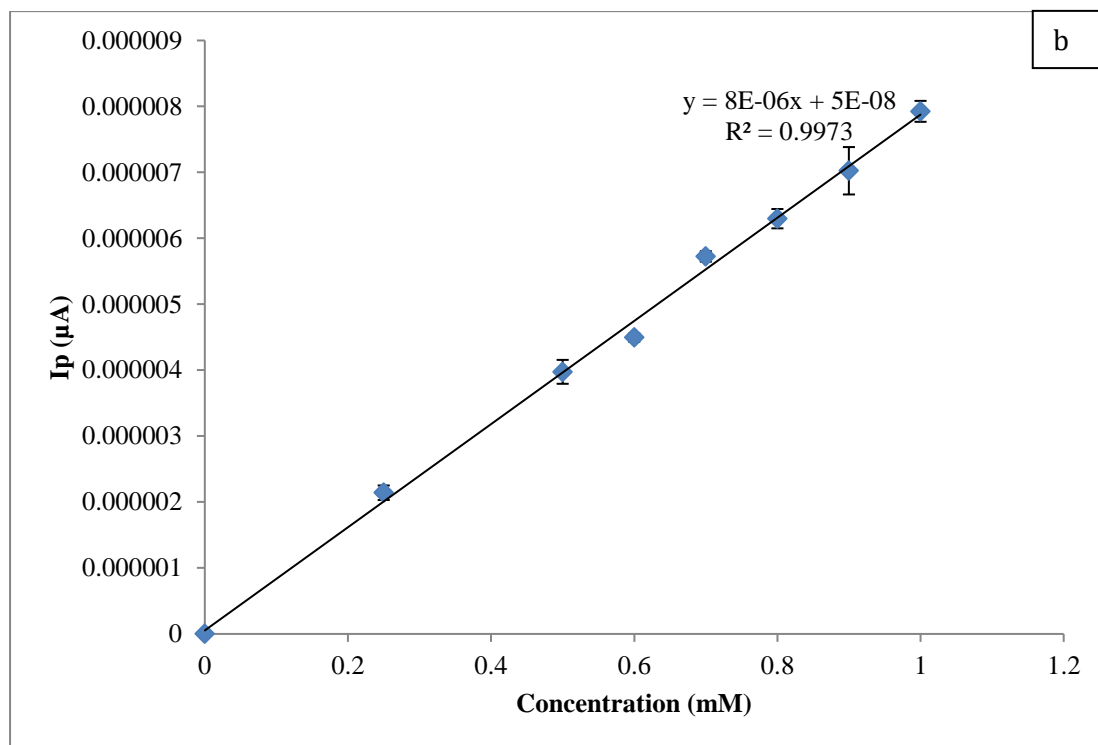


Many studies have reported the cyclic voltammetry of TMPD [19-21]. Thus, it was selected as a “model” compound to be used in this study for the development of an electrochemical method for the analysis of organic compounds in composting process. Figure 3(a) shows the cyclic voltammetry of TMPD in 0.1 M KCl solution. The result shows a characteristic single one-electron oxidation of TMPD to generate the cation

radical (TMPD<sup>+</sup>) [15,19]. In this electrochemically reversible voltammetry, the oxidation of TMPD to TMPD<sup>+</sup> occurred at +0.18 V, while the reduction of TMPD<sup>+</sup> back to neutral TMPD occurred at +0.07 V. The result obtained in this study is consistent with previous reports [15,19]. The peak current ( $I_p$ ) values for the oxidation peaks were calculated for each of the concentrations, and used to plot the

calibration curve as shown in Figure 3(b). The calibration curve was used in the determination of the limit of detection,

which was found to be 0.05 mM in this study.



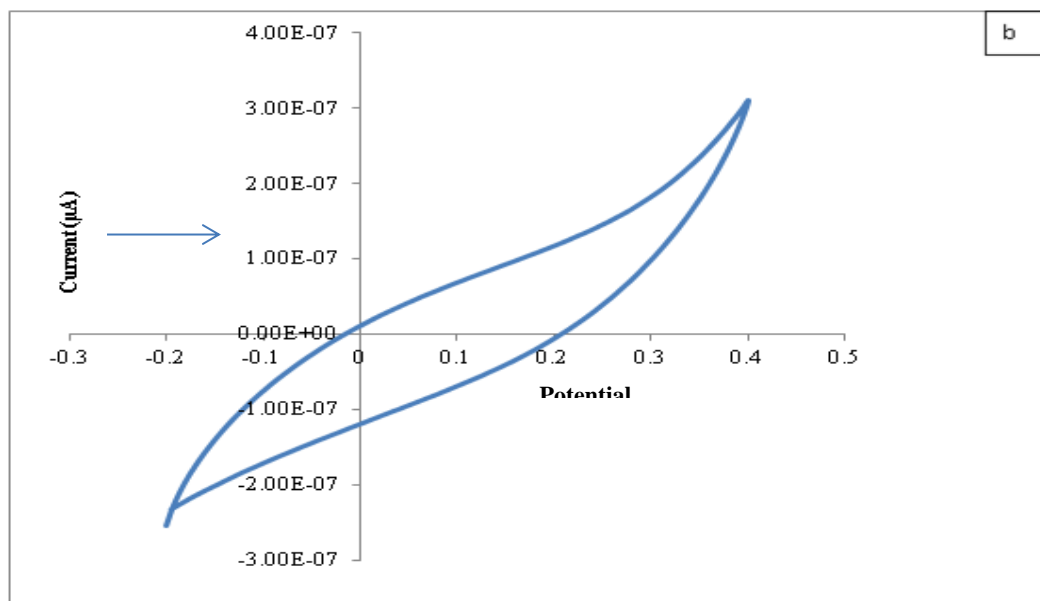
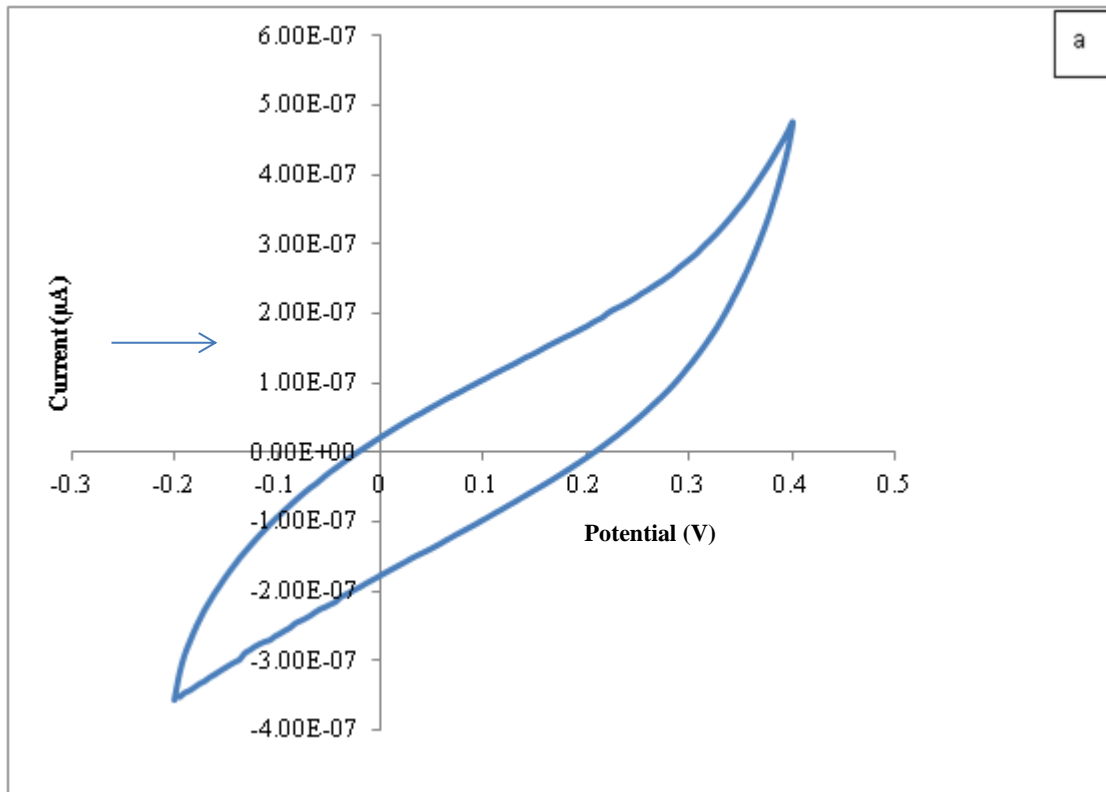
**Figure 3: (a) Cyclic voltammogram of TMPD in 0.1 M KCl (with arrow showing direction of scan), (b) Calibration curve for TMPD**

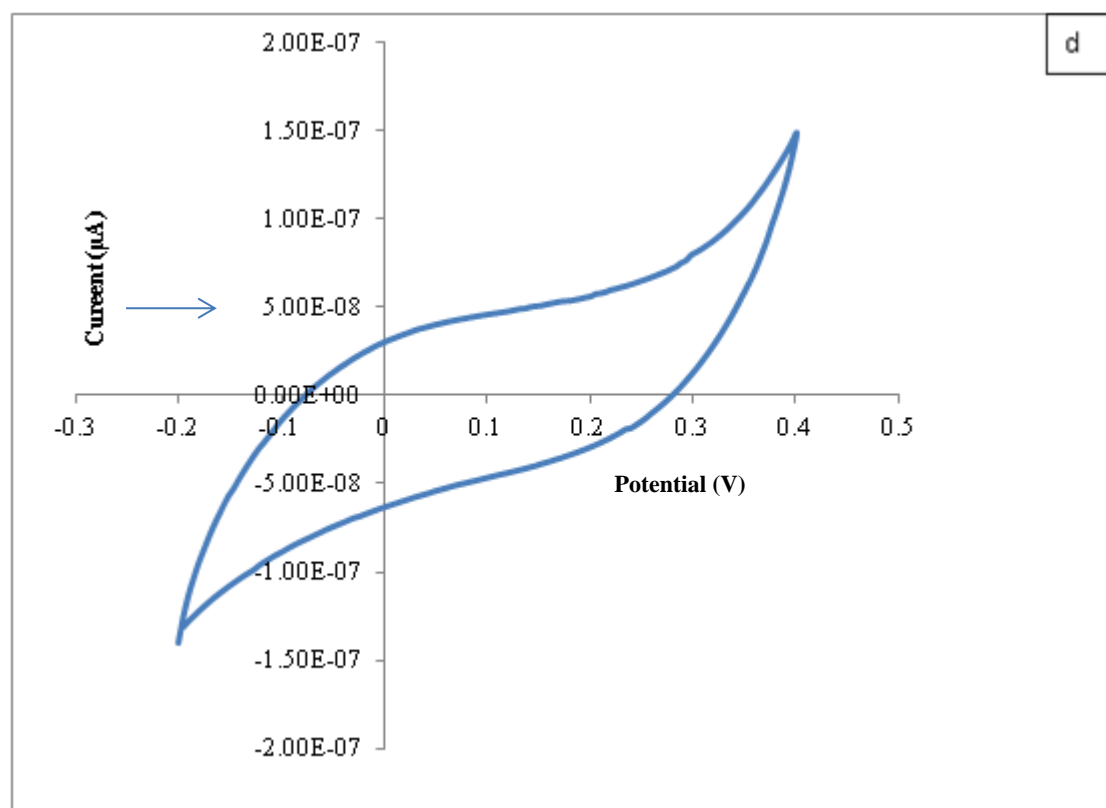
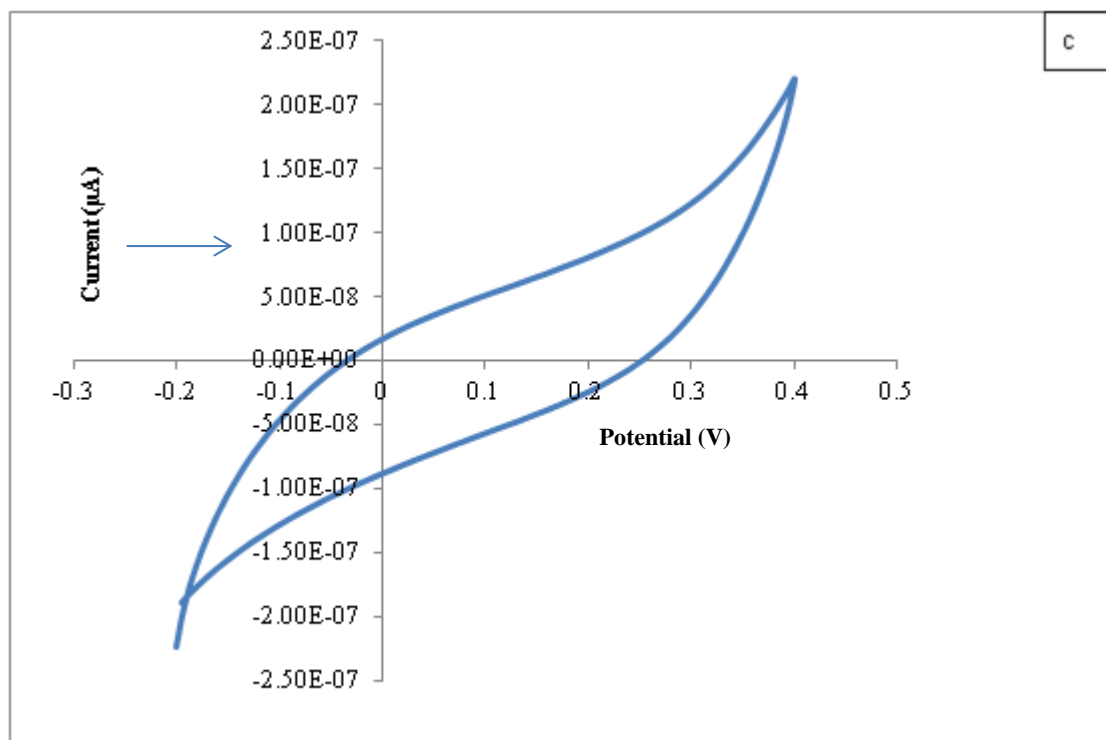
The different compost extracts obtained from four solvents of different polarity, namely hexane, dichloromethane, acetone and methanol (in order of increasing polarity) were subjected to cyclic voltammetry; none of the extracts revealed an oxidation or reduction peak (Figure 4 a-d), which implies that no electroactive species was present in the compost extracts. This could be interesting as it points to the possibility of using cyclic voltammetry as an analytical method for analysis of TMPD during the composting process. However, the cyclic voltammetry of the compost extracts spiked with TMPD showed neither

oxidation nor reduction peak. Similarly, the different non-coloured extracts obtained after the composting experiment with the TMPD did not show any oxidation or reduction peak. In each case, the obtained voltammograms (not shown) were similar to those of the compost extracts (Figure 4 a-d). Spaccini et al [22] reported that molecular components are held to the compost complex matrix by different intermolecular interactions. It is possible that this interaction could have been so strong that it prevented the oxidation of the TMPD in the compost extract. Therefore, the novel idea of using electrochemical

analysis as an inexpensive and rapid screening method to monitor the degradation of an organic compound

during composting process was ambitious and could not be achieved.





**Figure 4: Cyclic voltammogram of compost extracts, with arrow showing direction of scan (a) hexane extract, (b) dichloromethane extract, (c) acetone extract, (d) methanol extract**



## CONCLUSION

Cyclic voltammetry was explored as a cheap and rapid alternative screening method for the analysis of an organic compound during composting process. The results of the study showed that the technique is not suitable as an analytical method for this purpose, as it was unable to detect the presence of TMPD used as a model compound in the extracts. This might be as a result of the strong complex matrix of the compost, which prevented the oxidation of the TMPD within the compost extract, and making it difficult for it to be detected using this approach.

## REFERENCES

- [1] G. Lashermes, E. Barriuso, and S. Houot (2012), Dissipation Pathways of Organic Pollutants During the Composting of Organic Wastes. *Chemosphere* 87, 137.
- [2] S. Amir, M. Hafidi, G. Merlina, H. Hamdi, and J.C. Revel (2005), Fate of Polycyclic Aromatic Hydrocarbons During Composting of Lagooning Sewage Sludge. *Chemosphere* 58, 449.
- [3] C. Pakou, M. Kornaros, K. Stamatelatou, and G. Lyberatos (2009), On the Fate of LAS, NPEOs and DEHP in Municipal Sewage Sludge During Composting. *Bioresour. Technol.* 100, 1634.
- [4] R.J. Grosser, M. Friedrich, D.M. Ward, and W.P. Inskeep (2000), Effect of Model Sorptive Phases on Phenanthrene Biodegradation: Different Enrichment Conditions Influence Bioavailability and Selection of Phenanthrene-Degrading Isolates. *Appl. Environ. Microbiol.* 66, 2695.
- [5] K.T. Semple, B.J. Reid, and T.R. Fermor (2001), Impact of Composting Strategies on the Treatment of Soils Contaminated with Organic Pollutants. *Environ. Pollut.* 112, 269.
- [6] L.Y. Wick, R. Remer, B. Wurz, J. Reichenbach, S. Braun, F. Schafer, et al. (2007), Effect of Fungal Hyphae on the Access of Bacteria to Phenanthrene in Soil. *Environ. Sci. Technol.* 41, 500.
- [7] G. Cornelissen, O. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, and P.C.M. van Noort (2005), Extensive Sorption of Organic Compounds to Black Carbon, Coal, and Kerogen in Sediments and Soils: Mechanisms and Consequences for Distribution, Bioaccumulation, and Biodegradation. *Environ. Sci. Technol.* 39, 6881.
- [8] K.A. Thorn, J.C. Pennington, K.R. Kennedy, L.G. Cox, C.A. Hayes, and B.E. Porter (2008), N-15 NMR Study of the Immobilization of 2,4- and 2,6-Dinitrotoluene in Aerobic Compost. *Environ. Sci. Technol.* 42, 2542.
- [9] M. Kästner, and B. Mahro (1996), Microbial Degradation of Polycyclic Aromatic Hydrocarbons in Soils Affected by the Organic Matrix of Compost. *Appl. Microbiol. Biotechnol.* 44, 668.
- [10] S.M. Bamforth, and I. Singleton (2005), Bioremediation of Polycyclic Aromatic Hydrocarbons: Current Knowledge and Future Directions. *J. Chem. Technol. Biotechnol.* 80, 723.
- [11] A.L. Juhasz, and R. Naidu (2000), Bioremediation of High Molecular Weight Polycyclic Aromatic Hydrocarbons: A Review of the Microbial Degradation of Benzo[a]pyrene. *Int. Biodeter. Biodegr.* 45, 57.
- [12] E. Barriuso, P. Benoit, and I.G. Dubus (2008), Formation of Pesticide Nonextractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility. *Environ. Sci. Technol.* 42, 1845.

- [13] J.F. Joyce, C. Sato, R. Cardenas, and R.Y. Surampalli (1998), Composting of Polycyclic Aromatic Hydrocarbons in Simulated Municipal Solid Waste. *Water Environ. Res.* 70, 356.
- [14] T. Sayara, M. Sarrà, and A. Sánchez (2010), Effects of Compost Stability and Contaminant Concentration on the Bioremediation of PAHs-Contaminated Soil through Composting. *J. Hazard. Mater.* 179, 999.
- [15] J.E. Halls, N.S. Lawrence, and J.D. Wadhawan (2011), Electrochemical Estimation of Diffusion Anisotropy of N,N,N',N'-Tetramethylphenylenediamine within the Normal Hexagonal Lyotropic Mesophase of Triton X 100/Light Water: When Can the Effects of Cross-Pseudophase Electron Transfer be Neglected for Partitioned Reagents? *J. Phys. Chem. B* 115, 6509.
- [16] M.P. Bernal, A.F. Navarro, A. Roig, J. Cegarra, and D. Garcia (1996), Carbon and Nitrogen Transformation During Composting of Sweet Sorghum Bagasse. *BiolFertil Soils* 22, 141.
- [17] C. Paredes, A. Roig, M.P. Bernal, M.A. Sánchez-Monedero, and J. Cegarra (2000), Evolution of Organic Matter and Nitrogen During Co-Composting of Olive Mill Wastewater with Solid Organic Wastes. *Biol.Fertil. Soils* 32, 222.
- [18] A. García-Gómez, A. Roig, and M.P. Bernal (2003), Composting of the Solid Fraction of Olive Mill Wastewater with Olive Leaves: Organic Matter Degradation and Biological Activity. *Bioresour. Technol.* 86, 59.
- [19] J.S. Long, D.S. Silvester, A.S. Barnes, N.V. Rees, L. Aldous, C. Hardacre, and R.G. Compton (2008), Oxidation of Several p-Phenylenediamines in Room Temperature Ionic Liquids: Estimation of Transport and Electrode Kinetic Parameters. *J. Phys. Chem. C* 112, 6993.
- [20] R.G. Evans, O.V. Klymenko, C. Hardacre, K.R. Seddon, and R.G. Compton (2003), Oxidation of N,N,N',N'-Tetraalkyl-para-phenylenediamines in a Series of Room Temperature Ionic Liquids Incorporating the Bis(Trifluoromethylsulfonyl)Imide Anion. *Electroanal. Chem.* 556, 179.
- [21] M.J. Moorcroft, N.S. Lawrence, B.A. Coles, R.G. Compton, and L.N. Trevani (2001), High Temperature Electrochemical Studies using a Channel Flow Cell Heated by Radio Frequency Radiation. *J. Electroanal. Chem.* 506, 28.
- [22] R. Spaccin, S. Baiano, G. Gigliotti, and A. Piccolo (2008), Molecular Characterization of a Compost and Its Water-Soluble Fractions. *J. Agric. Food Chem.* 56, 1017.