WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.074
Volume 7, Issue 05, 157-165. Research Article ISSN 2277–7105

VOLTAMMETRIC DETERMINATION OF SULFAMETHOXAZOLE BY NICKEL HEXACYANOFERRATE FILM-CHEMICALLY MODIFIED ELECTRODE

Izabel C. Eleotério[1], Marco A. Balbino[1], José Fernando Andrade[1], Adelir Aparecida Saczk[2], Leonardo Luiz Okumura[3], Bruce R. McCord[4], Antonio Carlos Ferreira Batista[5], Marcelo F. de Oliveira*[1]

[1]Departamento de Química, FFCLRP, Universidade São Paulo, Ribeirão Preto-SP, 14040-901, Brazil.
[2]Departamento de Química, Universidade Federal de Lavras, 37200–000, Lavras, MG, Brazil.
[3]Departamento de Química, Universidade Federal de Viçosa, 36570–000, Viçosa, MG, Brazil.
[4]Chemistry Department – International Forensic Research Institute – Florida International University – Miami, FL – United States of America.
[5]Universidade Federal de Uberlândia - Campus do Pontal, 38304-402, Ituiutaba - MG, Brazil.

Article Received on
10 Jan. 2018,
Revised on 01 Feb. 2018,
Accepted on 22 Feb. 2018
DOI: 10.20959/wjpr20185-11342

***Corresponding Author**
Marcelo F. de Oliveira
Departamento de Química, FFCLRP, Universidade São Paulo, Ribeirão Preto-SP, 14040-901, Brazil.

ABSTRACT

Both human and veterinary medicine have relied on the antibiotic sulfamethoxazole to treat infections. However, high consumption of this compound culminates in environmental and public health problems. In this context, here we describe a voltammetric method to determine sulfametoxazole levels, using a glassy carbon disc electrode, chemically modified with nickel hexacyanoferrate film. We prepared the by cyclic voltammetry. The results provided a linear correlation coefficient (r) of 0.998 with a standard deviation (SD) of 0.053 µA, a limit of detection (based on the 3 SD/m ratio) equal to 6.8 nmol L^{-1}, and a limit of quantification (based on the 10 SD/m ratio) of 22.7 nmol L^{-1}.

KEYWORDS: Sulfamethoxazole, nickel hexacyanoferrate film, cyclic voltammetry, chemically modified electrodes.

INTRODUCTION

Electrode surface chemical modification plays an important role in the development of electrochemical sensors to determine organic compounds in complex samples. Chemically modified electrodes (CME) offer many advantages: they are inexpensive and selective, and their preparation is versatile.[1-32] In this context, nickel hexacyanoferrate (NiHCF) has emerged as an attractive compound to modify electrode sufaces.[1] NiHCF is a mixed-valence redox mediator with semiconducting characteristics, that can transfer electrons during reduction and oxidation processes. The electrodeposition technique promotes attachment of NiHCF films to electrode surfaces.[1] NiHCF resembles Prussian blue – cyanide interconnects its metal atoms, culminating in a crystalline structure consisting of alternating face-centered cubic Fe^{3+} and Ni^{2+} lattices that display interstitial potassium cations, to afford Ni(II)-CN-Fe(III) linkages.[6,16,25,28,29]

Several groups have investigated NiHCF film formation using supporting electrolytes containing the cations Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Al^{3+}.[1] NiHCF exhibits a well-defined, reversible, reproducible electrochemical response .The use of Group I cations has shown that different electrolyte compositions provide distinct voltammetric responses, and that the redox potential of the film couple rises with increasing ionic radius of the cation.[1]

Sulfamethoxazole (4-amino-N-(5-methyl-1, 2-oxazol-3-yl) benzene-1-sulfonamide, SMX)[33] consists on a widely employed antibiotic to treat infections in human and veterinary medicine. Figure 1 depicts the chemical structure of SMX. Unfortunately, the indiscriminate use of this drug may result in harmful environmental and public health issues.[34-36] For this reason, several investigators have pursued instrumental methods to determine this substance.

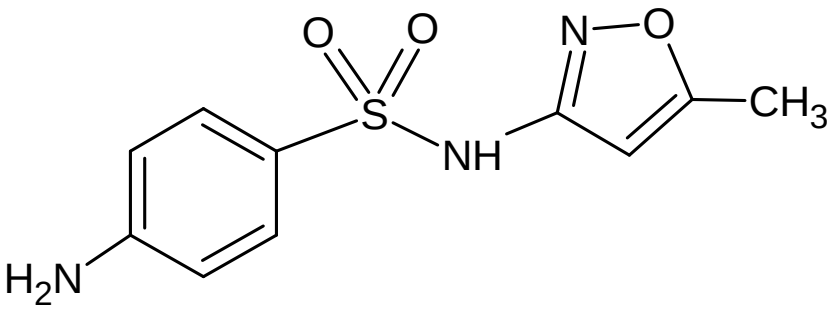

Figure 1: Chemical structure of sulfamethoxazole (SMX).

Several techniques have been used to determined sulfamethoxazole: chromatographic methods coupled with different detectors,[34,36] spectrophotometry,[37] and electroanalytical methods.[38-45] However, it is still necessary to establish a reliable and sensitive screening method that is simple to operate and is applicable for in situ analysis. In this context, the aim of this research was to investigate the voltammetric detection of SMX by using a glassy carbon disc electrode modified with a NiHCF.

Experimental

MATERIALS AND METHODS

Aqueous solutions of KNO_3 and $NaNO_3$ 1 mol L^{-1} (pH 7.0) were used as supporting electrolytes. The NiHCF film was prepared using 0.01 mol L^{-1} $Ni(NO_3)_2$ (Synth) and 0.01 mol L^{-1} $K_3[Fe(CN)_6]$ (Fluka) stock solutions. An SMX (Sigma Aldrich) $5x10^{-6}$ mol L^{-1} solution was prepared in methanol.

The cyclic voltammograms were registered on a potentiostat model μAUTOLAB III (Eco Chemie) connected to a microcomputer. A three-electrode configuration consisting of a commercial glassy carbon (GC) working electrode (3-mm diameter, Metrohm), an auxiliary (platinum wire spiral) electrode, and a Ag/AgCl reference electrode in a 5-mL electrochemical cell was employed. Before the experiments, the GC electrode was polished on alumina and washed with water and methanol. The solutions were purged with nitrogen gas for 15 min prior to recording the voltammetric curves.

NiHCF film preparation

The thin film was electrochemically deposited on the GC electrode by cyclic voltammetry. To this and, a solution containing 0.01 mol L^{-1} $Ni(NO_3)_2$, 0.01 mol L^{-1} $K_3[Fe(CN)_6]$, and 1 mol L^{-1} $NaNO_3$ electrolyte was used. Cyclic voltammetry was conducted for 15 successive cycles with applied potentials ranging from - 0.2 to 1.0 V (vs Ag/AgCl), at a scan rate of 100 mV s^{-1}. Then, CME stability was tested during 20 successive cycles between -0.2 and 1.0 V (vs Ag/AgCl) in a 1 mol L^{-1} $NaNO_3$, (pH 7.00) solution at a scan rate of 100 mV s^{-1}.

Voltammetric analysis

Voltammetric measurements were conducted in the potential range from - 0.2 to 1.0 V (vs Ag/AgCl). An accumulation time of 30 s and a scan rate of 100 mV s^{-1} were used. Analysis of SMX at different concentrations was performed by the standard addition method. For this purpose, the SMX standard aliquots were added to the cell between 2 and 100 μL.

RESULTS AND DISCUSSION

Nickel hexacyanoferrate film formation and stability studies

We used consecutive cyclic voltammetry between -0.2 and + 1.0 V to electrodeposit the NiHCF film on a GC electrode (Figure 2A), reduced $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, since the equilibrium $[Fe(CN)6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ has E ° = + 0.40 V. In other words, NiHCF film originated on the electrode surface in the presence of electrochemically reduced $[Fe(CN)_6]^{4-}$ and Ni^{3+} ions[1] (Figure 2A). We achieved stability studies in 1 mol L^{-1} $NaNO_3$ solution and 100 mV s^{-1}; the film remained stable for 20 successive cycles. Figure 2B reveals how the supporting electrolyte affected NiHCF film formation: Na^+ elicited a unique peak at 0.40 V, whereas K^+ generated two redox couples with peaks occurring at about 0.49 and 0.66 V.

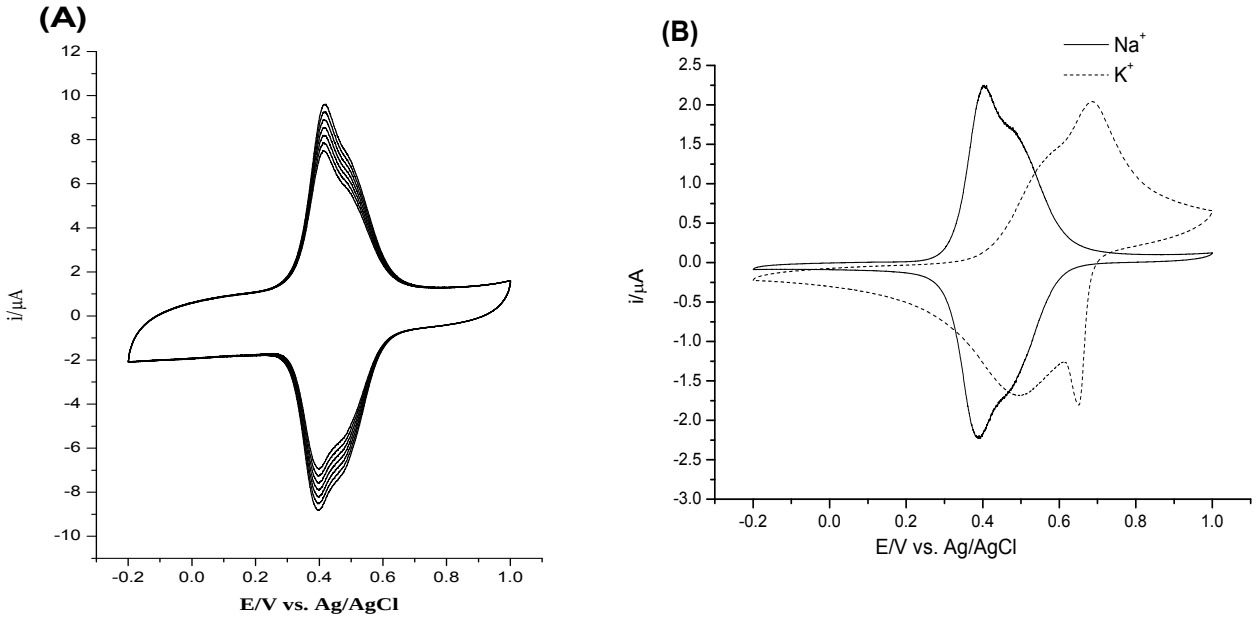

Figure 2: (A) Cyclic voltammograms of a glassy carbon electrode modified with 0.01 mol L^{-1} $Ni(NO_3)_2$ and $K_3[Fe(CN)_6]$ in 1 mol L^{-1} $NaNO_3$ aqueous solution (pH 7.0). (B) NiHCF film formation at the glassy carbon electrode in 0.01 mol L^{-1} $K_3Fe(CN)_6$ and $Ni(NO_3)_2$, solution. Supporting electrolyte = 1 mol L^{-1} KNO_3 or $NaNO_3$ solution. Scan rate: 100 mV s^{-1}.

Electrochemical behavior of SMX at a GC electrode chemically modified with a NiHCF.

The iap/icp ratio was around one during all SMX additions, which demonstrates that SMX and the NiHCF film interacted reversibly.

Figure 3A details cyclic voltammetric response recorded at the GC electrode modified with NiHCF film in the presence of SMX after successive SMX additions.

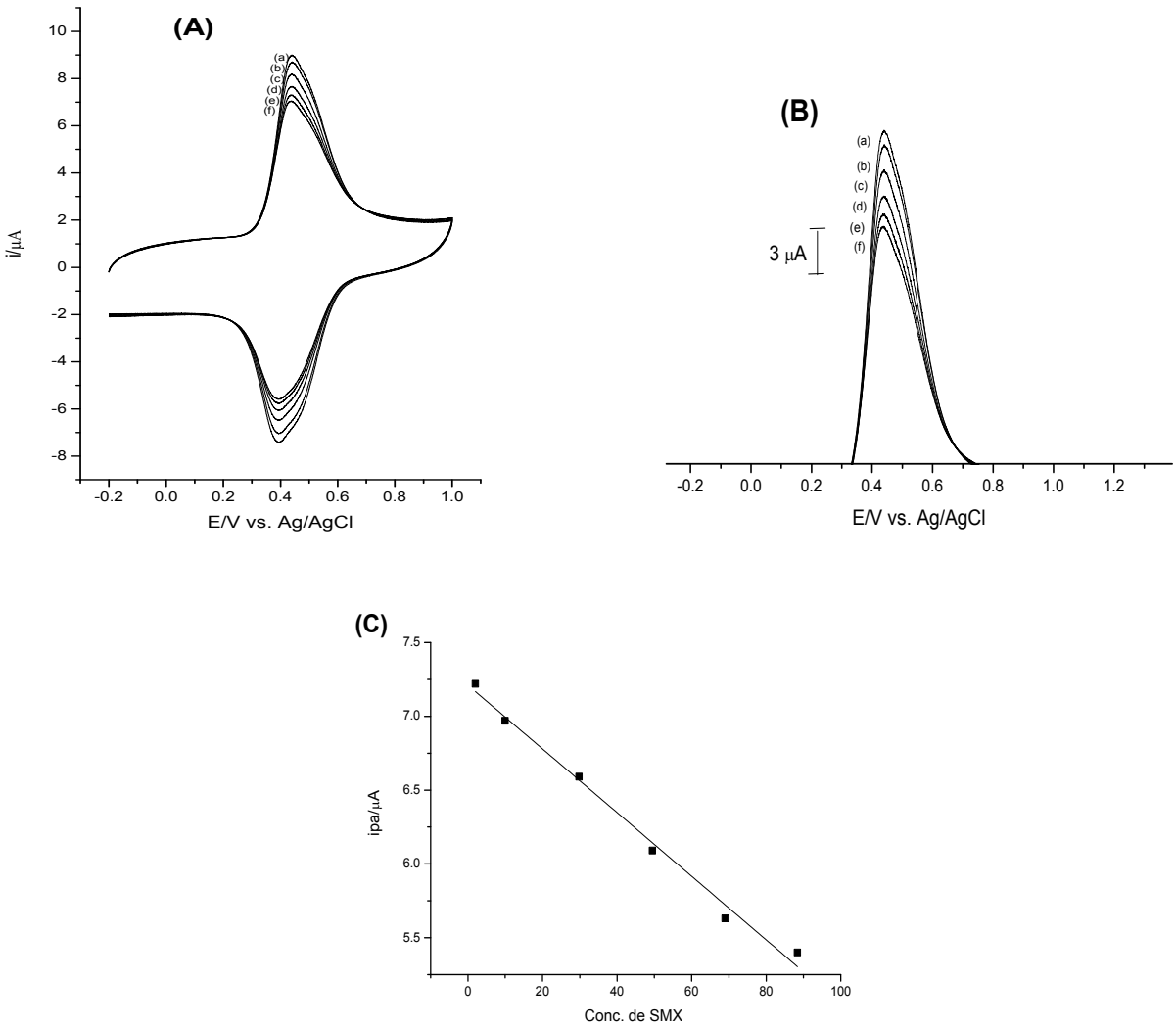

Figure 3: (A) and (B) influence of SMX concentration on the voltammetric response of the NiHCF film: (a) 2 nmol L^{-1}, (b) 9.98 nmol L^{-1}, (c) 29.8 nmol L^{-1}, (d) 49.5 nmol L^{-1}, (e) 69 nmol L^{-1}), and (f) 88.4 nmol L^{-1} cyclic voltammetry parameters: scan rate = 100 mV s^{-1} in the potential range -0.2 to 1.0 V, in 1 mol L^{-1} $NaNO_3$ solution; C) Analytical curve of the peak current (μA) vs TMP concentration (nmol L^{-1}).

The literature contains reports on the SMX electrocatalytic oxidation different voltammetric techniques and electrodes.[38-45] However, these reports have demonstrated that the redox system behaves irreversibly and that the electrochemical oxidation occurs at the primary amino group ($-NH_2$).[46] SMX has a catalytic effect and coordination may have taken place via the N-H; indeed, some researchers have investigated SMX complexes with metal(II)/(III),

and found that the ligand can also act as a bidentate ligand and acquire an octahedral molecular geometry.[47-56] We determined SMX employing the NiHCF film on the basis of partial film surface passivation by Ni-SMX. Figure 4 illustrates the proposed mechanism and the structure of the resulting complex.[55]

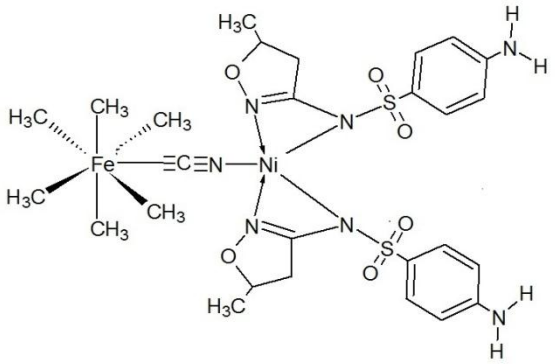

Figure 4: Schematic representation of NiHCF(SMX).

According to Figure 3B, the peak current decreases linearly with the SMX concentration. Figure 3 C shows the analytical curve, with a linear correlation coefficient (r) of 0.985 and a standard deviation (SD) of 0.053 µA. Its corresponding equation was ipa = 7.04 µA – 2. 2 x10 ^{6} µA /mol L^{-1} [SMX]. The limit of detection, calculated according to the 3 SD/m ratio (m = amperometric sensitivity of the analytical curve) was 6.8 nmol L^{-1}; the limit of quantification based on the 10 SD/m ratio, was 22.7 nmol L^{-1}.

CONCLUSIONS

Chemical modification of glassy carbon electrode surface with nickel hexacyanoferrate film allows SMX analysis at nmolL^{-1} levels. Hence, the proposed presence sensor is potentially applicable in the voltammetric determination of sulfamethoxazole in aqueous matrixes of environmental and pharmaceutical interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of FAPESP (Processes 2011/10216-5 and 2016/23825-3) and CAPES (Edital Pro-Forenses 25/2014). The authors also acknowledge Dr. Cynthia M. C. P. Manso for editing and revising the text.

REFERENCES

1. Chen, S.-M.; *J. Electroanal. Chem*, 2002; *521*: 29.
2. Zeng, B.; Zhao, F.; Ding, X.; *Anal. Sci*, 2001; *17*: 259.

3. Carpani, I.; Giorgetti, M.; Berrettoni, M.; Buldini, P. L.; Gazzanoc, M. Tonelli, D.; *J. Solid State Chem*, 2006; *179*: 3981.
4. Prabakar, S. J. R.; Narayanan, S. S.; *Electroanalysis*, 2009; *21:* 1481.
5. Chen, W.; Tang, J.; Xia, X-H.; *J. Phys. Chem.* C, 2009; *113*: 21577.
6. Jeerage, K. M.; Steen, W. A.; Schwartz, D. T.; *Chem. Mater*, 2002; *14*: 530.
7. Pandey, P. C.; Pandey, A. K.; *Analyst*, 2013; *138*: 952.
8. Zhang, S.; Huang, F.; Cao, X.; Yang, P.; Zhangc, W.; Jin, L.; *Analyst*, 2002; 127: 485.
9. Zhou, X.; Wang, S.; Wang, Z.; Jiang, M.; *Fresenius J. Anal Chem*, 1993; *345*: 424.
10. Steen, W. A.; Han, S-W.; Yu, Q.; Gordon, R.A.; Cross, J.O.; Stern, E. A.; Seidler, G. T.; Jeerage, K. M.; Schwartz, D. T.; *Langmuir*, 2002; *18*: 7714.
11. Lin, Y.; Cui, X. *J. Mater. Chem,* 2006; *16*: 585.
12. Lata, L.; Pundir, C. S.*; Bioprocess Biosyst Eng*, 2013; *36*: 81.
13. Cumba, L. R.; Bicalho, U. O.; Silvestrini, D. R.; do Carmo, D. R.; *Int. J. of Chem,* 2012; *4:* 66.
14. Shankaran, D. R., Narayanan, S. S.; *Fresenius J Anal Chem*, 1999; *365*: 663.
15. Upadhyay, D. N.; Yegnaraman, V.; Rao, P. G.; *Langmuir*, 1996; *12:* 4249.
16. Schneemeyer, L. F.; Spengler, S. E.; Murphy, D. W.; *Inorg. Chem*, 1985; *24*: 3044.
17. Haight, S. M.; Schwartz, D. T.; Lilga, M. A. *J. Electrochem. Soc*, 1999; *146*: 1866.
18. Giorgetti, M.; Scavetta, E.; Berrettoni, M.; Tonelli, D.; *Analyst*, 2001; *126*: 2168.
19. Lin, J.; Zhou, D. M.; Hocevar, S. B.; McAdams, E. T.; Ogorevc, B.; Zhang, X. *Frontiers in Bioscience*, 2005; *10:* 483.
20. Wessells, C. D.; Peddada, S. V.; Huggins, R. A.; Cui, Y.; *Nano Lett*, 2011; *11:* 5421.
21. De Tacconi, M. R.; Rajeshwar, K.; Lezna, R. O. *Chem. Mater*, 2003; *15*: 3046.
22. Untereker, D. F.; Lennox, J. C.; Wier, L. M.; Moses, P. R.; Murray, R. W.; *J. Electroanal. Chem*, 1977; *81:* 309.
23. Mimura, H.; Kimura, M.; Akiba, K.; Onodera, Y.; *J. of Nuclear Science and Technology*, 1998; *35:* 392.
24. Chen, S-M.; Liou, C-Y.; Thangamuthu, R.*; Electroanalysis*, 2007*; 19:* 2457.
25. Pandey, P. C Pandey, A..; K.; *Analyst*, 2012; *137*: 3306.
26. Bagkar, N.; Ganguly, R.; Choudhury, S.; Hassan, P. A.; Sawant, S.; Yakhmi, J. V.; *J. Mater. Chem*, 2004; *14*: 1430.
27. Hao, X; Schwartz, D. T.; *Chem. Mater*, 2005; *17:* 5831.
28. Wessells, C. D.; Peddada, S. V.; McDowell, M. T.; Huggins, R. A.; Cui, Y.; *J. Electrochem. Soc*, 2012; *159:* 98.

29. De Tacconi, M. R.; Rajeshwar, K.; Lezna, R. O. *Chem. Mater*, 2003; *15:* 3046.
30. Eleotério, I. C.; Balbino, M.A.; de Oliveira, M. F. *ECS Transactions*, 2012; 43: 345.
31. Oliveira. M. F.; Castro, S. S. L.; Stradiotto, N. R. *Int. J. Electrochem. Sci*, 2010; 5: 1447.
32. Oliveira, M. F.; Oiye, E. N.; Biziak, N.; De Andrade, J. F. Fernando; Tristão, H. M. *Forensic Sci. Int*, 2009; 192: 94.
33. Brunton, L.; Lazo, J. S.; Parker, K. L.; *Goodman & Gilman*. 11th ed. Porto Alegre: AMGH, 2010.
34. Chen, C-E.; Zhang, H.; Jones, C. K.; *J. Environ. Monit*, 2012 ; *14*: 1523.
35. Baran, W.; Adamek, E.; Ziemia´nska A., J.; Sobczak, *J. Hazard. Mater*, 2011; 196: 1.
36. Busetti, F.; Heitz, A.; *Intern. J. Environ. Anal. Chem*, 2011; *91*: 989.
37. Matysik, F-M.; *Electrochim. Acta*, 1998; *43:* 3475.
38. Shamsa, F.; Amani, L.; *Iranian J. Pharm. Res*, 2006; 1: 31.
39. Voorhies, J. D.; Adams, R. N.; *Anal. Chem*, 1958; 346.
40. Arvand, M.; Ansari, R.; Heydari, L. *Mater. Sci. Eng., C*, 2011; *31*: 1819.
41. Cai, M.; Zhu, L.; Ding, Y.; Wang, J.; Li, J. Du, X.; *Mater. Sci. Eng., C*, 2012*; 32*: 2623.
42. Sabry, S. M. *Anal. Lett*, 2007; *40*: 283.
43. Rao, T. N.; Sarada, B. V.; Tryk, D.A.; Fujishima, A. *J. Electroanal. Chem*, 2000; *491*: 175.
44. Momberg V., A.; Carrera B., M. E.; von Baer, D.; Bruhn F., C.; Smyth, M. R. *Anal. Chim. Acta*, 1984; *159*: 119.
45. Sinha, S.; Borcarsly, A. B.; *J. Electroanal. Chem*, 1982; *140*: 167.
46. Msagati, T. A. M.; Ngila, J. C. *Talanta*, 2002; *58*: 605.
47. Refat, M. S.; El-Korashy, S. A.; El-Deen, I. M.; El-Sayed, S. M.; *J. Mol. Struct*, 2010; *980*: 124.
48. Sharaby, C. M.; *Spectrochim. Acta A*, 2005*; 62: 326.*
49. Ganesh, K.; Satheshkumar, A.; Balraj, C.; Elango, K. P.; *Spectrochim Acta A Mol Biomol Spectrosc*, 2013; *107*: 156.
50. Elsaid, F. A. G.; Hamza, S.; Rizk, N.; Matter, H. A. B.; Amerah, E. A. S.; *Arab J. Sci Eng*, 2013; 38: 1681.
51. Karthikeyana, G.; Mohanraj, K.; Elango, K. P.; Girishkumar, K.; *Russ J. Coord. Chem*, 2006; *32*: 380.
52. Tella, A. C.; Obaleye, J. A.; *Orbital Electron. J. Chem*, 2010; *2*: 11.
53. Sharaby, C. M.; *Synth. React. Inorg. Met.-Org. Nano-Metal Chem*, 2005; *35*: 133.

54. Bamigboye; Oluwaseyi, M.; Obaleye; Abdulmolib, J, A.; Shola.; *Int J. Chem,* 2012; 2: 105.
55. Obasi, N. L.; Benedict, O. C. O.; Ukoha, P. O.; Anaga, A. O.; *E-J. Chem,* 2012; *9*: 2354.
56. AL-Hammoshi, M. HD.; Mustafa, Y. F.; Thannon, J.; *Tikrit J. of Pharm. Sci,* 2012; *8:* 59.