

Natural phosphate -modified carbon-paste electrode for the determination of trace Cu (II) by square-wave voltammetry

Tarik El Ouafy, Abdelilah Chtaini*, Hassan Oulfajrite, Rachida Najih

Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Faculté des Sciences et Techniques de Beni Mellal, Université Sultan Moulay Slimane, (MAROC)

BP: 523, Beni Mellal, (MAROC)

E-mail : a.chtaini@usms.ma

ABSTRACT

The electrochemical behavior of copper ions at natural phosphate modified carbon paste electrode (NP-CPE) is reported. The electrode paste was prepared as a mixture of finely powdered natural phosphate (NP) together with graphite powder. The influence of variables such as the accumulation time, pH solution, scan rate and concentration tested by cyclic and square wave voltammetry. The best results were obtained under the following optimized conditions: 3 min accumulation time. The electrochemical responses obtained by square wave voltammetry (SWV) and cyclic voltammetry (CV) at NP-CPE were found to be analytically suitable to develop a method for the determination of Cu(II) at low concentration levels. The proposed sensor presented good repeatability, and was applied for copper determination in tap water samples.

© 2015 Trade Science Inc. - INDIA

KEYWORDS

Copper;
Phosphate modified carbon
paste electrode;
CV;
SWV.

INTRODUCTION

Transition metal ions are playing an important role in biological processes in the human body^[1, 2]. For example copper (II), nickel (II), and zinc (II) ions are the most abundant transition metals in humans. They are found either at the active sites or as structural components of a good number of enzymes^[3, 4]. The heavy metal ions are hazardous to ecosystems and can cause serious danger to human population because of their accumulation in organs including liver, heart, brain etc^[5]. For this reason, up to now, several methods including atomic absorption spectrometry, UV-Vis spectroscopy, colorimetric analysis, ion chromatography, inductively coupled

plasma mass spectrometry and electroanalytical techniques have been proposed for the determination of heavy metals^[6, 7]. Among these techniques, electrochemical sensors have great potential for environmental and biological monitoring of toxic metal ions in drinking or waste water and biological samples as blood, urine etc. due to their portability and field-applicability, excellent sensitivity, automation, rapid analysis, low power consumptions and inexpensive equipment^[8-11]. The sensitivity of electrochemical sensors can be enhanced by modifying the electrode surface with a suitable chemical reagent liable to accumulate the target analyte^[12, 15]. This accumulation process induces a local increase of the analyte concentration at the electrode surface, which be-

Full Paper

comes considerably higher than in solution and enables various chemical species detection at trace levels using anodic stripping voltammetry. The general analytical procedure involves two main steps: a chemical accumulation performed at open circuit in the analyte solution, followed by voltammetric quantification of the analyte. The new electrochemical sensors based on electrochemical stripping appear to be a promising tool for determining aqueous heavy metal concentrations, being sensitive, compact, low cost and easily integrated into portable analysis systems^[16]. Carbon paste electrodes modified with functional ligands have been widely used to preconcentrate and quantify trace metal ions^[17-28], especially from environmental samples. In the present work, it describes the electrochemical investigation of Cu(II) at Phosphate Modified Carbon Paste Electrode. Many of the analytes have been detected by cyclic voltammetric technique by our research group^[29,30]. The aim of the work reported here was to investigate the electrochemical properties of Cu(II) on phosphate modified carbon paste electrode as well as the electrochemical characterization of electrodes by cyclic and square wave voltammetric technique.

EXPERIMENTAL

Instrument

All electrochemical experiments were performed by a potentiostat (model PGSTAT 100, Eco Chemie B.V., The Netherlands) interfaced to a personal computer and controlled by voltalab Master 4 software. A three electrode design consisting of a platinum counter electrode, SCE reference electrode and a modified carbon paste working electrode. Prior to any electrochemical measurements the solutions were thoroughly de-gassed with nitrogen (BOC Gases), whilst a continuous flow of the gas was maintained through the electrochemical cell during the experiments. The pH meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

Analytical procedure

The modified carbon paste electrode was im-

mersed in a cell containing 20mL of c sample to get a chemical accumulation. Meanwhile, the solution was rotated about 600rpm at open circuit. After a desired preconcentration time, the electrode was removed from the preconcentration cell, rinsed with DW and placed in the measurement cell containing the supporting electrolyte ($0.1\text{ mol L}^{-1}\text{ Na}_2\text{SO}_4$). The solution was deaerated with nitrogen for 10min. The voltammetric curve was recorded. Potential window of -0.8 to 0.7V was for all the voltammetric measurements. The same procedure was carried out in sample analysis and all electrochemical experiments were carried out at room temperature. The square wave voltammetry (SWV) was recorded in the range from -0.8 V to 0.7 V, for which the scan rate is $1\text{ mV}\cdot\text{s}^{-1}$, step potential 50 mv, amplitude 2 mV and duration 0.1 s The cyclic voltammetry was recorded in the range from -0.8 V to 0.7 V.

Electrodes synthesis

The working carbon paste electrode was prepared by mixing appropriate weight of natural phosphate with a graphite powder to give an appropriate ratio NP-CP. The whole cell modified carbon paste was subsequently packed firmly into the electrode cavity (0.1256 cm^2) and polished to a smooth shiny finish by gently rubbing over an ordinary weighing paper. Electrical contact was established with a bar of carbon. The resulting electrode is hereby denoted as NP-CPE. The carbon paste electrode (CPE) alone was prepared in a similar way.

RESULTS AND DISCUSSION

Voltammetric and EIS behavior of Cu(II)

Cyclic voltammetry

Figure 1 shows a cyclic voltammograms (CV) in the potential range -0.8 V to 0.7 V recorded for natural phosphate modified carbon paste electrode at $100\text{ mV}\cdot\text{s}^{-1}$. No peak is observed in the case of NP-CPE for the absence at Cu(II) Figure 1a, contrary to the Figure 1b shows as Cu(II) exhibits a pair of well-defined redox waves on the NP-CPE with $E_{pa} = 0.1\text{ V}$ and $E_{pc} = -0.25\text{ V}$.

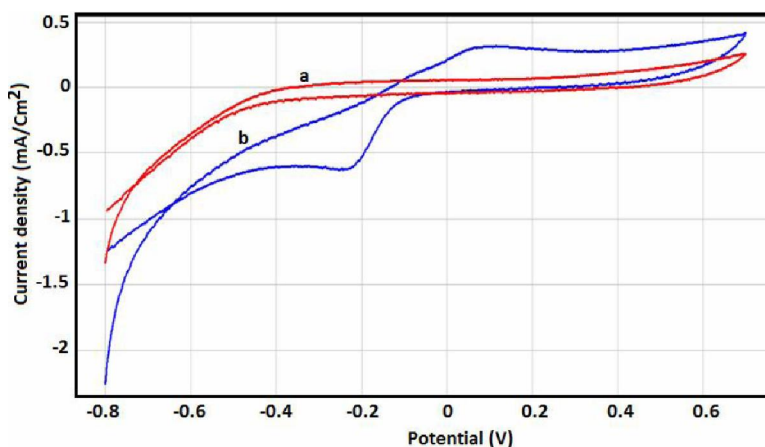


Figure 1 : CV recorded for 0.31 mM Cu(II) at pH=7 at bare NP-CPE (a) and NP-CPE/Cu(II) (b), Scan rate 100 mV/s, preconcentration time (t_p)= 3min

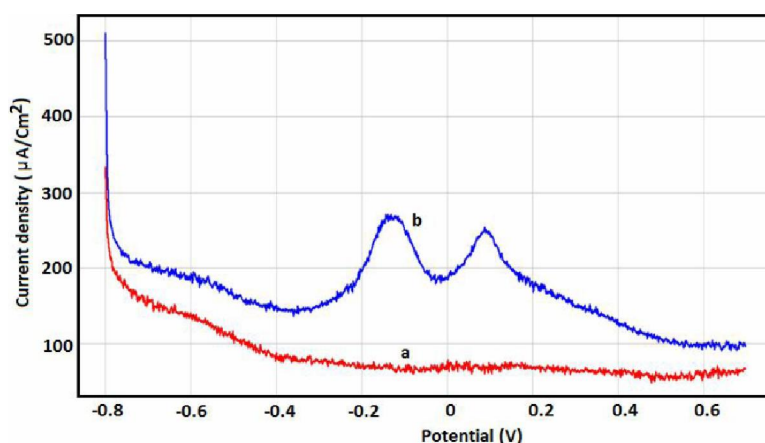


Figure 2 : SWV recorded for 0.31mM Cu(II) at pH 7 at bare NP-CPE (a) and NP- CPE/Cu(II) (b)

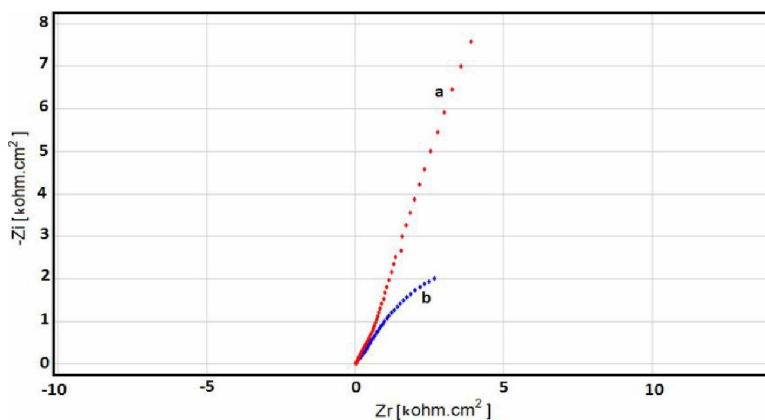


Figure 3 : Impedance spectra at 0 V (a) natural phosphate modified carbon paste electrode (a) and NP-CPE/Cu(II) 1,24mM

Square wave voltammetry

The square wave voltammograms recorded for 0.31mM Cu(II) at bare NP-CPE in Na_2SO_4 buffer solution at pH 7 are illustrated in Figure 2, this figure shows an oxidation and reduction peak of Cu(II).

EIS measurements

EIS was carried out on a NP modified CPE surface in $0.1 \text{ mol L}^{-1} \text{Na}_2\text{SO}_4$ in the absence and presence of Cu(II) (Figure 3). The charge-transfer resistance values decreased in the presence of Cu(II). This situation was the result of an increase in the surface coverage by the Cu(II), which led to an in-

Full Paper

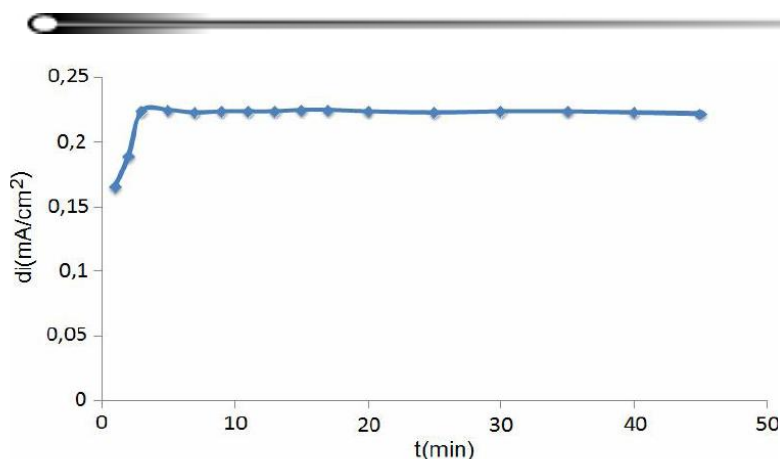


Figure 4 : Effects of accumulation time on Cu(II) oxidation peak currents

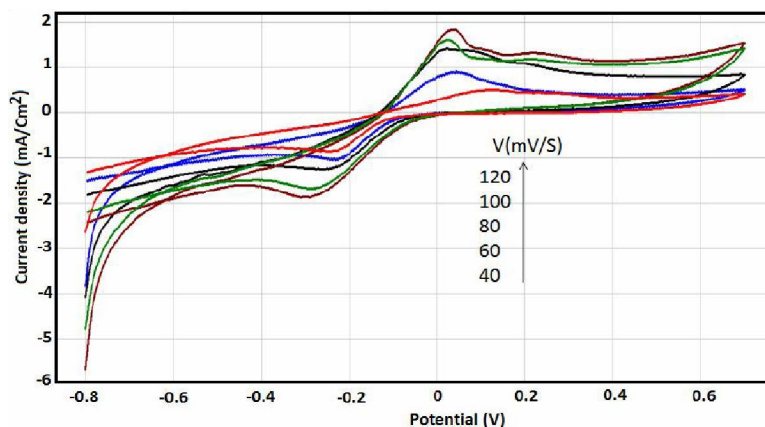


Figure 5 : CV acquired on NP-CPE with 1.8 mM Cu(II) in the buffer solution at different scan rates

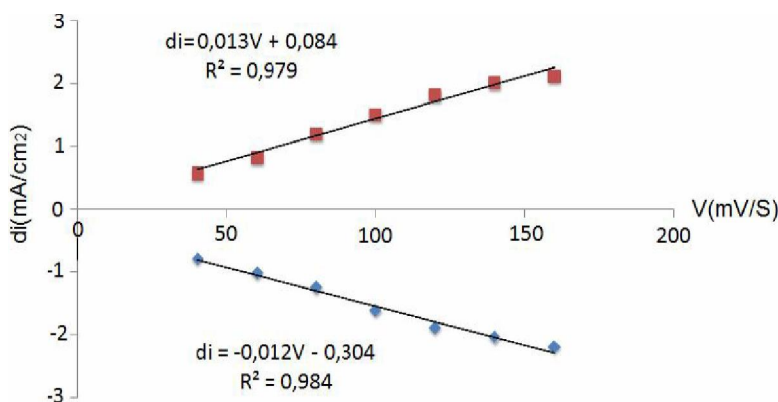


Figure 6 : Plot of peaks area versus scan rate

crease in the electrode conductivity. The observed decrease of the charge-transfer resistance means also that the modified electrode becomes more conductive, which can be explained by the presence of Cu on the electrode surface.

Influence of accumulation time

The dependence of peak current on the preconcentration time for $0.31 \text{ mmol L}^{-1} \text{ Cu(II)}$ was also investigated (Figure 4). The peak current in-

creases with the increasing in the preconcentration time between 0 and 45 min above which it became nearly constant due to the surface saturation. Hence, a 3 min preconcentration time was used in all subsequent experiments.

Effect of scan rate

The effect of scan rate on the redox of Cu(II) was examined in $0.1 \text{ M Na}_2\text{SO}_4$ buffer solution of pH7 as a supporting electrode. The Figure 5 shows

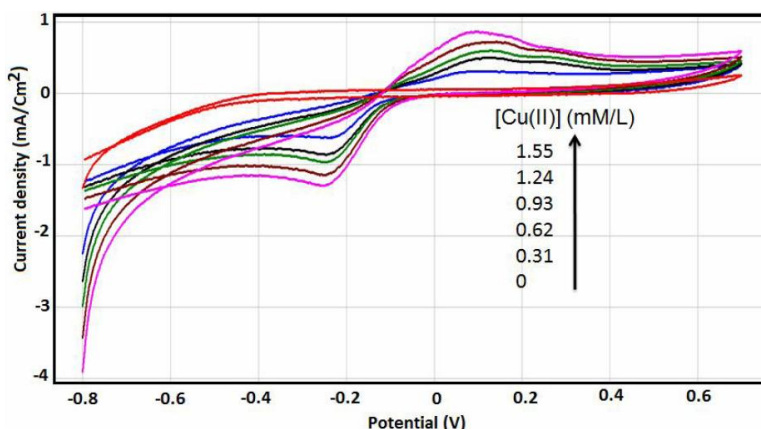


Figure 7 : Cyclic Voltammograms of different concentration of Cu(II) at NP-CPE in 0.1 M Na₂SO₄, Scan rate 100 mV/s

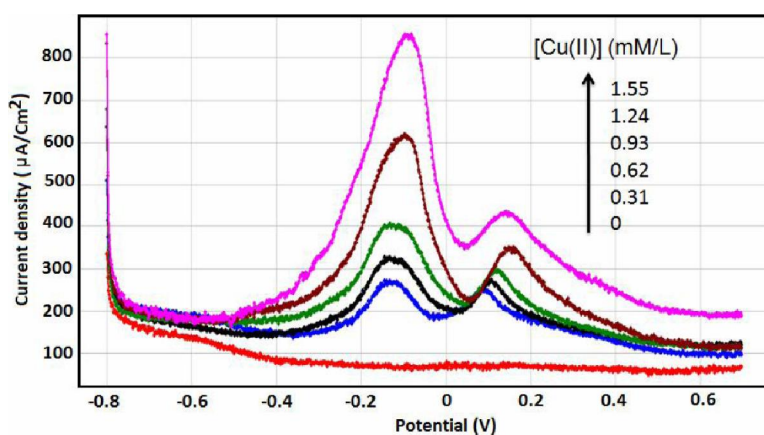


Figure 8 : Square wave Voltammograms of different concentration of Cu(II) at NP-CPE in 0.1 M Na₂SO₄

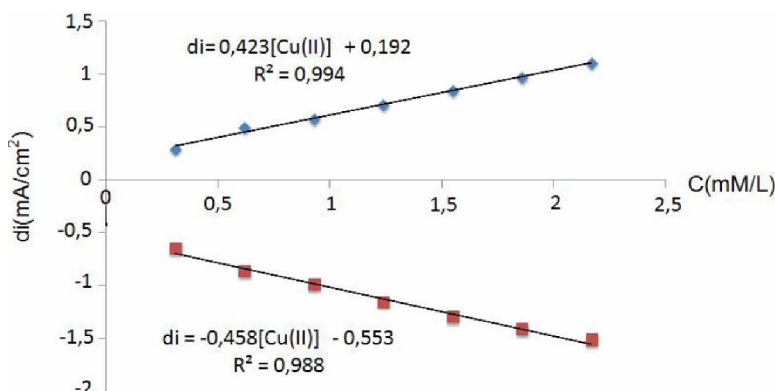


Figure 9 : Plot of peaks area versus added concentration of Cu(II)

both the anodic and the cathodic peak currents linearly increase with the scan rate over the range of 40 to 120 mVs⁻¹, suggesting that the electron transfers for Cu(II) at the phosphate modified CPE is adsorption controlled reaction. The Figure 6 shows the linear relationship between the scan rate anodic peak and cathodic peak currents of Cu(II) at NP-CPE.

Effect of concentration of Cu

Figure 7 and 8 shows the CV and SWV curves of different concentration of Cu(II) at NP-CPE was increased from 0.31 mM to 1.55 mM in 0.1 M Na₂SO₄ buffer solution at pH=7 at a sweep rate of 100 mVs⁻¹. Both the anodic and cathodic peak current increases linearly with the concentration of Cu(II). It was also observed that the cathodic peak potential shift towards

Full Paper

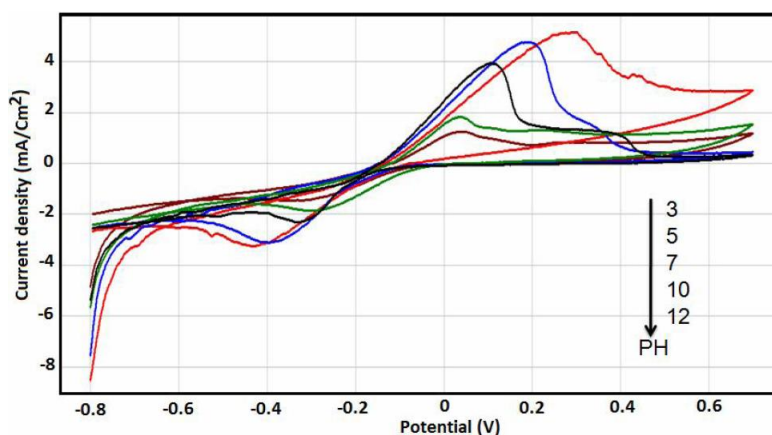


Figure 10 : Effect of pH on the oxidation and the reduction of Cu(II) at the NP-CPE

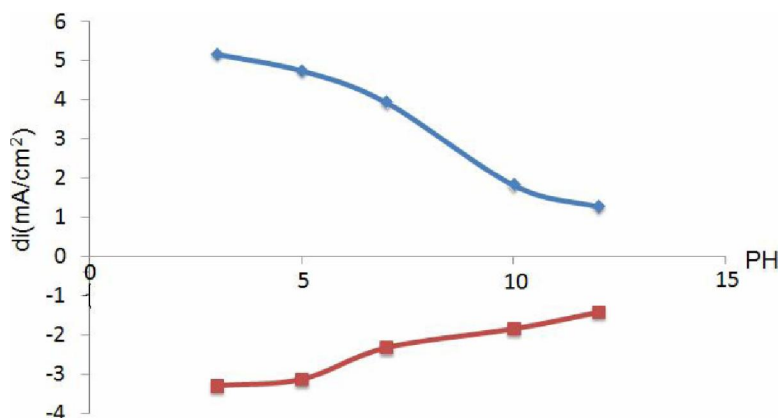


Figure 11 : Plot of the relationship between solution pH and the oxidation and reduction peak current

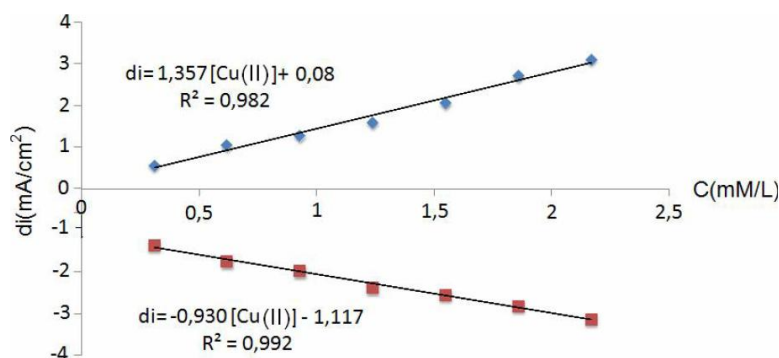


Figure 12 : Plot of peaks area versus added concentration of Cu(II)

negative values and anodic peak potential shift towards positive side. This kind of shift in E_p in the cathodic and anodic direction with increasing concentration of the Cu(II) indicates that the ion of Cu are adsorbed over the electrode surface.

Influences of pH

The Figure 10 shows the cyclic voltammograms of the Cu(II) at different pH. The current of the peak depend on the solution pH. The Figure 11 shows the graph of different pH versus peak current, it could

be confirmed that the current density decreases with increased PH.

Analytical application

Under the optimized conditions, the analytical system was used for copper determination in tap water sample without any pretreatment. The analytical curves were obtained by CV experiments in supporting electrode. It was founded that the peaks currents increase linearly versus Cu(II) added into the tap water (Figure 12).

CONCLUSION

This work demonstrated that carbon paste electrode modified with natural phosphate is a feasible alternative for the analytical determination of copper. In the present work, the influence of Cu(II) peak current has been evaluated. The oxidation of this compound on the modified electrode occurs in an reversible manner.

The modified electrode was successfully applied in tap water samples. The method could be improved in a simple way without introducing additional procedures.

REFERENCES

- [1] W.Kaim, B.Schwederski; *Bioinorganic Chemistry: Inorganic Elements of Life*, John Wiley and Sons: London, 39-262 (1996).
- [2] C.Xiao-Ming, Y.Bao-Hui, C.H.Xiao, X.J.Zhi-Tao; *Chem.Soc., Dalton Trans.*, 3465-3468 (1996).
- [3] F.A.Cotton, G.Wilkinson; *Advanced Inorganic Chemistry*, 5th Edition, John Wiley and Sons: New York, 1358-1371 (1988).
- [4] N.N.Greenwood, A.Earnshaw; *Chemistry of the Elements*, Pergamon Press: Oxford, 1392-1420 (1984).
- [5] H.J.Salavagione, J.Arias-Pardilla, J.M.Perez, J.L.Vazquez, E.Morallon, M.C.Miras, C.Barbero; *J.Electroanal.Chem.*, **576**, 139 (2005).
- [6] D.Bagal-Kestwal, M.S.Karve, B.Kakade, V.K.Pillai; *Biosens.Bioelectron.*, **24**, 657 (2008).
- [7] S.Senthilkumar, R.Saraswathi; *Sensor.Actuators B, Chem.*, **141**, 65 (2009).
- [8] D.Burshtain, D.Mandler; *J.Electroanal.Chem.*, **581**, 310 (2005).
- [9] W.Yantasee, B.Charnhattakorn, G.E.Fryxell, Y.Lin, C.Timchalk, R.S.Addleman; *Anal.Chim.Acta*, **620**, 55 (2008).
- [10] S.Betelu, C.Vautrin-UI, A.Chause; *Electrochem.Comm.*, **11**, 383 (2009).
- [11] M.Badihi-Mossberg, V.Buchner, J.Rishpon; *Electroanalysis*, **19(007)**, (2015).
- [12] B.Liu, L.Lu, M.Wang, Y.Zi; *Electroanalysis*, **20**, 2363 (2008).
- [13] J.Wang; "Stripping Analysis", VCH, Deerfield Beach, Florida, 63 (1985).
- [14] Kh.Brainina, E.Neyman; "Electroanalytical stripping methods", Wiley, New York, **4**, 55 (1993).
- [15] D.W.M.Arrigan, *Analyst*, **119**, 1953-1966 (1994).
- [16] S.Sayen, C.Gérardin, L.Rodehüser, A.Walcarius; *Electroanalysis*, **15**, 422-430 (2003).
- [17] I.Cesarino, G.Marino, J.R.Matos, É.T.G.Cavalheiro, *Talanta*; **75**, 15-21 (2008).
- [18] R.P.Baldwin, J.K.Christensen, L.Kryger; *Anal.Chem.*, **58**, 1790-1798 (1986).
- [19] S.V.Prabhu, R.P.Baldwin, L.Kryger; *Anal.Chem.*, **59**, 1074-1078 (1987).
- [20] B.Ogorevc, X.H.Cai, I.Grabec; *Anal.Chim.Acta*, **305**, 176-182 (1995).
- [21] W.Yantasee, Y.Lin, G.E.Fryxell, B.J.Busche; *Anal.Chim.Acta*, **502**, 207-212 (2004).
- [22] S.K.Alpat, U.Yuksel, H.Akcay; *Electrochem.Comm.*, **7**, 130-134 (2005).
- [23] I.Jureviciute, A.Malinauskas; *Chem.Anal*, **49**, 339-350 (2004).
- [24] A.Yamaguchi, N.Teramae; *Anal.Sci.*, **24**, 25-30 (2008).
- [25] M.Mazloun-Ardakani, Z.Akrami, H.Kazemian, H.R.Zare; *Int.J.Electrochem.Sci.*, **4**, 308-319 (2009).
- [26] N.Yu.Stozhko, N.A.Malakhova, M.V.Fyodorov, K.Z.Brainina; *J.Solid State Electrochem.*, **12**, 1219-1230 (2008).
- [27] A.M.Bond, W.Miao, T.D.Smith, J.Jamis; *Anal.Chim.Acta*, **396**, 203-213 (1999).
- [28] C.A.Borgo, R.T.Ferrari, L.M.S.Colpini, C.M.M.Costa, M.L.Baesso, A.C.Bento; *Anal.Chim.Acta*, **385**, 103-109 (1999).
- [29] M.Etienne, J.Bessiere, A.Walcarius; *Sensors and Actuators B*, **76**, 531-538 (2001).
- [30] M.A.El Mhammedi, M.Bakasse, A.Chtaini; *J.Hazardous Mat.*, **145**, 1-7 (2007).
- [31] M.A.El Mhammedi, M.Bakasse, R.Najih, A.Chtaini; *Appl.Clay Sci*, **43**, 130-134 (2009).