Dimethylglyoxime modified screen-printed electrodes for nickel determination

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ABSTRACT

This work reports the development of a dimethylglyoxime (DMG) modified sensor in which the complexing agent was successfully immobilized by drop-casting onto a screen-printed carbon electrode support (SPCE). The experimental conditions for the preparation of the DMG-SPCE sensor were optimized by means of a D-optimal design, and the built sensors were analytically evaluated for the determination of Ni(II) by adsorptive stripping voltammetry (AdSV). Its analytical performance suggests its suitability for the determination of Ni(II)-ions by AdSV at concentration levels of $\mu g\ L^{-1}$ (LOD of 2.3 $\mu g\ L^{-1}$, linear range from 7.6 to 200 $\mu g\ L^{-1}$). Finally, the applicability of the developed sensor was assessed by the determination of trace levels of Ni(II) by AdSV in a wastewater reference material with a very high reproducibility (0.005 %) and good trueness (0.1 %).

Keywords: dimethylglyoxime modified electrodes; adsorptive stripping voltammetry; screen-printed electrodes; modified electrodes; nickel

1. INTRODUCTION

"Heavy metals" (HMs) is a term that is used to refer to a group of metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity [1]. Despite the term is not defined by IUPAC, it appears in many publications and legislation, which provide their own definition and list of compounds to which they apply.

In this sense, Tchounwou *et al.* define HMs as those metallic elements with a density at least 5 times higher than that of water [2]. Despite being natural elements present in the terrestrial crust, their concentration has increased due to the anthropogenic activity. As a consequence, higher concern about their potential effects on the human health and the environment has grown as they are systemic toxicants known to induce multiple organ damage, even at very low concentrations. Furthermore, the half-life time of HMs in the organism is of the order of years, given its slow excretion from the different tissues. Consequently, the contamination of natural or drinking water by HMs such as cadmium, lead, mercury, arsenic, chromium, copper, manganese and nickel supposes a significant threat to natural ecosystems and human health, requiring methods that allow their on-site determination and monitoring at low concentrations [1-3].

Particularly, nickel is widely used to make coins, stainless steel, jewellery, magnets, electronics, and components of industrial machines. Consequently, it is a common industrial pollutant found in wastewater, contaminated soils and in the air around industrial areas [4, 5]. Nickel toxicity in humans has received important attention due to the carcinogenic character of this element [6-9]. Likewise, the toxicity of nickel to plants is well-known [10].

The conventional methodology for the determination of HMs is based on the use of atomic spectroscopic techniques [11]. However, these systems are expensive, bulky and

require qualified personnel capable of carrying out the analyses. In addition, they do not usually allow the on-site analysis of samples, requiring a sampling stage and its subsequent transport to the laboratory to carry out the analysis. For the on-site detection of HMs, the coupling of a powerful analysis technique with low cost miniaturized instrumentation is required.

In this regards, given the inherent redox activity of heavy metals, electrochemical devices offer attractive possibilities to meet these needs [12]. The advantages of electrochemical systems include its high sensitivity and selectivity, fast response, a broad linear range, compatibility with modern microfabrication techniques, low energy and space requirements (e.g. hand-held devices) and the low cost of their instrumentation; all of them characteristics that allow their on-site usage [13]. In this respect, screen-printed electrodes (SPEs) have recently undergone great advances, due to their reproducible and low-cost character, miniaturized size and their ability to be connected to portable instrumentation making them more suitable for on-site analysis [14-17]. Thus, electrochemical devices have great potential in the monitoring of different heavy metals.

Within the different electrochemical techniques, voltammetric stripping techniques are the most efficient for the analysis at trace levels due to their high sensitivity and selectivity, being particularly suitable for the determination of HM ions in environmental samples [18]. Anodic stripping voltammetry (ASV) is the preferred stripping technique for the determination of those metals (e.g. Cd, Zn, Cu, Pb, Hg, In, Tl, Sb or Bi) that can be accumulated by electrochemical deposition in Hg and Au electrodes or in Bi and Sb films [19]. However, the metals that cannot be directly electroplated onto the electrode surface (e.g. Ni, Co, Cr or Fe) must be determined by adsorptive stripping voltammetry (AdSV) using a complexing agent that facilitates its

adsorption. In particular, Ni(II) has been classically determined by AdSV using dimethylglyoxime (DMG) as complexing agent at different working electrodes (e.g. Hg, Bi or Sb based- electrodes) [19]. However the main problems of the classical AdSV determination are: (i) the complexing agent that must be present in solution is different for each metal or group of 2-3 metals, a circumstance that prevents the simultaneous determination of a large set of metals; and (ii) the required complexing agent in the solution hinders the on-site determination of metal ions.

In this regards, this work presents the development of a new voltammetric sensor based on carbon screen-printed electrodes (SPCEs) chemically modified with DMG for the determination of Ni(II) in environmental samples by AdSV.

2. EXPERIMENTAL

2.1. Chemicals and solutions

All chemicals used were of analytical grade. Ni(II) solutions were prepared from 1000 mg L^{-1} atomic absorption standard supplied by Alfa Aesar (Ward Hill, MA, United States) after appropriate dilution. Certificated reference material, wastewater SPS-WW2 was provided by Spectrapure Standards (Manglerud, Norway). Other reagents used were: dimethylglyoxime (DMG), hydrochloric acid, and ammonia purchased from Merck (Darmstadt, Germany); acetone provided by Acros Organics (Geel, Belgium); and ammonium chloride supplied by Probus S.A. (Badalona, Spain). Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

2.2. Instrumentation

Adsorptive stripping voltammetric (AdSV) measurements were carried out with an Autolab System PGSTAT12 (EcoChemie, The Netherlands) potentiostat, connected to a Metrohm 663 VA Stand (Metrohm, Switzerland) and a personal computer with GPES (v4.9) data acquisition software (EcoChemie).

A Ag|AgCl|KCl (3 M) and a Pt wire purchased from Metrohm (Herisau, Switzerland) were used as reference electrode and counter electrode, respectively. DMG-coated electrodes prepared from commercial carbon disk SPEs of 4 mm of diameter (ref. DRP-C110, DS SPE) supplied by DropSens (Oviedo, Spain) were used as the working electrode. A flexible cable (ref. CAC, DropSens) was used to connect the SPE to the Autolab System. All measurements were carried out in a glass cell at room temperature (20 °C).

2.3. Preparation of DMG-coated screen-printed electrodes (DMG-SPCEs)

DMG-SPCEs were prepared by repeated drop-casting of 25 µL (up to 225 µL) of a 0.02 M DMG solution in acetone onto the carbon working electrode surface. After each deposition, electrodes were allowed to dry in an oven at 25 °C for 15 min. At the end, electrodes were rinsed with water and stored at room temperature.

Prior to its usage for the first time, electrodes were activated by dipping them in a 1 µM Ni(II) solution for 5 seconds, rinsed with water and dipped in a 1 M HCl solution for 5 seconds to remove the bound Ni. This cycle of activation was repeated a total of three times, at the end of which the electrodes were rinsed with water again and ready to use.

All the above conditions were experimentally optimized through a D-optimal design, in which the amount (25 to 225 µL) and concentration (5 to 20 µM) of DMG, the drying temperature (25 to 160 ºC) and the activation conditions: number of cycles (0 to 12),

concentration of Ni(II) solution used (1 to 10 μM) as well as the activation time (5 to 60 s) and the rest time (0 to 24 h) were the factors included, whereas the voltammetric response as well as its RSD were the responses considered to build the response surface model (RSM). The choice of a D-optimal design was preferred as it is especially suitable for RSM and it will provide a more affordable number of runs in comparison to any classical design. For the optimization process MODDE® software from Umetrics (Umeå, Sweden) was used. Optimum theoretical obtained conditions were assessed experimentally to confirm those matched with the expected performance.

2.4. Voltammetric measurements

To carry out Ni(II) determination, AdSV was the chosen voltammetric technique. AdSV measurements were carried out in ammonium/ammonia buffer pH 9.2 [20, 21], and comprised three steps: accumulation, measurement and cleaning. Firstly, the electrode was immersed in a stirred cell containing 25 mL of sample for 60 s at 0 V to allow the Ni(II)-DMG interaction. Afterwards, reduction of Ni(II) adsorbed onto electrode surface took place by scanning the potential from -0.7 to -1.25 V [21], using a modulation amplitude of 50 mV, a step potential of 5 mV, and a modulation time of 50 ms. Finally, the sensor was regenerated by immersing it in a stirred cell containing 0.1 M HCl for 30 s [22].

Developed sensors were analytically characterized in terms of sensitivity, limits of detection and quantification, linear range, repeatability, reproducibility and durability. In order to obtain the linear calibration plots for the determination of Ni(II) on a DMG-SPCE by AdSV, metal ion concentrations were increased in 0.1 M ammonium/ammonia buffer at pH 9.2. Error bars in plots correspond to standard deviation.

Finally, the suitability of the developed DMG-SPCE for the determination of Ni(II) was tested in certificated reference material, wastewater (SPS-WW2). In the analysis of the certified wastewater sample, the sample was diluted 5:1000 in 0.1 M ammonium/ammonia buffer at pH 9.2, and placed in the cell where the scan was recorded. Calibration was performed by the standard addition method, three aliquots of Ni(II) standard solution were further added and the respective curves were recorded.

3. RESULTS AND DISCUSSION

3.1. DMG-SPCE sensor preparation

As mentioned above, the preparation of DMG-SPCEs was experimentally optimized through a D-optimal design to maximize sensor's response towards Ni(II). For each of the runs included in the design, modified SPEs were fabricated in duplicate, and its response evaluated towards a 50 µg L^{-1} Ni(II) solution. Averaged responses with their respective standard deviations were then used to build the RSM. Selection of the factors to be considered was based on the findings from previous works and some preliminary experiments [23, 24].

Initially, usage of acetone and absolute ethanol was evaluated as the solvent for DMG, but it was found that sensors prepared with ethanol did not gave any response. Consequently, acetone was the chosen solvent. As per the amount of DMG to be drop-casted, it is quite well-known that the obtaining of a homogeneous layer is very important to improve sensor's response. Therefore, both concentration and volume effect were considered. When the DMG concentration was too low, repeated drop-casting resulted in a poorer performance of the sensor; oppositely, for higher DMG concentrations, higher volumes lead to a higher response (Figure 1A). We hypothesize

that this distinguished behaviour could be attributed to DMG re-dissolution at low concentrations, thus leading to a similar effect as if higher volumes are drop-casted. For the drying of the electrodes, 15 min was the time fixed between depositions, but the temperature effect on the drying of the electrodes was evaluated, showing that an increase in the temperature did actually demote sensors' response (Figure 1B). Lastly, it was found that without the activation step, sensors response was almost negligible, which was assimilated to the common behaviour of potentiometric sensors which require an activation/conditioning step prior to its usage. Therefore, for the optimization at least 1 cycle was always considered, finding that a total of 3 cycles was the optimum number as a higher number of cycles of activation had a negative impact on sensors' responses (Figure 1C). As per the rest time, it was observed that it's better to activate sensors prior to usage, rather than trying to active them in advance. In this manner, optimum conditions were settled as the ones described in section 2.3.

Despite the total volume of DMG necessary to prepare the DMG-SPCE was optimized, the dropped volume at each deposition was fixed at 25 μL so as to avoid having a too complex design and model. However, since this was a bit lengthy and tedious when requiring the use of 225 μL, an increase of the volume as well as the time elapsed between additions (to ensure its drying) was evaluated. In this manner, two procedures were considered for the preparation of DMG-SPCE: (i) Procedure 1: nine additions of 25 μL of DMG solution with a rest period of 15 minutes between additions (DMG-SPCE-P1); and (ii) Procedure 2: three additions of 75 μL of DMG solution with a rest period of 30 minutes between additions (DMG-SPCE-P2). Both procedures were analytically compared in terms of repeatability, reproductibility, sensitivity, linear range, and limits of detection and quantification.

3.2. Analytical performance of DMG-SPCE

With the aim of characterizing and comparing the repeatability and reproducibility of DMG-SPCEs prepared according to procedure 1 and procedure 2, AdSV measurements in a solution containing 50 µg L^{-1} Ni(II) in ammonium/ammonia buffer pH 9.2 following the above-mentioned conditions were carried out. The repeatability was estimated as the relative standard deviation (RSD) of five repetitive measurements using the same unit (prepared according to either procedure 1 or procedure 2) producing a RSD of 4.3 % and 5.3 % for DMG-SPCE-P1 and DMG-SPCE-P2, respectively. The reproducibility calculated from three different units within a series of five repetitive measurements yielded a RSD of 10.2 % and 10.3 % for procedure 1 and 2, respectively. Calibration plots towards Ni(II)-ions ranging from 1.0 to 200.0 µg L^{-1} by AdSV on both DMG-SPCE-P1 and DMG-SPCE-P2 were built following the procedure described in the experimental section (Figure 2A and 2B, respectively). As it can be observed, in both cases, a well-defined and shaped stripping peak close to -1.1 V was obtained over the selected concentration range, although a less regular baseline was observed with DMG-SPCE-P2.

Table 1 summarizes the analytical parameters obtained for each of the procedures. Both sensors showed good response in terms of peak area *vs* Ni(II)-ion concentration, with good linearity maintained up to 200.0 µg L^{-1}. However, the sensitivity, obtained from the slope of the calibration curve, was higher in the case of DMG-SPCE-P1. Regarding the limits of detection (LOD) and limits of quantification (LOQ), calculated as 3 and 10 times the standard deviation of the intercept over the slope of the calibration curve respectively, those were also better for DMG-SPCE-P1, being at the level of µg L^{-1} in both cases. The differences seen in the linear range are due to calculated LOQ value was taken as the lowest value of the linear range.

Although the results obtained with both procedures were quite similar, it was seen that the increase in the deposition volume did have a negative impact on sensor's response. Consequently, this modified procedure (DMG-SPCE-P2) was discarded, and all further experiments were carried out following procedure 1 (from now on, simply referred to as DMG-SPCE).

Comparing to previous studies reported in the literature, the LOD and the linear range obtained for the determination of Ni(II) using the herein reported DMG-SPCE are similar or even slightly better than those obtained by DPV using a carbon paste electrode (ca. 3 µg L^{-1}) or AdSV using DMG as chelating agent with an *ex-situ* antimony screen-printed carbon electrode (*ex-situ* SbSPCE: 0.9 µg L^{-1}), an *ex-situ* bismuth screen-printed carbon electrode (*ex-situ* BiSPCE: 2.9 µg L^{-1}) or a commercial sputtered BiSPEs (Bi$_{sputtered}$SPE: 4.7 µg L^{-1}) [21, 23]. Moreover, it should be pointed out that using the developed DMG-SPCE sensor, Ni(II) can be determined by AdSV without having to add any chelating agent to the measuring solution enabling its applicability for on-site analysis. Besides, not requiring the application of a deposition potential also helps to diminish possible interferences from compounds present in water samples and that can also deposit at similar potentials. Lastly, it is worth noting that no studies are reported in the literature about the use of DMG-coated electrodes for the determination of Ni(II) by AdSV.

3.3. Sensor stability

After characterizing the analytical response of DMG-SPCEs developed sensors, their operational stability (durability), reusability and storage stability were studied. Regarding the durability, DMG-SPCEs were used for over 20 consecutive measurements without showing any degradation signs.

To study their reusability, upon completion of ten repetitive measurements, the modified sensor was immersed in absolute ethanol to remove the DMG layer and, after that, modified again following the same protocol. Then, the response of the sensor towards a 50 μg L^{-1} solution upon this measure-reuse cycle was evaluated (Figure 3A). The series of measurements demonstrate that the modified sensors can be reused by removing DMG layer and drop-casting a new layer. While herein we show that no signs of degradation are seen for at least two cycles, the decay after the third one might be more related to the disposable nature of SPEs and to any damage that such organic solvents can be causing to the printed materials.

Lastly, taking into account that one of the main objectives in the development of sensors is their applicability in real scenarios, storage stability is a key factor that was also evaluated. To this aim, a large set of DMG-SPCEs were simultaneously prepared under the same conditions and stored (without performing the activation step). Then, sensors were periodically activated and tested for over a one-month period. Concretely, four consecutive measurements of a 50 μg L^{-1} solution were carried with two different sensors every considered day, and the responses obtained compared, showing no decay over time (Figure 3B). Therefore, confirming that DMG-SPCEs can be prepared in advance and stored for its posterior usage, as long as they are not activated, for at least one month.

Therefore considering the good analytical features exhibited as well as the durability and storage time, the developed DMG-SPCE sensor appears to be a valuable option for the determination of metals ions such as Ni(II) at trace levels by AdSV without using an addition chelating agent in solution. In addition, it should be highlighted that the SPCEs which are the basis of the DMG-SPCE sensor are commercially accessible and do not need any polishing prior to the coating of the DMG layer.

3.4. Wastewater sample analysis

To confirm the applicability of the developed DMG-SPCE sensor for the determination of Ni(II) in natural or environmental water samples, its applicability on a wastewater certified reference material (SPS-WW2) was tested. The determination of Ni(II)-ions was carried out by means of the standard addition method. AdSV measurements following the above described conditions were carried out including three Ni(II) additions. For the determination of Ni(II) concentration by AdSV, three replicate measurements of the wastewater sample were performed and the same DMG-SPCE unit was considered for the measurements of a whole replicate. Characteristic AdS voltammograms achieved in the analysis of Ni(II) in wastewater samples at DMG-SPCE are shown in Figure 4A. Again, a symmetric Ni(II) peak can be observed when the concentration of Ni(II) increases.

The standard addition plot (Figure 4B) illustrates the good correlation of the AdSV measurements performed at DMG-SPCE. Table 2 reports the concentration of Ni(II) obtained from the three considered replicates of the sample. A good concordance between Ni(II) concentrations as well as with the certified Ni(II) value were obtained, confirming the use of this sensor as a suitable approach for the determination of Ni(II) at low μg L^{-1} levels in environmental samples. Moreover, the use of a SPE support for DMG modification ensures a simple connection to portable instrumentation, while the non-use of a chelating agent in solution enables on-site analysis.

4. CONCLUSIONS

In this study, a new sensor for the determination of Ni(II) based on the immobilization of DMG onto a SCPE support by drop-casting was successfully developed. This DMG-coated SPCE represents a very suitable alternative to common sensors for the Ni(II) determination by AdSV since the use of a chelating agent in solution is not required. Experimental conditions for the preparation of the DMG-SPCE sensor were optimized through a D-optimal design, and confirmed experimentally as the optimum. Two different protocols for drop-casting were evaluated, confirming that lower deposition volumes are a better choice. Prepared sensors were analytically characterized in terms of repeatability, reproducibility, sensitivity, linear range, LOD and LOQ. DMG-SPCE sensor generated a well-shaped peak for Ni(II), with LOD and LOQ values as well as the sensitivity and linear range obtained similar or even slightly better than those reported in the literature for *ex-situ* SbSPCE, *ex-situ* BiSPCE and $Bi_{sputtered}SPE$. Moreover, DMG-SPCE exhibits a good repeatability and reproducibility, can be used for a large number of stripping measurements without degradation signs, can be reused for up to two times, and can be prepared in advanced and stored for at least one month. The viability of the developed DMG-SPCE sensor for the determination of Ni(II) was successfully demonstrated using a wastewater certified reference material with very high reproducibility and good trueness inferred by the RSD (0.005 %) and the relative error (0.1 %) respectively.

Overall, the main advantages of the approach presented herein opposed to other methods include its reagent-less nature, portability and durability; making it a suitable candidate to carry out on-field determinations in a reliable and inexpensive way, especially for screening applications.

Finally, it should be considered that the DMG-SPCE developed sensor could also be used as part of a sensor array together with other sensors with complementary response

to achieve the multi-determination of a mixture of metals. This is especially relevant given no complexing agents in solution are required, in comparison to other Ni(II) sensors.

5. AKNOWLEDGMENTS

6. REFERENCES

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Table 1. Calibration data for the determination of Ni(II) on DMG-SPCE-P1 and DMG-SPCE-P2 in ammonium/ammonia buffer pH 9.2, applying 0 V for 60 s, and scanning the potential from -0.7 to -1.25 V.

Electrode	Ni(II)			
	Regression[a]	R^2	Linear range ($\mu g\ L^{-1}$)[b]	LOD ($\mu g\ L^{-1}$)
DMG-SPCE-P1	$y = 0.0323(\pm0.0005)\ x + 0.003(\pm0.05)$	0.999	7.6 – 200.0	2.3
DMG-SPCE-P2	$y = 0.0196(\pm0.0009)\ x - 0.05(\pm0.09)$	0.994	23.6 – 200.0	7.1

[a] y is the peak area (10^7/A·V) and x the concentration ($\mu g\ L^{-1}$); confidence intervals in brackets.

[b] LOQ was considered as the lowest value of the linear range.

Table 2. Total concentrations of Ni(II) determined in wastewater certified reference material (SPS-WW2) by AdSV on DMG-SPCE by standard addition calibration method in ammonium/ammonia buffer pH 9.2, applying 0 V for 60 s, and scanning the potential from -0.7 to -1.25 V.

	Ni(II)		
	c (μg L^{-1})	RSD (%)	Relative error (%)
DMG-SPCE	5005.9	0.005	0.1
Certified metal value	5000.0	0.5	—

n=3 for RSD (%).

FIGURE CAPTIONS

Figure 1. 3D response surfaces generated with the D-optimal design for (A) amount of DMG, (B) drying temperature and (C) activation cycles.

Figure 2. AdSV measurements and calibration plots of Ni(II) in 0.1 M ammonium/ammonia buffer (pH 9.2) using (A) DMG- SPCE-P1 and (B) DMG-SPCE-P2, applying 0 V for 60 s, and scanning the potential from -0.7 to -1.25 V.

Figure 3. (A) Reusability and (B) storage stability of DMG-SPCE-P1 sensor, evaluated as the variation in the response towards a 50 μg L^{-1} Ni(II) solution.

Figure 4. (A) AdSV measurements in wastewater samples with the DMG-SPCE in 0.1 M ammonium/ammonia buffer (pH 9.2), applying 0 V for 60 s, and scanning the potential from -0.7 to -1.25 V; and (B) Ni(II) standard addition plot.

Figure1
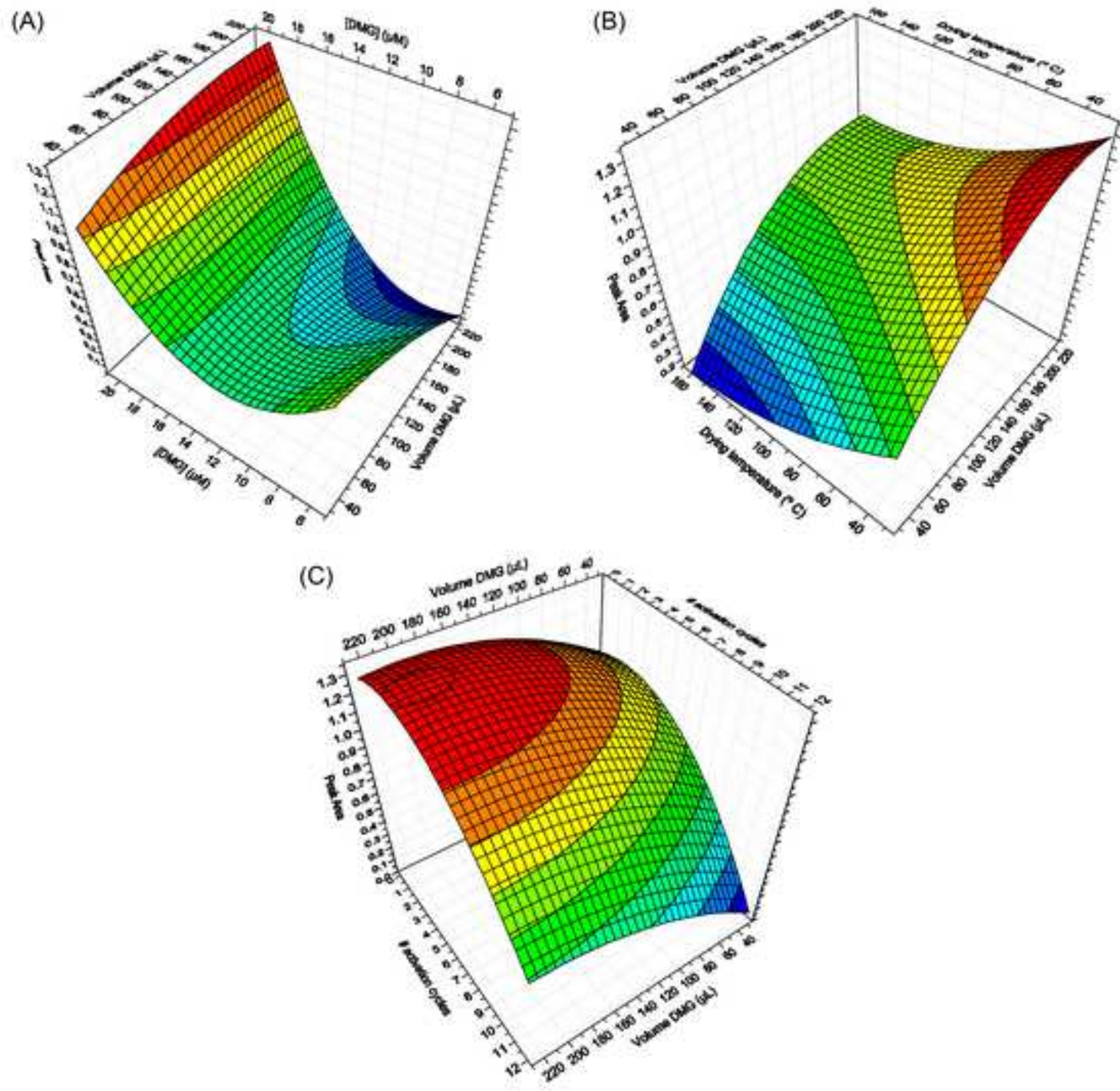**Click here to download high resolution image**

Figure2
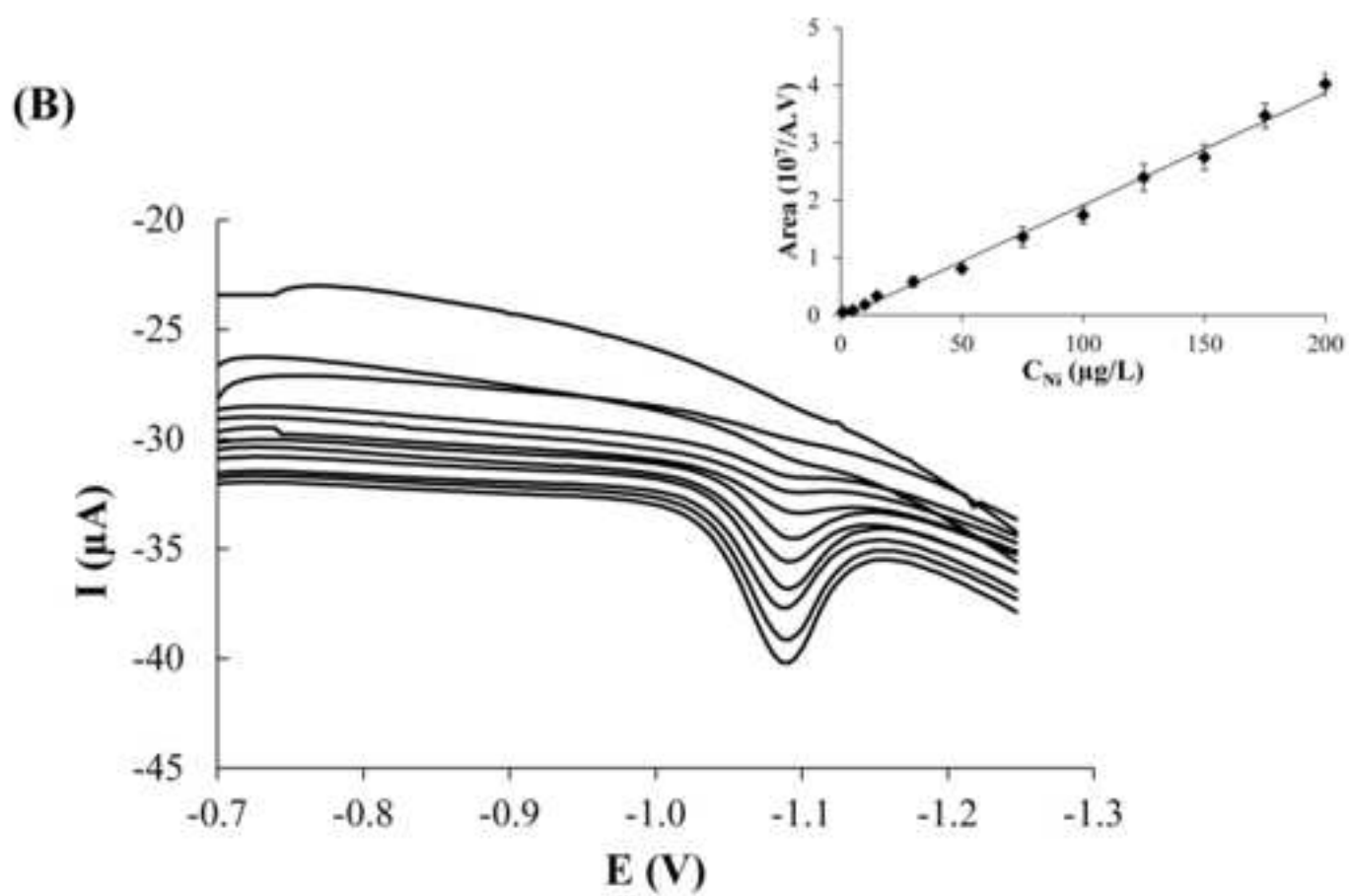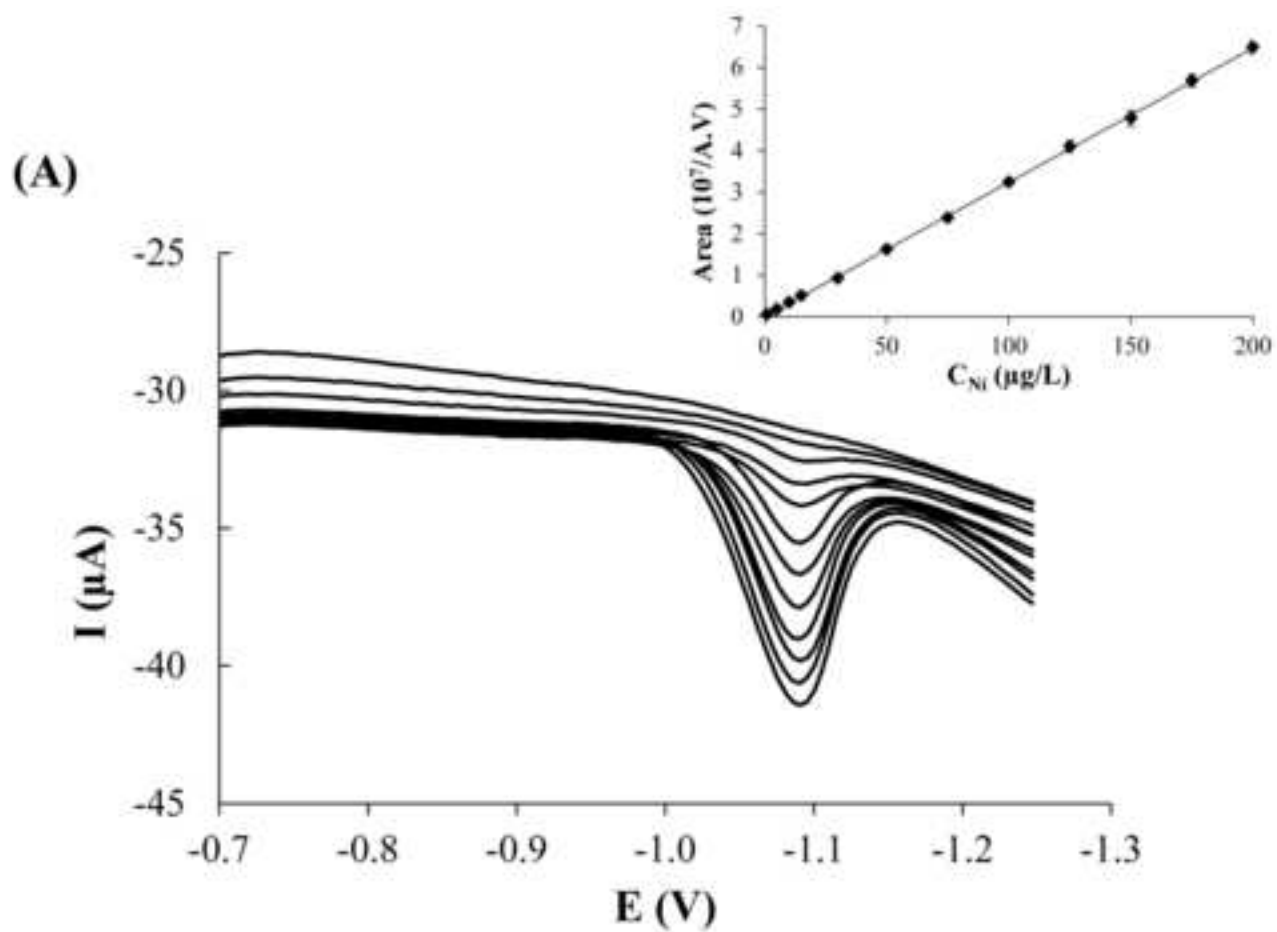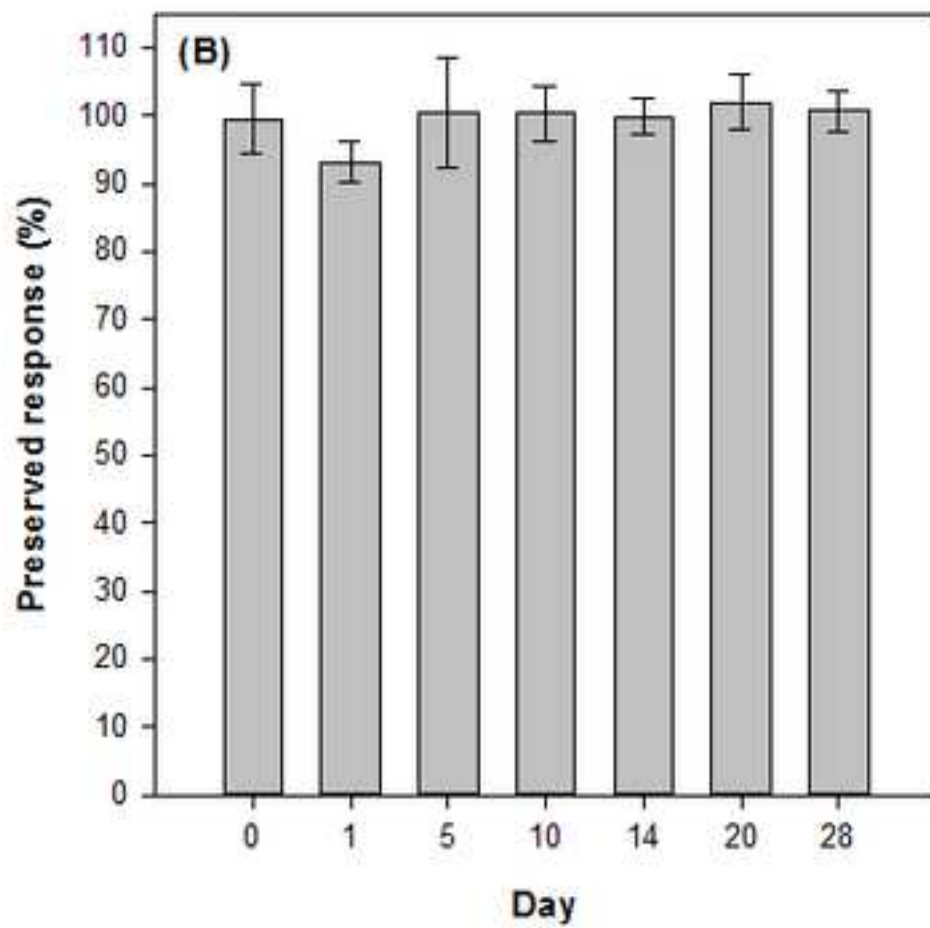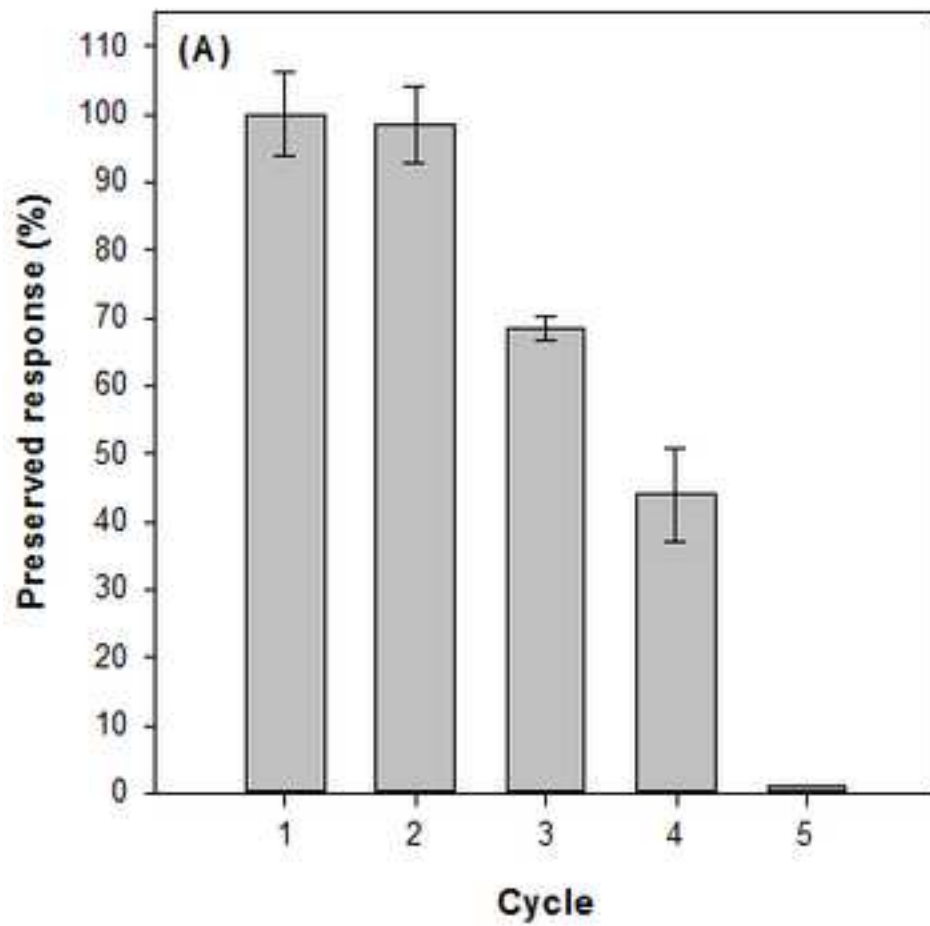**Click here to download high resolution image**

(A)

(B)

Figure3
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Figure4