



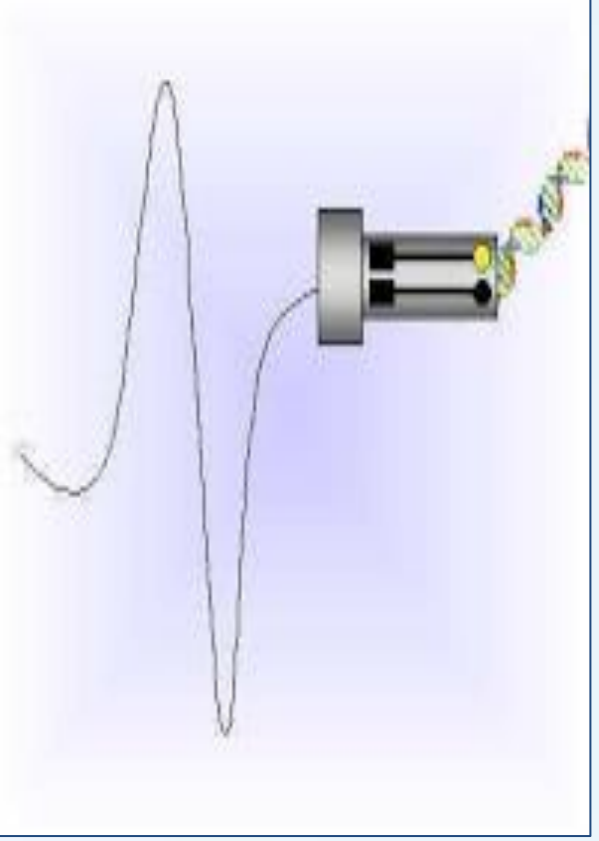
NANOPARTICLES MODIFIED SCREEN PRINTED ELECTRODES FOR ELECTROCHEMICAL DETERMINATION OF COD

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1. INTRODUCTION AND AIM OF THE WORK.

The Chemical Oxygen Demand (COD) is a widely used parameter to detect organic pollutants in water and represents the number of oxygen equivalents necessary to oxidize the organic compounds. The standard method for COD measurement (dichromate titration) suffers from several drawbacks such as long time and complexity of analysis and the consumption of toxic chemicals. Hence, interest is growing towards those methods employing electrochemical oxidation of organic compounds, as they allow to dispense with toxic reagents and above all to perform a continuous determination.

In this work, a nanoparticles based electrochemical method for COD measurement has been developed for the direct oxidation of organic molecules on suitable modified electrochemical surfaces. In particular, we have developed various modified electrochemical surfaces by electrodepositing copper oxide nanoparticles (CuONPs) onto several (graphite, G, multi walled carbon nanotubes, MWCNT, copper, Cu) commercial screen printed electrodes (SPEs) and we have compared their performances with an electrochemically modified Cu SPE surface with a copper oxide layer. Glucose was used as the standard compound for COD measurement [1]. The employing of SPEs allowed us to detect COD in continuous through a flow injection analysis (FIA) method. In this way we reduced the analysis time, improved the reproducibility and avoided the dilution of the real sample, necessary in a batch chronoamperometric detection.

2. ELECTROSYNTHESIS AND CHARACTERIZATION OF THE CuONPs ONTO THE DIFFERENT WORKING ELECTRODIC SURFACES.

- **G (SPE) – CuONPs**
 - **MWCNT (SPE) – CuONPs**
 - **Cu (SPE) ox**
 - **Cu (SPE) – CuONPs**
1. Electrodeposition of CuNPs (-0.40 V vs. Ag/AgCl for 120 s in 100 mM KCl and 10 mM CuCl₂, pre-purged with N₂);
 2. Oxidation to CuONPs (20 scans of cyclic voltammetry (CV) between -0.55 V and 0.30 V vs. Ag/AgCl at 100 mVs⁻¹ in a 100 mM NaOH solution).
1. Oxidation of the surface (20 scans of CV between -0.55 V and 0.30 V vs. Ag/AgCl at 100 mVs⁻¹ in a 100 mM NaOH solution).

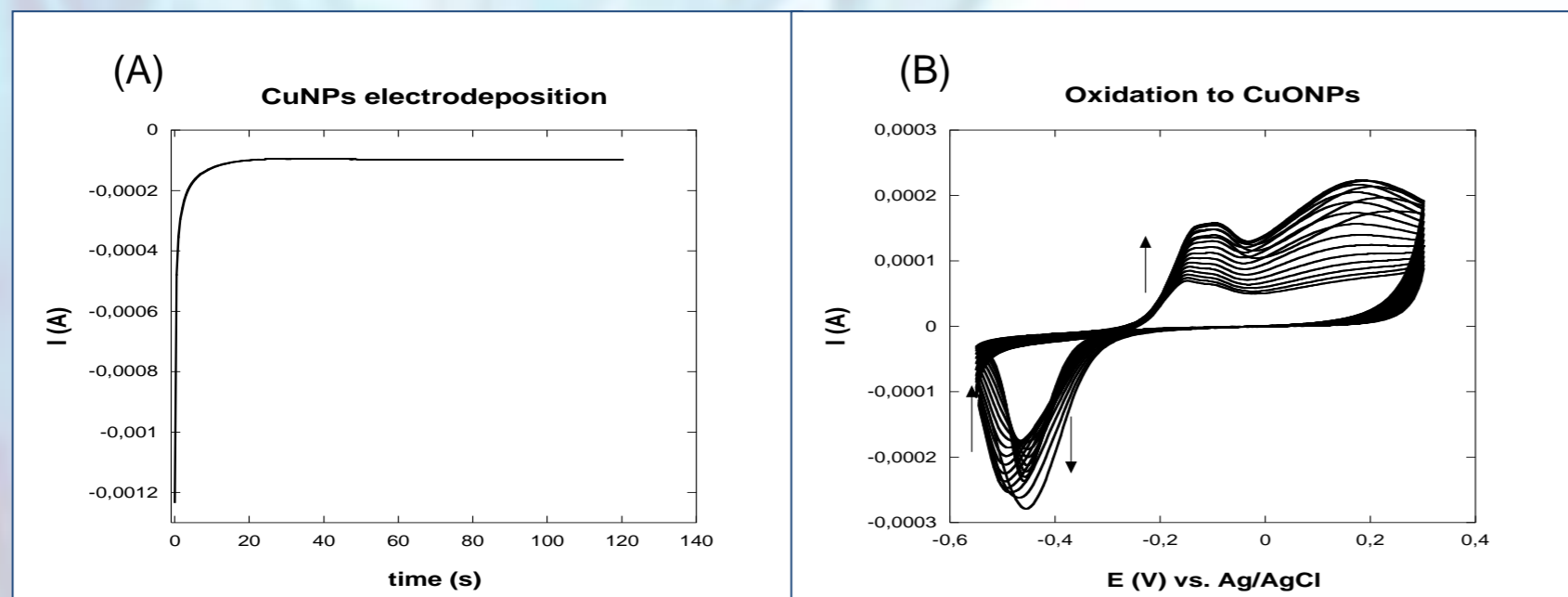


Figure 1. Electrochemical synthesis of the CuONPs onto Cu (SPE): (A) Electrodeposition of CuNPs; (B) Oxidation to CuONPs.

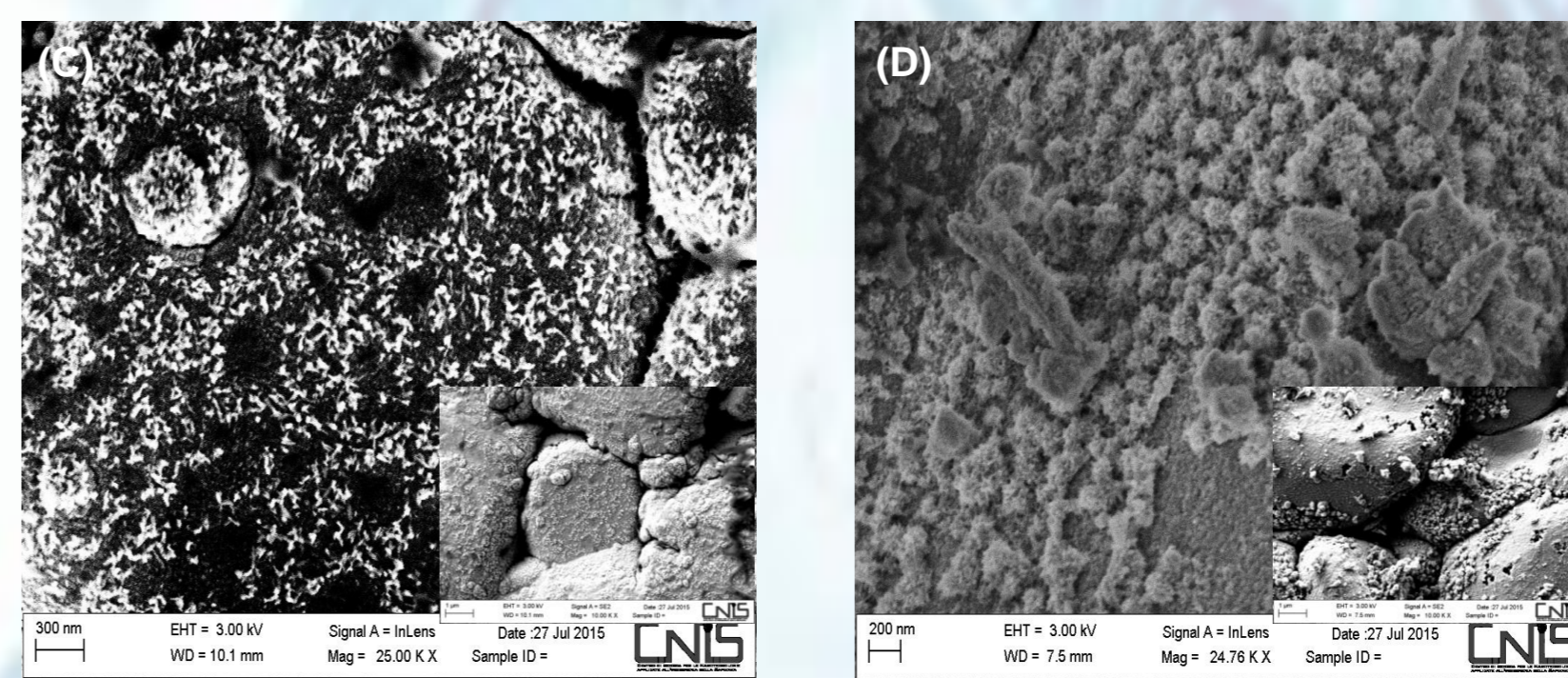
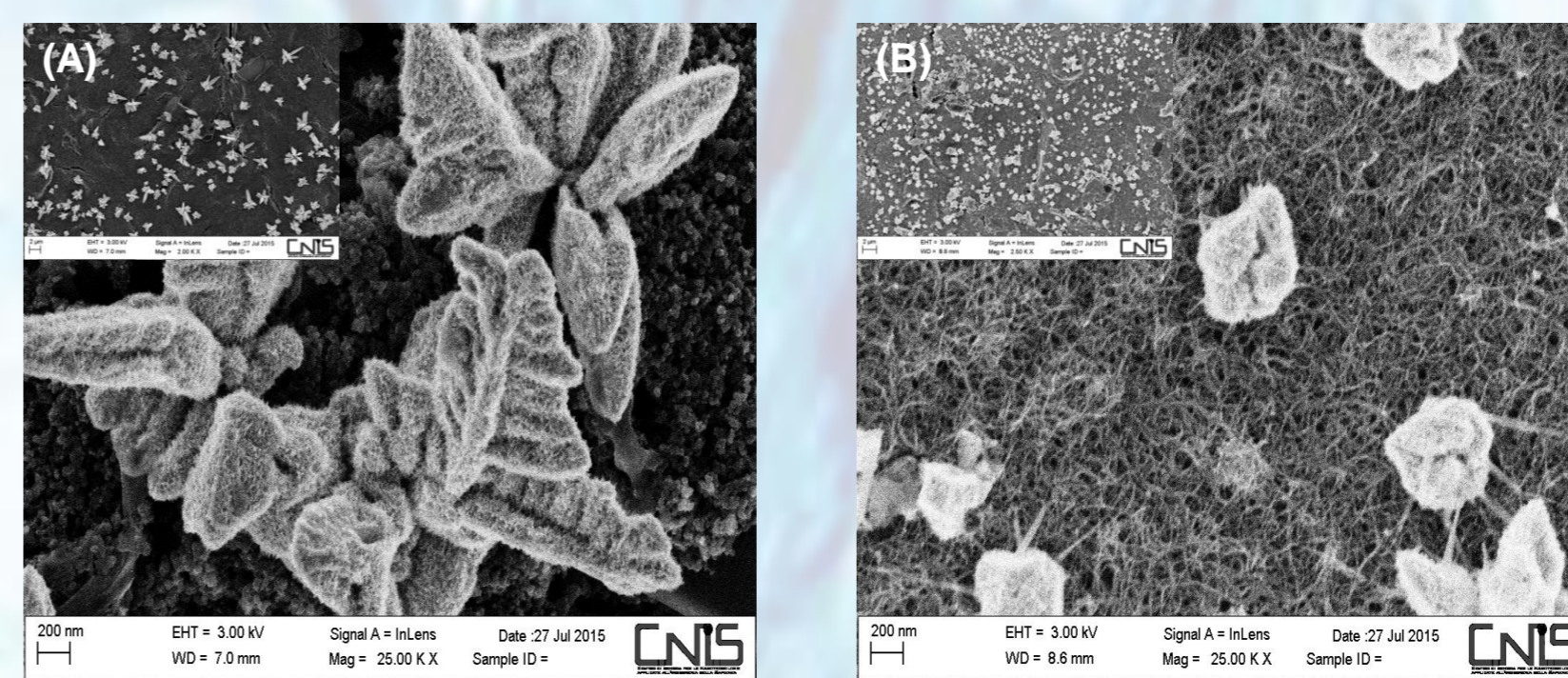


Figure 2. SEM images of the prepared modified COD sensors: (A) G(SPE)-CuONPs, (B) MWCNT(SPE)-CuONPs, (C) Cu(SPE)ox, (D) Cu(SPE)-CuONPs.

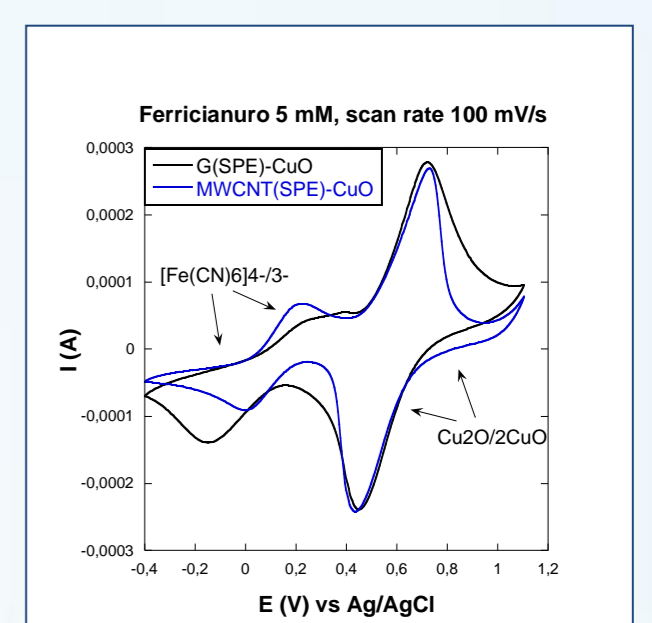
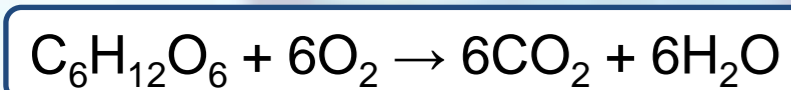


Figure 3. CV of G(SPE)-CuONPs (black) and MWCNT(SPE)-CuONPs (blue) in a solution of K₃[Fe(CN)₆].

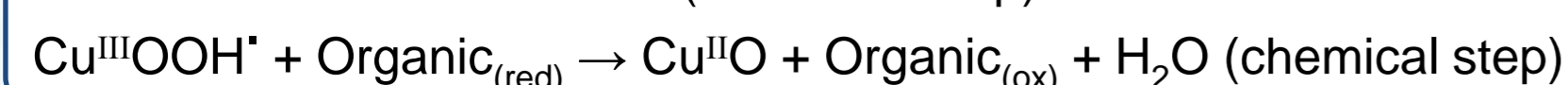


Figure 4. Cu(SPE)ox (left) and Cu(SPE)-CuONPs (right).

3. COD DETECTION USING A FIA METHOD.



Scheme 1. Oxidation reaction of glucose (COD standard): theoretical value of COD for a 1 mM glucose solution is 19.2 mgL⁻¹ of O₂.



Scheme 2. Mechanism of CuONPs catalysis of organic compound oxidation in basic media.



Figure 5. Apparatus of FIA method for COD electrochemical detection (loop volume: 1mL); inset a magnification of the SPE compartment.

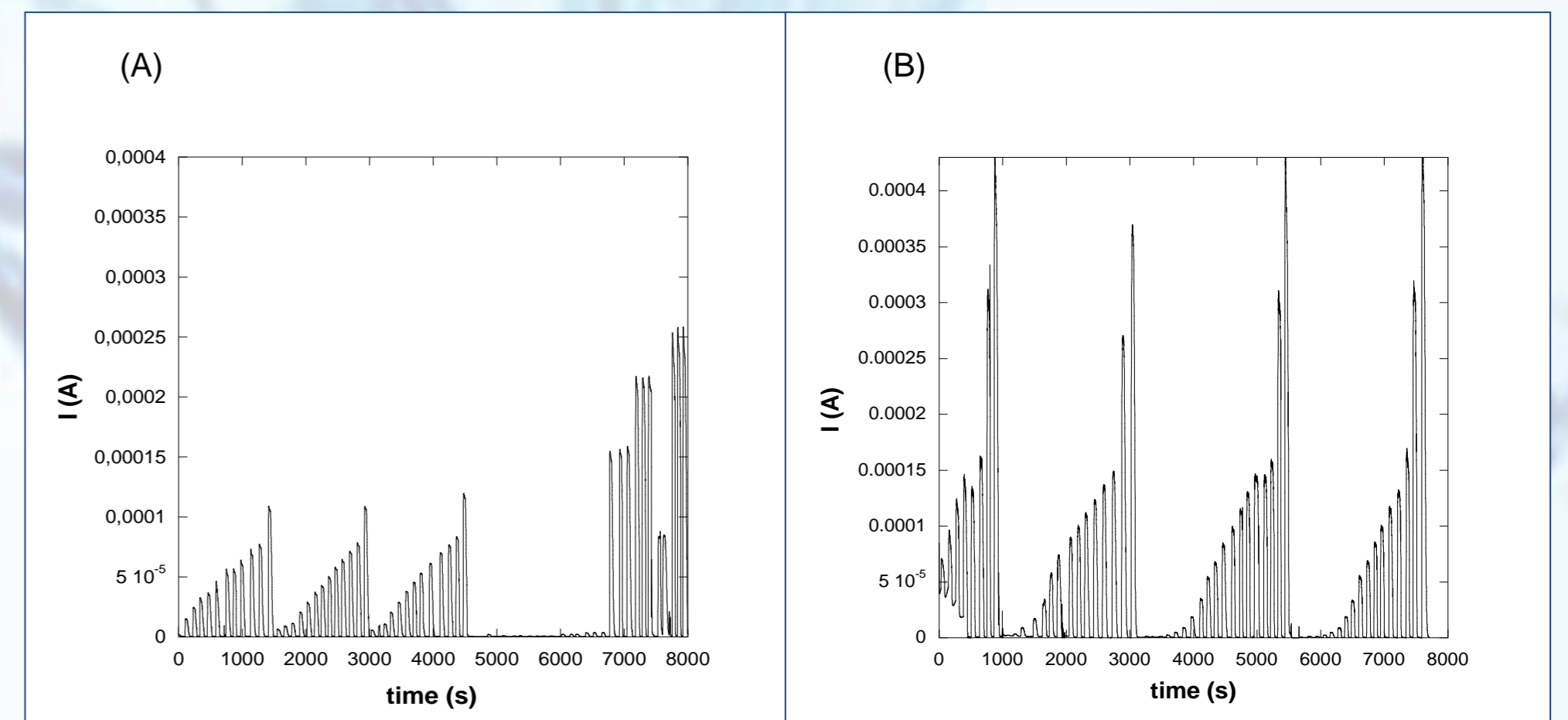


Figure 6. Electrochemical detection of increasing concentration of COD standard in 0.1 M NaOH solution by using FIA method with (A) Cu(SPE)ox and (B) Cu(SPE)-CuONPs: applied potential 0.55 V vs. Ag/AgCl (SPE pseudoreference), flow rate 1.4 mL/min, blank 0.1 M NaOH solution.

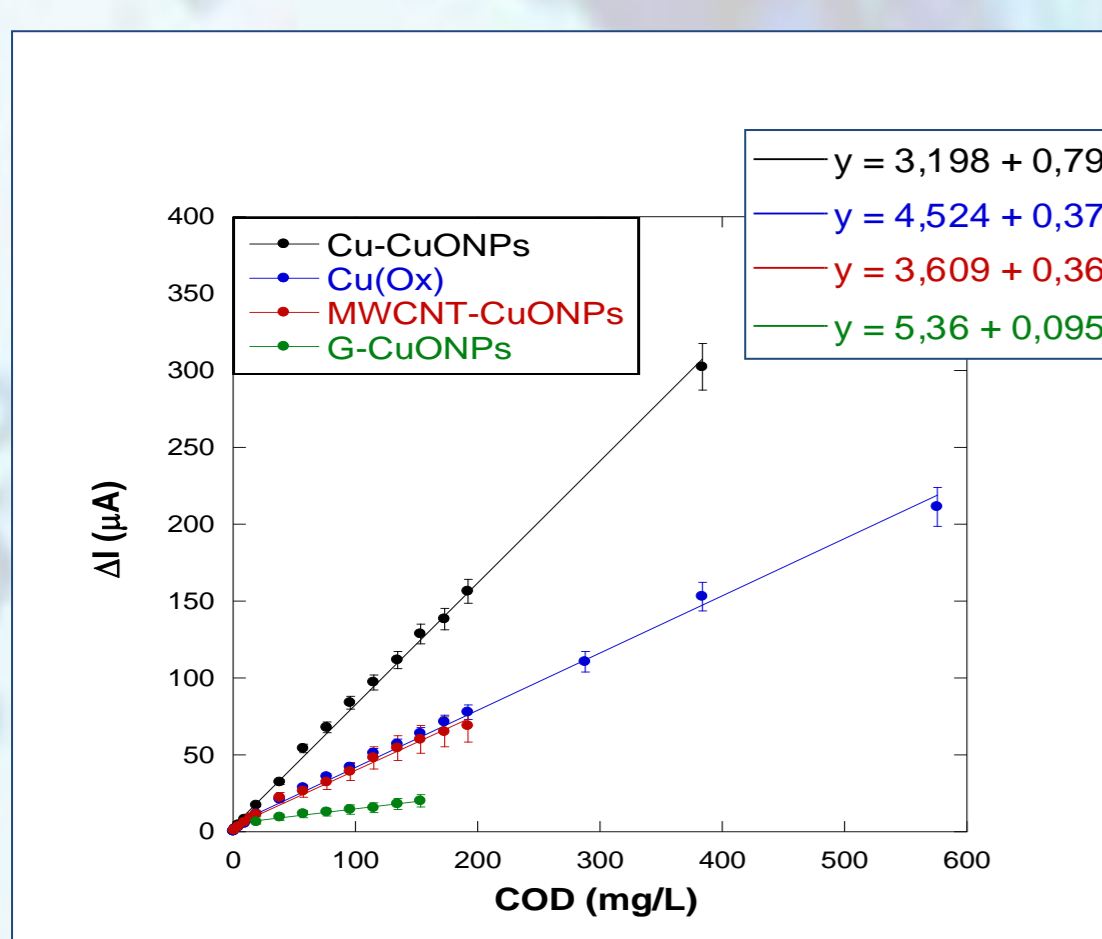


Figure 7. Calibration curves of electrochemical detection of COD standard by using FIA method with Cu(SPE)-CuONPs (black), Cu(SPE)ox (blue), MWCNT(SPE)-CuONPs (red) and G (SPE)-CuONPs (green).

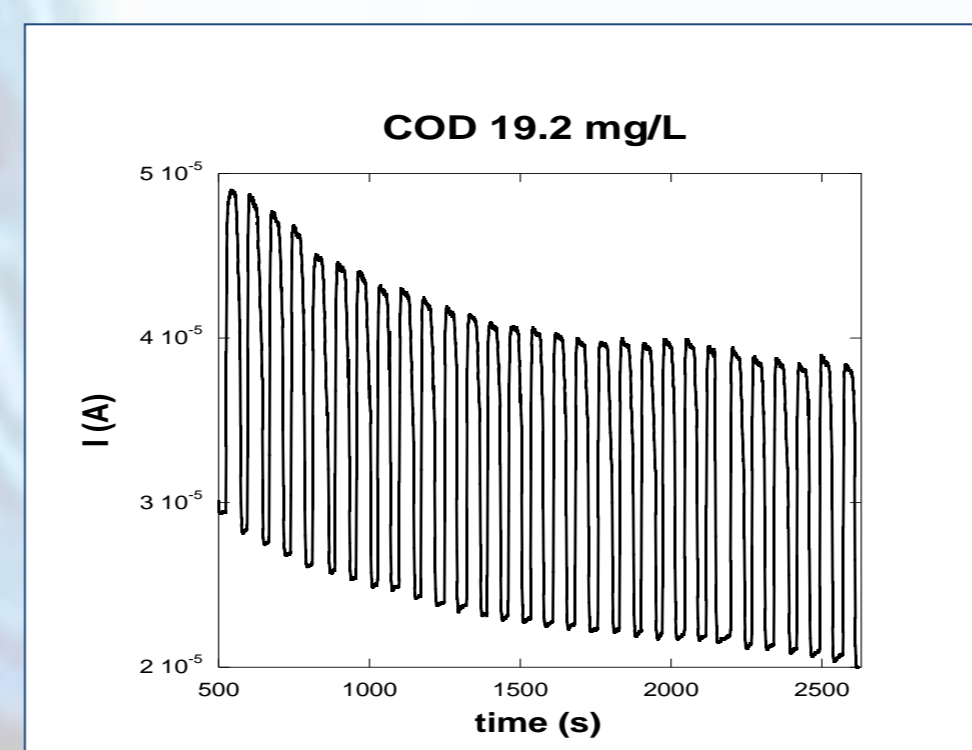


Figure 8. Repeated injections of 19.2 mgL⁻¹ of O₂ COD standard in 0.1 M NaOH solution with Cu(SPE)-CuONPs: applied potential 0.55 V vs. Ag/AgCl (SPE pseudoreference), flow rate 1.4 mL/min, blank 0.1 M NaOH solution; RSD 4% and loss of signal from the 1st to the 30th measure 9%.

Table I. Analytical parameters of COD electrochemical detection with Cu(SPE)-CuONPs and with other sensors [2].

Sensing Material	LOD (mgL ⁻¹ of O ₂)	Linearity Range (mgL ⁻¹ of O ₂)	Sensitivity (mALg ⁻¹)	Detection Potential vs. Ag/AgCl (V)
Cobalt oxide	1.10	1.70-170	1.000	0.80
Cu	3.60	4.80-600	0.454	0.80
Cu-Co	0.61	1.92-768	0.888	0.60
Boron Doped Diamond	1.00	2.00-175	0.091	2.80
Rh ₂ O ₃ /Ti	20	50-2000	0.022	1.30
Cu ₂ O-TiO ₂ Nanotube	15	20-300	1.450	0.30
Cu(SPE)-CuONPs [this work]	0.20	0.48-384	0.792	0.55

4. CONCLUSIONS AND FUTURE PERSPECTIVES.

In this work, different electrochemical COD sensors were developed. The modified SPEs were tested by using glucose as COD standard in 0.1 M NaOH medium with a continuous flow method. The copper oxide nanoparticles catalyzed the oxidation of the glucose, as well as of different organic pollutants, at relatively low potential (0.55 V vs. Ag/AgCl). After the sample injection, the oxidation of organic compound was detected in about 15 s. By alternating blank and sample solutions we avoided the dilution of the sample, improved our sensitivity to detect the sample signal from the blank and were able to analyze multiple samples in a single analysis. Cu(SPE)-CuONPs sensor showed the best performances, with a very small LOD (0.20 mgL⁻¹ of O₂), a very large linearity range (0.48-384 mgL⁻¹ of O₂), a high sensitivity (0.792 mALg⁻¹), also in presence of 0.5 M NaCl, and a good stability and reproducibility (RSD 4% up to 30 measurements). These findings provide an interesting strategy to obtain a simple, quick and cheap sensor for the on site monitoring of COD level in environmental matrices. In future, we will test the so developed Cu(SPE)-CuONPs to detect COD value in real sample of fresh and salt water, and we will compare the results obtained with the FIA electrochemical method and that obtained with standard dichromate titration method.



[1] C. R. Silva et al. J SolidState Electrochem 13 (2009) 665-669
[2] J. Wang et al. Microchim Acta 182 (2015) 515-522