Sensors for the Determination of Organic Load (Chemical Oxygen Demand) Utilizing Copper/Copper Oxide Nanoparticle Electrodes

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Abstract

This research project develops electronic sensors for determination of Chemical Oxygen Demand (COD) with the technique of cyclic voltammetry. This detection is based on the changes of current intensity followed by the oxidation reaction of organic substances in wastewater, which takes place on the surface of electrodes. Copper electrodes are chosen as the working electrodes based on the fact that copper in alkaline media acts as a powerful electrocatalyst for oxidation of aminoacids and carbohydrates, which are believed to be the major culprits for organic pollution. In this work, three kinds of copper/copper oxide electrodes were studied: electrodeposited copper nanoparticle electrode, copper nanoparticle-graphite composite electrode and copper oxide nanoparticle-graphite composite electrode.

Chemical Oxygen Demand (COD)

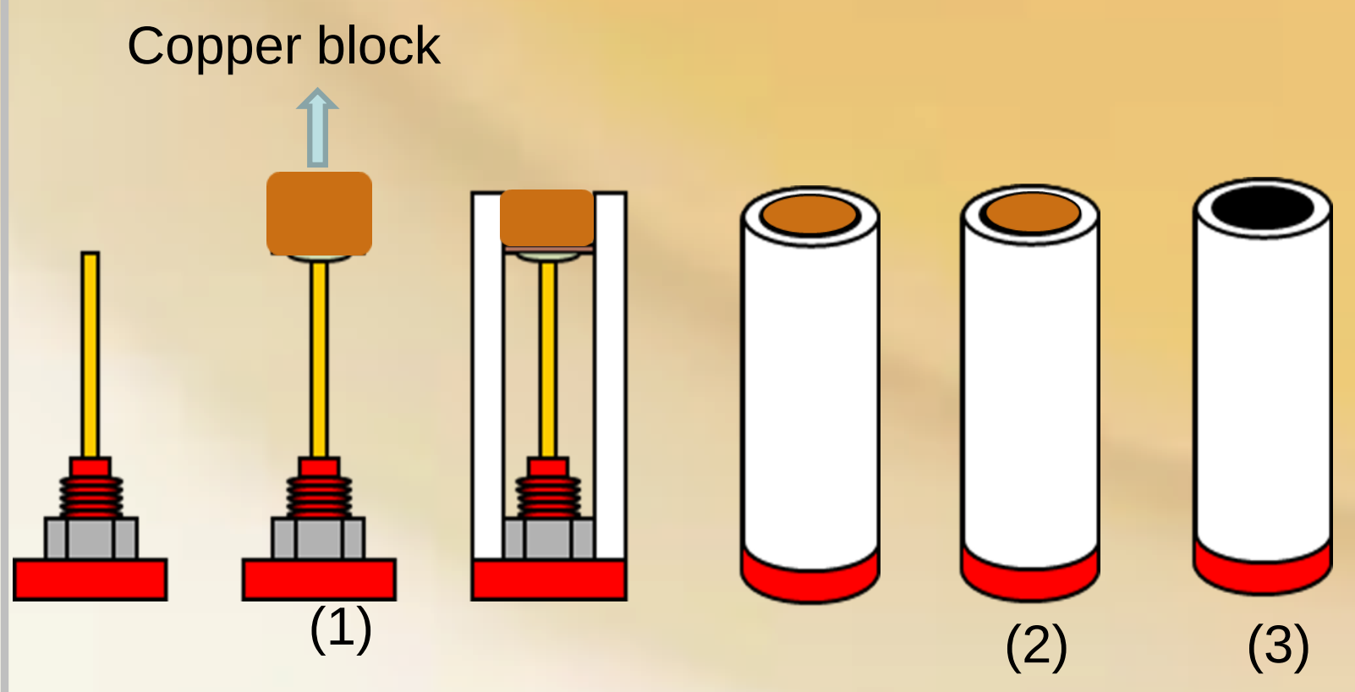
Free oxygen dissolved in water is very important for supporting aquatic life in ecosystems. The decomposition of organic contaminants will consume oxygen, which will affect the survival and qualities of these ecosystems. Chemical Oxygen Demand (COD) is a widely used parameter in analysing the extent of organic contamination of water samples[1]. The conventional method for COD determination is defined as the number of oxygen equivalents consumed in the oxidation of organic compounds by strong oxidizing agents such as dichromate and permanganate. However, this method requires the timeconsuming process of refluxing samples to achieve more complete oxidation; reproducibility of the results are dependent on the skill of the operator and expensive and toxic reagents. Electrochemistry methods of analysis are becoming more and more attractive for COD quantitation because they could be simple, accurate, sensitive and safe[2].

Why "copper"?

Copper in alkaline media acts as a powerful electrocatalyst for oxidation of carbohydrates and aminoacids. The oxidation process will result in the changes of current intensity, which can act as the signal for detection and analysis. In this sense, three electrodes with copper incorporated in different forms are designed: surface electrodeposited CuO/Cu electrode (**E1**) , copper nanoparticle-graphite composite electrode (**E2**), copper dioxide nanoparticle-graphite composite electrode (**E3**) and nickel/copper alloy nanoparticle-graphite composite electrode (**E4**).

Fabrication of Electrodes

1. Nafion film covered eletrodeposited CuO/Cu electrode **E1**



Scheme 1. Fabrication of deposited Cu/CuO electrode

1. Fix the copper block to electrical connector
2. Cover the copper surface with Nafion film
3. Electrodeposit

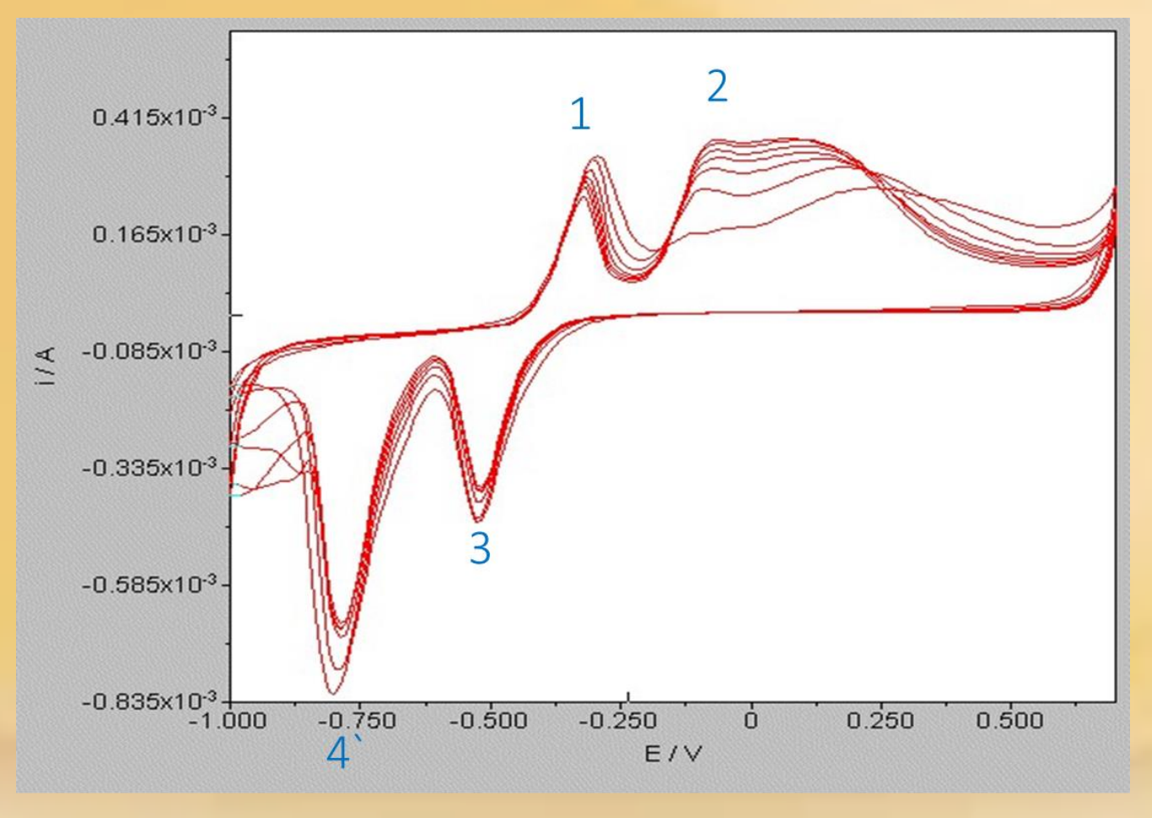
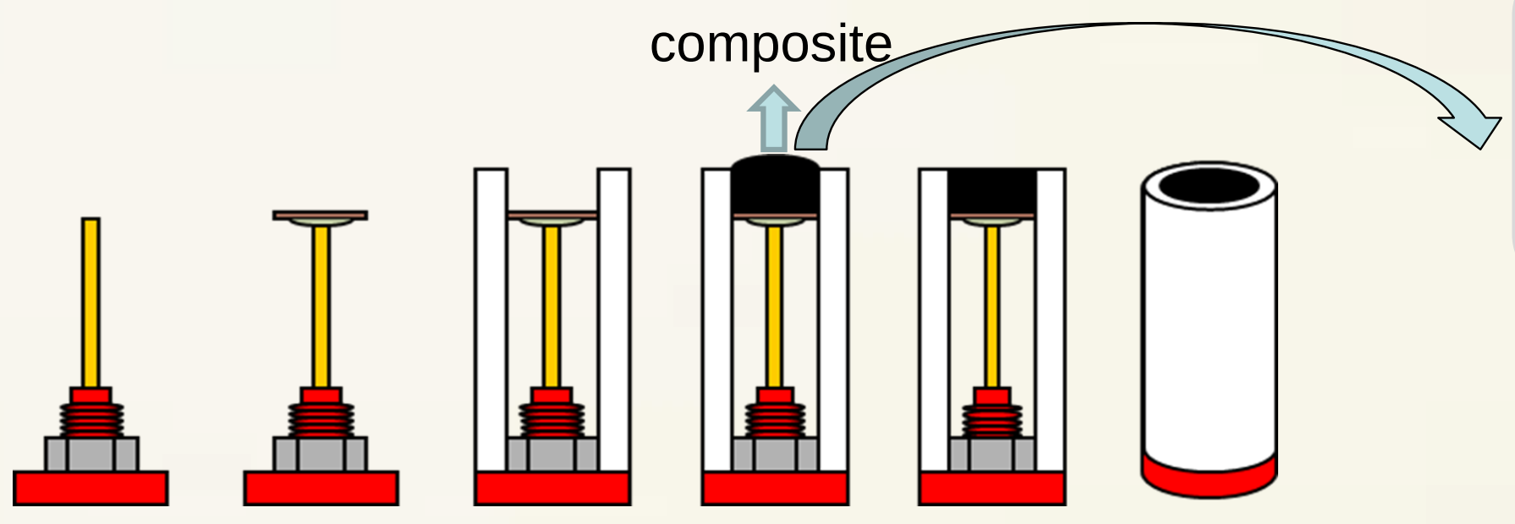


Figure 1. Series of cyclic voltammograms during preparation of the metallic copper electrode **E1** in 0.05 M NaOH-0.1 M KCl mixed solution. Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

Peak 1: Formation of a first layer of Cu_2O;
Peak 2: Formation of a second mixed layer of $CuO/Cu(OH)_2$;
Peak 3: Reduction reaction of Cu(Ⅱ)/Cu(Ⅰ);
Peak 4: Reduction reaction of Cu(Ⅰ)/Cu(0);

2. Nanoparticles composite Electrodes **E2**, **E3** and **E4**



E2: Cu nanoparticles + graphite + epoxy
E3 : CuO nanoparticles + graphite + epoxy
E4: Ni/Cu alloy nanoparticles + graphite + epoxy

Scheme 2. Fabrication of Nanoparticle Composite Electrodes

1. Fix the copper disk to electrical connector
2. Introduction of composite mixture
3. Polishing with emery paper

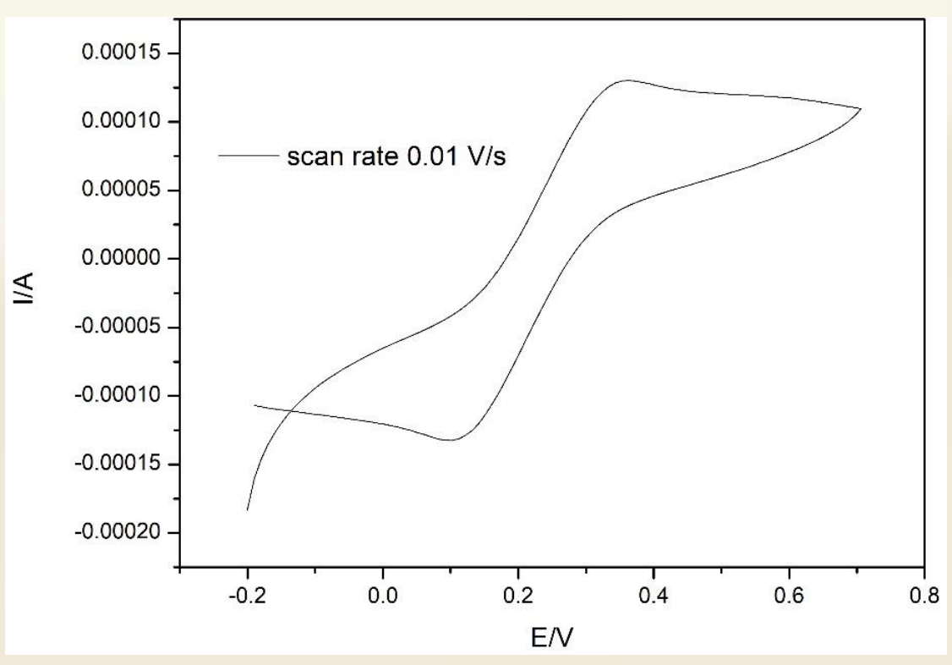


Figure 2. Cyclic voltammogram of electrode **E2** in the solution of 0.05 M $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$.

Application of four electrodes

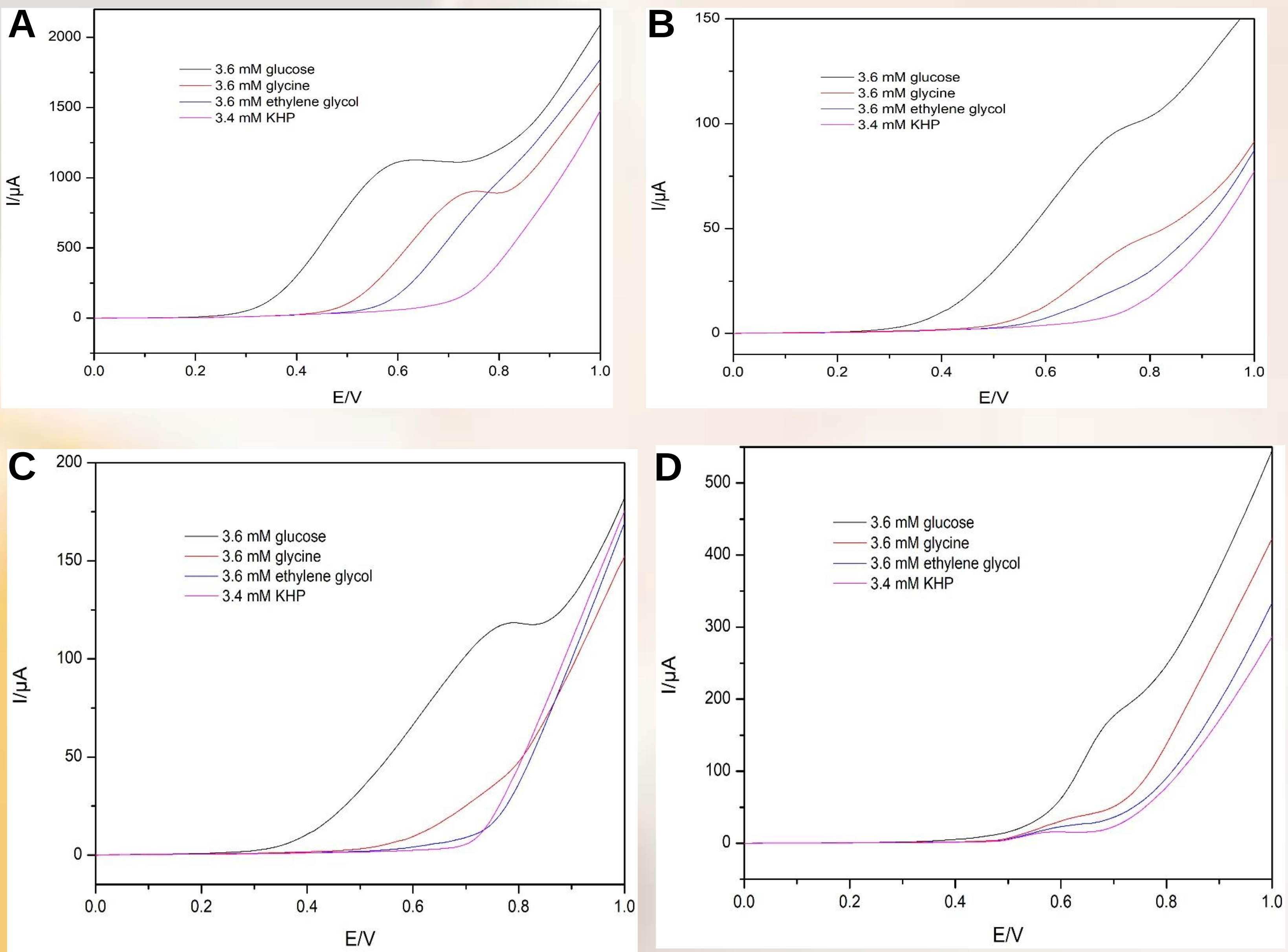


Figure 3. Oxidation curves of cyclic voltammetric responses of deposited copper electrode **E1** (A), **E2** (B), **E3** (C) and **E4** (D) to glucose, glycine, ethylene glycol, and potassium hydrogen phthalate in 0.05 M NaOH-0.1 M KCl mixed solution. Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

PCA results

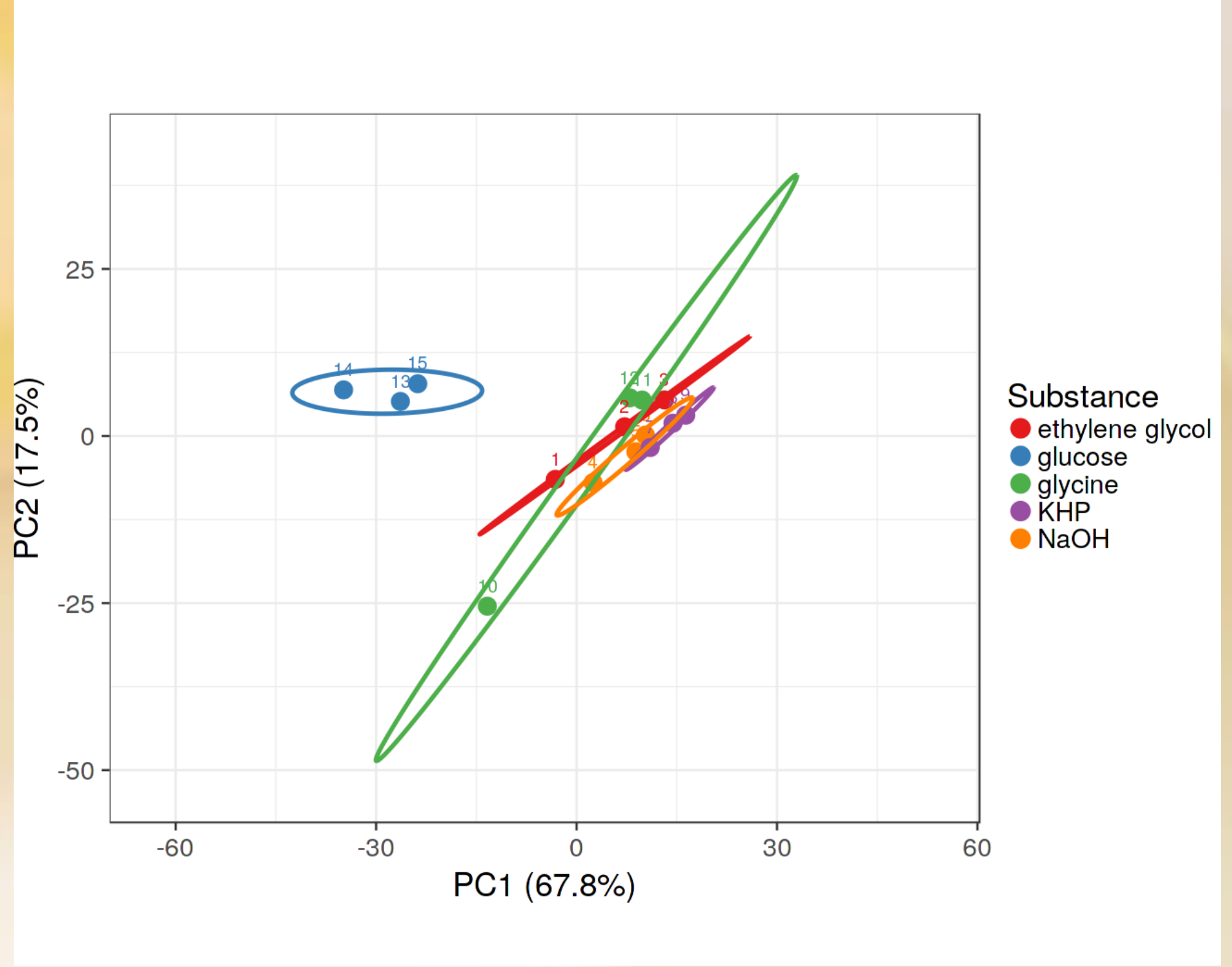
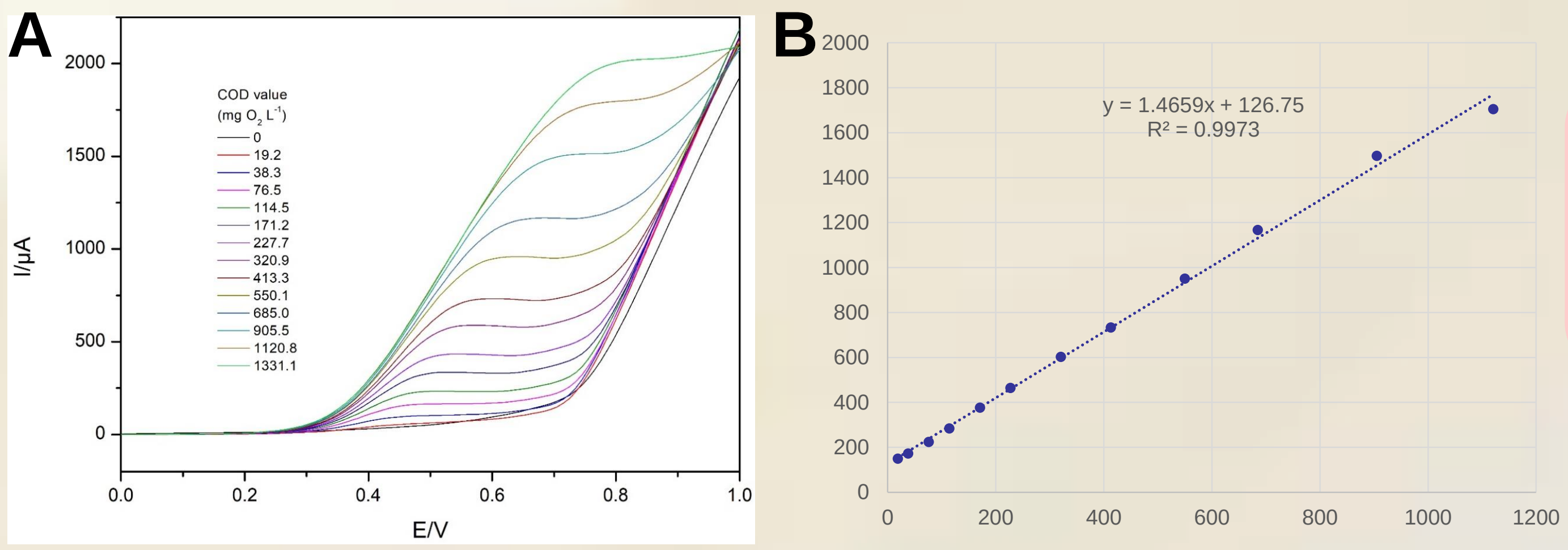


Figure 4. Score plot of the first two components obtained after PCA analysis.

In Figure. 4 are plotted the scores of samples corresponding to the two first principal components for the array response towards the 4 standard COD substances and NaOH. In there, it can be seen that not each compound sample is differentiated and clearly clustered, but glucose and potassium hydrogen phthalate (KHP) can be clearly clustered. Glucose can be oxidized easily and KHP is a compound that is hard to be oxidized, which implies that this sensor array can be used to distinguish different water samples that contains different organic contaminants.

Quantification



Linear range:
19.2~1120.8 mg O_2 L^{-1}
Limit of detection:
27.5 mg O_2 L^{-1} (LOD=3σ/k)

Figure 5. (A) Oxidation curves of cyclic voltammetric responses of electrode **E1** with the increase of addition of glucose in 0.05 M NaOH solution. (B) Calibration plot of intensity of current at E=0.7050 of electrode **E1** as a function of COD values (glucose as standard substance). Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

Conclusions

The performed calibrations showed that the electrodeposited copper electrode can detect COD values using standard substances. The linear range is from 19.2 to 1120.8 mg O_2 L^{-1} and the limit of detection is 27.5 mg O_2 L^{-1}, which shows a good performance. The conducted PCA analysis implies that this sensor array can be used to distinguish different water samples that contains different organic contaminants. The ongoing work is to optimize the detection condition and to analyse real samples.

Acknowledgements

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References

[1] C. R. Silva, C. D. C. Conceiçao et al., *J Solid State Electrochem*, **2009** (13), 665-660;
[2] T. Carchi, B. Lapo and L. Fernéndez et al., *Sensors*, **2019** (19), 669-685.