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.
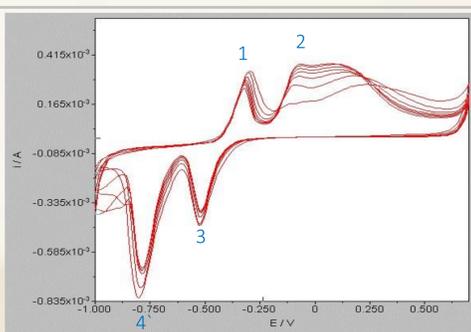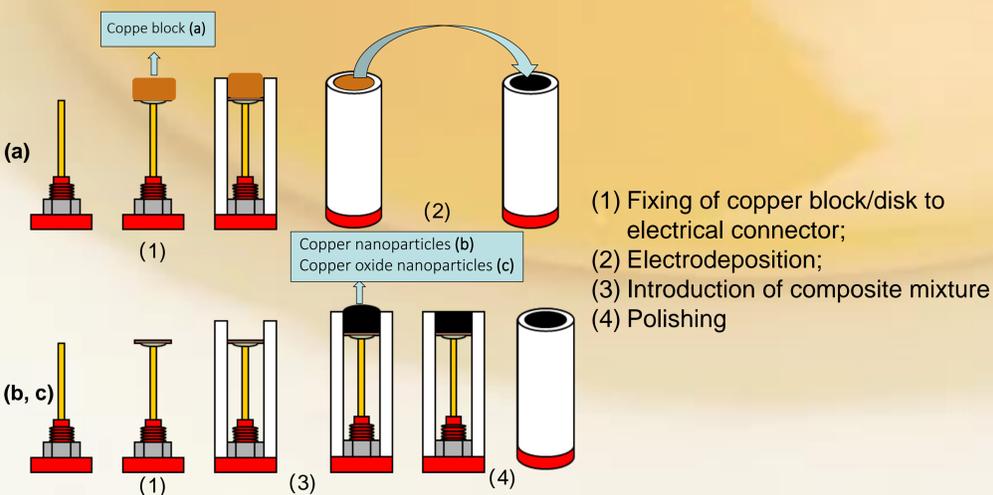
Chemical Oxygen Demand (COD)

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 nanoparticle electrode **(a)** , copper nanoparticle-graphite composite electrode **(b)**, copper dioxide nanoparticle-graphite composite electrode **(c)**.

Assembly of sensors (a), (b) and (c)

Coppe block (a)

Copper nanoparticles (b)
Copper oxide nanoparticles (c)

(1) Fixing of copper block/disk to electrical connector;
(2) Electrodeposition;
(3) Introduction of composite mixture
(4) Polishing

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 $Cu(I)/Cu(0)$;

Figure 1. Series of cyclic voltammograms during preparation of the metallic copper electrode 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.

Application of electrode (a)

The oxidation curves show different shapes with different organic substances, which reveals the possibility of distinguishing these organic substances.

Figure 2. Oxidation curves of cyclic voltammetric responses of deposited copper electrode **(a)** to ethylene glycol (4 mM), glucose (4 mM) and potassium hydrogen phthalate (4 mM) 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.
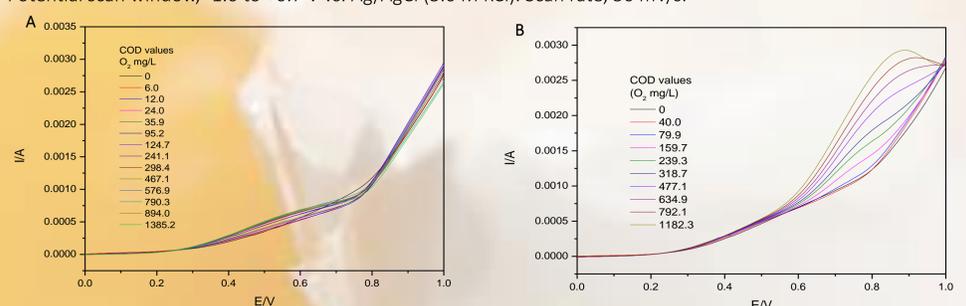
Figure 3. Oxidation curves of cyclic voltammetric responses of electrode **(a)** with the increase of addition of potassium hydrogen phthalate and ethylene glycol in 0.05 M NaOH-0.1 M KCl mixed solution. Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

$$y = 2E\text{-}06x + 9E\text{-}05$$
$$R^2 = 0.9955$$

Calculated Limit of Detection: 50.65 mg O_2 L^{-1}
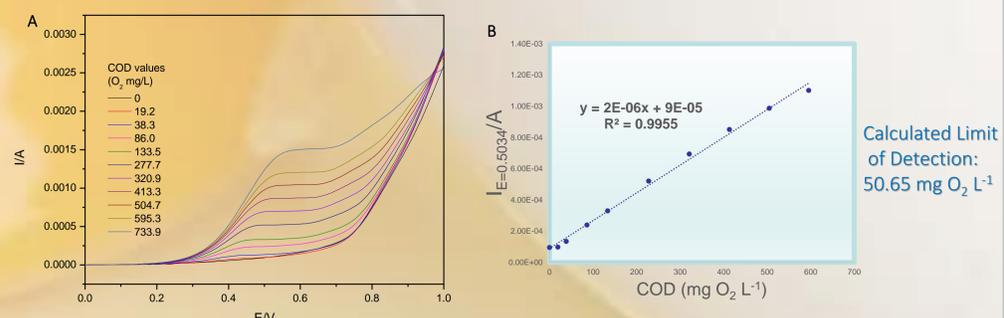
Figure 4. (A) Oxidation curves of cyclic voltammetric responses of electrode **(a)** with the increase of addition of glucose in 0.05 M NaOH-0.1 M KCl mixed solution. (B) Calibration plot of intensity of current at E=0.5034 of electrode **(a)** as a function of COD values (glucose as standard substance). Potential scan window, -1.0 to +0.7 V vs. Ag/AgCl (3.0 M KCl). Scan rate, 50 mV/s.

Application of electrodes (b) and (c)
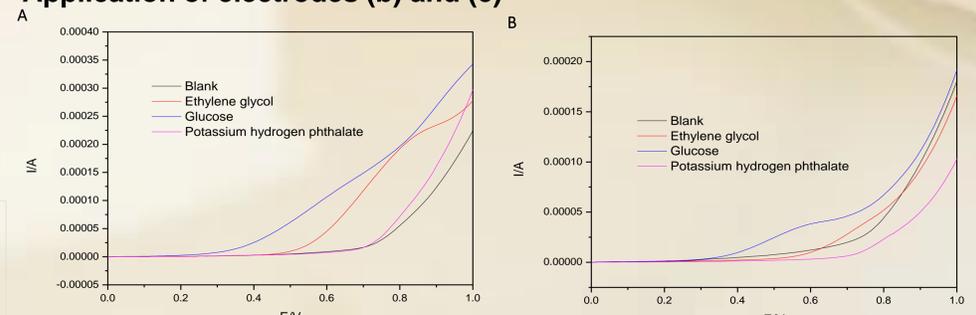
Figure 5. Oxidation curves of cyclic voltammetric responses of copper nanoparticle electrode **(b)** (A) to ethylene glycol (3.19 mM), glucose (4.12 mM) and potassium hydrogen phthalate (1.96 mM) and copper oxide nanoparticle electrode **(c)** (B) to ethylene glycol (6.95 mM), glucose (0.89 mM) and potassium hydrogen phthalate (1.69 mM) 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.

The performance of electrodes **(b)** and **(c)** show worse performance than surface electrodeposited electrode **(a)** in distinguishing these three organic substances.
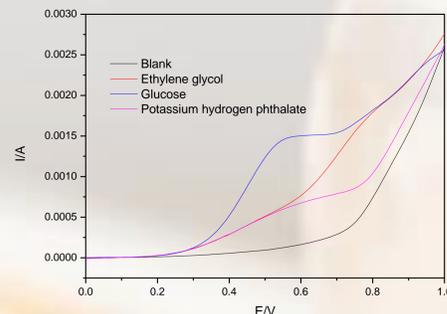
Conclusions

The performed calibrations showed that the electrodeposited copper electrode can detect COD values using standard substances. Besides, the obtained voltammetric profiles presented different shapes with the tested organic compounds, suggesting this can be used as a potential fingerprint for distinguishing organic compounds presented. Ongoing work is focused on modifying these three electrodes, optimizing measuring condition and detecting the COD values of real samples.

Acknowledgements

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.

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