Determination of Chemical Oxygen Demand (COD) Using Nanoparticle-Modified Voltammetric Sensors and Electronic Tongue Principles

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Abstract
This research focuses on the use of nanoparticle-modified voltammetric sensors for the rapid and green determination of Chemical Oxygen Demand in river waters and waters from agricultural waste. Four different variants of modified electrodes have been prepared: CuO nanoparticles electrogenerated over Cu and covered with Nafion film (CuO/Cu-Ni), and graphite-epoxy composites modified with Cu, CuO, and Cu-Ni alloy nanoparticles. The response features of these electrodes were assessed by calibrating them vs. glucose, glycine, ethylene glycol, and potassium hydrogen phthalate in alkaline media, as samples providing different difficulty in their (bio)degradation characteristics. The most sensitive electrode was demonstrated to be the (CuO/Cu-Ni) electrode, with an LOD of 12.3 mg O₂ L⁻¹. The joint information provided by the sensor array showed the ability of estimating both the organic load and the type of sample in terms of difficulty of degradation, in what can be named an intelligent sensor assembly.

Chemical Oxygen Demand (COD)
Chemical Oxygen Demand (COD) is defined as the amount of molecular oxygen (in milligrams of O₂) required to decompose all the organic compounds in 1 L of aqueous solution to carbon dioxide and water. There are many methods reported for COD determination, such as the conventional dichromate titration method. Electro-oxidizing the organic contaminants to completely transform them into CO₂ and H₂O using sensors is considered the best method for COD estimation [1-3].

Real Samples Analysis

1. Calibration

Table 1. Recovery yield of spiked glucose detected by electrode E1 towards Sample 1, 2 and 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added glucose (mg O₂ L⁻¹)</th>
<th>Spiked sample found</th>
<th>Recovery yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>&lt;LOD</td>
<td>38.32</td>
<td>109.5</td>
</tr>
<tr>
<td>Sample 2</td>
<td>&lt;LOD</td>
<td>38.32</td>
<td>108.6</td>
</tr>
<tr>
<td>Sample 1st</td>
<td>33.76</td>
<td>95.52</td>
<td>112.11</td>
</tr>
<tr>
<td>Sample 2nd</td>
<td>17.10</td>
<td>95.52</td>
<td>101.64</td>
</tr>
<tr>
<td>Sample 3rd</td>
<td>18.56</td>
<td>95.52</td>
<td>97.37</td>
</tr>
</tbody>
</table>

2. Spiking Tests

Figure 4. (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=+0.760 V of electrode E1 as a function of COD values (glucose as Standard substance). Potential scan window, -1.0 to +2.7 V vs. Ag/AgCl (1 M KCl). Scan rate, 50 mV/s.

3. PCA on Real Samples and Standard Compounds

Table 2. PCA score plots of the first two components obtained after PCA analysis to real samples and standard compounds.

This work developed an easy method of analyzing wastewaters quantitatively and qualitatively by combining the electrochemical electrodes with the electronic tongue technique. The COD values were calculated based on the calibration and the PCA technique can be used to evaluate the main component of a river sample, which is easy or difficult to be degraded. The resulting sensor-based method demonstrates great potential not only for estimating the precise value of organic load but for predicting the difficulty behavior in its degradation.

References