CUSTOMIZED SCREEN-PRINTED ELECTRODES BASED ON Ag-NANOSEEDS FOR ENHANCED ELECTROANALYTICAL RESPONSE TOWARDS Cd(II), Pb(II) AND As(V) IN AQUEOUS SAMPLES

KARINA TORRES-RIVERO*, CLARA PÉREZ-RÀFOLS, JULIO BASTOS-ARRIETA, NÚRIA SERRANO, VICENÇ MARTÍ AND ANTONIO FLORIDO
AGENDA

- Heavy Metals contamination problematic
- Objectives
- Methodology
- Results
- Conclusions
HEAVY METAL WATER CONTAMINATION

Heavy metal ions
- High toxicity
- Non-biodegradability
- Bioaccumulation
- Adverse health effects in humans

<table>
<thead>
<tr>
<th>Metal</th>
<th>WHO Limit</th>
<th>EU Directive 2020/2184 Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>10 µg/L</td>
<td>10 µg/L</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>3 µg/L</td>
<td>5 µg/L</td>
</tr>
<tr>
<td>As(V)</td>
<td>10 µg/L</td>
<td>10 µg/L</td>
</tr>
</tbody>
</table>


Source: http://water-purifiers.com/heavy-metal-contamination-in-drinking-water/
Heavy Metal Detection Methods

- Flameless atomic adsorption spectrometry (FAAS)
- Inductively coupled plasma mass spectrometry (ICP-MS)
- Hydride generation atomic fluorescence spectrometry (HG-AFS)
- ELECTROCHEMICAL TECHNIQUES: ANODIC STRIPPING VOLTAMMETRY (ASV)

Nanoparticles/Screen-printed electrodes

- Electrochemical response improvement
- ↓ Electron Transfer Resistance
- Catalyzing the electrode’s response at low analyte concentrations

Voltammetric determination of HMIs based on the use of carbon-nanofiber-based screen-printed electrodes (SPCNFEs) modified with silver nanoparticles (Ag-NPs)

- Synthesize Ag-NS
- Modify SPCNFE with the dropcasting technique
- Characterize the modified electrode surface.
- Characterize the modified electrode electrochemically using DPASV
- Study the applicability of the modified electrode in As(V) spiked tap water samples
METHODOLOGY

1. Ag-Seeds Synthesis

- AgNO₃ as metal precursor
- NaBH₄ as reducing agent
- Na₃C₆H₅O₇ (Trisodium citrate) as capping agent

2. Ag-Nanoseeds characterization

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)

3. SPCNFE Modification

- Dropcasting
  - 1 drop of 40 µL
- Heat at 50 ºC for 30 minutes

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4. Modified SPCNFE Surface characterization

**Scanning Electron Microscopy (SEM)**

5. SPEs Electrode characterization

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### DPASV Parameters

<table>
<thead>
<tr>
<th></th>
<th>Pb(II)</th>
<th>Cd(II)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$E_d$</strong></td>
<td>-1.4 V</td>
<td>-1.4 V</td>
<td>-1.3 V</td>
</tr>
<tr>
<td><strong>$T_d$</strong></td>
<td>180 s</td>
<td>180 s</td>
<td>120 s</td>
</tr>
<tr>
<td><strong>Scanning Potential</strong></td>
<td>-1.4 V - 0.0 V</td>
<td>-1.4 V - 0.0 V</td>
<td>-1.3 V - 0.65 V</td>
</tr>
</tbody>
</table>

---

### Buffer

<table>
<thead>
<tr>
<th></th>
<th>Pb(II)</th>
<th>Cd(II)</th>
<th>As(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Buffer</strong></td>
<td>0.1 mol/L Acetate buffer pH 4.5</td>
<td>0.1 mol/L Acetate buffer pH 4.5</td>
<td>0.01 mol/L HCl pH 2.0</td>
</tr>
<tr>
<td><strong>Standard</strong></td>
<td>1 mg/L</td>
<td>1 mg/L</td>
<td>1 mg/L</td>
</tr>
</tbody>
</table>
RESULTS

1. Ag-Nanoseeds characterization\textsuperscript{3}

- Spherical shape
- 12.2 ± 0.4 nm

2. Ag-NS-SPCNFE Surface characterization\textsuperscript{4}

Ag-Nanoseeds

- Spherical shape
- 12.2 ± 0.4 nm


\textsuperscript{4}Torres-Rivero, K.; Pérez-Ráfols, C.; Bastos-Arrieta, J.; Florido, A.; Martí, V.; Serrano, N. Direct As(V) determination using screen-printed electrodes modified with silver nanoparticles. Nanomaterials 2020, 10, 1–10
# RESULTS

**Ag-NS-SPCNFE Electrochemical Characterization**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD (µg.L⁻¹)</th>
<th>Linear Range (µg.L⁻¹)</th>
<th>R²</th>
<th>Sensitivity (nA µg⁻¹ L) (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>3.3</td>
<td>10.9-99.6</td>
<td>0.999</td>
<td>103 (3)</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>3.7</td>
<td>12.2-73.4</td>
<td>0.992</td>
<td>22 (1)</td>
</tr>
<tr>
<td>As(V)</td>
<td>2.6</td>
<td>8.9 - 40.0</td>
<td>0.991</td>
<td>260 (10)</td>
</tr>
</tbody>
</table>

![Graph](image-url)

- **As(V)**
- **Cd(II)**
- **Pb(II)**
Tap water samples were collected from the local water distribution network managed by Aigües de Barcelona Company
https://www.aiguesdebarcelona.cat/

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**Ag-NS-SPCNFE-Application in real sample**

<table>
<thead>
<tr>
<th>Method</th>
<th>CAs(V) (µg.L⁻¹)</th>
<th>SD (µg.L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPASV</td>
<td>10.04</td>
<td>0.37</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>10.70</td>
<td>0.20</td>
</tr>
</tbody>
</table>
CONCLUSIONS

✓ Ag-Nanoseeds were synthesized, microscopically characterized, and used for the modification of SPCNFE.
✓ Ag-NS-SPCNFE was suitable for determining Pb(II), Cd(II), and As(V) at low µg.L\(^{-1}\) levels.
✓ Electrochemical characterization showed wider linear ranges for Pb(II) and Cd(II) determination but lower sensitivities as compared to As(V).
✓ LODs achieved in this investigation are equal or lower than other LODs previously reported.
✓ The suitability of Ag-NS-SPCNFE for the determination of As(V) in spiked water samples, achieving comparable results with ICP-MS with good reproducibility.
Acknowledgments

This research has been funded by Ministerio de Ciencia, Innovación y Universidades, and European Union Funds for Regional Development (FEDER), projects CTM2015-68859-C2-2-R and CGL2017-87216-C4-3-R, as well as by the Generalitat de Catalunya (Project 2017SGR312).

PhD Grant: Spanish Ministry of Education, Culture and Sports
Thank you for your attention!
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*karina.torres.rivero@upc.edu