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Metal and Metal Oxide Nanoparticles in the Voltammetric Detection of Heavy Metals: A Review

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ABSTRACT

Most heavy metal ions are known to be toxic and carcinogenic when present in high amounts. Thus, rapid and reliable on-site detection of these ions is crucial. Voltammetry is a highly sensitive electrochemical method that has been widely used for heavy metal detection offering the advantages of sensitivity and rapidity. On the other hand, nanoparticles offer the advantages of high surface area and high selectivity. Thus, this review aims to highlight the application of metallic and metallic oxide nanoparticles for the voltammetric detection of heavy metals. The nanoparticles used were either applied solely on the electrode or as modifiers with various materials. In all cases, the synthesized devices showed an enhanced analytical performance, such that the limits of detection were lowered and the sensitivities were increased as compared to voltammetric systems not using nanoparticles. Moreover, the applicability of some of these systems was investigated in real samples.

1. Introduction

Heavy metals are defined as naturally occurring elements having a density or specific gravity greater than 5 g.cm^{-3} and atomic weights between 63.5 and 200.6 g.mol^{-1} [1]. Ions of heavy metals, even at trace levels, have been detected in different sources including food, beverages, soil, plants, natural waters, etc. The use of pesticides and fertilizers, burning of fossil fuels, mining, smelting and leaching from eating utensils and cookware are all sources of heavy metal contamination [2, 3]. In addition to human activities, natural sources of heavy metals include: weathering of metal-bearing rocks, volcanic eruptions and forest fires.

Upon their release into the environment, whether through natural or anthropogenic sources, and since they are non-biodegradable, heavy metals accumulate and become toxic when present at high concentrations [4]. They are also known to hinder the developmental activity, yielding capacity and growth of plants. Moreover, heavy metals cause soil pollution and continuous exposure is very harmful to aquatic and terrestrial plants and animals [5]. In addition to their adverse impact on the environment, heavy metals are dangerous to the human health. They enter natural waters and start accumulating in sediments and living organisms, until they reach the final consumers in the food chain, which are human beings [6]. Continued exposure to heavy metals over a prolonged period of time can cause chronic poisoning, growth and developmental abnormalities, nephrotoxicity, encephalopathy, cardiovascular diseases and cancer.

For this reason, for each heavy metal, especially those considered as toxic, several agencies including the World Health Organization (WHO), Environmental Protection Agency (EPA) and Food and Drug Administration (FDA) [7, 8] have set guideline values for the allowable intake and exposure of humans to these heavy metals. Some of these limits are summarized in Table 1.

Table 1: Comparison between the allowable levels of some heavy metals in drinking water following the EPA, WHO and EU guidelines.

| Heavy metal | EPA Guideline value in drinkable water ($\mu\text{g/L}$) | WHO Guideline value in drinkable water ($\mu\text{g/L}$) | EU Guideline value in foodstuff ($\mu\text{g/Kg}$) |
|-------------|--|--|--|
| Antimony | 20 | 5 | 40 |
| Arsenic | 10 | 10 | 2 |
| Cadmium | 3 | 3 | 50 |
| Chromium | 50 | 50 | 250 |
| Copper | 2000 | 2000 | 36 |
| Lead | 10 | 10 | 20 |
| Mercury | 6 | 1 | 1.6 |
| Nickel | 70 | 20 | n/a |

Conventional methods that have been used so far for the detection of heavy metals include Inductively Coupled Plasma- Mass Spectrometry (ICP-MS), Liquid Chromatography (LC) [9], UV-vis Spectrometry [10], Atomic Absorption Spectroscopy (AAS), Atomic Emission Spectrometry (AES) [11], Atomic Fluorescence Spectrometry (AFS) [12], Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) [13], Capillary Electrophoresis (CE) and

50 Laser-Induced Breakdown Spectroscopy (LIBS) [14]. Even though these techniques are highly sensitive and
51 selective, there still exists several challenges for their use in heavy metal detection [15]. These include high cost,
52 complex operational procedures, long detection time and difficulty in achieving the detection in real environments
53 [14].

54 On the other hand, electrochemical methods are gaining wide recognition in heavy metal detection. These
55 methods offer the same sensitivity with a lower cost, less complex operational procedures and fast on-site detection.
56 Different electrochemical platforms have been developed for heavy metal detection. Specifically, nanomaterials
57 have brought several advantages in this area due to their unique electronic, chemical and mechanical properties.
58 Accordingly, different electrochemical sensors using nanoparticles have been constructed for the detection of heavy
59 metals [16, 17].

60 To the best of our knowledge, recent reviews focus on the detection of heavy metals using either a specific
61 technique, or a specific type of nanoparticles [15, 17]. This review mainly discusses the use of voltammetry in the
62 past fifteen years for heavy metal detection that can be applied to water samples using metal or metal oxide
63 nanoparticles.
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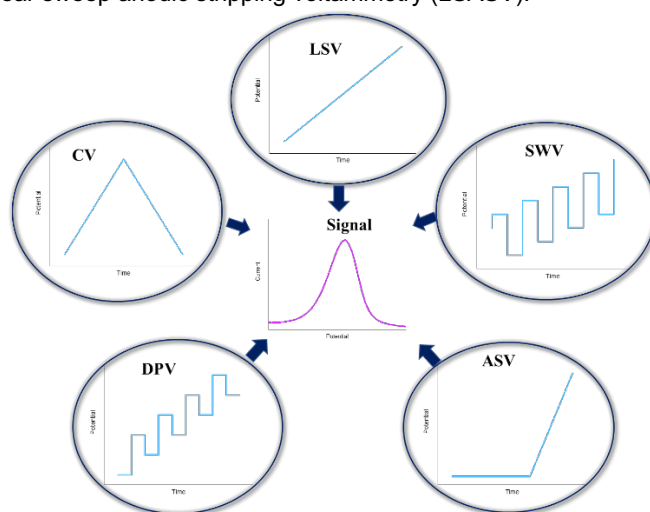
65 2. Voltammetric Techniques

66 Among the different known electrochemical methods, voltammetry is the most used in the detection of
67 heavy metal ions. Voltammetry in general describes all electrochemical systems which are based on potential-
68 dependent current measurements. A three-electrode electrochemical set-up typically consists of a working
69 electrode, a counter electrode and a reference electrode. The potential is applied between the working and the
70 reference electrodes, while the current is measured between the working and the counter electrodes. Upon varying
71 the method of potential change, one ends up with different techniques. Linear sweep voltammetry (LSV) is the
72 simplest technique such that the potential is swept linearly with time [18]. Cyclic voltammetry (CV) consists of linearly
73 scanning the potential in one direction followed by reversing the potential of a working electrode [17]. In other words,
74 a single or multiple triangular potential waveform [19] are involved.

75 The use of a pulse of voltage signal is the main concept behind pulsed voltammetry. By varying the shape
76 and amplitude of the pulses, different types of pulsed voltammetry exist [17]. Differential pulse voltammetry (DPV)
77 uses fixed magnitude pulses superimposed on a linear potential ramp [19]. Square wave voltammetry (SWV) is
78 when a waveform of a symmetrical square wave is superimposed on a base staircase potential and applied to the
79 working electrode [19].

80 Stripping voltammetry, and more specifically, anodic stripping voltammetry (ASV) is based on a two-step
81 process. The first step is a pre-concentration or electrodeposition of the heavy metal at the electrode surface
82 through the reduction of the metal ions. The second step is the stripping step, where the metal is oxidized back to
83 give the ion. Having taken the 2 steps into consideration, several factors are known to influence the analysis, such
84 as electrode material, deposition potential, deposition time [20] ... When the preconcentration step is non-
85 electrolytic, the analyte accumulates at the surface of the electrode by physical adsorption, a different method is
86 obtained: Adsorptive Stripping Voltammetry (AdSV) [21]. Figure 1 summarizes how the potential is varied with time
87 for CV, LSV, DPV, SWV and ASV to produce a signal.

88 A combination of some of these techniques results in increased sensitivities and limits of detection. The
89 combinations include differential pulse anodic stripping voltammetry (DPASV), square wave anodic stripping
90 voltammetry (SWASV) and linear sweep anodic stripping voltammetry (LSASV).



91
92 Figure 1: The graphs of potential vs time for some voltammetry techniques to produce a signal.

94 3. Metal Nanoparticles

95 Nanoparticles, specifically metal nanoparticles, present several advantages in the electrochemical sensing
96 field. Due to their small sizes, nanoparticles can increase the surface area of the electrode being used. Moreover,
97 metallic nanoparticles can increase the mass-transport rate and offer a fast electron transfer, both increasing the
98 sensitivity of the used electrodes [16]. In this section, we will present the use of different types of metallic
99 nanoparticles for the detection of the majority of heavy metals.

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101 3.1. Silver Nanoparticles

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102 Silver nanoparticles (Ag NPs) are one of the most well-developed nanoparticles because they are relatively
103 inexpensive and they have unique chemical and physical properties that make them useful in different catalytic,
104 optical and chemical applications. Silver nanoparticles have been combined with different materials for the detection
105 of Cd^{2+} , Cr^{6+} , Cu^{2+} , Hg^{2+} and Sb^{3+} . Two different ways have been employed for the synthesis of spherical Ag NPs:
106 reduction and electrodeposition. When the NPs were used along with graphene oxide, reduction of silver nitrate
107 (AgNO_3) was employed, either hydrothermally to produce Ag NPs with an average size of 10 – 20 nm [22] or using
108 hydrogen iodide HI as a reducing agent to yield Ag NPs with an average particle size of 9.7 nm [23]. The resultant
109 nanoparticles in both reports were homogeneously distributed on the reduced graphene oxide network. On the other
110 hand, the electrodeposition of silver nanoparticles [24, 25] produced larger particles with sizes ranging between 30
111 and 50 nm.

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112 Most recently, Cheng et al. synthesized reduced graphene oxide/silver nanoparticles composites for the
113 simultaneous detection of several ions. Trace levels of Cu^{2+} , Cd^{2+} and Hg^{2+} , using cyclic voltammetry were detected
114 with detection limits of 10^{-15} M, 10^{-21} M and 10^{-29} M respectively [22]. Although reporting exceptionally low LODs not
115 reported elsewhere, specifically for mercury, , this method could detect 1 atom in 166 m^3 of water! The detection
116 mechanism is different than all other papers such that it relies on the area of the entirety of the CV curve instead of
117 using that of a peak. Moreover, the paper lacks important data on the analytical performance such as the linear
118 range, sensitivity and reproducibility. Han et al. also used silver nanoparticles with reduced graphene oxide to detect
119 Hg^{2+} ions by differential square wave anodic stripping voltammetry. The synthesized nanoparticles were spherical
120 and uniformly distributed on the graphene sheet. The signal and analytical performance were compared with and
121 without the nanoparticles, and it was shown that the presence of nanoparticles enhanced the signal significantly
122 (figure 2). A linear concentration range was obtained between 0.1 and $1.8 \mu\text{M}$, the limit of detection was calculated
123 to be $0.11 \mu\text{M}$ and the sensitivity was $8 \mu\text{A}/\mu\text{M}$. Moreover, no interferences were detected from Cd (II) and Cu (II)
124 [23].

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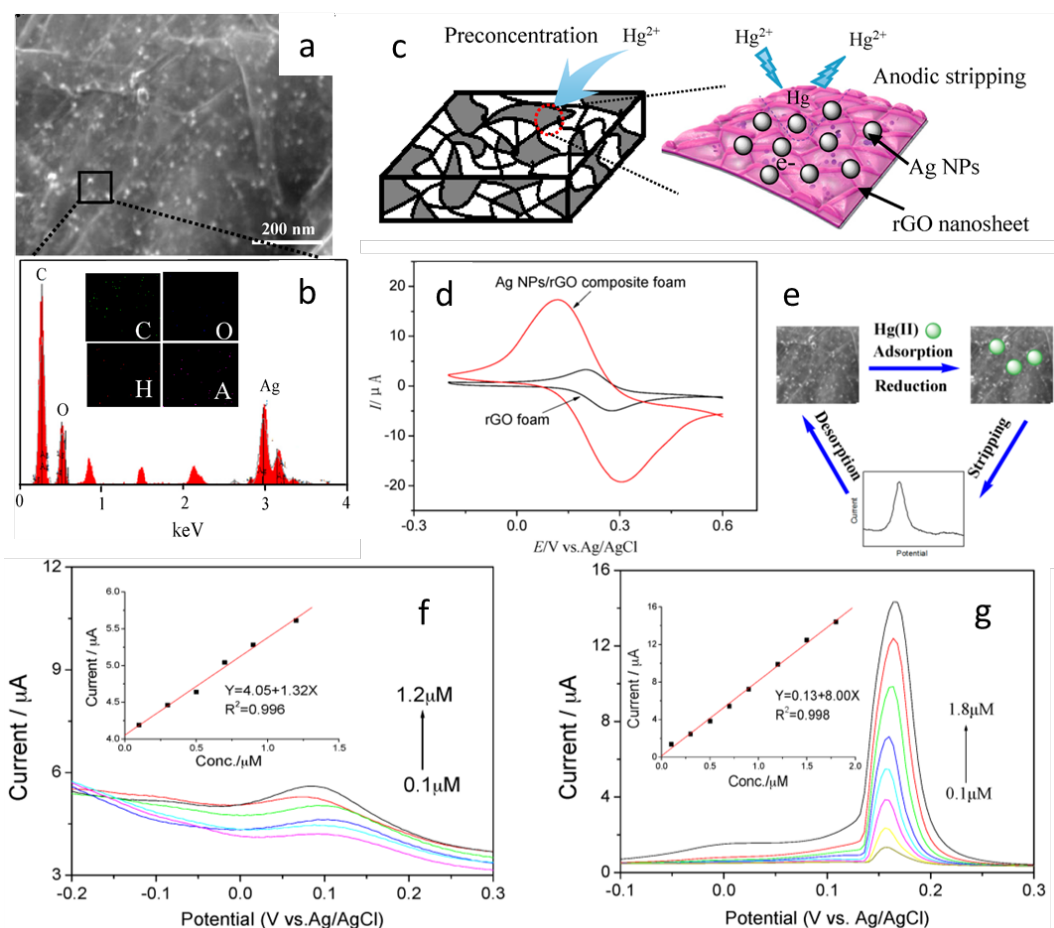
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125 Xing et al. modified a glassy carbon electrode with Nafion and electrodeposited silver nanoparticles on its
126 surface for the direct detection of Cr (VI) using linear sweep voltammetry. A linear range was obtained between 2
127 and 230 ppb and the limit of detection was 0.67 ppb with no interference from different ions. The applicability of this
128 sensor was studied using wastewater from a textile factory and the concentration of Cr (VI) was found to be $6.58 \pm$
129 $0.04 \mu\text{g}/\text{L}$ with a recovery of $99 \pm 5\%$ for spiked samples [24]. Renedo et al. also conducted a study using silver
130 nanoparticles modified screen printed electrodes for the detection of Sb by anodic stripping voltammetry. Differential
131 pulse anodic stripping voltammetry was used and the linear concentration range was between 9.9×10^{-8} M and
132 9.09×10^{-7} M, whereas the LOD in case of silver nanoparticles was 6.79×10^{-10} M. Three different seawater samples
133 were analyzed, and the amount of Sb (III) in all cases was below the detection limit and hence was not detected
134 [25].



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 137 Figure 2: (a) Scanning electron microscopy (SEM) image and (b) energy dispersive spectroscopy (EDS) spectrum
 138 with elemental mapping of Ag NPs/reduced graphene oxide. (c) Schematic diagram of the Ag NPs/reduced
 139 graphene oxide structure. (d) Cyclic voltammetry of pure reduced graphene oxide and Ag NPs/reduced graphene
 140 oxide. (e) Schematic representation of the electrochemical detection towards Hg (II) ions. (f) and (g) SWASV
 141 response of pure reduced graphene oxide and Ag NPs/reduced graphene oxide towards Hg (II) at different
 142 concentrations in a 0.1 M NH₃ solution; the insets correspond to the calibration plots, respectively [23].
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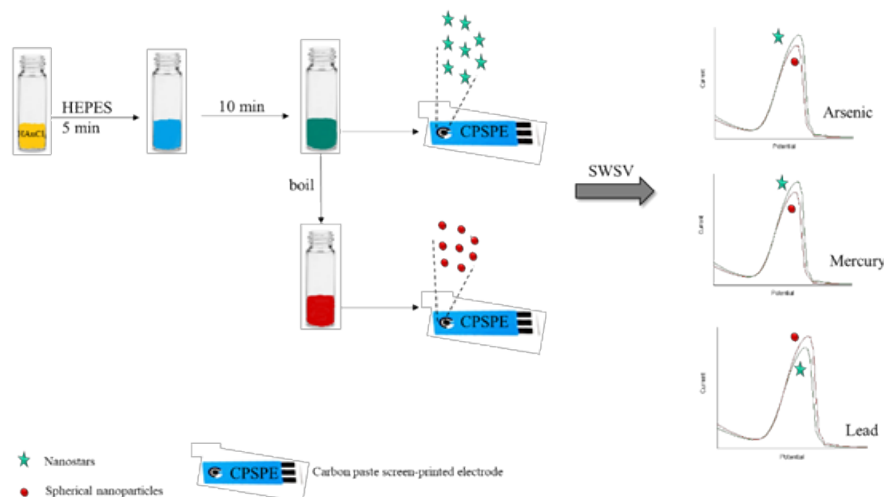
144 3.2. Gold Nanoparticles

145 The most used nanoparticles for the electrochemical detection of heavy metals are gold nanoparticles (Au
 146 NPs). Their properties vary depending on their size, but whatever the size, gold nanoparticles are known to be
 147 biocompatible and of low toxicity [26]. Table 2 summarizes the different voltammetric studies done to detect heavy
 148 metals using gold nanoparticles. Only a few reports focus on the use of gold nanoparticles alone; nonetheless,
 149 different materials have been associated with gold nanoparticles for the detection of heavy metals, and especially
 150 mercury and lead.

151 Similar to Ag NPs, the most common methods utilized for the synthesis of Au NPs are either
 152 electrodeposition or reduction. However, different synthesis conditions lead to different shapes and sizes of the gold
 153 nanoparticles. The most common shape used in the electrochemical detection of heavy metals is spherical. Most
 154 groups have successfully synthesized spherical Au NPs of sizes ranging between 4 and 298 nm. Hassan et al.
 155 reported the synthesis and use of different gold nanostructures for the detection of As (III). The synthesis involved
 156 the reduction of chloroauric acid using ibuprofen in a basic medium. They investigated the effect of different heating
 157 times on the shape of the produced nanoparticles, and the results indicated that with increased heating time,
 158 nanoflowers formed along with other structures [27]. Ouyang et al. used a more complex method for the synthesis
 159 of nanoflowers. In brief, they modified a glassy carbon electrode with a layer of gold nanoparticles, followed by a
 160 layer of 3-mercaptopropyl-trimethoxysilane. Then, the electrode was immersed in a solution containing Au NPs to
 161 form a second layer of nanoparticles and pyridinium was attached to the NPs after dipping in 4-pyridineethanethiol
 162 hydrochloride solution [28]. Dutta et al. synthesized gold nanostars and spherical gold nanoparticles and compared
 163 their performances in the detection of As (III), Hg (II) and Pb (II). The nanostars were prepared by mixing an auric
 164 chloride solution with 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) without stirring or shaking.
 165 Boiling the resultant nanostars for 5 minutes yielded spherical nanoparticles. Using these 2 structures, they modified
 166 a screen-printed electrode and optimized some conditions to conclude that the gold nanostar shape improved the

167 detection of arsenic compared to the spherical shape (figure 3) [29]. Later on, different studies used the same
 168 procedure for the gold nanostars synthesis to detect Cr (II), Cd (II), As (III) and Se (IV) [30, 31].

169 It is worthy to note that the use of gold nanoparticles associated with different sensors is gaining wide
 170 recognition. Even though the inhibition of enzymatic activity by heavy metals has been extensively studied, only
 171 one study uses enzyme-based biosensors with gold nanoparticles to detect mercury ions. The presence of gold
 172 nanoparticles considerably increased the analytical response [32]. Some researchers focus on the use of gold
 173 nanoparticles with amino acid- based biosensors. Amino acids and peptides (amino acid chains) have a high affinity
 174 towards some heavy metals which can be tuned by altering the peptide sequence [33]. Amino acids are known to
 175 bind heavy metal ions through cooperative metal-ligand interactions [34]. The use of gold nanoparticles with these
 176 biosensors amplifies the signal, improving the analytical performance [35]. The majority of authors focus on DNA-
 177 based biosensors with an emphasis on certain interactions between the DNA bases and certain heavy metal ions.
 178 Specifically, silver ion and mercury ion are well known to interact with cytosine-cytosine mismatch and thymine-
 179 thymine mismatch, respectively, to form stable base pairs [36 – 40].



180

181 Figure 3: Modification of carbon paste screen-printed electrodes by Au NPs for the detection of As³⁺,
 182 Hg²⁺ and Pb²⁺ [29].

183 Table 2: Comparison between the different studies using gold nanoparticles for heavy metal detection.

| HM | Technique | Electrode | LOD (μM) | Sensitivity (μA/μM) | Linear range (μM) | Addition to Au NPs | Real sample | Ref |
|------------------|-----------|----------------------|-----------------------|---------------------|---------------------------------|-------------------------------------|-----------------|-----|
| Ag ⁺ | DPV | Au | 3×10 ⁻⁵ | 124.6 | 10 ⁻⁴ – 0.12 | Oligonucleotide sequences | | 36 |
| As ³⁺ | SWV | GCE | 10 ⁻³ | 71.7 | | | River water | 41 |
| | SWV | GCE | 8.89×10 ⁻⁴ | 1985 | | Multiwalled Carbon nanotubes | | 42 |
| | ASV | CμF | 67.43 | 1318 | 0.067 – 0.8 | | Tap, well water | 43 |
| | SWASV | GNEE | 1.78×10 ⁻⁴ | 0.7492 | 0 – 0.2 | 3-(mercaptopropyl)trimethoxy silane | | 44 |
| | SWASV | SPE | 6.53×10 ⁻³ | | | | River water | 31 |
| | SWASV | GCE | 1.06×10 ⁻³ | 113.9 | 0.01 – 0.67 | | | 45 |
| | SWASV | SPE | 0.01 | | 0.03 – 10.2 | | Ground water | 29 |
| | LSV | GCE | 0.024 | | 0 – 1.2 | | | 47 |
| | LSV | GCE | 5.34×10 ⁻³ | 32.8 | | Multiwalled Carbon nanotubes | | 42 |
| | LSV | GCE | 2×10 ⁻³ | 14.2 | | | River water | 41 |
| LSASV | GCME | 0.01 | | 0.01 – 10.01 | Carbon nanotube | | 48 | |
| LSASV | GCE | 3.7×10 ⁻³ | 940 | 0.005 – 3 | Pt NPs | Tap, spring, river water | 49 | |
| LSASV | GCE | 2.9×10 ⁻³ | 230 | 0.005 – 1 | Porous graphitic carbon nitride | Tap, spring, river water | 50 | |
| DPV | GCE | 0.2 | 0.8075 | 4 – 40 | Crystal violet | Drinking water | 51 | |

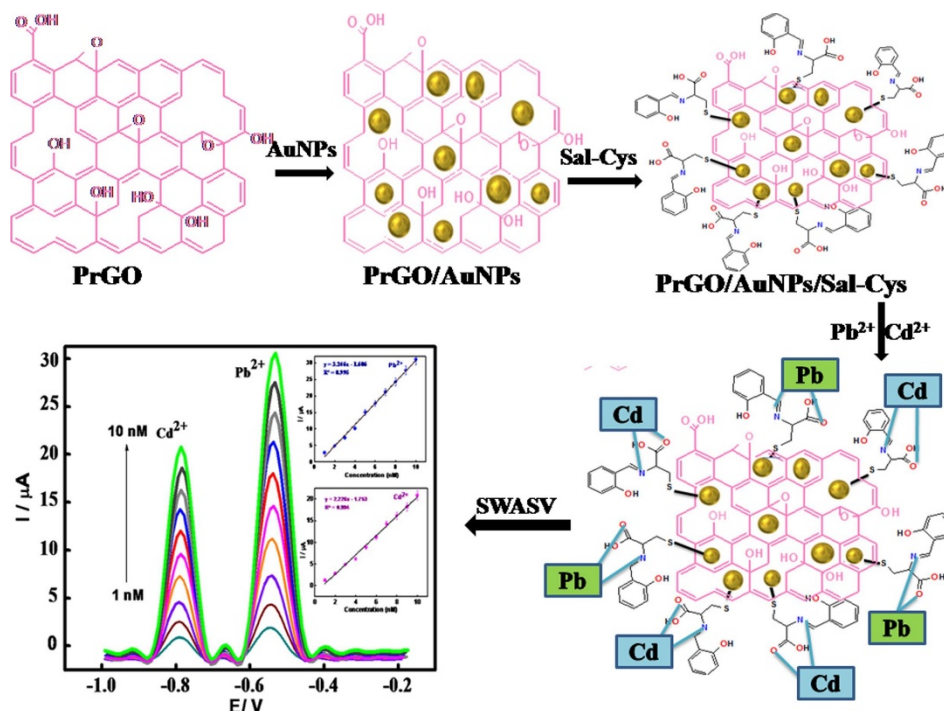
| | | | | | | | | |
|------------------------|-------|--------------------------------|-----------------------|--------------------------|--|---|------------------------------------|----|
| | DPSV | SPCE | 8.01×10^{-4} | | Up to 53.4 | Poly(L-lactide) | Ground, surface water | 52 |
| | CV | Basal-plane pyrolytic graphite | 0.8 | | | Glassy carbon microsphere | | 53 |
| | CV | SPCE | 2.4×10^{-4} | | $1.3 \times 10^{-3} - 24$ | Ibuprofen | Drinking, tap, river, ground water | 27 |
| Cd²⁺ | DPV | SPCE | 0.023 | 26.19 | 0.07 – 4448 | | River, tap water | 54 |
| | DPV | GCE | 0.022 | | 0.05 – 300 | Reduced graphene oxide, Tetraphenylporphyrin | Lake water | 55 |
| | DPASV | GCE | 0.3 | 3.24 | 0 – 1.4 | | | 56 |
| | SWV | GCE | 8.89×10^{-4} | | $4.4 \times 10^{-3} - 0.35$ | Graphene, cysteine | Spring water | 35 |
| | SWASV | GCE | 0.1 | 1.88 | 0.1 – 1 | Carbon nanofibers | | 57 |
| | SWASV | SPE | 0.015 | | | | River water | 31 |
| | SWASV | GCE | 6×10^{-5} | 2.2×10^3 | $10^{-3} - 0.01$ | L-cysteine, reduced graphene oxide | Lake, tap, sewage, ground water | 58 |
| Cr³⁺ | SWV | GCE | | | 100 – 400 | | | 59 |
| Cr⁶⁺ | SWV | SPE | 0.096 | | 0.19 – 96 | | River water | 60 |
| | SWV | GCE | 1.92×10^{-4} | 5.98 | $2.5 \times 10^{-3} - 0.86$ | | Sewage, tap water | 61 |
| | SWCSV | GCE | 5.58×10^{-5} | | $1.9 \times 10^{-4} - 23$ | 3-mercaptopropyl-trimethoxysilane | | 28 |
| | AdSV | Graphene | 0.02 | 1.94×10^{-4} | 0.48 – 5.77 | Reduced graphene oxide, 4-pyridylethylmercaptan hydrochloride | Waste water | 73 |
| | DPV | SPCE | 0.4 | 2.01×10^{-8} | 0.4 – 30 | | Tap, sea water | 74 |
| | CV | Indium tin oxide | 2 | 0.3025 | 5 – 100 | | Tap, sea, stream water | 75 |
| | LSV | SPE | 0.067 | | 0.19 - 1442 | | Ground water | 30 |
| Cu²⁺ | LSV | SPCE | 0.1 | 0.0572 | 0.38 – 3.8 | | River water | 76 |
| | DPV | SPCE | 0.126 | | 0.79 – 157 | L-cysteine | | 33 |
| | DPASV | GCE | 0.3 | 4.18 | 0 – 1.4 | | | 56 |
| | ASV | GCE | 5×10^{-5} | 3690 | Logarithmic | Graphene quantum dots, cysteamine | | 68 |
| | SWV | Au | 10^{-7} | 0.29435×10^{-6} | $10^{-4} - 10$ | 4-aminothiophenol, DNAzymes | Lake, tap water | 37 |
| | SWASV | SPE | 0.025 | 4.368 | 0.31 – 4.72 | | | 70 |
| | SWASV | GNEE | 2.22×10^{-3} | | $6.67 \times 10^{-3} - 0.2$ | 3-(mercaptopropyl)trimethoxy silane | | 44 |
| Hg²⁺ | SWASV | GCE | 0.1 | 4.41 | 0.1 – 1 | Carbon nanofibers | | 57 |
| | SWASV | GNEE | 9.97×10^{-5} | 2.006 | 0 – 0.07 | 3-(mercaptopropyl)trimethoxy silane | | 44 |
| | SWASV | SPE | 2.49×10^{-3} | | $7.5 \times 10^{-3} - 2.69$ | | Ground water | 29 |
| | SWASV | GCE | 2.99×10^{-5} | 708.3 7.37 | $3.99 \times 10^{-5} - 2.49 \times 10^{-4}$ $4.98 \times 10^{-4} - 0.3$ | Chitosan graphene | River water | 77 |
| | SWASV | SPCE | 3.99×10^{-3} | | $2.49 \times 10^{-5} - 10^{-4}$ | | Rain, river water | 78 |
| | SWASV | GCE | 4.2×10^{-4} | 1370 | $0.64 \times 10^{-3} - 4 \times 10^{-3}$ | | | 79 |

| | | | | | | | | |
|------------------------|-------|---------------------|-----------------------|-------------------|---|---|---------------------------------|----|
| | SWASV | Pencil graphite | 4×10^{-15} | | $10^{-13} - 10^{-4}$ | DNA, L-methionine | Sea water, fish | 80 |
| | SWV | Au | 5×10^{-4} | | 0.09-1.99 | MSO, linker probes | | 81 |
| | SWV | Carbon ionic liquid | 2.3×10^{-3} | | 0.01 – 20 | Thiolated amino acids | Waste, tap water | 34 |
| | SWV | SPE | 9.97×10^{-4} | 47.54 | $2.5 \times 10^{-3} - 0.25$ | Carbon nanotubes | Tap, river water | 71 |
| | DPV | GCE | 3×10^{-5} | 35.88 | $10^{-4} - 0.02$ | Multi-walled C nanotubes, DNA | Tap, lake water | 39 |
| | DPV | GCE | 7.48×10^{-6} | 1603.6 | $4.98 \times 10^{-5} - 4.98 \times 10^{-3}$ | Reduced graphene oxide, thymine-1-acetic acid, cysteamine | Tap water | 62 |
| | DPV | Au | 5×10^{-4} | | $10^{-3} - 0.1$ | DNA, methylene blue | Tap, river water | 38 |
| | DPV | Indium tin oxide | 7.8×10^{-4} | | $5 \times 10^{-3} - 0.11$ | Graphene oxide, 5-methyl-2-thiouracil | Tap, lake, bottled water | 63 |
| | DPV | Au | 7.38×10^{-6} | 333 | $5 \times 10^{-5} - 2.5 \times 10^{-3}$ | Thiolated probe DNA | Tap water | 40 |
| | DPASV | GCE | 8×10^{-5} | 749 | $4 \times 10^{-4} - 0.096$ | Single walled C nanotubes, poly(2-mercaptobenzothiazole) | River, tap water | 65 |
| | DPASV | GCE | 0.3 | 3.39 | 0 – 1.4 | | | 56 |
| | DPASV | GCE | 10^{-4} | 0.09 | $5 \times 10^{-4} - 1.25$ | Carbon nanotubes | | 82 |
| | DPASV | Indium tin oxide | 1.49×10^{-4} | | $4.98 \times 10^{-4} - 0.05$ | | Tap, lake water, milk, soil | 66 |
| | ASV | GCE | 0.16 | | 0.79 – 3.15 | | River water | 77 |
| | ASV | GCE | 7.48×10^{-7} | | Up to 0.25 | | Drinking water | 67 |
| | ASV | GCE | 2×10^{-5} | 2470 | $2 \times 10^{-5} - 0.1$ | Graphene quantum dots, cysteamine | | 68 |
| | CV | Au | 0.01 | | | MSO, ss-DNA | | 69 |
| Pb²⁺ | SWASV | GCE | 4×10^{-5} | 3.2×10^3 | $10^{-3} - 0.01$ | L-cysteine, reduced graphene oxide | Lake, tap, sewage, ground water | 58 |
| | SWASV | SPE | 0.02 | | 0.06 – 1.56 | | Ground water | 29 |
| | SWASV | SPE | 0.0106 | 31.91 | 0.096 – 0.96 | | | 70 |
| | SWASV | GCE | 0.1 | 19.08 | 0.1 – 1 | Carbon nanofibers | | 57 |
| | SWV | SPE | 4.34×10^{-4} | 17.612 | 0.01 – 1.2 | | Tap, river water | 71 |
| | SWV | GCE | 2.4×10^{-4} | | $2.41 \times 10^{-3} - 0.19$ | Graphene, cysteine | Spring water | 72 |
| | SWV | GCE | 800 | 455.83 | 0.01 – 0.15 | Graphene oxide | Tap water | 83 |
| | CV | Au | 2.8×10^{-5} | | | DNA | | 32 |
| | DPASV | GCE | 0.3 | 17.63 | 0 – 1.4 | | | 56 |
| | DPASV | GCE | 4.83×10^{-5} | 24.86 | $2.41 \times 10^{-3} - 0.48$ | Graphene oxide, chitosan | River water | 84 |
| | DPV | Au | 10^{-3} | | $5 \times 10^{-3} - 0.1$ | DNAzymes | | 64 |
| | DPV | GCE | 4.3×10^{-9} | | $10^{-8} - 5 \times 10^{-5}$ | Multi-walled carbon nanotubes, DNA | Tap, river, spring water | 85 |
| Sb³⁺ | DPASV | SPE | 9.44×10^{-4} | | $9.9 \times 10^{-2} - 0.909$ | | Sea water, drugs | 86 |
| Se⁴⁺ | SWASV | SPE | 0.01 | | | | River water | 31 |

184 Abbreviations: Au gold, GCE glassy carbon electrode, CuF carbon ultra-microfiber, GNEE gold nanoelectrode
185 ensembles, SPE screen printed electrode, GCME carbon nanotube flow-through membrane electrode, SPCE
186 screen printed carbon electrode.

187 From the above table, it can be concluded that the best analytical performance for the detection of As (III)
188 is obtained using gold nanoparticles modified carbon nanotubes [42]. The process of electrode modification and
189 arsenic detection using square wave voltammetry can be achieved within minutes producing a very high sensitivity
190 and low LOD compared to similar studies. Although the authors claim that this sensor can be used for the detection
191 of arsenic in natural waters, to the best of our knowledge, the study has not been conducted. The modification of a
192 glassy carbon electrode with gold nanoparticles, L-cysteine and reduced graphene oxide showed a superior

193 performance in the detection of Cd (II) by square wave voltammetry (figure 4). The modified electrode was used to
 194 assess the concentrations of cadmium in different water sources (lake, sewage, tap and ground water) and the
 195 obtained results were comparable with those of AAS [58]. The same electrode exhibited the highest reported
 196 sensitivity for the detection of Pb (II) as well; however, a better LOD was obtained by Zhu et al. [85] using differential
 197 pulse voltammetry. The latter team modified a glassy carbon electrode with gold nanoparticles, cysteine, graphene
 198 and bismuth film which exhibited a low LOD and good repeatability and reproducibility along with the possible usage
 199 in real water samples such as spring water. However, the preparation procedure was too complex compared with
 200 other studies. The modification of a GCE with graphene quantum dots and Au NPs is the method of choice for the
 201 detection of Cu (II) using anodic stripping voltammetry. Both the LOD and sensitivity are better than those obtained
 202 with different modifications, unfortunately the electrode was not tested with real samples [68]. This same electrode
 203 showed the highest sensitivity for the detection of Hg (II), while an outstanding LOD was obtained by Hasanjani et
 204 al. [80] who used DNA and L-methionine along with Au NPs for the modification of a pencil graphite electrode.
 205 Interestingly, for the detection of Cr (VI), the sensitivities are either not reported, or are very small, with the best
 206 limit of detection obtained by Ouyang et al. [28] who modified a glassy carbon electrode with Au NPs and 3-
 207 mercaptopropyltrimethoxysilane. It should be noted that the focus of most of the papers using gold nanoparticles
 208 was on the synthesis of the nanoparticles and not on testing the applicability of the sensor in real samples. However,
 209 it was implied in some of the studies that their fabricated sensors can be used in real samples.



210
 211 Figure 4: Schematic diagram of the possible interactions of Cd (II) and Pb (II) with gold nanoparticles, L-cysteine
 212 and reduced graphene oxide modified GCE electrode leading to the simultaneous analysis of the heavy metals [58].
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214 3.3. Bismuth Nanoparticles

215 The use of bismuth in different areas of chemistry (catalysis, organic synthesis, clusters...) has grown in
 216 the past decade. In electroanalytical chemistry, bismuth is used as an electrode coating, replacing the mercury
 217 electrode, because of its low toxicity and excellent peak resolution.

218 Lee et al. used bismuth nanopowder modified electrode to detect Zn, Cd and Pb ions using square wave
 219 anodic stripping voltammetry. Spherical bismuth was prepared with different particle size distribution in order to
 220 investigate its effect on the sensitivity and limit of detection of the studied metals. It was concluded that as the
 221 particle size decreases from 406 to 166 nm, both the sensitivity and the limit of detection are improved [87]. In
 222 another work, the same group modified a thick-film graphite electrode with bismuth nanopowder for the detection
 223 of thallium (Tl). Applying the same procedure, a limit of detection of 0.03 μg/L was obtained with the possibility to
 224 overcome any interference from divalent ions through the addition of EDTA [88]. Rico et al. [89] adopted the method
 225 of Lee et al. [87], to modify a screen-printed carbon electrode and detect the heavy metals. Optimization of the
 226 method included the accumulation configuration; both convective and flow configurations were tested. The limits of
 227 detection that were obtained at the flow cell for Zn (II), Cd (II) and Pb (II) were better than those at the convective
 228 cell. Those limits were 2.6, 1.3 and 0.9 ng/mL, respectively. Moreover, the reproducibility and sensitivity of the
 229 method were good after analyzing a certified reference sample and tap water, but further tests showed that high
 230 concentrations of Cu (II) interfered with the results. Saturno et al. modified a glassy carbon electrode with micro-
 231 nanoparticles/bismuth film for the determination of cadmium and lead by differential pulse voltammetry. The shape

232 and size of the nanoparticles were irregular, but they still obtained LODs of 11 µg/L for Cd (II) and 18 µg/L for Pb
233 (II) with the response being highly reproducible [90]. Sahoo et al. modified a carbon paste electrode with graphene
234 oxide and bismuth nanoparticles of diameter between 40 and 100 nm for the determination of zinc, cadmium, lead
235 and copper ions using differential pulse anodic stripping voltammetry. A linear concentration range was obtained
236 from 20 to 120 µg/L with limits of detection of 2.8, 0.55, 17 and 26 µg/L for Cd²⁺, Pb²⁺, Zn²⁺ and Cu²⁺, respectively.
237 The performance of the electrode was tested in two different water samples, ground and lake water, and the
238 concentrations of the divalent metals were determined [91]. The obtained LODs were comparable in the different
239 studies for lead and cadmium ions. However, the problem of Cu (II) interference was faced in more than one study.
240

241 3.4. Platinum Nanoparticles

242 Platinum metal has received a lot of attention in the catalysis industry. Platinum nanoparticles (Pt NPs)
243 have also found a lot of applications in electrochemical analyses due to their stability and conductivity [92]. Hrapovic
244 et al. electrodeposited spherical platinum nanoparticles on a glassy carbon electrode and on a boron doped
245 diamond electrode for the detection of Arsenite (As (III)). The electrodeposition resulted in a non-homogenous and
246 non-uniform distribution of the Pt NPs. Using linear sweep voltammetry, the boron-doped electrode was proven to
247 have a superior performance with a limit of detection of 0.5 ppb without interference from copper (II) ions. Moreover,
248 the analysis of drinking water and river water from Montreal confirmed that As (III) concentrations can be determined
249 without any interference [93]. Spherical platinum nanoparticles of diameters between 105 and 180 nm were also
250 electrodeposited on a glassy carbon electrode by Dai et al. for the detection of Arsenic (III) ions. Cyclic voltammetry
251 was applied and the measured limit of detection was 35 ppb. The performance of this electrode was compared
252 using different techniques (square wave voltammetry and differential pulse voltammetry) all giving the same results.
253 Moreover, possible interfering ions were investigated and the results still showed a clear peak for arsenic [94]. Both
254 studies rely on the oxidation of As (III) to As (V) electrocatalyzed by Pt on a BDD electrode. Dai et al. obtained a
255 LOD that is higher than recommended guidelines for water. Moreover, even though Hrapovic et al. obtained a lower
256 LOD, the electrodeposited Pt NPs were not uniform in size.
257

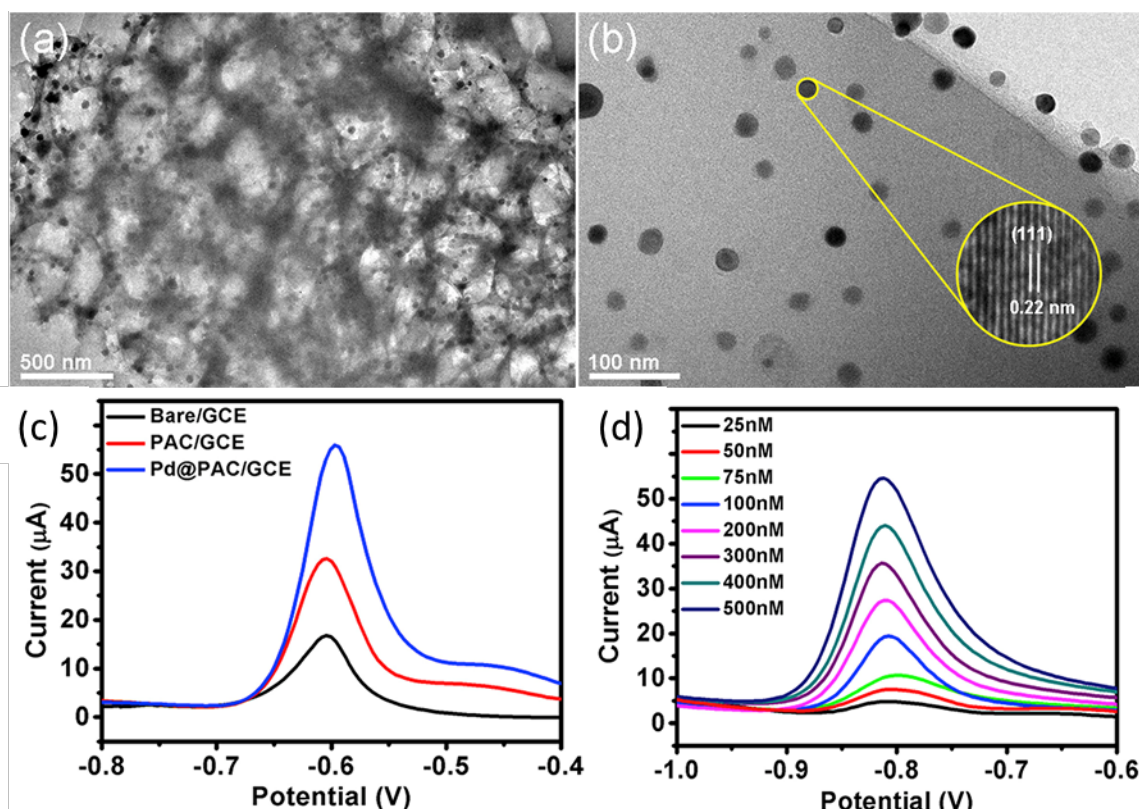
258 3.5. Other metal nanoparticles

259 Owing to the advantages of nanoparticles in the modification of electrodes in electrochemical analysis,
260 different metal nanoparticles have been used for the electrochemical detection of cadmium, copper, mercury and
261 lead.

262 Two groups have reported the use of palladium nanoparticles (Pd NPs) for the detection of heavy metals.
263 Both groups synthesized porous activated carbon (PAC), followed by the decoration of PAC with palladium
264 nanoparticles via a one-step thermal reduction method (with slightly different conditions). Spherical 20 – 30 nm Pd
265 NPs were used by Zhang et al. for the simultaneous and individual determination of Cd²⁺, Pb²⁺ and Cu²⁺ by applying
266 square wave anodic stripping voltammetry (figure 5). The obtained limits of detection for individual determinations
267 were 13.33, 6.6 and 11.92 nM for Cd²⁺, Pb²⁺ and Cu²⁺, while for simultaneous determinations the values were 20.9,
268 9.19 and 14.78 nM, respectively. The applicability of the sensor was successfully tested in practical water, without
269 specifying what this water is. [95]. Veerakumar et al. were able to obtain smaller crystals with an average size of 4
270 – 5 nm. They used differential pulse voltammetry for the detection of Cd²⁺, Pb²⁺, Cu²⁺ and Hg²⁺. Results showed
271 superior performance for both individual and simultaneous detections. For simultaneous detection of Cd²⁺, Pb²⁺,
272 Cu²⁺ and Hg²⁺, a linear response in the ion concentration ranges of 0.5 – 5.5, 0.5 – 8.9, 0.5 – 5.0 and 0.24 – 7.5
273 µM, with sensitivities of 66.7, 53.8, 41.1 and 50.3 µA µM⁻¹.cm⁻², and detection limits of 41, 50, 66 and 54 nM,
274 respectively, were observed [96].

275 Lee et al. have used tin nanoparticles (Sn NPs) with reduced graphene oxide on glassy carbon electrode
276 for the determination of Cd²⁺, Pb²⁺ and Cu²⁺. The Sn NPs of 50 nm diameter were synthesized using the
277 electrochemical reduction of Sn²⁺ with graphene oxide solution. Individual analysis of metal ions using square wave
278 anodic stripping voltammetry showed a high stability and detection limits of 0.63 nM, 0.60 nM and 0.52 nM,
279 respectively. However, simultaneous analysis of the heavy metal increased the detection limits to 7.56 nM, 6.77 nM
280 and 5.62 nM, respectively due to the possible formation of intermetallic compounds. The feasibility of the sensor
281 was tested in tap water samples with and without spiking. No peaks were observed before spiking, while recoveries
282 ranged between 97 and 102% after spiking [97].

283 Toghiani et al. modified a BDD electrode with Sb nanoparticles for the detection of Cd²⁺ and Pb²⁺ using linear
284 sweep anodic stripping voltammetry. The nanoparticles were electrochemically deposited on the electrode, with an
285 average size of 108 ± 70 nm, but due to the toxicity of Sb, the team tried to use the smallest possible concentration
286 of antimony. Based on this study, the addition of Sb nanoparticles didn't improve the individual detection of each
287 analyte as compared to the bare BDD. On the other hand, simultaneous detection of cadmium and lead was
288 improved and Pb did not inhibit Cd from nucleating on the electrode surface like previous works [98].



289
 290 Figure 5: (a) and (b) TEM and HR-TEM images of Pd@Pac. (c) SWASV curves for 500 nM each of Cd²⁺, Pb²⁺
 291 and Cu²⁺ on the bare, PAC-modified and Pd@PAC-modified GCEs in 0.1 M acetate buffer solution (pH 4.8).
 292 Conditions: deposition potential: 2.1 V; deposition time: 210 s; room temperature; amplitude: 50 mV; increment
 293 potential: 4 mV; and frequency: 15 Hz. (d) SWASV curves of the Pd@PAC/GCE for the individual analysis of Cd²⁺
 294 [95]. Reproduced with permission from Elsevier
 295

296 4. Metal oxide nanoparticles

297 Metal oxide nanoparticles are being extensively studied in electrochemical detection these past few years.
 298 They have been synthesized using different methods to obtain different sizes, stability, and morphology. These
 299 differences allow them to exhibit various electrical and photochemical properties resulting in different applications
 300 [99]. Various oxides of metals, mainly transition metals, have been used in the modification of electrodes for the
 301 detection of different analytes including heavy metals. Even though these oxides have been synthesized using
 302 almost all transition metals, only a few were used for the detection of heavy metals.

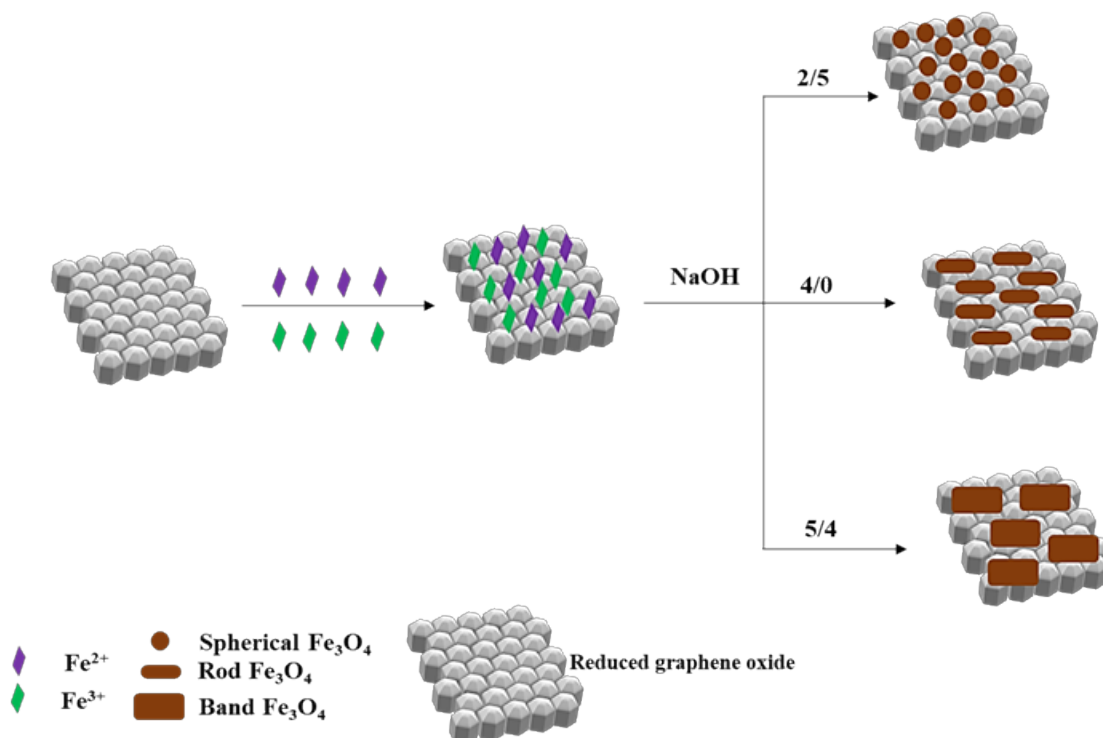
303 4.1. Iron oxide Nanoparticles

304 The most common metal oxide used for the detection of heavy metals is iron oxide in different forms
 305 (MnFe₂O₄, Fe₂O₃ and Fe₃O₄). While iron in the first 2 species is found as Fe³⁺, both Fe²⁺ and Fe³⁺ are present in
 306 Fe₃O₄, which permits an electron hopping process between the 2 ions, and thus increasing the electrical conductivity
 307 compared to MnFe₂O₄ and Fe₂O₃.

308 Lee et al. were the first group to report the use of iron oxide in the form of Fe₂O₃. Briefly, graphene oxide
 309 was prepared and reduced, after which Fe₂O₃/graphene composites were prepared using a solvent-less method by
 310 mixing iron (III) acetylacetonate and oleic acid with the prepared graphene. The synthesized spherical maghemite
 311 nanoparticles had an average size of 30 nm and uniformly decorated the graphene sheets. Prior to be used in the
 312 detection of Pb²⁺, Zn²⁺ and Cd²⁺ in tap water, the nanoparticles with graphene oxide were deposited on a cleaned
 313 glassy carbon electrode and dried under infrared heat lamp, and the electrode was modified with bismuth.
 314 Differential pulse anodic stripping voltammetry was applied and the analysis showed a linear range of detection
 315 between 1 and 100 μg.L⁻¹ for all the ions, and limits of detection of 0.11 μg.L⁻¹ for Zn (II), 0.08 μg.L⁻¹ for Cd (II) and
 316 0.07 μg.L⁻¹ for Pb (II) [100]. Li et al. later reported the synthesis of 2 different morphologies (nanorods and
 317 nanocubes) of Fe₂O₃ for the electroanalysis of Pb (II) by anodic stripping voltammetry. The limit of detection of Pb
 318 (II) by nanorods was much smaller (0.0034 μM) than that with nanocubes (0.083 μM). Moreover, Fe₂O₃ nanorods
 319 proved to be much more sensitive (109.67 μA.μM⁻¹) compared to nanocubes (17.68 μA.μM⁻¹). The practicability of
 320 the proposed sensor was evaluated in drinking water, and good recoveries were observed with a slightly decreased
 321 sensitivity for lead that could be the result of interfering ions [101].

322 On the other hand, Fe₃O₄ is the most common form of iron oxide used to detect heavy metals. Most
 323 recently, Fe₃O₄ nanoparticles have been investigated for heavy metal detection. Fe₃O₄ is known for having a high

324 affinity for heavy metal ions, but only a few reports that use iron oxide alone are available. This is due to the fact
 325 that iron oxide nanoparticles have the tendency to aggregate and become non-conductive units [102]. Most studies
 326 use either functionalized Fe₃O₄ or Fe₃O₄ combined with other materials. Table 3 summarizes the different studies
 327 done using Fe₃O₄ to detect heavy metals. Most of the magnetic nanoparticles used in heavy metal detection were
 328 spherical or quasi-spherical with sizes ranging between 5.8 nm and 200 nm. Sun et al. synthesized different Fe₃O₄
 329 shapes by varying the ratio of Fe²⁺ to Fe³⁺ ions. They used a one-step coprecipitation method with the following
 330 molar ratios of Fe²⁺/Fe³⁺: 2/5 to obtain spherical nanoparticles, 4/0 to get rod Fe₃O₄ (20 – 50 nm in width and 200
 331 – 300 nm in length) and 5/4 to obtain band Fe₃O₄ (80 – 120 nm in width and 300 – 400 nm in length) (Figure 6).
 332 Along with reduced graphene oxide, the iron oxide nanoparticles were used for the detection of Pb (II) and it was
 333 shown that the sensitivity is best with the band nanoparticles followed by spherical nanoparticles and then rod
 334 nanoparticles (the results are shown in decreasing order in Table 3). On the other hand, the limit of detection did
 335 not differ much between the three structures. Band NPs were also used for the detection of Cu (II) and Cd (II) [103].



336
 337 Figure 6: Synthesis of Fe₃O₄ nanoparticles, nanorods and nanobands done by Sun et al. [103]
 338

339 Table 3: Comparison between the different studies using Fe₃O₄ to detect heavy metals.

| HM | Technique | Electrode | LOD (μM) | Sensitivity (μA/μM) | Linear range (μM) | Addition to iron oxide NPs | Real sample | Ref |
|--|-----------|-----------|--|------------------------------------|---|--------------------------------|-----------------------------------|-----|
| Pb ²⁺ | SWV | GCE | 2.41×10 ⁻⁴ | | 0 – 0.24 | DMSA | Urine | 104 |
| Ag ⁺ Hg ²⁺ | SWV | GCE | 3.4×10 ⁻³ 1.7×10 ⁻³ | | 0.01 – 0.15 0.01 – 0.1 | Au NPs, DNA | Natural water, orange juice, wine | 105 |
| As ³⁺ | SWASV | GCE | 1.29×10 ⁻⁴ | 1015 | 1.33×10 ⁻³ – 0.27 | Au NPs | Natural water | 106 |
| Pb ²⁺ | SWASV | GCE | 0.15 | 10.07 | 0.5 – 8 | Amine | Waste water | 107 |
| Pb ²⁺ Cd ²⁺ | SWASV | GCE | 1.4×10 ⁻⁵ 9.2×10 ⁻⁵ | 235 196 | 5×10 ⁻³ – 0.6 0.02 – 0.59 | polydopamine | Aqueous effluent | 108 |
| Cd ²⁺ | SWASV | GCE | 0.056 | 14.82 | 0 – 0.8 | Reduced graphene oxide | | 109 |
| Pb ²⁺ | SWASV | GCE | 0.17 0.073 0.033 0.05 0.04 | 13.6 7.4 2.4 10.1 4.35 | 0.4 – 1.5 0.7 – 1.2 0.8 – 1.2 0.5 – 1.5 0.4 – 1.1 | Reduced graphene oxide | | 103 |
| Cu ²⁺ Cd ²⁺ Cd ²⁺ Cu ²⁺ | SWASV | CPE | 1.78×10 ⁻³ 0.014 | | | Macrocyclic Schiff-base ligand | Carrot, fish, rice, | 117 |

| | | | | | | | | |
|------------------------|-------|------|-----------------------|-------|------------------------------|--|------------------------------|-----|
| Hg²⁺ | | | 4.98×10^{-3} | | | | different waters | |
| Pb²⁺ | SWASV | GCE | 0.119 | 14.9 | 0.3 – 1.3 | | River water | 110 |
| Cd²⁺ | | | 0.154 | 3.18 | 0.3 – 1.3 | | | |
| Hg²⁺ | | | 0.0839 | 7.67 | 1.3 – 1.8 | | | |
| Cu²⁺ | | | 0.0765 | 4.73 | 0.3 – 1.7 | | | |
| Pb²⁺ | SWASV | GCE | 0.0422 | 50.6 | 0.1 – 1.3 | Chitosan | River water | 111 |
| Hg²⁺ | | | 0.0957 | 9.65 | 0.4 – 1.1 | | | |
| Cu²⁺ | | | 0.0967 | 4.24 | 0.3 – 1.2 | | | |
| Cd²⁺ | | | 0.0392 | 8.11 | 1.2 – 1.7 | | | |
| Cd²⁺ | SWASV | GCE | 0.2 | 12.15 | 0.4 – 1.1 | Terephthalic acid | River water | 102 |
| Pb²⁺ | | | 0.04 | 8.56 | 0.4 – 1.1 | | | |
| Hg²⁺ | | | 0.3 | 13.81 | 0.4 – 1.1 | | | |
| Cd²⁺ | SWASV | GCE | 1.52×10^{-3} | 8.4 | $4.4 \times 10^{-3} - 0.89$ | Glutathione | Natural water | 112 |
| Pb²⁺ | | | 8.78×10^{-4} | 27.37 | $2.41 \times 10^{-3} - 0.48$ | | | |
| Ni²⁺ | LSV | Pt | 3.5×10^{-3} | | $5 \times 10^{-2} - 1$ | Chitosan | Sewage water, urine | 113 |
| | | | | | 3 – 100 | | | |
| Cr⁶⁺ | LSV | SPCE | 0.01 | | 0.5 - 10 | Au NPs, Sephadex G-150 | Lake water | 114 |
| Ag⁺ | DPV | GCE | 0.059 | | 0.117 – 17.7 | Au NPs | Lake, tap, synthesized water | 115 |
| Cu²⁺ | DPV | GCE | 0.5×10^{-3} | | | Multi-walled carbon nanotubes, poly-3-nitroaniline | | 116 |

340 Abbreviations: CPE carbon paste electrode

341

342 Lead and cadmium are the most studied heavy metal ions with Fe₃O₄ NPs. The lowest LODs and highest
343 sensitivities for both ions were detected by Song et al. who coated the magnetic nanoparticles with polydopamine.
344 Additionally, the proposed method that uses SWASV was applied for the determination of lead in aqueous effluents
345 of a factory. The method proved to be successful and comparable with ICP-AES [108]. Moreover, it is worthy to
346 note that square wave voltammetry and glassy carbon electrodes are the most commonly used when working with
347 Fe₃O₄ NPs.

348 Recent studies have reported that the addition of another metal to iron oxide to produce spinel ferrites can
349 enhance its electrochemical behavior towards some heavy metals. All the groups relied on a solvothermal method
350 for the synthesis of MnFe₂O₄ along with surface modifications when applicable. The ferrite nanoparticles prepared
351 had a spherical morphology with sizes ranging between 200 and 400 nm.

352 In this regard, one group has done different studies on MnFe₂O₄ to detect different heavy metals. Zhou et
353 al. successfully synthesized MnFe₂O₄ nanocrystals and used them to modify a gold electrode and detect As (III)
354 using SWASV. A linear response was obtained at As concentrations between 10 and 100 ppb with a limit of
355 detection of 1.95 ppb and a sensitivity of 0.295 µA/ppb. The sensor was successfully applied in tap water for the
356 detection of arsenic in tap water with a recovery of 95.6% [118]. In another attempt to detect As (III), they modified
357 a glassy carbon electrode with MnFe₂O₄ and gold nanoparticles. Using SWASV, the electrode showed a sensitivity
358 of 0.315 µA/ppb and a LOD of 3.37 ppb with the sensor also being used to test tap water [119], proving that a similar
359 sensitivity and lower LOD for the detection of As (III) were obtained without modification with gold nanoparticles.
360 Then, the same group modified a glassy carbon electrode with these nanoparticles for the selective determination
361 of Pb²⁺. Using SWASV, a sensitivity of 19.9 µA.µM⁻¹ and LOD of 0.054 µM were obtained under optimized
362 conditions, while the response to Cd²⁺, Hg²⁺, Cu²⁺ and Zn²⁺ was poor. The modified electrode was successfully used
363 to detect a spiked lead concentration in river water [120].

364 In a later study, and in attempt to obtain a better analytical performance, Zhou et al. also used MnFe₂O₄
365 and graphene oxide to modify a glassy carbon electrode for the detection of Pb (II), Cd (II), Cu (II) and Hg (II). Using
366 square wave anodic stripping voltammetry, the best electrochemical response was obtained for Pb (II) with a
367 sensitivity of 33.9 mA/mM and a LOD of 0.0883 mM. The sensitivities for Cd (II), Cu (II) and Hg (II) were 13.5
368 mA/mM, 13 mA/mM and 5.79 mA/mM, respectively. Moreover, the limits of detection were calculated to be 0.778
369 mM, 0.0997 mM and 1.16 mM, respectively, with a successful application in the analysis of river water [121]. They
370 also tried modifying a glassy carbon electrode with L-cysteine functionalized MnFe₂O₄ to detect Pb (II), Hg (II), Cu
371 (II) and Cd (II) by SWASV. The developed sensor was particularly selective towards lead, with sensitivities of 57
372 µA/µM and 35.3 µA/µM and LODs of 0.0843 µM and 0.0607 µM under individual and simultaneous conditions of
373 detection. The sensor was also successfully used to monitor the concentration of lead in river water [122]. Thus, all
374 attempts to modify MnFe₂O₄ nanoparticles to detect different heavy metal ions have showed a higher selectivity and
375 preference for Pb (II). Moreover, although all studies have checked the practicability of the different modified
376 sensors in real water samples, more experimentation should be done in this regard by monitoring the ions in water
377 samples other than tap and river water.

378

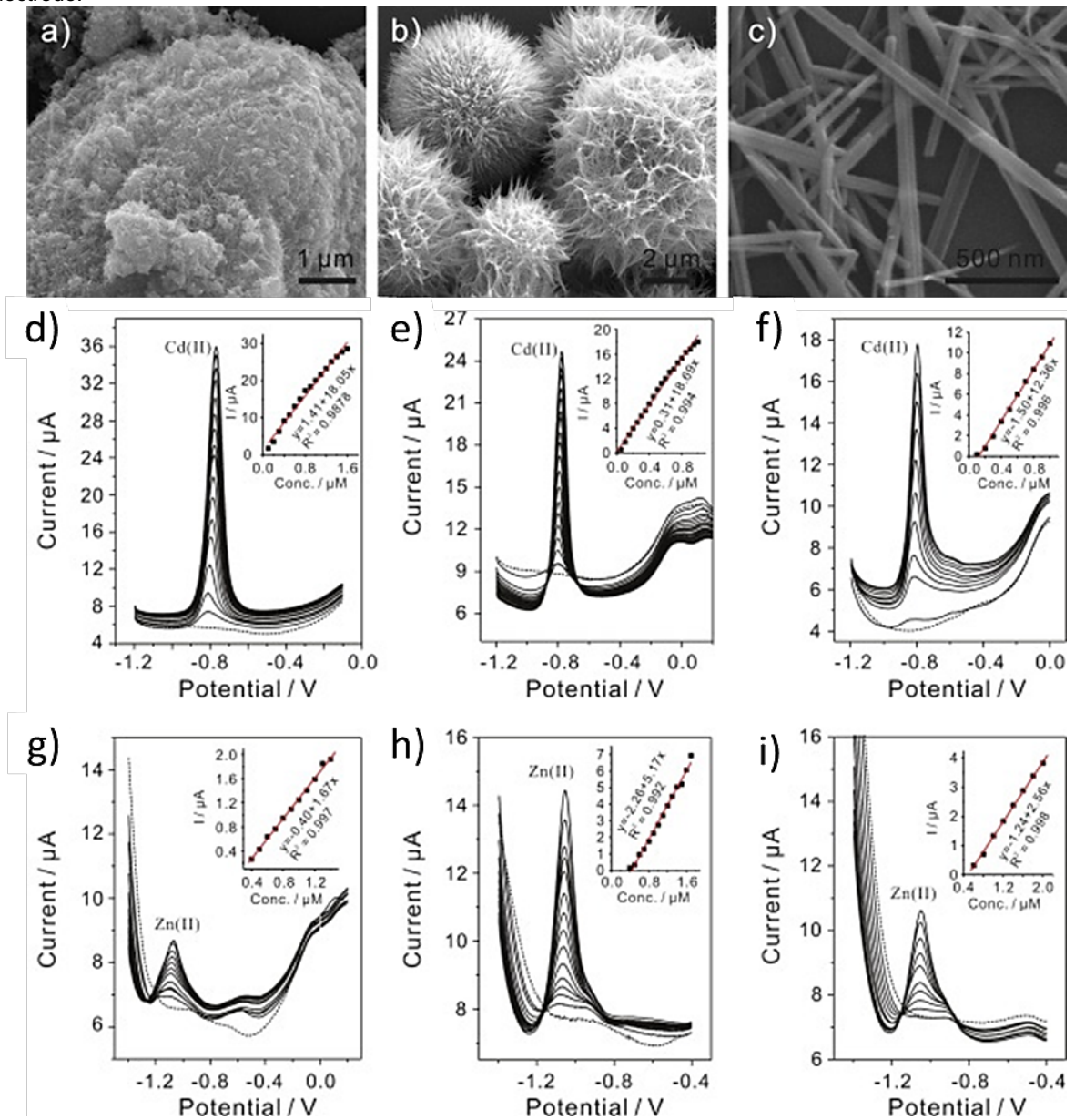
379 4.2. Other metal oxide nanoparticles

380 Co_3O_4 nanoparticles are one of the most versatile transition metal oxides mainly because of their high
381 reactivity, superior stability and excellent electrocatalytic activity. Salimi et al. electrodeposited cobalt oxide
382 nanoparticles on a glassy carbon electrode in order to detect Arsenic (III) using cyclic voltammetry. The
383 nanoparticles were small in size (100 nm) and uniformly distributed on the surface of the electrode. The results
384 exhibited a detection limit of 0.6 μM and no interferences in presence of other heavy metal ions with a linear range
385 of 10 – 50 μM . The possibility to use this sensor for the analysis of water samples was tested on drinking water
386 from a village in Kurdistan and a concentration of 2.1 μM of As was found in water and confirmed by atomic
387 absorption spectrometry [123].

388 On the other hand, titanium oxide nanoparticles have attracted attention due to their biocompatibility, high
389 conductivity, stability and low cost. TiO_2 nanoparticles were used to detect Hg (II) by Zhou et al. Titanium oxide
390 nanoparticles were prepared using sol-gel process. Briefly, tetrabutyl titanate was dissolved in ethanol and acetic
391 acid, after which water was added dropwise with vigorous stirring until a white transparent sol was formed. The sol
392 was transformed into a gel, dried and calcinated to obtain TiO_2 powder. The nanoparticles, along with gold
393 nanoparticles, were used to modify a gold electrode with the help of chitosan as a binder. Characterization showed
394 that TiO_2 nanoparticles had a size range between 5 and 15 nm, with gold nanoparticles on their surface. In a medium
395 buffered at a pH of 5 and using differential pulse anodic stripping voltammetry, the sensor showed a wide linear
396 concentration range of Hg (II) from 5 to 400 nM and a low detection limit of 1 nM with a sensitivity of 3.133 $\mu\text{A}\cdot\mu\text{M}^{-1}$
397 and no interference from different ions. Moreover, the sensor was tested for Hg (II) in some water samples, and
398 the recoveries were between 98 and 106% for all samples [124]. Zhang et al. used purchased titanium oxide
399 nanoparticle to modify a gold strip electrode to detect As (III) by linear sweep voltammetry. The linear range of
400 analysis was obtained between 10 $\mu\text{g/L}$ and 80 $\mu\text{g/L}$ with a limit of detection of 10 $\mu\text{g/L}$ and the possibility to use it
401 for arsenic determination in real samples. Moreover, the stability of the electrodes was investigated and 96% of the
402 initial response current was retained after 15 days [125]. Mao et al. incorporated TiO_2 nanoparticles into multiwalled
403 carbon nanotubes and a cationic surfactant to modify a glassy carbon electrode. LSASV was used for the
404 determination of mercury (II) and a linear range of 0.1 – 100 μM with a limit of detection of 0.025 μM were obtained.
405 The potential applicability of the sensor was evaluated in spiked and non-spiked samples of river and industrial
406 wastewater, and the sensor was able to successfully detect mercury in the wastewater even before spiking [126].
407 Ramezani et al. constructed an electrochemical sensor using spherical TiO_2 nanoparticles intermixed with graphite
408 powder and 1,2-bis-[o-aminophenyl thio] ethane. Using DPASV, and under optimum conditions, Cd (II) was
409 detected in a linear concentration range of 2.9 nM – 4.6 μM with a limit of detection of 2 nM. A spiked concentration
410 of Cd (II) ions in tap water was successfully detected without requiring any treatment of the water [127]. Liu et al
411 used an $\text{Fe}_3\text{O}_4\text{-TiO}_2$ core-shell nanoparticles on a glassy carbon electrode for the detection of Pb (II). Using square
412 wave voltammetry (SWV), the limit of detection of the proposed sensor was calculated to be 7.5×10^{-13} M with a
413 linear range of 4×10^{-13} M – 2.5×10^{-8} M. Different concentrations of Pb (II) were evaluated in river and rain water
414 samples with recoveries ranging between 99 and 110% [128]. Each one of these modifications with TiO_2 NPs
415 presents its advantages, from outstanding limit of detection of 7.5×10^{-13} M for Pb (II) [128] to the wide linear range
416 of detection of 2.9 nM – 4.6 μM for Cd (II) [127]; nevertheless, more experimentation is required in order to be able
417 to compare between the different methods.

418 Different forms of manganese oxide nanoparticles have been explored due to properties like low cost, non-
419 toxicity and high activity (mainly in alkali media). Zhang et al. focused on investigating the difference between
420 various MnO_2 structures, including nanoparticles, nanotubes and nanobowls on the mutual interference of Cd^{2+} ,
421 Pb^{2+} and Zn^{2+} (figure 7). The nanoparticles were prepared by dissolving potassium permanganate in ethanol,
422 washing the product with water and drying it. The nanotubes were prepared by dissolving $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and KMnO_4
423 in water, heating the mixture for 12 hours, washing the product with water and drying it. The nanobowls were
424 hydrothermally prepared by dissolving $\text{MnSO}_4\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in water, heating the mixture for 24 h, washing
425 the product with water and drying it. The group modified a glassy carbon electrode with MnO_2 and square wave
426 anodic stripping voltammetry was applied. The individual response was studied for Cd (II) and Zn (II) and the higher
427 sensitivities were observed with Cd (II) (18.05 $\mu\text{A}/\mu\text{M}$ for the nanoparticles, 12.36 $\mu\text{A}/\mu\text{M}$ for the nanotubes and
428 18.69 $\mu\text{A}/\mu\text{M}$ for the nanobowls). However, the interference mechanism was not clearly understood and
429 demonstrated. Upon fixing the concentration of Zn (II), the trend in the mutual interference between Cd (II) and Zn
430 (II) was similar on the three morphologies of MnO_2 . On the other hand, when fixing the Cd (II) concentration, the
431 interference between Cd (II) and Zn (II) on MnO_2 nanoparticles was different from that on the other structures.
432 Similarly, the interference between Cd (II) and Pb (II) on MnO_2 nanotubes was different from the other morphologies
433 [129]. Fayazi et al. used MnO_2 nanotubes for the detection of Hg (II) using differential pulse voltammetry. A simple
434 chemical precipitation followed by a hydrothermal method were used for the fabrication of halloysite nanotubes –
435 iron oxide – manganese oxide nanocomposite. The electrode displayed a limit of detection of 0.2 $\mu\text{g}\cdot\text{L}^{-1}$ in a linear
436 range of 0.5 – 150 $\mu\text{g}\cdot\text{L}^{-1}$. The proposed sensor was validated for mercury determination in well and aqueduct water
437 where the concentration of Hg (II) before spiking was below the detection limit and the recoveries after spiking were
438 close to 100%. [130]. Salimi et al. investigated the use of yet another form of manganese oxide nanoparticles:
439 nanoflakes. A glassy carbon electrode was first modified with chitosan and multiwalled carbon nanotubes followed
440 by the electrodeposition of manganese oxide. Using cyclic voltammetry, Cr (III) was detected in a linear range of

441 40 – 360 μM , and the electrode was used for the detection of chromium ions in drinking water samples such that
 442 the calculated Cr (III) concentration agreed with that measured by AAS [131]. All these studies were nicely
 443 elaborated, but at the same time each one of them still misses some important data on the analytical performance
 444 of each electrode.



445
 446 Figure 7: SEM images of (a) MnO_2 nanoparticles, (b) MnO_2 nanobowls and (c) MnO_2 nanotubes. SWASV responses
 447 of MnO_2 (d and g) nanoparticles, (e and h) nanobowls and (f and i) nanotubes modified electrode towards Cd (II)
 448 and Zn (II) at different concentrations in 0.1 M NaAc–HAc (pH 5.0), respectively. The insets are plots of current vs
 449 concentration of Cd (II) and Zn (II), respectively [129]. Reproduced with permission from Elsevier
 450

451 Wei et. al used tin oxide nanoparticles with reduced graphene oxide for the determination of Cd^{2+} , Pb^{2+} ,
 452 Cu^{2+} and Hg^{2+} by square wave anodic stripping voltammetry. SnO_2 nanoparticles are known to have a high electric
 453 conductivity and chemical sensitivity, along with the ability to adsorb heavy metal ions. The nanoparticles were
 454 prepared by a one-step wet chemical method after the preparation of reduced graphene oxide. This step involved
 455 mixing graphene oxide with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in water. After stirring and centrifuging, the product was heated to improve
 456 its crystallinity. The obtained nanoparticles were uniformly distributed on the graphene network, with an average
 457 diameter of 4 – 5 nm. Individual and simultaneous determination of these ions were done, and the limits of detection
 458 of the ions were 1.015×10^{-10} M, 1.839×10^{-10} M, 2.269×10^{-10} M and 2.789×10^{-10} M, respectively, with an enhanced
 459 sensitivity for Cu (II) and Hg (II) when analyzed simultaneously. The authors reported that even though the
 460 sensitivities and LODs are not the best, but the electrode can be used without needing regeneration [132]. Yang et
 461 al. synthesized an amino-based porous SnO_2 nanowires and modified a glassy carbon electrode for the detection
 462 of Cd (II) by means of SWASV. The sensor displayed a sensitivity of $124.03 \mu\text{A} \cdot \mu\text{M}^{-1}$ and a limit of detection of

0.0054 μM , with an effective determination of cadmium ions in water samples [133]. Cui and coworkers synthesized a 2-amino benzothiazole and 2-amino-4-thiazoleacetic acid derivative graphene enhanced with fluorine, chlorine and iodine on SnO_2 nanoparticles for the detection of Cu (II), Cd (II) and Hg (II). The nanoparticles were nearly spherical and well distributed on the graphene sheet. Using cyclic voltammetry, it was shown that the fluorine- SnO_2 sensor is the best suited for the detection of Cu (II), and thus differential pulse voltammetry was used. A linear range from 2 to 1000 nM and a LOD of 0.3 nM were obtained. The electrode was later used for the simultaneous detection of Cd (II), Cu (II) and Hg (II) such that all the linear ranges were between 20 and 2000 nM and the LODs were 5 nM, 3 nM and 5 nM, respectively, and hence the electrode was successfully evaluated for these ions in lake water, with results in agreement with those of AAS [134].

In addition to the general properties of nanoparticles, CeO_2 has a strong adsorption ability. Li et al. used a glassy carbon electrode modified with cerium oxide (CeO_2) nanoparticles, multi-wall carbon nanotubes, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4) and DNA to detect Pb (II). Differential pulse voltammetry was applied and the linear range for Pb (II) was between 10^{-8} and 10^{-5} M with the detection limit being 5×10^{-9} M hardly exhibiting any interference from five different metal ions with a practical application for the detection of lead in tap water [135].

Yukrid et al. used thermal pyrolysis for the synthesis of ZnO nanorods mixed with graphene solution through colloidal coagulation for the modification of a screen-printed carbon electrode. Anodic stripping voltammetry was used for the concurrent determination of Cd^{2+} and Pb^{2+} . The limits of detection obtained were $0.6 \mu\text{g.L}^{-1}$ for Cd (II) and $0.8 \mu\text{g.L}^{-1}$ for Pb (II) in a linear range of 10 – 200 $\mu\text{g.L}^{-1}$, respectively. These heavy metal ions were simultaneously determined in wastewater samples, with measurements in accordance with those obtained by ICP-OES [136]. Yuan-Yuan et al. prepared a ZnO nanotubes/reduced graphene modified glassy carbon electrode via electrospinning and thermal decomposition of zinc acetate-polyacrylonitrile-polyvinyl pyrrolidone. SWASV was used for the analysis of Pb (II). A linear concentration range of 2.4×10^{-9} – 4.8×10^{-7} M and the limit of detection was 4.8×10^{-10} M [137].

MgO nanoflowers were also used for the detection of Pb (II) and Cd (II). Their synthesis involved mixing a magnesium precursor with potassium carbonate and heating the mixture to obtain a white precipitate that was later collected and calcinated. These nanoflowers along with Nafion® were used to modify a glassy carbon macroelectrode and SWASV was used under optimized conditions. The results for Pb (II) and Cd (II) detection showed linear ranges between 1 and 30 nM for lead and between 20 and 140 nM for cadmium, sensitivities of 0.706 and $0.077 \mu\text{A.nM}^{-1}$ and limits of detection of 2.1×10^{-12} M and 8.1×10^{-11} M, respectively. The sensor was successfully tested for Pb (II) in Reservoir water samples from China [138].

5. Summary and Perspectives

Electrochemical methods have been extensively used for the detection of heavy metals. However, the use of metal and metal oxide nanoparticles for modifying electrochemical sensors, for the voltammetric detection of heavy metals, proves to be more promising. Taking advantage of the unique properties of nanoparticles along with the advantages of electrochemical detection over conventional detection techniques, the analytical performance of all the reported electrodes was enhanced. The result was a rapid response time, increased sensitivity, very low limits of detection, simplified operational procedures and enhanced reproducibility.

In this review, the emphasis was on electrochemical sensors that could be applied for water samples. However, different water systems exist, from sea water, river water, tap water, drinking water to wastewater. Thus, these matrices are considered complex, some more than others, with the presence of different heavy metals either free or complexed, cations and anions, organic and inorganic materials... Despite the claims that some of the fabricated sensors were tested in these complex matrices, transition to commercialization remains shy. Moreover, most of these sensors require significant improvements, especially in the selectivity and capability of simultaneous analysis, before they can be applied for commercial use. Besides, commercialization also presents the challenges of reusability and mass production, which question the simplicity and cost-effectiveness of some of the sensors. For example, great focus has been given to gold nanoparticles and some excellent electrochemical sensors have been developed for the detection of heavy metals with LODs much lower than those obtained with Fe_3O_4 NPs for instance. Nonetheless, noble metals such as gold and silver are known to be costly, and hence an alternative that presents high selectivity and can detect limits lower than the guidelines such as Fe_3O_4 NPs would be convenient. On the other hand, several materials were used along with the nanoparticles for the modification of the electrodes. However, with the use of all these nanoparticles, a few inconveniences, including toxicity and non-biocompatibility during the synthesis of the modified electrodes, still exist.

Recently, bimetallic nanoparticles are emerging as promising candidates that can overcome the challenges faced by mono-metallic nanoparticles. These materials are the result of combining two different metals, thus offering the advantages of each metal alone, along with new characteristics that arise from blending the two metals. Hence, we expect to see in the near future a major increase in research using bimetallic nanoparticles dedicated for the electrochemical detection of heavy metal ions.

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526

527 **Declaration of interests:**

528

529 The authors declare that they have no known competing financial interests or personal relationships that could
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