Research article

Electrochemical sensor based on gum Arabic nanoparticles for rapid and in-situ detection of different heavy metals in real samples

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ABSTRACT

The key solution to combat trace metal pollution and keep the environment, ecosystem, animals, and humans safe is earlier and rapid trace metal detection. For all these reasons, we propose in this work the design of a simple electrochemical sensor functionalized with green nanoparticles for electrochemical detection of the fourth most dangerous heavy metal ions namely copper, zinc, lead, and mercury. The green nanoparticles are fabricated by a one-step, consisting of reducing platinum nanoparticles by a natural gum Arabic polymer. To guarantee the success of these nanoparticles' design, the nanoparticles have been characterized by Fourier-transform infrared spectroscopy FTIR, and thermogravimetric TGA techniques. While, for the electrochemical characterization, we have adopted cyclic voltammetry CV and electrochemical impedance spectroscopy EIS to control different steps of surface modification, and the differential pulse anodic stripping DPAS was monitored to follow up the electrochemical detection of different heavy metals.

Results: have confirmed the good chemical and physical properties of the elaborated nanoparticles. As, the developed sensor showed a specific electrochemical response toward the heavy metal ions separately, with a lower limit of detection lower LOD than that recommended by the World Health Organization, in order of 9.6 ppb for Cu^{2+}, 1.9 ppb for Zn^{2+}, 0.9 ppb for Hg^{2+}, and 4.2 ppb for Pb^{2+}. Impressively, the elaborated sensor has demonstrated also high stability, outstanding sensitivity, and excellent analytical performance.

In addition, the elaborated analytical tool has been successfully applied to the determination of various heavy metal ions in real samples, reflecting then its promising prospect in practical application.

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1. Introduction

Heavy metal pollution has become one of the most worrisome threats to the safety of the environment, ecosystems, and public health [1,2]. The primary cause of the accelerated distribution of metals in the environment is increased industrialization and urbanization [3]. Metal processing, smelting, oil and gas, road traffic, and landfills have all contributed to the deterioration of the environment [4]. The dangers of these metals are related, in fact, to their persistence in the environment and then to their bioaccumulation in different parts of the ecosystem [5]. These toxic element has been identified in the atmosphere, the marine environment, groundwater, and the soil while damaging drinking water sources [6,7]. According to the World Health Organization WHO, globally, at least 2 billion people use a drinking water source contaminated with heavy metals [8]. In addition, heavy metals have achieved an important concentration in foods, facilitating, therefore, their penetration into the human organism. More dangerous, exposure in the long term to heavy metals can cause chronic poisoning, growth and developmental abnormalities, encephalopathy, nephrotoxicity, cardiovascular diseases, diarrhea, cholera, dysentery, typhoid, and cancer [9]. For example, Hg toxicity has been associated with nervous system damage in adults and neurodevelopmental disorders in infants and children [10]. While poisoning with Pb leads to 0.9 million deaths globally every year [11].

For all these reasons, several organizations, including the environmental protection agency (EPA), food and drug administration (FDA), and Agency for Toxic Substances and Disease Registry (ATSDR) have set guide values for the permissible human intake and exposure to these heavy metals, and they are adopting these values to control the daily maximum safe exposure levels. However, research has demonstrated that many regions have exceeded the recommended limit. Therefore, to control pollution, it is important to quantitatively identify the sources of HMs [12–17].

Different conventional methods, ion chromatography, coupled plasma-mass spectrometry (ICP-MS), UV–vis spectrometry, atomic absorption spectroscopy (AAS), atomic Emission, and inductively-coupled-plasma mass spectrometry (ICP/MS) have been used as the common quantification techniques for these metals [18]. Although their higher sensitivity and selectivity, these techniques are very expensive [18,19]. In addition, the operations are very complicated and the large amount of time required for sample processing limits the possibility to perform several measurements at the same time. There is, therefore an urgent need for the development of rapid, low-cost, and effective sensing devices for the detection of various heavy metals.

Sensor based on nanotechnology provides a gateway able to respond to all the mentioned challenges. In fact, nanomaterials promote various advantages such as high detection sensitivity, a large surface area, high stability, high thermal and electrical conductivity, enhanced electrical conductivity, and a low response time compared with the traditionally used biosensors [20–22], [23–25]. Among all the design pathways for nanomaterials, green methods are become a reliable, sustainable, and ecological for the synthesis of nanomaterials, especially nanoparticles. In fact, green chemistry require implementing principles dedicated to reducing toxic chemicals use and production [26,27]. As this approach provides potential remedies to the expensive processes, with simplicity and rapidity of fabrication, minimizes the risk, and of course reduces the harm to the environment and humans [28,29]. To design these nanoparticles, plant extracts are used as a reducing and capping agent of metals [30], including gold (Au), platinum (Pt), silver (Ag), iron oxide (Fe_2O_3) …

Owing to its biological, chemical and physical characteristics, gum Arabic (GA) has recently received much attention as a suitable biopolymer for the design of green nanoparticles [31–33]. The mentioned polymers are reported for their branched polysaccharide structure comprising various sugars, such as arabinose, rhamnose, galactose, glucuronic acid, etc [31–33]. The charged group's facilities then its adsorption onto the surface of a nanoparticle. Also, these groups enhanced the steric repulsion between nanoparticles, which improve their colloidal stability.

For all these reasons, we propose herein the design of electrochemical sensor functionalized with green nanoparticles based on gum Arabic as active biopolymer and platinum as metal center for several heavy metal's recognition, including copper, mercury, lead, and zinc. Fourier-Transform Infrared Spectroscopy (FTIR), Transmission electronic microscopy (TEM) and thermogravimetric measurements (TGA) are adopted to control the nanoparticles synthetises. While Differential pulse anodic stripping (DPAS), impedance spectroscopy, and cyclic voltammetry (CV) analysis were used to follow up different steps of sensor design as well as its metrological performances.

2. Materials and methods

2.1. Chemicals and reagents

Nanometal salts ($H_2PtCl_2 \cdot 6H_2O \geq 99.9\%$), acetates buffer, metals including $CuCl_2$, $Pb(NO_3)_2$, $ZnSO_4$ and $HgCl_2$ were obtained from Sigma Aldrich. Natural polymers (Gum Arabic) were purchased from Kingdom of Saudi Arabia market. Solvents like acetone (98%) and ethanol (98%) were from Thermo-Fisher (France). All chemicals were used without further purification. All the solutions were prepared in deionized (DI) water (18.2 MΩ-cm).

2.2. Instrumentation

2.2.1. Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR analyses were performed using a PerkinElmer spectrometer, connected to an attenuated total reflectance cell. Spectra were measured at room temperature from 500 to 4000 cm^{-1} with 2 cm^{-1} resolutions.
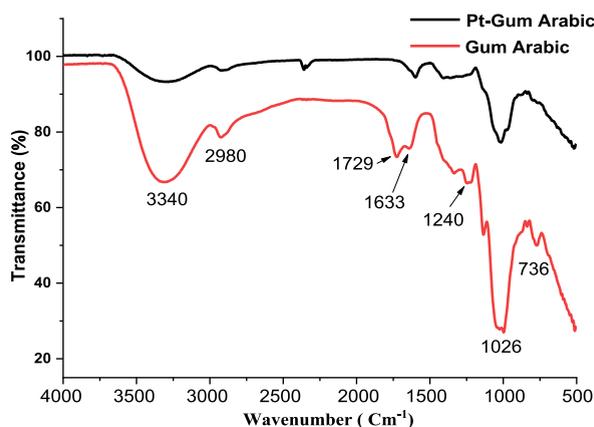
Fig. 1. FTIR characterization of platinum nanoparticles and platinum nanoparticles coated with gum Arabic.

2.2.2. Thermogravimetric measurements (TGA)

Thermogravimetric measurements were carried out with NETZSCH TG 209F1 Tris instrument. The catalytic powder with a mass of 6.575 mg is put in an alumina pan and heated under air with a range of 24 °C/10.0 (K/min)/800 °C.

2.2.3. Transmission electronic microscopy (TEM)

The nanoparticles morphology was analysed using a JEOL JEM-2100 LaB6 transmission electronic microscope (TEM). The acceleration voltage is in the order of 200 kV and equipped with a high tilt pole-piece characterized with a resolution of 0.25 nm.

2.2.4. Electrochemical measurements

Differential pulse anodic stripping voltammetry (DPASV), impedance spectroscopy, and cyclic voltammetry (CV) analysis were performed with the Potentiostat apparatus (Ivium technology) from the chemistry department in the faculty of science, at Majmaah University. Screen-printed electrodes were purchased from PalmSens. The active surface is gold, surrounded with platinum (auxiliary electrode) and Ag/AgCl (reference electrodes).

Electrochemical measurements were monitored at ambient temperature. All DPAS measurements are recorded in acetate buffer with acidic pH (5.5). To evaluate the surface modification, cyclic voltammetry (CV) and impedance spectroscopy response were carried out in the redox probe ferri/ferrocyanide $[Fe(CN)_6]^{3-/4-}$ with a concentration equal 5 mM, in PBS (0.1 M) with ionic strength I = 164 mM and pH 7.4.

2.3. Synthesis of Pt nanoparticles coated with nanoparticles

Pt nanoparticles were synthesized in one step, by dissolving (2.5 mg) of $(H_2PtCl_2 \cdot 6H_2O)$ in (1% and 5%) aqueous solutions of gum Arabic polymer. For high homogeneity and a well-dispersed structure, the solution was stirred gently at the desired temperatures (60 °C) for 24 h. After solution colour change, the nanoparticles are well rinsed with acetone as an anti-solvent. After that, the precipitated catalyst was centrifuged and dried in ambient air for 24 h. To control the preparation of the nanoparticles, they are characterized and investigated by FTIR, TGA, and electrochemical techniques.

2.4. Sensor surface preparation

The active surface of screen-printed electrode SPE was, firstly washed several times with deionized water. The cleaned electrode was, then dried at ambient temperature. In order to guarantee the well dissolved of the designed nanocomposites, 2 mg/mL of platinum gum Arabic were dissolved in DMF solution. The final obtained ratio is equal to 5 wt%. The mixture was sonicated for 1 h to achieve a homogenous solution. Then 5 μL of Pt-GA nanocomposite solution was dropped on the SPE surface overnight at 4 °C.

3. Results and discussions

3.1. Nanoparticles characterization

3.1.1. FTIR analysis

The proposed redox reaction between metal ions and gum chains during the manufacturing of the metallic nanocomposites could be achieved through a change in the molecular structure of the gum backbone, which in turn could be formerly detected in the FTIR data.

From the spectra presented in Fig. 1, the appearance of peaks at 3340 cm^{-1}, on the native GA spectrum, could be attributed to the –OH stretching vibration respectively. The peak at 2980 cm^{-1} is referred to –CH vibration. While the peaks observed at 1729, 1633,
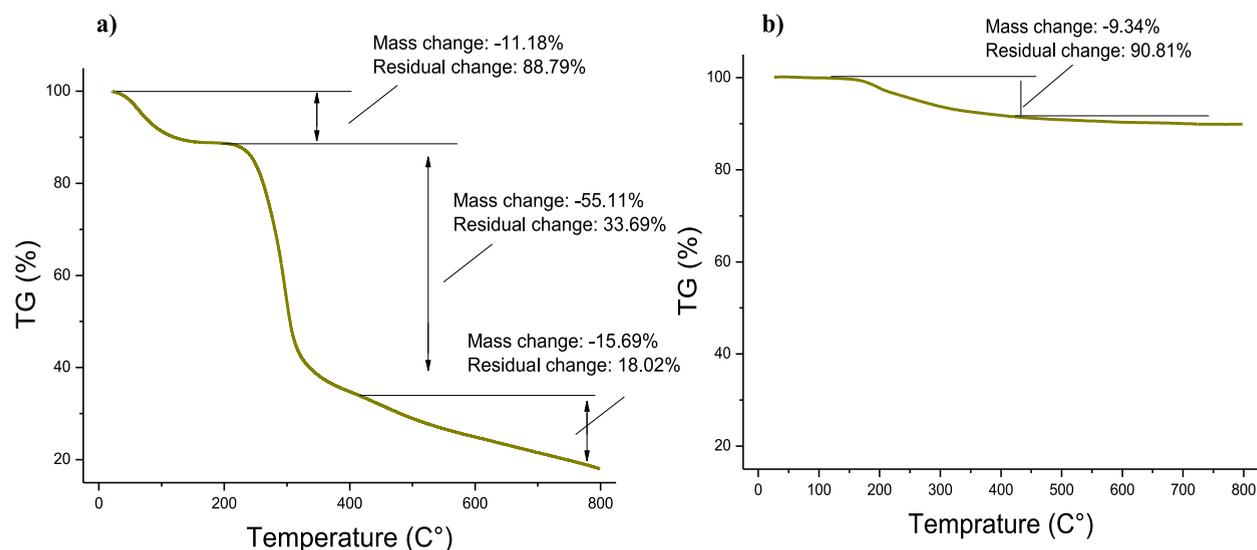
Fig. 2. Thermogravimetric TGA investigation: (a) of platinum nanoparticles; and (b) platinum nanoparticles coated with gum Arabic.
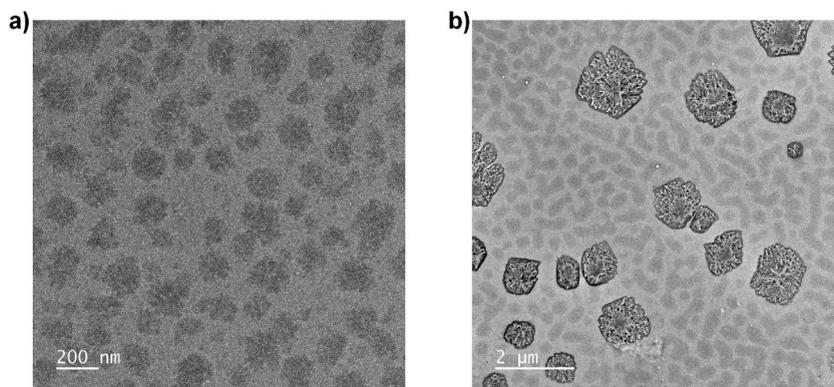
Fig. 3. Transmission electronic microscope (TEM) images of Pt-GA nanoparticles: (a) 200 nm; and (b) 2 μm.

1240, and 1026 cm^{-1} are fingerprints to the stretching of the C═O, C–O, and the C–O–C bending of the acid group, respectively. The found spectra are in good correlation with that found in the literature [34–36].

By comparing the GA spectra to that in the presence of Pt nanoparticles: i) the increase of peaks observed at 3319 cm^{-1} and 1026 cm^{-1}, and ii) the disappearance of peaks at 1729.7 and 1240 cm^{-1} indicate the formation of hydrogen bonding between the hydroxyl groups the carboxylic functional group of GA and Pt nanoparticles.

The spectral data approved then the successive formation of Pt nanoparticles coated by GA biopolymer.

3.1.2. Thermogravimetric measurement

Thermogravimetric TGA investigation elucidates the sintering and the thermal behaviour of platinum nanoparticles in the presence and in absence of GA. This technique characterizes, in fact, the mass loss through ligand removal as a function of temperature. The platinum nanoparticles and platinum-coated by gum Arabic thermograms were obtained by heating at room temperature 28 ± 2 C° under argon to 800 C° with a temperature rise rate of 10 C°/min. The characteristic thermograms of Pt-GA, visualized on Fig. 2(a), show three decomposition stages. The first, in the range of 0–180 C°, could be related to the loss of bound water that surround the gum Arabic polymer. The second decomposition stage, in the interval of 200–350 C°, is linked to the dehydration and decarboxylation of the polymer, leading to the formation of inter and intramolecular anhydride. The third one, in the range of 400–800 C°, is a result of the degradation of the residual gum Arabic polymer. More important, the following thermograms fit perfectly with precedent works reported by P.S. G et al. [37], et C. Cozic et al., [38].

After integration of gum arabic to the platinium nanoparticles surface Fig. 2(b), low mass losses are observer compared to the bare platinum nanoparticles. The mentioned spectra show a mass loss of 5%, confirming the fact that the gum Arabic formation on the platinum surface improve their thermal stability. In fact, the association between Pt-GA act as barrier layer, minimizing then the polymer degradation at higher temperature. Our funding provokes then the good structural as well as thermal stability of these
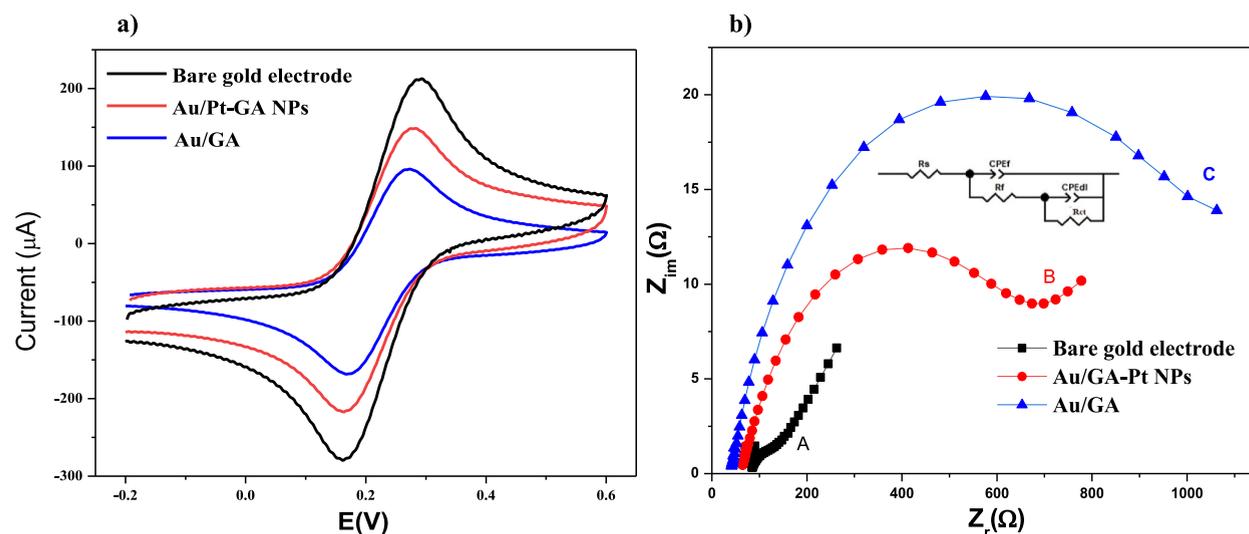
Fig. 4. (a) Cyclic voltammograms; and (b) Electrochemical impedance spectroscopy measurements of SPE surface, SPE modify with the gum Arabic polymer, and SPE functionalized with the nanocomposites Pt-GA. All measurements are recorded in Fe (CN$_6$)$^{3-/4-}$ solution with a concentration equal to 5 mM, dissolved in 20 mM phosphate buffer.

nanoparticles.

3.1.3. TEM characterization

The morphology as well as the size of the designed green nanoparticles were analysed using TEM technique. The TEM image illustrated in Fig. 3 reveals the presence of a homogeneous and well-structured nanoparticles of Pt-GA on the surface. The thickness, calculated based on Fig. 3(a–b) and ImageJ software, was found in order of 1 μm. All of these observations are in good accordance with results found by FTIR and TGA measurements.

Nevertheless, the implantation of these nanoparticles in the design of electrochemical sensors could provide a broad survey for the quantification of several types of heavy metals. For this purpose, these nanoparticles will be integrated with a sensor for the recognition four types of heavy metals.

3.2. Sensor design

The electrochemical sensors are selected herein to follow up the quantification of heavy metals in the regard to their ability to provide a low-cost, convenient solution for the detection of variable analyte with low detection limits, a wide linear response range, and good stability and reproducibility [36,37]. To succeed the sensor design, the transducer surface with be modified with the elaborated Pt-GA nanoparticles, to be ready after that to heavy metals quantification.

3.2.1. Sensor surface characterization

To establish Pt-GA as a sensing material and its validation in the design of chemical sensor, the electrochemical behavior of bare SPE, GA/SPE, and Pt-GA/SPE are investigated by using electrochemical measurement and the electrochemical response are recorded in 5 mM [Fe(CN)$_6$]$^{3-/4-}$ redox probe. As displayed in Fig. 4(a)–a well-resolved pair of redox peaks was observed in the red curve, confirming the surface clearness after treatment. According to the voltammograms presented on the black curve, the peak current of a redox couple on the surface was remarkably decreased and ΔEp declined, confirming the surface modification with the gum Arabic [32]. At pH neutral pH, the acidic groups' function became negatively charged, which minimizes the redox couples' penetration to the gold surface. Compared with the blue curve, a higher redox peak than that of the naked surface is observed after surface modification with nanocomposites. This enhancement is probably related to the large surface area of the transducer surface after modification with the nanoparticles, as well as the acceleration of the electron transfer at the electrode surface, resulting in larger current signals.

The electrochemical impedance spectroscopy measurements illustrated in Fig. 4(b) indicated the resistance of charge transfer increase from 96.5 KΩ to 633.8 KΩ after surface modification with Pt-GA and to 1090.6 KΩ after surface functionalization with the gum Arabic. The found results are in good correlation with cyclic voltammetry characterization, after each step of surface modification [32]. These results confirm then the ability of the nanoparticles to minimize the global negative charge of the gum Arabic and consequently the enhancement of the charge transfer.

3.2.2. Sensor optimization

To succeed the sensor configuration, several optimizations are recorded including the choice of the electrolyte support, the pH of the characterization media and the incubation time. For all measurements, we are based on DPASV method. Three electrolytes are
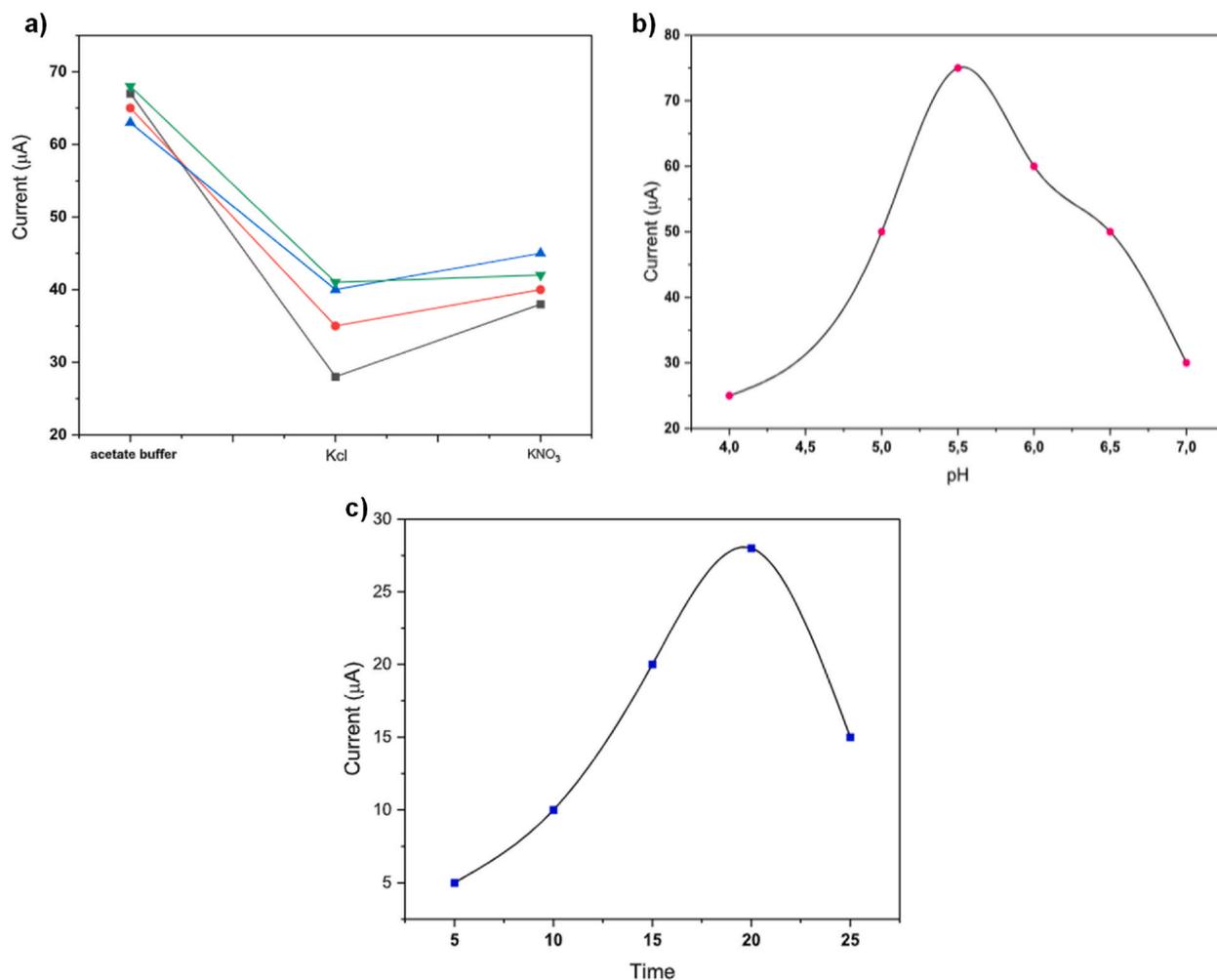
Fig. 5. Optimization of the nature the electrolyte) a**)**; Optimization of the pH of acetate buffer) b**)**, Optimization of the incubation time**) c)**, measurements were recorded with Cu^{2+} ion.

selected: acetate buffer, KCL and KNO_3 with a concentration equal to 0.1 M Fig. 5 (a). After surface incubation with 50 ppb of different ion Zn (II), Pb (II), Cu(II) and Hg (II), the current recording demonstrated that the highest current intensity is obtained in the acetate buffer case. Therefore, this buffer is selected for the rest of manipulations.

The pH, a critical parameter in the sensor design, control both the enhancement of the current intensity and the nanoparticles stability. For these reasons, the working pH effect on electrochemical response of the designed sensor was varied from 4 to 6.5. In this part, we have selected Cu^{2+}, as ion model. Results, grafted on Fig. 5) b (, showed the current intensity increase until reaching 5.5. From this value, the current decreases. This variation could be attributed to the protonation process of gum Arabic acid groups, minimizing then the electrostatic interactions between the acid groups and the positively charged leads ions. Based on the found results, all electrochemical measurements for different tested metal ions were carried out in 0.1 M acetate buffer solution at optimal pH of 5.5.

The last optimized parameter is the incubation time. This parameter could in fact influences the interaction time between the surface functionalization with the nanoparticles and the heavy metals, and then the sensors performances. The incubation time was optimized in the range time varying from 5 to 25 min Fig. 5) c). The current variation presents a parabolic variation with a maximum at 20 min. This time guarantees a good binding and interactions between heavy metals and the nanoparticles.

3.2.3. Electrochemical quantification of heavy metals

To investigate the ability of the designed nanoparticles to recognize different heavy metals namely Zn^{2+}, Hg^{2+}, Pb^{2+}, and Cu^{2+}, the transducer surface functionalized with the Pt-GA nanocomposites are incubated with different heavy metals concentration. It can be noticed on Fig. 6) a)- (c (, and d that the increase of different metals concentrations leads the current intensity increase. This variation could be attributed to the equilibrium acquirement after the adsorption of the investigated heavy metals. In fact, this equilibrium is related to the electrostatic interactions between the charged positive heavy metals and the negative charged acid groups.

In addition, a potential shift was also visualized towards positive potential with increasing concentration in the case of the fourth

a)

b)

c)

d)
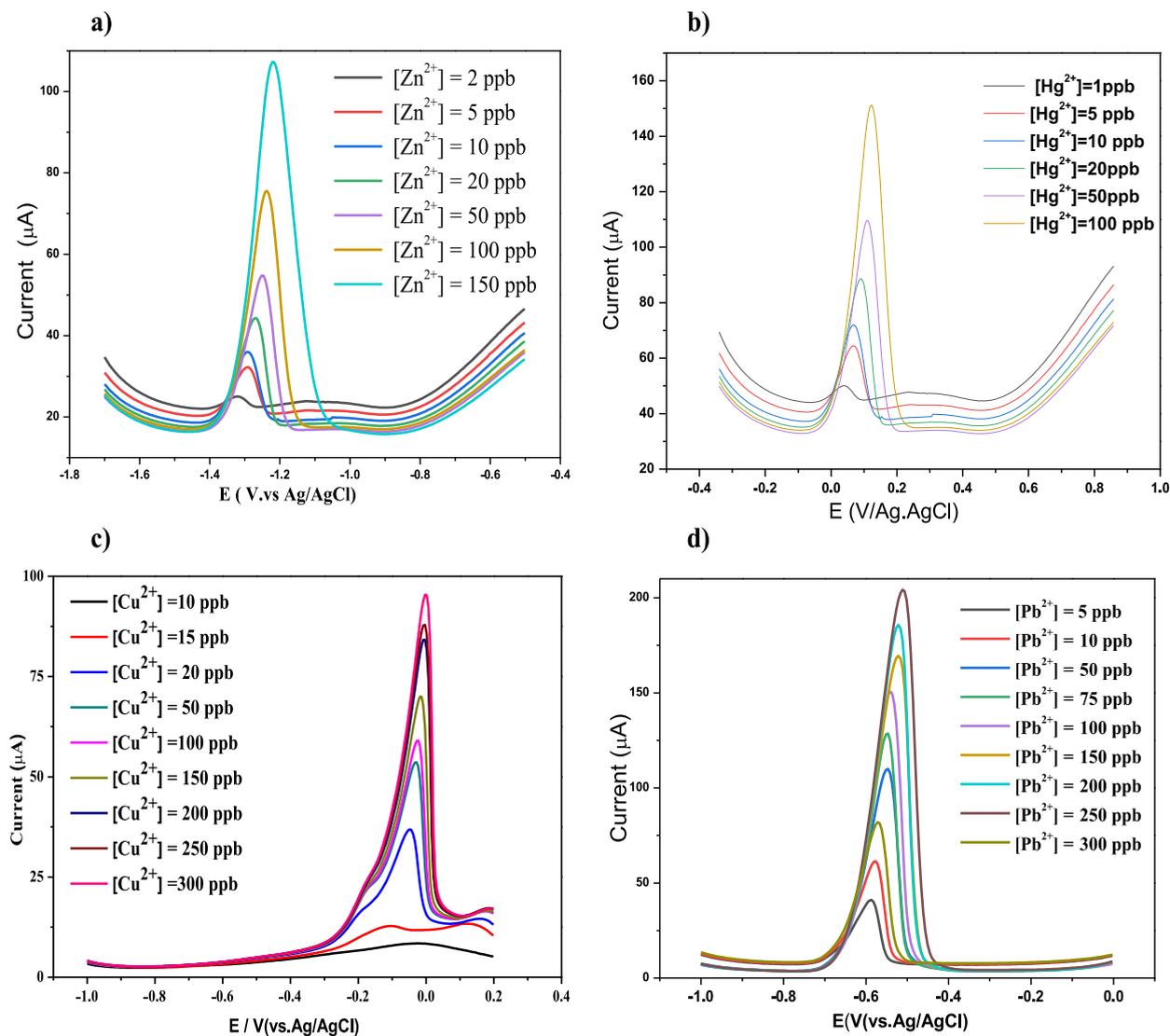
Fig. 6. Differential pulse anodic stripping voltammograms accumulated on the Pt-GA nanoparticles electrode for: (a) Zn^{2+}, (b) Hg^{2+}, (c) Pb^{2+}, and (d) Cu^{2+}. All measurements are recorded in 0.1 M acetate buffer pH 5.5.

ions. The potential shifting could be explained by the Nernst equation, a higher concentration lead to the potential increase [38]. In addition, the presence of a high concentration of analyte can cause a disordered diffusion, disturbing then the mass transport rate [38].

To more evaluate the capacity of these nanocomposites to the quantification with success several types of heavy metals, we make the choice to determine the linear responses of stripping peak currents variation of different ions on SPE modify with the gum Arabic polymer and SPE electrode functionalized with the nanoparticles. All results are illustrated on Fig. 7. The followed Fig. advert a good linearity with a good sensibility of the designed nanocomposites to recognize the different type a heavy metal.

In order to more compare the metrological performances of sensors modify with gum Arabic only and that functionalized with the nanoparticles, we have grouped the range game, limit of detection LOD, the correlation coefficient R^2, and the sensitivity in Table 1. The limit of detection is calculated from the standard deviation of the response (SD) and the slope of the calibration curve (S) according to the formula: LOD = 3(SD/S). While the sensitivities are calculated from the slope of the calibration plots.

Table 1 shows that nanoparticles have remarkably reduced the detection limit for all heavy metals, with an important enhancement in the correlation coefficient. As, the sensitivity has been increased four times for Zn^{2+}, Cu^{2+} and Hg^{2+}. More importantly, engineered nanoparticles improved further the sensitivity, attempting a seven-time increase for Pb^{2+}. The progressive amelioration in the electrocatalytic performance of these sensors is a result of the unique nanostructure of the elaborated nanoparticles, which increased the active surface of the transducer in first hand and provide more sites for metal ions entrapment through forming stable complex between the gum Arabic and metal ions, in the other hand. In fact, the gum Arabic present an acid dissociation constant (pKa) between 3 and 4 corresponding to the carboxylic group of the polysaccharide parts (uronic acid) [39]. In neutral pH, these acidic groups became
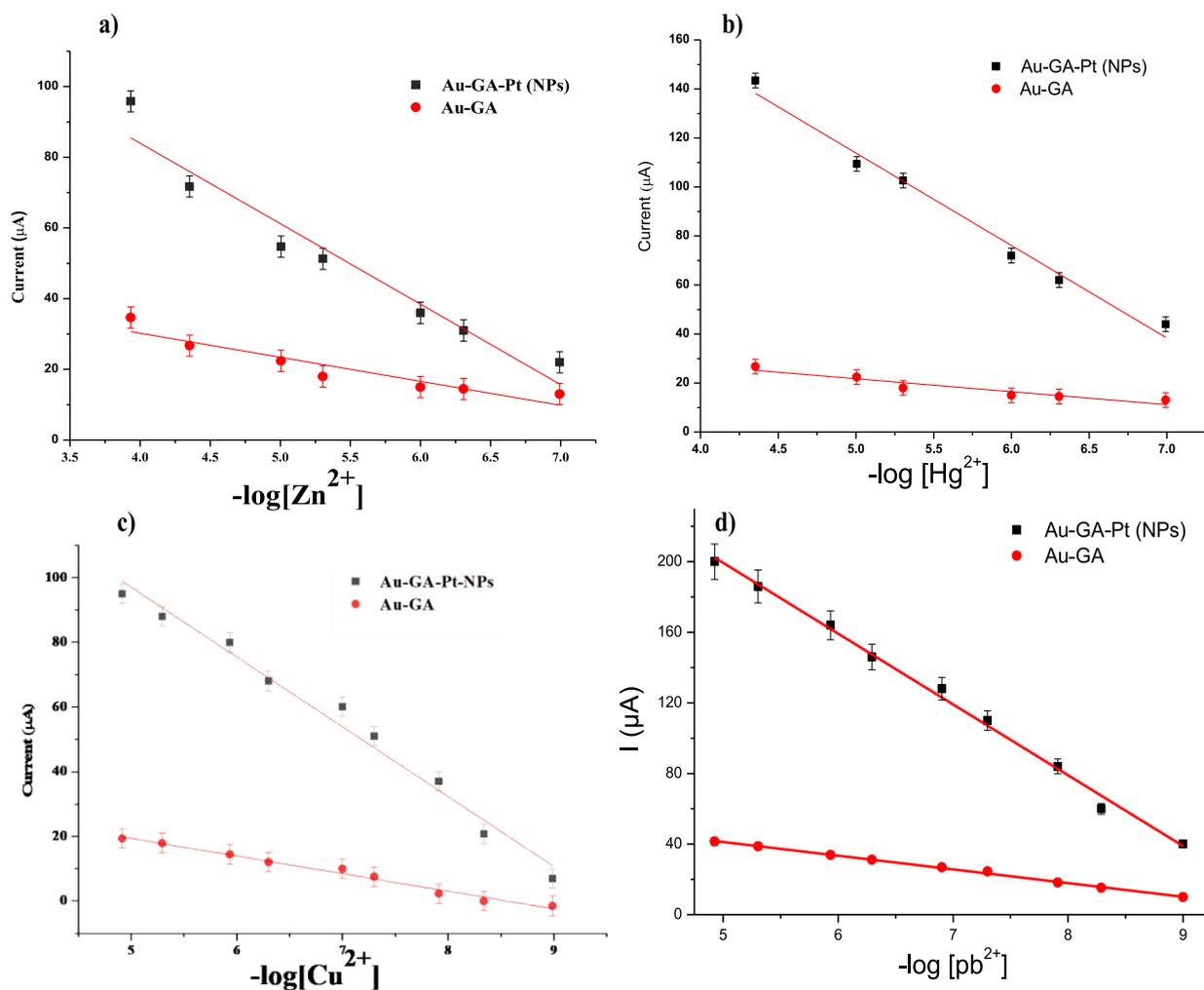
Fig. 7. Calibration curve of on GA/SPE and Pt-GA/SPE for GA and Au/GA-Pt-NPs electrodes: (a) Zn^{2+}, (b) Hg^{2+}, (c) Pb^{2+}, and (d) Cu^{2+}. All measurements are recorded in 0.1 M acetate buffer pH 5.5.

Table 1

Illustrative table of range game, limit of detection LOD, the correlation coefficient R^2, and the sensitivity of different heavy metals on the GA/SPE and Pt-GA/SPE.

	Zn^{2+}		Hg^{2+}		Pb^{2+}		Cu^{2+}	
	GA/SPE	NPs/SPE	GA/SPE	NPs/SPE	GA/SPE	NPs/SPE	GA/SPE	NPs/SPE
Range game (ppb)	2–150	2–150	1–200	1–200	5–300	5–300	10–300	10–300
LOD (ppb)	2	1.9	1	0.9	5	4.2	10	9.6
Correlation coefficient (%)	86	93	86	93	99	99	98	98
Sensitivity (µA/ppb)	6.82	22.76	6.82	22.76	7.81	40.16	5.44	21.58

negatively charged. This overall negative charge enhances the binding and the interaction between the metals and the acid groups. Therefore, sensor functionalized with GA-Pt nanoparticles provides a good chance to develop a high sensitivity device with a significant enrichment ability to metal ions trapping.

To more highlight the success of the elaborated nanoparticles to detect heavy metals, we have illustrated in Table 2, a comparative investigation between the metrological performances of the present work and several sensors modified with green nanoparticles elaborated to the heavy metal's quantification. The green nanoparticles are prepared using a green method based on gold or silver metals reducing by protein or polymer extracted from different plants. From the analytical parameters presented on Tables 2 and it can be concluded that the present investigation demonstrated that gum arabic present an enhancement in the metrological performances in terms of the limit of detection and the linear range compared to previous investigations. As it can be enumerated with a simplicity of

Table 2

Comparison of metrological performances of different sensor modified with green nanoparticles for heavy metals detection.

Surface modification	Transduction technique	Heavy metals	Linear range	LOD	Ref
L-tyrosine-Ag	Colorimetric	Hg^{2+}	20–100 nM	16 nM	[40]
L-tyrosine-Au		Pb^{2+}	20–100 nM	16 nM	
		Mn^{2+}	20–100 nM	16 nM	
β-cyclodextrin (β-CD)-graphene -Au	Electrochemical	Pb^{2+}	40–1200 µg L^{-1}	10.6 µg L^{-1}	[41]
		Cd^{2+}	40–1200 µg L^{-1}	29.9 µg L^{-1}	
		Cd^{2+}	5–160 ppm	0.048 ppm	
Grape Stalk Waste Extract-Ag	Electrochemical	Pb^{2+}	0.39–40 µg L^{-1}	0.12 µg L^{-1}	[42]
		Cd^{2+}	40.2–149 µg L^{-1}	12.1 µg L^{-1}	
		U^{4+}	17.4–49 µg L^{-1}	5.2 µg L^{-1}	
Grape Stalk Waste Extract-Au		Pb^{2+}	0.4–90 µg L^{-1}	0.12 µg L^{-1}	
		Cd^{2+}	47.5–162 µg L^{-1}	14.3 µg L^{-1}	
Flower extract of Acacia nilotica-Ag	Optical	Hg^{2+}	50–450 µM	50 µM	[43]
Gum Arabic-Pt	Electrochemical	Zn^{2+}	2–150 ppm	1.9 ppm	**The present work**
		Hg^{2+}	1–200 ppm	0.9 ppm	
		Pb^{2+}	5–300 ppm	4.2 ppm	
		Cu^{2+}	10–300 ppm	9.6 ppm	

Table 3

Cu^{2+}, Pb^{2+}, Hg^{2+} and Zn^{2+} heavy metals determination in farm water in Zulfi in Arabic Saudia.

	Heavy metals	Added (ppb)	Found (ppb)	Recovery %
Real samples of water	Hg^{2+}	80	83 ∓ 1.2	103.75
		90	88 ∓ 0.7	97.77
		100	95 ∓ 1.8	95
	Pb^{2+}	80	78.8 ∓ 1.3	98.5
		90	101 ∓ 0.77	112.22
		100	99.78 ∓ 1.6	99.78
	Cu^{2+}	80	74.6 ∓ 2.6	93.25
		90	98.4 ∓ 1.4	109.33
		100	83.8 ∓ 1.8	83.8
	Zn^{2+}	80	76.7 ∓ 2.1	95.87
		90	91 ∓ 0.5	101.11
		100	93.5 ∓ 1.8	93.5

sensor preparation, rapidity, good stability, and good reproducibility.

3.2.4. Real sample investigation

Sensor validation with real sample is a crucial step in sensor design, it determinate in fact the ability of sensor to recognize the specific analyte even in very complicated media. To investigate this parameter, real samples of water were taken from farm water in Zulfi in Arabic Saudia and were investigated by electrochemical measurements. A freshly prepared surface was incubated with water solution containing different heavy metals concentrations 80, 90, and 100 ppm. Table 3 showed that the recoveries of Cu^{2+}, Pb^{2+}, Hg^{2+} and Zn^{2+} ions using GA-Pt nanoparticles.

As presented in Table 3, the acceptable average recoveries for of Cu^{2+}, Pb^{2+}, Hg^{2+} and Zn^{2+} are obtained in the order of 95–110%. These good results suggest that the proposed sensors have a potential applicability in environmental monitoring.

4. Conclusion

Green nanoparticles based on gum Arabic have been investigated as a sensory electrode material for the simple, rapid and selective electrochemical detection of four heavy metals namely Zn^{2+}, Hg^{2+}, Pb^{2+} and Cd^{2+} ions. To successfully follow up the nanoparticle's elaboration as well as the sensor preparation, morphological, thermal and electrochemical technique namely Fourier-transform infrared spectroscopy FTIR, and thermogravimetric TGA, cyclic voltammetry CV and electrochemical impedance spectroscopy EIS differential pulse anodic stripping DPAS were used. Results have demonstrated a successful nanoparticles design, with a good structural, thermal stability, and small size in order of 1 µm.

More important, sensor functionalization with these nanoparticles have demonstrated a good analytical parameter, in terms of the limit of detection which was in order of 9.6 ppb for Cu^{2+}, 1.9 ppb for Zn^{2+}, 0.9 ppb for Hg^{2+}, and 4.2 ppb for Pb^{2+}. While the sensitivities are estimated in the order 21.58 for Cu^{2+}, 22.76 Zn^{2+}, 22.76 Hg^{2+} and 40.16 Pb^{2+}, respectively.

Regarding these encouraging performances, the elaborated sensor was applied for these metals' detection in real sample. The obtained results are comparable to those obtained with conventional methods, with a good reproducibility. Sensor modified with green nanoparticles based on gum arabic could be considered as an important and promising analytical chemistry for rapid and specific heavy metals' detection.

CRediT authorship contribution statement

Manahil Babiker Elamin: Investigation. **Amani Chrouda:** Methodology. **Shazalia Mahmoud Ahmed Ali:** Validation. **Laila M. Alhaidari:** Supervision. **Mahjoub Jabli:** Writing – original draft. **Rahaf Mutlaq Alrouqi:** Methodology. **Nicole Jaffrezic Renault:** Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr. Amani chrouda reports was provided by Majmaah University. Dr Amani chrouda reports a relationship with Majmaah University that includes: employment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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