MODIFIED GRAPHITE/GRAPHENE DOT MICROSENSORS FOR THE ASSAY OF TRACE AMOUNTS OF LEAD AND CADMIUM IN WATER CATCHMENTS AREAS USING DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

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In this study, dot microsensors based on graphite/graphene paste modified with iron (II) phthalocyanine, nickel (II) phthalocyanine and 5,10,15,20-tetra(4pyridyl)21H, 23H porphine chloride tetrakis(methochloride) manganese(III) were used for the determination of trace amounts of lead and cadmium from various water catchments areas using differential pulse anodic stripping voltammetry. The response of the proposed dot microsensors were sensitive enough to detect very low levels of both metals ions in drinking water resources to take corrective action for the supply of safe and suitable drinking water. The lowest limits of quantification for lead is $0.00207 \mu\text{g L}^{-1}$ and for cadmium $5.6 \mu\text{g L}^{-1}$, with a correlation coefficient (R^2) between 0.9951 and 0.9981 for lead, and between 0.9951 and 0.9984 for cadmium. The recovery of Pb(II) and Cd(II) in water samples were higher than 93.06 % with RSD(%) values lower than 0.29%. These results of the proposed dot microsensors compared favorably with the results from a standard ISO certified method.

INTRODUCTION

Exposure to various chemicals including transition and heavy metals occurs every day through multiple routes such as ingestion, inhalation, and skin contact and via the umbilical cord to the unborn child. Many chemicals and metals are harmless or even beneficial; others are a threat to our health and to the environment. There is a continuous increase production and pollution of these substances and subsequently the potential for chemical exposure. These substances are risky and hazardous to human health with possible development of allergies, tumors and serious

diseases and exposure could potentially be reduced or removed through environmental management with careful monitoring of metals like Cd and Pb. Water is essential for life. The amount of fresh water on earth is limited, and its quality is under constant pressure. Preserving the quality of fresh water is important for the drinking-water supply, food production and recreational water use. According to World Health Organization's (WHO) the maximum level for Pb^{2+} and Cd^{2+} ions in drinking water is $10 \mu\text{g L}^{-1}$ and $3 \mu\text{g L}^{-1}$. According to WHO and U.S. Environmental Protection Agency (EPA) the maximum level of Pb and Cd is 50 and $10 \mu\text{g L}^{-1}$, respectively.¹⁻⁷

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Cadmium is a toxic metal with a half-life of 10–30 years, being classified in the list of carcinogens in group 1.^{8,9} The main source of cadmium contamination is food. A disease caused by cadmium is the Itai Itai disease, which first appeared in Japan.^{10,11} Cadmium is, also, associated with breast cancer, chronic renal disease,^{12,13} and prostate cancer.¹⁴ No treatment against cadmium intoxication is known, but recent studies in rats have shown that *Tinospora Cordifolia* extract attenuates biochemical and histological changes induced by cadmium.¹⁵ Lead is a toxic metal that leads to Parkinson's disease, urological (kidney) disease. The treatment used is that of zinc supplements, meso-2,3-dimercaptosuccinic acid, 2,3-dimercapto-propanesulfonic acid, dimercaptopropanol.^{16–23}

The widely used and standard techniques for analysis of heavy metals are spectrometric procedures (graphite furnace atomic absorption spectroscopy, flame atomic absorption spectrometry, inductively coupled plasma mass spectrometry, atomic fluorescence spectrometry, inductively coupled plasma atomic emission spectroscopy), or chromatography methods (gas chromatography, high performance liquid chromatography, etc.). All these methods require complex equipment, are expensive to maintain, and need well trained people.^{24–30}

Recently, new electrochemical methods have been developed for the detection of heavy metals.^{31,32} The glassy carbon electrode is the most commonly used, usually modified with NiO morphologies consisting of rods NiO, flakes NiO and balls NiO³³, with mercury film,³⁴ screen printed electrodes modified with bismuth,^{35–38} or screen printed electrodes modified with some organic compounds such as: dibenzo-24-crown-8, tetrathiacyclododecane 12-crown-4,³⁹ crown-ether based membrane,⁴⁰ glutathione.⁴¹

We herewith developed a simple, sensitive and selective electrochemical method for the determination of cadmium and lead ions in water. The article presents a procedure with modified dot microsensors based on graphite/graphene paste for the detection of cadmium and lead ions from various water catchments areas (e.g., fresh water, underground water, geothermal waste water) using differential pulse anodic stripping voltammetry (DPASV).

MATERIALS AND METHODS

1. Reagents and instrumentation

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, KCl, NaCl, NaNO_3 , $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, Na_2HPO_4 for the preparation of the

solutions were purchased from Sigma-Aldrich. Graphite (G) and graphene (GR) were supplied by Sigma Aldrich, and paraffin oil by Fluka (Buchs, Sweden). Iron(II) phthalocyanine ($\text{Fe}(\text{II})\text{Pc}$), nickel(II) phthalocyanine ($\text{Ni}(\text{II})\text{Pc}$) and manganese(III) 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine chloride tetrakis(methochloride) ($\text{Mn}(\text{III})\text{TPP}$) were from Aldrich.

Phosphate buffer solutions (PBS, 0.1 mol L^{-1}) with $\text{pH} = 2\text{--}10$ were prepared by using different ratios between NaH_2PO_4 and Na_2HPO_4 . Hydrogen chloride (HCl , 0.1 mol L^{-1}) and sodium hydroxide (NaOH , 0.1 mol L^{-1}) were used for pH adjustment.

The standard solutions for differential pulse voltammetry (DPV) were prepared using $10^{-3} \text{ mol L}^{-1}$ of Cd^{2+} or Pb^{2+} as stock solutions. All standard solutions of Cd^{2+} or Pb^{2+} (10^{-4} – $10^{-12} \text{ mol L}^{-1}$) were prepared from the stock solution by serial dilution, with phosphate buffer solution (PBS) of different pHs containing KCl, NaCl or NaNO_3 (0.1 mol L^{-1}) as supporting electrolytes.

All solutions were prepared using deionized water obtained from a Direct-Q 3 Water Purification System (Millipore Corporation, France).

All measurements were recorded using a PGSTAT 128 N potentiostat/galvanostat connected to a three electrode cell, and linked to a computer via an Eco Chemie (Utrecht, The Netherlands) software version 4.9. An Ag/AgCl electrode served as reference electrode and a platinum electrode served as auxiliary electrode, new developed sensors served as working electrode in the electrochemical cell. The pH measurements were performed using a CyberScan PCD 6500 Multiparameter.

DPV curves have been recorded at 0.01 V s^{-1} , with a pulse height of 0.025 V and step potential of 0.05 V .

All measurements were performed at 25°C .

2. Design of dot microsensors

Graphite or graphene pastes were modified with iron(II) phthalocyanine ($\text{Fe}(\text{II})\text{Pc}$), nickel(II) phthalocyanine ($\text{Ni}(\text{II})\text{Pc}$) and manganese(III) 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine chloride tetrakis(methochloride) ($\text{Mn}(\text{III})\text{TPP}$) each. The modified graphite or graphene pastes were prepared as follows: 100 mg of graphite or graphene powder were mixed with 30 mL paraffin oil to form the graphite or graphene pastes. 25 mL from the solution of $\text{Fe}(\text{II})\text{Pc}$ ($10^{-3} \text{ mol L}^{-1}$, prepared in dimethyl sulfoxide) or $\text{Ni}(\text{II})\text{Pc}$ ($10^{-3} \text{ mol L}^{-1}$, prepared in N,N-dimethylformamide) or $\text{Mn}(\text{III})\text{TPP}$ ($10^{-3} \text{ mol L}^{-1}$, prepared in dimethyl sulfoxide) was added to the graphite or graphene pastes mixed with 25 mL paraffin oil. The

modified paste was placed into a very small plastic tube. Electrical contact was obtained with an Ag wire inserted into the paste. The surface of the electrode can be renewed by polishing with alumina paper. When not in use, the dot microsensors were stored in a dry place, away from day light and at room temperature.

RESULTS AND DISCUSSION

1. Optimization of working conditions

DPV curves (0.01 V s^{-1}) were recorded in order to optimize the working conditions for G, Fe(II)Pc/G, Ni(II)Pc/G, Mn(III)TPP/G, GR, Fe(II)Pc/GR, Ni(II)Pc/GR, Mn(III)TPP/GR dot microsensors, using a $10^{-6} \text{ mol L}^{-1}$ solution of Cd^{2+} or Pb^{2+} ions. Three different supporting electrolytes were tested (0.1 mol L^{-1} NaCl, 0.1 mol L^{-1} KCl and 0.1 mol L^{-1} KNO_3) in PBS pH = 2–10. Figure 1 shows the effect of pH and supporting electrolyte on the peak height for each sensor, using a solution of $10^{-6} \text{ mol L}^{-1}$ Cd^{2+} ions, and for a solution of $10^{-6} \text{ mol L}^{-1}$ Pb^{2+} ions. The sensor

sensitivity increases towards lower pH solutions. The following experimental conditions were used with the following eight dot microsensors for the working solution of $10^{-6} \text{ mol L}^{-1}$ Cd^{2+} ions. For Fe(II)Pc/GR, Ni(II)Pc/GR, Mn(III)TPP/GR dot microsensors the optimum performance were obtained in a 0.1 mol L^{-1} KCl, PBS pH = 2 solution. For the unmodified graphite dot microsensor the optimal response was obtained using a 0.1 mol L^{-1} KCl, PBS pH = 3 solution, and for the Fe(II)Pc/G sensor 0.1 mol L^{-1} KCl, PBS pH = 4 solution. For Ni(II)Pc/G and Mn(III)TPP/G dot microsensors we observed that two supporting electrolytes gave a good response: 0.1 mol L^{-1} KCl, PBS pH = 3 or 0.1 mol L^{-1} NaCl, PBS pH = 2, 3. Unmodified graphene dot microsensor have, also, a good response for two supporting electrolytes: 0.1 mol L^{-1} NaCl, PBS pH = 3 or 0.1 mol L^{-1} NaNO_3 , PBS pH = 2. In the case of Pb^{2+} ions, all sensors, except Ni(II)Pc/GR, gave the best response using a 0.1 mol L^{-1} KCl, PBS pH = 2 solution. Ni(II)Pc/GR sensors has a similar response in a 0.1 mol L^{-1} KCl, PBS pH = 2 or 0.1 mol L^{-1} NaCl, PBS pH = 2.

Fig. 1 – The effect of electrolyte and pH on the peak height for a concentration of a) and b) Cd^{2+} solution of $10^{-6} \text{ mol L}^{-1}$ unmodified graphite/graphene and modified graphite/graphene dot microsensors; c) and d) Pb^{2+} solution of $10^{-6} \text{ mol L}^{-1}$ unmodified graphite/graphene and modified graphite/graphene dot microsensors.

Fig. 2 – Influence of the deposition time for a) G, b) Fe(II)Pc/G, c) Fe(II)Pc/GR, d) Ni(II)Pc/GR, e) Mn(III)TPP/GR dot microsenors using a 10^{-6} mol L⁻¹ Cd²⁺ solution and for f) G, g) Fe(II)Pc/G, h) Ni(II)Pc/G, i) Mn(III)TPP/G, j) GR, k) Fe(II)Pc/GR, l) Mn(III)TPP/GR dot microsenors using a 10^{-6} mol L⁻¹ Pb²⁺ solution; inset: deposition potential, where H is the peak height (A).

Fig. 3 – Influence of the deposition time for a) Ni(II)Pc/G, b) Mn(III)TPP/G, c) GR dot microsensors using a 10^{-6} mol L⁻¹ Cd²⁺ solution; d) Ni(II)Pc/GR dot microsensors using a 10^{-6} mol L⁻¹ Pb²⁺ solution; inset: deposition potential, using different supporting electrolyte where H is the peak height (A).

Table 1

Optimum experimental conditions
for the Cd^{2+} 10^{-6} mol L $^{-1}$ and Pb^{2+} 10^{-6} mol L $^{-1}$ with different modified graphite and graphene dot microsensors

Heavy metal	Parameter Sensors	PBS pH	Supporting electrolyte	Reduction Time (V)	Deposition Time (s)
Cd^{2+}	G	3	KCl	-1.4	180
	Fe(II)Pc/G	4	KCl	-1.3	210
	Ni(II)Pc/G	3	NaCl	-1.4	180
	Mn(III)TPP/G	3	KCl	-1	180
	GR	3	NaCl	-1.3	210
	Fe(II)Pc/GR	2	KCl	-1	180
	Ni(II)Pc/GR	2	KCl	-1.5	240
	Mn(III)TPP/GR	2	KCl	-1.2	150
Pb^{2+}	G	2	KCl	-1.1	150
	Fe(II)Pc/G	2	KCl	-1.2	150
	Ni(II)Pc/G	2	KCl	-1.2	180
	Mn(III)TPP/G	2	KCl	-1.2	150
	GR	2	KCl	-1.2	150
	Fe(II)Pc/GR	2	KCl	-1.2	150
	Ni(II)Pc/GR	2	KCl	-1.2	180
	Mn(III)TPP/GR	2	KCl	-1.2	180

2. Optimization of deposition time and potential for maximum response

In order to obtain the maximum response of the dot microsensors, parameters like deposition potential and deposition time were optimized. Figures 2 and 3 show the influence of the deposition time with the corresponding position potential of the response of the dot microsensors using the best selected supporting electrolyte for each dot microsensor. For the sensors G, Fe(II)Pc/G, Fe(II)Pc/GR, Ni(II)Pc/GR, Mn(III)TPP/GR only one supporting electrolyte was used in a 10^{-6} mol L $^{-1}$ solution of Cd^{2+} . In the case of Ni(II)Pc/G, Mn(III)TPP/G, GR, these parameters were determined using two supporting electrolytes, in order to have the optimum response for the determination of Cd^{2+} . In the case of Pb^{2+} optimization, only one sensor (Ni(II)Pc/GR) with two supporting electrolytes were used for optimization of deposition potential with corresponding position time. Furthermore for maximum response of Pb^{2+} , using a 10^{-6} mol L $^{-1}$ Pb^{2+} solution with G, Fe(II)Pc/G, Ni(II)Pc/G, Mn(III)TPP/G, GR, Fe(II)Pc/GR, Mn(III)TPP/GR dot microsensors only one supporting electrolyte was used. Table 1 presents the final results for the deposition potential, for the deposition time and showed the supporting electrolyte used for the calibration curve and for various water catchments areas for Cd^{2+} ions and for Pb^{2+} ions.

3. Response characteristics for the Cd^{2+} and Pb^{2+} ions

Figures 4 and 5, as well as Table 2 presents the response characteristics for the Cd^{2+} and Pb^{2+} ions using the optimal parameters (supporting electrolyte, deposition potential and deposition time). It can be seen that for all sensors good correlation coefficients were obtained. The highest sensitivity for the sensors was recorded for Pb^{2+} ions when compared with the determination for the Cd^{2+} ions. Dot microsensors based on unmodified graphite and modified graphite with Ni(II)Pc have the highest sensitivity for the determination of Cd^{2+} ions (1.7×10^{-9} A $\mu\text{g L}^{-1}$ and 1.3×10^{-9} A $\mu\text{g L}^{-1}$, respectively).

The highest sensitivity, in case of determination of Pb^{2+} ions, was obtained with the dot microsensor based on graphene modified with Ni(II)Pc (8.7×10^{-7} A $\mu\text{g L}^{-1}$).

The lowest limit of quantification was obtained for the graphite sensor modified with Fe(II)Pc, for the determinations of Cd^{2+} ($5.6 \mu\text{g L}^{-1}$) and Pb^{2+} ($0.00207 \mu\text{g L}^{-1}$) ions. The same limit of quantification ($0.00207 \mu\text{g L}^{-1}$) for Pb^{2+} ions was also obtained for the graphene dot microsensors modified with Fe(II)Pc or modified with Ni(II)Pc, and for the graphite dot microsensor modified with Fe(II)Pc.

Fig. 4 – The calibration curves of the dot microsensors based on: a) G; b) Fe(II)Pc/G; c) Ni(II)Pc/G; d) Mn(III)TPP/G; e) GR; f) Fe(II)Pc/GR; g) Ni(II)Pc/GR; h) Mn(III)TPP/GR for the assay of Cd^{2+} ions; insert: the peak height (A) vs. the concentration of Cd^{2+} ions ($\mu\text{g L}^{-1}$).

Fig. 5 – The calibration curves of the dot microsensors based on: a) G; b) Fe(II)Pc/G; c) Ni(II)Pc/G; d) Mn(III)TPP/G; e) GR; f) Fe(II)Pc/GR; g) Ni(II)Pc/GR; h) Mn(III)TPP/GR for the assay of Pb^{2+} ions; insert: the peak height (A) vs. the concentration of Pb^{2+} ions ($\mu g L^{-1}$).

Table 2

Response characteristics of the electrodes used for determination of Cd^{2+} and Pb^{2+}

Heavy Metal	Parameter Sensors	Equation of calibration*	R	Sensitivity (A $\mu\text{g L}^{-1}$)	Linear conc. range ($\mu\text{g L}^{-1}$)	Limit of quantification ($\mu\text{g L}^{-1}$)
Cd^{2+}	G	$H = -1.2 \times 10^{-7} + 1.7 \times 10^{-9} \times C$	0.99886	1.7×10^{-9}	56 – 1120	56
	Fe(II)Pc/G	$H = -1.3 \times 10^{-8} + 4.5 \times 10^{-10} \times C$	0.99918	4.5×10^{-10}	5.6 – 1120	5.6
	Ni(II)Pc/G	$H = -4.1 \times 10^{-8} + 1.3 \times 10^{-9} \times C$	0.99792	1.3×10^{-9}	56 – 1120	56
	Mn(III)TPP/G	$H = -6.8 \times 10^{-9} + 2.4 \times 10^{-10} \times C$	0.99757	2.4×10^{-10}	11.2 – 560	11.2
	GR	$H = -2.8 \times 10^{-8} + 5.3 \times 10^{-10} \times C$	0.99904	5.3×10^{-10}	56 – 1120	56
	Fe(II)Pc/GR	$H = -4.9 \times 10^{-9} + 2.5 \times 10^{-10} \times C$	0.99806	2.5×10^{-10}	56 – 560	56
	Ni(II)Pc/GR	$H = -2.8 \times 10^{-8} + 7.1 \times 10^{-10} \times C$	0.99880	7.1×10^{-10}	11.2 – 1120	11.2
	Mn(III)TPP/GR	$H = -4.0 \times 10^{-8} + 7.3 \times 10^{-10} \times C$	0.99769	7.3×10^{-10}	11.2 – 1120	11.2
Pb^{2+}	G	$H = -2.5 \times 10^{-8} + 4.5 \times 10^{-7} \times C$	0.99753	4.5×10^{-7}	0.0207 – 1.035	0.0207
	Fe(II)Pc/G	$H = -4.9 \times 10^{-9} + 3.1 \times 10^{-7} \times C$	0.99810	3.1×10^{-7}	0.00207 – 1.035	0.00207
	Ni(II)Pc/G	$H = 2.4 \times 10^{-9} + 1.6 \times 10^{-7} \times C$	0.99905	1.6×10^{-7}	0.01035 – 1.035	0.01035
	Mn(III)TPP/G	$H = 1.2 \times 10^{-8} + 1.1 \times 10^{-7} \times C$	0.99868	1.1×10^{-7}	0.01035 – 10.35	0.01035
	GR	$H = -9.5 \times 10^{-10} + 4.9 \times 10^{-7} \times C$	0.99805	4.9×10^{-7}	0.01035 – 1.035	0.01035
	Fe(II)Pc/GR	$H = 1.8 \times 10^{-9} + 3.3 \times 10^{-7} \times C$	0.99804	3.3×10^{-7}	0.00207 – 1.035	0.00207
	Ni(II)Pc/GR	$H = -2.0 \times 10^{-8} + 8.7 \times 10^{-7} \times C$	0.99761	8.7×10^{-7}	0.00207 – 1.035	0.00207
	Mn(III)TPP/GR	$H = -2.1 \times 10^{-8} + 8.1 \times 10^{-8} \times C$	0.99923	8.1×10^{-8}	0.01035 – 10.35	0.01035

* H is the peak height (A); C is the concentration ($\mu\text{g L}^{-1}$) Fig. 6 – Differential pulse anodic stripping voltammetry obtained for a mix solution of $10^{-4} \text{ mol L}^{-1} \text{ Cd}^{2+}$ and $10^{-4} \text{ mol L}^{-1} \text{ Pb}^{2+}$ for KCl pH = 2 electrolyte for: a) G, Fe(II)Pc/G, Ni(II)Pc/G, Mn(III)TPP/G dot microsensors, and b) GR, Fe(II)Pc/GR, Ni(II)Pc/GR, Mn(III)TPP/GR dot microsensors.

4. Simultaneous determination of Cd^{2+} and Pb^{2+} ions

The DPV voltammograms with simultaneous determination of Cd^{2+} and Pb^{2+} ions were presented in Figure 6, using a mixed solution containing $10^{-4} \text{ mol L}^{-1} \text{ Cd}^{2+}$ and Pb^{2+} ions in $0.1 \text{ mol L}^{-1} \text{ KCl PBS pH}=2$. Table 3 shows the condition for these determinations, for all dot microsensors. It is clear from the DPV voltammograms in Figure 6 that a good separation was obtained for Cd^{2+} and Pb^{2+} ions in the mixed solution. The method is more selective for Pb^{2+} ions.

5. Real samples

Different types of waters (waste water, surface water, drinking water from spring water,

ground water) from different catchments areas were used for analytical determination of Cd^{2+} and Pb^{2+} ions. Buffered water samples (1:1, v/v) were screened using the proposed dot microsensors before and after the addition of certain amounts of Cd^{2+} and Pb^{2+} . The results obtained, using differential pulse anodic stripping voltammetry, as presented in Tables 4 and 5 excellently compared with the SR EN ISO 11885:2009 standard method (inductively coupled plasma atomic emission spectroscopy). It can be seen that all dot microsensors gave very good results for the determination of Cd^{2+} and Pb^{2+} ions in different types of water from different water catchment areas, with the relative standard deviation (RSD%) of less than 0.29 %.

Table 3

Experimental conditions for the determination of ions of Pb^{2+} and Cd^{2+} ions in mixture

Sensor	Conditions	Electrolyte	PBS	Reduction potential (V)	Reduction time (s)
G		KCl	pH=2	-1.4	180
Fe(II)Pc/G		KCl	pH=2	-1.3	210
Ni(II)Pc/G		KCl	pH=2	-1.4	180
Mn(III)TPP/G		KCl	pH=2	-1.2	180
GR		KCl	pH=2	-1.2	210
Fe(II)Pc/GR		KCl	pH=2	-1.2	180
Ni(II)Pc/GR		KCl	pH=2	-1.5	240
Mn(III)TPP/GR		KCl	pH=2	-1.2	180

PBS = phosphate buffer solution

Table 4

Sample results ($\mu g L^{-1}$) from different types of water samples for Cd^{2+}

	Sample 1		Sample 2		Sample 3		Sample 4	
	wastewater		surface water		drinking water from spring water		groundwater	
	ASV	ICP-OES	ASV	ICP-OES	ASV	ICP-OES	ASV	ICP-OES
G	0.46±0.002	0.5	0.46±0.002	0.5	0.49±0.003	0.5	0.36±0.002	0.4
Fe(II)Pc/G	0.48±0.003	0.5	0.43±0.001	0.5	0.44±0.003	0.5	0.37±0.001	0.4
Ni(II)Pc/G	0.45±0.002	0.5	0.47±0.004	0.5	0.47±0.003	0.5	0.38±0.003	0.4
Mn(III)TPP/G	0.48±0.002	0.5	0.47±0.002	0.5	0.49±0.004	0.5	0.39±0.008	0.4
GR	0.45±0.003	0.5	0.47±0.002	0.5	0.46±0.004	0.5	0.37±0.004	0.4
Fe(II)Pc/GR	0.46±0.004	0.5	0.46±0.002	0.5	0.46±0.002	0.5	0.37±0.004	0.4
Ni(II)Pc/GR	0.46±0.028	0.5	0.46±0.017	0.5	0.49±0.011	0.5	0.38±0.022	0.4
Mn(III)TPP/GR	0.45±0.005	0.5	0.43±0.005	0.5	0.46±0.005	0.5	0.35±0.004	0.4

ASV = anodic stripping voltammetry

ICP-OES = Inductively coupled plasma atomic emission spectroscopy

Relative standard deviation for 5 measurements (n=5)

Table 5

Sample results ($\mu g L^{-1}$) from different types of water samples for Pb^{2+}

	Sample 1		Sample 2		Sample 3		Sample 4	
	wastewater		surface water		drinking water from spring water		groundwater	
	ASV	ICP-OES	ASV*	ICP-OES	ASV*	ICP-OES	ASV*	ICP-OES
G	5.46±0.157	5.5	1.37±0.092	1.40	1.04±0.081	1.10	0.58±0.113	0.6
Fe(II)Pc/G	5.49±0.277	5.5	1.39±0.062	1.40	1.09±0.007	1.10	0.59±0.012	0.6
Ni(II)Pc/G	5.48±0.291	5.5	1.38±0.095	1.40	1.04±0.034	1.10	0.48±0.0223	0.6
Mn(III)TPP/G	5.16±0.138	5.5	1.35±0.109	1.40	1.09±0.045	1.10	0.53±0.073	0.6
GR	5.41±0.102	5.5	1.34±0.053	1.40	0.90±0.009	1.10	0.55±0.008	0.6
Fe(II)Pc/GR	5.42±0.193	5.5	1.36±0.078	1.40	1.02±0.014	1.10	0.59±0.0159	0.6
Ni(II)Pc/GR	5.31±0.201	5.5	1.38±0.041	1.40	0.98±0.037	1.10	0.58±0.0162	0.6
Mn(III)TPP/GR	5.21±0.179	5.5	1.35±0.069	1.40	1.06±0.059	1.10	0.54±0.0521	0.6

ASV = anodic stripping voltammetry

ICP-OES = Inductively coupled plasma atomic emission spectroscopy

Relative standard deviation for 5 measurements (n=5)

CONCLUSION

Several dot microsenors based on graphite or graphene unmodified or modified with Fe(II)Pc, Ni(II)Pc and Mn(III)TPP were proposed for the

determination of Cd^{2+} and Pb^{2+} ions. It can be seen that for all dot microsenors good correlation coefficients were obtained. The highest sensitivity for the dot microsenors was recorded for Pb^{2+} ions, in comparison with the determination for the

Cd^{2+} ions. A good separation was obtained as expected. All dot microsensors have good results for the determination of Cd^{2+} and Pb^{2+} ions in various water catchments areas.

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