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Nanostructured materials for sensing Pb(II) and Cd(II) ions: manganese oxyhydroxide *versus* carbonized polyanilines

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Abstract: Nanostructured materials including three different carbonized polyanilines and manganese oxyhydroxide were prepared and evaluated as electrode materials for sensing of lead and cadmium ions in aqueous media. Anodic stripping voltammetry results indicated that all prepared materials could be successfully used for determination of these two heavy metal ions. Carbonized polyaniline-based electrodes have higher signal and lower limits of detection (10^{-7} M) compared to manganese oxyhydroxide-based electrode. Among the three studied carbonized polyanilines, the one that was derived from polyaniline precursor produced in the presence of 3,5-dinitrosalicylic acid showed the highest electrocatalytic activity towards the lead and cadmium oxidation.

Keywords: lead ions; cadmium ions; carbonized nanostructured polyaniline; manganese oxyhydroxide; electrochemical sensors.

INTRODUCTION

Sensing of heavy metal ions in aqueous media, with lead (Pb^{2+}) and cadmium (Cd^{2+}) ions being the major metal pollutants, is one of the priority tasks in environmental monitoring. Lead has been introduced into the environment during automotive leaded fuel burning, as well as during lead mining, smelting and refining processes. Lead–acid batteries, paints and tin can solders represent further sources of lead in the environment, while nickel–cadmium batteries, cadmium pigmented plastics, ceramics, glasses, paints and enamels are major sources of cadmium.¹ Their consequent accumulation in the environment poses a serious risk to human health and safety.² Heavy metal ions are known to be non-biodegradable; for instance, lead in bone has a half-life of more than 20 years, while cadmium has a biological life of 10 to 30 years.³ The level of heavy metals

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toxicity mostly depends on their chemical forms and exposure levels.⁴ Lead poisoning was reported to be one of the most common environmental child health threats that can cause serious physical and mental problems, including brain and kidney damage, mental retardation, behavior problems and development delays.⁵

It has been estimated that nearly 20 % of human exposure to lead occurs through the consumption of contaminated drinking water.⁶ Therefore, the monitoring of these heavy metal ions in water resources is essential. Current methods for sensing of Pb^{2+} and Cd^{2+} include atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS) and X-ray fluorescence spectrophotometry.⁷⁻⁹ Although these methods show satisfactory sensitivity, they have the drawbacks of using expensive equipment in controlled laboratory conditions and requiring sample preparation and relatively large sample volumes.

On the other hand, electroanalytical methods offer not only high sensitivity but also intrinsic miniaturization and portability along with low cost.¹⁰⁻¹³ Stripping voltammetry techniques employing a mercury (Hg) electrode were found to allow the detection of trace heavy metals.¹⁴⁻¹⁶ However, the high toxicity of Hg has initiated the search for novel electrode materials for the sensing of heavy metal ions and different materials such as bismuth (Bi),¹⁷⁻¹⁹ gold (Au),²⁰ silver (Ag),²⁰ antimony (Sb),²¹ carbon (C),^{22,23} and boron-doped diamond (BDD)^{24,25} have been investigated.

Herein, the sensing of Pb^{2+} and Cd^{2+} has been explored employing four different electrode materials. The electrodes chosen for the study were glassy carbon electrode (GCE) modified with manganese oxyhydroxide (MnOOH) and GCE modified with three different carbonized nanostructured polyanilines (c-PANIs). The interest in studying a manganese oxide-based electrode arose from studies reporting the successful employment of carbon-supported manganese oxide electrodes for electroanalysis of different analytes, such as hydrogen peroxide, nitrite ions and ascorbic acid.²⁶⁻²⁹ Manganese oxides are economic, non-toxic and abundant.³⁰⁻³² They are present in a wide range of various crystal structures and their composition rarely corresponds to the stoichiometric formula but rather contains Mn in different oxidation states. The MnOOH studied herein has found application in rechargeable batteries, but it still has not been broadly investigated for application in electroanalysis. During a recent study of the sensing of the two named ions on composites of MnO_2 with different carbon materials, it was indicated that c-PANI (produced by the carbonization of PANI doped with 5-sulfosalicylic acid) showed activity for their sensing.³³ PANI in general has attracted significant attention during the last three decades due to its simple and inexpensive synthesis, acid-doping/base-dedoping chemistry, high stability and conductivity.³⁴ Carbonization of polyaniline and other N-containing aromatic polymers appeared during recent years as an efficient and simple way to produce new

N-containing (nano)materials with mainly preserved morphology of the polymer precursor and changed/improved physico-chemical properties, such as increased conductivity, specific surface area or pore volume, desirable for a variety of applications.^{34–40} It was shown that nanostructured c-PANIs exhibit excellent electrocatalytic properties toward oxygen reduction³⁹ and also represent promising materials for electrochemical capacitors.³⁷ The properties of c-PANI materials can be tuned by the protonation level, oxidation state, type of counter ions and morphology of PANI precursors.^{35–38}

The idea behind this study was to gather analytical information about the oxidation of Pb^{2+} and Cd^{2+} at MnOOH and different c-PANI electrodes, such as limit of detection (*LOD*), linear range response and reproducibility, and to compare their performances.

EXPERIMENTAL

Carbonized nanostructured PANIs were prepared by the procedures reported in previous works.^{35–38} PANI precursor salts were made by the gram-scale template-free oxidative polymerization of aniline with ammonium peroxydisulfate as an oxidant in three different media: a) in water (PANI),^{35,37} b) in 5-sulfosalicylic acid (SSA) aqueous solution (PANI–SSA)^{36,37} and c) in 3,5-dinitrosalicylic acid (DNSA) aqueous solution (PANI–DNSA).^{37,38} Subsequently, the precursors were carbonized by gradual heating in a nitrogen atmosphere up to 800 °C at a heating rate of 10 °C min⁻¹ to obtain c-PANI,^{35,37} c-PANI–SSA^{36,37} and c-PANI–DNSA,^{36,38} respectively. Detail characterization of the prepared materials was previously carried out using several physico-chemical techniques, including X-ray diffraction (XRD) analysis, scanning (SEM) and transmission (TEM) electron microscopy, Raman and Fourier transform infra-red spectroscopy.^{37,39}

Synthesis of MnOOH nanorods was done by oxidizing the saturated manganese sulphate aqueous solution by adding drop by drop of 10% hydrogen peroxide solution until the end of precipitation.

Catalytic ink was prepared by adding 4 mg of one of the investigated materials (c-PANI, c-PANI–SSA, c-PANI–DNSA or MnOOH) into 1 mL of a 2:3 water–ethanol mixture, followed by homogenization in an ultrasonic bath for 30 min. The working electrodes were prepared by pipetting 10 μl of a catalytic ink onto polished glassy carbon tip (5 mm diameter) and leaving the solvents to evaporate at room temperature.

Platinum (Pt) foil and saturated calomel electrode (SCE) served as the counter and reference electrode, respectively. All potentials in the paper are expressed *vs.* SCE. All electrochemical measurements were performed using Gamry PCI4/750 potentiostat, employing a cell of 15 cm³ volume. The supporting electrolyte was 20 mM H_2SO_4 + 30 mM KCl and all studies were performed at room temperature, without removal of oxygen from the supporting electrolyte.

Electroanalytical sensing of Pb^{2+} and Cd^{2+} was carried out using anodic stripping voltammetry. The electrode was kept at a potential of –1.3 V during the 120 s deposition step, with the electrolyte solution being stirred. Subsequently, the potential was swept in the anodic direction up to +0.6 V with no solution stirring. The same measurement was performed for a series of aqueous solutions of Pb^{2+} and Cd^{2+} with concentrations ranging from 5 to 100 μM .

RESULTS AND DISCUSSION

Pb²⁺ and Cd²⁺ sensing using the MnOOH-based electrode

Sensing of Pb²⁺ and Cd²⁺ employing MnOOH/GCE electrode was first studied. Linear scan voltammograms (LSVs) were initially separately recorded in 100 μM Pb²⁺ solution and 100 μM Cd²⁺ solution in the range from -1.3 to 0.6 V at a scan rate of 50 mV s⁻¹ (Fig. 1A). On each of the two LSVs, a clear peak originating from the oxidation of the corresponding heavy metal could be seen, *i.e.* a peak at *ca.* -0.46 V for Pb oxidation and a peak at *ca.* -0.69 V for Cd oxidation (Fig. 1A). Furthermore, it could be noticed that the Cd oxidation peak current (*I_p*) was *ca.* 33 % higher than that arising from Pb oxidation. No peak was observed in the LSV recorded on MnOOH/GCE in the absence of the studied heavy metal ions.

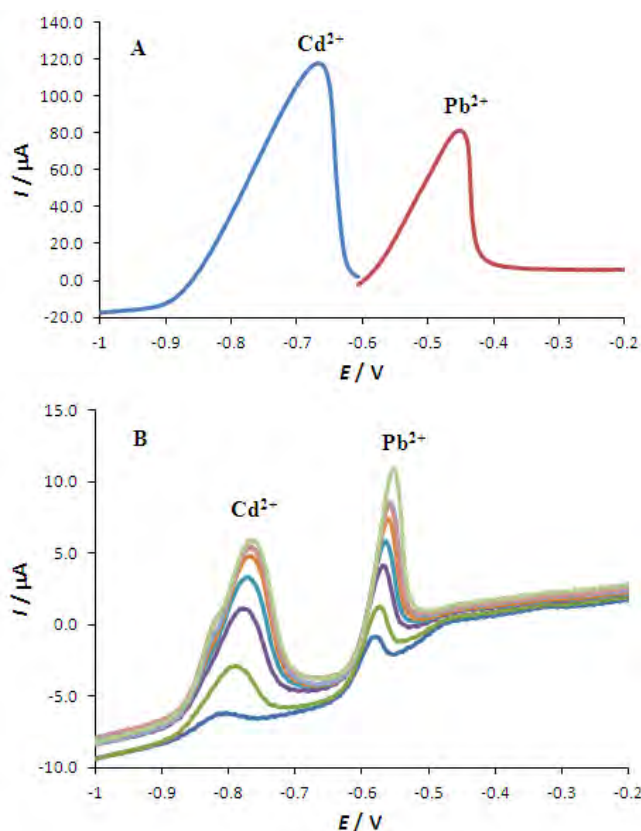


Fig. 1. A – LSVs of MnOOH/GCE recorded in 100 μM Pb²⁺ and Cd²⁺ solution in 20 mM H₂SO₄ + 30 mM KCl supporting electrolyte at a scan rate of 50 mV s⁻¹; B – increase in the peak currents of Pb and Cd oxidation with increasing concentration of heavy metal ions (between 5 and 40 μM). *E* in V vs. SCE.

Subsequently, the LSV was recorded on MnOOH/GCE in a solution containing both Pb^{2+} and Cd^{2+} in order to examine the possibility of the simultaneous detection of the two heavy metal ions and two distinct peaks could still be observed (Fig. 1B). The appearance of oxidation peaks of Pb and Cd at potentials that are *ca.* 0.25 V apart offers the possibility for the simultaneous detection of the two heavy metal ions with no mutual interference at MnOOH/GCE. Furthermore, good reproducibility of the signal was observed with the standard deviation of 6.8 % calculated for repeated measurements using a sample of constant concentration of 100 μM Pb^{2+} and Cd^{2+} ($n = 20$).

Next, the linear range and limits of detection of Pb^{2+} and Cd^{2+} sensing using the MnOOH-based electrode were determined. For these purposes, the blank solution was spiked with 5 μM additions of the two heavy metal ions and the recorded peak currents were observed to increase linearly with heavy metal ions concentration (*c*). The linear ranges were found to be limited up to 50 μM concentrations of the ions, which was reduced compared to linear ranges obtained when only one of the two studied heavy metal ions was present in the solution. The *LOD* values were calculated using 3σ method:

$$LOD = 3\sigma/b \quad (1)$$

where σ is the standard deviation of the regression line and b is the slope, *i.e.* sensitivity. The *LOD* values for Pb^{2+} and Cd^{2+} using the GCE modified with MnOOH were found to be 3.7 and 2.2 μM , respectively, and sensitivity to be 0.008 and 0.029 AM^{-1} , respectively. These *LOD* values are comparable with those obtained employing different electrodes (Table I). It should be mentioned that further improvement of MnOOH/GCE performance for sensing of the two

TABLE I. Comparison of the performance of different electrochemical sensors of various electrode materials for the sensing of Pb^{2+} and Cd^{2+} ; PolyL – poly(4-azulen-1-yl-2,6-bis(2-thiethyl)pyridine), GCD – glassy carbon disc, BDD – boron doped diamond, CPE – carbon paste electrode, SPE – screen printed electrode

Electrode	Pb^{2+}		Cd^{2+}	
	<i>LOD</i>	Deposition time, s	<i>LOD</i>	Deposition time, s
Bi-Modified Cu mini-sensor ⁴¹	8.3×10^{-7} M	120	5.3×10^{-7} M	150
PolyL film-modified GCD ⁴²	7×10^{-10} M	600	1×10^{-8} M	600
Sb-BDD ⁴³	25.4 $\mu\text{g L}^{-1}$	–	38.1 $\mu\text{g L}^{-1}$	–
Zeolite-modified CPE ⁴⁴	3.6 $\mu\text{g L}^{-1}$	–	1 $\mu\text{g L}^{-1}$	–
Benzoic acid-modified GCE ⁴⁵	0.2 $\mu\text{g L}^{-1}$	–	0.13 $\mu\text{g L}^{-1}$	–
Au-SP sensor ⁴⁶	0.5 $\mu\text{g L}^{-1}$	120	1.4 $\mu\text{g L}^{-1}$	120
BDD ^{47,48}	2 nM	900	2.5×10^{-8} M	60
			3.9×10^{-9} M	
SP microarrays ⁴⁹	3 μM	120	–	–
Nafion-modified GCE ⁵⁰	3 ppb	600	–	–
Nafion [®] -SPE ⁵¹	15 $\mu\text{g L}^{-1}$	–	–	–

heavy metal ions could be achieved by optimizing the experimental conditions, including solution pH, and deposition potential and time. For instance, relatively short deposition time of 120 s was used throughout this study as could be seen from comparison with some of those given in Table I.

A further study was performed in order to confirm the potential application of the investigated MnOOH-based electrode for heavy metal ions sensing in real samples. LSVs were recorded in a solution made with tap water. With no optimization of experimental conditions, such as optimization of solution pH value, two distinct peaks could still be observed (Fig. 2). The oxidation peak of Pb was somewhat suppressed in the studied solution as evidenced by smaller peak currents recorded, but was still clearly visible.

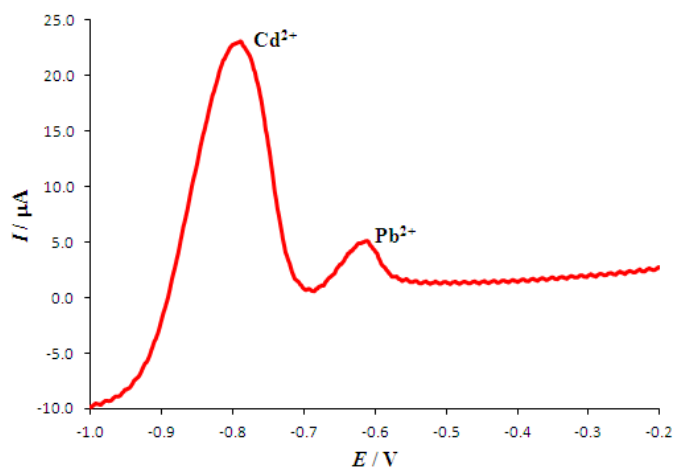


Fig. 2. LSV of MnOOH/GCE recorded in 25 μM Pb^{2+} and Cd^{2+} solutions in tap water at a scan rate of 50 mV s^{-1} ; E in V vs. SCE.

Pb²⁺ and Cd²⁺ sensing using c-PANIs-based electrodes

Control voltammograms of GCE modified with one of the three studied c-PANIs were recorded in the supporting electrolyte in the range from -1.3 to $+0.6$ V at a scan rate of 50 mV s^{-1} . The LSVs of all three electrodes showed no peaks in the absence of Pb^{2+} and Cd^{2+} . Upon the addition of 100 μM Pb^{2+} and Cd^{2+} , two clear peaks, at -0.37 and -0.64 V, could be seen at the LSVs of the GCE modified with each of c-PANI based electrodes (Fig. 3). In the case of c-PANI electrodes, the peak at -0.37 V, originating from Pb oxidation, was of significantly higher intensity compared to the peak at -0.67 V, corresponding to Cd oxidation. It should also be mentioned that only a small Pb oxidation peak could be observed on the LSV of the unmodified GCE, with no appearance of a Cd oxidation peak.

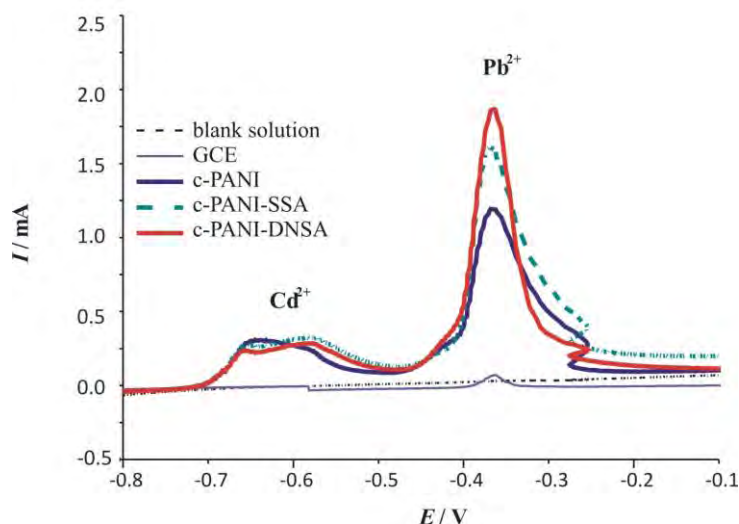


Fig. 3. LSVs of unmodified GCE and GCE modified with three different c-PANIs in 100 μM Pb^{2+} and Cd^{2+} solution in 20 mM H_2SO_4 + 30 mM KCl supporting electrolyte. A control voltammogram recorded in the absence of heavy metal ions is also presented; E in V vs. SCE.

The highest Pb oxidation peak current was obtained at the c-PANI–DNSA-based electrode, indicating its highest activity for the detection of the heavy metal ions. Peak current at the c-PANI–DNSA/GCE was *ca.* 17 % higher than that obtained at the c-PANI–SSA/GCE and 57 % higher than that recorded at c-PANI/GCE for the same Pb^{2+} concentration. This is most likely due to the high specific surface area S_{BET} of PANI–DNSA ($441 \text{ m}^2 \text{ g}^{-1}$ compared to $322 \text{ m}^2 \text{ g}^{-1}$ in case of c-PANI and $317 \text{ m}^2 \text{ g}^{-1}$ of c-PANI–SSA),³⁷ providing a high contact area for Pb^{2+} and Cd^{2+} during the deposition step. Other factors determining electroactivity of the c-PANIs include their structural and morphological properties, the presence of functional groups at their surface, and their pore structure and electronic structures. Peak currents corresponding to Cd oxidation were practically the same at all three studied carbonaceous electrodes. Using voltammetric sample of constant concentration of 100 μM Pb^{2+} and Cd^{2+} ($n = 20$), the standard deviation was found to be 7.2 %.

Compared to the MnOOH -based electrode, the first peak corresponding to Pb oxidation appeared at a somewhat less negative potential at the c-PANI-based electrodes, while the second peak corresponding to Cd oxidation was found at almost the same potential as at the MnOOH /GCE. Comparison of peak currents showed that the currents obtained at the electrodes based on the c-PANIs were one order of magnitude higher than those recorded at the MnOOH -based electrode. Significantly higher peak currents at the nitrogen containing carbon-based electrodes than at the manganese oxide-based electrode could be due to the diffe-

rence in the surface area of the materials. Manganese oxide electrocatalysts are reported to be active but they often suffer from having a small surface area and, in order to increase their electrochemical response, they have to be grafted onto carbon or other high surface supports.

Subsequently, the supporting electrolyte was spiked with 10 μM additions of the two heavy metal ions. The increase in the peak currents with increasing of Pb^{2+} and Cd^{2+} concentrations obtained at the c-PANI–DNSA/GCE are shown in Fig. 4, together with the corresponding I_p vs. C linear response plots in range up to a 100 μM solution. LOD values were calculated using the 3σ method (Eq. (1)) and are given in Table II. The lowest LOD of Pb^{2+} was obtained at the c-PANI–DNSA/GCE (0.58 μM), while lowest LOD of Cd^{2+} was obtained at the c-PANI/GCE (0.50 μM). The obtained results indicate that by choosing the right experimental conditions, c-PANI-based electrodes have potential application for the determination of the two heavy metal ions in aqueous media, offering a great benefit of eliminating use of mercury electrodes.

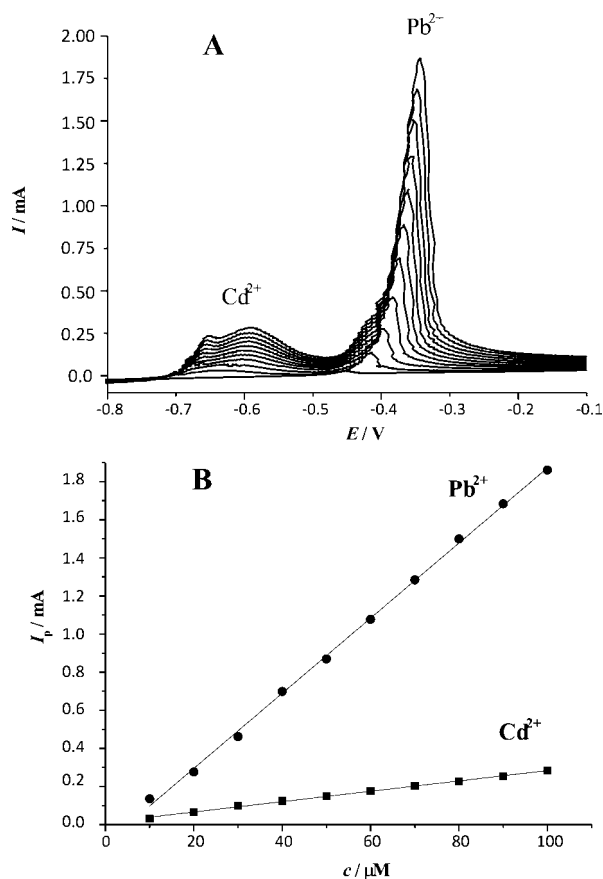


Fig. 4. A – Increase in the voltammetric response of the c-PANI–DNSA electrode with increasing Pb^{2+} and Cd^{2+} concentration from 0 to 100 μM ; B – linear dependences of peak current on the concentrations of the ions.

TABLE II. Limits of detection (μM) of Pb^{2+} and Cd^{2+} in aqueous media obtained using a GCE modified with MnOOH or different c-PANIs

Ion	MnOOH	c-PANI-SSA	c-PANI-DNSA	c-PANI
Pb^{2+}	3.70	0.69	0.58	1.70
Cd^{2+}	2.20	0.93	0.72	0.50

Other nanostructured carbon materials, including carbon nanoparticles, carbon nanotubes (CNTs), graphenes and fullerenes have been explored as electrode modifiers or electrode materials for the sensing of heavy metal ions and have shown themselves to be quite promising.^{52,53} Among them, CNTs have attracted the most attention due to their high electro-activity, originating from their high surface area and the presence of a high number of edge plane sites. Compared to CNTs, c-PANIs have the advantage of simpler and less expensive synthesis procedures, while still being characterized with high surface areas and number of edge plane sites.

CONCLUSIONS

Three different nanostructured carbonized polyanilines and nanostructured manganese oxyhydroxide were synthesized and examined with respect of their electrocatalytic activity in the sensing of lead and cadmium ions in aqueous solutions. Anodic stripping voltammetry showed that all the prepared electrodes gave a clear response corresponding to the oxidation of the two heavy metals. The method was further quantitatively evaluated and the limits of detection were found to be comparable to those reported in the literature for different electrochemical sensors. Comparison between peak currents recorded at MnOOH- and c-PANI-modified electrodes revealed significantly higher currents in the case of the c-PANIs. Among the three studied c-PANIs, c-PANI-DNSA gave the highest signal for Pb oxidation and lowest limit of detection, while response for Cd oxidation was similar at all three materials. The obtained results indicate that c-PANIs could be used for the fabrication of low-cost, rapid and sensitive electrochemical sensors for lead and cadmium ions determination.

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ИЗВОД

НАНОСТРУКТУРНИ МАТЕРИЈАЛИ ЗА ДЕТЕКЦИЈУ Pb(II) И Cd(II) ЈОНА: МАНГАН-ОКСИДИДРОКСИД И КАРБЕНИЗОВАНИ ПОЛИАНИЛИНИ

БИЈАНА ШЉУКИЋ, ДАРКО МИЦИЋ, НИКОЛА ЦВЈЕТИЋАНИН И ГОРДАНА БИРИЋ-МАРЈАНОВИЋ
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Наноструктурни материјали, укључујући три различита карбенизована полианилина као и манган-оксиидроксида, су синтетисани и испитани као електродни матери-

јали за одређивање јона олова и кадмијума у воденим срединама. Резултати анодне „stripping“ волтаметрије су показали да сви припремљени материјали имају потенцијалну примену у одређивању јона ова два тешка метала. Електроде на бази карбонизованих полианилина дале су значајно већи сигнал и ниже границе детекције (ред величине 10^{-7} М) него електрода на бази манган-оксихидроксида. Међу три испитивана карбонизована полианилина, материјал који је добијен карбонизацијом полианилина синтетисаног у присуству 3,5-динитросалицилне киселине је показао највећу електрокаталитичку активност за оксидацију олова и кадмијума.

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