

Organofunctionalized Mesoporous Silica Carbon Paste Electrode for Simultaneously Determination of Copper, Lead and Cadmium

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A new sensor has been developed for the simultaneous detection of copper, lead and cadmium, using square wave anodic stripping voltammetry (SWASV) at a carbon paste electrode modified with HMS mesoporous silica functionalized with acetyl-acetone by covalent coupling (AcAcNH₂-HMS). The heavy metal ions were preconcentrated on the surface of electrode where they complex with acetyl acetone ligand and are reduced to the metals and then reoxidized. The effects of several parameters were studied and the best results were obtained under the following conditions: - 1.1 V vs. SCE preconcentration potential, 210 s preconcentration time in Britton-Robinson buffer solution (pH 5.02). Optimum SWASV conditions lead to calibration plots with Nernstian slopes over a wide linear concentration range (0.01-1.1 ppm for Cu²⁺, 0.03-0.9 ppm for Pb²⁺ and 0.1-1.3 ppm for Cd²⁺) and ppb detection limits. The precision and accuracy were also investigated. The electrode was used for waste water analysis using standard addition method obtaining accurate results.

Keywords: copper, lead, cadmium; modified carbon paste electrode; organofunctionalized silica; square wave anodic stripping voltammetry

The environmental contamination with copper, lead and cadmium is a major concern worldwide because of the toxicity of these metals and their negative effects on the human health. They can easily enter in the aquatic systems by infiltrating into the soil and then leaching into the groundwater or by means of various industrial applications.

Copper is essential for the human body metabolism at a trace level (it has catalytic action in hem synthesis). Exposure to high levels of copper leads to eyes and skin irritation. The ingestion can cause cramps, stomach and intestinal irritation, liver and kidney damage, anemia, coma and even death.

Cadmium has been used extensively in industry in the production of pigments, anti-corrosion coatings, plastics, alloys and batteries. It presents great toxicological interest due to its long half-life and accumulation in soft tissues, especially in kidney and liver.

Lead pollution is one of the most serious environmental problems because of its stability in contaminated sites and the complex mechanism in the biological toxicity. Lead intoxication can cause irreversible neurological damage, renal diseases and cardiovascular effects.

Since these metals are not biodegradable, they can accumulate in vital organs, progressively exerting increasing toxic actions. This is why the regular monitoring of copper, lead and cadmium concentrations in different environmental samples is essential for the benefit of the human health.

Quantitative determination of these metals using techniques as atomic absorption spectrometry (AAS), *inductively coupled plasma mass spectroscopy* (ICP-MS) or gas chromatography (GC) is expensive.

Electrochemical techniques have certain advantages: are simpler, sensitive, precise, present a fast response and imply lower financial costs. Among these, electrochemical stripping voltammetry is frequently used, its advantage

being the lower detection limits due to the preconcentration step.

Currently, free-mercury chemically modified electrodes are used in stripping voltammetry, the modifier being employed to a better preconcentration of the analyte prior to its electrochemical detection.

Carbon paste electrode represents a convenient conductive matrix to prepare chemically modified electrodes by mixing the carbon paste with the modifier. These electrodes are inexpensive, present low background currents and wide range of used potentials, are easily prepared and can be rapidly regenerated by simple mechanical polishing [1-4].

Among the various modifiers of carbon paste electrodes, silica based materials showed growing interest in the last years. Ordered mesoporous silica based materials present special textural characteristics: high porosity, uniform pore size distribution, high surface areas and ordered pore arrangement. Hexagonal mesoporous silica (HMS) is one of the most important mesoporous materials used as adsorbents, separation membranes, catalyst supports. Attractive properties (great adsorption capacity, easy facial diffusion of analytes, fast sorption kinetics) of the mesoporous silica can be advantageously exploited in the accumulation of electroactive analytes before their electrochemical detection [5-7].

The possibility of silica surface functionalization with a variety of functional groups or ligands allows selectively sequestering a specific target species. By using these hybrid organic-inorganic materials, different modified carbon paste electrodes, applied for quantitative determination of copper [8-10], cadmium [11, 12] and lead [13-15] have been obtained. There was also studied the simultaneous determination of these metals [16-20] or of some of them along with mercury [21-23].

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The acetylacetonate anion (AcAc⁻) complexes by bonding each oxygen atom to the metallic cation to form a chelate ring. Because of this property, some acetylacetonates are commonly used in various catalysts and catalytic reagents for organic synthesis. Many researches have focused on the catalytic applications of acetylacetonates immobilized into mesoporous silica as catalysts [24, 25]. Acetylacetone bonded polyurethane foam sorbent was used for lead and cadmium preconcentration before their determination in tap water and apple leaves [26]. However, there are no reports about simultaneous determination of copper, cadmium and lead by using AcAc modified electrode.

In previous studies, individual quantitative determination of copper [27], cadmium [28] and lead [29], respectively, from natural and waste water samples using carbon paste electrodes modified with acetyl-acetone functionalized mesoporous silica by covalent coupling (AcAcNH₂-HMS) were reported.

This study presents the simultaneous quantitative determination of copper, lead and cadmium from waste water samples by square wave anodic stripping voltammetry (SWASV) in optimized conditions, using the acetyl-acetone functionalized mesoporous silica (AcAcNH₂-HMS) modified carbon paste electrode.

Experimental part

Reagents and solutions

All the solutions were prepared with double-distilled water. The supporting electrolyte for voltammetric experiments was a Britton-Robinson buffer solution. All the chemicals (CH₃COOH, H₃BO₃, H₃PO₄, NaOH) were of analytical grade. "Certipur" (Merck) stock solutions containing 1000 µg·L⁻¹ Cu²⁺, 1000 µg·L⁻¹ Cd²⁺ and 1000 µg·L⁻¹ Pb²⁺, respectively, were used for daily preparation of multicomponent working standard solutions by appropriate dilution.

Dodecylamine (Aldrich), tetraethoxysilane (TEOS) (Fluka), 3-aminopropyl-triethoxysilane (APTES) (Aldrich) and 3-bromo-2,4-pentandione were used for the synthesis and functionalization of the HMS mesoporous silica.

Graphite powder (with particles diameter < 20 µm) (Fluka) and paraffin oil (Merck) were used for the preparation of carbon paste electrodes.

High purity argon (Linde Gas 5.0) was used for solutions deaeration.

Apparatus

All the voltammetric measurements were carried out with a voltammetric analyzer Voltalab PST 050 Radiometer, controlled by the VoltaMaster 4.0 software, in a 20 mL cell equipped with a AcAcNH₂-HMS modified carbon paste electrode as working electrode, a saturated calomel as reference electrode (SCE) and a platinum wire as auxiliary electrode.

Preparation of the modified carbon paste electrodes

For modifying the carbon paste electrode, hexagonal mesoporous silica (HMS) was synthesised using dodecylamine as a template, TEOS as a silica precursor and ethanol as co-solvent by a procedure reported in a previous work [27]. For the acetyl-acetone functionalized HMS silica, the HMS silica was firstly silanized with APTES. Thereafter, the NH₂-HMS solid was reacted with 3-bromo-2,4-pentandione in order to obtain the AcAcNH₂-HMS mesoporous silica by a procedure already reported [27].

Organofunctionalized HMS modified carbon paste electrodes were prepared by homogenous mixing

AcAcNH₂-HMS with carbon powder at a typical ratio (1:6). Subsequently, paraffin oil was added, mixing thoroughly to obtain a homogenous paste. The carbon paste electrode was finally obtained by packing the paste into a plastic tube (2 mm interior diameter). A copper wire served as an external electric contact. The surface was smoothed on a weighing paper. When necessary, a new surface was obtained by pushing an excess of paste out of the tube, removing this excess, and again mechanically polishing the electrode surface. For comparison purposes, an unmodified carbon paste electrode was prepared using the same procedure.

Voltammetric analysis procedure

A Britton-Robinson buffer solution was used as a supporting electrolyte for the determinations. The Cu²⁺, Pb²⁺, Cd²⁺ multicomponent solution was deaerated with high purity argon for 5 min. If not stated otherwise, the measurements were carried out at pH 5.02, after a preconcentration step, in which the solution was stirred during the preconcentration time of 210 s at preconcentration potential of -1.1 V. After a rest period, the response curve was recorded by scanning the potential in the positive direction using square wave anodic stripping voltammetry (SWASV) technique (50 mV/s scan rate, 50 mV pulse amplitude, 1 mV ramp step amplitude, 0.02 s ramp step duration).

For the copper, cadmium and lead determination from waste waters, the filtered sample was mixed with the same volume of Britton-Robinson buffer solution (pH 5.02). The sample was analyzed in triplicate. In order to eliminate the interferences and the matrix effect standard addition method was used (3 additions).

Results and discussions

Functionalized mesoporous silicas are suitable modifiers to prepare chemically modified carbon paste electrodes. The chelation of acetylacetone with metal ions in solution has been previously studied [30]. AcAc was immobilized on the surface of the amino-functionalized HMS silica by covalent coupling. Due to the high surface area and strong adsorption ability of the mesoporous silica, effective reaction sites of AcAc with metal ions are considerably increased. Therefore, AcAcNH₂-HMS modified electrodes exhibit better adsorptive preconcentration capability, higher sensibility and selectivity than the electrodes modified only with HMS silica or the unmodified ones.

Previous studies [27-29] showed that AcAcNH₂-HMS can be used as modifier to prepare electrodes applied with success for individual voltammetric determination of Cu²⁺, Cd²⁺ and Pb²⁺, respectively. To achieve the accurate simultaneous determination of Cu²⁺, Pb²⁺, Cd²⁺ based on their voltammetric response at a carbon paste electrode modified with the above mentioned hybrid ligand-silica material, in this study the optimization of some parameters was performed.

Preconcentration potential, pH and preconcentration time influences

The effect of the preconcentration potential on the voltammetric responses obtained from the 0.5 ppm (each) multicomponent Cu²⁺, Cd²⁺, Pb²⁺ solution was observed in a preliminary study using the AcAcNH₂-HMS modified carbon paste electrode. The results are presented in figure 1.

Analyzing the obtained data, the preconcentration potential value of -1.1 V vs. SCE was considered the best preconcentration potential, regarding not only the values

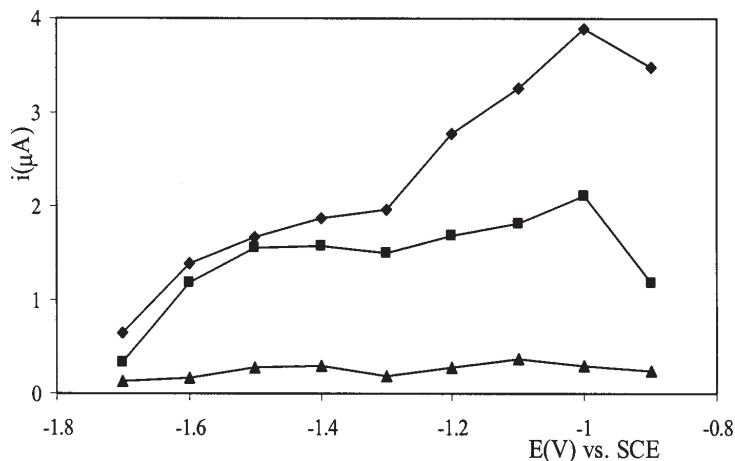


Fig. 1. The influence of the preconcentration potential on stripping peak currents intensities for 0.5 ppm (each) multicomponent Cu^{2+} (♦), Pb^{2+} (■) and Cd^{2+} (▲) solution, pH 6.80 Britton-Robinson buffer, preconcentration time 120 s

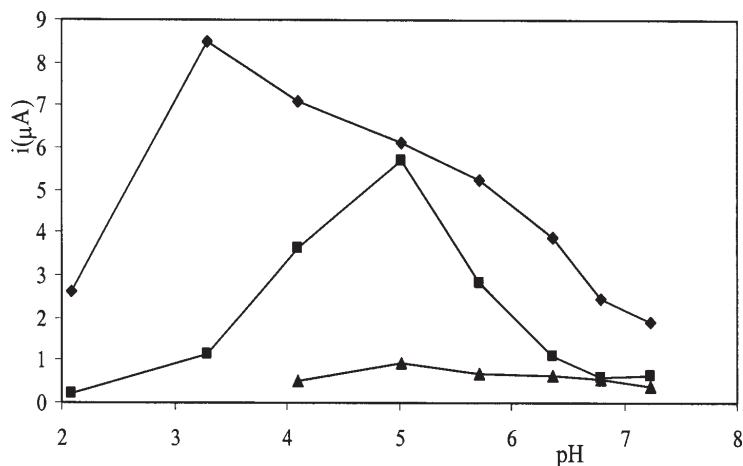


Fig. 2. Anodic peak currents intensities dependencies on the pH value for 0.5 ppm (each) multicomponent Cu^{2+} (♦), Pb^{2+} (■) and Cd^{2+} (▲) solution, in Britton-Robinson buffer, preconcentration potential -1.1 V vs. SCE, preconcentration time 120 s

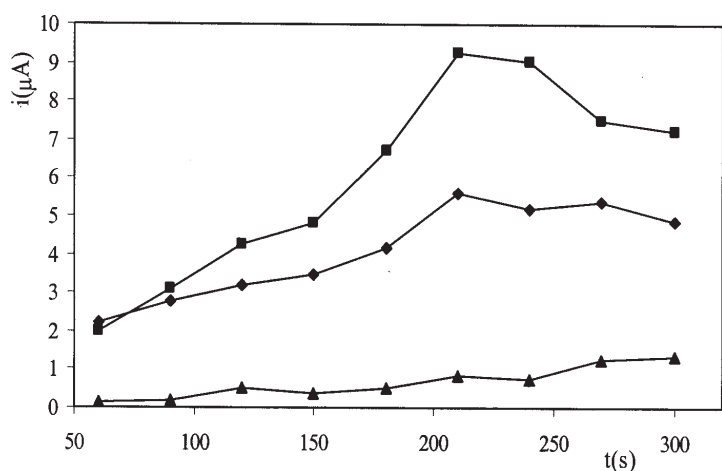


Fig. 3. Anodic peak currents intensities dependencies on the preconcentration time for 0.5 ppm (each) multicomponent Cu^{2+} (♦), Pb^{2+} (■) and Cd^{2+} (▲) solution, in Britton-Robinson buffer (pH 5.02), preconcentration potential -1.1 V vs. SC

of the current intensities, but also the shapes of the peaks and the allures of the voltammograms. This value was used in all subsequently studies.

Taking into account that in all previous studies [27-29] a Britton-Robinson buffer solution (with different pH values) was used as supporting electrolyte for voltammetric experiments, the same electrolyte was employed to study the peak currents intensities dependencies on the pH variation. The obtained results for the pH values within 2.09 - 7.24 range are presented in figure 2.

As it can be seen from figure 2, for Cu^{2+} the peak current increased very rapidly with pH increasing from 2.09 to 3.29 and then decreased slowly; for Pb^{2+} it increased relatively rapidly with pH increasing from 2.09 to 5.02 and then decreased. In the case of Cd^{2+} the peak appeared only at pH values above 4, reaching a maximum value at 5.02. At this pH (5.02) all three peaks are well defined and shaped.

In conclusion, the optimal pH value chosen and used for further studies was 5.02.

The influence of the preconcentration time on the anodic peak currents intensities for 0.5 ppm (each) multicomponent Cu^{2+} , Cd^{2+} , Pb^{2+} solution was also examined (fig. 3).

In the case of Cu^{2+} and Pb^{2+} , anodic peak currents intensities increased proportionally with time from 60 to 210 s (the AcAcNH_2 -HMS modified electrode has a high content of functional groups) and then remained almost constant or even decreased, due to electrode surface saturation. For Cd^{2+} , the anodic peak current intensity presented smaller increases with time, but the increase was from 60 to 300 s. For all subsequent measurements a 210 s preconcentration time was used, the value being a compromise between measurement sensitivity, analysis time and the resolution of the adjacent peaks.

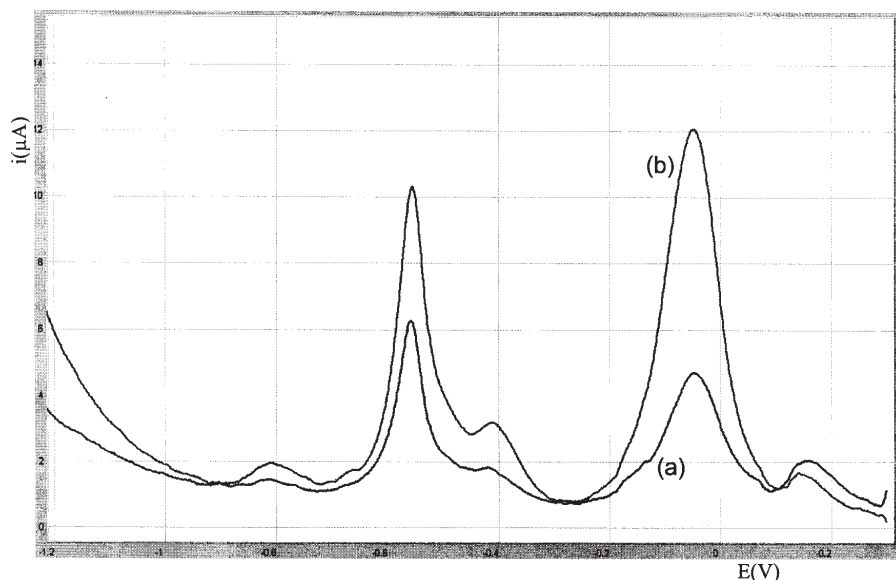


Fig. 4. Square wave anodic stripping voltammograms of 0.5 ppm (each) multicomponent Cu^{2+} , Pb^{2+} , Cd^{2+} solution, in Britton-Robinson buffer (pH 5.02) at: (a) unmodified carbon paste electrode; (b) AcAcNH_2 -HMS modified carbon paste electrode; preconcentration potential -1.1 V vs. ESC; preconcentration time 210 s

Voltammetric behaviour of copper, lead and cadmium on organofunctionalized silica modified carbon paste electrode

Voltammetric experiments were carried out to compare the 0.5 ppm (each) multicomponent Cu^{2+} , Pb^{2+} , Cd^{2+} solution behavior on unmodified and AcAcNH_2 -HMS modified carbon paste electrodes, in Britton-Robinson buffer (pH 5.02).

Figure 4 presents square wave anodic stripping voltammograms obtained on: unmodified carbon paste electrode (a) and AcAcNH_2 -HMS modified carbon paste electrode (b).

Anodic stripping voltammetric signals were obtained in both cases: (a) -0.046 V for Cu^{2+} , -0.556 V for Pb^{2+} , -0.803 V for Cd^{2+} ; (b) -0.047 V for Cu^{2+} , -0.554 V for Pb^{2+} , -0.806 V for Cd^{2+} vs. SCE. At the AcAcNH_2 -HMS modified carbon paste electrode (fig. 4b) the oxidation peaks present higher intensities of the anodic currents in comparison to those observed at the unmodified electrode. The increase in anodic current at the AcAcNH_2 -HMS modified electrode demonstrated that AcAcNH_2 -HMS plays an important role in the preconcentration process of the Cu^{2+} , Pb^{2+} and Cd^{2+} on the electrode surface, leading to a better sensitivity.

Calibration curve, detection limit, precision and accuracy

Table 1 presents the linear concentration ranges, the regression equations and the detection limits obtained for Cu^{2+} , Pb^{2+} and Cd^{2+} in the multicomponent solution under the optimized conditions.

To establish the concentration ranges, the homogeneity test was carried out. This test verifies if there are significant differences at concentration range limits. Measurements of Cu^{2+} , Pb^{2+} and Cd^{2+} peak currents were done using 10 replicates for the minimum concentration level and 10 for the maximum one ($n = 10$) for each concentration range (presented in table 1). Testing values (PG) were calculated

(5.11 for Cu^{2+} , 5.08 for Pb^{2+} and 4.92 for Cd^{2+}) and were compared with the tabled value of $F_{9,9;0,99}$ function (5.35) [31]. In all three cases $PG < F$, subsequently the concentration ranges were correctly chosen.

To prove that the method presents linearity on the proposed concentration ranges for each of the analytes the linearity statistical test was carried out [32].

The peak currents values for N standard solutions, whose concentrations were equidistant dispersed on the concentration range, were measured. After calculating the residual standard deviations for linear and nonlinear functions, the testing values were calculated (3.22 for Cu^{2+} , 3.52 for Pb^{2+} and 0.09 for Cd^{2+}) and compared with tabled $F_{N-3; N-3; 0,99}$ values (3.24 for Cu^{2+} , 3.91 for Pb^{2+} and 4.85 for Cd^{2+}) [31]. In all three cases the calculated testing values are smaller than the tabled values, resulting that nonlinear functions do not provide an improvement. In conclusion, the method presents linearity on the established concentration range for each analyte, the linear regression equations being those presented in table 1.

The detection limits were calculated as $3s/b$, where s is the background noise measured under the optimized conditions and b is the calibration curve slope (table 1).

In this study, the method precision was evaluated only on repeatability level. Repeatability is expressed as percentage relative standard deviation (RSD%) and the values obtained for 0.5 ppm Cu^{2+} , Cd^{2+} , Pb^{2+} multicomponent solution under the optimized conditions were: 5.60 % for Cu^{2+} , 7.02 % for Pb^{2+} and 5.60 % for Cd^{2+} . According to Horwitz equation [33], the predicted relative standard deviation (PRSD%) for this level of concentration is 17.63 % and the ideal RSD % is 8.81 %. As it can be seen, the obtained values of RSD % are within the specified limits. The HorRat value was also determined. This is a performance parameter that reflects the acceptability of a

Table 1

THE LINEAR CONCENTRATION RANGES, REGRESSION EQUATIONS, CORRELATION COEFFICIENTS (R^2) AND THE DETECTION LIMITS OF Cu^{2+} , Pb^{2+} AND Cd^{2+} AT AcAcNH_2 -HMS MODIFIED CARBON PASTE ELECTRODE

Analyte	Linear concentration range (ppm)	Regression equation $y = b \cdot x + a$, $y = i$, $x = c$, b – calibration curve slope, a – y -intercept	R^2	Detection limit (ppm)
Cu^{2+}	0.01-1.1	$i = 20.58 \cdot c - 0.24$	0.9949 ($N = 20$)	0.0042
Pb^{2+}	0.03-0.9	$i = 15.98 \cdot c - 0.05$	0.9977 ($N = 16$)	0.0054
Cd^{2+}	0.1-1.3	$i = 1.80 \cdot c - 0.13$	0.9954 ($N = 13$)	0.0474

Solution	Addition	Recovery %		
		Cu ²⁺	Pb ²⁺	Cd ²⁺
Solution I	1 st addition	101.76	98.87	81.09
	2 nd addition	104.99	87.53	103.54
	3 rd addition	92.15	100.49	95.31
Solution II	1 st addition	106.97	96.57	91.25
	2 nd addition	86.63	98.11	91.62
	3 rd addition	99.93	86.67	99.56
Solution III	1 st addition	92.16	105.41	103.00
	2 nd addition	85.24	97.12	108.81
	3 rd addition	102.36	95.31	90.25
Mean recovery %		96.91	96.23	96.05
RSD %		8.29	6.17	8.87

Table 2
RECOVERY VALUES OF THE ADDED ANALYTE FROM SPIKED STANDARD SOLUTIONS

Replicate	Addition number	c _{added} (ppm)	Cu ²⁺		Pb ²⁺		Cd ²⁺	
			c _{found} (ppm)	Recovery %	c _{found} (ppm)	Recovery %	c _{found} (ppm)	Recovery %
1	0	-	0.023	-	0.287	-	-	-
	1	0.210	0.218	93.65	0.444	89.36	0.211	100.69
	2	0.411	0.508	116.94	0.712	102.05	0.387	94.18
	3	0.604	0.582	92.84	0.899	100.96	0.620	102.60
2	0	-	0.025	-	0.284	-	-	-
	1	0.210	0.268	114.20	0.436	88.29	0.209	99.46
	2	0.411	0.407	93.48	0.688	99.02	0.408	99.39
	3	0.604	0.637	101.24	0.913	102.78	0.606	100.34
3	0	-	0.024	-	0.292	-	-	-
	1	0.210	0.239	102.28	0.455	90.83	0.194	92.64
	2	0.411	0.468	107.53	0.695	98.87	0.418	101.71
	3	0.604	0.604	96.16	0.917	102.39	0.605	100.09
Mean sample concentration in the voltammetric cell (ppm)			0.024		0.288		-	
Mean water sample concentration (ppm)			0.048		0.575		-	
RSD %			3.08		1.30		-	
c _{ICP-AES} (ppm)			0.047		0.550		-	
Relative error: $\epsilon r \% = ((c_{SWASV} - c_{ICP-AES}) / c_{ICP-AES}) * 100$			2.17		4.58		-	

Table 3
Cu²⁺, Pb²⁺ AND Cd²⁺ QUANTITATIVE DETERMINATION FROM WASTE WATER SAMPLES BY SWASV AND ICP-AES

chemical method of analysis with respect to precision and is calculated as the ratio between the obtained and the predicted relative standard deviation (HorRat = RSD/PRSD). The obtained values are: 0.30 for Cu²⁺, 0.40 for Pb²⁺ and 0.32 for Cd²⁺ and they are within the accepted limits (0.3 – 1.3) for an intralaboratory study [33].

The method accuracy was evaluated from the recovery degree of the added analyte from spiked standard solutions. The equation: Recovery % = $[(C_{TS} - C_U) / C_S] * 100$, (C_{TS} – total analyte concentration in spiked sample, C_U – analyte concentration in unspiked sample and C_S – total spike concentration) was used for the recovery calculation. There were used 3 identical standard multicomponent Cu²⁺, Cd²⁺, Pb²⁺ solutions (I, II, III) (0.2 ppm each) and for each one were made 3 additions of 0.2 ppm (each) Cu²⁺, Cd²⁺, Pb²⁺ (table 2). All the recovery values lie in the accepted range for this level of concentration [34].

Analysis of copper, lead and cadmium from waste water samples

The AcAcNH₂-HMS modified carbon paste electrode was applied for the SWASV simultaneous determination of Cu²⁺, Pb²⁺ and Cd²⁺ in waste water samples in optimized conditions: Britton-Robinson buffer (pH 5.02) as supporting electrolyte, -1.1 V preconcentration potential, 210 s preconcentration time.

The obtained results (concentrations, recoveries % and relative standard deviations (RSD %) values) are presented

in table 3. The average recovery values are 102.04 % for Cu²⁺, 97.17 % for Pb²⁺ and 99.01 % for Cd²⁺, these values indicating that there were no significant differences between the found and the added concentrations.

The determined concentrations in the waste water sample using the AcAcNH₂-HMS modified carbon paste electrode are comparable with the concentrations obtained by inductively coupled plasma atomic emission spectrometry ICP-AES (table 3).

These results indicate that the proposed modified electrode can be successfully used for the simultaneous determination of Cu²⁺, Pb²⁺ and Cd²⁺ in waste water samples, in optimized conditions with reliable results.

Conclusions

This study proved that the AcAcNH₂-HMS modified carbon paste electrode exhibited improved selectivity and high sensitivity toward the detection of copper, cadmium and lead, due to high surface area, numerous active sites, and strong adsorption ability of organically functionalized mesoporous HMS silica. This new electrode is a viable alternative for the simultaneous determination of copper, cadmium and lead by square wave anodic stripping voltammetry in waste water samples, after optimizing parameters such as pH value, preconcentration potential and time. An accurate and reproducible SWASV analysis can be done using standard addition method, taking into account the sample matrix, the results being comparable to those obtained by ICP-AES.

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