Chemometric Ways of Improvement of Heavy Metals Recovery Yields from Toxic Wastes using Mixtures of Strong Acids

KAPKOUMI NANA HUBERT[1], EDE BODOKI[2]*, BABALE DJAM DOUDOU[1], RADU OPREAN[2], ROBERT SANDULESCU[2]
[1] Université de Yaoundé I, Faculté des sciences, Laboratoire de Chimie Analytique, B.P. 812 Yaoundé, Cameroon
[2] "Iuliu Haţieganu" University of Medicine and Pharmacy, Faculty of Pharmacy, Analytical Chemistry Department 4 Pasteur Str., 400349, Cluj-Napoca, Romania

Chemometrical tools for experimental design were used to study ways of improvement of cadmium(II) and lead(II) ions recovery yields from toxic wastes using mixtures of strong acids. We report here a technique that takes advantage of the predictable electrochemical behavior of cadmium(II) and lead(II) ions in several strong acidic media and the effect of these strong acids to collect cadmium(II) and lead(II) ions from toxic wastes. The anodic peak intensity was used to compare the free forms of cadmium(II) and lead(II) in different aqueous mineral acids media. The experimental screening design show that only the sulfuric acid exhibits significant positive effects on cadmium(II) and lead(II) ions, therefore the free forms of cadmium(II) and lead(II) ions in this media are the highest. In perchloric and phosphoric acids media the cadmium(II) and lead(II) ions generate more stable, electroinactive ionic species of the heavy metals due to their different solvation properties and also probably by favoring the formation of insoluble colloidal particles of cadmium and lead, which gave lower electrochemical signals and also the shift of redox peak potentials recorded by square wave polarography. On the other hand, according to the designs coefficient plot, the influence of hydrochloric and nitric acid is not at all significant. Considering the anodic peak intensity as response of the screening experimental design, we can conclude that the nature and concentration of acid used in mixture with metallic ions exhibits positive, negative or no effect on the the formation of free, electroactive ionic complexes of the studied cations.

Keywords: heavy metal cations, strong acid mixtures, anodic peak intensity, square wave polarography, screening experimental design

Most of the heavy metals, which are generally persistent in the environment, are hazardous for any aquatic ecosystem as well as for human health. It results in an ever-increasing demand for the determination of trace metal contaminants [1]. The bioavailability and toxicity of metal ions to aquatic organisms is mainly related to concentrations of their free (hydrated) form [2]. Toxic metal have various sources: natural sources due to their presence in minerals or anthropic sources due to the human activities. The chemical properties of some metal ions give their toxicity effect in human body and other forms of life. Of such pollutants, heavy metals are the most important because of their non-biodegradability, with lead and cadmium ions being among the most toxic and hazardous. Cadmium(II) and its compounds are toxic and poisoning occurs through inhalation and ingestion [3]. Since lead(II) is a potent neurotoxic metal, its pollution is of major concern. The presence of lead in drinking water, even in low concentrations, may cause diseases such as anemia, hepatitis, nephrite syndrome, etc [4]. Recovery and recycling of metals will conserve the natural resources to meet the future demand of materials and reduce the environmental pollution. The processes usually employed for the recovery of metals are hydro/pyrometallurgical methods where material is first leached in acidic or alkaline solution to dissolve the metals directly or after thermal treatment [5]. The solution is subsequently processed to recover valuable constituents following precipitation, cementation, ion exchange, coagulation, adsorption, electrolysis, liquid-liquid or liquid-solid extraction etc. The majority of studies carried out with these techniques used different acid or mixture acids to adjust the pH of sample or to optimize the extraction method. It has been shown recently that concentrated solutions of mineral acids (phosphoric, hydrochloric, perchloric, nitric, sulfuric) having different solvation and redox properties. Hydrochloric and sulfuric acids have complexing properties and perchloric acid have little complexing properties. Nevertheless, phosphoric solutions are generally the less solvating toward most cations [6]. The interaction between anions of acid and metallic cations is possible. Cadmium(II) and lead(II) ions do not have the same reactivity in the various acids or acidic mixtures. However, under specific conditions (pH, concentrations), trace metals may form, with anions of various acids colloid particles or neutral complexes metallic. Usually, the presence of trace amounts of heavy metals in environmental samples is determined by spectrophotometric techniques [7]. However, the direct analysis of some complex samples presents some difficulties due to the high salt content or colloid particles, causing matrix interference and insufficient precision. Stripping voltammetric techniques are an interesting alternative for the detection of trace levels of heavy metals in high saline matrices. These techniques present a significant sensitivity due to their unique ability to preconcentrate target species during the accumulation step on the working electrode, next to its combination with pulse measurement techniques that generate a highly favourable signal-to background ratio. Mercury-based electrodes, such as mercury film electrodes (MFE), and hanging mercury drop electrodes (HMDE), have traditionally been used in stripping techniques due to their advantages, such as high sensitivity, reproducibility, purity of the surface, high hydrogen over potential, and possibility of amalgam formation. Therefore, they have been recognized as the most sensitive electrodes for the

determination of heavy metals. In particular, the HMDE has successfully been used for the determination of Pb^{2+} and Cd^{2+} in complex matrix like seawater samples [3]. The electroanalytical methods have been improved with the application of chemometrics for simultaneous quantitative prediction of analytes or qualitative resolution of complex overlapping responses [8]. The use of 'design of experiments' (DoE) is a revolutionary approach to optimization and screening of experimental parameters. Simple experimental designs and statistical tools for data analysis can provide much information about the system under investigation after only a few experiments. Such information can be key in decision-making for further experiments and can enable the development of robust and reliable protocols for chemical synthesis, analytical methods or biological assays [3].

The specific objectives of this study were (a) to screen the electrochemical behaviour of cadmium(II) and lead(II) in hydrochloric, perchloric, nitric, sulfuric and phosphoric acid or mixtures of two and more of these acids by square wave polarogrophy (SWP) and (b) to determine the significant main and interaction effects of cadmium(II) and lead(II) in single acid or acid mixtures using statistical tools. Chemometrics and particularly experimental designs of mixtures are applied to chemical processes to determine in an efficient way the set of optimal conditions that are required to obtain high quantities of free forms cadmium(II) or lead(II) ions in acidic media.

Experimental part
Chemicals reagents
The stock aqueous solution, containing Cd^{2+}, Pb^{2+}, hydrochloric acid, perchloric acid, nitric acid, sulfuric acid or phosphoric acid was prepared by dissolving analytical grade nitrate salts of the respective metals and respective fuming HCl (37% on weight basis), $HClO_4$ (70% on weight basis), HNO_3 (65% on weight basis), H_2SO_4 (97% on weight basis) and H_3PO_4 (85% on weight basis) in desionised water with an aqueous 0.2 M acetate buffer (pH 3.48). All the chemicals were purchased from Merck and were used without further purification.

Apparatus and experimental conditions
The square wave polarographic measurements were carried out on a MDE 150 polarographic stand (Radiometer Analytical SAS, France), using a hanging mercury drop electrode in a three-electrode arrangement with an AgCl/Ag (3M KCl) reference electrode and a Pt wire auxiliary electrode. The cell parameters were: drop number 2, drop growth time 0.5s, N_2 purge time 300s (with blanketing at the end), stirring time 300s, electrolysis time 0s and waiting time 5s. The signal parameters were: step duration 0.04s, step amplitude 1mV, pulse duration 20 ms, pulse amplitude 50mV, initial potential -800mV, final potential -100mV, minimum current range 10nA and maximum current range $100\mu A$. All measurements were made at 20°C. The general procedure for obtaining polarograms (square wave method) was as follows: in electrochemical cell, we introduced 10 mL of acidic solution (blank solution) with acetate buffer (pH 3.48) and the square wave polarogram was recorded. The appropriate quantities (in the range of 10^{-5}–10^{-4} mol/L) of Cd^{2+} or Pb^{2+} solution was added and the polarogram was recorded again. The obtained peak current is proportional to concentration of free, electroactive form of the metal ions in solution. A Personal computer controlled all settings and data processing of the system.

Design of Experiments (DoE) with Partial Least Square (PLS) fitting method
Design of experiments was applied to create the possibility of investigating and statistically validating the effect of acid or mixture acid media on free forms of cadmium(II) and lead(II) ions. The ideas of using DoE was to systematically vary the two parameters (variables), nature of acid and their quantity in the mixture, known to affect the outcome of free, electroactive forms of the metallic ions. The matrix of designed experiments (X) was then correlated by using the PLS method to the corresponding combined matrix of the obtained current intensities (Y) for the studied acid mixtures. In experiments with mixtures, a factor's value is its proportion in the mixture, which falls between zero and one. The sum of the proportions in any mixture recipe is one (100%). Multivariate analysis was performed using the MODDE 8.0 (Umetrics AB, Sweden) software, with an extended axial experimental design for screening, using a linear model with 5 model terms and a constant. The design comprised 15 runs, 3 centerpoints and 1 replicate for each run (total runs 36), the model being fitted by Partial Least Square (PLS). The anodic peak current intensities of Pb^{2+} (7 x $10^{-5}M$) and Cd^{2+} ($8 \times 10^{-5}M$) were the two followed responses. The worksheet of all the experiments is shown in table 1.

Results and discussion
The shift of normal potentials of Cd^{2+}/Cd and Pb^{2+}/Pb redox systems
Different levels of concentrated solutions of mineral acids (hydrochloric, perchloric, nitric, sulfuric, phosphoric) can change the standard potential of redox systems where the electrochemical reaction of cadmium and lead is carried out. The normal potentials of the Cd^{2+}/Cd and Pb^{2+}/Pb redox systems are given in tables 2 and 3 respectively. Their normal potential remain constant independent of the nature of acidic media when the acid concentration is lower than $10^{-3}M$. The normal potentials of these redox systems change significantly in more concentrated acidic media, which of course is also related to the change of ionic strenght. The range of variation depends on the nature of mineral acid, which in case of Cd^{2+}/Cd and Pb^{2+}/Pb redox systems is higher in hydrochloric, nitric and sulfuric acids than in perchoric and phosphoric acids. Reaction media with concentrated solutions of mineral acids, although in the same concentrations, involves different anions with different charges, capable of forming different ionic complexes with the lead or cadmium cations.

Calibration curves of cadmium and lead in different acidic media
Different concentrations of Cd^{2+} and Pb^{2+} were used to establish the calibration curve by plotting the anodic current intensities obtained for each concentration level in concentrated solutions ($10^{-3}M$) of hydrochloric, perchloric, nitric, sulfuric or phosphoric acids (fig. 1 and 2). In all cases, linearity ranging from $10^{-5}M$ to $4 \times 10^{-5}M$ was obtained with a correlation coefficient ≥ 0.99 for both cations. With Cd^{2+} and Pb^{2+} concentrations higher than $4 \times 10^{-5}M$, the correlation coefficient decreases and the calibration curves tend to show different shapes in function of the nature of the acid, except for perchloric and nitric acids in case of cadmium and perchloric and hydrochloric acids in case of lead, where the curves remain superimposed. Complexation phenomena can explain the observed variations. The effect of the different forms of studied acid anions on Cd^{2+} and Pb^{2+} is expressed in the formation of

Exp Name	Run Order	Factors					Responses	
		%, v/v HNO_3	%, v/v $HClO_4$	%, v/v HCl	%, v/v H_3PO_4	%, v/v H_3SO_4	I[µA] Lead	I[µA] Cadmium
N5	1	0	0	0	0	1	4.451	4.212
N2	2	0	1	0	0	0	3.237	2.87
N31	3	0.25	0.25	0	0.25	0.25	3.689	3.472
N18	4	0.2	0.2	0.2	0.2	0.2	3.741	3.451
N30	5	0.25	0	0.25	0.25	0.25	3.871	3.511
N29	6	0	0.25	0.25	0.25	0.25	3.609	3.539
N27	7	0.1	0.1	0.1	0.6	0.1	3.48	3.26
N26	8	0.1	0.1	0.6	0.1	0.1	3.355	3.295
N21	9	0	0	1	0	0	3.619	3.428
N3	10	0	0	1	0	0	3.789	3.448
N35	11	0.2	0.2	0.2	0.2	0.2	3.731	3.415
N28	12	0.1	0.1	0.1	0.1	0.6	3.974	3.957
N1	13	1	0	0	0	0	3.825	3.559
N14	14	0.25	0.25	0.25	0	0.25	3.773	3.637
N33	15	0.25	0.25	0.25	0.25	0	3.458	3.221
N10	16	0.1	0.1	0.1	0.1	0.6	4.078	3.927
N36	17	0.2	0.2	0.2	0.2	0.2	3.706	3.595
N20	18	0	1	0	0	0	3.117	3.07
N11	19	0	0.25	0.25	0.25	0.25	3.468	3.574
N22	20	0	0	0	1	0	3.027	3.126
N19	21	1	0	0	0	0	3.63	3.629
N32	22	0.25	0.25	0.25	0	0.25	3.786	3.647
N23	23	0	0	0	0	1	4.661	4.078
N15	24	0.25	0.25	0.25	0.25	0	3.365	3.256
N4	25	0	0	0	1	0	2.978	3.106
N7	26	0.1	0.6	0.1	0.1	0.1	3.425	3.203
N17	27	0.2	0.2	0.2	0.2	0.2	3.74	3.415
N6	28	0.6	0.1	0.1	0.1	0.1	3.597	3.387
N12	29	0.25	0	0.25	0.25	0.25	3.636	3.501
N9	30	0.1	0.1	0.1	0.6	0.1	3.383	3.211
N25	31	0.1	0.6	0.1	0.1	0.1	3.264	3.179
N8	32	0.1	0.1	0.6	0.1	0.1	3.44	3.336
N13	33	0.25	0.25	0	0.25	0.25	3.608	3.447
N16	34	0.2	0.2	0.2	0.2	0.2	3.747	3.461
N24	35	0.6	0.1	0.1	0.1	0.1	3.532	3.372
N34	36	0.2	0.2	0.2	0.2	0.2	3.756	3.441

Concentration [M]	HCl [mV]	$HClO_4$ [mV]	HNO_3 [mV]	H_2SO_4 [mV]	H_3PO_4 [mV]
10^{-1}	-585	-564	-567	-574	-566
10^{-2}	-566	-560	-560	-564	-561
10^{-3}	-564	-562	-562	-560	-562
10^{-4}	-563	-563	-563	-562	-564
10^{-5}	-562	-563	-563	-562	-564

Table 2
NORMAL POTENTIAL REDOX OF SYSTEM Cd^{2+}/Cd IN DIFFERENT CONCENTRATED SOLUTIONS

Concentration [M]	HCl [mV]	$HClO_4$ [mV]	HNO_3 [mV]	H_2SO_4 [mV]	H_3PO_4 [mV]
10^{-1}	-380	-370	-375	-380	-370
10^{-2}	-367	-364	-365	-372	-365
10^{-3}	-369	-368	-366	-369	-367
10^{-4}	-370	-371	-370	-371	-369
10^{-5}	-371	-371	-371	-371	-371

Table 3
NORMAL POTENTIAL REDOX OF SYSTEM Pb^{2+}/Pb IN DIFFERENT CONCENTRATED SOLUTIONS OF MINERAL ACIDS

Compounds	Solubility (g/L) at 20°C
$Pb_3(PO_4)_2$	1.2×10^{-6}
$PbHPO_4$	6.05×10^{-4}
$PbSO_4$	3.14×10^{-2}
$PbCl_2$	4.43
$Cd_3(PO_4)_2$	6.23×10^{-5}
$CdSO_4$	76.6

Table 4
SOLUBILITY TABLE FOR CERTAIN COMPOUNDS OF CADMIUM(II) AND LEAD(II)

ionic complexes with different solubilities and stabilities in the acidic media. Metallic ions do not have the same reactivity in the various acidic media [6]. Hydrochloric and sulfuric acids have complexing properties, nevertheless, complexes of cadmium and lead formed in hydrochloric acid are more stable than in sulfuric acid [8]. At certain point, phosphoric acid might form insoluble phosphates (colloidal particles), this is why observed current intensity levels are lower than in other acidic media, some of these compound solubility is given in table 4, which of course, is also influenced by pH and ionic strength.
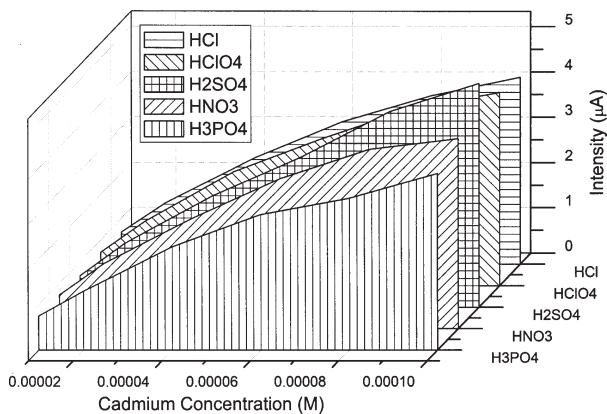
Fig. 1. Calibration curves of Cd^{2+} (10^{-5}...10^{-4})M in the presence of different 10^{-3}M acids buffer at pH =3.48 (0.2 M acetate buffer) at hanging mercury drop electrode

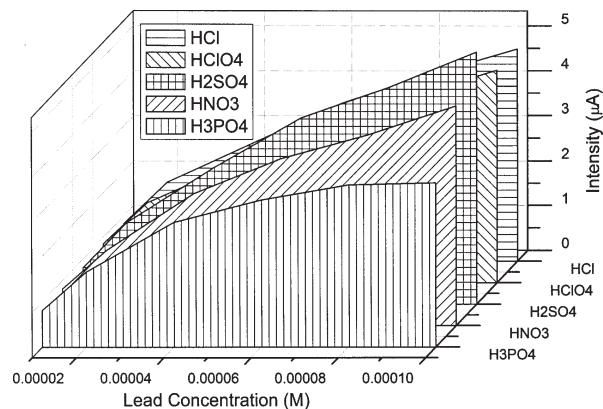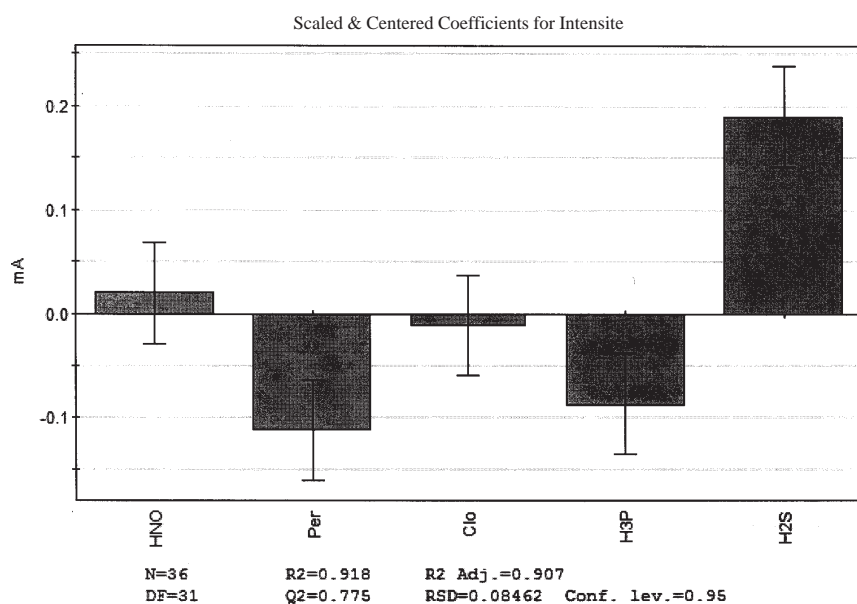Fig. 2. Calibration curves of Pb^{2+} (10^{-5}...10^{-4})M in the presence of different 10^{-3}M acids buffer at pH =3.48 (0.2 M acetate buffer) at hanging mercury drop electrode
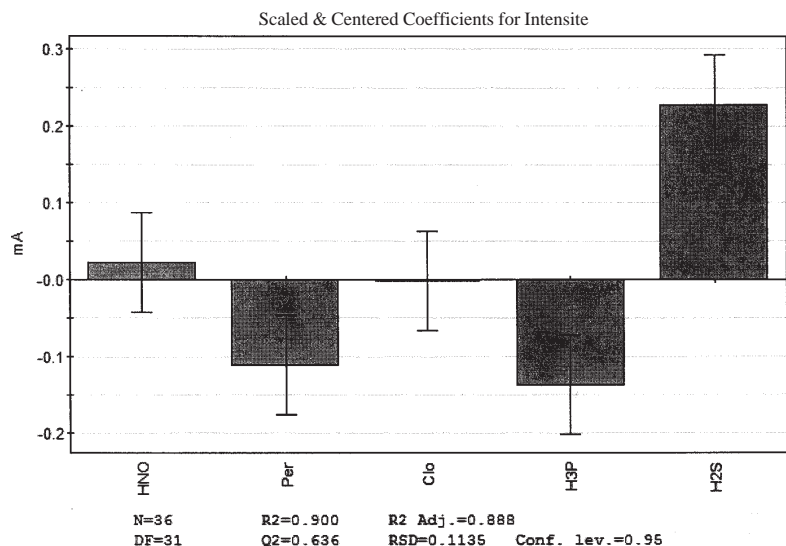

Fig. 3. Coefficient plot for cadmium

N=36   R2=0.918   R2 Adj.=0.907
DF=31   Q2=0.775   RSD=0.08462   Conf. lev.=0.95

Fig. 4. Coefficient plot for lead

N=36   R2=0.900   R2 Adj.=0.888
DF=31   Q2=0.636   RSD=0.1135   Conf. lev.=0.95

Screening design
Effect of mineral acids on cadmium and lead ions

Thirty-six experiments have been carried out according to the electrochemical protocol described above and the conditions fixed by the experimental design (table 1). The results are illustrated by the two histograms shown in figure 3 and 4, which represent the main effect of hydrochloric, perchloric, nitric, sulfuric and phosphoric acid respectively on the square wave anodic current of cadmium and lead ions. As it can be seen, hydrochloric and nitric acids have no significant effect and sulfuric acid exhibits significant positive effect on the recorded currents of cadmium and lead ions. This means that free forms of Cd^{2+} and Pb^{2+} are favored by the sulphuric acid. Perchloric and phosphoric acids, on the other hand, exhibit a negative effect. In conclusion, sulfuric acid is the only acid that shows an interesting positive effect on the response. Notice that level of a significant negative effect of perchloric acid is higher than level of phosphoric acid on cadmium ion. On lead ion,
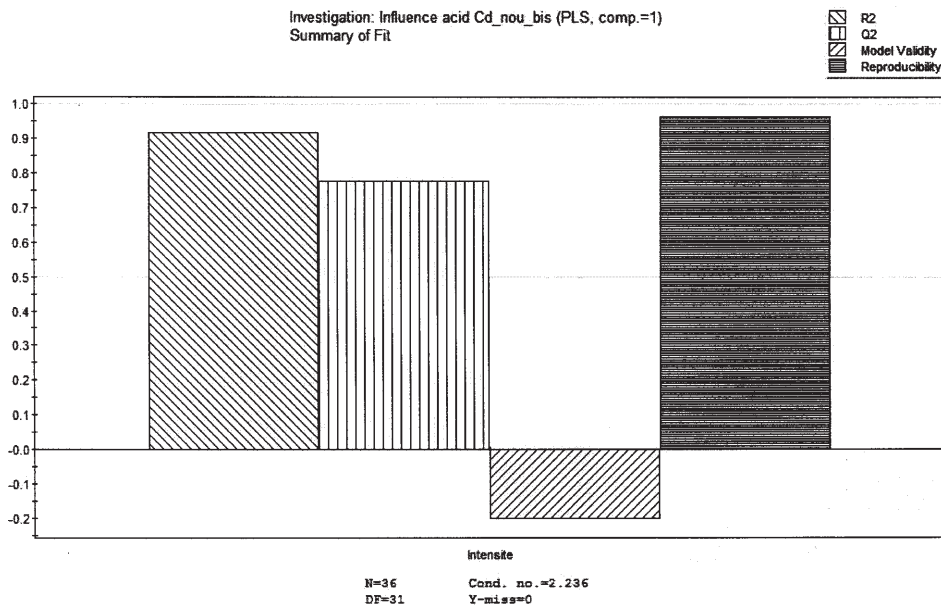
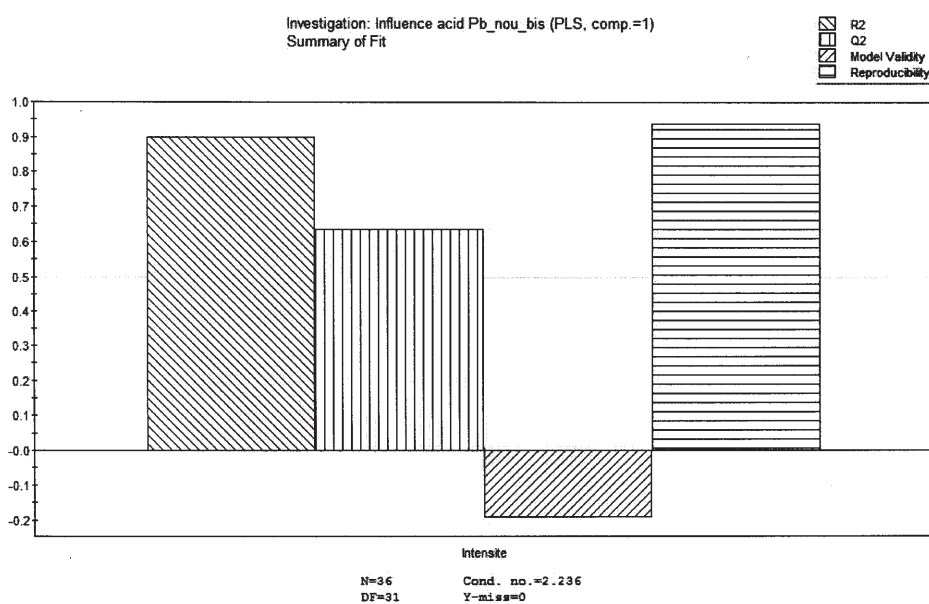Fig. 5. Summary plot of goodness of fit for cadmium
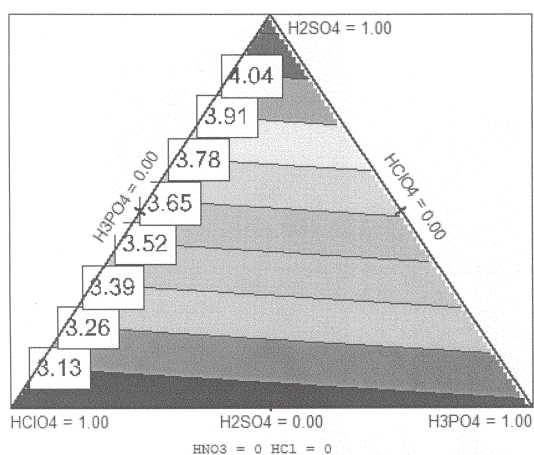

Fig. 6. Summary plot of goodness of fit for lead

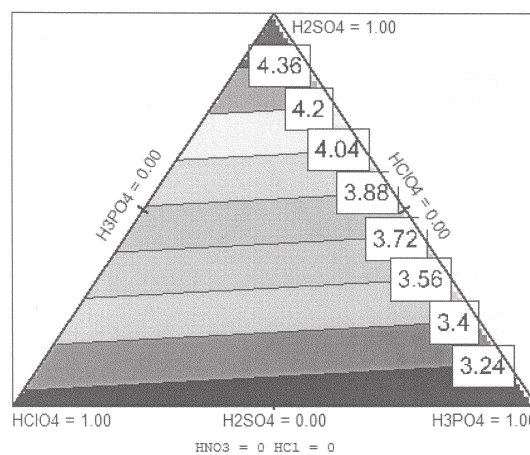Fig. 7. Mixture contour plot for cadmium

Fig. 8. Mixture contour plot for lead

levels of significant negative effect of these two acids are inversed.

Validation of the models

The goodness of fit obtained by PLS for the obtained models of the two cations is expressed by the factors R^2, Q^2, Model validity and Reproducibility shown in a summary plot (fig. 5 and 6). As it can be seen in both cases the model fits well the experimental data and has a fairly good predictive power ($R^2 > 0,90$; $Q^2 > 0,63$). The pure error compared with the total variation of the response is very small, showing a good reproducibility for both models (>0.93). Since the both models present relatively high R^2 and Q^2 and the pure error is not representative of the true experimental error, the indicated lack of fit is only artificial.

	% v/v HNO$_3$	% v/v HClO$_4$	% v/v HCl	% v/v H$_3$PO$_4$	% v/v H$_2$SO$_4$	I [μA]	Iterations	Log(D)
Cadmium	0	0	0	0	1	4.2263	220	0.7655
Lead	0	0	0	0	1	4.5504	209	0.1015

Interpretation of the response surface models

Following the interpretation of the main effect of mineral acids on the electrochemical behaviour of cadmium and lead ions (fig. 3 and 4) and the study of the obtained model validity (fig. 5 and 6), the mixture contour plots were constructed for the three acids that show significant effect on the response, keeping hydrochloric and nitric acid at their lowest level of concentration in the mixture (fig. 7 and 8). Examining the response surface plots gives us an insight towards the optimum five acid mixture composition capable of favoring the free forms of cadmium(II) and lead(II) and therefore the highest anodic currents. The red colored areas on response surface plot show the highest obtained response and the corresponding composition of the acid mixture.

Although, the objective of the experimental design was only for screening purposes, running the optimizer offered by Modde 8.0, the highest anodic current for both heavy metal cations is obtained using only sulphuric acid, without the addition of any other of the studied strong mineral acids (table 5).

Conclusions

Electrochemical behaviour of cadmium and lead ions in mineral acids and mixture mineral acids media has been studied by square wave polarography. Heavy metals form different ionic complexes of different stabilities with mineral acids and therefore they do not show the same electrochemical behaviour in hydrochloric, perchloric, nitric, sulfuric and phosphoric acids. Among the different mineral acids used, high free forms (electroactive forms) of cadmium and lead ions were obtained in sulfuric acid media. A screening experimental design carried out by the use of MODDE 8.0 allows the selection of the most influential acids as background electrolytes (perchloric, phosphoric and sulphuric acid) on the anodic current of the studied cations and also enables the assessment of some preliminary optimal conditions leading to the maximum of free forms of cadmium and lead in mineral acids media. Furthermore, chlorhydric acid and nitric acid exhibit no significant effect on stability of ionic complexes of cadmium and lead in solution. We can conclude that behaviour of cadmium and lead ions in aqueous solution depends of the nature and the concentration of mineral acid.

References

1. HEITZMANN, M., BUCHER, C., MOUTET, J.C., PEREIRA, E., RIVAS, B. L., ROYAL, G., SAINT-AMAN, E., Journal of Electroanalytical Chemistry, **610**, 2007, p.147
2. LOUIS, Y., CMUK, P., OVANOVIC, D., GARNIER, C., LENOBLE, V., MOUNIER, S., PIZETA, I., Analytica Chimica Acta, **606,** 2008, p.37
3. GUELLA, R., ARAGAYA, G., FONTAS, C., ANTICO, E., MERKOC¸ A., Analytica Chimica Acta, **627**, 2008, p.219
4. CHAKRAVARTY, S., MOHANTY, A., NAG SUDHA, T., UPADHYAY, A.K., KONAR, J., SIRCAR, J.K., MADHUKAR, A., GUPTA, K.K., Journal of Hazardous Materials, **173**, 2010, p.502
5. KUMAR, V., KUMAR, M., JHA, M. K., JEONG, J., LEE, J., Hydrometallurgy, **96**, 2009, p.230
6. LOUIS, C., BEBBA, A., BESSIERE, J., Canadian Journal of Chemistry, **66**, 1988, p.2422
7. RUBIO, R., HUGUET, J., RAURET, G., Water Research, **18**, 1984, p.423
8. Ni, Y., KOKOT, S., Analytica Chimica Acta, **626**, 2008, p.130
9. TYE, H., Drug Discovery Today, **9**, no.11, 2004, p.464
10. ACHOUR, S., YOUCEF, L., Larhyss Journal, **7**, no 02, 2003, p.68
11. GZARA, L., HAFIANE, A., DHAHDI, M., Revue des Sciences de l'Eau, **13**, no 3, 2000, p.289
12. ALGNACIL, F. J., ALONSO, M., Hydrometallurgy, **74**, 2004, p.195
13. SAYAR, N. A., FILIZ, M., SAYAR, A. A., Hydrometallurgy, **96**, 2009, p.148
14. ALAMDARI, E., MORADKHANI, D., DARVISHI, D., ASKARI, M., BEHNIAN, D., Minerals Engineering, **17**, 2004, p.89
15. MEUCCI, V., LASCHI, S., MINUNNI, M., PRETTI, C., INTORRE, L., SOLDANI, G., MASCINI, M., Talanta, **77**, 2009, p.1143
16. BAYEN, S., GUNKEL-GRILLON, P., WORMS, I., MARTIN, M., BUFFLE, J., Analytica Chimica Acta, **646**, 2009, p.104
17. SHRIVAS, K., AGRAWEL, K., HARMUKH, N., Journal of Hazardous Materials, **161**, 2009, p.325
18. DAATI, R., KAMOUN, A., CHAABOUNI, M., SERGENT, M., PHAN-TAN-LUU, R., Chemometrics and Intelligent Laboratory Systems, **80**, 2006, p.198
19. PARVEZ, J., VENKATARAMAN, C., MUKHERJI, S., Chemosphere, **73**, 2008, p.1049
20. NEZHADALI, A., LANGARA, P., ALI HOSSEINI, H., Journal of Chinese Chemical Society, **55**, 2008, p.271
21. APARICIO, J., MUHAMMED, M., Hydrometallurgy, **21**, 1989, p.385
22. PESAVENTO, M., ALBERTI, G., BIESUZ, R., Analytica Chimica Acta, **631**, 2009, p.129
23. ALMELA, A., ELIZALDE, M. P., Hydrometallurgy, **37**, 1995, p.47
24. BUFFLE, J., TERCIER-WAEBER, Voltammetric environmental trace-metal analysis and speciation: From laboratory to in situ measurements, Trends in Analytical Chemistry, **24**(3), 2005, p.172