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Optimization of Extraction Procedure for Selective Removal of Pb(II) Ions from Spreca River Sediment Samples

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***Abstract*- The toxicity of lead, as the most widespread heavy metal in nature still represents an environmental challenge, where scientists are trying to find the most efficient and cheapest way to safely remove it from the environment. In order to optimize the conditions for selective extraction and the highest efficiency of Pb(II) ion removal, the influence of different parameters was investigated. Factors that affect the selective extraction of Pb(II) ions: type of organic solvent and its volume, type of used ligand, counter-ion concentration in the feed solution, pH value of the feed and stripping solution and equilibrium time of extraction, were analyzed. The results showed that dicyclohexano-18-crown-6 dissolved in 50 mL of dichloromethane enable efficient removal of Pb(II) ions after 3 hours of stirring. The proposed procedure was finally applied to real samples and showed high selectivity for Pb(II) ions (over 90%) for all investigated samples.**

Keywords— Pb(II); solvent; extraction; macrocyclic ligands

I. INTRODUCTION

Since heavy metal ions are non-biodegradable, they can accumulate along the food chain and also can remain almost indefinitely in the soil environment. Removal of ions from their effluents has assumed of higher importance in the recent past due to the decreasing availability of natural resources and the increasing pollution in the environment [1]. Lead is one of the most abundant heavy metals and its toxic effects cause environmental and health problems because of its stability in the contaminated sites and complexity of mechanism in biological toxicity [2]. Lead is thought to be quickly absorbed in the bloodstream and is believed to have adverse effects on certain organ systems like the central nervous system, the cardiovascular system, kidneys, and the immune system [3]. Methods of efficient determination of heavy metals content in natural resources (water, air, industrial raw materials, and products) are increasingly occupying the attention of researchers [4]. Attempts to remove toxic heavy metal ions from the environment and from biological systems have utilized a variety of separation methods such as adsorption, precipitation, solvent extraction and liquid membrane transport [5]. The methods used so far for the determination of metal cations are mainly based on the principle of "molecular recognition" and involve the complexation of metal cations with suitable ligands, and removal in the form of formed complex compounds. The efficiency of complexation expressed through the stability of the formed complex is conditioned by the compatibility of cations and ligands. Polyether ligands are among the most suitable host molecules for many metal ions, due to the presence of oxygen atoms as electron donors in their structure, which enables the formation of a coordinate covalent bond. Crown ethers and related compounds [6] have widely been used as complexing agents for metal selective extractions, phase transfer catalysis, membrane transport and an ionophore for the fabrication of ion-selective electrodes. These compounds react with some bulky ions and the produced species were successfully used as neutral electrical carriers for some ions [7], [8]. Since the interactions between metal cations and ligands ("host-guest" interactions) depend on many factors, the resulting stability of the formed complex can be increased by varying experimental conditions during complex formation within the organic solvent during the extraction procedure [9]. Due to their ion size, selective nature and ability to transfer metal ions into organic media, crown ethers have been frequently used as extracts and phase transfer reagents in solvent extraction and liquid-liquid extraction [10], [11], [12]. Crown ethers have the specific macrocyclic structure of their molecules, consists of the polyether chain-forming "the crown" with hydrophilic cavity and hydrophobic surface. The macrocyclic structure of these ligands provides high stability of formed complexes with metal ions due to the "macrocyclic effect" [13]. The affinity of the ligand to the metal ion depends on the structural characteristics of the ligand, and primarily on: the number and type of donor atoms, polarity, the hydrophilic-lipophilic balance of the ligand, chirality, and other stereochemical indicators. The cations that best fit the cavity are located in the center and optimize interactions with heteroatoms (oxygen atoms).

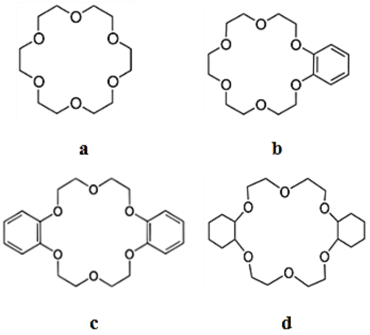

Fig 1. Structures of macrocyclic ligands:
a)18-crown-6 b) benzo-18-crown-6 c) dibenzo-18-crown-6 d) dicyclohexano 18-crown-6

For many years, solvent extraction has been one of the most used techniques for the removal and separation of heavy metal ions in industrial-scale processes, and crown ethers as ion carriers were successfully used for metal ion separation in solvent extraction. The general advantage of solvent extraction over traditional methods used for wastewaters treatment (chemical precipitation, coagulation-flocculation, ion exchange, adsorption, membrane filtration) is highly selective metal recovery from aqueous solutions (> 500 mg/L) during continuous operations. The efficiency of metal ion extraction depends on many parameters such as ligand structure, solution pH, type of solvent, temperature and the process duration, however, the extractant ability to form a metal-ligand complex has a crucial effect on the process selectivity. Reasearches [14] found that lipophilic nature is a decisive parameter for selecting a ligand in solvent extraction processes. Appropriate organic solvent selection,–extractant concentration, type of salt used for ionic strength …etc, have the highest influence on Pb extraction selectivity with new carboxylic acid extractant, and recovery of lead ions from industrial samples.

In this paper, the procedure for selective removal of Pb(II) ions from aqueous solutions was optimized and applied to heavy metal contaminated river sediment samples. The effect of various parameters, such as pH, type of macrocyclic ligand, type of organic solvent and its volume for extraction, equilibrium time, presence of counter ions, stripping agents for back-extraction, were investigated. Macrocyclic ligands with different substituents and the same cavity diameter (18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, and dicyclohexano-18-crown-6), were tested as carriers for Pb(II) ions. Different volumes of organic solvents (dichloromethane, chloroform, and 1,2-dichloroethane) were applied for solvent extraction. The effect of equilibrium time was also investigated through experiments with a duration between 1 and 4 hours. The feed solution was analyzed with calibration curve method, using flame atomic absorption spectrophotometry and efficiency of analyte removal was evaluated. An optimized procedure was applied for the removal of Pb(II) ions from river sediment samples.

II. MATERIALS AND METHODS

Materials

Feed solutions were prepared from:

- Standard Pb (II) solution (1000 mg/L), $Pb(NO_3)_2$ in 0,5 mol/L HNO_3, Merck,
- Picric acid ($C_6H_3N_3O_7$), c = $1\cdot10^{-3}$ mol/L, 99%, Kemika
- Acetate buffer solution (pH=5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck)
- Formic acid bufffer solution (pH=3), prepared from HCOOH and NaOH (g.r., Merck)

Organic solutions were prepared from:

- Organic solvents: chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and 1, 2-dichloroethane ($C_2H_4Cl_2$)
- Macrocyclic ligands: 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DCH18C6)

Stripping solutions were prepared from:

- Triton X-100 surfactant ($1{,}4\cdot10^{-3}$ mol/L)
- Disodium-EDTA ($1\cdot10^{-3}$ mol/L)
- Acetic acid buffer solution (pH=5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck).

Extraction procedure

For the optimized liquid-liquid extraction procedure, 10 mL of standard feed solutions containing the analyte Pb(II) ($1\cdot10^{-3}$mol/L) and counter ions (picrates, $1\cdot10^{-3}$mol/L) were mixed with 50 mL of organic solvent (chloroform, dichloromethane or 1,2-dichloroethane), contained the macrocyclic ligand (18C6, B18C6, DB18C6, or DCH18C6). The pH value of the standards, as well as the real samples, were adjusted to 3 with formic acid buffer solution. Macrocyclic ligands dissolved in organic solvent ($1\cdot10^{-3}$ mol/L) served to ″entrap″ the analyte in a hydrophobic medium. The contents of the flask were shaken at room temperature at 300 rpm, for 3 hours. After the phase separation, the lower organic phase was transferred to a flask for the back-extraction procedure. The upper aqueous phase was analyzed using the FAAS technique and results showed the content of the analyte remained in the feed solution.

The efficiency of extraction was calculated:

$$\%\ of\ E = \frac{(analyte\ concentration\ before\ extraction) - (analyte\ concentration\ after\ extraction)}{analyte\ concentration\ before\ extraction} \cdot 100$$

Back-extraction procedure

After separation of the organic layer, extracted metal ions were stripped from organic solution using 11 mL of an aqueous solution, buffered at pH=5 (acetic buffer) contained disodium-EDTA ($1\cdot10^{-3}$mol/L) and Triton X-100 surfactant ($1\cdot10^{-3}$mol/L). Analyte ions were transferred to the aqueous phase by mixing aqueous and organic phase at 300 rpm, for 3 hours. After the phase separation, back-extraction efficiency was determined through the FAAS measurements of Pb(II) content in aqueous stripping solutions after mixing.

FAAS measurements

Aqueous solutions after extraction and back-extraction procedures were analyzed with Flame Atomic Absorption Spectrometry, using the calibration curve method. A blank determination was simultaneously carried out in a matrix solution of standards (0.1 mol/L HNO_3) and samples using the same procedure and measurement conditions.

III. RESULTS AND DISCUSION

Optimization of Experimental Variables

A series of experiments were designed to investigate the effect of different parameters (type and volume of organic solvent, counter-ion concentration, pH value, type of macrocyclic ligand, stripping agent concentration, and extraction time) on the efficiency of the extraction procedure. All investigated parameters were optimized to achieve the highest possible extraction capability of Pb.

It was found that the extraction of analyte ions is not possible in absence of counter-ions in feed solutions, hence the preliminary experiments were carried out using picrate as counter-ions, as well as the final proposed procedure.

Effect of organic solvent type

The solvation of a metal ion strongly depends on its size, but also on the nature of the solvent. During complexation, the ligand should have the ability to replace the solvent molecules in the first cation solvation shell or that the cation has the ability to replace the solvent molecules with the ligand molecules [15]. Therefore, it can be concluded that by changing the type of solvent, we significantly alter the binding properties and selectivity of a particular ligand for a given metal cation. Researchers [16] highlight the necessity of having valid information for different solvent systems to understand their influence on thermodynamics and complexation kinetics. Some significant solvent parameters are given for solvents used in our experiments: dichloromethane (DCM), 1,2-dichloroethane (1,2-DCE), and chloroform (CH) in Table 1.

Table 1. Solvent parameters [17]

Solvent	Formula	Dielectirc constant	Dipole moment (D)	Viscosity (mPas)	Density (g/mL)
DCM	CH_2Cl_2	8.93	1.14	0.41	1.33
1,2-DCE	$C_2H_4Cl_2$	10.36	1.83	0.84	1.25
CH	$CHCl_3$	4.81	1.15	0.56	1.49

For liquid-liquid extraction purposes, the influence of three different organic solvents (contained macrocyclic ligands) was investigated: dichloromethane, 1,2-dichloroethane, and chloroform. The results showed the best extraction efficiency for dichloromethane (Table 2). The lower viscosity of DCM (0.41) compared to 1,2-DCE and CH (0.84 and 0.56 respectively) probably contributed to better solvent ability to extract analyte ions, due to less resistance to movement within the liquid which affects the removal of metal ions from feed solutions. Also, lower the dielectric constant for DCM (8.93) compared to dichloroethane (10.66) contributed to more efficient extraction, by stabilizing ionic pairs which are formed and transferred to the organic solvent layer where complexation takes place.

Table 2. The influence of solvent type in Pb(II) extraction experiments (feed solution contained: $1\cdot10^{-3}$mol/L of Pb(II) ions and $1\cdot10^{-3}$mol/L picrates; 50 mL of organic solvent contained $1\cdot10^{-3}$mol/L macrocycle ligand; stirring time is 3 hours, rotation 300rpm)

Organic solvent	Ligand	% of E
CH	B18C6	31.98
DCM		33.91
1,2-DCE		22.80
CH	**DCH18C6**	83.78
DCM		**92.10**
1,2-DCE		91.54
CH	18C6	64.06
DCM		63.47
1,2-DCE		71.06

Effect of organic solvent volume

In preliminary experiments, the addition of different volumes of organic solvent (chloroform) were applied and the results showed that 1:5 volume ratio for aqueous: organic phase was optimal for future investigation (Table 3.).

Table 3. The influence of solvent volume on Pb(II) extraction (feed solution contained: $1\cdot10^{-3}$mol/L of Pb(II) ions and $1\cdot10^{-3}$mol/L picrates; organic solvent chloroform contained $1\cdot10^{-3}$mol/L benzo-18-crown-6; stirring time is 1,5 hours, rotation 300rpm)

Solvent volume, mL	% of E
10	0
20	0
30	13.74
40	13.75
50	23.81

Effect of macrocyclic ligand type

Different macrocyclic ligands were investigated as possible carriers for Pb(II) ions: 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6) and dicyclohexano-18-crown-6 (DCH18C6). Since all macrocycles have the same cavity size (1,34-1,55), the influence of different substituents in their structures resulted in different extraction efficiencies for analyzed ions. Dichloromethane was used as an extraction medium and the results (Figure 1.) showed the highest removal of Pb(II) ions (92,10 %) was obtained with DCH18C6 as a ligand in the organic phase. A possible explanation of this effect lies in the fact that two cyclohexyl groups of DCH18C6 cause an increase in the basicity of the oxygen atoms which leads to the ability of the DCH18C6 to adapt to different conformations as required for greater stability of the complex.

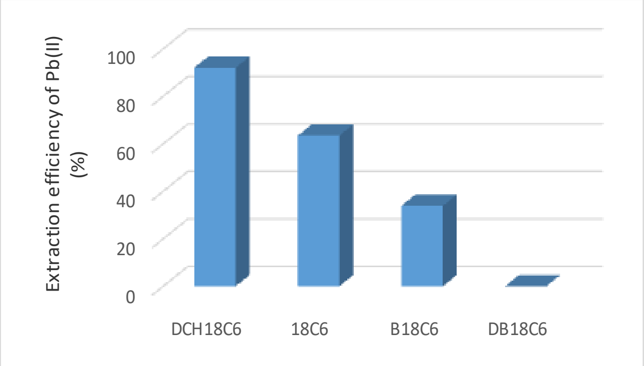

Fig 2. Comparison of the Pb(II) extraction efficiencies after 3 hours of stirring at 300rpm (feed solution contained: $1\cdot10^{-3}$mol/L of Pb(II) ions and $1\cdot10^{-3}$mol/L picrates; organic solvent dichloromethane contained $1\cdot10^{-3}$mol/L of macrocycle)

Effect of extraction time

The duration of mixing is an important parameter for every extraction procedure. Different experiments were designed to investigate this effect, using 50 mL of organic solvent phase mixed with 10 mL of aqueous feed solution phase. The results (Table 4.) showed that after 3 hours of mixing, maximum extraction efficiency was achieved (92,10 %), so this extraction time was chosen for the final procedure.

Table 4. The influence of stirring time on Pb(II) extraction (feed solution contained: $1\cdot10^{-3}$mol/L of Pb(II) ions and $1\cdot10^{-3}$ mol/Lpicrates; organic solvent DCM contained $1\cdot10^{-3}$mol/L DCH18C6; rotation 300rpm)

Stirring time, hours	% of E
1	82.75
2	83.48
3	92.10
4	73
24	91.74

Effect of feed solution pH on the Pb(II) extraction efficiency

Investigation of pH effect was designed through three experiments implementing different pH values of the feed solutions: 1, 3, and 5. The results (Figure 2.) indicate that 96% of Pb(II) ions can be extracted to the organic phase from feed solution at pH=1, which was very convenient for analyzing the real samples (prepared in the acidic medium after digestion). A slightly lower % of extraction was achieved at pH=3 (92,10 %) which was chosen for the majority of preliminary experiments where the influence of different parameters was investigated.

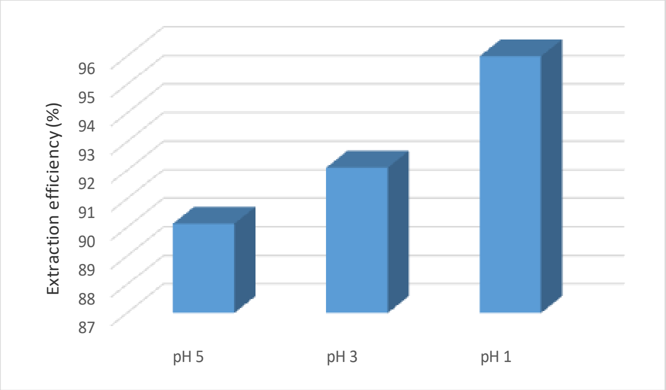

Fig 3. Effect of pH on the Pb(II) extraction efficiencies after 3 hours of stirring at 300rpm (feed solution contained: $1\cdot10^{-3}$mol/L of Pb(II) ions and $1\cdot10^{-3}$mol/L picrates; organic solvent dichloromethane contained $1\cdot10^{-3}$mol/L of DCH18C6)

Back-extraction optimization

Extraction Pb(II) ions from their Pb-CE complexes was the next step of the procedure we optimized, respectively back-extraction process. For this purpose, 11 mL of stripping aqueous solution (at pH=5), contained disodium-EDTA ($1\cdot10^{-3}$ mol/L) and Triton X-100 ($1,4\cdot10^{-3}$ mol/L) were used. The aqueous phase was analyzed after 3 hours of process. The results showed that, the content of the Pb(II) ions removed from the dichloromethane organic solvent layer (contained DCH18C6 as a ligand) was 94,12%, which led to the application of this back- extraction procedure in order to remove lead ions from river sediment samples.

Application of proposed procedure on collected soil samples

Based on the preliminary results, the final procedure was proposed for investigation of extraction possibility from the river sediment samples: 10 mL of the sample solution at pH=1 (original pH of samples after digestion) contained also $1\cdot10^{-3}$mol/L of picrates and the feed solution was mixed with 50 mL of dichloromethane as organic solvent (contained $1\cdot10^{-3}$mol/L DCH18C6 as ligand). After 3 hours of mixing at 300 rpm, the aqueous phase was analyzed with FAAS and extraction efficiency were calculated. After extraction and separation from feed solution, organic solvent layer was mixed with 11 mL of stripping aqueous solution (at pH=5), contained disodium-EDTA ($1\cdot10^{-3}$ mol/L) and Triton X-100 ($1,4\cdot10^{-3}$ mol/L) and back-extraction efficiency was evaluated. Prior to the extraction procedure, soil samples from different locations were collected and contents of metal ions were measured (Table 5). The samples were subjected to extraction procedure with dichloromethane, under proposed experimental conditions and after the organic layer was removed, aqueous solutions were analyzed with FAAS.

Table 5. Measured concentration of metal ions (mg/L) in sediment samples from different locations
(I-Bokavici, II-Lukavac, III-Devetak, IV-Berkovica)

Sample	**Concentration (mg/L)**				
	Pb(II)	Zn(II)	Ni(II)	Cu(II)	Co(II)
I	30	55	180	29	32
II	30	85	410	30	40
III	28	40	240	30	25
IV	17	25	350	15	35

The results showed that the proposed extraction procedure efficiently (>93%) removed Pb(II) ions from sediment samples and no interfering effects of coexisting ions were evident (Table 6).

After the extraction procedure, all organic solutions were used again for the back-extraction procedure with 11 ml of stripping solution, under the proposed experimental conditions. That stripping solution was analyzed after the procedure with FAAS (Table 6). Back-extraction efficiency was evaluated and it was found that, for two measured samples (I-Bokavici and IV-Berkovica) all amounts of Pb(II) ions were stripped from organic solution dichloromethane into the aqueous phase. More than 94% Pb(II) ions were stripped from the sample III-Devetak, while the lowest removal efficiency (<50%) was shown by the measured sample marked as II-Lukavac.

Table 6. Efficiencies of proposed extraction and back-extraction procedures applied on investigated sediment samples

Sample	Pb(II) content in sediment sample, mg/L	% of E	% of BE
I	30	93.2	100
II	30	100	49.83
III	28	99.2	94.82
IV	17	100	100

IV. CONCLUSSIONS

Several parameters, such as pH, type of macrocyclic ligand, type of organic solvent, were investigated to optimize the procedure for the removal of Pb(II) ions by extraction method and possibly apply it on the real samples. The present study showed that DCH18C6 ether is an excellent carrier for selective and efficient transport of Pb(II) ions through dichloromethane as an organic solvent. After 3 hours of experiment, more than 92,10 % Pb(II) ion has been removed by this extraction procedure. Back extraction optimization was also successful with 94,12% removed Pb(II) ions from the dichloromethane organic solvent layer with the same ligand. The optimized system for the removal of Pb(II) ions by extraction, showed high precision, efficiency, and selectivity, which led to successful application on river sediment samples. Results showed that the optimized system is effectively applicable to three of the four analyzed samples (Bokavici, Devetak, Berkovica), with an efficiency of over 94% removed Pb(II) ions and with an efficiency of only 50% for one sample (Lukavac). Different parameters, including a relatively short time for extraction and removal of Pb(II) ions, obtained by the optimized system investigated in this paper showed its potential applicability to the selective removal or purification of lead from its mixtures and actual samples.

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