

A useful approach towards solid–liquid extraction of metal cations with unsupported calixarenes

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Abstract

This article describes a convenient and effective method to study the extraction properties of unsupported calixarenes used as solid extracting agents. The solid–liquid extraction properties of different functionalized calixarene derivatives were studied. This method was compared to classic liquid–liquid extractions. The reproducibility of the solid–liquid extractions was studied among with the calixarene recycling. Results obtained for Cu^{2+} , Cd^{2+} and Pb^{2+} extractions using both methods have revealed the interest to use calixarenes as solid extracting agents. Moreover, a study of selective extraction has been carried out.

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1. Introduction

Motivated by environmental consideration, the extraction of metal cations from waste or drinking water is a current topic. Numerous studies have been performed to develop efficient methods for metals extraction like activated carbon adsorption, treatment with ion-exchange resins, membrane processes, and solvent extraction [1]. The efficiency of one of these techniques, the solvent extraction process, depends on the ligand nature. Indeed, the choice of the extractant often determines the success of this method. In this field among different families, extractants calixarenes were largely studied using liquid–liquid extraction method notably for the cation separation in radioactive waste [2]. These macrocycles have been modified in order to be immobilised onto various solid support materials as polymers [3], silica [4], resins [5],... Indeed the solid–liquid extraction approach is an attempt as one of the applications of chemically modified calixarenes to prepare selective chelating absorbents [6]. Several studies on ion recognition have been carried out using this method [7]. From an environmental and economic

view point, it remains a need to discover more selective and effective extractants for toxic heavy metals from waters and soils. The challenge is to find ligands that extract selectively one or some cations from a mixture and allow their release in pure form and that can be regenerated.

In this context, during the course of our continuing study on the synthesis and the use of calixarenes for cations extractions from an aqueous phase [8], we have studied the behaviour of unsupported calixarene derivatives as solid extractant using solid–liquid extraction, which has been never reported at our knowledge with such compounds. We have chosen for this study parent calixarenes (*p-tert*-butylcalix[4]arene and calix[4]arene), macrocycles functionalized with pendent proton-ionisable groups as carboxylic acid because of their potential for separations of polyvalent metal ions or sorption when immobilised on polymer matrices [9] and a calixarene amine. Additionally, calixarenes functionalized with no ionisable groups as ester have been selected for this study. All of these macrocycles have been used for liquid–liquid and solid–liquid extraction of three toxic metal cations (Cu(II), Cd(II) and Pb(II)) and both methods were compared. Moreover a study of the selectivity of these extractants towards the selected toxic cations has been measured. At last the regeneration of macrocycles and the recovery of the metal cations have been studied too.

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2. Experimental

2.1. Reagents

Fig. 1 shows the structure and the abbreviations of the calixarene derivatives used in the present study. The extractants *p*-*tert*-butylcalix[4]arene (noted **'Bu[4]**), calix[4]arene (noted **[4]**), *p*-*tert*-butylcalix[4]arene tetracarboxylic acid (noted **'Bu[4]CH₂COOH**); *p*-*tert*-butylcalix[6]arene hexacarboxylic acid (noted **'Bu[6]CH₂COOH**); *p*-*tert*-butylcalix[8]arene octacarboxylic acid (noted **'Bu[8]CH₂COOH**), tetraethyl *p*-*tert*-butylcalix[4]arene tetraacetate (noted **'Bu[4]COOEt**), hexaethyl *p*-*tert*-butylcalix[6]arene hexaacetate (noted **'Bu[6]COOEt**), octaethyl *p*-*tert*-butylcalix[8]arene octaacetate (noted **'Bu[8]COOEt**) and diaminobutoxy-*p*-*tert*-butylcalix[4]arene (noted **'Bu[4]di(CH₂)₄NH₂**) were synthesized according

to the literature procedure respectively [10–14]. Their spectroscopic data were conformed to those described.

Analytical-grade chloroform was employed as solvent in the liquid–liquid extraction. Deionised water was used for all extraction experiments. All other inorganic and organic reagents were standard reagent grade and used without further purification.

2.2. Instrumentation and analysis

All absorbance measurements were realised using a Perkin Elmer atomic absorption spectrometer with air-acetylene flame. Hollow cathode lamps manufactured by Varian were used in all the experiments. The parameters used were: current=5 mA, monochromator band pass=0.7 nm, flow of acetylene=2 L/min, flow of air=15 L/min, replicates: 5. Wavelengths used for

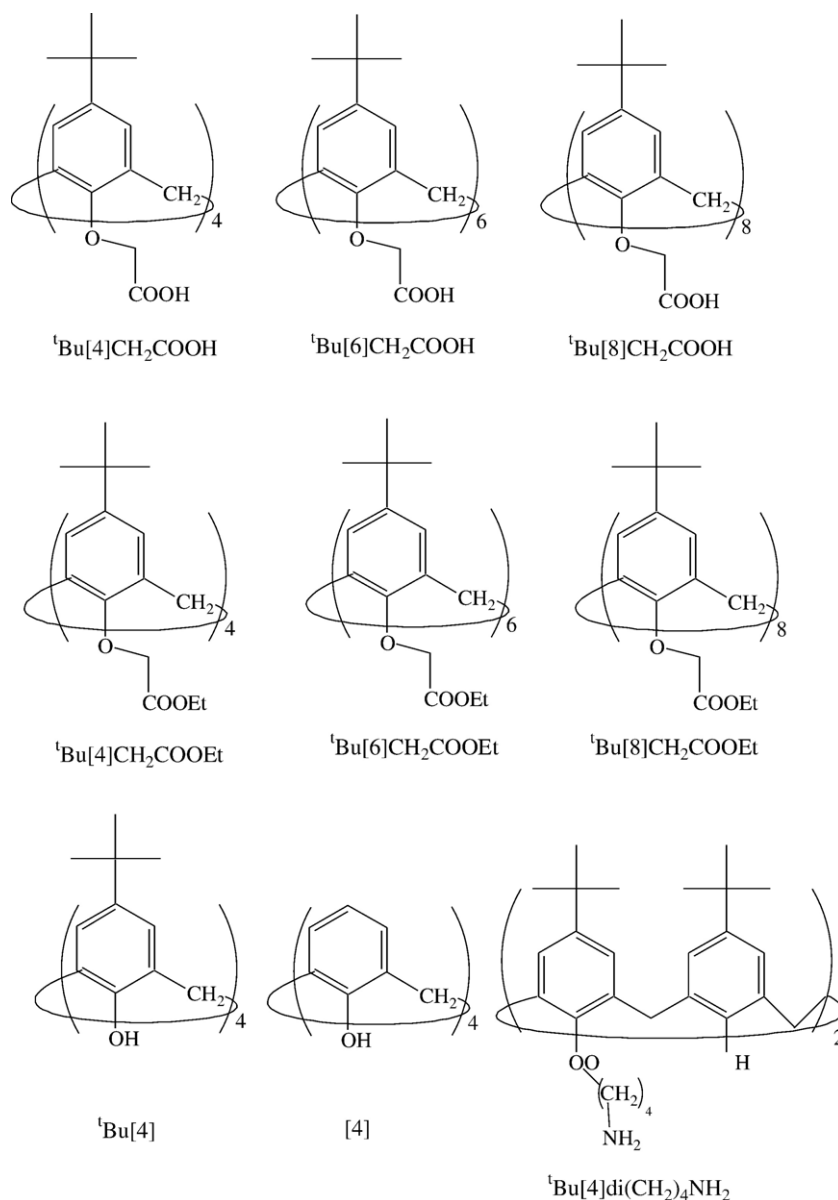


Fig. 1. Structure of studied calixarenes as extractant.

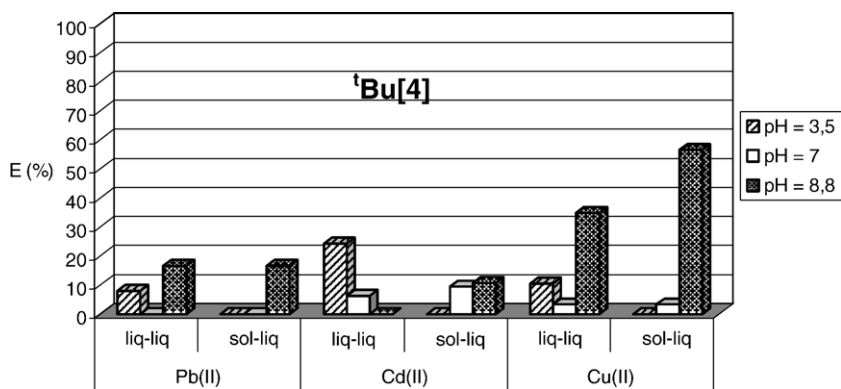


Fig. 2. Extraction percentage of cations as function of the pH value and the used method by **tBu[4]**.

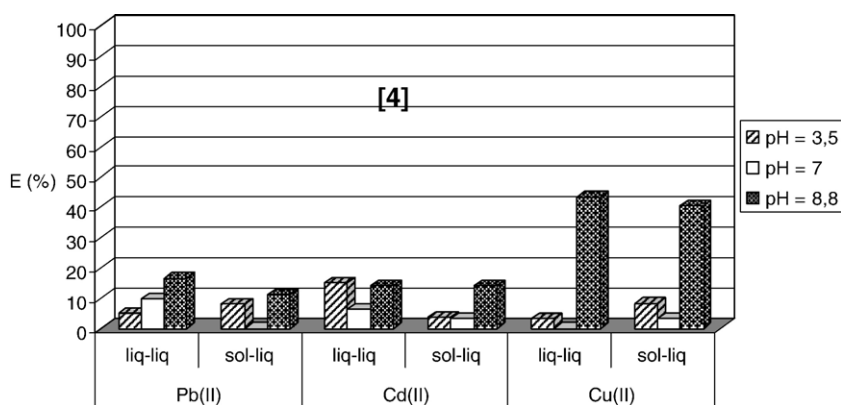


Fig. 3. Extraction percentage of cations as function of the pH value and the used method by **[4]**.

the determination of metal ion concentrations were Cd, 229 nm; Pb, 283 nm; Cu, 325 nm.

2.3. Metal ion extraction

2.3.1. Liquid–liquid extraction

The organic solutions were made by dissolving a weight amount of the ligand in chloroform. The aqueous solutions were

prepared at different pHs. One was buffered to pH 3.5 with acetate sodium (99%). A solution of pH 7 buffer was prepared from acetic acid (99.8%)–acetate sodium (99%) and another one of pH 8.8 was prepared by mixing appropriate volumes of 0.52 M ammonia and 0.52 M ammonium acetate. All these pH were measured before introducing the metal ion. Liquid–liquid extraction experiments were carried out in a flask by shaking (16 h; 30°C) 10 mL of an aqueous phase containing metal salt

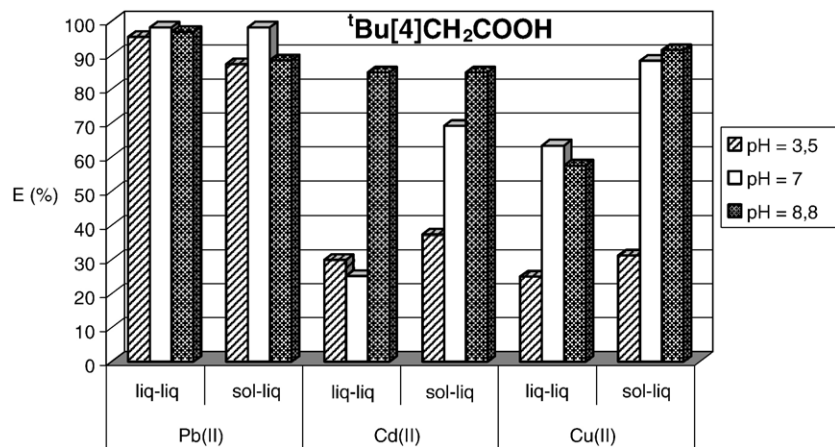


Fig. 4. Extraction percentage of cations as function of the pH value and the used method by **tBu[4]CH₂COOH**.

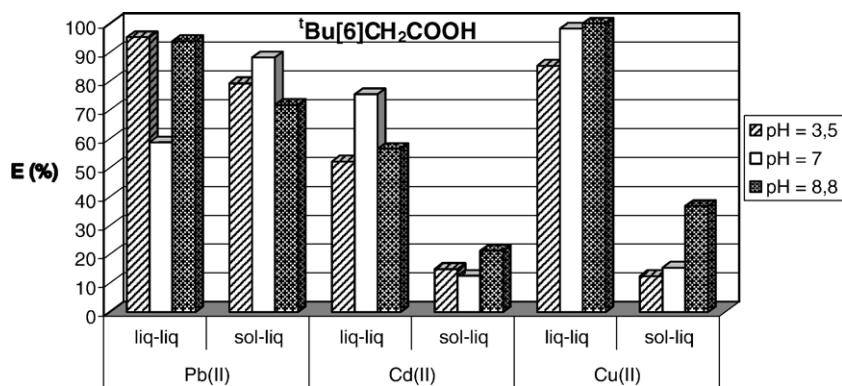


Fig. 5. Extraction percentage of cations as function of the pH value and the used method by ^tBu[6]CH₂COOH.

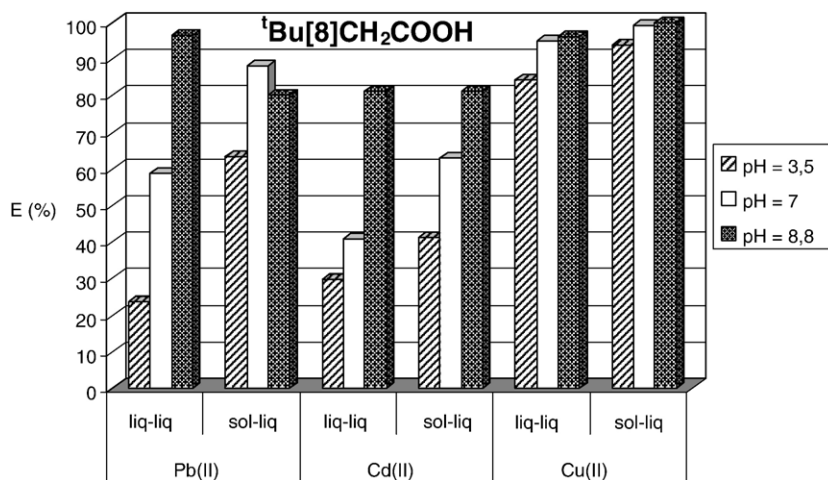


Fig. 6. Extraction percentage of cations as function of the pH value and the used method by ^tBu[8]CH₂COOH.

(2.10^{-3} M) and 10 mL of organic phase containing ligand (2.10^{-3} M). The extraction was not affected by further shaking, indicating that the equilibrium had been attained.

2.3.2. Solid–liquid extraction

A weighed amount of the ligand was introduced in the aqueous solution. Buffer aqueous solutions were prepared like

previously. Solid–liquid extraction experiments were carried out in flask by shaking (16 h; 30°C) 10 mL of an aqueous phase containing metal salt (2.10^{-3} M) and an amount of the calixarene (2.10^{-5} mol). This amount is exactly the same than that of the ligand involved in the liquid–liquid experiments of this study. The extraction was not affected by further shaking, indicating that the equilibrium had been reached.

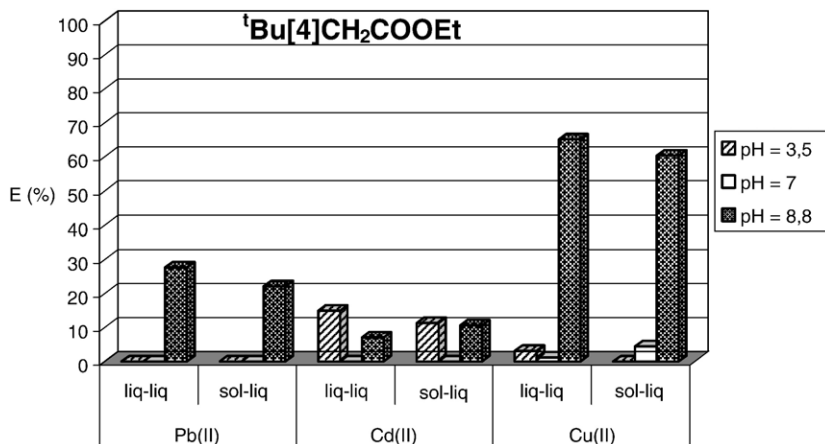


Fig. 7. Extraction percentage of cations as function of the pH value and the used method by ^tBu[4]CH₂COOEt.

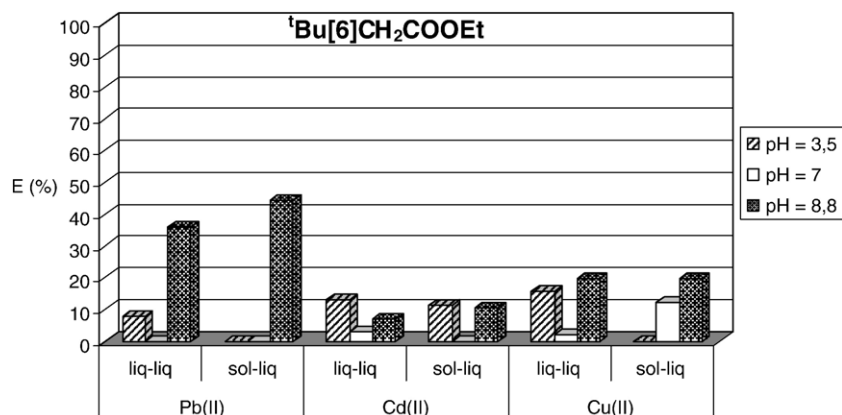


Fig. 8. Extraction percentage of cations as function of the pH value and the used method by ^tBu[6]CH₂COOEt.

2.3.3. For both methods

The aqueous phase was separated, centrifuged and analysed by atomic absorption spectrometry (Perkin Elmer) with an air-acetylene flame. The measurements have been carried out using standard conditions of calibration. The extent of extraction ($E\%$, Eq. (1)) was determined from the uptake of metal concentration from the aqueous phase:

$$E\% = \left\{ \frac{([\text{Metal}]_{\text{blank}} - [\text{Metal}]_{\text{water}}) \times 100}{[\text{Metal}]_{\text{blank}}} \right\} \quad (1)$$

where $[\text{Metal}]_{\text{blank}}$ and $[\text{Metal}]_{\text{water}}$ denoted for the liquid–liquid extraction, the metal concentration in the aqueous phase extracted respectively with pure chloroform and with the chloroform solutions containing extractants or, for the solid–liquid extraction, the metal concentration in the aqueous phase extracted respectively without and with the calixarene.

2.3.4. Regeneration of extractant

After solid–liquid extraction, the solid is filtered and washed with a 50 mL of HCl (1 M). Then the aqueous phase was analysed by atomic absorption spectrometry.

3. Results and discussions

The main objectives of this work are to find out an effective and simple method in order to study the extraction properties of

calixarenes toward toxic cations. During the past two decades the extraction properties of calixarene were studied using the liquid–liquid extraction method with or without aqueous metal picrates solution. Moreover calixarenes have been supported on various materials and used for solid phase extraction of transition metal ions from aqueous solution. But the use of unsupported calixarene as solid phase extraction of ions from aqueous solution have never been reported and seems be a useful approach to study the extraction properties of calixarenes.

The structures of all calixarene derivatives selected for this study and the used abbreviations are depicted in Fig. 1. The choice of the calixarene derivatives functionalized with carboxylic acid and ester function has been caused by their binding and extraction properties toward cations [15–19]. Moreover, parent calixarenes and a calixarene amine have been tested in the liquid–liquid and solid–liquid extraction as well.

The extraction results (Figs. 2–10) for each calixarene derivative have been calculated using both liquid–liquid and solid–liquid extraction methods toward three selected toxic metal cations (copper, cadmium, lead) at a slightly acid pH (3.5), neutral pH (7) and slightly basic pH (8.8) in order to avoid the dissolution of the calixarene in water. For these experiments, the shaking time has been optimized for both methods in order to obtain the best extraction percentages. Indeed no changes in extraction percentages were observed from 16h to 3days indicating that the equilibrium has been reached after 16h.

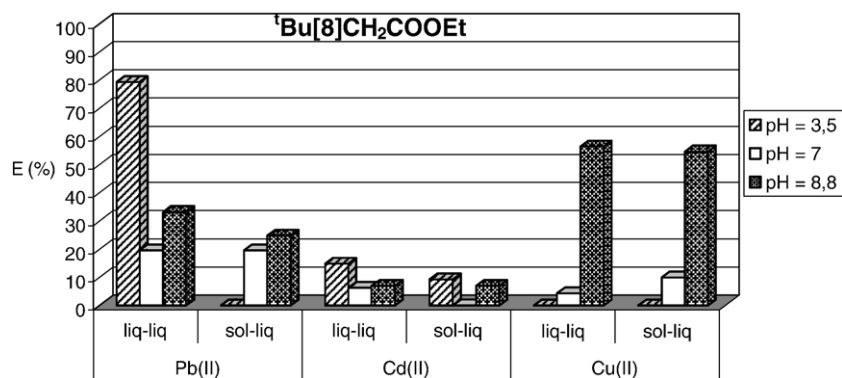


Fig. 9. Extraction percentage of cations as function of the pH value and the used method by ^tBu[8]CH₂COOEt.

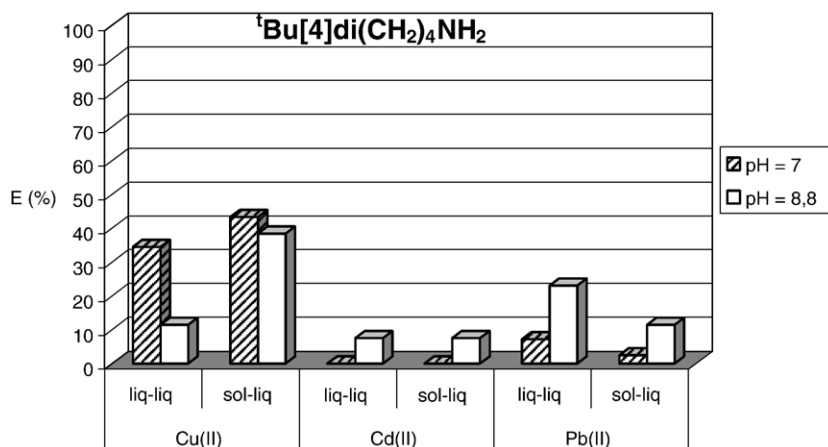


Fig. 10. Extraction percentage of cations as function of the pH value and the used method by ^tBu[4]di(CH₂)₄NH₂.

Moreover no precipitation of metallic salts or colour changes were observed for the aqueous phases at the different pHs. This indicates the full capacity of the metal ion to be complexed. In the case of *p*-*tert*-butylcalix[4]arene (^tBu[4]), the extraction percentages are reported in Fig. 2. They show that ^tBu[4] is poor extractant in acidic and neutral media for the metal cations used in the experiments but its extraction ability increases at pH = 8.8 above all in the case of the solid–liquid extraction. This may be due to the presence of phenolate ion on macrocycle which will facilitate the extraction process [20]. The best result is obtained in basic media where ^tBu[4] extract 35% and 56% of Cu(II) respectively with liquid–liquid (liq–liq) and solid–liquid (sol–liq) methods. The results obtained with both methods are similar for the extraction of lead and copper. The extractant [4] which differ from ^tBu[4] in the lack of *tert*-butyl groups has an affinity for Cu(II) at high pH and this result is similar for both used methods (43% for liquid–liquid extraction and 40% for solid–liquid extraction) (Fig. 3). Like ^tBu[4], [4] is poor extractant in acidic and neutral media for the selected metal cations and has very slightly affinity for Pb(II) and Cd(II). The extraction results of ^tBu[4] and [4] are similar indicating that the *tert*-butyl groups seem to have not a role in the extraction process by comparison with the hydroxyl groups. Indeed, in slightly basic media, we observed that the extraction is more efficient certainly due to the presence of phenolate groups [20]. A series of calixarenes carboxylic acid with four, six and eight phenolic units respectively ^tBu[4]CH₂COOH, ^tBu[6]CH₂COOH and ^tBu[8]CH₂COOH have been studied for the extraction and the extraction percentages are reported in Figs. 4, 5 and 6. An overall view of the results show that these macrocycles exhibited efficient Pb(II), Cd(II) and Cu(II) extraction and particularly at high pH in comparison with ^tBu[4] and [4]. Moreover the extraction percentages obtained by solid–liquid extraction method are very near to those obtained by solid–liquid extraction method. Only notable difference can be observed in the case of the Cu(II) and Cd(II) extraction by ^tBu[6]CH₂COOH. These results show that in this case, the size of the extractant may be involved in the extraction process.

Using the solid–liquid extraction method, at high pH, it is important to note that ^tBu[4]CH₂COOH extract 88% of Pb(II), 85% of Cd(II) and 91% of Cu(II); ^tBu[6]CH₂COOH extract 72% of Pb(II), 21% of Cd(II) and 37% of Cu(II); ^tBu[8]CH₂COOH extract 84% of Pb(II), 81% of Cd(II) and 100% of Cu(II) which show that the solid–liquid extraction is a very efficient method and as effective as the liquid–liquid extraction. In order to compare both extraction method, another series of calixarene derivatives functionalized with ester functions has been studied. The extraction percentages of cations by ^tBu[4, 6 and 8]CH₂COOEt are reported in Figs. 7, 8 and 9. We can observe that the results obtained for both methods are very similar indicating that the solid–liquid extraction method gives coherent result depending on the type of extractant used. In comparison to the extraction percentage reached with calixarenes carboxylic acids, calixarenes esters are less efficient extractant. It confirms that the ionisable groups play an important role in the extraction process. Moreover calixarene esters are more efficient as solid extractant at high pH where 60% and 55% of Cu(II) are extract by respectively ^tBu[4, 8]

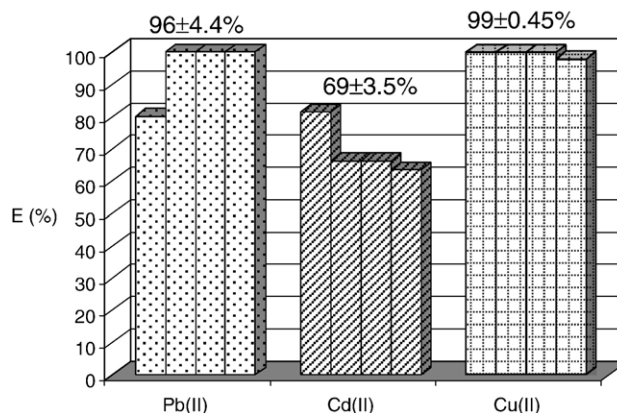


Fig. 11. Reproducibility study of solid–liquid extraction of cations by ^tBu[8]CH₂COOH at pH = 8.8.

Table 1
Selectivity study: extraction (%) of cations by calixarene derivatives from an aqueous solution containing a mixture of Cu(II), Cd(II) and Pb(II) at pH=3.5

Ligands	pH 3.5					
	Cu(II)		Cd(II)		Pb(II)	
	Sol-liq	Liq-liq	Sol-liq	Liq-liq	Sol-liq	Liq-liq
^t Bu[4]	0	0	25	15	0	0
[4]	0	0	15	9	2	5
^t Bu[4]CH ₂ COOH	30	15	22	40	91	95
^t Bu[6]CH ₂ COOH	26	29	19	9	77	88
^t Bu[8]CH ₂ COOH	24	38	9	15	49	93
^t Bu[4]CH ₂ COOEt	10	9	3	3	7	9
^t Bu[6]CH ₂ COOEt	10	11	0	0	7	9
^t Bu[8]CH ₂ COOEt	8	20	0	0	7	21
^t Bu[4]di(CH ₂) ₄ NH ₂	/	23	/	6	/	5

CH₂COOEt and 44% of Pb(II) by ^tBu[6]CH₂COOEt than as extractant in liquid–liquid extraction method. Additionally an example of a calixarene derivative functionalized with amine functions (^tBu[4]di(CH₂)₄NH₂) was studied in order to evaluate its efficiency as extractant more particular at low pH in opposition to calixarenes carboxylic acids. The experiments were realised at only pH=7 and 8.8 due to the solubility of the compound in water at pH=3.5. The results show that the extraction percentages obtained with both methods are coherent. ^tBu[4]di(CH₂)₄NH₂ is more efficient as solid extractant of Cu(II) (43% at pH=7 and 39% at pH=8.8) than extractant of Cd(II) or Pb(II) (*E*(%) ≤ 10%). All of these results show that the solid–liquid extraction method using calixarenes as solid extractant is an efficient and useful method. In spite of some differences between the extraction percentages of both methods, this process gives good results. The reproducibility of the solid–liquid extraction method was calculated repeating assays four times with one calixarene giving high level extraction. The selected calixarene derivative ^tBu[8]CH₂COOH extract 96% (±4.4%) of Pb(II), 69% (3.5%) of Cd(II) and 99% (0.5%) of Cu(II) (Fig. 11) showing the good reproducibility of this method. Moreover, the regeneration of the ^tBu[8]CH₂COOH ligand after extraction of Cu(II), Cd(II)

Table 2
Selectivity study: extraction (%) of cations by calixarene derivatives from an aqueous solution containing a mixture of Cu(II), Cd(II) and Pb(II) at pH=7

Ligands	pH 7					
	Cu(II)		Cd(II)		Pb(II)	
	Sol-liq	Liq-liq	Sol-liq	Liq-liq	Sol-liq	Liq-liq
^t Bu[4]	0	0	0	4	0	0
[4]	0	0	8	8	2	2
^t Bu[4]CH ₂ COOH	28	28	16	44	63	97
^t Bu[6]CH ₂ COOH	18	32	16	12	51	95
^t Bu[8]CH ₂ COOH	8	57	16	28	29	97
^t Bu[4]CH ₂ COOEt	0	4	0	0	0	10
^t Bu[6]CH ₂ COOEt	0	6	0	0	5	17
^t Bu[8]CH ₂ COOEt	4	3	4	4	10	7
^t Bu[4]di(CH ₂) ₄ NH ₂	43	34	0	0	2	7

Table 3
Selectivity study: extraction (%) of cations by calixarene derivatives from an aqueous solution containing a mixture of Cu(II), Cd(II) and Pb(II) at pH=8.8

Ligands	pH 8.8					
	Cu(II)		Cd(II)		Pb(II)	
	Sol-liq	Liq-liq	Sol-liq	Liq-liq	Sol-liq	Liq-liq
^t Bu[4]	0	0	15	11	0	7
[4]	2	0	15	15	12	2
^t Bu[4]CH ₂ COOH	48	33	41	60	90	0
^t Bu[6]CH ₂ COOH	22	44	23	26	74	97
^t Bu[8]CH ₂ COOH	50	65	38	34	85	99
^t Bu[4]CH ₂ COOEt	14	18	11	11	21	18
^t Bu[6]CH ₂ COOEt	16	30	15	8	16	28
^t Bu[8]CH ₂ COOEt	17	18	11	11	18	18
^t Bu[4]di(CH ₂) ₄ NH ₂	11	38	8	8	23	12

and Pb(II) have been done by washing the ligand with HCl solution which allows a full regeneration of the starting material as described in the case of liquid–liquid extraction [21]. About the extraction mechanism, the exchange between the metal cations dissolved in the aqueous phase and the calixarene (as solid or dissolved in organic solution) is achieved by means of interfacial reactions of complexation at the interface between the phases in contact. These interfacial reactions may be based on the hydrophilic groups of the calixarene containing donor atoms like oxygen or nitrogen which are capable of selective binding with some metals ions [22].

A selectivity study of the extractants was developed by mixing the three metal cations in aqueous phase in the same concentration and condition that the previous described experiments. The extraction percentages were calculated for each pH and each cation (Tables 1–3). In the case of carboxylic acid calixarenes, high level of extraction is reached but no selectivity toward one metal is observed and it is the same thing at all pH. From the results at pH=3.5 reported in Table 1, the most efficient and selective ligand is ^tBu[4] which extract 25% of only Cd(II) from the mixture of cations using the solid–liquid extraction method as against 15% using the liquid–liquid extraction. Table 3 shows that ^tBu[4]di(CH₂)₄NH₂ is a selective solid extractant for Cu(II): %*E* values are 43% for solid–liquid extraction method as against 34% for liquid–liquid extraction method.

4. Conclusion

The extraction properties of calixarenes can be studied by a simple and efficient method using unsupported calixarenes as solid extractant in solid–liquid extraction method. The method is reproducible and the calixarene can be regenerate. Calixarenes containing ionisable groups like carboxylic acid are good extractant for Cd(II), Cu(II) and Pb(II) but are not very selective. The studied calixarene parents are interesting extractant and can be selective in extraction of Cd(II). To the best of our knowledge, the use of calixarene as solid extractant of metal from aqueous solution is new and offer large possibilities to study the extraction properties of calixarenes.

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