

# Natural Silicate as a Solid Support for the Calix[4]Thiophosphorus Derivative for Removal Mercury (II), as Picrate from Water

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**How to cite this paper:** Aparicio-Aragon, W.B. and Deza-Ramos, T. (2024) Natural Silicate as a Solid Support for the Calix[4]Thiophosphorus Derivative for Removal Mercury (II), as Picrate from Water. *Advances in Chemical Engineering and Science*, 14, 74-83.

<https://doi.org/10.4236/aces.2024.142005>

**Received:** March 20, 2024

**Accepted:** April 20, 2024

**Published:** April 23, 2024

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## Abstract

Currently a technique widely used for gold extraction is mercury by amalgamation technique, the tailing produced pollutes water of all kinds, so it is necessary to develop a form of selective mitigation, for which it is necessary to use complexing agents based on calixarene functionalized with mercury sequestering agents. These are immobilized by adding supports based on natural silica to form polymers and make them insoluble in all types of solvents, so that they can be used as an extractor and at the same time regenerate to their original properties for continuous reuse.

## Keywords

Extraction, Amalgamation, Polymer, Natural Silicate, Calixarene

## 1. Introduction

Calixarenes are benefiting from their three-dimensional structures and easily chemically modified both at the upper and lower rim as well as having potential receptor properties for cations, anions and neutral molecules [1]-[8]. In particular the easy accessibility of *p-tert-butylcalix[4]arene* has made this member of the series increasingly popular as a building block or platform for assembling more elaborate structures with ligating side arms or podands for the reception of guest species [9]-[16]. In addition, calixarene derivatives are a family in which the phenolicoxygens are attached to two pendant arms containing oxygen, nitrogen, sulphur and phosphorusdonoratoms, while the upper rim of the calixarene derivative is attached to a polymeric support of a silicate chain.

However, calixarene based polymers have just begun to receive attention, as

these new polymers may then be processed into materials suitable for the chemical sensor devices such as ion selective electrodes and filtration/extraction membranas [17] [18] [19] [20] [21]. Previously reported sensor devices based on calixarenes have been fabricated by blending the calixarene molecules into polymer melts or other membrane composites

Yilmaz and co workers [22] [23] [24] [25] [26], reported a synthesis of polymeric calixarenes by lower and upper rim and investigation of these ionophoric material with alkali and transition metal cations, in all cases the polymeric support reported are organic compounds. We report the used inorganic support as silicate in this work.

Harris *et al.* [18] have prepared a polymeric calixarene complex with Na<sup>+</sup> analogue that was reported by Shinkai [27] which they prepared by reacting *p*-(chlorosulphonic)calyx[6]arene with poly(ethylene-imine) and used the polymer for selective adsorption of UO<sub>2</sub><sup>2+</sup>.

Robledo *et al.* [28] have prepared a polymeric calcium silicate-based product as a cementitious agent for the repair of reticular perforations in teeth.

In this work we have discussed by synthesis and extraction properties of silicate support polymer, show higher selectivity for soft metal cation as Hg<sup>2+</sup> and Ag<sup>+</sup> similar to the parent calixarene.

## 2. Experimental Part

### Chemicals

*p*-*tert*-Butylcalix[4]arene, bromoacetonitrile, potassium carbonate, potassium hydrogen carbonate,  $\alpha$ ,  $\alpha$  dichloromethyl methyl ether, sodium cyanoborane hydride, stannum tetrachloride and aluminium chloride were purchased from Aldrich. Lithium aluminium tetrahydride, 18-crown-6 (18-C-6), diethyl chlorothiophosphate, phenol and tetra-*n*-butyl ammonium bromide purchased from Fluka were used without further purification. Metal-cation (silver and mercury) perchlorates were purchased from Aldrich. These were dried over P<sub>4</sub>O<sub>10</sub> under vacuum for several days before use.

Acetonitrile (HPLC grade, Hayman Limited, high purity reagent), THF (tetrahydrofuran), methanol (Fisher reagent, 99%) ethanol (HPLC grade, Fisher) dichloromethane (Fisher), Toluene (Fisher), acetone (Fisher, AR) were used without further purification.

### Synthesis of polymeric resin material

In order to anchor the *p*-*tert*-butylcalix[4]arene, amine thiophosphorus to a natural solid support framework, several routes were followed starting to the removal of the *p*-*tert*-butyl groups from the parents calix[4]arene as described below.

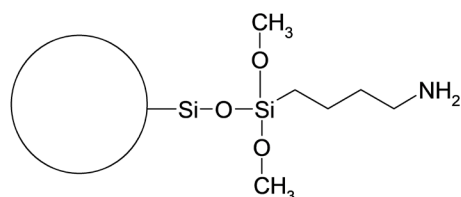
### Synthesis of L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub>

L<sub>1</sub>, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub> were synthesized following the pathway described by Aparicio *et al.* [29], L<sub>5</sub> is the receptor material that is added to a polymeric matrix composed of natural clay as described below.

### Synthesis of 3-aminopropyltrimethylsilylated natural silica (L<sub>6</sub>)

The natural silicate from the Marrakech region, of the many samples of this region, by analysis of the physic-chemical properties selected two samples has the following characteristics **Table 1**.

Previous treatment of this silicate carried out for removal water-soluble salts by washing many times with deionized water and 5 M solution of hydrochloric acid for removal  $\text{Fe}_2\text{O}_3$ , after dry and get the neutral pH for this clay used as the solid support for synthesise  $\text{L}_6$ .



### 3-aminopropyltrimethylsilylated natural silica ( $\text{L}_6$ )

In a three-necked round-bottomed flask (250 ml) equipped with condenser and nitrogen atmosphere. Dried silica (5 g) was dispersed in anhydrous toluene (100  $\text{cm}^3$ ). To the resulting slurry 3-aminopropyltrimethylsilane (2.5 g, 22.3 mmol) was added. The resulting mixture was refluxed for 6 h and then cooled to 25°C, filtered and washed first with toluene and then with methanol in order to furnish.

Elemental analysis was carried out at the University of Surrey, calculated %: C 10.65, H 1.68, N 1.83; found %: C 11.20, H 1.71, N 1.93.

### Synthesis of the polymer calix[4]arene amine phosphorus derivative, ( $\text{L}_7$ )

In a three-necked round-bottomed flask (250 ml) equipped with condenser and nitrogen atmosphere. (1 g, 0.75 mmol) of anhydrous 3-aminopropyltrimethylsilylated silica ( $\text{L}_6$ ) in absolute methanol and dichloromethane mixer solvent (50  $\text{cm}^3$ ), the pH of solution kept in 1 by addition of methanolic solution of HCl, after check the pH condition, was added  $\text{L}_5$  (0.70 g, 0.96 mmol) and sodium cyanoborohydride (0.07 g, 0.96 mmol). The resulting slurry was stirred at 25°C for 72 h. Concentrated HCl was added to the slurry until the pH = 1. The acidified slurry was filtered and the resulting solid was washed with dichloromethane (50  $\text{cm}^3$ ), chloroform (50  $\text{cm}^3$ ), acetone (50  $\text{cm}^3$ ), ethanol (50  $\text{cm}^3$ ), methanol (50  $\text{cm}^3$ ), aqueous NaOH (50  $\text{cm}^3$ ) and water (50  $\text{cm}^3$ ) before being dried over  $\text{CaCl}_2$  in vacuo for 12 h.

Elemental analysis was carried out at the University of Surrey, calculated %: C, 21.82, H 3.01, N 2.72; found %: C 20.82, H 2.91, N 2.66.

**Table 1.** Chemical composition of the natural silicate used in this work<sup>a</sup>.

Sample	$\text{Fe}_2\text{O}_3$	MnO	$\text{TiO}_2$	CaO	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	MgO	$\text{Na}_2\text{O}$	LOI	Total
	%	%	%	%	%	%	%	%	%	%	%	%
O1-RT	6.23	0.06	1.08	1.23	2.95	0.15	64.54	14.41	2.02	0.50	7.10	100
SR1-RT	4.89	0.07	0.83	0.4	2.10	0.06	74.45	11.49	0.70	0.50	5.01	100

<sup>a</sup>Chemical analysis result from department of geology, UAB Spain.

### Extraction experiments

In order to investigate the extraction ability of the polymeric material, in accorded of behavior of parent ligand, was check of extraction process by filtered a solution of mercury(II) as picrate into of a column contained polymeric material (0.4 g), the remain solution is analyze for determine concentration of mercury(II), as picrate by use UV spectroscopy Cecil 8000 Scanning spectrophotometer.

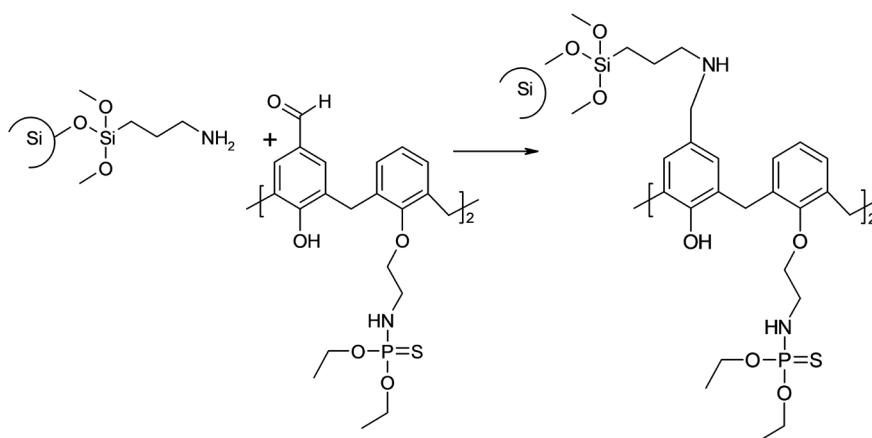
## 3. Results and Discussion

### Synthesis of 3-aminopropyldimethylsilylated silica ( $L_6$ )

This natural silicate material (light yellow crystals) was prepared in 90% yield.

In the microanalysis data confirmed the presence of amine groups that mean the 3-aminopropyldimethylsilylated silica is obtained in good yield.

### Synthesis of the polymer calix[4]arene amine thiophosphorus derivative in natural silicate as a support ( $L_7$ )



### Analysis for nitrogen

Microanalysis data reported in **Table 2** of the experimental section, [Synthesis of the polymer calix[4]arene amine phosphorus derivative, ( $L_7$ )] indicate that the percentage of nitrogen found is 2.66%, this amount of nitrogen is higher by 0.58% in amount of nitrogen found in  $L_6$ , [Synthesis of 3-aminopropyldimethylsilylated natural silica ( $L_6$ )], **Table 3**, on the other hand, the complete insolubility of this compound in any solvent (organic and inorganic) means that the calix[4]amino-phosphorus ligand derivative is bound to the natural silicate support. These amounts of nitrogen in the silicate material are representing 0.29 moles of ligand are attached of a mol of silicate material.

### Extraction experiments

In the way of determine extraction capacity for this silicate polymer calix[4]aminothiophosphorus, the follow technique was use 0.7126 g. of material amino thiophosphorus silacte polymer filled in a small column for to determine capacity of the absorption of this material, all experimental carried out with a solution of mercury(II), as picrate ( $1.21 \text{ mol}\cdot\text{dm}^{-3}$ ), this results are show now, the remained solution analysis by UV spectrophotometer technique at 354.5 nm

of wave length. A representative result of 10 experiments is shown in the following section, **Figure 1**, **Figure 2** and **Figure 3**.

The exactly concentration of mercury(II), picrate was determine by use volumetric titration technique, for replacement titration with EDTA  $0.01 \text{ mol}\cdot\text{dm}^{-3}$  and used the following relation:

1 ml, expended of  $0.01 \text{ mol}\cdot\text{dm}^{-3}$  EDTA is equal to 2.0061 mg Hg detected [30].

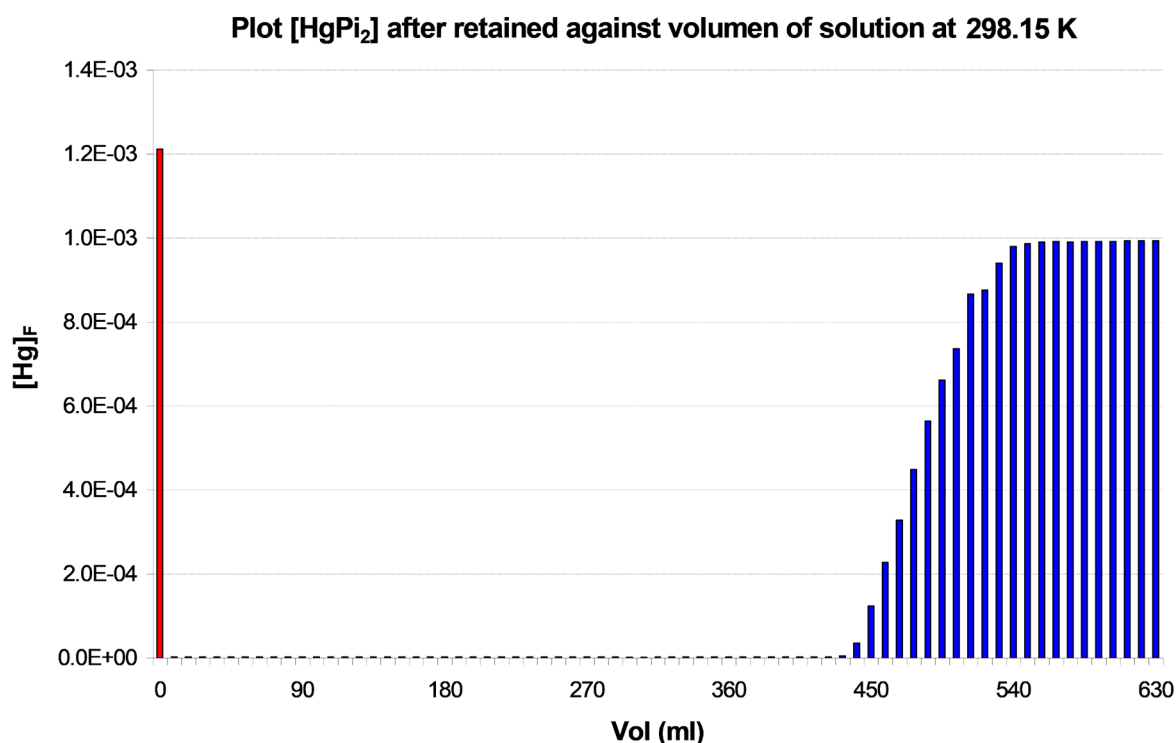
To determine the initial concentration of mercury(II), picrate was used for the evaluate capacity of retained of the calix[4]aminethiophosphorus natural silicate as solid support is  $1.56 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ .

**Table 2.** Microanalysis report of L<sub>6</sub>, (Synthesis of 3-aminopropyldimethylsilylated natural silica); Experimental Part.

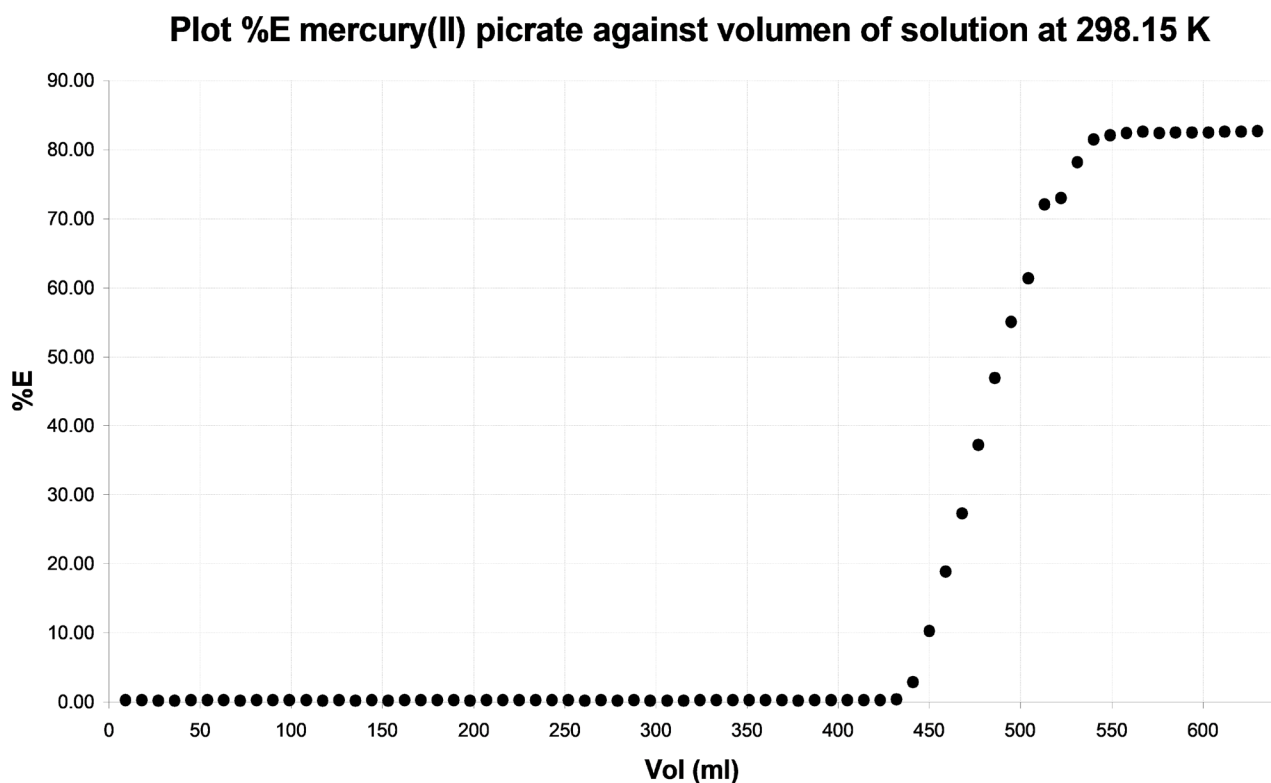
Element	% C	% H	%N
Found	11.20	1.71	1.93
Calculate	10.65	1.68	1.83

**Table 3.** Microanalysis report of L<sub>7</sub>, (Synthesis of the polymer calix[4]arene amine phosphorus derivative); Experimental Part.

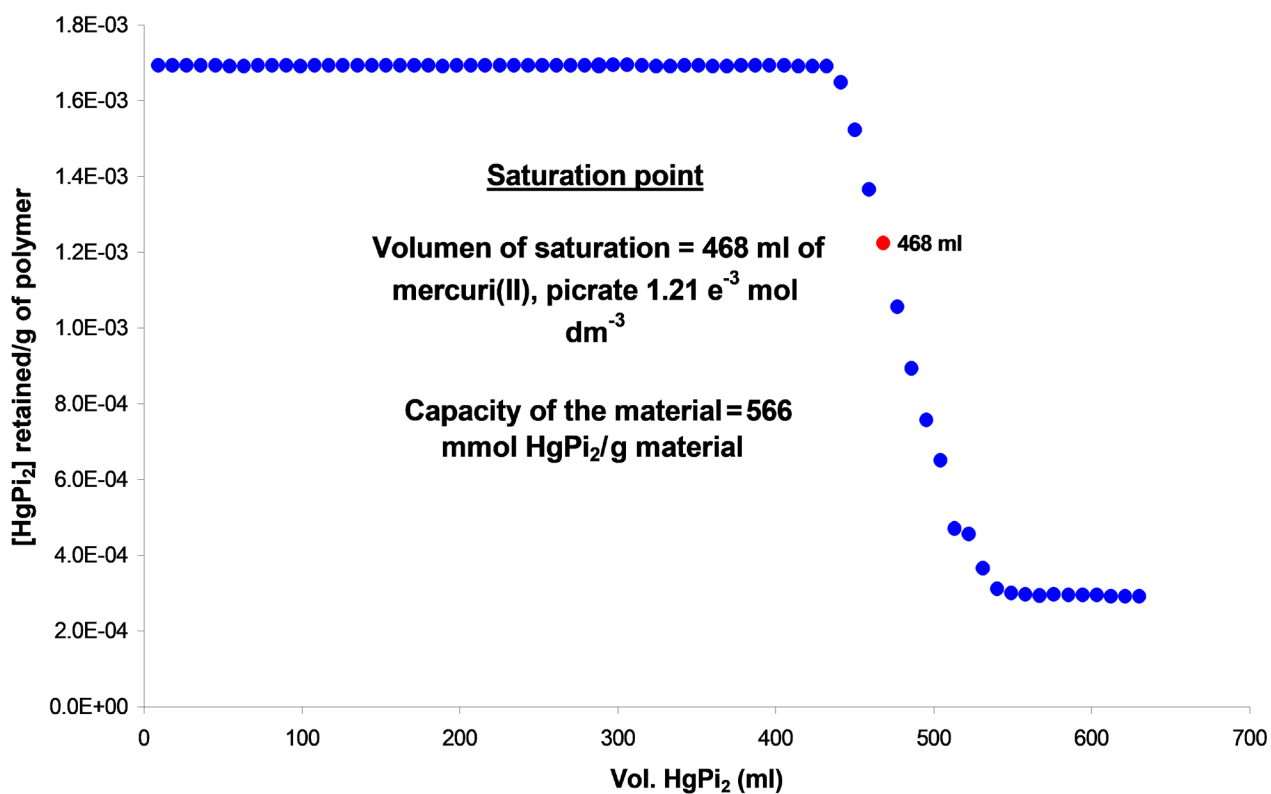
Element	% C	% H	%N
Found	20.82	2.91	2.51
Calculate	21.05	3.01	2.72



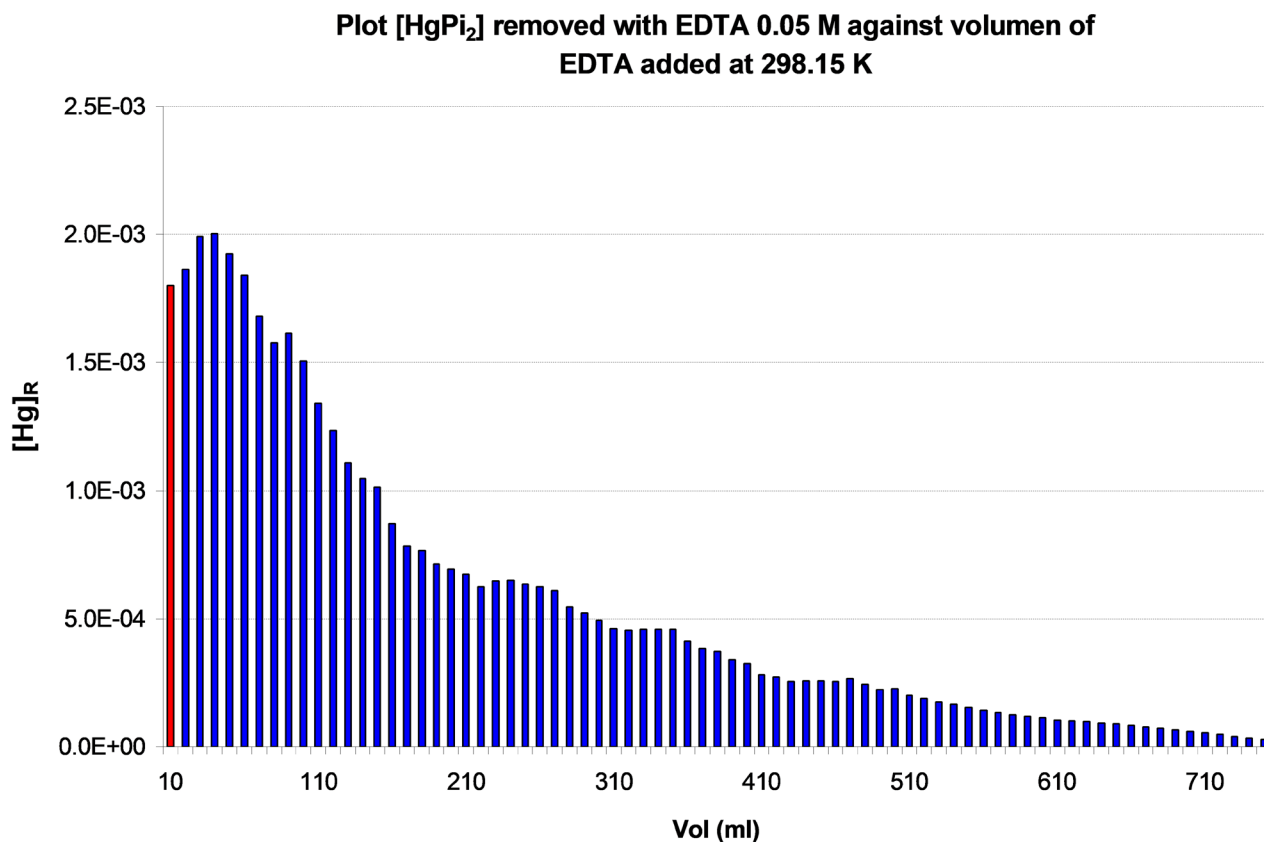
**Figure 1.** Mercury(II), picrate remainder after extraction with natural silicate polymer calix[4]arene thiophosphorus in water at 298.15 K.



**Figure 2.** % E extraction of mercury(II), picrate from water by calix[4]arene thiophosphorus attach to a natural silicate as solid support at 298.15 K.



**Figure 3.** Saturation capacity of calix[4]arene thiophosphorus attach to a natural silicate as the solid support at 298.15 K.



**Figure 4.** Regeneration of the polymeric calyx[4]arene thiophosphorus derivative with EDTA at 298.15 K.

**Figure 1** shows the capacity of retainer of the material is higher, this plot shows what before saturation point the efficiency of the polymer is total, after saturation point decrease remainder capacity of the material, on the other hand in **Figure 2** shown % of extraction again the volume of the solution.

We used **Figure 3** for the determine absorption capacity of the silicate polymer for grams of the material, as well as for the used solution of mercury(II), picrate in  $1.56 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ , 0.7126 grams of calix[4]amine thiophosphorus, natural silicate polymer is saturate with 468 ml of this solution, the data analysis shown the capacity of saturation is:

**Capacity of saturation = 878.40 mmol of mercury(II), picrate/g of polymer.**

#### Regeneration of the polymer

When the animothiophosphorus silicate polymer is saturate with mercury(II), picrate solution, for the restore initial properties of this material is necessary to remove mercury(II) picrate into the polymeric material, for this purpose used EDTA solution  $0.05 \text{ mol}\cdot\text{dm}^{-3}$ . The results show in **Figure 4**.

## 4. Conclusions

On the basis of these discussions, can be drawn:

- 1) The natural silicate after previous treatment is possible to use as a solid

support for getting out polymeric material.

2) Attaching calix[4]amino thiophosphorus ligand to natural silicate support is in same yields if compared with silicate pure.

3) The capacity of absorption mercury(II), as picrate of this polymer is the 566 mmol of mercury(II) picrate, if this value is compared with that obtained for the previous polymer fixed on pure silicate, its adsorption capacity is (878 mmol of Hg/g of material), when the support is natural silicate, this capacity decreases by 312 mmol of Hg/g of material. This is why the natural silicate has same impurities impossible to remove completely.

4) Same in the previous polymer is possible to regenerate this material.

## Acknowledgements

The author thanks the University of Surrey for the great opportunity to study in their classrooms. Many thanks to my supervisor Prof. Angela F. Danil de Namor. I feel very privileged for having worked under her supervision.

## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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## List of Abbreviations

- L<sub>1</sub>: De-*tert*-butylacion de *p-tert*-butylcalix[4]arene.
- L<sub>2</sub>: 25,27 bis[nitrilo]metoxi, 26,28 dihidroxicalix[4]arene.
- L<sub>3</sub>: 25,27 bis[amino]ethoxi, 26,28 dihidroxicalix[4]arene.
- L<sub>4</sub>: 5,11,17,23 tetra-*tert*-butyl,25,27 bis(dietil tiofosfato amino)ethoxi,26,28 dihidroxicalix[4]arene.
- L<sub>5</sub>: 5,17-*p*-aldeido-25,27-bis(dietiltiofosfato amino)ethoxi-26,28-dihidroxicalix[4]arene.
- Hg: mercury.