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Novel D2EHPA-polysiloxane-based Sorbent for Titanium (IV) Extraction and Separation

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Abstract. In this work the synthesis, characterization and evaluation of a novel sorbent material used for the solid-phase extraction of titanium (IV) from hydrochloric acid medium is described. The material was prepared by the sol-gel route incorporating bis(2-ethylhexylphosphoric acid) (D2EHPA) as extractant within a polymeric matrix based on polysiloxanes and characterized through FTIR-ATR, XRD, ^{29}Si and ^{31}P NMR, TGA and DSC. In studies of titanium sorption and desorption in batch mode several factors related with the extraction and back-extraction operations were evaluated, such as: contact time, titanium concentration, nature and composition of the aqueous media, and extractant concentration in the sorbent. The maximum sorption was observed at 30 min of contact time in a 1 mol L^{-1} HCl + 0.1% KCl medium, while the maximum desorption was observed at 60 min in a 1.5 mol L^{-1} H_2SO_4 + 20% v/v H_2O_2 medium when titanium concentration was 70 mg L^{-1}. Under optimal conditions the recovered percent of titanium was nearly 90%. In addition, the characterization of the extraction equilibrium was performed. The selectivity of the method was studied adding Al(III), Fe(III) and V(V) to the extraction medium. A high selectivity for Ti over Al and Fe was observed, even at high concentrations of the interferents; 50% of Ti, only 7% of Fe, 3% of Al and less than 1% of V were recovered under the established conditions. The method was finally applied for titanium recovery from a certified fly ash sample generated from a municipal incineration plant.

Keywords: titanium (IV), solid-phase extraction, polysiloxanes.

Resumen. Se describe la síntesis, caracterización y evaluación de un material adsorbente novedoso utilizado para la extracción en fase sólida de titanio (IV) a partir de medio de ácido clorhídrico. El material se sintetizó mediante la técnica de sol gel, incorporando el ácido bis(2-etilhexilfosfórico) (D2EHPA) como extractante dentro de una matriz polimérica a base de polisiloxanos y fue caracterizado mediante FTIR-ATR, XRD, ^{29}Si y ^{31}P NMR, TGA y DSC (por las siglas en inglés). En los estudios de sorción y desorción en lote de titanio se evaluaron diversos parámetros relacionados con las operaciones de extracción y re-extracción tales como: tiempo de contacto, concentración de titanio, naturaleza y concentración de los medios acuosos, y concentración del extractante en el material sorbente. La máxima sorción se presentó a los 30 min de contacto en un medio HCl 1 mol L^{-1} + KCl 0.1%, mientras que la máxima desorción ocurrió a un tiempo de 60 min en un medio compuesto de H_2SO_4 1.5 mol L^{-1} + H_2O_2 20% v/v para una solución que contenía 70 mg L^{-1} de titanio (IV). En condiciones óptimas el porcentaje de recuperación de Ti(IV) fue cercano a 90%. Adicionalmente, se realizó la caracterización del equilibrio de extracción. La selectividad del método se estudió adicionando los cationes Al(III), Fe(III) y V(V) al medio de extracción. Se observó que el método fue selectivo para titanio incluso a concentraciones muy elevadas de Al y Fe bajo las condiciones establecidas, obteniendo una recuperación de 50% del titanio inicial en comparación al 7% de Fe, 3% de Al y menos del 1% de V. Finalmente el método se aplicó para la recuperación de titanio de una muestra real certificada de cenizas de un incinerador municipal de desechos.

Palabras clave: titanio (IV), extracción en fase sólida, polisiloxanos.

Introduction

Due to its high strength-to-weight ratio and inertness to corrosion, titanium is not only known as a space-age metal but also has numerous high-technological industrial applications. Because of its widespread use, the primary sources of titanium are becoming exhausted and efficient recovery methods from low-grade ores and secondary sources, such as fly ash or red mud, need to be developed [1, 2]. About 70 percent of coal ash is fly ash, and although most fly ash is disposed in landfills, high technology recycling operations include metal recovery and filling of metal bearing composite materials. Fly ash is a complex composition of silicon and aluminum oxides together with oxides of iron, calcium, titanium, potassium and trace metals. From a hydrometallurgical point of view, solvent extraction (SX) is the most employed separation method for titanium [3]. Among the most frequently extractants used are organophosphorus reagents [4-6]. In fact, the commercially available reagent, bis(2-ethylhexylphosphoric) acid (D2EHPA) has been used for the extraction of Ti(IV) from chloride media [7-10] not only in SX experiments but also in other separation methods such as liquid membranes [11]. The use of liquid membranes for metal recovery has increased in the past years because they present as main advantages high transport rates and less consumption of organic reagents (solvents and extractants). However, membrane systems are frequently unstable thus the development of new inorganic or hybrid organic-inorganic supports containing selective extractants in their matrix has received considerable attention [12-14]. Solid-phase extraction (SPE) is another approach that offers a number of important benefits as it reduces solvent usage and exposure, disposal costs and extraction time [15]. However, in spite that TiO_2 sorbents have been extensively used for metal preconcentration in solid-phase extraction techniques [15, 16] reports on Ti(IV) preconcentration and separation using solid-phase separation techniques are scarcely found. Nanometer size zirconium dioxide [17] and 2-nitroso-1-naphthol impregnated MCI GEL CHP20P resin [18] are two of the adsorbents which have been used for such purposes.

In this work we report the development of an environmentally friendly procedure for titanium extraction and separation from a secondary source, such as fly ash, from hydrochloric acid solutions based in the use of a sorbent material containing D2EHPA as extractant. The sorbent material was synthetized by a sol-gel procedure and characterized by several analytical techniques (FTIR-ATR, XRD, ^{29}Si and ^{31}P NMR, TGA and DSC). Results of the studies performed for the extraction-back extraction of titanium(IV) in single and multicomponent chloride solutions in batch mode are discussed. A model for the extraction equilibrium is proposed as well.

Results and discussion

Homogeneity of the sorbent

It was observed that the distribution coefficient defined as:

$$D=\left(\frac{C_0}{C_i}-1\right)\left(\frac{V}{m}\right) \tag{1}$$

(where C_0 stands for Ti analytical concentration, C_i for its equilibrium concentration after sorption, V for the aqueous volume (mL) and m for the sorbent mass (g)) was independent of the amount of sorbent used in the 0.05 − 0.12 g range, denoting a homogeneous solid phase when such amounts are employed in sorption experiments [19], thus further work was performed using 0.05 g of the sorbent.

Extraction and back-extraction kinetics

As for sorbents containing 2.29, 1.20 and 0.43 mmol g^{-1} of D2EHPA experiments showed that Ti sorption increases with time during the first 15 min of contact time after which constant sorption values of 211.7 ± 7.6 mmol kg^{-1} were attained within 90 min. For a blank material containing no extractant only 2.5 mmol kg^{-1} of titanium was loaded in the same time interval, denoting low affinity for sorption of the analyte in the absence of extractant. Otherwise stated, further experiments were performed with 30 min of shaking time to allow the establishment of equilibrium conditions. Back-extraction of the loaded organic phase (2.29 mmol g^{-1} of D2EHPA) was accomplished using 1 mol L^{-1} H_2SO_4 + 10% v/v H_2O_2 solution. It was observed that after 50 min of contact time the percent recovered of Ti (67% of the loaded Ti) was independent of time so further experiments were performed using 60 min. The difference between extraction and back-extraction kinetics may be attributed to the formation of Ti (IV)-H_2O_2 species in the latter step together with differences in the rate constants which have been reported to be lower for back-extraction in comparison with the extraction step in HCl media [9].

Effect of extractant concentration

Different sorbents containing variable amounts of extractant (0.5 − 1.67 mmol g^{-1}) were prepared and used in titanium extraction. The plot of $\log D = f(\overline{[(\mathrm{HA})_2]}_{eq\,[\mathrm{HCl}]_{tot},[\mathrm{TiO}^{2+}]_{tot}})$ (where $(HA)_2$ stands for D2EHPA dimmer and the bar denotes species in sorbent phase) shown in Figure 1A indicates a linear increase between both variables due to the extracting effect of D2EHPA. The slope and intercept of the line equal 1.25 ± 0.66 and 3.81 ± 0.37 (α = 0.05), respectively.

Effect of acid concentration

The HCl concentration in the feed phase was varied between 0.5 and 3 mol L^{-1} using a solution containing 70 mg L^{-1} of Ti (IV). A decrease in the distribution coefficient with the increase of HCl concentration was observed. This result has been previously reported in a similar solvent-extraction system [8] and explained taking into account the acidic dependence of the extraction equilibrium (see the extraction equilibrium section). Experiments performed at 1 mol L^{-1} HCl and varying the concentration of chloride ion (as KCl) in the extracting phase within the range 0.1-0.5 mol L^{-1} confirm that chloride ion has no noticeable effect on the distribution coefficient due to the fast conversion of $TiOCl_2$ to TiO^{2+} [8], in addition to the low values of the global formation constants of the $TiOCl^+$ and $TiOCl_2$ species [15]. The $\log D = f([\mathrm{HCl}]_{tot\,\overline{[(\mathrm{HA})_2]},tot[\mathrm{TiO}^{2+}]_{tot}})$, plot (Figure 1B) showed a linear function with a slope of −1.07 ± 0.30 and an intercept of 3.06 ± 0.10 (α = 0.05).

Effect of titanium concentration in the aqueous phase

The $\log D = f([\mathrm{TiO}^{2+}]_{eq\,\overline{[(\mathrm{HA})_2]}_{tot},[\mathrm{HCl}]_{tot}})$ plot (Figure 1C) showed a linear function with a slope of −0.72 ± 0.08 and intercept of 0.28 ± 0.19 (α = 0.05). The titanium adsorption isotherm in 1 mol L^{-1} HCl medium was obtained in the 0.15 – 6.25 mmol L^{-1} range using a material containing 2.29 mmol g^{-1} of total D2EHPA concentration. The results are shown in Figure 1D. The S-shape profile observed is characteristic of a type-v adsorption isotherm (according to IUPAC classification) and indicates a lack of energetic uniformity of the extracting groups within the material for titanium ion binding i. e., a certain degree of restriction in the availability of the extracting sites [20], possibly due to the confinement of D2EHPA within the inorganic matrix which favors the interactions between both components (see the characterization section). Isotherms similar to the one presented in Figure 1D have also been observed for Hg^{2+} adsorption on thiol-functionalized mesoporous silica microspheres with large particle sizes and little textural porosity [20], characteristics similar to those of the adsorbent used in this work. The maximum loading capacity obtained under the established conditions was just about 0.215 mmol g^{-1}, being this value on the upper limit of different sorbents used for metal preconcentration [15] and comparable to that of nanometer size zirconium dioxide as Ti (IV) sorbent [17].

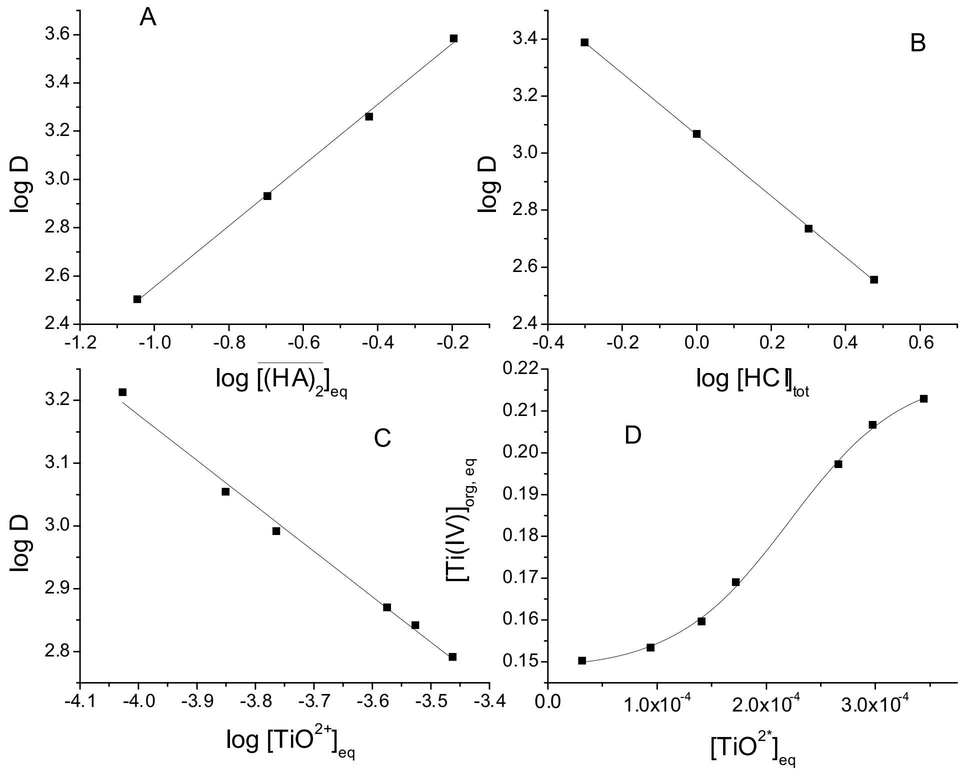


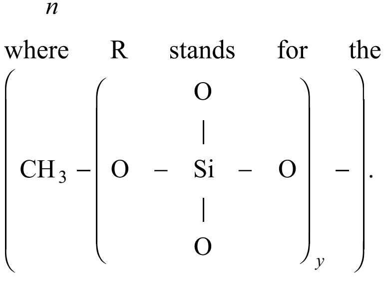
Figure 1. Effects of (A) D2EHPA (70 mg L^{-1} Ti(IV), 1.2 mol L^{-1} HCl), (B) HCl ((70 mg L^{-1} Ti(IV), 2.29 mmol g^{-1} D2EHPA), and (C) metal ion concentration (1 mol L^{-1} HCl, 2.29 mmol g^{-1} D2EHPA), on the distribution coefficients and extraction isotherm (D) for titanium (IV) sorption. The units of the x-axis variables are: A) mmol g^{-1}, B), C) and D) mmol mL^{-1}.

Extraction equilibrium

Taking into account polymerization of Ti(IV) in the aqueous phase, negligible polymerization of the organic-phase species due to the low Ti(IV) concentration in the aqueous phase used (below 10 mM [21]), evidence from the characterization section pointing out two possible chemical forms of D2EHPA within the adsorbent related to residual silanol moieties interacting strongly with the extractant, and the shape of the isotherm data confirming unavailability of adsorption sites, the results from previous sections can be conceptualized considering the following reaction:

$$\frac{1}{n}(\mathrm{TiO}^{2+})_n + \overline{(\mathrm{HA})_2\,,\ \mathrm{RS}i\mathrm{OH}} \Leftrightarrow \overline{\mathrm{T}i\mathrm{OA}_2\,,\mathrm{RS}i\mathrm{OH}} + 2\,\mathrm{H}^+ \quad (2)$$

where R stands for the polysiloxane matrix:



$$\left(\mathrm{CH_3} - \left(\begin{array}{ccccc} & & \mathrm{O} & & \\ & & | & & \\ \mathrm{O} & - & \mathrm{Si} & - & \mathrm{O} \\ & & | & & \\ & & \mathrm{O} & & \end{array}\right)_y - \right).$$

Equation (2) can be simplified considering a constant activity of the matrix acting as a solvent under given experimental conditions in such a form that the equilibrium can be rewritten as:

$$\frac{1}{n}(\mathrm{TiO}^{2+})_n + \overline{(\mathrm{HA})_2} \Leftrightarrow \overline{\mathrm{T}i\mathrm{OA}_2} + 2\,\mathrm{H}^+ \qquad (3)$$

with an extraction equilibrium constant given by:

$$K_E = \frac{\overline{[\mathrm{T}i\mathrm{OA}_2]}[\mathrm{H}^+]^2}{[(\mathrm{TiO}^{2+})_n]^{1/n}\,\overline{[(\mathrm{HA})_2]}} \qquad (4)$$

Taking into account the distribution coefficient expressed by:

$$D = \frac{\overline{[\mathrm{T}i\mathrm{OA}_2]}}{n[(\mathrm{TiO}^{2+})_n]} \qquad (5)$$

the following expression is deduced once logarithms are taken:

$$\begin{aligned} \log D = \log K_E - \log(n) - \left(1 - \frac{1}{n}\right) \\ \log[(\mathrm{TiO}^{2+})_n] + \log\overline{[(\mathrm{HA})_2]} - 2\,\log[\mathrm{H}^+] \end{aligned} \qquad (6)$$

Equation (6) explains the linear relationships of the plots $\log D = f(\overline{[(\mathrm{HA})_2]}_{eq_{[\mathrm{HCl}]_{tot},[\mathrm{TiO}^{2+}]_{tot}}})$ and $\log D = f([\mathrm{HCl}]_{tot_{\overline{[(\mathrm{HA})_2]}_{tot},[\mathrm{TiO}^{2+}]_{tot}}})$ together with the value of the slope of the former plot. From the slope of the $\log D = f([\mathrm{TiO}^{2+}]_{eq\,\overline{[(\mathrm{HA})_2]_{tot},[\mathrm{HCl}]_{tot}}})$ plot it is possible to compute the value of n in equation (6). The calculated value of 3.6 ± 1.1 is consistent with the value of 3 reported for a similar solvent extraction system with 1 mM Ti (IV) concentration [21]. The 1: 1 Ti (IV): $(HA)_2$ stoichiometric ratio has also been observed in solvent extraction of this analyte with D2EHPA in conditions in which the extractant is limited [8]. As for the deviation of the slope from the theoretical value of 2 in the $\log D = f([\mathrm{HCl}]_{tot\,\overline{[(\mathrm{HA})_2]_{tot},[\mathrm{TiO}^{2+}]_{tot}}})$ plot, this is not attributable to non ideality of the aqueous phase since the replacement of activities instead of HCl concentrations in the evaluation of these parameters modified the slope to –0.75 ± 0.11 and the intercept to 2.99 ± 0.05 ($\alpha = 0.05$). It is more likely that co-extraction of HCl consumes hydrogen ions decreasing the expected dependency, and the equilibrium concentration differs significantly from the total HCl concentration employed in the evaluation. From the intercept values of the previous figures an estimated value of 2.9 ± 0.4 for the logarithm of the extraction equilibrium constant was computed. In this case a lower value is obtained in comparison with other extraction systems that use liquid organic solvents [8, 22], due to the different interactions that are present in the solid phase. In addition it has been reported in liquid-liquid extraction that the extraction equilibrium constant for titanium (IV) with D2EHPA can vary significantly, from 10 to 10^8, depending on titanium concentration [22].

Effects of H_2O_2 and acid concentration in back-extracting phase

The results obtained when H_2O_2 concentration in the stripping phase was varied from 10 to 30% v/v in 1 mol L^{-1} H_2SO_4 solution are shown in Figure 2. From this plot an increase in extraction percent with the increase of hydrogen peroxide concentration was noticed and explained considering an augment in the concentration of the Ti(IV) – (H_2O_2) complex [23] in the back-extraction medium. At 20% of H_2O_2, the acidy of such phase was also varied in the 0.5 – 1.5 mol L^{-1} range using both H_2SO_4 and HCl. The back-extraction percent increases as acid concentration increases for both media; however, on the average a 20% increase in the percent of extraction was observed when sulfuric instead of hydrochloric acid was employed, as previously reported [24]. A lower co-extraction of H_2SO_4 in comparison to HCl or the formation of $Ti(OH)_4(H_2O_2)SO_4$ species [25] may be responsible for this behavior.

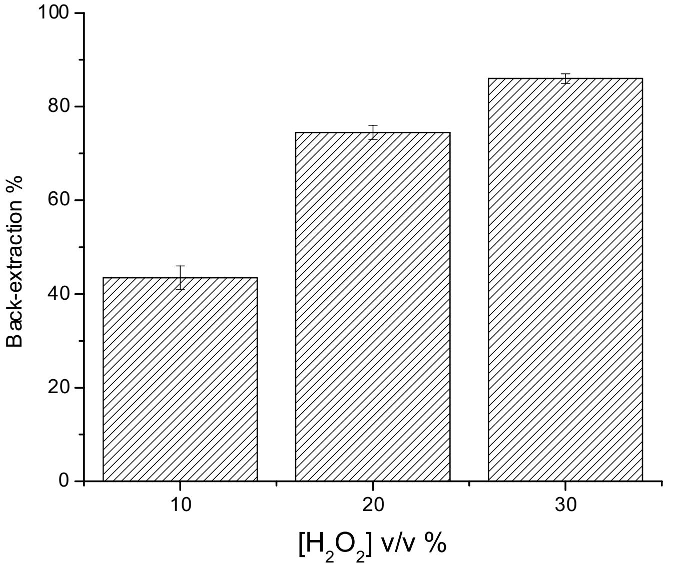


Figure 2. Influence of hydrogen peroxide concentration on titanium back-extraction using 1 mol L^{-1} H_2SO_4.

Presence of interfering ions

Table 1 reports some parameters for the extraction of monoelemental solutions of different ions which can interfere with titanium extraction. As observed, the highest percent of extraction is obtained for the target ion although Fe (III) can significantly compete due to a high distribution coefficient value.

The results from a multi-component mixture of Al (III), Fe (III) and Ti (IV) indicate a 10% decrease in titanium extraction with regards to that obtained when the cation is alone (Table 2); as Fe (III) extraction remains constant but Al (III) extraction decreases, this behavior may be explained considering a variation in the titanium extraction kinetics due to interfacial activity of the different ions, as previously observed with other type of solid sorbents [26]. From the same Table it is also observed that the interfering effect of Fe (III) is minimized in the back-extraction step due to a low recovery of this ion under the experimental conditions employed.

Using the reported procedure a multielemental solution containing 300 mg L^{-1} of Fe (III), 700 mg L^{-1} of Al (III), and 70 mg L^{-1} of Ti (IV) (proportions similar to those found in fly ash) were extracted with the synthesized sorbent. With the aim of increase titanium recovery in the presence of high amounts of aluminum, two different back-extracting media were assayed: 20% H_2O_2 + 1 mol L^{-1} H_2SO_4 (Figure 3, left) and 20% H_2O_2 + 1.5 mol L^{-1} H_2SO_4 (Figure 3, right). From Figure 3 an increase is observed in the percent recovered of Ti (IV) with the increase of sulfuric acid concentration. In addition, the amount recovered of Al (III) is reduced, while that of Fe (III) increases slightly from 8 to 15%.

Table 1. Extraction parameters during sorption for monoelemental solutions of different cations each at 70 mg L^{-1}. 2.29 mmol g^{-1} D2EHPA, 1.2 mol L^{-1} HCl, 60 min of contact time.

Cation	Extraction %	Retained amount of metal (mmol Kg^{-1})	log D
Al(III)	7	34.6	1.2
Fe(III)	59	148.0	2.5
V(V)	2	5.2	0.6
Ti(IV)	75	220	2.9

Table 2. Extraction and back-extraction parameters during sorption of multicomponent solutions of different cations each at 70 mg L^{-1}.

Metal	Extraction %	Retained amount of metal (mmol Kg^{-1})	log D	Back-extraction %	Recovery %
Ti (IV)	65	191.6	2.7	72	47
Al (III)	1	3.7	0.1	nd*	nd*
Fe (III)	60	149.5	2.5	5	2

*nd: no detectable

Table 3. Application of the developed method for the recovery of Ti (IV) from fly ash.

Sample	Extraction %	Back-extraction %	Certified value (mg Kg^{-1})	Ammount recovered (mg Kg^{-1})	Recovery %
IRM-019	66.5%	64.1%	2870 ± 143.5	1231.9 ± 123.2	43 ± 4%

Titanium recovery from a real sample

The results obtained after application of the method to a certified fly ash sample generated from a municipal incineration plant (IRM-019 CRM) are presented in Table 3. Nearly 43% of the analyte was recovered from this complex material demonstrating the potentiality of the method for titanium recovery from this type of samples. However, although further work is required to recover the analyte in a more quantitative form, a successive extraction procedure could be implemented.

Material characterization

FTIR-ATR analyses of materials containing different amounts of extractant (0.43 – 2.29 mmol g^{-1}) showed D2EHPA characteristic bands at 1015 cm^{-1} ($\nu_{\text{P-OH}}$), 1226 cm^{-1} ($\nu_{\text{P=O}}$), 1381 cm^{-1} ($\nu_{\text{(CH3)2CH-}}$), 1463 cm^{-1} ($\nu_{\text{CH3-}}$), and 2800-2900 cm^{-1} ($\nu_{\text{CH3-, CH2-}}$) indicating its immobilization within the polisiloxane matrix. A blank material containing no D2EHPA showed characteristic bands at 800 cm^{-1} ($\nu_{\text{Si-O-Si, Si-O-C}}$), 940 cm^{-1} ($\nu_{\text{Si-O}}$), 1200 cm^{-1} ($\nu_{\text{Si-O-Si-}}$), and 3400 cm^{-1} ($\nu_{\text{SiO-H}}$) which were also present in the D2EHPA-containing materials. However, the overlapping of bands in the 900-1250 cm^{-1} region did not allow to evidence any kind of interaction between the extractant and the matrix. ^{29}Si NMR signals at –51.5, –106.2, and –113.5 ppm were assigned to hydroxylated T$^{\text{OH}}$ units or D$^{\text{OH}}$ [27], Q^3, and Q^4 units, respectively, indicating the presence of residual silanol moieties in the sorbent. Polysilsesquioxanes and polysiloxanes are compounds with low dielectric constant values, within the range from 2 to 2.9 [28, 29] and D2EHPA is known to form dimmers due to hydrogen bonding in most hydrocarbon media of low dielectric constant, such as kerosene ($\varepsilon = 2.2$) [30]; consequently, it is expected that in the polysiloxane sorbent the extractant behaves in a similar manner showing only one phosphorous peak in NMR spectra. ^{31}P MAS solid state NMR spectra of solvent impregnated resins (SIRs) composed of D2EHPA and Lewatit MP600 (DVB-crosslinked polystyrene resins bearing strongly basic di-methyl-ethyl-ammonium groups) as polymeric support has shown a signal at about 2 ppm which is an overlap of two peaks, one related to the extractant that is chemically associated with the polymeric support in the macropores and the other to the extractant that exists as a liquid occupying the pore volume [31]. A similar result has been observed in polysilsesquioxanes doped with D2EHPA (PSSDD) with such signals at –1.24 and –1.39 ppm [32]. In the present case ^{31}P NMR spectrum showed the presence of two clearly different signals at 2.076 and –2.607 ppm. The first one is attributed to the dimmers of the extractant based on the chemical shift that the pure extractant shows (1.969 ppm), while the second was attributed to the extractant interacting with the polysiloxane matrix. Due to the magnitude of the observed chemical shift, this interaction is stronger than those observed in SIRs and PSSD taking into account that the chemical shift of the Si-O-P bond is reported at –10.0 ppm [33]. TGA analyses indicated weight losses from 32.1 to 54.5% for

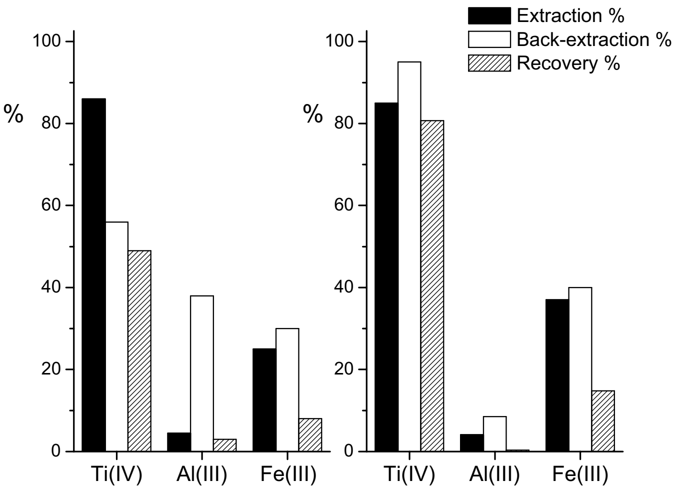


Figure 3. Application of the solid-phase extraction method for titanium (IV) recovery from a multielemental solution (300 mg L^{-1} of Fe(III), 700 mg L^{-1} of Al(III), and 70 mg L^{-1} of Ti(IV)) using: 20% H_2O_2 + 1 mol L^{-1} H_2SO_4 (left) and 20% H_2O_2 + 1.5 mol L^{-1} H_2SO_4 (right) in the stripping phase. 2.29 mmol g^{-1} D2EHPA, 1.2 mol L^{-1} HCl in the feed phase, 60 min of contact time.

the D2EHPA-containing materials within the 220-236°C range corresponding to the volatilization of the extractant (boiling point 218°C in its pure form), and of 13.8% within the range 60-75°C for the blank material corresponding to evaporation of the azeotropic ethanol-water mixture remaining from the synthesis. From DSC thermograms the absence of chemical bonding between D2EHPA and the polysiloxane is clearly established since only one endothermic peek independent of the extractant content at 230°C was present. XRD difractograms revealed an amorphous material without crystalline parts, as expected due to the randomly branched structure of these materials. Taking all the characterization evidence into account two possible forms of D2EHPA within the adsorbent related to residual silanol moieties interacting strongly with the extractant were identified, supporting the formation of species during titanium extraction through the species immobilized in the sorbent.

Experimental

Reagents

All reagents and solvents were purchased from commercial sources and used as received. Tetraethyl orthosilicate (TEOS, 98%); di-2-ethylhexyl phosphoric acid (D2EHPA, 98%); titanium chloride ($TiCl_4$, 99.9%); hydrogen peroxide (30%) and ethanol were Aldrich products, and hydrochloric acid (37%), vanadium pentoxide (99.8%) and potassium chloride (99.6%) were J. T. Baker reagents. Aluminum (III) and iron (III) were atomic absorption standard solutions (985 and 1000 mg L^{-1}, respectively, from Aldrich). The IRM-019 CRM was purchased from Resource Technology Corporation, Laramy, WY. Its composition is given below (Table 4):

Table 4. Elemental composition of the IRM-019 CRM

Element	mg kg^{-1}	Element	mg kg^{-1}
Aluminum	32759	Magnesium	6310
Antimony	223	Manganese	480
Arsenic	77.2	Mercury	2
Barium	3.52	Molybdenum	26
Beryllium	2	Nickel	22.2
Boron	336	Silver	7.35
Cadmium	432	Lead	4540
Calcium	51949	Potassium	49344
Cobalt	26	Selenium	4.11
Cupper	279	Sodium	50522
Chrome	55.2	Tellurium	42
Tin	410	Titanium	2870
Strontium	173	Vanadium	28.9
Phosphorous	No detectable	Zinc	22400
Iron	12693		

Apparatus

Characterization of the material was carried out using wide angle X-Ray diffraction, FTIR spectroscopy and thermal analysis. Crystallographic data were obtained with an X-ray diffractometer D 5000 Siemens (30 kV and 30 mA) using the Cu K_α radiation. A Perkin Elmer Spectrum GX FTIR spectrometer equipped with a diamond DuraSampl IR II ATR-sampling accessory from SensIR Technologies was used to identify the functional groups using the Spectrum QUANT+ v4.51 software. A Mettler Toledo Star Thermal Analysis System (DSC 821 differential scanning calorimeter with nitrogen cooling and TGA/SDTA 851e thermogravimetric analyzer) with STAR 610 software was employed to test the thermal stability of the synthesized samples. Thermograms were obtained under oxygen atmosphere at a heating rate of 10ºC min^{-1}. ^{29}Si and ^{31}P solid-state NMR experiments were conducted on a Bruker ASX3000 spectrometer using the Mest Re-C 2.3a 1996-2000 software. Samples were supported on a 7 mm diameter ZrO_2 rotor at 5kHz of spinning rate at room temperature using Q_8M_8 ($(HSiMe_2O)_8Si_8O_{12}$, octakis (hydridodimethlysiloxy) octasilsesquioxane) and phosphoric acid as references. Metal concentrations were determined by FAAS using a Perkin Elmer 3100 spectrometer under the recommended conditions of the manufacturer. A Burell-75 mechanical shaker was used to perform extraction and back-extraction experiments and the synthesized material was grinded in an 800 mill Spex Mixer.

Material preparation

The materials were synthesized using a sol-gel technique. Tetraethoxysilane was mixed with de-ionized water (1:1), at which time 25 mL of a D2EHPA-ethanolic solution were added (0.15-0.8 mol L^{-1}), in the presence of HF as catalyst. The mixture was agitated during 30 min in an ultrasonic bath and allowed to gel. The gel was dried at room temperature until constant weight, washed with de-ionized, grinded and sieved to a 90-250 μm particle size. A material without extractant was also prepared for use in background experiments. The amount of D2EHPA in the material was controlled by monitoring P content by elemental analysis. As for free-D2EHPA concentrations needed for graphical analysis, they were calculated assuming a given stoichiometry ($x = 1$, i.e., monomer species in the organic phase) for the organic complex and the corresponding mass balance equation according to: $\overline{[(HA)_2]}_{eq} = \overline{[(HA)_2]}_{tot} - x[TiO^{2+}]_{eq}$ [21].

Homogeneity of the sorbent

Different amounts (0.03, 0.050, 0.070, 0.090 and 0.120 g) of a material containing 2.29 mmol g^{-1} of D2EHPA and 70 mg L^{-1} of Ti in 1 M HCl medium were contacted for 30 min according to extraction kinetics experiments and the distribution coefficient was measured as a function of the amount of sorbent.

Titanium (IV) extraction and back-extraction

Batch experiments were carried out at room temperature (20 ± 2°C) by shaking 10 mL of aqueous solutions of $TiCl_4$ of known concentrations (50-90 mg L^{-1}) with appropriate amounts of the sorbent (0.030 – 0.120 g) until equilibrium was attained. The equilibrium time was previously determined by kinetics experiments using 0.050 g of material loaded with D2EHPA at 1 mol L^{-1} HCl medium. The aqueous media studied were 0.5, 1, 2, and 3 mol L^{-1} HCl solutions + 0.1 w/v% KCl. Back-extraction experiments were performed once titanium was loaded in the sorbent using 10 mL of two different media: (0.5, 1, 1.5 mol L^{-1}) H_2SO_4 + (10%, 20%, 30% v/v) H_2O_2 and (0.5, 1, 1.5 mol L^{-1}) HCl + (10% v/v) H_2O_2. Back-extraction kinetics in 1 mol L^{-1} H_2SO_4 + 10% v/v H_2O_2 was also studied.

As for experiments in which concomitant metal ions were added (Fe (III), Al (III), V (V)) to a solution containing 70 mg L^{-1} of Ti (IV), molar ratios of 1:1 for all metals and 1:5 for Ti:Fe and 1:10 for Ti:Al were employed using the established conditions for titanium sorption and desorption experiments using a sorbent containing 2.29 mmol g^{-1} of extractant. Experiments were performed at least 3 times. The deviation observed was within 5%.

Certified reference material (CRM) treatment

An amount of 2.5 g of the IRM-019 CRM was digested according to the USEPA method SW846 3050b. After filtration, 1.1074 g of the digested sample were diluted to 100 mL using deionized water and used in sorption experiments.

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