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Extraction and recovery of rare earths by chelating phenolic copolymers bearing diglycolamic acid or diglycolamide moieties

C. Arrambide Cruz^a, G. Arrachart^{a,*}, S. Berthalon^a, M. Wehbie^a, S. Pellet-Rostaing^a

^a ICSM, CEA, CNRS, ENSCM, Univ Montpellier, Marcoule, France.

* Corresponding author. E-mail address: guilhem.arrachart@cea.fr

Abstract

Extraction and recovery of rare earth elements (REEs) have been studied using ion-exchange and chelating process thanks to phenol copolymeric resins. The ion-exchange and chelating resins have been prepared through an alkaline polycondensation reaction of phenolic diglycolamide derivatives with admixture of phenol, catechol or resorcinol in the presence of formaldehyde as crosslinker. The phenol copolymeric resins were fully characterized and involved in sorption experiments. The sorption experiments of rare earth elements have been investigated in different acidic conditions. Lanthanum (La), europium (Eu) and ytterbium (Yb) were chosen to represent the light, medium and heavy REEs respectively. Changes in the extraction properties of the copolymeric resins have been observed depending on the nature of chelating groups in the phenolic matrices and the extraction conditions. The results indicate that the synthesized materials are good sorbent for REEs with cation uptake capacity in the range 50–100 mg/g and in some cases above 150 mg/g.

Keywords

Chelating phenolic copolymers; sorbents materials; rare-earth elements; liquid-solid extraction

1. Introduction

Lanthanides are elements with atomic numbers ranging from 57 (lanthanum) to 71 (lutetium), together with scandium and yttrium form the rare-earth series of elements. Despite their name, rare-earth elements (REEs) are not as rare as their name suggests, they are more abundant than copper. However, these metals are very difficult to exploit because of their geochemical properties, dispersion and are usually not often found in high concentration in geologic deposits.

Due to their peculiar electronic structure, these elements present specific chemical, optical, and magnetic properties, they have thus become essential to almost all aspects of modern life. Indeed, REEs are involved as catalytic converters, lighting devices, high coercivity magnets (electric cars, wind turbines, hard disk drives), rechargeable batteries and much more. Therefore due to their economic importance and supply risk (China is the predominant producer and supplier) these metals are classified as strategic materials.¹ It is expected that their average annual demand will increase by more than 8% every year by 2020.² To decrease the stress on the supply of rare earth elements new REE deposits should be exploited, also an attractive and viable approach relies on the recovery from industrial wastes or the recycling of these elements from end-of life products such as e-waste or Waste of Electrical and Electronic Equipment's (WEEE).³

Whatever the resources of REEs, these metals can be extracted and recycled by hydrometallurgy. Liquid-liquid extraction processes are widely used in hydrometallurgy for separation and purification of REEs; however, such method requires large volume of solvents during the repeated steps of extractions. Alternatively, among hydrometallurgical methods, solid-liquid extraction appears to be a promising alternative thanks to its simplicity on one hand and on the other hand, the use of organic diluents is not required in this process and therefore makes it more environmentally friendly.

The REEs are classified into two categories based on their atomic numbers, light rare earth elements (LREE) from La-57 up to Gd-64, and heavy rare earth elements (HREE) from Tb-65 up to Lu-71. Increasing atomic numbers across the lanthanides series results in a decreasing of the atomic radii, a phenomenon called lanthanide contraction.⁴ Due to this phenomenon HREEs have smaller atomic sizes but higher charge densities than LREEs. REEs are considered as hard acids according to Pearson's HSAB concept,⁵ and they are preferentially bounded by oxygen donor hard bases such as malonamides,⁶ and diglycolamides.⁷⁻¹⁰ Indeed, amides are weak bases whose protonation occurs only on the oxygen atom. In diamides, electron density transfer between the two carbonyls is important and greatly increases the basicity. The nature of the metal–amide binding have been investigated showing that bidentate coordination to a cation requires a cis arrangement of the carbonyl groups.^{11, 12} Diglycolamides (DGA) derivatives seems to be more efficient extractants than malonamides because of their architectural shapes in which they form stable complexes through tridentate O-donating ligands.¹³ The organization of DGA moieties on preorganized platforms have been proved to boost the efficiency of the DGA ligand in regard to the extraction of lanthanides in liquid-liquid extraction.⁷ Another good extractant is the monoacid derivative of diglycolamides, namely the diglycolamic acid. This derivative extracts the trivalent ions from a diluted nitric acid solution,¹⁴ unlike the diglycolamides which extract actinides and lanthanides at a concentration of acid greater than 0,1 mol/L.¹⁵

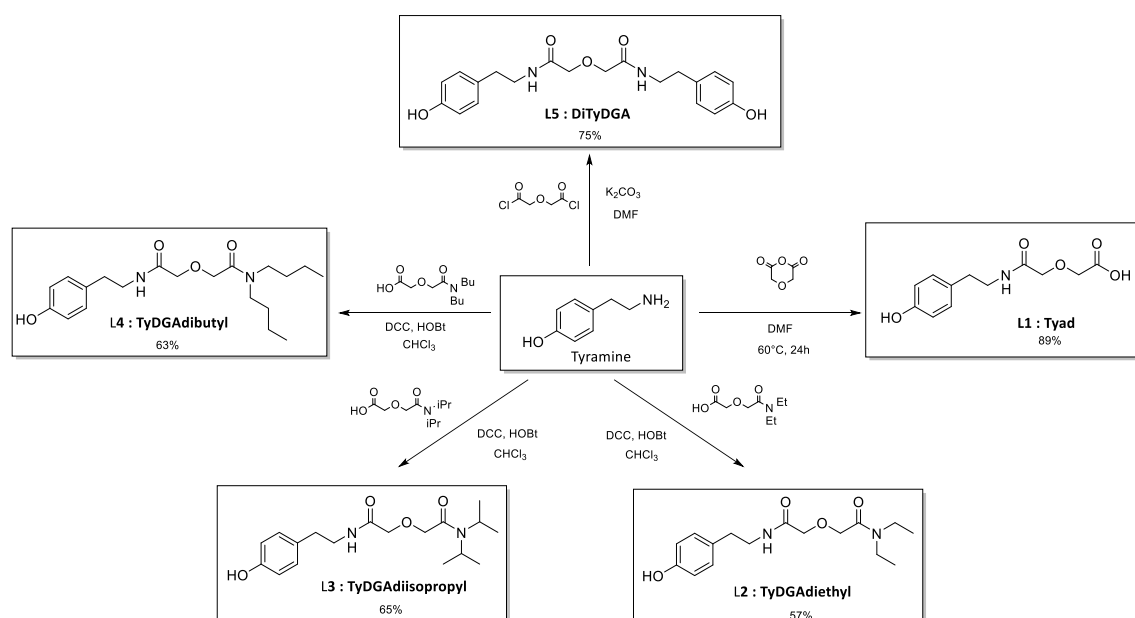
Based on these well-known ligands used in liquid-liquid extraction applications functionalized sorbents have been developed for REE separation.¹⁶ For instance, an acrylic ester matrix (Amberchrom-CG71) impregnated with DGA derivatives is commercially produced using TODGA (N,N,N',N'-tetra-n-octyldiglycolamide; Normal DGA Resin) and TEHDGA (N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide; Branched DGA Resin) (Eichrom Technologies Inc.).¹⁷ Other impregnation strategies have been employed such as impregnated functional polymeric composite (TODGA/SiO₂-P).¹⁸ Unfortunately, leaching into the aqueous phase is frequently observed as the ligand is only supported on the stationary phase. This problem limits its reuse and applicability. To overcome such drawbacks, the extractant can be chemically anchored to the solid support. A literature survey show that diglycolamides and diglycolamic acid extractants have been grafted on polyamide matrix,¹⁹ in a film-type adsorbent,²⁰ as well as on silica gel particles,^{21, 22, 23} mesoporous silica,^{24, 25} and oxide particles.²⁶

Interestingly, to the best of our knowledge, there is no evidence in the literature of the use of phenolic resin with incorporation of diglycolamides derivatives for REEs extraction.

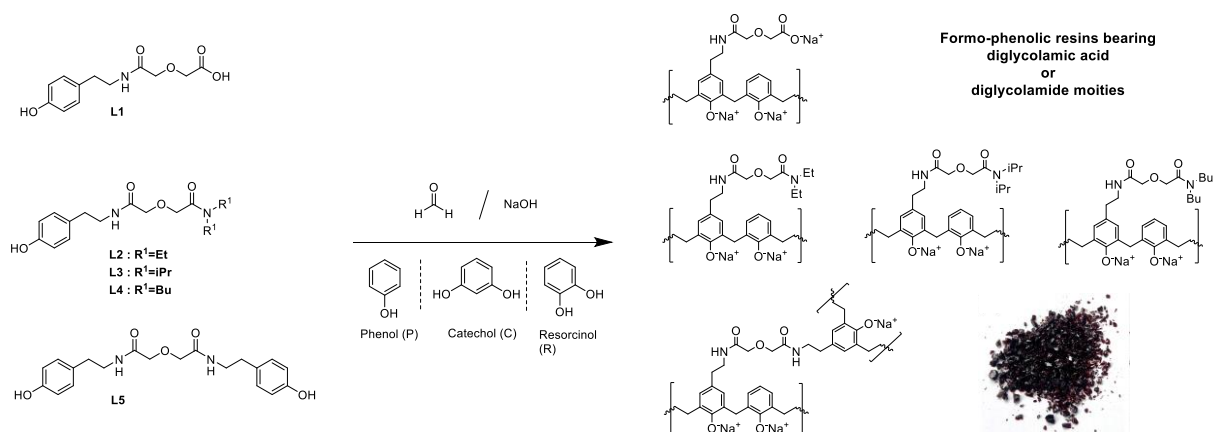
These types of resins are widely studied and described in the literature since the discovery of Baekeland.²⁷ The thermosetting resole resins are used for liquid solid extraction. They exhibit ion exchange properties thanks to the -OH groups in their polymeric structure. Chelating groups can be incorporated in order to increase the sorb or modify the selectivity of ions.^{28, 29} So, phenolic resins have been used for extraction of heavy metals,³⁰⁻³⁵ lanthanide metal ions,³⁶⁻⁴⁰ and radionuclides.^{29, 41-48}

It is believed that polymers with a combination of diglycolamide derivatives and phenolic group can improve the existing sorbents system developed for REEs extraction. Therefore, herein we described the synthesis of novel phenol based copolymeric resins that incorporate diglycolamides derivatives. The different resins obtained have been implemented in solid-liquid extraction of three REEs

respectively La, Eu, and Yb representing the light, medium and heavy rare earth elements. The investigation has been carried out at different aqueous phase acidities, resin concentrations and resins type. The presence of diglycolamides or diglycolamic acid on formol-phenol resins could have a positive influence on the efficiency as well as on the increase of extraction of lanthanide cations. Therefore, five new phenolic precursors bearing diglycolamic acid or diglycolamide moieties have been synthesized (Scheme 1). The diglycolamic acid derivative (**L1** : Tyad) was chosen as the reference derivative in order to evaluate the best sorption conditions. We have implemented a procedure for the synthesis of diglycolamic acid in a matrix of the resol type in alkaline conditions. The copolymerization was carried out in the presence of Phenol (P), Catechol (C) or Resorcinol (R) (Scheme 2). After the choice of the high-performance resin for the extraction of lanthanides, the other diglycolamide derivatives (Ligand **L2** : TyDGAdiethyl; **L3** : TyDGAdiisopropyl; **L4** : TyDGAdibutyl and **L5** : DityDGA) were engaged in the synthesis of phenolic resins in a similar way. The resulting formo-phenolic resins were studied in regards to their efficiencies for REEs extraction.



Scheme 1. Synthetic route for phenolic precursors bearing diglycolamic acid or diglycolamide moieties investigated in this study



Scheme 2. Schematic illustration of the synthetic route for the diglycolamic acid and diglycolamide formo-phenolic copolymers.

2. Experimental part

2.1. Material and methods

All chemicals were analytically pure (Sigma-Aldrich or Alfa Aesar) and used without further purification, anhydrous solvent (AcroSeal) were obtained from Acros. Thin layer chromatography (TLC) were performed on silica plate 60F254 adsorbed onto alumina sheet (Merck TLC Silica Gel 60 F254).

NMR and mass analysis and melting point were performed for the characterization of the different compounds. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz instrument. Displacements are reported in ppm using the solvent (CDCl_3 : 7.26 ppm for ^1H ; 77.16 ppm for ^{13}C) as an internal reference. Electrospray ionisation mass spectrometry (ESI-MS) was implemented on a Flexar SQ 300 MS instrument. A Buchi M-560 instrument was used for manual determination of melting points.

After mechanical grinding at 50 Hz for 10min using a Retsch mixer mill MM 200 with a Zr ball, the synthesized polymers have been characterized by several techniques such as solid state NMR, FT-IR, TGA, microscopy and elemental analysis. Solid state MAS (Magic Angle Spinning) ^{13}C NMR spectra were recorded with a Varian VNMRS 300 solid spectrometer at rotation speed of 12 KHz (3.2mm outer diameter rotors). Attenuated total reflection FTIR (ATR) was recorded on a Perkin Elmer 100 spectrometer equipped with ATR crystal (working range: 4000 – 400 cm^{-1} ; resolution 4 cm^{-1}). Thermal analyses were carried out using a TGA/DSC 2 STAR^e system from Mettler Toledo (heating rate of 10°C/min from 25 to 950°C under N_2 atmosphere). Environmental scanning electron microscope and X-EDS analyses were performed using a Bruker AXS X-Flash 5010 detector coupled with SEM (model FEI QUANTA 200 ESEM FEG). Elemental analysis was carried out with an Elementar Vario Micro Cube instrument.

The sorption behaviour of the polymers were highlighted from the determination of the total ion-exchange capacity by titration and batch contact experiments. Acide-base titration was performed using a Metrohm 809 Titrando by titration with HCl 0.1 M (Fluka analytical). Cation concentration in solution (before and after batch experiments) was quantified using an ICP/AES SPECTRO ARCOS spectrometer. The wavelengths were chosen to avoid any spectral interference between the elements: La (333.749, 379.478, 408.672, 412.323 and 419.655 nm), Eu (372.494, 390.710, 393.048, 412.970 and 420.505 nm), and Yb (275.048, 297.056, 328.937 and 369.419 nm).

2.2. Synthesis

2.2.1. General procedure for the synthesis of diglycolamic acids (1-3)

A mixture of 1.2 eq of amine R_2NH with 1 eq of diglycolic anhydride in anhydrous THF (50 mL) was stirred at 0°C and then at room temperature for 48h under nitrogen atmosphere. The solvent was evaporated and the crude product dissolved in CHCl_3 , the organic phase was washed successively with dilute aq HCl and with water (2 times). The organic phases were then combined and dried over sodium sulfate and concentrated under vacuum. The residue was recrystallized from Et_2O to give the final product as a solid.

2-(2-(diethylamino)-2-oxoethoxy) acetic acid (**1**) (65% yield, m.p: $51.6 \pm 0.2^\circ\text{C}$) was prepared starting from 3 g of diethylamine (41 mmol) and 3.97 g of diglycolic anhydride (34.2 mmol) in anhydrous THF (50 mL). See supporting information Figure SI-1a and Figure SI-1b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 10.69 (s, 1H, O=C-OH), 4.37 (s, 2H, O=C-CH₂), 4.16 (s, 2H, O-CH₂-C=O), 3.37 (t, 2H, $J = 8\text{Hz}$, N-CH₂-CH₃), 3.18 (t, 2H, $J = 8\text{Hz}$, N-CH₂-CH₃), 1.18, 1.17, 1.15, 1.13, 1.12, 1.10 (m, 6H, N-CH₂-CH₃).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 172.21 (HO-C=O), 170.18 (O=C-N), 72.10 (O-CH₂-C=O), 70.86 (O=C-CH₂-O), 41.04 (N-CH₂-CH₃), 13.78, 12.67 (N-CH₂-CH₃).

2-(2-(diisopropylamino)-2-oxoethoxy) acetic acid (**2**) (73% yield, m.p: 58.4 \pm 0.2°C) was prepared starting from 2.84 g of diisopropylamine (35.58 mmol), 3.44 g of diglycolic anhydride (29.65 mmol) in anhydrous THF (50 mL). See supporting information Figure SI-2a and Figure SI-2b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.35 (s, 2H, O=C-CH₂), 4.19 (s, 2H, O-CH₂-C=O), 3.64, 3.63, 3.61 (m, 2H, N-CH-(CH₃)₂), 3.53, 3.52, 3.50 (m, 2H, N-CH-(CH₃)₂), 1.41 (d, 6H, J = 8Hz, N-CH-(CH₃)₂), 1.23 (d, 6H, J = 8Hz, N-CH-(CH₃)₂).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 172.26 (HO-C=O), 169.79 (O=C-N), 72.76 (O-CH₂-C=O), 72.07 (O=C-CH₂-O), 47.81, 46.84 (N-CH-(CH₃)₂), 20.46, 20.19 (N-CH-(CH₃)₂).

2-(2-(dibutylamino)-2-oxoethoxy)acetic acid (**3**) (91% yield, m.p: 53.6 \pm 0.2°C) was prepared starting from 3.15 g of dibutylamine (41 mmol) and 3.97 g of diglycolic anhydride (34.2 mmol) in THF (50 mL). See supporting information Figure SI-3a and Figure SI-3b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 4.40 (s, 2H, O=C-CH₂), 4.24 (s, 2H, O-CH₂-C=O), 3.36 (t, 2H, J = 8Hz, N-CH₂-CH₂), 3.11 (t, 2H, J = 8Hz, N-CH₂-CH₂), 1.59, 1.57, 1.55, 1.54, 1.51, 1.50 (m, 4H, CH₂-CH₂-CH₂), 1.34, 1.32, 1.30, 1.29 (m, 4H, CH₂-CH₂-CH₃), 0.98, 0.96, 0.95, 0.94, 0.91 (m, 6H, CH₂-CH₃).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 171.99 (HO-C=O), 170.61 (O=C-N), 72.73 (O-CH₂-C=O), 71.10 (O=C-CH₂-O), 46.62, 46.52 (N-CH-CH₂), 30.63, 29.46 (CH₂-CH₂-CH₂), 20.14, 20.02 (CH₂-CH₂-CH₃), 13.77, 13.70 (CH₂-CH₃).

2.2.2. Preparation of 2-[2-[2-(4-hydroxyphenyl)ethylamino]-2-oxoethoxy]acetic acid - (**L1: Tyad**)

5 g of tyramine (36.5 mmol) was dissolved in anhydrous DMF (60 mL), and 4.66 g of diglycolic anhydride (40.2 mmol) were added. The resulting solution was stirred for 24h at 60°C after which the solvent was evaporated, and the crude product was dissolved in MeOH (10 mL) and precipitated by adding CH₂Cl₂ (80 mL) drop by drop. The resulting precipitate was filtered and evaporated under reduced pressure to give 8.23 g of **L1** as white solid (89% yield), m.p: 137.5 \pm 0.5°C. See supporting information Figure SI-4a, Figure SI-4b and Figure SI-4c.

^1H NMR (400MHz, DMSO-d₆) δ (ppm): 7.88 (t, 1H, J = 8Hz, NH-C=O), 7.00, 6.98 (m, 2H, Ar-H), 6.69, 6.67(m, 2H, HO-Ar-H), 4.09 (s, 2H, O-CH₂-C=O), 3.94 (s, 2H, O=CH₂-O), 3.29, 3.28, 3.26, 3.24 (m, 2H, CH₂-CH₂-NH), 2.62 (t, 2H, J = 8Hz, Ar-CH₂-CH₂).

^{13}C NMR (100MHz, DMSO-d₆) δ (ppm): 171.89 (O-CH₂-C=O), 169.06 (NH-C=O), 156.08(OH-C), 129.90(HC-CH=C), 129.77 (C-CH₂-CH₂), 115.58 (HO-C-CH=C), 70.57 (O=C-CH₂-O), 68.34 (O-CH₂-C=O), 34.80 (Ar-CH₂-CH₂).

^{13}C NMR DEPT-135 (DMSO-d₆) δ (ppm): 129.91(HC-CH=C), 115.58 (HO-C-CH=C), 70.57 (O=C-CH₂-O), 68.34 (O-CH₂-C=O), 40.57 (CH₂-CH₂-NH), 34.80 (Ar-CH₂-CH₂).

ESI-MS (m/z): 254.10 [(M-H)⁺]

2.2.3. General procedure for amidation of diglycolamic acids (**L2-L5**)

The amidation of diglycolamic acid was performed by amide coupling using HOBt and DCC following a procedure adapted from the literature.⁷

N,N-diethyl-2-[2-[2-(4-hydroxyphenyl)ethylamino]-2-oxoethoxy]acetamide - (**L2: TyDGAdiethyl**) was prepared starting from 2 g of 2-(2-(diethylamino)-2-oxoethoxy) acetic acid (**1**) (10.58 mmol); 1.573 g of hydroxyl benzotriazole (11.64 mmol); 2.402 g of dicyclohexylcarbodiimide DCC (11.641 mmol); and 1.452 g of tyramine (10.58 mmol). Ligand 2 (**L2 : TyDGAdiethyl**) was obtained as a yellow powder (57% yield), m.p : 55.8 \pm 0.2°C. See supporting information Figure SI-5a and Figure SI-5b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.41 (s, 1H, **HO-Ar**), 7.91 (t, 1H, $J = 8\text{Hz}$, $\text{H}_2\text{C-NH-C=O}$), 7.04 (d, 2H, $J = 12\text{Hz}$, HC-CH=C), 6.79, 6.77 (d, 2H, $J = 8\text{Hz}$, C=CH-CH), 4.18 (s, 2H, $\text{O-CH}_2\text{-C=O}$), 4.06 (s, 2H, $\text{O=C-CH}_2\text{-O}$), 3.54, 3.52, 3.51, 3.49 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}$), 3.45, 3.43, 3.41, 3.39 (m, 2H, $\text{N-CH}_2\text{-CH}_3$), 3.21, 3.19, 3.17, 3.16 (m, 2H, $\text{N-CH}_2\text{-CH}_3$), 2.76 (t, 2H, $J = 8\text{Hz}$, $\text{Ar-CH}_2\text{-CH}_2$), 1.20, 1.18, 1.16, 1.15 (m, 6H, $\text{CH}_2\text{-CH}_3$).
 ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.55 (NH-C=O), 167.91 (O=C-N), 155.30 (HO-C), 129.82 (C-CH_2), 129.69 (C-CH=C), 115.47 (C=CH-C), 71.35 ($\text{O=C-CH}_2\text{-O}$), 69.16 ($\text{O-CH}_2\text{-C=O}$), 41.02, 40.72 (N-CH_2), 40.59 ($\text{CH}_2\text{-NH}$), 34.75 ($\text{Ar-CH}_2\text{-CH}_2$), 14.12, 12.93 ($\text{CH}_2\text{-CH}_3$).
ESI-MS (m/z): 309.18 [(M-H) $^+$]

N,N-diisopropyl-2-[2-[2-(4-hydroxyphenyl)ethylamino]-2-oxoethoxy]-acetamide - (**L3**: TyDGAdiisopropyl) was prepared starting from 2.522 g of 2-(2-(diisopropylamino)-2-oxoethoxy) acetic acid (**2**) (11.61 mmol); 1.725 g of hydroxyl benzotriazole (12.77 mmol); 2.635 g of dicyclohexylcarbodiimide DCC (12.77 mmol) and 1.592 g of tyramine (11.61 mmol). Ligand 3 (**L3**: TyDGAdiisopropyl) was obtained as a white solid (65% yield), m.p: $79.6 \pm 0.5^\circ\text{C}$. See supporting information Figure SI-6a and Figure SI-6b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.99 (t, 1H, $J = 4\text{Hz}$, $\text{H}_2\text{C-NH-C=O}$), 7.06 (d, 2H, $J = 8\text{Hz}$, HC-CH=C), 6.82 (d, 2H, $J = 8\text{Hz}$, C=CH-CH), 4.16 (s, 2H, $\text{O-CH}_2\text{-C=O}$), 4.06 (s, 2H, $\text{O=C-CH}_2\text{-O}$), 3.66 (t, 2H, $J = 8\text{Hz}$, CH-CH_3), 3.55, 3.53, 3.51, 3.49 (m, 2H, $\text{CH}_2\text{-NH}$), 2.77 (t, 2H, $J = 4\text{Hz}$, $\text{Ar-CH}_2\text{-CH}_2$), 1.45, 1.43 (d, 6H, CH-CH_3), 1.23, 1.21 (d, 6H, CH-CH_3).
 ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.43 (NH-C=O), 167.27 (O=C-N), 155.33 (HO-C), 129.86 (C-CH_2), 129.68 (C-CH=C), 115.49 (C=CH-C), 71.19 ($\text{O=C-CH}_2\text{-O}$), 70.20 ($\text{O-CH}_2\text{-C=O}$), 47.63 (N-CH), 46.33 (N-CH), 40.68 ($\text{CH}_2\text{-NH}$), 34.88 ($\text{Ar-CH}_2\text{-CH}_2$), 20.69 (CH-CH_3), 20.46 (CH-CH_3).
ESI-MS (m/z): 337.21 [(M-H) $^+$]

N,N-dibutyl-2-[2-[2-(4-hydroxyphenyl)ethylamino]-2-oxoethoxy]acetamide - (**L4**: TyDGAdibutyl) was prepared starting from 2.743 g of 2-(2-(dibutylamino)-2-oxoethoxy) acetic acid (**3**) (11.18 mmol); 1.662 g of hydroxyl benzotriazole (12.3 mmol); 2.538 g of dicyclohexylcarbodiimide DCC (12.3 mmol) and 1.534 g of tyramine (11.18 mmol). Ligand 4 (**L4**: TyDGAdibutyl) was obtained as a white solid (63% yield), m.p: $81.2 \pm 0.5^\circ\text{C}$. See supporting information Figure SI-7a and Figure SI-7b.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.30 (s, 1H, **HO-Ar**), 7.93 (t, 1H, $J = 8\text{Hz}$, $\text{H}_2\text{C-NH-C=O}$), 7.04 (d, 2H, $J = 8\text{Hz}$, HC-CH=C), 6.80 (d, 2H, $J = 12\text{Hz}$, C=CH-CH), 4.19 (s, 2H, $\text{O-CH}_2\text{-C=O}$), 4.06 (s, 2H, $\text{O=C-CH}_2\text{-O}$), 3.54, 3.52, 3.50, 3.49 (m, 2H, $\text{CH}_2\text{-CH}_2\text{-NH}$), 3.36 (t, 2H, $J = 8\text{Hz}$, O=C-N-CH_2), 3.10 (t, 2H, $J = 8\text{Hz}$, O=C-N-CH_2), 2.76 (t, 2H, $J = 8\text{Hz}$, $\text{Ar-CH}_2\text{-CH}_2$), 1.58, 1.56, 1.55, 1.54, 1.52, 1.51, 1.50 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 1.38, 1.36, 1.34, 1.32, 1.30, 1.28 (m, 4H, $\text{CH}_2\text{-CH}_2\text{-CH}_3$), 0.98, 0.96, 0.94, 0.93 (m, 6H, $\text{CH}_2\text{-CH}_2\text{-CH}_3$).
 ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 169.52 (NH-C=O), 168.26 (O=C-N), 155.28 (HO-C), 129.86 (C-CH_2), 129.67, 115.47 (C-CH=C), 71.38 ($\text{O=C-CH}_2\text{-O}$), 69.12 ($\text{O-CH}_2\text{-C=O}$), 46.65 ($\text{N-CH}_2\text{-CH}_2$), 46.06 ($\text{N-CH}_2\text{-CH}_2$), 40.64 ($\text{CH}_2\text{-CH}_2\text{-NH}$), 34.83 ($\text{Ar-CH}_2\text{-CH}_2$), 30.90 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$), 29.67 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$), 20.20 ($\text{CH}_2\text{-CH}_2\text{-CH}_3$), 20.08 ($\text{CH}_2\text{-CH}_2\text{-CH}_3$), 13.85 ($\text{CH}_2\text{-CH}_2\text{-CH}_3$), 13.77 ($\text{CH}_2\text{-CH}_2\text{-CH}_3$).
ESI-MS (m/z): 365 [(M-H) $^+$]

2,2'-oxybis(*N*-(4-hydroxyphenethyl)acetamide) – (**L5**: DiTyDGA)
6 g of tyramine (43.8 mmol) and 6.05g of K_2CO_3 (36.5 mmol) were poured into round bottomed flask in 60mL of anhydrous DMF at 0°C . Then 3.4 g of diglycolyl chloride (19.9 mmol) was added drop by drop. The mixture was stirred for 24 h and filtrated. The filtrate was washed with DMF and the product was precipitated from the filtrate solution in 1 M HCl. After filtration, the filtrate was washed with water, saturated solution of NaCl and acetone. The organic phases were collected, dried over anhydrous Na_2SO_4 and then evaporated under vacuum. Ligand 5 (**L5**: DiTyDGA) was obtained as a white

powder (75% yield), m.p: $190.3 \pm 0.5^\circ\text{C}$. See supporting information Figure SI-8a, Figure SI-8b and Figure SI-8c.

^1H NMR (400 MHz, DMSO- d_6) δ (ppm): 9.19 (d, 2H, $J = 8\text{Hz}$, HO-Ar), 8.07 (t, 2H, $J = 8\text{Hz}$, O=C-NH-CH₂), 7.01 (d, 4H, $J = \text{Hz}$, CH-CH=C), 6.69 (d, 4H, $J = 8\text{Hz}$, C=CH-CH), 3.91 (s, 4H, O=C-CH₂-O), 3.31, 3.29, 3.28, 3.26 (m, 4H, CH₂-CH₂-NH), 2.64 (t, 4H, $J = 8\text{Hz}$, Ar-CH₂-CH₂).

^{13}C NMR (100 MHz, DMSO- d_6) δ (ppm): 168.87 (O=C-NH), 156.12 (HO-C), 129.91 (C-CH₂), 129.76 (CH-CH=C), 115.59 (C=CH-CH), 70.75 (O=C-CH₂-O), 34.92 (Ar-CH₂-CH₂).

^{13}C NMR DEPT-135 (DMSO- d_6) δ (ppm): 129.91 (C-CH₂), 129.76 (CH-CH=C), 115.59 (C=CH-CH), 70.74 (O=C-CH₂-O), 40.63 (CH₂-CH₂-NH), 34.92 (Ar-CH₂-CH₂).

ESI-MS (m/z): 373.18 [(M-H)⁺]

2.3. Resins synthesis

2.3.1. Thermosetting phenolic resins.

The thermosetting phenolic resins were synthesized by alkaline polycondensation of formaldehyde (F) (37% aqueous solution) with phenolic compounds Phenol (P), Catechol (C) or Resorcinol (R) according to procedure adapted from the literature.⁴⁶

Typically, a phenolic compound / formaldehyde / NaOH / H₂O molar ratio of 1:2.5:1.5:25 were used. After the addition, the mixture was stirred for 1h at room temperature and 2h at 50°C. Catechol and Resorcinol were not stirred for 2h at 50°C because of their low temperature gel point. After stirring, only phenol / formaldehyde / NaOH / H₂O mixture was stirred for 1h30 at 100°C. The phenol prepolymer was heated in an air oven from 100°C to 130°C at 3°C/h after 130°C for 24h. Catechol and resorcinol compounds was heated in an air oven from 50°C to 130°C at 3°C/h after 130°C for 24h. After curing, the thermosetting resin compounds was crushed by ball-milling. The resins were then submitted to a washing step with 1 M HCl/H₂O/1 M NaOH/H₂O cycles in order to remove the unreacted compounds and the oligomers which have not been well crosslinked. The resins were converted in their Na⁺ form by washing in 1 M NaOH and water until neutral. Finally, the resins were dried in air at 80°C for 24h.

2.3.2. Thermosetting diglycolamic acid phenolic copolymers resins

The homopolymerization of Ligand 1 (**L1**) lead to a water-soluble material which can not be used as a sorbent material for solid-liquid extraction. Therefore, a copolymerisation reaction between the phenolic ligand and Phenol, Catechol or Resorcinol was performed.

Mixture **L1** - phenolic precursor P, C or R (1 mmol) were done in different molar ratios by two steps. In a first step, a **L1**/ formaldehyde / NaOH / H₂O molar ratio of 1:2.5:1.5:25 was used. Then a mixture of phenolic precursor (P, C or R) / formaldehyde / NaOH / H₂O in a 1:2.5:1.5:50 molar ratio was added to the **L1** mixture solution. The mixture for the **L1** - Phenol was stirred for 1h at room temperature and 16h at 50°C and finally 1h30 at 100°C leading the **L1** - Phenol prepolymer. The prepolymer was heated in an air oven from 100°C to 130°C at 3°C/h and maintained at 130°C for 24h. The mixture for the **L1** - Catechol or **L1** - Resorcinol was stirred for 24 h at room temperature. After the mixture was heated in an air oven from 25°C to 100°C at 3°C/h, 24 h at 100°C, from 100°C to 130°C at 3°C/h and finally at 130°C for 24h in order to form the copolymers. After curing, the diglycolamic acid copolymers resins were crushed and washed in the same way as the phenolic resins. The resins were converted in their Na⁺ form by washing in 1 M NaOH and water until neutral. Finally, copolymers resins were dried in air at 80°C for 24h.

Table 1 summarizes the different phenolic resins synthesized in this study from Ligand 1 (**L1**), Phenol (P), Catechol (C) and Resorcinol (R).

Table 1. List of polymeric resins synthesized in this study starting from Ligand 1 (**L1**), Phenol (P), Catechol (C) and Resorcinol (R).

Polymer	Composition
I	100% L1
II	80% L1 – 20% P
III	60% L1 – 40% P
IV	40% L1 – 60% P
V	20% L1 – 80% P
VI	100% P
VII	80% L1 – 20% C
VIII	60% L1 – 40% C
IX	40% L1 – 60% C
X	20% L1 – 80% C
XI	100% C
XII	80% L1 – 20% R
XIII	60% L1 – 40% R
XIV	40% L1 – 60% R
XV	20% L1 – 80% R
XVI	100% R

2.3.3. Thermosetting diglycolamide phenolic copolymers resins

Mixture diglycolamide phenolic Ligand (**L2**, **L3**, **L4** and **L5**) - Resorcinol (1 mmol) were prepared in different molar ratios in two steps as described for the diglycolamic acid – phenolic copolymers. A list of synthesized diglycolamide phenolic copolymers resins - resorcinol is summarized in Table 2.

Table 2. List of polymeric resins synthesized by alkaline polycondensation : Ligand 2 - 5 (**L1** – **L5**) and Resorcinol (R).

Table 2. List of polymeric resins synthesized in this study starting from Ligand 2 (**L2**), Ligand 3 (**L3**), Ligand 4 (**L4**) or Ligand 5 (**L5**) with Resorcinol (R).

Polymer	Composition
XVII	60% L2 – 40% R
XVIII	60% L3 – 40% R
XIX	60% L4 – 40% R
XX	60% L5 – 40% R

Moisture regain was determined by a thermal treatment at 100°C for 24 hours, the percentage of water in the resin are summarized in Table SI-1 (see supporting information).

The ion-exchange capacities summarized in Table SI-1 (see supporting information) have been determined by titration of the resins in their H-form following the procedure from the literature and are close to value obtained in the literature.³⁹

2.4. Sorption experiment

The metallic solutions engaged in sorption experiments were prepared after dilution from lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Europium (III) nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), and Ytterbium (III) nitrate pentahydrate ($\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) with acid solutions.

Extraction experiments were conducted with different resins concentrations and acid conditions:

- i) 5 mM of Eu with 5 g/L diglycolamic acid phenolic copolymers resins from 10^{-4} mol/L to 10^{-2} mol/L in HNO_3 or H_2SO_4 solution;
- ii) 5 mM of Eu with from 1 g/L to 10 g/L diglycolamic acid phenolic copolymers resins (60% **L1** – 40% phenolic resins compounds) from 10^{-4} mol/L to 10^{-2} mol/L HNO_3 ;
- iii) 2 mM of La, Eu, Yb with 5 g/L diglycolamic acid or diglycolamide copolymers resins (**L1**, **L2**, **L3**, **L4** and **L5** - R) from 10^{-4} mol/L to 10^{-1} mol/L HNO_3 .

Back extraction experiments at 2 mol/L HNO_3 were conducted on resins loaded with REEs after extraction experiments performed by contacting 300 ppm of La, 300 ppm of Eu and 300 ppm of Yb with 5 g/L 60% **L1** - 40% C and 60% **L1** - 40% R resins from 10^{-4} mol/L HNO_3 and H_2SO_4 .

For concentrated solutions higher than 3 M of nitric acid a partial degradation of the resins could be observed which is not the case for the sulphuric acid media.

Batch contacts were generally performed for 24h under rotary agitation (1 rotation/s). Various volume to solid ratio (V/m) have been used from 1000 (1 g/L) to 100 (10 g/L). After the contact, the mixtures were filtered through a 0.2- μm cellulose acetate membrane and the remaining metal ion concentration in the liquid phase was determined by ICP/AES.

The cation uptake capacity Q (mg/g) and adsorption efficiency E (%) were calculated respectively using the following equation $Q = (C_i - C_f) \times V/m$ and $E = ((C_i - C_f)/C_i) \times 100$. C_i refers to the initial concentration of the metal ion in solution while C_f is the residual metal ion concentration after the batch contact, V/m is the ratio of the volume of the solution to the mass of the solid (V = volume of the treated solution and m = mass of the resin used). The separation factor $SF_{Yb/M}$ was determined according to the equation $SF_{Yb/M} = Q_{Yb}/Q_M$.

The back-extraction or stripping efficiency S (%) is defined as follows : $S = ((Q_E - Q_F)/Q_E) \times 100$; in which Q_E is the concentration of the metal ion loaded into the polymer and Q_F is the residual metal ion concentration in the polymer.

Kinetics experiments performed in the same way as for the batch contacts, highlighted that equilibrium was reached in 4h. A 24h shaking-time at 25°C was used in all the experiments to ensure thermodynamic equilibrium.

Langmuir isotherm parameters were estimated using the equation : $C_{eq}/Q_e = 1/(K_L \times Q_{max}) + C_{eq}/Q_{max}$; in which C_{eq} is the concentration of the metal ion adsorbed at equilibrium, Q_e is the amount of metal ion adsorbed at equilibrium, Q_{max} is the maximal amount of metal ion adsorbed at equilibrium and K_L is the Langmuir constant.

3. Results and Discussion

3.1. Synthesis

3.1.1. Ligand synthesis

Tyramine (2-(4-Hydroxyphenyl)ethylamine) was used in order to synthesize the chelating phenolic precursor (Scheme 1).

The tyramine was engaged in an opening ring reaction with diglycolic anhydride leading the chelating ligand **L1**. The chelating ligands **L2**, **L3** and **L4** were prepared by coupling the tyramine with corresponding diglycolamic acid in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) /

hydroxybenzotriazole (HOBT) as coupling reagent for amide formation. The chelating ligands **L5** was synthesized by nucleophile substitution of diglycolic acid chloride with tyramine. The products were fully characterized by NMR, FT-IR, and ESI-MS analysis and then engaged in the polymerisation reaction (see experimental part and supporting information Figure SI1 to SI-8).

3.1.2. Resin synthesis and characterizations

The formo-phenolic resins were prepared using formaldehyde as crosslinker in the presence of alkaline hydroxide as catalyst (NaOH) by adjusting the conditions described in the literature in order to obtain the solubilisation of the phenolic precursors in basic conditions before the addition of formaldehyde.^{28, 29} Preliminary investigation of the homopolymerization of **L1** gave a water-soluble material (polymer I), which can be not useful in solid-liquid extraction. Water soluble oligomers are obtained in link with a low degree of polymerization which may be due to the presence of two reactive sites (two ortho positions- on its phenol ring) in the precursor **L1** which are difficult to homopolymerize.

To increase the degree of polymerization, a copolymerization reaction between the phenolic ligands and phenolic precursors was used, resulting in an uncontrolled crosslinking through a methylene linkage between the diglycolamic acid or diglycolamide with the phenolic precursors. By changing the nature of ligands and the phenolic precursors, various amorphous crosslinked polymers are obtained (Table 1 and 2). After the washing step, which allows to remove the partially soluble oligomeric species (mass decrease around 25-30%, see Table SI-1 supporting information), insoluble resins are obtained which can be investigated as sorbent materials for solid-liquid extraction. Examination of the crushed resins by SEM showed smooth glass-like surfaces particles that lack pore structure with sizes of the order of 25 μm (Figure SI-9).

FT-IR ATR spectra of the polymers I-VI in Figure 1 exhibit the characteristics band of the phenolic resins as well as the ligands in the copolymers. The phenolic contribution was highlighted by the O-H bond stretching from phenolic hydroxyl at 3300 cm^{-1} (broad band), the C-H stretching at 2920 cm^{-1} corresponding to the methylene linkages between the phenolic rings and the aromatic C-H out-of-plane deformation band at around 1600 cm^{-1} . The amide bands corresponding to **L1** are observed at 1655 and at 1540 cm^{-1} and their intensity increase by increasing the **L1** ratio in the copolymer.

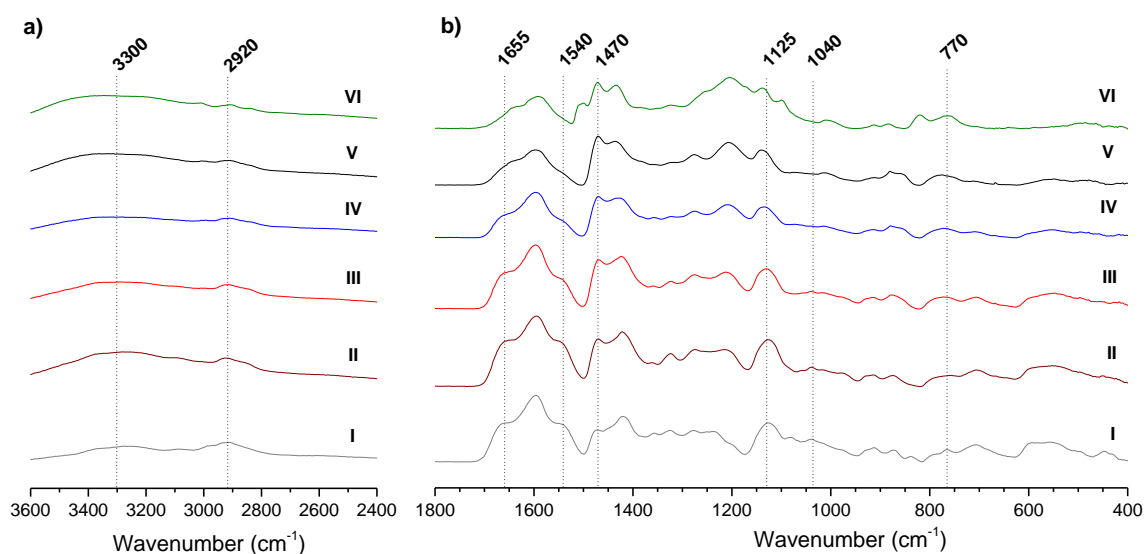


Figure 1. FTIR spectra a) 3600-2400 cm^{-1} and b) 1800-400 cm^{-1} region of phenolic polymers bearing **L1** ligand: Polymer I (100%**L1**) Polymer II (80% **L1** – 20% P), Polymer III (60% **L1** – 40% P), Polymer IV (40% **L1** – 60% P), Polymer V (20% **L1** – 80% P).

Also, the band at 1125 cm^{-1} indicating $-\text{CH}_2-$ bond from $-\text{CH}_2-\text{O}-\text{CH}_2$ function while C-O bond is present at 1040 cm^{-1} . Similar observations have been noticed for the polymers prepared starting from ligand **L2** to **L5** (Figure SI-10 see supporting information).

The corresponding ^{13}C CP-MAS NMR spectra of the resins exhibits a signal at around 33 ppm corresponding to bridging methylene carbon ($\text{Ar}-\text{CH}_2-\text{Ar}$), while the presence of a peak at 130 ppm and between 156.7 and 151.5 ppm corresponding respectively to the aromatic and phenolic carbons (Figure 2). Evidence of the introduction of the **L1** ligand in the polymer was highlighted by the presence of the peaks at 70 ppm, 177 and 172 ppm corresponding respectively to the methylene group close to the central oxygen and the carbonyl C=O unit of ligand **L1**. A comparison between the prepolymer and resulting polymer after curing is illustrated in Figure SI-11 in the supporting information. The increase in intensity of these peaks was correlated with the increase of **L1** ratio in the polymeric resin. This was also confirmed thanks to elemental analysis (Figure SI-12 supporting information). The ^{13}C -NMR spectrum of Polymer XII showed a peak at 118 ppm corresponding to the bridging methylene carbon between the two hydroxyl groups in the resorcinol moieties.⁴⁹

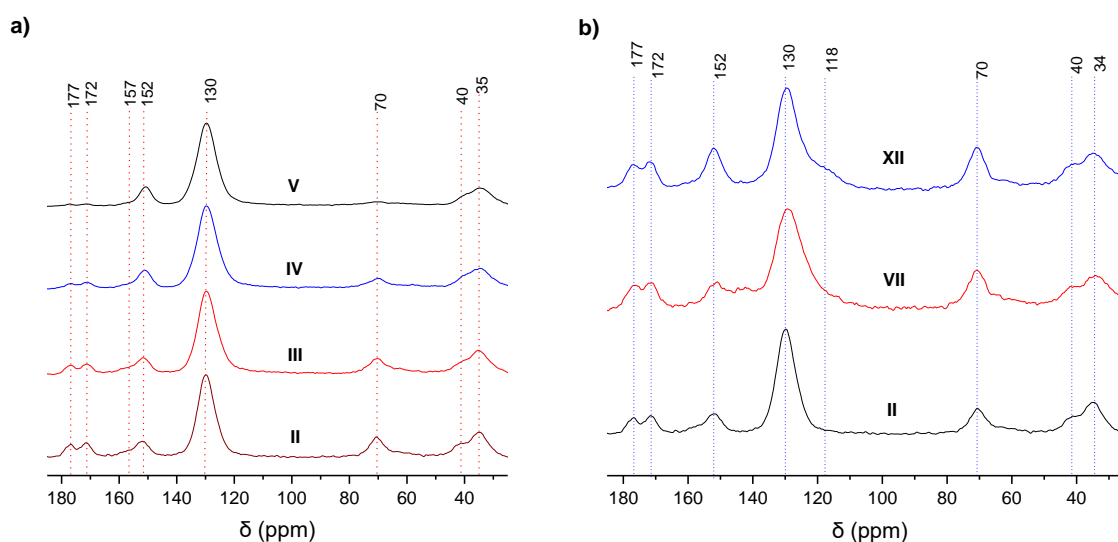


Figure 2. ^{13}C solid state NMR spectra of a) Phenolic polymers bearing **L1** ligand: Polymer II (80% **L1** – 20% P), Polymer III (60% **L1** – 40% P), Polymer IV (40% **L1** – 60% P), Polymer V (20% **L1** – 80% P); b) Phenol, Catechol, Resorcinol polymer bearing **L1** ligand: Polymer VII (80% **L1** – 20% C), Polymer XII (80% **L1** – 20% R).

The TG/DTG curves (thermogravimetry and differential thermal analysis) of polymers bearing **L1** ligand (from Polymer I to Polymer V) and phenol resin (Polymer VI) are shown in Figure 3a and 3b. The mass loss of Polymer I appears in several stage decompositions indicating that is not well cross-linked. There is less rigidity in its skeleton in comparison to the copolymers, consequently decomposition is easier and is carried out at 182°C. Endothermic peaks in derivatives thermogravimetry curves (Figure 3b) highlight this decomposition. The release of free phenol, formaldehyde, short oligomers in their polymer matrix were main contributors to the weight loss around 200°C.⁵⁰ Other decomposition takes place between 330 and 400°C. Ammoniac derivatives and CO_2 from carboxylic acid groups in the ligand release occurs certainly in their decomposition.

Thermoset copolymers present two endothermic peaks overlapping between 360 and 390°C. Polymer II, III and IV show the largest endothermic peak where the most important decomposition products take place. When the temperature increases after 390°C, degradation of polymeric matrix form CO, CO₂, benzaldehyde and char.⁵¹ The presence of the ligand in the Polymer V shows two endothermic peaks which differ from polymer without L1 (Polymer VI). We demonstrated that thermal decomposition behaviour changes when L1 is incorporating in the phenolic matrix. Similar observation has been noticed for the L1 polymers prepared with Catechol and Resorcinol (Figure SI-13 and SI-14 see supporting information).

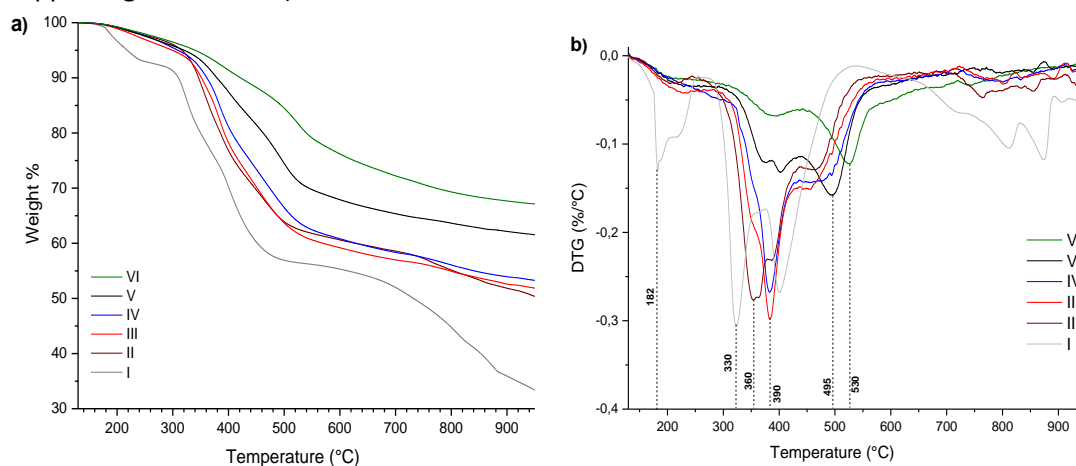


Figure 3. Thermal analysis data of the Phenolic polymers bearing L1 ligand: Polymer I (100%L1), Polymer II (80% L1 – 20% P), Polymer III (60% L1 – 40% P), Polymer IV (40% L1 – 60% P), Polymer V (20% L1 – 80% P) and Polymer VI (100%P). (a) TG and (b) DTG curves at 10°C/min under an N₂ atmosphere.

3.2. Extraction experiments

During preliminary sorption experiments conducted in a 10⁻⁴ – 2 M acid range, a low metal adsorption was observed at high acid concentration due to the competition between the extraction of the metallic species and the protonation of hydroxyl group. This has been also highlighted by the increase of the pH after the batch contact, which indicate that Na⁺ groups are exchanged with H⁺. Starting from a pH= 4 for the feed aqueous solution the pH reached a value of 5 at the equilibrium. The ion-exchange sorption of the cation is controlled by deprotonation of the phenolic groups.³⁹ This drawback in terms of extraction performance at high acidity allows however to consider the possibility of using such a medium for a back extraction step. In addition, in the H⁺-form of the resin, the weakly acidic phenolic groups of the resins displayed a low metal adsorption in the acid range. Based on these results, it appears necessary to convert the resins into their Na⁺-form in order to enhance the sorption properties of the resins.

3.2.1. Resins bearing the diglycolamic acid ligand

3.2.1.1. Extraction of Eu³⁺

The efficiency of the extraction properties of the resins for Eu³⁺ was conducted for the resin with and without the L1 diglycolamic acid ligand. Typically, 50 mg of resin was submersed with 10 mL (V/m=200 ; resin concentration= 5 g/L) of nitric acid solution (10⁻⁴ – 10⁻² M) with 5 mmol/L (760 ppm) of Eu³⁺. In each case, in comparison with purely phenolic resins when the ligand is introduced the efficiency for Eu³⁺ extraction is clearly improved (Figure 4). Also, the increase in the acidity of the initial feed solution results in decreased sorption performance of each resins. Good extraction performance was observed

at low pH (4), these results are in good agreement with those observed for DGA-modified silica materials.^{24, 25} A comparable set of experiments has been performed by replacing nitric acid with sulfuric acid, similar extraction behavior has been observed for each resin (see Figure SI-15 supporting information).

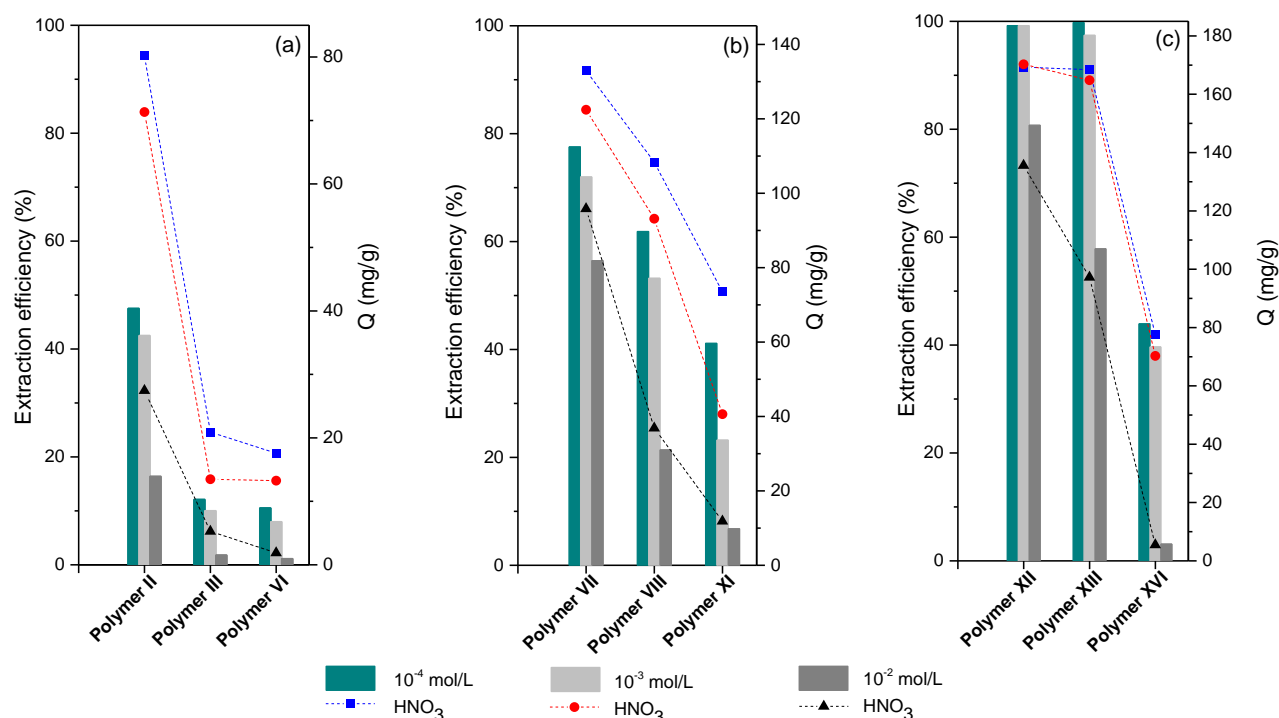


Figure 4. Extraction efficiency (bar) and cation uptake capacity (symbol) of Eu³⁺ for a) Phenol based materials: Polymer II (80% L1 – 20% P), Polymer III (60% L1 – 40% P), Polymer VI (100% P) ; b) Catechol based materials: Polymer VII (80% L1 – 20% C), Polymer VIII (60% L1 – 40% C), Polymer XI (100% C) ; c) Resorcinol based materials: Polymer XII (80% L1 – 20% R), Polymer XIII (60% L1 – 40% R), Polymer XVI (100% R). Polymer concentration (5 g/L), nitric acid solution (10⁻⁴ – 10⁻² M) with 5 mM of Eu³⁺ (760 ppm), 24h of contact at 25°C.

When resorcinol was used instead of phenol or catechol for the diglycolamic acid-containing resins an increase of sorption capacities has been observed. As illustrated for the resorcinol based resins in the Figure 5, the Eu³⁺ sorption efficiency is raised by the introduction of the chelating ligand.

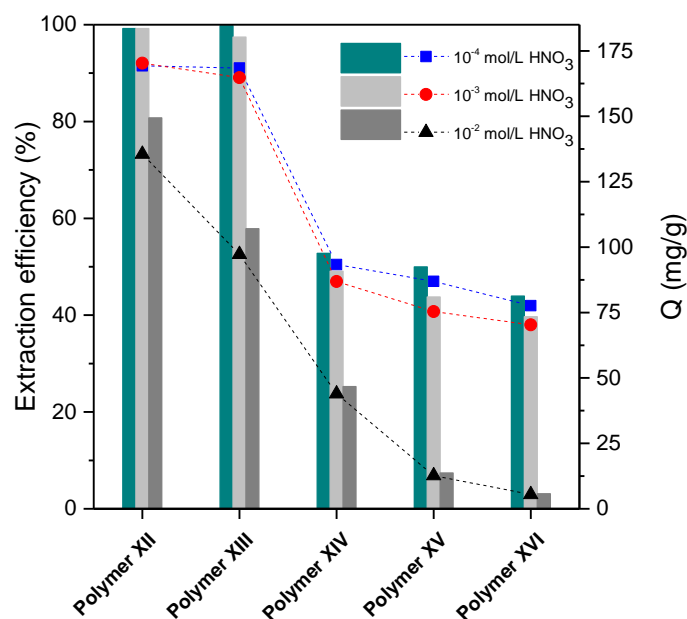


Figure 5. Extraction efficiency (bar) and cation uptake capacity (symbol) of Eu^{3+} for Resorcinol based materials: Polymer XII (80% L1 – 20% R), Polymer XIII (60% L1 – 40% R), Polymer XIV (40% L1 – 6% R), Polymer XV (20% L1 – 80% R), Polymer XVI (100% R). Polymer concentration (5 g/L), nitric acid solution (10^{-4} – 10^{-2} M) with 5 mM of Eu^{3+} (760 ppm), 24h of contact at 25°C.

It appears that the resins with the highest amount of chelating ligand is the most efficient. However, a high amount in chelating ligand also reflects an inferior crosslinking as we have been able to point out with the mass losses after the washing step. A compromise must be made between sorption performance and crosslinking properties. For this reason, in the following extraction experiments we focused on resins based on resorcinol and bearing the chelating ligand at a molar percentage up to 60%. A plateau was observed for the extraction efficiency of Eu^{3+} by the polymer after 4h at 25°C, suggesting that equilibrium state is reached. To illustrate this result a kinetic study is provided in Figure SI-16 (see supporting information). Also, X-EDS analyses (Figure SI-17, see supporting information) confirm the presence of europium in the polymer after the extraction experiments. The possibility to extract quantitatively the Eu^{3+} from a 10^{-2} M acidic solution has been demonstrated by varying the amount of resins involved (Figure 6).

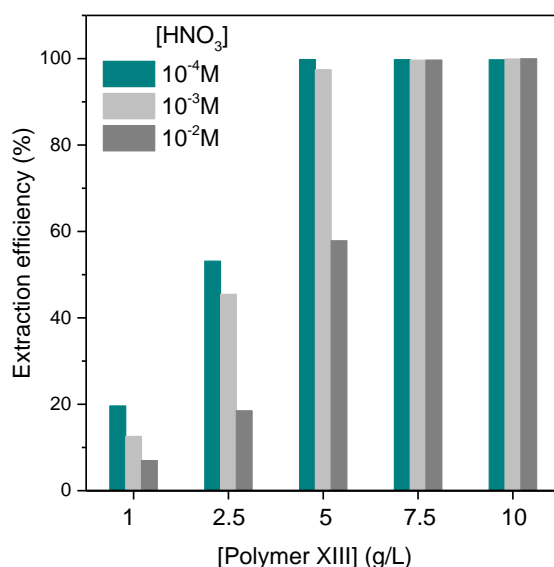


Figure 6. Extraction of Eu^{3+} by Polymer XIII (60% L1 – 40% R) at various concentration (1–10 g/L) from nitric acid solution (10^{-4} – 10^{-2} M) with 5 mM of Eu^{3+} (760 ppm), 24h of contact at 25°C.

The extraction isotherm of Eu^{3+} by Polymer XIII at 5 g/L from nitric acid solution 10^{-4} M is shown in Figure 7. Extraction of Eu^{3+} increase with concentration of metal adsorbed at equilibrium (Q_e) increase until 0.3 mM (40 ppm). Extraction gradually increases from this concentration where Q_e is 153 mg/g, until the saturation of the chelating sites in the polymeric matrix. This experimental adsorption was correlated with Langmuir model in order to calculate Q_{max} . From Langmuir fitting the Q_{max} was determined to be 171.7 mg/g and K_L was 0.121 L/mg. The nature of slope of the initial portion of the curve of Figure 7 seems the H adsorption isotherm from Giles⁵² which indicated a high affinity of metal ions in the extraction by ion-exchange.

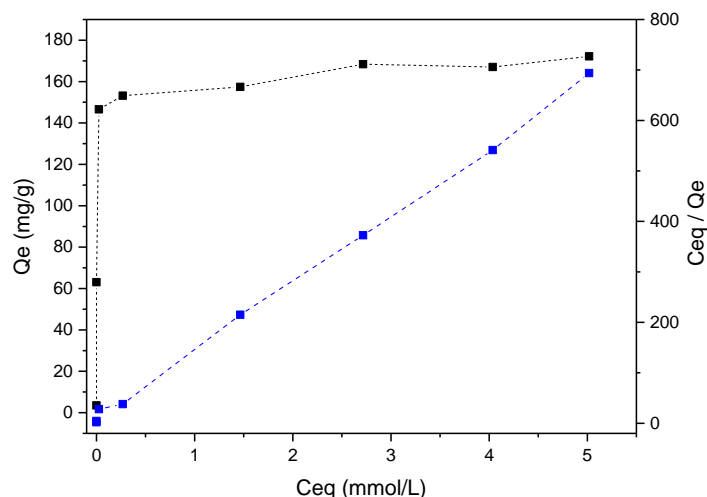


Figure 7. Extraction of Eu^{3+} by Polymer XIII (60% L1 – 40% R) at 5 g/L from nitric acid solution 10^{-4} M with several solutions of Eu^{3+} from 5 μM to 5 mM (0.5 ppm to 760 ppm), 24h of contact at 25°C.

3.2.1.2. Extraction and stripping of REEs

The extraction profile of the polymer XIII (60% L1 – 40% R) was then established for La, Eu and Yb as light, medium and heavy REEs respectively. The results presented in Figure 8a indicate that the extraction performance of REEs by polymer XIII is quantitative for each cations in the studied condition. The behaviour of the extraction values for the three REEs is quite similar in regard to the feed nitric acid solution.

The solid phase loaded with the REEs initially present in the aqueous phase was then suggested to stripping step in order to recover the REEs from the polymer. As mentioned, ion-exchange sorption of the cation is controlled by protonation / deprotonation of the phenolic groups of the resin and the protons of the carboxylic acid groups of the ligand. Therefore, protonation of hydroxyl group allows to back-extract the metallic species loaded in the polymer. The data shows that approximately up to 80% of REEs already extracted by the polymer can be recovered thanks to a stripping step with a 2M nitric acid solution (Figure 8b).

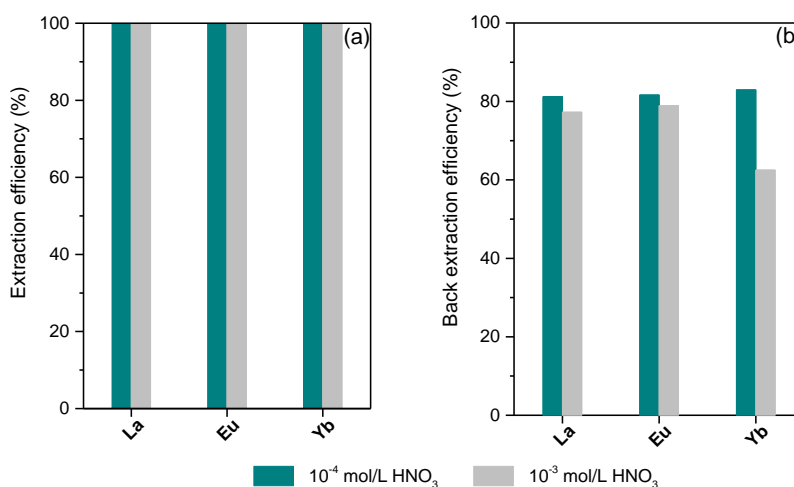


Figure 8. a) Extraction of La^{3+} , Eu^{3+} and Yb^{3+} by Polymer XIII (60% L1 – 40% R) at 5 g/L ($V/m=200$) from nitric acid solution (10^{-4} and 10^{-3} M) with 2 mM of each cations (La^{3+} (305 ppm), Eu^{3+} (285 ppm), Yb^{3+} (285 ppm) , contact 24h at 25°C; b) Back-extraction of La^{3+} , Eu^{3+} and Yb^{3+} from loaded Polymer XIII using HNO_3 2M ($V/m=200$), 24h of contact at 25°C.

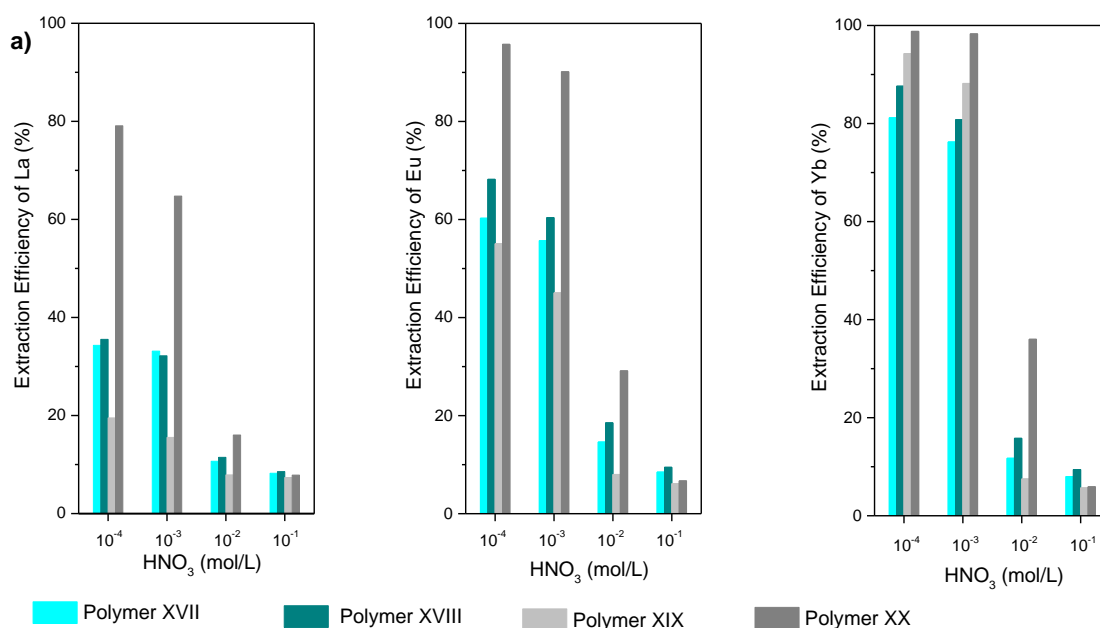
3.2.2. Resins bearing the diglycolamide ligands

A strong influence of the ligand on the efficiency of phenolic resins has been highlighted and the efficiency is enhanced when resorcinol is used as comonomer. The influence of the other chelating compounds **L2** to **L5** on ion-exchange selectivity was then examined for polymeric resins based on resorcinol and bearing the chelating ligand at a molar percentage up to 60%.

As previously showed, the extraction efficiencies are highly dependent on the concentration of the feed nitric acid. It appears that the polymer which incorporate the ligand **L5** is more efficient than the other diglycolamide ligand with respect to the 3 studied REEs. The results in Figure 9 and Figure SI-18 (see supporting information) also suggest that in comparison to Eu and La, the polymers preferentially extract the Yb.

These tendencies are in agreement to the one encountered in the literature, with a preferential extraction of HREEs by the DGA. The highest separation factors $SF_{Yb/La}$ and $SF_{Yb/Eu}$ are obtained for the polymer XIX at low acidity (pH= 3 - 4) with value of about 5 and 2 respectively. In comparison for TODGA impregnated resins, estimated values for heavy to medium REE separation are close ($SF_{Yb/Eu} \approx 2.5$) while for heavy to light REE separation higher separation factors are found ($SF_{Yb/La} > 50$).¹⁷ By changing the concentration of the resin it is possible to consider a more pronounced selectivity for HREEs towards LREEs. At higher acidity, there is no pronounced selectivity with a mutual extraction of the REEs.

All tested polymers showed a comparable adsorption behaviour with a quantity of adsorbed metal in the range 50–100 mg/g and in some cases above 150 mg/g. As sorption efficiencies depend on both the composition of the feed solution as well as the ion-exchanger used, it is difficult to provide a relevant comparison. For chelating function close to those studied here, results from the literature showed that the DGA-TODGA resin has a capacity of around 30 mg/g towards europium.^{17, 53} Also, DGA-functionalized mesoporous silica materials highlighted an adsorption capacity of about 25 mg/g for DGA-SBA-15 or DGA-MCM41 for a series of REEs²⁵ and up to 170 mg/g towards europium using a DGA-KIT-6 hybrid material in a dynamic process.⁵³ In comparison to the literature, it appears that the phenolic polymers bearing diglycolamic acid or diglycolamides moieties, which exhibit competitive Q values with respect to the studied extraction condition, are good sorbent for REEs.¹⁶



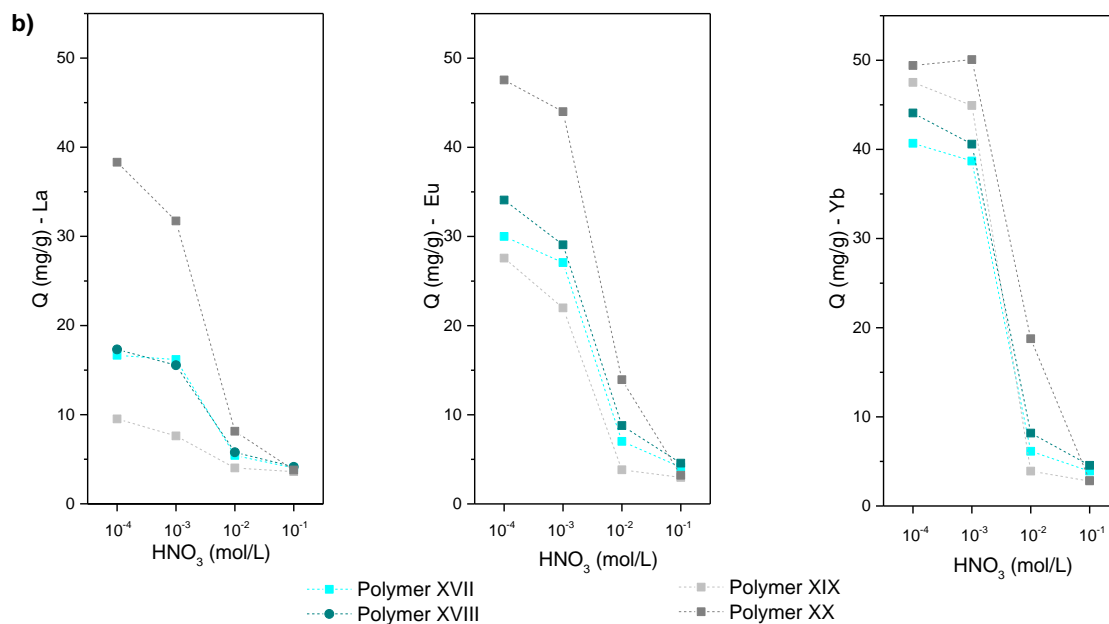


Figure 9. a) Extraction efficiency and b) cation uptake capacity of La³⁺, Eu³⁺ and Yb³⁺ for Resorcinol based materials: Polymer XVII (60% **L2** – 40% R), Polymer XVIII (60% **L3** – 40% R), Polymer XIX (60% **L4** – 40% R), Polymer XX (60% **L5** – 40% R). Polymer concentration (5 g/L), nitric acid solution (10⁻⁴ – 10⁻¹ M) with 2 mM of each cations (La³⁺ (305 ppm), Eu³⁺ (285 ppm), Yb³⁺ (285 ppm), 24h of contact at 25°C.

4. Conclusion

Five new phenolic precursors bearing diglycolamic acid or diglycolamides moieties have been synthesized. They were then engaged in a copolymerisation reaction by alkaline polycondensation with formaldehyde with admixture such as phenol, catechol or resorcinol. The immobilization of the functional group in the polymeric resins has been demonstrated thanks to complementary characterization techniques. The resins have been then engaged in sorption experiment in regards to rare earth elements. The europium extraction by the phenolic polymers demonstrates that the incorporation of the ligands enhances the extraction efficiencies of the REE by the polymers. It was highlighted that the resorcinol based polymer bearing the ligand exhibits higher properties in comparison to those based on phenol and catechol.

The present work displays competitive Q values and promising application with respect to the simplicity of implementation of these materials as well as their low cost.

The recovery of REEs was verified with an acidic eluting solution (2 M nitric acid), demonstrating the potential reusability of these sorbents.

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