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Diglycolamide phenolic foams as sorbent for rare earth elements

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ABSTRACT

In this present study, we developed a new series of sorbents based on phenolic foam resin for the extraction of rare earth elements. Chelating phenolic foams were prepared using appropriate formulation of blowing agent, surfactant and curing acid agent and a prepolymer resulting from an alkaline polymerisation reaction of phenolic diglycolamide derivative with admixture of phenol, catechol or resorcinol in the presence of formaldehyde as crosslinker agent. The foaming copolymer resins were completely described and engaged in sorption studies with three types of lanthanide (La, Eu, Yb), which represent light, medium and heavy REEs, respectively.

KEYWORDS: Phenolic foam, Sorbents materials, Diglycolamide, Rare-earth elements, Liquid-solid extraction

1. INTRODUCTION

Rare-earth elements (REEs) play a major role in the development of new current technologies such as optical, electronics and renewable energy [1]. Whatever the sources of the REEs (mining deposit, exploitation of secondary sources or recycling), these strategic metals are recovered via hydrometallurgical processes. Solid liquid extraction (SLE) of metal ions is increasingly developed due to its various advantages over other hydrometallurgical methods, since it is free from the use of toxic or volatile organic solvents, which are involved in conventional liquid–liquid extraction processes. As a result, this has led to the research for insoluble polymers such as ion-exchange or chelating resins with good stability and high capacity for metal ions. Among them, formo-phenolic resins, which result from the alkaline polycondensation of formaldehyde with a phenolic compound, have demonstrated sorption properties from their phenolic OH groups and/or from active chelating groups for various metal ions [2–4] including REEs [5–7]. Recently, the use of resol-type resins incorporating diglycolamide derivative for the extraction of REEs showed promising results [8].

In most of these applications, the resins are studied in the form of powders but the advantage of the phenolic resin is that they can be obtained in different forms in particular in the form of foams [9].

To the best of our knowledge, no study has yet been reported on the phenolic foams (PFs) with active chelating groups dedicated to the extraction of REEs. The present study aims for the synthesis of a new class of foaming chelating copolymers based on phenolic resin that was synthetised by alkaline polycondensation of formaldehyde and phenolic compound with diglycoamide derivative. The different copolymers obtained were expanded or foamed by using a blowing agent, a surfactant and a curing acid agent (Figure 1). Then the materials were engaged for the extraction of La, Eu, Yb, which represent light, medium and heavy rare-earth elements, respectively.

2. MATERIALS AND METHODS

2.1 Synthesis

The diglycolamide (DGA) phenolic precursor was synthetised according to the procedure previously described in the literature [8]. The experimental procedure for the preparation of prepolymer was adapted from previous studies [8,10,11].

In a first part, a mixture of DGA/formaldehyde/solution NaOH (6 M in aqueous solution)/H_2O in a 1/2.5/1.5/30 molar ratios was prepared. Then, a mixture of phenolic compound (phenol (P), catechol (C) or resorcinol (R))/formaldehyde/NaOH/H_2O in a molar ratio 1/2.5/1.5/ 50 was added to the initial mixture. The reaction mixture with phenol was stirred 24 h at 50°C, then at 95°C for 2 h while with catechol or resorcinol the mixture was stirred for 24 h at room temperature and 1 h at 60°C. The resulting pre-polymers were then engaged in the preparation of the foam. Foaming resin was prepared from the pre-polymer mixed thoroughly at room temperature with 10 wt.% of n-pentane as blowing agent, 3 wt.% of Tween 80 as surfactant and then 12 wt.% sulphuric acid (50 wt.%) as curing agent. The mixture was heated for 1 h at 80°C for expansion and then the temperature was increased gradually from 100°C to 130°C for 24 h. After the curing, the foaming phenolic resins were submitted to a washing step with 1 M HCl/H_2O/1 M NaOH/H_2O cycles for removing the unreacted compounds and the oligomers that have not been crosslinked. Finally, for the sorption experiments the resins were converted in their Na+ form by washing step with 1 M NaOH and then water until neutralisation, followed by drying in air oven at 80°C for 24 h. In the present study, DGA-polymeric foams with a 50% of functional group and 50% of phenolic precursor were studied (Table S1).

2.2 Materials

^1H and ^{13}C liquid NMR spectra and ^{13}C CP MAS NMR spectra were recorded on a Brucker advance 400 ultra-shield VS spectrometer. Chemical shifts are reported in ppm using D2O as an internal reference and using a MAS probe using 3.2 mm outer diameter rotors with a spinning rate of 12 KHz (typical contact: 2–3 ms, typical recycle delay: 5 s). FT-IR spectra were recorded with a Perkin Elmer 100 spectrometer on a range 4000–380 cm^{-1} using ATR crystal with 4 cm^{-1} resolution. Thermal gravimetric analysis (TGA) measurements were performed on a Mettler Toledo instrument (heating rate of 10°C/min from 30°C to 950°C under N_2 atmosphere). Microstructure and morphology of phenolic foams were characterised by environmental scanning electron microscopy (model FEI QUANTA 200 ESEM FEG) with X-EDS analyses using a Bruker AXS X-Flash 5010. Quantification of cation concentration in solution (before and after batch experiments) was conducted by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) using a SPECTRO ACROS spectrometer.

2.3 Adsorption experiments

The sorption experiment was carried out using feed aqueous solutions consisting in REEs at 500 ppm in nitric acid at pH = 4. The solutions were prepared from La $(NO_3)_3.6H_2O)$, Eu $(NO_3)_3$. $6H_2O$ and Yb $(NO_3)_3.6H_2O$ in nitric acid solution in order to get a pH = 4. Batch contacts were performed for 24 h; even then, kinetic studies have shown that the equilibrium was reached in 1–3 h. The mixtures were shaken at 1 rotation/s under rotary agitation. Then, the mixtures were filtered through a 0.2 µm cellulose acetate membrane filter and analysed by ICP-OES to determine the residual metal concentration. The adsorption capacity Q (mg/g) and extraction efficiencies E (%) were calculated, respectively, using the formulae: $Q = (Ci\text{-}Cf) \times V/m$ and $E = (Ci\text{-}Cf)/Ci \times 100$, where Ci denote the initial concentration of metal in solution while Cf denote the residual concentration of metal in solution, V is the volume of solution and m is the mass of resin used.

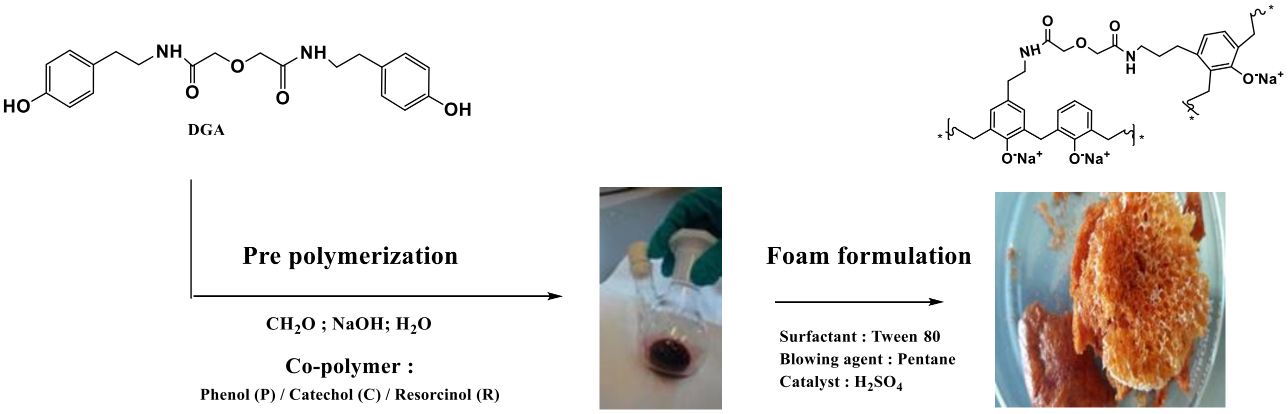

Figure 1. Illustration of the synthesis of the DGA-phenolic foams.

3. RESULTS AND DISCUSSION

As already described [8], the homopolymerisation of chelating ligand in basic conditions with formaldehyde as crosslinker lead generally to water-soluble oligomers. The same behaviour was observed for the foaming resin prepared in similar conditions. In order to use these functionalised resins in a SLE process, a copolymerisation with phenolic precursors (50% molar ratio) was implemented. The copolymerisation lead to uncontrolled crosslinking through a methylene linkage between chelating ligand and phenolic precursors.

Foaming chelating phenolic resins were prepared based on previous studies involving: i) Tween 80 a non-ionic surfactant [12] that stabilises the emulsion before the foaming, with an interfacial tension decrease and hindering coalescence phenomenon; ii) Pentane [13], as blowing agent which produces gas bubbles in the phenolic matrix when the temperature increases during the curing step and/or the exothermic reaction between the pre-polymer mixture and the acid catalyst; iii) H2SO4 as catalyst/curing agent, which accelerates the curing reaction [14]. After curing, the resins were washed in order to remove the partially soluble oligomeric species.

All foaming chelating phenolic resins exhibit the same characteristic FT-IR bands and ^{13}C CP/MAS NMR peaks corresponding to the functional group and the phenolic moiety (Figure 2).

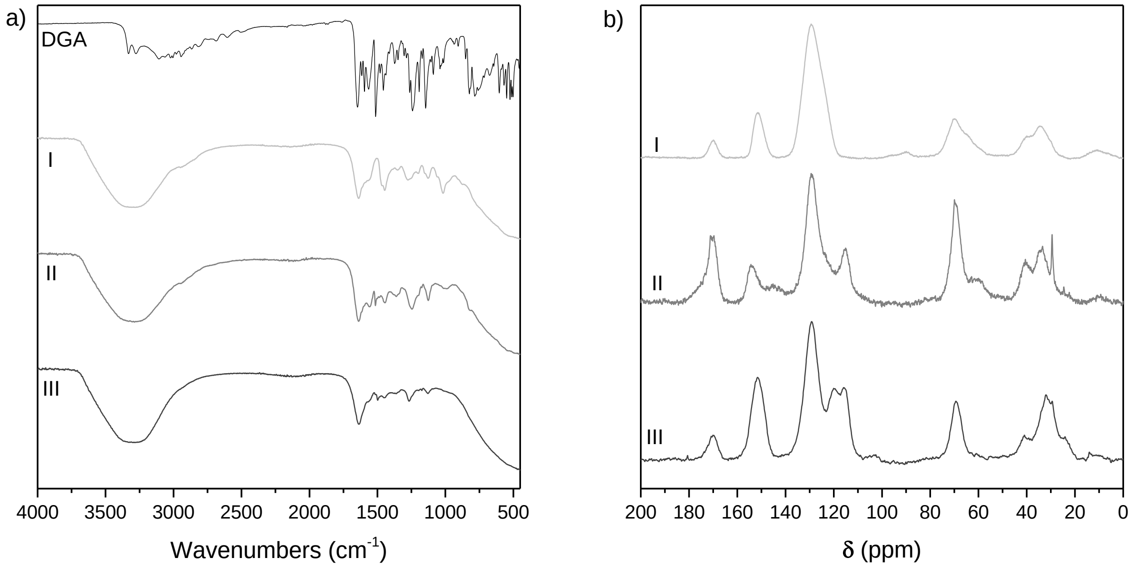

Figure 2. a) FTIR spectra and b) ^{13}C solid state NMR spectra of chelating PFs **I** (DGA-Phenol), **II** (DGA-Catechol) and **III** (DGA-Resorcinol).

The presence of amide bands indicating that the ligand has been incorporated in the final polymer was observed at 1650 and 1560 cm^{-1}. This was also confirmed with the band at 1130 cm^{-1} assigned to the ether group function of the DGA group ($–CH_2–O–CH_2$). The presence of the DGA moiety was confirmed from the signals at 70ppm and at 170ppm in the solid state NMR spectra corresponding, respectively, to the methylene between the central oxygen and the carbonyl C=O. A comparison of the ^{13}C spectra of the prepolymer in the liquid state and the resulting foam in the solid state is provided in the ESI (Figure S1). In addition, elemental analysis indicates the presence of nitrogen according to the incorporation of the DGA functional group.

The process of thermal decomposition observed from the thermogravimetric analysis could be divided into three different stages (Figure 3) [15].

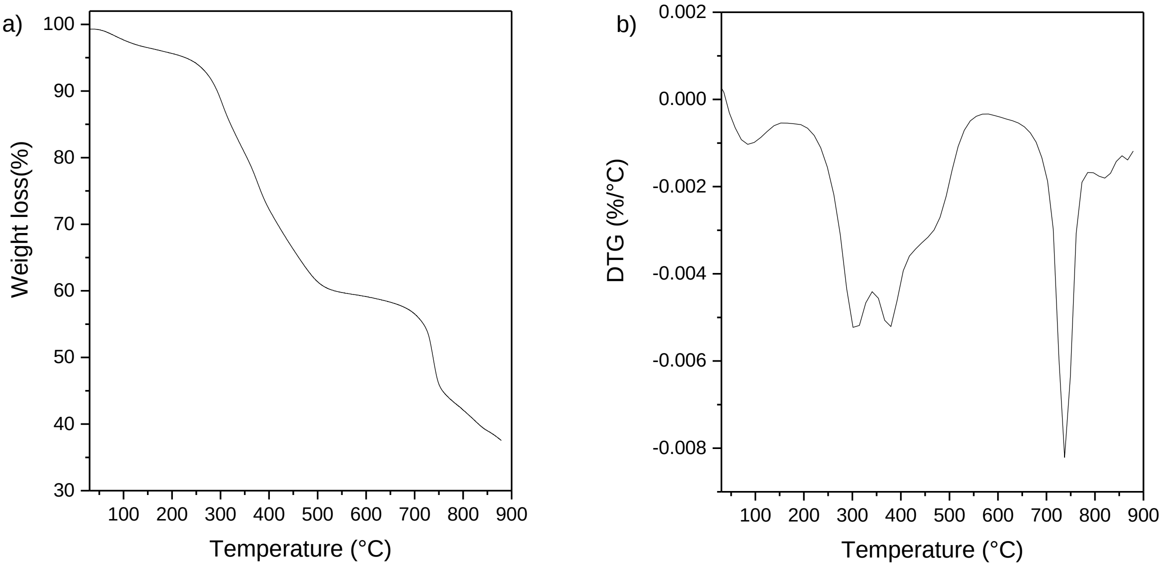

Figure 3. Thermal analysis data of chelating foaming phenolic polymers **I** (DGA–Phenol).
a) TG and b) DTG curves at 10°C/ min under N_2 atmosphere.

The first thermal degradation peak was below 300°C attributed to the release of excess phenol, formaldehyde, short oligomers and water [16] as well as the DGA functional group. The second stage in the thermal decomposition was observed in the range of 300– 450°C; during this stage, the reaction of pyrolysis and polymerisation reaction of pyrolysis start to occur. The third stage, in the range of 450–900°C, was the main process of thermal mass loss; during this process, the methylene-bridged structure and the long-chain molecules degraded of all phenolic foaming polymer and formation of carbonaceous char.

The SEM morphologies of the foaming polymers are presented in Figure 4. All phenolic foams showed cells which are roughly spherical. High volatile hydrocarbons such as pentane are known to induce the formation of open cells. The cells exhibit some perforation, which may be caused by the presence of water in the foaming polymer.

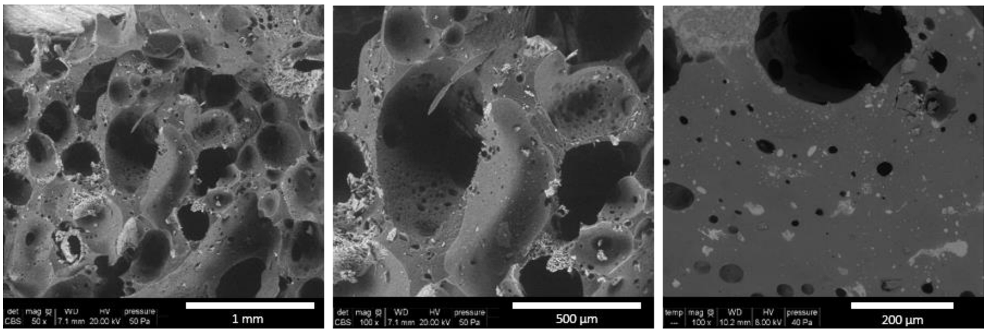

Figure 4. SEM images of chelating PF **I** (DGA-Phenol).

The efficiency of the foam for the REEs extraction was demonstrated from the sorption experiments results, which show that most of the cation were extracted (Figure 5). An interesting point is that the DGA foam exhibits higher efficiencies for Yb>Eu>La which is in agreement with previous studies showing that the DGA functional group exhibits higher affinity for heavier REEs [17].

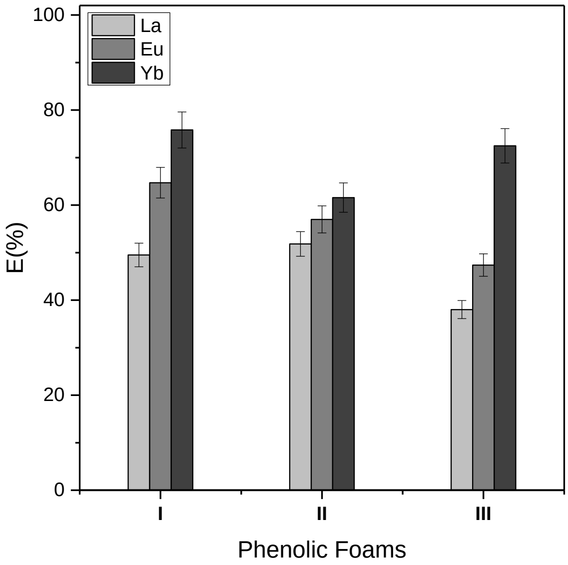

Figure 5. Extraction efficiency of La^{3+}, Eu^{3+} and Yb^{3+} for chelating PFs **I** (DGA-Phenol), **II** (DGA-Catechol) and **III** (DGA-Resorcinol). Polymer concentration (5 g/L: V/m=200), nitric acid solution (10^{-4}mol/L) with 500 ppm of La^{3+}, Eu^{3+} or Yb^{3+}, 24 h of contact at 25°C.

Indeed, the extraction increases by increasing the atomic number or by decreasing the ionic radius of the rare earths. This can be attributed to the charge density, which is higher in heavy rare earths due to their smaller ionic radii, which facilitates their complexation by the DGA functional group [18].

The uptake was also demonstrated by submitting the solid phase loaded with the REEs to an X-EDS analysis (Figure S2).

4. CONCLUSION

For the first time, diglycolamide phenolic foams have been synthesised by a copolymerisation process with diglycolamide moieties and various phenolic groups using pentane as foaming agent. The expanded phenolic resins were subjected to sorption experiments in order to determine their extraction efficiency for REEs showing a preferential extraction of HREEs by the DGA. Ongoing studies are in progress in order to improve the toughness of the PFs.

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SUPPORTING INFORMATION

Table S1 Foaming chelating phenolic resins prepared in this study.

Phenolic foams	Composition	Elemental analysis*			
		C %	H %	O %	**N %**
I	50% DGA – 50% Phenol	53.0	4.6	29.1	**3.7**
II	50% DGA – 50% Catechol	54.2	5.5	26.0	**3.7**
III	50% DGA – 50% Resorcinol	42.6	4.7	32.0	**3.4**

* Uncertainties are related to the determination of O% which is obtained by combustion

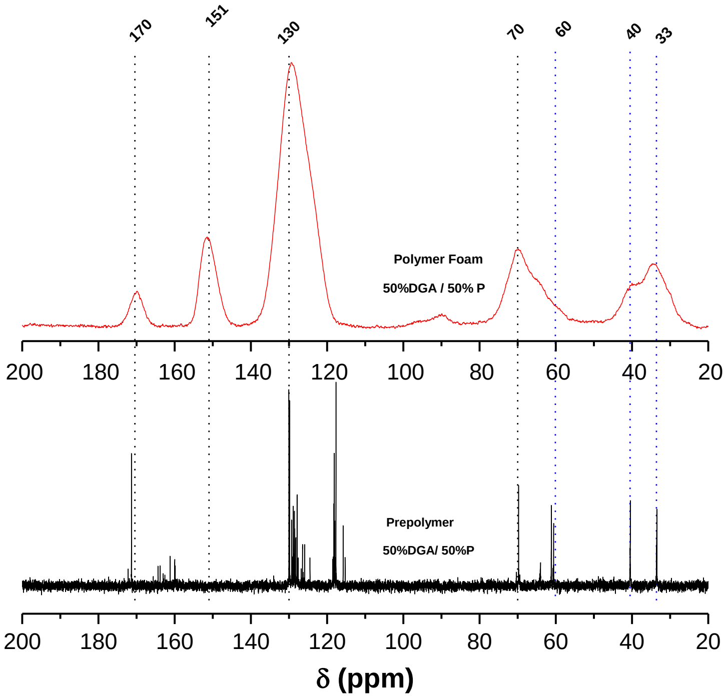

Figure S1. ^{13}C liquid (D_2O) NMR spectra of prepolymer **I** (DGA-Phenol) and ^{13}C CP MAS NMR of foaming chelating polymer **I** after curing.

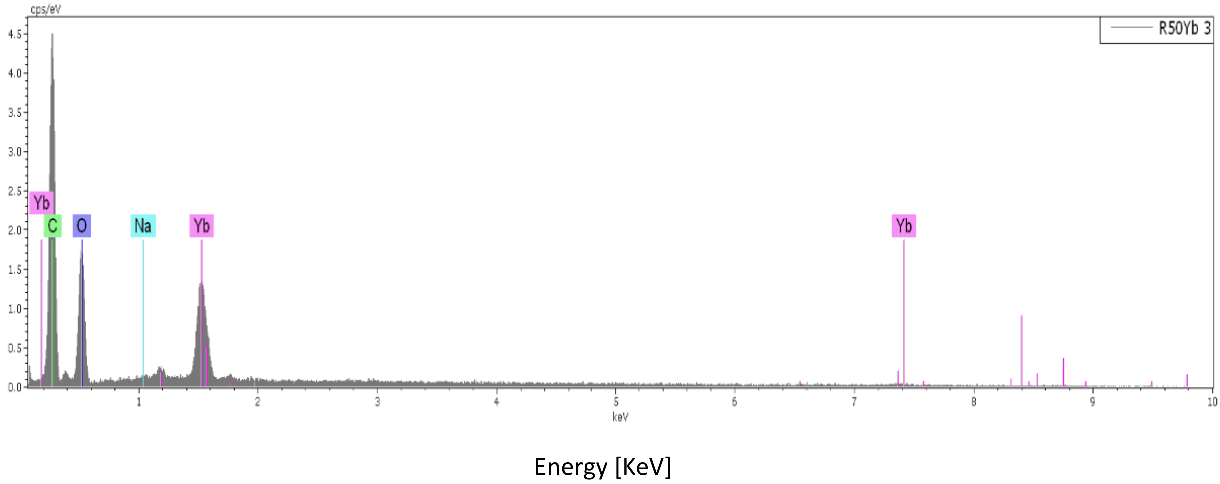

Figure S2. X-EDS spectra of polymer II (DGA–Resorcinol) after extraction of Yb^{+3} .Polymer concentration (5g/L, V/m=200), nitric acid solution (10^{-4}mol/L) with 500ppm of Yb^{+3} , contact 24h at 25°C.