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Diazabenzo crowns grafted on the polystyrene and application of extraction of metal cations

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ABSTRACT

The study of the new structures mainly useful in the synthesis of more efficient and selective new extractants led to the development of new series of macromolecules. Hence, in our present experiment, the expanded polystyrene packaging waste was chemically modified. Then, the functionalization of polystyrene recovered by the direct blending and grafting of a benzenic crown ether group was carried out. The obtained resins were characterized by elemental analysis, infrared spectroscopy, differential scanning calorimetry, differential thermal analysis, thermogravimetric analysis, and X-ray diffraction. The ability to extract metallic cations (Cr^{3+}, Fe^{3+}, Ni^{2+}, Cd^{2+}, and Pb^{2+}) contained in an aqueous solution was done by the grafted or ungrafted polymers by crown ethers. Obtained results showed higher extraction percentages for resin 4, thus, suggesting it had important extracting capacity compared with resin 3.

Keywords: Recovered polystyrene; Diazabenzo crowns; Metallic cations extraction

1. Introduction

Macrocyclic ligands are known for their remarkable complexing properties for both neutral and ionical molecules [1]. However, the formed complexes are generally substantially soluble in water, which sometimes makes their recovery delicate. Hence, the ligands are usually immobilized on a polymer support [2,3], notably on the Merrifield resin such as Morin (2´,3,4´,5,7-pentahydroxyflavone), used for the extraction of heavy metals (Cu, Pb, Zn, and Cd) [4] or macrocycle grafted on aminobenzo-15-crown-5 and aminobenzo-18-crown-6 resins, used for the separation of lithium isotopes [5,6] (see Fig. 1).

In subsequent studies, the microporous polypropylene membranes (Celgard 2500, 2400) were used as a supporting medium to hold an organic solution containing the crown ether dissolved in a mixture of ethanol and chloroform (v/v) [7]. Besides, in some investigations, the cellulose triacetate membranes were doped with imidazoleazocrown derivatives, fixed as carriers and used for facilitated transport of Zn(II), Cd (II), and Pb(II) ions from aqueous nitrate source phase [8]. Solid phase extraction (SPE) offered a number of important benefits [9]. In fact, it has been shown that it allowed the reduction of solvent usage, solvent exposure, disposal costs, and extraction time during sample preparation, which resulted in its successful role in the separation and sensitive determination of metallic ions, mainly in water samples [10].

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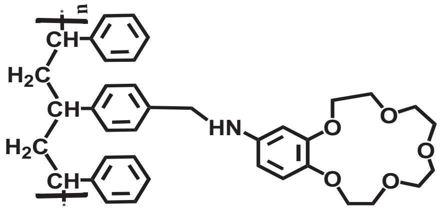

Fig. 1. Merrifield resin grafted with aminobenzo-15-crown-5 [5].

Polymeric resin has been widely used as a solid support for metal extraction in the SPE technique, especially polystyrene divinylbenzene (PS-DVB), due to its high porosity and ease of surface modification [11]. The modification methods of PS-DVB have been recently reported. Among these methods there may be mentioned, impregnation and functionalization with chelating agents or ligands containing electron donor atoms, such as nitrogen, oxygen, and sulfur. During impregnation, ammonium pyrrolidine dithiocarbamate was used for the preconcentration of seven heavy metals in drinking water and sea water [12]. However, in practice, resins prepared by the impregnation of the ligands are difficult to reuse, due to partial leaching of the ligands during the elution process [10]. In addition, in literature, most chelating agents were macromolecules, painful to synthesize, and expensive [13–17]; and the small or commercial ligands have poor selectivity [10,18–22]. Thus, most of these ligands were functionalized on PS-DVB through an azo spacer [14,15,18–27]. Other authors have converted the waste of polystyrene into a cation exchange resin [28] and used it for the removal of lead and cadmium metals from aqueous solution [29].

The present work is aimed to perform a functionalization by a chelating agent (B15C5 and DB18C6), with waste polystyrene (after nitration and its transformation into polyamine polymer) through azo coupling, in order to use it in the extraction of metallic cations from aqueous solution.

2. Experimental

2.1. Materials and apparatus

2.1.1. Materials

Products used were: polystyrene foam from packaging waste (PS), chloroform (99–99.4%, Sigma–Aldrich), absolute ethanol (Prolabo), nitric acid (65%, Scharlau Chemie SA), sulfuric acid (95–97%, Scharlau Chemie SA), hydrochloric acid (37%, Scharlau SL), $SnCl_2$, (Panreac Quimica SA), sodium hydroxide (Prolabo), acetone (99.8%, Prolabo), acetic acid (Prolabo), benzo-15-crown-5 (99%, Acros Organics), and dibenzo-18-crown-6 (98%, Sigma–Aldrich). $CdCl_2{\cdot}H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $CrCl_3{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and $Pb(NO_3)_2$ were produced by Fluka and used as such.

2.1.2. Apparatus

Characterizations were carried out as described below. Infrared analysis, using the attenuated total reflectance technique (ATR/FTIR), was made on a Nicolet IR 200 spectrometer with a scanning range between 4,000 and 400 cm^{-1}. Elemental analysis was performed by using Perkin Elmer Analyzer CHN Series II 2400. Differential scanning calorimetry (DSC) was performed on a Setaram DSC 131 apparatus. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Setaram TGA92 device. X-ray diffraction (XRD) was recorded on a Bruker D8 Advance device. The amount of remaining metal ions in solution was evaluated by flame atomic absorption spectroscopy (FAAS) analysis on a Perkin-Elmer PinAAcle 900T. The instrumental parameters are the following: the wavelengths used were 228.8, 248.33, 357.87, 232, and 283.31 nm for Cd, Fe, Cr, Ni, and Pb, respectively, and the detection limits were 15 $mg\,L^{-1}$ for Pb(II), 3 $mg\,L^{-1}$ for Cr(III), 5 $mg\,L^{-1}$ for Fe(III), 6 $mg\,L^{-1}$ for Ni(II), and 0.8 $mg\,L^{-1}$ for Cd(II).

2.2. Preparation of resins

2.2.1. Functionalization of PS

2.2.1.1. By physical mixing of PS with crown ethers. Unmodified PS (1 g) was dissolved in chloroform, followed by the addition of crown ether (B15C5 or DB18C6) with different weight percentages (5, 10, 15, and 20%). The mixture was stirred until complete dissolution of the crown ether occurred. The solution was then evaporated in order to obtain a thin film of whitish color. The result led to the formation of polymers M1, M2, M3, and M4 for the mixture with different percentages of B15C5 5, 10, 15, and 20%, respectively, and polymers P1, P2, P3, and P4 for the mixture with DB18C6 for the same different percentages.

2.2.1.2. By chemical grafting of crown ethers.

2.2.1.2.1. Nitration of PS. PS (5 g) was dissolved in chloroform (50 mL) and nitric acid (65%, 20 mL). Sulfuric acid (98%, 25 mL) was added dropwise into the solution under vigorous stirring. The nitration

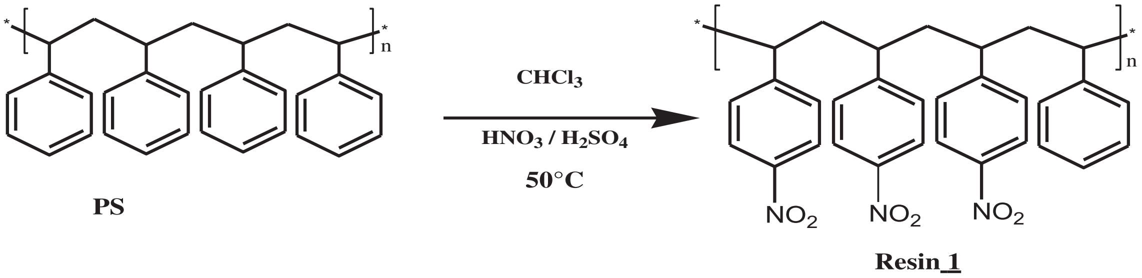

Fig. 2. Nitration of PS.

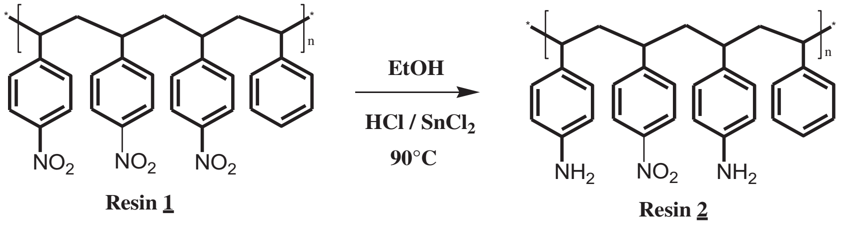

Fig. 3. Amination of PS.

reaction was carried out for 2 h at 50°C. Thereafter, the reaction mixture was poured into distilled water. The nitrated resin was filtered, washed with water until freed from acid and dried at 50°C for 12 h (Fig. 2).

2.2.1.2.2. Reduction of the nitro groups. The nitrated resin (4 g) was mixed with 10 g $SnCl_2$, 20 mL concentrated HCl, and 20 mL ethanol. The mixture was refluxed for 10 h at 90°C. The solid precipitates were filtered, washed with water and 2 M NaOH to ensure the deprotonation of ammonium salts and dried at room temperature, and then at 50°C for 12 h (Fig. 3).

2.2.1.2.3. Diazotization of functionalized PS by diazo-B15C5 and diazo-DB18C6. The amino resin (1 g) was first washed with 2 M HCl and then with excess of water. It was slurried in an ice–water mixture (50 mL) and treated with 1 M HCl and 1 M $NaNO_2$ (added in small aliquots of 1 mL). The diazotized resin was filtered, washed with cold water and was treated with B15C5 or DB18C6 (0.5 g in 35 mL of glacial acetic acid and 15 ml of acetone) at 0–4°C for 24 h, and the resulting brown-colored material was filtered, washed with chloroform and dried at room temperature (Figs. 4 and 5).

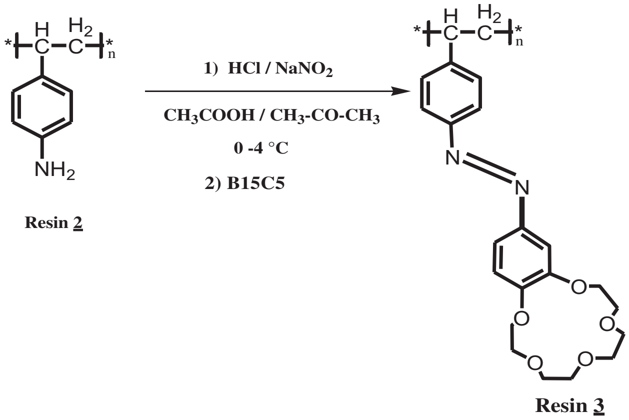

Fig. 4. Functionalization of PS by a diazo-B15C5.

2.3. Metal ion extraction method

Aqueous monometallic solutions of $CdCl_2{\cdot}H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $NiCl_2{\cdot}6H_2O$, $Pb(NO_3)_2$, and $Cr(Cl)_3{\cdot}6H_2O$ were prepared at a concentration of $2.10^{-4}\,mol\,L^{-1}$ in relation with each metal ion in distilled water (pH 6). The polymer (0.10 g) was incubated with 20 mL of the metal ion solution at 25°C for 24 h. The suspension was filtrated on filter paper. The amount of remaining metallic ions in solution was analyzed by FAAS of the filtrate after dilution in distilled water on a Perkin-Elmer PinAAcle 900T. The results were demonstrated as percentages of metal extraction, based on its initial concentration (Figs. 15 and 16).

The extraction percentage (%) was calculated using the following equation:

$$\%\ \text{Extraction} = ((C_i - C_f)/C_i) \times 100 \tag{1}$$

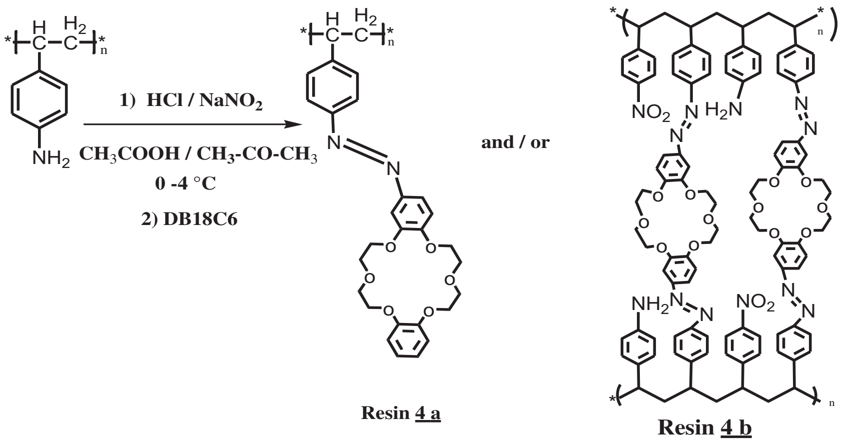

Fig. 5. Possible structures of grafting of diazo-DB18C6 on polymer.

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, respectively.

3. Results and discussion

We carried on PS two structural change methods. The first is to directly mix the crown ethers with PS in varying amounts (from 5 to 20% by weight of polymer) in chloroform. This was conducive to polymers M1, M2, M3, and M4 when mixing PS with benzo-15-crown-5 (B15C5). Then, the mixture of PS with dibenzo-18-crown-6 (DB18C6) in varying amounts resulted in polymers called P1, P2, P3, and P4. The second step was to chemically modify the PS by nitration, using a mixture of (HNO_3/H_2SO_4) in chloroform, that yielded the nitro polystyrene (resin **1**), followed by grafting these crown ethers on the backbone of amino polystyrene. Concerning the aminated polystyrene (resin **2**), it was obtained by the reduction of nitro groups by Sn–HCl [30]. The amine functions underwent diazotization by the method described in the literature [31], followed by condensation: first with B15C5, to achieve resin **3** and then with DB18C6, to yield resin **4**.

3.1. Characterizations of PS by ATR/FTIR, DSC, and DTA–TGA

The IR spectra of the PS (performed on a film prepared in chloroform) showed the presence of three bands of stretching vibration of (–CH) aromatic between 3,075 and 3,039 cm^{-1}, two vibration bands of symmetrical and asymmetrical distortion(–CH_2), between 2,940 and 2,859 cm^{-1}, and three bands (C=C) aromatic rings between 1,607 and 1,454 cm^{-1}, respectively, and various substitutions of benzene nucleus between 752 and 697 cm^{-1} (Fig. 12(a)). Table 1 summarizes dominant infrared frequencies for PS.

Table 1
Infrared frequency for the PS

Characteristic vibration	Wave number (cm^{-1})
CH aromatic	3,075–3,039
C=C aromatic	1,607–1,454
–CH_2 asymmetric and symmetric vibrations	2,940–2,859
Various substitutions of benzene nucleus	752–697

The DSC curve of PS recorded from a sample of mass $m = 4.2$ mg with a heating rate of 20˚C/min in the temperature range from 25 to 300˚C showed that the T_g is 105˚C (Fig. 6) and an endothermic peak around 410˚C, which probably indicates the decomposition of polymer (Fig. 10). Similar result was reported in the literature [32]. On the other hand, the DTA–TGA curves of PS recorded from a sample of mass $m = 7.2$ mg with a heating rate of 5˚C/min showed two

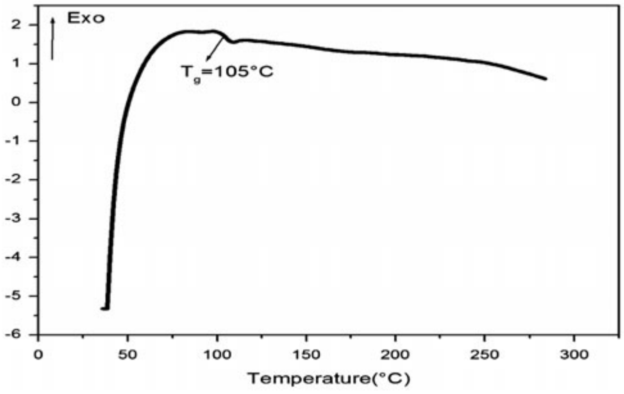

Fig. 6. DSC diagram of PS.

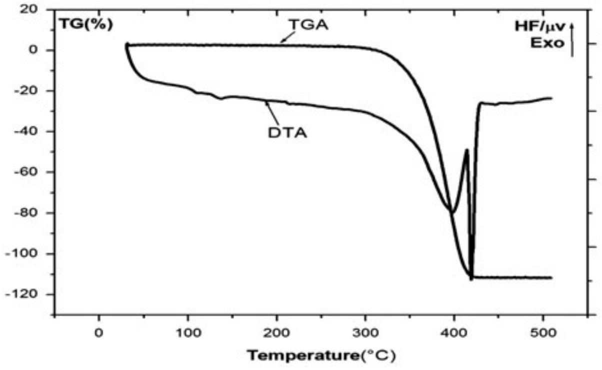

Fig. 7. DTA–TGA curves of PS.

endothermic peaks at 390 and 420°C. The first peak at 390°C was accompanied by a very large mass loss of 92.6%. This peak could be attributed to the decomposition of polystyrene. The second thin peak was observed at 420°C and can be explained by a small loss of mass of 2.08% due to the end of the polymer decomposition of polymer (Fig. 7). Obtained TGA agrees with the literature [32].

3.2. *ATR/FTIR analysis of polymers obtained by mixtures of PS with different percentages of crown ethers*

Figs. 8 and 9 showed the superposition of the IR spectra of PS blends with different percentages of crown ethers (5, 10, 15, and 20%). Obtained results revealed an increase in the intensities of the valence bands corresponding to C–O–C and Ar–O–C of crown ethers (which appear at around 1,248–1,130 cm^{-1} for B15C5 and at 1,248–1,139 cm^{-1} for the DB18C6) with the increase in weight percentages of crown ethers added to the mixtures.

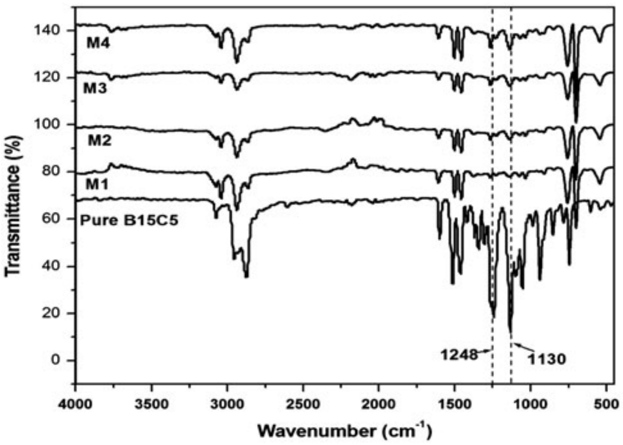

Fig. 8. ATR/FTIR spectra of the pure B15C5 and films M1, M2, M3, and M4.

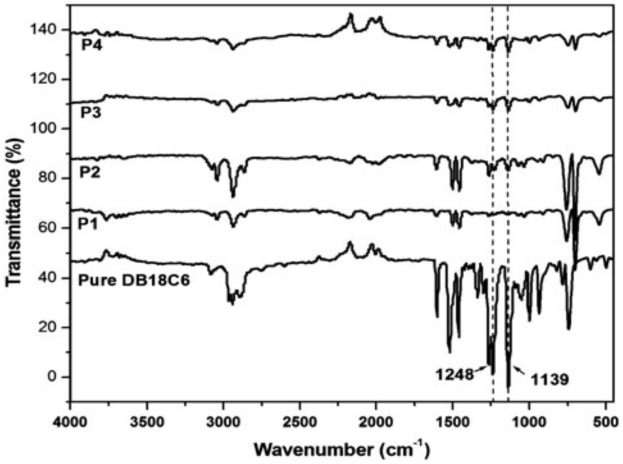

Fig. 9. ATR/FTIR spectra of the pure DB18C6 and films P1, P2, P3, and P4.

3.3. *Elemental analysis of PS and the resins* ***1–4***

The results of the elemental analysis of the PS, nitro, amino, diazo-B15C5, and diazo-DB18C6 derivative of the resin are given in Table 2. The nitrated (resin **1**) and aminated (resin **2**) polystyrene were found to contain 7.65 and 9.27% of nitrogen, respectively. Elemental analysis of the resin **3** showed 31.11, 4.68, 5.19, and 35.5%of C, H, N, and O, respectively. Elemental analysis of the resin **4** showed 34.98, 4.70, 5.34, and 31% of C, H, N, and O, respectively (Table 2).

3.4. *DSC analysis of the PS and the resins* ***1–4***

DSC curves of the different polymers, stored in a temperature range of 25–500°C with a heating rate of 5°C/min, showed different thermal stability between the different types of polymers (Fig. 10 and Table 3).

3.5. *DTA–TGA analyses of the resin* ***1*** *and* ***2***

The DTA–TGA curve of resin **1** (Fig. 11(a)) recorded in a sample of a mass $m = 16$ mg with a heating rate of 5°C/min in the temperature from 25 up to

Table 2
Elemental analysis of the PS and the resin: **1–4**

Sample name	C (%)	H (%)	N (%)
PS	80.39	7.47	–
Resin **1**	36.72	3.79	7.65
Resin **2**	52.52	6.55	9.27
Resin **3**	31.11	4.68	5.19
Resin **4**	34.98	4.70	5.34

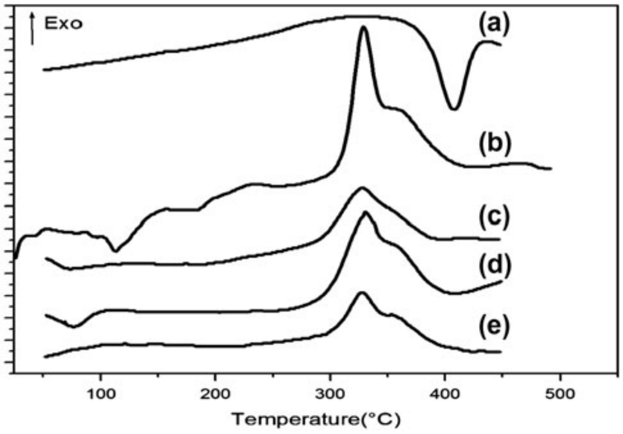

Fig. 10. DSC diagrams of (a): PS, (b): resin **1**, (c): resin **2** (d), resin **3**, and (e): resin **4**.

Table 3
DSC studies of the PS and the resin: **1–4**

Sample name	T_g (°C)	T_{Di} (°C)	T_{Dmax} (°C)	T_{Df} (°C)
PS	106	350	410	450
Resin 1	200	268	327	450
Resin 2	–	204	327	380
Resin 3	–	261	330	430
Resin 4	–	238	328	400

Notes: T_g: Glass transition temperature, it clearly appears in the case of PS (Fig. 6) and resin **1** (Fig. 10(b)). T_{Di}: Decomposition starting temperature. T_{Dmax}: Maximum temperature of decomposition. T_{Df}: End temperature of decomposition.

500°C, showed four peaks: one endothermic and three exothermic observed at 85, 225, 340, and 370°C. The first peak at 85°C was accompanied by a significant mass loss of 18.8%, corresponding to the departure of surface water molecules. Other peaks observed at 225, 340, and 370°C showed that the decomposition of the polymer took place in steps. The DTA–TGA curve of resin **2** (Fig. 11(b)) recorded from a sample of a mass $m = 8$ mg with a heating rate of 5°C/min in the temperature range from 25 to 500°C, appeared at three peaks, a broad endothermic peak centered at 55°C accompanied by a mass loss of 4.12%, corresponding to the departure of surface water molecules. The last two exothermic peaks at 330 and 360°C were accompanied by a significant mass loss of 30.5%, showing that the decomposition of the polymer continued until 600°C.

3.6. FTIR/ATR analysis of the PS and the resins 1–4

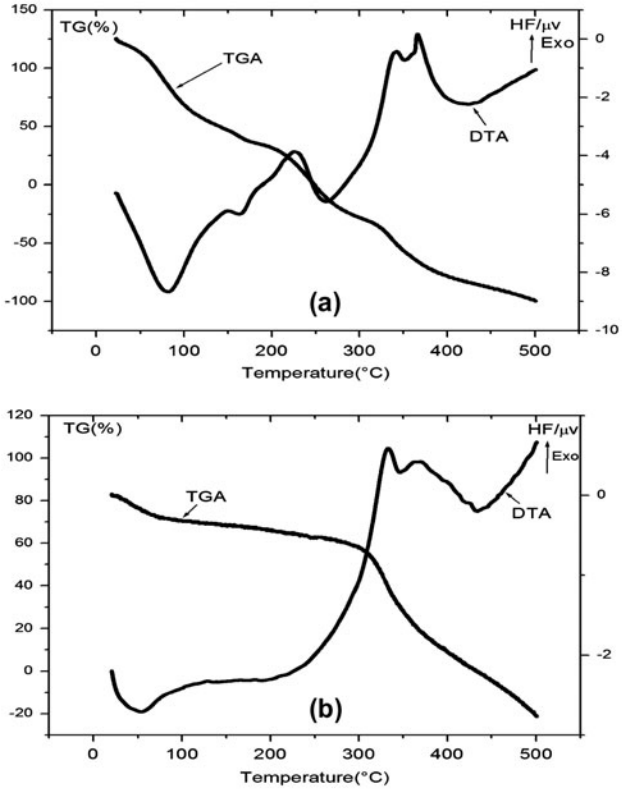

Fig. 11. DTA–TGA curves of (a): resin **1** and (b): resin **2**.

The success of the nitration and amination processes was confirmed by infrared spectroscopy. The IR spectra of polystyrene, resin **1**, and resin **2** were shown in Fig. 12. After nitration, the IR spectrum of the polymer showed peaks at 1,517 and 1,347 cm^{-1}, corresponding to NO asymmetric and symmetric stretches, respectively. A stretching vibration band at around 860 cm^{-1}, corresponding to C–N of Ar–NO_2, was characteristic of para-substituted aromatics. After amination, two broad peaks were recorded at around 3,345 and 3,228 cm^{-1} and a sharp one was recorded at 1,626 cm^{-1}, which are typical of the N–H stretching and bending modes in primary amines. A stretching vibration band at 1,265 cm^{-1} corresponds to C–N of Ar–NH_2. These findings agree with the literature [30]. The IR spectra of the resin **3** (Fig. 13(a)) showed the appearance of a strong band around 1,598 cm^{-1}, characteristic of the –N=N– and a valence wide band centered at 1,049 cm^{-1}, characteristic of the functions of ethers of benzo-15-crown-5. The IR spectra of the resin **4** (Fig. 13(b)) showed the appearance of a strong band at 1,590 cm^{-1}, characteristic of the –N=N– and valence bands between 1,238 and 1,085 cm^{-1}, characterizing ethers functions of dibenzo-18-crown-6. Table 4 summarizes dominant infrared frequencies for modified polystyrene.

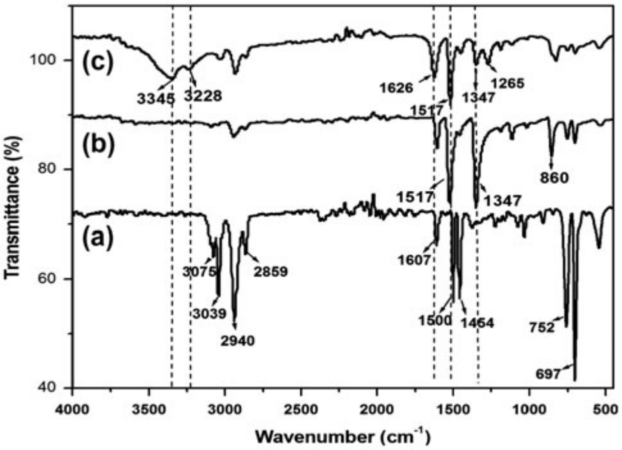

Fig. 12. ATR/FTIR spectra of (a): PS, (a) resin 1, and (b): resin 2.

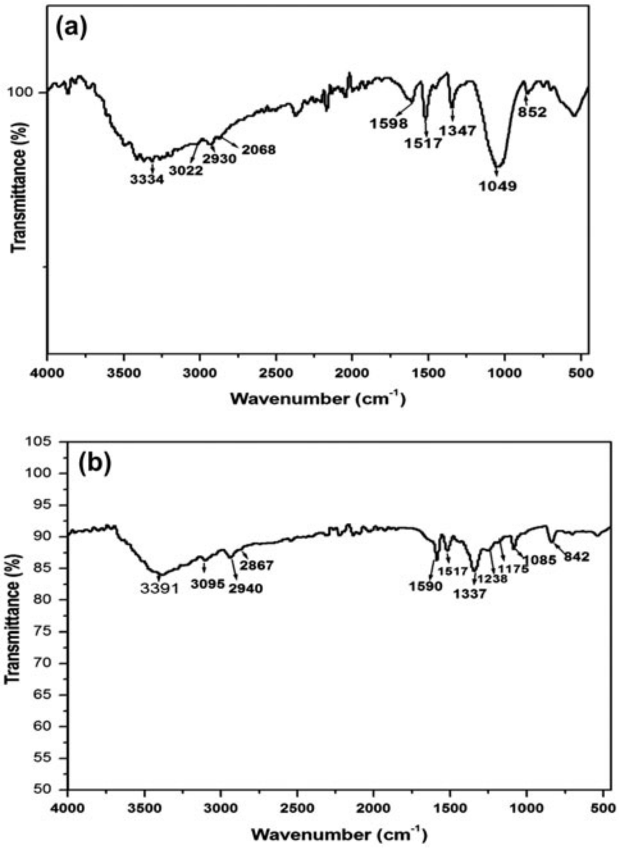

Fig. 13. ATR/FTIR spectra of (a): resin 3 and (b): resin 4.

3.7. XRD analysis of the PS and the resins *1–4*

The XRD patterns recorded for 2θ between 2 and 50° of resin samples **1–4** (Fig. 14) showed changes occurring in the polystyrene during the process of functionalization; but no peak was observed for the different patterns, which suggests that the polymers have probably amorphous structures. The extent of amorphousness can be explained by the absence of an exotherm of crystallization or melting endotherm in diagrams DSC (Fig. 10).

3.8. Metal ion extraction by the modified polymer

The metal extraction of pure crown ethers was less than that of PS mixed with crown ethers and extracted less than those of polystyrene grafted with crown ethers. Furthermore, our results suggest that the azo coupling plays an important role in improving the metal complex. When the extraction of metals was studied by the resin 3, percentages varied from 61 to 97%. The power metallic extraction studied by grafting crown ethers through azo coupling polymers conformed the following order of increasing selectivity: Cr < Ni < Cd < Pb < Fe, for resin 3 (Fig. 15).

When studied by the resin 4, the percentages of extracted metals varied from 88 to 98%. The extraction power accorded with the sequent order of selectivity: Cr < Cd < Pb < Ni < Fe. In addition, it seems that the extracting power of the resin 4 toward the metals Cr, Fe(III), Ni, Cd, and Pb was greater than that of the resin 3 (Fig. 16). The strong improvement in the extraction due to resin 4 percentage is not observed for resin 3. However, the extraction power for both resins 3 and 4 revealed more selectivity for Cd compared to Pb. Similar results were reported in literature [4] when resin of different structures was used and when polymer inclusion membranes were doped with imidazoleazocrown ethers [8].

On the other hand, crown ethers dispersed in a polystyrene film of mixtures (Fig. 17), made crowns less effective during extraction: their cavities being hindered by the polymer chains. While crown ethers grafted onto a polymeric support through an azo coupling provide a good extraction yield which suggests a sandwich complex (Fig. 18) known in the literature for isolated crown ethers [33].

The order of selectivity depends upon the compatibility between the size of metal cation and complexing ligand cavity size, the number, and the type of hetero atom ligands (oxygen atom of crown ether and nitrogen atom of azo group –N=N– or –NH_2 in resin).

Hence, it appears that resin 3 exhibited good efficiency for Fe^{3+} (97%) and Pb^{2+} (88%) while resin 4 exhibited good efficiency for Fe^{3+} (98%), Pb^{2+} (93%), and Ni^{2+} (92%). This high extraction selectivity could be explained by the high affinity of Fe(III) ions to the crown ether group in resin. On the basis of the hard-soft

Table 4
The FTIR data of grafted or ungrafted polystyrene

	Wave number (cm^{-1})				
Characteristic vibration	PS/crown ether	Resin **1**	Resin **2**	Resin **3**	Resin **4**
NO asymmetric and symmetric vibrations	–	1,517–1,347	–	–	–
–NH_2 asymmetric and symmetric vibrations	–	–	3,345–3,228	–	–
N–H bending	–	–	1,626	–	–
C–N stretching	–	860	1,265	–	–
–N=N– vibration	–	–	–	1,598	1,590
C–O–C ether	1,248–1,130	–	–	1,049	1,238–1,085

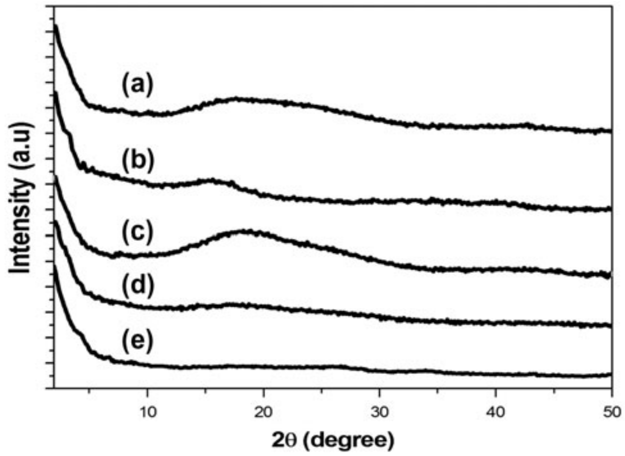

Fig. 14. X-ray diffractograms of (a): PS, (b): resin **1**, (c): resin **2**, (d): resin **3**, and (e): resin **4**.

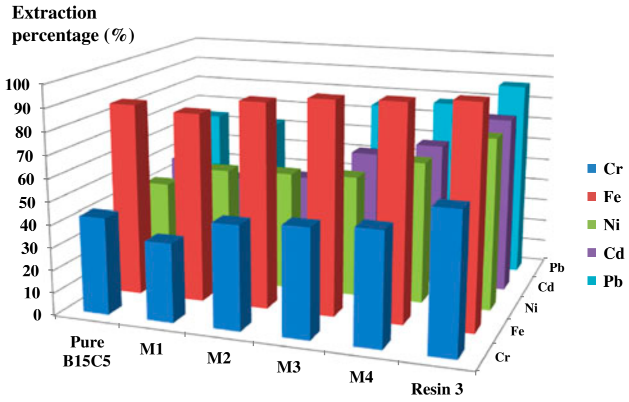

Fig. 15. Percentages of metal cations extraction for the polymers M1, M2, M3, M4, and the resin **3**.

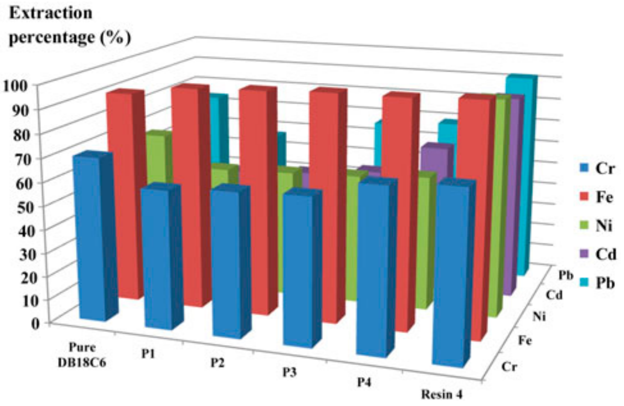

Fig. 16. Percentages of metal cations extraction for the polymers P1, P2, P3, P4, and the resin **4**.

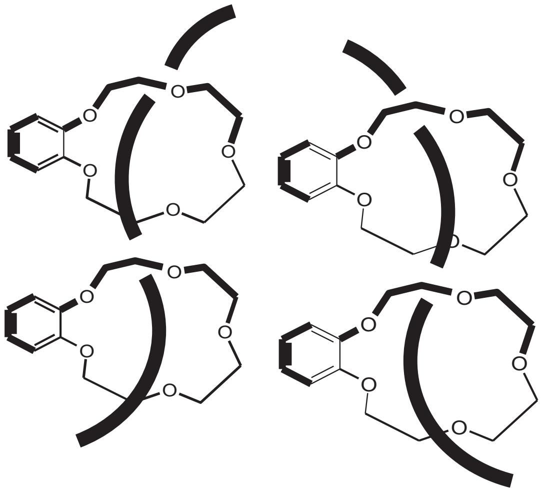

Fig. 17. Chains of PS from cycles through the crowns.

acid-base theory, Fe(III) was classified as a hard ion, and has affinities to hard ligands which contain oxygen atoms of crown ether group, but Pb(II) and Ni(II) were classified as intermediate ions. Therefore, they have affinities to two types of soft ligands which contain nitrogen atoms of –N=N– or –NH_2 groups and hard ones which contain oxygen atoms of crown ether group.

The results also show that Cr(III) is less a extracted metal by the resins **3** and **4**. This may be explained by the high charge density of metal Cr(III) and also it is

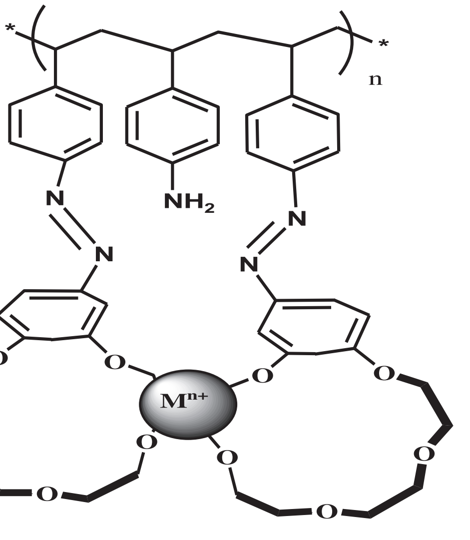

Fig. 18. Formation of a sandwich complex in a polymer chain.

probable that the steric constraint imposed by the overall size of crown ethers prevents them to take the conformation necessary for optimal complexation of this metal.

Crown ethers have appreciable solubility in aqueous media and are difficult to recover. There are several advantages of grafting crown ethers on polymers or their lives as polymeric backbones. The incorporation of crown ethers in a polymer greatly reduces the loss of the latter using a coupling agent for fixing on insoluble polymers covalently. When a supported polymer by a crown ether is used as complexing agent to metal cation, it may be simply filtered and reused repeatedly after simple washing with a solution of diluted hydrochloric acid and then with the distilled water.

4. Conclusions

In this paper, we have suggested a new technique to purify wastewater by solid–liquid extraction process using modified waste polystyrene. After chemical modification, the waste polystyrene led to resins, grafted groups diazabenzo-15-crown-5 and diazadibenzo-18-crown-6, and were used as adsorbents of metals. The polymers M1, M2, M3, M4, P1, P2, P3, P4, and the resins <u>3</u> and <u>4</u> were tested for extraction of five metals (Cr, Ni, Cd, Pb, and Fe(III)). The extraction percentages of metals by the polymers M1, M2, M3, M4, P1, P2, P3, and P4 are smaller than those of resins <u>3</u> and <u>4</u>. Resin <u>3</u> improved the extraction of Fe^{3+} rates ranging from 86% by the pure benzo-15-crown-5 to 97% by the resin. Thus, the Fe^{3+}, Pb^{2+}, Cr^{3+}, Ni^{2+}, and Cd^{2+} cations and extracted with 91, 74,70, 67, and 48% by the pure DB18C6 respectively, and were extracted with 98, 92, 71, 93, and 88%, respectively, by the resin <u>4</u> containing the DB18C6 grafted polystyrene chains on a diazo condensation reaction. The resins obtained in the present work by the grafting of a crown through a diazo function have significantly improved the rate of extraction of metals such as Fe^{3+} or Ni^{2+}.

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