SCIENTIFIC PAPER

INVOLVEMENT OF AMINOALKYLATED MERRIFIELD RESINS RETRACTED BY BIS(CHLORODIETHYL) ETHER IN METAL EXTRACTION.

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ABSTRACT

Merrifield resin, a cross-linked polystyrene resin with chloromethyl functional groups, is an extremely resilient material resistant to water and environmental degradation. Our objective is to develop novel substituted polymers with functional groups capable of chelating heavy metals for depollution applications. Cross-linked polymer networks, which are predominantly insoluble and adaptable to diverse chemical environments, are invaluable for pollution management. A key area of environmental significance is the selective retention of organic contaminants for purifying polluted water sources. This work focuses on creating new chelating polymeric sorbents for metal extraction by grafting ethylenediamine (EDA) and triethylenetetramine (TETA) onto Merrifield resin, resulting in two polymers: MR-EDA and MR-TETA. These modified polymers are further reticulated with bis(chlorodiethyl) ether to produce two novel reticulated polymers, MR-TETA-BCEE and MR-EDA-BCEE.To characterize the polymers, differential thermal analysis (DTA) and infrared (IR) spectroscopy are employed. The resins are subsequently tested for their ability to extract lead (Pb^{2+}) and lithium (Li^{+}) ions from aqueous solutions using the solid-phase extraction (SPE) method. Conductivity and atomic absorption spectrometry (AAS) analyses demonstrate high extraction efficiencies, ranging from 50% to 85% for both Pb^{2+} and Li^{+} ions.

These results demonstrate the potential of MR-EDA-BCEE and MR-TETA-BCEE as effective polymeric sorbents for environmental remediation and heavy metal removal from water.

Keywords: Merrifield resin, ethylenediamine (EDA), chlorodiethyl, metal extraction

Highlights

- Merrifield resin is robust, resisting water and environmental degradation.
- MR-EDA and MR-TETA were synthesized by grafting EDA and TETA onto Merrifield resin.
- Crosslinking with bis(chlorodiethyl) ether produced MR-EDA-BCEE and MR-TETA-BCEE.
- Polymers extracted 50%-85% of Pb^{2+} and Li^{+}, with MR-TETA-BCEE performing best.

- Modified resins show promise for metal ion recovery and environmental depollution.

Introduction

The extraction of metals from water remains a critical area of research, driven by the need to address water pollution caused by toxic metals and their harmful effects on the environment and human health, as well as the necessity to recover and recycle certain metal ions that play vital roles in various applications. For instance, lithium has garnered particular attention due to the increasing demand for energy storage materials, such as lithium batteries, and the gradual depletion of natural reserves of this element. Among the various separation techniques, solid-phase extraction (SPE) has emerged in recent years as a preferred method, owing to its technical and economic feasibility. The chemical modification of polymeric resins through the incorporation of functional groups and polar compounds enhances the efficiency of extraction by increasing the surface interaction between the sorbent and aqueous samples. Organic resins based on styrene–divinylbenzene copolymers are especially valued for their mechanical stability, resistance to hydrolysis, pH variations, and relatively high-temperature conditions.In this context, several studies have focused on functionalizing Merrifield resins (chloromethylated polystyrene). For example, Slimi et al. grafted piperazine-based chelating units onto the resin for extracting metals such as Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}. Similarly, Lukashova et al. substituted tetrahydroxy-thiacalixarenes and tetraphosphonates on Merrifield resin to selectively remove europium (Eu^{3+}) from aqueous solutions. Adeleye et al. functionalized Merrifield resin with 2,2-pyridylimidazole, enabling selective separation of nickel from other base metals in synthetic sulfate solutions. Furthermore, the immobilization of bioactive compounds, such as quercetin, on these resins has led to the development of adsorbents capable of recovering Pb^{2+} ions. Other modifications, such as the introduction of polyamines and phosphorus derivatives, have shown effectiveness in extracting metals like Cd, Cu, and Fe. Recent studies have also highlighted the efficiency of a polychloromethylstyrene-based resin modified with heterofluorenone pendant groups and polymers like poly(6-acryloylamino-N-hydroxyhexanamide), which exhibited remarkable adsorption capacities for Cu^{2+} and Pb^{2+}ions under optimal pH conditions. In this study, two polyamine-supported polymers were prepared from Merrifield resin, modified respectively with ethylenediamine (EDA) and triethylenetetramine (TETA), and subsequently crosslinked using bis(chlorodiethyl)ether. The complexing properties of these novel sorbents were then studied for the extraction of a heavy metal (lead) and an alkali metal (lithium).

EXPERIMENTAL

Materials

Merrifield resin (MR reticulated by 2% divinylbenzene, 200–400 mesh, 2.1 mmol Cl. g^{-1}, Fluka), ethylenediamine (EDA), triethylenetetramine (TETA), Bis-(chlorodiethyl) ether (BCEE) and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Absolute ethanol, triethylamine (TEA), and diethyl ether were purchased from Prolabo. Lithium bromide (LiBr), and Lead (II) nitrate $Pb(NO_3)_2$ were purchased from Fluka.

Synthesis of Merrifield Resin with Ethylenediamine Group (MR-EDA)

MR-EDA was synthesized following the procedure reported in the literature [14]. Commercially available Merrifield resin (2 g) was suspended in 30 cm^3 of dimethylformamide (DMF) and allowed to swell for 10 hours. Ethylenediamine (EDA, 8.4 mmol) was then added to the suspension. An excess of EDA was used to act as a base and accelerate the reaction. The reaction mixture was stirred at room temperature for 1.5 hours, followed by heating at 70–80°C for 24 hours. Upon completion of the reaction, the resin was thoroughly washed multiple times with deionized water, followed by absolute ethanol, to remove unreacted reagents. The final product (MR-EDA) was dried under vacuum at 50°C for 48 hours. The resulting material is depicted in **Figure 1.**

Synthesis of Merrifield Resin with Triethylenetetramine Group (MR-TETA)

The reaction involved 2g of MR, 30 cm^3 of DMF, and excess of TETA (8.4 mmol). The reaction conditions of the product were similar to that of MR-EDA **Figure 1**.

Synthesis of MR-EDA Reticulated by Bis-(chlorodiethyl) ether (MR-EDA-BCEE)

MR-EDA-BCEE was synthesized according to the method described in the literature [15]. The starting material, Merrifield resin functionalized with ethylenediamine (MR-EDA, 2 g), was dissolved in 30 cm^3 of dimethylformamide (DMF), a polar aprotic solvent that facilitates efficient dissolution and ensures the homogeneous mixing of reactants. Bis(chlorodiethyl) ether (BCEE, 6 cm^3) was then added to the solution. BCEE was used as a crosslinking agent to introduce additional functional groups, enhancing the resin's chemical properties for its intended application. The reaction mixture was stirred to ensure uniform distribution of BCEE throughout the solution and heated to 125°C for 24 hours. The elevated temperature was necessary to activate the reaction and promote covalent bonding between MR-EDA and BCEE, ensuring effective crosslinking.Upon completion of the reaction, the resulting product was isolated by filtration to separate the modified polymer from the reaction mixture. The resin was thoroughly washed with distilled water to remove any residual reactants or by-products, ensuring the purity of the final Product. The modified polymer was initially dried at room temperature for 24 hours to remove surface moisture. It was subsequently washed with diethyl ether to remove non-polar impurities and rinsed again with distilled water to ensure all solvents and residual chemicals were eliminated. Finally, the obtained resin (**depicted in Figure 1)** was dried under controlled conditions. It was first oven-dried at 60°C for 12 hours to remove residual solvents and stabilize the polymer. To achieve complete drying, the resin was subjected to vacuum drying at 70°C for 48 hours, which removed any remaining moisture or volatile components, resulting in a stable and ready-to-use product.

Synthesis of MR-TETA Reticulated by Bis-(chloroethyl) ether (MR-TETA-BCEE)

The reaction medium contained MR-TETA, DMF, BCEE, and TEA. The reaction conditions of the product were similar to that of MR-EDA-BCEE **Figure 1**.

Insert Figure 1

Extraction Procedure of Metal Cations

The work consists in using the modified resins by amino and Bis-(chlorodiethyl) ether groups for the removal of metal ions (Pb^{2+} and Li^{+}) using solid phase extraction method (SPE).

Metal Ion Extraction Method

The kinetics of metal extraction in this experiment involves the interaction between the metal ions (Pb^{2+} and Li^{+}) and the polymer, where the rate of chelation depends on factors like polymer and metal ion concentration, temperature, pH, and the incubation time. During the incubation, the polymer binds to the metal ions, reducing their concentration in the solution. This chelation process is typically time-dependent, and a time study could be performed to model the kinetics, often following first- or second-order reaction models depending on the reaction dynamics. After the incubation, the filtrate is analyzed for the remaining metal ions using Flame Atomic Absorption Spectrometry (FAAS), which detects the metal concentration by measuring the absorption of light at characteristic wavelengths. In this method, the sample is aspirated into a flame where the metal ions are atomized, and their absorption of light is proportional to their concentration. A calibration curve is created using known concentrations of the metal, allowing for the determination of the metal concentration in the filtrate. FAAS detection is sensitive, with detection limits typically in the range of 10^{-8} to 10^{-9} mol/L, and potential interferences such as spectral, ionization, and chemical effects must be considered to ensure accurate measurements. The results were expressed as percentages of extraction of the metal (Table 1, Figure 2). The percentage was calculated using the following expression:

$$\%E=(\sigma i-\sigma f)\div\sigma i$$

Where: σi – the initial conductivity of the metal in aqueous solution, σf – the final conductivity of the metal.

Methods of testing

The infrared analysis using the (ATR FT-IR) technique was carried out on a Thermo Scientific Nicolet FTIR 200 spectrophotometer with a scanning range between 4000 and 400 cm^{-1}. Differential thermal analysis (DTA) was performed on a SETARAM TGA 92 device. The pH was measured with a pH and conductivity meter, VWR / CO 3000L.

RESULTS AND DISCUSSION

IR spectroscopy

The structures of the resulting chelating resins, MR-EDA and MR-TETA, were confirmed using ATR-FTIR spectroscopy, as shown in **Figure 2**. The ATR-FTIR spectra provided evidence for the successful functionalization of the Merrifield resin. A key observation was the disappearance of the characteristic CH_2–Cl bond, which appears at 1266 cm^{-1} in the spectrum of the Merrifield resin [7]. This disappearance indicates the loss of the chloromethyl functional group during the substitution reaction. In addition, new peaks were observed at 1644 cm^{-1}, corresponding to the deformation vibration of NH groups, confirming the incorporation of ethylenediamine (EDA) or triethylenetetramine (TETA) into the resin structure. Amines exhibit characteristic bands in infrared spectroscopy, enabling their identification. The N-H stretching vibrations typically appear in the region **3300–3500 cm^{-1}**. Primary amines ($-NH_2$) show two bands in this region, corresponding to symmetric and asymmetric stretching, while secondary amines (−NH) display only one. These bands are usually broad and of moderate intensity. Another characteristic band, associated with N-H bending vibrations, is found in the region **1500–1650 cm⁻¹**. Lastly, the C-N stretching vibration appears between **1200 and 1350 cm⁻¹**. These features help distinguish between primary, secondary, and tertiary amines in a mixture or compound.This observation is consistent with findings by Kadous et al. [12], who reported a similar peak at 1602 cm⁻¹ in polystyrene resin grafted with ethylenediamine. These spectroscopic changes collectively support the substitution of the chloro group by polyamine groups. For the resins MR-EDA-BCEE and MR-TETA-BCEE, the ATR-FTIR spectra (Figure 2) displayed all the characteristic bands observed for MR-EDA and MR-TETA. Additionally, a new valence band was detected at 1100 cm⁻¹, corresponding to the C–O–C stretching vibration. This band indicates the successful grafting of the bis(chlorodiethyl) ether group onto the amino-functionalized Merrifield resins. Similar findings were reported by Mbarki et al. [12], who observed a C–O–C band in the range of 1050–1170 cm⁻¹ for amino-PVC modified with bis(chlorodiethyl) ether.

Insert Figure 2

DTA Analyses

The DTA curves of MR-EDA, MR-TETA, MR-EDA-BCEE, and MR-TETA-BCEE **Figures 2** showed that all resins present tow peaks, an exothermic peak between 300 and 360°C that could indicate their decomposition and an endothermic peak between 65 and 115°C that can be explained with the evaporation of residual water. Dardouri et al. [10] observed the same decomposition peaks at 305, 330, and 509 °C.

Metal Ion Extractions by the Synthesized Polymers

The extraction was performed also using the atomic absorption spectrometry technique. Table 1 shows the heavy metal extraction determined by conductivity measurements and by AAS. The difference between the extraction percentages deter- mined by these two methods (The absorption method and the conductivity method) is between 8 % and 12 %.

Insert Table1

Effect of Initial pH on modified Merrifield resins

The pH of the aqueous phase plays a crucial role in the extraction of Pb^{2+} and Li^{+} ions by an extracting agent. It influences both the chemical behavior of the functional groups in the functionalized resin and the nature of the species present in solution. Studying the retention efficiency of lead and lithium ions as a function of pH helps determine the optimal conditions for the extraction process. The effect of pH on the extraction of these ions was examined within the pH range [1.0 - 6.0], using an aqueous solution containing 2×10^{-4} M of Pb^{2+} and Li^{+}. A volume of 30 mL of this solution was treated with 0.1 g of resin, while the agitation speed was kept constant at 250 revolutions per minute (rpm) using a vibrating platform.The results show that the extraction efficiency of Pb^{2+} and Li^{+} ions increases with pH, reaching a maximum of 80% at pH 6.1(**Table 2**). At low pH, the high concentration of H^{+} ions in solution leads to competition between protons and Pb^{2+}/Li^{+} ions for extraction. Additionally, in an acidic medium, the lone electron pairs of the nitrogen and oxygen atoms in the Merrifield resin are blocked by H^{+} ions, reducing their availability for complexation with metals. Furthermore, in an environment rich in H^{+}, these ions strongly adsorb onto the resin, giving it a positive charge that creates electrostatic repulsion, thereby limiting the approach of Pb^{2+} and Li^{+} ions.

Insert Figure 3.

The extraction percentages of metal ions Pb^{2+} and Li^{+} with the chelating resins M_1, M_2, M_3 and M_4 are shown in **Table 1 and Figure 3.** The values are between 50% and 85% which indicate that all resins are high metal nature for both Pb^{2+} and Li^{+}. **Figure 3** showed that the order of adsorption capacity of the chelating resins against $Pb^{2+}$and Li^{+} ions is as follows: MR-TETA > MR-EDA, which is similar to other investigation [9,11]. This result was explained by the higher content of nitrogen groups (% N) in modified resins which improves more coordination with metallic ions. The extraction percentages of Pb^{2+} with the synthesized polymers MR-EDA, MR-TETA, MR-EDA-BCEE and MR-TETA-BCEE varied between 65.6 and 85.5 % and between 50 and 87 % for the ion Li^{+}. All the synthesized polymers showed more selectivity for the Pb^{2+} which has a higher size than Li^{+}, these results can be explained by the compatibility factor between the size of Pb^{2+} ion and the size of the complexing cavity in the polymers, which could be influenced by the cross-linking degree, the length of amine chain and the cross-linking by the Bis-(chlorodiethyl) ether is directly proportional. However, the active sites are less readily available and efficiency of the resin is reduced. The orders of adsorption capacity for Pb^{2+} were respectively: MR-TETA-BCEE > MR-EDA-BCEE > MR-TETA > MR-EDA. Besides, the orders of adsorption capacity for Li^+ are as follows: MR-TETA-BCEE > MR-TETA> MR-EDA-BCEE> MR-EDA. When looking at all the results, as an average of all polymers, we can observe that the synthesized polymer that is the best extractant and the more selective for both Pb^{2+} and L^+ is MR-TETA-BCEE, respectively with 85.5% and 78%. This high adsorption selectivity could be explained by the high affinity of Pb^{2+} and Li^+ ions to the polyamine and oxygen groups in studied resins which are able to fix the metal through non covalent bonds (van der Waals bonds) as shown on **Figure 5**. This extraction effiency also could be partially explained by the electro-negativities of the substituted nitrogen of the polyamine and oxygen groups. In the case of Li^+, the polymer M_4 (78 %) is the better extractant; Li^+ is less voluminous than Pb^{2+}. Based on the hard-soft acid-base theory, Li^+ has affinities to hard ligands which contain oxygen atoms like in M_4 more than Pb^{2+} **[18-19].**

Insert Figure 4.

Kinetic study

Figures 3 show variation curves of average electrical conductivity with time for metal cations $Pb^{2+}$and Li^+ in contact with the modified polymers (M_1, M_2, M_3 and M_4). The kinetic study showed that the optimum extraction time obtained is of approximately 35 h for Pb^{2+} extraction and 22 h for Li^+ extraction. The extraction results are the average of three experiments. These results show that all modified resins M_1, M_2, M_3 and M_4, give better results (shorter extraction durations) with Li^+ cation. However, the development of new chelating ion exchange materials with special chelating properties can provide better kinetics of interaction between metal ion and chelating groups [6]. The demonstration that metal coordination occurs through amines and not simply via "entanglement" in the Merrifield resin is based on several observations from the figure. Graph (a) shows that resins functionalized with amines (MR-EDA, MR-TETA, and their derivatives) exhibit higher adsorption rates for Pb^{2+} and Li^+, suggesting a specific chemical interaction involving amine groups. Graphs (b) and (c) illustrate a progressive decrease in solution conductivity over time, indicating the extraction of metal ions. The difference in kinetics among the resins (M_1, M_2, M_3, M_4) and their superior performance for Pb^{2+}, which has a higher affinity for amines due to its electronic properties, supports the hypothesis of metal-amine coordination. This selective behavior and the dependence on the type of amine confirm that the interaction is chemical and specific, rather than a mere physical entanglement.

Influence of extracted metals on the IR spectra of new resins

The IR absorption spectra of the studied complexes **Figure 4** indicate that the influence of free polymers and their complexes on IR spectra is not very significant. Ammari et al [17] find the same observation with functionalized PVC; he has explained these results by the effect of the counter-anions of used salts.

Insert Figure 5.

CONCLUSION

In this study, we demonstrated the efficiency of modified Merrifield resin-based polymers for extracting Pb^{2+} and Li^{+} ions from aqueous solutions. The integration of polyamine groups, followed by crosslinking with bis(chlorodiethyl) ether, enhanced the adsorption capacity of the polymers, with a particularly high performance for lead extraction. Among the synthesized materials, MR-TETA-BCEE proved to be the most effective, highlighting the influence of functional group type and structure on selectivity and extraction efficiency. These findings suggest that the developed polymers could be promising candidates for water decontamination and the selective recovery of industrially valuable metals. Further investigations, particularly on the reusability of the resins and their efficiency under real-world conditions, will be necessary to fully assess their potential for industrial and environmental applications.

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Conflicts of Interest: The author declares no conflict of interest.

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Figure capture

Figure 1 a) Aspect of M_0 and M_1, b) M_0 and M_2, c) M_0 and M_3, d) M_0 and M_4

Figure 2 a) ATR-FTIR of M_0, M_1, M_2, b) ATR-FTIR of M_0, M_3, M_4, c) DTA curves of M_0, M_1 M_2, d) DTA curves of M_0, M_3, M_4.

Figure 3 a) Percentages of metal ions extraction for the polymers M_1, M_2, M_3 and M_4, b) Curves of the optimal duration of Pb^{2+} extractions, c) Curves of the optimal duration of Li^+ extractions.

Figure 4 IR spectra of (a) polymer M_1 and complex M_1-Pb^{2+}, M_1-Li^+; (b) polymer M_2 and complex M_2-Pb^{2+}, M_2-Li^+; and (c) polymer M_4 and complex M_4-Pb^{2+}, M_4-Li^+.

Figure 5 a) Proposed of polyamine resin's structure, b) Proposed Complex structures of M_1, M_2, M_3 and M_4 with M^{n+}: Li^+ or Pb^{2+}

Table capture

Table 1 Extraction percentage results of metal ions ($Pb^{2+,}$ Li^{+}) by the synthesized polymers.

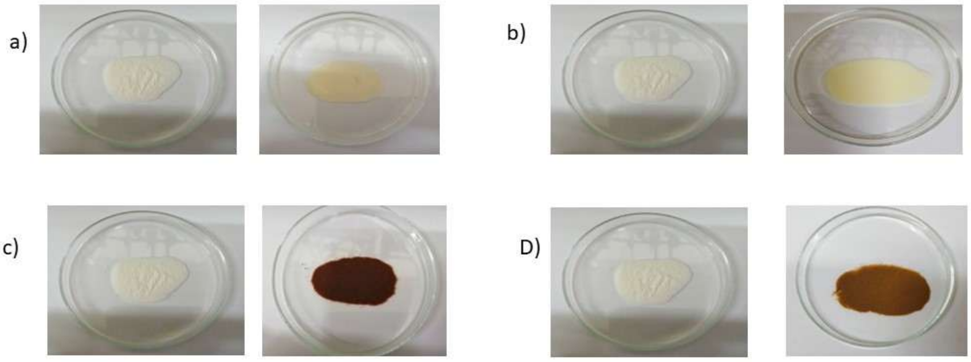


Figure 1

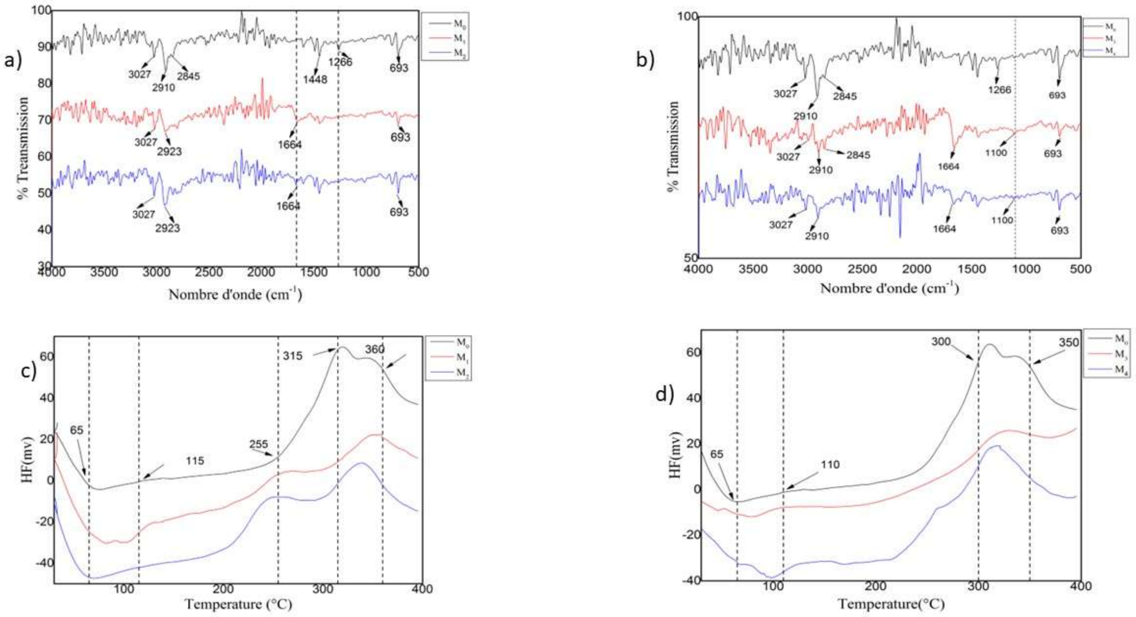


Figure 2

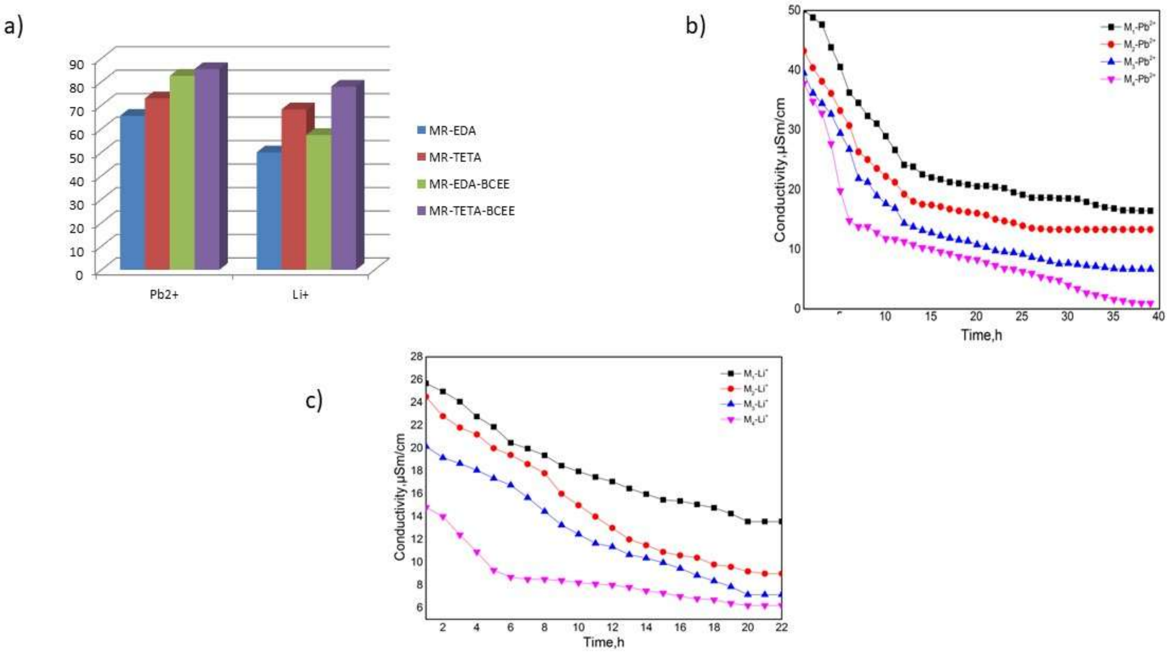


Figure 3

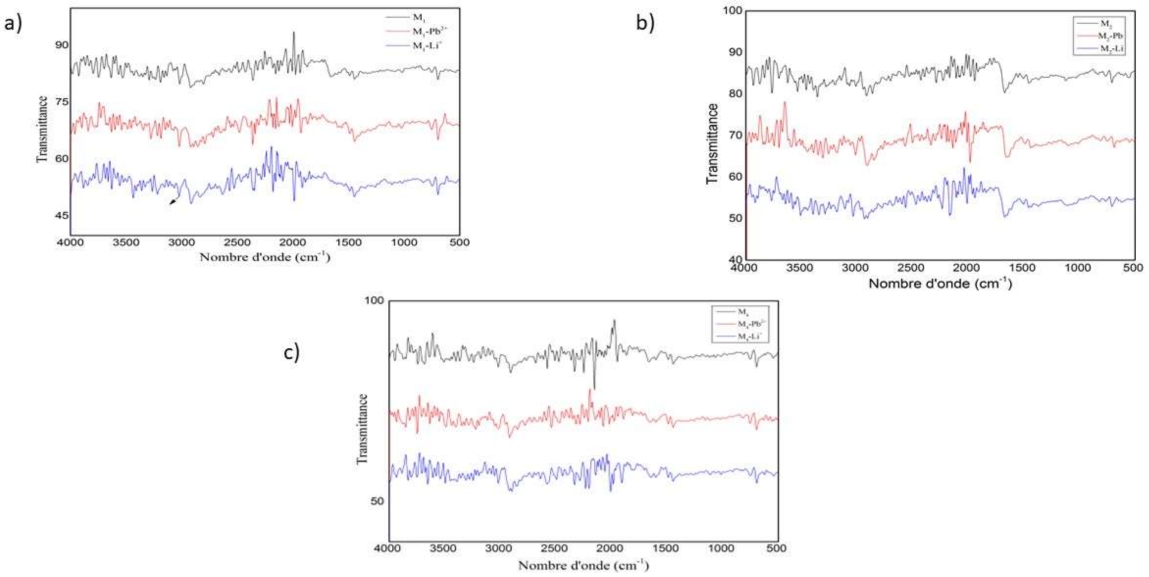
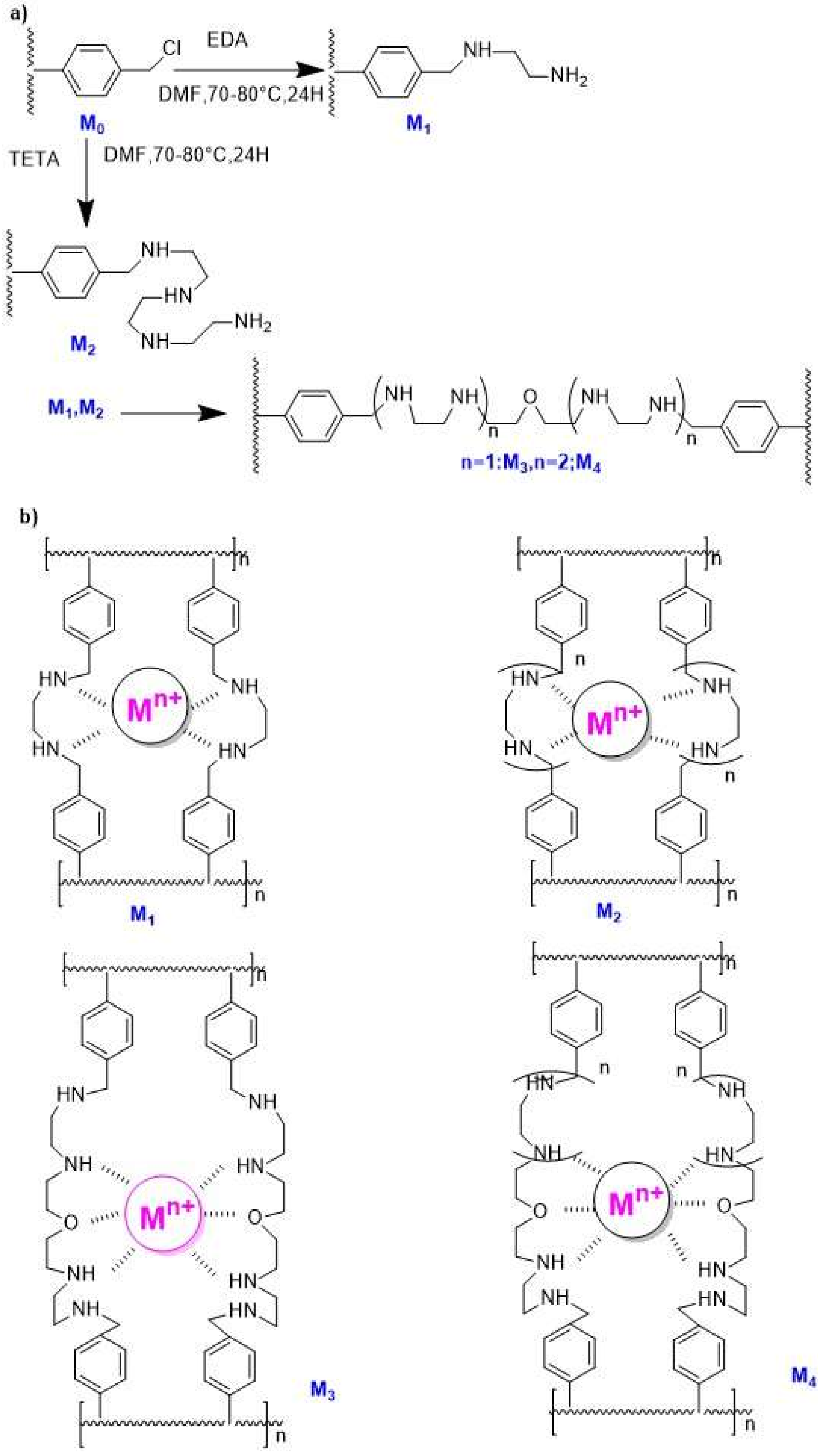


Figure 4


a)
Cl
EDA
DMF,70-80°C,24H
NH
NH2
M0
M1
TETA
DMF,70-80°C,24H
NH
HN
NH
NH2
M2
M1,M2
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NH
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n
n
n=1:M3,n=2;M4
b)
Mn+
HN
NH
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M1
M2
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Figure 5

Table 1

Metal Cation	%WithM1		%WithM2		%WithM3		%WithM4	
	Conductivity	AAS	Conductivity	AAS	Conductivity	AAS	Conductivity	AAS
Pb^{2+}	65.6	57.6	73	61	82.6	72.6	85.5	75
Li^+	50	42	68.3	55.7	57.4	47	78	68

Table 2

Metal Cation	%WithM1 To PH=2.0	%With M2 To PH=3.0	%With M3 To PH=5.1	%With M4 To PH=6.1
Pb^{2+}	62	70	80	83
Li^+	45	63	55	75