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# A poly (vinyl chloride) functionalized by diethylenetriamine, 2,6-bis-(chloromethyl) pyridine and a crowded aromatic amine. Inductively coupled plasma study of the extraction of La(III) and Bi(III) by modified PVC polymers

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ABSTRACT

The aim of this study was to evaluate the efficiency of three new polymers obtained by functionalization of a commercial poly (vinyl chloride) (Mw = 48,000) by grafting diethylenetriamine, 2,6-bis-(chloromethyl) pyridine and 1-chloro-2-phenylaminomethyl-6-phenyl aminomethylene-cyclohex-1-ene groups to extract some metal cations from aqueous solutions. The structural properties of the polymers were systematically investigated by different analytical methods; namely elemental analysis, differential scanning calorimetry and infrared spectroscopy (FT-IR). The percentage of extraction was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). One of the obtained polymers gave an extraction ratio of $La^{3+} = 99.57\%$ which highlights the importance of the substitution of chlorine atoms by amino groups.

*Keywords:* Poly (vinyl chloride); Functionalization; Metal cations; Extraction; Inductively coupled plasma-atomic emission spectrometry

## 1. Introduction

Pollution of aquatic environment by heavy metals from industrial and consumer wastes is considered as a major threat to the aquatic organisms including fishes and thus to the human health.

Heavy metals are of serious concern due to their persistence in the environment and carcinogenicity to human beings. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another. Thus, it would be interesting to develop new materials in order to remove heavy metals from natural waters.

From PVC and to extract metal cations, several products based on polymers have been synthesized. Shortly after the work of Frye–Horst on the PVC and their theory “of mechanism of reversible blocking” [1], several researches were dedicated to illustrate the presence of the unstable atoms of chlorine by undertaking chemical modifications on the commercial PVC (i.e. plasticized PVC) as well as samples prepared in laboratories.

PVC has been subjected to many modifications, mainly chemical modifications which are the most

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widely used. Several chemical reactions were applied such as the substitution, the elimination, the reduction and the degradation. Bicak et al. [2] synthesized poly (vinyl chloride) amine in two steps. The first step consists of the nitration of PVC, while in the second one the reduction of the nitro group ($NO_2$) was done. Azoturation of the PVC was produced by Lakshmi et al. [3] using sodium azide ($NaN_3$) in the presence of tetrabuthylammonium bromide (TBAB) as phase transfer catalyst. Abdelaal and Sobahi [4] modified PVC in a charged polymer triazole and imidazole. The functionalized polymer was used in the absorption of heavy metals due to its ability to interact with metal ions. Using a two-step process, Kurt and Mercimek [5] have made the following chemical modification of PVC. Initially, they used the amine derivative (N,N´-bis(3-aminopropyl)-ethylene diamine) in THF as solvent. This mixture was heated at reflux for 48 h, and then they used benzoyl isothiocyanate in acetone under stirring for 6 h. The functionalized compound obtained by this reaction was used as the ligand in a large heavy metal analysis. Shaglaeva et al. [6] studied the nucleophilic substitution on the PVC by Pyrazole (Pz) and dimethylpyrazole (dmPz). The modification reaction was studied in DMF, dimethylsulfoxide (DMSO) and cyclohexanone as solvents and at temperatures ranging from 0 to 45˚C. The yields are in the order of 14–24%. Kruglova et al. [7] were able to add azole units (triazole and tetrazole) on the PVC matrix.

This type of modification plays a key role in the manufacture of new organic materials for specific applications (purification, depollution) [8–11], generally in the removal of toxic organic compounds [12,13]. Several extraction tests of metal cations have been made. In fact, Bagheri et al. [14] studied efficient removal of $Cr^{3+}$, $Pb^{2+}$ and $Hg^{2+}$ ions from industrial effluents by hydrolysed/thioamidated polyacrylonitrile fibres.

In some investigations, the cellulose triacetate membranes were doped with imidazole azocrown derivatives, fixed as carriers and used to facilitate the transport of Zn(II), Cd(II) and Pb(II) ions from aqueous nitrate source phase [15].

In another study, Behnamfard and Salarirad studied characterization of coconut shell-based activated carbon and its application in the removal of Zn(II) from its aqueous solution by adsorption [16].

From PVC and to extract metal cations, several products based on polymers have been synthesized. Moulay [17] presented many chemical modifications of PVC based on reports over the last decade along with related applications. These modifications were presented according to the $C_{PVC}$-X bond formed between the PVC carbon $C_{PVC}$ and atom X (X = N, O, S, Hal) of the modifying molecule.

In this work, new products were synthesized by grafting diethylenetriamine, 2,6-bis(chloromethyl) pyridine and 1-chloro-2-phenylaminomethyl-6-phenyl aminomethylene-cyclohex-1-ene groups on PVC for use in the extraction of two metal cations such as bismuth and lanthanum which are widespread in the environment and known to be dangerous to human health.

## 2. Experimental

### 2.1. Chemicals and instrumentation

#### 2.1.1. Chemicals

The commercial poly (vinyl chloride) Mw = 48,000 (packed in Switzerland) was purchased from Fluka. Diethylenetriamine (DETA) and 2,6-bis-(chloromethyl) pyridine were purchased from Aldrich-Chemistry D-7924 Steinheim, West Germany. 1-chloro-2-phenylaminomethyl-6-phenylaminomethylene-cyclohex-1-ene was a gift from C. Girard laboratory ENSCP, France. Diethyl ether, triethylamin (TEA) and Tetrahydrofuran (THF) were purchased from Prolabo (Groups Rône Poulenc). Chemicals including $Bi(NO_3)_3{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}H_2O$ were obtained from Germany (Aqueous monometallic solutions of $Bi(NO_3)_3{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}H_2O$ were prepared at a concentration of $2 \times 10^{-4}$ mol $L^{-1}$ in relation with each metal ion in distilled water (pH 6)).

#### 2.1.2. Instrumentation

IR analyses were accomplished with a Thermo Scientific Nicolet FTIR 200 spectrophotometer, using the ATR/FTIR technique (Verona road Madison WI 53711-4495 USA). Setaram DSC 131 (7 L'oratory street 69300 Caluire, France) was used for differential scanning calorimetry (DSC) analyses. Elemental analysis (EA) of N was performed by using a Perkin–Elmer Analyser CHN Series II 2400. ICP-AES: HORIBA JOBIN (HORIBA Jobin Yvon S.A.S., 16-18 Canal Street, 91165 Longjumeau Cedex).

### 2.2. Synthesis

#### 2.2.1. Preparation of amino-PVC ($P_1$)

In a hydrogenating bomb, 4.8 g of commercial PVC, 8 g of diethylenetriamine and 1 g of potassium iodide were mixed in 70 ml of THF. After stirring for 3 h at 160˚C, we obtained a paste which was washed several times with distilled water to obtain a yellow

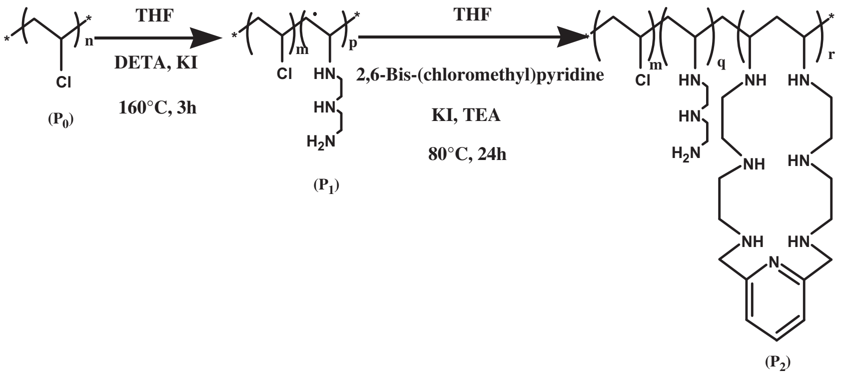

Fig. 1. Synthetic scheme of amino-PVC ($P_1$) and amino-methylpyridine-PVC ($P_2$).

powder that was crushed and then washed several times with distilled water, with diethyl ether and finally dried in an oven at 65˚C to obtain a mass $m = 3.7$ g ($P_1$). The obtained yellow solid was then crushed and washed several times with distilled water until the wash water no longer drains any salt (verification of the electrical conductivity of the wash water).

### 2.2.2. Preparation of amino-methylpyridine-PVC ($P_2$)

In a hydrogenating bomb, 2 g of amino-PVC ($P_1$), 1 g of 2,6-bis(chloromethyl) pyridine, 4 ml of triethylamin and 2 g of potassium iodide were mixed in 70 ml of THF. After stirring for 24 h at 80˚C a paste was obtained. Washed several times with distilled water, it turns into powder which was crushed and washed several times with distilled water, with diethyl ether and finally dried in an oven at 65˚C to get a yellow-brown powder ($P_2$) of mass $m = 2.41$ g.

### 2.2.3. Preparation of the polymer ($P_3$)

In a hydrogenating bomb, 0.5 g of amino-PVC ($P_1$), 0.5 g of 1-chloro-2-phenylaminomethyl-6-phenylaminomethylene-cyclohex-1-ene, 1 ml of triethylamin and 0.5 g of potassium iodide were mixed in 70 ml of THF. After stirring for 24 h at 80˚C a paste was obtained. Washed several times with distilled water, it turns into powder which was crushed and washed several times with distilled water, with diethyl ether and finally dried in an oven at 65˚C to get a brown powder ($P_3$) of mass $m = 0.6$ g.

### 2.2.4. Proposed structures of amino-PVC ($P_1$) and of amino-methylpyridine-PVC ($P_2$)

Based on the analytical results obtained by different physicochemical analyses, (EA, infrared spectroscopy (FT-IR) and DSC) we propose the following structures for the materials ($P_1$) and ($P_2$) in Fig. 1.

The proposed structure for the material ($P_3$) is shown in (Fig. 2).

### 2.2.5. Technique of extraction by ICP-AES

In a 30-ml vial, 20 ml of aqueous solution of metal salt ($2 \times 10^{-4}$ M) has been mixed with 100 mg of each polymer ($P_0$, $P_1$, $P_2$ or $P_3$) at 25˚C for 24 h. At the extraction equilibrium and after filtration, each sample was diluted with distilled water and assayed to determine the final concentration of metal remaining at the extraction equilibrium.

The extraction percentage of the metal is given by the following relationship:

$$\%E = (C_0 - C_f)/C_0 \times 100$$

where $C_0$ is the initial concentration of the metal in the aqueous solution and $C_f$ is the final concentration of the metal in the aqueous solution at the extraction equilibrium.

In this work, ICP-AES was performed in order to assay the metals using a HORIBA JOBIN spectrometer. The used wavelengths were 223.061 and

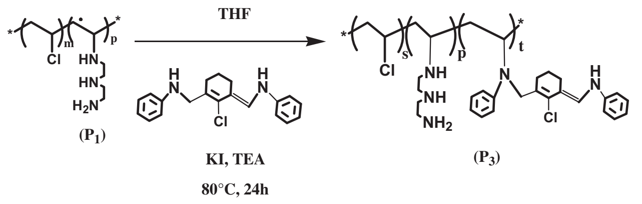

Fig. 2. Synthetic scheme of the material ($P_3$): use of the crowded amine; 1-chloro-2-phenylaminomethyl-6-phenylaminomethylene-cyclohex-1-ene.

331.749 nm for Bi and La, respectively (Power 1,050 W, flow nebulization 0.75 l/min, nebulization pressure 2.74 bar).

## 3. Results and discussion

### 3.1. IR spectroscopy

Fig. 3 shows the IR spectra of the powder form of the studied polymers ($P_0$), ($P_1$) and ($P_2$). On the commercial PVC ($P_0$) spectrum, we notice a high intensity band assigned to the stretching vibration $\nu_{\text{C–Cl}}$ at 689 and 609 $\text{cm}^{-1}$. The spectrum of ($P_1$) shows two broad peaks around 3,374 $\text{cm}^{-1}$ attributed to the stretching vibration of NH primary and secondary amines, a bending vibration of NH at 1,627 $\text{cm}^{-1}$ and a stretching vibration of CN at 1,302 $\text{cm}^{-1}$. In the case of ($P_1$), we observe that the band $\nu_{\text{C–Cl}}$ at 689 $\text{cm}^{-1}$ becomes very low compared to that corresponding to the polymer ($P_0$) as a result of the high-temperature reaction which induces the increase in the number of chlorine atoms substituted by diethylene triamino groups. The IR spectrum of the polymer ($P_2$) shows some bands of stretching vibration $\nu_{\text{C=N}}$ at 1,639 $\text{cm}^{-1}$, $\nu_{\text{C=C(arom)}}$ at 1,609 and 1,455 $\text{cm}^{-1}$ and bending vibration bands $\delta_{\text{Ctrigonal–H(arom-sub)}}$ at 781 $\text{cm}^{-1}$. In the case of ($P_3$) we notice the appearance of the peaks $\nu_{\text{C=C(arom)}}$ at 1,605 $\text{cm}^{-1}$, $\nu_{\text{C–Cl}}$ at 699 $\text{cm}^{-1}$ and bending vibration bands $\delta_{\text{Ctrigonal–H(arom-sub)}}$ at 766 $\text{cm}^{-1}$ (Fig. 4).

### 3.2. DSC analysis

DSC was performed on 9-mg samples and the results were recorded between 50 and 380°C at a speed of 5°C $\text{min}^{-1}$.

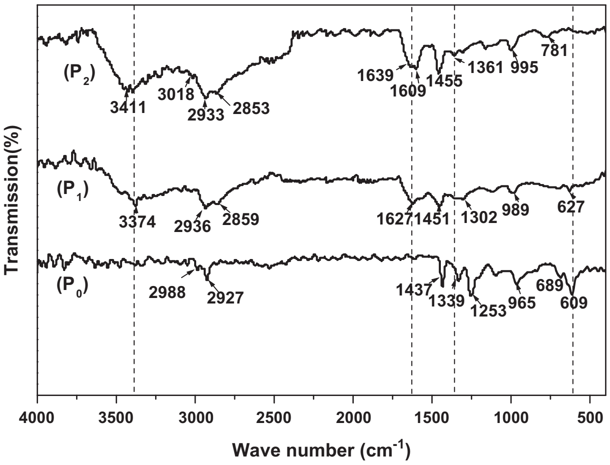

Fig. 3. IR spectra of PVC ($P_0$); amino-PVC ($P_1$) and amino-methylpyridine-PVC ($P_2$).

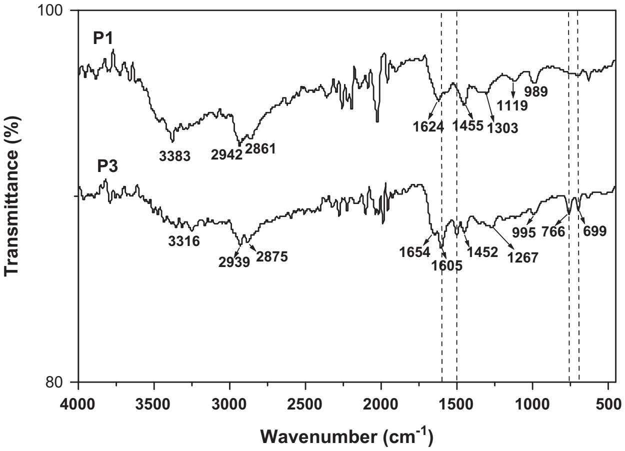

Fig. 4. IR spectra of the polymers ($P_1$) and ($P_3$).

The DSC diagram (Fig. 5) of the polymer ($P_1$) presents an endothermic transformation at 121°C and an exothermic peak at 352°C. In the case of polymer ($P_2$), we note the presence of three endothermic transformations at 99, 319 and 337°C and an exothermic peak at 276°C. Finally, the diagram of the polymer ($P_3$) exhibits three endothermic transformations at 91, 175 and 329°C with the absence of an exothermic peak up to 380°C (Table 1).

In this type of polymer, the endothermic peaks observed in the DSC thermograms are generally attributed to the loss of water molecules retained in the structures; in spite of the drying at 65°C. The release of water molecules by the obtained polymers is slightly difficult at 91°C for $P_3$, at 99°C for $P_2$ and at 121°C for $P_1$ because of differences of the structures of substituents introduced into the PVC backbone.

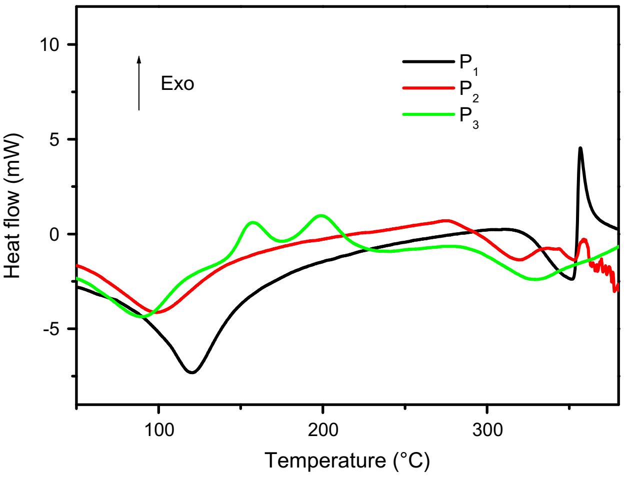

Fig. 5. DSC diagrams of polymers ($P_1$), ($P_2$) and ($P_3$).

Table 1
DSC analysis of the synthesized polymers

| Sample name | Endothermic transformation $T_{\text{endo.}}$ (°C) | Exothermic transformation $T_{\text{exo.}}$ (°C) |
|---|---|---|
| ($P_1$) | 121 | 352 |
| ($P_2$) | 99, 319 and 337 | 276 |
| ($P_3$) | 91, 175 and 329 | – |

### 3.3. Elemental analysis

Table 2 presents the N percentage in polymers determined by elemental analyses. An EA was also used to prove the success of the reaction as well as to estimate the reaction yield based on the mole fraction concept [4]. The obtained results show that the content of N in these polymers ($P_1$), ($P_2$) and ($P_3$) were, respectively, 11.697, 9.188 and 9.422. These findings suggest that the polymer structure, particularly polyamine chain length and nitrogen atoms composition, influence the N content.

### 3.4. Results of extraction by ICP-AES

Table 3 and Fig. 6 show the extraction percentages obtained by ICP-AES for the studied metals. These results demonstrate that the material ($P_1$) gives the best extraction percentage with the cation $La^{3+}$ (99.57%). This can be explained by the fact that ($P_1$) is the single polymer which does not have a cyclic amine chain. While the best extraction percentage of $Bi^{3+}$ (97.38%) was obtained with the material ($P_2$).

The material ($P_2$) becomes a poorer extractant than ($P_1$) and ($P_3$) for cation $La^{3+}$ which is probably due to the presence of aromatic amino groups in ($P_2$) that makes it less accessible. The material ($P_2$) gives extraction percentage, for $Bi^{3+}$, slightly better than those obtained by ($P_1$) and ($P_3$). A priori ring closure in the polymer ($P_2$) increases the extraction of the metal.

Table 2
EA of the synthesized polymers

| Sample name | C (%) | H (%) | N (%) |
|---|---|---|---|
| ($P_1$) | 78.851 | 8.548 | 11.697 |
| ($P_2$) | 67.95 | 6.783 | 9.188 |
| ($P_3$) | 82.348 | 7.332 | 9.422 |

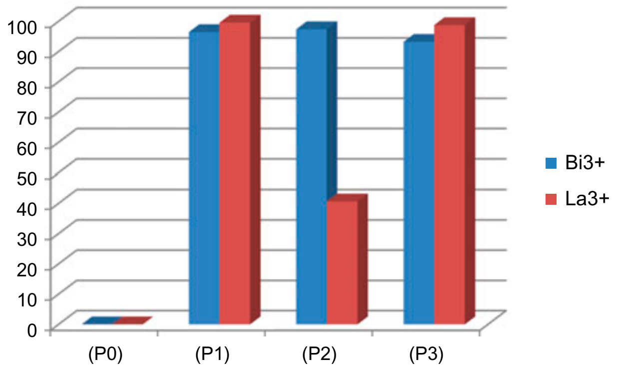

Fig. 6. Percentages of metal cations extraction (La and Bi) by commercial PVC ($P_0$), polymers ($P_1$), ($P_2$) and ($P_3$).

Moreover, on the basis of hard–soft acid–base (HSAB) theory, La(III) was classified as hard ion and Bi(III) was classified as intermediate ions, they have affinities to soft ligands which contain nitrogen atoms of polyamine groups. In addition, the deference of adsorption capacity of $La^{3+}$ and $Bi^{3+}$ by the three synthesized polymers $P_1$, $P_2$ and $P_3$ can be mainly explained by the compatibility factor between the cations' size and the ligands' cavity size in polymer matrix, which was probably influenced by the cross-linking degree.

This type of complex structures (Fig. 7) is well known in supramolecular chemistry [18].

### 3.5. Influence of extracted metals on IR spectra of new materials

The IR absorption spectra of the studied complexes (Fig. 8) indicate that the influence of free polymers and their complexes on IR spectra is not very significant. This could be due to the counter-anions of metal

Table 3
Extraction percentages with the synthesized polymers obtained by ICP-AES

| Metal cation | Percentage of extraction with ($P_0$) | Percentage of extraction with ($P_1$) | Percentage of extraction with ($P_2$) | Percentage of extraction with ($P_3$) |
|---|---|---|---|---|
| $Bi^{3+}$ | 0 | 96.45 | 97.38 | 93.22 |
| $La^{3+}$ | 0 | 99.57 | 40.69 | 98.78 |

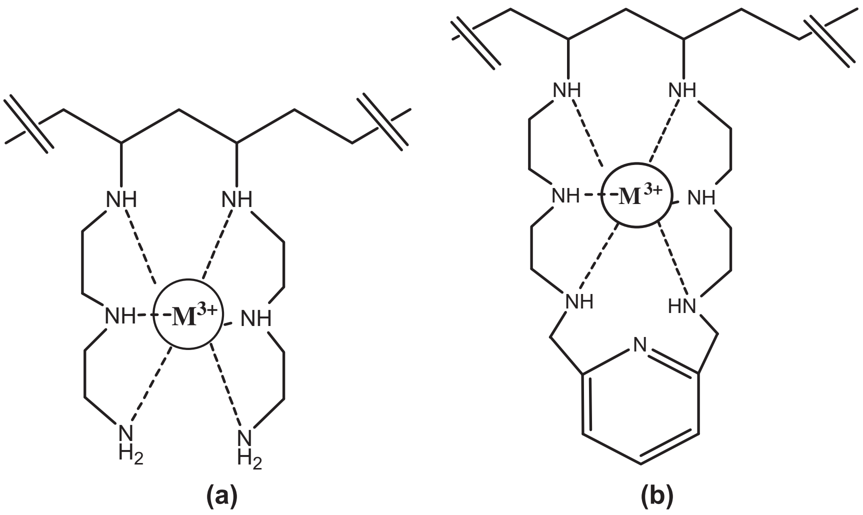

Fig. 7. Structures of (a) complex ($P_1$-$M^{3+}$) and (b) complex ($P_2$-$M^{3+}$). M = Bi or La.

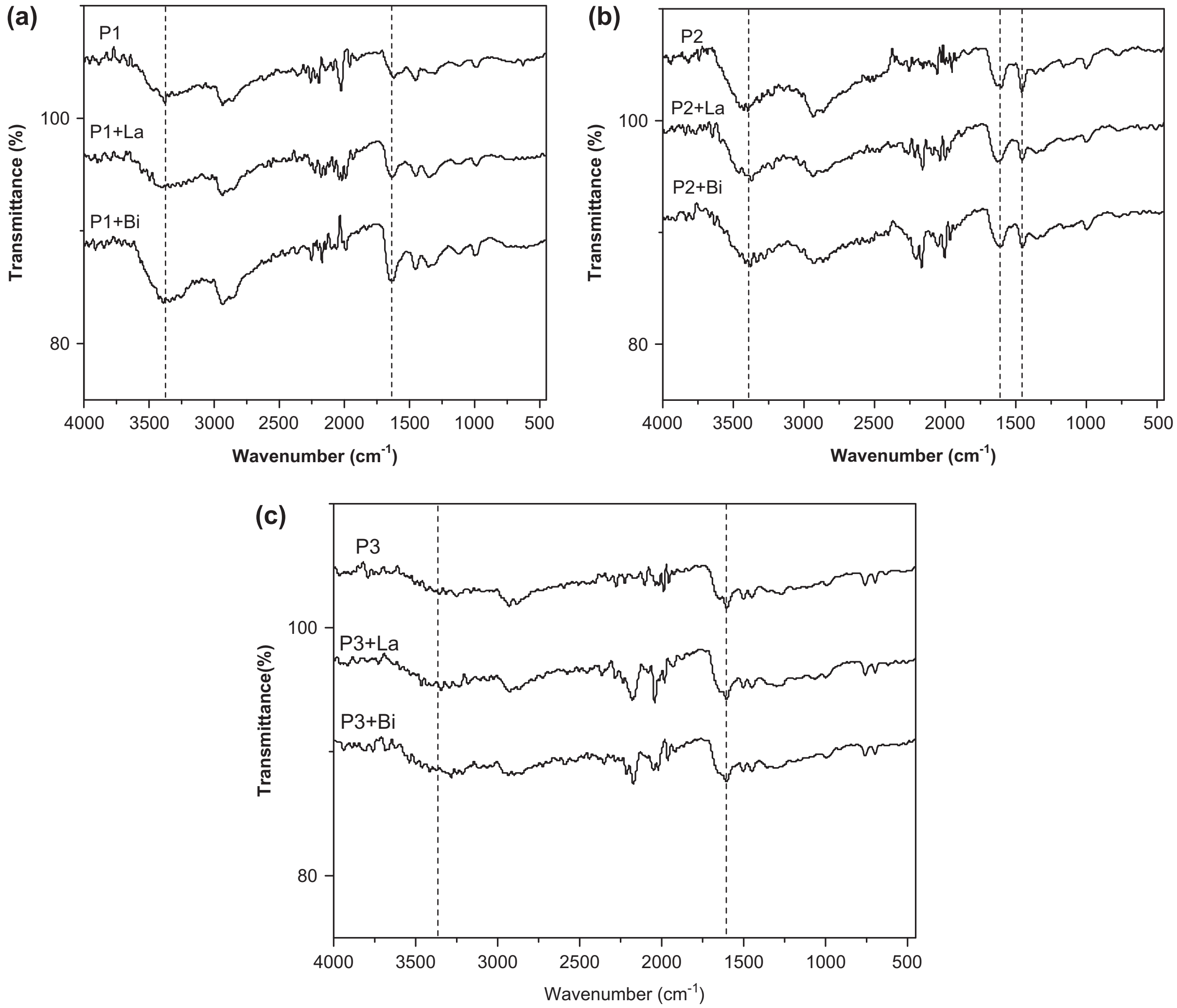

Fig. 8. IR spectra of (a) ($P_1$) and complex ($P_1$-$La^{3+}$), ($P_1$-$Bi^{3+}$); (b) ($P_2$) and complex ($P_2$-$La^{3+}$), ($P_2$-$Bi^{3+}$) and (c) ($P_3$) and complex ($P_3$-$La^{3+}$), ($P_3$-$Bi^{3+}$).

cations because of the use of these salts: Bi $(NO_3)_3{\cdot}5H_2O$ and $La(NO_3)_3{\cdot}H_2O$. Apparently, the anion $NO_3^-$ fixes easily to water molecule via hydrogen bonds which makes the drying of new materials difficult. We note the extension of the band at 3,374 $cm^{-1}$ due to the complexation of the polymers and the increase in the band at 1,637 $cm^{-1}$.

## 4. Conclusion

This work allowed us to obtain three new polymeric materials by functionalization of PVC (Mw = 48,000) namely amino-PVC ($P_1$), amino-methyl-pyridine-PVC ($P_2$) and polymer ($P_3$). The synthesized polymers were characterized with DSC, FTIR analyses and EA. The polymers were tested for the extraction of metals (La and Bi). The study of this extraction with the obtained polymers was followed by ICP-AES.

The percentage of extraction of cation $Bi^{3+}$ was found to increase from 93.22% for ($P_3$) to 97.38% for ($P_2$) and those of $La^{3+}$ from 40.69% for ($P_2$) to 99.57% for ($P_1$). Thus, ($P_1$) and ($P_2$) are better extractants of toxic metals $La^{3+}$ and $Bi^{3+}$, respectively.

In conclusion, synthesized polymers were able to minimize the negative effects of toxic metals on the environment.

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