

Recovered poly(vinyl chloride) grafted by amino groups and evaluation in metal ions extraction

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Abstract: The amount of plastic materials used is rapidly increasing and so are the problems caused by municipal plastic waste. Therefore this kind of waste requires an effective control to prevent its negative economic and environmental impact. For this reason the recycling process, chemical processing operations or purification of plastic waste have become an essential process for depollution nowadays. This work studies the purification of recovered Poly(vinyl chloride) (PVC) and its functionalization by grafting amino groups. The purified polymer was substituted with p-phenylenediamine and with p-methoxyaniline to obtain polymers (P₁) and (P₂). In another modification, diethylenetriamine was introduced on the modified PVC skeleton, obtaining polymers (P₃) from (P₁) and (P₄) from (P₂). The obtained polymers were characterized by elemental analysis (CHN), infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). After these chemical modifications, the modified polymers were tested for metal cation extraction from the aqueous phase containing (Cr(III), Pb(II), Cd(II), Zn(II) or Co(II)) using the solid-phase extraction (SPE) method. The study of these extractions with modified PVC (P₁, P₂, P₃ and P₄) was followed by Atomic Absorption measurements in aqueous solutions. The extraction percentage of Cd(II) was 84.8% by P₃, 79.4% by P₄, 18.7% by P₂, and 25.8% by P₁.

Key words: PVC grafting, p-phenylenediamine, p-methoxyaniline, diethylenetriamine, metal extraction.

INTRODUCTION

Polymer science is very important to produce new materials for new applications. Poly(vinyl chloride) is currently one of the most popular and used polymers due to its good and various properties [1-3], such as chemical stability, corrosion resistance and low cost [4-6], especially its ease of processing, recycling and important compatibility with additives [7]. There is currently considerable public interest in the issue of plastic waste [8,9]. The question about the disposal of used PVC has become increasingly important in the public debate due to the negative impact of said waste [10,11].

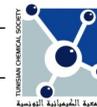
PVC has been subjected to many modifications, mainly chemical ones which are the most widely used. This type of modification plays a key role in the manufacture of new organic materials for new applications, generally in the removal of toxic organic compounds [12,13]. It is well known that PVC can be chemically modified by nucleophilic substitution reactions of its chlorine atoms [14,15].

In the present study we are interested in recovered PVC containing various additives such as phthalate esters, which have been extensively used as plasticizers to improve various properties such as flexibility and softness [16-18]. These types of additives are widely used in the manufacture of PVC and are toxic such as phthalate plasticizers. These plasticizers can migrate from the plasticized PVC products to the environment [18,19].

In this work those additives were eliminated in order to obtain purified PVC which would later allow the performance of heavy metal complexation following chemical transformations and assemblies. Moreover, environmental contamination by heavy metals could be largely avoided since the resulting PVC no longer contains toxic additives.

The second part of this work consisted in using the obtained polymers for the extraction of metal cations (Cr³⁺, Cd²⁺, Zn²⁺, Pb²⁺ or Co²⁺) from aqueous solutions to limit the negative effects of heavy metals in waste water [20,21].

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EXPERIMENTAL SECTION

1. Materials

The used polymer is recovered PVC (tubes and pipes). Commercial PVC ($M_r = 48000 \text{ g}\cdot\text{mol}^{-1}$), p-phenylenediamine and p-methoxyaniline were purchased from Fluka. Tetrahydrofuran (THF) provided by Sigma-Aldrich was distilled under nitrogen prior to its use. Diethylenetriamine (99%) and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%) were provided by Sigma-Aldrich. $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (98%), $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$ (98%), $\text{Pb}(\text{NO}_3)_2$ (98%) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99%) were produced by Fluka. Diethyl Ether was bought from Panreac. Potassium Iodide (KI) and Acetone were purchased from Prolabo.

2. Instrumentation

IR absorption spectra were recorded using a Thermo Scientific Nicolet FTIR 200 spectrophotometer, using the ATR/FTIR technique. Differential scanning calorimetry (DSC) was carried out on a SETARAM DSC 131. The pH was measured with a pH and conductivity meter, VWR / CO 3000L. Elemental analysis of N was performed by using a Perkin-Elmer Analyzer CHN Series II 2400. The extraction percentage of each metal cation by modified polymers was obtained using atomic absorption spectroscopy (AAS) analysis on a Perkin-Elmer PinAAcle 900T.

3. PVC purification

Recovered PVC (tubes and pipes) was water washed, dried and cut into 2 x 2 mm pieces. 5 g of this recovered PVC was placed in a 250 mL Erlenmeyer flask with 50 mL of acetone. After stirring at 50 °C for 1 h the PVC pieces increased in volume and became easy to grind. After grinding them, they were returned to the flask with 50 mL of acetone and were stirred at 50 °C for 6 h. The resulting solution was filtered in order to obtain two separate products, a (white) dissolved powder (DP) in acetone and a (grey) undissolved powder (UDP). These were finally dried in the oven at 60 °C.

(DP is the polymer which contains the ester plasticizer and UDP is similar to commercial PVC, these results were shown by IR analysis).

4. Chemical modification of the purified PVC (UDP)

In order to make the polymer more reactive, the Conant-Finkelstein reaction was carried out [22, 23]. This consisted of substituting a certain number

of chlorine atoms of the initial PVC (UDP) with iodine atoms by using a nucleophilic substitution mechanism before reacting with amines.

4.1. Substitution of purified PVC with an aromatic amine

6 g of an aromatic amine (p-phenylenediamine or p-methoxyaniline) was mixed in an autoclave (hydrogenating bomb) with 6 g of purified PVC and 2 g of KI in 100 mL THF. The mixture was reacted at 160 °C for 4 h. After cooling, the resulting product was washed with distilled water, dried in the oven at 65 °C for 24 h, crushed and washed with diethyl ether and distilled water. Finally, the product was dried for 48 h to obtain a brown-colored powder. The PVC substituted by p-phenylenediamine was designed as P_1 and the PVC substituted by the p-methoxyaniline was designed as P_2 .

4.2. Substitution of modified PVC with an aliphatic triamine

The two previously obtained polymers P_1 and P_2 (4 g) were substituted with diethylenetriamine (8 mL) in 70 mL of THF as described above. The PVC substituted by the p-phenylenediamine and the diethylenetriamine was designed as P_3 and the PVC substituted by the p-methoxyaniline and the diethylenetriamine was designed as P_4 .

5. Extraction study

5.1. Extraction of some metal cations

In this study, the extraction of a series of metals by the modified polymers (P_1 , P_2 , P_3 and P_4) was tested. The extraction degree of metal cations such as Cr^{3+} , Pb^{2+} , Cd^{2+} , Co^{2+} or Zn^{2+} from aqueous solutions, was evaluated through atomic absorption measurements. The modified polymers (P_1 , P_2 , P_3 and P_4 as powders) were put in contact with aqueous solutions of metal cation in order to determine the optimal extraction time according to the change in conductivity (σ) of the metal aqueous solution with time.

Solid phase extraction has already been successfully used in determining and separating metal ions [24], and has many advantages such as rapidity, reproducibility and versatility [25].

5.2. Extraction procedure: Kinetic study of the solid phase extraction

The modified polymer was washed a few times with distilled water until the electrical conductivity of the water became stable ($\sigma_{\text{water}} = 2\text{-}4 \mu\text{S}/\text{cm}$). 20 mL of the aqueous metal salt solution with a

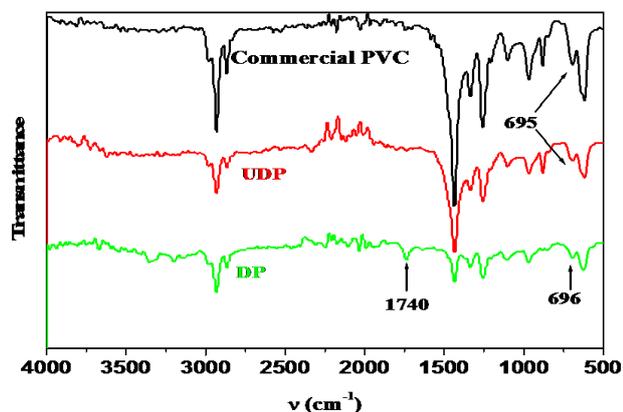


Figure 1. FTIR spectra of Commercial PVC, UDP and DP.

concentration of 2.10^{-4} mol.L⁻¹ was added to a 30 mL flask containing 0.1 g of the modified PVC (powder was crushed in a mortar).

At certain 't' time intervals, the electrical conductivity of the solution in contact with the modified PVC was measured until extraction equilibrium was reached (the conductivity of the metal aqueous solution becomes stable when the modified PVC is loaded with metal ions).

RESULTS AND DISCUSSION

1. Characterization of the purified PVC

The IR analysis showed that the carbonyl group exists only in DP and doesn't exist in UDP. The treatment with acetone therefore showed that the ester plasticizer (for example) had been eliminated from the recovered PVC. The acetone extracted a small amount of the PVC along with the plasticizers, which is visible in the IR spectrum of the DP (Figure 1) where the ν_{C-Cl} band at 696 cm^{-1} is also seen (Table I).

Through the differential scanning calorimetry analysis (DSC) (Figure 2 and Table II), it was found that the glass transition ($81\text{ }^{\circ}\text{C}$) and the

endothermic transformation ($295\text{ }^{\circ}\text{C}$) of the UDP are comparable to those of commercial PVC ($T_g=83\text{ }^{\circ}\text{C}$, $T_{\text{endo}}=279\text{ }^{\circ}\text{C}$). In the case of the DP, only an exothermic peak at $280\text{ }^{\circ}\text{C}$ was observed marking the decomposition of the obtained product.

2. Analysis of the substituted polymers

2.1. IR spectroscopy

The IR absorption spectra for P₁ and P₂ showed characteristic bands of an amine between 3200 and 3500 cm^{-1} . Bands were also observed at: around 3045 cm^{-1} which corresponds to $\nu_{C_{\text{sp}^2-H}}$; at 1620 cm^{-1} corresponding to δ_{N-H} ; two stretching vibration bands at 1524 and 1441 cm^{-1} which correspond to $\nu_{C=C}$ of the benzene ring; and one band at 1250 cm^{-1} which corresponds to ν_{C-N} . One must also note the presence of deformation vibration bands at 821 cm^{-1} out of the aromatic cycle γ_{Ar-H} , which confirms the para-substitution of the benzene ring. In the meantime, the characteristic bands of the ether function: ν^s_{C-O-C} and ν^a_{C-O-C} at 1040 cm^{-1} and at 1185 cm^{-1} respectively were only observed for P₂ (Figure 3).

All the characteristic bands observed for P₁ and P₂ were also seen in the IR spectra for P₃ and P₄. One must also note the absence of the stretching vibration band ν_{C-Cl} between 600 and 800 cm^{-1} in the spectra of both P₃ and P₄. This confirms that chlorine atoms of polymers P₁ and P₂ have been substituted by the diethylenetriamine (Figure 3).

2.2. Elemental analysis

An elemental analysis was also carried out to prove the success of the reaction as well as to estimate the yield of the reaction which was based on the concept of molar fraction for each element [26]. The percentage of elements C, H and N for P₁ increased from 38.88%, 4.38% and 0% to 83.50%, 4.8% and 5.21% respectively. An increase in the percentages of said elements (C, H and N) was also observed for P₂ (Table III).

Table I. Comparison of characteristic bands of UDP and DP with commercial PVC.

Characteristic vibration	Wave number (cm^{-1})		
	Commercial PVC	UDP	DP
—CH ₂ asymmetric and symmetric vibrations	2930-2870	2929-2869	2930-2875
C—Cl stretching vibration	695	695	696
C=O stretching vibration	—	—	1740

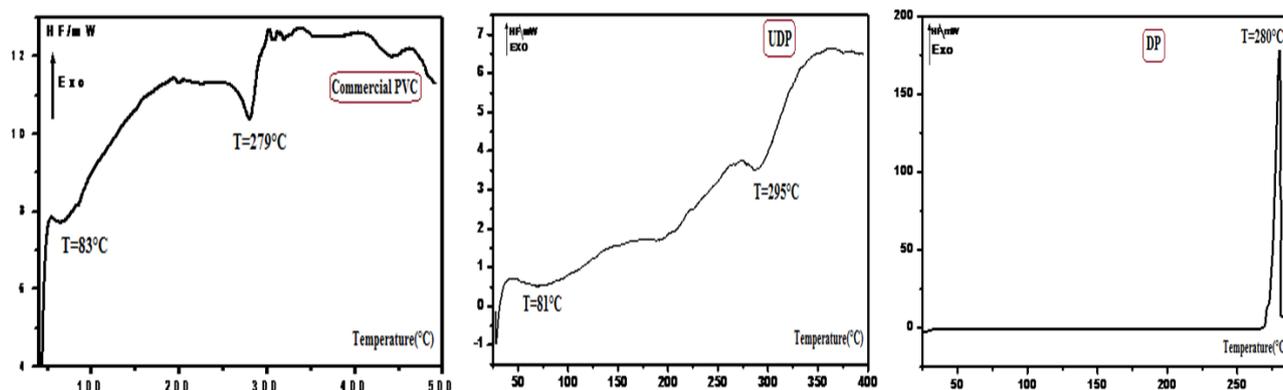


Figure 2. DSC diagrams of (a): Commercial PVC, (b): UDP and (c): DP

Table II. DSC analysis of Commercial PVC, UDP and DP.

Sample name	T_g (°C)	T_{endo} (°C)	T_{exo} (°C)
Commercial PVC	83	279	—
UDP	81	295	—
DP	—	—	280

Notes: T_g : Glass transition temperature,
 T_{endo} : Endothermic transformation,
 T_{exo} : Exothermic transformation.

The percentages of nitrogen for P_3 and P_4 which were 6.41 and 7.25% respectively were found to be higher than those obtained with the undissolved powder.

2.3. DSC characterization of P_1 , P_2 , P_3 and P_4

Differential scanning calorimetry (DSC) was performed on 5 mg samples and the results were recorded between 50 and 500 °C at a heating speed of 5°C min⁻¹ (Figure 4).

The DSC analysis of modified PVC shows a glass transition and endothermic and exothermic transformations. The glass transition (T_g) was observed for all polymers at around 70 °C but the endothermic transformations (T_{endo}) were observed at 191, 450 and 293 °C for P_1 , P_3 and P_4 , respectively, and the exothermic transformation was observed at 175 °C for P_2 (Table IV).

3. Proposed structures

The obtained results show that the chlorine atoms of the purified PVC (starting product) have

been substituted by p-phenylenediamine to produce P_1 and by p-methoxyaniline to produce P_2 . The IR spectrums of P_1 and P_2 show that the chlorine stretching vibration bands ($\nu_{\text{C-Cl}}$) have not entirely disappeared. The proposed structures, inspired from a published work [27], are suggested

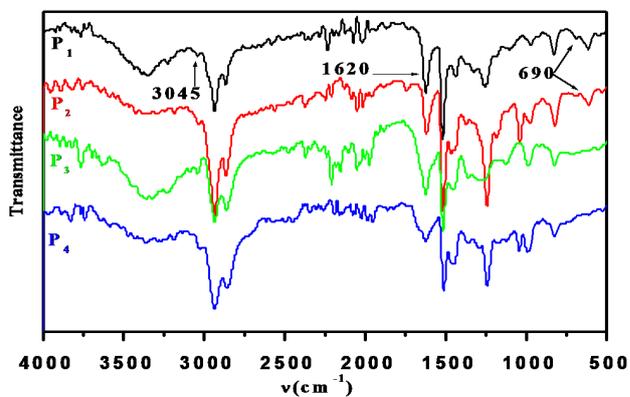


Figure 3. FTIR Spectra of polymers: P_1 , P_2 , P_3 and P_4 .

Table III. Elemental analysis for Purified PVC (UDP) and modified polymers (P_1 , P_2 , P_3 and P_4).

Sample name	C (%)	H (%)	N (%)
UDP	38.88	4.38	0.00
P_1	83.50	4.80	5,21
P_2	84.45	5.17	4,71
P_3	65.96	6.66	6,41
P_4	64.35	8.20	7,25

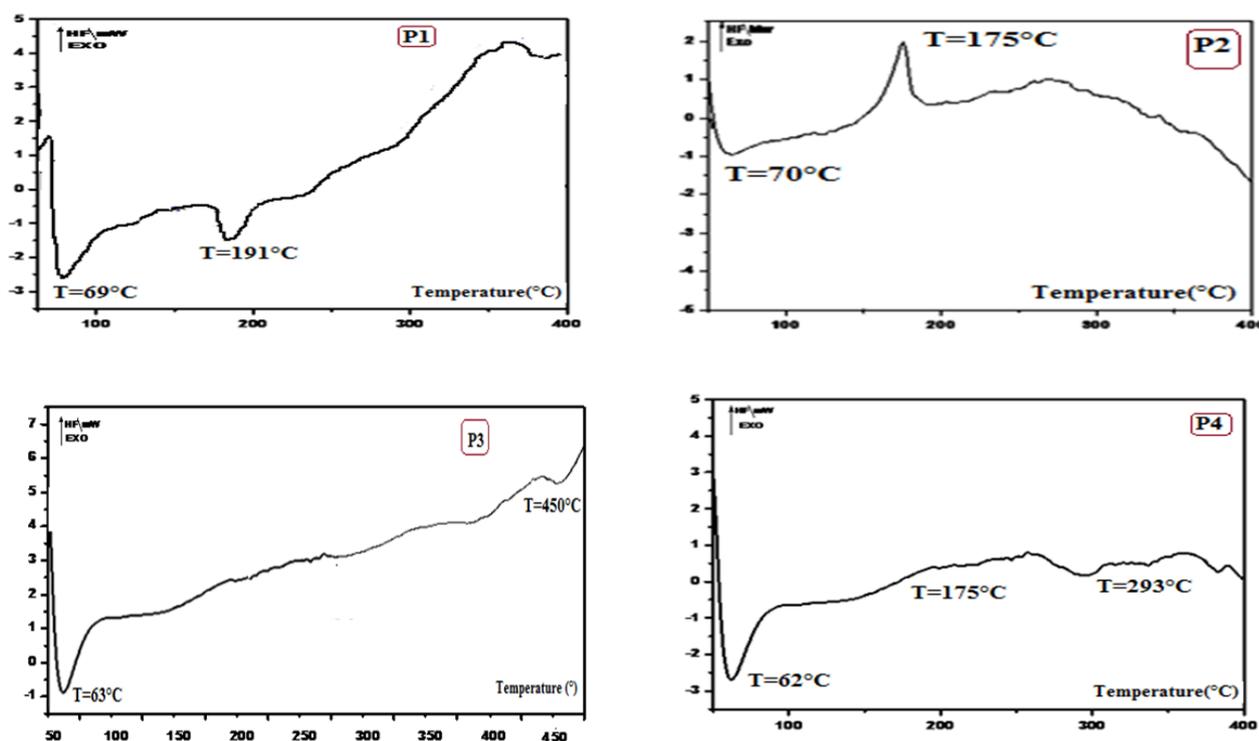


Figure 4. DSC diagrams of (a): P₁, (b): P₂, (c): P₃ and (d): P₄.

Table IV. DSC analysis of P₁, P₂, P₃ and P₄

Sample name	T _g (°C)	T _{endo} (°C)	T _{exo} (°C)
P ₁	69	191	—
P ₂	70	—	175
P ₃	63	450	—
P ₄	62	293	175

Notes: T_g: Glass transition temperature,
 T_{endo}: Endothermic transformation,
 T_{exo}: Exothermic transformation.
 These polymers (P₁, P₂, P₃ and P₄) have amorphous structures based on their DRX diffractograms.

by the presence of some chlorine atoms in structures of P₁ and P₂ (Scheme 1).

P₁ and P₂ were substituted with diethylenetriamine. A possible structure of P₃ and P₄ are shown in Scheme 2. The proposed structures are suggested by the complete disappearance of the ν_{C-Cl} band from the IR spectrums.

4. Metal cations extraction by synthesized polymers

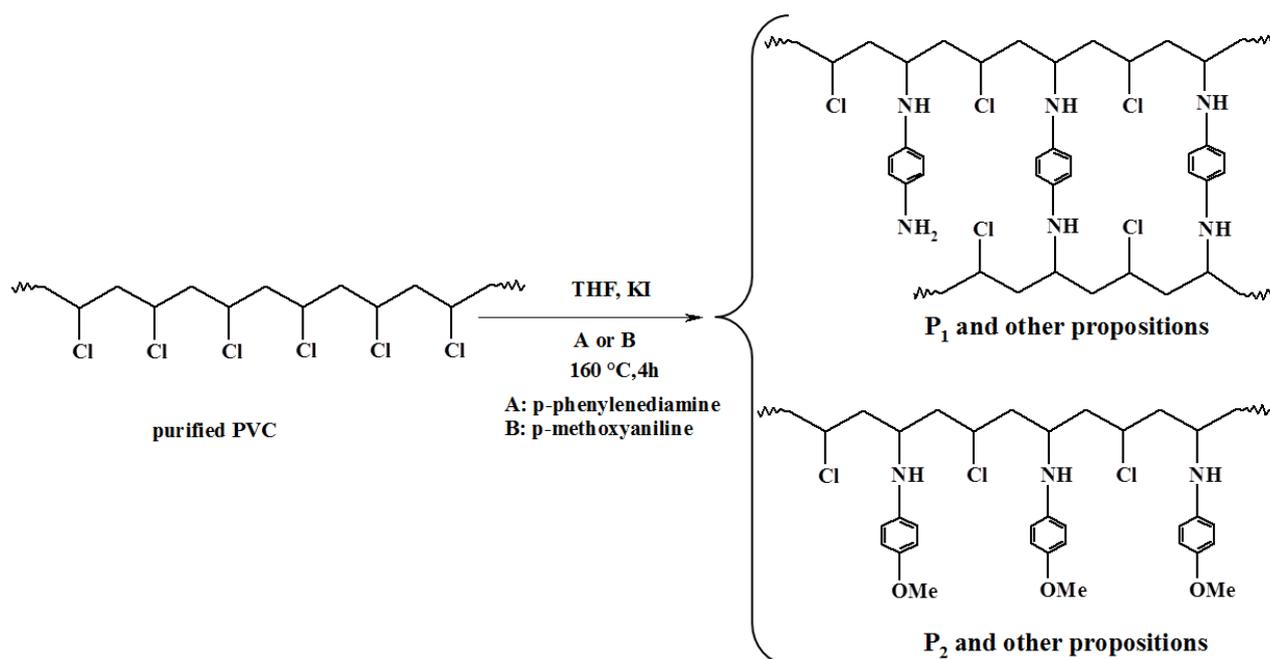
4.1. Kinetic study

The kinetic study showed that the optimum extraction time obtained with polymers P₃ and P₄ is of approximately 8 h whereas for the other polymers (P₁ and P₂) it was of 24 h. The extraction results are the average of three experiments.

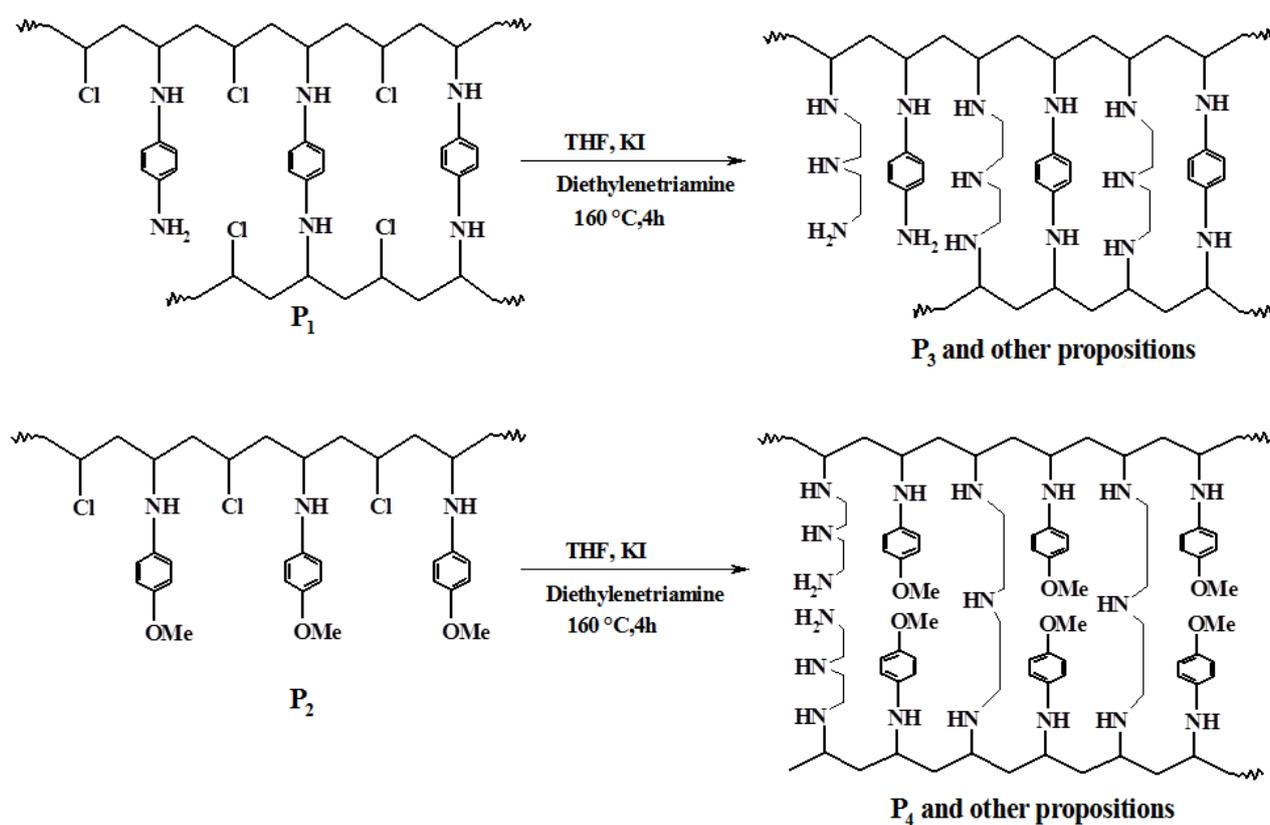
Figure 5 Shows curves corresponding to variations of the electrical conductivity averages as a function of time in the case of Cr³⁺ and Pb²⁺ extraction by the modified polymers (P₁, P₂, P₃ and P₄).

4.2. Extraction followed by the atomic absorption method

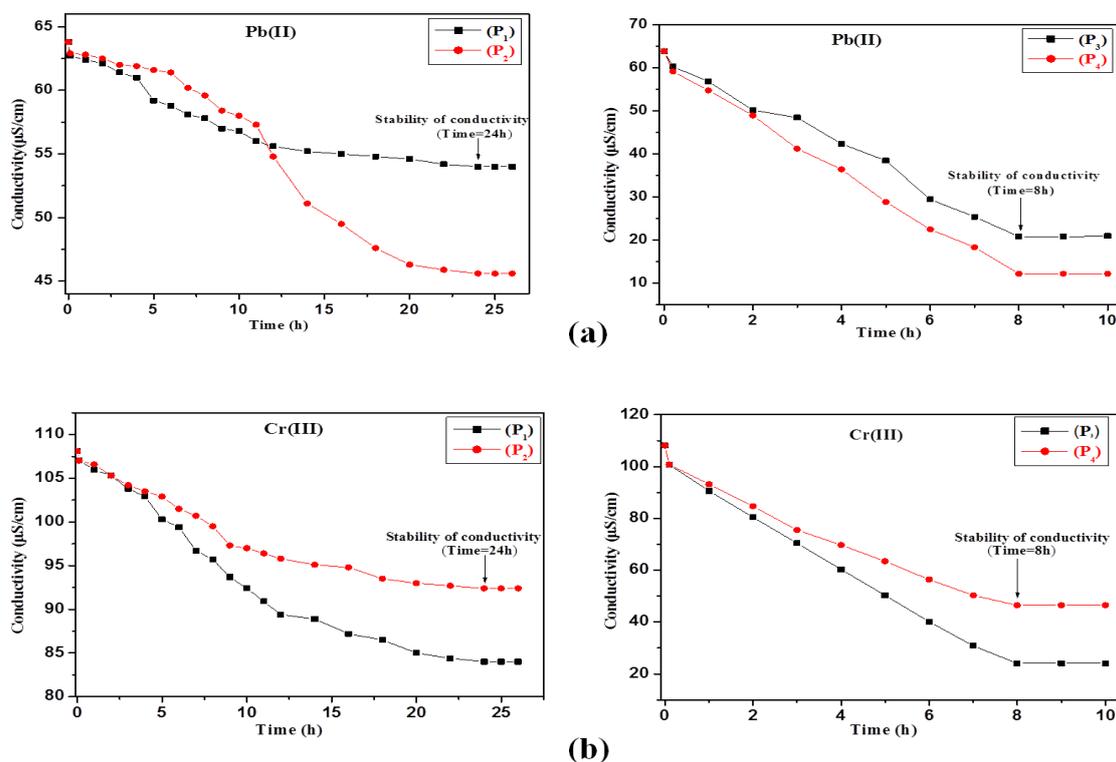
Aqueous monometallic solutions of Cr(NO₃)₃·9H₂O, CdCl₂·H₂O, ZnCl₂·6H₂O, CoCl₂·6H₂O and Pb(NO₃)₂ were prepared at a concentration of 2.10⁻⁴ mol.L⁻¹ in relation with each metal ion in distilled water. The pH of the prepared aqueous solutions varied between 3.7 and 4.7. The modified polymer was washed a few times with distilled water. 20 mL of the aqueous metal salt solution was added to a 30 mL flask containing 0.1 g of the modified PVC. The extraction equilibrium of obtained polymers (P₃ and P₄) was reached after 8 h but after 24 h for the other polymers (P₁ and P₂).



Scheme 1. Substitution reactions by p-phenylenediamine or by p-methoxyaniline of purified PVC.



Scheme 2. Substitution reactions of P₁ and P₂ by Diethylenetriamine.



5. Curves of variation of electrical conductivity with time for Pb(II) (a) and Cr(III) (b) in contact with P₁, P₂, P₃ and P₄

The suspension was filtrated on filter paper (which was previously washed with water). The amount of remaining metal ions in solution was evaluated by atomic absorption spectroscopy (AAS) analysis of the filtrate which was diluted in distilled water. The AAS measurement was evaluated on a Perkin-Elmer PinAAcle 900T.

The results were expressed as extraction percentages of the metal, based on its initial concentration.

4.3. Extraction percentage

The extraction percentage of metal cations is given by the following formula:

$$E(\%) = (C_i - C_f) / C_i * 100$$

Where: C_i is the initial concentration of the metallic aqueous solution before extraction.

C_f is the concentration of the metallic aqueous solution at extraction equilibrium.

4.4. Interpretation

Extraction percentages of metal cations (Cr³⁺, Cd²⁺, Zn²⁺, Pb²⁺ or Co²⁺) by polymers P₁ and P₂ which vary between 7% and 32% were found to be lower than those obtained with polymers P₃ and P₄ which were between 62% and 90%.

The metal extraction percentages by P₃ and P₄ varied from one metal to another. For P₃ they were found to be 89.7%, 84.8%, 82.15%, 79.45%, and 71% respectively for Cr³⁺, Cd²⁺, Zn²⁺, Pb²⁺ and Co²⁺. For P₄ they were 90.1%, 79.8%, 79.4%, 65.8% and 62.2% respectively for Pb²⁺, Zn²⁺, Cd²⁺, Cr³⁺ and Co²⁺. The extraction power of P₃ with the studied metals followed this increasing order: Co²⁺ < Pb²⁺ < Zn²⁺ < Cd²⁺ < Cr³⁺, while polymer P₄ followed a different order: Co²⁺ < Cr³⁺ < Cd²⁺ < Zn²⁺ < Pb²⁺. These polymers P₃ and P₄ provide better extraction results with the studied metals than P₁ and P₂ (Figure 6).

An increase in extraction percentage of cadmium was observed from UDP (0%) to P₂ (18.7%) and to P₁ (25.8%), and also an amelioration in extraction percentage from P₂ (18.7%) to P₄ (79.4%) and another percentage increase from P₁ (25.8%) to P₃ (84.8%). Therefore, cadmium extraction percentages by P₁ are better compared to P₂ and they are better for P₃ compared to P₄. These percentages can be explained by the presence of different types of complexing cavities with steric complementarity (shape and size) compatible with the used metals. In this study, the obtained

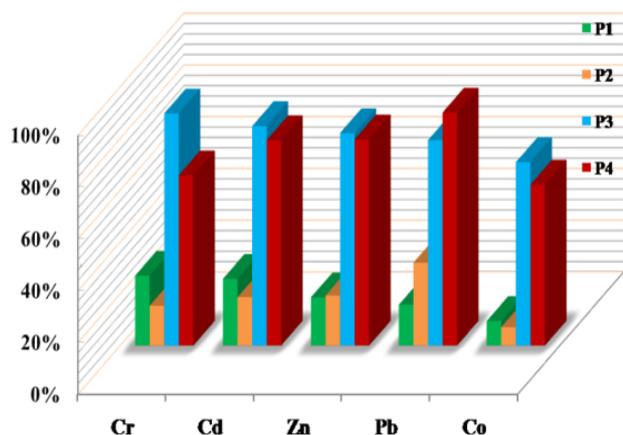


Figure 6. Extraction percentages of metal cations (Cr^{3+} , Cd^{2+} , Zn^{2+} , Pb^{2+} or Co^{2+}) by P₁, P₂, P₃ and P₄.

complexing cavities were coated with donor atoms (N, O) [12, 28], this type of atom is able to fix the metal M^{n+} ($\text{M}^{n+} = \text{Cr}^{3+}$, Cd^{2+} , Zn^{2+} , Pb^{2+} or Co^{2+}) through noncovalent bonds (Van Der Waals bonds). The fixing of M^{n+} can also be explained by the presence of an electron-rich π system (benzene ring), this type of noncovalent interaction was explained by the noncovalent cation- π interactions theory [29, 30].

The complexation with M^{n+} may be the best for P₃ because of the combination of amino groups (the ligands of p-phenylenediamine are ambidentate) and the π -electron system (benzene ring) [31] (Figure 7).

The modified polymer P₃ has well defined cavities thanks to the rigidity of the cross-linking chain p-phenyleneamine which doesn't accept as easily

Pb^{2+} , which is the most voluminous ion ($R_i = 1.19 \text{ \AA}$) of the studied series.

Polymer P₄ (90.1%) is a better extractant than P₃ (79.4%) for Pb^{2+} . These polymers have the same polyamine chains but P₄ has more flexible chains with p-anisidine groups.

The obtained results with those modified polymers can be compared to some of those published in the literature but, of course, the studied PVC does not exhibit the same composition or structure. In the case of Pb^{2+} , the extraction percentage by modified polymers, which has been substituted by diethylenetriamine and p-anisidine (90.1%), is more important compared to the percentage obtained in another publication (18.1%) [32].

CONCLUSIONS

In this study, recovered PVC was purified (from discarded tubes and pipes) and amino groups were grafted on the purified PVC. The modified polymers were characterized by DSC, FT-IR and elemental analysis (CHN). The polymers were tested for the extraction of a series of metals (Cr, Cd, Zn, Pb or Co). The study of this extraction with the obtained polymers was followed by atomic absorption spectroscopy (AAS).

Percentages of metal cation extraction by polymers P₁ and P₂ (grafted by amino aromatic groups) were lower than those obtained by P₃ and P₄ (grafted by aliphatic and aromatic amino groups). Thus the chemical modification by two types of amino groups plays an important role in improving the complexation and extraction of heavy metals. The extraction percentage of Cd^{2+}

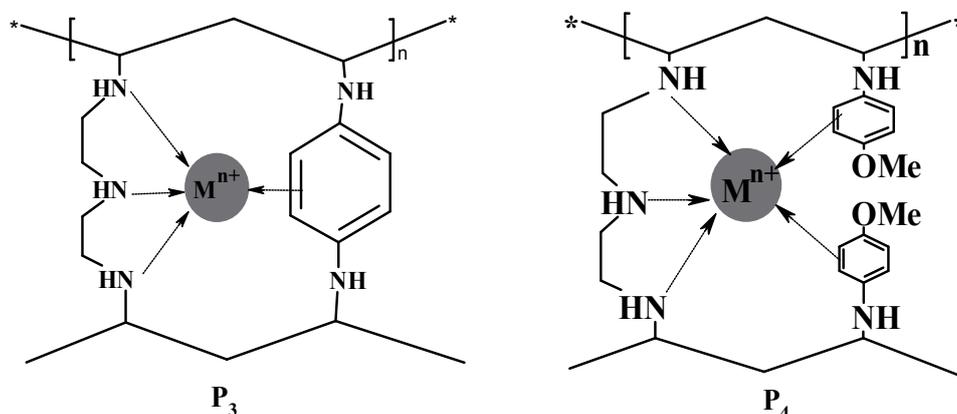


Figure 7. Possible interactions of P₃ and P₄ with M^{n+} .

was found to increase from 25.8% for P₁ to 84.8% for P₃ and from 18.7% for P₂ to 79.4% for P₄. In conclusion, polymers P₃ and P₄ have many complexing cavities with N atoms and are better extractants than P₁ and P₂; therefore they are able to minimize the negative effects of toxic metals on aquatic environments.

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