CHEMICAL MODIFICATION OF COMMERCIAL AND RECOVERED POLY(VINYL CHLORIDE) WITH AMINO GROUPS - ADSORPTION OF HEAVY METALS (Cr(III), Pb(II), Cd(II), OR Co(II)) BY MODIFIED PVC POLYMERS

Faten Mbarki\textsuperscript{a,b} & Fayçel Ammari\textsuperscript{a}

\textsuperscript{a} Laboratory of Organic Synthesis, Carthage University, Faculty of Sciences of Bizerte, 7021 Jarzouna, Bizerte, Tunisia.

\textsuperscript{b} Department of Chemistry, College of Science, University of Hafr Al Batin, Hafr Al Batin, Saudi Arabia.

E-mail: mbarkifeten12@yahoo.fr, ammari1971@gmail.com

Faten Mbarki\textsuperscript{a,b}, Assistant professor qualified at the College of Sciences of Hafr Al Batin, University of Hafr Al Batin (Saudi Arabia), 02 Publications and 07 Communications in polymer chemistry and wastewater treatment.

Fayçel Ammari\textsuperscript{a}, Associate Professor at IPEST, STCHA member, co-president of two scientific committees and of the JICHA2-2020 organisation, Supervision of 6 Masters, co-supervision of 4 PhD theses. Supervision of the current thesis, Jury member of 4 Masters, 3 theses and one accreditation. 18 Publications, 4 Books, 2 Plenary Conferences and 19 communications in Polymer chemistry and wastewater treatment.

Abstract

The adsorption process has been evolved to produce a new molecular structures based on modified polymers by functional groups known by their extracting powers. In this context, the present work is conducd, and it is devided into two main parts. The first part studies the purification of the recovered Poly (vinyl chloride) (PVC) and its functionalization by grafting amino groups. The purified polymer was substituted by the p-phenylenediamine and the p-methoxyaniline to obtain the polymers (P\textsubscript{1}) and (P\textsubscript{2}). In another modification, the diethylenetriamine was added to the modified PVC skeleton, to obtain the polymers (P\textsubscript{3}) from (P\textsubscript{1}) and (P\textsubscript{4}) from (P\textsubscript{2}). The second part describes the chemical modification of the Commercial PVC by the aliphatic and aromatic amines (benzylamine and diethylenetriamine) through nucleophilic substitution reactions of its chlorine atoms to obtain the (P\textsubscript{5}) polymer. The modified polymer was subsequently reticulated with dichlorodiethyl ether to obtain the...
After these chemical modifications, the modified polymers were tested for metal cation extraction from the aqueous phase containing (Cr(III), Pb(II), Cd(II), or Co(II)) using the solid phase extraction (SPE) method and the inductively coupled plasma atomic emission spectrometry (ICP-AES) technique. For Pb\(^{2+}\), the extraction percentage was 98% using (P\(_5\)) and 90.3% using (P\(_6\)).

**Keywords**: poly (vinyl chloride), p-phenylenediamine, p-methoxyaniline, diethylenetriamine, benzylamine, dichlorodiethyl ether, substitution reaction, metal cation extraction, grafting amino groups.

**Introduction**

Poly (vinyl chloride) is one of the most common materials these days due to its good and various properties [1-3], such as the chemical stability, the corrosion resistance the low cost [4-6], and especially its ease of processing and recycling, and its important compatibility with additives [7]. There is currently considerable public interest in the issue of plastic wastes [8, 9]. The question about the disposal of the 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 numerous reactions, mainly the dehydro chlorination [12], the nucleophilic substitutions [13,14], the degradation [15,16], the grafting and the cross-linking [17-19]. The chemical modification of the PVC has been important in the development of the macromolecular chemistry. 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 [20,21]. It is well known that PVC can be chemically modified by nucleophilic substitution reactions of its chlorine atoms [22,23].

In the present study we are interested in the 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 [24-26]. These types of additives are widely used in the PVC manufacture and they are toxic, such as the phthalate plasticizers. These plasticizers can migrate from the plasticized PVC products to the environment [26,27].

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 has consisted in using the commercial PVC. In the first step, these commercial polymer was chemically modified with aliphatic and aromatic amines (benzylamine and diethylenetriamine), and in the second step the modified polymer was reticulated with dichlorodiethyl ether.

The new products based on the modified PVC have been able to remove toxic pollutants from wastewater. Several techniques are available for the study of the elimination of these toxic products from wastewater. Adsorption process is one of the most important methods for the removal of toxic organics, using several types of adsorbents, such as polymeric adsorbents [28].

This work has evaluated the efficiency of modified polymers in the removal of toxic metals from the environment and especially from wastewater, since water pollution is a major worldwide issue caused by contamination from several toxic pollutants [29,30].
Purification of recovered PVC and its functionalization by grafting amino groups

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

Figure 1. Representation of DP and UDP and recovered PVC.

Chemical modification of the purified PVC (UDP)

In order to make the polymer more reactive, the Conant-Finkelstein reaction was carried out [31]. 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.

Substitution of purified PVC with an aromatic amine (p-phenylenediamine or p-methoxyaniline)

The reaction between the purified PVC and an aromatic amine (p-phenylenediamine or p-methoxyaniline) with KI gives a brown-colored powder. The PVC substituted by p-phenylenediamine was designed as P₁ and the PVC substituted by the p-methoxyaniline was designed as P₂.

The obtained results show that the chlorine atoms of the purified PVC (starting product) have been substituted by p-phenylenediamine to produce P₁ and by p-methoxyaniline to produce P₂. The IR spectrums of P₁ and P₂ show that the chlorine stretching vibration bands (ν\(_{\text{C-Cl}}\)) have not entirely disappeared. The proposed structures, inspired from a published work [32], are suggested by the presence of some chlorine atoms in structures of P₁ and P₂.
Substitution of modified PVC with an aliphatic amine

The two previously obtained polymers $P_1$ and $P_2$ were substituted with diethylenetriamine 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 $P_4$. $P_1$ and $P_2$ were substituted with diethylenetriamine. A possible structure of $P_3$ and $P_4$ are shown in scheme 2. The proposed structures are suggested by the complete disappearance of the $\nu_{C-Cl}$ band from the IR spectrums.

Scheme 1. Substitution reactions by p-phenylenediamine or by p-methoxyaniline of purified PVC.
**Scheme 2.** Substitution reactions of P₁ and P₂ by Diethylenetriamine.

**Analysis of the modified polymers**

**IR spectroscopy**

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 where the $\nu_{\text{C-Cl}}$ band at 696 cm$^{-1}$.

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 $\nu_{\text{Csp2-H}}$; at 1620 cm$^{-1}$ corresponding to $\delta_{\text{N-H}}$; two stretching vibration bands at 1524 and 1441 cm$^{-1}$ which correspond to $\nu_{\text{C=C}}$ of the benzene ring; and one band at 1250 cm$^{-1}$ which corresponds to $\nu_{\text{C=N}}$. One must also note the presence of deformation vibration bands at 821 cm$^{-1}$ out of the aromatic cycle $\gamma_{\text{Ar-H}}$, which confirms the para-substitution of the benzene ring.

In the mean time, the characteristic bands of the ether function: $\nu^s_{\text{C-O-C}}$ and $\nu^a_{\text{C-O-C}}$ at 1040 cm$^{-1}$ and at 1185 cm$^{-1}$ respectively were only observed for P₂.

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 $\nu_{\text{C-Cl}}$ 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.
Elemental analyses

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 [33]. 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. The percentages of nitrogen for P₃ and P₄ which were 6.41 and 7.25% respectively were found to be higher than those obtained with the undissolved powder.

Table 1. Elemental analysis for Purified PVC (UDP) and modified polymers (P₁, P₂, P₃, P₄).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
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<tr>
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<tr>
<td>P₂</td>
<td>84.45</td>
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<td>P₃</td>
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<td>6.41</td>
</tr>
<tr>
<td>P₄</td>
<td>64.35</td>
<td>8.20</td>
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Chemical functionalization of Commercial PVC

Nucleophilic substitution mechanism of PVC

In order to make the polymer (PVC) more reactive, we performed the Conant–Finkelstein reaction with the aim to replace the chlorine atoms of the pure PVC with iodine ones through a nucleophilic substitution mechanism [31].
Preparation of amino-PVC

The new polymer (P₅) was prepared by reacting between the commercial PVC (P₀), benzylamine, KI and diethylenetriamine. The compound was collected by filtration, treated with a 0.1 M aqueous solution of NaOH, filtered and washed several times with distilled water and with diethylether. A possible structure of P₅ is shown in scheme 3. Some chlorine atoms are still present in the proposed structures. The IR spectrum of P₅ shows that the chlorine stretching vibration bands (ν_C-Cl) have not entirely disappeared; this suggests the presence of some chlorine atoms in P₅ structures.

Grafting of dichlorodiethyl ether on amino-PVC

Previously modified PVC (P₅) reacts with dichlorodiethyl ether to lead, after purification, at the polymer (P₆).

P₅ has been grafted with dichlorodiethyl ether. A possible structure of P₆ is shown in Scheme 4. The proposed structures are suggested by the complete disappearance of the ν_C-Cl band from the IR spectrum.

Scheme 3. Modification mechanism of P₀ with benzylamine and diethylenetriamine.
Scheme 4. Cross-linking of P₅ by dichlorodiethyl ether.

Analysis of the modified polymers

IR spectroscopy

The IR spectroscopy analysis of the modified polymer (P₅) clearly shows that a substitution reaction takes place, as indicated by the appearance of characteristic bands of the amingroup at 3434 and 3310 cm⁻¹ corresponding to NH₂ and NH, respectively, and also absorption at 1650 cm⁻¹ corresponding to N-H bending in plane. An absorption at 1467 cm⁻¹ corresponding to aromatic C=C is also observed, confirming the presence of the benzene ring in polymeric chains of PVC. However, the spectrum also shows the presence of the chlorine stretching vibration bands (ωC-Cl) with low intensity at 701 cm⁻¹. This indicates that some chlorine atoms have not entirely disappeared. All the characteristic bands observed for P₅ were also seen in the FT-IR spectrum of P₆, with an increase in the intensity of the valence band corresponding to C–O–C which appears at around 1050–1170 cm⁻¹. This finding confirmed the grafting of ether group (dichlorodiethyl ether) on the amino-PVC.
Figure 4. FT-IR spectra of P₀ (a), P₅ (b) and P₆ (c).

Elemental analysis
Comparing the element percentages (% C, % H, and% N) for P₅ and P₆ with those of P₀ clearly proves that a chemical change has happened. This is especially clear from the nitrogen percentage which increased from 0% (P₀) to 6.31% and 5.08 % for P₅ and P₆, respectively. The percentage of other elements (C and H) also increased.

<table>
<thead>
<tr>
<th>Sample name</th>
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<th>H (%)</th>
<th>N (%)</th>
</tr>
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<tr>
<td>P₅</td>
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<td>6.31</td>
</tr>
<tr>
<td>P₆</td>
<td>69.08</td>
<td>5.43</td>
<td>5.08</td>
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Metal cation extraction by modified polymers

Extraction of some metal ions
The work consisted in using the modified polymers for the removal of metal ions (Cr³⁺, Cd²⁺, Pb²⁺ or Co²⁺) with methods such as the adsorbent by solid phase extraction (SPE) method.

Analysis method
The modified polymer, (powder) was crushed in a mortar and was sieved through a ≤ 100μm sieve was washed several times with distilled water to remove any possible salts present, was added to aqueous metal salt solutions of Cr(NO₃)₃·9H₂O, CdCl₂·H₂O, Pb(NO₃)₂, and CoCl₂·6H₂O (2×10⁻⁴ mol/dm³) with the pH of each aqueous solution varying between 3.5 and 4.5 and subjected to stirring in order to determine the optimal extraction time according to the change in conductivity (σ) of the aqueous solution with time. Finally, the suspension was filtrated and the metal content in the filtrate evaluated by the inductively coupled plasma to mice mission spectrometry (ICP-AES) analysis.
Extraction percentage of modified polymers

Extraction percentage of $P_1$, $P_2$, $P_3$ and $P_4$

Extraction percentages of metal cations ($\text{Cr}^{3+}$, $\text{Cd}^{2+}$, $\text{Pb}^{2+}$ or $\text{Co}^{2+}$) by polymers $P_1$ and $P_2$ which vary between 7% and 32% were found to be lower than those obtained with polymers $P_3$ and $P_4$ which were between 62% and 90%.

The metal extraction percentages by $P_3$ and $P_4$ varied from one metal to another. For $P_3$ they were found to be 89.7%, 84.8%, 79.45%, and 71% respectively for $\text{Cr}^{3+}$, $\text{Cd}^{2+}$, $\text{Pb}^{2+}$ and $\text{Co}^{2+}$. For $P_4$ they were 90.1%, 79.4%, 65.8% and 62.2% respectively for $\text{Pb}^{2+}$, $\text{Cd}^{2+}$, $\text{Cr}^{3+}$ and $\text{Co}^{2+}$.

The extraction power of $P_3$ with the studied metals followed this increasing order: $\text{Co}^{2+} < \text{Pb}^{2+} < \text{Cd}^{2+} < \text{Cr}^{3+}$, while polymer $P_4$ followed a different order: $\text{Co}^{2+} < \text{Cr}^{3+} < \text{Cd}^{2+} < \text{Pb}^{2+}$. These polymers $P_3$ and $P_4$ provide better extraction results with the studied metals than $P_1$ and $P_2$.

An increase in extraction percentage of cadmium was observed from UDP (0%) to $P_2$ (18.7%) and to $P_1$ (25.8%), and also an amelioration in extraction percentage from $P_2$ (18.7%) to $P_1$ (25.8%). A large increase was observed from $P_2$ (18.7%) to $P_4$ (79.4%) and another percentage increase from $P_1$ (25.8%) to $P_3$ (84.8%). Therefore, cadmium extraction percentages by $P_1$ are better compared to $P_2$ and they are better for $P_3$ compared to $P_4$. 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 complexing cavities were coated with donor atoms (N, O), this type of atom is able to fix the metal $M^{n+}$ ($M^{n+} = \text{Cr}^{3+}$, $\text{Cd}^{2+}$, $\text{Pb}^{2+}$ or $\text{Co}^{2+}$) through noncovalent bonds (Van Der Waals bonds). The fixing of $M^{n+}$ can also be explained by the presence of an electron-rich $\pi$ system (benzene ring), this type of noncovalent interaction was explained by the noncovalent cation-$\pi$ interactions theory [34,35].

The complexation with $M^{n+}$ may be the best for $P_3$ because of the combination of amino groups (the ligands of $p$-phenylenediamine are ambidentate) and the $\pi$-electron system (benzene ring) [36].

The modified polymer $P_3$ has well defined cavities thanks to the rigidity of the cross-linking chain $p$-phenyleneamine which doesn’t accept as easily $\text{Pb}^{2+}$, which is the most voluminous ion ($R_i = 1.19$ Å) of the studied series.

Polymer $P_4$ (90.1%) is a better extractant than $P_3$ (79.4%) for $\text{Pb}^{2+}$. These polymers have the same polyamine chains but $P_4$ 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 $\text{Pb}^{2+}$, 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 publications (18.1%) [37].
Figure 5. Extraction percentages of metal cations (Cr\textsuperscript{3+}, Co\textsuperscript{2+}, Pd\textsuperscript{2+} or Pb\textsuperscript{2+}) by PND, P\textsubscript{1}, P\textsubscript{2}, P\textsubscript{3} and P\textsubscript{4}.

**Extraction percentage of P\textsubscript{5}, P\textsubscript{1} and P\textsubscript{2}**

The extraction percentages of metal ions (Cr\textsuperscript{3+}, Co\textsuperscript{2+}, Cd\textsuperscript{2+} or Pb\textsuperscript{2+}) by the synthesized polymer (P\textsubscript{5}) varied between 45% and 98% and between 65.1% and 96.65% for the other polymer (P\textsubscript{6}). The extraction power of P\textsubscript{5} with the metals studied followed the following increasing selectivity order: Cr\textsuperscript{3+} << Co\textsuperscript{2+} < Cd\textsuperscript{2+} < Pb\textsuperscript{2+}, while the second polymer followed another order: Co\textsuperscript{2+} << Pb\textsuperscript{2+} < Cd\textsuperscript{2+} < Cr\textsuperscript{3+}. The extraction percentages by P\textsubscript{5} indicated more selectivity of Pb(II) with a percentage of 98%, while P\textsubscript{6} showed more selectivity of Cr(III) with a percentage of 96.65%.

Complexation with M\textsuperscript{2+} (Pb\textsuperscript{2+}, Cd\textsuperscript{2+} and Co\textsuperscript{2+}) proved to be the best for P\textsubscript{5} given that the extraction percentages were 98%, 97.2% and 73.5% respectively for Pb\textsuperscript{2+}, Cd\textsuperscript{2+} and Co\textsuperscript{2+}. These results can be explained by the compatibility between the size of the metal ion and the size of the complexing cavity and the type of hetero-atom ligands (oxygen and nitrogen atoms or -NH\textsubscript{2}). According to the P\textsubscript{5} and P\textsubscript{6} structures, there are several types of macrocyclic cavities. The retention of metal cations can also be explained by the presence of an electron-rich \(\pi\) system (benzene ring), this type of interaction was explained by the noncovalent cation-\(\pi\) interactions theory [34]. In the case of Cr(III), the polymer P\textsubscript{6} (96.65%) is a better extractant than P\textsubscript{5} (45%); P\textsubscript{6} accepts Cr\textsuperscript{3+} better, which is the least voluminous ion of those studied. Based on the hard-soft acid-base theory, Cr(III) was classified as a hard ion, and has affinities to hard ligands which contain oxygen atoms in the P\textsubscript{6} cavity, but Cd(II) was classified as a soft ion and Pb(II) and Co(II) were classified as intermediate ions.

Therefore, the chemical modification of commercial PVC is important for the extraction of heavy metals, and the cross-linking with a bifunctional group has an important effect on extraction. In our case it improved the extraction power of P\textsubscript{5} to the point that the percentage of the trivalent Cr ion increased from 45 to 96.65%.
Figure 6. Percentages of metal cations extraction with the polymers P₀, P₅ and P₆.

Scheme 5. Possible interactions of P₃ and P₄ with Mⁿ⁺.

Scheme 6. Possible interactions of P₅ with Mⁿ⁺.
Conclusion

The substitution reactions of commercial PVC ($M_r = 48000$) and of purified PVC by amino groups show the importance of chemical modification for the synthesis of long polymer chain functionalized materials. In this work these new materials containing electron-donating atoms such as nitrogen and oxygen were used as chelating agents for heavy metal extraction. The simple preparation procedure of the reactions depends on the used solvent, the temperature, and the reaction time. The simple (SPE) technique based on polymeric adsorbents proved to be an effective method for the metal ion extraction from aqueous phases [Pb(II), Cd(II), Co(II), or Cr(III)].

For synthesized polymers from recovered PVC, the extraction percentage of Cd$^{2+}$ was found to increase from 25.8% for P$_1$ to 84.8% for P$_3$ and from 18.7% for P$_2$ to 79.4% for P$_4$ [38].

For modified polymers from commercial PVC, the extraction percentage was 97.2% by P$_5$ and 94.8% by P$_6$ for Cd$^{2+}$ [39].

This work has enabled us to evaluate the extraction of heavy metals by new adsorbents based on modified PVC polymers.

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