Synthesis and characterization of Polyalkylamines modified Poly (vinyl chloride) used for removing of Bi(III) and Cr(III) from aqueous solutions

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Abstract: Three polyamine-functionalized poly (vinyl chloride) prepared by ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) called respectively: PVC-EDA, PVC-DETA and PVC-TETA. The synthesized modified polymers have been investigated as high-capacity chelating agents for trivalent cations Bi(III) and Cr(III) from aqueous solutions. The structural properties of the polymers were characterized by elemental analysis and infrared spectroscopy (FT-IR). These new polymers were found to be highly effective for the extraction of Bi(III) and Cr(III) ions. Kinetic data revealed that the extraction process was achieved within 24 hours. The functionalized polymer by TETA: PVC-TETA had a high selectivity of extraction for the metals Bi(III) and Cr (III) with percentages of extraction respectively about 97 % and 90 %.

Keywords: Poly (vinyl chloride), Polyalkylamines, Functionalization, Metal cations, Extraction.

INTRODUCTION

Wastewaters containing organic and inorganic contaminants such as dyes, heavy metal ions, salts, and surfactants are a serious environmental problem in human society [1]. Heavy metals are discharged into waters mainly within the effluents and wastes from the industries of mining, smelting, surface finishing, and electroplating [2,3]. These are characterized to be non-biodegradable and they can be accumulated in internal organs and cannot be utilized by living organisms, thus causing serious problems and metabolic disorders [4-7]. In point of view of worldwide environmental concern, the removal of the above mentioned toxic substances from wastewaters has become a crucial issue [8]. Several well-known conventional techniques are commonly employed for treatment of toxic heavy metals from aqueous solutions as well as industrial water effluents [9-12]. Some of these methods are well characterized by many drawbacks such as high cost, slow process, high energy consumption and production of toxic sludge [13]. Among many techniques, solid phase extraction (SPE) is an adequate technique for trace metals separation/preconcentration, and it consists on a simple and flexible principle, it is also easy of automation, and having a high enrichment factor [14]. However, new extractants, which are locally available with a high removal capacity and economic feasibility, are still needed and developed. The development of polymeric materials as extractants for removal of some metal ions from aqueous solutions is considered as a research priority in the environmental field. In this context, many researchers prepared synthetic polymers to use them in the removal of metal ions such as activated carbon [15,16], clay minerals [17,18], ion exchangers [19-21], polystyrene [22,23] and Poly vinyl chloride [24]; Therefore, by chemical modifications reactions of PVC with appropriate compounds, new polymers with improved physical properties can be obtained [25, 26]. Moreover, Poly (vinyl chloride) due to many advantages including high specific surface value, physical and chemical stability especially in concentrated acidic, basic media and organic

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solvents for long-time is a suitable support for SPE. To be well operating polymer, the surface of PVC could be modified by sorbent to obtain reversible and efficient enrichment of metal ions capture [27]. In this context, chemical modifications of Poly vinyl chloride with polyalkylamines have been successfully used for the removal of harmful metal ions from their aqueous solutions with solid phase extraction.

In this work, we attempt to investigate chelating polymers synthesized by grafting three polyamines: ethylenediamine, diethylenetriamine, and triethylenetetramine on polyvinyl chloride: PVC-EDA, PVC-DETA, and PVC-TETA to extract hazardous metal cations bismuth and chrome which are widespread in the environment and known to be dangerous to human health.

EXPERIMENTAL

1. Materials

Poly (vinyl chloride), high molecular weight (MW = 48,000 g.mol^{-1}, 16 mmol of Cl.g^{-1}, 99 %) as purchased from Fluka. All reagents were purchased from commercial suppliers and used without further purification. Ethylenediamine (99 %), diethylenetriamine (99 %) and triethylenetetramine (97 %), reagents used were supplied by the Sigma-Aldrich and used without further purification. Tetrahydrofuran (THF) was used as the solvent. Triethylamine (TEA) and diethyl ether were purchased from Prolabo. Iodide potassium (KI) (99 %), $Cr(NO_3)_3 \cdot 9H_2O$ (99 %) and $Bi(NO_3)_3 \cdot 9H_2O$ (98 %) were produced by Sigma-Aldrich: Aqueous monometallic solutions were prepared at a concentration of 2×10^{-4} mol.L^{-1} in relation with each metal ion in distilled water (pH = 6-7).

2. Apparatus

Elemental analysis of C, H and N was performed by using Perkin Elmer Analyzer CHN Series II 2400. Infrared analysis was carried out by using the attenuated total reflectance technique (ATR/ FTIR), with a Nicolet FTIR 200 spectrophotometer (Thermo Scientific, France). The amount of remaining metal ions in solution was evaluated by ICP-AES: HORIBA JOBIN (HORIBA Jobin Yvon S.A.S., 16-18 Canal Street, 91165 Longjumeau Cedex). Kinetic measurements were carried out by conductometric method using conductometer: VWR /CO 3000L (Germany). The calibration of the conductivity is carried out using standard solutions for each metal.

3. Synthesis of Poly (vinyl chloride) modified with Ethylenediamine: PVC-EDA

PVC (1 g, 16 mmol Cl) was suspended in 40 ml THF, KI (1g) and ethylenediamine (3.84g, 4 eq.) were added. The reaction mixture was charged in a hydrogenating bomb at 100 °C for 24 h. The product was precipitated. Then filtered and washed with distilled water and diethyl ether. Finally, the obtained polymer was dried at room temperature, and then at 65°C for 24 h. The obtained product had a weak solubility in THF and not soluble in organic solvents such as: ethanol, methanol, acetone, chloroform and dichloromethane. The obtained polymers are rated PVC amino: PVC-EDA. A brown powder was obtained for PVC-EDA.

4. Synthesis of Poly (vinyl chloride) modified with Diethylenetriamine: PVC-DETA

The reaction involved (1 g, 16 mmol Cl) of PVC, 40 ml THF, 1g of KI and (6.6g, 4 eq.). The reaction conditions, time, and purification procedure of the product were similar to that of PVC-EDA. The obtained polymer was rated PVC amino: PVC-DETA. A brown powder was obtained for PVC-DETA.

5. Synthesis of Poly (vinyl chloride) modified with Triethylenetetramine: PVC-TETA

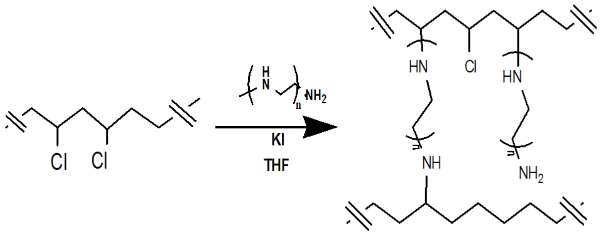
The reaction involved (1 g, 16 mmol Cl) of PVC, 40 ml THF, 1g of KI and (9.35g, 4 eq.) The reaction conditions, time, and purification procedure of the product were like that used for PVC-EDA. The obtained polymer was rated PVC amino: PVC-TETA. A dark brown powder was obtained for PVC-TETA.

6. Proposed structures of PVC-EDA, PVC-DETA and PVC-TETA

Based on the analytical results obtained by different physicochemical analyses, (EA, infrared spectroscopy (FT-IR)) we propose the following structures for the materials PVC-EDA, PVC-DETA, and PVC-TETA (Fig.1).

7. Extraction Procedure of Metal Cations

Two aqueous metallic solutions of $Bi(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were prepared at a concentration of 2.10^{-4} mol.L^{-1} in relation with the metal cations, and were filtrated on filter paper prewashed with distilled water before their use in the extraction of metals. Then, 0.1 g of modified PVC (PVC-EDA, PVC-DETA, and PVC-TETA)



n=1, PVC-EDA ; n=2, PVC-DETA ; n=3, PVC-TETA

Fig.1. Synthetic scheme of polymers PVC-EDA, PVC-DETA, and PVC-TETA

was introduced with 20 mL of the metal ion solution at 25°C for 24 h. These polymers were separated by filtration and washed in deionized water. The filtrate was analyzed by ICP-AES. The results were demonstrated as percentages of metal extraction, based on its initial concentration. The extraction percentage of the metal is given by the following relationship:

$$\%\ \text{Extraction} = \frac{C_0 - C_f}{C_0} \times 100$$

C_0: Concentrations of the metal ion in initial solutions.
C_f: Concentrations of the metal ion in final solutions.

8. Determination of the Equilibration Time

Conductimetric method was performed to determine kinetic extraction properties of PVC-EDA, PVC-DETA and PVC-TETA for Bi(III) and Cr(III) ions. Then, we decided to estimate the equilibration time by conductimetric method. A typical procedure is: 0.1 g of each new resin was shaken with 20 mL of solution containing metal ions for different hours. Variation of the conductivity was monitored with a conductometer for 24 hours.

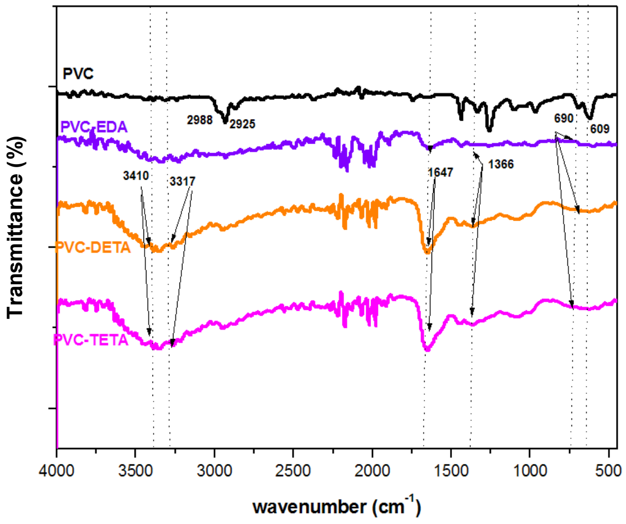


Fig.2. ATR-FTIR spectra of polymers: PVC, PVC-EDA, PVC-DETA and PVC-TETA.

RESULTS AND DISCUSSION

1. ATR-FTIR Analysis

The FTIR spectroscopy was applied to characterize the surface structure of PVC-EDA, PVC-DETA, and PVC-TETA chelating resins by comparing the spectra of PVC before and after reaction with polyamines EDA, DETA and TETA (**Fig. 2**). The spectra of the commercial PVC show a high intensity band assigned to the stretching vibration C–Cl at 690 cm^{-1}, agrees with IR spectral data of Ammari et al [28]. PVC-EDA, PVC-DETA, and PVC-TETA show the appearance of new bands around 3410-3317 cm^{-1} due to the stretching vibration of NH primary and secondary amines. A bending vibration of NH appears at 1647 cm^{-1}. A stretching vibration of CN was recorded at 1366 cm^{-1}. The most significant change in each spectra of the modified PVC was the characteristic band of C-Cl at 690 cm^{-1} that becomes very low in polymers PVC-EDA, PVC-DETA, and even missing in PVC-TETA compared to that corresponding to commercial PVC. These results affirm the increasing of the number of chlorine atoms substituted by amine groups. These results confirm the crosslinking occurred between polyalkylamines and commercial PVC.

2. Elemental Analysis

Table I gives the N content of the chelating polymers determined by elemental analysis. An elemental analysis was also used to prove the success of the reaction as well as to estimate the reaction yield based on the mole fraction concept

Table I. Elemental analysis results for the synthesized polymers

Sample Name	C (%)	H (%)	N (%)
PVC-EDA	67.16	6.36	2.89
PVC-DETA	76.53	8.18	8.45
PVC-TETA	79.57	8.71	11.96

[29]. The elemental analysis results showed that the content of polyamine in the three kinds of chelating polymers PVC-EDA, PVC-DETA, and PVC-TETA are the presence of 2.89%, 8.45% and 11.96 % of nitrogen in polymers respectively. These results confirm the success of grafting the three polyamines EDA, DETA and TETA on commercial PVC. However, these findings suggest that the resin structure, nitrogen atoms composition and polyamine chain length, influences the N content [30].

3. Removal of the metal cations from the synthesized polymers

The functionalized polymers obtained: PVC-EDA, PVC-DETA and PVC-TETA were tested for its extractant properties of hazardous metals Bi(III) and Cr(III) from aqueous solutions of $Bi(NO_3)\cdot 9H_2O$ and $Cr(NO_3)_3\cdot 9H_2O$ prepared at 2 .10^{-4} mol.L^{-1}. The study of the extraction showed that the time required to extract hazardous metal ions is 24 hours. The metals studied extractions percentages varied from metal to another.

When looking at metal extraction results obtained with the modified polymers PVC-EDA, PVC-DETA, and PVC-TETA, the first observation was that most polymers are highly selective for the studied metal cations of Bi(III) and Cr(III) and they have extraction efficiencies. The polymers PVC-EDA, PVC-DETA, and PVC-TETA were found to extract these ion at high level (> 97 %) with a clear selectivity Cr(III)< Bi(III) and showed a same affinity order. In comparison study of capacity extraction it was found that, polymers PVC-TETA, PVC-DETA, have better extraction percentage for Bi(III) and Cr(III) ions than PVC-EDA, especially polymer PVC-TETA (more than 97% extraction capacity for Bi and more than 90% of extraction capacity for Cr). However, the order of extraction capacity of the chelating resins against Bi(III) and Cr(III) ions was, respectively, PVC-TETA > PVC-DETA > PVC-EDA, which agree with the other investigation [31] in the case of Merrifield resin. This increase in extraction percentage could be explained by the higher content of nitrogen atoms in functional groups and thus imposed more coordination with metallic ions. Those functional groups play a dominant role in the extraction removal of heavy metals.

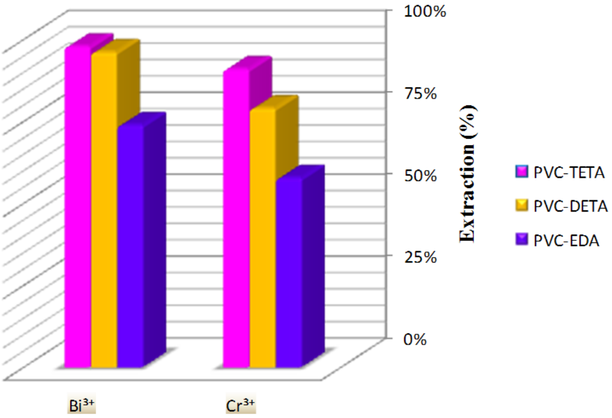
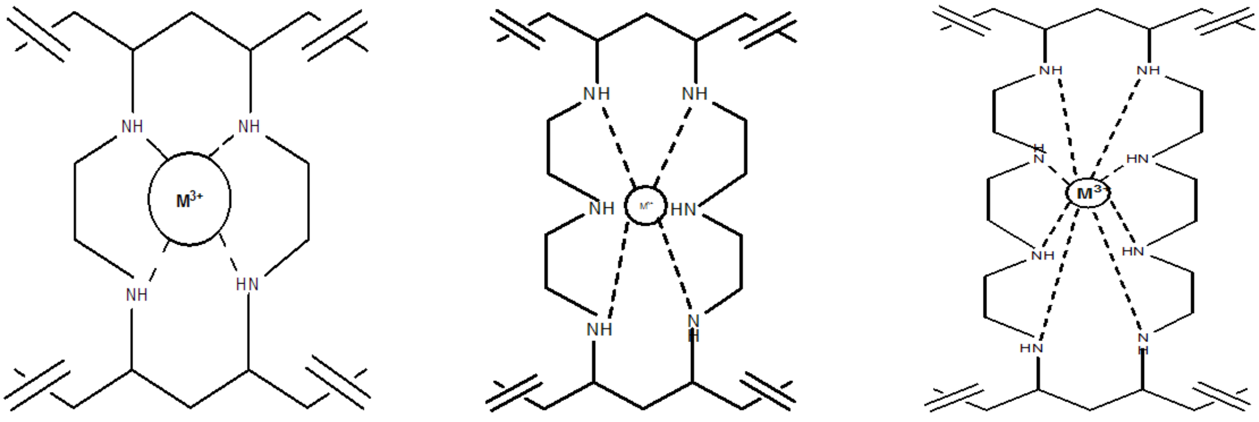


Fig. 3. Percentages of metal cations extraction for the polymers.

Polymers modified with Alkylamines (EDA, DETA, TETA) have been successfully used as extracting agents for bismuth (III) and chrome(III) from aqueous solutions. The extraction was attributed to the interaction of the metals to nitrogen atom of alkylamines. The special functional groups on the surface of the extractants provide significant interactions with heavy metals, resulting in the extraction separation of heavy metals from water **Fig.3**. Moreover, polyamines resins with nitrogen donor atoms have been characterized that the amine is the most effective functional groups for metal adsorption [32]. In addition, the deference of extraction percentage of Bi(III) and Cr(III) can be mostly explained by the compatibility factor between the cation size and the ligands cavity size in different polymers, also, the differences in form and volume between the two kinds of extractant ions **Fig. 4**.

Modified PVC exhibits chelating property by forming complex through reactive groups. The groups that are responsible for complex formation are mainly amine groups. Nitrogen in amine groups is proven to be a major effective binding site for Metal ions. Moreover, based on hard-soft acid-base (HSAB) theory, Cr(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.

To explain the order of selectivity and high extraction percentage find in these new chelating polymers: PVC-EDA, PVC-DETA, and PVC-TETA, we admit that's depend from the compatibility between the size of metal cations and complexing ligands cavity size, the number, and the type of hetero atom ligands. The studied polymers can be used as complexing agents that can be simply filtered and reused repeatedly after simple



(a) (b) (c)

Fig. 4. Structures of (a) complex (PVC-EDA-M^{3+}), (b) complex (PVC-DETA-M^{3+}) and (c) complex (PVC-TETA-M^{3+}). M = Bi or Cr.

washing with a solution of diluted hydrochloric acid (10^{-2} M) and with distilled water.

4. Kinetic Study

The conductivity of two metal ions solutions was investigated to determine the time equilibration. Conductimetric method [33] was chosen as an alternative to estimate time span for the equilibrium of the metal exchange, in which conductivities of dilute metal ion solutions ($2 .10^{-4}$ M) were monitored while contacting with wetted resin samples. **Fig. 5** show conductivity-time plots of Cr(III) and Bi(III) solutions contacting with prepared chelating polymers, as representative examples shows the conductivity curves of two metal ions at the optimal pH.

The Conductivity decreased sharply within 8 h and then trended toward equilibrium until 24 h. Abid et al. [34] and Ammeri et al. [35] pointed out that the time required to reach equilibrium during extraction of different metal ions on polystyrene from aqueous solutions is equal to 24 hours. This phenomenon might be explained by the existence of plentiful sites at first, and as the conductivity decreased, the available sites decreased, resulting in the reduction in the rate. However, the initial extraction rate was very fast may be due to the existence of greater number of resin sites available for metal ions

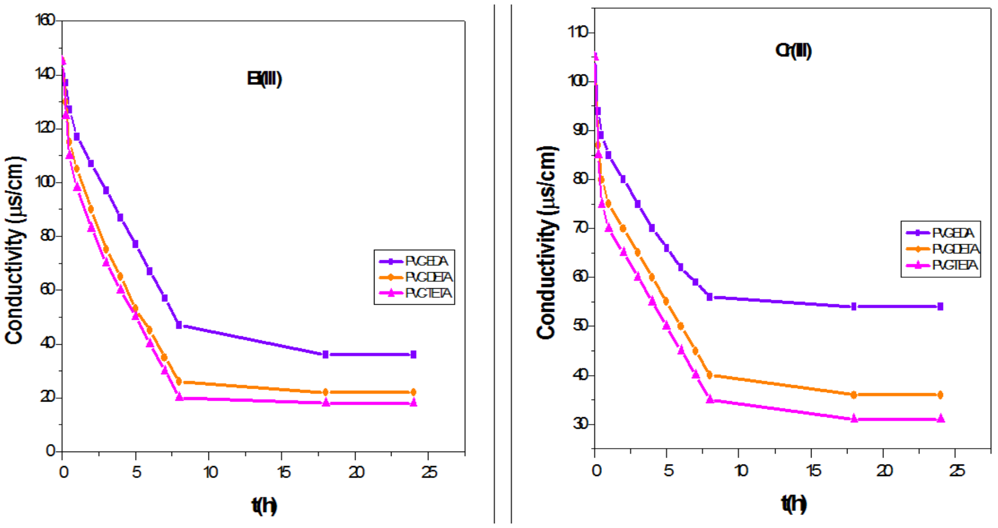


Fig. 5. Conductivity-time plots of Bi(III) and Cr(III) while interacting with polymers.

extraction. As the remaining vacant surface sites decreasing, the extraction rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase.

CONCLUSION

In this work, three chelating resins were synthesized via chemical grafting of polyamine groups on poly (vinyl chloride), leading to resin polymers named PVC-EDA, PVC-DETA, and PVC-TETA. FT-IR and EA characterization results confirmed the existence of the components and active functional groups, which are responsible for metal extraction. The polymers were tested for the extraction of metals ions (Cr and Bi). The removal extent of these hazardous and toxic metals was substantial, more than 97%; better extraction efficiency was observed towards Bismuth ions as the more selected one. The polymers were found to extract these ions with a clear selectivity, it seems to have an affinity following the order of Cr < Bi. These chelating polymers can be used as complexing agents that can be simply filtered, regenerated and reused repeatedly. Although the actual supported ligands prepared in this paper could minimize and decrease the negative effects of hazardous metals on the environment.

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