Involvement of hybrid materials based on natural clay and poly(vinyl chloride) into extraction of metal cations

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Abstract: The solid-liquid extraction is one of the most used methods for protection of the environment against organic and inorganic pollutants. The hybrid materials have been synthesized by a simple method from natural clay and modified poly(vinyl chloride) (PVC). The obtained products were characterized by various techniques, infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The final materials were successfully used for entrapping heavy metal ions (Fe, Cu, Cd, Zn, Pb, Mn, and Co). The quantities of adsorbed metal cations were determined by atomic absorption analysis. It has been revealed that the metals extraction was governed essentially by the affinity between the functional groups of the hybrid material and the investigated metal ion. The cations are extracted in the following decreasing order of effectiveness: $Fe^{3+} > Cu^{2+} > Co^{2+} \approx Mn^{2+} > Pb^{2+} > Cd^{2+} \approx Zn^{2+}$.

Keywords: modified poly(vinyl chloride), clay, hybrid material, metal cations, extraction.

Wykorzystanie materiałów hybrydowych na bazie modyfikowanego poli(chlorku winylu) napełnionego naturalną glinką w ekstrakcji kationów metali

Streszczenie: Proces ekstrakcji w układzie ciało stałe-ciecz jest najczęściej stosowany w celu ochrony środowiska przed działaniem szkodliwych, organicznych i nieorganicznych zanieczyszczeń. Materiały hybrydowe zsyntetyzowano w prosty sposób z modyfikowanego poli(chlorku winylu) i naturalnej, tunezyjskiej glinki. Otrzymane materiały badano różnymi metodami: spektroskopii w podczerwieni (FT-IR), analizy termograwimetrycznej (TGA) oraz różnicowej analizy termicznej (DTA). Oceniano przydatność otrzymanych materiałów hybrydowych w procesach ekstrakcji kationów metali ciężkich: Fe, Cu, Cd, Zn, Pb, Mn i Co w układzie ciało stałe-ciecz. Ilości zaadsorbowanych kationów oceniano metodą absorpcji atomowej. Wykazano, że ekstrakcja metali jest możliwa dzięki powinowactwu grup funkcyjnych kompozytów hybrydowych z jonami metali. Za pomocą wytworzonych materiałów hybrydowych ekstrahowano badane jony w stopniu określonym następującą kolejnością: $Fe^{3+} > Cu^{2+} > Co^{2+} \approx Mn^{2+} > Pb^{2+} > Cd^{2+} \approx Zn^{2+}$.

Słowa kluczowe: modyfikowany poli(chlorek winylu), glinka, materiał hybrydowy, kationy metali, ekstrakcja.

Lamellar clays are constituted by multiple organized elementary layers. Smectites are among the well studied clay minerals belonging to the family of the phyllosilicate 2:1, which structure involves colloidal particle size (< 2 μm). Negatively charged layers are composed of two tetrahedral sheets that sandwich the octahedral one [1–3]. Thanks to their important physicochemical properties as high permeability, large specific area, and high cation exchange capacity (*CEC*), these materials are widely used in diverse applications. Indeed, smectites were considered as a promising material in order to resolve problems related to engineering barriers against radioactivity and used as an adequate host matrix to immobilize metal cations, occurring essentially in industrial wastewater [4–8]. Numerous investigations have been carried out to improve the sorption performance of these clay minerals by intercalating diverse polymers into the smectite matrix [9–12]. Different terminologies have been used in the literature to describe the morphology and the state of dispersion of the hybrid materials [13]. The "interposed system" has been agreed as a performed system in which the degree of swelling of the clay in the polymer exceeds the original state.

The hybrid materials including polymer matrix and clay particles have been developed and the obtained clay-containing products were used as nanofillers and extractors of metals. As a part of this approach, the current study describes a synthesis of hybrid materials using natural clay from Gafsa region from Tunisia (STG) and modified PVC. The resulting materials were used to remove heavy metals (Fe, Cu, Pb, Cd, Zn, Co, and Mn) from aqueous solutions.

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EXPERIMENTAL PART

Materials

Commercial poly(vinyl chloride) (PVC, *M* = 48 000, Fluka).

Tetrahydrofurane (THF, Sigma Aldrich), ethylenediamine (ED, Sigma Aldrich), diethylenetriamine (DET, Sigma Aldrich), triethylenetetramine (TET, Sigma Aldrich), 2-aminopyrimidine (Sigma Aldrich).

The clay is a dioctahedral phyllosilicate (2:1) represented by the following molecular formula: $Ca_{0.537}\ K_{0.263}Na_{0.038}(Si_{7.418}\ Al_{0.582})\ (Al_{2.442}Fe_{0.954}Mg_{0.468})\ O_{22}$ [14] and taken from Gafsa region (Tunisia).

Salts $Fe(NO_3)_3 \cdot 9\ H_2O$, $CuCl_2 \cdot 2\ H_2O$, $Pb(NO_3)_2$, $CdCl_2 \cdot H_2O$ and $ZnCl_2 \cdot 6\ H_2O$ were produced by Fluka, $MnCl_2 \cdot 4\ H_2O$, and $CoCl_2 \cdot 6\ H_2O$ were produced by Riedel-de-Haen AG.

Samples preparation

Synthesis of P_1

Poly(vinyl chloride) (5 g) was dissolved in THF (100 cm^3), 2-aminopyrimidine (4 g), ethylenediamine (6 cm^3) and KI (2 g) [14, 15]. The mixture was heated at 100 °C for 8 h. Thereafter, the reaction mixture was poured into distilled water (300 cm^3) . The modified PVC was filtered, washed with water and diethyl ether to remove the amine adsorbed on the polymer and dried at 65 °C for 24 h. The final obtained powder was brownish in color (6.7 g), the obtained polymer was labeled $\mathbf{P_1}$.

Synthesis of P_2

The reaction conditions were similar to that of $\mathbf{P_1}$, except that we changed the aliphatic amine (diethylenetriamine). The final obtained powder was brownish in color (6.2 g), the obtained polymer was labeled $\mathbf{P_2}$.

Synthesis of P_3

In this reaction, triethylenetetramine was used and the obtained powder was in dark brown color (7.1 g), the resulted polymer was called $\mathbf{P_3}$.

Preparation of clay

The natural clays were taken at 40 cm under ground surface. The raw clay (STG) was powdered, sieved (100 μm) and used for the purification procedure (sodium exchange). The purified clay was obtained by suspending 20 g of the sieved raw clay in 400 cm^3 of aqueous solution of sodium chloride (1 M). The suspension was stirred (100 rpm) for 12 h before being centrifuged (4 000 rpm, 10 min). The supernatant was removed and the clay was treated in the same way five times using fresh NaCl aqueous solutions. The excess of NaCl was removed by stirring in water (400 cm^3, 100 rpm, 5 min) and centrifugation (4 000 rpm, 10 min), followed by dialysis. The dialysis was performed on 2 g samples suspended in 200 cm^3 of distilled water placed in a dialysis membrane [cellulose, 20 cm long, 20.4 mm diameter, molecular weight cut-off (MWCO) 6–8 kD] against 1 dm^3 of distilled water. Distilled water was changed from time to time until complete disappearance of chloride ions using silver nitrate test (1 M $AgNO_3$). After over-night standing, the suspension was decanted, evaporated and dried at 50 °C in order to obtain the purified and sodium exchanged clay (**STG-Na$^+$**) [16].

Preparation of hybrid materials

The preparation technique is called exfoliation/adsorption [17]. It is divided into three main steps: 1 g of purified clay was first swollen in 30 cm^3 of THF, then 1 g of modified PVC was introduced into this mixture, finally the solvent was removed by evaporation and the obtained thin film was crushed and dried in an oven at 60 °C for 24 h.

The obtained final products were called $\mathbf{STG\text{-}P_1}$, $\mathbf{STG\text{-}P_2}$ and $\mathbf{STG\text{-}P_3}$.

Extraction of some metal ions

The following metal cations (Fe^{3+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+}) were used in the extraction study of the synthesized hybrid materials. Aqueous solutions $Fe(NO_3)_3 \cdot 9\ H_2O$, $CuCl_2 \cdot 2\ H_2O$, $CdCl_2 \cdot H_2O$, $ZnCl_2 \cdot 6\ H_2O$, $Pb(NO_3)_2$, $MnCl_2 \cdot 4\ H_2O$, and $CoCl_2 \cdot 6\ H_2O$ were prepared at a concentration of 50 mg/dm^3 of each salt. Then 0.1 g of the prepared adsorbent was incubated in 20 cm^3 of the metal ion aqueous solution at 25 °C for 48 h. The suspension was filtered and the aqueous solution analyzed.

Methods of testing

The obtained compounds were characterized by infrared analysis using the attenuated total reflectance technique (ATR/FT-IR). A Nicolet IR 200 FTIR spectrometer (France) was used for IR spectra, differential thermal analysis (DTA), thermogravimetric analysis (TGA) were performed on a SETARAM TGA92 (France). The samples (23 mg) were placed in 0.04 cm^3 aluminum pans, and recorded under argon atmosphere between 30 and 600 °C at a speed of 10 °C/min.

Elemental analyses (EA) of C, H, and N were performed by Perkin Elmer analyzer CHN series II 2400.

The amount of remaining metal ions in aqueous solutions was evaluated by atomic absorption spectroscopy on a Jenna NovAA 400 (Japan).

The results of the metal ion extraction for each hybrid material were expressed as percentages, of their initial concentration. The percentage was calculated using the following expression:

$$E = [(Ci - Cf) / Ci] \cdot 100\ \%$$

where: *Ci* – the initial concentration of the metal in aqueous solution, *Cf* – the concentration of the remaining quantity of the metal ion in aqueous final solution.

RESULTS AND DISCUSSION

Modified PVC

Infrared spectroscopy

The IR spectra (Fig. 1) of the **P**$_1$, **P**$_2$ and **P**$_3$ obtained products show the presence of the characteristic band of aromatic carbons $\upsilon_{C=C}$ located at 1450 cm^{-1}, their hydrogen υ_{CAr-H} at 3250 cm^{-1}, while the characteristic valence band of the primary amine (υ_{N-H}) appears at 3380 cm^{-1} [18]. The characteristic deformation band in the plane of N-H group, and the vibration (υ_{C-N}) appear respectively at 1660 cm^{-1} and 1290 cm^{-1}. The characteristic band of the aliphatic CH$_2$ is located at 2862 and 2940 cm^{-1}. It is necessary to mention that there is a decrease in the intensity of the stretching vibration band of the C-Cl group that appears around 650 cm^{-1} (Fig. 1).

Elementary analysis

The results of the elemental analysis (C, H, and N) of modified PVC are given in Table 1. The polymers **P**$_1$, **P**$_2$ and **P**$_3$ were found to contain 8.99, 6.7 and 11.87 % of nitrogen, respectively.

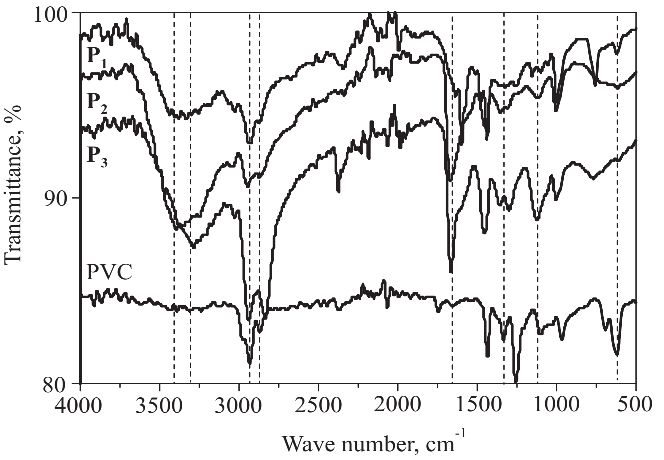


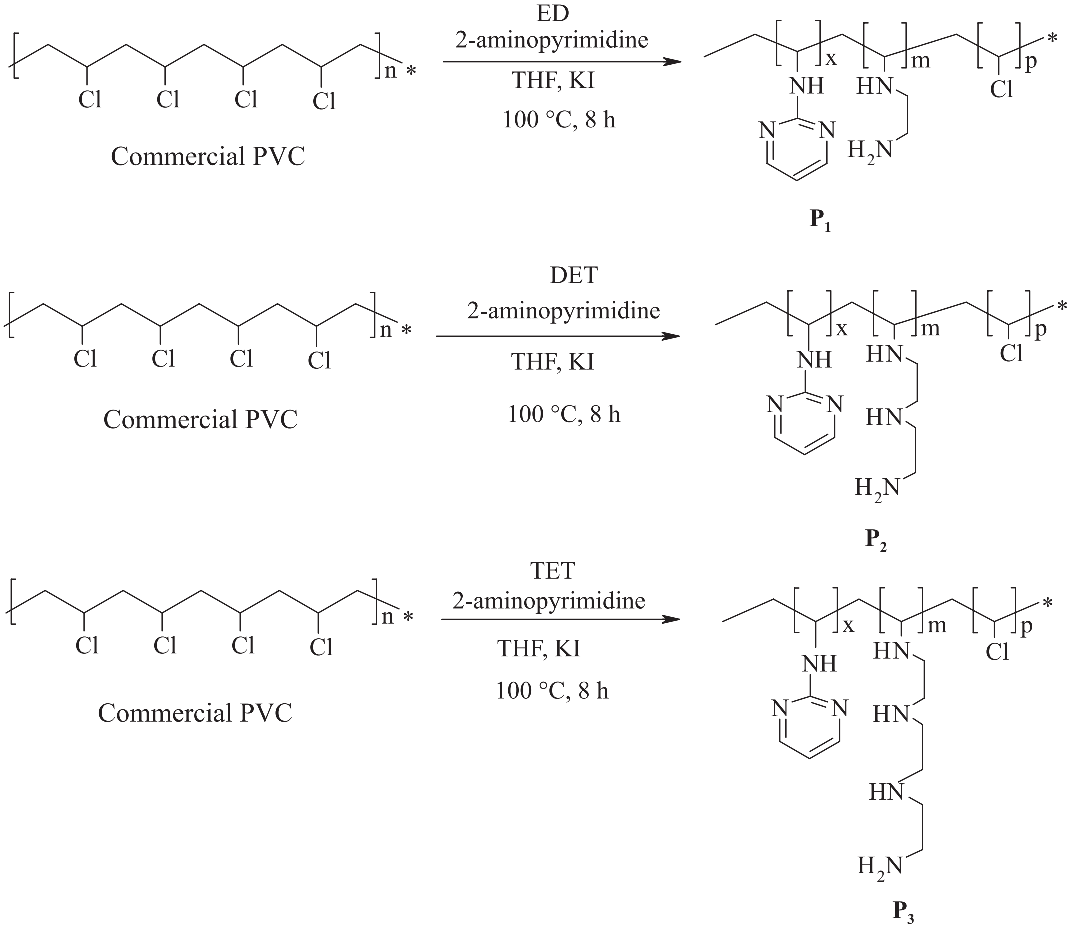
Fig. 1. IR spectra of poly(vinyl chloride) modified by amines molecules

Based on the analytical results obtained by different physicochemical analyses we propose the following structures for the three materials **P**$_1$, **P**$_2$ and **P**$_3$ in Scheme A.

Hybrid materials based on PVC

IR spectroscopy

IR spectra (Fig. 2, Fig. 3) of the obtained hybrid materials **STG-P**$_1$, **STG-P**$_2$ and **STG-P**$_3$ show the presence of the characteristic band of the function Si-O at 1036 cm^{-1} [19].



Scheme A

T a b l e 1. Results of elemental analysis of amine-modified PVC

Sample	Atom percentage, %		
	C	H	N
P_1	55.031	8.316	8.995
P_2	61.545	6.366	6.700
P_3	56.352	8.933	11.876

The characteristic bands of aromatic ring $\upsilon_{C=C}$ are located at 1450 cm^{-1}, C-H at 3200 cm^{-1}, characteristic band of the valence of the primary amine (υ_{N-H}) appears at 3380 cm^{-1}, characteristic band of the deformation in-plane δ_{NH} appears at 1640 cm^{-1}. Stretching mode vibration (υ_{C-N}) corresponds to the band at 1290 cm^{-1}, two characteristic bands of aliphatic CH_2 are located at 2862 and 2940 cm^{-1} and stretching mode vibration band of Al-OH at 3640 cm^{-1} [20].

DTA-TGA analysis

We followed the thermal stability of the hybrid materials by DTA-TGA analysis. The DTA-TGA thermograms of hybrid materials (Fig. 4, Table 2) show three endothermic peaks observed at 72 °C, 330 °C and 497 °C for **STG-P$_1$** accompanied by a mass loss of 5, 9 and 6 wt %, respectively. For **STG-P$_2$** these peaks are observed at 74 °C, 334 °C, 500 °C accompanied by a mass loss of 6, 10 and 7 wt %, respectively. For **STG-P$_3$** these peaks appear at 78 °C, 340 °C and 510 °C accompanied by a mass loss of 6, 9.2 and 8.4 wt %, respectively. The first peak for such hybrid materials corresponds to the solvent evaporation. The second shows the decomposition of organic element, whereas the last one corresponds to the removal of -OH group from clay.

Extraction of some metal ions

Extraction with same mass mixtures 50/50

The average of three experiments was expressed as a percentage of the extraction of the metal, based on its initial concentration (Fig. 5).

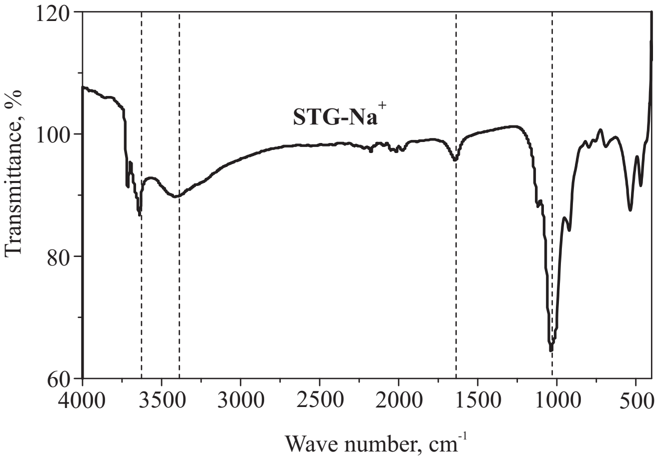


Fig. 2. IR spectra of purified clay

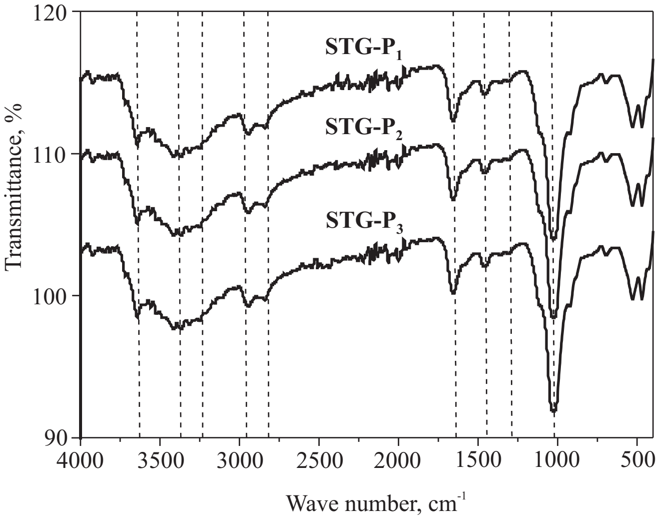


Fig. 3. IR spectra of studied hybrid materials

Figure 5 shows that the extraction percentage of the studied metals by purified clay (**STG-Na$^+$**) is higher than with the use of raw washed clay. The histogram shows also that the extraction of Fe^{3+}, Cu^{2+}, and Mn^{2+} using mixed clay with modified polymers gives better results than that using the sodium exchanged clay. The extraction percentages of Fe^{3+}, Cu^{2+}, and Pb^{2+} by mixed clays with modified polymers was in the order of 78 ± 1.4 %, 71 ± 1.7 % and 60 ± 2.1 %. The extraction efficiency of cations such as Fe^{3+} and Cu^{2+} by sodium exchanged clay was from 60 ± 1.3 % to 51 ± 2 %. The extraction of Co^{2+} was from 32 ± 1.7 % with studied clays. Exceptionally for Pb^{2+} the yield is 33 ± 1.4 % with **STG-Na$^+$**. The examination of Fig. 5 reveals that the extraction of Cd^{2+} and Zn^{2+} was low

T a b l e 2. Results of DTA-TGA of studied hybrid materials

Sample	DTA	TGA	Interpretation
STG-P$_1$	72 °C (endo) 330 °C (endo) 497 °C (endo)	5 wt % 9 wt % 6 wt %	Solvent evaporation [21] Decomposition of organic element [22] Removal of OH group from clay [21]
STG-P$_2$	74 °C (endo) 334 °C (endo) 500 °C (endo)	6 wt % 10 wt % 7 wt %	Solvent evaporation Decomposition of organic element Removal of OH group from clay
STG-P$_3$	78 °C (endo) 340 °C (endo) 510 °C (endo)	6 wt % 9.2 wt % 8.4 wt %	Solvent evaporation Decomposition of organic element Removal of OH group from clay

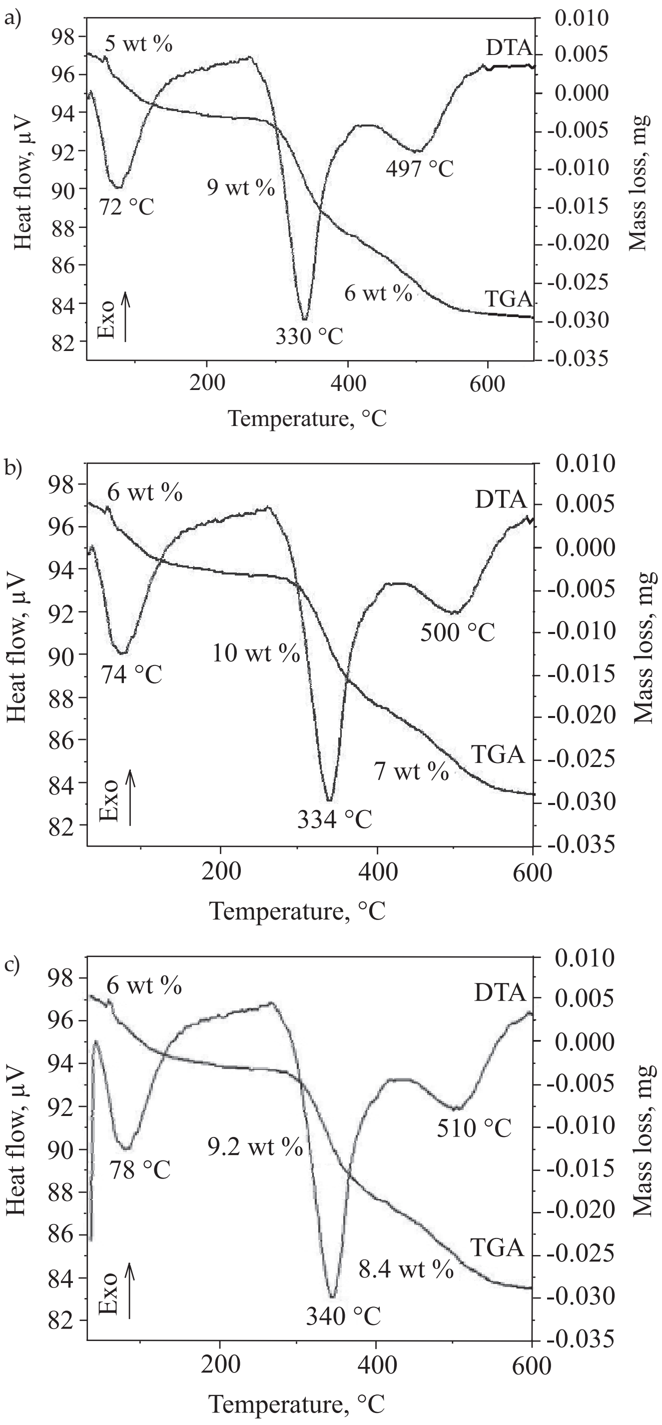


Fig. 4. DTA-TGA thermograms of studied hybrid materials: a) STG-P_1, b) STG-P_2, c) STG-P_3

using modified clays, and the extraction yield was in the order of 20 ± 1.8 %. Metals extraction by modified clays varied in the following decreasing order $Fe^{3+} \geq Cu^{2+} \geq Mn^{2+} > Pb^{2+} > Co^{2+} > Cd^{2+} \approx Zn^{2+}$.

The investigation results show that the modified PVC: **P_1**, **P_2** and **P_3** used in metal cations extraction have an extraction power much higher than the purified clay **STG-Na$^+$**. For the prepared hybrid materials **STG-P_1**, **STG-P_2** and **STG-P_3** the level of extraction increases with the same selectivity scheme like as for other used adsorbents **P_1**, **P_2**, **P_3**.

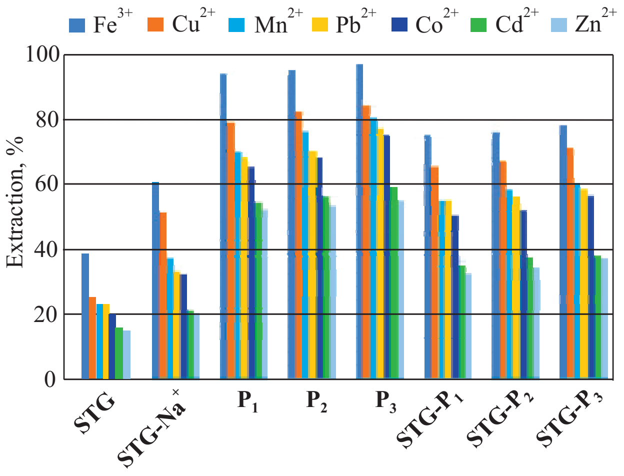


Fig 5. Percentages of extraction of metal cations with: raw clay (STG), STG-Na$^+$, P_1, P_2, P_3, 50/50 mixture of STG-Na$^+$ and P_1, 50/50 mixture of STG-Na$^+$ and P_2, 50/50 mixture of STG-Na$^+$ and P_3

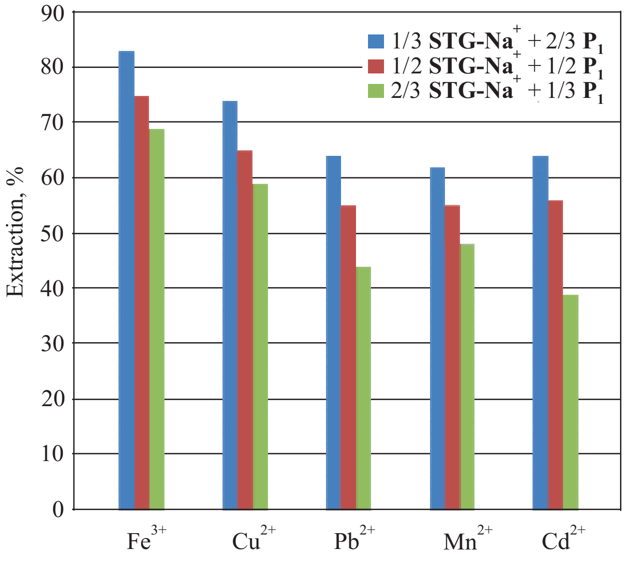


Fig. 6. Percentages of extraction of metal cations with mixtures of different mass ratio between STG-Na$^+$ and modified polymer P_1

Extraction with different mass mixtures

The extraction results given in Fig. 6 show that the extraction yield increases with an increase in PVC-amine mass in the hybrid material. This consequence can be explained by the complexing cavity structures with nitrogen atoms. The presence of the heteroatom (N) enables the formation of non-covalent bonds (van der Waals bonding) with the metal, which stabilize the formed complexes. The percentage of metal extraction varies from one metal to another, reaching the maximum value and high selectivity for Fe^{3+}. It has been notable that the average time of extraction with clays and modified clays was within 3 days. However, the extraction times using the synthesized polymers **P_1**, **P_2**, **P_3** did not exceed 12 h.

CONCLUSIONS

In the present paper, three polymers were synthesized *via* chemical modifications of PVC with 2-aminopyrimidine, ethylenediamine, diethylenetriamine and triethylenetetramine on a commercial poly(vinyl chloride), leading to the formation of polymers called $\mathbf{P_1}$, $\mathbf{P_2}$, and $\mathbf{P_3}$. These polymers were mixed (50/50) with a purified clay (**STG-Na**$^+$) to get various hybrid materials named **STG-P**$_1$, **STG-P**$_2$ and **STG-P**$_3$, respectively. The structures of polymers and hybrid materials were evaluated by ATR FT-IR, EA, TGA and DTA analysis. The obtained hybrid materials were used to extract metal ions from aqueous solutions. The orders of adsorption capacity for Fe^{3+}, Cu^{2+}, Pb^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+} cations were as follows: **STG-P**$_3$ > **STG-P**$_2$ > **STG-P**$_1$ in relation with variable number of nitrogen atoms. These studies show also that all hybrid materials exhibited good adsorption capacity for Fe(III).

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