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POLIMERY

CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

Synthesis of new polymers containing 1,2,3-triazole units from poly(vinyl chloride) *via* "click" chemistry catalyzed by copper iodide and its application in extraction of nitrates and metals contained in wastewater

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Abstract: New polymers with potential application in a wastewater purification from inorganic contaminants were synthesized *via* a chemical modification of poly(vinyl chloride) by "click" method based on copper(I)-catalyzed Huisgen reaction. The structure of the resulting polymers containing 1,4-disubstituted triazole units was confirmed by infrared spectroscopy (ATR-FTIR), nitrogen elemental analysis and differential thermal analysis (DTA). The obtained polymers were subsequently used in the elimination of nitrate ions and metal ions from the wastewater of Beja region (Tunisia). It was found that new polymers were most efficient in capturing of zinc ions, the average extraction percentage of Zn^{2+} was 28 %, while the average extraction percentage of nitrates did not exceed 12.5 %. The selectivity of the binding of investigated ions can be arranged in the following order: $Zn^{2+} > NO_3^- > Ca^{2+} > Mg^{2+}$.

Keywords: "click" chemistry, poly(vinyl chloride), 1,4-triazoles, extraction, nitrates, metals, wastewater.

Nowe polimery zawierające jednostki 1,2,3-triazolowe, syntetyzowane z poli(chlorku winylu) w reakcji „click" katalizowanej przez jodek miedzi, stosowane do ekstrakcji ze ścieków jonów azotanowych i jonów metali

Streszczenie: W wyniku chemicznej modyfikacji poli(chlorku winylu) metodą „click", opartej na reakcji Huisgena katalizowanej za pomocą miedzi, zsyntetyzowano nowe polimery o potencjalnym zastosowaniu do oczyszczania ścieków z zanieczyszczeń związkami nieorganicznymi. Nowe zsyntetyzowane polimery zawierają w swojej budowie jednostki 1,4-dwupodstawionego triazolu. Strukturę otrzymanych polimerów potwierdzono metodami spektroskopii w podczerwieni (ATR-FTIR), analizy elementarnej azotu i analizy termicznej (DTA). Polimery te wykorzystano następnie do eliminacji jonów azotanowych i jonów metali występujących w wodach ściekowych w regionie Beja (Tunezja). Stwierdzono, że nowe

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polimery najefektywniej wychwytują jony cynku (Zn), średni procent ekstrakcji (% E) wynosił 28 %, a średni procent ekstrakcji azotanów nie przekraczał 12,5 %. Selektywność wychwytu badanych jonów przez zsyntetyzowane polimery można uszeregować następująco: $Zn^{2+} > NO_3^- > Ca^{2+} > Mg^{2+}$.

Słowa kluczowe: reakcje „click", poli(chlorek winylu), 1,4-triazole, ekstrakcja, azotany, metale, ścieki.

In the countries with semi-arid climate, such as Tunisia, Algeria, Morocco, and many southern Mediterranean countries, wastewater present a significant source to minimize the deficit of water [1]. The use of wastewater can cause several risks to environment and human health. Nitrates, phosphates, organic compounds, metals and chlorides present the major pollutants in the origin of these risks [2–9]. The elimination of these pollutants was not usually achieved by natural processes. Farmers use this wastewater in irrigation, because they were rich in nutrients elements [10]. These pollutants can be accumulated in the soil, absorbed by plants [11, 12], and can also pollute groundwater [13]. The toxicity of heavy metals was mainly due to their tendency to accumulate in living organisms and to concentrate along trophic chains [14]. To eliminate these toxic pollutants, an attempt to synthesize new polymers by modification of poly(vinyl chloride) was made in this study. The "click" chemistry based on the Huisgen reaction catalyzed by copper(I) iodide was used in this synthesis [15–19]. The polymers containing 1,4-triazoles were tested in the removal of nitrates and metal ions contained in wastewater taken from the Beja region (Tunisia). Scheme A summarizes the approach used in this synthesis and the elimination mechanism of nitrates and metal ions present in studied wastewater.

EXPRIMENTAL PART

Materials

Poly(vinyl chloride), with high molecular weight (*Mw* = 48 000, 16 mmol of Cl/g; 99 %), were used as-received from Fluka (France), 1-chloro-2-[2-(2-chloroethoxy)-ethoxy]ethane ($C_6H_{12}O_2Cl_2$, *M* = 187.065 g/mol; 99 %), quinic acid ($C_7H_{12}O_6$, *M* = 192.17 g/mol), propargyl amine (C_3H_5N, *M* = 55.08 g/mol; 98 %), dipropargyl amine (C_6H_7N, *M* = 93.13 g/mol; 97 %), copper(I) iodide (99.5 %), sodium azide (99 %), sodium sulfate (99 %), acetone (97 %), *N'N*-dimethyl formamide (DMF), diethyl ether (99 %), methylene chloride (CH_2Cl_2), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), methanol (MeOH) and triethylamine (Et_3N) were purchased by Sigma Aldrich (France).

The samples of wastewater were taken from the treatment station of Beja region (36°44' North, 9°11' East, Tunisia). The collection of samples of wastewater was taken in the first week of January 2017. The sampling of wastewater was taken by immersing the glass bottle in the basin at 15 cm in depth. The sample was maintained at 4 °C and filtered before treatment.

Synthesis of 1-azido-2-[2-(2-azidoethoxy)ethoxy]-ethane (A)

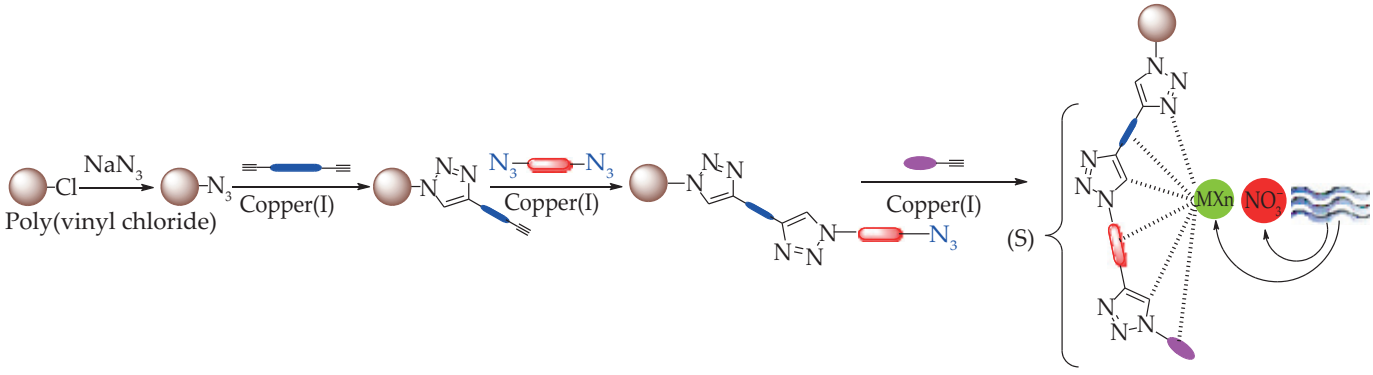
Sodium azide (5.85 g, 90 mmol) was added to a solution of 1-chloro-2-[2-(2-chloroethoxy)ethoxy]ethane (5.61 g, 30 mmol, 33 %) in 50 cm^3 of DMF. The reaction mixture was stirred under nitrogen at 80 °C for 20 h. The resulting product was washed with distilled water (750 cm^3) and extracted by diethyl ether (3 · 50 cm^3). The organic phase was washed three times with distilled water (3 · 50 cm^3) for removing sodium azide unreacted and dried over $MgSO_4$. After filtration, the solvent was evaporated under vacuum (4.18 g, 70 %) (Scheme B).

^{1}H NMR (**A**), $C_6H_{12}N_6O_2$: (300 MHz, $CDCl_3$, δ): 3.63 (t, 4H), 3.67 (t, 4H), 3.78 (t, 4H) ppm.

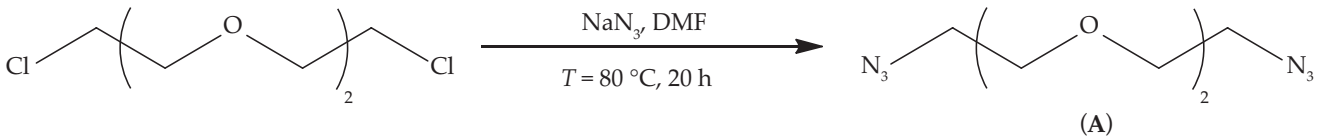
ATR-FTIR (**A**): 2873 (ν_{CH_2}), 2094 (ν_{N_3}), 1288 (ν_{C-N}) cm^{-1}.

Synthesis of (1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2-dimethyl-*N*-(prop-2-yn-1-yl)hexahydro-2H-1,3-benzodioxole-5-carboxamide (C)

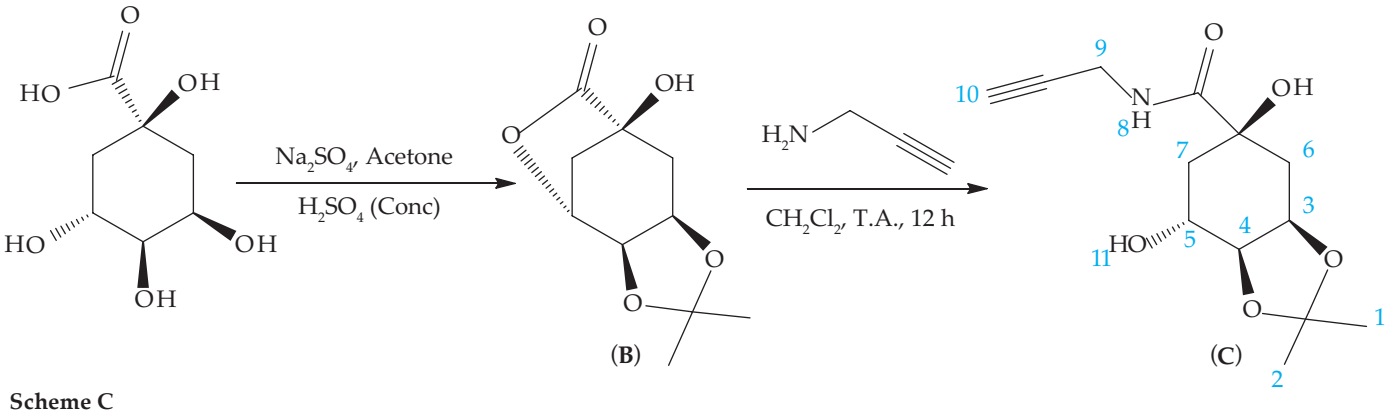
The alkyne (1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2-dimethyl-*N*-(prop-2-yn-1-yl)hexahydro-2H-1,3-benzodioxole-



Scheme A



Scheme B



Scheme C

Scheme D

-5-carboxamide (**C**) was prepared using the method described in the literature [20]. The synthesis protocol is presented in Scheme C.

^{1}H NMR (**B**), $C_{10}H_{14}O_5$: (300 MHz, $CDCl_3$, δ): 1.36 (s, 3H), 1.55 (s, 3H), 2.23 (dd, *J* = 15 Hz, *J* = 3 Hz, 1H), 2.40 (m, 2H), 2.68 (dd, *J* = 15 Hz, *J* = 3 Hz, 1H), 3.71 (s, 1H), 4.31–4.35 (m, 1H), 4.51–4.54 (m, 1H) and 4.72–4.75 (m, 1H) ppm.

^{1}H NMR (**C**), $C_{13}H_{19}NO_5$: (300 MHz, $CDCl_3$, δ): 1.36 (s, 3H, H-1), 1.52 (s, 3H, H-2), 2.01–2.44 (m, 5H, H-6, H-7 and H-10), 3.42–3.43 (d, 1H, H-11), 3.86–4.14 (m, 4H, H-3, H-4 and H-9), 4.56–4.58 (m, 1H, H-5) and 7.41 (d, 1H, H-8) ppm.

ATR-FTIR (**B**): 2984 (ν_{C-H}), 1747 ($\nu_{C=O}$), 1051 (ν_{C-N}), 1122 (ν_{C-O}) cm^{-1}.

ATR-FTIR (**C**): 3417 (ν_{O-H}), 3286 (ν_{NH}), 2985–2928 (ν_{CH}), 1653 ($\nu_{C=O}$), 1043 (ν_{C-N}) cm^{-1}.

Synthesis of poly(vinyl azide) (D)

The method of synthesis of poly(vinyl azide) was described in the literature [21]. The substitution reaction of Cl group by N_3 was characterized by elemental analysis, IR spectroscopy and thermal analysis (DTA). Protocol of synthesis is reported in Scheme D.

Elemental analysis: % N = 33.334 resulting 7.93 mmol N_3/g or 23.79 mmol N/g for the obtained resin. The yield of substitution reaction was 49.6 %.

ATR-FTIR: 2928 (ν_{CH_2}), 2097 (ν_{N_3}), 1663 ($\nu_{C=C}$) cm^{-1}.

[4-(*N*-propynylaminomethyl)triazol-1-yl] poly(vinyl chloride) (E)

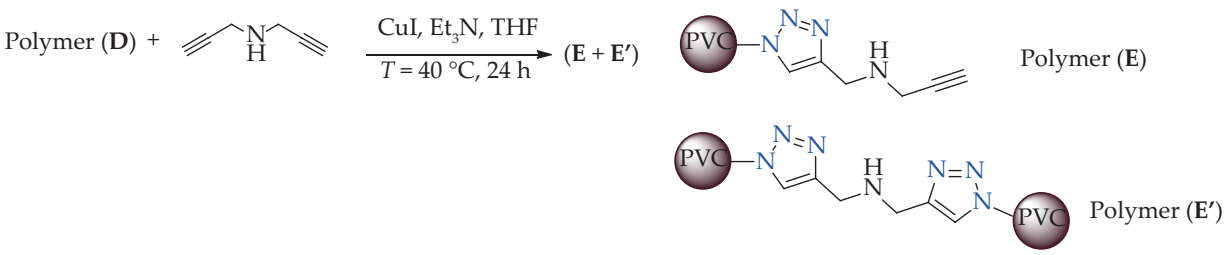
The new polymer alkyne (**E**) was synthesized by condensation reaction between the polymer azide (**D**) and dipropargyl amine (Scheme E). Poly(vinyl azide) (**D**) (1.6 g, 12.7 mmol of N_3) was suspended in 30 cm^3 of THF, after stirring for 30 minutes at room temperature, dipropargyl amine (2.33 g, 25 mmol, 2 eq), copper iodide (0.07 g, 0.37 mmol, 3 %) and triethylamine (21.5 cm^3, 16.12 g, 159 mmol, 12.5 eq) were added. The mixture was stirred at 40 °C for 72 hours. After filtration under vacuum, the polymer was washed three times with THF (10 cm^3), Et_3N (10 cm^3), methylene chloride (10 cm^3) and MeOH (10 cm^3) alternatively and then dried at 40 °C for 48 hours. The weight of the mixture (**E** + **E'**) was 2.28 g.

Elemental analysis: % N = 19.627, which give 14.01 mmol N/g for the obtained resin.

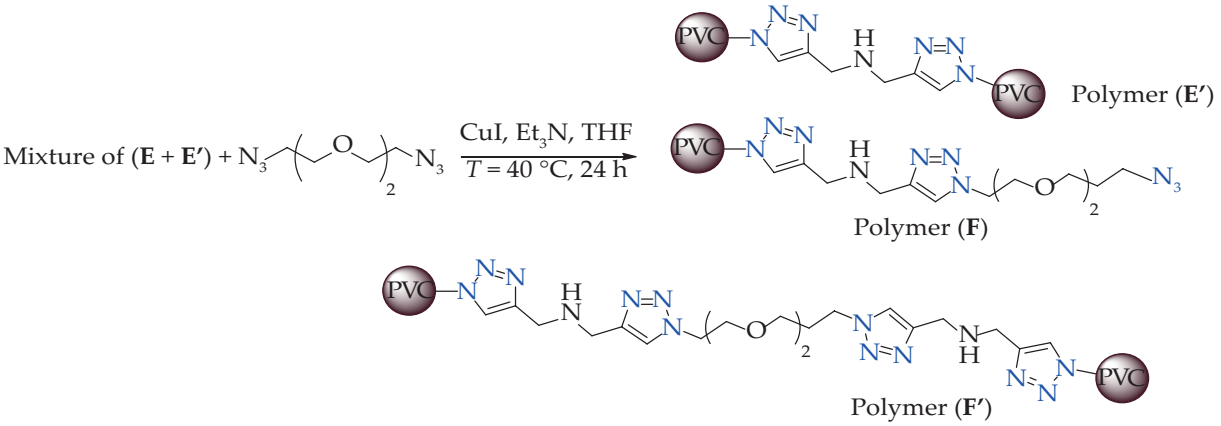
ATR-FTIR: 3361 (ν_{NH}), 2982 (ν_{CH_2}), 2124 ($\nu_{C\equiv C}$), 1651 ($\nu_{N=N}$) cm^{-1}.

[4-{2-[2-(2-azidoethoxy)ethoxy]ethyl}triazol-1-yl-(*N'*,*N*-dimethylamino)triazol-1-yl] poly(vinyl chloride) (F)

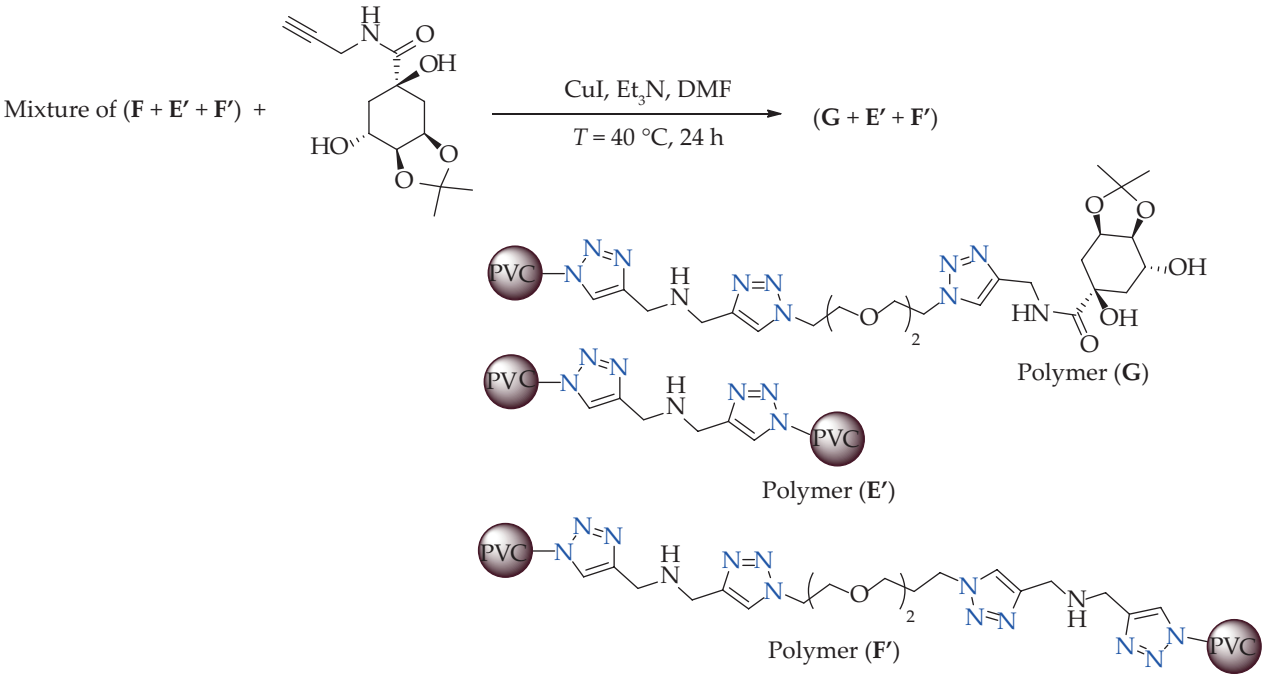
The reaction between polymer (**E**) and 1-azido-2-[2-(2-azidoethoxy)ethoxy]ethane (**A**) (Scheme F) gave



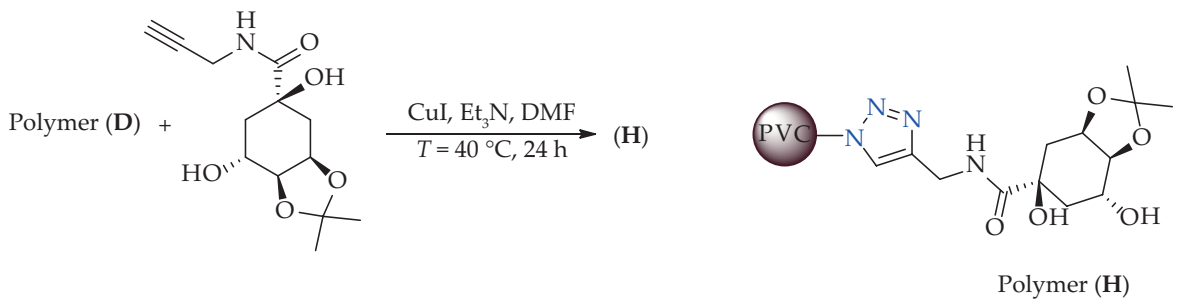
Scheme E



Scheme F



Scheme G



Scheme H

new polymer-supported triazole (**F** + **E′** + **F′**). Polymers (**E** + **E′**, 2 g) in 40 cm^3 of THF were stirred for 30 minutes, then 1-azido-2-[2-(2-azidoethoxy)ethoxy]ethane (**A**, 11.2 g, 56 mmol), copper iodide (0.06 g, 0.3 mmol) and Et_3N (31.5 g, 311 mmol) were added and the mixture slowly stirred at 40 °C during 72 hours. In order to avoid the coupling of two sites of compound containing azide groups, after filtration, the obtained polymer was washed three times with THF (10 cm^3), Et_3N (10 cm^3), methylene chloride (10 cm^3) and MeOH (10 cm^3) alternatively and then dried at 40 °C for 48 hours. The weight of obtained polymer (**F** + **E′** + **F′**) was 2.05 g.

Elemental analysis: % N = 18.9, which give 13.49 mmol N/g for the obtained resin.

ATR-FTIR: 2909 (ν_{CH_2}), 2106 (ν_{N_3}), 1606 ($\nu_{N=N}$) cm^{-1}.

[4-{4-(2-{2-(4-[(1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2--dimethylhexahydro-1,3-benzodioxole-5--carboxamidomethyl]triazol-1-yl)ethoxyethoxy}ethyl)-triazol-1-yl-(*N′*,*N*-dimethylaminotriazol-1-yl)triazol-1--yl}] poly(vinyl chloride) (G)

In 23 cm^3 of DMF, the mixture of polymer (**F** + **E′** + **F′**, 1 g), alkyne (**C**, 5.5 g, 20.42 mmol), copper iodide (50 mg, 0.26 mmol) and 10 cm^3 of Et_3N (7.5 g, 74 mmol) was prepared. The suspension was stirred at 40 °C during 24 hours, after filtration under vacuum, the obtained polymer (**G** + **E′** + **F′**), presented in Scheme G, was washed three times with DMF (10 cm^3), Et_3N (10 cm^3), CH_2Cl_2 (10 cm^3), MeOH (10 cm^3) and distillated water (50 cm^3) alternatively. Finally the polymer (**G** + **E′** + **F′**) was dried under vacuum at 60 °C for two days, the obtained experimental mass was 1.5 g.

ATR-FTIR: 3335–3450 (ν_{OH} and ν_{NH}), 2964 (ν_{CH_2}), 1735 ($\nu_{C=O}$), 1646 ($\nu_{N=N}$) cm^{-1}.

[4-{(1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2-dimethyl-hexahydro-1,3-benzodioxole-5-carboxamidomethyl}-triazol-1-yl] poly(vinyl chloride) (H)

By the condensation reaction between 1 g (7.93 mmol N_3) of PVC-azide (**D**) and alkyne (**C**, 5.5 g, 20.42 mmol, 2.57 eq) in presence of copper iodide (0.05 g, 0.26 mmol, 3.4 %) and 10 cm^3 of Et_3N (7.5 g, 74 mmol, 9.3 eq) in 24 cm^3 of DMF, the polymer (**H**) given in Scheme H was synthesized. The suspension was stirred at 40 °C during 72 hours, after filtration under vacuum, the polymer **H** was washed three times with DMF (10 cm^3), Et_3N (10 cm^3), CH_2Cl_2 (10 cm^3), MeOH (10 cm^3) alternatively and finally washed with 150 cm^3 of distillated water, this polymer was dried under vacuum at 60 °C for two days. The isolated mass of polymer was 0.9 g, which give the yield 29 %.

ATR-FTIR: 3441 (ν_{O-H}), 2937 (ν_{CH_2}), 1743 ($\nu_{C=O}$), 1646 ($\nu_{N=N}$) cm^{-1}.

Application of synthesized polymers in the extraction of nitrate and metals contained in wastewater

Polymers (**F** + **E′** + **F′**, **G** + **E′** + **F′** and **H**) have been studied independently in this treatment. 0.2 g of polymer was incubated with 20 cm^3 of wastewater at room temperature for 48 h, the suspension was filtrated on filter paper and washed several times with distilled water (5 · 50 cm^3), after drying, the polymer was washed with 50 cm^3 of distilled water at 50 °C during 20 min, the obtained new liquid phase was analyzed by atomic absorption spectroscopy and UV-Vis for dosing the quantity of metals and nitrate ions respectively, retained by these polymers.

Methods of testing

– Infrared analysis using the attenuated total reflectance technique (ATR-FTIR) was made on a Nicolet IR 200 FTIR (France) spectrometer between 4000 and 400 cm^{-1}. The relevant absorption bands of vibrations (ν) were indicated.

– Elemental analysis of nitrogen (N) was performed by using Perkin Elmer Analyzer CHN Series II 2400.

– Proton nuclear magnetic resonance spectra (NMR) were recorded on a Bruker Avance 300 at 300 MHz.

– Differential thermal analysis (DTA) was performed on a SETARAM TGA92. The samples (23 mg) were placed in 40 mm^3 aluminum pans and analyzed under argon between 15 and 400 °C at a heating speed of 10 °C/min.

– The UV-Vis spectra were measured using a UV--Vis spectrophotometer UV-5100B. The aqueous solution obtained after washing the polymer was analyzed to determine the concentration of nitrate ions retained on these polymer based on wavelengths of 204 and 215 nm. Distilled water was used as a blank in this study, calibration of spectrophotometer was performed by aqueous solutions of $NaNO_3$ at λ = 204 nm (absorbance = 0.1015 C + 0.0861; R^2 = 0.9922) and at λ = 215 nm (absorbance = 0.0693 C + 0.0415; R^2 = 0.9972).

– The amount of metal ions bound by synthesized polymers was evaluated by atomic absorption spectroscopy (AAS) analysis (Perkin–Elmer AAnalyst 200) calibrated with solutions of the studied metal (0.5–5 mg/dm^3). The results, average of three experiments, were expressed as percentages of extraction of metal, based on its initial concentration.

The percentage of nitrate removal was evaluated using the following equation [22]:

$$\% \text{ Extraction} = \frac{C_0 - C_i}{C_0} \cdot 100 \qquad (1)$$

C_0 – concentration of nitrate contained in wastewater before extraction, C_i – concentration of nitrate determined after extraction.

RESULTS AND DISCUSSION

Characterization of polymers synthesized from poly(vinyl chloride)

In this part, the chemical modification of poly(vinyl chloride) was carried out using a series of addition reaction. First, the substitution of chlorine by azide group was performed. Infrared spectroscopy (Figs. 1 and 2), elemental analysis of nitrogen and thermal analysis (Fig. 3 and Table 1) were used for characterization of the products of PVC modification. The glass-transition temperatures (T_g) of these polymers were determined by DTA (Table 1).

T a b l e 1. DTA studies of synthesized polymers from poly(vinyl chloride)

Polymer	T_g, °C	T_{exo}, °C	ΔH_{exo}, J/g
D	88	190	-958
E + E′	135	312	-556
F + E′ + F′	131	384	-281
G + E′ + F′	139	322	-651
H	148	Not observed	Not measured

Poly(vinyl azide) (D)

PVC-azide (**D**) containing 23.79 mmol N/g or 7.93 mmol N_3/g was synthesized by method described in literature [21], the yield of this substitution was 49.6 %. The structure of PVC-azide was confirmed by IR spectroscopy, the strong band observed at 2097 cm^{-1} (Fig. 1) was attributed to the valence vibrations of azido group (N_3). This substitution reaction was accompanied by removal of HCl molecule [23]. IR spectrum showed the existence of double bond observed at 1663 cm^{-1}. The results of DTA (Fig. 3) show the exothermic peak at 190 °C attributed for the decomposition of azido group [24], the other peak observed at 272 °C confirmed the deformation of polymer.

[4-(*N*-propynylaminomethyl)triazol-1-yl] poly(vinyl chloride) (E)

The coupled reaction between dipropargylamine and PVC-azide (**D**) give a mixture of two polymers **E** and **E′** (Scheme E). The structure of polymer (**E**) was confirmed by infrared spectroscopy (Fig. 2), and coherent with those find from the literature [25]. This mixture of obtained polymers contained 19.627 % of nitrogen or 14 mmol N/g. The IR spectrum of (**E**) shows a low band at 2124 cm^{-1} characterized the terminal alkyne (C≡CH), and the bands observed at 1651, 3361 cm^{-1} attributed for the vibration of N=N and NH groups, respectively (Fig. 1). The results of DTA (Fig. 3) show the exothermic peak observed at 312 °C attributed for the deformation of this polymer.

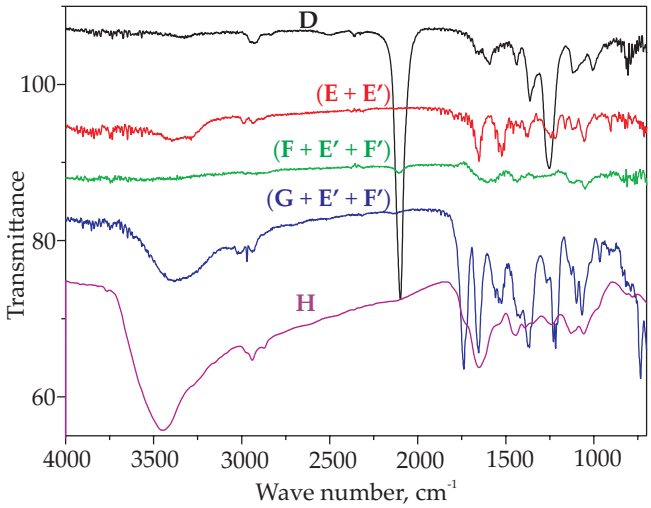


Fig. 1. IR spectra of synthesized polymers from poly(vinyl chloride) (D to H)

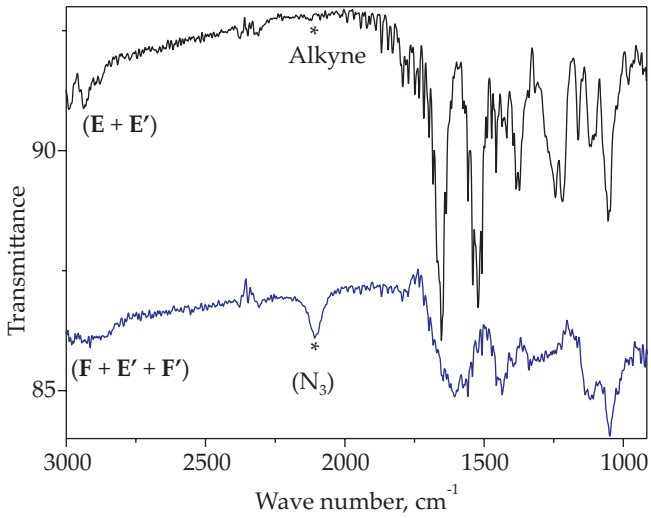


Fig. 2. IR spectra of polymers (E + E′) and (F + E′ + F′)

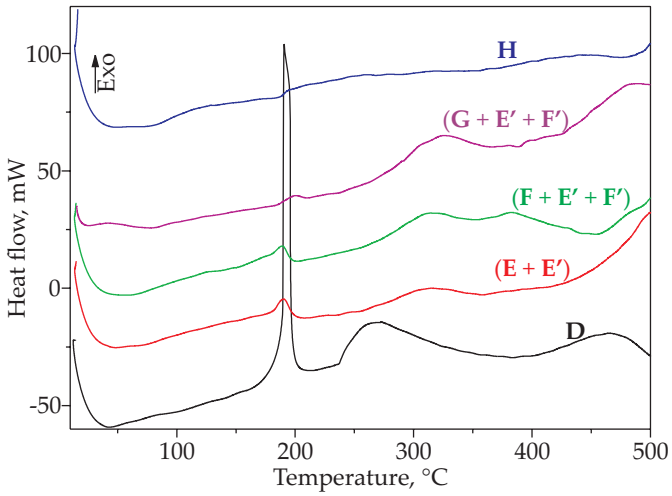


Fig. 3. Differential thermal analysis (DTA) of synthesized polymers from poly(vinyl chloride) (D to H)

[4-{2-[2-(2-azidoethoxy)ethoxy]ethyl}triazol-1-yl-(*N'*,*N*--dimethylamino)triazol-1-yl] poly(vinyl chloride) (F)

The polymer **E** was coupled with 1-azido-2-[2-(2-azidoethoxy)ethoxy]ethane (**A**) to obtain a mixture of polymers (**F** + **E′** + **F′**). The structure of **F′** was coherent with those obtained by Chernykh *et al*. [26]. The quantity of nitrogen present in the mixture of (**F** + **E′** + **F′**) was 0.189 N/g. The IR spectrum of (**F** + **E′** + **F′**) shows the existence of the characteristic bands N=N and N_3 observed, respectively, at 1606 and 2106 cm^{-1} (Fig. 2). The results of DTA (Fig. 3) show an exothermic peak observed at 384 °C attributed for the deformation of the polymer.

[4-{4-(2-{2-(4-[(1S, 3R, 5R, 7R)-5,7-dihydroxy--2,2-dimethylhexahydro-1,3-benzodioxole-5--carboxamidomethyl]triazol-1-yl)ethoxyethoxy}ethyl)-triazol-1-yl-(*N'*,*N*-dimethylaminotriazol-1-yl)triazol-1--yl}] poly(vinyl chloride) (G)

1 g of the (**F** + **E′** + **F′**) was reacted with terminated alkyne (1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2-dimethyl-*N*-(prop--2-yn-1-yl)hexahydro-2H-1,3-benzodioxole-5-carboxamide (**C**) to give the polymer (**G** + **E′** + **F′**). The IR spectrum presented in Fig. 1 confirms this coupling reaction, by the disappearance of the band observed at 2106 cm^{-1} characterized the N_3 group, and the appearance of the C=O group observed at 1735 cm^{-1} and N=N of heterocyclic triazole observed at 1655 cm^{-1}. The results of DTA (Fig. 3) show the exothermic peak at 322 °C attributed for the deformation of this polymer.

[4-{(1S, 3R, 5R, 7R)-5,7-dihydroxy-2,2-dimethyl-hexahydro-1,3-benzodioxole-5-carboxamidomethyl}-triazol-1-yl] poly(vinyl chloride) (H)

1 g of polymer (**D**) was coupled with terminated alkyne (**C**) in DMF to give the polymer (**H**). The IR spectrum presented in Fig. 1 confirms this coupling reaction by the disappearance of the N_3 group (2097 cm^{-1}) and the appearance of C=O and OH groups observed at 1743 and 3441 cm^{-1}, respectively. The results of DTA diagram presented in Fig. 3 show no adequate transformation for this polymer.

The results of thermal analysis by DTA are presented in Table 1 and Fig. 3.

Application of synthesized polymers in the extraction of nitrate ions contained in wastewater

The recent application of polymers synthesized from PVC was the treatment of wastewater of Beja region. The distilled water used in washing polymers (**F** + **E′** + **F′**), (**G** + **E′** + **F**′) and **H** after treatment was analyzed by the UV-Vis spectrophotometry to dose the concentration of nitrate ions retained by these polymers at 204 [27] and 215 nm [28]. The nitrate concentrations of the wastewater before treatment are 37.65 and 40.10 g/dm^3 at 204 and 215 nm, respectively, the average concentration was in the order of 38.87 ± 1.73 g/dm^3. The concentrations of the distilled water used in washing the mixture of polymers (**F** + **E′** + **F′**) after treatment are 5.58 ± 0.82 and 4.86 ± 0.62 g/dm^3 at 204 and 215 nm, respectively. The average concentration of nitrate was 5.22 ± 0.51 g/dm^3. Concentrations of nitrate ions present in distilled water used in washing (**G** + **E′** + **F′**) are 5.23 ± 0.20 and 4.15 ± 0.71 g/dm^3, respectively, at 204 and 215 nm. The average concentration was 4.69 ± 0.76 g/dm^3. Distilled water used in washing polymer **H** after treatment has the lowest concentration 3.08 ± 0.18 and 1.95 ± 0.80 g/dm^3 at 204 and 215 nm, respectively, the average concentration was 2.51 ± 0.80 g/dm^3.

By evaluating the percentage of nitrate extraction after the treatment by synthesized polymers (Table 2), it can be noticed that the polymer (**F** + **E′** + **F′**) gave the highest degree of nitrate removal 13.64 ± 2.00 % and 11.37 ± 1.45 %, determined, respectively, at 204 and 215 nm. The average value was 12.50 ± 1.60 %.

The polymer (**G** + **E′** + **F′**) gives a percentage of nitrate elimination comparable to that found by (**F** + **E′** + **F′**), with an average value of 11.25 ± 2.18 %.

The polymer **H** gave the lowest yield of nitrate removal, with a mean percentage of 6.05 ± 2.11 %.

From this study, it can be concluded that the derivative of quinic acid grafted on the polymer has no effect on the removal of nitrate ions, because the polymer **H** containing this derivative and not spacer (S) presented in Scheme A gave the smallest percentage of nitrate elimination (6.05 ± 2.11 %), whereas the polymer (**F** + **E′** + **F′**) containing the spacer (S) and not derivative of quinic acid gave the best nitrate removal efficiency (12.50 ± 1.60 %). On the other hand, the percentage of removal of nitrate ions obtained after treatment by polymer (**G** + **E′** + **F′**) was slightly decreased by comparison to the results obtained with polymers (**F** + **E′** + **F′**). This decrease was mainly due to the effect of the quinic acid derivative grafted on this polymer.

The pH of wastewater was 8.15 before treatment. After treatment by polymers (**F** + **E′** + **F′**), (**G** + **E′** + **F′**) and **H**, the pH values are 7.29, 6.61 and 7.97, respectively. This decrease in pH of wastewater after treatment by synthesized polymers was attributed at the fixation of some basic anions: nitrates, sulfates, phosphates and amines by these polymers [29].

Application of synthesized polymers in the extraction of metals contained in wastewater

The distilled water used in washing of (**F** + **E′** + **F′**, **G** + **E′** + **F′** and **H**) after treatment at 50 °C was analyzed by atomic absorption spectrometry to determinate the concentration of Mg, Zn and Ca retained by these polymers. Distilled water was used as a blank in this work. The concentrations of metals Mg, Zn, Ca in the wastewater before treatment are 17.45, 0.175 and 57.747 g/dm^3, respectively. The

T a b l e 2. Elimination of nitrate ions by synthesized polymers

Polymer	$[NO_3^-]$, g/dm^3 λ = 215 nm	% E λ = 215 nm	$[NO_3^-]$, g/dm^3 λ = 204 nm	% E λ = 204 nm
F + **E′** + **F′**	4.86 ± 0.62	11.37 ± 1.45	5.58 ± 0.82	13.64 ± 2.00
G + **E′** + **F′**	4.15 ± 0.71	9.71 ± 1.65	5.23 ± 0.20	12.80 ± 0.50
H	1.95 ± 0.80	4.56 ± 1.46	3.08 ± 0.18	7.54 ± 0.43
Wastewater	37.65	–	40.1	–

percentage retention of the metals studied was the average of three repetitions for each metal. Figure 4 shows the percentage of extraction (% E) of metals Mg, Zn and Ca retained, the conductivity (C) and the turbidity (TDS) of the distilled water obtained after washing the polymers used in this treatment. If we look at the Fig. 4, it can be seen that the polymers (**F** + **E′** + **F′**, **G** + **E′** + **F′** and **H**) have no efficiency for retaining the two metals: Mg and Ca, the percentage extraction does not exceed 4.85 ± 0.65 % for Ca and 1.2 ± 0.03 % for Mg. The extraction of Zn was better than that obtained for Mg and Ca. The percentages extraction of Zn are 28.67 ± 2.02, 21.83 ± 2.25 and 33.09 ± 2.29 % with the polymers (**F** + **E′** + **F′**, **G** + **E′** + **F′** and **H**), respectively. The average percentage of Zn extraction was 28 %. This result of Zn extraction was comparable with studies obtained by Taouil *et al*. [30], better than those found by Slimi *et al*. [31] and those found by Wang *et al*. [32]. The polymer **H** has a slightly better efficiency (33.09 ± 2.29 %) than (**F** + **E′** + **F′**) (28.67 ± 2.02 %) and (**G** + **E′** + **F′**) (21.83 ± 2.25 %), the polymers (**F** + **E′** + **F′** and **G** + **E′** + **F′**) contain the spacer (S), but the polymer **H** does not contain this spacer. We conclude that the spacer (S) has no effect on the extraction of Zn. The conductivities of distilled water obtained after washing the polymers (**F** + **E′** + **F′**, **G** + **E′** + **F′** and **H**) are 39.1 ± 5.23 μs/cm, 26.8 ± 0.84 μs/cm and 14.55 ± 0.64 μs/cm, respectively. These results show that the extraction of the mineral salts by the polymer (**F** + **E′** + **F′**) containing the spacer (S) and not the derivative of the quinic acid was better than that obtained with the polymer **H** not containing the spacer (S) and containing the quinic acid derivative. The polymer (**G** + **E′** + **F′**) containing the spacer (S) and the quinic acid derivative gives a slightly yield than (**F** + **E′** + **F′**) and better than **H** for the extraction of mineral salts. The conductivities of the distilled water obtained after washing the synthesized polymers used in treatment are consistent with results obtained for the turbidity of these same waters (**F** + **E′** + **F′**) 33.5 ± 9.19 mg/dm^3, (**G** + **E′** + **F′**) 26.8 ± 5.77 mg/dm^3, and **H** 14.66 ± 5.51 mg/dm^3. The distilled water used as blank has a conductivity of 5.8 μs/cm and a turbidity of 5 mg/dm^3.

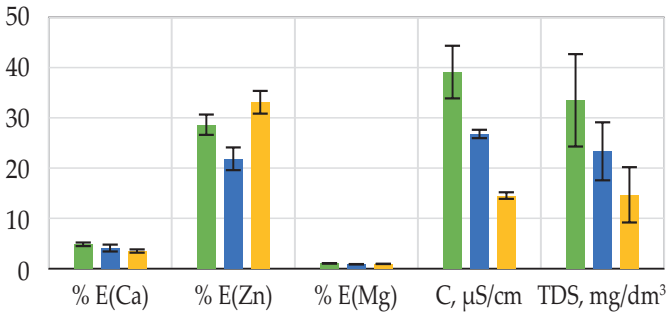


Fig. 4. Percentages of extraction (% E) of Ca, Zn and Mg retained by studied polymers, conductivity (C) and turbidity (TDS) of distillated water obtained after washing polymers (F + E′ + F′, green), (G + E′ + F′, blue) and H (yellow)

CONCLUSIONS

In this work, new polymers containing 1,4-triazoles units were synthesized from PVC using the concept of "click" chemistry. The obtained polymers were characterized by IR spectroscopy and thermal analysis (DTA). These polymers were tested for the extraction of nitrates and ions of metals (Ca, Mg and Zn) contained in wastewater of Beja region (Tunisia). This study shows that Zn was most efficiently retained by these polymers, the average percentage was 28 %. The synthesized polymers gave lower yields of the extraction of nitrates contained in the wastewater, the average extraction percentage did not exceed 12.5 % using the polymer (**F** + **E′** + **F′**). The selectivity order of tested ions was defined as follows: $Zn^{2+} > NO_3^- > Ca^{2+} > Mg^{2+}$.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

A. Klozinski, M. Barczewski – Porównanie technik pomiarowych typu *off-line*, *on-line* i *in-line* stosowanych w ocenie właściwości reologicznych kompozytów polietylenowych z węglanem wapnia (*j. ang*.)

M. Bhuvaneshwaran, P.S. Sampath, Suresh Sagadevan – Wpływ długości i zawartości włókien oraz ich obróbki alkalicznej na właściwości mechaniczne kompozytów epoksydowych wzmacnianych włóknami naturalnymi (*j. ang*.)

J. Kozakiewicz, J. Przybylski, K. Sylwestrzak – Synteza i charakterystyka elastomerów poli(siloksano-uretanowych) zawierających segmenty poli(tlenku etylenu) – jako potencjalnych materiałów membranowych (*j. ang*.)

D. Kuśmierczyk, J. Turło, P. Podsadni, K. Małkiewicz – Stabilność chemiczna klejów ortodontycznych opartych na sieci polimerowej w zależności od temperatury środowiska zewnętrznego (*j. ang*.)

M. Barczewski, J. Andrzejewski, D. Matykiewicz, A. Krygier, A. Kloziński – Wpływ przyspieszonego starzenia na mechaniczne i termomechaniczne właściwości kompozytów poli(kwasu mlekowego) z napełniaczem z odpadów naturalnych (*j. ang*.)

A. Drogoń, M. Pyda – Badanie procesu fizycznego starzenia amorficznego polilaktydu metodą różnicowej kalorymetrii skaningowej

K.J. Wilczyński, K. Buziak – Symulacja wytłaczania jednoślimakowego kompozytów polimerowo-drzewnych na podstawie pomiaru ciśnienia on-line (*j. ang*.)