

Article

“High-Throughput” Evaluation of Polymer-Supported Triazolic Appendages for Metallic Cations Extraction

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Abstract: The aim of this work was to find and use a low-cost high-throughput method for a quick primary evaluation of several metal extraction by substituted piperazines appendages as chelatants grafted onto Merrifield polymer using click-chemistry by the copper (I)-catalyzed Huisgen’s reaction (CuAAC). The polymers were tested for their efficiency to remove various metal ions from neutral aqueous solutions (13 cations studied: Li^+ , Na^+ , K^+ , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Ba^{2+} , Ce^{3+} , Hg^+ and Pb^{2+}) using the simple conductimetric measurement method. The polymers were found to extract all metals with low efficiencies ($\leq 40\%$), except for Fe^{3+} and Hg^+ , and sometimes Pb^{2+} . Some polymers exhibited a selectivity for K^+ , Cd^{2+} and Ba^{2+} , with good efficiencies. The values obtained here using less polymer, and a faster method, are in fair correspondence (average difference $\pm 16\%$) with another published evaluation by atomic absorption spectroscopy (AAS).

Keywords: polymer functionalization; click chemistry; CuAAC; complexants; metallic cations; complexation; depollution; catalysis

1. Introduction

Water pollution by metallic ions and other pollutants is becoming an increasing concern nowadays. This modification of the water, in all his reservoirs, is mainly due to Human activities with uncontrolled rejects of such pollutants. The pollution has a strong impact onto the global ecosystem as well as drinkable water sources. There is thus a strong need for methods to analyze traces and to remove the pollutants from water. Usual methods for removing metallic salts from water range from distillation to the use of engineered materials such as zeolites, polymers, membranes, *etc.* The long time known ion-exchange resins can be used for this purpose [1–3]. Usually, the polymers are engineered is such a way that their nature can be hydrophilic [4–7] or phobic [8,9], to meet the requirements for their use [10–14]. Many polymers have been designed in order to include chelatants to fix metal ions to be used in applications such as purification, depollution or catalysis [15–20].

Due to our interest into metal chelation, supported catalysis and Huisgen's reaction, we became interested into the preparation of polymers based on this approach [21–23]. We thus started to use the "click-chemistry" concept for polymer functionalization and especially copper (I)-catalyzed Huisgen's cycloaddition ("copper (I)-catalyzed azide/alkyne cycloaddition" or CuAAC) [24–29]. The use of CuAAC has the advantage to give a quick access of controlled substitutions onto the polymer by the use of its azided version and alkynes with various substituents [30–35]. This CuAAC is linking the azided polymer and the substituents bearing alkyne by forming the 1,4-triazole linkage. All the introduced substituents and the triazole can be implicated into chelation through a "triazole design", or a "pendant design", or both parts implicated into an "integrated design". The chelation can be a mono- or multi-dentate mode due to the vicinity of other chelating entities and the flexible structure of the polymer chains. (Figure 1) [34,35].

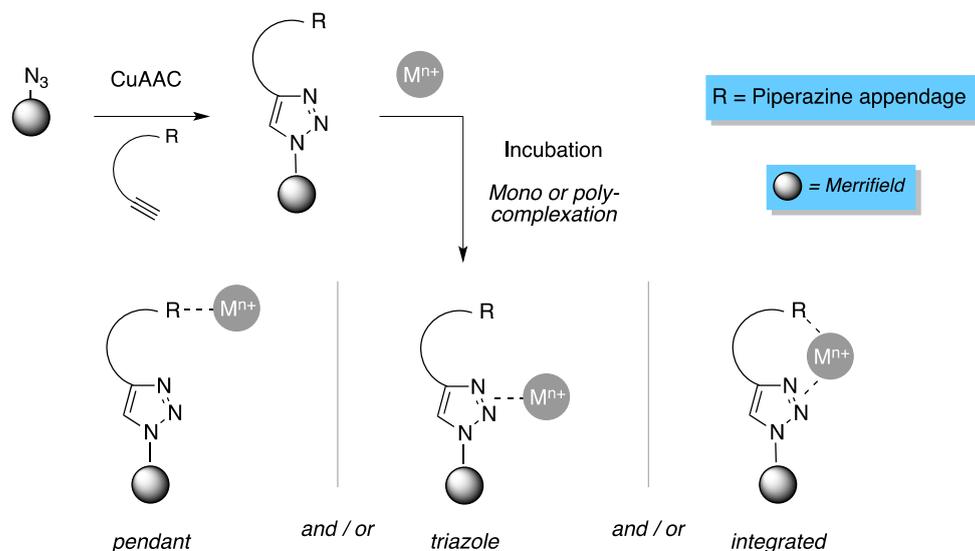


Figure 1. Functionalization of azido-Merrifield polymer by complexing appendages using copper (I)-catalyzed azide/alkyne cycloaddition (CuAAC) for a 1,2,3-triazole linkages and possible chelation modes.

The goal of this work was to try to find a faster method, using less polymer, for the evaluation of several metal cations complexation evaluation. We present in this communication the use of the less

sensitive conductimetric method for the study of piperazine-triazole-substituted poly(styrenes). The polymers were tested for their ability to extract metal cations salts (Li^+ , Na^+ , K^+ , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Ba^{2+} , Ce^{3+} , Hg^+ and Pb^{2+}) from neutral aqueous solutions. The results were found to be fair enough to be used for a primary evaluation at a “high-throughput” level when compared to our previous atomic absorption spectroscopy measurements (within $\pm 16\%$ average difference) [36].

2. Experimental Section

2.1. *N*-Substituted Piperazine Propargylcarbamates and Polymers

Poly(azidomethylstyrene) was prepared from Merrifield polymer as already reported. *N*'-propargylcarbamates of *N*-substituted piperazine, and the corresponding polymers containing triazole-linked piperazines preparations were described in a another publication as depicted in Figure 2 [36,37]. Typical procedures are indicated below.

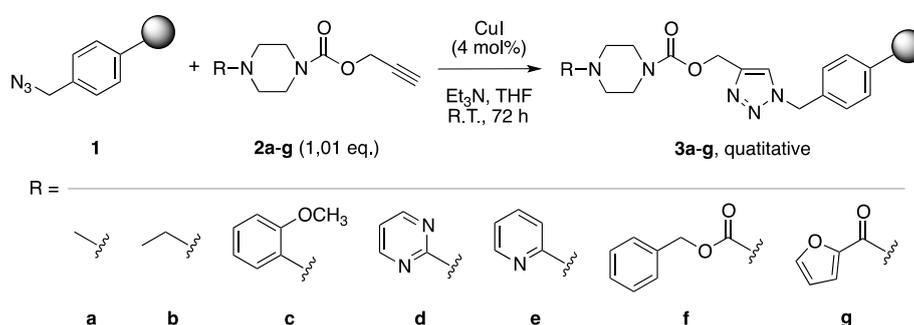


Figure 2. Synthesis of the polymers by CuAAC procedure.

2.1.1. General Procedure for the Synthesis of Propargylcarbamates Derivatives of Piperazines **2a–2g**

To a solution of the required *N*-substituted piperazine **1a** to **1g** (12.0 mmol) in acetonitrile (45 mL) was added Na_2CO_3 (1.27 g, 12.0 mmol, 1 eq.). Propargyl chloroformate (1.42 g, 1.17 mL, 12.0 mmol, 1 eq.) was then added dropwise. The reaction mixture was stirred for 48 h at room temperature and then filtered and evaporated under vacuum. The resulting carbamates **2a–2g** were sufficiently pure to be used without further purification.

2.1.2. General procedure for the Synthesis of Polymers **3a–3g**

Coupling reactions onto the polymer using CuAAC were conducted accordingly to the general procedure indicated below in round bottom flasks equipped with a reflux condenser. To a suspension of 3.00 g of azidomethyl polystyrene **A** ($1.82 \text{ mmol N}_3 \text{ g}^{-1}$, 5.46 mmol N_3) in THF (60 mL) was added 6.30 mmol (1.15 eq.) of the alkyne (**2a–2g**), 9.00 mL of triethylamine (6.75 g, 66.7 mmol, 12.2 eq.) and 2.40 mg of copper (I) iodide ($12.6 \mu\text{mol}$, 4 mol%). The suspension was slowly stirred at room temperature 72 h. After this time, the complete disappearance of the IR band of the azide of the polymer **A** (2103 cm^{-1}) was observed. The resulting polymer was filtered on sintered glass and washed sequentially with CH_2Cl_2 , pyridine, and MeOH (60 mL each), the sequential washings being repeated two other times. The resulting polymers **3a–3g** were finally dried overnight in an oven at $50 \text{ }^\circ\text{C}$.

2.2. Conductimetric Quick Primary Evaluation of Metals Complexation

2.2.1. Extraction

Neutral aqueous solutions of metal salts were prepared with 50 mg of LiCl (1.179 mmol), NaCl (0.856 mmol), KCl (0.671 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.253 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.124 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.210 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.210 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.293 mmol), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (0.248 mmol), $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.205 mmol), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (0.134 mmol), HgNO_3 (0.190 mmol) and $\text{Pb}(\text{NO}_3)_2$ (0.151 mmol) in 1 L of distilled water.

Aliquots of the each polymers (100 mg; **3a**: 0.137 mmol, **3b**: 0.134 mmol, **3c**: 0.121 mmol, **3d**: 0.126 mmol, **3e**: 0.126 mmol, **3f**: 0.117 mmol and **3g**: 0.123 mmol piperazine) were incubated in triplicate with 20 mL (50 mg L^{-1} , equals to 1 mg of salt) of each metal ion solution ($23.6 \mu\text{mol Li}^+$, $17.1 \mu\text{mol Na}^+$, $13.4 \mu\text{mol K}^+$, $5.05 \mu\text{mol Mn}^{2+}$, $2.47 \mu\text{mol Fe}^{3+}$, $4.20 \mu\text{mol Co}^{2+}$, $4.21 \mu\text{mol Ni}^{2+}$, $5.87 \mu\text{mol Cu}^{2+}$, $4.97 \mu\text{mol Cd}^{2+}$, $4.09 \mu\text{mol Ba}^{2+}$, $2.68 \mu\text{mol Ce}^{3+}$, $3.81 \mu\text{mol Hg}^+$ and $3.02 \mu\text{mol Pb}^{2+}$) at $25 \text{ }^\circ\text{C}$ for 24 h. The suspension was then filtrated on filter paper, which was previously washed with distilled water until no difference in conductimetry was observed between the washes and water.

2.2.2. Conductimetric Measurements

Evaluation of the chelated metal was done by conductimetric measurements on a bench Conductivity/TDS/ $^\circ\text{C}$ Meter CO 3000 L, pHenomenal[®] by VWR (Paris, France) on the filtrate by comparison with the conduction of the initial solution of the metal salt. The results, average of three experiments, were expressed as percentages of extraction of the metal (Figures 3 (below) and 4, Section 3.2).

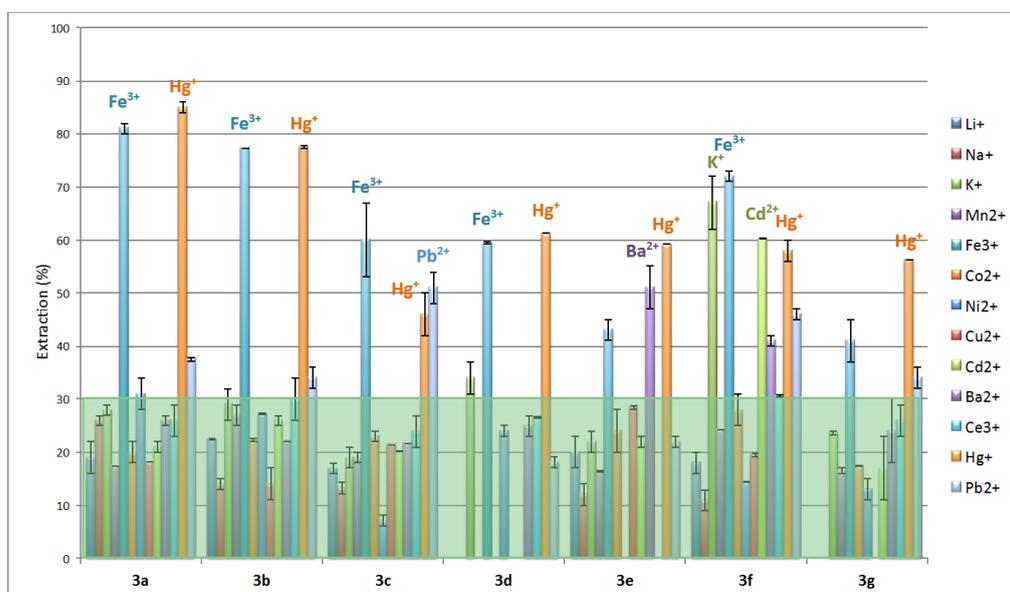


Figure 3. Extraction efficiencies of metal cations by the triazolic piperazine polymers **3a–3g** (cations extracted at levels $\geq 50\%$ are indicated).

3. Results and Discussion

3.1. Polymers Preparation

The polymers needed for this study have been prepared elsewhere [36]. They were easily accessible, in different substitution motifs, using poly(azidomethylstyrene) (**1**) and various *N*-substituted-piperazine-*N'*-propargylcarbamates (**2a–2g**). A CuAAC procedure afforded a quantitative reaction to form the triazole linkage onto the polymers **3a–3g** (Figure 2, Section 2.1) [36,37].

3.2. Extraction Results

After 24 h incubation on a 100 mg scale of the polymers in 20 mL of 50 mg L⁻¹ solutions of the salts (1 mg of salt, see Section 2.2.1 for details), the percentages of extraction for each metal were calculated by conductimetric differences between the initial and final solutions, each experiment having been carried out in triplicate. The results for each polymer as a function of the metallic cations are presented in Figure 3 (Section 2.2.2).

When looking at the whole results, we can observe that most of the cations were poorly extracted, at 30% or below, but exceptions. Since the polymeric structure differs only by the R substituent on the nitrogen (Figure 2, Section 2.1), an analysis has been done to understand the influence of the substituent's nature on the extraction.

In the alkyl series, polymer **3a**, R = Me, was a very good extractant for Fe³⁺ (81% ± 1%) and Hg⁺ (85% ± 1%), less for Pb²⁺ (37.5% ± 0.3%), and not very good for other metals (≤30%). When changing R for Et, in polymer **3b**, the same extractive properties were found, only at a little lower level, for Fe³⁺ (77.35% ± 0.05%) and Hg⁺ (77.5% ± 0.3%), less for Pb²⁺ (34% ± 2%), the other metals being around or below 30%, as for the previous one.

When entering the aryl series, an obvious decrease in the extraction potentials was observed, alongside some other interesting behaviors. For the uncited cations in the following paragraph, they were extracted ≤30%. For R = 4-methoxyphenyl in **3c**, Fe³⁺ (60% ± 7%) and Hg⁺ (46% ± 4%) were less extracted. However, Pb²⁺ (51% ± 3%) was better extracted. By replacing the phenyl group by a nitrogen containing aromatic one, like in the 2-pyrimidyl (**3d**), Fe³⁺ (59.4% ± 0.2%) was extracted at the same level, lower than the alkyl family (**3a**, **3b**). Hg⁺ (61.25% ± 0.05%) was a little less extracted than by *N*-alkyl substituted polymers **3a** and **3b** but better than the 4-methoxyphenyl polymer **3c**. In the case of polymer **3d**, Pb²⁺ (18% ± 1%) extraction dropped, but K⁺ (34% ± 3%) uptake increased. It is interesting to point out that some metals were not at all extracted by **3d**: Li⁺, Na⁺, Mn²⁺, Co²⁺, Cu²⁺ and Cd²⁺. When the substituent borne by the nitrogen was 2-pyridyl (**3e**), the extraction level dropped for Fe³⁺ (43% ± 2%), but stayed similar for Hg⁺ (59.19% ± 0.04%) and Pb²⁺ (22% ± 1%). Interestingly, another metal was extracted, Ba²⁺ (51% ± 4%), while Ni²⁺ and Ce³⁺ were not extracted.

By changing the nature of the substituent by introducing a carbamate function in **3f** (R = C(O)OCH₂Ph), the polymer became less selective. This polymer (**3f**) still extracted Fe³⁺ (72% ± 1%), but at the same level as the *N*-alkyl substituted ones (**3a**, **3b**), it extracted Pb²⁺ (46% ± 1%) at the level of the 4-methoxyphenyl polymer **3c**, and stayed in the same range as the

previous one for Hg^+ ($58\% \pm 2\%$) and Ba^{2+} ($41\% \pm 1\%$). Furthermore, the polymer **3f** was a good extractant for K^+ ($67\% \pm 5\%$) and Cd^{2+} ($60.3\% \pm 0.1\%$).

Finally, when the piperazine nitrogen onto the polymer was an amide of 2-furoic acid (**3g**), The extraction behavior came back to the triade Fe^{3+} ($41\% \pm 4\%$), Hg^+ ($56.23\% \pm 0.04\%$), and Pb^{2+} ($34\% \pm 2\%$). The levels were similar as the ones of **3e**. Once again some cations were not extracted like Li^+ , Na^+ , and Cu^{2+} .

From this first analysis, based only on the difference of the R group, it seems that the presence of an alkyl substituent (**3a**, R = Me, **3b**, R = Et) is giving the best extraction levels for Fe^{3+} and Hg^+ , probably due to the increased electronegativity of the amine. Inductive and steric hindrance effects can explain the differences between **3a** and **3b**. The introduction of a 2-methoxyphenyl group on the nitrogen (**3c**) changes it to an aniline, less basic, which is extracting less Fe^{3+} and Hg^+ . However, the presence of the methoxy group in *ortho* position seems to help in Pb^{2+} extraction. It is possible that this oxygenated group is implicated into the chelation of this metal. Replacement of this aromatic by a 2-pyrimidyl (**3d**) and 2-pyridyl (**3e**), less and more basic respectively when compared one to the other, still gives polymers capable of extracting Fe^{3+} and Hg^+ , with similar levels as **3c**. Special features of these polymers are higher extraction of K^+ for **3d** and Ba^{2+} for **3e**, as well as exclusion of some cations: Li^+ , Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} and Cd^{2+} for **3d**, and Ni^{2+} and Ce^{3+} for **3e**.

The electronegativities and chelating capabilities of these amino-R groups are however difficult to put in relation with their extracting properties. The most puzzling effect is the presence of a benzylcarbamate onto the nitrogen of the polymer (**3f**). This group is totally modifying the properties of the polymer. In this case, more metallic ions are extracted, with the classical Fe^{3+} and Hg^+ . This includes K^+ , Cd^{2+} , Ba^{2+} , and Pb^{2+} . This may suggest another chelation mode introduced by the presence of the carbamate. Finally, the presence of a derivative of furoic acid as an amide on the nitrogen (**3g**) do not seems to helps since extraction levels are going down with extraction of the usual Fe^{3+} , Hg^+ , and Pb^{2+} , and exclusion of Li^+ , Na^+ , Cu^{2+} .

The electronegativities of the substituted nitrogen of the piperazine can in part explain some of the relative extraction efficiencies. However, it is difficult to draw a clear conclusion. We have also tried to rationalize the interactions between the polymers and the metal ions based on their electropositivities, ionic radii and water solvation. Once again, no clear link can be drawn about the extraction efficiencies based on the metal cation properties. The only difference that can explain, once again in part, the preference of the polymers for Fe^{3+} and Hg^+ , and in some cases Pb^{2+} , is the counter-ion of the salt used for the study. All metallic salts were chlorides except for Fe^{3+} , Hg^+ , and Pb^{2+} , which were used as their nitrates.

The final analysis we have tried to make is to try to find out the chelation mode from the piperazine-triazole in relation with the metal cations. For the best extraction results, over 40%, it was not possible to make a clear discrimination between the three modes (pendant, triazole and integrated). The ratios piperazine-triazole:metal cation varied from 13:1 (**3f** and K^+ , $67\% \pm 5\%$) to 118:1 (**3e** and Fe^{3+} , $43\% \pm 2\%$), since the chelating moieties were in large excess. This cannot gives a clear hit on the chelation mode, which can be of polydentate type or simply a statistical repartition on the chelation sites, without knowledge of the chelation type.

All the results and analyses cannot clearly identify the discrete complexation behavior of the metal by the polymers at the solid/liquid interface. However, we were able to obtain better results than with

our first series of triazolic polymers based on propargyl amides and propiolic anilides onto poly(styrene) [38].

Figure 4 presents our results by cation absorption to help to find the best extractant. By drawing a cut-off for selection at 40% extraction level, it is clear that none of the polymers is very efficient for the removal of Li^+ , Na^+ , K^+ , Co^{2+} , Ni^{2+} , Cu^{2+} and Ce^{3+} . For K^+ , polymer **3f** is the best with $3.51 \text{ mg K}^+ \text{ g}^{-1}$.

- In the case of Fe^{3+} , as said before, all polymers are complexing this ion. The best results are $1.12 \text{ mg Fe}^{3+} \text{ g}^{-1}$ **3a**, $1.07 \text{ mg Fe}^{3+} \text{ g}^{-1}$ **3b** and $1.00 \text{ mg Fe}^{3+} \text{ g}^{-1}$ **3f**; followed by $0.83 \text{ mg Fe}^{3+} \text{ g}^{-1}$ **3c** and $0.82 \text{ mg Fe}^{3+} \text{ g}^{-1}$ **3d**, while **3e** and **3g** were borderline.
- Cd^{2+} and Ba^{2+} are more efficiently removed by **3f** ($3.37 \text{ mg Cd}^{2+} \text{ g}^{-1}$, $2.31 \text{ mg Ba}^{2+} \text{ g}^{-1}$) and **3e** ($2.87 \text{ mg Ba}^{2+} \text{ g}^{-1}$).
- For Hg^+ , as for Fe^{3+} , all polymers can be used. In order, by sorption capacities, are **3a** ($6.49 \text{ mg Hg}^+ \text{ g}^{-1}$), **3b** ($5.92 \text{ mg Hg}^+ \text{ g}^{-1}$), **3d** ($4.68 \text{ mg Hg}^+ \text{ g}^{-1}$), **3e** ($4.52 \text{ mg Hg}^+ \text{ g}^{-1}$), **3f** ($4.43 \text{ mg Hg}^+ \text{ g}^{-1}$), **3g** ($4.30 \text{ mg Hg}^+ \text{ g}^{-1}$) and **3c** ($3.51 \text{ mg Hg}^+ \text{ g}^{-1}$).
- Finally, in the case of Pb^{2+} , polymers **3c** ($3.19 \text{ mg Pb}^{2+} \text{ g}^{-1}$) and **3f** ($2.88 \text{ mg Pb}^{2+} \text{ g}^{-1}$) are the more efficient.

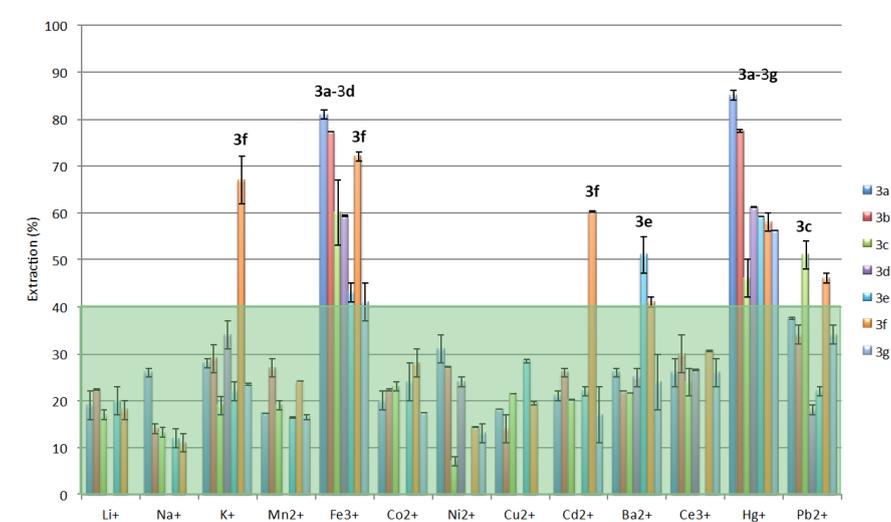


Figure 4. Extraction efficiencies of metal cations by the triazolic piperazine polymers **3a–3g** (polymers extracting at levels $\geq 50\%$ are indicated).

4. Conclusions

In this work, we studied chemical grafting of piperazine chelating units onto commercial poly[styrene] (Merrifield resin) using CuAAC procedure between the azided polymer and selected piperazine-*N*-propargylcarbamates. The synthesized polymers were characterized by FTIR. They were then tested for their efficiency to extract metallic ions from aqueous solution (Li^+ , Na^+ , K^+ , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+} , Ba^{2+} , Ce^{3+} , Hg^+ and Pb^{2+}). All polymers were found to extract most of the ions at low level ($\leq 40\%$), with the exception of Fe^{3+} , Hg^+ and Pb^{2+} . Some polymers showed selectivity for K^+ , Cd^{2+} and Ba^{2+} . Extraction efficiencies reached up to 85%, with the highest sorption capacity of $6.49 \text{ mg Hg}^+ \text{ g}^{-1}$ of polymer (**3a**).

The conductimetric method used, even having a less precise reputation, was good enough to have a quick evaluation of several cations removal. This method has been selected both for its lower cost in apparatus when compared to AAS and ICP methods. It is also faster and easier to do the measurements in order to speed up the process to find the best and highly selective extractant for a range of engineered polymers.

Even if no clear interpretation can be done with the results for the interfacial chelation process, the good extraction properties encourage us to continue polymers modifications using CuAAC in order to find new polymeric complexants for depollution and catalytic applications. Further studies will be reported in due course.

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Author Contributions

This is a part of the Ph.D. thesis of R. Slimi under the supervision of C. Girard. Experiments were conducted by R. Slimi. R. Slimi and C. Girard analyzed the data.

Conflicts of Interest

The authors declare no conflict of interest.

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