# Study of copper ions adsorption by itaconic-based hydrogels

**Angelika Wesołowska, Szczepan Bednarz, Dariusz Bogdał**

*email: angelikawesolowska18@wp.pl,
sbednarz@pk.edu.pl, pcbogdal@cyf-kr.edu.pl*

*Cracow University of Technology. Faculty of Chemical Engineering and Technology
Department of Biotechnology and Physical Chemistry
ul. Warszawska 24. 31-155 Kraków. Poland*

## Abstract

Hydrogels are macromolecular, insoluble polymers, capable of absorbing large quantities of water. Their properties make them widely utilized superabsorbents. Recently, a novel family of ionic solvents called deep eutectic solvents (DES) have been applied to prepare the hydrogels [1–3].

In this work. poly(itaconic acid) - based hydrogels prepared by free-radical polymerization-crosslinking of itaconic acid in deep eutectic mixture with choline chloride. were prepared and characterized by elemental analysis. FTIR spectroscopy and SEM. The process of removal of copper cations ($Cu^{2+}$) from aqueous solutions by the gels was studied. The Freundlich and Langmuir adsorption isotherm models were applied to quantitative describe the metal binding.

## Keywords:

hydrogels; free-radical polymerization; crosslinking; ionic liquids; deep eutectic solvents.

**INTRODUCTION**

Itaconic acid (IA) is an α-substituted acrylic acid derivative, having two carboxylic groups and a double bond. IA is acompound with a wide range of applications in polymer chemistry, pharmacy and agriculture. IA can be obtained either by chemical synthesis, or through biotechnological methods from fructose, glucose or xylose under the influence of fungi of the species: *Aspergillus terrus and Aspergillus itaconicus, Ustilago maydis,* as well *as Pseudozyma antartic* [1],[4].

Polymer gels can be defined as a three-dimensional polymer network filled with solvent. This network immobilizes the solvent, leading to the loss of its liquidity, giving the gels properties specific to both solids and liquids. These include the ability to absorb water, quick absorption of fluid in a reversible manner, high absorption capacity, non-toxicity, sorption of heavy metal ions and organic compounds, flexibility and good mechanical strength, as well as resistance to aggressive chemicals and high temperature. Hydrogels can be obtained through chemical or radiation methods. As the reaction initiators in chemical methods persulfates are used. One of the most common methods of synthesis of these materials is copolymerization of monofunctional free-radical hydrophilic monomers with two- or polyfunctional monomers carried out in a solution. This way the acrylamide-based and acrylic acid-based hydrogels can be obtained, as well as their derivatives [5], [6].

*Deep Eutectic Solvents* (DES) are mixtures of two or more components with a specified composition, interacting with each other through hydrogen bonds. Eutectic mixtures are characterised by lower melting point comparing to the temperatures of pure components, whereas during solidification at a specific temperature their individual components do not precipitate. DES show similar physicochemical properties to the traditionally used ionic liquids (IL's), including low vapour pressure, biodegradability, and often are much cheaper, easier to manufacture, and more environmentally friendly than IL's [2],[7]. The polymerization of IA is usually carried out in an aqueous medium. The reaction takes a long time, resulting in higher costs [8].

Recently, synthesis of itaconic-based polymers in DES as new media have been described [1]. The aim of the research was DES-assisted synthesis of bisacrylamide-crosslinked hydrogels based on itaconic acid and investigation the sorption capacity of obtained polymers with respect to $Cu^{2+}$ ions.

**EXPERIMENTAL**

*Materials*

Itaconic acid (IA), choline chloride (CC), *N.N′*-Methylenebisacrylamide (BisAA), and ammonium persulfate (APS) were from Sigma- Aldrich. All the chemicals were analytical grade and used as received.

*Preparation of polymers*

The hydrogels were prepared as described previously [1]. Briefly, eutectic mixture was obtained through melting at $110^o$C for 1h of IA (5.20g; 40mmol) with the CC in (5.58g, 40mmol). The process was performed in glass beakers with a capacity of 25 cm$^3$, equipped with a stir bar. To the obtained melts BisAA was added (0.308 g; 2 mmol) and the mixture was stirred until complete dissolution of the crosslinking agent. The resulting homogeneus mixture was cooled to the room temperature and then APS (0.456g; 2mmol) dissolved in 0.7 cm$^3$ of distilled water was added. Polymerisation was continued for two hours at 65ºC.
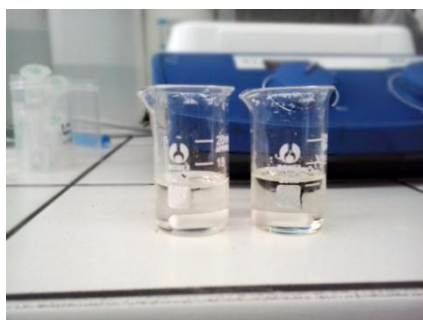


*Figure 1. Eutectic mixtures IA : CC.*

After completion of the reaction, the beakers with the polymer were transferred to beakers filled with 1dm$^3$ of distilled water in order to wash out the choline chloride, unreacted itaconic acid and low molecular weight reaction products. Then every day (for approx. 8 days) the water in beakers was replaced until complete removing of the impurities. After that, the obtained hydrogels were weighed, and then freezdrieded for 24 hours at -30 °C under 0.3 mbar.

*Figure 2. The appearance of swollen itaconic-based hydrogel.*

### *Examination of the absorption capacity of PIA-co-BisAA hydrogels*

A series of solutions of $CuSO_4$ with concentrations of: 0.002; 0.003; 0.004; 0.005; 0.008; 0.010; 0.020mol/dm$^3$ was prepared. Samples of the hydrogel (3g) were immersed in 50 cm$^3$ of the solutions of $Cu^{2+}$ (Fig.3.). The metal ions uptake were measured after 14 days (336 h) using spectrophotometric method with $NH_3$ as complexing agent. On the basis of the results the graphs of dependency of the sorption capacity on the equilibrium concentration of copper ions qe = f(Ce) were drawn.. The data were analysed using the Freundlich and Langmuir isotherm models. Characteristic parameters for each model were determined.

Calculations of the concentrations, the sorption capacity of the hydrogel were carried out according to the formulas:

$$C_{Cu^{2+}} = \frac{C_{sample} \cdot V_{sample}}{V_{Cu^{2+}}}$$

$V_{Cu^{2+}}$ - volume of the solution of copper sulphate (II) used for measurement;

$V_{sample}$ - volume of the solution of ammonia water + volume of the solution of copper sulphate (II) used for the measurement.

$$q_e = \frac{V(C_o - C_e)}{m}$$

where:

$q_e$- sorption capacity [mg/g];

$V$- sample volume [dm$^3$], V=50ml;

$C_o$- the concentration of the starting solution of copper sulphate [mg/dm$^3$];

$C_e$ – equilibrium concentration of ions Cu$^{2+}$ [mg/dm$^3$];
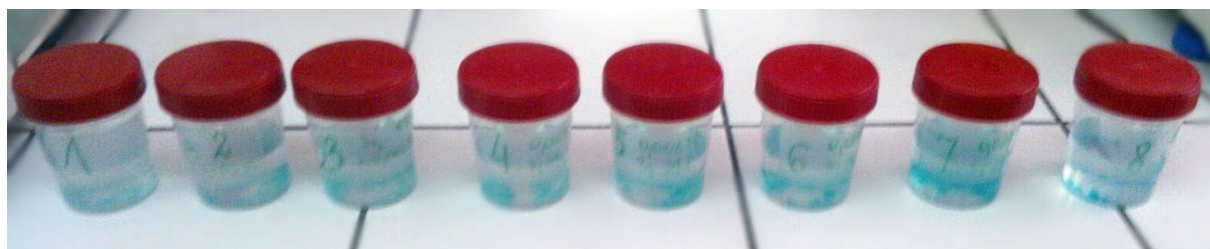
$m$ – amount of the hydrogel sample (m=3g).



*Figure 3. The change in colour of the hydrogels from transparent to blue as an effect of sorption Cu$^{2+}$.*

## *RESULTS AND DISCUSSION*

After initialising the polymerization reaction a significant increase of viscosity of the mixture was observed, and after 20 minutes the mixture completely solidified. During the purification in water of the resulting products they underwent swelling. The structure of bisacrylamide-crosslinked poly(itaconic acid) was examined using the elemental analysis, infrared spectroscopy (FTIR) and by scanning electron microscopy (SEM)

As a result of the polymerization of itaconic acid and N'N-methylenebisacrylamide, a copolymer was obtained with the simplified structure shown below.
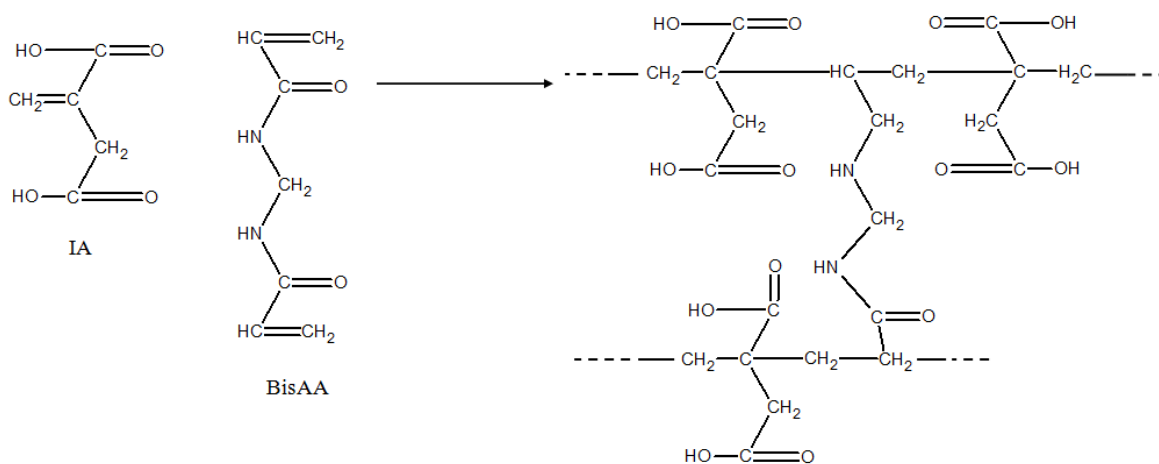
*Figure 4. Simplified structure: PIA-co-BisAA.*

### Elemental analysis

The approximate amount of carbon in the PIA is 41%, while about 5% is hydrogen (Tab. 1). The resulting contents of C and H differ from the calculated value for the hypothesized dry polymer (C = 46.16%. H = 4.65%). This is due to side reactions, e.g. decarboxylation or the presence of hydration water in the polymer, which, despite carried out lyophilisation, was probably not completely removed. The analysis of the amount of nitrogen confirms the creation of IA-BisAA copolymer. The calculations indicated average 13 units of IA per one unit of BIsAA.

*Table 1. Results of elemental analysis of PIA-coBisAA.*

|  | C [%] | H [%] | N [%] |
|---|---|---|---|
| **PIA-co-BisAA** | 41.26 | 5.43 | 1.43 |

### Infrared spectroscopy studies

Analysis of FTIR spectra of PIA-co-BisAA confirms the presence of the characteristic functional groups: stretching vibration bands of the carbonyl group C=O in the range of 1730-1690cm$^{-1}$, bending vibrations of the group C-H in the range of 1320-1210cm$^{-1}$. Also small bands are visible in the range of 780- 900cm$^{-1}$ which may indicate the presence of itaconic anhydride groups formed probably during drying of the samples. A strong and broad band (2600-3600cm$^{-1}$) can be noticed characteristic for stretching vibrations of the –OH group [1].
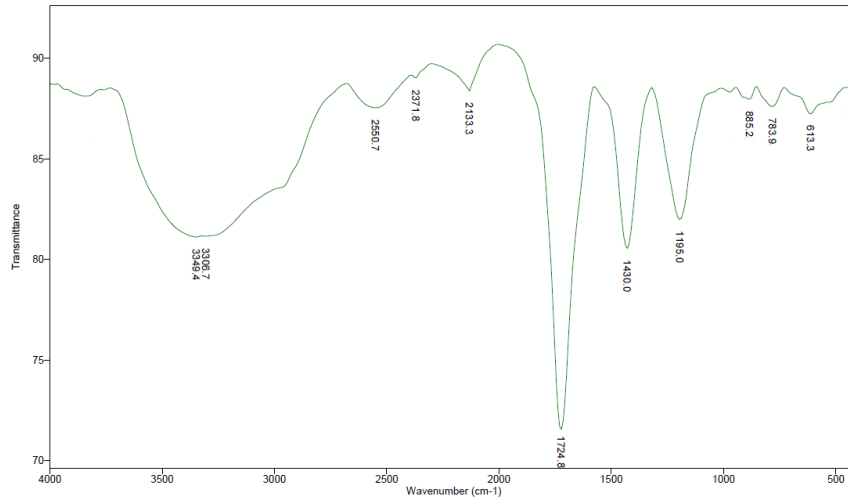
*Figure 5. The IR spectrum of PIA-co-BisAA xerogel.*

### Sorption studies

Tab. 2 shows results of sorption experiments. Based on the data, a plot of dependence of sorption capacity on the equilibrium concentration $q_e = f(C_e)$ was prepared and theoretical Langmuir and Freundlich models were applied to describe the sorption process (Fig. 7 and 8). Based on the mathematical equations for each isotherm the characteristic parameters were determined (Table 3).

*Table 2. The equilibrium concentrations of Cu $^{2+}$ in individual experiments after 336 hours of sorption and calculated sorption capacities.*

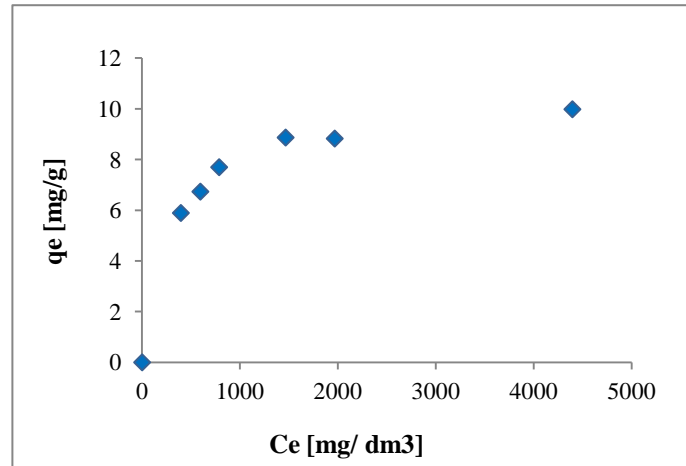| The parameter | Initial concentration $Cu^{2+}$ [mol/dm$^3$] | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.002 | 0.003 | 0.004 | 0.005 | 0.008 | 0.010 | 0.20 |
| Equilibrium concentration of ions $Cu^{2+}$ ($C_e$) [mg/dm$^3$] | 86 | 395 | 595 | 787 | 1465 | 1967 | 4395 |
| Sorption capacity of the sorbent ($q_e$) [mg/g] | 6.7 | 5.9 | 6.7 | 7.7 | 8.8 | 8.8 | 9.9 |

*Figure 6. Dependency of sorption capacity on the equilibrium concentration of $Cu^{2+}$.*

The following linearized equations were used:.

For Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e$$

where: *qe* is the amount of adsorbate adsorbed per unit mass of adsorbate [mg/g]; *Ce* is the adsorbate equilibrium concentration in solution [mg/dm$^3$]; $K_F$ and $a_L$ are Langmuir isotherm constants [dm$^3$/mg]. The value of $a_L$ was determined from slope of the line, which is equal to $a_L/K_L$. Maximal adsorption capacity for a particular monolayer is equal to the numerical value $K_L/a_L$.

For Freundlich isotherm:

$$ln_{q_e} = \ln K_F + \frac{1}{n_F} ln C_e$$

where: $K_F$ is the Freundlich constant [dm$^3$/g], $n_F$ – is the Freundlich isotherm exponent; $q_e$- is the amount of a substance adsorbed at equilibrium [mg/g]; $C_e$ – is the liquid phase adsorbat concentration at equilibrium [mg/dm$^3$].
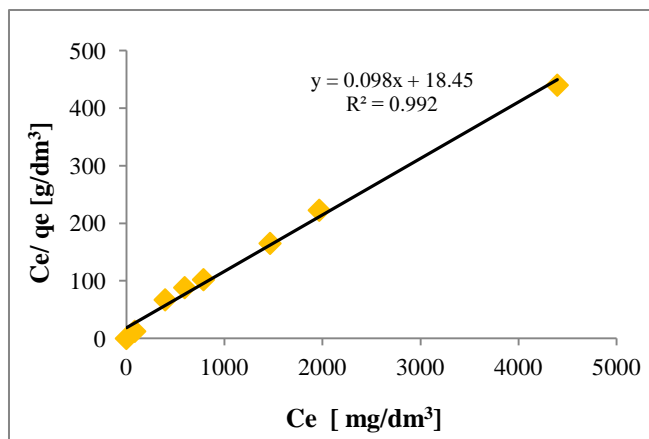
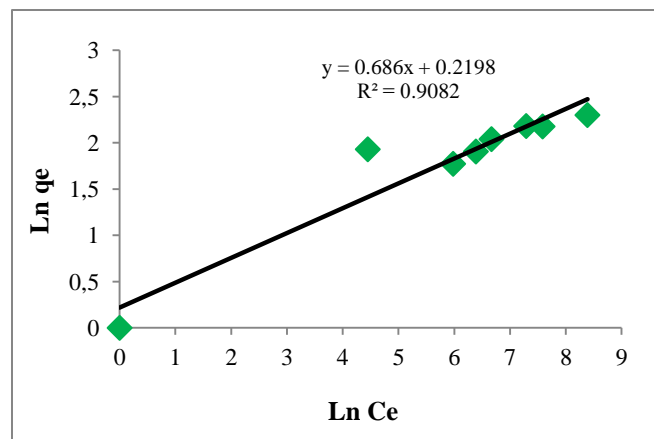*Figure 7. Linear Langmuir isotherm adsorption model for sorption of $Cu^{2+}$ ions ontoPIA-BisAA hydrogels.*



*Figure 8. Linear Freundlich isotherm adsorption model for sorption of $Cu^{2+}$ ions ontoPIA-BisAA hydrogels.*

*Table 3. Isotherm parameters of Langmuir and Freundlich models.*

|  | K [dm$^3$/g] | n$_F$ | a$_L$ [dm$^3$/mg] | R$^2$ |
|---|---|---|---|---|
| **Langmuir Isotherm** | 0.054 | - | 0.0053 | 0.99 |
| **Freundlich Isotherm** | 1.25 | 1.46 | - | 0.91 |

Matching the appropriate model of isotherm is done based on the value of correlation coefficient $R^2$. Table 3 shows appropriate parameters with the correlation coefficients. Based on them it is possible to conclude that the presented results are better described by the Langmuir isotherm model. Additionally, the Freundlich and Langmuir models parameters are similar to those presented by Gregorio Crini in [9], where the process of cationic dyes adsorption on polymers of cyclodextrin was studied ($K_F$ =4.86, n$_F$ =2.45; $K_L$ =1,65, $a_L$=0,046) and also to the results describing process of $Cu^{2+}$ removal by cryogels based on polyacrylamide and anionically modified potato starch ($K_F$ =8.07; $K_L$ =0.163) [10]. Hydrogels PIA-BisAA contain free –COOH groups derived from IA that could interact with cations, e.g. $Cu^{2+}$. It is probable, that during the sorption process copper ions form salt with the structure outlined below:

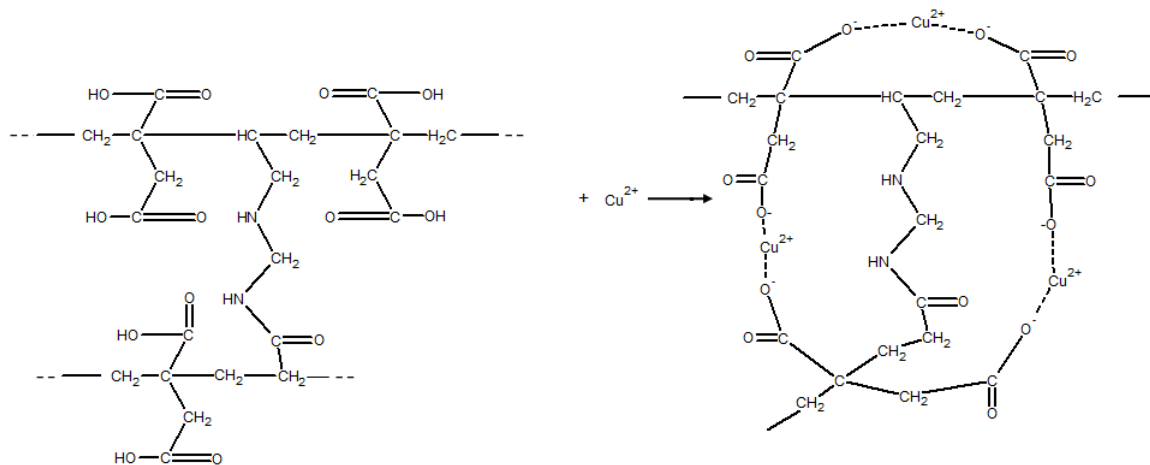*Figure 9. Simplified scheme of binding $Cu^{2+}$ on PIA-co- BisAA*

It should be noted that, it is possible to recovery of copper adsorbed in hydrogel through contact the polymer with a solution containing strong complexing agent e.g. EDTA.

**Scanning electron microscopy (SEM)**

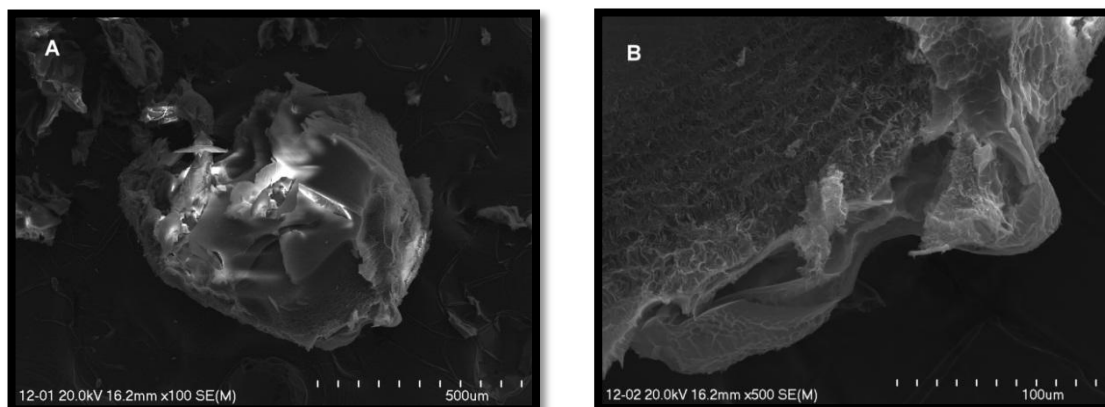Morphology of the hydrogels after freeze-drying (xerogels) were studied using SEM (Fig.10.).



*Figure 10. The morphology of the PIA-co-BisAA xerogels magnified 100x (A) and 500x (B)*
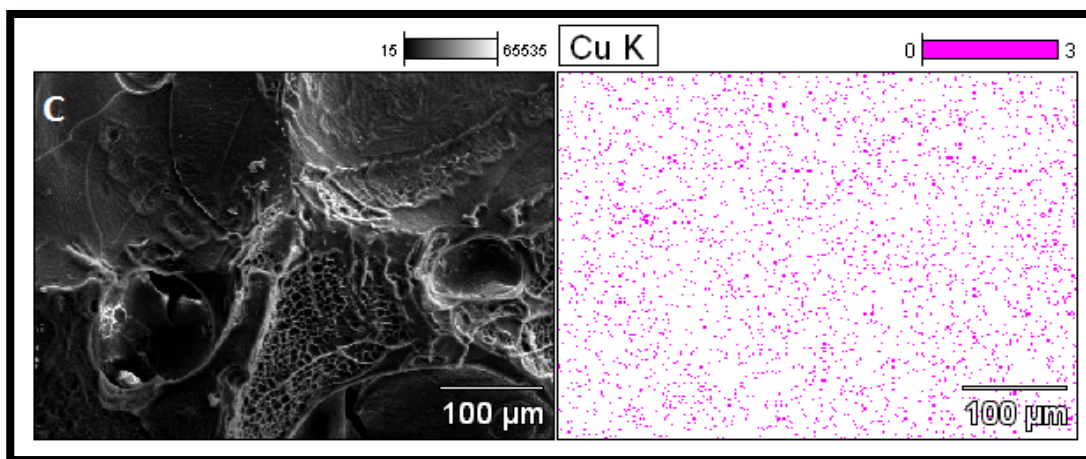
*Figure 11. Mapping of Cu $^{2+}$ cations on the surface of sample B*

The figure shows the morphology of the copolymer characterized by a well-developed, porous surface. The pores of uniform size are arranged in characteristic curves (Figure 10. B). Photograph C shows the morphology of the sample after the absorption of $Cu^{2+}$ ions. Based on the analysis of ions' distribution on the matrix's surface it can be seen that copper is uniformly distributed on the entire surface of the sample.

**CONCLUSIONS**

Itaconic-based hydrogels can be obtained via DES-mediated free-radical polymerization-crosslinking. The polymers have the affinity to $Cu^{2+}$ cations and the sorption process can be described by Langmuir model. This makes the materials usefull in environmental applications, i.e. for water purification.

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