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ORIGINAL PAPER

Synthesis and characterization of a new copper(II) ion-imprinted polymer

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Abstract In this study, a new copper(II) ion-imprinted polymer (Cu(II)-IIP) was synthesized by the precipitation method. Itaconic acid, ethylene glycol dimethacrylate and 2,2′-azobisisobutyronitrile were used as functional, cross-linking monomer and a free-radical initiator, respectively. This polymer has been characterized on the basis of Fourier transform infrared spectroscopy and surface area measurements. The imprinted Cu(II) ions were completely removed from the polymer by leaching with the mixture of 0.1 M EDTA and 1 M HCl. The optimum pH for the adsorption of Cu(II) on to the polymer was 6. The selective performance of the polymer was compared to non-imprinted polymer (NIP) for the binary mixture Cu^{2+}/Ni^{2+} and Cu^{2+}/Zn^{2+}. The relative selectivity of Cu(II)-IIP was 12.8 and 32.4 times greater than that of NIP as compared with the Zn^{2+} and Ni^{2+} ions, respectively. At optimal pH value, the maximum static adsorption capacity of Cu(II)-IIP and NIP was found to be 14.8 and 4.08 mg/g, respectively.

Introduction

Copper is a common environmental pollutant, which is encountered with food and drink in urban countries. The World Health Organization (WHO) evaluated regulations concerning the copper(II) content in drinking water. The maximum recommended concentration of Cu(II) in drinking water is 2 mg/L (31 mM) [1]. Copper is an essential trace element and plays an important role in various biological systems. It is a functional component of essential enzymes (eg.

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cytochrome *c* oxidase, lysyl oxidase, ferroxidase, tyrosinase, dopamine beta-monooxygenase, D-hexozo oxidoreductase, superoxide dismutase), takes part in cell transpiration, etc. [1–4]. Both, its excess and deficiency can cause damage to human body systems. Copper deficiency can lead to symptoms such as hypochromic anemia, leucopenia and osteoporosis [5]. On the other hand, its excessive intake may result in a number of adverse health effects including liver and kidney damage, immunotoxicity and developmental toxicity [6]. As a result, it is really important to control the concentration of Cu in body fluids as well as environmental samples (sewage sludge, drinking water), which is usually accomplished by atomic absorption spectroscopy, inductively coupled plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry methods. The concentration of Cu in urine and blood of a healthy person lays in the range 13–108 μg/L [7]. The presence of Ni, Zn and Cu at the similar concentration level in those samples can lead to matrix effects, which influence the accuracy of Cu determination by ET AAS [8]. Due to the complexity of the samples' matrix, often prior to their analysis, it is necessary to separate and enrich the copper ions using the following methods: liquid–liquid extraction [9, 10], co-precipitation [11], solid-phase extraction (SPE) [12, 13] and cloud point extraction [14, 15]. The basic principle of SPE is the transfer of analytes from the aqueous phase to the active sites of the adjacent solid phase, which is stimulated by the selection of appropriate optimal conditions in the system of three major components: water (liquid phase); analyte; and, sorbent [16]. It seems that among the methods of solid-phase extraction those where copper(II) ion-imprinted polymers were used were relatively simple to perform [17].

The first metal-imprinted polymers were synthesized in 1976 by Nishide et al. [18, 19]. They co-polymerized poly(4-vinylpyridine) with 1,4-dibromobutane in the presence of metal ions. Next, they analyzed the adsorption of Cu(II), Zn(II), Co(II), Ni(II), Hg(II) and Cd(II) on acquired resins. It turned out that the resins preferably adsorbed the metal ions, which have been used in the process of synthesis. In the past years, a rapid increase in number of publications concerning metal-imprinted polymers including copper(II)-imprinted polymers, their characteristics and application can be observed [20–41]. Baghel et al. reported a fabrication of an ion-selective electrode using Cu(II) ion-imprinted polymer for sensing Cu(II) ion [33]. Cu(II)-IIP were also used in the development of a fluorescent Cu(II)-IIP-based optosensor [41, 56]. These materials can also be applied as sorbents in SPE, which enable selective determination of copper in various water samples: mineral water, seawater, distilled water, well water, river water, spring water and tap water samples from water installation containing copper elements [21, 23, 25, 26, 31, 32, 37, 40]. Besides water analysis, Cu(II)-IIP was used in a selective preconcentration for a trace Cu(II) determination in biological samples, such as human urine, serum samples [42] and fish samples [32].

The metals analysis performed when determining important parameters of the ion-imprinted polymers was carried out by the following methods: atomic absorption spectrometry [25, 29, 32, 33, 37, 38, 57] and inductively coupled plasma optical emission spectrometry [31, 35, 40, 42].

In our work, we applied wavelength-dispersive X-ray spectroscopy (WD-XRF), which effectively allows for a quantitative determination of an element directly in

the ion-imprinted polymer matrix. WD-XRF has been used for the determination of metals in polymers. It is a non-destructive method that enables determination of elements in solid-state samples. This technique has been applied very successfully to industries, to the routine determination in polyethylene and polypropylene samples of the following elements: aluminum, bromine, calcium, chlorine, magnesium, potassium, sodium, titanium and vanadium [43]. The WD-XRF method was also used for the determination of elements in the commercial polymers produced by zirconocene (Al), Ziegler-Natta (Ti and V), Philips (Cr) and metallocene (Zr) technology [44, 45]. Another application of this technique is the determination of metals (Co, Cu, Fe, Ni and Zn) in polybutadiene, polyisoprene and polyester resins [46].

The aim of this work was the synthesis of a copper(II) ion-imprinted polymer, which applied in the solid-phase extraction system, can selectively adsorb copper(II) ions from the samples of a complex matrix, including biological and environmental samples. The analytical method—the wavelength-dispersive X-ray spectrometry was for the first time used for the evaluation of the ion-imprinted polymer properties, such as selectivity, adsorption properties, etc. In this study, a new copper(II)-imprinted polymer was synthesized via a precipitation polymerization. Itaconic acid was used to prepare a pre-polymerization compound with the copper (II) ion. The polymerization was performed in the presence of EDMA and AIBN as a cross-linking monomer and initiator, respectively. The properties of the obtained polymer such as characteristics of the structure, selectivity and sorption were evaluated.

Materials and methods

Apparatus

In this study, the following spectrometers were used: the Fourier Transform Infrared (FT-IR) spectrometer (Perkin Elmer, SPECTRUM 1000), the UV–VIS spectrophotometer (Shimadzu, UV-1800) and wavelength-dispersive X-ray spectrometer (WD-XRF) (Thermo, ARL Advant'x series sequential XRF Intelli PowerTM) equipped with: the Rh-anode X-ray tube of power 3,6 kW, seven crystals (LiF 200, LiF 220, Ge 111, PET, AX 03, AX 09, AX 16c), two detectors (Flow Proportional Counter and Scintillation Counter) and four collimators (0.15; 0.25; 0.6; 2.6 mm).

The operating parameters of the WD-XRF spectrometer are summarized in Table 1.

Materials

Itaconic Acid (IA) (>99 %), the monomer and ethylene glycol dimethacrylate (EDMA) (98 %), the cross-linking agent, were supplied from Sigma Aldrich (Sigma Aldrich, Germany). 2,2′-Azobisisobutyronitrile (AIBN, Aldrich, Germany) was used as an initiator for polymerization and methanol (>99.9 %) (Sigma Aldrich, Germany) was used as the porogenic solvent.

Table 1 Operating parameters of WD-XRF spectrometer

Crystal	LiF 220
Collimator	0.6 mm
kV/mA	40/60
Counting time	2 s
2θ angle range	64.8–66.4
Increment	0.02
Detector	FPC

Stock solutions of Cu(II), Ni(II) and Zn(II) of concentration 1000 mg/L were purchased from Merck (Darmstadt, Germany). Working solutions were prepared by diluting the stock solutions with deionized water. The eluent solutions were prepared by dilution of concentrated hydrochloric acid (pure for analysis) and EDTA (<99 %), purchased from Merck (Darmstadt, Germany). The Britton–Robinson buffers were prepared according to the procedure given in the literature [47], by mixing the acidic solution (0.04 mol phosphoric acid, 0.04 mol boric acid and 0.04 mol acetic acid L^{-1}) with 0.2 mol L^{-1} sodium hydroxide solution in appropriate ratios. All reagents were of pure for analysis grade, POCh (Gliwice, Poland).

Polymer synthesis

Cu(II)-IIP (Fig. 1) was prepared by thermal polymerization. Copper (II) ion (1 mmol) was mixed with itaconic acid (2 mmol) in methanol (30 mL). This solution was then mixed with ethylene glycol dimethacrylate (20 mmol) and 2,2′-azobisisobutyronitrile (50 mg). To prevent any side reactions, the oxygen of the solution was removed by bubbling of argon through it for 15 min. The polymerization reaction was performed in an oil bath at 60 °C for 24 h. After completion of polymerization, the solid polymer was crushed and ground. To remove the template ion, the particles were treated with the mixture of 2 M HCl and 0.1 M EDTA until no copper could be detected in the polymer material by the WD-XRF method. The excess amount of HCl/EDTA was washed by methanol and deionized water. Finally the particles were dried in a vacuum oven at 60 °C.

Non-imprinted polymer (NIP) was also prepared under similar conditions except for adding the template ion.

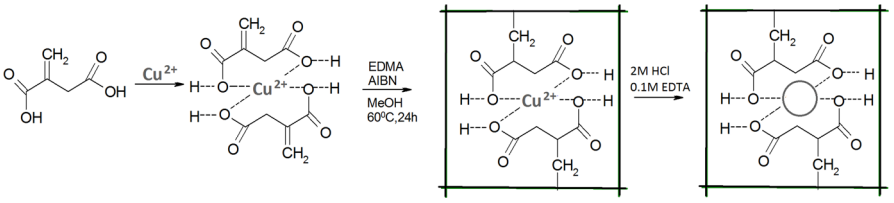

Fig. 1 Schematic illustration of imprinting process for the preparation of copper (II)-imprinted polymer

Sample preparation

Calibration standards preparation

The WD-XRF method was used to evaluate the concentration values of Cu(II), Ni(II) and Zn(II) in the samples.

First, calibration curves were constructed by measuring a series of ten calibration standard samples containing a known amount of Cu (II), Ni(II) and Zn(II) ions. The procedure of preparing calibration standards was as follows: 2.000 g of microcrystalline cellulose was weighed into glass bottles. To that quantity 50 mL of a standard solution of metal ions (Cu(II), NI(II) and Zn(II)) of known concentration was added. The mixtures were shaken for 2 h and finally the standard samples were dried in a vacuum oven for 72 h (temperature 60 °C). A mortar and pestle made of agate was used to homogenize the samples. Next, accurately weighed powdered standard samples (50.00 mg) were pressed with the hydraulic press machine (pressure 10 *t*, time 20 s) to obtain pellets of 13 mm diameter. 150.00 mg of boric acid per each sample was used as backing. The backing absorbs stress and shock in the pressing process, and gives a smooth pellet surface. The standard pellets were measured by the WD-XRF method. The calibration curves were prepared in the following concentration range: 0.020–20 mg/g. The linearity of the calibration curves for Cu(II), Ni(II) and Zn(II) was satisfactory—the value of R^2 was 0.9935, 0.9984 and 0.9958, respectively.

The preparation of the polymer samples

All of the analyzed polymer samples were homogenized with a mortar and pestle made of agate. Next, accurately weighed powdered polymer samples (50.00 mg) were pressed with the hydraulic press machine (pressure 10 *t*, time 20 s) to obtain pellets of 13 mm diameter. 150.00 mg of boric acid per each sample was used as backing. The polymer pellets were measured by the WD-XRF method. The concentration of Cu, Ni and Zn in the polymer samples was determined from the obtained calibration curves.

Procedure

Effect of pH

The samples of the Cu(II)-IIP and NIP (50 mg) were equilibrated with the solution of copper (II) ions and the buffer in 100-mL glass bottles. The total concentration of Cu(II) was 10 mg/L and the volume 40 mL. The set of five test solutions of pH varying from 2.09 to 6.09 was prepared. The solutions were shaken for 5 h at room temperature (20 °C). Then the polymers were filtered off through a membrane filter (Sumplep LCR 25-LG, Nippon Millipore Ltd., Japan), washed with the appropriate buffer solution and dried overnight in a vacuum oven.

Static adsorption capacity

A sample of 100 mg of Cu(II)-IIP (or NIP) particles was added into a 50-mL solution containing Cu^{2+} in the concentration of 10 ppm, and the solution was sealed in a test bottle (100 mL volume). The pH was adjusted to 6.0 and the mixture was shaken for 5 h at a room temperature (20 °C). Then the polymers were filtered off through a membrane filter (Sumplep LCR 25-LG, Nippon Millipore Ltd., Japan), washed with the appropriate buffer solution and dried overnight in a vacuum oven.

Adsorption kinetics

The adsorption isotherm was evaluated in batch experiments. Seven solutions of Cu(II) over the concentration range of 0.7–10 ppm were maintained at the optimum pH and shaken with 100 mg of Cu(II)-IIP. The mixtures were shaken for 5 h at room temperature (20 °C). Then the polymers were filtered off through a membrane filter (Sumplep LCR 25-LG, Nippon Millipore Ltd., Japan), washed with the appropriate buffer solution and dried overnight in a vacuum oven.

Selectivity studies

The selectivity of the Cu(II)-IIP towards Cu^{2+} in the presence of competitive ions was investigated. The sorption studies were performed from binary solution of the copper ions and the competitive ions. 100 mg of the polymer (Cu(II)-IIP or NIP) was placed in a glass bottle (250 mL) and mixed with a solution containing Cu^{2+} (10 mg/L) and Ni^{2+} (1 or 10 mg/L) or Zn^{2+} (1 or 10 mg/L). After adjusting pH to 6.0, the solutions were shaken for 5 h at room temperature (20 °C). Then the polymers were filtered off through a membrane filter (Sumplep LCR 25-LG, Nippon Millipore Ltd., Japan), washed with the appropriate buffer solution and dried overnight in a vacuum oven.

The distribution ratio (D), selectivity factor of Cu(II) with respect to Zn(II) and Ni(II) (α) and relative selectivity factor (α_r) were calculated using the Eqs. 1–3 [21, 48].

$$D = C_i/C_e \tag{1}$$

$$\alpha = D_{Cu}/D_M \tag{2}$$

$$\alpha_r = \alpha_i/\alpha_n \tag{3}$$

where C_i is the concentration of Cu(II) in the polymer (mg/g), C_e is the equilibrium concentration of Cu (II) (mg/L), D_{Cu} and D_M is the distribution ratios of Cu(II) and Zn(II) or Ni(II), α_i, α_n is the selectivity factors of Cu(II)-IIP and NIP, respectively, α_r is the relative selectivity factor.

Surface area measurement

The surface area of the leached Cu(II)-IIP and NIP was measured by methylene blue adsorption method. Methylene blue is known to be adsorbed as a monolayer only on solid adsorbents [49]. A standard stock solution of methylene blue was prepared (0.0178 g L^{-1}). A set of the working standards was analyzed by UV–VIS spectrophotometry ($\lambda = 600$ nm) to draw a calibration curve for methylene blue. To calculate the surface area, 0.1 g of Cu(II)-IIP and NIP was treated with 25 mL of methylene blue solution of concentration 0.0178 g L^{-1}. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on the difference between the initial and equilibrium concentration, which were measured spectrophotometrically.

Results and discussion

Characterization of polymer

Figure 1 represents the scheme of the reactions that led to prepare Cu(II)-IIP.

The IR spectra of unleached copper (II)-imprinted polymer (Cu(II)-IIP) and non-imprinted polymer (NIP) materials were recorded using KBr pellet method (Fig. 2).

The majority of the FT-IR spectra bands recorded for the Cu(II)-IIP and NIP polymers are similar indicating that the synthesis of Cu(II)-IIP was successful. The only difference was an additional IR band at 1550–1610 cm^{-1} present for Cu(II)-IIP, which originates from Cu–O bond and indicates formation of a salt of copper(II) and the itaconic acid. The precise structure of the salt is unknown and need to be determined by more sophisticated analytical methods (e.g., NMR).

To confirm that the copper ions were incorporated in the polymer network, the WD-XRF spectra of Cu(II)-IIP and NIP were recorded (Fig. 3).

It can be observed that an intense signal of copper appears only for Cu(II)-IIP.

To evaluate the concentration of Cu(II) in the synthesized polymers, a quantitative analysis was performed. The concentration of copper was found to be 21.5 mg g^{-1} and was below the detection limit in the Cu(II)-IIP and NIP, respectively.

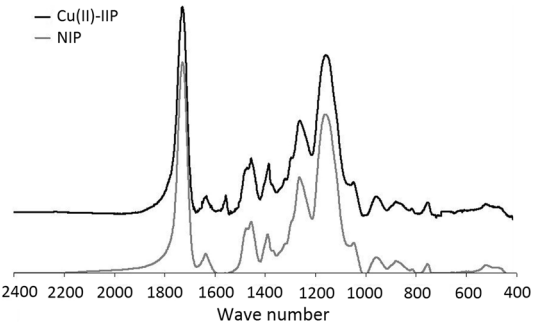

Fig. 2 FTIR spectra of Cu(II)-imprinted polymer (Cu(II)-IIP) and non-imprinted polymer (NIP)

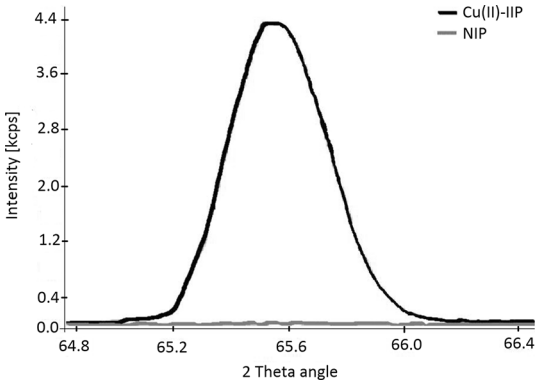

Fig. 3 The WD-XRF spectra of Cu(II)-imprinted polymer (Cu(II)-IIP) and non-imprinted polymer (NIP)

Surface area measurement

The surface area of IIP and NIP was calculated using the Eq. 4 [49].

$$A_s = \frac{G \cdot N_{AV} \cdot \emptyset \cdot 10^{-20}}{M \cdot M_W} \quad (4)$$

where A_s is the imprinted polymer surface area in $m^2\ g^{-1}$, G is the amount of methylene blue adsorbed (g), N_{AV} is the Avogadro's number ($6.02 \times 10^{23}\ mol^{-1}$), Ø is the methylene blue molecular cross section (197.2 $Å^2$), M_W is the molecular weight of methylene blue (373.9 g mol^{-1}), M is the mass of adsorbent (g).

The calculated surface area of leached Cu(II)-IIP and NIP was 14.56 and 11.65 $m^2\ g^{-1}$, respectively.

Effect of pH

One of the most critical parameters influencing adsorption of metal ions is pH of the solution. Thus, the effect of varying pH values on Cu(II) uptake was investigated using a batch procedure. The binding capacity of Cu(II)-IIP and NIP was evaluated in the pH range of 2.09–6.09. In consideration of hydrolysis, pH above 6.09 was not tested [31].

As can be observed in Fig. 4, the adsorption capacity of Cu(II) increases with the pH increasing, reaching the maximum at pH 6.0. Below pH 4.0, the adsorption capacity was low due to the protonation of the polymers. This occurrence was in a good agreement with the data reported in the literature [22, 30, 35]. The optimum pH exploited for further experiments was 6.0.

Adsorption properties

One of the most important properties characterizing the ion-imprinted polymers is the adsorption capacity (Q), defined as the total amount of ion adsorbed per gram of the sorbent particles [50].

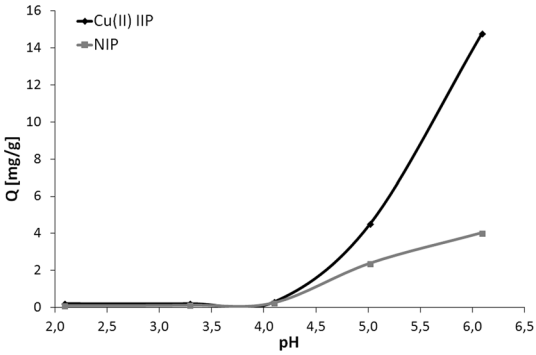

Fig. 4 Effect of pH on Cu^{2+} adsorption

Static adsorption capacity

The static adsorption capacity is the maximum concentration of ions that can be adsorbed by the polymer at equilibrium state [51]. The adsorption of copper (II) ions from the metal ion-containing aqueous solution was investigated. The static adsorption capacity for Cu(II)-IIP and NIP was 14.8 and 4.08 mg/g, respectively. The adsorption capacity of the polymer reported in the previous publications was in the following range: 0.3–28 mg/g [21–23, 25, 26, 35, 36, 38, 57]. Only one polymer characterized in the literature had a higher value of the Q parameter ($Q = 76$ mg/g) [37]. It should be pointed out that the majority of authors determined the adsorption capacity only for the copper ion-imprinted polymers. They have not compared this result with the adsorption capacity of the non-imprinted polymers. The question arises as to what we can actually discover from these data? Is the adsorption capacity of the imprinted polymer higher than that of the control polymer? Do the synthesized imprinted polymers have in their structure the specific cavities that are able do adsorb only the copper ion?

The adsorption capacity of our Cu(II)-IIP is 3.6 times higher than that of NIP which, according to the data available in the literature, is the highest value [21].

Adsorption kinetics

The adsorption properties of IIPs can be evaluated by the adsorption isotherms in the batch experiments. These isotherms provide a relationship between the concentration of the analyte metal ion in a solution and that adsorbed on the solid sorbent, when the two phases are in equilibrium. The Langmuir adsorption isotherm model was used to evaluate the adsorption properties of the particles of Cu(II)-IIP. This model is a theoretical equation that is applicable to homogeneous binding sites and assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent and distant to each other so that there are no interactions between molecules adsorbed on adjacent sites [52, 53].

The Langmuir adsorption isotherm is expressed by the Eq. 4 [24, 29, 54].

$$\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{(Q_m b)} \quad (5)$$

where C_e is the equilibrium concentration of metal ions (mg/L), Q is the amount of metal ions adsorbed (mg/g), Q_m is the maximum adsorption capacity of metal ions (mg/g), and b is the Langmuir adsorption equilibrium constant (L/mg) [55, 56].

Figure 5 shows the dependence of the equilibrium concentration on the adsorbed amount of Cu^{2+} onto the Cu(II)-IIP particles.

The equilibrium adsorption data of the Cu(II) ions were highly correlated according to the Langmuir adsorption model ($R^2 = 0.9969$), which indicates that the adsorption obeys the Langmuir model assumptions. The maximum adsorption capacity Q_m was 16.12 mg/g.

Selectivity studies

To evaluate the selectivity of the imprinted polymer, the competitive sorption of Cu^{2+}/Ni^{2+} and Cu^{2+}/Zn^{2+} from their binary mixtures was investigated in batch experiments. It is worth mentioning that the interfering ions have the same charge and similar ion radii with copper (II) ion (Cu^{2+}—71 pm, Ni^{2+}—69 pm, Zn^{2+}—74 pm) [38]. The results in Table 2 indicate that the relative selectivity coefficients of the Cu(II)-IIP increased with increasing ratio of Cu^{2+}/M^{2+}. Depending on the interfering ion and its concentration referring to Cu^{2+}, the enrichment factors were 3.30–32.4 times greater than those of the non-imprinted polymers. It indicates that the synthesized copper(II) ion-imprinted polymer can selectively adsorb copper ions in the presence of interfering ions.

Table 3 shows a comparison of the values of the adsorption capacity and relative selectivity coefficients of the new Cu(II)-IIP and polymers reported in the literature.

Although the adsorption capacity of the polymer characterized in this work is lower than other copper(II) ion-imprinted polymers [31, 37, 57], the data presented in Table 3 indicate that it is showing the best selectivity towards Ni^{2+} ions and very high selectivity towards Zn^{2+} ions.

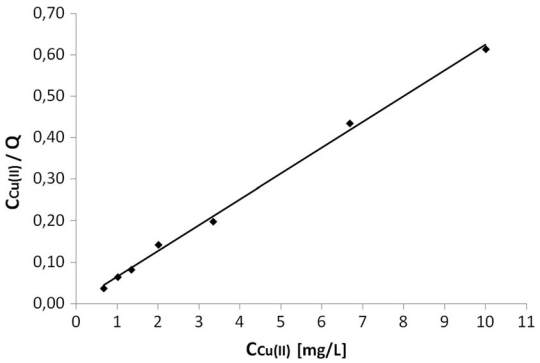

Fig. 5 Langmuir adsorption isotherm

Table 2 Distribution ratio (D), selectivity coefficient (α) and relative selectively coefficient (α_r) values of copper (II) ion-imprinted polymer (Cu(II)-IIP) and control non-imprinted polymeric (NIP) material for different metal ions and various concentration ratios of copper(II) and interfering ion (M^{2+})

	Cu^{2+}/M^{2+}	Polymer	D_{Ni}	D_{Zn}	D_{Cu}	α	α_r
Cu^{2+}/Ni^{2+}	1:1	NIP	24.8		429	17.3	
		Cu(II)-IIP	6.38		804	126	7.28
	10:1	NIP	108		283	2.63	
		Cu(II)-IIP	10.0		855	85.1	32.4
Cu^{2+}/Zn^{2+}	1:1	NIP		218	435	1.99	
		Cu(II)-IIP		120	789	6.57	3.30
	10:1	NIP		132	228	1.73	
		Cu(II)-IIP		37.0	823	22.2	12.8

Table 3 A comparison of selectivity of Cu(II)-IIP prepared in this work and in other publications

Publication	Adsorption capacity (mg/g)		Selectivity			
	Q Cu(II)-IIP	Q NIP	αCu/Ni	αCu/Zn	α_rCu/Ni	α_rCu/Zn
This work	14.8	4.08	126	22.2	32.4	12.8
[21]	0.3096	0.1997	13.6	4.12	2.47	3.17
[29]	2.033	[a]	7.45	5.68	6.83	5.98
[31]	14.91	[a]	107	175	18.7	18.1
[37]	76	[a]	1.44	3.26	1.58	3.10
[57]	22.2	[a]	11.6	6.04	10.9	5.92

[a] Data not available

Conclusions

This work reports the preparation and characterization of a new copper(II) ion-imprinted polymer. Prior to the precipitation polymerization, the compound of copper(II) and itaconic acid was prepared in methanol. The cross-linking monomer and an initiator were ethylene glycol dimethacrylate and 2,2′-azobisisobutyronitrile, respectively.

It should be pointed out that in this work WD-XRF method was first applied do determine the copper (II) content directly in the ion-imprinted polymer matrix, which allows checking, e.g., the effectiveness of leaching of the Cu(II) ions from the synthesized polymer. Furthermore, it enables to determine of the copper ions concentration in the polymer after synthesis.

The new Cu(II)-imprinted polymer exhibits good characteristics for adsorption of Cu^{2+} and shows very good selectivity towards Zn^{2+} and Ni^{2+} ions. It is worth mentioning that among other copper ion-imprinted polymers, the new Cu(II)-IIP

exhibits the best selectivity towards the nickel ion. Therefore, it can be successfully applied for the enrichment and selective adsorption of copper (II) ion from the samples of a complex matrix (e.g., biological fluids, environmental samples) prior to their analysis by the spectroscopic methods.

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