

Cu(II)-imprinted copolymer microparticles: effect of the porogen solvents on particle size, morphology and sorption efficiency

I. G. Dakova^{1*}, V. A. Dakov², M. Karadjov³, I. B. Karadjova¹

¹ Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski",
1 James Bourchier Blvd., Sofia, Bulgaria

² University Laboratory of Ecology and Environmental Protection, University of Forestry,
10 Kliment Ohridsky Blvd., Sofia, Bulgaria

³ Geological Institute, Bulgarian Academy of Science, Acad. G. Bonchev St. Bl. 24,
Sofia 1113, Bulgaria

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New Cu(II)-imprinted poly(hydroxyethyl methacrylate-co-trimethylolpropane tri-methacrylate) copolymer gels (Cu-IIPs) were prepared by precipitation copolymerization for the selective solid phase extraction of Cu(II). The Cu-IIPs were characterized by elemental analysis, Fourier transform infrared spectroscopy, scanning electron microscopy and nitrogen physisorption. The effect of the porogen solvents acetonitrile, toluene and their mixtures on particle size and morphology was presented. The adsorption properties of the synthesized copolymers were determined using batch experiments. At optimal chemical parameters the Cu-IIPs show fast sorption/desorption kinetics, high selectivity and satisfied adsorption capacity for adsorption of Cu(II). Finally, the prepared in acetonitrile Cu-IIPs were successfully applied to the selective recognition and determination of copper ions in surface waters.

Key words: Cu(II)-imprinted copolymer microparticles, copper ions, solid phase extraction.

INTRODUCTION

Copper is an essential micronutrient and participates in the cell growth, metabolism and enzyme activities, but slightly above the background concentrations copper can be highly toxic in surface waters to invertebrates and fish [1]. In natural surface waters the concentrations of Cu(II) are usually low with an average concentration of 2 µg/L [2]. Due to the influences of coexisting substances in real water samples, development of analytical procedures for reliable and accurate determination of Cu(II) in surface waters is still an analytical challenge [3]. A great variety of analytical procedures for Cu(II) separation and enrichment are proposed, based mainly on liquid–liquid extraction and micro-extraction [4–6], cloud point extraction [7, 8], coprecipitation [9] and solid phase extraction (SPE) [10–13]. However, SPE is preferred among them because of its significant advantages such as simplicity of performance, low solvent consumption, fast separation of phases without emulsion forma-

tion, high enrichment factor, good reproducibility and flexibility [14, 15]. Relatively low selectivity of conventional sorbents used is the main disadvantage of this approach. It could be significantly improved by using ion-imprinted polymers (IIPs) as sorbents. Generally, IIPs are a new generation of materials with ionic recognition sites having high affinity towards the analytes of interest as compared to the competing species which may also be found in the same matrices [16]. Properties of IIP are remarkable because of their high selectivity towards the target ion due to a memory effect resulting from their preparation process [17]. The general procedure for IIP preparation consists in the formation of a ligand-metal complex and its copolymerization with a cross-linker in order to create three dimensional recognition cavities inside the polymer network. Two main factors are responsible for their high selectivity: the affinity of the ligand toward the imprinted metal ion and the suitable size and shape of the generated cavities [18, 19]. Although polymer matrix is accepted as inert support its binding and sorption properties could influence sorption characteristics and efficiency of synthesized sorbents. Various types of functional monomers have been used in the synthesis of Cu(II) imprinted co-

* To whom all correspondence should be sent:
E-mail: ahid@chem.uni-sofia.bg

polymer gel matrixes: new-synthesized vinylated chelating agents [20, 21], acrylamide [22], N-vinyl-2-pyrrolidone [23], styrene [24], and 4-vinylpyridine (4-VP) [25, 26]. Recently, our group reported a simple procedure for synthesis of microspheric Cu-IIPs via precipitation copolymerization using methacrylic acid (MAA), 4-VP or their mixtures as functional monomers, trimethylolpropane trimethacrylate (TMPTMA) as a cross-linking agent and 4-(2-pyridylazo)resorcinol (RAR) as a specific Cu(II) ligand [27, 28]. However, the carboxylic and pyridine groups in MAA and 4-VP, respectively, are deprotonated in neutral and alkali solutions and this leads to decreased selectivity due to non-specific interactions with other cations. Replacement of MAA (acidic monomer) and 4-VP (basic monomer) with 2-hydroxyethyl methacrylate (HEMA) as neutral functional monomer could improve polymer selectivity. According to authors' knowledge, the Cu-IIPs containing HEMA as a functional monomer have not been synthesized and studied.

In this study, new Cu-IIPs was prepared via precipitation copolymerization using HEMA as a functional monomer, TMPTMA as a crosslinking agent and PAR as a specific for Cu(II) ligand in the presence of different porogen solvents. The synthesized Cu-IIPs were further characterized by scanning electron microscopy (SEM), nitrogen adsorption-desorption isotherms, Fourier transform infrared spectroscopy (FTIR) and elemental analysis. The effect of the type of porogen_solvents used on the morphology and the sizes of polymer particles were defined. The extraction efficiency and selectivity of synthesized Cu-IIPs and non-imprinted polymer gels toward Cu(II) were compared and most suitable of them proposed and applied for Cu(II) determination in surface water samples.

EXPERIMENTAL

Materials

All reagents were of analytical-reagent grade and in all experiments deionized water (DW) (Millipore Corp., Milford, MA, USA) was used. The stock standard solutions of Cu(II), Cd(II), Ni(II) and Pb(II) (1000 µg/mL) were Titrisol, Merck (Germany), in 2 % HNO₃. Working standard solutions were daily prepared by appropriate dilution with DW. PAR (as Na salt, Koch-Light Laboratories Ltd, England), HEMA, TMPTMA, 2,2'-azo-bis-isobutyronitrile (AIBN) (Merck, Germany), acetonitrile (ACN) and toluene (T) (Labscan, Ireland) were used without further purification. The pH was adjusted with the following buffer solutions: CH₃COONa/CH₃COOH for pH 4–6; KH₂PO₄/NaOH for pH 7 and 8.

Apparatus

Electrothermal atomic absorption spectrometric (ETAAS) measurements were carried out on a Perkin Elmer Zeeman 3030 spectrometer (Uberlinden, Germany) with an HGA-600 atomizer. The light source used was a hollow cathode lamp for Cu. The spectral bandpass was 0.7 nm. Pyrolytic graphite-coated graphite tubes were used as atomizers. Solutions (20 µL) were introduced into the graphite atomizer using an AS-60 autosampler. Only peak areas were used for quantification. The IR-spectra (4000–400 cm⁻¹) in KBr disks were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA). A scanning electron microscope (SEM, JEOL JSM-5500, Japan) was used for the determination of the microparticles shape and size. Elemental analysis was carried out with an universal CHNOS elemental analyzer Vario EL III (Elementar Analysen systeme GmbH, Germany). Specific surface area and pore size distribution were measured through nitrogen adsorption-desorption isotherms at 77 K using a Quantachrome NOVA 1200 apparatus (Quantachrome UK Ltd, England). A microprocessor pH meter (Hanna Instruments, Portugal) was used for pH measurements. A centrifuge EBA-20 (DJB Labcare Ltd, England) was used to separate microparticles and extracted metal ion solution in batch experiments.

Preparation of Cu(II)-IIPs

The synthesis of Cu(II) ion-imprinted and non-imprinted polymer gels was adapted from the procedure reported by Dakova et al. [27]. The Cu-IIPs (called P(Cu-PAR-HEMA)) were prepared via a precipitation copolymerization using HEMA (0.57 mmol) as a functional monomer, TMPTMA (0.93 mmol) as a cross-linking agent, AIBN (0.10 mmol) as an initiator, complex of the imprinted ion (Cu(II)) with PAR (0.08 mmol) as a template. Various porogen solvents: ACN, toluene, mixtures of ACN with toluene (25 mL) were tested. Briefly the solution was saturated with dry nitrogen for 15 min and copolymerization was carried out at T = 60 °C for 24 h. The polymer particles obtained were recovered by centrifugation, washed with ACN to remove unreacted monomers and other ingredients. Copper was removed from the sorbent by several, sequential elution steps using 2 M HNO₃. This procedure was repeated until the Cu concentration (template ions) in the eluate solution is below the limit of quantification (LOQ, 10σ criteria) as measured by ETAAS. Non-imprinted polymer sorbent (called P(HEMA)) was synthesized in the same way as described above, in the absence of Cu(II)-PAR complex. Cu(II) ion-imprinted polymer gels and

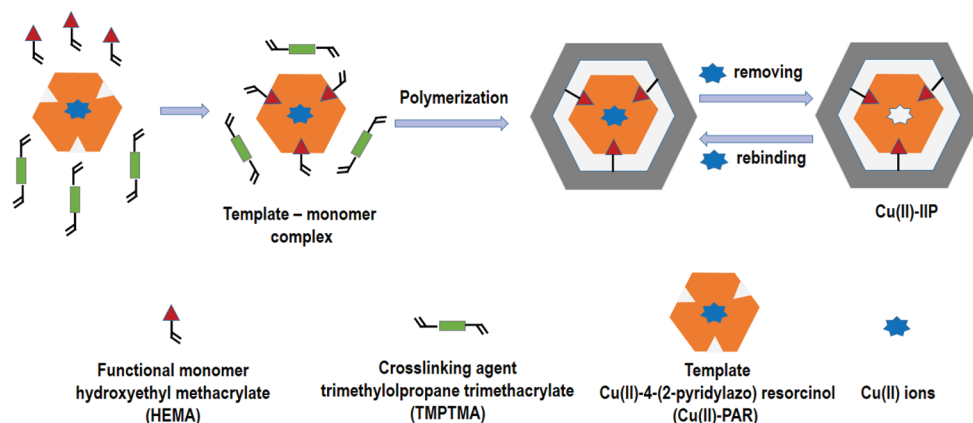


Fig. 1. Schematic representation of ion imprinting process

P(HEMA) were dried in a vacuum oven at 60 °C. The preparation of IIPs is presented schematically in Fig. 1.

Sorption experiments

The effect of pH on the sorption of Cu(II) was tested by equilibrating 50 mg of the prepared imprinted and non-imprinted polymer gels with 10 mL of the buffer solutions containing 0.1 µg of Cu(II) under different pH conditions for 30 min. The sample was centrifuged (5000 rpm), supernatant removed and polymer particles washed twice with DW. The Cu(II) was eluted from the sorbent with 1 mL 2 M HNO₃. Copper content in the effluante (supernatant after sorption) and eluate solutions was determined by ETAAS measurements. The kinetics of the Cu(II) sorption and desorption were investigated in a batch system by adding 50 mg of the P(Cu-PAR-HEMA) particles to 10 mL of Cu(II) solution at pH 7 for 5–40 min. Samples were regularly collected at appropriate time intervals, separated and analyzed for Cu(II) content. To measure the sorption capacity, 50 mg of P(Cu-PAR-HEMA) and P(HEMA) were equilibrated with 10 mL Cu(II) containing solutions with increasing initial concentrations (50–450 µmol/L) under optimum conditions at room temperature. Competitive loading of Cd(II), Cu(II), Ni(II) and Pb(II) by Cu(II)-imprinted and non-imprinted polymer gels was examined in aqueous solutions containing 0.1 µg/mL Cu(II), 0.1 µg/mL Cd(II), 0.3 µg/mL Ni(II) and 0.3 µg/mL Pb(II) at pH 7.

Sorption characteristics of the polymer particles

The degree of sorption (E%), distribution ratio (D), selectivity coefficient ($S_{Cu/Me}$) and relative se-

lectivity coefficient (k') were calculated by the following equations:

$$E \% = [(A_i - A_{eff}) / A_i] \cdot 100 \quad S_{Cu/Me} = D_{Cu} / D_{Me}$$

$$D = (A_i - A_{eff}) / A_{eff} \quad k' = S_{imprinted} / S_{non-imprinted}$$

where A_{eff} (µg) is the cation amount in the effluante solution after sorption from a solution with an initial cation amount A_i (µg); D_{Cu} and D_{Me} are the distribution ratios for Cu(II) and Cd(II), Ni(II) or Pb(II), respectively.

RESULTS AND DISCUSSION

Synthesis of Cu(II)-IIP and characterization studies

Cu-IIPs were synthesized by “trapping” technique, i.e. complexes between target metal ion and non-vinylated chelating agent get trapped inside the polymer matrix during the polymer formation. In this case, preparation of Cu(II)-IIPs included several steps (Fig. 1). Firstly, the template-monomer (prepolymerization) complex was formed by non-covalent interactions between the functional monomer (HEMA) and the template molecule (Cu(II)-PAR complex). Secondly, the copolymer network was formed by the precipitation copolymerization of the prepolymerization complex with TMPTMA as a cross-linker. Finally, Cu(II) ions were removed from copolymer network prepared leaving behind some specific binding sites with functional groups in a predetermined orientation and cavities with special size of templates.

In the present investigation, initially four types of Cu-IIPs were synthesized using varying solvent composition: ACN, toluene and mixture of ACN-toluene (80:20 and 60:40, v/v) to observe

the solvent effect on the morphology of the polymer gels. The SEM micrographs of prepared P(Cu-PAR-HEMA)s are presented in the Fig. 2. It is seen that spherical particles with mean diameters of about 3 μm and about 1 μm were obtained when ACN and ACN-toluene (80:20) were used as porogen solvents (P_{ACN} (Cu-PAR-HEMA) and ($P_{\text{ACN-T(80:20)}}$ (Cu-PAR-HEMA)), respectively (Fig. 2, A and B). Irregular shaped and agglomerated particles can be seen in the SEM images of Cu-IIPs synthesized in the presence of mixture of ACN-toluene (60:40) ($P_{\text{ACN-T(60:40)}}$ (Cu-PAR-HEMA)) (Fig. 2, C). It might be concluded that when the quantities of toluene in the ACN-toluene mixture were low (0% or 20%), large spherical Cu-IIPs particles with relative uniformity and monodispersity were obtained. However, as the percentage of toluene in the solvent mixture increased to about 40%, the particle shape changed from globular to agglomerates formed by smaller particles (Fig. 2, C). A similar influence of the quantity of toluene in the ACN-toluene mixture on the size of molecularly imprinted microspheres prepared by precipitation polymerization was also found by Pardeshi et al. [29]. The SEM micrographs of the particles P_{T} (Cu-PAR-HEMA) prepared in toluene showed irregular aggregates of bigger particles packed together with a smoothly spherical surface (Fig. 2, D).

The specific surface area, total pore volume and average pore diameter, for the Cu-IIPs and non-imprinted P(HEMA) were determined from nitrogen adsorption-desorption isotherms. Both P_{ACN} (Cu-PAR-HEMA) and P_{T} (Cu-PAR-HEMA), have similar surface areas (4 m^2/g and 3 m^2/g) and average pore diameters (15 nm and 12 nm), while P(HEMA) has higher surface area (9 m^2/g) and average pore diameters (18 nm). As it is evident, all the polymer gels studied present a mesoporous structures. The imprinted P_{ACN} (Cu-PAR-HEMA) shows more narrow pore size distribution than non-imprinted P(HEMA) particles (Fig. 3, A and B).

To evaluate the degree of PAR incorporation, the elemental analysis of the Cu-IIPs and non-imprinted P(HEMA) were performed. The nitrogen content in all synthesized Cu-IIPs was in the range from 2.25 wt% to 2.15 wt%. This increase in nitrogen content for imprinted gels compared to P(HEMA) (0.02 wt%) suggests that the PAR molecules are successful incorporated into copolymer network of imprinted sorbents.

FTIR spectroscopy was used to prove the presence of HEMA, TMPTMA and PAR in the chemical structure of the imprinted and non-imprinted copolymer gels. FTIR spectra of Cu-IIPs and P(HEMA) have the characteristic C=O stretching bands which

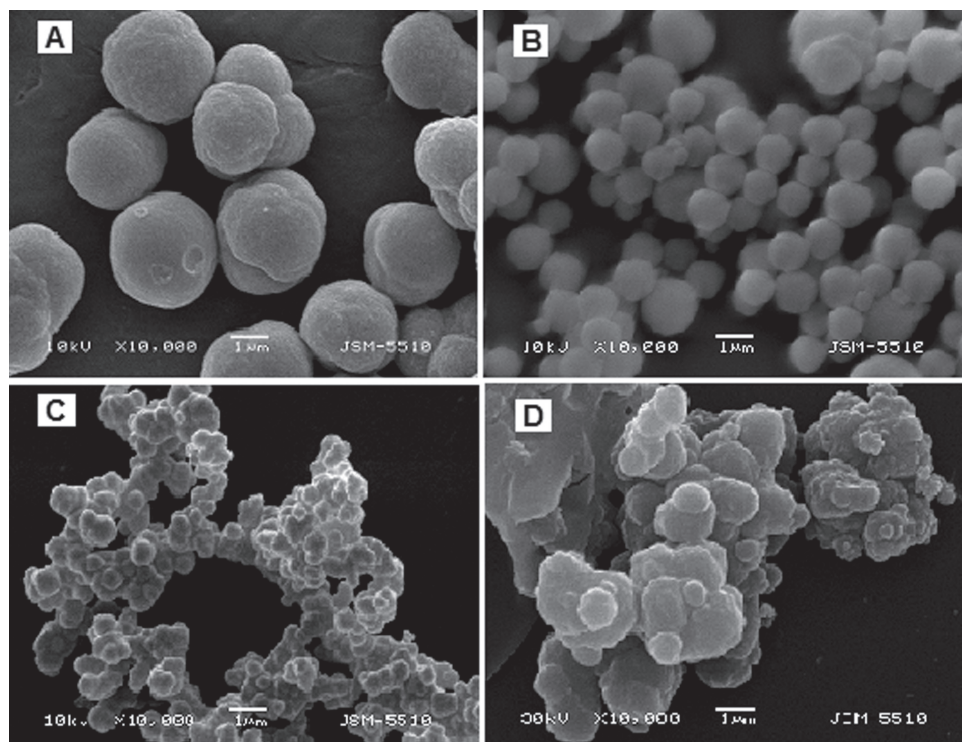


Fig. 2. Scanning electron micrographs of Cu-IIPs: (A) – P_{ACN} (Cu-PAR-HEMA); (B) – $P_{\text{ACN:T(80:20)}}$ (Cu-PAR-HEMA); (C) – $P_{\text{ACN:T(60:40)}}$ (Cu-PAR-HEMA); (D) – P_{T} (Cu-PAR-HEMA)

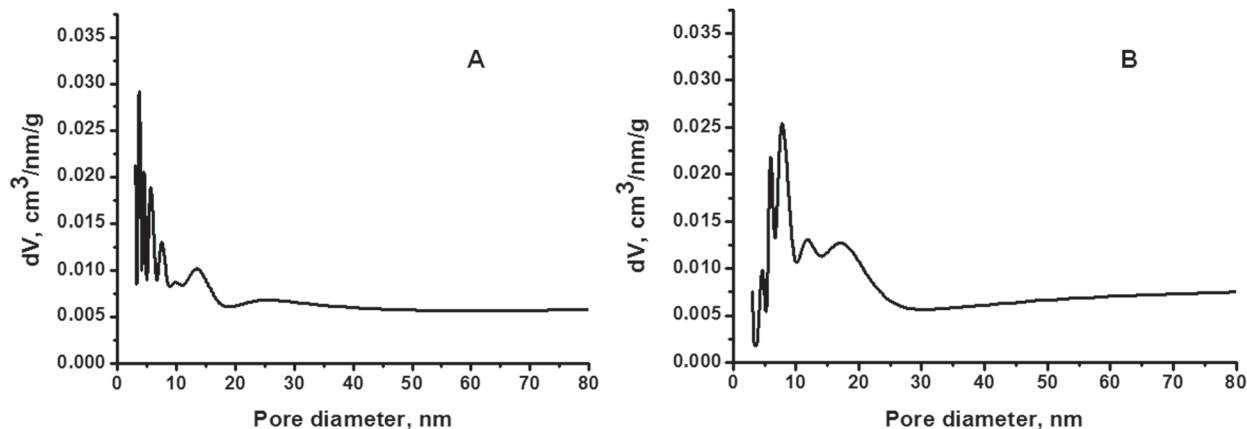


Fig. 3. Pore-size distributions for the imprinted $P_{ACN}(Cu-PAR-HEMA)$ (A) and non-imprinted $P(HEMA)$ (B) prepared in ACN

belongs to the ester functional group of TMPTMA (observed at 1730 cm^{-1} and 1728 cm^{-1} for $Cu(II)$ -IIP and $P(HEMA)$ cm^{-1} , respectively). The four ring stretching bands of pyridine were observed in the $1650\text{--}1450\text{ cm}^{-1}$ region (1640 cm^{-1} , 1596 cm^{-1} , 1560 cm^{-1} and 1465 cm^{-1}) [30, 31]. These data confirmed the presence of PAR in the synthesized Cu-imprinted copolymer gels.

The practical application of any sorbent depends from one side on its chemical properties and from other side on its particles shapes and size and their size distribution. The results obtained for the Cu-IIPs synthesized in the presence of various porogen solvents showed that $P_{ACN}(Cu-PAR-HEMA)$ is the most suitable material for routine application in the analytical practice.

Extraction efficiency of $P_{ACN}(Cu-PAR-HEMA)$ in comparison with $P(HEMA)$

The pH value plays an important role in the adsorption performance of the IIPs toward different ions since it affects on the interaction of the metal ions with the “trapped” chelating agents and functional groups of the polymer matrix. The pH-dependence (in the range 3–9) on the degree of sorption (E , %) of $P_{ACN}(Cu-PAR-HEMA)$ and non-imprinted ($P(HEMA)$) sorbents is presented in Fig. 4. The results show that the E values achieved for imprinted polymer gel are well above those for the non-imprinted $P(HEMA)$ sorbent. The quantitative sorption of $Cu(II)$ ions on the $P_{ACN}(Cu-PAR-HEMA)$ was achieved at pH 7, while the maximal degree of sorption on $P(HEMA)$ was 51%. Evidently, the specific interaction between chelating agent PAR and $Cu(II)$ ions does not take place in the case of $P(HEMA)$, thus explaining the observed lower degree of sorption. The degree of sorption for both

studied sorbents decreased at $pH > 7$, most probably this is related to the $Cu(II)$ ability to form stable complexes with hydroxide groups ($Cu(OH)_4^{2-}$). The formation of these complexes prevents quantitative sorption of $Cu(II)$ ions and reduces $Cu(II)$ sorption on $P_{ACN}(Cu-PAR-HEMA)$ and $P(HEMA)$ as a whole (Fig. 4) at pH 7–9.

Quantitative elution of $Cu(II)$ retained on both sorbents was achieved using 2 M HNO_3 with minimum volume of 1 mL. The kinetic investigations of both processes of sorption and desorption of $Cu(II)$ showed that quantitative sorption was reached for 20 min while for quantitative desorption 30 min has to be used for both sorbents. The average maximum adsorption capacities were $57.8\text{ }\mu\text{mol/g}$ and $21.5\text{ }\mu\text{mol/g}$ for $P_{ACN}(Cu-PAR-HEMA)$ and $P(HEMA)$, respectively. As it might be expected the adsorption capacity of $P_{ACN}(Cu-PAR-HEMA)$ was higher versus the non-imprinted polymer particles $P(HEMA)$, indicating that the cavities created after

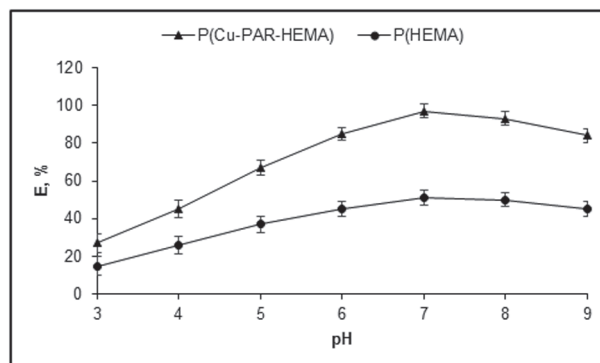


Fig. 4. pH-dependence of the degree of sorption (E , %) of $Cu(II)$ ions with $P_{ACN}(Cu-PAR-HEMA)$ and $P(HEMA)$

Table 1. Degree of sorption (E, %), distribution ratios (D), selectivity coefficients ($S_{Cu/Me}$) and relative selectivity coefficients (k') of $P_{ACN}(Cu-PAR-HEMA)$ and $P(HEMA)$ for Cu(II)

Metal Ion	P(Cu-PAR-HEMA)			P(HEMA)			k'
	E	D	$S_{Cu/Me}$	E	D	$S_{Cu/Me}$	
Cu(II)	97±1	32.3		51±1	1.0		
Cd(II)	42±2	0.5	60.5	31±2	0.4	2.3	26.1
Ni(II)	49±2	0.7	47.1	35±2	0.5	1.9	24.4
Pb(II)	53±1	1.1	28.7	42±2	0.7	1.4	19.9

removal of template ions ensures higher affinity of Cu(II) toward the $P_{ACN}(Cu-PAR-HEMA)$ than to the $P(HEMA)$ confirming the imprinting effect.

In order to examine the selectivity of the imprinted $P_{ACN}(Cu-PAR-HEMA)$ and $P(HEMA)$ sorbents toward Cu(II) ions, competitive adsorption of Cd(II), Cu(II), Ni(II) and Pb(II) from their model mixture was studied. The Cd(II), Ni(II) and Pb(II) ions were chosen as the competitor species because these ions often coexisted in environmental water samples. Although these ions have similar chemical properties and ionic radii ((Cd(II)=0.109, Cu(II) = 0.080, Ni=0.083 and Pb=0.133 nm [32]), significant differences were observed in their extraction characteristics (Table 1). Results presented in Table 1 could be summarized as follows: higher extraction efficiency for Cu(II) than those for Cd(II), Ni(II) and Pb(II); higher $S_{Cu/Me}$ values for $P_{ACN}(Cu-PAR-HEMA)$ compared to $P(HEMA)$; high values of the relative selectivity coefficients (k') which confirmed the selectivity of the imprinted $P_{ACN}(Cu-PAR-HEMA)$.

Application of the method

The applicability of $P_{ACN}(Cu-PAR-HEMA)$ for Cu(II) determination in surface waters was tested for sea and river water samples. Samples of Black sea water and water from river Iskar were spiked with known amounts of Cu(II) in the range (1 and 5 µg/L) and passed through the procedure: 50 mL water sample with pH adjusted to 7, was stirred with 50 mg $P_{ACN}(Cu-PAR-HEMA)$ for 20 mins. After centrifugation supernatant was removed, sorbent washed with 10 mL DW and finally eluted with 1 mL 2 M HNO_3 . The concentration of Cu(II) in the eluate was determined by ETAAS. Results obtained showed that Cu(II) recoveries achieved varied between 94–95% and 95–97% for sea water and river water, respectively. Relative standard deviations are in the range 5–9% for both types of water. Overall $P_{ACN}(Cu-PAR-HEMA)$ could be successfully applied for Cu determination in surface waters.

CONCLUSIONS

In the present paper new Cu(II) imprinted copolymer gels were successfully synthesized by a precipitation copolymerization with HEMA as a functional monomer. It was shown that the polymer particles size and morphology depend on porogen solvent used and ACN was proposed as more suitable reagent which ensures their better uniformity and monodispersity. The prepared $P_{ACN}(Cu-PAR-HEMA)$ sorbent is characterized with good binding properties, fast sorption/desorption kinetics and high selectivity toward Cu(II).

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CU(II)-ОТПЕЧАТАНИ СЪПОЛИМЕРНИ МИКРОЧАСТИЦИ: ВЛИЯНИЕ НА РАЗТВОРИТЕЛЯ ВЪРХУ РАЗМЕРА И МОРФОЛОГИЯТА НА ЧАСТИЦИТЕ И СОРБЦИОННАТА ИМ ЕФЕКТИВНОСТ

И. Г. Дакова^{1*}, В. А. Даков², М. Караджов³, И. Б. Караджова¹

¹ Факултет по химия и фармация, СУ „Св. Климент охридски“, бул. „Джейм Баучер“ 1, София, България

² Университетска лаборатория по екология и опазване на околната среда, Лесотехнически университет бул. „Климент Охридски“ 10, София, България

³ Геологически институт, Българска академия на науките, ул. „Акад. Г. Бончев“, бл. 24, София 1113, България

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(Резюме)

Нови Cu(II)-отпечатани поли(хидроксиетилметакрилат-съ-триметилпропан триметакрилат) съполимерни гелове (Cu-IPs) са получени чрез утаителна съполимеризация и са използвани за селективна твърдофазна екстракция на Cu(II). Cu-IPs са охарактеризирани чрез елементарен анализ, инфрачервена спектроскопия с Фурие преобразуване, сканираща електронна микроскопия и нискотемпературна сорбция на азот. Представено е влиянието на порогени разтворители като ацетонитрил, толуен и техни смеси върху размера и морфологията на частиците. Адсорбционните свойства на получените съполимери са определени чрез експерименти в статичен режим. При оптимални химични условия Cu-IPs показват бърза кинетика на сорбция/десорбция на Cu(II), висока селективност и адсорбционен капацитет. Получените в ацетонитрил Cu-IPs са успешно приложени за селективно определяне на медни йони в повърхностни води.