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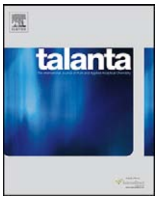

# New use of polypyrrole-chloride for selective preconcentration of copper prior to its determination of flame atomic absorption spectrometry

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ABSTRACT

Polypyrrole-chloride was studied as a new sorbent for preconcentration of copper(II) using solid-phase extraction prior to determination by flame atomic absorption spectrometry. The sorbent showed an extremely high selectivity towards copper(II) as an anionic chelate, i.e. Cu (pyrocatechol violet)$_2{}^{2-}$ in the pH range of 4–7. Copper(II) as Cu (pyrocatechol violet)$_2{}^{2-}$ was selectively retained on a column containing 1.0 g of polypyrrole-chloride and quantitatively eluted by 3 mL of 2.0 mol L$^{-1}$ nitric acid. The calibration graph was linear with a correlation coefficient of 0.999 at levels near the detection limit and up to at least 50 μg L$^{-1}$. When applied for preconcentration and determination of copper in tap water, waste water and hot spring water, the recoveries were found to be 96, 101 and 95%, respectively, with high precision (% relative standard deviation <4%) and low detection limit (0.87 μg L$^{-1}$). Verification of the accuracy was carried out by the analysis of a standard reference material (BCR 715 wastewater-SRM). The relative error was +3.33%. The proposed method was successfully applied to the determination of copper in tap water, waste water and hot spring water samples.

## 1. Introduction

Copper is an essential trace element that is vitally important for the human body. Human organs with the highest concentrations are kidney and liver, followed by brain, heart and bone in decreasing order. These organs contain more than half the copper in the body. It functions as a co-factor in various enzymes and in copper-based pigments. Almost all of the copper in the body is bound to proteins. Copper is a heavy metal that is toxic in its unbound form. Copper(II) ion is prone to bind to the cell membrane, hindering the transport process through the cell wall heavily [1]. Excessive amount of copper can cause abnormal metabolism [2]. So, there is a critical need for timely evaluation of the existing level of copper in environmental samples like water. Copper concentration in potable water is usually very low ($\leq$20 μg L$^{-1}$) [3]. The concentration of copper in lakes and rivers ranges from 0.5 to 1000 μg L$^{-1}$ with an average concentration of 1 μg L$^{-1}$. In groundwater the average of copper concentration is almost 5 μg L$^{-1}$. As the levels of copper in natural water samples are low, a preconcentrative separation and determination of trace copper from the natural water samples is essential and needs much more attention.

Solid-phase extraction (SPE) is one of the most important preconcentration and separation methods, due to its advantages like simplicity, selectivity, eco-friendliness, reusability, flexibility to choose the solid phase, high preconcentration factor, low consumption of the organic solvents or no requirement of toxic solvent, low cost and extraction time for preconcentration of trace metals. In the SPE procedures based on adsorption, trace species are usually retained on non-polar polymeric sorbents (reversed phase) through van der Waals forces or hydrophobic interaction. However, because most trace metal species are ionic, they will not be retained by such polymeric sorbents. The most simple SPE to be used in practice is based on adsorption of heavy metal ions as chelates and/or inorganic complexes in neutral form. So, in some cases, chelating agents may be directly added to the sample for chelation of trace elements, the chelates being further retained on an appropriate solid-phase sorbent [4–8]. The selectivity of the solid-phase polymeric sorbents mainly depends on the selectivity of chelating agent forming chelate with metal ions and functional groups in structure of the sorbent.

On the other side, the sites having positive or negative charges in the polymer skeleton can occur during a polymer synthesis [9,10]. In this case, electroneutrality of the polymer matrix is maintained by the incorporation of cation [11,12] or anion [13,14] as a counter-ion from the reaction solution. The associated counter-ions can be exchanged with relevant ions in a solution. Thus, these polymers can retain trace metal ions in convenient chemical form by electrostatic attraction. In addition to the surface properties, the structure of most polymers having ion exchange properties can be included some groups such as π-electrons, rings and/or functional group atoms, which are responsible from adsorption of trace metal ions in appropriate form. The polymers having adsorptive and ion

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exchanger properties may provide interesting results for selective retention of metal chelates in ionic form.

Based on the discussion above, it can be concluded that polypyrrole having extremely intrinsic surface properties will be useful for preconcentration of trace heavy metal ions. Because polypyrrole possesses adsorptive and ion exchanger properties. It is also one of the few polymers that can be synthesized both chemically [15–18] and electrochemically [18–20] from both aqueous and non-aqueous solvents. The chemical synthesis of polypyrrole is very important as it is a more feasible route for producing polypyrrole on a large scale, required for SPE application. During chemical polymerization of pyrrole, physical, chemical or electrical properties of polypyrrole can be altered by doping polypyrrole with various dopants or agents. For example, when $FeCl_3$ is used as oxidants, $Cl^-$ ion is incorporated as counter-ion into the polymer matrix. The anion excahange properties of polypyrrole-chloride (PPyCl) may be used to uptake anions or metal complexes in anionic form in aqueous solutions. Polypyrrole-based adsorbents, polypyrrole coated various materials and polypyrrole have attracted some research interest as an sorption material in this regard. However, these are limited with adsorption of organic and biological species from aqeuous samples [9,15,21–23]. There are a couple of studies for heavy metal ions adsorption onto polypyrrole-impregnated materials [24–26]. Also, the conducting polymer materials as polypyrrole, polythiophene and their derivatives in electromodulated extractions are used for various sample clean-up operations and preconcentrations of some cations and anions [27]. Up to now, according to our best knowledge, directly, polypyrrole-chloride has not been used to concentrate trace metal ions.

Pyrocatechol violet (PV) as a chelating agent has been widely used because of its high complex formation constants with metal ions for spectrophotometric metal determinations [28] and for preconcentration of trace metal ions from aqueous solutions [5,29–31]. Furthermore, pyrocatechol violet forms anionic chelates with metal ions [32].

These outcomes discussed above encourage us to examine the efficiency of PPyCl as a sorbent for preconcentration of trace copper ions. This research thus focused on the use of PPyCl for a highly selective solid-phase extraction and preconcentration of Cu(II) as an anionic chelate, i.e. $Cu(PV)_2{}^{2-}$, for improving the detection limit of the determination by flame atomic absorption spectrometry (FAAS). The performance was evaluated by applying the proposed method to the determination of Cu(II) in a variety of water samples.

## 2. Experimental

### 2.1. Instrumentation

A PerkinElmer Model Aanalyst 700 flame atomic absorption spectrometer with deuterium background correction was used throughout this work. A copper hollow cathode lamp was used as light source at a wavelength of 324.8 nm and operated at 4.0 mA with a 0.7 nm spectral bandpass. An air–acetylene burner was used for the determination of copper.

The pH measurements were conducted by a pH meter Hanna instruments model pH 211 calibrated against two standard buffer solutions, pH 4.0 and 7.0.

### 2.2. Material and chemicals

All chemicals used in this work were of analytical reagent grade and were used without further purification. Ultra-pure (UP) quality water (resistivity 18.2 MΩ cm$^{-1}$) obtained with a reverse osmosis system (Human Corporation, Seoul, Korea) was used for all dilutions. All the plastic and glasswares were cleaned by soaking in dilute $HNO_3$ (1 + 9) and then thoroughly rinsed with UP water prior to use. Standard and working solutions of Cu(II) was prepared by stepwise dilution of 1000 mg L$^{-1}$ Cu(II) stock solution supplied by Merck (Darmstadt, Germany).

Blank solution was prepared by UP water and adjusted pH at 5.0. A 0.05% (m/v) pyrocatechol violet (PV) solution using solid PV from Merck was prepared daily in UP water. 2 mol L$^{-1}$ $HNO_3$ used as an eluent was prepared using concentrated $HNO_3$ from Merck.

The pH of the model solution was adjusted to pH 2–3 with phosphate buffers, pH 4–6 with $CH_3COONH_4/CH_3COOH$ buffers, while pH 8–10 with $NH_3/NH_4{}^+$ buffers. Pyrrole (99%) from Merck and $FeCl_3{\cdot}6H_2O$ (97%) from Aldrich were used to synthesize polypyrrole doped with the chloride. Polypropylene empty solid-phase extraction (SPE) tubes (6 mL) were purchased from Supelco.

### 2.3. Synthesis of polypyyrole

PPyCl was synthesized from pyrrole by chemical oxidation–polymerization method, with Fe(III) as oxidant [10]. Polymerization was carried out in aqueous solution. In brief, 1.75 mL of pyrrole (0.025 mol) was added in droplets into 150 mL of aqueous $FeCl_3{\cdot}6H_2O$ (13.5 g, 0.05 mol) solution with stirring at room temperature. The mixture was continuously mixed for 3 h to allow the oxidation–polymerization reaction to be fully proceeded. Then, the resultant black precipitates were separated by filtration, thoroughly washed with ultra-pure (UP) water and methanol to remove any possible iron residues, and then dried at temperature about 40 °C (in an oven), for 24 h. The black powders so obtained were PPyCl, i.e. PPy doped with chloride and used to fill a empty cartridge column without further any pre-treatment.

### 2.4. Solid-phase extraction cartridges

Polypyyrol-chloride packed cartridges were prepared by an empty SPE tube (6 mL). 0.7 or 1.0 g of PPyCl was packed into the cartridge after a PTFE frit was set at the cartridge bottom. In the front of the cartridge, another PTFE frit was set to fix the height of the polymer. The polymer bed was approximately 3.5–4 cm long for 0.7 and 1.0 g polymer, respectively.

### 2.5. Column procedure

The column method was used to define an optimum condition for the sorption and desorption of the metal ions. For column procedure, test solutions containing 5 μg Cu(II) and some examined heavy metal ions were prepared in a 25 mL volumetric flask using pure water. 2.0 mL of buffer solution to give the desired pH between 1.0 and 10.0 and 2.0 mL of 0.05% (m/v) PV solution were added. The test solutions were passed through a column at a flow rate of 2.0 mL min$^{-1}$ by vacuum. The flow rates were controlled by a stopcock of the column. The analytes retained by the PPyCl column were eluted by 3 mL of 2.0 mol L$^{-1}$ $HNO_3$ at a flow rate of 2 mL min$^{-1}$. The concentration of copper in the effluent was determined by FAAS with conventional nebulization or after the effluent is evaporated up to 1 mL; it is determined by FAAS adopted with a micro-injection technique based on use of a micropipet tip (100 μL) connected to the capillary tube of nebulizer [33,34].

After each elution, it was ready for use without further pretreatment. To clean and condition the column, the column was washed with 1.0–2.0 mL of relevant buffer solution before loading the sample solution. The performance of the column was stable at least over 500 preconcentration cycles.

The effect of loading flow rate, concentration of eluent solution, sample volume and interfering ions were evaluated in quadruplicate, i.e. in duplicate for each of two columns in parallel. The sample volume was 10.0 mL for the study of the effect of loading flow rate

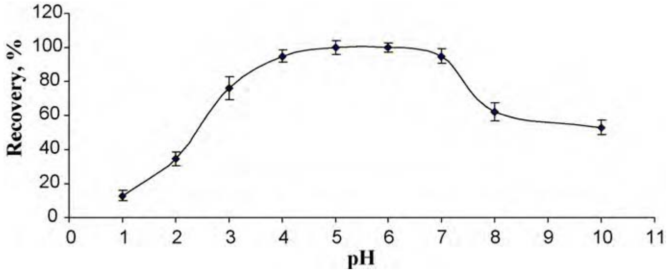

**Fig. 1.** Dependence of copper retention on PPy-chloride with the pH of sample solution (eluent: 1 mol $L^{-1}$ $HNO_3$; eluent vol.: 2 mL; flow rate: 2 mL $min^{-1}$; PPyCl: 0.7 g, $n = 4$).

and it varied from 10 to 150 mL for the study of the effect of sample volume.

### 2.6. *Analysis of water*

Tap water was taken from a tap in our laboratory at Pamukkale University, filtered through 0.45 μm cellulose acetate membranes (Millipore, Bedford, MA, USA) under vacuum and immediately analyzed using the procedure given above. Waste water sample was taken from a municipal waste water treatment plant for Denizli city, Turkey. Karahayıt hot spring water sample was obtained from a famous source of hot spring water known as red water in Karahayıt, Denizli, Turkey. Both waste water and hot spring water samples were brought to the laboratory in 1 h and filtered using 0.45 μm cellulose acetate membranes. Then, the filtered water samples were buffered to pH 5 and immediately analyzed using the proposed procedure above given.

## 3. Results and discussion

### 3.1. *Effect of pH on the retention of copper*

As a generally accepted rule, the pH value of solutions is a key parameter for quantitative extraction of metal species due to its important influence not only on functional site dissociation of solid-phase extractor surface, but also on the solution chemistry of metal ions including hydrolysis, complexation by chelating and inorganic ligands, redox reactions, precipitation of the metals. So, the effect of pH on the retention of Cu, Pb, Ni, Cr, Cd, Mn and Zn as their pyrocatechol violet chelates in this study was firstly investigated in the pH range of 2 and 10. The results showed that copper among the examined analytes was quantitatively and selectively retained at pH 4 and 6. Therefore, in further studies, we examined the effect of pH on the recovery of copper ions as Cu(PV) anionic chelate in detail.

Results concerning the effect of pH on the solid-phase extraction of copper are presented in Fig. 1. An obvious increase in the retention efficiency was observed as the pH value increased from 2.0 to 4.0, and it kept virtually unchanged in the range of 4.0–7.0; thereafter an important decline of the efficiency appeared upon the further increasing the pH of solution. It is thus apparent that pH = 5 is appropriate for the quantitative retention efficiency of Cu(II) as an anionic chelate, i.e. $Cu(PV)_2{}^{2-}$ on the PPy. The influence of volume of buffer was investigated; addition of 1.0–5.0 mL of buffer did not have any effect on the sorption of $Cu(PV)_2{}^{2-}$. Therefore, 2.0 mL of the acetate buffer was used in all the subsequent experiments.

The changing of retention efficiency with changing pH may be explained by formation of an anionic chelate, i.e. $Cu(PV)_2{}^{2-}$, between pyrocatechol violet (PV) and copper(II) ion [31], and the dissociation constants of PV ($pK_a$ values: 1; 7.82; 9.76; 11.79) [35,36].

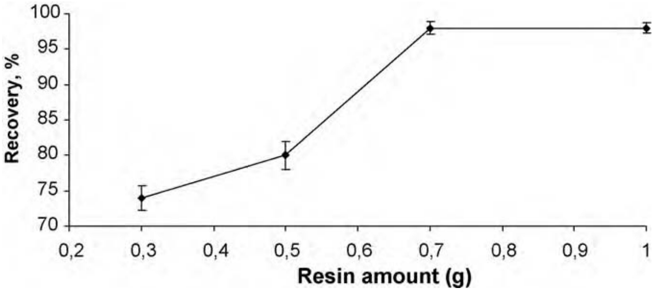

**Fig. 2.** The effect of resin amount on retention of copper (pH = 5; eluent: 1 mol $L^{-1}$; eluent vol.: 2 mL; flow rate: 1–2 mL $min^{-1}$; PPyCl: 0.7 g, $n = 4$).

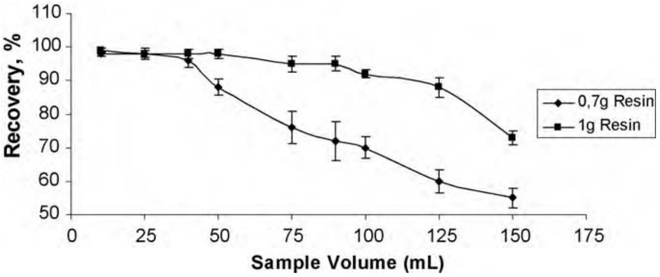

**Fig. 3.** Effect of sample volume on retention of copper (pH = 5, flow rate: 1–2 mL $min^{-1}$, $n = 4$).

Based on $pK_a$ values of PV, it is concluded that PV at lower than pH 7.82 ($pK_{a2}$) is in mono-anionic form because of ionic equilibrium of the sulfonic acid in PV at higher than pH 1 ($pK_{a1} = 1$). Therefore, Cu(II) as $Cu(PV)_2{}^{2-}$ is found in the acidic solution. Thus the Cu–PV anionic chelate as $Cu(PV)_2{}^{2-}$ is retained by PPy-chloride, i.e. $PPy^+Cl^-$, in cationic form ($PPy^+$) because of exchanging of divalent $Cu(PV)_2{}^{2-}$ with chloride on $PPy^+Cl^-$. At pH values close to pH 7.82 and after pH 7.82, because of decreasing of mono-anionic form of PV, the retention drops from pH 6 to pH 8.

On the other hand, by decreasing until pH 1, the equilibrium of the sulfonic acid shifts to the sulfonic acid form (neutral structure) in a way that will decrease the amount of sulfonate form of PV. Therefore, the recovery values for copper ion decrease because of decreasing of $Cu(PV)_2{}^{2-}$ amount. The discussions above indicate that the Cu–PV divalent anionic chelate is mostly retained with anion exchange mechanism by PPy-chloride, i.e. $PPy^+Cl^-$, in cationic form. However, because of both PPyCl and $Cu(PV)_2{}^{2-}$ having π-electrons, also, it may be concluded that additional π–π interaction is responsible from retention of copper through the column packed with filled PPy-chloride.

### 3.2. *Sorbent amount and sample breakthrough volume*

Sorbent amount is a significant parameter to obtain the quantitative retention of Cu–PV chelate. Also it concludes the capacity of a sorbent for given initial concentration of analyte at the operating conditions. The influence of PPyCl amount on retention of copper in the column is represented in Fig. 2. The sorption of copper–PV anionic chelate increases by increasing the amount of PPyCl and the sorption was almost constant at higher amount of 700 mg.

On the other hand, breakthrough volume is the maximum sample volume that should percolate through a given mass of sorbent after which an analyte starts to elute from the sorbent resulting in nonquantitative recoveries. It was determined by varying the sample volume over a range of 10–150 mL, at two different resin amounts (0.7 and 1.0 g). The percentage of retention efficiency against sample volume is depicted in Fig. 3. The results indicate that breakthroughs occur at volumes 40 and 90 mL for 0.7 and 1.0 g sorbent, respectively. The eluents used to elute copper from the columns filled with 0.7 and 1.0 g PPyCl were 2 mL of 1 mol L$^{-1}$ $HNO_3$ and 3 mL of 2 mol L$^{-1}$ $HNO_3$, respectively.

### 3.3. *Effect of eluent type, volume and concentration*

Up to now, several acid solutions have been widely used for the elution of metal ions or metal chelates retained by a sorbent. In this work, at lower pH level there is a sharp decrease in the recovery yields of copper (Fig. 1). Due to this fact, nitric acid as an eluent was chosen for desorption of the retained copper from the column. Also, nitric acid does not interfere in the subsequent determination by FAAS which is an advantage for determination.

The suitable acid concentration and volume are other important factors to prevent the contamination from eluent and to obtain a high preconcentration factor. Therefore, the desorption of the retained copper–PV anionic chelate from a column filled with 1.0 g PPyCl was examined using $HNO_3$ solutions at various concentrations. The quantitative recoveries (>95%) were obtained for copper with 10 mL of 1.5–3.0 mol L$^{-1}$ $HNO_3$. To achive higher preconcentration factor, the effect of eluent volume in the range of 2 and 4 mL on the recovery of copper was examined using 2 mol L$^{-1}$ $HNO_3$ as an eluent. The results showed that the smallest usable volume of 2 mol L$^{-1}$ $HNO_3$ is 3.0 mL for quantitative desorption of copper from a column filled with 1.0 g PPyCl. In this case, the preconcentration factor with 90 mL of sample volume was calculated as 30. However, if necessary, the preconcentration factor can be increased up to 90 using 1.0 g resin and evaporating effluent up to 1.0 mL. To examine this lower volume for the flame atomic absorption spectrometric measurements, we used a micro-injection method for sampling from 1.0 mL effluent [33,34]. For further studies, 1.0 g of the sorbent material with 3.0 mL of 2 mol L$^{-1}$ $HNO_3$ which is evaporated to 1.0 mL was used to preconcentrate copper from 90 mL of sample volume.

Regeneration is one of the key factors in evaluating the performance of the sorption materials. The stability and regenerability of the column filled with PPyCl were examined. The experiments were carried out using the PPyCl column for Cu–PV retention in different days and the number of these experiments was noted down. The results showed us that PPyCl is stable in operation process, enabling more than 500 loading and elution cycles without decrease in the recoveries of Cu–PV chelate. Beyond 500 cycles, there was a drop in the retention of Cu–PV.

### 3.4. *Ligand amount*

The ligand concentration plays an important role in the retention of analytes because in its absence, solid-phase material does not retain completely the metal ions. However, excess PV prevents the retention of copper ion due to sorptive competition between Cu–PV chelate and PV itself on PPyCl. Therefore, the influence of the pyrocatechol violet (PV) amount on the retention of copper(II) was examined by varying the amounts of PV from 0 to 2.5 mg. It was found that, the recovery of the metal ions increased with increasing amounts of PV added and reached a quantitative value with at least 1 mg PV. It was also quantitative at 1.25 mg PV. After that, the recovery values decreased. The amount of PV in the sample solution is recommended as 1 mg for further studies.

### 3.5. *Effect of flow rates on retention and elution*

Flow rate of sample solution is one of the important parameters in SPE studies. The time must be enough, i.e. the slow flow rate, for complete retention of Cu as PV chelate by PPyCl but should be short, i.e. the fast flow rate, for an efficient preconcentration step. Thus, the effect of sample flow rates on the retention was investigated in the range of 0.5–3.5 mL min$^{-1}$ at constant elution flow rate as 2 mL min$^{-1}$. A flow rate ranging between 0.5 and 2.5 mL min$^{-1}$ was found to be suitable for quantitative retention of copper on the PPyCl-packed column. Higher flow rates of sample solution did not lead to quantitative retention of copper. This could be probably due to insufficient contact time between the sample solution and the PPy-chloride. Elution flow rate was also examined for quantitative recovery of copper. It was found that the quantitative recovery, ≥95%, of copper does not depend on the elution flow rates in the examined range of 0.5–4 mL min$^{-1}$. Therefore, all the studies were carried out for flow rates of sample and eluent solutions at a flow rate of 2.0 mL min$^{-1}$.

**Table 1**
Effect of foreign ions on the determination of copper.

| Ions | Added as | Tolerable limits (mg L$^{-1}$), as ion |
|---|---|---|
| $Na^+$, $K^+$ | $NO_3^-$ salts | 40 000 |
| $Ca^{2+}$, $Mg^{2+}$ | $Ca(NO_3)_2$ $MgSO_4$ | 20 000 |
| $SO_4^{2-}$ $HPO_4^-$ | $NH_4^+$ salts, | 30 000 |
| $CO_3^{2-}$ | $Na^+$ salt | 5000 |
| $CH3COO^-$ | $NH_4^+$ salt | 4000 |
| $Cl^-$ | $Na^+$ salt | 1200 |
| $Ni^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Cr^{3+}$, $Zn^{2+}$, $Mn^{2+}$ | $NO_3^-$ salts ($SO_4^{2-}$ for except $Mn^{2+}$) | 700 |
| $Fe^{3+}$ | $NO_3^-$ salt | 75 |
| $Fe^{2+}$ | $SO_4^{2-}$ salt | 75 |
| $Hg^{2+}$ | $Cl^-$ salt | 75 |

**Table 2**
Recovery of copper spiked to water samples ($n = 3$).

| Sample | Spiked (μg L$^{-1}$) | Found (μg L$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Tap water | 0 | <LOD | – |
| | 0.5 | 0.50 | 100 |
| | 2 | 1.95 | 98 |
| | 4 | 3.92 | 98 |
| Waste water | 0 | 0.27 | – |
| | 0.5 | 0.74 | 94 |
| | 1 | 1.24 | 97 |
| | 2 | 2.15 | 94 |
| Hot spring water (Karahayıt) | 0 | 0.22 | – |
| | 0.25 | 0.45 | 92 |
| | 1 | 1.16 | 94 |
| | 2 | 2.30 | 104 |

**Table 3**
Determination of copper in water samples by proposed procedure.

| Sample | Copper concentration (μg L$^{-1}$)[a] |
|---|---|
| Tap water | <LOQ |
| Waste water | 2.29 ± 0.21 ($n = 5$) |
| Hot spring water (Karahayıt) | 2.80 ± 0.18 ($n = 6$) |

[a] Mean expressed as 95% tolerance limit; <LOQ, lower than quantitaion limit.

### 3.6. *Effect of foreign ions*

Under optimized conditions, in order to evaluate the feasibility of the proposed method for water analysis, the effects of possible matrix ions were also examined. The column method was applied to binary mixtures (90 mL) of 5 μg of Cu(II) and each interfering ion at increasing concentrations and the results are presented in Table 1. The tolerance limit of a foreign ion was taken as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and determination of copper ion. The ions normally present in natural water do not interfere under the experimental conditions used. Also, some of the transition metals at mg L$^{-1}$ levels have no interference on the recoveries of copper.

**Table 4**
Comparative data from some recent studies on preconcentration.

| Extraction technique | Extractive system | Analytes | EF | LOD ($\mu$g L$^{-1}$) | RSD (%) | $E_r$ (%) | Refs. |
|---|---|---|---|---|---|---|---|
| Solid-phase extraction | Activated carbon/pyrocatechol violet | Cu | 100 | 0.025 | <8 | – | [30] |
| Solid-phase extraction | Tetradecyldimethyl-enzylammonium chloride-treated analcime zeolite/pyrocatechol violet | Cu | 200 | 0.05 | 5.4 | −7.5 | [31] |
| Solid-phase extraction | Dowex Optipore SD-2/5-methyl-4-(2-thiazolylazo) resorcinol | Cu | 50 | 1.03 | 7 | +3.3 | [40] |
| Solid-phase extraction | Amidoamidoximesilica | Cu | 20 | 9 | <4 | (−4)–(+1) | [41] |
| Solid-phase extraction | Naphthalene methyltrioctyl ammonium chloride/methylthymol blue | Cu | 100 | 0.54 | 1.4 | – | [42] |
| Cloud point extraction | Amino acid | Cu | 22 | 5 | 2.8 | – | [43] |
| Dispersive liquid liquid microextraction | 1,2-Diclorobenzene and ethanol | Cu | – | 0.5 | 1.4 | – | [44] |
| Electrochemical | A thin mercury film electrode | Cd, Tl, Pb | – | 13 | – | 7.5 | [45] |
| Electrochemically controlled deposition and stripping | Glassy carbon electrode | Cu | 30/2 min | 1.4 | 2.3 | – | [46] |
| Coprecipitation | Erbium hydroxide | Cu, Mn, Co, Cr, Fe, Pb | 25 | 0.04–0.87 | 1–9 | 1.9–8 | [47] |
| Solid-phase extraction | PPyCl/pyrocatechol violet | Cu | 90 | 0.87 | 3.4 | +3.3 | This work |

EF, enrichment factor; LOD, limit of detection; RSD, relative standard deviation; $E_r$, relative error.

These results indicate that the proposed method could be applied for the determination of copper ion in natural water. The tolerable limit for chloride as 1200 mg L$^{-1}$ was lower than those of other anions examined in this study. It refers to a competition between chloride and anionic Cu–PV chelate. This could be expected with increasing concentration of chloride as a counter-ion in the PPyCl. However, interference of chloride is not relevant to the proposed procedure because chloride is typically found in natural water samples in concentrations lower than the tolerable limit.

### 3.7. Adsorption capacity

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. To determine the adsorption capacity, 40–400 $\mu$g of Cu as chelate was loaded to the column containing 0.7 g of resin and eluted according to the recommended procedure. The recoveries were investigated. The maximum adsorption capacity was obtained using a model Langmuir adsorption isotherm, based on the following equation: [$C/n = 1/n_m k + C/n_m$]. The concentration of adsorbed copper in mg g$^{-1}$ ($n$) onto PPyCl as a function of its concentration in solution in mg/L (C) was investigated. The adsorption isotherms for copper were shown in Fig. 4. The adsorption capacity ($n_m$) of PPyCl for copper was found to be 388 mg g$^{-1}$.

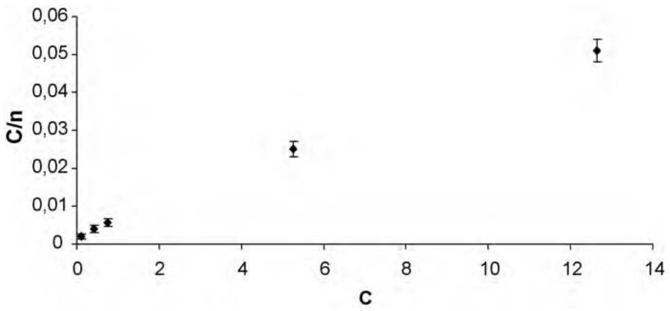

**Fig. 4.** Adsorption isotherm for sorption capacity of PPyCl.

### 3.8. Analytical performance of the proposed system

The solid-phase extraction/preconcentration method developed using PPy-chloride allowed the determination of Cu in the concentration range of 0.00–0.07 $\mu$g mL$^{-1}$ by FAAS coupled micro-injection technique. The calibration equation was $A = 1.3322 \times C$ [Cu, $\mu$g mL$^{-1}$] + $8.5 \times 10^{-3}$ ($r = 0.9987$). Without preconcentration, in the concentration range of 0.0–4.0 $\mu$g mL$^{-1}$ Cu, the calibration equation was $A = 0.0153 \times C$ [Cu, $\mu$g mL$^{-1}$] + $1.87 \times 10^{-3}$ ($r = 0.9992$). The experimental enhancement factor, calculated from the ratio of the slopes of the calibration equations, was 87. The theoretical preconcentration factor, calculated as the ratio of the sample volume (90.0 mL) to the final effluent volume (1.0 mL), was 90.

The accuracy of the proposed procedure was verified by determination of copper(II) in a certified reference material, namely BCR 715 wastewater-SRM, a reported copper content of 0.90 $\mu$g L$^{-1}$.

Using the proposed procedure the copper content determined in this BCR was found to be 0.93 ± 0.06 (mean ± $ts/\sqrt{n}$, $n = 4$). The $t$-test demonstrated that there is no significance difference between the certified value and the experimental result at the significance level of 0.05 [37]. The relative error was calculated to be +3.33%.

In order to further validate this procedure, spiking recovery test of copper(II) was also performed for tap water, waste water and hot spring water samples using the proposed procedure. The results in Table 2 showed that favorable recovery for the real environmental sample had been achieved. Recoveries from 94 to 104% were estimated indicating that the procedure is free from matrix effects.

The detection limit was estimated as 0.87 $\mu$g L$^{-1}$ Cu(II) according to IUPAC recommendations at the 99.7% confidence level, with an preconcentration factor of 90[38,39]. The quantitation limit was calculated 1.68 $\mu$g L$^{-1}$ Cu(II).

The relative standard deviation (RSD) was calculated as 3.4% for 20 independent measurements on different days with a 10 $\mu$g L$^{-1}$ Cu(II) solution, using the proposed procedure. The RSDs were found to be 7.4% ($n = 5$) and 6.1% ($n = 6$) for copper contents of waste water and hot spring water, respectively (Table 3).

### 3.9. Application

The proposed SPE preconcentration procedure was applied to the determination of copper in tap water, waste water and hot spring water samples. The results obtained are showed in Table 3.

The copper contents in waste water and hot spring water samples were above quantitation limit of the procedure as $2.29 \pm 0.25$ ($n = 5$) and $2.80 \pm 0.20\,\mu g\,L^{-1}$ ($n = 6$), respectively. The content of copper in tap water sample was lower than quantitation limit of the procedure.

### 3.10. *Comparison with other solid-phase adsorbents*

The proposed method was compared to a variety of preconcentration methods reported recently in the literature (Table 4). It is evident that the enrichment factor, limit of detection relative standard deviation and relative error obtained with PPyCl is comparable to or even better than most of the other methods.

## 4. Conclusions

It can be concluded from the results that PPyCl is an effective and selective sorbent for trace amounts of copper and can be used for preconcentration of Cu(II) ion from the diverse kind of water samples. The recovery obtained through the standard addition technique and analysis of the reference standard material revealed that the procedure has good accuracy. The detection and quantitation limits achieved were satisfactory for determination copper in the examined samples. The successful applications of the proposed procedure for Cu(II) determination in various real water samples show the viability of the use of PPyCl as a synthetic sorbent in solid-phase extraction processes.

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