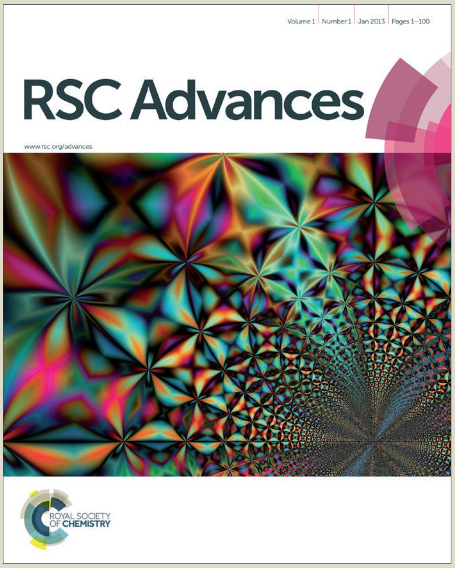
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Copper selective self-sort polymeric resin with mixed-mode functionality for column preconcentration and atomic absorption spectrometric determination

Aminul Islam[*]**, Hilal Ahmad, Noushi Zaidi, Suneel Kumar**

Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh, India-202 002

Abstract

A new approach for the synthesis of highly Cu(II) selective mixed-mode solid phase extractant is proposed. In aqueous medium triethylenetetramine (trien) reacts with Dowex 50 resin and forms a self assembled product. The self-sorting trien molecules get attached by forming a hydrogen bond with the sulfonic acid groups of the resin, where nitrogen-containing functional groups flexibly change their orientation in order to selectively coordinate with Cu(II) with square-planar geometry. This enables the solid phase to behave in a manner similar to free monomeric ligand in liquid-liquid system. A column procedure for preconcentration/separation of Cu(II) was developed optimizing various experimental variables which exhibits low preconcentration limit (3.3 μg L^{-1}) and high sorption capacity (101.6 mg g^{-1} of resin). Analytical method coupling column preconcentration procedure with flame atomic absorption spectrometry (FAAS) was validated analyzing standard reference materials and recovery of the spiked analyte. The proposed method was successfully applied for the preconcentration and determination of Cu(II) in tap water, river waters, electroplating wastewater, and tea sample.

---

[*] Corresponding author: Analytical Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh, India -202 002 Tel.: +91 9358979659; E-mail address: aminulislam.ch@amu.ac.in

Keywords: Copper, Selectivity, Triethylenetetramine, Flame atomic absorption spectrometry.

Introduction

Copper is an essential element for many biological system and necessary micronutrient at very trace levels. However, it becomes toxic at higher levels due to its association with cell membranes, prevents the transport mechanism across the cell wall.[1] Copper ions are components of more than 30 enzymes (in an organism), but long term exposure to high concentrations of copper leads to chronic toxicosis. Functioning of copper in living organisms, and its deficiency or excess effects have been described in detail in numerous books, reports by Agency for Toxic Substances and Disease Registry,[2] International Copper Association[3] and World Health Organisation.[4,5] Aqueous systems are especially more sensitive to copper exposure. Cu(II) concentration in fresh waters is typically about 0.5–50 μg L^{-1}. However, in industrial areas or also to near mines its concentration can increase several folds. Copper concentration in tap water is at the μg L^{-1} level, but, when water is sampled from a copper-made installation system, the concentration of copper can reach several mg L^{-1} level just after opening the tap.[6] Assessment and monitoring of Cu(II) content in the environment, food and drinking water is necessary due to its anthropogenic sources and the possibility of its accumulation in living system.

The development of preconcentration techniques like solid phase extraction (SPE)[7-9], liquid-liquid extraction [10], precipitation [11] and cloud point extraction [12] with selective separation potentiality for the accurate determination of metal ions from samples of complex matrices is frontier area of ongoing research in analytical chemistry. SPE using chelating resins enables accurate determination of trace metal ions using analytical techniques with less sensitivity such as atomic absorption spectrometry as well as sophisticated simultaneous, multi-element capability which usually suffers from interferences.[13] Numerous chelating sorbents for sequestering of metal ions including polymeric resins,[7-9] metal–organic framework,[14] graphene oxide sheets,[15] carbon nanotubes[16] and monoliths[17] are useful with certain shortcomings likely lack of selectivity,[7] low sorption capacity,[7] slower kinetics,[8] and reusability of sorbent.[9] Chelating resins tailored with a variety of organic ligands (smaller in size, containing hydrophilic groups and donor atoms) in order to have better accessibility of ligands, faster kinetics of metal ion sorption and higher metal-ligand stability constant. Such resins possess several advantages namely good sorption capacity with selectivity,[8] mechanical and chemical stability,[15] multiple quantitative sorption-desorption cycles with good reproducibility[9,15] and high preconcentration factor.[8,9,15] However, the selectivity towards metal ions from the matrix containing other metal ions for the chelating resins possessing ligands with two or more bulky groups, decreases due to restricted free spatial movement of coordinating groups. It depends strongly on the specificity of interaction between flexible configuration of the immobilized ligand, the charge/size of the metal ion and coordination geometry. Several approaches have been made to enhance the selectivity of resin by improving steric flexibility of the ligand either by incorporation of spacer arms between the ligand and the matrix[18,19] or by development of mixed-mode sorbents in a hybrid of ion exchange sorbents.[20]

Accordingly, our concern is to fabricate a hydrophilic polymeric resin incorporating simple building blocks to exhibit self-sorting[21,22] due to the orthogonality of the interactions between their reactive sites, resulting into active structures with high selectivity and sorption capacity. Thus, we simply mixed a sulfonated polystyrene resin with trien to self-organize which in turn produced a highly hydrophilic mixed-mode sorbent; that is, both capacity and selectivity are combined together in a single material. Dowex was selected for assembling with trien due to its porous structure and the ease of hydrogen bond formation through sulfonic acid groups, which also results in hydrophilicity. The smaller linear size of multi-dentate trien ligand would increase the probability of incorporation by virtue of lesser steric hindrance. The high porosity as well as surface area of resin would favor better accessibility to the incorporating ligand, thereby increasing the number of analyte binding sites and the presence of hydrophilic sulfonic acid groups would improve accessibility of metal ions to the binding sites. Advantages of this system are the inexpensive with the easy route, self-assembly of mixed-mode sorbents in aqueous medium, free from the use of organic solvents and catalyst, elimination of gases/side products, hence, making it environmentally safer. The trien molecules get attached forming a hydrogen bond with the sulfonic acid groups of the resin, where preferably the ligand flexibly change their orientation in order to selectively coordinate with the target metal ion inside the porous resin. Steric flexibility of trien can be attributed to the presence of three ethylene unit between nitrogen atoms acting as spacer arm and the large volume of free space within channels which allows the stable rearrangement of the bonding geometry once a metal ion interacts. Such stable geometry allows trien to less coordinate with other competing ions of the solution. Hence, trien functionality inside the resin can selectively binds with Cu(II) to form the most stable square planar complex.[23] Such self-sorting chelates in which ligand reconstruct its molecular framework to selectively recognize the target metal ions may results higher sorption capacity and improved selectivity as compared to the recent researches on SPE including commercially available chelates (Table 1). The resin was explored for the development of solid phase extraction procedure for selective separation/preconcentration of Cu(II) in real samples and its subsequent determination by FAAS.

Table 1. Comparision of some previous SPE studies for Cu(II).

Solid support	Chelating agent	Cu(II) selective	Capacity (mg g^{-1})	PF[a]	Technique	Detection limit ($\mu g\ L^{-1}$)	Ref.
Polystyrene divinyl benzene	Triethylenetetramine	✓	101.6	300	FAAS	2.5	This work
Nobias-chelate PA1	EDTA[b] and IDA[c]	×	-	8	ICP-MS	0.001	24
Nobias-chelate PA1	EDTA[b] and IDA[c]	×	-	10-13	ICP-MS	0.003	25
Muromac A-1	IDA[c]	×	83.9	50	ICP-OES	0.007	26
Polystyrene divinyl benzene	Dodecylsalicylaldoxime	✓	1.8	74	FAAS	0.4	27
Polystyrene divinyl benzene	Pyridoxal salicyloylhydrazone	✓	-	100	FAAS	0.004	28
Amberlite XAD-16	Hydroxyquinoline	×	-	80	FAAS	0.5	8
Ion-imprinted polymer	Methacrylic acid-divinyl benzene	✓	15.9	30	ICP-OES	0.9	29
Alumina	Diphenylcarbazone	×	-	100	FAAS	1.4	30
Silica	Dithizone	×	0.76	42.6	FAAS	0.2	31
Silica	Amidoamidoxime	✓	10.2	-	FAAS	9.0	32
Chloromethylated polystyrene	1-phenyl-1,2-propanedione-2-oxime thiosemicarbazone	×	0.82	-	FAAS	0.56	33

[a] Preconcentration factor
[b] Ethylenediaminetriacetic acid
[c] Iminodiacetic acid

Materials and procedures

Reagents and solutions

All chemicals used were of analytical reagent grade. Stock solutions (1000 mg L^{-1} in 1% HNO_3/HCl) of nitrate salts of Mn(II), Co(II), Ni(II), Cu(II), Fe(II), Pb(II) and chloride salts of Cr(III) and Zn(II) were purchased from Merck (Darmstadt, Germany). All glassware was cleaned by soaking in 2 % HNO_3 and rinsed carefully with triply distilled water. Working solutions were prepared on a daily basis diluting the stock solution with triply distilled water (TDW) prior to use. The buffer solutions used were of HCl-$C_2H_5O_2N$, CH_3COOH-CH_3COONa, Na_2HPO_4-$C_6H_8O_7$, and NH_4Cl-NH_3 for the pH 2.0-3.6, 4.0-6.0, 7.0-7.8, and 8.0-9.0, respectively. The chelating reagent trien (N,N-Bis(2-aminoethyl)ethane-1,2-diamine) and Dowex 50 (Na) (with 8% cross linking, moisture content of 50-58 %) 20-50 mesh was procured from Merck (Mumbai, India) and S D fine Chem. Ltd. (Mumbai, India), respectively. Fulvic acid powder and soluble humates containing 75% humic acid and 10% potassium were received as a gift from Nutri-Tech Solutions (Yandina, Australia). Standard reference materials like vehicle exhaust particulates NIES 8 and Zinc base die-casting alloy C NBS 627 were provided by the National Institute of Environmental Studies (Ibaraki, Japan) and National Institute for Standards and Technology (NIST), (Washington, DC, USA), respectively. All the reagents (HNO_3, HCl, $HClO_4$ and H_2O_2) used for wet digestion and elution studies of the samples were procured from Merck (Mumbai, India).

Experiments

Instruments

The GBC 932+ (Dandenong, Australia) FAAS (conditions for Cu: wavelength; 324.7 nm, lamp current; 4 mA, Slit width; 0.5 nm, burner height; 11 mm, and fuel flow rate; 2.3 L min^{-1}) was used for determining metal ion concentration. Blank run was performed before all FAAS measurements An Elemental analysis was carried out on Flash EA 1112 Organic Elemental Analyzer (Thermo Fischer Scientific). A thermostatted mechanical shaker NSW−133 (New Delhi, India) was used for the batch studies. A water distillation apparatus (Popular Science Apparatus Workshops Pvt. Ltd. India) was used to obtained triply distilled water. PerkinElmer Spectrum Two spectrometer (Waltham, MA, USA) was used to record Fourier Transform Infrared spectra (FT-IR) using KBr disk method and the interferograms were recorded by accumulating 32 scans. Far infrared spectra (FIR) were recorded using a PerkinElmer Spectrometer in polyethylene pellet under nitrogen atmosphere at 25 ^{0}C in the range between 50 to 500 cm^{-1}. A Shimadzu TGA/DTA simultaneous measuring instrument, DTG-60/60H (Kyoto, Japan) was used for thermo gravimetric analysis (TGA) from the temperature 50 ^{0}C to 600 ^{0}C at a heating rate of 10 ^{0}C/min under an inert atmosphere (N_2 flow rate of 50 mL/min). An Autosorb iQ Station 1 gas sorption analyzer, Quantachrome Instruments (Boynton Beach, FL, USA) was used for pore size distribution studies. Energy dispersive X-ray analysis spectra (EDS) for micro compositional analysis of the resin were performed with a Jeol JSM-6510LV (Tokyo, Japan) after coated with gold overlayer to avoid charging during electron irradiation. A solid state 1D ^{13}C cross-polarization-magic-angle-spinning (^{13}C{1H} CP/MAS) NMR spectra were recorded using a Jeol JNM-ECA 400 spectrometer (MA, USA) using a 4 mm triple resonance MAS probe. The proton 90° pulse length was 5 μs and the proton RF field for spinlock during cross polarization (CP) was set to 40 kHz. The spinning speed was set to 4000 Hz. The spectra are referenced using the CH_2 carbon peak of adamantane as an external reference. Other conditions are: contact time 5 ms; relaxation delay 5 s; repetition time 5 s; initial wait 1 s. A column (1×10 cm), for dynamic studies, was obtained from J-SIL Scientific Industries (Agra, India).

Preparation and characterization of mixed-mode resin

The mixed-mode Dow-trien resin was prepared by mixing sulfonated polystyrene divinyl benzene and trien reagent (ESI Figure S1). First, Dowex 50 resin was first completely converted to H^+-form by immersing the resin beads in 50 mL of 1 M HCl solution for 12 h and subsequently rinsed with triply distilled water until pH of the supernatant became neutral. An amount of 5 g of air dried resin was then mixed with 10 mL of trien (diluted with 50 mL of triply distilled water) in a round bottom flask. The reactant mixture was stirred for about 48 h and allowed to stand for 6 hour. The resin was then filtered, washed with triply distilled water and dried at 60 ^{0}C for 12 h before further studies. The functionalized resin (Dow-trien) was characterized on the basis of FT-IR, FIR, EDS, ^{13}C-NMR and thermal studies.

Recommended SPE procedures

Batch procedure

Batch experiments were carried out by equilibrating 50.0 mL of metal ion solutions of 500 mg L^{-1} (except for effect of resin amount (250 mg L^{-1}) and selectivity studies (356 mg L^{-1})) at constant pH with 0.2 g Dow-trien in an Erlenmeyer flask stirred at 25±0.2 ºC.

The sorbed metal ions were desorbed by shaking with 5 mL of 2 M HNO_3 and subsequently subjected for FAAS determination.

Fixed-Bed column procedure

All column experiments were conducted in a glass column (10 cm × 1.0 cm) fitted with porous disc. The column was slurry packed with water soaked Dow-trien (0.2 g) with a bed height of ∼1.0 cm and preconditioned with 5 mL of buffer solution of pH 5.5. The 100 mL of solution containing 5 μg of Cu(II) buffered to pH 5.5 ± 0.1 was passed through the column at an optimum flow rate of 5 mL min^{-1}. The column was then washed with triply distilled water to ensure complete removal of unretained Cu(II) and a 3 mL of 2 M HNO_3 was used at a flow rate of 2 mL min^{-1} to percolate through the bed whereby, the retained metal ions get eluted and measured by FAAS.

Optimization of preconcentration procedure

In order to optimize the experimental variables for the preconcentration/separation of Cu(II) on Dow-trien, the univariate approach was followed to establish all the experimental parameters. For this each optimum condition was established by varying one experimental parameter while others remain constant following the recommended SPE procedure. A batch method was preferred to study the effect of pH, effect of contact time, effect of resin amount and performing selectivity experiments. The other experimental variables were optimized using fixed-bed column method.

Collection and digestion of samples and SRMs

The proposed method was evaluated for preconcentration of Cu(II) in the Ganga river water (collected from the two different cities; Narora and Kanpur, India), electroplating wastewater (collected from an area in the vicinity of local nickel electroplating industry, Aligarh, India), tap water (collected from University campus) and tea sample (Tata tea, India). The water samples were preliminarily filtered through Millipore cellulose membrane filter (0.45µm pore size), acidified to pH 2 with 2 M HNO_3, stored in precleaned polyethylene bottles and then subjected to the analysis. The tea sample (3x50 g) of different batches was agitated and washed with acetone, dried in an oven at 70 ºC and subsequently ground to a fine powder. An amount of 1g of sample was digested by heating with 5 mL of a mixture of nitric acid and perchloric acid in a ratio of 3:2 (v/v) at 100 ºC for 2 h. The digested sample was then diluted with TDW to 100 mL and filtered through Millipore cellulose membrane filter. The solutions of 375 mg of NIES 8 and 100 mg of NBS 627 were digested as reported in earlier work.[34] The residue obtained after digestion was dissolved in 3 mL of 0.5 M HNO_3 and made up to a 500 mL volume in a calibrated flask. From this an aliquot (100 mL of each prepared SRMs solutions) consisting of 75 mg of NIES 8 and 20 mg of NBS 627, respectively, were taken for the determination of Cu(II). The pH was optimized accordingly and all the samples were preconcentrated by the given column procedure. The concentration of desorbed Cu(II) in the eluent was determined by FAAS.

Result and discussion

Characterization of Dow-trien

The incorporation of trien onto the Dowex 50 was characterized by elemental analysis, FT-IR, FIR, $^{13}C\{1H\}$ CP/MAS NMR spectroscopy, and EDS. The Color differences shown in the photographs (Figure 1) of Dowex 50 and Dow-trien after Cu(II) sorption also depicts the immobilization of trien onto the resin.

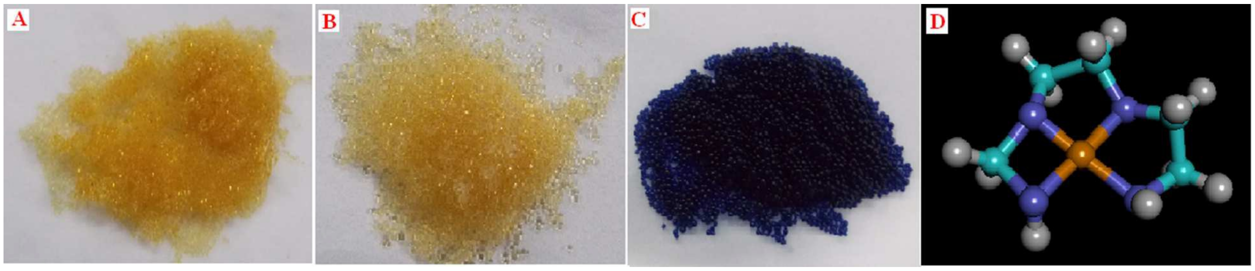


Fig. 1. Photographs showing the color change in (A) Cu(II) loaded host Dowex 50, (B) Dow-trien resin (C) Cu(II) loaded Dow-trien resin and (D) corresponding Dow-trien-Cu complex (Resin amount 0.2 g; Sample volume 50 mL; Sorption pH 5.5; Cu(II) 500 µg mL^{-1}).

Elemental analysis. The comparative results of C, H, N, S, and O elemental analysis of Dowex 50 and Dow-trien were shown in Table S1. From the % N content data of Dow-trien, the amount of trien molecules immobilized (L0; mmol g^{-1}) onto the resin estimated to be 1.73 mmol g^{-1} using the following equation[35] $\mathrm{L0} = (\%\mathrm{N}/\mathrm{Nitrogen\ atomic\ weight}) \times 10$ whereas, host Dowex resin shows the absence of nitrogen. Correlating this data with Cu(II) uptake capacity of nascent Dowex resin (1.3 mM g^{-1}) and Dow-trien (1.59 mM g^{-1}) as shown in Fig 2, it may be concluded that possibly one sulfonic acid sites are associated per trien ligand.

FT-IR and FIR spectra. In the FT-IR spectrum of Dow-trien (ESI Figure S2), the characteristic peaks at 3437.32 cm^{-1} (N–H stretching vibrations of amine groups),[36] 1515.94 and 1453.90 cm^{-1} (C–N stretching vibrations of primary and secondary amine),[36,37] 1410.78 and 1033.82 cm^{-1} (symmetric and asymmetric stretching vibrations of $-SO_3$),[36] 832.18, 774.82, 671.88 cm^{-1} and 578.77 cm^{-1} (N–H out of plane and in plane bending),[36] 1628.42 cm^{-1} (N–H deformation vibration),[36] and 3020 and 2926 cm^{-1} (for sp^3 C–H and sp^2 C–H stretching vibrations)[37] supports the presence of trien moieties into the resin beads. Conclusive evidence of the bonding was shown in the FIR spectrum (ESI Figure S3) obtained after Cu(II) sorption the spectral bands in the region 500–400 cm^{-1} indicates stretching vibrations of Cu–N in the complex.[38]

^{13}C{1H} CP/MAS NMR spectra. In the solid state ^{13}C{1H} CP/MAS NMR spectra of Dow-trien resin the peaks in between the region 40-55 ppm (ESI Figure S4) belongs to the $-CH_2$ groups bonded to primary amine (δC=44.2 ppm; δC=53.3 ppm) and secondary amine (δC=44.2 ppm; δC=53.3 ppm) of the trien depicts the successful incorporation of trien into the resin. The peak at δC=126.85 ppm (ar-C without sulfonic groups) and δC=142.09 ppm (ar-C bonded without sulfonic groups) are corresponds to the polymer backbone carbon.

Both in FT-IR and ^{13}C{1H} CP/MAS NMR spectra of Dow-trien the observed characteristic peaks confirm the incorporation of trien ligand onto the Dowex 50 resin without any new covalent bond formation.

EDS analysis. The EDS results (ESI Figure S5A and S5B) of the Dow-trien and their corresponding elemental weight% illustrating the presence of C, O, S, N and Cu respectively, in Dow-trien resin. The presence of nitrogen moiety in the EDS spectra also ascribes the incorporation of trien in the functionalized resin.

The observed decrease in pore diameter of 3.721 nm (adsorption) and 0.276 nm (desorption) in Dow-trien resin using the Barrett-Joyner-Halenda (BJH) method may be ascribed due to the incorporation of trien molecules into the channels of nascent Dowex resin.

Effect of pH

The metal binding capacity of the chelating resin over a wide pH range is a prerequisite and depends on the metal-proton competition in aqueous solutions for the same basic sites on the ligand moiety. To study such effects, pH of the model solution (500 µg mL^{-1}) was adjusted within a range of 1−9 by using corresponding buffer solutions. As shown in Figure 2A, the uptake of Cu(II) by Dow-trien starts from the acidic medium (pH 1±0.1), and >50% uptake of total capacity (101.6 mg g^{-1}) achieved in acidic medium at pH 2. According to hard and soft acid base concept[39] trien with soft base 'N-donor atom' of the resin would shows the chelating ability with a soft acid 'Cu(II)' and thereby impart selective complexation with a specific metal ion, hence the positive charge on the trien due to the protonation event does not much affect the basicity of the nitrogen atom. Above pH 2 the extent of protonation decreases, the competition between metal and hydrogen ion also decreases simultaneously the basicity of ligand increases, results in increasing the sorption capacity of resin and gets constant for a wide pH range, afterward at pH 7−9 the uptake of Cu(II) slightly decreases which may be due to the hydroxide formation at basic pH values. The Dow-trien resin showed selectivity towards Cu(II) at pH< 2 over the other similar metals. However, maximum sorption capacity for Cu(II) requisite for efficient preconcentration of trace analyte was achieved at pH range 3.5-5.5. Moreover, a significant selectivity of Dow-trien towards Cu(II) at pH 5.5 was achieved (as shown in Figure 6A) with enhanced sorption capacity of 25.4 mg g^{-1} of Cu(II) in comparison to sorption capacity at pH 2 (76.3 mg g^{-1}). Hence, advantage of higher capacity has been taken into account. A similar study was carried out for the host Dowex resin (Figure 2B) to understand the effect of solution pH. Thus, for subsequent experiments, pH 5.5±0.1 was selected as the working pH.

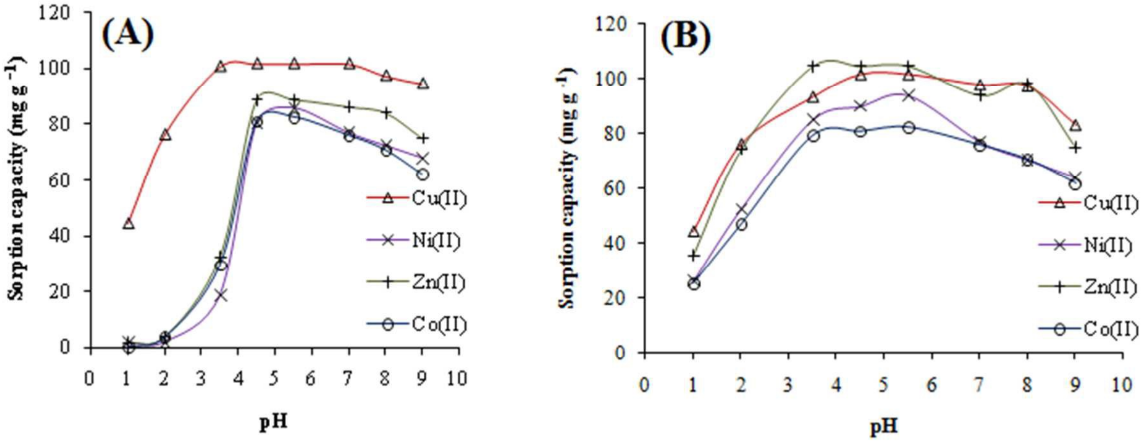


Fig. 2. Effect of solution pH on the uptake of Cu(II) on (A) Dow-trien resin and (B) Dowex resin (Resin amount 0.2 g; Sample volume 50 mL; Cu(II) 500 µg mL^{-1}; Eluent 5 mL of 2M HNO_3).

Effect of contact time

The sorption kinetics of Cu(II) (500 µg mL^{-1}) from 2 min to 1 h (at optimum conditions) shows that (Figure 3) the sorption of Cu(II) increased remarkably at the beginning of the experiment and was 50% sorbed of its total capacity in about 5 min and then reached to equilibrium in 20 min. A further increase in the contact time does not shows any increase in sorption. Hence, it was concluded that 20 min stirring of sample solutions with sorbent was enough to reach the saturation level which reflects better accessibility of the active sites of the resin.

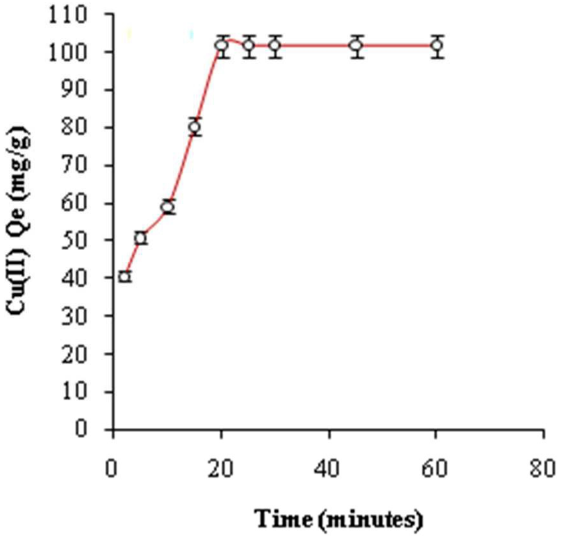


Fig. 3 Effect of contact time on the sorption of Cu(II) (Resin amount 0.2 g; Sample volume 50 mL; Sorption pH 5.5; Cu(II) 5 µg; Eluent 5 mL of 2M HNO_3).

Effect of resin amount

After examine the effect of loaded resin amount on the sorption of Cu(II) (500 µg mL^{-1}), it can be deduced that retention of the Cu(II) per gram resin increased with the increase in resin amount up to 200 mg, afterward a maximum uptake (1.6 mM g^{-1}) almost remains constant this may due to the fact that at low resin amount, there is insufficient number of active sites on the resin to contact or achieve equilibrium with the analyte ion. Similarly, a maximum uptake of 1.3 mM g^{-1} of Cu(II) while using Dowex (200 mg) was obtained which was 19.06 mg (of Cu(II)) less than the Dow-trien. Such remarkable increase in sorption capacity of Dow-trien was due to the immobilized trien ligand.

Type of eluting agent and column reusability test

A series of experiments were performed to elute the retained Cu(II) from Dow-trien using different mineral acids namely nitric acid (HNO_3) and hydrochloric acid (HCl) by varying their volumes and concentrations (Figure 4). Among them quantitative recovery for Cu(II) (>99%) was achieved by using 3 mL of 2 M HNO_3 . Therefore, 3 mL of 2 M HNO_3 was used as an eluting agent in further studies.

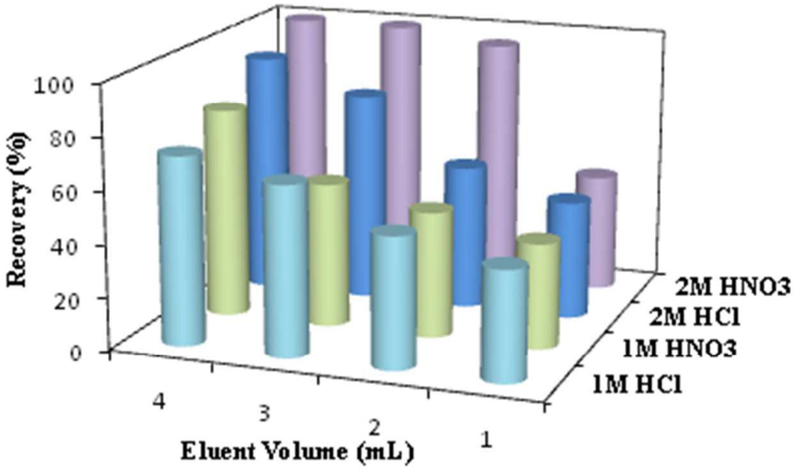


Fig. 4. Effect of type and volume of eluting agents on the recovery of retained Cu(II) (Resin amount 0.2 g; Sample volume 50 mL; Sorption pH 5.5; Cu(II) 5 µg; Eluent 5 mL of 2M HNO_3).

To test the reusability of Dow-trien the functionalized resin was subjected to several sorption and elution cycles. A 100 mL of solution containing 5 µg of Cu(II) buffered to pH 5.5 ± 0.1 was passed through the column at an optimum flow rate of 5 mL min^{-1} and a 3 mL of 2 M HNO_3 was passed at a flow rate of 2 mL min^{-1} to elute the retained Cu(II). The column bed was successfully reused up to 35 cycles without loss of any sorption capacity (Figure 5A). Afterward 6.25 % decrease in uptake capacity was observed upto 40th sorption/elution cycles. This may due to the leaching of trien ligand from the solid matrix. The superposition of Cu(II) uptake capacity achieved from the identical column in the 1st and 35th cycle indicated the reusability of Dow-trien without any significant capacity loss indicating only a negligible loss of trien during the sorption/elution cycles.

Therefore, multiple use of the Dow-trien in the selective separation/preconcentration of Cu(II) through complex formation from contaminated waters is feasible.

Optimal flow rate for sorption/desorption of Cu(II)

To optimize the influence of column flow rate on sorption/elution, a 100 mL solution containing 5 µg of Cu(II) buffered at pH 5.5 ± 0.1 was passed through the column in the range of 2−10 mL min^{-1}. The results showed that the quantitative retention of the analyte ion on the column was unaffected up to a flow rate of 5 mL min^{-1} indicating a fairly fast kinetics. On further accelerating the sorption flow rate the retention of Cu(II) gradually decreases up to 88.2% at 6 mL min^{-1} due to the decrease in equilibration time between two phases. Hence, 5 mL min^{-1} sorption flow rate was chosen and applied for subsequent experiments. The residence time calculated taking into consideration the optimum flow rate of 5 mL min^{-1} was found to be 9.6 sec (0.16 min) for the column bed volume of 0.2 g of resin packed in 10 cm × 1.0 cm diameter of column. In the elution studies the effect of elution flow rate was also studied using 3 mL of 2 M HNO_3, > 99% of the retained Cu(II) was eluted from the Dow-trien at a flow rate of 2 mL min^{-1} and considered optimum henceforth.

Preconcentration studies

To investigate the effect of sample volume on the recovery of Cu(II), an increasing sample volume in the range of 500−2000 mL containing a constant amount of Cu(II) (5 µg) was preconcentrated. Following the column procedure, retained Cu(II) was eluted using 5.0 mL of eluant and subjected to FAAS determination. The result (Figure 5B) shows that the quantitative recovery (> 99%) of analyte can be possible from a maximum of 1500 mL of sample volume corresponding to a preconcentration limit of 3.3 µg L^{-1} and a high preconcentration factor of 300. Moreover, this particular concentration (3.3 µg L^{-1}) cannot be quantitatively recovered from 100 mL of sample volume because this meant to be very low amount of analyte (0.33 µg/100 mL) and subsequently will not show linear calibration curve.[40]

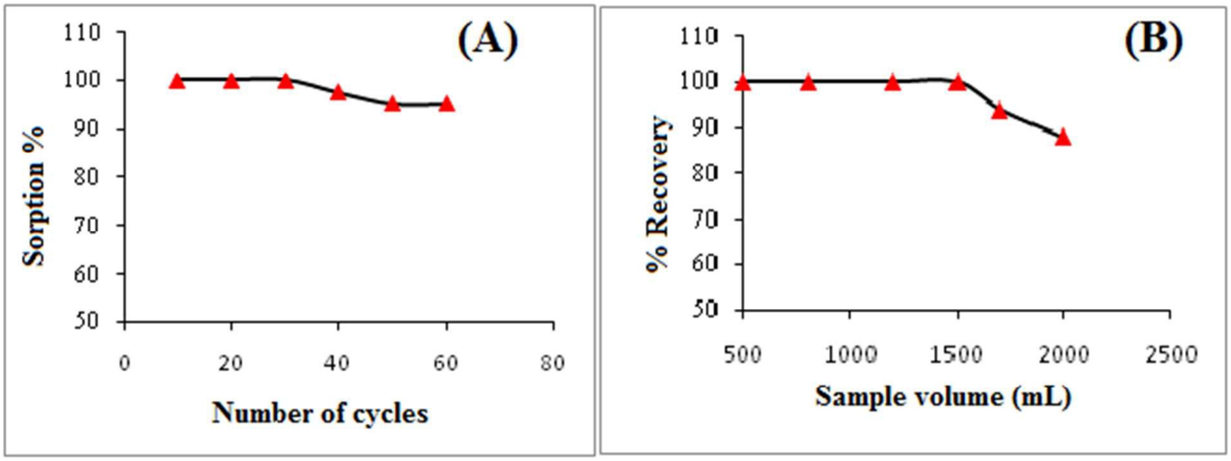


Fig. 5. (A) Shows reusability of Dow-trien and (B) Effect of sample volume on the recovery of trace Cu(II) ((Resin amount 0.2 g; Sample volume 50 mL (A), 500-2000 mL (B); Sorption pH 5.5; Cu(II) 5 µg; Eluent 5 mL of 2M HNO_3).

Selectivity studies of Dow-trien

Competitive sorption of Cu(II) with Zn(II), Ni(II), Co(II), Fe(II), Mn(II), Cr(III) Cd(II) and Pb(II)

The selectivity of Dow-trien for Cu(II) was established based on the recovery of Cu(II) from a binary mixtures of Cu(II) with competitive metal ions such as Zn(II), Ni(II), Co(II), Fe(II), Mn(II), Cr(III), Cd(II) and Pb(II). Experimentally, a 50 mL solution containing 0.28 mM of Cu(II) (which can be quantitatively uptaken by 0.2 g Dow-trien) and other metal as competitive ions (2.8 mM) were equilibrated with Dow-trien resin following recommended batch procedure at optimized pH (pH= 5.5) and the host cation exchanger Dowex 50 resin was also studied for reference. For Dowex 50 resin due to ion exchange mechanism, the % recovery of Cu(II) was less than 65.5 % under competitive condition while, for Dow-trien > 97.4% (among Fe, Mn, Cr, Cd) and > 79.6% (among Zn, Ni, Co, Pb) recovery of Cu(II) was observed under competitive conditions for the same binding sites (Figure 6A and B). This unique selectivity of Dow-trien towards Cu(II) is due to the fact that Cu(II) prefers to bind with nitrogen than to oxygen atom of ligand, and because trien has four nitrogen groups, it fits in the most stable square-planar geometry with Cu(II).[22] Therefore, Dow-trien prefers to bind Cu(II) and restricts other competitive metal ions from co-sorption. The results are further supported based on the relevant knowledge of the formation constants[41,42]; trien having a comparatively high stability constants with greater log K_1 values for Cu(II) than Ni(II), Zn(II), Co(II), Pb(II), Fe(II), Cd(II) and Mn(II) at 25 ^{0}C corresponding to log K_1 values of 20.5, 14.1, 12.1, 11.0, 10.4, 7.8, 10.0 and 4.9, respectively[42,43]. Hence, up to 10 times presence of these competitive ions did not significantly hinders Cu(II) binding and allows strong complexation between Dow-trien and Cu(II). The intense blue color development of resin (Figure 1B) on equilibration with Cu(II) in the presence of co-existing ions also revealed the specific interactions of Cu(II) with Dow-trien. This color change is due to the blue shift of d-d transition in the visible spectra of the intercalated Cu(II)-trien complexes indicates an increased ligand-field splitting as the geometry of the complexes changes to the predominantly square-planar (Figure 1C).[23,43,44] Moreover, comparatively there is no such color change was observed when the simple Dowex resin was saturated with Cu(II). These findings and discussions seem to imply a specific interaction of Dow-trien with Cu(II) and the structure of chelate is not feasible for recognition of other cations in presence of Cu(II). Therefore, Dow-trien can be effectively use for the selective recovery of Cu(II) from water samples.

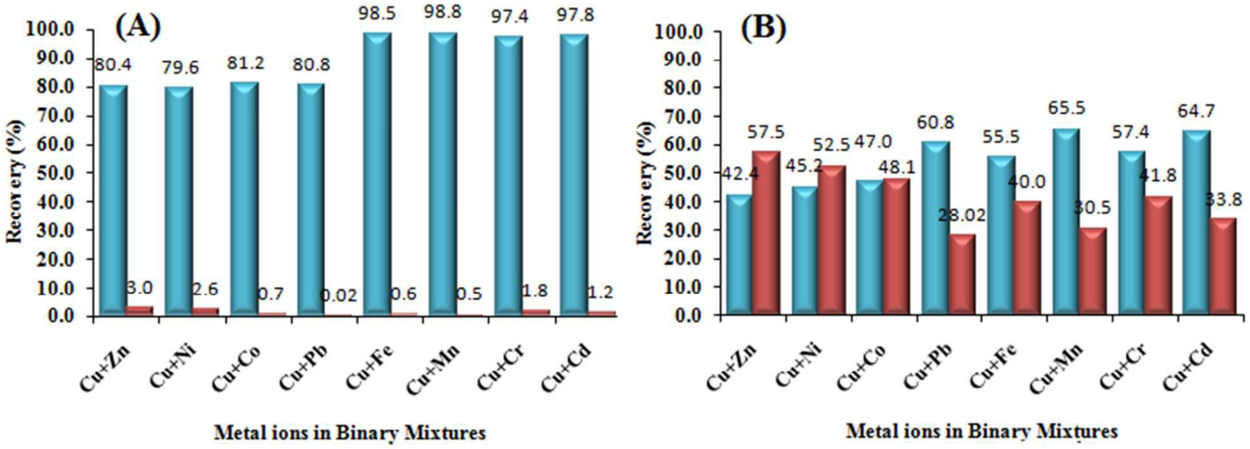


Fig. 6. (A) Selective sorption of Cu(II) on Dow-trien resin and (B) sorption of Cu(II) on cation exchanger Dowex 50 resin from binary mixtures of competitive metal ion (Resin amount 0.2 g; Sample volume 50 mL; Sorption pH 5.5; Cu(II) 0.28 mM and 2.8 mM other metal ions; Eluent 5 mL of 2M HNO_3).

Chemistry of selective Cu(II) complexation

The basis of metal ion selectivity was highly dependent on the characteristics of ligand incorporated onto polymer matrix. We envisioned that the stability constant, stoichiometry of the complex, basicity and orientation of coordinating atoms and metal-ligand geometry are the key factors that plays a determining role in metal ion selective complex formation. Copper is a moderate soft Lewis acid. Due to its incomplete d-orbital (Cu(II) : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^9$), it forms inner-sphere complexes with a trien ligand (tertiary or secondary amines are soft Lewis bases). Since, trien is a linear polar ligand without benzene ring structure, flexible to desired orientation, behave in a manner similar to free monomeric ligand in homogenous system (liquid-liquid system) and forms stable chelate with Cu(II) as compare to those ligands that have steric hindrance due to presence of bulky groups/benzene ring in the ligand structure. [18,19] Trien with Cu(II) shows high stability of complex as depicted from stability constant data in the literature,[41,42] and as a result of Jahn-Teller distortions, the complex enters to a square-planar configuration with 1:1 stoichiometry while others metals like Ni(II) and Zn(II) forms tetrahederal complexes.[21,43,44]

Interference studies in the SPE coupled FAAS procedure

Although the stability constant of the Cu(II)-trien is perhaps the foremost obstacle, steric and electronic factors are also limit the activity by which the metal ion may react with the potential concomitants existing in different water samples which may affect selectivity and preconcentration leading to decrease in extraction recovery. Interference of such coexisting inorganic/organic species on the preconcentration of Cu(II) was investigated by preconcentrating a 50 mL solution containing 5 μg of Cu(II) and varying amount of interfering substances. The results are shown in Table 2. The tolerance level was set as the maximum concentration of the concomitants causes an error in the absorbance of eluent concentration not more than ± 5%, when compared with the absorbance of eluent for 100.0 μg L^{-1} of Cu(II) alone after SPE. The results shows that all the coexisting ions with added concentration level did not interfere in the selective preconcentration and determination of Cu(II). Thus, Dow-trien shows two distinctive features; first, it separates copper from the interference of inorganic and organic interferent through selective chelation; and second, it simultaneously preconcentrate trace amount of copper in the sample solution.

Table 2 Effect of foreign ions on the recovery of Cu(II) using SPE coupled FAAS procedure (column parameter: resin amount 200 mg, sample volume 50 mL, Cu (II) loaded 100 μg L^{-1}, N= 3)

Foreign ions	Concentration (μg L^{-1})	Cu(II) Recovery (%)	RSD
Cl^-	7.6×10^6	100	0.86
Br^-	8.2×10^6	96	0.76
PO_4^{--}	2.1×10^6	100.0	1.28
NO_3^-	3.0×10^5	100.0	0.50
CO_3^{--}	2.3×10^5	100.0	0.97
$C_2O_4^{--}$	1.0×10^5	100.0	0.63
CH_3COO^-	1.0×10^5	102.2	0.74
$C_6H_5O_7^{---}$	2.0×10^5	100.0	0.19
Na^+	5.0×10^6	96.0	3.85
K^+	4.0×10^5	100.2	2.38
Ca^{++}	8.0×10^5	100.8	1.54
Mg^{++}	1.0×10^6	98.0	1.83
Fulvic acid	1.0×10^3	100.0	2.34
Humic acid	1.0×10^3	100.0	1.76
EDTA	2.0×10^3	98.4	2.50
Ni^{++}	250	98.2	3.62
Zn^{++}	250	97.5	4.15
Co^{++}	250	98.0	2.52
Pb^{++}	300	99.2	1.87
Fe^{++}	250	98.7	3.00
Mn^{++}	350	99.0	2.23
Cr^{+++}	250	97.6	3.75
Cd^{++}	250	98.8	2.76

Analytical method validation

The accuracy of the method was assessed by analyzing SRMs and recovery of the spiked analyte from the real samples using optimized column procedure. The Student's t (t-test) values for mean concentration of Cu in SRMs (NIES 8; 1.19 and NBS 627; 1.83) were found to be less than the critical Student's t-value of 4.3030 at 95% confidence level for

N= 3 (Table 3) indicating absence of bias even in the presence of other minor and major elements. Recovery experiments were performed after spiking with two levels of known amount of Cu(II) in water and tea samples and are reported in Table 3. The mean percentage recoveries were found to be 98.8 - 102.1% with relative standard deviation (RSD) <5%, indicating the reliability of the present method for the determination of Cu(II) in real samples of various matrices without significant interference. The method had good precision, as the coefficient of variation for 5 replicate measurements of 5 µg Cu in 100 mL was < 5%. The calibration curve for Cu(II) was obtained after preconcentrating a series of standards (50-250 µg L^{-1}) under optimized conditions against a blank run which contains no metal ions. This experiment was limited to a volume of 100 mL and a minimum amount of 5 µg which is the quantity taken for preconcentration studies. Least squares method was used to compute the correlation coefficient (R^2) = 0.985 and regression equation; $A = 0.148C_{Cu(II)} + 0.037$. However, 3.3 µg L^{-1} is the minimum concentration which can be preconcentrated from 1500 mL with >99% recovery of analyte ion without any non-linearity. The limit of detection and limit of quantification evaluated as the ratio of three and ten times the standard deviation of the mean blank absorbance signal to the slope of calibration curve[45] corresponding to a preconcentration factor of 20[46,47] were found to be 2.5 and 8.2 µg L^{-1} respectively, after 20 blank runs. Procedural blank run was performed applying the recommended column procedure with 100 mL of aqueous solution prepared by adding suitable buffer (excluding metal ions) and finally eluting the same in 5 mL before subjecting it to FAAS determination.

Table 3 Validation of the proposed separation/preconcentration method by analysis of SRMs for Cu(II) concentration.

SRM	Matrix composition[a]	Certified value (μg g^{-1})	Found[b] (RSD) (μg g^{-1})	Calculated Student's *t* value[c]
Vehicle exhaust particles (NIES 8)	0.33% Al, 0.53% Ca, 25.5µg g^{-1} Cr, 219 µg g^{-1} Pb, 0.101% Mg, 18.5 µg g^{-1} Ni, 0.115% K, 0.192% Na, 89µg g^{-1} Sr, 17 µg g^{-1} V, 0.14% Zn	67	66 ± 4 (2.4)	1.25
Zn base alloy (NBS 627)	3.88% Al, 0.030% Mg, 0.023% Fe, 0.0082% Pb, 0.0051% Cd, 0.0042% Sn, 0.0038% Cr, 0.014% Mn, 0.0029% Ni, 0.021% Si	1320	1317 ± 16 (0.5)	0.79

[a] Elements at concentration below 10 µg g^{-1} are not included in the table.
[b] Mean value ± 95% confidence limit; N = 3
[c] At 95% confidence level.

Application of the method

To explore the applicability of the proposed SPE method for practical use, Cu(II) concentration in various real water samples (1 L) and tea sample (1 g) were selectively determined with 95% confidence limit after preconcentration following optimized column procedure and was found to be 14.38, 24.26 and 22.73, and 50.14 µg L^{-1} for tap, rivers and electroplating wastewater, respectively and 2.69 µg g^{-1} for tea sample (Table 4). The presence of constant errors in the developed method was ruled out by varying the sample size and henceforth proves the applicability of reported method for Cu(II) determination with good efficiency.

Table 4 Determination of Cu(II) in spiked real samples after column preconcentration.

Samples	Added (μg L^{-1})	Found[a] (μg L^{-1}) (RSD)	% Recovery[a]
Tap water	0	14.4±1.3 (3.8)	-
	5	19.4±1.2 (2.6)	100.4±24
	10	24.6±1.8 (3.0)	102.1±18
River water (The Ganga, Narora)	0	24.3±1.7 (2.7)	-
	10	34.2±2.3 (2.7)	99.6±23
	15	39.3±2.6 (2.7)	100.2±17
River water (The Ganga, Kanpur)	0	22.7±1.5 (2.6)	-
	10	32.6±2.4 (2.9)	99.1±23
	15	37.8±2.5 (2.6)	100.2±16
Electroplating wastewater	0	50.1±3.0 (2.4)	-
	10	60.2±4.4 (2.9)	100.4±43
	15	65.0±4.5 (2.8)	99.1±30
Tea[b]	0	2.7±0.3 (3.7)	-
	5	7.6±0.6 (2.8)	98.8±10
	10	12.6±0.5 (1.9)	99.7±5

[a] Mean value ± 95% confidence limit; N = 3; [b] μg g^{-1}.

Conclusion

The choice of ligand selection and the approach for the preparation of resin adopted in this work have proved to be fairly successful in a single step, facile one-pot green synthesis. Self-assembled non-covalently bound trien ligand flexibly orients and free from steric restriction forms stable square planar geometry with Cu(II) resulting in enhanced Cu(II) selectivity similar to that of the homogeneous system. The selectivity of Cu(II) over other studied metals was favored due to complex geometry, ligand basicity, and solution pH. The Dow-trien resin is persistent, mechanically robust and highly selective for Cu(II) at wider acidic pH range and attains equilibrium within 20 min for its maximum sorption capacity, thus can also be used for the removal of Cu(II). The proposed column method promises simple handling, accuracy, repeatability, and environmental innocuousness. The method shows its ability to preconcentrate Cu(II) from a concentration as low as 3.3 μg L^{-1} and its accurate determination by cheap ideally suited single-element technique (FAAS) without any interference from commonly occurring coexisting ions. Potential application was exhibited by the analysis of tap water, river water, electroplating wastewater and tea sample for its Cu(II) content. The application of the proposed procedure for Cu(II) preconcentration/determination in various real samples with and without spiking and in certified reference materials validate the reliability of the proposed method with good accuracy and precision. Thus, in the designing of metal selective polymeric sorbents it is noteworthy to understand the mechanism of interaction by which metal ions specifically coordinates to a ligand.

Note

ESI (Electronic supplementary information) available.

Acknowledgments

The authors are grateful to the University Grant Commission India, for providing research fellowship to Hilal Ahmad (UGC-BSR) and Noushi Zaidi (UGC-SRF). The authors acknowledge the support provided by, UGC-SAP program and DST (FIST & PURSE), New Delhi.

References

[1] M. Diaz-de Alba, M. D. Galindo-Rianon, M. Garcia-Vargas, *Talanta,* 2012, **100**, 432–438.

[2] Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Department of Health and Human Services, Toxicological profile for copper, Atlanta, GA, 1990.

[3] International Copper Association (ICA), The biological importance of copper– final report of project no. 223, 1995.

[4] WHO, International programme on chemical safety, Environmental health criteria 200, Copper, 1998.

[5] WHO, Copper in drinking-water, Background document for development of WHO guidelines for drinking-water quality,WHO/SDE/WSH/03.04/88, 2004.

[6] A. Tobiasz, S. Walas, *Trac trends in Anal. Chem.,* 2014, **62**, 106–122.

[7] A. Islam, A. Ahmad and M. A. Laskar, *Anal. Methods,* 2011, **3,** 2041−2048.

[8] R. Saxena and P. L. Meena, *RSC Adv.*, 2014, **4,** 20216–20225.

[9] A. Islam, N. Zaidi, H. Ahmad and S. Kumar, *Environ. Sci. Poll. Res.*, 2015, **22**, 7716–7725.

[10] Funda Aydin, E. Yilmaz, M. Soylak, *RSC Adv.*, 2015, **5**, 40422–40428.

[11] A. Komjarova, R. Blust, *Anal. Chim. Acta,* 2006, **576**, 221–228.

[12] D. Citak, M. Tuzen, *Food Chem. Toxicol.*, 2010, **48,** 1399–1404.

[13] V. Camel, *Spectrochim. Acta Part B,* 2003, **58,** 1177−1233.

[14] Y. Wang, J. Xie, Y. Wu and X. Hu, *Microchim. Acta,* 2014, **181**, 949–956.

[15] A. Islam, H. Ahmad, N. Zaidi and S. Kumar, *ACS Appl. Mater. Interfaces*, 2014, **6**, 13257−13265.

[16] C. H. Latorre, J. A. Mendez, J. B. Garcia, S. G. Martin, R. M. P. Crecente, *Anal. Chem. Acta*, 2012, **749**, 16–35.

[17] S. Wang and R. Zhang, *Anal. Chem. Acta*, 2006, **575**, 166–171.

[18] H. Kumagai and Y. Inoue, *Anal. Chem.* 1998, **70**, 4070–4073.

[19] M. A. L. Tanco, D. A. P. Tanaka, V.C. Flores, T. Nagase and T.M. Suzuki, *React. Funct. Polym.*, 2002, **53,** 91–101.

[20] N. Fontanals, P. A.G. Cormack, R. M. Marce and F. Borrull, *Trends Anal. Chem.*, 2010, **29**, 765–779.

[21] Y, Ma, S. V. Kolotuchin and S. C. Zimmerman, *J. Am. Chem. Soc.*, 2002, **124**, 13757–13769.

[22] R. K. Shervedani, Z. Rezvaninia, H. Sabzyan, H. Z. Boeini, *Anal. Chem. Acta*, 2014, **825**, 34–41.

[23] D. Grohol and E. L. Blinn, *Inorg. Chem.,*1997, **36,** 3422–3428.

[24] T. Minami, W. Konagaya, L. Zheng, S. Takano, M. Sasaki, R. Murata, Y. Nakaguchi, Y. Sohrin, *Anal. Chim. Acta*, 2015, **854,** 183–190.

[25] V. D. Biller, K. W. Bruland, *Mar. Chem.,* 2012, **130-13**, 12–20.

[26] E. Vassileva, N. Furuta, *Spectrochim. Acta, Part B*, 2003, **58,** 1541–1552.

[27] A. Tobiasz, S. Walas, L. Landowska, J. Konefal-Goral, *Talanta*, 2012, **96**, 82– 88.

[28] M. Diaz-de Alba, M. D. Galindo-Rianon, M. Garcia-Vargas, *Talanta*, 2012, **100**, 432–438.

[29] C. Cui, M. He, B. Chen, B. Hu, *Talanta*, 2013, **116**, 1040–1046.

[30] S. Dadfarnia, A. M. Salmanzadeh, A. M. H. Shabani, *J. Anal. At. Spectrom.*, 2002, **17**, 1434–1438.

[31] H. M. Yu, H. Song, M. L. Chen, *Talanta*, 2011, **85**, 625–630.

[32] W. Ngeontae,W. Aeungmaitrepirom, T. Tuntulani, A. Imyim, *Talanta*, 2009, **78**, 1004–1010.

[33] M. A. Chamjangali, G. Bagherian, A. Mokhlesian, B. Bahramian, *J. Hazard. Mater.*, 2011, **192**, 1641– 1649.

[34] A. Islam, M. A. Laskar and A. Ahmad, *Talanta*, 2010, **81**, 1772–1780.

[35] S. A. Idris, C. M. Davidson, C. McManamon, M. A. Morris, P. Anderson and L. T. Gibson, *J. Hazard. Mater.,* 2011, **185**, 898–904.

[36] G. Socrates, Infrared Characteristic Group Frequencies, John Wiley & Sons, New York, 1980.

[37] R.S. Drago, Physical Methods in Inorganic Chemistry, Litton Education Publishing, 1965.

[38] D. Prabhakaran and M. S. Subramanian, *Talanta*, 2003, **59**, 1227–1236.

[39] R. G. Pearson, *J. Chem. Educ.*, 1968, **45**, 643–648.

[40] A. Islam, N. Zaidi, H. Ahmad and S. kumar, *Environ. Sci. Pollut. Res.*, 2015, **22**, 7716–7725.

[41] H. B. Jonassen and A. W. Meibohm, *J. Phys. Chem.* 1951, **55**, 726–733.

[42] A.E. Martell and R. M. Smith, Critical Stability Constants, Springer Science + Business Media, New York, 1989.

[43] C. P. Kulatilleke, S. N. Goldie, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg. Chem.*, 1999, **38**, 5906–5909.

[44] V. M. Nurchi, G. Crisponi, M. Crespo-Alonso, J. I. Lachowicz, Z. Szewczuk, G. J. S. Cooper, *Dalton Trans.*, 2013, **42** 6161–6170.

[45] G. L. Long and J. D. Winefordner, *Anal. Chem.*, 1983, **55**, 712A–724A.

[46] A. Bartyzel and E.M. Cukrowska, *Anal. Chim. Acta*, 2011, **707**, 204–209.

[47] B. Godlewska-Zylkiewicz, B. Lesniewska and I. Wawreniuk, *Talanta*, 2010, **83**, 596–604.

Graphical Abstract