



## Zincon polymer as a new modifier for selective separation and determination of copper and zinc from synthetic, water and drug samples

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**Abstract:** Chloromethyl polystyrene polymer (CMPS-polymer) has been modified with 2-carboxy-2-hydroxy-5-sulfoformazyl benzene (Zincon) to be used as a new reagent for preconcentration of Cu(II) and Zn(II) ions. The modified polymer (Z-polymer) has been characterized by elemental analysis and IR spectra. Batch and column modes were operated. The newly designed polymer sorbs Cu(II) and Zn(II) quantitatively at pH 7 with flow rate of 5 ml min<sup>-1</sup>. The maximum sorption capacities for Cu(II) and Zn(II) ions were 1.26 and 1.04 mmol g<sup>-1</sup>. The preconcentration factors were 250 and 200 for Cu(II) and Zn(II) ions. The limit of detection was 4 and 5 ng ml<sup>-1</sup> for Cu(II) and Zn(II) ions. The desorption was effective by using 5 ml of 0.1 mol l<sup>-1</sup> HCl or HNO<sub>3</sub> prior to detection using AAS. The modified polymer was highly ion-selective even in the presence of large concentration of electrolytes or organic media, with a preconcentration ability for Cu(II) and Zn(II) ions. The modified polymer was tested on its utility with synthetic, natural water and drug samples, showing RSD value of < 3% which reflects good accuracy and reproducibility.

**Keywords:** Chloromethyl polystyrene polymer; preconcentration of Cu(II) and Zn(II) ions.

### Introduction

Although atomic absorption spectrometry (AAS) (Narin *et al.*, 2000; Soyak *et al.*, 2005) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Gjerde *et al.*, 1993; Jamali *et al.*, 2007; Xu *et al.*, 2007; Beiraghi & Babaee, 2008) are among the most widely used methods for trace metal determination, they are usually insufficient due to the matrix interferences and the very low concentration of metal ions. Therefore, a separation/preconcentration step is required. The traditional separation and preconcentration methods for metal ions include liquid-liquid extraction, co-precipitation and ion exchange. These methods often require large amount of high purity organic solvents, some of which are harmful to health and cause environmental problems. Recently, several methods have been used for pretreatment of the samples; solid phase extraction (SPE) (Chaudhari *et al.*, 2003; Rao & Daniel, 2003; Soyak *et al.*, 2003; de IL Alcantara *et al.*, 2004; Godlewska-Zylkiewicz, 2004; Tuzen *et al.*, 2004) is one of them. Its advantages (Shamsipur *et al.*, 1999) are: (i) the fast, simple and direct application in very small sample amounts ( $\mu$ L volume) without any loss; (ii) low risk of contamination and (iii) time and cost saving. So, SPE has been widely used for the preconcentration of analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical,

environmental and food chemistry (Lemos *et al.*, 2005). The choice of sorbent is therefore a key point in SPE, because it controls the analytical parameters such as selectivity, affinity and capacity (Hafez *et al.*, 2001; Tokalioglu *et al.*, 2006). Chelating and modified polymers have found a widespread applications in the separation and preconcentration of metal ions from various sources and have some advantages over another SPE such as a higher preconcentration factor, higher selectivity, higher stability, better efficiency and great simplicity in handling and transfer (Narin *et al.*, 2004; Hassanien *et al.*, 2007).

In this work, a new modified polymer was prepared by reacting 2-carboxyl-2-hydroxy-5-sulfo-formazyl benzene (Zincon) with chloromethyl polystyrene polymer and its sorption behavior towards Cu(II) and Zn(II) ions has been investigated in batch and column modes. Trials to optimize procedure for separation and preconcentration of Cu(II) and Zn(II) ions from natural water samples have been done.

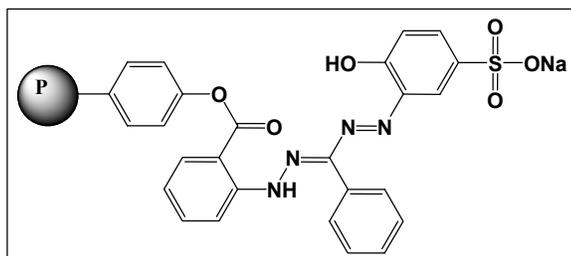
### Experimental

#### Reagents

Commercial chloromethyl polystyrene copolymer with divinylbenzene (CMPS-polymer) (MP-500A; Bayer Co., Germany); 2% DVB; specific surface area (BET) is 66 m<sup>2</sup> g<sup>-1</sup> and 46 meq g<sup>-1</sup> resin was used. 2-Carboxy-2-hydroxy-5-sulfo-formazyl benzene, cetyltrimethyl ammonium bromide (CTAB) and the metal salts (Aldrich) were used. The reaction was followed up with the aid of FTIR spectroscopic analysis. The pH-metric measurements were performed using a Metrohm E53b Potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized before and checked after each titration with buffer solutions produced by FISHER (New Jersey, USA). All titrations were carried out at temperatures 28-40 °C and ionic strength of 0.04-0.12 mol l<sup>-1</sup> KCl.

#### Preparation of Z-polymer

In a 100 ml round bottom flask, 1 g of chloromethyl polystyrene polymer was soaked for three days in 25 ml chloroform as swelling medium. To the swollen polymer, 0.5 g Zincon; 0.1 g CTAB and 5 ml of 30% aqueous solution of Na<sub>2</sub>CO<sub>3</sub> were added. The reaction mixture was heated under reflux on a water bath with magnetically stirring for 10 h. On cooling, the polymeric product was filtered off, washed thoroughly with acetic acid, distilled water, methanol, acetone and finally diethyl ether. The product was dried at 40°C overnight and characterized by elemental analysis and FTIR spectroscopy. The suggested structure of Z-polymer is shown in Scheme 1.



Scheme 1. Structure of the modified polymer (Z-polymer)

### Equipment

A Perkin-Elmer Model 2380 Atomic Absorption Spectrometer, USA, was used. The IR spectra were recorded using Mattson 5000 FTIR Spectrophotometer at 4000–200  $\text{cm}^{-1}$ . The pH values were measured using a pH-meter (Hanna- Instruments, 8519, Italy) with an accuracy of  $\pm 0.01$  standardized with 0.05  $\text{mol l}^{-1}$  potassium hydrogen phthalate yielding pH 4.01 and a standard pH tablet (9.2) at 25  $^{\circ}\text{C}$ .

### pH metric titrations

All pH titrations were carried out at  $25 \pm 2$   $^{\circ}\text{C}$ . The following solutions were titrated against 0.0052  $\text{mol l}^{-1}$  NaOH at ionic strength of 0.1  $\text{mol l}^{-1}$  KCl:

- 1 ml KCl + 2.5 ml HCl (0.0135  $\text{mol l}^{-1}$ )
- Solution (a) + 50 mg Z-polymer
- Solution (b) + 1 ml Cu(II) ions [ $1 \times 10^{-3}$   $\text{mol l}^{-1}$ ]
- Solution (c) + 1 ml Zn(II) ions [ $1 \times 10^{-3}$   $\text{mol l}^{-1}$ ]

The volume was completed to 25 ml with bidistilled  $\text{H}_2\text{O}$ , stirred and the pH was recorded.

### Investigation of the optimal conditions for Z-polymer

**Batch method:** A sample solution (100 ml) containing a known concentration (50  $\mu\text{g/ml}$ ) of Cu(II) or Zn(II) ions was transferred to a glass stoppered bottle (250 ml) and after adjusting its pH to the optimum value, 50 mg of Z-polymer was added. The mixture was shaken for 30 min with a mechanical stirrer, filtered, washed with bidistilled water; the sorbed metal ion was eluted with 5 ml of a suitable concentration of HCl. The resulting solution was adjusted to 100 ml and determined using AAS.

**Column method:** Z-polymer (0.5 g) was first swollen for 24 h, packed in a glass column (40x6 mm) treated with 20 ml of 1  $\text{mol l}^{-1}$  HCl at the optimum flow rate and washed with bidistilled water until the polymer became free from acid. A 100 ml of 100  $\mu\text{g/ml}$  metal ion solution buffered at the optimum pH, was passed through the column at optimum flow rate. After this sorption step, the column was washed with 100 ml of bidistilled water to remove excess metal ions from the polymer bed. The stripping of metals from the polymer was carried out by HCl or  $\text{HNO}_3$ . The eluted solution was collected in a 100 ml calibrated flask and analyzed.

## Results and discussion

### Characterization of Z-polymer

In order to verify the presence of the active functional groups of Zincon in the modified polymer, the IR spectra of CMPS-polymer and Z-polymer were recorded. The spectrum of CMPS-polymer exhibits a characteristic band at 701  $\text{cm}^{-1}$  attributed to  $\nu(\text{C-Cl})$  and a broad band at 3400  $\text{cm}^{-1}$  attributed to  $\nu(\text{OH})$  of water.

Upon modification of CMPS-polymer with zincon (Scheme 1), additional bands appeared at 3600–3500, 3160, 1708, 1655, 1630 and 1050  $\text{cm}^{-1}$  attributed to  $\nu(\text{OH})_{\text{phenolic}}$ ,  $\nu(\text{NH})$ ,  $\nu(\text{N=N})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C=N})$  and  $\nu(\text{N-N})$  bands, respectively (El-Shazly *et al.*, 2005). Also, the high decrease in intensity of the 701  $\text{cm}^{-1}$  band, the formation of a new one at 1050  $\text{cm}^{-1}$  and the presence of the phenolic OH were taken as evidence for the progress of the reaction through ester link.

Metal-Z-polymer interaction was confirmed by the change in color from red in Z-polymer to blue in the complexes. Also, by the shift of  $\nu(\text{C=O})$  and  $\nu(\text{N=N})$  bands to lower wavenumbers by 30 and 20  $\text{cm}^{-1}$ , respectively, and the absence of  $\nu(\text{OH})_{\text{phenolic}}$  band indicating the interaction of Z-polymer with Cu(II) and Zn(II) ions.

The C, H and N content in the Z-polymer was estimated by elemental analysis [Found (Calcd. %): C = 58.9 (60.2%), H = 4.1 (4.0%), N = 9.0 (9.7%)] indicating the formation of Z-polymer. The modification was carried out by 92%. The nitrogen content was measured in Z-polymer which absent in CMPS-polymer.

The shift observed in the pH titration curves (Fig. 1) of Z-polymer with Cu(II) and Zn(II) ions than the Z-polymer was taken as a support for the interaction of Z-polymer with the studied metal ions *via* liberation of hydrogen ions. The Cu(II)- Z-polymer is found below Zn(II)- Z-polymer and Z-polymer curves indicating that Cu(II) ions interact with the modified polymer more strongly than Zn(II) ions.

Water regain values were measured by recording the weight difference of the modified polymer after its storage at 120  $^{\circ}\text{C}$  for 48 h. The water regain value was found 0.30  $\text{g g}^{-1}$  for Z-polymer. Comparison of this value with 0.12  $\text{g g}^{-1}$  of CMPS-polymer indicates appreciable improvement of the sorption capacity of Z-polymer (Das & Das, 1989).

### Preliminary investigations

Preliminary experiments for batch and column were carried out to investigate the quantitative sorption of Cu(II) and Zn(II) ions by CMPS-polymer and Z-polymer. CMPS-polymer does not show any tendency for the sorption of these metal ions; Z-polymer is found efficient. This is probably due to the strong interaction between metal ions and the loaded organic ligand through complexation *via* the active functional groups. The analytical variables such as pH, sorption kinetics, temperature and matrix effects have been studied.

Fig. 1. The pH-metric titrations of HCl, (HCl + Z-polymer), [HCl + Z-polymer + Cu(II)] and [HCl + Z-polymer + Zn(II)] against  $0.0052 \text{ mol l}^{-1}$  NaOH.

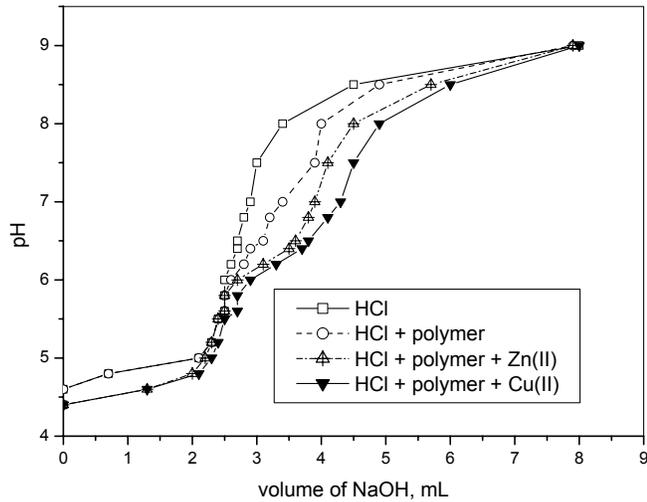
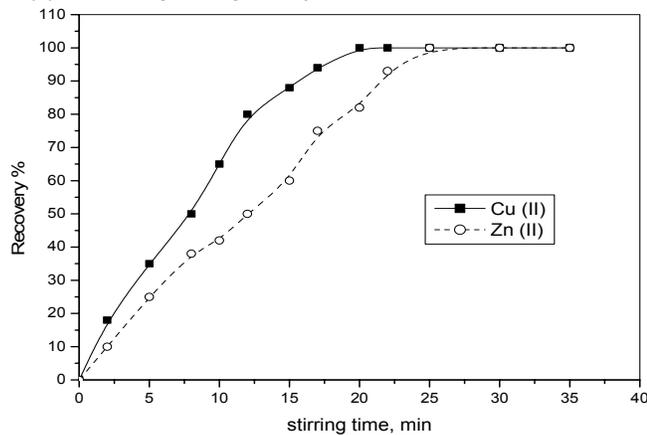


Fig. 3. Effect of stirring time on the recovery of Cu(II) and Zn(II) ions using 50 mg Z-polymer at  $25^\circ\text{C}$ .



#### Batch technique

**Effect of pH:** The effect of pH on the sorption of the studied metal ions has been investigated (1-8 pH range). The experiments were elaborated by shaking solutions containing the metal ions with the Z-polymer of variable pH for sufficient equilibrium time (the pH was adjusted using HCl/KCl or acetic/acetate buffers). The data represented in Fig. 2 showed that the maximum sorption efficiency was achieved at pH 6-7; subsequent experiments were carried out at this pH.

**Determination of sorption capacity:** The sorption capacity of Z-polymer towards Cu(II) and Zn(II) ions was determined by shaking solution containing excess metal ions with 50 mg of the polymer under the operating conditions. The maximum sorption capacity for Cu(II) and Zn(II) ions is  $1.26$  and  $1.04 \text{ mmol g}^{-1}$ , respectively.

**Effect of the amount of polymer:** The amount of Z-polymer is an important parameter that affects the recovery of metal ion. The sorption is not quantitative

Fig. 2. Effect of pH on the recovery of Cu(II) and Zn(II) ions using 50 mg Z-polymer and stirring time 30 min at  $25^\circ\text{C}$ .

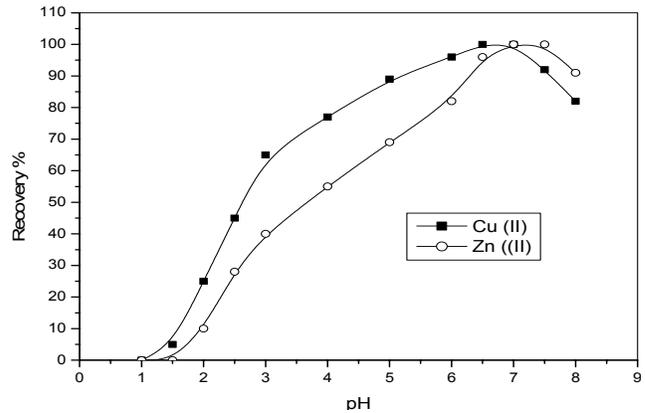
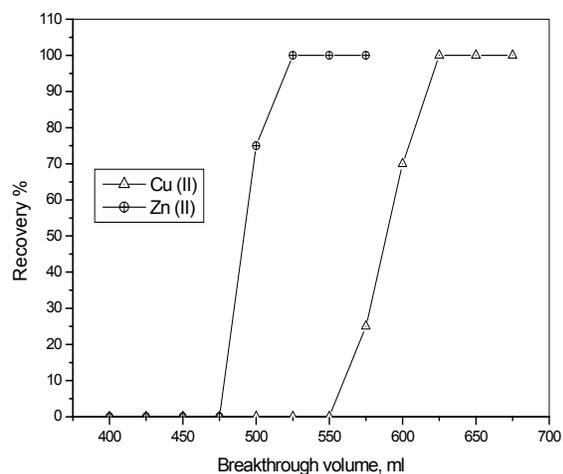


Fig. 4. Breakthrough curves for Cu(II) and Zn(II) ions with flow rate of  $5 \text{ ml min}^{-1}$  at  $25^\circ\text{C}$  and pH 7.



by using amount of polymer smaller than the optimum amount (50 mg). On the other hand, excess polymer prevents quantitative elution of the sorbed metal ion by a small volume of eluent. For this reason, the amount of polymer was optimized. To test the polymer amount for quantitative sorption of Cu(II) and Zn(II) ions, 25-500 mg of Z-polymer were used. Quantitative recoveries of Cu(II) and Zn(II) ions were obtained in the range of 50-200 mg of the modified polymer. Thus, 50 mg of Z-polymer has been used for the subsequent experiments.

**Stirring time:** To determine the rate of sorption of metal ions on Z-polymer, a solution containing the metal ion with 50 mg of Z-polymer was shaken at room temperature ( $25^\circ\text{C}$ ). Aliquot of 1 ml solution was taken out for analysis at pre-determined intervals. The concentration of the metal ion in the supernatant solution was determined and its sorbed amount on the polymer was calculated by mass balance. The sorption half-time ( $t_{1/2}$ ) was estimated from Fig. 3; the maximum



sorption of Cu(II) and Zn(II) ions with Z-polymer reached its equilibrium time after 15 and 25 min, respectively. However, the time required for 50% sorption of Cu(II) and Zn(II) ions was 8 and 12 min, respectively.

*Table 1. Influence of interfering cations and anions on the recovery % of  $10 \mu\text{g ml}^{-1}$  Cu(II) and Zn(II) ions under investigation using Z-polymer and shaking for 30 min at  $25^\circ\text{C}$ .*

Interfering Ion	Concentration ( $\mu\text{g ml}^{-1}$ )	Recovery %	
		Cu(II)	Zn(II)
K <sup>+</sup>	200	98	98
Mg <sup>2+</sup>	200	97	98
Ca <sup>2+</sup>	200	98	97
NH <sub>4</sub> <sup>+</sup>	200	99	99
Acetate	200	99	98
Oxalate	200	76	89
Tartrate	200	79	76
Citrate	200	70	75
Thiourea	200	65	80
NO <sub>3</sub> <sup>-</sup>	200	98	99
Cl <sup>-</sup>	200	99	98
F <sup>-</sup>	200	98	98
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	200	10	98
EDTA	200	97	98
SO <sub>4</sub> <sup>2-</sup>	200	99	98

*Effect of temperature:* It was expected that temperature would affect the equilibrium and sorption of Cu(II) and Zn(II) ions. The sorption of Cu(II) and Zn(II) ions was investigated over a temperature range  $25\text{--}70^\circ\text{C}$ , which reflects typical laboratory ambient conditions. A steady, almost linear, decrease in sorption time with increase in temperature declining from 15 to 11, and 25 to 18 min for Cu(II) and Zn(II) ions, respectively. The change in sorption time with temperature may be taken for analysis of the samples from the native source without thermostating.

*Polymer stability:* Z-polymer (50 mg) was shaken with 100 ml ( $1\text{--}6 \text{ mol l}^{-1}$  HCl or NaOH), electrolyte ( $0.001\text{--}5.000 \text{ mol l}^{-1}$  NaCl, KCl or NaNO<sub>3</sub>) or organic solvent (ethanol, acetone or chloroform) for 24 h, filtered and washed with bidistilled water. It was found that, no change in its composition suggesting a stable nature of Z-polymer. The exchange capacity of Cu(II) and Zn(II) ions on the polymer was subjected to several sorption and desorption (batch) operations. The Z-polymer (50 mg) was stirred with 100 ml of  $25 \text{ mg l}^{-1}$  solution containing Cu(II) and Zn(II) ions for 1 h at room temperature. The polymer was separated where the Cu(II) and Zn(II) ions were desorbed using 5 ml of

appropriate concentration of HCl. It was found that, the sorption capacity after 50 cycles for Cu(II) and Zn(II) ions varied by less than 2%. Therefore, the reuse of Z-polymer is feasible. The capacity of the polymer stored for more than 6 months under ambient conditions found unchanged.

*Choice of eluent:* Choice of the most effective eluent for quantitative stripping of the retained metal ions on Z-polymer is of special interest. The metal ions sorbed on Z-polymer can be eluted with HCl into the aqueous phase. Other approach was the use of sodium tartarate or EDTA for elution of the sorbed metal ions. Literature survey showed that, complex organic matrix causes severe suppression of the analyte signal; inorganic acid is analytically preferred. The data obtained indicate that, 5 ml of  $0.1 \text{ mol l}^{-1}$  of HCl could afford quantitative elution of Cu(II) and Zn(II) ions from Z-polymer. Subsequent elution of the metal ions were carried out with HCl taking that, Cl<sup>-</sup> is an acceptable matrix for both AAS and spectrophotometric determination.

*Effect of some interfering species:* In competitive reactions of the loaded separating agent with various metallic species, a reduction of the sorption efficiency of the target metal species should be expected. The effect of interfering ions on the recovery of the analytes was studied for several reasons: (1) to avoid any effect during application, (2) to choose a selective eluent as predicted from its interfering effect, (3) to study the preferred positions of different metal ions, and (4) to enhance the selectivity. No change on the recovery % of Cu(II) and Zn(II) ions was observed from nitrate, sulfate, chloride, acetate; Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions (Table 1) on Z-polymer. However, oxalate, citrate, tartrate and thiourea caused a remarkable suppression of the metal ion sorption; EDTA has no effect. Moreover, thiosulfate prevents the loading of Cu(II) on Z-polymer and loaded Zn(II); the behavior could be taken for the separation of Cu(II) from Zn(II).

#### Column technique

*Effect of flow rate:* The effect of flow rate on the metal sorption was investigated by varying the flow rate from

*Table 2. Determination of Cu(II) and Zn(II) (5 ppm each) from synthetic samples: flow rate =  $5 \text{ ml.min}^{-1}$ ,  $n = 5$  at  $20^\circ\text{C}$ .*

Mixture taken	Cu(II)			Zn(II)		
	ppm	R%	R.S.D	ppm	R%	R.S.D
Hg(II)+Mn(II) <sup>a</sup>	4.98	99.6	0.55	4.99	99.8	0.45
Co(II)+ Pb(II) <sup>a</sup>	4.97	99.4	0.70	4.96	99.2	0.21
Ni(II)+ Cd(II) <sup>a</sup>	4.98	99.6	0.20	4.97	99.4	0.53
Co(II)+ Cd(II) <sup>a</sup>	4.98	99.6	0.85	4.98	99.6	0.22
Al(III)+Cr(III) <sup>b</sup>	4.94	98.8	0.50	4.94	98.8	1.10
Al(III)+Fe(III) <sup>b</sup>	4.90	98.0	1.25	4.91	98.2	2.25

<sup>a</sup> at pH 7 in presence of EDTA; <sup>b</sup> at pH 7 in presence of EDTA and NaF

*R.S.D is the relative standard deviation =  $s.100/\bar{x}$ ,  $s$  is the standard deviation and  $\bar{x}$  is the experimental average.*



0.5 to 10 ml min<sup>-1</sup> under the optimum conditions. It was found that, the optimum flow rate for the maximum sorption capacity of Cu(II) and Zn(II) ions was 5 ml min<sup>-1</sup> for both. In flow rate greater than 5 ml min<sup>-1</sup>, Cu(II) and Zn(II) ions do not reach equilibrium. The faster sorption of Cu(II) and Zn(II) ions on Z-polymer is taken as an indication for its higher reactivity.

Table 3. Water quality measurements for samples collected from different locations

Location	Parameters				
	pH	TDS (g l <sup>-1</sup> )	TSM (g l <sup>-1</sup> )	TDO (mg O <sub>2</sub> <sup>-1</sup> )	Alkalinity (mg CaCO <sub>3</sub> l <sup>-1</sup> )
Tap water (Mansoura city)	7.22	0.12	4.00	6.38	125.00
Nile river (Mansoura city)	7.83	0.50	4.00	5.54	144.00
Wastewater (Talkha, Meat Antar)	8.25	0.55	4.00	7.85	180.00
Nile water (Dameitta city )	8.20	29.20	321.00	5.56	185.00
Wastewater (Ras El-Bar, Elborg)	8.14	14.30	150.00	6.24	154.00
Sea water (Port Said, Suez canal)	8.19	46.10	346.00	5.74	132.00

**Breakthrough capacity.** It was used to evaluate the amount of metal ion sorbed per gram on the modified polymer under the operating conditions. In order to obtain a breakthrough capacity, a glass column was packed with 0.5 g of Z-polymer, 50 µg ml<sup>-1</sup> of Cu(II) and Zn(II) solution at the optimum pH was passed through the column with the selected flow rate. The receiving effluent after 5 min was fractionalized into 5 ml portions and each metal ion was determined. The breakthrough capacity (Fig. 4) indicates that, the column is exhausted with 62.5 and 55.0 mg of Cu(II) and Zn(II)/g polymer.

**Column reuse.** To test the long-term stability of the column containing the modified polymer, successive sorption and desorption cycles were subjected by passing the metal ion solution through the column at the optimum flow rate. The sorbed metal ion is then eluted from the polymer with 5 ml of 0.1 mol l<sup>-1</sup> HCl. The procedure was repeated several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed metal ions. The results of fifty sorption/desorption cycles indicated that, the recovery decreased by 2-3 % for Cu(II) and Zn(II) ions, which reflect a good stability of Z-polymer.

**Effect of volume and preconcentration factor.** Aqueous solution (0.1-1.5 L) containing 10 µg of Cu(II) and Zn(II) was passed through Z-polymer bed, eluted with 5 ml of appropriate concentration of HCl and determined. It was found that, Cu(II) and Zn(II) ions could be removed quantitatively from volume up to 1125 and 1000 ml, respectively, then the recovery decreased remarkably. Therefore, by using 5 ml of 0.1 mol l<sup>-1</sup> HCl, a practical maximum of 250 folds preconcentration factor

for Cu(II) and 200 folds for Zn(II) ions were obtained.

**Detection limits of the metal ions:** It means the lowest concentration of metal ion below which a quantitative sorption by the polymer is not perceptibly seen. It was investigated for Cu(II) & Zn(II) ions at 10<sup>-1</sup>-10<sup>-3</sup> µg ml<sup>-1</sup> passed through Z-polymer bed at a suitable flow rate. The limit of detection (LOD) is 4 and 5 ng ml<sup>-1</sup> for Cu(II) and Zn(II) ions, respectively, showing a high sensitivity of the polymer to preconcentrate trace analyte.

### Applications

#### Selective separation of Cu(II) and Zn(II) ions from synthetic mixtures

In order to separate selectively Cu(II) and Zn(II) from their mixtures containing some metal

ions, an aliquot of aqueous solution (0.5 L) containing 5 mg of the studied metal ion and 50 mg of other cations was taken and the recommended procedure (column mode) was followed. The results summarized in Table 2 show that Cu(II) and Zn(II) ions each are sorbed by the polymer, even up to 50 mg of the other interfering cations where no effect on their recovery in presence of 0.1 g EDTA under the optimum conditions.

#### Selective separation of Cu(II) and Zn(II) ions from natural water

Surface water samples were collected from Nile River water (Mansoura, Dameitta, Ras EL-Bar) and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and the suspended matter is determined. The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg CaCO<sub>3</sub> l<sup>-1</sup>) were determined (Table 3) according to the previous methods [21]. The samples were acidified with concentrated HNO<sub>3</sub> to pH ~ 2 and preserved in polyethylene vessel. The organic matter was digested prior to the separation process. K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (0.5 g) and 5 ml of 98% (w/v) H<sub>2</sub>SO<sub>4</sub> were added to 500 ml of the water sample and heated for 30 min at 95 °C. After cooling to room temperature, 100 mg of Z-polymer, and

Table 4. Determination of Cu(II) and Zn(II) ions on water samples using AAS after preconcentration with Z-polymer at pH 7, flow rate = 5 ml min<sup>-1</sup>, n = 5 at 20 °C.

Sample (location)	Experimental value of Cu(II) µg l <sup>-1</sup>	Experimental value of Zn(II) µg l <sup>-1</sup>
Tap water (Mansoura city)	5.45 ± 0.65	160.50 ± 2.64
Nile river (Mansoura city)	6.52 ± 0.81	120.10 ± 1.02
Wastewater (Talkha, Meat Antar)	4.26 ± 0.87	96.54 ± 2.52
Nile water (Dameitta city )	16.21 ± 0.52	140.55 ± 1.87
Wastewater (Ras El-Bar, Elborg)	11.32 ± 0.95	155.50 ± 1.55
Sea water (Port Said, Suez Canal)	3.50 ± 0.42	28.60 ± 0.50



Table 5. Preconcentration and determination of Cu(II) and Zn(II) in pharmaceutical tablets (mg tablet<sup>-1</sup>), pH 7, stirring time 30 min, n 5 at 25°C

Drug	Metal content (mg tablet <sup>-1</sup> )	Recovery % of Cu(II)	Recovery % of Zn(II)
Gerimax	Mg (150); Fe (14); Mn (2.5); Zn (15); Cr (0.05); Se (0.05); Mo (0.15); Cu (2.00)	1.96 ± 0.02	14.50 ± 0.55
Centrum Recovery %)	Ca (162); Fe (27); Mg (100); Mn (7.5); K (7.5); Zn (22.5); Cu (3.00)	2.88 ± 0.20	22.45 ± 0.08
Totavit (Recovery %)	Cr (25); Mn (2.5); Fe (18); Cu (2); Ni (0.005); Zn (15)	0.20 ± 0.05	15.00 ± 0.02

1 ml ( $5 \times 10^{-3}$ ) EDTA solution was added to the sample and the pH was adjusted to 7 and stirred for 30 min then filtered off. To the filtrate, another 100 mg of Z-polymer was added and the pH was again controlled. The sample was then stirred for 30 min and filtered. The total residue was gathered and the collected Cu(II) and Zn(II) ions were eluted by 5 ml of 0.1 mol l<sup>-1</sup> HCl to give a concentration factor of 200 folds. The eluates were analyzed as previously described.

The quality of water is mentioned in Table 3. The tap, Nile and Sea waters were analyzed for Cu(II) and Zn(II) ions by the described procedure. Preliminary investigation showed that the method able selectively to sorb Cu(II) and Zn(II) ions with high efficiency. Samples of wastewater from Talkha (Table 4) showed high concentration of Cu(II) and Zn(II) ions (the water of this area is relatively polluted by agricultural effluents and domestic sewage and was chosen because many water creatures were dead). The RSD % was found to be 1.9 - 3.5.

#### Determination of Cu(II) and Zn(II) ions in pharmaceutical samples

A drug or vitamin tablet containing metal ions was digested using 5 ml of concentrated HNO<sub>3</sub> and heated to near dryness. After cooling, the residue was dissolved in another 5 ml of conc. HNO<sub>3</sub>. The solution was gently evaporated on a steam bath till a residue was again left. It was heated with 50 ml of bidistilled water, filtered off and completed to 100 ml in a calibrated flask. After adjusting to optimum pH, the recommended procedure for determination of Cu(II) and Zn(II) ions was applied. The amounts recovered and determined are listed in Table 5.

#### Conclusion

The introduced modified polymer (Z-polymer) is found suitable and efficient for trace enrichment of Cu(II) and Zn(II) ions. The proposed procedure is simple, selective and fast for sorption and preconcentration of the metal ions without using organic solvents. In comparison with the other modified resins, Z-polymer has found superior due to its higher preconcentration factor, higher sorption capacity, low

matrix effect, good precision, strong stability in different media, quantitative sorption at a very low concentration of Cu(II) and Zn(II) ions in samples having complicated and variable matrices, recycling over 50 cycles, and a short loading time ( $t_{1/2}$ ). From the economic point of view, the sorption capacity of the modified polymer is practically unchanged by use for 6 months or stored under ambient conditions.

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