

## EFFICIENT PRECONCENTRATION OF $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ AND $\text{Fe}^{3+}$ WITH AN AGAROSE-SCHIFF BASE SORBENT

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Sorption and preconcentration of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  on a salen-type Schiff base, 2,2'-(ethane-1,2-diylbis(nitrilomethylidene))bis(2-methylphenol), chemically immobilized on a highly crosslinked agarose support, were studied. Kinetic studies showed higher sorption rates of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  in comparison with  $\text{Zn}^{2+}$ . Half-times ( $t_{1/2}$ ) of 31, 106 and 58 s were obtained for sorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  by the sorbent, respectively. Effects of pH, eluent concentration and volume, ionic strength, buffer concentration, sample volume and interferences on the recovery of the metal ions were investigated. A 5-ml portion of 0.4 M HCl solution was sufficient for quantitative elution of the metal ions from 0.5 ml of the sorbent packed in a 6.5 mm i.d. glass column. Quantitative recoveries were obtained in a pH range 5.5–6.5 for all the analytes. The volumes to be concentrated exceeding 500 ml, ionic strengths as high as 0.5 mol l<sup>-1</sup>, and acetate buffer concentrations up to 0.3 mol l<sup>-1</sup> for  $\text{Zn}^{2+}$  and 0.4 mol l<sup>-1</sup> for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  did not have any significant effect on the recoveries. The system tolerated relatively high concentrations of diverse ions. Preconcentration factors up to 100 and detection limits of 0.31, 0.16 and 1.73  $\mu\text{g l}^{-1}$  were obtained for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ , respectively, for their determination by a flame AAS instrument. The method was successfully applied to the metal ion determinations in several river water samples with good accuracy.

**Keywords:** Agarose; Schiff bases; Chelating sorbents;  $\text{Cu}^{2+}$ ;  $\text{Zn}^{2+}$ ;  $\text{Fe}^{3+}$ ; Flame AAS; Salene complexes; Metal cations.

The residence time of an analyte in a small preconcentration column is generally quite short. Hence, the rate of sorption of metal ions by a sorbent is an important factor that can influence its recovery. The kinetics of sorption or removal of metal ions has been extensively studied for different sorbents<sup>1-8</sup>.

The rate of removal of zinc, cadmium, lead and copper ions from solution with Chelex-100 in bulk experiments was reported by Schulze and Elsholze<sup>1</sup>. The observed first-order rate constants, corresponding to half-lives of about 1 min, did not differ by more than 10%, which indicates that

mass transfer, rather than the rate of complexation was the main resistance in the accumulation process. The sorption rates of copper, cobalt and nickel ions on three agarose-based chelating sorbents have been reported elsewhere<sup>3</sup>. The study indicated marked differences between the sorption rates of different metal ions and different ligands used which implies the high mass transfer rate of the agarose support. One can conclude that the rate-determining step for the agarose-based sorbents is chelation rather than mass transfer. In a previous study<sup>2</sup> the much higher sorption rates of some metal ions on an agarose-based sorbent in comparison with Chelex-100 were shown. Study of the rates of sorption of different metal ions by an immobilized ligand on an agarose support can be very helpful because it affords their relative chelation rates by the ligand and can be used for prediction of their behavior in a preconcentration system.

Salens, which are formed by condensation between salicylaldehyde and ethylenediamine, are good chelating agents and make stable complexes with transition metals<sup>9-13</sup>. Salens have been used for the determination of metal ions<sup>14-17</sup> but there exist only few reports on their use in preconcentration systems<sup>18-20</sup>.

Recently, we reported the synthesis of a novel salen, 2,2'-[ethane-1,2-diyl-bis(nitrilomethylidyne)]bis(2-methylphenol), and its chemical immobilization on Novarose (a highly crosslinked agarose)<sup>21</sup>. The study indicated the possibility of application of the sorbent as a column packing for quantitative preconcentration of Pb<sup>2+</sup> in water samples. The sorbent showed relatively high capacities for some other metal ions as well. In this paper the kinetics of sorption of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>3+</sup> by the Novarose-Schiff base sorbent and its use for the preconcentration of the metal ions in natural waters will be reported.

## EXPERIMENTAL

### Apparatus

A flame atomic absorption spectrometer (Shimadzu AA-670, Japan) with an air-acetylene flame was used for determination of elements under the conditions recommended by the manufacturer. Hollow-cathode lamps were employed as radiation sources. No background correction method was applied. An ET-AAS (Shimadzu AA6650, Japan) with a deuterium lamp background correction served for direct determinations of copper, zinc and iron in natural water samples. pH determinations, were performed with a Jenway model 3020 (U.S.A.) with a combined glass electrode, after calibration with standard Merck buffers. A glass preconcentration column (Omnifit) with 6.5 mm i.d. and adjustable length and a peristaltic pump (EYLA, Japan) were used for pumping solutions through the column.

## Chemicals and Reagents

All chemicals and reagents were of analytical reagent grade (Merck, Germany) and were used as received. Doubly distilled water, prepared with a totally glass Fisons (U.K.) double distiller, was used for all the dilutions. Crosslinked and epoxy-activated agarose (Novarose) with 40–60  $\mu\text{m}$  particle size was a gift from Inovata AB (Stockholm, Sweden).

## Methods

The salen type Schiff base, 2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]bis(2-methylphenol), was synthesized and chemically immobilized on Novarose using a method described elsewhere<sup>21</sup>.

Kinetic studies were performed in batch mode. 100 ml of a solution containing 100  $\mu\text{g}$  of a metal ion was prepared in 0.01 M acetate buffer, pH 5.5. An 0.5-ml portion of the packed sorbent was added to the metal ion solution while stirring with a magnetic bar. A syringe, equipped with a filter, was used for sampling of the solution. The samples were collected in small capped bottles and analyzed by flame AAS. Graphs of the relative metal ion concentration vs contact time were plotted and the rate constants ( $k$ ) were calculated from the first part of the curves assuming pseudo-first-order reaction rates. Calculation of  $k$  and  $t_{1/2}$  were based on the known equation of

$$\ln (c_t - c_\infty)/(c_0 - c_\infty) = -kt$$

in which  $c_0$ ,  $c_\infty$  and  $c_t$  are initial, equilibrium and instantaneous (at time  $t$ ) concentrations, respectively.

Preparation and buffering of metal ion solutions, packing and pretreatment of columns and analysis of field samples were performed as reported elsewhere<sup>21</sup>.

Preconcentration and recovery experiments were performed usually by pumping 30 ml of a buffered test solution, 0.01 M acetate buffer, through a pretreated 0.5-ml column. The column was then washed with a few ml of 0.01 M acetate buffer and eluted with 5 ml of 1 M hydrochloric acid (unless stated otherwise). The eluate was collected in small capped vessels and analyzed by flame AAS against standards.

The detection limit ( $DL$ ) was calculated using the equation

$$DL = \frac{\bar{S}_{bl} + 3\sigma}{m} P_F$$

in which  $\bar{S}_{bl}$  and  $\sigma$  are the mean and standard deviations of the system's blank signal for ten replicated measurements, respectively;  $m$  is the calibration curve slope and  $P_F$  stands for the preconcentration factor of the system.

## RESULTS AND DISCUSSION

### *Kinetic Studies*

Sorption profiles of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  on the Novarose–Schiff base sorbent are shown and compared in Fig. 1. As the figure indicates,  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$

were quickly accumulated by the sorbent and their concentrations in solution leveled off to about zero in approximately 15 min. Sorption of  $\text{Zn}^{2+}$ , however, was relatively slower with a high equilibrium concentration of about  $0.3 \text{ mg l}^{-1}$ . Assuming pseudo-first-order sorption rates in the first few minutes of the accumulation, resulted in rate constants of  $0.71 (\pm 0.02)$ ,  $0.39 (\pm 0.02)$  and  $1.31 (\pm 0.04) \text{ s}^{-1}$  and  $t_{1/2}$  values of 58, 106 and 31 s for  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ , respectively. The relatively large variation in the sorption rates of agarose based sorbents in this work as well as some previous works<sup>2,20,21</sup>, suggests that the chelation by the immobilized ligand rather than the diffusion or the convective transport of the ions in the solution is the rate determining step in the kinetics of sorption.

In comparison with an iminodiacetate (IDA) agarose sorbent<sup>3</sup>, the  $t_{1/2}$  of the Novarose–Schiff base sorbent for copper ion is higher by a factor of about 5. The  $\text{Cu}^{2+}$  sorption rate of the sorbent is also slower than that of tris(2-aminoethyl)amine (TREN) and even dipicolylamine sorbents (DPA)<sup>3</sup> with the same support and particle sizes. There exist no data on the sorption rates of  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$  by other agarose-based sorbents. Although the sorption rate of the Schiff base sorbent seems to be somewhat slow, it is sufficient when moderate sample flow rates are used. This conclusion is based on reported quantitative recoveries for sorbents with substantially smaller sorption rates<sup>1,4–8</sup>.

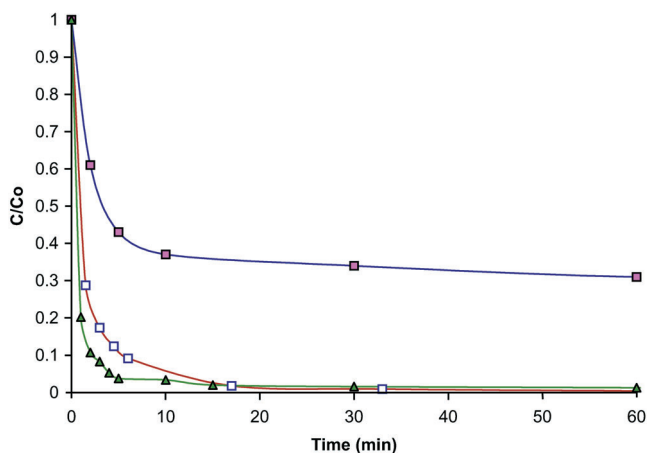


FIG. 1

Sorption profiles of  $\text{Fe}^{3+}$  ( $\square$ ),  $\text{Zn}^{2+}$  ( $\blacksquare$ ) and  $\text{Cu}^{2+}$  ( $\blacktriangle$ ) on the Novarose–Schiff base sorbent. Sorbent volume 0.5 ml; buffer concentration  $0.01 \text{ mol l}^{-1}$ ; pH 5.5; sample volume 100 ml; initial metal ion concentration  $1 \text{ } \mu\text{g ml}^{-1}$

### Effect of Different Parameters on the Column Recovery

Our previous studies<sup>21</sup> indicated that the binding capacities of the Novarose–Schiff base sorbent are reasonably high for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ . The capacities at pH 6 were calculated to be 3813 ( $\pm 137$ ), 3792 ( $\pm 83$ ) and 2011 ( $\pm 62$ )  $\mu\text{g ml}^{-1}$ , respectively; they seem to be sufficiently high for quantitative recovery in natural waters. Hence, the effects of different parameters on the column recoveries of these metal ions were carefully studied.

Figure 2 indicates the effect of pH on the recovery of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$  from the column. The recoveries were found to be quantitative over a pH range of 5.5–6.5 for all the studied metal ions.

Elution of the metal ions accumulated on the column was tested using various HCl volumes (1–9 ml) and concentrations (0.01–2 mol  $\text{l}^{-1}$ ). The study indicated that the analytes can be eluted quantitatively with a minimum 5-ml portion of 0.4 M HCl solution.

Sample flow rates up to 2.5 ml  $\text{min}^{-1}$  did not affect the recoveries of the metal ions and in higher flow rates a high back pressure was observed. Therefore, the flow rate of 2.5 ml  $\text{min}^{-1}$  was used in subsequent experiments.

The tolerance of the method for high ionic strengths was tested by recovery measurements at various sodium chloride concentrations. Using concentrations up to 0.5 mol  $\text{l}^{-1}$  of the salt, no significant changes were monitored in the recoveries. The study was repeated for various acetate

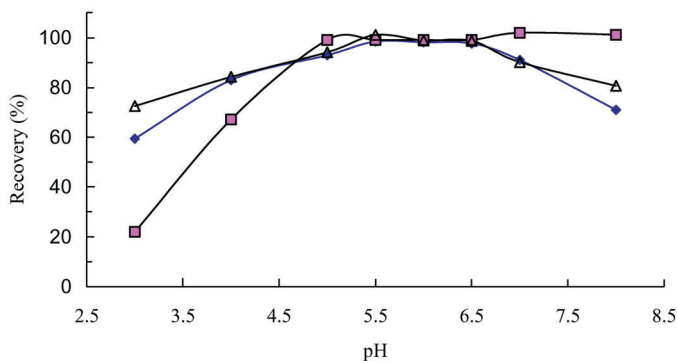


FIG. 2

Effect of pH on the uptake of  $\text{Cu}^{2+}$  ( $\Delta$ ),  $\text{Zn}^{2+}$  ( $\blacksquare$ ) and  $\text{Fe}^{3+}$  ( $\blacklozenge$ ) on a 0.5 ml Novarose–Schiff base column. Eluent 5 ml of 1 M HCl; sample volume 30 ml; buffer concentration 0.01 mol  $\text{l}^{-1}$ ; flow rate 2.5 ml  $\text{min}^{-1}$ ; analyte concentration 0.3 mg  $\text{l}^{-1}$

buffer concentrations. The maximum acetate concentration that could be used with still quantitative recoveries was  $0.4 \text{ mol l}^{-1}$  for  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  and  $0.3 \text{ mol l}^{-1}$  for  $\text{Zn}^{2+}$ . Hence, the tolerance of the method to matrix ions is reasonably high; this is an indication of a chelation mechanism, rather than a simple ion exchange, operating in metal sorption.

The preconcentration procedure for trace metals can be strongly affected by diverse ions that are present in a sample. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions in natural waters. Table I shows the recoveries of the analytes in presence of some specified amounts of diverse ions.

### Preconcentration Factors and Detection Limits

Using the optimized experimental conditions, different sample volumes (up to 500 ml) were concentrated on the column; no significant losses were observed for any of the metal ions. Hence, by using 5 ml of the eluent, preconcentration factors up to 100 can be obtained.

TABLE I

Recoveries of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  from the Novarose–Schiff base column in the presence of maximum concentrations of matrix ions tolerated (for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{Na}^+$ ) or tested (for the other ions)<sup>a</sup>

Matrix ion		$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$	$\text{Cd}^{2+}$	$\text{Fe}^{3+}$
$\text{Fe}^{3+}$	Mass ratio <sup>b</sup>	500	500	30000	50	50	50	50	–
	Recovery, %	101	98.0	99.2	101	102	98.4	98.1	–
	RSD (n=3)	4.4	3.2	3.5	2.2	2.8	4.9	6.7	–
$\text{Zn}^{2+}$	Mass ratio	500	330	38000	50	–	50	50	50
	Recovery, %	98.2	98.8	101	99.2	–	98.6	98.1	98.9
	RSD (n=3)	1.7	2.9	2.8	3.5	–	2.3	2.1	3.6
$\text{Cu}^{2+}$	Mass ratio	660	660	38000	–	50	50	50	50
	Recovery, %	97.6	101	101	–	101	99.3	101	99.3
	RSD (n=3)	3.2	4.1	3.5	–	2.9	2.1	2.9	2.1

<sup>a</sup> Eluent 5 ml of 1 M HCl; sample volume 30 ml; buffer concentration  $0.01 \text{ mol l}^{-1}$ ; flow rate  $2.5 \text{ ml min}^{-1}$ ; analyte concentration  $0.3 \text{ mg l}^{-1}$ . <sup>b</sup> Matrix ion concentration (in  $\text{mg l}^{-1}$ ) divided by the analyte concentration (in  $\text{mg l}^{-1}$ ).

By applying a preconcentration factor of 100, detection limits of 0.31, 0.16 and 1.73  $\mu\text{g l}^{-1}$  were obtained for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Fe}^{3+}$ , respectively, using a flame AAS apparatus.

### *Application to Real Samples*

The proposed method was applied to the determination of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in four river water samples; two from Korram Abad river (Khorram-Abad, Iran), and the other two from Koot-Abdollah and Tembi rivers

TABLE II  
Application of the Novarose-Schiff base sorbent to the determination of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in river and spiked river water samples<sup>a</sup>

Analyte	Water sample	Added analyte $\mu\text{g l}^{-1}$	Measured <sup>b</sup> $\mu\text{g l}^{-1}$	Reference $\mu\text{g l}^{-1}$
$\text{Fe}^{3+}$	Khorram Abad River-1	–	21.30 ( $\pm 0.8$ )	–
		20	41.07 ( $\pm 1.6$ )	41.30 ( $\pm 0.8$ ) <sup>c</sup>
	Khorram Abad River-2	–	14.63 ( $\pm 0.5$ )	–
		20	33.88 ( $\pm 1.4$ )	34.63 ( $\pm 0.5$ ) <sup>c</sup>
	Koot-Abdollah River	–	82.55 ( $\pm 4.0$ )	85.05 ( $\pm 2.2$ ) <sup>d</sup>
	Tombi River	–	85.16 ( $\pm 2.8$ )	90.54 ( $\pm 1.8$ ) <sup>d</sup>
$\text{Zn}^{2+}$	Khorram Abad River-1	–	8.13 ( $\pm 0.2$ )	–
		10	18.22 ( $\pm 0.7$ )	18.13 ( $\pm 0.2$ ) <sup>c</sup>
	Khorram Abad River-2	–	5.57 ( $\pm 0.2$ )	–
		10	15.64 ( $\pm 0.6$ )	15.57 ( $\pm 0.2$ ) <sup>c</sup>
	Koot-Abdollah River	–	7.84 ( $\pm 0.31$ )	7.54 ( $\pm 0.08$ ) <sup>d</sup>
	Tombi River	–	10.30 ( $\pm 0.25$ )	9.84 ( $\pm 0.21$ ) <sup>d</sup>
$\text{Cu}^{2+}$	Khorram Abad River-1	–	6.56 ( $\pm 0.2$ )	–
		20	26.94 ( $\pm 0.6$ )	26.56 ( $\pm 0.2$ ) <sup>c</sup>
	Khorram Abad River-2	–	7.23 ( $\pm 0.28$ )	–
		20	26.19 ( $\pm 0.8$ )	27.23 ( $\pm 0.28$ ) <sup>c</sup>
	Koot-Abdollah River	–	10.15 ( $\pm 0.44$ )	9.56 ( $\pm 0.45$ ) <sup>d</sup>
	Tombi River	–	15.28 ( $\pm 0.45$ )	15.90 ( $\pm 0.18$ ) <sup>d</sup>

<sup>a</sup> Eluent 5 ml of 1 M HCl; sample pH 6.0; buffer concentration 0.01 mol  $\text{l}^{-1}$ ; flow rate 2.5 ml  $\text{min}^{-1}$ . The numbers in parentheses are standard deviations for three replicate analyses. <sup>b</sup> Measured by flame AAS, after preconcentration on the column. <sup>c</sup> Calculated by summing up the added analyte and the measured value in the unspiked water sample.

<sup>d</sup> Measured directly by ET-AAS.

(Khuzestan, Iran). Since the concentrations in the Khorram Abad's samples were too low to be precisely confirmed by the ET-AAS method, they were spiked with the metal ions before analysis. The results obtained by the proposed method are listed in Table II. A two-tailed *t*-test at 95% confidence level was performed for comparison of the measured and reference data reported in the table and no significant difference was observed. Hence, the method possesses a good accuracy and show negligible matrix effects for the field samples.

## CONCLUSION

The study of the effect of different parameters on the metal sorption indicates that all the studied metal ions can be quantitatively accumulated on the column and efficiently eluted. Relatively slower sorption kinetics is observed for  $\text{Zn}^{2+}$ , but it does not significantly influence its column recovery. One expects that at higher flow rates some losses of zinc may show up. However, the effect of higher flow rates was not studied because of high back pressures encountered.

One can conclude that, in general, the Novarose–Schiff base sorbent can be used as an efficient, inert, stable and moderately selective column packing for the preconcentration and matrix separation of  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  (and also  $\text{Pb}^{2+}$  that was reported elsewhere<sup>21</sup>) in natural waters. The analytes do not show any interference, can be preconcentrated simultaneously and determined by any of the atomic absorption or emission spectrometric methods.

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