

Comparison of Three Agarose Based Chelating Adsorbents and Their Application to the Preconcentration of Some Metal Ions in Water

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The properties of two agarose based chelating ion exchangers with, respectively, dipicolyl amine (DPA) and tris(2-aminoethyl) amine (TREN) as functional groups are investigated and compared to those of a previously studied adsorbent functionalized with iminodiacetic acid (IDA), with the same matrix, for preconcentration of Cu, Co and Ni in water. Binding capacities, adsorption rates and column recoveries of the metal ions are carefully investigated. An ICP-AES instrument is used for measurements. The capacity of the IDA adsorbent for Cu, Co and Ni was similar and is averaged to $50 (\pm 7) \mu\text{mol/mL}$, while for the DPA and TREN sorbents the capacity was more variable and pH-dependent. The highest capacity of the new adsorbents was obtained for copper, which is averaged to $18.3 (\pm 0.3)$ and $120 (\pm 6) \mu\text{mol/mL}$, respectively. Kinetic studies indicated relatively high adsorption rates of Cu on all the sorbents. Nickel, on the other hand, showed relatively slow rates on the DPA and TREN chelators. High column recoveries were obtained for all the studied metal ions on the IDA adsorbent and only some loss of Ni was observed at high pHs. The column recoveries for the DPA sorbent, on the other hand, were quite low for Cu and Ni. It indicated high recoveries only for Co, which rose up to $93.8 (\pm 1.8)\%$. Copper was almost quantitatively recovered on the TREN sorbent, with low and pH dependent recoveries for Co and Ni. The method was evaluated by preconcentration of spiked river water samples. Good agreement was obtained between the results obtained for natural samples and standard solutions. In general, more selectivities, slower adsorption rates and lower and more pH dependent recoveries were identified for the DPA and TREN sorbents compared to that with the IDA groups.

Key Words: Chelating ion exchangers, Preconcentration, Agarose, ICP-AES.

INTRODUCTION

Chelating ion exchangers have been frequently used for preconcentration, separation and speciation of metal ions prior to their determination in both off-line¹ and on-line² modes. Efficiency and usefulness of a chelating sorbent in an analytical application depends on its physico-chemical properties, e.g., acid base characteristics, metal binding capacity, chemical stability and hydrophobicity³. High binding capacity and strong bonds with metal ions are usual

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considered as advantages. These properties may, however, be problematic in the elution step for desorption of metals from an adsorbent⁴. Chelators are usually useful only in a limited range of pH and the hydrophobicity of their solid matrix also affects adsorption kinetics⁵. It may be concluded that properties of both the adsorbents' matrix and the chelating groups fixed (or adsorbed) on them determine the characteristics of a chelating adsorbent.

Agarose⁶ is a highly hydrophilic matrix and its physical properties have been largely improved by crosslinking procedures^{7,8}. In previous works^{9,10} a highly cross-linked agarose (Novarose) with iminodiacetic acid (IDA) as its functional group was shown to have superior kinetic properties for accumulation of metal ions. This adsorbent was also successfully applied to preconcentration of heavy metals in humic rich waters using an on-line system of buffering acidified samples¹⁰. Study of other commercially available agarose based adsorbents, currently used as immobilized metal ion affinity chromatography (IMAC) reagents, for preconcentration of metal ions, can explore properties and possible applications of them to metal preconcentration experiments.

In our knowledge, tris(2-aminomethyl) amine (TREN) has not yet been used as a functional group for column preconcentration of metal ions. This ligand contains four amino groups and is known as a good chelator^{11,12}. Limited studies have been performed^{13,14} on dipicolyl amine (DPA) using styrene-divinylbenzene, which is a hydrophobic polymer, as the matrix and a high selectivity for copper and nickel over iron has been reported. In this work, adsorption properties of TREN-Novarose and DPA-Novarose for preconcentration of some metal ions, both commercially available as immobilized metal ion affinity chromatography (IMAC) reagents, is studied and compared to that of IDA-Novarose.

EXPERIMENTAL

IDA-, DPA- and TREN-Novarose adsorbents were a generous gift from Inovata AB, Stockholm. Their nominal capacities were 50, 18 and 120 $\mu\text{mol Cu/mL}$ adsorbent, respectively.

Experimental solutions of metal ions were prepared by dilution of Titrazol (Merck) atomic absorption standards. All other chemicals were of analytical grade from Merck. Double distilled and deionized water was used for dilutions.

Apparatus and Analysis: Metal ion concentrations were measured by an ICP-AES instrument (Turbo-Varian, Liberty 150 AX, Australia). A digital pH-meter (Corning, UK) was used for pH measurements after calibration by Merck buffers. Magnetic stirring (IKAMAG RH, Germany) was used for suspending adsorbent particles during kinetic studies.

Polypropylene tubes with 5.7 mm i.d. were used as preconcentration columns with 0.5 mL adsorbents confined in the columns between two frits (Omnifit, UK) with 25 μm pore sizes. Exact volume of the packing between two frits was used in calculations of capacity and in recording adsorbent volume. Columns were packed as discussed elsewhere⁹. A peristaltic pump (Desaga GmbH, Germany) or polyethylene syringe was used for flow path through the columns. The columns

were first washed with 5 mL 1 M HCl and conditioned by the same volume of 0.1 M acetic acid-sodium acetate buffer (pH 5) before loading with samples. Sample flow rate was between 10 to 15 mL/min.

Capacity measurements were performed in column mode. Solutions of metal ions were prepared in 0.1 M acetate buffer and the pH was adjusted, if necessary, by a few droplets of 1 M HCl or 2 M NaOH solution. Some 50 mL portions of the solutions were passed through the column, usually by a 60 mL syringe. Column saturation was ensured by comparison of metal concentration in the initial solution and last few mL of column effluent. The column was then washed by a few mL of the buffer to displace non-bound metals from the void volume and then eluted by 5 mL 1 M HCl. Eluates were collected in polypropylene tubes and analyzed by ICP-AES after dilution. The capacity was calculated by dividing the total eluted metal ion by the adsorbent volume.

Kinetic studies were performed in batch mode. A 200 mL solution of a metal ion was prepared in 0.1 M acetate buffer, pH 5.5, which contained less than 10% of the adsorbent's capacity. The solution was transferred into a beaker and a 0.5 mL portion of the packed adsorbent was added while the solution was being stirred by a magnetic bar. A syringe equipped with a filter, 25 μm pore, was used for sampling the solution from the beaker at different times. The samples were collected in polypropylene tubes and analyzed later by ICP-AES. The $t_{1/2}$ and rate constant (K) calculations were performed assuming pseudo first order reaction rates for the adsorption of metal ions. The calculation of K was performed from the equation

$$\ln (C_t - C_\infty)/(C_0 - C_\infty) = -Kt$$

in which C_0 , C_∞ and C_t are initial, equilibrium and time t concentrations, respectively.

For preconcentration and recovery measurements standard solutions of 0.2 μg metal ions/mL, buffered in a 0.1 M acetic acid-sodium acetate media were used. A 100 mL portion of solutions was pumped through the column with a flow rate of about 10 mL/min. The column was then washed by a few mL of a buffer solution before elution with 5 mL of 1 M HCl. The eluate was collected in 10 mL polypropylene tubes and analyzed by ICP-AES.

River water samples, taken from Khoramabad river, were acidified to pH 2 on collection and spiked, after filtration, to a concentration of 0.2 $\mu\text{g}/\text{mL}$ of Cu, Co and Ni. The pH of 100 mL portions of the samples was adjusted by addition of droplets of 1 M sodium hydroxide before column preconcentration. The preconcentration experiment was then performed as mentioned above. Blank concentrations also were measured by preconcentration of an unspiked river water portion in the same way.

RESULTS AND DISCUSSION

Capacity: Binding capacity, in a pH range of 4 to 6.5, was the first parameter studied for the three agarose based sorbents. The adsorbents were functionalized to different extents with the functional groups; hence, their nominal capacities were different.

In agreement with previous studies¹⁰, the binding capacity of IDA-Novarose was found to be similar for Cu, Co and Ni in the pH range of 4 to 6.5, i.e., $50(\pm 7)$ $\mu\text{mol/mL}$. TREN- and DPA-Novarose, on the other hand, showed to be more selective and pH-dependent adsorbents in comparison to IDA-Novarose.

The capacity of DPA-Novarose was $18.3 (\pm 0.3)$ $\mu\text{mol/mL}$ and independent to pH for copper but, it was quite low ($\mu\text{mol/mL}$) for Co. The sorbent's capacity for Ni changed from $3.0 (\pm 0.2)$ to $16 (\pm 3)$, when the pH changed from 4 to 6.5.

The capacity of TREN-Novarose for copper was $93 (\pm 4)$ at pH 4 and increased to $120 (\pm 6)$ $\mu\text{mol/mL}$ at pH 5.5 (the nominal capacity). The binding capacity of the sorbent measured for Co was quite low ($\mu\text{mol/mL}$) and it increased for nickel from $7.25 (\pm 0.7)$ to $16.6 (\pm 0.9)$ at pH 6.5.

Fig. 1 compares the maximum capacities of the sorbents for the studied metal ions. The uniform response of IDA-Novarose for different elements and the much greater variation in the results for the two other sorbents is obvious.

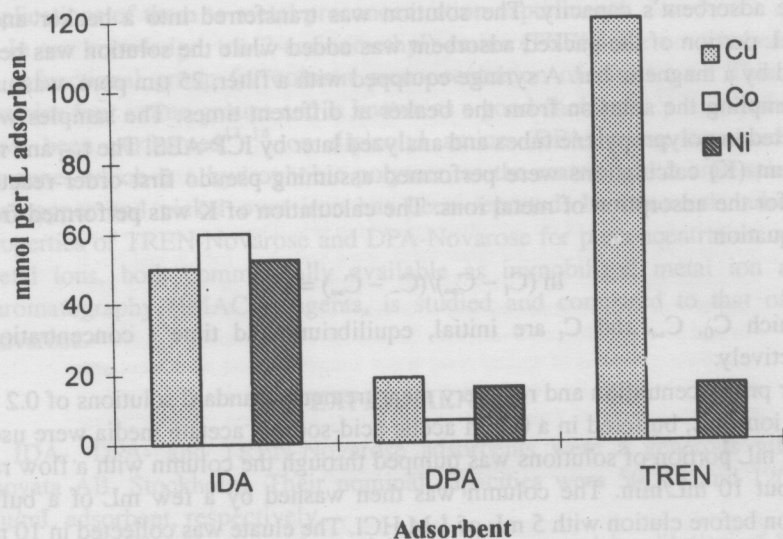


Fig. 1. Maximum capacities of the IDA-, DPA- and TREN-Novarose adsorbents for different metal ions. Adsorbent volume 0.5 mL, packed in 5.7 mm i.d. columns, flow rate 10 mL/min, sample matrix 0.1 M acetate buffer.

Kinetic studies: Batch mode adsorption rates were determined for comparison of adsorption kinetics of the adsorbents for different metal ions. Metal ion concentration was plotted as a function of contact time between the ion and suspended adsorbent. Rate constants (K) and half times of adsorption ($t_{1/2}$) were calculated, assuming pseudo first order reaction rates. The results are summarized in Table-1.

The results depict that IDA-Novarose shows its highest adsorption rate for Cu, with $t_{1/2} < 15$ s. The rates for Co and Ni were also high and the $t_{1/2}$ values for them average $49 (\pm 12)$ s. It should be noted that equilibrium concentrations of the metal ions were also quite low in this case.

TABLE-1
 KINETIC DATA FOR THE BATCH MODE ADSORPTION OF METAL IONS ON THE
 IDA-, DPA-, AND TREN-NOVAROSE ADSORBENTS

Adsorbent volume 0.5 ml, pH 5.5, 0.1 M acetate buffer.
 RSD for duplicate measurements is considered 5 to 10% for all the data.

Element	IDA		DPA		TREN	
	$t_{1/2}$	K (min^{-1})	$t_{1/2}$	K (min^{-1})	$t_{1/2}$	K (min^{-1})
Cu	10	4.07	20	2.04	36	1.16
Co	35	1.20	55	0.92	6	6.50
Ni	52	0.80	450	0.09	233	0.18

For the DPA-Novarose, similar and relatively high adsorption rates of Cu and Co were noticed, as well. A high $t_{1/2}$ value of 450 s was, however, obtained for nickel that implies a slow complexation rate of this element by the DPA sorbent. It is known that Ni complexation rate is relatively slow¹² and this fact was confirmed by a slow taking up of this element on TREN-Novarose, as well ($t_{1/2}$, 233 s). Fig. 2 compares the adsorption profiles for the taking up of nickel on the three studied sorbents. The much higher scavenging rate of Ni by IDA-Novarose is evident in the figure. Because all adsorbents had the same support material, this can be attributed to their different chelation rates for this metal ion by the DPA and TREN ligands.

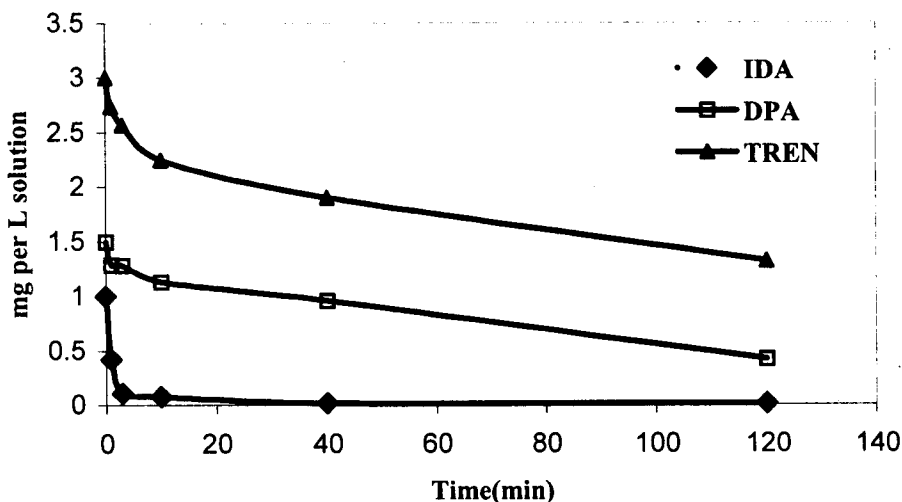


Fig. 2. Adsorption profiles for batch mode accumulation of nickel on the three agarose based adsorbents. Experimental conditions are as in Table-1.

The adsorption rates of the other studied elements on TREN-Novarose were similar and their $t_{1/2}$ values averaged 18 (± 11) s. For both TREN and DPA adsorbents, Cu and Co came to a fast equilibrium with quantitative adsorption on the sorbents but quantitative uptake of Ni was not achieved in the batch mode.

Recovery experiments: Recovery experiments were performed in column mode for some synthetic standard solutions. Table-2 summarizes the results at pH 5.0 and 6.5.

TABLE-2
PER CENT RECOVERY OF METAL IONS FROM STANDARD SOLUTIONS OF
0.2 µg/mL CONCENTRATION ON DIFFERENT ADSORBENTS

The figures between brackets are standard deviations for triplicate measurements.

Element	IDA		DPA		TREN	
	pH 5	pH 6.5	pH 5	pH 6.5	pH 5	pH 6.5
Cu	98.4 (0.5)	97.5 (0.5)	2.5 (0.4)	-0.3 (0.8)	99.1 (0.1)	99.7 (0.4)
Co	99.4 (0.8)	99.5 (1.3)	91.1 (1.6)	93.8 (1.8)	-0.4 (0.6)	49.1 (1.1)
Ni	100.7 (1.4)	75.1 (1.1)	5.6 (3.8)	11.6 (1.2)	-0.6 (0.9)	38.0 (1.2)

The IDA-Novarose showed quantitative recoveries for all the analytes. Its recovery for Ni, however, decreased to 75.1 (+1.1) at pH 6.5, probably due to kinetic reasons or its precipitation. The DPA-Novarose showed quite low recoveries for Cu and Ni but its recovery for Co was up to 93.8% at pH 6.5. The TREN-Novarose, on the other hand, depicted quantitative recoveries for Cu, while its recovery for Co and Ni was low and quite dependent on pH.

A comparison between the capacity and recovery experiments indicates that the two factors can be quite independent. The capacity of DPA-Novarose for Co, for instance, is quite low, while this element can be recovered almost quantitatively from the same adsorbent.

TABLE-3
PER CENT RECOVERY OF METAL IONS FROM SPIKED RIVER WATER SAMPLES

The samples were spiked by 0.2 mg/L of the analytes. The figures between brackets are standard deviations for duplicate measurements.

Element	IDA		DPA		TREN	
	pH 5	pH 6.5	pH 5	pH 6.5	pH 5	pH 6.5
Cu	97.6 (0.7)	96.9 (1.3)	0.9 (0.6)	-0.3 (0.5)	99.6 (0.6)	99.3(0.8)
Co	99.6 (0.4)	96.5 (0.7)	89.1 (1.2)	91.3 (0.5)	0.05 (0.2)	49.4 (0.4)
Ni	99.0 (1.4)	71.6 (0.5)	2.1 (0.8)	11.0 (1.2)	0.25 (0.4)	38.8 (0.1)

Analysis of real samples: Table-3 summarizes the results for some spiked river water samples. The blank concentration was generally very low for all the measurements. A very good agreement between the results of Table-2 and Table-3, *i.e.*, the recoveries for standard solutions of the elements, is evident. The river water matrix, hence, has no effect on the recoveries. Regarding the fact that the spiked samples contained all the three elements indicates that in the condition used there was no significant interference among the analytes.

Conclusions

The study demonstrates that DPA-Novarose and TREN-Novarose are more selective adsorbents than IDA-Novarose. The relatively high selectivities of the new sorbents and the pH dependence of their behaviour can be well used in separation procedures. IDA-Novarose, on the other hand, is a more efficient sorbent and shows better kinetics and higher recoveries for the studied elements. However, it shows lower selectivities and its behaviour is less affected by pH. The slow kinetics of the new sorbents for Ni, compared to that of IDA-Novarose is evident.

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