Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Metallic Cations on Silica Gel-Immobilized 8-Hydroxyquinoline

J. P. Bernal[a]; E. Rodríguez De San Miguel[a]; J. C. Aguilar[a]; G. Salazar[a]; J. De Gyves[a]
[a] DEPARTAMENTO QUÍMICA ANALÍTICA, UNIVERSIDAD NACIONAL AUTÓNOMA DE MEXICO, CIUDAD UNIVERSITARIA, COYOACÁN, MEXICO D.F., MEXICO

To cite this Article Bernal, J. P. , Miguel, E. Rodríguez De San , Aguilar, J. C. , Salazar, G. and De Gyves, J.(2000) 'Adsorption of Metallic Cations on Silica Gel-Immobilized 8-Hydroxyquinoline', Separation Science and Technology, 35: 10, 1661 — 1679

To link to this Article: DOI: 10.1081/SS-100100247

URL: http://dx.doi.org/10.1081/SS-100100247

SEPARATION SCIENCE AND TECHNOLOGY, **35**(10), pp. 1661–1679, 2000

Adsorption of Metallic Cations on Silica Gel-Immobilized 8-Hydroxyquinoline

J. P. BERNAL, E. RODRÍGUEZ DE SAN MIGUEL, J. C. AGUILAR,
G. SALAZAR, and J. DE GYVES*
DEPARTAMENTO QUÍMICA ANALÍTICA
FACULTAD DE QUÍMICA
UNIVERSIDAD NACIONAL AUTÓNOMA DE MEXICO
CIUDAD UNIVERSITARIA, COYOACÁN 04510, MEXICO D.F., MEXICO

ABSTRACT

TLC-grade silica gel was functionalized with 8-hydroxyquinoline via a catalyzed Mannich amminomethylation reaction. The resulting solid was characterized by FT-IR and used as a sorbent for 0.05–5 mmol·L^{-1} Cu(II), Cd(II), Zn(II), Pb(II), and Fe(III) from aqueous solutions in the batch mode. Experiments were carried out in both single and multiple cation solutions. The influence of the aqueous media composition on the adsorption process, the possible adsorbed species, and the adsorption kinetics are discussed. Overall equilibrium constants for these processes are reported.

INTRODUCTION

Solid-phase extraction techniques have been used extensively for the separation and preconcentration of different analytes. It is well known that chemical modification of adsorbents may improve their performance by increasing the selectivity and retention abilities (1–3). In 1973, Hill (4) proposed 8-hydroxyquinoline immobilization on silica gel via an azo compound formation reaction. Since then, considerable work has been done to optimize the immobilization of 8-hydroxyquinoline on silica gel as well as to evaluate related adsorption phenomena (5, 6). Also, several authors have reported the immobilization of 8-hydroxyquinoline in solid supports such as cellulose (7) and

---

* To whom correspondence should be addressed.

www.dekker.com

polymeric resins (8). Silica-immobilized 8-hydroxyquinoline adsorbents have mainly found application for the preconcentration of metal species (1, 2, 9, 10). The development of on-line trace element preconcentration routines has recently been a subject of interest (11). However, in order to predict or correlate simple batch assays with on-line behavior or to scale-up separation processes, it is important that both chemical and kinetic data are available. Consequently, pH, complexation effects, and metal ion speciation, as well as adsorption rate constants, must be evaluated in order to establish their overall effect on the solid-phase extraction efficiency. Furthermore, the study of competitive adsorption phenomena is also of relevance since, from a practical point of view, several metal ions are expected to be present in real samples.

In the present work, kinetic and equilibrium studies on the single and multiple solid-phase extraction of Cu(II), Pb(II), Cd(II), Zn(II), and Fe(III) using a silica gel immobilized 8-hydroxyquinoline adsorbent in a batch mode were carried out. Characterization of the modified surface was done by FT-IR. Conditional adsorption equilibrium constants were calculated from adsorption isotherms. The pH and pL (where L stands for ligand) effects were studied in order to obtain information about the adsorption equilibrium and metal ion species involved.

THEORY

Two different approaches are generally used in the study of adsorption processes: a) Helfferich's kinetic approach (12) which describes the time-dependent adsorption behavior of a system and, b) the equilibrium approach derived from the Langmuir adsorption theory (13). The former states that, for film diffusion controlled processes, the equilibrium may be described as

$$\mathrm{M} \Leftrightarrow \overline{\mathrm{M}} \tag{1}$$

A correct mass balance, valid throughout the extraction process, is

$$C = [\mathrm{M}] + \overline{[\mathrm{M}]}\, W/V \tag{2}$$

where C is the total concentration of M. It follows from Eqs. (1) and (2) that

$$\left(\frac{\partial\overline{[\mathrm{M}]}}{\partial t}\right)_T = k_{\mathrm{ads}}C - (k_{\mathrm{ads}}(W/V) + k_{\mathrm{des}})\overline{[\mathrm{M}]} \tag{3}$$

Equation (3) can be solved by assuming that, at the beginning of the adsorption process, the concentration of M at the solid phase is completely negligible, that is, at $t = 0$, $\overline{[\mathrm{M}]} = 0$. Then:

$$\ln(1 - \frac{k_{\mathrm{ads}}(W/V) + k_{\mathrm{des}})}{k_{\mathrm{ads}}}\overline{[\mathrm{M}]} = -(k_{\mathrm{ads}}\,(W/V) + k_{\mathrm{des}})\mathrm{t} \tag{4}$$

Using Helfferich's definition (12) for the attained fraction of equilibrium, F_t:

$$F_t = \overline{[\mathrm{M}]}_t/\overline{[\mathrm{M}]}_{\mathrm{eq}} \tag{5}$$

Where $0 \leq F_t \leq 1$, Eq. (4) can be reduced to

$$\ln(1 - F_t) = -[k_{\mathrm{ads}}\,(W/V) + k_{\mathrm{des}}]t = -Kt \tag{6}$$

where

$$K \propto \frac{\Delta C}{r_0 \delta \overline{C}} \frac{W}{V} \tag{7}$$

Equation (6) differs from the one proposed by Helfferich (12) in the phase relation (W/V) considered in the mass balance (Eq. 2). Although the latter consideration produces a slightly different definition of the proportionality constant K, no significative implications or effects are expected. However, care should be taken if kinetic data are to be compared among different sources.

According to Eq. (6), a logarithmic plot of $(1 - F_t)$ versus time should give a straight line with a negative slope that intercepts the y-axis at zero value. Although this model was first developed for ion-exchange kinetics, it has recently been reported for chemically modified silica gel (14) with satisfactory results.

The second approach, derived from the Langmuir adsorption theory (13), states that any adsorption process depends on the adsorbate concentration in the liquid and solid phases as well as on the number of free adsorption sites. That is:

$$V_{\mathrm{ads}} = k_{\mathrm{ads}}[\mathrm{M}](S - S_{\mathrm{oc}}) \tag{8}$$

and for desorption:

$$V_{\mathrm{des}} = k_{\mathrm{des}} S_{\mathrm{oc}} \tag{9}$$

Therefore, at equilibrium, the fraction ϕ of occupied adsorption sites may be expressed as follows:

$$\phi = \frac{k_{\mathrm{ads}}\,[\mathrm{M}]}{k_{\mathrm{des}} + k_{\mathrm{ads}}[\mathrm{M}]} \tag{10}$$

Considering an 8-hydroxyquinoline modified silica gel where the adsorption sites correspond only to the 8-hydroxyquinoline moieties, then

$$\phi = \overline{[\mathrm{M}]}/\overline{[\mathrm{HOX}]} \tag{11}$$

and

$$\overline{[\mathrm{M}]} = \frac{k\overline{[\mathrm{HOX}]}[\mathrm{M}]}{1 + k[\mathrm{M}]} \tag{12}$$

which is the expression of a normal Langmuir isotherm for monolayer formation.

Equation (12) is important because it allows calculation not only of the adsorption capacities but also of the experimental values of conditional adsorption equilibrium constants (*k*). For infinite dilution conditions, i.e., [M]→0, Eq. (12) can be written as

$$\overline{[\mathrm{M}]} \cong k\overline{[\mathrm{HOX}]}[\mathrm{M}] \tag{13}$$

A predictive model based on the Gouy–Chapman surface potential has also been used in order to predict adsorption of selected ions over a reduced pH range (9), but as recently stated by Smith (15), conclusions obtained with this approximation are comparable with those from adsorption isotherms.

It should be noticed that both the kinetic and equilibrium approaches give fundamental data. The information obtained by one approach complements the other, and both are necessary to completely characterize the adsorption phenomena.

EXPERIMENTAL

Reagents

The 8-hydroxyquinoline was immobilized on TLC grade silica gel (Merck-Darmstaadt, 40 μm average particle size, 490 $m^2 \cdot g^{-1}$ surface area), using γ-aminopropyltriethoxysilane (Aldrich Chemical Co.), formaldehyde (Aldrich Chemical Co.), and 8-hydroxyquinoline (Aldrich Chemical Co.)

All acids, salts, and solvents used in the present work were of analytical grade. Metal stock solutions were prepared by dissolving the corresponding metal (Aldrich Chemical Co.) in concentrated nitric acid and diluting with deionized water (18 MΩ) with the exception of Fe(III) which was prepared by dissolving $Fe(NO_3)_3 \cdot 5H_2O$ in 0.5 v/v% nitric acid solution. Unless otherwise stated, ionic strength was fixed for all experiments at 0.1 $mol \cdot L^{-1}$ with $NaNO_3$.

Instruments

Metal ion concentrations were determined either by flame-atomic absorption spectrometry (Perkin-Elmer 3110 spectrometer) or inductively coupled plasma atomic emission spectrometry (Jobin Yvon 24 sequential spectrometer). The solid-phase extraction experiments were carried out by shaking the sample and the adsorbent with a mechanical shaker (Burrell 75). The pHs of the aqueous phases were measured using a Metrohm model 620 pH-meter with a combined glass electrode Cole-Parmer 62014. FT-IR spectra were obtained from pressed KBr pellets (Perkin-Elmer FT-IR 1600 spectrometer).

Synthesis

Silica gel (50 g) was successively washed with 100 mL of 1 $\mathrm{mol{\cdot}L^{-1}}$ HNO_3, 100 mL of 1 $\mathrm{mol{\cdot}L^{-1}}$ NaOH, and deionized water until neutral pH was obtained, and it was then left overnight in an oven at 110°C. The silica was then stirred in a covered PTFE beaker with 100 mL of 10 v/v% γ-aminopropyltriethoxysilane in dry acetone and heated at 50°C for 4 hours. After this time the solid was vacuum filtered, washed several times with dry acetone, and stored in a dessicator. The resulting silica-gel (pale yellow solid) was then refluxed and stirred with a 0.1 $\mathrm{mol{\cdot}L^{-1}}$ 8-hydroxyquinoline/formaldehyde solution in dry ethanol and glacial acetic acid (0.2 mL). The resulting orange solid was filtered and washed with dry ethanol, then with 200 mL of a 0.1 $\mathrm{mol{\cdot}L^{-1}}$ hydrochloric acid solution, and finally with deionized water until no desorption of HCl was potentiometrically observed. The resulting solids were characterized by FT-IR. As described elsewhere (6), Cu(II) uptake was used as an indirect measure of the amount of functionalized 8-hydroxyquinoline in the silica-gel surface.

Solid-Phase Stability

The stability of the modified surface was studied by carrying out several (up to 5) Cu(II) adsorption–desorption assays. The loaded adsorbent was regenerated by washing it successively with 1 $\mathrm{mol{\cdot}L^{-1}}$ HCl solution and deionized water.

Solid-Phase Extraction (SPE)

Single metal ion solutions (10 mL) at various concentrations were mechanically shaken with approximately 0.1 g of the modified silica gel for different periods of time, pH, and pL values. These mixtures were vacuum filtered and the aqueous phases analyzed by F-AAS or ICP-AES. Three replicates of each experiment were carried out. Metal ion concentrations in the solid phases were calculated with Eq. (2).

The pH working range was selected on the basis of metal ion and solid-phase solubilities. Poor adsorption efficiencies ($<2.5\%$) were obtained in the 1–5 pH range at low metal ion concentrations (0.5 $\mathrm{mmol{\cdot}L^{-1}}$) when nonmodified silica gel was used as the adsorbent.

Multiple Cation SPE

Extraction assays were carried out mixing 0.1 g of the adsorbent with 10 mL of a solution containing four of the cations studied [five when Fe(III) was soluble], all at the same initial concentrations. Equilibrium time, pH curves, and adsorption isotherms were obtained using the same procedures as described above for the single element experiments.

RESULTS AND DISCUSSION

Synthesis of 8-Hydroxyquinoline–Silica Gel

Figure 1 shows the oxine concentration profile in ethanolic media as a function of time in the presence of small amounts of acetic acid. The data presented were determined on the basis of the decrease of 8-hydroxyquinoline from the reaction media by UV spectrometry at 315 nm using a 10-mm length quartz cuvette. As the reaction proceeds, 8-hydroxyquinoline concentration in solution drops during the first 4 hours and remains almost constant for the following 68 hours, indicating that completion of the reaction is attained in a short period of time.

The FT-IR spectrum of the modified silica gel, when compared with those obtained for the unmodified material and the pure 8-hydroxyquinoline, shows heavy Si—O—Si and Si—OH absorptions which completely block the Si—C and C—N vibration bands, respectively. However, it is possible to compare the spectra at the 1300–1700 cm^{-1} frequency range (Fig. 2), where C=C and C=N stretching bands of the quinoline group are observed for the pure 8-hydroxyquinoline and the modified silica gel, but none for the unmodified silica. Consequently, the bonding of 8-hydroxyquinoline with the silica gel can be assumed. Figure 3 shows the spectra in this zone for the modified silica gel af-

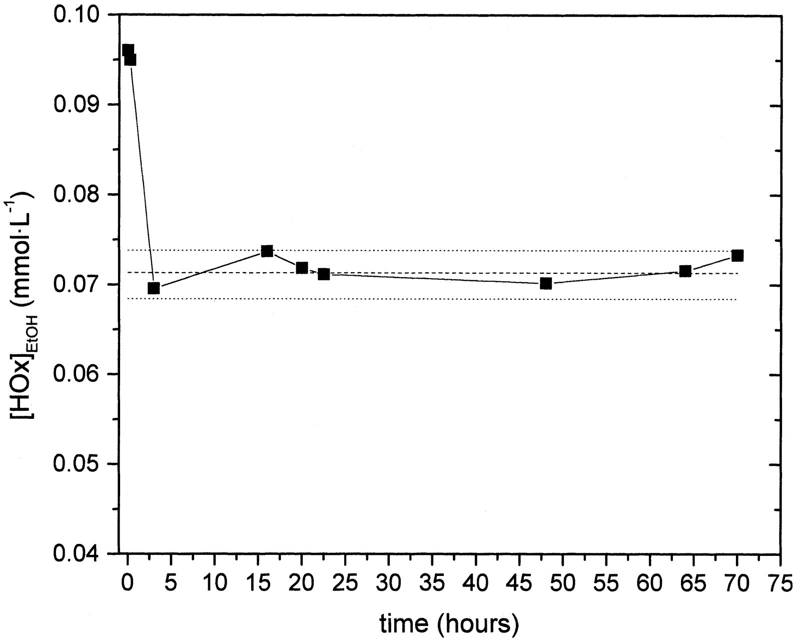

FIG. 1 Variation of 8-hydroxyquinoline concentration in ethanolic solution as a function of time in catalyzed media. Dotted lines are confidence interval for equilibrium concentration ($\alpha = 0.05$, $n = 7$).

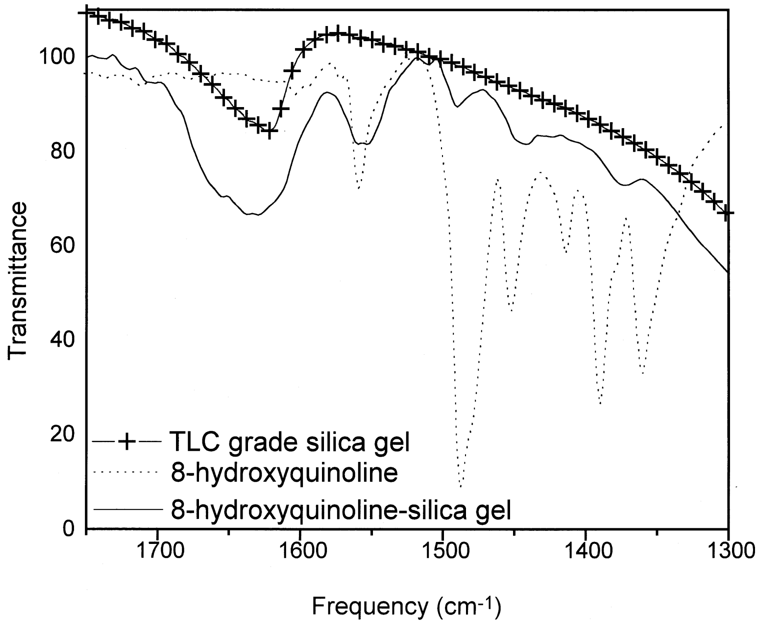

FIG. 2 FT-IR spectra of TLC silica gel, 8-hydroxyquinoline, and modified silica gel.

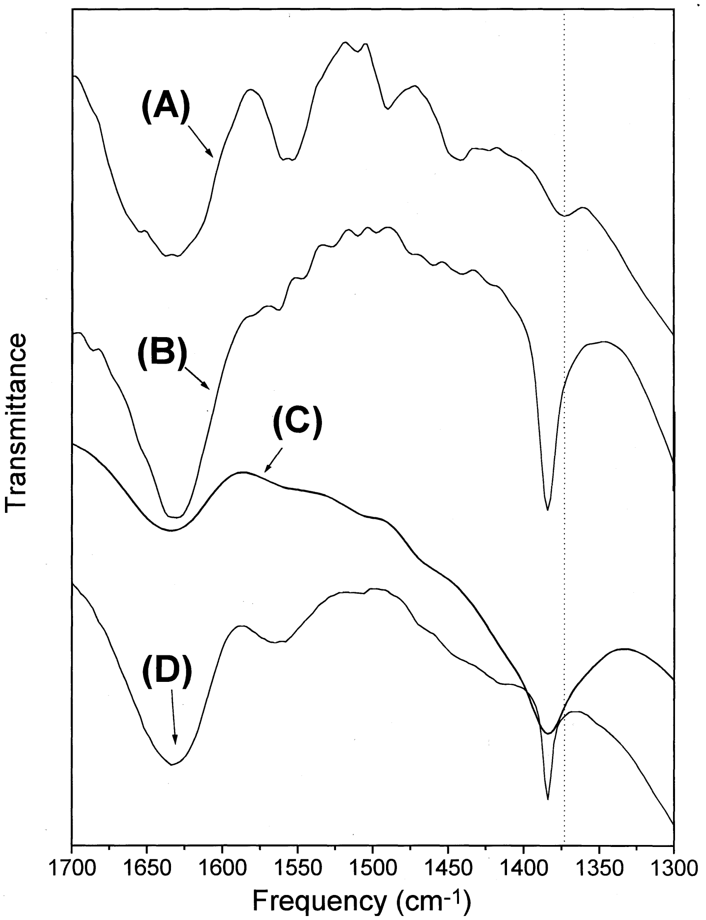

FIG. 3 FT-IR spectra of adsorbed complexes: (A) 8-hydroxiquinoline-silica gel, (B): (A) + Cd(II), (C): (A) + Fe(III), (D): (A) + Cu(II).

ter its contact with Cu(II), Cd(II), and Fe(III). A reduction of the absorption bands is observed except for the one at 1372 cm^{-1} which is related to a C═N vibration (16). This band changes to 1384 cm^{-1} in the presence of the adsorbed cations.

Solid-Phase Equilibrium

Figure 4 shows the metal ion concentration at the solid phase as a function of time at different pH values for single cation solutions. According to this figure, equilibrium is completely achieved after 30 minutes. This time is extremely fast when compared with those of polymer-supported 8-hydroxyquinolines (8, 17). Several factors may allow for this difference, i.e., the type of diffusion process controlling the kinetics of adsorption (12), surface area,

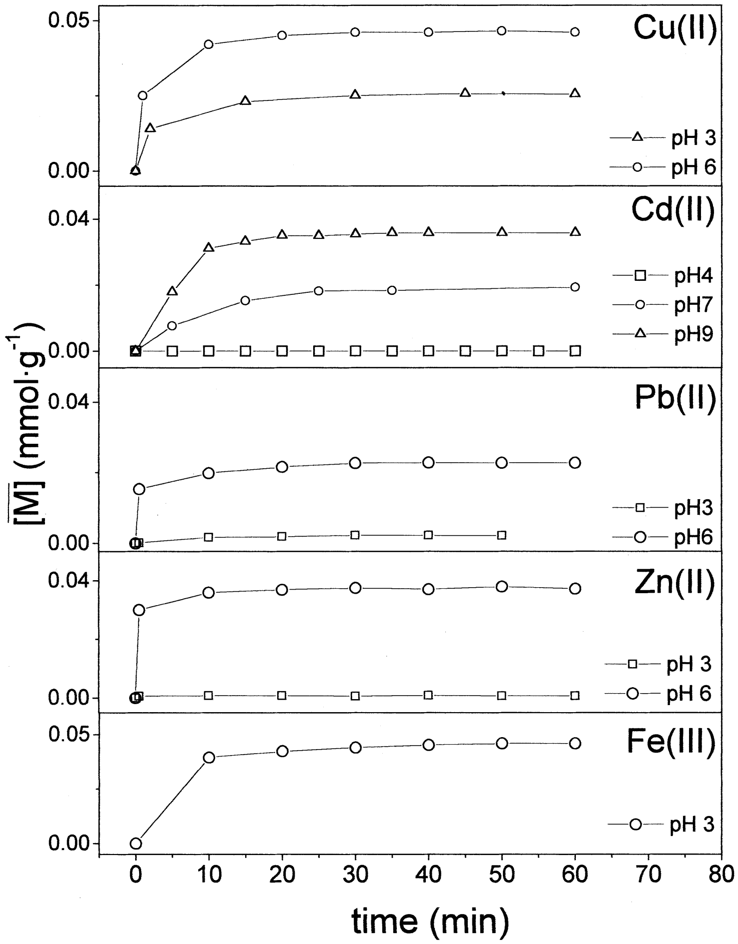

FIG. 4 Determination of equilibrium time for Cu(II), Cd(II), Pb(II), Zn(II), and Fe(III) at different pH values. All data obtained at $NaNO_3$ 0.1 mol·L^{-1} ionic strength, $[M]_{0,aq}$ = 0.0005 mol·L^{-1}.

TABLE 1
Cu(II) Concentration at the Solid Phase after Five Adsorption–Desorption Cycles[a]

	Assay							
	0	1	2	3	4	5	Average	% RSD
[Cu], (mmol/g)	0.035	0.035	0.034	0.034	0.034	0.033	0.034	2.2

[a] Initial [Cu(II)] = 0.001 mol·L^{-1}, pH 4.0, % RSD = percentage relative standard deviation.

and particle size. Table 1 presents the results of the stability study of the modified surface obtained under equilibrium conditions for a Cu(II) solution. An average of 0.034 mmol·g^{-1} of Cu(II) was adsorbed, and no significant difference was observed among the successive assays.

Figure 5 shows the effect of pH values on adsorption efficiency for Fe(III), Cu(II), Cd(II), Zn(II), and Pb(II). As expected for the present system, it increases quantitativity along the pH scale. The pH-dependent extraction profiles do not present the typical sigmoidal form observed in liquid–liquid extraction; however, these profiles are similar to those reported by Honjo and coworkers (2) for 8-hydroxyquinoline supported via an azo compound over

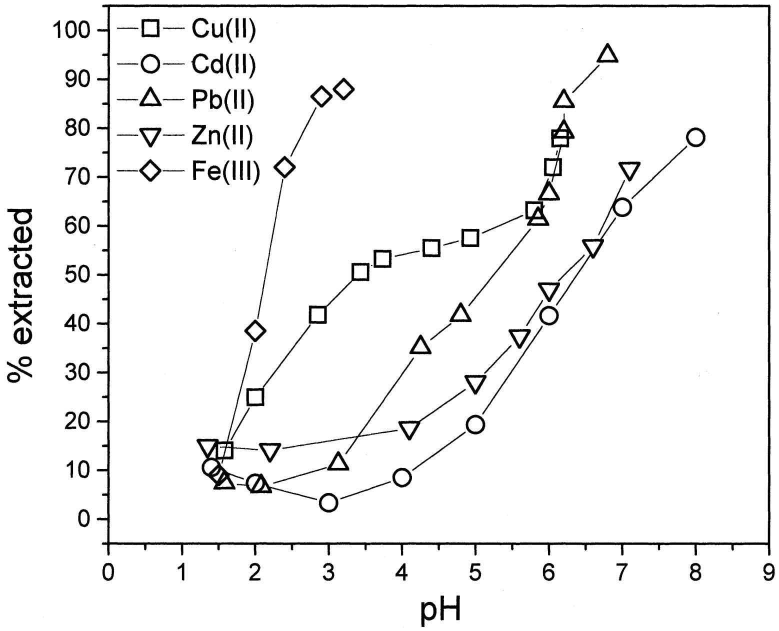

FIG. 5 Extraction profiles as a function of equilibrium pH for Cu(II), Cd(II), Pb(II), Zn(II), and Fe(III). $[M]_{0,aq}$ = 0.0005 mol·L^{-1}.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

controlled pore glass beads. It has also been reported (10) for these solid phases that the extracted species have a 1:1-stoichiometry between the ligand and the cation. Considering the 8-hydroxyquinoline content on the silica gel (data in Table 1) and the nominal surface area (490 $\mathrm{m^2 \cdot g^{-1}}$), it is possible to assume that there are no two functionalized terminals close enough to form a neutral complex; consequently, under the experimental conditions used, a similar stoichiometry is assumed for the present system.

As neutral complexes must be formed at the solid phase, the extraction (cosorption) of an anion is thus necessary in order to maintain electrical neutrality. Therefore, the following equilibrium is proposed:

$$\mathrm{M}^{m+} + (m-1)\mathrm{X}^- + \overline{\mathrm{HOX}} \Leftrightarrow \overline{\mathrm{OXMX}_{m-1}} + \mathrm{H}^+ \qquad (14)$$

where X^- may be extracted to form a coordination compound with M or through electrostatic interaction with the surface complex. Consequently, an increase of X^- concentration in the aqueous phase will produce an increase of $\overline{\mathrm{M}}$.

Figure 6(a) shows the solid-phase concentration of Zn(II) when the concentration of nitrate is modified. As clearly seen, a significant increase on the extraction efficiency is observed for this metal when the $\mathrm{NO_3^-}$ concentration in the aqueous phase is increased. Figures 6(b) and 6(c), respectively, show the Cu(II) and Cd(II) solid-phase concentrations when the concentration of acetate in the solution is increased at constant pH. As seen, the extraction efficiency is improved when the acetate concentration is about 0.1 $\mathrm{mol \cdot L^{-1}}$. However, at higher acetate concentration a decrease in Cd(II) and Cu(II) concentrations on the solid phase is observed. If the concentration profiles are compared with the calculated fraction (Φ) of the $\mathrm{MAcO^+}$ [M = Cu(II) or Cd(II)] complex under the experimental conditions, it is then possible to directly correlate the metal ion concentration at the solid phase with the concentration of this complex, and therefore assume that this compound is preferably extracted over others due to the achievement of electroneutrality.

Adsorption Kinetics

Figure 7 shows single cation $\ln(1 - F_t)$ vs time plots for Fe(III), Cu(II), Cd(II), Zn(II), and Pb(II) at different pH values. Proportionality constants (K, Eq. 6) are given in Table 2. As good regression coefficients are obtained, it may be assumed that a diffusional barrier is controlling the overall adsorption processes (18). Three significantly different cases are observed: a) no adsorption in a long time interval, b) adsorption ($K = 0.08 \pm 0.015$), and c) quantitative adsorption ($K = 0.15 \pm 0.015$).

As the plotted data are normalized, ($F_t < 1$ in all cases), the differences observed in the slopes of the plots cannot be attributed to quantitative changes due to collateral equilibria such as acid–base or complexation in the aqueous

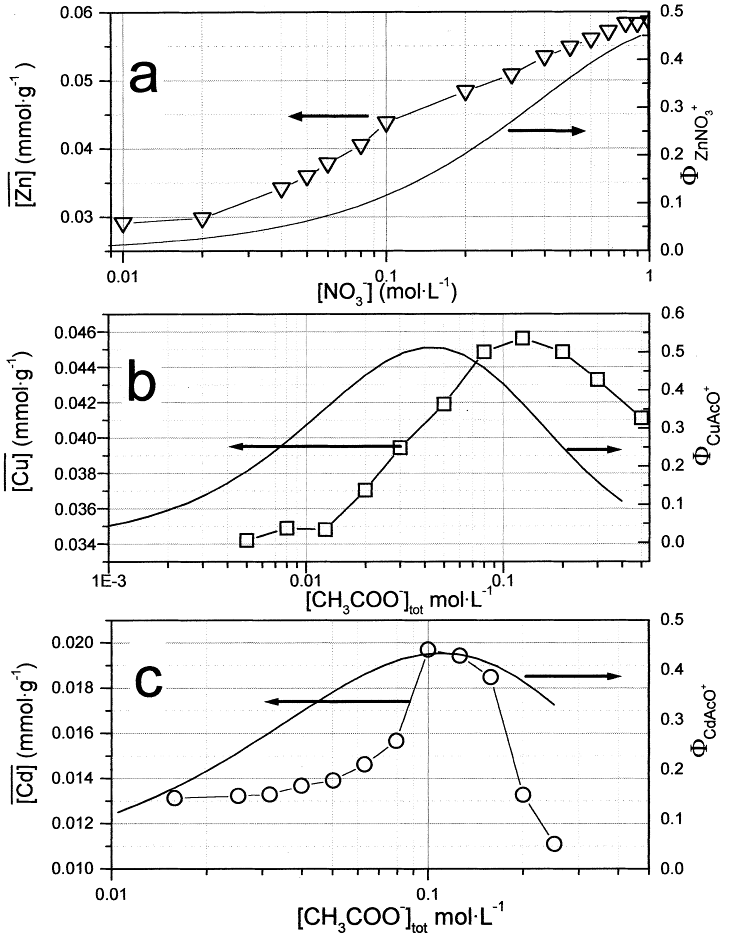

FIG. 6 Metal ion concentration on the solid phase as a function of complexing agent concentration compared with theoretical abundance of monocharged complex ($\Phi_{MX_n^{m-n}}$).

phase, but rather to ligand selectivity toward the cations (14). Since the ionic strength was controlled (0.1 mol·L^{-1}), changes in the physical properties at the solid–liquid interface were minimized.

Adsorption Isotherms

The adsorption isotherms for all metal cations at different pH values are presented in Fig. 8. As expected, monolayers are observed in most cases. However, under specific conditions for Cu(II), Pb(II), and Fe(III) a second layer is formed. The experimental differences observed in the isotherm profiles, together with the particular solution chemistry of the three metal ions and their coordinating properties [with oxygen atoms: Fe(III) >> Cu(II) > Pb(II); with nitrogen atoms: Cu(II) > Pb(II) > Fe(III)] allow us to assume that different adsorbed species are involved in the formation of the second layer (19). For Fe(III), the particular behavior observed can be explained on the ba-

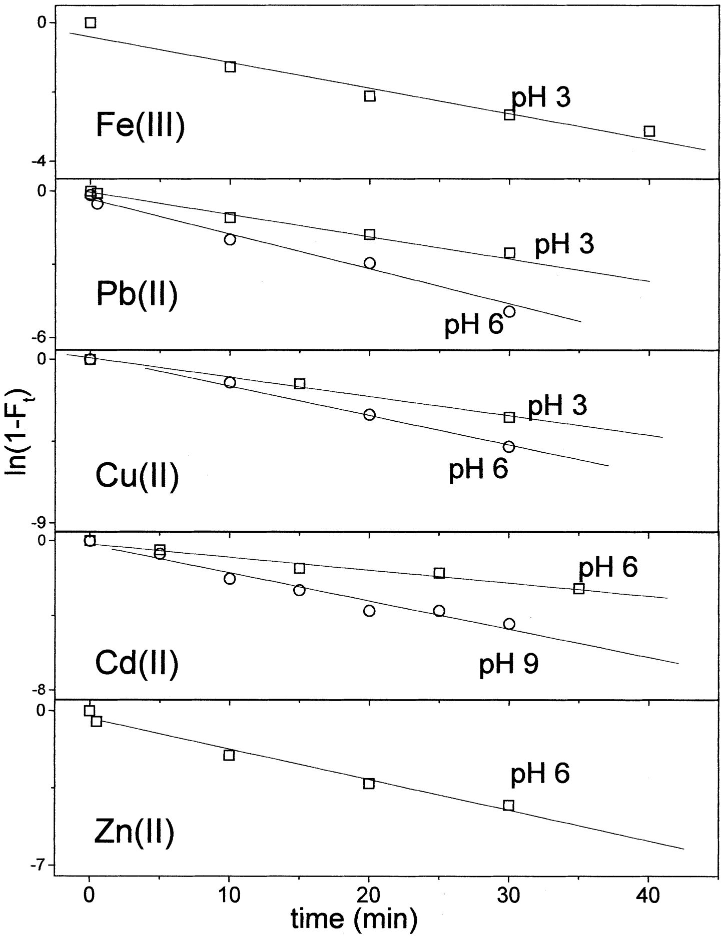

FIG. 7 Logarithmic plots (1 - F_t) as a function of extraction time for Cu(II), Cd(II), Pb(II), Zn(II), and Fe(III) at different pH values. Regression data are given in Table 3. $[M]_{0,aq} = 0.0005$ $mol \cdot L^{-1}$; aqueous phase: 10 mL; solid phase: 0.1 g.

TABLE 2
Proportionality Constants and Correlation Coefficients Obtained Using Eq. (6) and the Data from Fig. 7[a]

	Cu(II)	Cd(II)	Fe(III)	Zn(II)	Pb(II)
pH 3	0.094	NA	0.073	NA	0.090
r^2	0.9953	NA	0.9899	NA	0.9938
pH 6	0.161	0.069	—	0.136	0.143
r^2	0.9972	0.9842	—	0.9887	0.9878
pH 9	—	0.151	—	—	—
r^2	—	0.9796	—	—	—

[a] Ionic strength = 0.1 $mol \cdot L^{-1}$, NA = no adsorption observed, — = cation is not soluble.

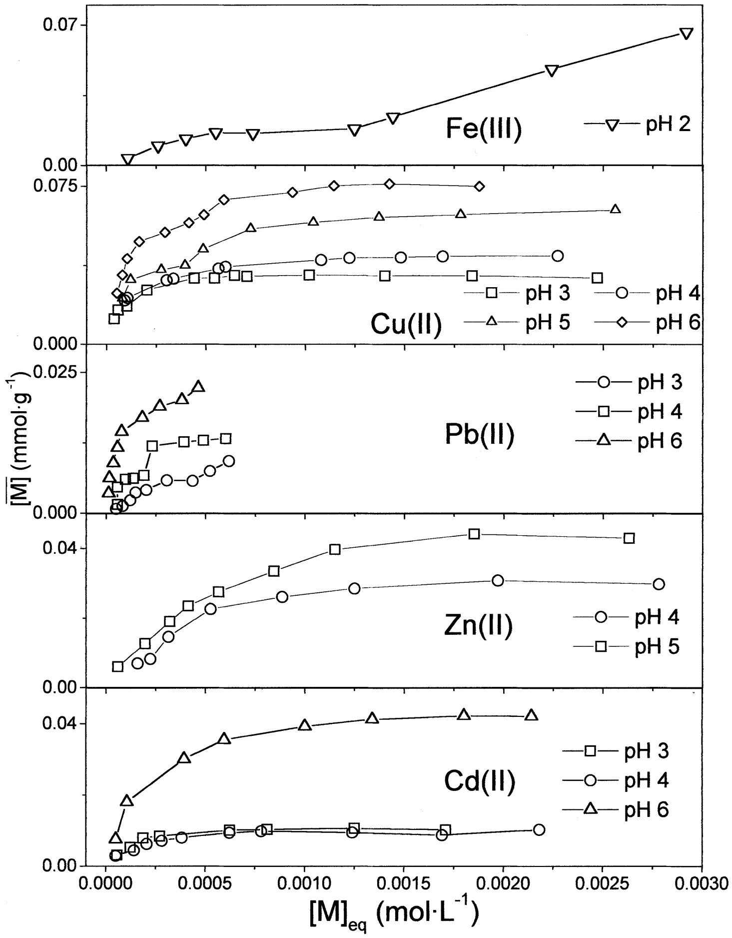

FIG. 8 Adsorption isotherms for Fe(III), Pb(II), Cu(II), Cd(II), and Zn(II) in 0.1 mol·L^{-1} NaNO$_3$.

sis of the adsorption of hydroxide complexes on the —OH terminals of the silica gel, since the theoretical fraction of total metal concentration in a solution of these species can not be neglected under the experimental conditions used ($<$0.001 mol·L^{-1}) (20). For Cu(II) and Pb(II), where the bilayers observed are located at twice the metal concentration value of the first layer, the phenomenon can be explained by the formation of a complex similar to the one shown in Fig. 9, where the amine group of the ligand may act as a second ad-

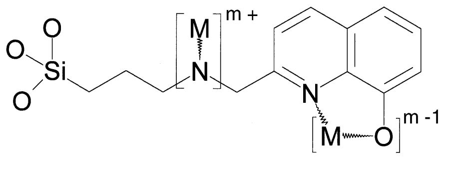

FIG. 9 Proposed structure for the complex formed at high metal concentrations.

TABLE 3

Maximum Adsorption Capacities and Conditional Equilibrium

Cation	Fe(III)	Zn(II)		Cd(II)		
pH	2	4	5	3	4	6
Adsorption capacity ($mmol \cdot g^{-1}$)	0.016	0.031	0.044	0.010	0.010	0.042
Log k	1.33	1.64	1.64	1.20	1.40	1.67

sorption–complexation site. The formation of this complex could not be confirmed by FT-IR spectroscopy due to absorption and the complete overlapping of the —OH bands from the silica gel.

Adsorption equilibrium constants (Table 3) were obtained from experimental data using Eq. (13). The maximum uptake capacities, as well as the overall conditional adsorption equilibrium constants for each cation, are also presented in Table 3. It is observed that capacity values decrease in acidic media. This is most probably due to the protonation of 8-hydroxyquinoline, although changes in the liquid–solid interface with the acidity of the bulk solution cannot be ruled out. Dissolution of silica gel (21) in more alkaline media makes adsorption in this media unsuitable for practical purposes.

Multiple Cation SPE

Aqueous pH and Time Effects

The results obtained in these experiments are quite different to those observed for the single cation assays. Figure 10 shows the metal ion concentration for the five metal ions as a function of extraction time. Although almost all metal ions reach their maximum adsorption efficiency in a short period of time [Cu(II), Pb(II), Cd(II) and Zn(II)], there is an important decrease after 20 minutes of contact time which, in some cases, may lead to null adsorption after long periods [Cd(II) and Zn(II) after 50 and 60 minutes, respectively]. In contrast, Fe(III) adsorbs more slowly (ca. 30 minutes) but shows no decrease, and its content in the solid phase remains constant with time. The reason for the former observation is not well understood; however, the rate of formation and the thermodynamic stability of the involved species may play an important role in the competitive adsorption equilibrium and kinetics.

Figure 10 also presents the total metal concentration in the solid phase ($\overline{[M]}_{total} = \overline{[Cu(II)]} + \overline{[Cd(II)]} + \overline{[Zn(II)]} + \overline{[Fe(III)]} + \overline{[Pb(II)]}$). The curve presents a maximum at approximately 120 $\mu mol \cdot g^{-1}$ after 20 minutes of ex-

Constants at Different pH Values

Cu(II)				Pb(II)		
3	4	5	6	3	4	6
0.041	0.041	0.060	0.076	0.057	0.012	0.022
1.48	1.67	1.80	2.33	1.65	1.90	2.27

traction time and then decreases until it reaches a constant value of ca. 60 $\mu mol \cdot g^{-1}$.

The pH effect on the simultaneous solid-phase extraction is shown in Fig. 11. Although Cu(II) presents a similar adsorption profile to the one observed in the single cation assay, the extraction of Pb(II), Cd(II), and Zn(II) is com-

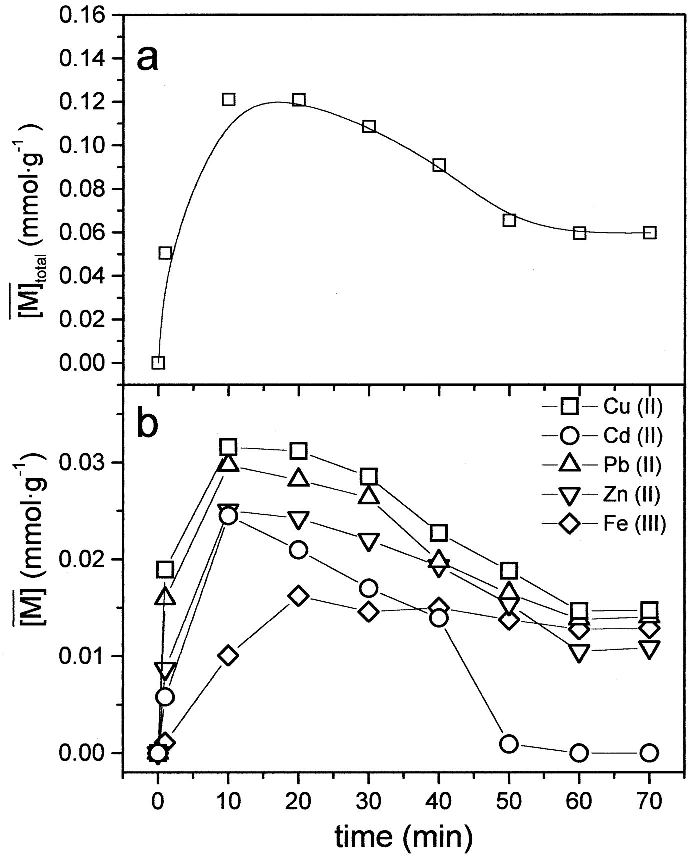

FIG. 10 Metal ion concentration as a function of time for the multiple cation SPE. (a): Total metal ion concentration at the solid phase, $\overline{[M]}_{total}$. (b): Single cation concentration.

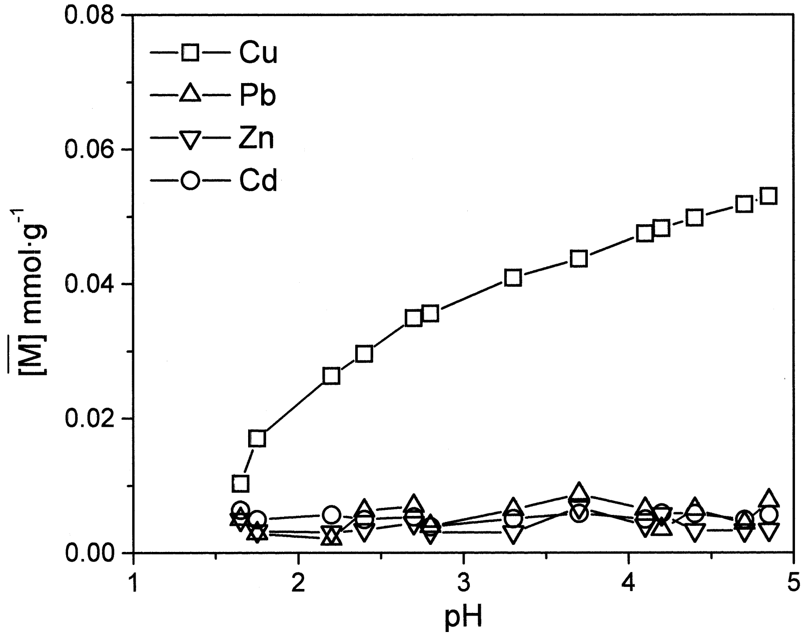

FIG. 11 Extraction profiles as a function of pH in the multiple cation SPE.

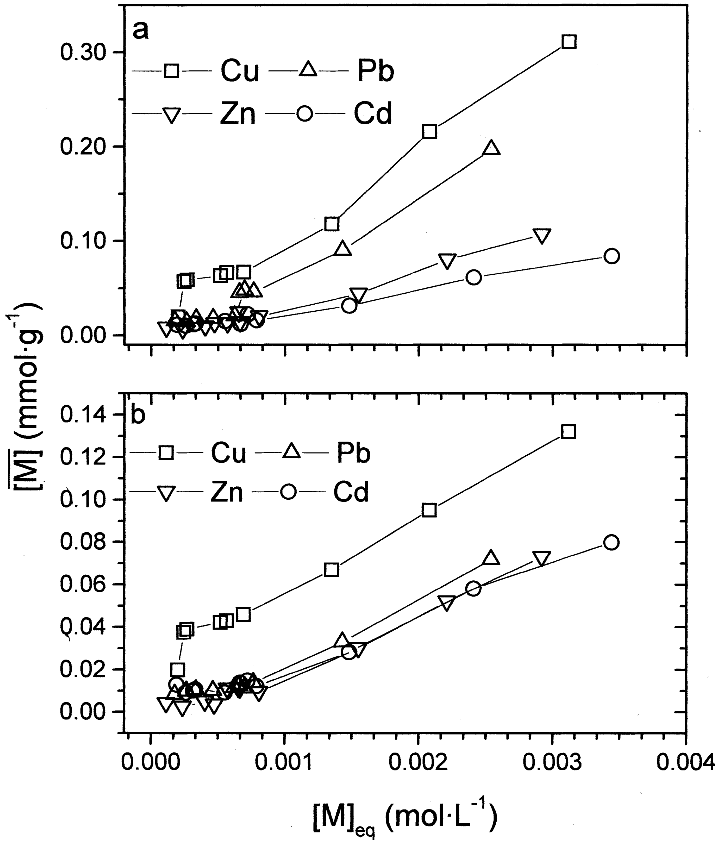

FIG. 12 Adsorption isotherms in the multiple cation SPE. (a): pH 5. (b): pH 4.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

pletely negligible to that of Cu(II) when the pH is below 5. The stability of the formed complexes can be again considered as the ruling factor in the competitive media.

Adsorption Isotherms

From Fig. 12 it is possible to observe that, in the absence of Fe(III), Cu(II) is preferentially extracted over Pb(II), Zn(II), and Cd(II) at pH 4 and 5. Consequently, these latter cations are adsorbed when the first adsorption layer is full. It is also worth noting that when each cation concentration is about 0.001 $\text{mol}\cdot\text{L}^{-1}$ (thus $[\text{M}]_{\text{total}} = 0.004\ \text{mol}\cdot\text{L}^{-1}$), the amount of metal ion adsorbed increases with metal concentration even in those cases in which adsorption was not significant at lower concentrations. The Langmuir adsorption model proposed above (Eqs. 8–13) is no longer applicable under these conditions.

CONCLUSIONS

Modification of silica gel via amminomethylation of 8-hydroxiquinoline in the presence of small quantities of acetic acid allows completion of the reaction in approximately 4 hours. Although FT-IR analysis of the modified silica does not confirm the covalent adsorption of the ligand, its behavior throughout the experiments led us to think that covalent adsorption was accomplished. However, FT-IR spectra revealed the role of the 8-hydroxiquinoline terminal and its interaction with the adsorbed cations.

Extraction of monocharged cationic species is not surprising as a 1:1 stoichiometry for similar adsorbent:cation systems and experimental conditions has been previously reported (10). However, although it has been generally considered that the addition of complexing agents or pH buffers may result in a decrease in the adsorption efficiency, our results suggest that the careful selection of a cosorbed anion concentration may increase adsorption of the cation. Consequently, the operating conditions must be selected in such a way that the monocharged complex cation is predominant in solution in order to achieve a more favorable extraction.

For SPE systems like the one studied in this work, the 8-hydroxyquinoline terminal may not be the only factor responsible for cation adsorption and retention. This should be taken into account when evaluating the expected theoretical loading capacities based on the number of available coordination sites.

The results observed in the multiple cation SPE demonstrate that conclusions obtained from single cation assays are not necessarily true for multicomponent systems. Our first results from these experiments suggest that the adsorption–complexation mechanisms may not be the same as in the single element assays. Future work will be focused on the physical and chemical characterization of the competitive adsorption phenomena for similar systems.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

SYMBOLS

[M]	concentration of the adsorbable cation in the aqueous phase ($mol\cdot L^{-1}$)
$\overline{[M]}$	concentration of the adsorbed cation in the solid phase ($mol\cdot g^{-1}$)
$\overline{[HOX]}$	concentration of 8-hydroxyquinoline in the solid phase ($mol\cdot g^{-1}$)
W	mass of the solid phase (g)
V	volume of the aqueous phase (L)
k_{ads}	adsorption rate constant (s^{-1})
k_{des}	desorption rate constant (s^{-1})
t	time (s)
K	proportionality constant
r_0	particle radius (cm)
Δ	diffusion coefficient of the extracted species ($cm^2\cdot s^{-1}$)
δ	diffusional barrier thickness (cm)
Φ_M	fraction of M concentration
S	total number of adsorption sites
S_{oc}	occupied number of adsorption sites
T	temperature (K)
ϕ	fraction of free adsorption sites
k	observed conditional adsorption equilibrium constant
V_{ads}	observed adsorption rate
V_{des}	observed desorption rate

ACKNOWLEDGMENTS

The authors express their gratitude to Marisela Gutierrez Franco for her collaboration and help to acquire the FT-IR spectra used in this work, and Ma. Teresa de Jesús Rodríguez Salazar for the ICP-AES analysis. J.P.B. thanks CONACyT for the scholarship granted. This work was possible thanks to FQUNAM and CONACyT supports.

REFERENCES

1. K. Terada. "Preconcentration by Sorption," in *Preconcentration Techniques for Trace Elements* (Z. B. Alfassi and C. M. Wai, Eds.), CRC Press, Ann Arbor, MI, 1992.
2. T. Honjo, H. Kitayama, K. Terada, and T. Kiba, *Fresenius Z. Anal. Chem., 330*, 159 (1988).
3. T. Shilling, P. Scharamel, B. Michalke, and G. Knapp, *Mikrochim. Acta, 116*, 83 (1994).
4. J. M. Hill, *J. Chromatogr., 76*, 455 (1973).
5. M. A. Marshall and H. A. Mottola, *Anal. Chem., 55*, 2089 (1989).
6. C. R. Lan and M. H. Yang, *Anal. Chim. Acta, 287*, 101 (1994).
7. K. S. Huang and S. J. Jiang, *Fresenius J. Anal. Chem., 347*, 238 (1993).

8. B. Mohammad, M. A. Ure, and D. Littlejohn *J. Anal. At. Spectrom., 8*, 325 (1993).
9. A. K. Kostad, P. Y. T. Chow, and F. F. Cantwell, *Anal. Chem., 60*, 1569 (1988).
10. J. R. Jezorek, C. Fulcher, M. A. Crowell, R. Bayliss, B. Greenwood, and J. Lyon, *Ibid., 131*, 223 (1981).
11. C. R. Lan and M.-H. Yang, *Anal. Chim. Acta., 287*, 111 (1994).
12. F. Helfferich. "Ion Exchange Kinetics," in *Ion Exchange, Vol. 1* (J. A. Marinsky, Ed.), Dekker, New York, NY, 1966.
13. B. Al-Duri, and G. McKay, "Prediction of Multisolute Adsorption Equilibrium," in *Modeling in Environmental Chemistry* (S. E. Jørgensen, Ed.), Elsevier Science, The Netherlands, 1992.
14. E. P. Horwitz, R. Chiarizia, and S. D. Alexandratos, *Solv. Extr. Ion Exch., 13*, 831 (1994).
15. E. H. Smith, *Sep. Sci. Technol., 33*(2), 149 (1998).
16. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Halsted Press, London, 1975.
17. R. Purohit, and S. Devi, *Talanta, 38*, 753 (1991).
18. J. L. Cortina and N. Miralles, *Solv. Extr. Ion Exch., 15*(6), 1067 (1997).
19. A. E. Martell and R. M. Smith *Critical Stability Constants, Vols. 3 and 4*, Plenumm Press, New York, NY, 1997.
20. A. Ringbom, *Formación de Complejos en Química Analítica, Ed. Alhambra*, Barcelona, 1977.
21. R. K. Ilker, *The Chemistry of Silica*, Wiley, New York, NY, 1979.

Received by editor June 1, 1999
Revision received October 1999

Downloaded At: 10:58 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100100247