

Solid-phase extraction employing 5-methyl-4-(2-thiazolylazo) resorcinol entrapped in sol-gel glass as a sorbent resin to remove zinc ions

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ABSTRACT

Aim: The ligand 5-methyl-4-(2-thiazolylazo)resorcinol (5-Me-TAR) was encapsulated in an optically transparent, inert and porous sol-gel glass to produce a solid resin. The synthesized composite (resin) was used as a solid phase extractant to remove (as a filter) zinc ions from water samples. Materials and Methods: A solution of the ligand in ethanol was mixed with selected alkoxysilanes in the presence of water to produce a homogeneous mixture. By hydrolysis and condensation of the alkoxysilanes, solid glass forms around the dopant. The ligand molecule is entrapped inside the glass pores, while small Zn(II) metal ions can diffuse into the pores where they are complexed by the ligand and retained inside the pores. Absorption and fluorescence spectroscopy were used to characterize 5-Me-TAR ligand and 5-Me-TAR-Zn complex both in solution and sol-gel glass. The sol-gel glass precursors were carefully selected to produce a glass composite material doped with the ligand with no leaching, especially when the glass is soaked in the solution. Results: Complexation using the batch method was employed, in which a known weight of the sorbent resin is mixed with a known concentration of Zn(II) ions. In order to attain the maximum metal ion complexation capacity; the filter was optimized to the optimum separation/pre-concentration conditions of analytes, including the effect of pH, capacity of the solid, equilibration time and coexisting ions; afterwards, the solution was filtered. The amount of zinc metal ion complexed/adsorbed was determined by the difference between the initial concentration in aqueous solution and that found in the supernatant, using flame atomic absorption. The optimum conditions (maximum uptake) was obtained at pH = 6 using 30 min shaking time, and the capacity of the solid was 0.153 mmol Zn/g. **Conclusion:** The ligand was successfully trapped inside the sol-gel pores, and no diffusion of the ligand was observed. Soaking of the sorbent in a solution containing Zn(II) ions results in diffusion of the zinc ions through the sorbent pores into the ligand for complexation.

KEY WORDS: Absorption, complex, emission, filter, ligand, sol-gel, solid-phase extraction, Zn(II), 5-methyl-4-(2-thiazolylazo) resorcinol

INTRODUCTION

Heavy metals, to a large extent, are dispersed in the environment through industrial effluents, organic wastes, refuse burning, transport and power generation. They can be carried to places far away from the sources by the wind. Metallic pollutants are ultimately washed out of the air by rain into land or the surface waters [1].

Heavy metal pollution of water is a major environmental problem facing the modern world. By heavy metals we shall understand the most toxic elements, primarily lead, cadmium, mercury, arsenic, selenium, tellurium, as well as copper, nickel, cobalt, zinc, chromium, silver, and some other metals [2]. Zinc, copper, and lead are three of the most common heavy metals released from road travel; about half of the zinc and copper contribution to the environment from urbanization is from automobiles [3]. Brakes release copper, whereas tire wear releases zinc. Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores [4,5].

Zinc-shortages can even cause birth defects. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea, and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism,

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Received: May 15, 2014 Accepted: September 09, 2014 Published: September 24, 2014 and cause arteriosclerosis [6]. Extensive exposure to zinc chloride can cause respiratory disorders [7]. In the workplace environment, zinc contagion can lead to a flu-like condition known as metal fever. Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc, the children may be exposed to it through blood or milk of their mothers. The world's zinc production is still rising, this basically means that more and more zinc ends up in the environment. Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactorily. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters. Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish, it is able to biomagnify up the food chain [2,4,8].

Determination of heavy metals in natural water was extensively studied [9-16]. To environmental remediation and clean-up, what is more important than determination is the pre-concentration and selective separation (removal) of heavy metals from food and water [17]. The traditional separation and pre-concentration methods for metal ions include liquid-liquid extraction, coprecipitation, and ion exchange. These methods often require large amounts of high purity organic solvents, some of which are harmful to health and cause environmental problems [18].

Solid phase extraction (SPE) is being widely utilized as a powerful tool for pre-concentration and separation technique of various organic and inorganic analytes [19,20]. SPE has several major advantages that include (i) simple operation, (ii) safety with respect to hazardous samples, (iii) higher enrichment factors, (iv) high selectivity, (v) low cost and less time, and (vi) the ability to combine with different modern detection techniques [21]. A variety of solid sorbents such as activated carbons, minerals, metal oxides, ion exchange and chelating resins have been used for removal of metal ions. However, these traditional sorbents have some common limitations such as low binding strength and selectivity, and low resistance to chemicals, heat and radiation [22]. To overcome the above limitations, many new sorbents have been developed as promising materials (i) covalently bonding the ligand to silica gel, and (ii) trapping of the ligand into silica gel by the sol-gel method. Silica gel has been one of the most widely used solid substrates [23] because it does not swell, has good mechanical strength, and can sustain high temperatures. However, covalent binding on silica gel and other substrates is often difficult, complicated, time-consuming and expensive. It usually involves surface modification followed by covalent binding [24]. An efficient adsorbing material should be simple, inexpensive, easy to make, possess a stable and insoluble porous matrix, and having suitable active groups (organic groups) that interact with metal ions [25]. Solution-gelation (sol-gel) method is a simple entrapment method that can be used to prepare solid sorbents. The sol-gel method can be used to prepare solid sorbents, in which the complexing or chelating reagents are entrapped in porous substrates. This method offers a low-temperature alternative to traditional melting glasses. Sol-gel silicate glasses are glass monoliths made by the sol-gel process using silicate precursors. Silicon alkoxide is hydrolyzed by water (-OR of the alkoxide is changed to -OH), once the hydrolyzed products are formed condensation starts. At this stage (sol), the dopant (guest)

is mixed with the sol to produce a homogeneous solution in which the dopant is completely dispersed within the pores of the host silica solution; this process provides good homogeneity and uniformity within the sample. Condensation continues in all directions to produce a polymeric Si-O-Si network, and we reach the gel point. Slow evaporation (drying) of the gel over a period of several days causes the glass to shrink until a constant weight monolithic glass is formed. The sol-gel doping method is gaining importance as a result of its generality and simplicity [26,27]. The synthesized glass material is inert, porous, optically transparent, and easy to fabricate; the concept of so-gel glass has provided a general and inexpensive route for immobilization of dopants (organic, inorganic, and biochemical). Prior to the sol-gel work, the incorporation of organic, organometallic and metallic species in solids generally was restricted to the use of frozen solvents or organic polymer matrices. The present approach represents a totally new type of inorganic/organic composite material because the oxide skeleton not only offers a significantly more ionic environment, but also is thermally, chemically, and dimensionally more stable [28-33]. Studies of organic, organometallic or metallic doped sol-gel glasses have begun to develop substantial breadth; from investigation of doped glasses for luminescent materials, to the development of recognition phases of optical chemical sensors. The highly porous and optically transparent silica gel matrix has been used in both chemical and biochemical sensors [34,35]. Zusman et al. [36] have demonstrated the success of doped gels in chemical analysis. Ragents like ethylenediaminetetraacetic acid has been prepared for removal of heavy metals [37]. The dye Cibacron Blue was entrapped in sol-gel glass and was used to remove heavy metals [38]. The two precursors method was also employed to remove metal ions, in this method a tetraalkoxysilane, e.g., $Si(OCH_3)_4$ and a trialkoxysilane derivative of the complexing reagent, e.g., R-Si(OCH₂)₂ where R is the reagent [39].

In this paper, the feasibility of the sol-gel as a host matrix to trap high-affinity ligands to form sorbents that are used to removal metal ions from aqueous solutions is demonstrated. 5-methyl-4-(2-thiazolylazo)resorcinol (5-Me-TAR) [Figure 1], a multi-dentate ligand with many nitrogen and oxygen donor atoms available to bind metal cations was encapsulated in sol-gel glass matrix employing a quite easy and inexpensive approach using (3-glycidyloxypropyl) trimethoxysilane (GPTMS), 3-(diethoxymethylsilyl)propylamine (DEMPA), and (3-aminopropyl) triethoxysilane (APTES) as the sol-gel precursors [Figure 2]. To ascertain the activity of the ligand in the sol-gel glass pores, spectrophotometry and spectrofluorometry were used to diagnose the encapsulated ligand where absorption and emission were compared to those for the ligand in solution. Capacity of the sorbent glass was determined by comparing the initial concentration of Zn(II) to that of Zn(II)in the filtrate using flame atomic absorption (AA).



Figure 1: Chemical structure of 5-methyl-4-(2-thiazolylazo)resorcinol

MATERIALS AND METHODS

GPTMS, tris-(2-aminoethylamine), DEMPA, APTES, potassium hydrogen phthalate (KHP), potassium dihydrogen phosphate, hydrochloric acid, sodium hydroxide, potassium chloride, and $Zn(NO_2)_2$ were purchased from Aldrich and were used without any further purification. De-ionized, ultra filtered water was used for all preparations. Buffer solutions of 1-7 pH were prepared by using appropriate volumes of solutions of KCl and HCl (pH 1-2.2), KHP/HCl (pH 2.2-4), KHP/NaOH (pH 4.1-5.9) and KH₂PO₄/NaOH (pH 5.8-8) according to the Table 1.

Standard stock solutions of Zn²⁺ (1000.0 mg/L) were prepare by dissolving spectral pure grade $Zn(NO_3)$, in deionized water. Standard working solutions (2.0, 10.0, 20.0, 30.0, 50.0, 100.0 and 200.0 mg/L) were further prepared by dilution with the desired buffer solution; for the 2.0 mg/L solution for example, 0.20 mL from the stock solution (1000.0 mg/L) were taken into a 100.0 mL volumetric flask and the solution was adjusted to the mark with the required buffer to prepare nine solutions (pH = 1, 2, 3, 4, 5, 5.5, 6, 6.5 and 7).

A certified reference material, namely 1000 mg/L Zn²⁺ was obtained from Fluka-Switzerland. Similarly, standard working solutions of these reference materials (2, 10, 20, 30, 50, 100 and 200 mg/L) were further prepared by dilution with the desired buffer solution.

The fabrication of the sorbent resin glass was performed using the monomers GPTMS, DEMPA and APTES. The hybrid matrix GPTMS/DEMPA/APTES mixed in the proper mole ratio in ethanol/water produces a sol that provides the required specifications.

In a typical run, 1.00 g of the 5-Me-TAR ligand was dissolved in 75 mL ethanol followed by the addition of 75 mL DEMPA and the solution were sonicated for 15 minutes. A volume of 50 mL GPTMS and 10 mL APTES were added to the mixture. This solution was hydrolyzed by gradually dropping 10 mL of deionized water and sonication for 25 min. The resultant clear and homogeneous solution was transferred to polystyrene cuvettes sized 10 mm \times 10 mm \times 40 mm. The cuvettes were sealed with parafilm and kept at room temperature for aging. Samples gelled in 24 h (gel point), a weak later the parafilms were punched for drying. In additional 14 days, the monolith shrunk to $6 \text{ mm} \times 6 \text{ mm} \times 0.72 \text{ mm}$ forming a constant weight optically transparent xerogel glass. Some of the prepared xerogel samples were used for optical measurements (absorption and emission) the rest of them were ground into small particles (125 μ m in diameter). The sorbent resin was then were washed with water, ethanol, and methanol to remove residuals prior to use. Metal ion Zn²⁺ complexation/adsorption (removal) by the sol-gel silica sorbent were carried out in batch method [18,40,41], in which a working, standard, or sample (10.0 mL) containing Zn²⁺ were transferred into a small beaker, 0.050 g of sorbent resin was added to the beaker and the mixture was shaken gently and continuously for a certain fixed time (equilibration time) on a mechanical shaker to facilitate complexation/adsorption of the metal ions onto the sorbent resin.

Our goal was to find the best experimental conditions that produce the maximum percent metal extracted. The synthesized resin sorbent extraction process was optimized to the optimum separation/pre-concentration conditions of analyte metal cation. The following parameters were studied.

Effect of pH

To study the effect of pH on the extraction process (complexation/adsorption), 10.0 mL of the desired buffer solution (containing Zn^{2+}) are added to 0.050 g of the sorbent resin resin (125 μ m particle size), the mixture was shaken gently and continuously for 30.0 min on a mechanical shaker to facilitate complexation/adsorption of the metal ions onto



Figure 2: Chemical structure of (3-glycidyloxypropyl)trimethoxysilane, 3-(diethoxymethylsilyl) propylamine and (3-aminopropyl) triethoxysilane

Table 1: B	uffer preparations						
Buffer A pH=1.0-2.2 50 mL 0.2 M KCI+ 0.2 M HCI (mL)		Buffer B pH=2.2-4 100 mL 0.1 M KHP+ 0.1 M HCI (mL)		Buffer C pH=4.1-5.9 100 mL 0.1 M KHP+ 0.1 M Na0H (mL)		Buffer D pH=5.8-8 100 mL 0.1 M KH2P04+ 0.1 M Na0H (mL)	
1	134	3	44.6	5	45.2	5	45.2
2	13	4	0.2	5.5	732	5.5	73.2

the sorbent resin. After filtration, the concentration of the metal ions in the solution was determined by Flame AA. To find the best pH at which extraction is the highest, a plot of % metal extracted versus pH was performed, that the pH of 6.0 was a more efficient pH value, and it was considered for additional tests.

Effect of Shaking Time

Our goal was to study the uptake (% extraction) as a function of time. Experiments were carried out by shaking mechanically the sorbent resin (0.05 g, 125 μ m size resin) with 10.0 mL of 200.0 mg/L metal ion solution (Zn²⁺) prepared at the optimum pH value (pH = 6.0) in a small beaker and the experiment was performed by varying the shaking time (1, 5, 15, and 30 min) then (1, 6, and 24 h). After this time, the solution was filtered and analyzed by flame AA.

Capacity of the Solid

In order to determine the capacity of these sorbent resin solids, experiments were performed at the optimum pH range using 10.0 mL of 200.0 mg/L metal ion solution. Sorbent resins that were ground and sieved to $125 \,\mu\text{m}$ in diameter were employed (0.050 g). The mixture was shaken for 30 minutes, after filtration the samples were analyzed by flame AA.

Effect of Coexisting Ions

The effect of common coexisting ions on the adsorption/ complexation of Zn^{2+} on sorbent resin was investigated. The existence of Co^{2+} , Ni^{2+} or Cu^{2+} with the target analyte ion (Zn^{2+}) was studied by recording any changes on the % extraction of Zn^{2+} .

Standard stock solutions (1000) mg/L of Co²⁺, Ni²⁺ and Cu²⁺ were prepared using spectral grade nitrate salts. In a 10.0 mL volumetric flask, 2.0 mg/L of the coexisting ion (Co²⁺, Ni²⁺ or Cu²⁺) were mixed with 2.0 mg/L of the analyte ion (Zn²⁺) and the volume was adjusted to the 10.0 mL mark using buffer of pH = 5.5. The 10.0 mL were then transferred into a small beaker and 0.05 g of sorbent resin (125 μ m) were added. After shaking for 30 min, the solution was filtered and the filtrate was tested for remaining uncomplexed analyte ions.

Test for Leaching

The extent of leaching was evaluated by immersing the sol-gel sorbent resin doped with SiGPTMSTAEA in buffer solution of different pH for 24 h. After filtration, the filtrate was tested by UV-vis spectrophotometer for any leached ligand.

Spectroscopic Measurements

The optical absorption measurements of Zn-5-Me-TAR complex in solution and that confined in the pores of the silica monoliths were determined using a Perkin Elmer (Lambda 25) spectrophotometer, the spectra were recorded in the visible region

using 1.00 cm quartz cuvettes. Photoluminescence data were obtained under continuous Xe lamp (150 W) excitation in a Jobin Yvon Fluoromax P spectrofluorometer at room temperature. The emission was collected at 90°C from the excitation beam. The slits were placed at 5.0 nm for excitation and emission.

RESULTS

Figure 1 shows the chemical structure of 5-Me-TAR. Figure 2 displays the chemical structure of the monomers GPTMS, DEMPA, and APTES.

Figures 3 and 4 shows the UV-Vis. absorption spectra for 5-Me-TAR ligand in ethanol and in sol-gel glass, respectively. A careful look at Figures 3 and 4 indicate a broad absorption band in the range 400-550 nm with maximum at around 470 nm.

The formation of a complex between Zn(II) and 5-Me-TAR ligand in ethanol solution was also diagnosed using spectrophotometry, Figure 5 displays the absorption spectrum of 5-Me-TAR-Zn complex in ethanol. Complexation is clearly evaluated by comparing Figures 3 and 5. Complexation resulted in the appearance of a new broad absorption broadband (450-550) nm.

Emission spectroscopy was also used as a characterizing tool to prove that the sol-gel glass poses no chemical changes to the 5-Me-TAR ligand and that the ligand is a suitable one to form



Figure 3: Absorption spectrum for 5-methyl-4-(2-thiazolylazo)resorcinol ligand in ethanol (0.010 g ligand in ethanol)



Figure 4: Absorption spectra for 5-methyl-4-(2-thiazolylazo)resorcinol ligand in sol-gel glass

a stable complex with zinc ions. Figures 6 and 7 displays the emission spectra ($\lambda_{exc} = 300 \text{ nm}$) for 5-Me-TAR ligand in ethanol and in sol-gel glass, respectively. Both spectra display a broad emission peak that extends from 530 to 720 nm and a sharp peak at 830 nm that has higher intensity in Figure 6 compared to Figure 7. The resemblance of the two emission peaks again proves an active ligand in the sol-gel glass. The minor differences are again attributed to the change of the local environment surrounding the ligand. Figure 8 shows the emission spectrum of Zn-5-Me-TAR ligand in ethanol ($\lambda_{exc} = 300 \text{ nm}$). By comparing Figures 6 and 8, it can be clearly concluded that complexation between Zn(II) ions and 5-Me-TAR ligand resulted in the disappearance of the broad emission band (530-720 nm) and



Figure 5: Absorption spectrum for 5-methyl-4-(2-thiazolylazo) resorcinol -Zn complex in ethanol



Figure 6: Emission spectrum for 5-methyl-4-(2-thiazolylazo)resorcinol ligand in ethanol ($\lambda_{\rm exc}$ = 300 nm)



Figure 7: Emission spectrum for 5-methyl-4-(2-thiazolylazo)resorcinol ligand in sol-gel glass (λ_{exc} = 300 nm)

To evaluate the suitability of the newly synthesized sol-gel sorbent for metal ion extraction and binding, the effect of pH of metal ion solution on the metal capacity values was studied. A plot of % Zn extracted versus pH can be seen in Figure 9. The conditions at which Figure 9 was obtained include: 10 mL of 2.0 mg/L of the desired buffer solution (containing Zn²⁺, 0.050 g of the sorbent resin (125 μ m particle size), the mixture was shaken gently and continuously for 30 min on a mechanical shaker, after filtration, the concentration of the metal ions in the solution was determined by Flame AA (three trials for each pH).

In order to determine the capacity of the solid sorbent (rersin), experiments were performed at pH = 6 and with 200 mg/L Zn(II) and 50 mg sorbent resins of 125 μ m particle size. Under these conditions, the percent uptake of Zn(II) was 22.4 ± 0.45.

For the study of the equilibration time, we employed 10 mL of 200 mg/L Zn(II) at pH = 6 as the sample and 100 mg of sorbent resin (125 μ m particle size), the extraction yield after 5, 10, 20, 25, 30, and 35 min were 30, 33, 37, 41, 43, and 43% respectively.



Figure 8: Emission spectrum for 5-methyl-4-(2-thiazolylazo)resorcinol -Zn complex in ethanol ($\lambda_{\rm exc}$ = 300 nm)



Figure 9: Effect of pH on the reaction between Zn(II) and 5-methyl-4-(2-thiazolylazo)resorcinol that is encapsulated in sol-gel glass

The effect of coexisting ions was performed using 10.0 mL of 2.0 mg/L Zn(II) in pH 6.0 buffer as the sample, the extraction yield by 0.05 g resin was $83 \pm 4\%$ in 30 min. Repeating the experiment with 2.0 mg/L Ni(II) and with 2.0 mg/L Co(II) as the sample decreased the extraction yield to $64 \pm 5\%$ and $65 \pm 4\%$, respectively.

DISCUSSION

Compared with the traditional ion exchange and chelating sorbents based on organic polymers, the sol-gel method has several advantages that include: ease of preparation at room temperature of an optically transparent and porous sorbent, homogeneous dispersion of the guest molecules, the synthesized sorbent glass has higher resistance to heat, chemicals and radiation. Since the metal ions removed will be entrapped inside silica gel pores, sintering the sol-gel silica sorbent (fusion) will cause the pores to shrink and eventually collapse, leading to complete and a permanent entrapment of the metal ions in the fused silica. This could be used as a new method for permanent waste disposal.

5-Me-TAR ligand is an organic ligand that is used in this study for several reasons. Firstly, the derivatives of resorcinol principally 4-(2-pyridylazo)resorcinol, 4-(2-thiazolylazo) resorcinol, 5-Me-TAR and 4, 6-diacetyl resorcinol have been employed to facilitate concentration and determination of many metals [42-44]. Second, the ligand is readily soluble in ethanol, inexpensive and readily available.

For the synthesized sol-gel glass sorbent to work as a filter, the sol-gel glass must act as an inert host that doesn't interact with the guest 5-Me-TAR ligand. An active ligand dispersed in the pores of the glass with all functional groups available for chelation is a major requirement for a working filter.

We used absorption and emission (fluorescence) spectroscopy to diagnose any changes to the 5-Me-TAR ligand in the sol-gel glass pores compared with that in solution. The minor changes in absorption that appears in Figures 3 and 4, may be attributed to differences in the local environment (Si-O-Si network) in sol-gel compared with ethanol solution and the possible interaction between the 5-Me-TAR ligand molecules trapped inside the pores and the silanol groups of the silica matrix.

Optimization of Sol-gel Method

The sol-gel method involves the following steps: (i) hydrolysis of some of the $-OC_2H_5$ and $-OCH_3$ groups in DEMPA, GPTMS and APTE to form -OH, (ii) condensation (water is released) to produce the colloidal particle (sol), (iii) hydrolysis and condensation continues on the remaining $-OC_2H_5$ and $-OCH_3$ groups which produce a network of -Si-O-Si- in all directions in a step called gelation, finally (iv) drying and shrinkage form the xerogel (air dried gel). The guest (target ligand) is usually added to the glass material before the gelation step (at the sol-stage). After drying one usually ends up with a solid, porous, transparent material that serves as a host to accommodate the ligand guest. In a previous work [45,46], we only used GPTMS and DEMPA to prepare a workable sol-gel glass that we employed to the trap variety of compounds. In this work, the precursor APTES is carefully selected and added to the recipe. APTES is added in order to increase porosity, maintain good optical quality, and at the same time enable the reaction between the immobilized ligand and metal cations [47]. APTES is one of the most frequently used organo-silane coupling agents because it has excellent affinity for glass silanols, and it also provides a means of binding between organic indicators and inorganic substrates [48]. Moreover, addition of APTES to the sol inherently decrease the network connectivity and a more open framework is formed with easier diffusion of the analyte metal cations to the trapped ligand [49]. Finally, it possesses a hydrophilic amino group that is not involved in the sol-gel reaction that will participate in adsorption/ chelation of metal cations because our ultimate goal is to capture as much metal cations as possible. The careful selection of the above precursors resulted in no leaching of the ligand even when the ligand was soaked in different buffer solutions for periods that extend to more than 2 weeks.

To study the optimization conditions (effect of pH, shaking time, capacity and effect of coexisting ions), removal efficiency (% removal) is defined using the following expression [50],

% Removal = $([C_0 - C_e]/C_0) \times (100)$ (1)

Where: C_0 is the initial metal ion concentration (mg/L); C_e is the equilibrium metal ion concentration (mg/L).

It is well-known that binding of metal ions to chelate compounds either in solution or loaded on a solid support is mainly dependent on several factors such as nature, charge and size of the metal ions, nature of the donor atoms and their binding characteristics; the buffering conditions [51,52].

Effect of pH

Figure 9 has the expected sigmoidal shape that is a result of the competition between H_3O^+ and metal ions for the ligand sites.

The amount of removal was small at low pH because H⁺ ions compete with Zn(II) ions. Measurements were not made at pH >7 in this work in order to avoid precipitation of Zn(II) hydroxides. Two factors determine the observed pH dependence of Zn(II) removal, the surface charge of the sol-gel glass and the acid-base equilibrium of 5-Me-TAR ligand. The removal of Zn(II) increases with increasing pH because of the deprotonation of the OH groups in 5-Me-TAR and surface -SiOH groups on silica. To avoid hydrolyzing at higher pH, pH 6 was selected as the enrichment acidity for further study.

Capacity of the Solid

The concentration was selected in a range were the amount extracted was below 25 %. From the data at pH = 6 and the mass of the solid, a capacity of 0.153 mmol Zn/g was obtained.

Effect of the Shaking Time

The shaking time is an important factor in determining the possibility of application of the sol-gel sorbent for the selective

extraction of metal ions. The study of Zn(II) remained in solution as a function of shaking time give us an idea about the kinetics of Zn(II) removal by the doped sol-gel glass.

From obtained results, a 43% removal was the optimum we could reach in 30 min. The use of 30 min equilibration time was selected.

Effect of Coexisting Ions

Our SPE method is performed with a general complexing agent in the batch method; we anticipate interference from mixtures of metal ions, particularly if the formation constant of the interferent with 5-Me-TAR is greater than that of the targeted metal (Zn(II)). Further improvements could include more specific ligands that selectively reacts with the desired ion.

CONCLUSION

This study was undertaken in order to evaluate the potential application of sol-gel chemically immobilized-5-Me-TAR ligand for pre-concentration of Zn(II) in natural water samples. The sol-gel glass was carefully engineered to accommodate 5-Me-TAR ligand and the matrix formed was used as a solid phase extractant. The preparation of the sorbent was relatively simple and convenient. The synthesized sorbent showed a high affinity and good accessibility for Zn(II) ions.

The shortcomings of the proposed method include the slow removal kinetics and the small removal capacity, which can be attributed to the nature of the entrapment method. The properties and performance of the synthesized sorbent could be improved by future optimization. Further studies are in progress to optimize the properties and performance of this new sorbent and to develop sorbents doped with other complexing or chelating ligands that are both selective and have a higher affinity for metal cations.

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