

Functionalized Sol-Gel Silica as Solid Phase Extractant

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ABSTRACT

8-Hydroxyquinoline (8-HQ) functionalized sol-gel silica (HQSG) was prepared and investigated as a solid phase extractant for mercury from aqueous solutions. Various parameters: effect of pH, contact time, effect of foreign ions and complexing agents that could influence the extraction have been studied at room temperature. Fast equilibration was observed and equilibration was achieved in less than five minutes. The maximum sorption capacity of Hg^{+2} on to HQSG from non-competitive solutions at pH 6 was found 0.066 mM g^{-1} . The adsorption data was best fitted to Langmuir adsorption isotherm. Extraction data from effect of foreign ions on the extraction of mercury shows that the proposed sorbent has reasonable selectivity for mercury against various metal ions. Extraction route and stripping of the extracted mercury with different solutions have been discussed. HQSG has been compared with some reported alternate sorbents investigated for solid phase extraction of mercury.

Key words: Sol-gel silica; 8-Hydroxyquinoline; mercury

INTRODUCTION

In recent years, there has been a pronounced tendency to use functionalized silica support materials as solid phase extractant for the separation and concentration of different analytes. Functionalization of silica may improve their performance by increasing selectivity and adsorption capacities. Two approaches are used for loading the surface with specific organic compounds, chemical immobilization and physical adsorption. In the first approach, the organic compound is directly adsorbed on the silanol groups of silica gel surface (impregnation or loading), either by passing the reagent solution through a column packed with the absorbent, or by soaking the absorbent in the reagent solution /1/. In the second case, a chemical bond is formed between the silica gel surface groups and those of the organic compounds. Numerous reagents have been investigated for impregnation of silica gel as a means of increasing retention capacity and selectivity of

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the sorbent for elements, namely (2-mercapto-N-2-naphthylacetamide) /2-3/, 2-mercaptobenzothiazole (MBT) /4/, 1-nitroso-2-naphthol (NN) /5/, 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone (MPSP) /6/, salicylaldehyde /7/, dimethylglyoxime (DMG) /8/, Aliquat 336 (methyl-tricaprylammonium chloride) and Calcon (hydrophobic sodium sulfonate) /9/.

Conventional methods of silica surface modification by chemical routes involve reaction of surface hydroxyl group with commercial silane coupling reagents that act as precursors for further immobilization. Normally these silylating agents react with the surface silanol groups in one step, allowing the surface to embrace the desirable terminal functional group /10/. Humic acid was immobilized by the treatment of aminopropyl modified silica HA with the modified silica /11/. 2-Mercaptobenzothiazole (MBT) was synthesized by the Mannich reaction between MBT and γ -aminopropyltriethoxysilane modified silica gel /12/. The immobilization of 8-hydroxy quinoline on different supports including silica, and the use of these supports for preconcentration of metal species has been reported by several authors /13-21/. The chemical processing, including activation of silica followed by modification with functional organic reagent, is considered a major disadvantage of the second route of modification of silica. Tremendous developments in the low temperature sol-gel processing in the last decades of the 20th century, and introduction of new simple, economical, single pot route for modification of silica "doping method" by Aviner and his coworkers at Hebrew University /22/, opened new doors for the design of functionalized sol-gel silica sorbents. The doping is considered intermediate between impregnation and covalent grafting techniques. The doping of organic reagent is achieved during the formation of sol-gel matrices, which provides uniform distribution of organic reagent almost at molecular level in the silica support.

In the present work, sol-gel silica modified with 8-hydroxy by doping method has been reported for solid phase extraction of mercury from aqueous solutions. The modified material exhibited fast equilibration, reasonable selectivity and capacity for extraction of mercury. The effect of pH, foreign ions, uptake mechanism, stripping of the extracted mercury and comparison of the material proposed with alternate sorbents has been discussed.

MATERIALS AND METHODS

Reagents and Chemicals

The chemicals in this study including tetraethoxysilane (TEOS) 98.5% (Aldrich, USA), ethanol and ammonium fluoride (Merck, Germany) and 8-hydroxyquinoline (8-HQ) (Fluka, Switzerland) were used as received. Double-distilled water was used in the preparation of solutions, sol-gel and washing of sorbents. All other chemicals were of analytical grade.

The radiotracer ^{203}Hg was prepared by neutron irradiation of spec-pure mercuric oxide in the research reactor PARR-1 of PINSTECH at a flux of $7 \times 10^{13} \text{ n sec}^{-1}$. A known amount of mercury oxide was sealed in a polythene capsule before irradiation. The irradiated material was dissolved in concentrated HNO_3 acid, the acid was removed by repeated evaporation with distilled water and diluted to 25 ml. Further dilution was made from this stock solution. The radiochemical purity of the tracer was checked using a $25 \text{ cm}^3 \text{ Ge (Li)}$

detector coupled with a 4k series of 85 Canberra, USA multichannel analyzer.

Buffer solutions of 1-10 pH with an ionic strength of 10mM were prepared by using appropriate volumes of solutions of KCl and HCl (pH 1-2), sodium acetate- acetic acid (pH 3-6) sodium di-hydrogen phosphate – di-sodium hydrogen phosphate (pH7-8), sodium hydrogen carbonate –sodium carbonate (9-10).

Apparatus/Instruments

All pH measurements were made on a Metrohm-605 pH meter. The shaking was performed in a 30 ml pyrex culture vial having teflon lined screw- type polythene cap. Gross gamma – ray measurements were made on a Tennelec, USA counting assembly equipped with a well type 25 cm³ NaI(Tl) crystal.

Preparation of Doped. and Plain Sol–Gel Silica

The ligand doped sol-gels were prepared by mixing 40.0 ml of tetraethoxysilane, 40.0 ml of double distilled water and 100 ml ethanol solution of 8-Hydroxyquinoline in the presence of 10⁻² M ammonium fluoride as a catalyst, a gel started to appear in about five minutes. The prepared gel was placed at room temperature 28°C±2 for 24 hours to complete the gelation and then placed in an oven at 48°C. During drying shrinkage of the gel occurred and the gel cracked into hard and transparent fragments; pieces of 0.5-1cm size were obtained. The hard pieces were crushed, ground and sieved to obtain material of uniform size. Plain sol-gel silica was also prepared for comparison according to the above procedure without 8-HQ.

Conditioning of Doped Sol-Gel-Silica

The dry powder HQSG was soaked in water for three days to leach the non-doped reagent. In this process, some of the free reagent leached out of the sol-gel. No further leaching was observed after three days soaking. After the leaching process, the sol-gel powder was oven-dried at 48 °C for 48 hours and stored in a vacuum desiccator till use. The sorbent was conditioned in appropriate buffer before it was used for the removal of metals. The amount of doped reagent was determined by spectrophotometric determination of leached dye in the washings.

Procedures

Hg (II) extraction from the single metal aqueous solutions was investigated in batch adsorption-equilibrium experiments at room temperature (28 ± 2 °C.). Sorption isotherm of mercury (II) ion was studied by equilibrating 50mg of the sorbent with 5ml of the solution at certain pH, containing an appropriate quantity of tracer alone or tracer plus carrier of mercury. After equilibration, the vials were centrifuged and 1ml supernatant aqueous phase was radio-assayed for Hg²⁰³ by gamma scintillation counter after checking for any type of precipitation or turbidity. Control trials were performed for experiments when and where required. The concentration of adsorbed metal ions (Q) was calculated using the following equation:

$$Q = [(C_i - C_f)/m_a] V \text{ (mg/L)}$$

Here, Q is the amount of metal ion adsorbed (mg g^{-1} sol-gel); C_i and C_f are the concentration of aqueous phases before and after equilibration respectively (mgL^{-1}); m_a is the quantity of adsorbent (g); and V is the suspension volume (ml).

The effect of pH has been studied by varying the solution pH from 1-10, keeping the quantity of sorbent and concentration of sorbate constant. The following equation was used to compute the percentage removal:

$$\% \text{ Sorption} = \frac{C_i - C_f}{C_i} \times 100$$

C_i = Initial activity of solution

C_f = Final activity of solution

The kinetic study was performed by following discontinuous method. A series of screw-cap test tubes was prepared, each containing the same weighed amount of sorbent and concentration of mercury. At various time intervals one of the test tubes was removed from the shaker and quickly centrifuged at high speed, 1 ml aliquot of the supernatant solution was assayed for metal ion and a plot of amount of metal ion retained on the sorbent as a function of time was drawn, where each experimental point is the result of the measurements performed on a single test tube.

RESULTS AND DISCUSSION

Effect of pH

Figure 1 represents the extraction of mercury from aqueous solutions of different pH (1-10). Adsorption of mercury was sensitive to pH of solutions and increased with increase of pH and became quantitative at pH 6. The increase of mercury extraction with increase of pH may be attributed to the increase of non-protonated mercuric ions and chelating molecules due to less availability of H^+ ions at pH higher than 6. Moreover, lower pH may favour formation of non extractable species like HgCl_3^- and HgCl_4^{2-} .

Equilibration time

The effect of shaking on the extraction of mercury was studied by keeping the concentration of mercury in solution, amount of sorbent and pH of solution constant. The extraction of mercury was very fast and equilibration was achieved in less than five minutes. The fast equilibration could be attributed to the free availability of mercuric ions, high affinity of mercuric ions towards the reagent, easy approach of chelating reagent molecule to mercuric ions, least steric hindrance exhibited by the structure of chelating reagent and three-dimensional solid sol-gel net-work around the doped organic reagent (8-HQ).

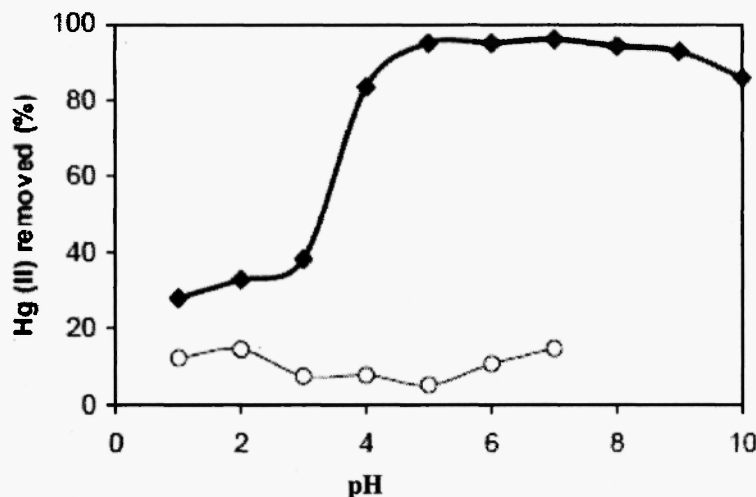


Fig. 1: Removal of Hg(II) as a function of pH of solution (Hg(II) = 5.0ppm, volume = 5ml, sorbent=50.0mg, shaking time=30minutes). ♦ Doped Sol-Gel Silica ○ Plain Sol-Gel silica

Adsorption isotherm

Figure 2 depicts the results collected from the equilibration concentration of Hg^{2+} in solutions to determine adsorption capacities of the sorbent, using 50 mg sorbent and varying the initial amount of mercury in solution from 0.1 to 5mg / 5m at pH 6. Initially the extraction increased with increase of mercuric concentration and the curve attained plateau form when the sorbent was saturated with Hg^{2+} , which shows optimum capacity of 0.066mM Hg(II) per gram of HQSG. The adsorption capacity of plain sol-gel silica is 0.001mM Hg (II) per gram. The high difference in adsorption capacities for doped and plain HQSG minimized the role of surface of silica in adsorption and suggests that doping of 8-HQ was the major reason for enhancement in adsorption capacities, and extraction of mercury might take place by ion exchange and / or complexation of mercury with 8-HQ.

Figure 3 depicts the decrease of distribution ratio with increase of initial concentration of mercury; it was achieved by plotting initial concentration of mercury versus distribution ratios (Rd) for mercury between sorbent and initial mercuric solutions, using 50mg sorbent at pH 6. The following equation was used to determine distribution ratios (Rd):

$$\text{Rd} = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \text{ml g}^{-1},$$

where C_i and C_f are the concentration of aqueous phases before and after equilibration respectively, W is the weight of dry sol-gel silica (g) and V is the volume of the aqueous phase (ml).

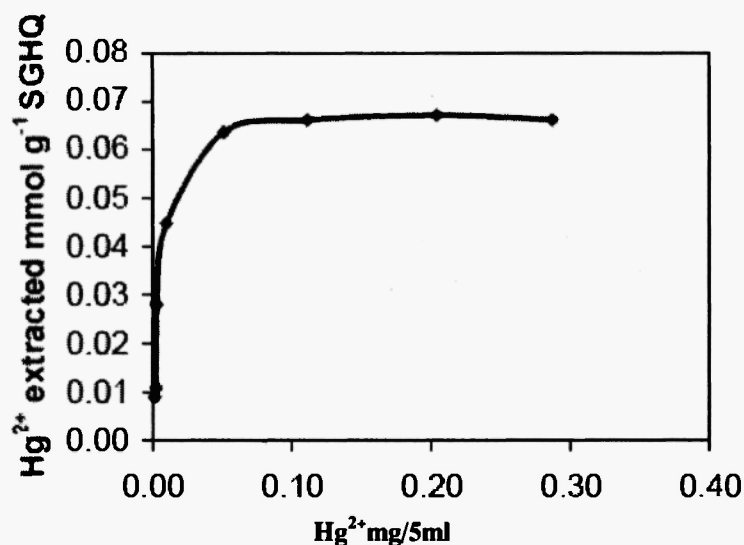


Fig. 2: Isotherm for removal of Hg(II) by doped sol gel silica (SGHQ) (sorbent = 50mg, volume = 5ml, shaking time = 10 minutes, initial quantity of Hg(II) in solutions = 20, 40, 60, 80, 100, 180, 260, 320, 420 ppm)

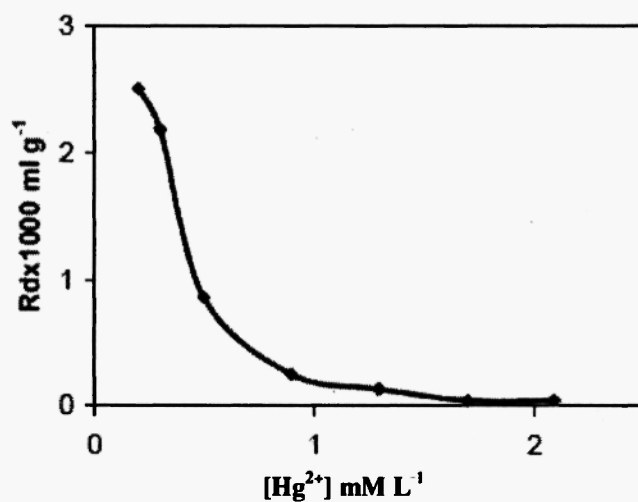


Fig. 3: Variation of the distribution ratio (Rd) of Hg(II) as a function of initial concentration of Hg²⁺.

The extraction data were best fitted to Langmuir adsorption isotherm presented in Fig. 4, using the following form of Langmuir Equation:

$$\frac{C_e}{q_e} = \frac{1}{Nb} + \frac{C_e}{N}$$

where C_e is concentration of mercuric ions at equilibrium, q_e shows sorption capacity of sorbent and N , b are

Langmuir constants. The values of N and b were found 0.07 mM g^{-1} and 35.7 L mmol^{-1} respectively. The value of N 0.07 mM g^{-1} is in close agreement with the experimental value 0.066 mM g^{-1} obtained from extraction data.

Effect of foreign ions and recovery of extracted mercury

Table 1
Effect of foreign ions (5 mg/ml) in the determination of
0.1mg / ml Hg (II) from PH 6 solutions

Substance added	Ag(I) extraction %
Cd (II)	93.4
Cr (III)	71.9
Mn (II)	68.8
Cu (II)	97.9
Zn (II)	95.9
Co (II)	95.7
Sb (II)	Nil
Au (III)	96.4
Pb (II)	68.3
Fe (III)	12.9
Bi (III)	97.7
Ce (III)	92.0
SCN-	29.3
thiourea	29.5
ascorbic acid	44.9
oxalate	20.4
citrate	33.2

Table 1 shows the effect of foreign ions; aqueous solutions that contain ions such as Cd (II), Cu (II), Zn (II), Co (II), Au (III), Bi (III) do not interfere in the extraction, whereas the extraction of mercury was seriously affected by cations such as Sb (II) Fe (III), Cr (III) and complexing agents SCN^- , thiourea, ascorbate, oxalate and citrate. The presented data suggest that mercury can be separated from Cd (II), Cu (II), Zn (II), Co (II), Au (III) and Bi (III).

Different solutions have been used for the stripping of extracted mercury. It was observed that more than >99% of adsorbed mercury can be stripped by 10ml solution of 1M NaCl, 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$) and 0.5 EDTA.

Comparison with alternate sorbents

The proposed sorbent has been compared with different alternate reported sorbents in Table 2. The modified silica sorbent presented has very fast equilibration (< five minutes), reasonable selectivity, physical stability. In addition its synthesis is simple (one-pot preparation), low cost and is free from activation of silica.

Table 2
Comparison of HQSG with some reported sorbents for mercury

Adsorbent	Capacity (mmol /g)	Equilibration time	Separation of mercury from:	Reference
Dithiocarbamate-incorporated monosize polystyrene microspheres	0.16	30 min	Cu (II), Cd(II) and Pb(II)	/23/
Procion Brown MX 5BR immobilized poly(hydroxyethyl-methacrylate/chitosan) composite membranes	0.34	45 min	Cd (II), Pb (II)	/24/
Dithiocarbamate grafted on silica gel	0.30	2 Hours	Effect of metal ions not reported	/25/
Carboxymethylcellulose and immobilized <i>Phanerochaete chrysosporium</i>	0.41, 0.51	1 Hour	Not reported	/26/
Moroccan stevensite	0.166	2 Hours	Not reported	/27/
Hg(II)-imprinted diazoaminobenzene-vinylpyridine copolymers	0.205	24 Hours	Cu (II), Zn (II), Cd (II)	/28/
H-Hydroxyquinoline functionalized sol-gel silica	0.066	<5min	Effect of foreign metal ions suggest separation of mercury from Cd (II), Cu (II), Zn (II), Co (II), Au (III), Bi (III)	Presented work

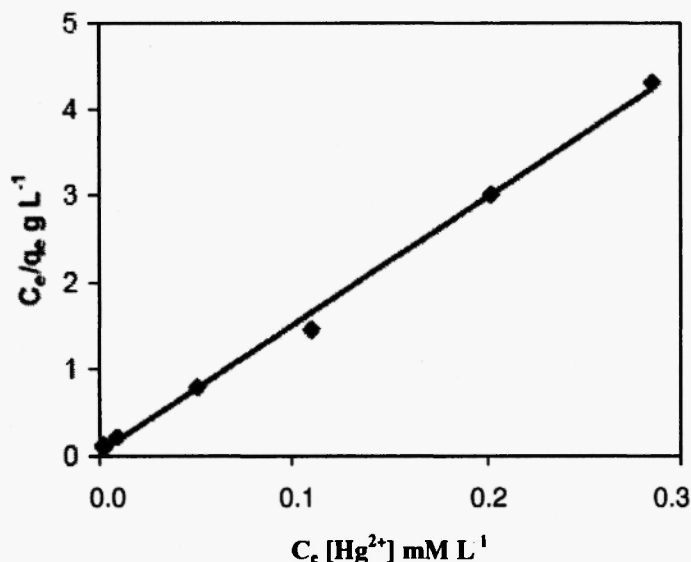


Fig. 4: Langmuir adsorption isotherm for sorption of Hg(III) by SGHQ sol-gel silica.

CONCLUSION

8-Hydroxyquinoline doped sol-gel silica having functional groups –N-, –OH has been introduced as solid phase extractant for mercury from aqueous solutions. The fast equilibration, simple one-pot economic synthesis, reasonable selectivity for mercury and chemical stability make this material potentially useful for extraction-separation of mercury from aqueous solutions.

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