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Modification of Silica Gel with 1,10-Phenanthroline for Cd(II) and Pb(II) Adsorption

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Silica gel was modified via silylation using 3-chloropropyltrimethylsilane and functionalization using 1,10-phenanthroline. FTIR, DSC and quantitative SEM-EDX data were obtained to confirm functionalization. The uptakes of cadmium (II) and lead (II) by the phenanthroline-modified silica (Phen-Si) were determined using equilibrium and dynamic methods. For the equilibrium method, percent adsorbed for 5 to 200 ppm metal ion solutions ranged from 0 % to 93.2 % (for Cd) and from 81.6 % to 95.2 % (for Pb) The maximum uptake of Phen-Si is 91.89 mg Pb/g silica and 93.06 mg Cd/g silica for the equilibrium method while for the dynamic method, maximum uptake was 25.65 ± 6.52 mg Pb/g silica and 17.68 ± 2.33 mg Cd/g silica.

Keywords: *silica gel; phenanthroline; Pb(II)-phenanthroline complex; Cd(II)-phenanthroline complex*

INTRODUCTION

The immobilization of chelating agents in an inert support has been examined for various purposes like chromatographic applications and analytical preconcentration of toxic metals in the environment. Information on design, synthesis, characterization and factors that affect the properties of the supported materials abound in the literature and the practical applications of such materials are now gaining the attention of scientists working on chemically modified surfaces. Silica gel is commonly used for this purpose because of the following advantages: a variety of silylating agents can be used to allow different functional groups to be attached to the surface, it has high resistance to organic solvents and high temperatures, and it has a large surface area that has constant composition which allows easy analysis and interpretation of results (Jal et al., 2004).

A review of chemical modification of silica (Jal et al., 2004) lists various ligands immobilized on the surface and used for analytical preconcentration or removal of toxic metals from waste waters. Examples are: thiosemicarbazide for Pd(II), dithizone for Ag(I), Hg(II) and Pb(II), 2,4-dichloro-phenoxyacetic acid (2,4-D) for Cu(II), Ni(II), Zn(II) and Cd(II), 1-allyl-3-propylthiourea for (Hg(II), and dithiocarbamate derivatives for Pb(II), Cd(II) and Zn(II). Other modifiers mentioned in the review (Jal et al., 2004) were macrocyclic crown ethers (for separation of alkali and alkaline earth metal cations) and octadecyl (C18) bonded silica gel (for

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separation and preconcentration of the platinum group metals Ru, Rh, Pd, and Os).

1,10-Phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) is a white crystalline powder with melting point of 93-94^{O}C. It forms a complex compound with ferrous ions and is normally used as an indicator in oxidation-reduction systems. It is also used in spectrophotometric determination of nickel, ruthenium, silver and other metals. Several studies have used silica with physically adsorbed phenanthroline as preconcentrating ligand for various metals (Zaporozhets et al., 1998; Part et al., 1993; Mikula et al., 2009). However, these materials are non-reusable since desorption of metals would mean desorption of the adsorbed chelating material, 1,10-phenanthroline, as well. A possible solution to make these materials reusable is to covalently graft phenanthroline on the surface of the silica. However, literature is sparse on chemical surface modification of silica by this ligand. Only one reference (Zaytsev and Trofimchook, 1984) was found by the authors of this study, and it was in Russian. This study is an attempt for this chemical modification based on the reaction of alkali metals with aromatic hydrocarbons containing two or more joined, conjugated or fused aromatic rings (Coates et al., 1965) and on the unpublished dissertation of the primary author of this study (where 2,2'-dipyridylamine-functionalized silica synthesis was reported). The resulting phenanthroline-modified silica (Phen-Si) was tested for adsorption of the health-impacting Pb and Cd ions from their aqueous solutions.

METHODOLOGY

Silylation. Silica gel Grade 62, 60-200 mesh, 150 Å (Sigma-Aldrich) was first dried in vacuo at 150^{O}C for six hours. Six grams of the predehydrated silica gel was dispersed in 200 mL of low water toluene (AR, Merck) in a 250mL flask. 6.4 mL of 3-chloropropyl-trimethoxysilane (Aldrich) was added and the solution was stirred magnetically under nitrogen for 48 hours. The silylated silica was filtered and the unreacted silane was removed by Soxhlet extraction using dry toluene (AR, Scharlau) for 24 hours. Any polar contaminants in the product were removed by washing the silylated silica 3x50mL of toluene, followed by 3x50 mL acetone (AR, Merck), and finally 3x50mL diethyl ether (AR, Merck), then dried in vacuo at 100^{O}C for 6 hours. The remaining surface silanols in the product were silylated by suspending the chloropropyl-modified silica in 100mL of chloro-trimethylsilane (Fluka). The mixture was refluxed for 6 hours and left overnight. Excess silane was removed by distillation and the product is again dried in vacuo at 80^{O}C for 12 hours. This procedure was based on the unpublished dissertation of the primary author of this study and on reference (Huang et al., 2008).

Comparing the unpublished dissertation to reference (Huang et al., 2008), both involve the same reagents and general procedure but differs in minor details like ratio and amounts of starting materials used. Activation of silica gel was also mentioned, which was not done in this study.

Modification using 1,10-phenanthroline. 2.23 grams of 1,10-phenanthroline mono-hydrate (Univar) was dissolved in 25mL of THF (AR, JT Baker) in an inert atmosphere. 0.44 grams of potassium metal (Aldrich) was added to the solution and refluxed under nitrogen until the metal is completely dissolved and a blue solution was produced. 2.5 grams of silylated silica was added into the solution and then refluxed for another 24 hours under nitrogen. The excess metal and other contaminants were removed by Soxhlet extraction with methanol (AR, Merck) for 24 hours. The modified silica is filtered, washed with 3x50mL methanol, then dried in vacuo at 80^{O}C.

Heavy Metal Adsorption. *Equilibrium Method.* 25mL of cadmium and lead solutions with concentrations varying from 5-200ppm were prepared (pH 5) by diluting AAS metal standard (Merck) using deionized water. 50mg of phenanthroline-modified silica were added to the solution and magnetically stirred for 30 mins. The solution was filtered and the concentration of heavy metal left after

adsorption was determined using an AA-6501S Atomic Absorption Flame Emission Spectrophotometer (Shimadzu). The instrumental parameters recommended for the instrument were followed and the wavelengths selected were 228.8 nm for cadmium and 217 nm for lead.

Dynamic Method. 50mg of phenanthroline-modified silica gel was placed in a Bio-Rad Econo Column. The column is washed repeatedly with HCl solution and deionized water to clean and equilibrate the silica (pH of the last washing: 6-7) before adsorption. Adsorption of the metal was done by passing 25mL of 100ppm cadmium and lead solutions (pH 5), prepared using AAS Metal Standard (Merck) diluted using deionized water, to the column with a flow rate of 1mL/min. Desorption of the adsorbed metal in the silica was done by washing the column with 5mL of either 0.1 M HCl or 1 mM EDTA followed by 15mL of deionized water (pH of last washing: 5-6). The modified silica gel in the column was used three times, repeating the desorption step after each adsorption. The filtrates, after adsorption, were collected and analyzed for the concentration of the heavy metal left using flame AAS after each cycle. The washings, after each desorption step, were also collected and analyzed by flame AAS to calculate the amount of the heavy metal desorbed.

Characterization. Differential Scanning Calorimetry was performed on the samples using TA Differential Scanning Calorimeter Q10. The silica samples were heated from ambient temperature to 500^{O}C at a rate of 10^{O}C/min. The infrared spectra were recorded using IR-Prestige 21 Fourier Transform Infrared Spectrophotometer (Shimadzu) between 4000 and 500 cm^{-1} with KBr as background. Scanning Electron Microscope/Energy Dispersive Using X-Ray (SEM-EDX) analysis was done on the samples using Philips XL 30 Field emission scanning electron microscope/ Energy dispersive x-ray analyzer (FESEM/EDX).

RESULTS AND DISCUSSION

1,10-Phenanthroline (phen) is a hetero-aromatic compound, and as such, is likely to react with alkali metals producing a charge-delocalized organoalkali compound. Poly-nuclear aromatic haydrocarbons react with alkali in strongly donor ethers, the reaction consisting of an electron transfer from the metal to the lowest vacant π-molecular orbital (Coates et al., 1965). Though the metal cations and hydrocarbon anions exist mainly as ion-pairs, the alkali metal atom is not associated with any particular carbon atoms since the negative charge is spread over the whole of the extended π -orbital involved (Coates et al., 2006). With the nucleophilic ring, nucleophilic substitution on the alkyl halide functional group on the surface of the silica is proposed. One possible reaction is shown in Figure 1.

Characterization. It was observed that the white chloropropyl-silica turned to pale yellow powder at the end of the reaction with phenanthroline. Aside from the observed color change, FTIR, DSC and SEM-EDX were used to confirm the success of the surface modification using phenanthroline. The results are shown in Figures 2A and 2B (for FTIR), Figures 3A and 3B (for DSC) and Table 1 (for SEM-EDX).

The group of small peaks found in the region 1350-1950 (Fig. 2B), which is not present in the silylated silica spectrum (Fig 2A), could be the representative peaks for the phenanthroline ring: C=C stretch of aromatic

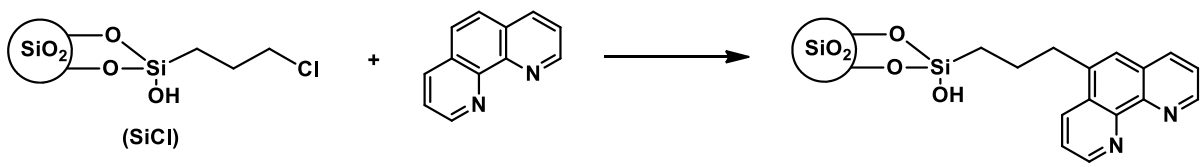

Figure 1. *Modification reaction of chloro-functionalized silica gel with phenanthroline.*

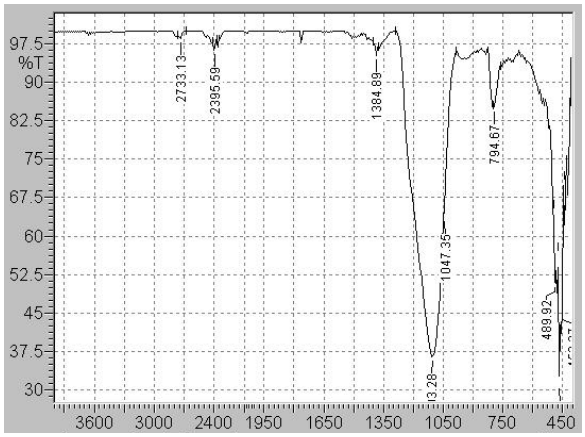

***Figure 2A**. FTIR of silylated silica.*

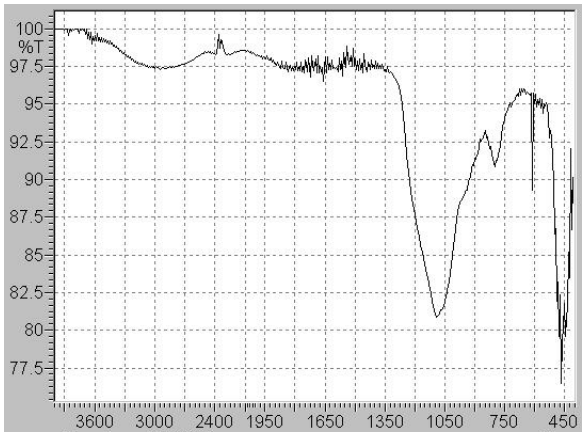

***Figure 2B**. FTIR of Phen-Si.*

rings at 1500 and 1600 cm^{-1} and C-H stretch of aromatic rings at 3000-3100 cm^{-1} (Silverstein et al., 2005). The absorption bands are not well defined since silica is the abundant material in the sample and the silane peaks obscured the peaks of the relatively small amount of phenenthroline on the surface.

A sample of silica gel with phenanthroline physically adsorbed (Fig. 3A) and Phen-Si (the phenanthroline-modified silica gel in Fig. 3B) were both subjected to DSC analysis. An

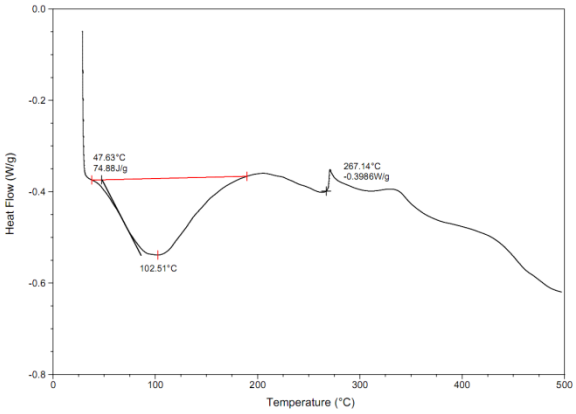

***Figure 3A**. DSC of silica with adsorbed phenanthroline.*

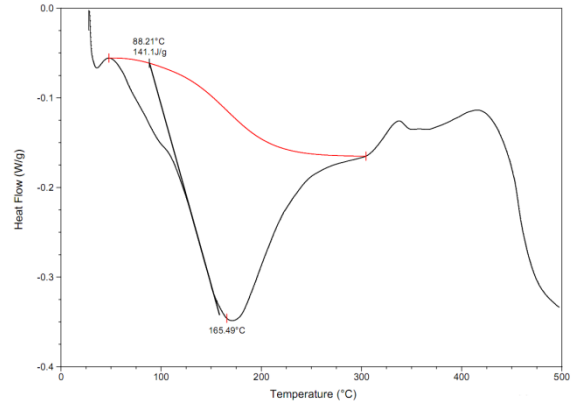

***Figure 3B**. DSC of Phen-Si.*

increase in the phase change temperature peak of Phen-Si (165.49 °C) compared to that of silica gel with physically adsorbed phenanthroline (102.51 °C) could be attributed to the additional energy needed to break the covalent bond of phenanthroline to silica.

Elemental analysis using Scanning Electron Microscope/Energy Dispersive X-Ray Fluorescence (SEM-EDX) confirmed the presence of N, coming from the phenanthroline ring, on the surface (Table 1).

Table 1. SEM/EDX – Quantitative (weight %)

	Si	O	N	Cl	K
silylated silica	39.85±4.77	57.40±5.47	0	2.75±0.72	0
phen-modified silica	40.57±0.85	44.25±0.14	1.93±0.27	1.34±0.09	11.91±1.09

The product was subjected to Soxhlet extraction with methanol to remove the potassium metal used. Since potassium was still detected, longer Soxhlet extraction will be explored in future experiments.

Heavy Metal Uptake. *Equilibrium Method.* The capability of the modified product to uptake heavy metals in solution was determined using the equilibrium method. Figure 4 and Table 2 show that the maximum uptake of Phen-Si was 91.89 mg Pb/g silica and 93.06 mg Cd/g silica. However, Table 2 shows that Pb was more efficiently adsorbed from solution (with high % metal adsorbed of around 80 % to 95 % in both high and low concentrations of 5 to 200 ppm) compared to Cd (with 0 % to around 33 % at the lower 5 to 50 ppm concentrations and increasing to 74 % to 93 % at the higher 100 to 200 ppm concentrations). This does not seem to agree with the known thermodynamic overall formation constants (Padmaja et al., 1990) of the aqueous Pb-phenanthroline complexes: log β1 = 2.872, log β2 = 6.498, which are less than the β's of aqueous Cd-phenanthroline complexes: log β1 = 4.912, log β2 = 9.007, log β3 = 11.213, unless there are kinetic factors involved. These β's are for the soluble complexes, while the study deals with complexes of the metal with a ligand attached to a solid phase. The heterogeneous nature of the interaction might also affect the equilibria.

Heavy Metal Uptake. *Dynamic Method.* The possibility of reusing the modified silica was explored in the dynamic method using 0.1 M HCl or 1mM EDTA to desorb the metal that

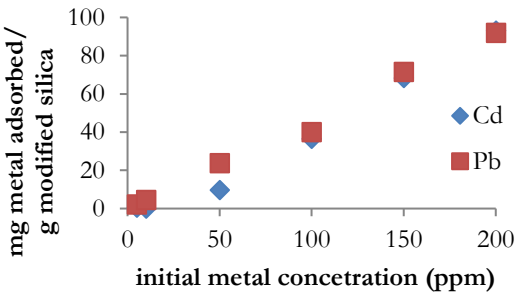

Figure 4*. Cd and Pb Adsorption (Equilibrium Method)*

the modified silica had adsorbed. The results of the dynamic method for both metal ions (Tables 3A and 3B) seem more consistent with the β's of the aqueous metal-phenanthroline complexes. Around 70 % of the initially adsorbed Cd was retained by Phen-Si after 3 cycles (each cycle consisting of passage of 100 ppm metal solution followed by a washing or desorption), but none of the initially adsorbed Pb was retained, after 3 cycles, by Phen-Si. Pb (II) has no d electrons in the valence shell, hence the small extent of overlap of metal-ligand orbitals leads to the formation of weak complexes which may become dissociated, the dissociation being much faster than formation (Padmaja et al., 1990). On the other hand the Cd (II) ion has filled d orbitals which make possible dπ-pπ interaction with the ligand (Padmaja et al., 1990).

CONCLUSIONS

Infrared spectroscopy, differential scanning calorimetry and SEM-EDX confirmed the

Table 2. Cd and Pb Adsorption (Equilibrium Method)

Initial Metal Solution Conc. (ppm)	% Cd Adsorbed from Solution	mg Cd Adsorbed per g Phen-Si	% Pb Adsorbed from Solution	mg Pb Adsorbed per g Phen-Si
5	17.8	0.45	85.2	2.14
10	0	0	91.8	4.52
50	33.7	9.62	95.7	23.70
100	74.6	36.49	81.6	39.95
150	92.2	68.36	95.2	71.41
200	93.2	93.06	92.1	91.89

Table 3A. Dynamic Adsorption of Cd.

Cd	% Cd Adsorbed from 100 ppm Solution*		mg Cd adsorbed per gram of Phen-Si**		% Cd Desorbed from Phen-Si***	
	0.1 M HCl	1mM EDTA	0.1 M HCl	1mM EDTA	0.1 M HCl	1mM EDTA
cycle 1	38.66	32.06	19.33	16.03	-	-
after wash 1	-	-	-	-	90.94	69.53
cycle 2	14.8	16.93	9.15	13.35	-	-
after wash 2	-	-	-	-	23.21	13.31
cycle 3	17.35	7.35	**15.72**	**15.26**	-	-
after wash 3	-	-	**13.51**	**13.41**	13.79	12.15

** the results of each cycle give % of metal adsorbed from the 100 ppm solution*
***amount is sum of adsorbed in present and previous cycle minus desorbed in previous wash*
****% metal desorbed calculated from AAS analysis of accumulated washings, per wash*

Table 3B. Dynamic Adsorption of Pb.

Pb	% Pb Adsorbed from 100 ppm Solution*		*mg Pb adsorbed per gram of Phen-Si**		% Pb Desorbed from Phen-Si***	
	0.1 M HCl	1mM EDTA	0.1 M HCl	1mM EDTA	0.1 M HCl	1mM EDTA
cycle 1	58.51	40.09	29.26	20.04	-	-
after wash 1	-	-	-	-	100	71.72
cycle 2	24.14	11.48	12.07	11.41	-	-
after wash 2	-	-	-	-	92.9	97.37
cycle 3	5.49	12.43	**3.72**	**6.51**	-	-
after wash 3	-	-	**0**	**0**	100	100

** the results of each cycle give % of metal adsorbed from the 100 ppm solution*
***amount is sum of adsorbed in present and previous cycle minus desorbed in previous wash*
****% metal desorbed calculated from AAS analysis of accumulated washings, per wash*

successful modification of silica surface with phenanthroline. Initial studies on the uptake of cadmium and lead using equilibrium and dynamic methods at pH 5 show its possible application for wastewater treatment. However, additional studies should be done to improve the metal uptake and reusability of the modified silica gel.

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