Report as of FY2006 for 2006DC76B: "Silica and Siliceous Surfaces as Host for Hazardous Metals in Water"

Publications

Project 2006DC76B has resulted in no reported publications as of FY2006.

Report Follows

Silica and Siliceous Surfaces as Hosts for Hazardous Metals in Water

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Silica and Siliceous Surfaces as Hosts for Hazardous Metals in Water

Executive Summary

Systematic studies of the uptake of Cu and Pb from dilute aqueous solutions showed that the sorption of these ions on silica gel reached constant levels in less than two hours, indicative of the establishment of equilibrium. Consistent with this observation, the uptake gradually decreased with increasing temperature. Observed increase in uptake at higher pH was also in agreement with equilibrium constant expressions. Dissolved Pb was sorbed in preference to Cu. The effects of pre-treatment of silica gel on the sorption of Pb and Cu could be summarized by the following sequence:
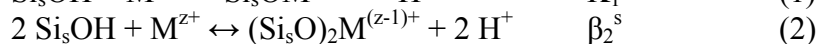$HNO_3 = HCl = H_2SO_4 << H_2O << NH_4OH/NaNO_3 < NH_4OH$
The use of silica gel with a larger value of specific surface area associated with narrower pores caused a slight decrease in the uptake of Cu and Pb. Dissolution of silica from the sorbent, unlike the sorption of Cu and Pb, was kinetically controlled. Thus, the extent of silica dissolution was observed to grow with increases in time, temperature, and specific surface area of the silica gel.

Introduction

Sorption of polyvalent metal ions on siliceous surfaces is of great importance to water quality. For instance, if such sorption takes place on rocks or soils bordering a contaminated stream, it can facilitate removal of dissolved hazardous species such as Pb, Cr, Cu, Ni, Hg, U, or Ra ions from the water. On the other hand, sorption of such ions on small suspended particles in the water, such as corrosion products in water distribution systems, can facilitate the transport of hazardous species and reduce the efficiency of household filters in removing them from drinking water (Senftle *et al.*, 2007). Many studies of the applied aspects of the sorption of metal ions on the surfaces of siliceous solids (e.g., silica gel) have been performed. However, much work remains to be done in order to provide accurate models of the extent of sorption and its effects on water quality in contaminated environmental streams and water distribution systems.

Sorption of various metal ions on siliceous surfaces as a function of pH was characterized and the relative tendency of various ions to undergo sorption was established. The results were expressed in terms of models that describe the sorption equilibria of metal ions on siliceous surfaces in terms of complex formation between the metal ions and the surface silanol groups. These models assign equilibrium constants to such complex formation processes (Schindler *et al.*, 1976). These models account for the strong pH dependence of the extent of sorption of a given metal ion on a siliceous surface.

$$Si_sOH + M^{z+} \leftrightarrow Si_sOM^{(z-1)+} + H^+ \qquad K_1^s \qquad (1)$$
$$2\,Si_sOH + M^{z+} \leftrightarrow (Si_sO)_2M^{(z-1)+} + 2\,H^+ \qquad \beta_2^s \qquad (2)$$

Si_sOH denotes a surface-bound silanol group, and K_1^s and β_2^s are equilibrium constants. According to such models, the surface-bound silanol group Si_sOH behaves as a ligand similar to HOH, and the extent of sorption varies between 0% and 100% of the surface capacity (reflecting the number of surface-bound silanol groups) over a narrow pH range. For instance, in the cases of Cu^{2+} and Pb^{2+}, this pH range is between about 4 and about 7, with the extent of sorption reaching 50% of ultimate capacity around pH 6.

However, such simple reaction schemes are not sufficient to account for all aspects of the sorption of metal ions from solutions, especially when such solutions contain constituents that form insoluble precipitates or complexes with the metal ions, or when the siliceous sorbent had been pre-treated with solutions containing such constituents. For instance, in the case of radium ions, very different results were obtained for the extent of sorption on fine quartz grains and also for the extent of desorption of Ra into EDTA solutions depending on whether these grains had been pre-washed with HCl or with H_2SO_4 (Nirdosh *et al.*, 1987). Chelating agents such as EDTA, poly(ethylene amine) and N-[-3-(trimethoxysilyl) propyl]-ethylenediamine were found to have large effects on adsorption/desorption equilibria whether such reagents were present in the solution or on the siliceous surface (Nirdosh *et al.*, 1987; Ghoul *et al.*, 2001; Chiron *et al.*, 2003). Other studies on the sorption of radium ions also showed that differences in the nature of the siliceous sorbent were also very important (Ames *et al.*, 1983). In addition to the thermodynamic characteristics of silica-metal system, various system parameters also affect the sorption kinetics. For instance, as metal concentrations are decreased, charge

reversal occurs and a longer period of time is required for the system to reach equilibrium (Vithayaveroj *et al.*, 2003).

The present study was intended to explore in a systematic manner the effects of system parameters, including contact time, temperature, pH, specific surface area, weight-to-volume ratio, and pre-treatment of the sorbent in various environments, on the sorption of Cu and Pb ions on silica surfaces. In order to minimize the effects of uncontrolled impurities, pure silica gel was used as the sorbent.

Experimental

Combined solutions of copper and lead were prepared by dissolving appropriate amounts of copper acetae dihydrate, $Cu(CH_3COO)_2 \cdot 2H_2O$, and of lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$, in de-ionized water. The pH of the combined copper/lead solutions usually did not require adjustment to bring it 5.0 ± 0.1. Whenever necessary, a slight adjustment with acetic acid was used to bring it to within this range. In several experiments, the pH of the combined solution was brought to 8.0 ± 0.1 using sodium acetate. The reaction vessels consisted of 60-mL polyethylene bottles. The sorbents used in the experiments consisted of two varieties of silica gel. The sorbent most commonly used was silica gel, Merck, grade 10184, 7-230 mesh, 100Å pore size, Sigma-Aldrich 403601-100G, Batch # 10203AO, surface area 300 m^2/g. The other sorbent was silica gel, Merck, grade 10180, 70-230 mesh, 40Å, Sigma-Aldrich 403563-100G, Batch # 09018CD, surface area 750 m^2/g, distinguished from the former type of silica gel by having smaller pores and a larger surface area. Samples of the two types of silica gel were dissolved in warm dilute solution of HF and analyzed to determine the concentration of impurities using a Perkin-Elmer Plasma 400 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer). The results of the analysis are shown in Table 1.

Table 1
Impurity Content of Silica Gel Sorbents

Impurity	Concentration, mg/kg	
	Merck grade 10184, 300 m^2/g	Merck grade 10180, 750 m^2/g
Ca	782	563
Na	358	558
Al	242	<10
Mg	113	69
Ti	75	5
Pb	<60	<100
K	37	20
Cr	20	20
Fe	11	<10
Ni	5	4
Cu	1	<2
Zn	1	1
Mn	<1	<1

Sorbent powders were used without pre-treatment or following a pre-treatment with de-ionized water, an acidic solution or a basic solution. The pre-treatment consisted of rotating a 5-g sample of the grade 10184 (300 m^2/g) silica gel at 30 rpm for 50 hours with one of the following aqueous phases: de-ionized water, 2 M H_2SO_4, 4 M HCl, 4 M HNO_3, 4 M NH_4OH, or 4 M NH_4OH + 3 M $NaNO_3$. Each of the pre-treated samples was filtered using grade 42 Whatman filter paper. The solid accumulated on each filter paper was washed with 500 mL of de-ionized water. The final pH of the wash water was 5 in the cases of the samples pre-treated with H_2SO_4, HCl, or HNO_3 and 9 in the cases of the samples pre-treated with ammonia solutions. The last stage of the pre-treatment consisted of air-drying the samples at room temperature.

In each of the sorption experiments, a quantity of 0.5 g or 1.0 g of an as-received or pre-treated sorbent was placed in a polyethylene bottle, together with 50 mL of the combined Cu-Pb solution. Mixing was performed using either a TCLP rotator, operated at 30 rpm, or a magnetic stirrer. Contact times ranged between 2 and 240 hours. Temperatures varied between 1.5 and 40 ^{o}C. All experiments at temperatures other than ambient were carried out using a magnetic stirrer/hot plate. Experiments at a low temperature were conducted by placing the beaker containing the sorbent powder and the test solution within a larger beaker filled with ice water. At the end of each experiment, the bottle was removed from the rotator or stirrer. The mixture was filtered through a filter paper with very fine (2.5-μm) pores (Whatman grade 42), and the filtrate was collected. The solid sorbent accumulated on the filter was washed with 100 mL of de-ionized water, and the spent wash solution was collected for analysis. The starting solution, the filtrate and the used wash solution were analyzed for Cu, Pb and Si. The sorbent was then rotated with 10 mL of 0.1 M HCl for 16 hours, and the eluate was filtered through Whatman grade 42

filter paper and collected for analysis. Following the elution, the sorbent was washed with a second volume of 10 mL of 0.1 M HCl. The spent wash solution was then combined with the original eluate, and the combined 20 mL of acidic solution was analyzed. This procedure allowed determination of the amount of the amount of copper and lead adsorbed on the sorbent in two independent ways. One method was based on the subtraction of amounts of these elements in the filtrate and the de-ionized water wash from the corresponding amounts of these elements in the starting solution which was contacted with the silica gel. The other method was based on the determination of the amounts of Cu and Pb in the combined acidic eluate and acidic wash solution. In addition to the amounts of Cu and Pb sorbed on the silica gel, the amount of SiO_2 dissolved during the contact with the copper/lead solution and the subsequent water wash was also determined. The analysis of Cu, Pb and Si in the solutions was performed using a Perkin-Elmer Plasma 400 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometer). The results of the Cu and Pb analysis were expressed in terms of the percentage of Cu or Pb initially present in the test solution that was taken up by the sorbent during the test period. The results of the Si analysis were expressed in terms of the percentage of the weight of the sorbent that was dissolved during the test period.

Five sets of sorption experiments were performed. The experimental conditions used in the experiments included in each test are summarized in Table 2.

Table 2
Experimental Conditions

Set	Sorbent			Starting solution				Temper-ature, ^oC	Contact time, hours	Mixing method
	Material	Pre-treatment	Weight, g	Cu conc., mg/L	Pb conc., mg/L	pH	Volume, mL			
1	Merck 10184, 300 m^2/g	DIW	0.5,1	5,10	5,10	5	50	20	2,6,24, 72,240	TCLP rotator
2	Merck 10184, 300 m^2/g	DIW	0.5	10	10	5,8	50	1.5,20, 40	6,24	Magnetic stirrer
3	Merck 10184, 300 m^2/g, Merck 10180, 750 m^2/g	DIW,2M H_2SO_4, 4M HCl, 4M NH_4OH, 4MNH_4OH +3M $NaNO_3$, 4M HNO_3	0.5	10	10	5	50	20	6,24	Magnetic stirrer
4	Merck 10184, 300 m^2/g, Merck 10180, 750 m^2/g	DIW,2M H_2SO_4, 4M HCl, 4M NH_4OH, 4MNH_4OH +3M $NaNO_3$, 4M HNO_3	0.5	10	10	5	50	20	6,24	TCLP rotator
5	Merck 10184, 300 m^2/g	DIW,2M H_2SO_4, 4M NH_4OH, 4MNH_4OH +3M $NaNO_3$	0.5	10	10	5	50	20	6,24	TCLP rotator

Results

The results of the five sets of experiments outlined in Table 2 are shown in Tables 3-7, respectively.

The sorbent used in the first set of experiments (Table 3) was Merck grade 10184 silica gel (300 m^2/g) without any pre-treatment.

Table 3

Effects of time, solute concentration, solute concentration, and mass of sorbent on the sorption of Cu and Pb on silica gel

Amount of sorbent, g	Concentration of initial solution, mg·L^{-1}		Time, hr	Amount of metal ion sorbed, %				Amount of silica dissolved, %
	Cu	Pb		Based on subtraction		Based on elution		
				Cu	Pb	Cu	Pb	
0.5	5	5	2	75.2	65.6	71.8	92.8	0.225
0.5	5	5	6	74.8	66.8	79.0	99.6	0.411
0.5	5	5	24	75.2	66.4	80.2	91.4	0.627
0.5	5	5	72	74.0	66.0	100.0	100.0	0.753
0.5	5	5	240	77.2	68.0	100.0	78.0	1.162
0.5	10	10	2	59.6	88.0	44.0	57.3	0.201
0.5	10	10	6	48.8	83.4	30.5	33.3	0.394
0.5	10	10	24	49.4	82.8	49.9	61.9	0.614
0.5	10	10	72	49.0	82.4	38.5	42.6	0.674
0.5	10	10	240	57.2	85.6	69.0	90.0	1.068
1.0	5	5	2	77.6	66.4	6.8	6.4	0.225
1.0	5	5	6	78.8	67.6	55.6	40.8	0.291
1.0	5	5	24	78.0	66.8	49.6	44.4	0.413
1.0	5	5	72	78.0	66.8	89.2	86.0	0.428
1.0	5	5	240	78.0	67.2	92.4	88.0	0.287

The type of silica gel used in the second set of experiments (Table 4) was the same as the one used in the first set (Merck grade 10184, 300 m^2/g).

Table 4
Effects of temperature, pH, and time on the sorption of Cu and Pb on silica gel

Temperature, ^{o}C	pH	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		based on elution		
			Cu	Pb	Cu	Pb	
1.5	5.02	6.0	12.5	56.0	9.4	16.2	0.079
1.5	5.02	6.0	7.7	28.8	9.1	16.6	0.083
1.5	7.98	6.0	54.6	61.7	32.0	41.3	0.563
1.5	7.98	6.0	47.3	56.7	19.2	21.5	0.507
21.0	5.02	6.0	0	0	6.7	11.6	0.165
21.0	5.02	6.0	5.5	10.3	6.2	9.1	0.175
21.0	7.99	6.0	56.2	63.9	25.4	29.4	1.545
21.0	7.99	6.0	53.9	54.6	36.1	40.9	0.766
40.2	5.02	6.0	0	4.2	8.1	11.8	0.449
40.2	5.02	6.0	5.2	13.3	9.0	13.5	0.501
40.2	7.99	6.0	71.5	73.9	45.1	34.2	1.371
40.2	7.99	6.0	68.2	71.2	46.0	37.6	1.363
1.7	5.01	27.7	46.3	75.6	13.5	33.2	0.126
1.7	5.01	27.7	0	55.8	13.2	25.8	0.128
1.7	7.96	27.6	43.4	31.7	5.4	8.2	0.458
1.7	7.96	27.6	30.9	40.5	5.7	8.9	0.528
19.7	5.01	26.2	0	57.0	15.5	27.9	0.058
19.7	5.01	26.2	4.6	48.0	12.4	24.1	0.417
19.7	7.96	27.1	34.1	11.6	5.0	7.0	0.901
19.7	7.96	27.1	27.3	21.7	5.4	7.6	1.020
39.3	5.01	25.1	0	53.1	14.8	27.7	1.262
39.3	5.01	25.1	0	11.8	18.6	90.5	0.881
39.3	7.96	25.4	32.1	9.9	6.2	10.3	1.476
39.3	7.96	25.4	42.8	35.4	5.4	8.4	1.301

The third set of experiments (Table 5) examined the difference in sorption behavior between the two types of silica gel and the effects of various pre-treatments.

Table 5
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10184, 300 m^2/g	De-ionized water	6	71.0	86.5	49.9	77.0	0.415
Grade 10184, 300 m^2/g	De-ionized water	6	69.9	87.2	33.9	48.3	1.095
Grade 10180, 750 m^2/g	De-ionized water	6	79.9	90.7	40.9	64.3	0.319
Grade 10180, 750 m^2/g	De-ionized water	6	65.0	83.7	41.8	65.2	0.717
Grade 10184, 300 m^2/g	2 M H_2SO_4	6	44.3	64.8	21.0	37.5	0.167
Grade 10184, 300 m^2/g	2 M H_2SO_4	6	19.2	36.6	13.5	26.9	0.235
Grade 10184, 300 m^2/g	4 M HCl	6	29.4	38.6	13.2	24.3	0.116
Grade 10184, 300 m^2/g	4 M HCl	6	36.9	56.6	11.6	21.1	1.279
Grade 10184, 300 m^2/g	4 M NH_4OH	6	99.5	98.7	79.4	82.0	0.627
Grade 10184, 300 m^2/g	4 M NH_4OH	6	98.9	98.4	26.9	26.3	2.261
Grade 10184, 300 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	6	55.3	75.9	42.1	62.6	2.837
Grade 10184, 300 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	6	87.4	79.4	90.0	84.7	1.393
Grade 10184, 300 m^2/g	4 M HNO_3	6	24.0	45.0	14.8	27.5	0.218
Grade 10184, 300 m^2/g	4 M HNO_3	6	17.9	26.9	14.6	26.1	0.186
Grade 10184, 300 m^2/g	De-ionized water	24	64.1	79.5	36.0	50.1	0.920
Grade 10184, 300 m^2/g	De-ionized water	24	62.0	81.5	49.7	78.6	0.730
Grade 10180, 750 m^2/g	De-ionized water	24	51.4	77.0	45.5	68.6	0.759
Grade 10180, 750 m^2/g	De-ionized water	24	84.5	92.8	45.5	68.9	0.911
Grade 10184, 300 m^2/g	2 M H_2SO_4	24	93.5	93.2	15.3	28.5	0.400
Grade 10184, 300 m^2/g	2 M H_2SO_4	24	96.2	94.9	15.5	29.3	0.364
Grade 10184, 300 m^2/g	4 M HCl	24	15.6	30.4	14.6	25.3	0.285
Grade 10184, 300 m^2/g	4 M HCl	24	6.9	18.7	9.6	17.9	0.362
Grade 10184, 300 m^2/g	4 M NH_4OH	24	98.1	96.8	42.3	42.1	2.520
Grade 10184, 300 m^2/g	4 M NH_4OH	24	99.0	97.7	66.4	65.5	1.018
Grade 10184, 300 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	24	94.3	89.5	83.9	88.9	1.557
Grade 10184, 300 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	24	84.6	90.8	72.4	76.6	1.281
Grade 10184, 300 m^2/g	4 M HNO_3	24	97.6	96.6	15.4	27.0	0.340
Grade 10184, 300 m^2/g	4 M HNO_3	24	39.7	58.4	15.5	28.8	0.466

The fourth set of experiments (Table 6) was similar to the third set, except that the mixing of the sorbent with the starting solution was performed using the TCLP rotator instead of a magnetic stirrer.

Table 6
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10184, 300 m^2/g	De-ionized water	6	65.8	89.3			0.451
Grade 10184, 300 m^2/g	De-ionized water	6	61.1	87.1	61.8	81.3	0.441
Grade 10180, 750 m^2/g	De-ionized water	6	55.7	83.3	53.3	77.4	0.610
Grade 10180, 750 m^2/g	De-ionized water	6	54.5	84.4	54.0	79.6	0.640
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	6	15.1	41.6	17.9	31.1	0.263
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	6	17.0	38.0	18.3	30.5	0.265
Grade 10184, 300 m^2/g	4 M HCl	6	19.5	34.3	14.5	24.0	0.242
Grade 10184, 300 m^2/g	4 M HCl	6	17.4	27.4	14.2	23.1	0.231
Grade 10184, 300 m^2/g	4 M NH$_4$OH	6	99.7	97.6	96.6	92.8	0.798
Grade 10184, 300 m^2/g	4 M NH$_4$OH	6	100.0	98.8	97.6	95.3	0.834
Grade 10184, 300 m^2/g	4 M NH$_4$OH + 3 M NaNO$_3$	6	89.3	97.2	87.2	100.0	4.482
Grade 10184, 300 m^2/g	4 M NH$_4$OH + 3 M NaNO$_3$	6	90.8	95.8	90.6	102.9	4.383
Grade 10184, 300 m^2/g	4 M HNO$_3$	6	21.6	35.8	17.1	28.1	0.282
Grade 10184, 300 m^2/g	4 M HNO$_3$	6	13.3	25.6	15.4	26.0	0.259
Grade 10184, 300 m^2/g	De-ionized water	24	62.5	84.4	66.7	90.3	0.721
Grade 10184, 300 m^2/g	De-ionized water	24	61.2	84.3	67.8	89.8	0.736
Grade 10180, 750 m^2/g	De-ionized water	24	56.0	81.3	57.3	82.9	0.976
Grade 10180, 750 m^2/g	De-ionized water	24	56.0	82.2	59.0	84.1	0.937
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	24	10.3	29.2	18.4	30.5	0.608
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	24	12.4	27.9	18.9	31.2	0.588
Grade 10184, 300 m^2/g	4 M HCl	24	8.4	20.0	14.2	24.4	0.454
Grade 10184, 300 m^2/g	4 M HCl	24	13.5	22.9	13.6	24.0	0.443
Grade 10184, 300 m^2/g	4 M NH$_4$OH	24	100.0	97.3	105.4	106.6	1.001
Grade 10184, 300 m^2/g	4 M NH$_4$OH	24	100.0	97.5	103.3	102.0	0.997
Grade 10184, 300 m^2/g	4 M NH$_4$OH + 3 M NaNO$_3$	24	87.2	96.1	86.5	103.7	1.731
Grade 10184, 300 m^2/g	4 M NH$_4$OH + 3 M NaNO$_3$	24	89.5	94.8	90.5	107.9	1.788
Grade 10184, 300 m^2/g	4 M HNO$_3$	24	18.8	36.6	19.4	33.9	0.449
Grade 10184, 300 m^2/g	4 M HNO$_3$	24	12.4	25.3	15.9	27.1	0.471
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	336	67.0	75.7	18.3	31.5	0.875
Grade 10184, 300 m^2/g	2 M H$_2$SO$_4$	336	15.3	43.2	20.3	33.7	0.822

The fifth set of experiments (Table 7) was similar to the fourth set, except that Merck grade 10180 silica gel (750 m^2/g) was used in all experiments.

Table 7
Effects of type and pre-treatment of silica gel and of time on the sorption of Cu and Pb

Type of silica gel	Pre-treatment of silica gel	Time, hours	Amount of metal ion sorbed, %				Amount of silica, dissolved, %
			Based on subtraction		Based on elution		
			Cu	Pb	Cu	Pb	
Grade 10180, 750 m^2/g	De-ionized water	6	52.1	70.9	28.6	52.7	1.249
Grade 10180, 750 m^2/g	De-ionized water	6	42.8	74.9	31.7	56.8	0.963
Grade 10180, 750 m^2/g	2 M H_2SO_4	6	35.0	77.9	26.5	47.4	0.943
Grade 10180, 750 m^2/g	2 M H_2SO_4	6	17.5	51.1	28.9	48.8	0.866
Grade 10180, 750 m^2/g	4 M NH_4OH	6	88.1	96.6	73.7	84.0	1.605
Grade 10180, 750 m^2/g	4 M NH_4OH	6	85.9	95.8	66.4	82.9	1.658
Grade 10180, 750 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	6	80.5	92.8	74.8	99.5	5.338
Grade 10180, 750 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	6	86.6	91.1	76.8	95.3	5.385
Grade 10180, 750 m^2/g	De-ionized water	24	79.9	83.0	31.2	57.4	0.980
Grade 10180, 750 m^2/g	De-ionized water	24	36.6	69.4	30.6	53.0	0.830
Grade 10180, 750 m^2/g	2 M H_2SO_4	24	19.5	44.8	26.4	47.4	0.881
Grade 10180, 750 m^2/g	2 M H_2SO_4	24	29.5	59.0	25.4	47.3	0.851
Grade 10180, 750 m^2/g	4 M NH_4OH	24	92.5	96.2	83.8	95.4	1.455
Grade 10180, 750 m^2/g	4 M NH_4OH	24	93.8	98.2			1.395
Grade 10180, 750 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	24	86.6	95.3		77.9	4.905
Grade 10180, 750 m^2/g	4 M NH_4OH + 3 M $NaNO_3$	24	90.8	96.4	36.9	50.4	5.077

Discussion

The results summarized in Tables 3-7 shed light on the effects of various parameters on the sorption of cupper and lead on silica surfaces. The results reported here exhibit considerable inconsistencies with respect to the quantitative determination of the uptake of copper and lead on the silica gel substrates. The results based on subtraction of the concentrations of these dissolved metals in the test solutions after contact with the silica gel from the initial concentrations are, in many cases, considerably different from those obtained by extracting the silica gel with acid following the sorption process. In addition, considerable disagreement has been observed between the two individual results when an experiment was carried out in duplicate. Discrepancies were also observed in some cases between the results of an experiment included in a given set and those of a similar experiment included in another set. Clear trends for the dependence of the uptake of Cu and Pb on specific parameters were difficult to discern, especially in the earlier experiments. Throughout the experimental program, efforts have been made to identify the causes of the discrepancies and eliminate or minimize them. Indications were obtained, for instance, that variation in the time interval between the end of the experiment and the analysis, the material of which the test vessels were made (CPE, LDPE, HDPE), the geometric shape of the vessel (wide mouth, narrow mouth), the number of test vessels placed on a single magnetic stirrer and the size of that stirrer, and the details of the techniques of filtration, washing the precipitate and its elution with acid, and the small number (one or two) of replicate experiments performed under each set of conditions might have contributed to the observed inconsistencies. In general, the results obtained based on subtraction (i.e., on differences in concentration between the original test solution and the same solution following contact with silica gel) appeared to be more consistent and more reliable than those based on elution by acid, especially in the earlier experiments. Standardization of the experimental procedures with respect to these initially overlooked factors was thought to account for the improvement of the consistency of the results observed in the more recent sets of experiments (see Tables 6 and 7). Improved control of these secondary parameters is necessary in order to make it possible to obtain more quantitative trends and conclusions.

Notwithstanding the limitations of the data, it was possible to establish a number of trends and to arrive at useful conclusions.

* At room temperature, a contact time as short as 2 hours between the silica gel and the solution is sufficient to remove most of the Cu and Pb from the solution under the conditions employed in the first set (Table 3) of the experiments (pH 5, 0.5 or 1 g of silica gel, 5 or 10 mg/L of Cu and Pb). Upon extending the contact time to periods as long as 240 hours, a statistically significant increase in the extent of sorption was not observed. Comparison between data obtained in 6-hour experiments and in 24-hour experiments included in the other sets has led to a similar conclusion. Of course, the uptake or sorption process is expected to take a certain amount of time, but the results of the present experiments indicate that the time required for this process to reach its maximum extent is smaller than 2 hours.

* Trends observed upon measuring the uptake of Cu^{2+} and of Pb^{2+}, respectively, on silica gel as a function of time, temperature, pH, etc., are generally similar, but, under the same conditions, the absolute extent of sorption of Pb^{2+} is usually larger than the extent of Cu^{2+} sorption. This observation is consistent with previous findings regarding the relative magnitudes of the equilibrium constants of sorption of these metal ions on siliceous surfaces (Saeki, 2006).

* According to the data (in particular, the more reliable data based on subtraction rather than elution) of the second set (Table 4), using a higher temperature within the range between 2 °C and 40 °C decreases the extent of Cu and Pb sorption. The temperature effect appears to be more noticeable at pH 5 than at pH 8.

* The decrease in Cu and Pb uptake upon increasing the temperature is consistent with the absence of an increase in uptake upon extending the contact time beyond 2 hours. Both observations indicate that the values obtained for the uptake of Cu and Pb under the conditions of the experiments reported here reflect sorption capacities under equilibrium conditions, which are expected to decrease with increasing temperature, rather than sorption rates, which are expected to increase with increasing temperature.

* Raising the pH of the solution enhances the uptake of Cu from the solution in 6-hour experiments as well as in 24-hour experiments (Table 4), as expected on the basis of equations (1) and (2). The same trend is observed in the 6-hour experiments on the sorption of Pb, but not in the corresponding 24-hour experiments. Upon prolonged immersion at pH 8, some Pb appears to de-sorb from the silica gel surface.

* According to the data of the fourth set (Table 6), the use of silica gel with a small pore size (40Å) and a correspondingly high surface area (750 m^2/g) is not more effective, and may actually be slightly less effective, in removing Cu and Pb from solution compared with the use of silica gel with a larger pore size (100 Å) and a smaller surface area (300 m^2/g). The same trend is observed upon comparing the results given in Table 6 with those shown in Table 7. This observation may be attributed to limited penetration of the solution containing the Cu or Pb ions into narrow pores, especially as regards the deep regions of such pores. The small diameter of such pores retards effective transport and replacement of solution depleted with respect to Cu and Pb within the pores by fresh test solution.

* The effects of pre-treatment of the silica gel sorbent by contacting it with various aqueous media have been explored in the experiments of the third, fourth and fifth sets (Tables 4, 5 and 6, respectively). Discounting a few obvious outliers (in particular, the subtraction-based data for 2 M H_2SO_4 in Table 5), the data show that the uptake of Cu and Pb is smallest in the cases of silica gel pre-treated with acids (HNO_3, HCl, or H_2SO_4), larger in the case of silica gel pre-treated with de-ionized water, and largest in the case of silica gel pre-treated with NH_4OH. These results generally agree with the model of Schindler *et al.* (1976) described above, which represents the sorption equilibria in terms of equations (1) and (2) above. Since the pre-treatment with acids generates a local low-pH environment around the surface, while pre-treatment with ammonia gives rise to a

high local pH, sorption on the ammonia-treated silica gel is much greater than on the acid-treated silica gel. Consistent differences among silica gel powders pre-treated with HNO_3, HCl, and H_2SO_4, respectively, were not observed. Silica gel pre-treated with de-ionized water exhibits an intermediate extent of Cu and Pb sorption because the local environment is near-neutral. Of course, the effective pH of the surface is not solely determined by the pre-treatment but is also influenced by the pH (originally 5) of the test solution. However, the acetate concentration in that solution (10 mg/L Cu introduced as copper acetate and 10 mg/L Pb introduced as lead acetate) is only $4.1 \cdot 10^{-4}$ M. This accounts for the observation that some Cu and Pb are sorbed even on the silica gel pre-treated in acid solutions, but the low concentration of acetate in insufficient to overwhelm the local pH resulting from the introduction of H^+ or OH^- ions into the surface sites during the preceding pre-treatment. It should be emphasized that following pre-treatment, the silica gel powders (5 g each) were washed with several portions of de-ionized water, and the total volume of wash water was 500 mL water. The final portion of wash water was near-neutral (pH = 5) in the cases of the powders pre-treated with acids, but was still basic (pH = 9) in the cases of those pre-treated with ammonia.

* High uptake of Cu and Pb is observed with silica gel samples pretreated with 4 M NH_4OH alone or with 4 M NH_4OH + 3 M $NaNO_3$, but the extent of sorption in the case of the combined solution is slightly smaller. It was noted (Patrick and Barclay, 1925; Simmons, 1981) that polyvalent metal ions such as Cu^{2+} can be effectively incorporated into the surfaces of silica gel or porous high-silica, either through a single treatment with a solution of the ion of interest, or through a two-step process consisting of ion-exchange with an alkali ion such as Na^+ followed by immersion in a solution of the polyvalent ion. The two-step process was found to result in more effective sorption only when the polyvalent ion was loaded onto the siliceous surface from a neutral or acidic solution; the amount of Cu^{2+} taken up directly from an ammoniacal solution was similar to, or even slightly larger than, the uptake of Cu^{2+} in the two-step process. The present findings are in agreement with the reported observations. The slight reduction in uptake observed in the present studies upon using silica gel pre-treated with NH_4OH + $NaNO_3$ rather than with NH_4OH alone may be attributed to a greater reduction in the effective surface area of the silica gel due to corrosion when it is exposed to the former solution. Such enhanced corrosion is reflected in the larger concentrations of dissolved silica observed in the NH_4OH + $NaNO_3$ solutions following contact with silica gel compared with the corresponding concentrations in the NH_4OH solutions. In addition, $-Si-NH_2$ groupings may form a hydrogen-bonded ammoniacal layer on the siliceous surface. [A similar structure is formed with -Si-OH groups (Dove and Crerar, 1990; Dove and Elston, 1992)] Such a layer would tend to complex polyvalent ions such as Cu^{2+} and Pb^{2+}. In contrast, Na^+ ions bound to $-Si-O^-$ sites would compete against, and even repel, Cu^{2+} and Pb^{2+} ions.

* The extent of silica dissolution in the experiments exhibits consistent increase with increasing time, temperature, amount of silica gel, pH, and Na^+ concentration. The use of silica gel with a larger surface area also appears to result in a higher concentration of dissolved silica (Table 6). These findings indicate that under the conditions of the present experiments the dissolution of the silica gel, unlike the sorption of Cu and Pb, is

largely controlled by kinetics rather than by equilibrium solubility. As in the case of Cu and Pb sorption, within the uncertainty of the experiments performed here no consistent differences were observed among the silica dissolution data obtained in HNO_3, HCl, and H_2SO_4 solutions, respectively. As noted above, the extent of silica dissolution is larger in $NH_4OH + NaNO_3$ solution than in a solution of NH_4OH. This finding can again be interpreted according to the model of Dove et al. (Dove and Crerar, 1990; Dove and Elston, 1992). According to this interpretation, ammonia, like water, forms a hydrogen-bonded layer which covers the siliceous surface and protects it against hydrolysis, while Si-O-Na^+ groups are perpendicular to the surface and allow water to penetrate, hydrolyze the siliceous surface, release dissolved silica, and transport this silica to the bulk solution (Wickert *et al.*, 1999; Pulvirenti *et al.*, 2006).

* The low content of impurities in the silica gel used in the study (Table 1) indicates that the findings truly reflect the properties of siliceous surfaces rather than the effects of minor components.

The study described above has led to the identification of a number of experimental issues involved in the characterization of the sorption of metal ions in silica gel and to the resolution of the majority of these issues. Further work is necessary in order to obtain an accurate and fully quantitative picture of all aspects of the sorption process so as to give proper consideration to such sorption in the analysis of issues of water quality in environmental streams and in drinking water systems.

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