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Colloids and Surfaces A: Physicochem. Eng. Aspects 320 (2008) 25–35

COLLOIDS AND SURFACES A

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Functionalized SiO_2 with N-, S-containing ligands for Pb(II) and Cd(II) adsorption

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Received 15 November 2007; received in revised form 2 January 2008; accepted 3 January 2008
Available online 8 January 2008

Abstract

Five novel organosilicas SiO_2-L have been prepared by grafting organic ligands (L) bearing thiazolidine (TAMS), thiazole (TIMS), imidazole (DTIMS), mercaptopropyl (DETATS) or pyridine (DETAPS) functional groups. The SiO_2-L materials have been evaluated for their capacity for Pb^{2+} and Cd^{2+} uptake from aqueous solution as a function of the pH. The present data demonstrate that the grafting of the silica may result in significant enhancement of metal uptake by the SiO_2-L adsorbent. Noticeably, multifunctional ligands such as DTIMS and DETAPS, have exhibited the highest metal capacity between the studied materials. Significant metal uptake was observed for both Pb and Cd on those materials independent of pH. The adsorption data have been analyzed based on a surface complexation model (SCM) with FITEQL by considering the grafted ligands as additional surface sites. FT-IR data are provided in support of this approach. Based on the theoretical speciation results, we may conclude that the determining factors for the metal uptake by the modified silica are the following three: (a) the presence or absence of protonable groups on the ligand determines the pH-edge profile, (b) the complexing affinity of the particular ligand towards each metal, and (c) the amount of grafted ligand on the silica surface. The interplay of these factors will determine the final maximum loading capacity of the sorbing material. Both the nature of the ligand as well as its surface concentration are of equal importance for the sorbing capacity of the material.

Keywords: Modified SiO_2; Cd; Pb; Metal uptake; Speciation; FITEQL; Surface complexation model; FT-IR

1. Introduction

The presence of heavy metals in polluted waters is a matter of environmental concern due to their acute and long-term toxicity. Cadmium, copper, lead, mercury, nickel and zinc are considered the most hazardous and are included on the US Environmental Protection Agency's (EPA) list of priority pollutants. Among the different techniques applied to the removal of heavy metal ions from solution, the metal adsorption onto solid supports such as activated carbon, zeolites, clays and metal oxides has been used [1]. However, the efficiency and selectivity of these solid supports are quite low and improved metal absorbents have been prepared by coupling chelating ligands to support matrixes. The organic functionalities typically serve to form complexes with heavy metal ions, and the solid support allows easy removal from the liquid waste for example by filtration. Various functionalized absorbents with heavy metal complexing ligands have been reported [2,3] based mainly on polymers [4,5], clays [6,7], silica gel [8] and mesoporous silica [9,10].

Modified silica gel with various organic compounds has attracted a great attention for metal uptake [11]. The silica support is chosen for its high surface area, high mechanical and thermal stability. In addition, it is easily modified [12], by reacting with organofuctionalized silanes through its surface silanol groups. These covalently bonded organic groups are highly stable and resistant to removal from the surface by organic solvents or water. Further treatment is also possible in order to immobilise new molecules with a variety of other organic functions even more active as chelating agents.

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doi:10.1016/j.colsurfa.2008.01.007

Several ligands containing N or O donor atoms have been successfully immobilised onto silica and applied to heavy metal extraction and preconcentration. In this context, 5-formyl-3-(1′-carboxyphenylazo) salicylic acid-bonded silica gel [13] has been used for the quantitative adsorption of Cd(II), Zn(II), Fe(III), Cu(II), Pb(II), Mn(II), Cr(III), Co(II) and Ni(II) from natural aqueous systems at pH 7.0–8.0. 2,4-Dichlorophenoxyacetic acid [14] was applied to the separation and preconcentration of Cu(II), Cd(II), Ni(II) and Zn(II). 4-Amino-3,5,6-trichloropicolinic acid [15] has been used for the adsorption of Cu, Ni, Zn, and Cd metal ions from aqueous solutions at room temperature and exhibited maximum capacities at pH 4–5. 8-Hydroxyquinoline-modified silica gel has been used in the extraction of Cu(II), Cd(II),Co(II), Fe(III), Ni(II), Zn(II) and Pb(II) and has shown a higher capacity for copper ions. 1,8-Dihydroxyanthraquinone [16] anchored on silica gel has been prepared and used for the preconcentration of Pb(II), Zn(II) and Cd(II). Diethylenetriamine mono- and bis-salicyaldehyde and naphthaldehyde Schiff's bases onto silica gel have been used in the selective extraction or separation of Fe(III), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) [17].

In other works, chelating agents containing S in addition to N atoms were also immobilised onto silica and their capacities towards highly toxic heavy metals ions such as Hg(II), Pb(II) and Cd(II) were investigated. Benzimidazol-2-ylmethylthioether immobilised onto silica exhibited high selectivity in the removal of copper from an aqueous solution containing a mixture of divalent metal anions Cu(II), Ni(II), Cd(II), Co(II) and Zn(II) [18]. 2-Aminothiazole [19] was applied to the selective adsorption towards mercury(II) ions when measured by both batch and chromatographic column techniques. 2-Mercapto-imidazole [20]-modified silica exhibited high selectivity in the removal of mercury(II) ions from a mixture of metal ions in aqueous solution. 2-Mercapto-5-phenylamino-1,3,4-thiadiazole [21] was applied to preconcentration of Pb(II), Cu(II) and Cd(II). Thiol functionalized silica such as aminoethanethiol [22] and aminoethylthioethanethiol [23] have shown high capacities for the extraction of Pb(II), Cd(II) and Hg(II) from aqueous solutions.

The aforementioned works show that improved materials can be obtained by immobilising metal chelating functionalities onto matrices. In this context of equal importance is the theoretical understanding of the observed phenomena and physicochemical mechanisms. This is of intermediate relevance since it allows more improved materials to be designed.

This paper reports the immobilisation of a series of molecules containing N, S atoms onto silica gel. The obtained materials were characterised and their adsorption properties for Pb and Cd ions were determined as a function of pH of the aqueous solution. Finally, the observed metal sorption onto modified silica was simulated using a surface complexation model (SCM) and the intrinsic stability constants of the various surface complexes were determined.

Table 1
Specific surface area and surface site density of SiO_2

SiO_2-specific surface area ($m^2\ g^{-1}$)	254 (BET)
SiO_2 surface site density (sites nm^{-2})	4.7 (pH titration) or 2000 mmol/kg

2. Experimental

2.1. Chemicals and materials

All reagents were purchased form Aldrich Chemical Company and were used as received. Solvents were purchased from Merck and dry toluene was obtained by standing over preactivated 4 Å molecular sieves.

Silica (Kieselgel 100) with particle size in the range of 63–200 μm was purchased from Merck and was activated at 200 °C for 12 h before use. The specific surface area, as determined by the BET method is 254 $m^2\ g^{-1}$, while the SiO_2 surface sites density, determined by pH-titration was 4.7 sites nm^{-2}, listed in Table 1.

All metal solutions were prepared with analytical grade chemicals and ultra pure water (Milli-Q Academic system) with a conductivity of demineralized water 18.2 μS cm^{-1} and degassed prior to use. Stock solutions of $Pb(NO_3)_2$, and $Cd(NO_3)_2$ (Aldrich > 99.5%) were prepared at a concentration of 3 mM and kept in a polyethylene bottle at pH value <2.

The working solutions of metal ions were made by suitable dilution of stock solutions with a buffer system of 10 mM *N*-morpholino-ethanesulfonic acid (MES) and 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES). This system presented a significant buffer capacity at range pH 4–7.5 with an average deviation from the adjusted pH value <10%. The pH values were adjusted with small volumes of NaOH or HNO_3 (0.1 N). Screening experiments indicated that under the conditions of our experiments the buffer molecules caused no interferences on the adsorption phenomena [24].

2.2. Analysis and spectroscopy

Elemental analyses (C, H, N, S) were obtained using a PerkinElmer Series II 2400 elemental analyzer. FT-IR spectra were recorded using a Spectrum GX PerkinElmer FT-IR System with a DRIFT set-up.

Determination of metal concentrations in aqueous phase was carried out by anodic stripping voltammetry using a Trace Master5-MD150 polarograph by Radiometer Analytica as described earlier [24]. The measuring cells were borosilicate glass cell from Radiometer. The working electrode was a hanging mercury drop electrode (HMDE), with an Hg drop with 0.4-mm diameter generated by a 70-μm capillary. The reference electrode was an Ag/AgCl electrode with a double liquid junction. The counter electrode was a Pt electrode. Initially, before the stripping step N_2 gas (99.999% purity) was passed from the measuring solutions to remove any trace O_2. During this step the solution was under continuous stirring at 525 prm. During the stripping step the solution was not stirred. Square wave (SW) measurements were performed in the anodic direction, i.e. square wave anodic stripping voltammetry (SW-ASV), to quantify metal ions. Typically under our experimental conditions, 1.05×10^{-6} M $Pb(NO_3)_2$ in 0.01 M KNO_3 resulted in