



Calorimetric Approach for the Detection of Modified Silica Efficiency as Chelating Agent for Heavy Metal Ions

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Authors' contributions

This work was carried out in collaboration between both authors. Author YK designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author HA managed the analyses of the study. Authors YK and HA managed the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

Chelating molecules with carboxyhydrazide functional group was immobilised on silica surface. The functional group was covalently bonded to the silica surface by sequential reactions of silica with dibromobutane, malonic ester and hydrazine in different media. The grafting reaction was confirmed by elemental analyses and thermal stability analysis (TGA). The flow microcalorimeter (FMC) was used as an approach to assess the performance of modified silica sorbent toward heavy metal ions. The FMC results show that this modification enhances remarkably the silica ability to retain a series of heavy metal ions on its surface. The selectivity of adsorption on modified silica was determined and the strength of the chemical bonding between metal ions and modified silica was quantified.

Keywords: Flow microcalorimeter; silica particles; chelating molecules.

1. INTRODUCTION

The extraction of metal ions from their mother solutions is a common technique used to concentrate a solute or decontaminate a solution [1-3]. The basic principle is to transfer an ion from the aqueous phase to the active sites of the adjacent solid phase. Such transfer is not obvious without some acting driving forces. New types of sorbents are now under development to allow either more effective extractions or more selective ones. Specific adsorbent materials provide a selective extraction [4-6]. Silica based supports are successfully used as adsorbing agents, as they are mechanically stable, chemically simple and support heat treatment. However, in order to be quantitatively efficient and chemically selective, chelating agents should be loaded on silica surface. It is well known that chemisorption of the chelating molecules covalently grafted on silica surface provides immobility, mechanical stability and water insolubility, thereby increasing the efficiency of extraction [7]. The surface of silica is stamped by a characterized number of silanol groups. Nevertheless, silanols are poor ion-exchangers and have very low selectivity [1-4,8-11]. Therefore, silica modification is usually performed to obtain efficient sorbents with greater acceptable selectivity. Different modification routes with various numbers of steps have been used for loading the surface with specific organic compounds. A covalent bond between the silica surface and the organic compound (functionalized sorbent) offers the chelating molecules insolubility, immobilization and mechanical stability [5,6,8,9,12-15]. Suitably designed organic chelating group acts as ion-exchanger. Silanization is the most common way to functionalize silica surface among most numerous modification methods presented in the literature [10,11,16,17].

The measurement of the sorbent efficiency and/or its selectivity on the laboratory scale required calibration steps. It is often excessively material consuming and needs long and sophisticated detection methods [18].

Therefore in the present work we use a known modification method to synthesize chelating molecules on the surface of silica, in order to focus our attention on a new calorimetric approach providing a precise measurement of

the amount of adsorbed ions as well as the enthalpy of adsorption [7,12].

2. MATERIALS AND METHODS

2.1 Materials

The silica selected for this study was the pyrogenic Aerosil A130 (from Degusa-Evonik, Germany), a non-porous silica having a specific surface of $130 \pm 15 \text{ m}^2/\text{g}$. Its surface structure is quite well known with a relatively few reactive sites randomly distributed; it is generally considered as a plane at a molecular scale. Hydrochloric acid, sodium hydroxide, 1,4 dibromobutane, sodium, methanol and hydrazine hydrate were purchased from Sigma Aldrich (France) and used without further purification.

2.2 Methods

The chemical modification of silica was performed according to the procedure employed by Jal et al. (Fig. 1) [7,12].

Briefly, silica was first treated with 6 N hydrochloric acid, for 4 hours in order to remove contamination and regenerate its silanol surface groups. The conditioned silica was stirred with 2 N Sodium hydroxide for 10 hours using a magnetic stirrer, it was then washed with triply distilled water till the washing became non-alkaline. The alkali-treated silica was stirred with 1,4 dibromobutane solution (2 mL) in demineralized deionized water (100 mL) for 12 hours and then was filtered. The silica, as obtained, was then stirred with diethylmalonate (2 mL) in presence of sodium methoxide (prepared by dissolving 1 g of sodium in 50 mL of methanol) for 12 h. The final hydrazine terminated silica, which was obtained by using hydrazine hydrate under reflux for 4 h with constant stirring, was filtered, washed with ethanol and dried at 85-90°C for 4 hours.

2.3 Characterization

2.3.1 Thermal stability analysis (TGA)

The thermal stability analysis (TGA) was taken on Mettler Toledo Thermogravimetric 851e (Viroflay, France) in nitrogen atmosphere. The samples were heated in the 20-600°C temperature range at a heating rate of 10°/min.

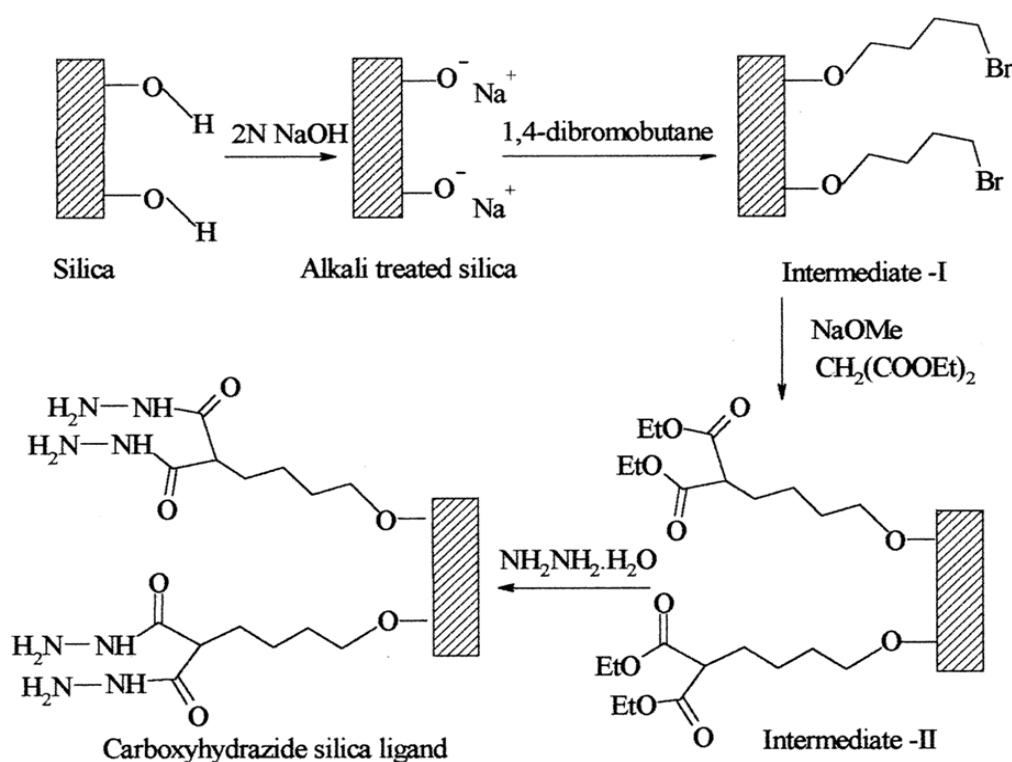


Fig. 1. Surface modification reaction of silica particles inspired from Jal et al. [7,12]

The grafting ratio was deduced according to the equation:

$$T = \Delta m_1 \times 10^3 / (m_{\text{sample}} - \Delta m_2) M_{\text{organic}}$$

Where the loss weight Δm_1 , Δm_2 are respectively the dehydration of the silica, and the decomposition of organic graft, m_{sample} is the mass of the sample, M_{organic} is atomic mass of organic graft.

2.3.2 Elemental analyses

The Elemental analyses were performed using Inductively Coupled Plasma (Service Central d'Analyse de Solaize, Villeurbanne, France). The grafted molecules per surface unit in nm² was deduced from the percentage of carbon, %C, according to the following equation

$$N_g = N_A \%C / n_c \cdot M_c \cdot S_0$$

Where n_c and M_c are the number and atomic mass of carbon contained in organic graft, S_0 is the specific surface area of the unmodified silica, and N_A is Avogadro number. The percentage of nitrogen can be calculated in the same way.

2.3.3 Calorimetry

A Flow Micro Calorimeter (FMC) developed by Microscal (London, United Kingdom) was used to

measure metal ions solution heat of adsorption on the silica. A schema of the measurement cell is presented in Fig. 2.

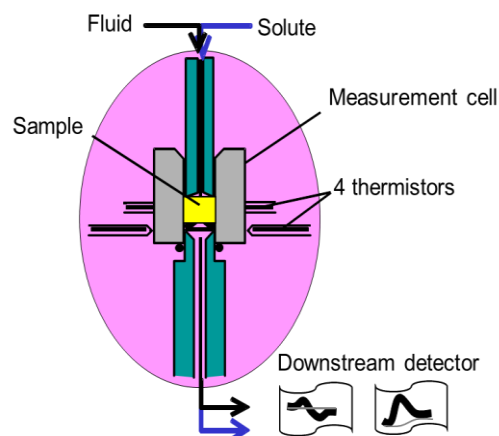


Fig. 2. Scheme for representing the FMC cell

The FMC was operated under a constant flow rate (3.3 ml/h) of carrier solvent, distilled water, at 25°C. In a pulse mode, a known amount of the solute dissolved in the carrier solvent was injected in the flow path through a calibrated sample loop. If any thermal exchange occurs when the solute comes into contact with the particles being studied, a peak was registered

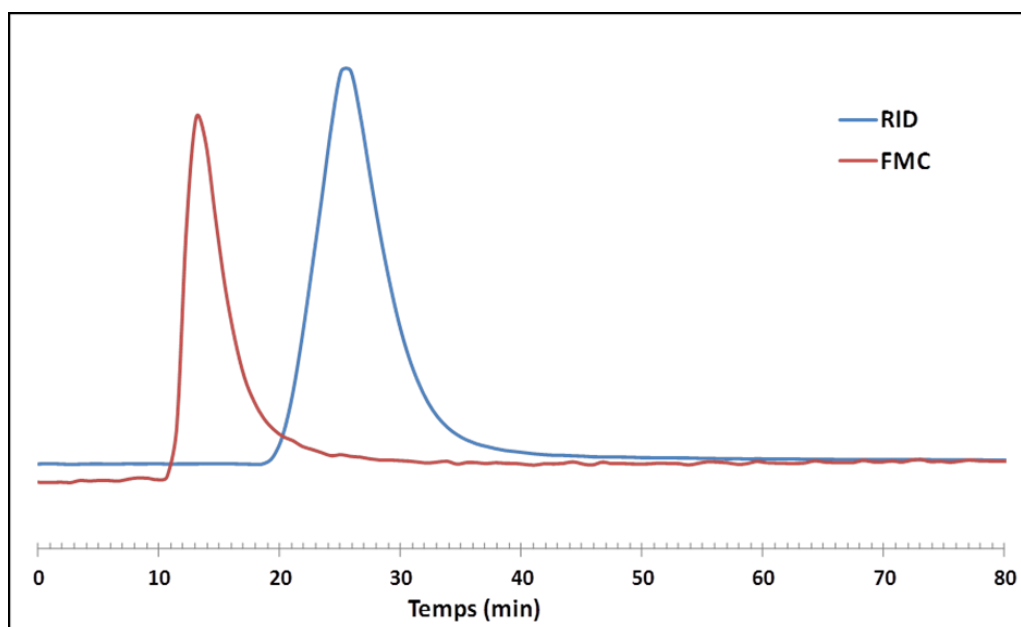


Fig. 3. Typical FMC and downstream detector peaks

(positive or negative corresponding to exo- or endothermic events respectively, as presented in (Fig. 3).

The adsorbed fraction of the solute, if any, was then detected by a downstream detector, a differential refractive index detector (RID-10A, Shimadzu) and UV detector. Metal ions solutions were injected through 5-100 μl sample loops. The solute concentration of each metal ion was fixed at 1×10^{-3} M. Results were averaged out of 5 measurements for each ion. The FMC principles and the experimental setup were described elsewhere [13,14,19,20]. In this paper only the positive exothermic event was observed reflecting the solute adsorption process.

3. RESULTS AND DISCUSSION

3.1 Thermal stability analysis (TGA)

The TGA results are presented in Fig. 4.

We can split the TGA into two temperature domains, below and above 200°C . The former is associated essentially with desorption of adsorbed water the latter is generally attributed to dehydration dihydroxylation in the case of pristine silica while, in the case of grafted silica, the decomposition of organic grafts comes into the mass-loss process. From the weight loss results above 200°C of the grafted silica presented in Table 1 we can calculate the grafting ratio (expressed in mol/g) and the grafts surface-concentration (molecule/ nm^2). Since

some weight loss of unmodified silica takes place in this same temperature range, we preferred to make the estimation of grafting ratio between two limits. For the upper limit we consider the whole weight loss (4.4%) as attributable to the grafted hydrazine, while for the lower one, we subtract from this amount the weight loss of the ungrafted silica sample in the same temperature range (1.5%). This gives a grafting content between 1.1 and 0.7 molecule/ nm^2 . Such ratio is very close to the saturation of the accessible silanols. In fact, it is accepted that the surface concentration of the free silanol groups ranges from 1.5 to 2.4 -OH/ nm^2 , the value of 1.1 -OH/ nm^2 has been even given for the number of OH groups very close to the surface [14,15,20,21].

Table 1. TGA results after silica modification

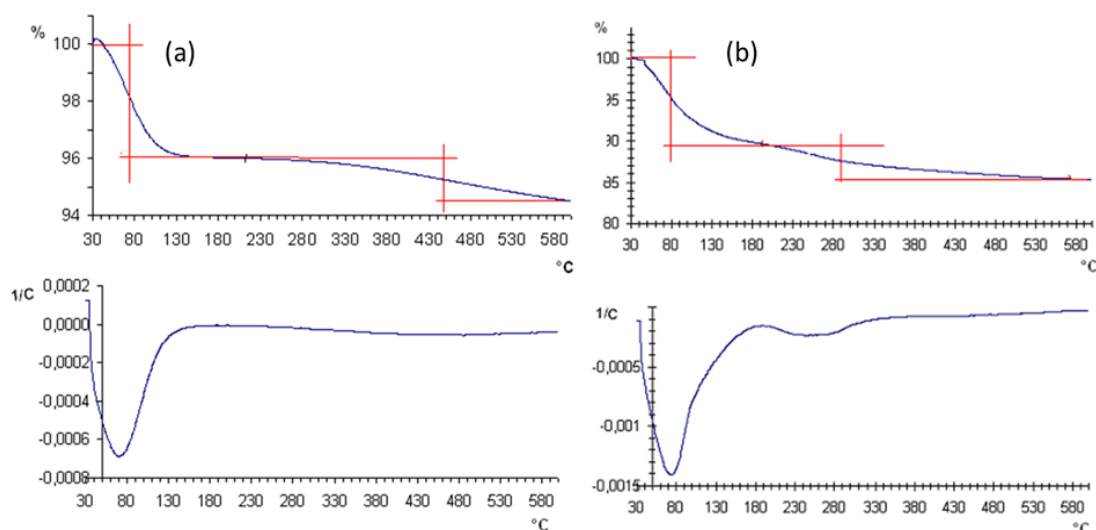
	Upper estimation	Lower estimation
Weight loss, %	4.40	2.90
Hydrazine, mol/g. 10^4	2.40	1.60
Hydrazine molecule/ nm^2	1.10	0.70

3.2 Elemental Analysis

Elemental analysis of carbon (C) and nitrogen (N) elements were performed before and after silica modification by Hydrazine molecules. Results are collected in Table 2.

Table 2. Elemental analysis results after silica modification

	based on (C) content		based on (N) content	
	%	graft/nm ²	%	graft/nm ²
Silica				
Un-grafted silica	<0.30	-	<0.10	-
NH ₂ -NH ₂ -terminated Silica	1.06	0.60	0.63	0.50

**Fig. 4. Thermal stability analysis (TGA) curves (weight loss % in function of the temperature variation) results and their derivatives for (a) the silica and (b) the grafted silica in the 30-600°C temperature range****Table 3. Heat of adsorption and % of adsorbed ion per injection**

Adsorption efficiency	Metal ion		Ungrafted silica		Grafted silica	
	Oxidation number	Symbol	ΔH kJ/mol ± 8	% adsorption ± 3	ΔH kJ/mol ± 8	% adsorption ± 2
1	II	Pb	7	3	160	65
2	II	Cu	5	7	157	55
3	II	Ca	8	6	180	50
4	I	K	4	2	140	47
5	II	Zn	12	4	167	45
6	II	Ni	12	10	210	10

The presence of nitrogen after treatment is related to the success of the modification reaction. The graft surface concentrations calculated on the base of carbon content show a slightly higher value, 0.6 graft/nm², compared to the one deduced from nitrogen content, 0.5 grafts/nm². This indicates that a fraction of the grafts remains as ethoxy rather than hydrazine terminated. Furthermore, both values are much closer to the lower estimation, 0.7 graft/nm², given by TGA results, which indicates that part of the weight loss of the modified silica is effectively not associated with the graft decomposition but should be linked to the dehydration of silica surface.

3.3 FMC Results

Heat of adsorption was measured on modified and unmodified silica. The results are gathered in Table 3.

It appears clearly that silica modification increases not only the adsorption efficiency in comparison with unmodified one; it also enhances the surface selectivity of the adsorption process. Heats of adsorption as well as the amount of adsorbed ions are increased by one to two orders of magnitude. Heat of adsorption on modified silica is in the strong chemical bonding range (100 kJ/mol) while it is in

the range of weak physical-to-hydrogen bonding on unmodified silica. Strong chemical bonding does not seem to be the only factor controlling adsorption and selectivity of adsorption. All measured ions have more or less strong interaction with the silica surface. However, the efficiency of the adsorption (the adsorption %) are very different from 65 to 10%. This difference can be related to a selective affinity to metal ions. The order of efficiency, from 1 to 6 in Table 3, seems depend on numerous factors (specific surface area, particle size, spatial arrangement) that are out of our reach in the present study.

4. CONCLUSION

The thermal stability analysis and the elemental analyses results confirmed that carboxyhydrazide functional group was immobilized on the silica surface. The modified silica was used to extract heavy ions from their water based solutions.

We showed that calorimetric approach using FMC technique can be used, as a suitable method, to demonstrate the ability of carboxyhydrazide modified silica to adsorb heavy metal ions from aqueous solution. Our results showed that the modified silica have a selective affinity to metal ions. The origin of this selectivity was not investigated in the present work.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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