

A fractional factorial design applied to organofunctionalized silicas for adsorption optimization

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Received 28 December 1994; accepted 18 March 1996

Abstract

A 2^{4-1} fractional factorial design is employed to study Cu(II) adsorption on organofunctionalized silicas. Two types of immobilized silicas, Sil-et-1 and Sil-et-2, two solvents, water and ethanol, two copper salts, chloride and acetate, as well as 100 and 200 mg quantities of silica are used. For this design, substituting water for ethanol results in an average increase in copper adsorption of $3.57 \times 10^{-4} \text{ mol g}^{-1}$. An increase in silica mass from 100 to 200 mg decreases adsorption by a significant amount. Three important binary effects involving the solvent, salt and silica mass factors are found. All of these effects indicate the existence of antagonistic interactions between these factors. Large values of Cu(II) adsorption, $\approx 6 \times 10^{-4} \text{ mol g}^{-1}$, are found when 100 mg of silica in ethanol solvent is used in the presence of either Cu salt or silica type.

Keywords: Chemometrics; Factorial design; Metal adsorption; Organofunctionalized silicas

1. Introduction

Silica gel is an amorphous inorganic polymer with siloxane groups (Si–O–Si) in the interior and silanol groups (Si–OH) on the surface [1,2]. The latter are responsible for chemical modifications that can occur on the silica surface. Organofunctionalization using alcoxysilanes as surface-modifying agents has become commonly reported in published work since this type of ligand possesses high thermal and hydrolytic stability [3,4].

Normally molecules are immobilized on pure silica gel previously heated at 423 K for about 8 h to eliminate physically adsorbed surface water [5,6]. However, some alcoxysilanes are immobilized by means of the sol–gel process, normally

using $\text{Si}(\text{OET})_4$ as a skeletal forming agent for silica gel [7,8]. Characterization studies of these materials using ^{13}C and ^{29}Si nuclear magnetic resonance in the solid state [7,9,10] showed that a larger quantity of silicon agent can be immobilized by precipitation. Once the ligand is immobilized, the new silica has a high capacity to adsorb metal cations on its surface [11] and has wide applicability in diverse areas such as adsorption of metal cations from solvents [4,12] and sea-water [13], use as a stationary phase in high performance liquid chromatography [15], and catalysis of enzymatic reactions [16] as well as metal-supported organic reactions [17]. Adsorption capacity is intimately related to the levels or values of several experimental factors. The types of immobilized ligand and metal cation involved, the solvent used, the contact time of the cation with the surface and the quantity of silica in contact with the metal

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solution can determine the quantity of metal cations adsorbed.

Various papers have already been published by different research groups, including those of our laboratory, involving the utilization of several organofunctionalized silicas and some metal cations in aqueous and non-aqueous media [12,18,19]. However, only a few of the relevant experimental factors have been systematically studied. A more profound study should be carried out, permitting the evaluation not only of the isolated factor effects but also possible synergic and antagonistic interaction effects involving two or even more factors on the quantity of adsorbed metal cations [20]. Since such a study can involve a prohibitively large number of experiments, chemometric procedures based on multivariate statistical techniques are employed here. Besides economizing experimental effort, these methods are capable of measuring interaction effects on metal adsorption as well as the isolated effects of each experimental factor on this response in the most precise way possible. More specifically, a fractional factorial design [20] adequate for studying four of the factors mentioned above has been carried out. This factorial design requires the execution of only eight distinct experiments. To determine the statistical significance of the effects evaluated in this study, duplicate determinations were made for each of these experiments.

2. Experimental

2.1. Materials

Water was used after bidistillation and ethanol was refluxed with calcium oxide previously dried at 873 K and then distilled. A new treatment was carried out by refluxing ethanol with resublimated iodine and magnesium. After distillation the solvent was conditioned in a polyethylene flask. Two copper salts, chloride and acetate (Merck), were used. Both salts were dried in a vacuum line at 300 K for 8 h. Ethylenediamine (Merck) was distilled before use. The tetraethoxysilane (Baker), the silylating agent 3-trimethoxysilylpropylethylenediamine (Aldrich) and the 25% glutaral-

dehyde solution (Aldrich) were utilized without purification.

2.2. Synthesis of organofunctionalized silicas

The precipitation reaction of organomodified silicas was carried out using a procedure described previously [21]. 50 cm³ of tetraethoxysilane and 25 cm³ of 3-trimethoxysilylpropylethylenediamine were mixed in a 500 cm³ beaker maintained in an ice bath. Dropwise addition of 30 cm³ of a concentrated HCl solution was performed with manual agitation. The silica obtained (Sil-et-1) was filtered and washed with 100 cm³ of doubly-distilled water and 100 cm³ of 5% sodium bicarbonate (pH 8) solution. The silica was again washed with doubly-distilled water and with 15 cm³ of ethylether and dried in a vacuum line at room temperature for 6 h. A slightly yellow material of nonuniform granulometry was obtained.

This silica was treated with 2.5% glutaraldehyde in a citrate buffer of pH 7.0 [21,22]. The product (Sil-glut) was filtered and dried, yielding a light brown product of irregular granulometry. The reaction of this silica with ethylenediamine [21] was carried out in a pH 9.20 carbonate–bicarbonate buffer solution. The product obtained was reduced with sodium borohydrate in the same buffer to give the final product (Sil-et-2). This silica showed the same light yellow color as Sil-et-1. This fact can be taken as qualitative evidence of the success of the reactions performed since these silicas have only simple carbon–nitrogen bonds, whereas when glutaraldehyde is incorporated carbon–nitrogen double bonds are inserted in the immobilized structure [21].

Fig. 1 shows a schematic diagram of proposed products of the organic compounds anchored on the silica surface. The quantitative determination of the number of anchored molecules was made by nitrogen analysis, using the Kjeldhal method described earlier [12]. The results are given in Table 1.

2.3. Adsorption of Cu (II)

The adsorption studies were realized using a batch procedure [12,18,19] where the silica quanti-

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