

Mesoporous materials for heavy metal ion adsorption synthesized by displacement of polymeric template

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A successful application of the template displacement synthesis to the polymer templated mesoporous silica SBA-15 resulted in the preparation of materials with high surface area and open porosity. It was shown for the first time that such procedure is applicable for neutral polymer templated silica-based materials. Some of the materials, particularly the sample with attached 1-allyl-3-propylthiourea functionality, exhibited promising properties towards mercury ion adsorption. The maximum mercury loading from aqueous solution is 0.16 g Hg²⁺/g or 0.8 mmol Hg²⁺/g. The mercury desorption was accomplished by washing the mercury-loaded samples with aqueous thiourea solution.

1. INTRODUCTION

Pollution with heavy metals represents a serious threat for environment and constitutes a great concern for ecologists in developed countries. One of the approaches to this problem is the removal of harmful metal ions through binding them to the insoluble matrixes, adsorbents [1-4], which later can be disposed or regenerated and reused. Such materials can be designed by combining advantageous properties of mesostructured silicas (high surface area, large pore size and outstanding transport properties) [5, 6] with metal-specific organic functionality [7-9].

Specificity of functional groups can be described in terms of the hard-soft acid-base theory [10]. According to this theory the common metal ions such as Na⁺, K⁺, Mg²⁺ and Ca²⁺ are classified as hard acids, but Hg²⁺, Cd²⁺, Ag⁺ and Pb²⁺ metal ions are soft acids, and consequently only the second group of ions would strongly interact, for instance, with sulfur-containing ligands, which are soft bases. This fact allows designing potential adsorbents for environmental cleanup via attaching soft bases (e.g. sulfur-containing ligands) to the silica surface. Such materials would selectively bind heavy metal ions from aqueous solutions and their regeneration can be achieved by utilization of acid, complexing agent solutions or their mixtures.

In the most favorable case, there is 1:1 interaction between Hg²⁺ ions and SH-ligands. The smallest, readily available, sulfur-containing silane that is suitable for mercury adsorption and subsequently, for silica modification, is 3-mercaptopropyltrimethoxysilane

[8, 9]. The attachment of mercaptopropyl groups to the silica surface would increase molecular weight of the material by 119.25 g/mol. The highest population of silanols on the silica surface is ca. 4.9 groups/nm² that results in the maximum of ca. 6 mmol/g groups for most common silicas, and even less, ca. 4 mmol/g for mesoporous silicas [11]. Thus, in the case of the most optimal scenario one mol (200.59 g) of mercury(II) would be adsorbed on one mol (119.25 g) of the SH-ligands attached through one mol of silanols present on the silica surface, the mass of which should be at least 167 g (in order to assure the 6 mmol/g silanol concentration). This calculation shows that the highest attainable loading of mercury ions on mercaptopropyl functionalized silica would be ca. 0.7 g Hg²⁺/g of functionalized material. The actual number would be much lower if one takes into account several factors such as much lower concentration of silanols present on the high surface silicas (typically 1.5 times lower), difficulties in achieving the ligand coverage higher than 75% and the pore wall curvature restrictions. Taking into account the aforementioned factors one could provide a more realistic estimation of the maximum mercury adsorption for a hypothetical "superadsorbent" as ca. 0.5 g Hg²⁺/g. That number is very close to 0.505 g Hg²⁺/g, which was reported for the material showing an unprecedented 100% ligand coverage [9].

Two conclusions arise from the above calculations: (i) there is an evident limitation for the maximum adsorption capacity of materials with a given framework, which can be increased by using "lighter" matrices, for example, active carbon; (ii) there are other areas which could be improved, e.g., regeneration and stability of the adsorbing materials.

The objective of this study was to explore the applicability of the template displacement synthesis (TDS) for preparation of modified materials by using polymer-templated silica, SBA-15. One of the goals is to synthesize functionalized silica-based mesoporous materials suitable for removal of heavy metal ions from aqueous solutions and to elucidate their adsorption performance with respect to mercury(II) ions.

2. MATERIALS AND METHODS

Tetraethyl orthosilicate, 3-aminopropyltriethoxysilane, 3-cyanopropyltrimethylchlorosilane, allyl isothiocyanate and pyridine (anhydrous) were from Aldrich Chemical Co. (Milwaukee, WI). Toluene (p.a.), ethyl alcohol and isopropyl alcohol (anhydrous) were from Fisher Scientific (Pittsburgh, PA). All materials were used as received.

The SBA-15 mesoporous silica was synthesized using Pluronic P123 triblock copolymer (EO₂₀PO₇₀EO₂₀) at 35°C following the procedure described elsewhere [12]. TEOS was used as a silica source and low-temperature preparation was followed by aging for 2 days at 90°C. The solid product was filtered out without washing to obtain a material with templating polymer inside of mesopores.

The uncalcined and unmodified sample of SBA-15 is denoted as S-U. The unwashed and uncalcined sample was subjected to the template displacement synthesis (TDS) [13, 14] in order to remove polymer from mesopores and to attach functional groups. The resulting samples are designated as follow: sample treated with tetraethyl orthosilicate, S-UT, sample treated with 3-cyanopropyltrimethylchlorosilane, S-UCN, sample treated with 3-aminopropyltriethoxysilane, S-UNH₂. The TDS procedure included dispersion of ca. 0.2 g of uncalcined silica in 10 ml of silane-toluene (1:3) mixture followed by refluxing for 8 h. The mixture was filtered and washed several times with small portions of toluene, isopropyl alcohol, and finally the modified mesoporous material was dried overnight in an oven at

