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Biosynthesis of mesoporous functionalized silicates and their efficiency in water treatment

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ABSTRACT

Removal and detection of contaminants from waste water or other water sources continue to be a focus of research and a significant challenge when concentrations of the contaminant are low and water volumes are high. During the treatment of wastewater, removal of heavy metal ions is one of the main problems encountered by most of the industries. In order to optimize wastewater treatment process, low cost materials are required with high pollutant-removal efficiency. In this study Mesoporous silica has been synthesized using biotemplate and later functionalized (FMS) as potential sorbent for the removal of heavy metal ions. They have a combined advantage of inorganic-organic composites with large surface area, uniform pore size distributions. In this work, functionalization of silica nanostructures with thiol-group has been investigated as a general method for chemical binding of various metal or metal oxide particles to thiol-functionalized silica gel as adsorbent to remove toxic metal species from aqueous solutions. Since the FMS system has a large surface-to-volume ratio, surface modification of such materials with -SH group and chemical adsorption of metals can be useful in separation processes.

KEYWORDS

Functionalised mesoporous silica;
Thiol;
Starch.

INTRODUCTION

Numerous processes such as ion exchange, adsorption, precipitation, ultra filtration, or reverse osmosis have been successfully used for removing heavy metal ions, but they offer the disadvantages related to removal efficiency like wide distribution of pore size, heterogeneous pore structure and relatively low metal loading capacities. One of the promising technique in order to remove low levels of metal ions from water is to trap them using donor ligands modified on the surface of mesoporous materials[1-3]. A lot of literature is available on synthesis of mesoporous material. The method of using a 'template' is probably the most effective method for this purpose. Conventionally there are many templates, which are used for mesoporous material synthesis. However, two main limitations exist: (a) limited wall thickness, which is a serious limitation regarding stability for catalysis application (b) limited pore size offered by molecular surfactants. Therefore, it is highly desirable to develop a facile method to synthesize mono dispersed mesoporous metal oxides with controllable porosities. In the present work we are aiming at green polysaccharide assisted synthesis of metal oxides using starch. Since the starch granules are practically inert towards chemical reactions, they need to be pretreated to activate them, for example by enzymatic hydrolysis.

Among various adsorbent materials, mesoporous silicas are used widely because of large surface areas, high porosities, narrow distributions of the pore size, and ease of modification[4-7]. Moreover, silica and silicates are being considered as one of the most promising mesoporous supports because the silanol groups can be easily modified with functional groups. Thiol-functionality is most promising due to the strong metal-sulfide interaction, that can be utilized in removal of heavy metal ions. Thiol-functionalized silicas have been examined for mercury, silver and lead remediation. This study deals with the preparation of a thiol-functionalized porous silica via the co-condensation of TEOS and 3-mercaptopropyltrimethoxysilane (MPTMS) using starch as a pore forming agent[8-10]. The thiol-functionaled mesoporous silica (FMS) has been used as an adsorbent for removal metal ions from water.

EXPERIMENTAL

Synthesis of the starch templated mesoporous silica

Corn starch was immersed into buffer solution (pHH”4.7) with stirring to form a starch suspension solution. After being added with an enzyme mixture of glucoamylase and α-amylase (3:1, w/w), the suspension solution in a beaker was placed in a water bath and was stirred for 24 h at 43 °C. Ultrasonic treatments were included before, during, and after glucoamylase treatments. The concentrations of starch slurry were 40, 60, and 80%, respectively (solid content were 8, 12, 16 g in 20 mL buffer, respectively). The temperature was maintained at 40 °C for ultrasonic treatments. When the mixture turned in to a homogeneous emulsion, 2 mL TEOS was added dropwise into the bulk solution under vigorous stirring to get a final gel with mass ratio of Water : TEOS : Ethanol 1 : 4 : 6. The reaction proceeded at room temperature for 12 h, after which the resultant white precipitate was filtered, washed with Millipore water, and dried overnight at 60 °C in a vacuum oven. Finally, the as-synthesized powder was calcined at 600 °C for 4 h (heating rate: 1 °C min^{-1}, O_2 atmosphere) in a muffle furnace to completely remove the organic template. The samples were designated as (Si-8, Si-12, Si-16).

Synthesis of thiol-functionalized silicas

The thiol-functionalization on silica (denoted as Si-SH) was done using tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) template by starch under acidic conditions. The addition was done in the raio : (0.6 g) starch : (15.0 g) H_2O: (5.2 g) 37% HCl: (1 g) TEOS +MPTMS. The whole mass was agitated for 24 hours at 4o °C. Starch was later removed by refluxing with ethanol solution for 1 day to yield the desired produt Si-SH. It was found that per gram of silica contained 1.1 mmol of thiol group.

Adsorption of metal ions

The ability of the functionalized mesoporous materials (FMS) to adsorb metal ions[11] from solutions was tested by stirring Si-SH in the individual aqueous solution of the metal ions at room tempearature. 10 mg of Si-SH in 100 ml of $[M^{2+}]$was taken for measurement. The amount of metal ions left was determined by titration with EDTA solution.

Characterization

The nature and morphology of particles was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Other physical properties were studied using N_2 adsorption (BET), Particle Size distribution analysis and Small angle Neutron Scattering (SANS).

RESULTS AND DISCUSSION

Powder X-ray diffraction

The XRD patterns in Figure 1 shows that all the samples exhibit mesoporous nature. An almost similar trend indicates surface immobilization of the enzyme with unchanged internal molecular arrangement.

Scanning and and transmission electron microscopy

The SEM micrographs of the Si-8, Si-12 and Si-16 are shown in Figure 2. Depending on the synthesis parameters, the structure of colloidal particles varied from isolated spherical particles to agglomerates.

Particle size distribution analysis

The particle size analysis of the Si-8, Si-12 and Si-16 are shown in Figure 5. The particle sizes of Si-8 (~352) are enlarged due to low cross linking of starch with TEOS before calcination, while S-12 (~321nm) and S-16(~56nm) show decrease in the particle size due to large amount of cross linking with TEOS.

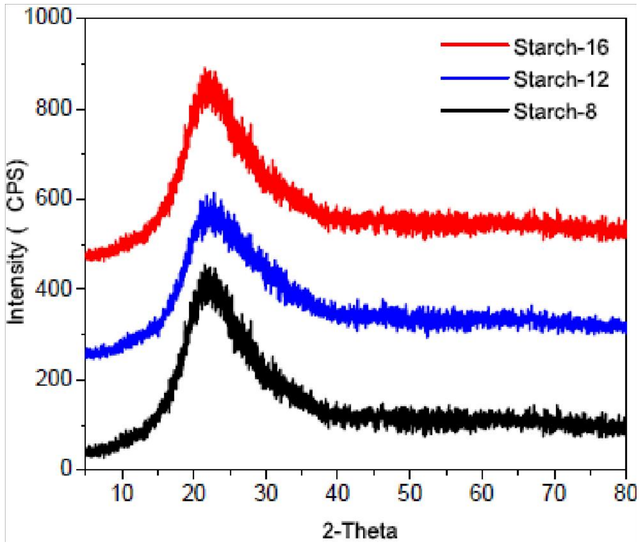

Figure 1 : Xray diffraction of silica without functioalisation

Small angle neutron scattering

The silica nanoparticles are considered to be formed via aggregation process in which fractal aggregates assemble into the resultant silica nanoparticle with a fractal dimentionality of 3.4 which is almost constant for all the three type of silica.

N_2 adsorption desorption studies

Results of BET surface area, BJH pore diameter and total pore volume of samples are given TABLE 1 Surface area, total pore volume and pore diameter showed an increase with increase of starch concentration. The typical N_2 adsorption desorption curve of silica exhibits a type IV isotherm with BET surface area characteristic of mesoporous materials. The higher pore volume may be attributed to a stronger permeation power of the precursor into the starch template compared to others having less amount of starch. The reason for such a trend might be due to the availability of a surface where the precursor could diffuse not only onto the surface but also the near surface layers. The surface area, total pore volume and pore size of Si-SH showed a significant decrease (TABLE 1), revealing that the surface modification must have occurred inside the pores.

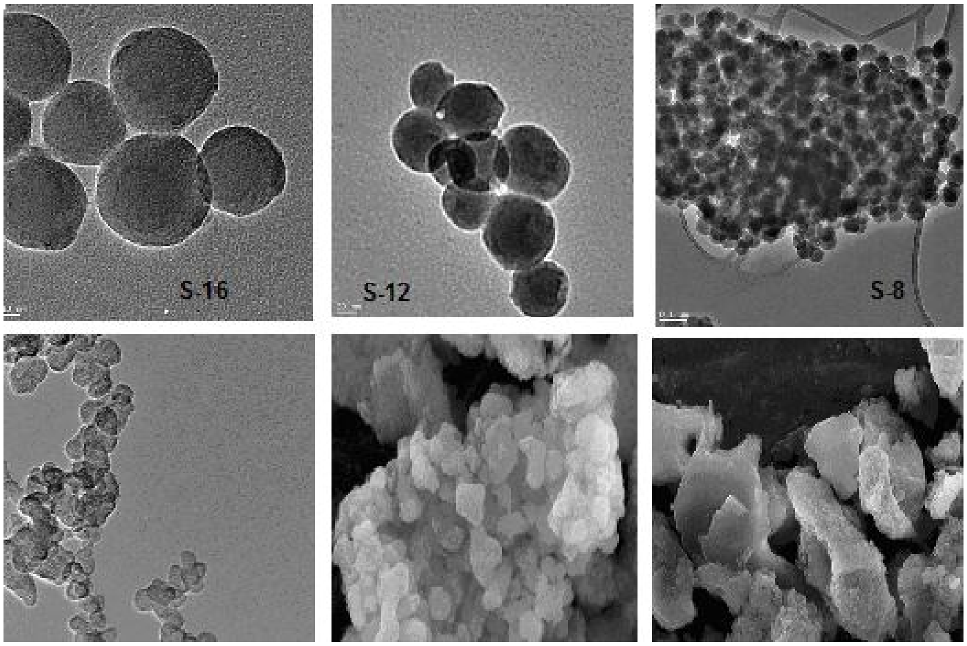

Figure 2 : TEM and SEM micrographs of silica particle

TABLE 1 : Physical properties of silicas and Functionalised mesoporous silica

Sample	BET Surface Area m²/g	Pore Diameter in nm	Total Pore Volume cm³/g
Si(8)	146	8.4	0.22
Si(12)	251	9.3	0.34
Si(16)	438	10.4	0.63
Si-SH	225	7.4	0.51

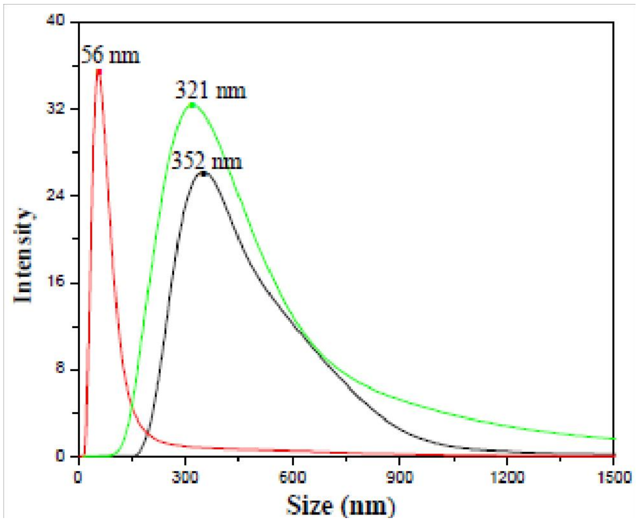

Figure 3 : Particle size distribution analysis

Adsorption of Metal ions by FMS

The adsorption capacity of the FMS for various metal ions ranged from 2.8 mg/g to 11.3 mg/g adsorbed per gram of adsorbent. Results of the metal ion adsorption are summarized in TABLE 2. As seen a maximum adsorption of copper(II) was observed compared to other ions.

CONCLUSION

Spherical silica particles with a very narrow particle size distribution have been synthesized using starch as a template. The morphology and the average diameter of silica particles depend on the proportion of the template taken. A novel functionalized mesoporous material has been synthesized by co-condensation of TEOS and MPTMS in the presence of starch as a biotemplate. Furthermore, the adsorption capacity of the FMS was found to be greatest for ions like lead, cadmium and copper, thus allowing them to be promising adsorbents for wastewater treatment.

ACKNOWLEDGEMENTS

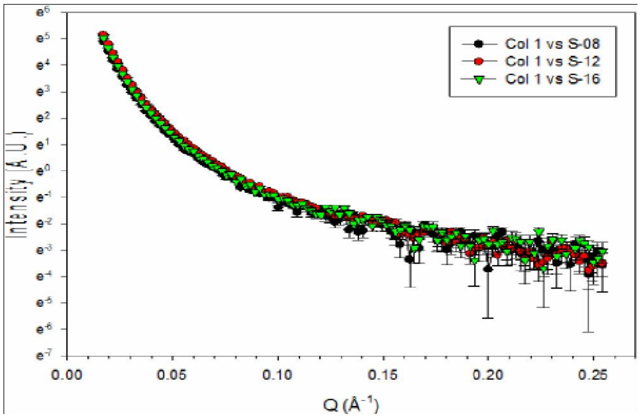

Figure 4 : SANS data in a log-log Plot

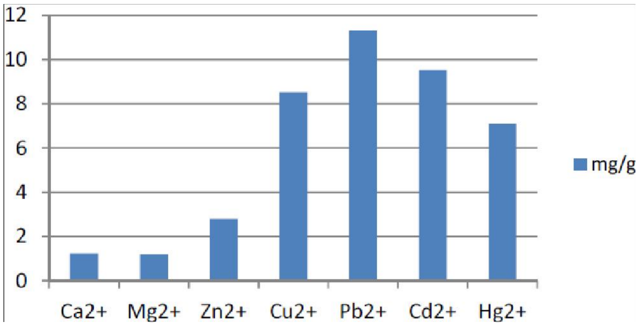

Figure 5 : Quantity of various metal ions adsorbed by Si-SH

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