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Synthesis and characterization of guar gum templated hybrid nano silica

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ABSTRACT

The objective of the present study was the fabrication of green adsorbent hybrids for which native guar gum was used as template to polymerize tetraethoxysilane. The properties and performances of the hybrids could be tailored by using varying molecular sizes of the partially depolymerized guar gum templates of various molecular sizes as control. Zn(II) uptake from aqueous solution was used as a criterion for evaluating the adsorbent efficiency. The optimum material (H4) in terms of maximum Zn(II) uptake, was obtained when the template size used was 375 kDa at a calcination temperature of 700 °C. H4 was also evaluated for Ca(II), Mg(II), Cd(II) and Hg(II) adsorption. To explore the other applicability areas, the hybrids have been extensively characterized using FTIR, XRD, TGA-DTA, PL, SEM, TEM and BET analyses. H4 was found to be as efficient as previously reported vinyl modified-silica nanohybrids. It had a high surface area (264 m^2/g) with silica nanoparticles in the size range of 90–140 nm. Being thermally very stable and photoluminescent, the material can be potentially used for many biological, medical and environmental applications.

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1. Introduction

Hybrid porous materials with well-defined pore structures and tailored components are of great interest for high performance applications [1]. Mesoporous hybrid materials are obtained from the organic inorganic assembly by using soft matter, that is, organic molecules or supramolecules as templates. Self-assembly of inorganic precursors with biomolecules and/or biomolecule-initiated nucleation and growth processes result in hybrid organic–inorganic biomaterials having complex structures and shapes [2]. Mesoporous silicates have been synthesized by surfactant [3] or polymer templating [4] but such materials may have some disadvantages in terms of environmental compatibility. While some of the surfactants are known to be toxic to animals, ecosystems and humans, and can increase the diffusion of other environmental contaminants [5], majority of the polymer used for templating are petrochemical based, toxic and expensive. Their removal from silica network is often difficult making these materials unfit for biological applications.

Much of these limitations can be overcome by the use of polysaccharide templates which are renewable biodegradable natural materials [6]. Polysaccharides are reported to manipulate the formation of hybrid silica nanocomposites by sol–gel processes [7–10]. In the literature, different polysaccharides/mineral oxides are described such as cellulose/silica [11], alginate/silica [12] chitosan/silica [13–16], and cellulose/titania [17,18]. Conducting sol–gel chemistry in presence of biopolymer template furnishes hybrids which on calcination >450 °C results into porous materials. Polysaccharide self-assemblies are capable of templating novel mesophasic inorganic materials [19]. Templating techniques have been used to control the structural properties of materials including outer shape, inner porosity, and surface area [20] such as the fibrous superstructure of collagen was used to produce tubular silica [21], cellulose [22], and its derivatives [23,24] and dextran-based polymers [25,26] have resulted in both meso- and macroscopic porous inorganic structures; and α-chitin [27] and starch [28] gave large scale sponge-like architecture to the final silica or silicalite materials.

Guar gum is a abundantly available [29] polysaccharide material having backbone of β-D(1 → 4) mannopyranosyl units with α-D-galactopyranosyl units as side chains. Our research group have previously used saponified poly(acrylonitrile) modified guar gum and poly(acrylamide) grafted guar gum as templates to synthesize novel hybrid nanocomposites with excellent ability to bind Zn(II) [30,31] and Cd(II) [32], respectively. However synthesis of these composites involved vinyl modification of the guar gum as a preparatory step which adds to cost as the used monomers were pertrochemically derived. The synthetic ingredients make these materials undesirable for biological applications.

In continuation to our previous study on the vinyl modified guar gum-silica nanocomposites [33,34], in the present study, a new

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kind of hybrid adsorbent and photoluminescent material having no synthetic polymeric component, is targeted. In the present study, instead of vinyl modified guar gum, guar gum in its native form has been used as template to obtain cost effective environmentally benign hybrid sorbent [33,34].

The partial acid hydrolysis under mild acidic conditions breaks guar gum in to smaller fragments in terms of molecular sizes and weights [35,36]. These depolymerized gum samples have been used in templating the polymerization of TEOS such that hybrids of controlled particle sizes and shapes [37] were synthesized to obtain maximum Zn(II) binding. These materials were calcined to further tailor their adsorbent and photoluminescent properties [38]. The chemical, structural and textural characteristics of the synthesized hybrids have been determined and in a preliminary investigation, the optimum zinc(II) sorbent was also evaluated for cadmium(II), mercury(II), calcium(II) and magnesium(II) uptake. Present communication mainly deals with the synthesis and characterization; however detailed study on the adsorption behavior of the material is under progress and will be communicated as a separate study.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (98% TEOS; Aldrich) was used as silica precursor. NH_4OH (30% NH_3; Merck), H_2SO_4 (Merck) were used. Commercial sample of guar gum (Merck) was used after purification. $ZnSO_4$, $MgSO_4$, $CdNO_3$, $HgCl_2$ and $CaCO_3$ (Merck) were used for making the respective standard metal ion solutions. $BaCO_3$, EDTA, Eriochrome Black-T (Merck) were used.

2.2. Analysis

Schott AVS 470 viscometer was used for viscosity measurements. Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer using KBr mulls in reflectance mode. X-ray diffraction (XRD) was carried out on Rigaku D/MAX-2200 X-ray powder diffractometer. Wavelength used to compute *d*-spacing was 1.54056 °A (Cu/K-alpha 1). TGA was done at Perkin-Elmer TGA-7 at a heating rate of 10 °C per min under nitrogen atmosphere. SEM analysis was done on EDAX, FEI Quanta 200 machine. Transmission electron micrographs were obtained using a Philips® EM208 operating at 200 kV. For TEM, a drop of aqueous suspension containing the material was placed on the carbon coated copper grid to form a film and then dried under IR lamp. Temperature treatment of the hybrids was done in Mac (India) electric Muffle Furnace under atmospheric conditions. Photoluminescence spectra were recorded in Perkin-Elmer LS55® Spectrofluorimeter using 90° illumination. Based on the excitation maximum (275 nm), emission scan was carried out in the range of 380–800 nm. The excitation and emission slit widths were kept at 2.5 and 5.0 nm, respectively. The entire scanning was done at the speed of 100 nm/min. The data were analyzed using the FL Winlab® software. The BET surface area was measured by nitrogen adsorption at 77.3 K using Quanta chrome ASIC-9 Autosorb Automated Gas Sorption System, using outgas temperature 300 °C.

2.3. Methods

Purification of the guar gum. The guar gum (GG) was purified by barium complexing as described elsewhere [32]. The pure gum was finally washed with 70, 80, 90, 95% ethanol and dried.

2.3.1. Hydrolysis of the guar gum

For partial hydrolysis, the purified GG sample was refluxed [37,38] with 0.01 N H_2SO_4. In different sets of experiments, the hydrolysis was allowed for 20, 30, 40, 60, 80 and 100 min, respectively to obtain depolymerized GG samples of different molecular sizes GGA, GGB, GGC, GGD, GGE and GGF, respectively (Table 1). The hydrolyzates were precipitated in excess of 95% ethanol after neutralization with barium carbonate.

Table 1
Viscosity average molecular weight of guar gum (GG) and hydrolyzed GG for different time intervals using 0.1 N H_2SO_4.

Samples	Hydrolysis time (min)	Intrinsic viscosity [η]	Mol. wt (KDa)
GG	–	15.5	2610
GGA	20	9.00	1546
GGB	30	7.10	1214
GGC	40	4.50	762
GGD	60	2.50	418
GGE	80	2.25	375
GGF	100	1.80	299

2.3.2. Intrinsic viscosity and molecular weight of the guar gum and hydrolyzed guar gum

The molecular weights of the GG/hydrolyzed GG samples (GGA to GGF) were determined by viscosity method. Intrinsic viscosities [32] of the samples were calculated from their respective relative viscosities.

The viscosity average molecular weight of the depolymerized GG samples were calculated using their intrinsic viscosities according to the Mark-Houwink equation reported for the galactomannans [39] (Eq. (1)).

$$[\eta] = 11.55 \times 10^{-6}[(1-r)\overline{\mathrm{Mw}}]^{0.98} \qquad (1)$$

Where $[\eta]$ is the intrinsic viscosity of the seed gum in dL g^{-1}. *r* is the galactose/(mannose + galactose) ratio. The reported [6] galactose to mannose ratio in the guar gum is 1:2.

2.3.3. Preparation of hybrid materials

GG and the depolymerized GG samples (GGA to GGF) (1.0 g each) were dissolved separately in 10 ml of distilled water. To each solution, solution of TEOS (2.5 ml) in ethanol (2.5 ml) and 1.75 ml of 12 N ammonium hydroxide were poured rapidly with stirring. The solutions were kept under gentle stirring for 18 h at room temperature. The ensuing mixtures were then subjected to slow evaporation at 40 °C (3 h), 60 °C (4 h), 70 °C (2 h) and 80 °C (2 h) until dry monolithic nanohybrids (coded as GG_{80}, GGA_{80}, GGB_{80}, GGC_{80}, GGD_{80}, GGE_{80}, GGF_{80}, respectively) were obtained. Each of them was further calcined (in air) inside a furnace at 250 °C, 500 °C, 700 °C, 800 °C and 1100 °C (for 2 h at each temperature) to obtain a series of heat treated samples. For example, the GGA series was coded as GGA_{80}, GGA_{250}, GGA_{500}, GGA_{700}, GGA_{800}, GGA_{1100}. A comparative evaluation in terms of Zn(II) binding was done for each series calcined at 80 °C, 250 °C, 500 °C, 700 °C, 800 °C and 1100 °C, respectively (Table 2), keeping adsorption efficiency as the criterion. GGE was chosen as the representative series (GGE_{80}, GGE_{250}, GGE_{500}, GGE_{700}, GGE_{800}, GGE_{1100}) for further studies as it showed maximum binding with zinc.

Since our study involves only the GGE series, for simplification we have recoded GGE_{80}, GGE_{250}, GGE_{500}, GGE_{700}, GGE_{800}, GGE_{1100}, the samples obtained by the calcination of GGE hybrid at 80 °C, 250 °C, 500 °C, 700 °C, 800 °C and 1100 °C as H1, H2, H3, H4, H5 and H6, respectively.

2.3.4. Preparation of control silica

To a solution of TEOS (5 ml TEOS in 5 ml ethanol), 3.5 ml of 12 N NH_4OH solution was added and the resulting mixture was stirred in a conical flask for 18 h at 32 °C followed by 3 h stirring at 80 °C. The dry product thus obtained at 80 °C (S1) was washed well with distilled water, filtered, and dried. S1 was thermally treated (for

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