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Synthesis and characterization of gum acacia inspired silica hybrid xerogels for mercury(II) adsorption

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ABSTRACT

In a sol–gel process, gum acacia inspired silica xerogels have been synthesized from tetraethylorthosilicate. Besides showing photoluminescence under ultraviolet excitation, the hybrid xerogels were very efficient in capturing mercury(II) from synthetic solution. To synthesize the optimum sample (in terms of Hg(II) uptake), different ratios of H_2O:TEOS:EtOH were taken at fixed GA and catalyst concentrations where 4:1:1 ratio was found to be most favorable. Calcination in air further enhanced the mercury binding capacity of this sample. Optimum sample (H4) was obtained on calcination of the gel at 600 °C. The hybrids have been structurally characterized using Infrared spectroscopy, X-ray diffraction, scanning electron microscopy, thermo gravimetric analysis, photoluminescence spectroscopy and Brunauer–Emmett–Teller analysis. In a preliminary batch adsorption experiment, H4 was evaluated to be highly efficient in the removal Hg(II) from synthetic aqueous solution.

1. Introduction

Organic-(bio)–inorganic hybrid materials are of great significance as they have the combined characteristics of both organic (or bio) and inorganic components [1]. The growing environmental consciousness [2] has prompted the use of abundant, low cost and environmentally friendly biopolymers in the synthesis of hybrid materials. In last 15 years [3,4], the development of biopolymer/inorganic oxide materials has got much attention and reports on many polysaccharide/mineral oxide hybrids are available in the literature such as cellulose/silica [5], alginate/silica [6], chitosan/silica, [7–10] and cellulose/titania [11,12]. Use of biopolymeric template in a sol–gel reaction of metal oxide precursor results into hybrid materials which on calcination >450 °C, result porous inorganic oxide xerogels. Polysaccharide self-assemblies are capable of templating novel mesophasic inorganic materials [13]. Templating techniques have been used to control the structural properties of materials including outer shape, inner porosity, and surface area [14]. The porosity can only be obtained after the removal of templates from inorganic–organic hybrids for example, the fibrous superstructure of collagen was used to produce tubular silica, [15] cellulose, [16] and its derivatives, [17,18] and dextran-based polymers [19,20] have resulted in both meso and macroscopic porous inorganic structures; and â-chitin [21] and starch [22] gave large scale sponge-like architecture to the final silica or silicalite materials. The technique has also been demonstrated for the oxides of titanium, zirconium, niobium, and tin [23]. Hierarchical morphologies in metal oxides are advantageous for many applications [15,24] including controlled drug release, photocatalysis, catalysis, synthetic biomaterials and adsorption and separation technologies. Silica compounds are among the most extensively studied materials, especially those prepared by the sol–gel process [25–27]. The sol–gel polymerization of silicon alkoxides has been widely used for the preparation of a variety of silica-based materials, including monoliths, thin films, small particles, and porous materials.

Availability of acacia tree as a renewable resource makes gum acacia a green material. Furthermore, gum acacia is particularly attractive for the preparation of hybrids due to the presence of hydroxyl and carboxylic acid groups in most of their polymer units.

In this manuscript, we demonstrate the use of an acacia gum as a template for the formation of porous hybrid silicon oxide suitable for adsorption applications. Gum acacia (GA) is a complex arabinogalactan which contains a small proportion of proteinaceous materials and has been classified as arabinogalactan–protein complex [28]. The gum has a highly variable composition and its physical and chemical properties can vary considerably depending upon the source of the nodules [29]. It is composed of D-galactose, L-arabinose, L-rhamnose, D-glucuronic acid and 4-*O*-methyl-D-glucuronic acid [29].

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The gum is very soluble in water and forms solutions over a wide range of concentrations without becoming highly viscous. The combination of this behavior and of its structure and composition confers on acacia gum its highly valued emulsifying, stabilizing, thickening and suspending properties [30]. A novel magnetic nano-adsorbent has been developed by treating Fe_3O_4 nanoparticles with gum Arabic to remove copper ions from aqueous solutions [31]. Gum Arabic has been reported to complex magnesium ions but in small quantity [32]. Though the gum has functionalities that may be suitable for binding metal ion from solution, it cannot be exploited as metal ion sorbent under aqueous conditions due to its solubility in water. Unique properties of the gum in combination with that of silica can be exploited to obtain hybrid for various applications such as adsorbent, photoelectronic devices and optical sensors for heavy metal ions. In the present study the synthesis and characterization of gum acacia–silica hybrid xerogels have been undertaken. Hg(II) uptake ability and photoluminescent behavior of these hybrids have also been investigated at a preliminary level in order to explore potential applicability areas for these hybrids.

2. Experimental

2.1. Materials

Gum acacia sourced from Acacia Senegal. (Merck, India) having acid insoluble ash ≤0.5%; insolubles ≤ .5%; ash ≤ 5% was used as supplied. Tetra ethylorthosilicate (98% TEOS; Aldrich) was used as silica precursor. NH_4OH (30% NH_3; Merck) was used as catalyst. Working standards of Hg(II) solutions were prepared by progressive dilution of stock mercury solution (1000 mg/L) that was prepared by dissolving 1.354 g of $HgCl_2$ in 700 mL deionized distilled water in the presence of 1.5 mL of conc. HNO_3 and then making up the solution in 1000 mL of deionized distilled water. HCl, NaOH and buffer solutions (Merck) were used to adjust the solution pH.

2.2. Instrumentation

Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer making 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 0.71056 Å (Mo/K-alpha1). TGA was done at Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopy was done on EDAX, FEI Quanta 200 machine. The hybrids were calcined in air using Mac (India) electric muffle furnace. Photoluminescence spectra were recorded in Perkin-Elmer LS55® Spectrofluorimeter using 90° illumination. Prescan was performed to find out the excitation and emission maxima for the silica nanoparticles. Based on the excitation maximum (234–340 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. Systronics single beam visible Spectrophotometer (model 105) was used for photometric measurements.

2.3. Preparation of the hybrids

Gum acacia (1.0 g) was dissolved in 10 mL of deionized distilled water. Separately, a known amount of TEOS was also dissolved in known amount of ethanol. A third solution incorporating 1.75 mL of 12 N ammonium hydroxide was prepared separately. Afterwards, the three solutions were rapidly poured together into a reaction glass flask, which was kept under gentle stirring for 14 h at room temperature to grow monodisperse SiO_2 particles within the biopolymer medium. The ensuing mixture was then subjected to slow evaporation at 40 °C (4 h) and 60 °C for about 1 h to obtain a dry material (H1) [30] which was subsequently washed several times with distilled water. Varying the H_2O, TEOS and EtOH ratio at fixed starch and catalyst concentration, hybrid samples A–E were prepared and evaluated for mercury binding in a preliminary batch adsorption study where hybrid sample "A" was found to be most efficient. Sample "A" was renamed as H1 for convenience and was calcined in air inside an electric furnace at 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C for 2 h at each temperature to obtain H2, H3, H4, H5 and H6, respectively.

2.4. Hg(II) sorption by the hybrids

In a preliminary investigation, hybrid samples (A–E) were evaluated for mercury binding from synthetic Hg(II) solutions using batch adsorption method. For each experimental run, 20 mL of 100 mg/L Hg(II) solution of pH 6.5 was taken in 100 mL stoppered reagent bottle to which 0.05 g of the hybrid was introduced as sorbent. The solutions in the bottles were agitated at room temperature (30 °C) using a mechanical stirrer for 16 h to attain equilibrium. At the end, the samples were taken out and the respective supernatant solutions were separated from the adsorbent by centrifugation at 20,000 rpm for 20 min and the centrifugates were analyzed for the concentration of mercury by spectrophotometric method at λ_{max} 575 nm using Rhodamine 6G/KI buffer and gelatin solution as stabilizer [33].

Blank solution was treated similarly (without hybrid) and the concentration was taken as initial concentration. All the batch experiments were carried out in triplicate and the values reported are the average of three readings.

2.5. Hg(II) sorption by gum acacia

In a control experiment, 20 mL of 100 mg/L Hg(II) solution of pH 6.5 was taken in 100 mL stoppered reagent bottle to which 0.05 g of the gum acacia was introduced and the solution was agitated at room temperature (30 °C) using a mechanical stirrer for 16 h to attain equilibrium. The contents of the bottle were centrifuged as above and the centrifugate was analyzed for mercury concentration by spectrophotometric method as determined in the case of hybrid.

3. Results and discussions

3.1. Characterization of the hybrid

3.1.1. Infrared spectroscopy

In IR spectrum of gum acacia, O–H and C–H stretching peaks are observed at 3421 cm^{-1} and 2927 cm^{-1}, respectively. Salt nature of carboxylic acid groups at gum acacia is indicated by the –C=O asymmetrical stretching at ν_{max} 1616 cm^{-1} along with a weaker symmetrical stretching band at 1423 cm^{-1}. O–H bending peaks are observed at ν_{max} 1029 cm^{-1}.

Incorporation of silica in the polysaccharide (composite H1) is evidenced by Si–O stretching modes that are observed below [30] 1250 cm^{-1} (Fig. 1). IR absorption bands at 1099 cm^{-1} (Si–O stretching) and 802 cm^{-1} (Si–OH stretching) evidenced the formation of Si–O–Si bonds (by dehydration polymerization of silanols). Stretching peaks due to GA hydroxyl and silanols are observed as merged broad peak at 3421 cm^{-1}. In the hybrid (H1), carbonyl stretching peak is seen shifted to 1639 cm^{-1} (due to possible dipolar interactions between carboxylate anion at GA and positively polarized silicon atom in the gel which interrupts the delocalization of negative charge at carbonyl oxygen). On calcination at 600 °C (H4),