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Mesoporous organic–inorganic hybrid aerogels through ultrasonic assisted sol–gel intercalation of silica–PEG in bentonite for effective removal of dyes, volatile organic pollutants and petroleum products from aqueous solution

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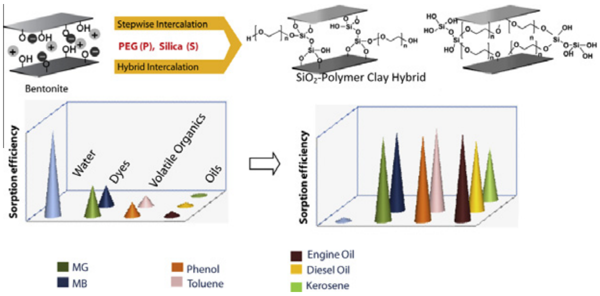
HIGHLIGHTS

- ▶ Hybrid organic–inorganic aerogels by ultrasonic assisted sol–gel intercalation.
- ▶ PEG grafted silica in the interlayer of bentonite clay.
- ▶ Hybrids showed mesoporous nature, high surface area and thermal stability.
- ▶ Hybrids demonstrated as good adsorbents for dyes and VOCs from aqueous solution.
- ▶ Hybrid aerogels exhibited good oil absorption efficiency with petroleum products.

GRAPHICAL ABSTRACT

Hybrid organic–inorganic aerogels with predominant mesoporous and marginal microporous nature, high surface area and thermal stability were obtained through a facile ultrasonic assisted sol–gel intercalation of SiO_2 and PEG in bentonite clay. The hybrids acted as highly efficient, multifunctional adsorbents for different environmental pollutants.



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ABSTRACT

Hybrid mesoporous materials with high surface area (1144 m^2/g) and enhanced thermal stability were achieved through ultrasonication assisted sol–gel-intercalation technique using bentonite clay and PEG grafted sol gel silica. Solvent extraction with mixed solvents showed efficient aerogel formation of the hybrids. The products were characterised by small angle X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, scanning electron microscopy, transmission electron microscopy, zeta potential measurement and BET surface area analysis. The XRD analysis showed interlayer spacing of ~43.28 Å. The increasing spacing is interesting in a way that the available interior pore volume can be tailored for the enhanced adsorption of different pollutants. Clay-hybrid porous materials showed hydrophobic nature with high adsorption capacities for organic dyes (methylene blue and malachite green), volatile organic pollutants (phenol and toluene) and petrochemical derivatives (kerosene, engine oil and diesel). The contact time necessary to attain adsorption equilibrium and the optimum pH were found to be 2 h and 5.0–6.0, respectively. Kinetics of adsorption was rapid film diffusion with a pseudo-second-order rate constant. The best interpretation for the equilibrium data was given by the Langmuir isotherm indicative of homogenous surface and maximum adsorption capacity of clay-hybrid towards methylene blue, malachite green, phenol and toluene from aqueous solution was found to be 101.55, 98.42, 116.75 and 114.10 mg/g, respectively, and was found to be greater than commercial adsorbents like activated carbon, zeolite and activated alumina. Thermal regeneration studies were carried out by calcinating the exhausted adsorbents. Clay-hybrid aerogels were then demonstrated using different petroleum products to exhibit excellent oil absorption properties.

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1. Introduction

Organically modified layered-silicates have become a prospective class of hybrid porous materials with wide range of applications such as gas and energy storage, rheological control agents, effluent treatment and drug delivery carrier [1–3]. The hybrid nature of these materials brings together the hardness, optical properties, thermal and chemical stability of inorganic materials with elasticity, ease of processibility and excellent impact resistance of organic polymers [4]. Synthesis of hybrid composites constituting highly thin layered frameworks is challenging. They are very crucial for many applications because these materials permit the final nanoporous materials to have a more exposed surface and higher specific surface area because of the thin walls. Bentonite as a representative layered-silicate is a very promising ceramic host-matrix for the fabrication of organic–inorganic hybrid composites, the main part of which is mineral montmorillonite, a 2:1, type of alumino silicate [5]. The introduction of robust propping species like metal oxide nanoparticles inside the alumino silicate layers by pillaring and intercalation techniques is a frequently practiced approach for obtaining nanoporous layered structures with high thermal stabilities and interesting catalytic properties [6]. There had been attempts to introduce silica pillars in clays using positively charged sol particles of metal hydrate and organometallic pillaring agents like tris(acetylacetonato) silicon cations ($Si(acac)^{3+}$),polyhedral oligosilsesquioxane compounds and octadecyltrimethylammonium assisted intercalation of mixed hydroxides of silicon and titanium [7,8]. However, the resulting SiO_2 pillared clays showed relatively low surface areas and a small interlayer spacing, indicating the presence of only monolayer siloxane chains between the layers. This problem seriously confines their applications as catalysts and catalyst supports. A direct intercalation of metal oxide sols was attempted by Moini and Pinnavaia, who mixed commercial hydrolysed silica sol with montmorillonite and obtained relatively large surface area solids of 250–460 m^2/g, though those were not a regular intercalation phase [9].

Recently, the adsorption of polyethylene-block–poly(ethylene glycol) copolymers onto Na^+-montmorillonite has been reported as a possible surface treatment to facilitate the formation of clay polyethylene nanocomposites [10]. Nanocomposites of hydrophilic polymers such as poly ethylene oxide or polyvinyl alcohol intercalated between the aluminosilicate layers of the clay were reported to show a *d*-spacing which varies from 14 Å to 19 Å depending on the different surfactant loading [11,12]. There are many limitations to achieve intercalation of polymer beyond monomer depth, which in turn limit many valid applications of clay-polymer composites and hamper their progress towards commercialisation [13]. By making an organic polymer present simultaneously in sol–gel media, it is possible to achieve novel organic–inorganic polymer hybrids containing ordered, molecular porous architectures which is in fact an area that is not well explored to the best of our knowledge. In this direction we designed a novel multi component meso-porous clay nanohybrid aerogels by *in situ* step-wise intercalation as well as direct *in situ* hybrid intercalation using silica sol and polyethylene glycol (PEG) onto the interlayer of bentonite clay of Indian origin. The clay-hybrid porous materials were attempted in this study with an aim to achieve a novel, multifunctional adsorbents.

Adsorption process has been shown to be highly efficient for the removal of harmful, toxic environmental pollutants due to its sludge-free cleaning operation and simplicity [14,15]. The present work investigated the possible application of the clay–silica–PEG hybrid materials as an adsorbent for organic dyes (methylene blue (MB) and malachite green (MG)), volatile organic components (VOCs) such as phenol and toluene from aqueous solutions. Dyes in wastewaters under aerobic conditions decomposes into carcinogenic aromatic amines which can cause serious health problems to humans and animals, while VOCs are the major contributors to the formation of photo chemical ozone and secondary organic aerosol, which would result in serious environmental problems [16,17]. Further the hybrids were explored for their sorption efficiency for petrochemical products such as kerosene, engine oil and diesel oil which are major source of ground water contamination and ocean pollution.

2. Experimental

2.1. Materials and methods

The Indian origin bentonite, extrapure was obtained from Central Drug House [CDH], India. The starting material TEOS to prepare silica–PEG intercalated clay hybrid gels were obtained from Sigma Aldrich. NaCl, isopropanol, hexane, MB, MG, phenol, toluene, HCl, PEG 300 were supplied by E. Merk India Ltd. Engine oil, diesel oil and kerosene were purchased from local market and used as received. Activated carbon (granular) was purchased from Hi-Media Laboratories Private Ltd. Zeolite and activated alumina were purchased from S. D. Fine-Chemicals, India. All chemicals were of analytical grade and were used without further purification. All solutions were prepared with deionised water of specific conductivity less than 1 $\mu/\Omega/cm$.

Crystal structure of the hybrids were analysed by powder X-ray diffraction using Philips X-ray diffractometer (X'Pert Pro, Cu Kα radiation, $\lambda = 0.154$ nm) in the scanning angle range of $1^\circ < 2\theta < 10^\circ$. Crystallite size was calculated using the well known Scherrer's formula:

$$\text{Crystallite size} = 0.9\lambda/\beta\cos\theta \tag{1}$$

where λ is the X-ray wavelength, θ, the Bragg angle and β, line broadening which is measured from the increased peak width at half the peak height. FTIR analysis was carried out with Nicolet Magna-560, in the range 400–4000 cm^{-1}, using KBr pellet technique. The bulk surface area was determined by the Brunauer–Emmet–Teller (BET) technique using a Micromeritics Gemini 2370 instrument that uses a N_2/77 K adsorption–desorption method. The total pore volume was determined from the amount of N_2 adsorbed at a relative pressure of 0.95 and meso-pore volume and micro-pore volume calculated by *t*-plot method. The surface morphology of the adsorbent samples was analyzed using a JEOL 5600 SL scanning electron microscope. Transmission electron microscopy images were also recorded using a JEOL, 200 CX, TEM apparatus. The TGA curves of the samples were taken from a Mettler TG 50 (Shimadzu, Kyoto) in air. A Mettler Toledo pH meter (model μ-8603) was used for pH measurements. A UV–visible spectrophotometer (Jasco model V-530) was used for the determination of MB, MG, phenol and toluene from aqueous solution.

2.2. Preparation of silica–PEG intercalated clay hybrids

The clay-hybrids were synthesized using a sonication assisted sol–gel intercalation technique. The schematic representation of synthesis process of the hybrid materials is shown in Scheme 1. Table 1 presents the details of the hybrids and their sample codes as per the synthesis procedures used in the present work.

The preparation of the Na-saturated bentonite (B) was performed by stirring 10 g of the raw sample with 1 L of 1.0 M NaCl solution for 12 h to replace all exchangeable cations with Na^+, separation by centrifugation and washing several times with distilled water until Cl^- was free. The product was dried at 105 °C, ground