



Microporous nanohybrids of carbon xerogels and multi-walled carbon nanotubes for removal of rhodamine B dye

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ABSTRACT

In the current paper, microporous nanohybrids of carbon xerogel and multi-walled carbon nanotubes (CX/MWCNTs) with different loadings of MWCNTs (1, 2 and 4 g/L) were synthesized. Scanning electron microscope (SEM) and transmission electron microscope (TEM) assessed the decoration of microspheres of carbon particles in CX matrix with bundles of MWCNTs. Nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$ revealed that the N_2 uptake was enhanced when CX was decorated with MWCNTs and the specific surface area (S_{BET}) increased from 192 to 643 m^2/g . The resulting hybrids are mainly microporous materials. Raising the amount of MWCNTs from 1 to 4 g/L led to a decrease in the S_{BET} from 643 to 515 m^2/g (i.e. decreased approximately 20%). Fourier transform infrared spectra (FTIR) and Boehm's titration showed that both acidic and basic oxygen functional groups were equally distributed while carboxylic groups were increased considerably by increasing the amount of MWCNTs. The efficiency of adsorption and catalytic oxidation properties of CX/MWCNTs nanohybrids towards removal of rhodamine B (RB) was examined. Adsorption equilibrium data were analyzed using five different adsorption isotherms, i.e. Langmuir, Freundlich, Flory-Huggins, Halsey and Elovich models. The equilibrium adsorption results proved that adsorption of RB dye onto these nanohybrids can be well-fitted using Langmuir and Halsey isotherms. These nanohybrids exhibited considerable adsorption capacities that varied from 154 to 256 mg/g . The catalytic performance indicated that the investigated nanohybrids could eventually be used for the removal of RB dye in presence of H_2O_2 and visible light within 60 min, affirming that the CX/MWCNTs obtained are effective materials in liquid-phase applications for treating dye-contaminated industrial wastewater.

1. Introduction

Synthesis of organic gels and their carbon gels (i.e. xerogels, aerogels and cryogels) by sol-gel polycondensation was first reported by Pekala [1]. These materials are classified as one class of nanostructure carbon materials [2]. Due to their fascinating properties such as low mass density, high surface area, continuous porosities, three-dimensional network interconnected nodules and high conductivity; they are also recognized as unique materials for high temperature thermal insulation [3] and capacitive deionization systems [4]. Furthermore, such materials contain a hierarchical structure of pores formed during two stages of their synthesis. The first stage associated by the formation of mesoporous structure during sol-gel process as a result of phase separation, while microporous structure is created as a result of carbonization in the second step. Furthermore, the possibility of easy alteration in their textural and structural properties towards particular applications declares their use as adsorbents, catalyst supports and electrode materials for supercapacitors and rechargeable batteries [5–14].

In order to expand the potential applications of these unique materials, some additives such as metals and carbon nanotubes (CNTs) can be incorporated into the carbon gels matrix [15]. In recent years, CNTs are emerged as one of the best additives in the design of carbon-carbon nanohybrids due to their intrinsic properties such as electrical conductivities as high as 10^6 Sm^{-1} [16], thermal conductivities as high as $3000\text{ Wm}^{-1}\text{ K}^{-1}$ [17] and elastic moduli on the order of 1 TPa and being extremely flexible [18]. Also, the large surface-to-volume ratio of CNTs (100–1000) making low addition of CNTs (less than 1 vol%) can produce a composite with novel properties [19]. Particularly, Worsley et al. [20] synthesized a monolithic of double-walled carbon nanotubes (DWCNTs)/carbon aerogels nanocomposites during sol-gel polymerization of resorcinol and formaldehyde in an aqueous solution containing a surfactant stabilized dispersion of DWCNTs [20]. In a further investigation, they studied properties of single-walled carbon nanotubes-based carbon aerogels as a function of nanotube loading (0 – 55 wt%) [21]. Earlier research by Haghgoo et al. [22] documented the preparation of multi-walled carbon nanotubes (MWCNTs) dispersed

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in resorcinol-formaldehyde (RF) aerogel using sodium dodecyl benzene sulfonate and studied the dispersion effect of MWCNTs on the final properties of RF matrix. Also, Haghgoo and coworkers [23] studied the correlation between morphology and electrical conductivity of dried and carbonized multi-walled carbon nanotube/resorcinol-formaldehyde xerogel composites, where the maximum surface area of the MWCNTs/carbon xerogels (CXs) reached to 685 m²/g. Fathy et al. [24] synthesized carbon nanotube/carbon xerogel hybrid (CNT/CX) during chemical vapor decomposition of camphor in presence of RF xerogel loaded with nickel catalyst. Results showed that this hybrid exhibited a specific surface area of 95 m²/g and a maximum capacitance of 50 F/g. However, the chemical activation of this hybrid with phosphoric acid led to an enhancement in both the specific surface area and electrochemical capacitance reaching to 215 m²/g and 151 F/g, respectively. Therefore, incorporating of CNTs into the carbon gels matrix through sol-gel step can produce valuable nanohybrids accompanying with an improvement in their chemical, electrical, thermal and mechanical properties. On the basis of these promising findings, the nanohybrids consisting of carbon xerogel and carbon nanotubes (CX/CNTs) were used effectively as electrodes in an energy storage application [24–26]. These studies indicated that good dispersion of CNTs through preparation of organic gels could enhance the capacitance performance of CX/CNTs electrodes rather than the individual component alone (CX or CNTs). The most likely explanation of this finding is due to the presence of mesopores through CNTs bundles and the micropores developed on the CX surface that could serve as active sites for fast electrolyte ions transfer which strengthened the electrochemical performance of electric double layer capacitors (EDLCs). Accordingly, to the author's knowledge, the use of CX/CNTs nanohybrids in liquid-phase adsorption and catalysis processes has not yet been published.

Recently, few studies were carried out to prepare low cost CNTs using agricultural wastes [27,28]. In this study, synthesized multi-walled carbon nanotubes (MWCNTs) from chemical vapor deposition of both rice straw as natural substrate and camphor as carbonaceous gas source [27] were successfully used as additives with carbon xerogel.

In sum, the aim of this paper was to investigate the adsorptive and catalytic oxidation behaviors of carbon xerogels and MWCNTs microporous nanohybrids towards removal of rhodamine B dye (RB). To find the optimum conditions, different concentrations of MWCNTs that well-dispersed in sodium dodecyl sulfate surfactant were performed during sol-gel of resorcinol-formaldehyde reactants to evaluate their effect on the adsorption and catalytic properties of obtained nanohybrids. Further investigation using SEM, TEM, N₂ adsorption and FTIR was also carried out. Rhodamine B (RB) dye is a synthetic dye and used extensively in textile, leather, paper and cosmetic industries and its resistance to biological and chemical degradation implies that it is an excellent compound for this study. Adsorption and catalytic experiments for the removal of rhodamine B (RB) dye from aqueous solutions were employed.

2. Experimental

2.1. Materials

Resorcinol (C₆H₆O, Panreac, 99%), formaldehyde (HCHO, Adwic, 36–38%), methanol (CH₃OH, Sigma-Aldrich, 99%), sodium carbonate (Na₂CO₃, POCH SA, 99%), sodium bicarbonate (NaHCO₃, POCH SA, 99%) and sodium dodecyl sulfate (SDS, CH₃(CH₂)₁₁OSO₃Na, Sigma-Aldrich, 98%) as an anionic surfactant were purchased and used without prior purification.

2.2. Preparation of MWCNTs

Fathy [27] prepared laboratory-multiwalled carbon nanotubes (MWCNTs) via chemical vapor deposition of camphor as carbon source onto as catalyst support of a hydrothermally treated rice straw loading

with iron and nickel oxides at 850 °C for 30 min. Prior to preparation of nanohybrids, the produced MWCNTs were purified with a mixture solution of HNO₃:H₂SO₄ = 3:1 (v/v) at 100 °C for 4 h, followed by washing for several times with distilled water till pH of filtrate becomes ~6. Then the sample was dried in an air-oven at 80 °C overnight. The outer diameters of MWCNTs were between 22 and 66 nm and the specific surface area of MWCNTs was about a 35 m²/g.

2.3. Preparation of carbon xerogels/MWCNTs nanohybrids

A sol-gel procedure of resorcinol-formaldehyde-sodium dodecyl sulfate (R-F-SDS) was carried out according to the following recipe: reactants of R, SDS and Na₂CO₃ as alkaline catalyst (C) were dissolved in distilled water (W) and then formaldehyde solution (F) stabilized by 10% methanol was added into this mixture under vigorous stirring to form the hydrogel. The hydrogel was obtained after 30 min at 80 °C. The molar ratios of the used reactants with respect to resorcinol were calculated as; R/F = 0.5, R/C = 500, R/W = 0.027 and R/SDS = 9.36 × 10⁻⁶. The pH of the sol was adjusted to 6.0 by 0.1 M NaOH solution. The prepared hydrogel was then transferred into a stoppered glass bottle and heated in an air-oven at 80 °C for 24 h to complete curing and gelling process. Afterwards, the sealed bottle was opened to allow the gel obtained for drying at the same temperature for another 48 h. After cooling, the obtained xerogel was carbonized as follows. The carbonization of xerogel prepared from sol-gel of resorcinol-formaldehyde-SDS was carried out at 350 °C for 1 h and gradually raised up to 750 °C for 2 h under flowing of N₂ gas (heating rate 10°/min). Finally, the carbon xerogel produced was washed thoroughly with hot distilled water for several times, filtered, dried and denoted as CX.

In preparation route of CX/MWCNTs nanohybrids, initially three different concentrations of MWCNTs (1, 2 and 4 g/L) were dispersed in an aqueous surfactant solution containing sodium dodecyl sulfate (SDS) and water with a fixed weight ratio of MWCNTs/SDS = 2/3 [22]. This mixture was thoroughly stirred for 30 min followed by sonication for 1 h to form homogeneous solution. A solution of R, F and C with the same fixed molar ratios as abovementioned was added to MWCNTs/SDS under stirring and heated at 80 °C for 30 min. The sol-gel mixture was transferred into sealable glass moulds and kept in an air-oven at 80 °C for 1 day to complete polymerization process. Brownish-black monolithic gels were formed and dried by evaporation at 80 °C for 2 days and then exposed to carbonization process. A vertical tubular reactor was used to carry out the pyrolysis of dried gel composites at two subsequent temperatures of 350 °C for 1 h and 750 °C at 2 h under passing N₂ gas. The resulting samples were denoted as the following; CX/1-MWCNTs, CX/2-MWCNTs and CX/4-MWCNTs, respectively. Arabic numerals in the notations refer to the concentrations of MWCNTs incorporated into CX matrix.

2.4. Characterization of the prepared samples

The surface morphology and content of elements in the obtained nanohybrids were determined using field-emission scanning electron microscope (FEI-SEM, Quanta FEG-250) attached to energy-dispersive spectroscopy and electron backscatter diffraction (EDAX). The structure of the prepared samples was estimated deeply by high resolution-transmission electron microscopy (HR-TEM, JEM-1230, Japan).

The textural parameters such as Brunauer-Emmett-Teller surface area (S_{BET}, m²/g), total pore volume (V_p, cm³/g) and average pore diameter (\bar{r} , Å) were determined using nitrogen adsorption analysis at -196 °C (BEL-Sorp, Microtrac Bel Crop, Japan) [29]. In addition, some textural parameters were evaluated using α_s – method such as total surface area (S_t^α, m²/g), non-microporous surface area (S_n^α, m²/g), and the micropore volume (V_o^α, cm³/g) [30]. To estimate the pore size distributions, N₂ gas adsorption data were analyzed using NLDFT method which allows the quantification of both micro- and mesopores

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