Hierarchical hybrid carbon nano-structures as robust and reusable adsorbents: Kinetic studies with model dye compound

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HIGHLIGHTS

- A new design for robust and reusable carbon nanostructures has been demonstrated.
- Aligned nanotube arrays anchored on porous foams create super-adsorbing sponges.
- High capacity Langmuir adsorption demonstrated with model contaminant.
- Advantages of carbon nanotubes available without environmental dispersion risks.

GRAPHICAL ABSTRACT
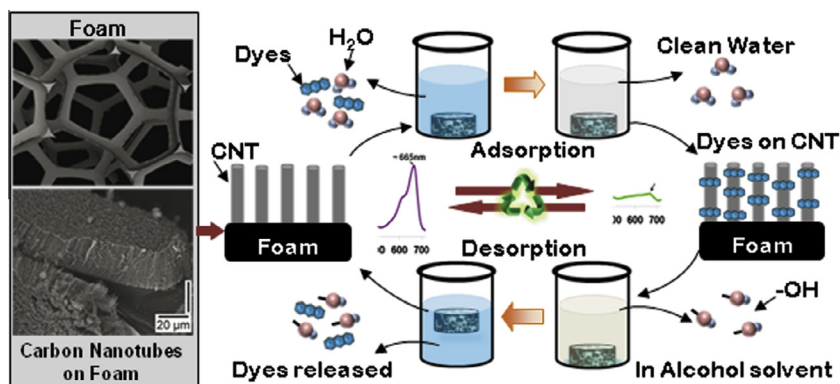
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ABSTRACT

This study demonstrates the potential of using multi-scale hierarchical carbon structures as robust, reusable solids suitable for removal of aqueous pollutants such as dye molecules from wastewater. Carpet-like vertical arrays of carbon nanotubes (CNT) were attached on surfaces of porous carbon foams by pre-coating with silica buffer layer followed by chemical vapor deposition (CVD). The surface morphology and specific surface areas were varied by controlling the buffer layer thickness and CVD deposition times. Surface characteristics have been correlated with adsorption thermodynamics and kinetics by investigating the removal rates of methylene blue (MB) dye in simulated water. The results show that MB adsorption capacity correlates well with total CNT surface area in the carpet, indicating full utilization of the nanotube surfaces. Adsorption rates fit well with pseudo second order kinetics model. Maximum MB adsorption capacity of the CNT surfaces in this structure was estimated by extrapolating equilibrium adsorption amounts at different dye concentrations using the Langmuir isotherm. This was found to be about 43.5 mg/g, which compares favorably with adsorption capacity of isolated nanotubes. It must be noted that whereas isolated nanotubes can disperse in the liquid and pose environmental threats, the hierarchical solids as demonstrated in this study can be repeatedly agitated in water without the loss of CNT or performance deterioration. These results indicate promising application potential for these types of hybrid materials in environmental purification applications.

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1. Introduction

The contamination of water bodies is an ever-growing problem worldwide, and water pollution issues are impacting all aspects of

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life [1–3]. In addition to population growth, water contamination is increased by widespread industrialization that can produce unprecedented contaminants [4]. These include byproducts containing heavy metals, chemical toxins, petroleum derivatives, dyes, and other emerging contaminants [5,6]. Dyes are common contaminants from textile, plastic, and paper industries. They are complex aromatic synthetic compounds that have potential carcinogenic and mutagenic effects [2,3,6,7], and are difficult to treat due to their chemical stability and resistance to natural biological degradation. Several techniques have been developed for dye degradation including chemical precipitation, filtration [8], adsorption [9–11], photo-catalysis [12,13], electrochemical [14], ion-exchange [15] and oxidation/catalytic degradation [16,17]. Among these techniques, adsorption is the most attractive due to its simplicity, high efficiency, ease of operation, and its ability to remove multiple components simultaneously. Moreover, adsorption technique can be coupled with other mechanisms such as photo-degradation or catalysis, whereby the adsorbed and immobilized toxic compounds and their derivatives can be subsequently treated [18]. This has led to the study of a wide range of natural and synthetic materials as potential adsorbents [19,20]. It is recognized that the desirable material characteristics of an adsorbent are chemical stability, structural durability, and high specific surface area. Hence, there has been growing emphasis on developing innovative adsorbent solids that can maximize the above characteristics.

Carbon-based materials such as activated carbon, carbon fibers, aerogels, and nanostructures of carbon are well-suited as adsorbents [21–23]. Nanostructures of carbon such as graphene, carbon nanotubes (CNT), and bucky-balls, have recently gained significant interest [22–27]. Among them, CNT have shown special promise due to their high aspect ratio, fibrous meso-porous structure, and large specific surface area [27]. These have been reportedly used in the isolated powder form and have shown high adsorption performance, but successful recovery of nanostructures pose a significant challenge and calls for additional separation steps [9,28]. This is a serious limitation of stand-alone CNT and all isolated nanomaterials in general, since their dispersion in water can relate to uneconomical material loss and pose toxicity risks to the aquatic environment [29,30]. Moreover, the cost-effectiveness will be significantly reduced if the material cannot be recovered and reused easily. Possible approaches proposed to address this limitation include centrifugation and attachment of magnetic iron nanoparticles that can be separated from liquid media using a magnet [31–34]. Both options add cost and complexity to the adsorption process.

More recent investigations have focused on designing aggregated materials containing nanostructures of carbon [35–42]. Vecitis et al. has reported a thin sheet of multiwalled carbon nanotubes – MWCNT (50 μm) as filter material held with PTFE membrane and encased in filter casing [39]. Zhao et al. have developed a graphene sponge [40] and Ai et al. have reported a graphene-carbon nanotube hybrid structure as adsorbent material [41]. These structures are improvements over isolated nanotubes, but still consist of loosely aggregated nanostructures that are not sustainable in flowing water because they lack the structural integrity of a covalently bonded continuous solid.

In this study, we demonstrate a new class of hybrid solid consisting of tall vertical carbon nanotube arrays chemically bonded to larger carbon supports through a reactive buffer layer of silicon dioxide. The CNT arrays are structurally robust, and provide the flexibility of tunable surface area, which can be several orders of magnitude higher than that of conventional high-porosity solids. The hybrid structures can be used as effective reusable adsorbents since the nanotubes do not detach in liquid media, and therefore no additional recovery step is needed. Moreover, these structures, if successful as adsorbents, can be functionalized with suitable nanocatalysts in future for degradation of the adsorbed species. These types of hierarchical materials are already proven to effectively host metal nanoparticles [43], which were successful in repeatable use for degradation of carbon tetrachloride [44] and biological contaminants in water [45].

The present study focuses on bench-scale investigation of the CNT-Foam hybrid structures for removal of a model organic contaminant: methylene blue dye (MB). Methylene blue is a well-known cationic dye that has wide applications in textile, printing, biology, and chemistry. MB has some harmful effects to the environment, but it is less toxic than most aromatic dyes and hence it is suitable as a good model pollutant.

Two different types of foam structures having different geometry and porosity have been compared: micro-cellular carbon foam (Ce-foam) consisting of spherical cell walls (80% porous) and reticulated vitreous carbon foam (RVC-foam) consisting of triangular struts (97% porous). Carefully controlled CNT arrays have been grown on these porous materials using a previously published process [46,47] that covered, not only the outer surfaces, but also the deeper interior pores of the foams.

Methylene blue adsorption experiments were studied using UV–Vis spectroscopy to monitor dye concentration in water. Rate kinetics and isotherm analysis for adsorption of MB on CNT arrays on foam structures have been performed, and results are compared with those from other advanced materials reported in the literature. The results suggest that CNT arrays on foams of this study compares well with other reported materials, while providing the additional benefit of structural durability and repeated use.

2. Materials and methods

2.1. Materials and chemicals

The chemical reagents used in this study were of analytical grade and consumed without further purification. These include hexamethyl-di-siloxane (HMDSO, Sigma–Aldrich chemicals), xylene (PTI Process Chemicals), ferrocene (99%, Alfa-Aesar Ltd.), methylene blue ($C_{16}H_{18}N_3SCl$, MW: 319.85 g/mol, λ_{max}: 665 nm, Sigma–Aldrich chemicals), and 2-propanol (99.9%, HPLC Grade, Fisher Scientific). Other materials are de-ionized water (DI water) and laboratory grade gases that include argon and hydrogen. The micro-cellular carbon foam (Ce-foam) used in this study is of L1a grade, which was obtained from Koppers© Inc. The reticulated vitreous carbon foam (RVC-foam) is 80 ppi (pores per inch) grade obtained from Ultramet© Inc.

2.2. Fabrication of CNT on porous carbon – hybrid material preparation

Vertically aligned carbon nanotubes were fabricated on porous foam structures using a two-step coating process described in earlier publications [46,47]. The first step involves plasma enhanced deposition of a nano-layer of silicon dioxide followed by carbon nanotube (CNT) growth using floating catalyst chemical vapor deposition (CVD) technique. Silica was deposited on porous structures using oxygen and gas phase HMDSO as precursors in the microwave plasma reactor (V15GL manufactured by PlasmaTech Inc.). In the second step, CNT growth was carried out using a multi-zone CVD furnace reactor (MTI Corporation Ltd.). A mixture of ferrocene and xylene (catalyst and carbon sources) was injected in the pre-heated zone maintained at 380 °C. Reactions were allowed to happen for a specific length of time in the reaction zone where the substrates were maintained at 700 °C in an Ar/H$_2$ environment. Subsequently, the furnace was allowed to cool down to room temperature in a reduced flow of Ar. The structural