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Outstanding adsorption performance of high aspect ratio and super-hydrophobic carbon nanotubes for oil removal

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HIGHLIGHTS

- The performance of Produced CNT with high aspect ratio is analyzed for oil-water separation.
- As hydrophobicity of CNT increased the removal of oil from water increased too.
- The Produced CNT showed adsorption capacity of more than 7 g/g.
- Removal efficiency of 100% is achieved using produced CNT.

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ABSTRACT

Oil removal from water is a highly important area due to the large production rate of emulsified oil in water, which is considered one of the major pollutants, having a negative effect on human health, environment and wildlife. In this study, we have reported the application of high quality carbon nanotube bundles produced by an injected vertical chemical vapor deposition (IV-CVD) reactor for oil removal. High quality, bundles, super hydrophobic, and high aspect ratio carbon nanotubes were produced. The average diameters of the produced CNTs ranged from 20 to 50 nm while their lengths ranged from 300 to 500 μm. Two types of CNTs namely, P-CNTs and C-CNTs, (Produced CNTs from the IV-CVD reactor and commercial CNTs) were used for oil removal from water. For the first time, thermogravimetric analysis (TGA) was conducted to measure maximum oil uptake using CNT and it was found that P-CNT can take oil up to 17 times their weight. The effect of adsorbent dosage, contact time, and agitation speed were examined on the oil spill clean-up efficiency using batch sorption experiments. Higher efficiency with almost 97% removal was achieved using P-CNTs compared to 87% removal using C-CNTs.

1. Introduction

Owing to the rapid growth in energy demand worldwide, oil production from conventional and unconventional resources is growing annually. The production of each barrel of oil is associated with the production of 2–3 barrels of contaminated water, the so called "produced water" (Khatib and Verbeek, 2002). Accordingly, significant amounts of produced brine waters are generated during the exploitation and production processes (Wang et al., 2011). Generally, the normal practices in the oil and gas industries are discharging the produced water to the spent reservoir or into water bodies such as seas or tailing ponds (Martins et al., 1995). Water produced from oil wells contains almost 30–50% of free oil and emulsified hydrocarbons, and many other heavy metals such as arsenic, strontium, barium, etc. (Fakhru'l-Razi et al., 2009). Free and emulsified oil in produced water contains many toxic/phytotoxic compounds such as aromatic hydrocarbons, organic acids, phenols, etc (Fakhru'l-Razi et al., 2009).

Abbreviations: CNT, carbon nanotube; CVD, chemical vapor deposition; IV-CVD, Injected Vertical Chemical Vapor Deposition; XRD, x-ray powder diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; BET, Brunauer–Emmett–Teller; TGA, thermogravimetric analysis; TOC, total organic carbon; D-R, Dubinin–Radushkevich isotherm; IC, inorganic carbon; TC, total carbon.

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Owing to the presence of such compounds in produced water, it has become a significant environmental concern. Based on the United States Environmental Protection Agency (USEPA) limits, the daily maximum limit for oil and grease in water is 42 mg/L and the monthly average limit is 29 mg/L (EPA). Consequently, to meet environmental regulations and to endorse the recycling of produced water, many research projects are under consideration for treating oily, saline produced water (Kaatz et al., 2006).

Different techniques are used for treating oil-contaminated water including reverse osmosis, filtration (ultra and micro), various flotation methods (dissolved air, column flotation, electro and induced air), adsorption, gravity separation, activated sludge treatment, membrane bioreactors, biological treatment, chemical coagulation, electro-coagulation and coalescence (Gu et al., 2014; Kong et al., 2015). Sorption is a widely used technique due to its simplicity and high efficiency (Fakhru'l-Razi et al., 2009).

The selection of adsorbents/absorbents and the development of new functional materials that can remove oil depends on many factors such as availability, cost, and safety of the adsorbent material. High carbon or oxygen content is also important since this property leads to good oil removal from water. Another physical factor such as the surface area of the sorbent is also of importance. Nevertheless, only a limited numbers of materials meet all the practical demands for selectivity, sorption capacity, sorption rate and recyclability. These parameters, which are mainly governed by the structure of the sorbents that exhibit super-hydrophobicity and super-hydrophilicity, high porosity, suitable pore sizes, and reversible deformation under a high level of strain, must be studied and considered (Nishi et al., 2002; Nguyen et al., 2012; Zhao et al., 2012; Zhang et al., 2014b) (Zou et al., 2010). To date, the synthesis of sorbents with superior oil sorption performance remains a great challenge.

Generally, three types of materials are used for oil sorption and classified as (i) synthetic polymers, (ii) natural fiber materials, and (iii) inorganic minerals (Gui et al., 2011). The synthetic polymers are widely used due to their hydrophobic and oileophilic characteristics. Examples of such synthetic polymers are polyurethane (Duong and Burford, 2006), polypropylene(Tu et al., 2016), polyethylene and butyl rubber (Zou et al., 2010). However, the drawback of synthetic polymers is their very slow degradability, which makes them an environmental concern. Moreover, these materials are prone to fouling by blocking their surfaces pores (Masuelli et al., 2009). Natural fiber materials represent another sorption material characterized with low sorption capacities and are mostly hydrophilic (Gui et al., 2011). Examples are corn stalk (Husseien et al., 2009), bagasse pith (Hussein et al., 2008), nonwoven wool (Radetic et al., 2008) and cotton fibers (Deschamps et al., 2003). The inorganic sorbents are the most widely used; examples of such materials are vermiculite (Moura and Lago, 2009), exfoliated graphite (Toyoda and Inagaki, 2000), sepiolite (Rajaković-Ognjanović et al., 2008), zeolites (Rajaković-Ognjanović et al., 2008), CNTs (Fard et al., 2016), etc. Recently carbon nanotubes (CNT) caused a lot of interest in oil removal studies due to their exceptional one-dimensional structure, large specific surface area, and oileophilic and hydrophobic nature (Gupta and Tai, 2016).

Super-hydrophobicity is a function which is mainly found on hydrophobic surfaces with enhanced surface roughness because of the minimization of contact areas between the surface and water by trapped air (Evershed et al., 1983; Dong et al., 2012). Therefore, multiwalled carbon nanotubes (MWCNTs; referred to in this paper as CNTs for the sake of simplicity), have been widely used for the synthesis of super-hydrophobic surfaces because of their large aspect ratio, chemical inertness, and hydrophobicity (Ci et al., 2007; Gui et al., 2010). In this study, we used ultra-long CNTs synthesized using the chemical vapor deposition (CVD) technique and the performance for oil removal has been compared with commercial multiwalled CNT. MWCNTs are an outstanding raw material that can be widely applied in many fields (Lan et al., 2014; Patiño et al., 2015). Since being introduced in 1991 CNTs have gained a lot of interest due to their chemical, mechanical, and thermal stability (Upadhyayula et al., 2009; Ihsanullah et al., 2015). Oil-water purification using CNTs as an adsorbent has been reported by a limited number of researchers and considered to be a new field. The reported studies in the literature for oil-water separation are mainly on cleanup of oil spill from the surface of water but it was not tested for separation of oil from an oil-water emulsion (Gu et al., 2014; Kong et al., 2015), (Gui et al., 2013; Pham and Dickerson, 2014; Khosravi and Azizian, 2015). The results in our study are quite unique due to adsorption of oil molecules on the surface of the carbon nanotubes using powder (as received CNTs). Other reported studies consider the adsorption by entrapment of the oil molecules in the pores of the sponge or highly porous material, which results in very large sorption capacity. Therefore, the mechanism is based on adsorption of pure oil and not the separation of dispersed oil from water as reported in this study (Li et al., 2016).

The main objective of this study is to compare the removal efficiencies of CVD-produced CNT (termed produced CNT in the context) and commercial CNT as raw adsorbents and determine the optimal parameters for efficient removal of oil from water. The raw and modified CNTs were characterized using field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis (TGA), X-ray diffractometer (XRD), the Brunauer, Emmett and Teller (BET) nitrogen adsorption technique, and high-resolution transmission electron microscopy (HR-TEM). The effect of different parameters such as sorbent dosage, contact time, and oil concentration were investigated for the removal of oil from water. The sorption experimental data were analyzed by the Freundlich, Halsey, Temkin, and Dubinin–Radushkevich isotherm models and the data were correlated to the appropriate kinetic model.

2. Experimental section

2.1. Materials

Two types of CNTs were used in this study, commercial CNT (C-CNT) and produced CNT (P-CNT). Commercial CNT was purchased from the Chengdu Organic Chemicals Co Ltd. (China). The CNTs have a lengths of 1–10 μm and outer diameters of 10–20 nm with purity of >95% and BET surface area of 141 m^2/g while the other types of CNTs were produced using an Injected Vertical Chemical Vapor Deposition (IV-CVD) Reactor. Analytical grade hydrocarbon liquid xylene was purchased from Sigma-Aldrich Co. Ltd. and the gasoline liquid used as synthetic oil was purchased from a local Petrol Distribution Company, Woqod, Doha, Qatar with an octane number of 97. All the chemicals were used as received without purification.

2.2. Synthesis of carbon nanotubes

The IV-CVD reactor was designed and fabricated to produce high quality and high purity CNTs. The production of CNT (referred to P-CNT for sake of simplicity) in the present study was conducted in a vertical reactor. As shown in Schematic 1, the vertical reactor consists of a quartz tube of 100 mm in diameter and 1200 mm in length with flanges fixed at both ends. The top flange has two inlet ports, one for gas inlet and the other for injecting the aqueous solution of hydrocarbon with the iron source catalyst using a syringe pump. The P-CNTs were collected from the bottom of the reactor into a receiving collector. Two types of gases, hydrogen and argon gases were used and controlled by mass flow controllers. The