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Sol-gel derived flexible silica aerogel as selective adsorbent for water decontamination from crude oil

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ABSTRACT

Oil spills are the most important threat to the sea ecosystem. The present study is an attempt to investigate the effects of sol-gel parameters on seawater decontamination from crude oil by use of flexible silica aerogel. To this goal, methyltrimethoxysilane (MTMS) based silica aerogels were prepared by two-step acid-base catalyzed sol-gel process, involving ambient pressure drying (APD) method. To investigate the effects of sol-gel parameters, the aerogels were prepared under two different acidic and basic pH values (i.e. 4 and 8) and varied ethanol/MTMS molar ratios from 5 to 15. The adsorption capacity of the prepared aerogels was evaluated for two heavy and light commercial crude oils under multiple adsorption-desorption cycles. To reduce process time, desorption cycles were carried out by using roll milling for the first time. At optimum condition, silica aerogels are able to uptake heavy and light crude oils with the order of 16.7 and 13.7, respectively.

1. Introduction

Over the last decade, there has been an increasing worldwide concern about controlling the release of organic liquids into the environment. Generally, the main sources of the seawater contamination are oil tankers accidents, war, oil rig drilling and natural events, which cause severe environmental damage. For example, in Exxon Valdez incident, over 112 million gallons of crude oil spilled into Alaska seawater, during the Gulf war in 1991, several thousand tons of crude oil spilled into the sea as well (Carmody et al., 2008; Teas et al., 2001; Westermeyer, 1991).

In this regard, special efforts have been made to use of environmentally friendly materials in oil spill out technology. Hence, in recent years a large number of studies have been carried out implementing a wide range of materials namely, adsorbents, booms, solidifiers and dispersants (Olalekan et al., 2014). Adsorbents are a class of attractive nanometer/micrometer size materials due to the high ability of collection and complete removal of hydro-carbonic contaminations from oil spill sites. Using adsorbents in oil spill areas facilitates a change from liquid to semi-solid phase causing easy decontamination by removal of the adsorbent. Furthermore, these materials have the potential to be recycled and used for further decontamination operations. Oleophilicity and reusability as well as textural properties of adsorbents are significant factors for effective oil spill clean-up applications. Modified polymers, resins and inorganic hybrids are some general examples of adsorbents used to remove oils and organic pollutants from the marine ecosystem (Ceylan et al., 2009; Li et al., 2012; Lin et al., 2012; Wei et al., 2005). However, few studies have focused on the reusability of both adsorbents and adsorbed crude oil, ignoring the reuse of latter on would contribute to great loss of energy sources.

Recently, nano-engineering has opened up new perspectives in commercial and special fields of engineering applications (Sun et al., 2017; Liu et al., 2017; Wang et al., 2017; Li et al., 2017; Yang et al., 2017; Zhang et al., 2017a; Zhang et al., 2017b; Zheng et al., 2017). Nanoporous materials are organic or inorganic based materials with the micro, *meso* or macro pore size distributions. Zeolites, activated carbon, ceramics, inorganic porous hybrids, and aerogels are some typical examples of this kind of natural or synthetic materials. Thanks to the valuable intrinsic properties of nanoporous materials such as high porosity, high surface area, and tuneable pore size distribution they are used in many various engineering applications. In recent years, this type of materials has been recognized as promising candidates for the engineering applications such as energy storage, solar cells, separation technologies, catalysis, sorption applications, environmental remediation, and electromagnetic devices (Jenkins, 2010; Rao et al., 2004). With rising concerns about the environmental pollutions from the organic materials, the use of nanoporous materials in the removal of polluting components from the different media has become more significant (Albuquerque Júnior et al., 2008; Mangun et al., 2001; Hristovski et al., 2009a, 2009b; López-Muñoz et al., 2005; Mattigod

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et al., 1999; Standeker et al., 2007; Wu and Ritchie, 2006).

Aerogels are a class of nanoporous materials, which are prepared with various chemical compositions and produced by the sol-gel process of both inorganic and organic precursors. Typical high-quality silica aerogels are sol-gel derived materials, which are formed in open three-dimensional silica network with unique properties such as high surface area (800–1200 m^2/g), high porosity (~%98) and very low density (0.06 g/cm^3) (Aegerter et al., 2011). These materials have found potential applications in various fields such as thermal super insulation, oil spill cleanup, aerospace, and intelligent sensing (Alippi, 2016; Haiyang et al., 2016; Padhy and Sidhartha, 2017; Zhang et al., 2016). Silica aerogel is a low density inorganic type of aerogels, which possesses a three-dimensional nanoporous structure with unusual properties such as high specific surface area (500–1200 m^2/g), high porosity (80–99.8%) and low index of refraction (~ 1.05). Due to the intrinsic properties of this type of nanoporous materials, silica aerogel has drawn a lot of interest in engineering application (Aegerter et al., 2011; Soleimani Dorcheh and Abbasi, 2008). For example, silica aerogel has found special attention in biological applications for the purpose of the development of both drug delivery systems and enzyme encapsulation (Guenther et al., 2008; Rajanna et al., 2015; Smirnova et al., 2004). High surface area accompanied with a high porosity of the aerogels also gives it a great potential to use as a heterogeneous catalyst or catalyst carriers in both gas and liquid phase systems (Orlović et al., 2002; Yousefi Amiri et al., 2016; Yu et al., 2015). Using as a Template, thermal insulator, using in refrigerators, Skylights, and Windows are some general examples of commercial applications of silica aerogel (Hasan et al., 2017; Rubin and Lampert, 1983; Thapliyal and Singh, 2014; Wei et al., 2008). From recent literature, it can be understood that silica aerogel has gained widespread acceptance as green and efficient material used primarily in hydrocarbonic decontamination and environmental applications due to its non-toxicity nature. Hutbesh et al. (Hrubesh et al., 2001), reported the comparative study between perfluoro modified silica aerogel and granular activated carbon for cleaning the certain hydrocarbon components (i.e. toluene, ethanol, chlorobenzene) from wastewater. The adsorption capacity of the modified silica aerogels exceeded the capacity of comparable granular activated carbon by a factor of 30 to 130 for high and low water miscible components, respectively. The group of Rao et al. (Parale et al., 2011) reported about the adsorption-desorption properties of the chemical surface modified TEOS based silica aerogel for use in hydrocarbon cleanup application. The study deal with adsorption of pure organic components and the results reveal that, in light hydrocarbon components, aerogel adsorbents are able to adsorb neat organic liquids (i.e. acetone) approximately 12 times per unit mass of silica aerogel.

It is well known that in adsorption of hydrocarbonic components, especially in the oil spill cleanup process, it is necessary to use hydrophobic materials. Hydrophobic aerogels were prepared by rendering their hydrophilic network to a hydrophobic surface by chemical surface modification or using a special silica precursor containing hydrocarbonic groups in its molecular structure (Aegerter et al., 2011; Teas et al., 2001). Although its non-toxicity and special textural properties provide high potential as a green adsorbent, its brittleness, hydrophilicity and cost of production (i.e. chemical surface modification) strongly limit its industrial applications especially in the field of environmental protection. Therefore, special efforts have been made to synthesize cost effective hydrophobic silica aerogel. In this regard, several groups have reported well-tailored intrinsic hydrophobic silica aerogel with an improved adsorption property of organic components (Bhagat et al., 2007; Brinker and Scherer, 1990). However, only a few experiments have focused on the effect of synthesis parameters on both recyclability of the adsorbent materials and to reuse the adsorbed oil. Based on the discussed considerations, the aim of this study was to investigate the effect of sol-gel parameters on the adsorption-desorption performance of flexible silica aerogels to be used in crude oil decontamination applications. In this study, we characterize the textural properties of the prepared aerogels in detail and discuss the relationship between sol-gel parameters and porous morphology to enable the good design of nano-porous silica network for use in oil spill cleanup applications. The decontamination performance of the resulted methyltrimethoxysilane (MTMS) based silica aerogels was examined in terms of adsorption-desorption capacity in a real condition of seawater/crude oil bath. To this aim, different sets of experiments were performed in which the molar ratio of EtOH/MTMS systemically varied in three different values (i.e. 5, 10, 15) and gelation proceeded under two acidic and basic conditions (i.e. pH of 4 and 8, respectively). With the best knowledge of the authors, this is the first study about the comprehensive investigation of the effect of sol-gel parameters on crude oil decontamination performance of MTMS based silica aerogel and use of roll milling in desorption step of decontamination.

2. Materials and methods

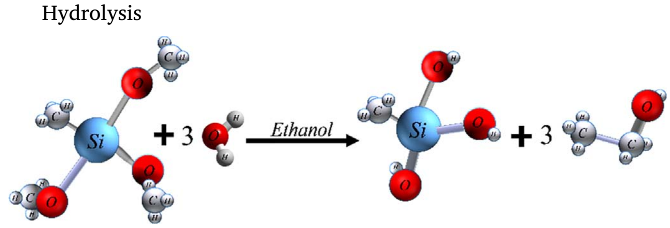
2.1. Materials

All chemical reagents including methyltrimethoxysilane (MTMS), oxalic acid, ammonium hydroxide solution, ethanol (EtOH) and NaCl were purchased from Merck and used as received. In this research, two different types of heavy (Persian Gulf) and light (North Brent Sea) crude oils were used for adsorption-desorption examinations. These are the general types of commonly used crude oil and were selected due to their frequent applications in refinery processes. The properties of the used crude oils are listed in Table 1.

2.2. Aerogel preparation

An overview of the fabrication scheme for hydrophobic silica aerogel is shown in Fig. 1. To synthesize MTMS-based aerogels, alcogels were prepared via two-step acid-base process. First of all, silica sols were prepared by dilution of MTMS in ethanol. For hydrolysis, desire amount of water in form of 0.01 M oxalic acid, as an acidic catalyst, was added to the EtOH/MTMS mixture. For complete hydrolysis, the solution was stirred for 6 h. at room temperature. For the purpose of acidic and basic conditions of gelation, different amount of basic water (ammonium hydroxide with 0.005 molarity) was added to EtOH/MTMS/acidic water solution. pH monitoring was conducted by using high accurate portable pH meter (Mettler-Toledo inc). In all cases, the total molar ratio of H_2O/MTMS was kept constant at 6. Afterward, alcosols were transferred into an airtight container and placed in an oven for gelation at 50 °C. Mechanisms of hydrolysis and polycondensation of MTMS-based silica aerogels are as per the following chemical reactions (Bhagat et al., 2007; Rao et al., 2005; Wu et al., 2011).

Hydrolysis



(1)

Table 1
Properties of the crude oil samples.

Property	North Brent Sea	Heavy Persian Gulf	Method
Density (g/ml)	7.4	8.7	ASTM D-1298
API gravity (°)	35	29	ASTM D-1298
Kinematic viscosity 40 °C, c.St.	4.4	9.2	ASTM D-445