Plasma polymer facilitated magnetic technology for removal of oils from contaminated waters☆

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ABSTRACT

Oil pollution of waters is one of the most serious environmental problems globally. The long half-life and persistence within the environment makes oil particularly toxic and difficult to remediate. There is a significant need for efficient and cost-effective oil recovery technologies to be brought in to practice. In this study, we developed a facile and efficient magnetic separation method. The surface of 316L stainless steel nanoparticles was modified by plasma deposition of 1,7-octadiene and perfluorooctane, producing relatively hydrophobic coatings having water contact angles of 86 and 100°, respectively. Both coatings had high oil removal efficiency (ORE) of >99%. The captured oil could be easily separated by applying an external magnetic force. The ease of material preparation and separation from the water after the oil is captured, and its high ORE is a compelling argument for further development and optimization of the technology to possible utilization into practice. Furthermore, the capacity of plasma polymerization to deliver desired surface properties can extend the application of the technology to removing other chemical and biological contaminants from polluted waters.

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1. Introduction

With the growth of industrial development and exploration, production, and refining, the possibility for oil pollution of the environment presents a significant risk. Oils are considered particularly dangerous contaminants because of their persistence and extremely long half-lives in the environment (Guix et al., 2012). Some sources often causing water pollution by oil contaminants are factories waste, petroleum transport and refinement, transportation leakages and household waste (Jha et al., 2008; Seifi et al., 2011; Wang et al., 2012). Furthermore, common strategies and technologies implemented for oil removal are gravity separation, physical separation, flotation, evaporation, chemical extraction, membrane separation, and adsorption (Arthur et al., 2005; Fakhru'l-Razi et al., 2009).

The adsorption method is by far the most popular technique because of its efficiency, low cost, simplicity of utilization and the ease of the application (Ali et al., 2012). This process exploits the physical adhesion of the pollutant to a solid physical surface. The essential requirement for adsorbent materials is to be hydrophobic and oleophilic (Chu and Pan, 2012). Such materials have already been applied for water-oil separation, particularly for high viscosity oils (Xue et al., 2011). Recently, considerable efforts have been made to develop efficient adsorbents by modifying material surface properties. Typical chemistries used to generate hydrophobic surfaces are hydrocarbon (Nash et al., 2015; Venkateswara Rao et al., 2007; Wang et al., 2012), fluorocarbon (Gürsoy and Karaman, 2016; Kylián et al., 2014; Tomina et al., 2011; Zhu et al., 2005), or siloxane (Ferrara and Pattarini, 2016; Tsoi et al., 2004; Zhang et al., 2007). These adsorbents have been demonstrated to deliver good outcomes when applied for removing oil spillage, organic solvents and toxic organic compounds (Bi et al., 2012; Dong et al., 2012; Monopoli et al., 2011; Zhang et al., 2017b; Zhu et al., 2011).

One of the current challenges related to the methods for material surface modification is that the procedures are commonly conducted by wet-chemistry and rely on complex reactions, which are highly substrate type dependent and produce an excess of potentially toxic waste products (Hernandez-Lopez et al., 2003; Morent et al., 2011). This complexity leads to limitations in the selection of carrier material and prohibitive costs associated with west solvent treatment. Thus, it is logical to develop methods which can potentially overcome these limitations. An example of such alternatives is a technique called plasma polymerization. The methods involve the deposition of polymer–like, highly cross-linked coating from the vapor of an organic precursor (Denes and Manolache, 2004; Vasilev, 2014; Yasuda and Matsuzawa, 2005).

Plasma polymerization offers many benefits compared to wet processes. It is substrate independent, which means that identical coatings can be deposited on the surface of different materials using the same process (Vasilev et al., 2009). The techniques consist of a single step and do not require the use of any solvents. Furthermore, coatings can be deposited on substrates of compact sizes and shapes, including micro and nanoparticles. Finally, there is substantial body of literature from our group and others pointing that hydrophobic coatings can be prepared in a very facile way using plasma-based techniques (Akhavan et al., 2013a; Hegemann et al., 2001; Michelmore et al., 2011; Ramiasa-MacGregor et al., 2016; Vaswani et al., 2005).

Another challenge is to separate the adsorbent material from the contaminated continuum. Processes such as centrifugation and filtration give excellent results in some situations, but they are too expensive or inapplicable in some instances. In this work, we selected to use as hydrophobic coating carrier 316L stainless steel nanoparticles because they can be easily separated by the contaminated medium by an external magnetic field. Nanoparticles also have a very high surface to volume ratio, thus providing a large surface area to which oil contaminants could be concentrated. The surface of magnetic and others particulate can be modified by plasma polymerization using customized systems developed by our group and others (Cavallaro and Vasilev, 2015; De Vietro et al., 2012; Jarvis and Majewski, 2012; Michl et al., 2015; Mierczynska-Vasilev et al., 2017; Wahono et al., 2016).

The hypothesis underpinning this work is that 316L stainless steel nanoparticles modified by hydrophobic plasma polymer layers can be successfully utilized for the removal of oils from aqueous media. To validate this hypothesis, we coated the surface of magnetic nanoparticles using two precursors known to deliver coatings with different levels of hydrophobicity. After characterizing the chemical and physical properties of the coatings, we evaluated the capacity of newly developed plasma polymer coated magnetic adsorbents to oils from model aqueous media.

2. Materials and methods

2.1. Materials

For plasma precursor, 1,7-octadiene and perfluorooctane (octadecafluorooctane) were purchased from Sigma-Aldrich and used as received. Two types of crude oil samples from the waste store of the University of South Australia were used as model oils. Density and viscosity of the oil samples were measured. The density measurements were conducted using $25\,cm^3$ pycnometer and the JF1004 ProSciTech, whereas the viscosity measurements were conducted using the LVT-93405 Brookfield Viscometer with spindle number LV 1, LV 2 and 60, 30 rpm. All measurements were performed at $23.0 \pm 0.5\,°C$. 316L stainless steel nanoparticles (Hongwu International Group, Guangzhou, China) were chosen as the base for the adsorbent material due to their magnetic properties and size. This

material is a black powder with a purity of 99,99% and size of 70 nm.

2.2. Plasma deposition

The nanoparticles were coated with hydrophobic polymers using 1,7-octadiene and perfluorooctane (octadecafluorooctane). The coating process utilized a cylindrical custom built plasma reactor, which is supported by the U-shaped upper electrode, round-shaped bottom electrode, and powered by RF plasma generator of 13.56 MHz. The reactor was equipped with agitation platform for coating of powder or particulate material (Cavallaro and Vasilev, 2015; Wahono et al., 2016). Octadiene and perfluorooctane were coated using the pressure of 16 Pa and 23 Pa, respectively. In both cases, deposition was carried out using RF power of 50 W. Total deposition times varied between 600 and 2400 s.

2.3. Characterization

SEM analysis was conducted to determine the morphology of the magnetic nanoparticles and possible changes of the plasma polymerization treatment. SEM was performed on the Hitachi SU3500 at the Indonesian Institute of Sciences. The sample was dried in the oven at $110\,°C$ for an hour to remove water. A small quantity of powder sample was splashed on carbon tape surface as preparation before analysis. The results of this analysis show in Supplementary Information part.

To investigate the coatings thickness, wettability, and stability, $1\,cm^2$ silicon wafers were also coated with the same polymers. Ellipsometry was used to determine the thickness of the coatings. All measurements were conducted using J. A. Woollam Co., Inc. V-VASE Ellipsometer with the plasma polymers deposited on silicon wafers and data collected and analyzed using the WVASE32 software. Surface wettability was used to investigate the hydrophobicity of surface coatings. A sessile drop method was employed, and all images were captured by Logitec digital camera and contact angles determined by ImageJ software. The thickness changes caused by polymer loss were measured to determine the relative stability of the coatings in aqueous environments. The stability test was conducted by soaking silicon wafers coated with the hydrophobic polymers in ultra-pure water for an hour and measuring the thickness by ellipsometry (as above).

XPS analysis was used to determine the surface composition of bare and plasma coated magnetic nanoparticles. XPS spectra were recorded on a Specs SAGE XPS spectrometer. The results were processed and fitted using CasaXPS software. The XPS was operated with Mg Kα radiation source (hv = 1253.6 eV) at 10 kV and 20 mA. It used a Phoibos 150 with MCD-9 detector as the hemispherical analyzer. The atomic composition was calculated from the survey spectra in the energy range 0–1000 eV at the pass energy of 30 eV and resolution of 0.5 eV. The C1s neutral carbon peak of 285 eV was used a reference for all the binding energies to compensate the surface charging effect.

2.4. Oil capture experiments

A mixture of water $(20\,cm^3)$ and crude oil $(400\,mm^3 = 20,000\,ppm)$ was prepared. The coated magnetic nanoparticles as adsorbent were used in various oil-to-adsorbent-weight ratios (between 8 mg and 1200 mg of adsorbents). The adsorbent was added to the oil/water samples then agitated for 30 s and allowed to rest for 600 s. A magnet was then used to collect the adsorbent after capturing oil from the oil/water solution which shown in **video 1**. The rest of the solution was mixed with n-hexane to determine oil residue within the samples. The oil residue content