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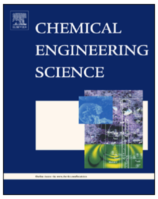


# Modification of formaldehyde-melamine-sodium bisulfite copolymer foam and its application as effective sorbents for clean up of oil spills

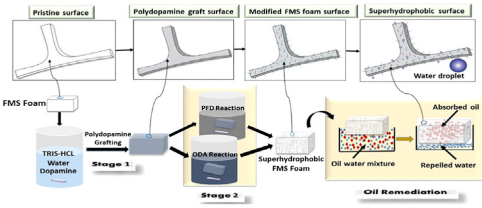
Oluwasola Oribayo [a], Xianshe Feng [b], Garry L. Rempel [b], Qinmin Pan [a,*]

[a] College of Chemistry, Chemical Engineering and Material Science, Soochow University, 199 Ren'ai Road, Suzhou 215123, People's Republic of China
[b] Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada N2L 3G1

## HIGHLIGHTS

- FMSF-PDA-PFD and FMSF-PDA-ODA spill clean-up sorbents were successfully fabricated.
- Hydrophobic molecule incorporation into pristine foam template was achieved.
- Sorbents exhibits high sorption capacity and recovery for oil spill clean-up.
- Excellent reusability and oil/water selectivity is displayed by sorbents.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Oil spills have serious impact on the environment, and its effective remediation for environmental protection is of global significance. Thus, oil sorbents with interconnected microporous structures having superoleophilic and superhydrophobic properties have attracted significant interest as sorption materials for oil spill clean-ups. In this study, an approach inspired by the adhesive proteins secreted by mussels was used in modifying a commercially available formaldehyde-melamine-sodium bisulfite copolymer foam (FMSF) as a thiols and amine functionalized oil/solvent sorption material, resulting in significantly improved hydrophobicity and oleophilicity. Our strategy was based on facile conjugation of octadecylamine (ODA) and 1H,1H,2H,2H perfluorodecanethiol (PFD) molecules to polydopamine (PDA) adhered to the interior micropores of FMSF. The FMSF-PDA-PFD and FMSF-PDA-ODA foams so prepared showed excellent oil/water selectivity, without damaging its intrinsic 3-D porous structure. In oil and solvent sorption experiments using engine oil and chloroform, a very high oil sorption capacity (amounting to 84 and 152 times its own weight) was obtained respectively. They also showed excellent reusability, and the same good oil sorption capacity was retained after 50 cycles of sorption-squeezing steps. The absorbed oil in the foams could be removed and collected simply by squeezing, and the foams became ready for reuse. The superhydrophobic and superoleophilic foams exhibited a significant potential as an effective and low-cost oil absorbent for applications in large-scale oil-spill clean-ups and recovery.

## 1. Introduction

Oil spills have become a critical worldwide issue that has a significant impact on environment and ecological systems, needless to say the energy loss due to discharge of oil into the environment. Over the past few years, there have been several oil spill events with serious consequences on human health and wildlife (Annunciado et al., 2005; Arbatan et al., 2011; Bande et al., 2008; Dave and Ghaly, 2011; Duan et al., 2015; Suni et al., 2004). For instance, the oil spill accident that occurred in the China National Offshore Oil Corporation in June 2011 at the Penglai 19-3 Oilfield in Bohai Bay resulted in more than 840 sq km of coastal

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* Corresponding author.
*E-mail address:* qpan@suda.edu.cn (Q. Pan).

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water polluted, causing huge economic losses in the aquatic farming and tourism industries of Hebei and Liaoning provinces (Zhou and Wang, 2011). To address this challenge, various oil spill remediation techniques (including the uses of sorbents, chemical dispersants, solidifiers, bioremediation, mechanical clean-up methods, and in-situ burning of oil in water) have been employed to facilitate clean-up and recovery of the spilled oil from water surface (Al-Majed et al., 2012; Chu and Pan, 2012; Wei et al., 2003; Yuan and Chung, 2012). Among these techniques, the application of three dimensional (3D) porous oil absorbent materials is particularly attractive and promising because not only is it able to absorb and hold the oil pollutants into its matrix structure, subsequent recovery of the oil from its semisolid phase is also achievable (Lü et al., 2016; Ruan et al., 2014; Wu et al., 2015; Yang et al., 2015; Zhu et al., 2011). In addition, such properties as selective oil/water separation, high oil sorption capacity, fast sorption uptake, hydrophobicity and oleophilicity, reusability, biodegradability, and environmentally friendliness must also be satisfied for effective applications.

In recent years, interconnected microporous sorbent materials having favourable superoleophilic and superhydrophobic surface properties and excellent oil sorption capacity have attracted significant interest for potential applications in oil/water separation because of their self-cleaning properties. The water droplet on a superhydrophobic sorbent material surface can roll off even at inclinations of only a few degrees, while still retaining the oil contaminants encountered on its way into its matrixes (Li et al., 2012; Pham and Dickerson, 2014; Reyssat et al., 2010). Motivated by these endowed properties, many efforts have been devoted to developing novel and advanced 3D porous materials, possessing hydrophobic surface properties and interconnected macro-porous structures with excellent absorption performance for the separation and recovery of organic pollutants from water. It may be mentioned that these efforts in developing functional architectural materials have significantly improved the absorption performance towards various oil and organic solvents.

Duan et al. (2014) synthesized a highly hydrophobic and oleophilic chitin sponge via a freeze-dry method, followed by thermal chemical vapour deposition of methyltrichlorosilane at different relative humidities. The 3D sorbent material was reported to possess a high sorption capacity that was effective for absorption of organic solvents from both the surface and bottom of the water and solvent mixtures. Liu et al. (2013) reported the fabrication of an oil sorption material by grafting graphene oxide, modified by dodecane diamine onto polyurethane foam. This process was reported to enhance the foam surface roughness and reduce its surface energy, making it hydrophobic. The modified foam exhibited excellent oil sorption capacities and recyclability for organic liquids. Wang et al. (2014) fabricated a superhydrophobic sorption material by coating an ultrathin functionalized layer onto polyurethane (PU) foams. This was done via atomic layer deposition of $Al_2O_3$ transition layer onto the skeleton of polyurethane foam, followed by coupling of a single-molecule layer of silanes to the foam via hydroxyl groups on the surface of the $Al_2O_3$ layers. The modified PU foams exhibited outstanding water-repelling ability and oil-affinity without compromising their high porosity and elasticity. Wu et al. (2014) fabricated a superhydrophobic and superoleophilic sponge by modifying a commercial polyurethane foam with $TiO_2$ sol and n-octadecylthiol successively, and this sorption material was reported to show a high oil–water selectivity and high absorption capacity for a variety of oils and organic solvents at both static and dynamic conditions. However, most of the sorption material fabrication processes reported in the literature are complicated and costly, and they often require sophisticated equipment. In addition, the superhydrophobic stability of these sorption materials have not been fully elucidated, which restrict their deployment for industrial applications.

Inspired by the adhesive proteins secreted by mussels for attachment to wet surfaces (Lee et al., 2007a; Reyssat et al., 2010; Wu et al., 2015; Xu et al., 2010), the innate self-polymerization attribute of dopamine to form surface-adherent polydopamine (PDA) has attracted considerable interest in polymer coatings for special applications (Lynge et al., 2011). Dopamine, commonly known as neurotransmitter or hormone, is a unique molecule mimicking adhesive proteins secreted by mussels. It self-polymerizes at a weak alkaline pH to form polydopamine on a wide range of surfaces (Lee et al., 2007a, 2007b; Lynge et al., 2011). This adhesive protein, which contains catechol and amine functional groups, exhibits excellent affinity for most inorganic and organic substrate surfaces, including metals, metal oxides and polymers. Moreover, these substrates can be further surface functionalised and modified by reaction between quinone (oxidized form of catechol produced during dopamine self-polymerization reaction) and such functional groups as thiols and amine via Michael addition or Schiff base reaction, forming covalently-grafted functional layers (Lee et al., 2007b, 2008; Xu et al., 2010).

Therefore, due to its covalent and non-covalent bonding capabilities for a broad range of inorganic, organic, and metallic substrates, polydopamine has potential applications for self-cleaning surfaces, microfluidic channels, antibacterial/antifungal/antifouling membranes, drug delivery systems, and tissue engineering (Dreyer et al., 2012; Lynge et al., 2011). Lee et al. (2007a, 2007b), for example, reported multifunctional polymer coatings onto a wide range of inorganic and organic materials through simple dip-coating of the objects in an aqueous solution of dopamine. This may be followed by a secondary reaction, creating ad-layers via grafting with macromolecules for various industrial applications.

Inspired by the endowed adhesive ability of dopamine and its capability of undergoing secondary reaction with macromolecules, this paper presents the chemical modification of a superhydrophobic formaldehyde-melamine-sodium bisulfite copolymer foam (FMSF) for oil spill remediation application, using a facile cost-effective two-step method. The sorption material was prepared by anchoring polydopamine on the skeleton of FMSF via dopamine self-polymerization, followed by functionalization with thiols and amine functional groups. In addition, the properties and performance of the material as an oil absorbent, fabricated using thiol and a low-cost hydrophobic functionalisation molecule (ODA), were also investigated.

## 2. Experimental

### 2.1. Materials

Formaldehyde-melamine-sodium bisulfite copolymer foam (FMSF) was purchased from SINOYQX, China, nonwoven polypropylene sorbent (PPS) was purchased from Suzhou YJ Environmental protection co. Ltd, China and SJ MA 10W-50 engine oil was purchased from Sinopec, China. Dopamine hydrochloride, oil red, methylene blue, and tris(hydroxymethyl) aminomethane (Tris), were purchased from Energy Chemicals (Shanghai, China). 1*H*,1H,2*H*,2H-Perfluorodecanethiol was purchased from Sigma–Aldrich and used as received. Octadecylamine was purchased from Aladdin Reagent. 1, 2-dichloromethane, toluene, cyclohexane, acetone, ethanol, carbon tetrachloride, chloroform and silicone oil were purchased from Shanghai Chemical Reagents Co. Ltd. All chemicals were used as received.