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PAPER

6 Reduced Graphene Oxide-Coated Microfibers for Oil-Water 7 Separation

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10 Reduced graphene oxide (rGO)-coated microfibers (GCMs) have been developed through a straightforward synthesis by
11 soaking microfiber cloths in graphene oxide (GO) aqueous dispersions and followed by reduction with hydrazine vapors in
12 autoclave at 80 °C. The produced GCMs show high hydrophobicity and oleophilicity, which can be used to recover crude oil
13 from oil-in-water mixtures. The microscopic structures have been analyzed under optical microscopy and scanning electron
14 microscopy; confirming the presence of rGO on the microfibers' surface. Thermal gravimetric analysis measurements
15 showed that GCMs are stable up to 300 °C. Raman spectroscopy indicated a strong quenching of the polymers' peaks in
16 GCMs and the appearance of graphene's D and G peaks due to the rGO coating. The maximum uptake capacity of the GCMs
17 is 6.78 g of oil per gram of material with a reduction of 13.5% after 10 adsorption-desorption cycles. Removals of 97.90%
18 and 87.58% of crude oil have been achieved after a single application of GCMs in 1% (v/v) oil-water and oil-artificial seawater
19 mixtures respectively. Oil concentrations below 35 ppm have been reached after the second and the fifth application of
20 GCMs in oil-water and oil-artificial seawater mixtures respectively. The adhesion strength of the rGO coating has been
21 assessed by different means such as sonication and vigorous mixing in water; the highest amount of rGO released in water
22 was 8.3 ppm after 30 minutes of sonication. These properties suggest that GCMs can be used, as prepared or combined in
23 filter devices, as a possible oil recovery method in case of oil spills.

24 Introduction

25 Crude oil is an important source of energy and chemicals
26 in the world; it provides raw material for the production
27 of a large variety of polymers, plastics, rubbers and
28 organic solvents.^{1,2} Nowadays, maritime oil transport and
29 production from offshore oil reservoirs have become
30 more frequent in order to meet the demand of this
31 precious resource.³ This increases the chance of
32 environmental disasters that have an impact on marine
33 and coastal wildlife, tourism, fishing and on the local
34 economies of the impacted regions.^{4,5} Additionally, the
35 cost of a major oil spill is remarkably high due to the loss
36 of oil and the enormous remediation tasks for clean-up.⁶
37 During the Deepwater Horizon oil spill in 2010, it has been
38 estimated that 4.9 million barrels of oil have been
39 released in the Gulf of Mexico and around 2.1 million
40 gallons of dispersants were used to mitigate the
41 environmental damages caused by the spill.⁷
42 Apart from dispersants, numerous different remediation
43 techniques have been developed. Physical remediation

44 methods consist in booms and skimmers: the former are
45 used to confine the oil spill while the latter can absorb or
46 suck the oil in.^{4,8} Other remediation methods are in-situ
47 burning, use of sorbents^{4,5,7} and bioremediation through
48 microorganisms.⁹ However, most of these techniques use
49 toxic chemicals, produce harmful by-products or are time
50 consuming. In addition, they will degrade or change the
51 physico-chemical composition of the oil, making its
52 recovery impractical for further use. Skimmers, boom and
53 sorbents are the only remediation methods that do not
54 alter the properties of the spilled oil, allowing it to be
55 reused. Skimmers generally need an oil-water separation
56 step of the influent liquids due to the high amount of
57 water collected in the process.¹⁰ In contrast, sorbent
58 materials can avoid this thanks to their hydrophobic and
59 oleophilic properties. These materials can be produced
60 from natural fibers such as cotton, rice husks or kapok
61 fibers and treated to improve their hydrophobic
62 properties and surface area.^{4,7,11} Synthetic sorbents
63 alternatives to the ones obtained from natural fibers can
64 be made of polymers such as polypropylene, which
65 already presents a strong hydrophobic behavior and can
66 be easily produced as a porous foams and fibers;
67 achieving high absorption capacities per gram of
68 material.^{4,7,12}
69 In contrast to common organic solvents such as toluene
70 and chloroform, which are single compounds with specific
71 molecular structures and physical-chemical properties,

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crude oil is a complex mixture of numerous different compounds, mostly hydrocarbons, and thus its properties can significantly vary depending on its composition, which is often related to its geographical origin.¹³ On average, the majority of the crude oils are composed by 50% naphthenes or cycloalkanes, 30% paraffins or alkanes, 15% aromatics and 5% polar compounds containing nitrogen, sulfur and oxygen called NSO compounds and metals in trace amounts.^{14,15}

Graphene, in addition to various applications in catalysis and electrochemistry,^{16–22} has been recently used to coat different types of substrates such as polyurethane, melamine foams and cotton fibers; achieving remarkable separation and recovery of organic solvents and oils from water^{23–27}. This is due to graphene's strong hydrophobicity, oleophilicity and large surface area.^{28–31}

Graphene, an allotrope of carbon,³² consists of a monoatomic layer of sp² hybridized carbon atoms (120° angle) with a C-C bond length of 1.42 Å. Graphene has extremely low resistivity ($1.0 \cdot 10^{-8} \Omega\text{m}$), high Young's modulus (1 TPa) and its theoretical calculated surface area has been estimated to be 2630 m²/g while experimental values are between 270 and 1550 m²/g.³³ The high hydrophobicity of graphene and other carbon nanomaterials, e.g. carbon nanotubes, comes from their chemical and topological structures. Graphene, being composed exclusively by carbon atoms, is extremely efficient in repelling polar molecules such as water and, when used as a coating, it can increase the roughness of a substrate, further enhancing the hydrophobicity of the composite material.³⁴ On the other hand, the carbon lattice of graphene and its derived materials have a strong affinity towards a wide range of organic solvents, hydrocarbons and oils and can be easily wetted by graphene-derived materials due their comparable surface energies.³⁵ This properties, combined with high thermal, mechanical and chemical stability, makes graphene-derived materials excellent choices for oil-water separation.³⁴

Three-dimensional (3D) graphene-derived structures, such as porous free-standing aerogels and foams, have been reported as effective selective sorbents for heavy metals³⁶, oils³⁷ and organic solvents³⁸; achieving some of the highest oil uptake capacities per gram of material.⁷ The main disadvantages of the 3D graphene-derived structures are their delicate mechanical structure, lack of a large-scale production technology and poor reusability. Flexible and spongy graphene-derived 3D structures were developed to overcome these problems, however their synthesis is often complicated and requires expensive materials and reagents.^{39–43}

Reduced graphene oxide (rGO)-coated microfibers (GCMs) offer another approach for oil remediation due to the combination of high hydrophobicity and the technology versatility when it comes to the matrix selection, which allows designing composite materials with the desired flexibility, resistance to mechanical

solicitation and reusability. Given their straightforward preparation, technology scalability and possibility to be used in harsh conditions, they can be considered an alternative to other oil sorbents. rGO can be obtained in large quantities via chemical routes from graphene oxide (GO). Although its properties and morphology are not identical to single-layer pristine graphene, the residual oxygen containing groups present on rGO after the reduction of GO, have been reported to enhance the affinity towards polar solvents that are difficult to remove with pristine graphene,⁴⁴ thus increasing its effectiveness towards a wider range of polar molecules present in crude oils such as NSO compounds.

In this work, the authors report cost-effective and reliable rGO-coated microfibers (GCMs) for selective absorption of crude oil from oil-in-water mixtures. Commercial microfibers were coated with rGO using mild temperatures and scalable synthesis. The developed GCMs have been characterized through a series of techniques such as scanning electron microscopy (SEM), Raman spectroscopy and thermal gravimetric analysis (TGA) to map their structures and properties. Various qualitative and quantitative oil absorption analyses have been performed on the GCMs to assess their reusability, oil uptake capacity and oil removal efficiency in both oil-water and oil-seawater mixtures. The GCMs developed here are promising and could be implemented for oil-water separation, wastewater treatment and oil spills remediation.

Experimental section

Materials and Chemicals

All glassware was cleaned thoroughly with detergent and rinsed with deionized water. Milli-Q water (Millipore) was used in the determination of aromatic compounds through Ultraviolet-visible light (UV-Vis) spectrophotometry and for the preparation of stock solutions. Hydrazine hydrate (N₂H₄•H₂O 99%), 2-propanol (CH₃CH(OH)CH₃ 99.9%), ethanol (C₂H₅OH 99%) and ammonium hydroxide (NH₄OH 30%) were purchased from Sigma Aldrich (USA). GO was purchased from The Sixth Element (China). The two different crude oils used in the experiments were extracted in Mexico and the North Sea (Denmark). The viscosity and density of North Sea oil were 7.29 mPas and 0.8461 g/ml respectively (25°C). The viscosity and density of Mexican oil were 12.45 mPas and 0.8668 g/ml respectively (25°C). The North Sea crude oil was used in every test while the Mexican crude oil was used only in the oil uptake capacity test. Artificial seawater stock solution was prepared following the method proposed by Kester *et al.*⁴⁵ The salts were purchased from Sigma Aldrich (USA) and were reagent grade. All the purchased chemicals were used as received. GO dispersions (1 and 4 mg/ml) were prepared by dispersing appropriate amounts of GO powder in Milli-Q water, followed by 30 minutes of

Scheme 1. Schematic illustration of the procedure used for the preparation of GCMs.

sonication. The main commercial microfiber used for the preparation of GCMs was Ultra Terry 300 gsm Microfiber from Microfiber Tech (USA) composed of 80% polyester and 20% polyamide, as stated by the supplier. Alternative types of GCMs have been prepared using different microfibers. Details on these alternative fabrics and their preliminary experiments are given in the supplementary information.

Fabrication of GCMs

The microfiber cloth was cut into 6.0x6.0 cm² pieces and soaked with 20 ml of 1.0 or 4.0 mg/ml aqueous GO dispersion. After being soaked for 30 minutes, the textiles were removed from the dispersion. The excess of GO dispersion was removed by dripping. The samples were placed in a clean glass container and heated in an oven at 60 °C until completely dry. A 10 ml glass beaker was positioned upside down on the bottom of a homemade Teflon-lined autoclave equipped with stainless steel jacket (8 cm in height and 5 cm in diameter). The samples were then cut in to 3.0x3.0 cm² pieces of approximately 0.35 g each and placed on the top of the beaker inside the autoclave. 3 drops (Ca. 150 µl) of 99% hydrazine hydrate were carefully added to the bottom of the Teflon container by a pipette, avoiding direct contact with the samples or the beaker. The autoclave was then sealed and heated at 80 °C for 4 hours in an oven to reduce GO by hydrazine vapors. Once the reduction was completed, the autoclave was removed from the oven, cooled down to room temperature, opened, and left in a fume hood for 2 hours to eliminate hydrazine residues. After this step, the reduced GCMs were collected, and stored in a sealed container. Pure microfiber is hereafter defined as MF

while microfiber samples coated with 1.0 and 4.0 mg/ml GO solution are defined as MF1 and MF4 respectively. **Scheme 1** shows the main steps for the preparation of GCMs.

Characterization

A Leica DFC 295 optical microscope (Germany) and a Carl Zeiss Merlin field emission SEM (Germany) have been used to analyze the microstructure of the GCMs. A Mettler Toledo TGA/differential scanning Calorimetry (DSC) 1 STARe System (Switzerland) has been employed for TGA to obtain information on thermal stability of GCMs and their degradation temperatures. A Horiba Labram HR (Japan) equipped with a 488 nm laser was used for Raman spectroscopy analysis. Details on the characterization methods are described in the supplementary information.

Oil uptake capacity

The weight of dry GCMs was measured. Subsequently, the GCMs were dipped in crude oil until completely soaked. The excess of oil was removed by dripping until drops stopped falling. Afterwards, the samples were weighted again. The amount of oil absorbed was obtained by subtracting the dry sample weight from the wet sample weight. By calculating the grams of oil per gram of material ratio, the oil uptake capacity was obtained.

Reusability

Figure 1. (a) A piece of microfiber before treatment, (b) coated with GO and (c) after reduction. The brownish color is due to the deposited GO, which turns black and hydrophobic once reduced to rGO. (d) A larger piece of GO-coated microfiber ready for reduction.

After having measured the dry weight of GCMs, the samples were soaked in crude oil, dripped from the excess and weighted again following the same procedure used for the oil uptake capacity. The samples were then squeezed to extract the absorbed oil and weighted to evaluate how much oil has been retained by the GCMs. To determine whether the oil uptake capacity has been reduced, the samples were then re-soaked in the oil, dripped and weighted again. Each sample has been soaked and squeezed for 10 times and its dry and wet weight noted. The overall behavior of the GCMs after various absorption-desorption cycles and mechanical stresses has been evaluated.

Quantitative absorption

The absorption capabilities of GCMs were quantified by UV-Vis spectrophotometry according to the method described by Bastow T. *et al.* (1997).⁴⁶ Many aromatic compounds present in crude oil show an absorption peak at 226 nm; another peak at 256 nm can be attributed to benzene. 2-propanol was used as a co-solvent to facilitate the solution of crude oil in water. Measurements were performed with a Shimadzu UV-2401PC spectrophotometer (Japan) and Hellma Analytics High precision cell-SUPRASIL quartz (Germany) with 10 mm optical path length. The detailed description of the method is given in the supplementary information.

Residue of rGO in water

To assess the environmental safety of GCMs, the amount of rGO released by GCMs after sonication or stirring in water has been quantified by UV-Vis spectrophotometry. The detailed description of the method can be found in the supplementary information.

Results and Discussion

Development of GCMs

The clean microfibers were completely wetted by both 1 and 4 mg/ml GO dispersions rapidly. After being dried in oven, the samples changed their color uniformly from white to light brown (Figure 1a and Figure 1b respectively), indicating that GO has been deposited on the microfibers successfully. After the reduction, the samples turned black (Figure 1c); this is a clear sign of the conversion of GO to rGO. It was possible to upscale the production of GCMs by simply using larger pieces of microfibers and appropriate amounts of reagents (Figure 1d). Nevertheless, due to the limited size of the available autoclaves, the GO-coated microfibers were cut into smaller pieces before reduction. The use of bigger

Figure 2: (a) Oil uptake capacity of GCMs. MF1 performs better compared to MF4. Higher uptake capacities are measured with the more viscous Mexican oil. (b) Reusability test of MF1 with North Sea oil. (c) Reusability test of MF4 with North Sea oil.

Figure 3. (a, b, c) Optical micrographs of MF, MF1 and MF4 respectively. (d, e, f) SEM micrographs of MF, MF1 and MF4 respectively; the latter shows presence of rGO agglomerates. (g, h, i) SEM micrographs of MF1 obtained with InLens detector and higher magnifications.

autoclaves would easily overcome this limitation, allowing the fabrication of large GCMs cloths.

Compared to the initial pure microfibers, no difference in the mechanical properties of the GCMs was noticed; all

the samples could be pressed, stretched and twisted as the pure microfibers without visible losses of the rGO coating. Hydrophobicity was tested by leaving the materials in a beaker full of water for 24 hours. No visible changes or wetting occurred after the elapsed time. Additionally, when immersed underwater and subsequently released, the GCMs quickly rose back to the surface completely dry. In contrast, pure microfibers would rapidly absorb water, losing most of their buoyancy.

Quantitative and reusability tests on GCM

The oil uptake capacity, reusability and oil removal efficiency of each GCM has been determined. **Figure 2a** shows the maximum oil uptake capacity of the GCMs for oils with different viscosities

and densities. The oil uptake capacity of MF4 was 5.15 g/g for North Sea oil and 5.42 g/g for Mexican oil. GCMs coated with 1 mg/ml GO absorb more oil in general with 5.42 and 6.78 g/g for North Sea and Mexican oil respectively; nevertheless, the difference in oil uptake capacity between the two GO concentrations is usually small. The higher absorptions of the Mexican oil can be attributed to its higher viscosity, thus less dripping of the oil excess. **Figure 2b**, presents the results of the reusability test for MF1. The measurements were conducted with the North Sea oil. MF1 first measurement showed a lower uptake capacity compared to the second cycle. This might be due to the incomplete impregnation of the internal fibers. After squeezing the MF1 for the first time, the free internal spaces in and among the fibers have been forced to absorb oil due to the pressure exerted. Thus, it is more representative to consider the difference in uptake capacity between the second and the last cycle, which results in a reduction of the MF1 uptake capacity of 13.5%. An average of 1.35 g of oil per gram of MF1 is retained within the material's bulk volume after each squeezing cycle. A similar behavior has been observed with MF4 (**Figure 2c**): the initial oil uptake capacity tends to increase after few cycles due to incomplete impregnation of the fibers; it then decreases rather steadily with every single further cycle. Compared to MF1, MF4 needs more cycles to be fully saturated with oil; this is possibly due the presence of rGO agglomerates observed with SEM (**Figure 3f**). The reduction in oil uptake capacity between the 4th cycle (highest value) and the last is 13.3%. The average amount of retained oil per gram of material after squeezing is 1.41 g.

Optical microscopy and SEM

Optical microscopy micrographs showed that the white color of pure microfiber changes to a metallic grey-black once turned to MF1 (**Figure 3a** and **Figure 3b** respectively). The darker color of MF4 in **Figure 3c** is possibly due to a higher concentration of rGO on the surface. The dense but airy network of pure microfibers changed to a more compact network in MF1 (**Figure 3e**)

Figure 4. (a) TGA curves of MF, MF1 and MF4. (b) Raman spectra of MF, MF1 and MF4.

Figure 5. (a) 100 ml of 1% (v/v) oil-in-water mixture before the first oil removal with a 3.0x3.0 cm² piece of MF1. (b) The same oil-water mixture after oil absorption with a piece of MF1.

and especially in MF4; with the latter showing rGO agglomerates with sizes ranging between 50 and 200 μm (Figure 3f). Nevertheless, the presence of rGO on MF1 becomes clearly visible only at higher magnifications and with the use of an InLens detector. In Figure 3g is possible to observe the presence of the rGO coating on the microfibers along with some rGO sheets extending out from the microfibers' surface. Figure 3g, Figure 3h and Figure 3i confirm the presence of a thin coating of rGO along all the entirety of the microfibers' length.

TGA

All samples showed a linear and slow weight loss due to moisture desorption until 375 $^{\circ}\text{C}$ when a sudden weight loss occur due to the degradation of polyester and polyamide^{47,48} (Figure 4a). The last weight variation at 500 $^{\circ}\text{C}$ is attributed to the oxidation of carbon and rGO into gaseous products.⁴⁹ MF and MF4 are completely burnt off at 535 $^{\circ}\text{C}$. In contrast, MF1 decomposes entirely at 570 $^{\circ}\text{C}$ possibly due to the presence of the more uniform rGO coating observed with the SEM. In conclusion, All GCMs are stable up to 300 $^{\circ}\text{C}$.

Raman Spectroscopy

MF shows polyester peaks at 1614 and 1723 cm^{-1} ^{50,51} and a possible polyamide peak at 1284 cm^{-1} that is slightly shifted to the left compared to the peak at 1298 cm^{-1}

found in literature.⁵⁰ The rGO coating quenches the intensities of the polymeric peaks. The quenching is more significant for MF4 compared to MF1. In addition, rGO generates the characteristic D and G peaks at 1361 cm^{-1} and 1582 cm^{-1} respectively due to its similarities with graphene (Figure 4b).⁵²

Determination of GCMs oil removal efficiency by UV-Vis spectrophotometry

Considering the lower values of oil uptake capacity, presence of rGO agglomerates and the need of a significant large amount of GO for the synthesis, MF4 has not been investigated further. MF1 has been chosen as the GCM of choice due to its higher performance in oil uptake capacity and finer rGO coating. 100 ml of 1% (v/v) oil-in-water mixtures (1 ml of North Sea oil in 99 ml of water) were measured with the UV-Vis spectrophotometer before and after being repeatedly cleaned by appropriate pieces of MF1 (3.0x3.0 cm^2), capable of absorbing all the oil present in the mixture. In Figure 5, a reduction in oil content was already noticeable by naked eye.

Three filtrations can reduce the amount of oil from 8461 to 23.9 ppm in oil-water mixtures. On the other hand, seawater has a stronger interaction with the oil and requires five filtrations to bring the oil concentration down to 34.4 ppm (Figure 6). These experiments confirm

Figure 6. (a) UV-Vis absorption curves for repeated filtration of a 100 ml, 1% (v/v) oil-in-water mixture using a 3.0x3.0 cm^2 piece of MF1. (b) Repetition of the previous test using a 1% (v/v) oil-in-seawater mixture. (c) Residual oil concentration in water and (d) seawater after each treatment.

Figure 7. (a) UV-Vis absorption curves for released rGO in a water sonicated together with a 3.0x3.0 cm² piece of MF1 for 10, 20 and 30 minutes. (b) Repetition of the previous test with mild and vigorous stirring instead of sonication. (c) rGO concentration in water after each treatment.

that MF1 is efficient in absorbing oil from the oil-water mixtures and can reach oil concentrations close or below to the 30 ppm limit defined by the OSPAR Commission for offshore water discharges.⁵³

rGO residue in water

rGO is firmly immobilized on the microfibers. MF1 do not lose the typical black color of rGO after any of the sonication or stirring treatments. After 30 minutes of treatment, sonication released 8.3 ppm of rGO in water while vigorous and mild stirring released up to 4.8 and 3.3 ppm of rGO respectively (Figure 7). We shall emphasize that each measurement in Figure 7 has been performed on an individual sample of MF1 of the same size. Due to the impossibility to synthesize two samples with identical coating, our analysis reaches its limitation to identify a difference at a level of 0.5 ppm. Thus difference more than 0.5 ppm can be regarded as significant. It is important to notice that there is no steady increase of the amount of rGO in water over time. The difference between 10 and 20 minutes treatment is significantly larger than between 20 and 30 minutes. This indicates that only the small amount of loosely adhered rGO was detached from the fabrics while the majority of rGO is firmly adhered on the microfibers' surface. The 30 minutes measurement was repeated for the vigorous stirring treatment since it showed lower concentrations compared to the 20 minutes measurements.

Nevertheless, almost identical values were measured for the repetition. This suggests that after 20 minutes, no additional rGO is being released in the solution and it is confirmed by the fact that the 20 and 30 minutes measurements have practically the same concentrations: 4.8 and 4.5 ppm (or 4.6 ppm considering the repetition). In conclusion, these experiments demonstrate a strong adhesion between rGO and the microfibers' surface and prove the good stability of MF1 in aqueous media.

Conclusion

Commercially available microfiber cloths have been used for the preparation of GCMs. The main advantages of these coated microfibers are a straightforward synthesis, low costs, versatility and scalable production. GCMs showed excellent performance in the selective separation of crude oil from oil-water mixtures. Oil uptake capacities between 5.15 and 6.78 g/g were achieved. The reusability test indicated a decrease in oil uptake capacity of 13.5% after ten cycles. High oil removal efficiencies values of 97.90% and 87.58% were reached after a 30-seconds single application of MF1 on oil-water and oil-seawater systems respectively. A more uniform and fine coating has been observed through SEM on the fabrics coated with 1 mg/ml GO dispersions. In contrast, the fabrics coated with 4 mg/ml GO dispersions presented signs of rGO agglomerates, which did not bring any benefit to the absorbing capabilities of the material. TGA measurements

confirmed that all the GCMs are stable up to 300 °C in air. In conclusion, two to five applications of MF1 are able to reduce the oil concentrations in both oil-water and oil-seawater mixtures to values between 25.1 and 34.4 ppm respectively, which are close or even below the OSPAR limit of 30 ppm for offshore discharged waters. Moreover, MF1 can be considered safe for the marine ecosystem due to the very low release of rGO in the media after intense mechanical stresses.

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Conflicts of interest

There are no conflicts to declare.

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Reduced graphene oxide (rGO)-coated microfibers demonstrating efficient separation of oil-water mixtures and minimal release of rGO in the marine environment.