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POST-CONSUMER MoS_2-MODIFIED POLYURETHANE FOAMS FOR OFFSHORE OIL SPILL SORPTION: A SIMPLE AND INEXPENSIVE TECHNIQUE

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ABSTRACT

Offshore oil spills are unfortunately common during extraction and transport processes. When it happens, the first action is contingency, followed by oil removal. Skimmers, incineration, and sorption in porous structures are some of the techniques commonly used. Polyurethane foams (PU), for example, are highly porous polymers. Due to a lack of legislation and environmental education, post-consumer PU foams are found irregularly discarded throughout Brazilian cities. This work aims to promote the reuse of this residue to sorb offshore oil spills. Post-consumer PU foams were cleaned and surface modified through sonication technique for impregnation with MoS_2. Scanning Electron Microscopy (SEM) + Energy-Dispersive X-ray Spectroscopy (EDS) and contact angle were the characterizations performed. SEM images showed that the unchanged post-consumer PU foam (Un-PC) surface went from smooth to rough after MoS_2 impregnation (MoS_2-PC). C, N, and O together represented 99.05 %atoms of Un-PC composition. For MoS_2-PC, C, N, plus O represented 66.13 %atoms, while S and Mo represented 26.92 %atoms and 6.95 %atoms, respectively. The contact angle increased from 104.4° (Un-PC) to 123.3° (MoS_2- PC). This increase was due to hydrophobization caused by MoS_2 particles. Three sorption tests were performed. In the first one, when only seawater was used, MoS_2-PC (7.42 ± 0.22 $g \cdot g^{-1}$) sorbed statistically less seawater than Un-PC (9.98 ± 0.22 $g \cdot g^{-1}$). In the second system, only with lubricating oil S46 (~46 cSt), MoS_2-PC increased about 16.5x the sorption capacity compared to Un-PC, reaching up to 24.13 ± 0.00 $g \cdot g^{-1}$. The third sorption test was performed in a multi-component system formed by seawater (92%):(8%) lubricating oil S46. While Un-PC was able to absorb 0.08 ± 0.00 $g \cdot g^{-1}$ of seawater and 3.20 ± 0.28 $g \cdot g^{-1}$ of lubricating oil S46, MoS_2-PC absorbed 0.75 ± 0.06 $g \cdot g^{-1}$ and 32.81 ± 0.02 $g \cdot g^{-1}$ of seawater and lubricating oil S46, respectively. Although there was an increase in seawater sorption between Un-PC and MoS_2-PC, the increase in oil sorption was much more significant (925% or 10.25x). The roughness caused by the MoS_2 particles on the polyurethane surface combined with the increase in intermolecular forces of Van der Waals type proved its strong influence in increasing the sorption capacity and its selectivity for oil over water. Here one waste was successfully used to remove another, which showed that post-consumer foams are a viable and highly cost-effective option for oil spill recovery.

Keywords: *oil spill, environment, polymers technology, surface modification.*

INTRODUCTION

Scientists worldwide are studying ways to accelerate the energy transition to cleaner and renewable sources. However, petroleum dependence might persist for decades. Offshore oil exploration, production, and transport can result in spillage in the oceans. When it happens, the first measure is to contain the leak both at the source and over the ocean surface. The use of booms is currently the primary way to prevent the spread of oil, which is caused due to the movement of waves and wind.

After the containment of the spilled oil, different techniques for oil removal can be used. Depending on the wind conditions, the oil layer on the water, and other factors, techniques such as pumping, incineration, or dispersion with surfactants can be used. Another possibility for oil removal is through oil sorption by porous structures. There are studies using polydimethylsiloxane [(1)] and polyurethane [(2)] foams, two highly porous polymers, as oil sorbents capable of absorbing oil spilled into the water.

One of the primary sources of polyurethane is mattresses, which are often made from 100% of this polymer. Unfortunately, due to flaws in environmental legislation, it is common to find post-consumer mattresses irregularly discarded throughout Brazilian cities. In addition, since 2014, Brazil has produced more than 1 million m^3 of new polyurethane foam per day, which increases the need for studies on its reuse and recycling [(3)].

In this study, post-consumer polyurethane foam obtained from irregular disposal was modified using a deposition technique with molybdenum disulfide. This modification's purpose was to enhance the affinity for oil over water aiming for oil capture in seawater. In addition, water and oil sorption tests were carried out and analyzed quantitively. This work highlights the reduction, recycling, and reuse of post-consumer polyurethane foams to remove oil spilled in seawater through a simple surface modification. Thus, two apparently unrelated problems are addressed and one waste is used to remove another.

MATERIALS AND METHODS

A 100% polyurethane mattress with a density of 18 $kg \cdot cm^{-3}$ was obtained from an irregular disposal area. There was no visible damage or mechanical compaction, but there were characteristic time-of-use stains likely from urine and sweat as well as dust and hairs. Samples were cut into 1cm x 1cm x 1cm cubes and washed multiple times with distilled water and 70% (v/v) ethanol. Seawater was obtained directly from the Atlantic Ocean (5° 52′ 52″ S, 35° 10′ 16″ W) in Natal, Brazil, and filtered on blue band filter paper to remove suspended solids. Diesel, lubricating oil S46, and engine oil 20W40 were purchased from a national fuel chain. Turpentine solvent was purchased at a local supermarket. Anhydrous ethanol (99%), and molybdenum disulfide (MoS_2) were purchased from Dinâmica Química Contemporânea, Brazil. All analytical reagents were used without further purification.

MoS_2 deposition

A 6.25 x 10^{-3} $mol \cdot L^{-1}$ MoS_2 suspension in anhydrous ethanol was prepared and kept under mechanical agitation at 510 rpm for 1 h. In this solution, the post-consumer polyurethane foam cubes were kept immersed for 5 min. Then, the cubes were slightly compressed to drain excess liquid and cured in a vacuum oven for 13 min at 160 °C and -27 mmHg. The process from immersion in the solution was repeated twice more for a more significant deposition of MoS_2

particles. Next, post-consumer MoS_2-modified foams (MoS_2-PC) were washed with distilled water and 70% ethanol to remove unfixed particles. Finally, the foams were dried in an oven at 60 °C until constant mass.

Characterization

The post-consumer polyurethane foams morphology, modified and unmodified, was analyzed by Scanning Electron Microscopy (SEM), and chemical elements were semi-quantified by Energy-Dispersive X-ray Spectroscopy (EDS) (JSM - 6610LV, Jeol, Japan). In addition, hydrophobic and oleophilic characteristics were evaluated in a Drop Shape Analyzer (DSA 100, Kruss, Germany).

Sorption capacity tests

The sorption tests were performed following ASTM F726-12: Standard Test Method for Sorbent Performance of Adsorbents [(4)]. In addition, the test for determining the amount of water/oil sorbed was performed following ASTM D95-13: Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation [(5)]. All tests were performed in triplicate. Data were evaluated using analysis of variance in Statistica 5.0 software.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images for post-consumer polyurethane foams before and after modification.

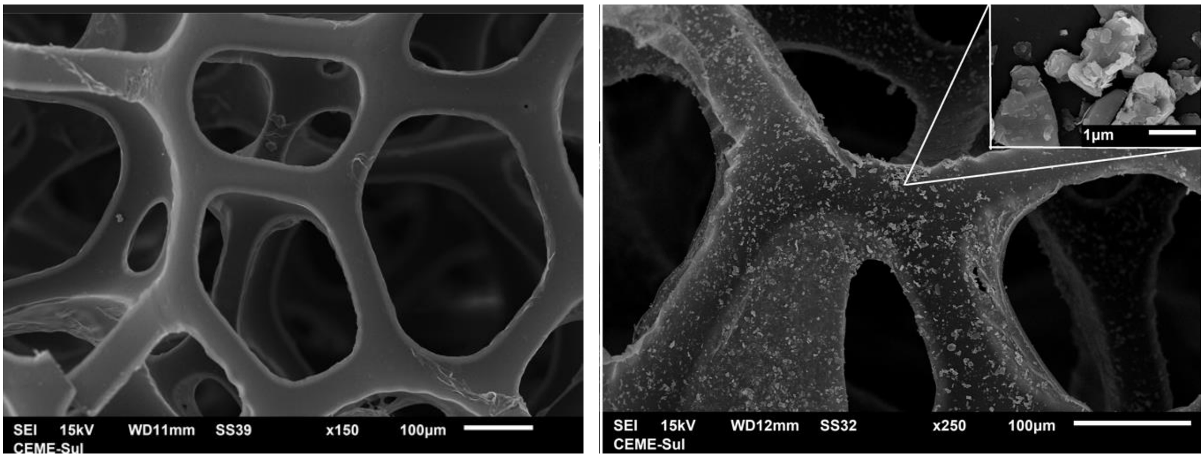

Figure 1: SEM images for post-consumer polyurethane foams before (left) and after (right) modification. Highlighted, with 10000x magnification, the MoS_2 granules deposited on the surface.

In Figure 1 it is possible to observe that the unmodified post-consumer polyurethane foam (Un-PC) surface was smooth and had well-defined pores and channels. However, post-consumer polyurethane foams modified by deposition with molybdenum disulfide particles (MoS_2-PC) presented a rough surface. In the highlight of Figure 1, the granules of MoS_2 deposited and fixed on the foam's surface could be observed.

EDS analyses in Figure 2 identified the presence of carbon, nitrogen, and oxygen in all foams evaluated. These elements were already expected since they are widely found in the repeater structure of the polyurethane polymer. Calcium was also determined for Un-PC because mattress manufacturers presently use calcium carbonate as a "filler" while manufacturing foams.

The presence of hydrogen is also assured in all foams. However, due to the limitations of the technique employed, it was not possible to quantify light elements, such as hydrogen (atomic mass = 1 u).

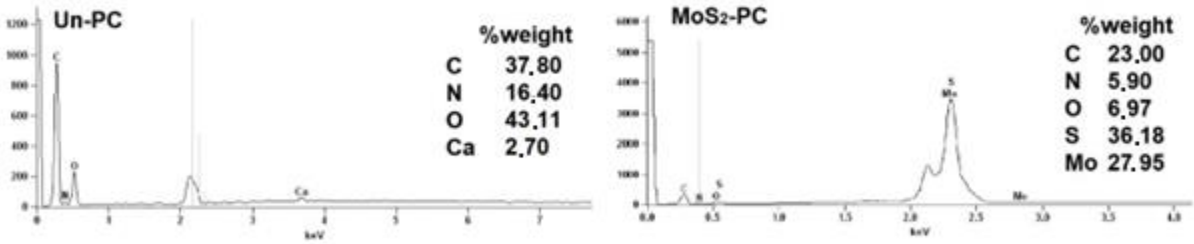

Figure 2: EDS for polyurethane foams unmodified (Un-PC) and modified with molybdenum disulfide particles (MoS_2-PC).

As expected, sulfur and molybdenum were also identified for MoS_2-PC (in addition to C, N, and O), indicating successful deposition of MoS_2 particles.

Figure 3 shows the contact angles between water/oil droplets on the foam surfaces obtained from Drop Shape Analyzes (DSA).

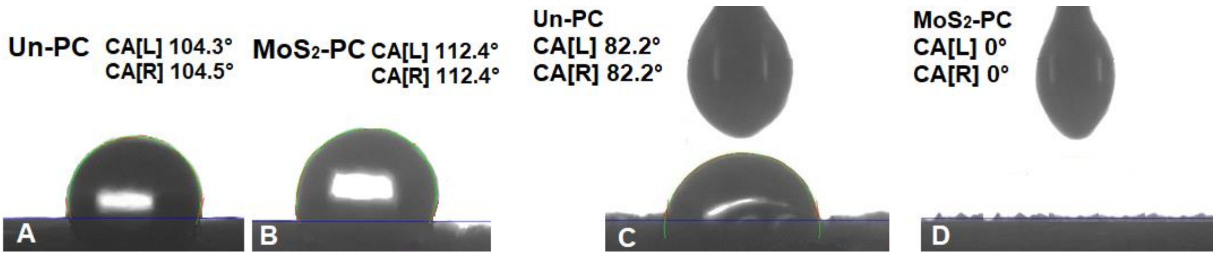

Figure 3: DSA for polyurethane foams unmodified (Un-PC) and modified with molybdenum disulfide particles (MoS_2-PC) using seawater (A and B) and lubricant oil S46 (C and D) drops.

For contact angles between the seawater droplet and the foam surface (Figure 3, A and B), there was a slight increase between the unmodified (Un-PC) and the modified foam (MoS_2-PC), ranging from 104.4° to 112.4°. The closer to 180°, the more hydrophobic the surface.

For the contact angles between the drop of lubricating oil S46 and the surface of the foams (Figure 3, C and D), there was a notable reduction between Un-PC and MoS_2-PC, dropping from 82.2° to 0°. The closer to 0°, the more oleophilic the surface.

The 0° angle observed between the lubricating oil droplet S46 and the surface of MoS_2-PC (Figure 3, D) was obtained from the instantaneous passage of the oil drop through the pores and channels of the modified foam. The same was not observed for Un-PC (Figure 3, C). This comparison makes it possible to state that the modification effectively increased the foam's affinity for the oil.

Figure 4 presents the results of the first, second, and third sorption tests performed with the modified and unmodified foams.

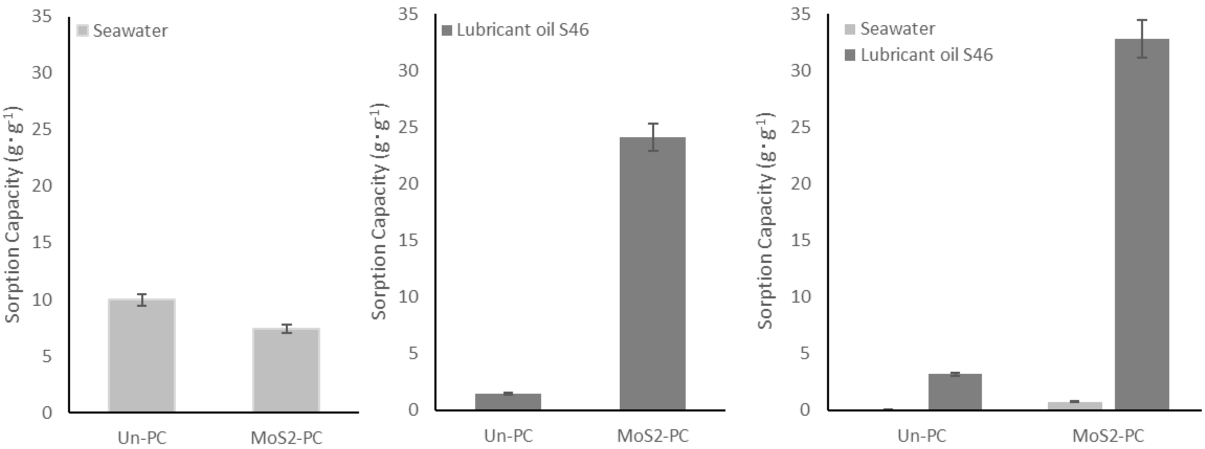

Figure 4. From the left to the right: test 1 single component with seawater; test 2 single component with lubricating oil S46; test 3 multicomponent with a mixture of seawater (92%):(8%) lubricating oil S46.

In test 1, composed only of seawater, the Un-PC foam sorbed 9.97 ± 0.22 $g{\cdot}g^{-1}$ of seawater while the MoS_2-PC foam sorbed 7.42 ± 0.22 $g{\cdot}g^{-1}$. The 25.58% reduction in seawater sorption capacity after modification was statistically significant.

In test 2, composed only of S46 lubricating oil, Un-PC sorbed only 1.46 ± 0.02 $g{\cdot}g^{-1}$ of oil, while MoS_2-PC sorbed 24.13 ± 0.00 $g{\cdot}g^{-1}$. The sorption capacity of S46 lubricating oil after modification was statistically significant and increased approximately 16.5 times (>1500%) when compared to the unmodified foam (Un-PC).

In test 3, with a mixture of seawater and S46 lubricating oil, the Un-PC foam sorbed 0.08 ± 0.00 $g{\cdot}g^{-1}$ and 3.20 ± 0.28 $g{\cdot}g^{-1}$ of seawater and lubricating oil S46, respectively. The modified MoS_2-PC foam sorbed 0.75 ± 0.06 $g{\cdot}g^{-1}$ and 32.81 ± 0.02 $g{\cdot}g^{-1}$ of seawater and S46 lubricating oil, respectively. When compared to Un-PC, oil sorption by MoS_2-PC foam was statistically significant, reaching 10.25 times more oil sorption. This result confirms that the modification was able to increase the oil sorption capacity even in a multicomponent medium where water and oil compete for the foam pores.

In a recent study [1], researchers synthesized polydimethylsiloxane foam and coated it with particles of MoS_2. Tests evaluating the sorption capacity of standard shipboard bilge mix showed that the modified foams were able to sorb approximately 100% of their own mass in oil. In another study [6], polyurethane foams were synthesized and coated with graphene oxide and MoS_2. The sorption test results showed that the modified polyurethane foams reached between 83% and 94% of selectivity for oil. When compared, the unmodified and modified foams showed a sorption capacity of diesel in water of 111.68% and 402.15%, respectively. Compared to these studies, this present work stands out showing that post-consumer polyurethane foam coated with MoS_2 was able to sorb 75% and 3281% of its own mass in seawater and S46 lubricating oil, respectively.

CONCLUSIONS

The use of post-consumer polyurethane foams for oil sorption was feasible regardless of their age or time of use. Oil sorption from Un-PC to MoS_2-PC increased 16.5 times in the single component test and 10.25 times in the multicomponent test. Moreover, post-consumer polyurethane foam coated with MoS_2 was able to sorb 75% and 3281% of its own mass in seawater and S46 lubricating oil, respectively. MoS_2-PC deposition proved to be a simple, cheap, and effective surface modification to increase the oil sorption capacity of post-consumer foams.

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