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Greasy Raw Wool for Clean-up Process of Marine Oil Spill: from Laboratory Test to Scaled Prototype

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Greasy raw wool, as sheared, was proposed as natural, cost effective adsorbent material for oil recovery and remediation of marine surface contaminated by oil spills. In this way, an effective cleaning of sea surface can be coupled with the revaluation of a sheep breeding waste, suitable for the purpose thanks to its oilphilic behaviour.
A characterization of wools of different origin was carried out by sorption test of IFO 380 oil, either pure or mixed with Diesel, layered on a water surface. The wool has been characterized in terms of humidity, lipids, adherent and not adherent dirt while viscosity, density and surface tension were evaluated for the different oil mixes. Preliminary tests on the process efficiency, performed with reduced volumes of water and oil in a static system, assessed the sorption kinetics, the yield of the process for fresh wool and the number of sorption-regeneration cycles at which the wool can be submitted without reduction of the original adsorption properties.
The obtained results were used to set a scaled up series of tests, on a pilot prototype, suitable for reproduce the real recovery conditions of a ship on the sea. The possible destination of the exhausted wool was also taken into account.
The obtained results suggest that wool wastes can be a suitable sorbent material for spilled oil recovery on marine surfaces, with performance that are competitive with the materials of synthetic origin proposed for similar applications.

1. Introduction

Oil spill accidents, that are caused by activities related to oil production, storage and transportation, give rise to serious effects when occur on water because the spill spreads rapidly, as shown by the April 2010 explosion of the drilling offshore rig that released a huge amount of crude oil into the Gulf of Mexico and on the far coast of Louisiana. (National Commission on BP Deepwater, 2011) Spilt oil can be dispersed or burned but the removal should be the best response when both environmental remediation and oil recovery are considered. In some cases, when the response to the accident is constrained by equipment availability or limited by weather and hydrodynamic conditions of seas, the application of dispersant or ignition of oil slick are the alternative methods usually employed. (Oebius, 1999) As a usual procedure, spilled oil are contained by floating booms and then removed by means of mechanical skimmers and/or sorbent materials. Sorbents can be applied as preferred solution for oil spill clean-up since this technique is the most rapid, effective and cost saving for reducing the environmental damage in a very short time. (Gheorghiu et al. 2014) The application of sorbents as single solution can be decided for small areas and when the window-of-opportunity is too short and limited by problems in organizing, coordinating and transporting the clean-up technologies. (Paltrinieri et al. 2014)
Synthetic organic polymers have emerged as materials with significantly high sorption capacity. However the major drawback of organic synthetic sorbents deals with the problem of recycling or disposal after usage. (Cojocaru et al. 2011) In the last decades, an increasing interest for cheap sorbents of natural origin has emerged, the main advantages involving their low-cost, availability as renewable and abundant natural supply,

good oil sorption performance and their property to be “ecofriendly” in terms of biodegradabilit. (Hussein et al. 2011)
In the present work, raw greasy wool from sheep breeding for no textile purposes was choose as a natural oil sorbent. The morphology and the chemical composition of wool fibers together with the presence of surface lipids makes this substrate particularly hydrorepellent and oilphilic, suitable for the selective absorption of oil in presence of water. Moreover, in this way an effective cleaning of sea surface can be coupled to the revaluation of a sheep breeding waste.

2. Materials and Method

Greasy raw wool, as shared, was provided from local sheep breeders of the Biella district (Italy). It was divided in two sets: the first one with a high amount of dirt, both organic and mineral, adherent to the fibres (wool 2), the second one (wool 1) a cleaner raw wool, without apparent presence of heterogeneous materials. The wool was used as received, without any cleaning action.
The foreign materials present on each wool set was determined. The humidity percentage was evaluated by weight loss of wool samples submitted to 105 °C for 12 h. The dirt not strongly adherent to the fibres was evaluated by weight loss after rinsing cycles in cold water up to constant weight of the dried wool. On the same samples, the lipid content was determined by weight loss after extraction in soxhlet with dichloromethane (2 h, about 50 cycles). The inorganic dirt adherent to wool fibres was evaluated by a thermal treatment at 500 °C for 2h; the residual ashes were collected and weighted according to Ferrero et al. 1988. Finally, the water potential sorption was estimated by dipping flocks of wool in water and evaluating the weight increase after 5 seconds of contact followed by 5 s of dripping.
Tip water was salted with sea salt (35 g/L) to simulate the Mediterranean sea water while the IFO 380, a marine fuel oil whose characteristics are reported in Table 1, was used to simulate the oil spill. Samples of oils with different viscosity and surface tension were obtained by mixing the IFO 380 with different amount of commercial gasoil and the spreading of the oil on the water surface, in terms of spot thickness or covered area, was correlated with the physical properties of the oil. The viscosity was measured at 20 °C through a SV 10 vibro-viscometer (A&D, Tokyo) and the contact angle on glass surface was evaluated through a KRUSS DSA 10 instrument.

Table 1: Characteristics of IFO 380 oil

A.P.I.	Specific Gravity	Viscosity at 50°C [cSt]	Flash point [°C]	Sulphur Wt %
15.7	0.9607	370	148.9	3.18

Preliminary efficiency tests on the proposed process were performed in a static laboratory system to assess the required sorption times, the sorption capacity of the pristine and recycled wool and the maximum number of sorption-regeneration cycles at which the wool can be submitted without a significant reduction of the original sorption properties. For this purpose, an open container 40 x 40 cm^2 was filled with 15 L of salted water; the oil was spread on the water surface and covered with wool fibers layered on the liquid surface by means of cylinder rolling on the surface and plunged about 2 cm in the water free surface. Both fresh and recycled wool were used for the test, and the influence of contact time on the oil sorption was investigated. The sorption of liquid was evaluated after recovery and few seconds of dripping of the wool before and after squeezing. The oil sorption was determined by difference between the mass of the squeezed liquid and the mass of water obtained by the azeotropic distillation of the liquid in presence of toluene.
The data obtained at laboratory scale were used to set a scaled up series of tests, on a pilot prototype (Figure 1), realized in such a way to simulate the real recovery conditions of a ship on the sea. Water was circulated in the channel by high performance pumps, to simulate a ship velocity of 1.4 knots and controlled amount of oil with 50/50 IFO380/Diesel ratio, was spread on the water by a volumetric pump for 15 s, in order to have an homogeneous deposition of oil on the water surface with a thickness of about 1 mm. In the same time, wool fibres were thrown on the liquid surface by a mechanical tape in such a way to completely cover the oil spot. A rolling metallic cylinder enhanced the contact between wool and oil by sinking the wool under the surface of the flowing liquid. The impregnated wool was recovered and squeezed by continuous automated mechanical devices. The oil was separated from soaked water by decantation while the squeezed wool was recharged on the feeding tape to be used for the following cycle test. From these tests, the minimum amount of wool fibres necessary for each cycle, the maximum number of cycles the pristine wool can be submitted to, the process yield, that is the percentage of recovered oil with respect to the introduced amount, and the selectivity, that is the percentage of recovered oil with respect to total recovered liquid, were determined.

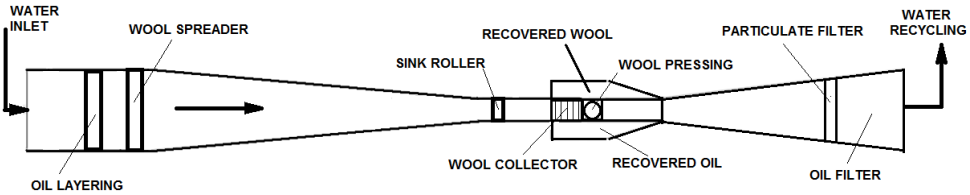


Figure 1: scheme of the pilot prototype for scaled up tests. (Total length: 14 m, water surface velocity: 0 - 0.75 m/s, oil flow: 16.4 L/min)

3. Results and Discussion

3.1 Wool characterization

The main difference between the two considered wool sets, namely less and more dirt, was toward water sorption. The dirty wool showed a higher tendency to absorb water with a partial sinking that can hinder the following wool recovery when wool is layered on the water surface. On the contrary the cleaner fibres show high hydrophobic behaviour when deposited on the water surface and the amount of absorbed water was negligible, as reported in Figure 2. It is clear that wool 1 shows a negligible water affinity while wool 2 shows strong weight increases, till 2-3 times its initial weight, in particular if the amount of dirt is higher. In fact, test 3 was carried out choosing the most dirty wool fibres of each set, so the relevance of the dirty grade is pointed out.
The foreign material present in each wool set is reported in Figure 3. The main difference is the amount of not adherent dirt present on the fibres: on wool 2, 10.56% of the weight was due to it while on wool 1 the amount was negligible (0.16 %). Humidity (8.4 %), inorganic dirt adherent to fibres (4 %) and lipids (10 – 12 %) were similar for both the considered substrates.

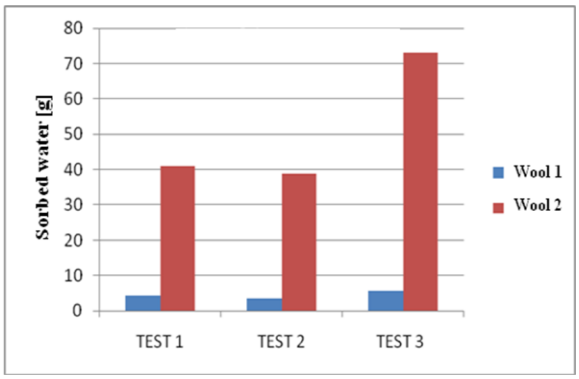


Figure 2: Water sorption test on 25 g wool samples.

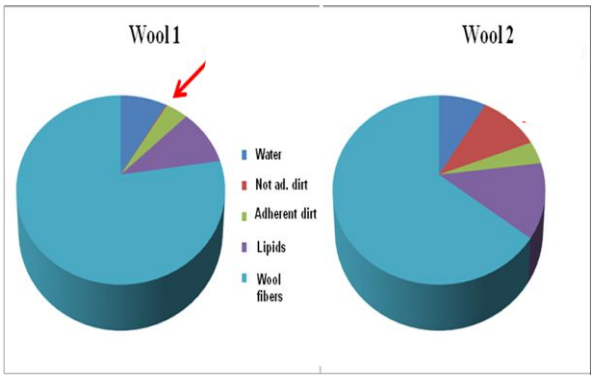


Figure 3: Wool composition.

3.2 Oil characterization

Oils with different physical properties were obtained by mixing IFO 380 and Diesel in different ratios. The physical properties of the oil should control the thickness of the oil layer on the water surface and, as a consequence, the amount of wool that must be spread per unit of liquid surface for the complete spill removal. Density, viscosity and contact angle on glass were evaluated and were correlated to the oil layer thickness, calculated by the oil volume and the measured diameter of the oil spot observed on the water surface. Results are reported in Table 2.
The correlation between density and the thickness of the oil layer was quite linear, as can be observed by Eq(1) that provides a good fitting of the experimental data (R^2 = 0,9237).

$$\text{Spot thickness} = 3{,}7586 * \text{density} - 2{,}7312 \quad (1)$$

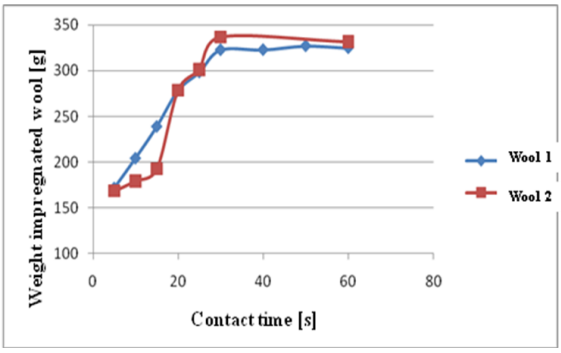
A strong decrease of the viscosity, measured at ambient temperature, can be related to the presence of Diesel as dilution media. Contact angle on glass is an index of the surface tension of the different mixes: the lower is the measured value, the highest is the drop tendency to spread on the glass surface, and on water surface as consequence. The lowest value was found for the 50/50 mix, corresponding in fact to a spot with higher dimensions and lower thickness. In general, all measured values were low, typical of a liquid with high tendency to wet the substrate on which it is spread.
Among the evaluated parameters, density was the one with a good linear correlation with the spot thickness, while viscosity and contact angle do not show any apparent correlations.

Table 2: Oil characterization.

Diesel/IFO 380 ratio	Density [g/ml]	Viscosity	Contact angle [°]	Spot diameter [cm]	Spot area [cm^2]	Volume [ml]	Thickness [cm]
50/50	0.785	44.6 mPa s	7	14.9	174.28	31.84	0.18
35/65	0.805	89.7 mPa s	16.5	12	113.04	31.05	0.27
18/82	0.824	1.21 Pa s	18.7	10.5	86.55	30.33	0.35
7/93	0.87	1.96 Pa s	19.1	7.4	42.99	28.73	0.66
0/100	0.958	4.64 Pa s	19.4	6.4	32.15	26.09	0.81

3.3 Results of laboratory test

The influence of the contact time between wool and the spread liquid on the amount of recovered pure IFO 380 oil was first investigated for both clean and dirty wool. A suitable volume of oil, sufficient to generate a layer of about 0.9 cm, was spread on the water surface inside the container. Wool fibres, homogeneously distributed on the liquid surface, were sunk by the rolling cylinder for contact times in the 5 - 120 s range. For both the wool samples, the oil sorption increases with contact time, reaching a stable value at times higher than 30 s. (Figure 4) The mean weight increase of the wool samples was 12 L for wool 1 and 12.5 times for wool 2.
In all experiments, after 50 seconds of contact, the wool recovery becomes difficult because the wool fibres show the tendency to sink. The behaviour of the two wool sets was similar, apart a different tendency toward water absorption. By allowing the phase separation of the absorbed liquid, it has been observed that for wool 1 the amount of water was negligible while for wool 2 the absorbed water was 1.4 times the weight of the wool. This amount can increase up to 3.2 times when the oil does not cover completely the water surface. The absorbed water showed a great tendency to drip off during the wool recovery. The dripping was tested for both the wools in order to evaluate the behaviour during the recovery and transport of the impregnated wool to the squeezing unit. The difference was evident: wool 1 showed a limited dripping for a very short time whereas from wool 2 the dripping of water and oil went on for more than 10 min. A loss of liquid close to the amount of absorbed water evaluated on squeezed liquid was observed. (Figure 5)
Wool capacity on oil adsorption was tested in recycled wool by reusing the same fibers up to 15 consecutive times. The results, in terms of absorbed oil and wool weight, are reported in figures 6 and 7. It was observed that wool 1 could be reused 10 times, then it becomes stringy, its volume collapses and both the dispersion and squeezing become difficult. After the tenth cycle, the wool absorbed, in total, oil 86 times its initial weight, that is 2,150 g/25 g. On wool 2 no problem was found during squeezing while recovery became difficult only after 15 cycles. For these reasons wool 2 has been chosen for the further tests on the pilot prototype. At 10th cycle wool 2 recovered oil 100 times its initial weight while at 15th cycle 140 times were reached. However, the evaluation of the amount of water sorbed with the oil revealed that about 1/10 of the sorbed liquid was water.
In the tests with recycled wool, a peak in the amount of the absorbed oil after 2 or 3 cycles and a higher amount of water absorbed in the first cycles has been observed. The phenomenon has been ascribed to the partial cleaning of the wool fibres, an obvious consequence of the sorption and squeezing cycles that involves the loss of the not adherent dirt, a decreasing of the hydrophilicity and an improved performance with respect to the fresh wool.



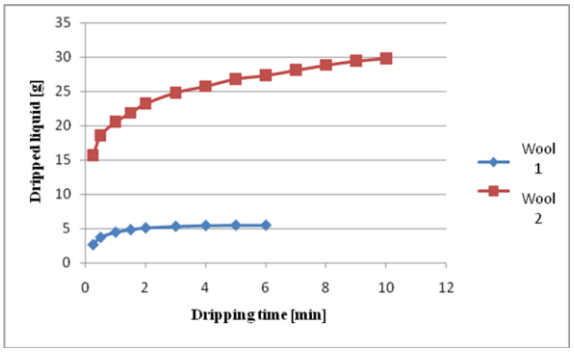
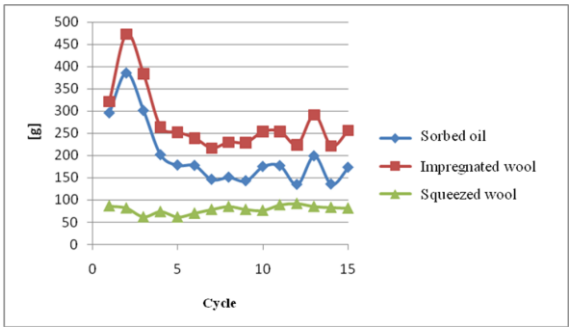


Figure 4: Influence of contact time on oil sorption.

Figure 5: Dripping test.



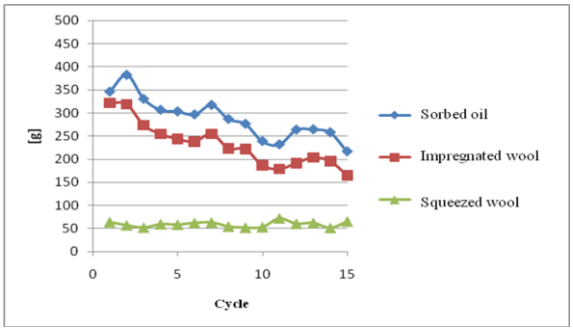


Figure 6: Tests with recycled wool (wool 1)

Figure 7: Tests with recycled wool (wool 2)

3.4 Results of test on the pilot prototype

The tests carried out on the scaled up prototype highlighted the importance of wool opening before the feeding on the oil spot. The reused wool occupy a reduced volume with respect to fresh wool, due to the wetting and compaction generated by the previous squeezing cycles. It means that the spreading of the fibres on the liquid and the wool-oil contact surface are reduced. A good opening of the fibres and their homogeneous distribution on the rolling feeding belt was crucial to enhance the sorption performance. Otherwise, some areas of the channel were not reached by the wool and the oil there present could not be sorbed. Moreover, the effect of the rolling cylinder was lower because it could not get in touch with the wool.

A first set of test was aimed to evaluate the minimal amount of wool necessary to clean the channel from the spread oil. Different amounts of wool were charged on the belt conveyor, in the 0.5-1.0 kg range, the absorption-regeneration cycle was repeated three times with the same charge and the total yield and selectivity (RE %) was evaluated. Obviously the best results were obtained with the higher charge of wool and this charge, namely 1 kg of wool per cycle, was maintained for the following test on the prototype.

A process yield of about 96 % was reached, meaning that the oil fed to the channel was quite totally removed. Taking in account the results of analysis on the squeezed recovered liquid, it was found a RE % of about 77 %. The synthetic sorbents proposed for the removal of oil spills show RE% varying from 42 % to 92 % (Fingas, 2011), meaning that the performance of raw wool results higher than the average.

A second set of test was aimed to prove the wool performance during repeated cycles of reuse. An amount of 1 kg of wool was continuously cycled 22 times and all data of oil sorption, wool degradation, recovery and squeezing problems due to the mechanical stress were analysed. A mean value of 53 % for yield and of 68 % for RE% was obtained. The results of the test, reported in figure 8, show that both yield and RE% have acceptable values for each step without evidence of a decreasing activity with the increasing number of reuse steps. The wool that did not show any problem on collection or squeezing after 22 cycles could probably go on with further cycles of sorption and squeezing without problems. Data obtained from cycles where the water flux in the channel was stopped for a short time or was significantly decreased, show a relevant increase of yield and RE%. Even if the influence of water flux was not considered as varied parameter in this study, this evidence that the water speed can play a critical role for the process performance: low rates are coupled with higher amounts of absorbed oil and low amounts of absorbed water. It explains also the difference between results obtained on prototype and at laboratory scale, where static test were carried out.

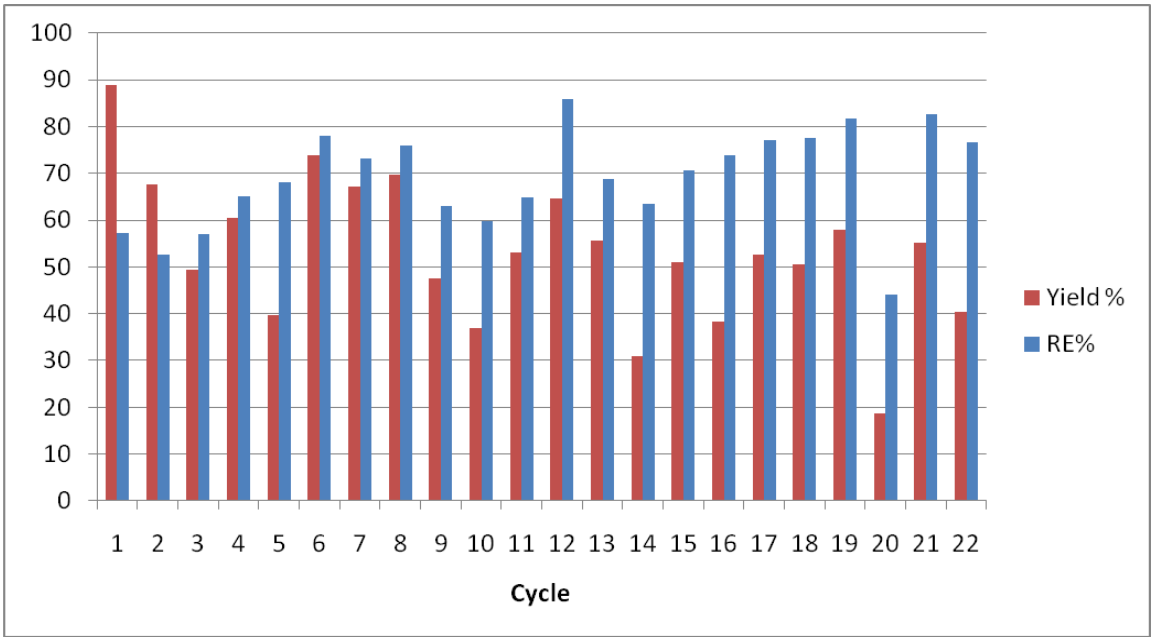


Figure 8: Continuous assessment test of wool reuse.

4. Conclusions

The obtained results suggest that greasy raw wool is a good candidate for the clean-up process of marine oil spill, competitive with other synthetic sorbents normally used. In this way, an effective cleaning of sea surface can be coupled with the revaluation of a sheep breeding waste, suitable for the purpose thanks to its hydrorepellent and oilphilic behaviour. Satisfactory performance were found both on laboratory test and on the scaled up prototype: dirt grade of the wool, contact area, contact time between wool and oil and ship speed were identified as the crucial parameters for the optimisation of the process. Promising results can encourage a deeper research on the topic and the real application of the tested device on a suitable ship.

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