Cork Sorbents for Aquatic Oil Spills Clean Up

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Abstract

Oil spills may happen due to simple dumping of crude from tankers up to major environmental catastrophes, and may contribute to severe environmental impacts and economic losses. Fast and efficient removal of oil from the aquatic environment is desirable. The use of sorbents is considered one of the most efficient techniques in oil and polycyclic aromatic hydrocarbons removal from water, especially due to their lower costs. However, sorbents should be employed with caution to minimize secondary environmental problems, particularly when using synthetic sorbent material. In this work, the response of a heat treated cork sorbent was analyzed and compared with two other commercial sorbents. Cotton fiber showed a better performance in both sorption rate and sorption capacity, but worse results regarding oil loss after compression and floatability in water. Heat treated cork presented a better floatability and a better retention capacity than the other two sorbents. These results suggest that the use of heat treated cork as a sorbent has potential for oil removal in aquatic environments with the advantage of being a natural and ecological product.

1. Introduction

Oil spills may happen due to simple illegal dumping of crude from tankers up to major environmental catastrophes, like the recent Gulf of Mexico disaster that spilled over 750,000 cubic meters of oil. Illegal oil discharges incidents in Europe occur at an average number of 3,000 per year (EEA, 2010).

Oil spills contribute to major environmental impacts, killing birds, dolphins, imparting genetic mutations on shrimps and crabs, among other things, and may even be toxic to humans (Aguillera et al., 2010). Economic losses are also significant, hurting the fishing, tourism and oil industry (EEA, 2010; Karan et al., 2011). Therefore, fast and efficient removal of oil from the aquatic environment is desirable.

There are several approaches to cleaning oil spills. One approach is the use of physical methods that will contain the spill and then remove the oil from the water surface either by skimming or by using adequate sorbents. Another one is the use of chemical methods, like using dispersants to break up the oil and speed up natural degradation, and still the use of solidifiers or *in situ* burning (Karan et al., 2011). Biological methods are also used, introducing bacteria and other microorganisms to promote biodegradation of oil.

Sorbents are insoluble materials that recover liquids through absorption, adsorption, or both, and that should be both oleophilic (oil attracting) and hydrophobic (water repellent) (EPA, 2012; Adebajo et al., 2003). Retention over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent are also important factors for oil sorption success (Teas et al., 2001; Adebajo et al., 2003).

Absorbents retain liquid through their molecular structure by swelling of the material, whereas adsorbents attract the oil to the surface of the material. Once sorbed, removal of oil by removal of the sorbent is easier (Adebajo et al., 2003). The use of sorbents is considered one of the most efficient techniques in oil and polycyclic aromatic hydrocarbons (PAHs) removal from water, especially due to their lower costs. However, sorbents should be employed with caution to minimize secondary environmental problems, particularly when using synthetic sorbent material (ITOPF, 2012).

Sorbents may be natural or synthetic. Natural sorbents may also be organic or inorganic (EPA, 2012; ITOPF, 2012). Natural organic sorbents include cotton and cork, whereas polyethylene is a synthetic sorbent. Natural organic sorbents can adsorb up to 15 times their weight and are being used for oil spill cleanup (EPA, 2012; Adebajo and Frost, 2004). However, some organic sorbents tend to also adsorb water and sink (EPA, 2012), therefore floatability tests are also important to evaluate sorbent performance. Floatability is an important issue, especially when using skirt booms with ballast.

High porosity materials, like most natural organic sorbents, have higher initial oil pickup but might have poor retention capacity (Wei et al., 2003). Nonetheless, natural organic sorbents have the advantage of biodegradability and cost-effectiveness in comparison to the synthetic polymeric fibres (Abdullah et al., 2010; Karan et al., 2011; Adebajo and Frost, 2004). Low cost materials for hydrocarbon removal (e.g. cork) have been searched for in recent years and studies are being carried out for removal performance (Olivella et al., 2011).

Cork is a natural and renewable raw material obtained from the bark of the cork oak (*Quercus suber L.*). A new product based on cork has been developed for oil spill absorption purposes, and has recently been introduced in the market with the trade name CORKSORB®. This product is based on cork previously treated with heat and pressure, in order to improve its hydrophobic behaviour and absorption capacity. The use of heat treated cork in aquatic oil spills cleanup is recent, and the available scientific information regarding its performance is still scarce.

The objective of this study is to analyze and compare the response of a heat treated cork sorbent with two other commercial sorbents – melt-blown polypropylene and cotton fiber, representing synthetic and natural sorbents, respectively. Sorption and retention capacities, and floatability, were evaluated over time.

2. Material and Methods

Three commercial booms with different sorbents were used in this study – CORKSORB® (heat treated cork); ECOSORB R® (melt-blown polypropylene); and ECOSORB® (cotton fiber), with densities 65.8 kg/m^3, 65.5 kg/m^3, and 52.4 kg/m^3 respectively. All booms were cylindrical 3.0 m long and with a diameter of 0.18 m for both ECOSORB R® and ECOSORB®, and 0.20 m for CORKSORB®. The booms of cork and polypropylene had a non-woven fabric between the sorbent and the outer sleeve. In the cotton fiber boom the sorbent was directly in contact with the outer sleeve.

2.1 Measurement of Oil Sorption Rate

Sorption of oil was simulated in nine beakers (three replicates for each sorbent), filled with a 0.09 m layer of sorbent material extracted from the booms, and maintaining boom density. The top of the beakers with cork and polypropylene were covered with the fabric materials used in the respective booms. The beakers with cotton fiber were covered with fishing thread with the only purpose of preventing sorbent to fall from the beaker. The beakers were placed top-down on a metallic grid immersed in crude oil (Arabian Light 110) in a stationary condition. Specifications of the crude oil used in experiments are shown in Table 1.

Figure 1 shows the experimental set-up. At given times the beakers were removed from the oil, drained for 20 s and wiped to remove excess oil from the beakers' outer glass, and their weight was monitored. Oil sorption was calculated as grams of oil sorbed per gram of sorbent for times up to 8 days and at a constant temperature of 20 ºC.

Table 1: Specifications for Arabian Light 110 crude oil (data provided by the supplier of the oil sample)

Property (units)	
Specific gravity at 15 ºC	0.8605
API gravity (º)	32.8
Kinematic viscosity at 20 ºC (m^2/s)	11.24×10^{-6}
Kinematic viscosity at 40 ºC (m^2/s)	6.11×10^{-6}
Sulfur content (%wt)	1.89
Pour point (ºC)	-57
Acidity (mg KOH/g)	0.05

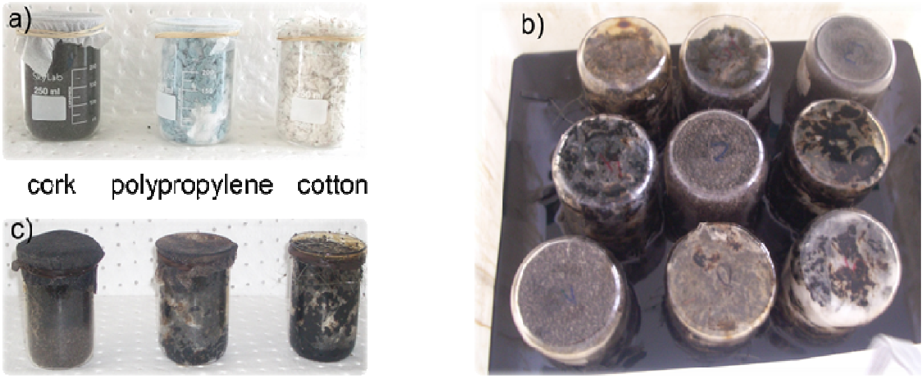

Figure 1 – Experimental set-up for the oil sorption capacity determination of heat treated cork, melt-blown polypropylene, and cotton fiber: a) initial stage, b) during experiment; c) after 8 days.

2.2 Measurement of Retention Capacity after Compression

Three replicates of each sorbent from oil sorption experiments were put together at the end of the sorption experiments, and each sorbent was submitted during 1 min to a 2,000 $N.m^{-2}$ compression test. In order to evaluate retention capacity each sorbent was weighted before and after compression.

2.3 Measurement of the Floatability of the Booms

Two measuring tapes were placed around the perimeter of each boom, at 1 m distance from the boom's end on both sides. The distance between the measuring tapes in the same boom was also 1 m. The booms were then placed in water, and their floatability was evaluated by measurement of the submersed perimeter in each tape during a 42 days experiment. Figure 2 shows the experimental set-up for this essay.

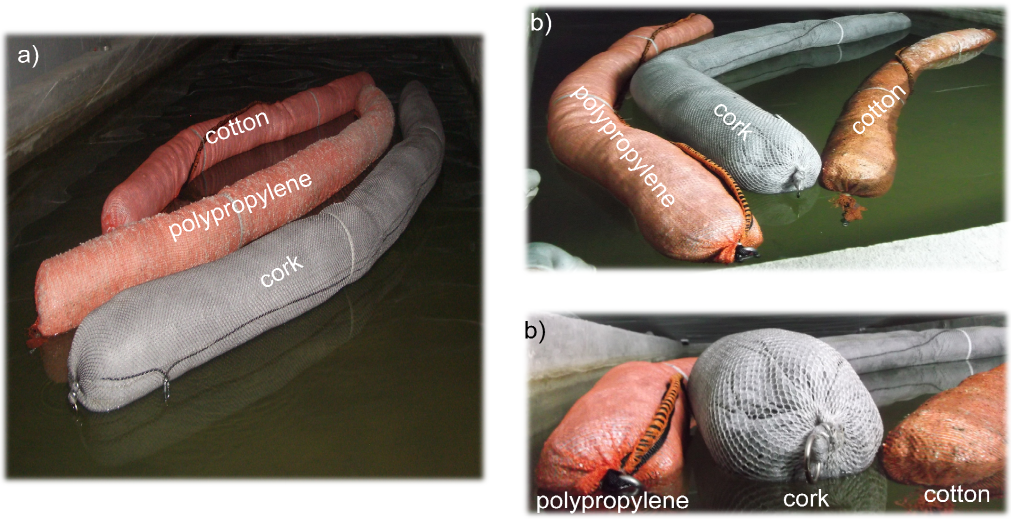

Figure 2 – Floatability essays for booms of heat treated cork, melt-blown polypropylene and cotton fiber: a) initial stage; b) 34 days later.

3. Results and Discussion

Figure 3 shows the global results for the oil sorption experiments. All three sorbents tested showed similar behavior: the initial rate of sorption is higher, in an intermediate phase the sorption rate lowers until the process reaches a steady-state phase where no further sorption occurs. Table 2 shows the results obtained for the sorption capacity at a steady-state for each sorbent. It is important to refer that these results do not represent maximum oil sorption capacities, since it was observed that the material on the top of the beakers was clearly dryer than the material closer to the oil surface. Therefore this steady-state stage was achieved without total saturation of the sorbents.

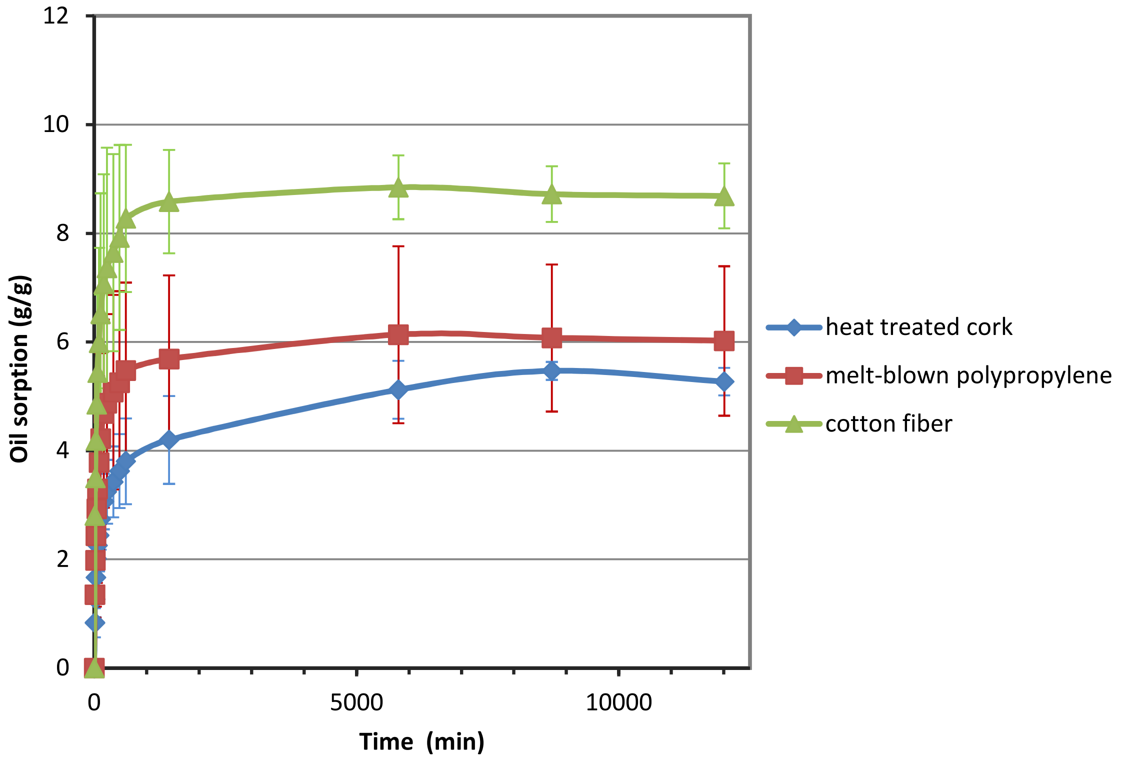

Figure 3 – Oil sorption results (dots and error bars represent, respectively, mean value and two standard deviations of the three samples).

Table 2 – Maximum amount of oil sorbed in the oil sorption experiments.

sorbent	Maximum oil sorbed	
	g oil / g sorbent	g oil / cm^3 sorbent
heat treated cork	5.3 ± 0.4	0.35 ± 0.03
melt-blown polypropylene	6 ± 1	0.40 ± 0.08
cotton fiber	8.8 ± 0.5	0.46 ± 0.03

The results for the initial stage of the experiments are shown in more detail in Figure 4. It can be seen that the initial rate of oil sorption is higher for cotton fiber.

It is important to refer that these results were obtained under static conditions, and therefore in a real aquatic oil spill cleanup situation, the rate of oil sorption is expected to be higher due to convection processes.

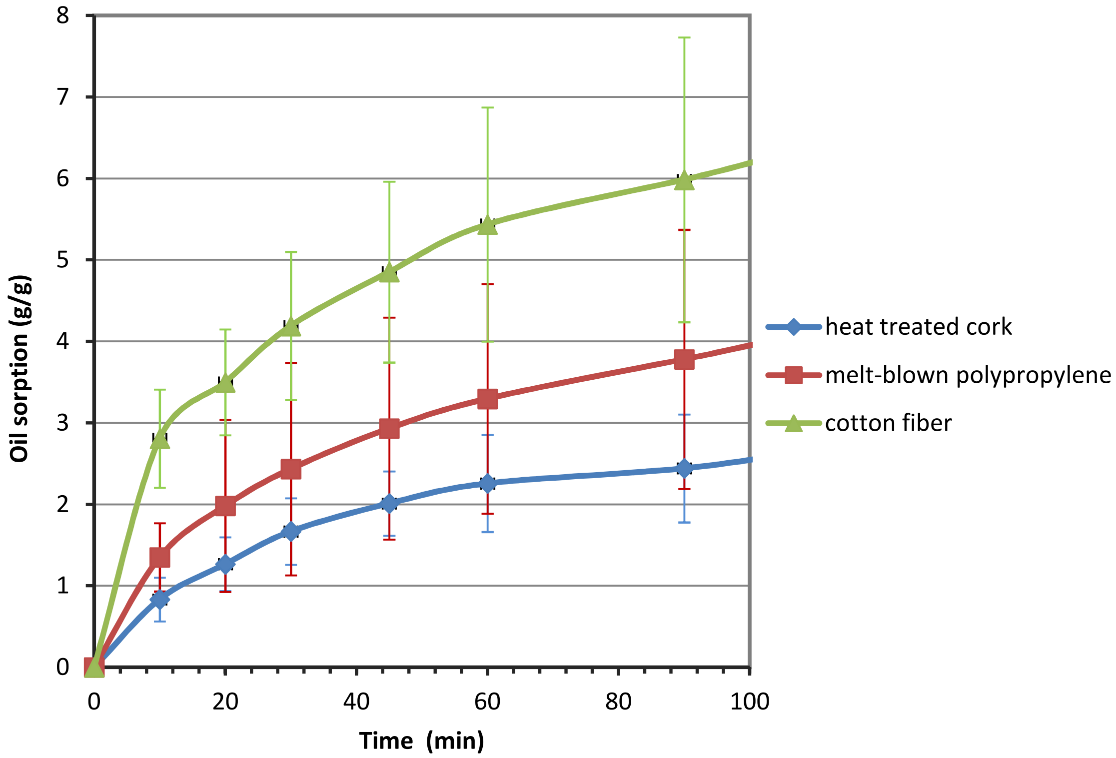

Figure 4 – Oil sorption results for the initial stage of the experiments (dots and error bars represent, respectively, mean value and two standard deviations of the three samples).

Regarding the retention capacity of the three sorbents, the results obtained in our experiments are shown in Table 3. The results show that cotton fiber exhibits poor performance regarding retention capacity, loosing around 8 % of the oil previously absorbed, when compressed at 2,000 $N.m^{-2}$. The retention capacity is an important property of sorbents since after the oil spill clean-up with booms, these have to be manipulated for removal from the water and proper disposal, and during these operations the booms are exposed to compression forces. Heat treated cork showed the best results in this test.

Table 3 – Oil loss from sorbent after compression.

Heat treated cork	Melt-blown polypropylene	Cotton fiber
0.2%	2.7%	7.9%

Regarding the floatability of the booms, Figure 2b and Figure 5 show the results obtained in this experiment. It was observed that the heat treated cork boom also had the best performance in this test, since at least 80 % of the boom remained above the water level during the entire experiment. Melt-blown polypropylene partially sank during the initial 8 days, but remained approximately stable below 35 % of volume immersed for the rest of the experiment. The cotton fiber boom showed a higher tendency to sink, with 70 % of its volume submersed after 42 days.

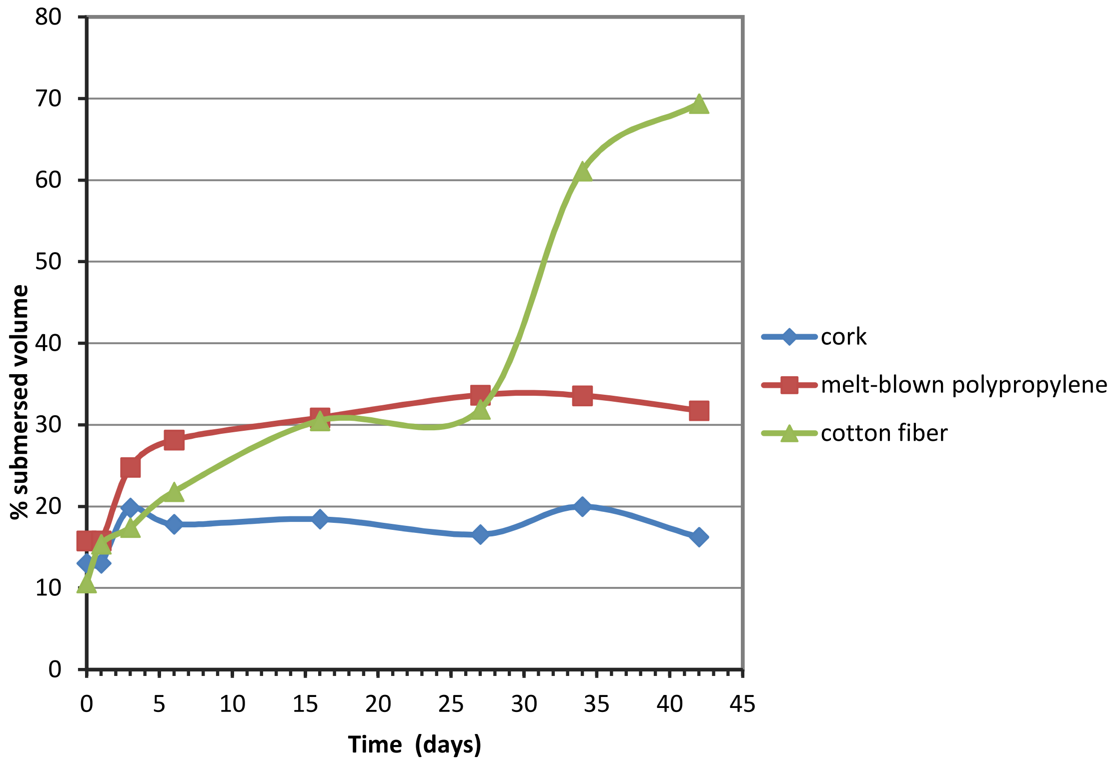

Figure 5 – Floatability essays – percentage volume of submersed boom over time.

4. Conclusions

Regarding the oil sorption experiments, our results show that cotton fiber has a better performance than the other two sorbents, both in sorption rate and in sorption capacity. However, cotton fiber has shown to have worse results regarding oil loss after compression and floatability in water. Heat treated cork presented a better floatability and a better retention capacity after saturation than the other two sorbents. These results suggest that the use of heat treated cork as a sorbent has a potential for oil removal in aquatic environments with the advantage of being a natural and ecological product.

5. Aknowledgements

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6. References

Abdullah, M. A., Rahmah, A. U., Man, Z. (2010). Physicochemical and Sorption Characteristics of Malaysian *Ceiba pentandra* (L.) Gaertn. as a Natural Oil Sorbent. *In: J. Hazardous Materials,* 177, pp. 683–691.

Adebajo, M. O., Frost, R. L., Kloprogge, J. T., Carmody, O., Kokot, S. (2003). Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *In: Journal of Porous Materials,* 10, pp. 159–170

Adebajo, M. O., Frost, R. L. (2004). Acetylation of Raw Cotton for Oil Spill Cleanup Application: A FTIR and ^{13}C MAS NMR Spectroscopic Investigation. *In: Spectrochimica Acta Part A,* 60, pp. 2315–2321.

Aguilera, F., Mendez, J., Pásaro, E., Laffon, B. (2010). Review on the Effects of Exposure to Spilled Oils on Human Health. *In: J. App. Toxicology*, 30, pp. 291–300.

EEA – European Environment Agency (2010). *The European Environment State and Outlook 2010 - Marine and Coastal Environment.* Copenhagen, Denmark. Available at http://www.eea.europa.eu/soer/europe/marine-and-coastal-environment.[Retrieved on 04/01/2013].

EPA (2012) [On line]. Available at http://www.epa.gov/oem/content/learning/sorbents.htm. [Retrieved on 03/09/2012].

ITOPF (2012). Use of Sorbent Materials in Oil Spill Response. Technical Paper 8. [On line]. Available at http://www.itopf.com/information-services/publications/technical-reports/ [Retrieved on 03/09/2012].

Karan, C. P., Rengasamy, R. S., Das, D. (2011). Oil Spill Cleanup by Structured Fibre Assembly. *In: Indian J. Fiber Textile Res.*, 36, pp. 190-200.

Olivella, M. A., Jové, P., Sen, A., Pereira, H., Villaescusa, I., Fiol, N. (2011). Sorption Performance of *Quercus Cerris* cork with Polycyclic Aromatic Hidrocarbons and Toxicity Testing. *In: BioResources,* 6(3), pp. 3363-3375.

Teas, C., Kalligeros, S., Zanikos, F., Stoumas, S., Lois, E., Anastopoulos, G. (2001). Investigation of the Effectiveness of Absorbent Materials in Oil Spills Clean Up. *In: Desalination,* 140, pp. 259-264.

Wei, Q. F., Mather, R. R., Fotheringham, A. F., Yang, R. D. (2003). Evaluation of Nonwoven Polypropylene Oil Sorbents in Marine Oil-spill Recovery. *In: Marine Pollution Bulletin*, 46, pp. 780–783.