

Clay-based materials for the control and removal of oil spills

G. Jock Churchman^{1,2}, Jenny S. Anderson² and Eric H. Dunlop³

¹University of Adelaide, School of Agriculture, Food and Wine, Private Mail Bag No.1, Glen Osmond, South Australia 5064, Australia. jock.churchman@adelaide.edu.au

²Commonwealth Scientific and Industrial Research Organisation, Land and Water, Private Mail Bag No.2, Glen Osmond, South Australia 5064, Australia.

³Pan Pacific Technologies Pty. Ltd., P.O. Box 523, Glenside, South Australia 5065, Australia

Introduction

The disastrous 2010 oil spill in the Gulf of Mexico has reminded the world of the lack of reliable technologies for the control and clean-up of spills of fuel oils at sea.. Its cause aside, the methods used in attempts to prevent the pollution of beaches and coastal ecosystems are not only old-fashioned, but have also proven to be ineffective. Essentially they comprise physical restraint - through floating booms, and chemical dispersion of the oil slicks. While oil spills have been highlighted for the public by the massive well 2010 spill from the breakdown of a well and those caused by tankers sinking, 82% of all oil spills annually involve the loss of fewer than 7 tonnes of oil (ITOPF, 2010), but these also bring local problems and demand better solutions than booms and dispersants. For larger spills, especially, it is most important that the solution to be employed is easily accessible so that it can be deployed at short notice. For small spills, it is particularly crucial that the solution to the problem is relatively inexpensive. For all spills, it is a great advantage if the method used to restrain the oil also enhances its removal for degradation on land.

In the course of experiments on clearing films of lubricating oils on water through the addition of powdered hydrophobic clays produced by reacting quaternary ammonium salts with bentonites, we discovered that powdered solid wastes from bleaching cooking oils (spent bleaching earths, or SBEs) were also effective for clearing these films. A bleaching earth (BE) is a clay-based material that is used to remove compounds which impart colour, undesirable odour and also taste to edible oils, which may derive from plants or land or marine animals (Anderson and Williams, 1962; Siddiqui, 1968). Generally, it is a smectitic clay that has been acid activated by its controlled, partial dissolution in mineral acids, giving rise to a mixture of protonated aluminosilicate clay with amorphous silica that exhibits a higher surface area, porosity and Brønsted acidity than the original smectite (Adams, 1987; Rhodes and Brown, 1994; Breen et al., 1995; Komadel, 1999; Gates et al., 2002). Edible oils and fats are contacted with BEs to remove their colour and undesirable compounds, sometimes at elevated temperatures until the BEs are saturated. The resulting SBEs comprise both chemically and physically adsorbed organic compounds and also invariably include residual edible oil or fat that is closely incorporated.

Materials

Arabian light crude oil and Marine diesel oil were obtained from oil refineries. The sorbent materials tested included: three from the processing of tallow by different companies, one from sunflower oil (from Meadow Lea), and one from vegetable oil (from Unilever). Some experiments only used (1) complexes formed between two Australian bentonites and (a) a pure quaternary ammonium salt, dimethyl dioctadecyl ammonium bromide (DMDOAB) and (b) a commercial quaternary ammonium salt, 2HT.75, (2) the commercial organoclay 'Petro Lock', comprising a modified clay, which was developed by the Lockheed Corporation as an oil spill containment agent.

Methods

Oil sorption tests were carried out by a standard ASTM procedure (ASTM, 1999). The objective of the tests was to measure the sorption of oil by the solid samples in the absence of water. Dynamic degradation tests were carried out using a scaled-down version of the ASTM standard (ASTM, 1999). The objective of this test, carried out in stoppered glass jars, was to determine the buoyancy of the sorbent materials on water. Tests of the ability of the different sorbent materials to aggregate the oil into removable semi-solid 'clumps' were also carried out. It was found necessary to confine the SBE materials into bags to ensure their containment and that of the oil they removed from water surfaces. Bags made out of spun-bonded polypropylene were tested for their suitable weight grade and for retention of SBE material. These were filled with the materials and were subjected to the same dynamic degradation tests as the powders in two shapes, viz. tubes and pillows. After the tests with SBEs in bags, the original oil, the residues of oil in water and the oil sorbed into the SBE in the bags were each extracted into hexane and the extracted water-insoluble components were analysed by GC-MS to determine the efficiency of the treatments. Successively higher amounts of the oils were added to water to test the capacity of SBEs in bags to remove the oils. Biodegradation was carried out by adding soil, maintained at 70% water holding capacity to the SBE-fuel oil complex at a ratio of 20:1 w/w and removing the samples at different time intervals for extraction with hexane and analyses by GC-MS. Large scale tank tests were carried out in a tank designed to hold 1 tonne of water in which waves were generated from one end that approximated the nature and frequency of waves in the ocean. The tank ended at the other end in a beach-like structure that was able to dampen the wave motion and prevent their return. At this scale, SBE from tallow was sewn into sets of pillow-shaped bags ("Spillows"TM) that together spanned the width of the tank.

Results

Process and outcomes are illustrated in Figure 1.



a



b



c



d

Fig. 1. a: SpillowsTM being filled with SBE. b: Addition of crude oil to water in tank. c: Uptake of crude oil occurring on SpillowsTM in tank. d: Uptake of crude oil largely complete.

Key outcomes

- SBEs from the manufacture of tallow sorbed fuel oils more effectively than those from vegetable and sunflower oil manufacture.
- SBEs generally ‘clumped’ oils more rapidly than modified clays, including Petro Lock.
- SBE from tallow was able to remove all of both a crude oil and a diesel from slicks on water, until its sorption capacity (~1g oil/g SBE) was reached.
- When they were contained in porous bags of spun bond polypropylene, SBEs passed the ASTM test for buoyancy, including under agitation.
- Mineral oil that had been sorbed by SBE from tallow could be microbially degraded in soil provided the concentration of the waste in soil was not too high.
- Sorbents were similarly effective at a larger scale as at a small scale (~1g oil sorbed/g SBE).
- In a tank with simulated wave action, SBE from tallow contained in a number of flattish porous bags (“spillows”) tied together successfully removed the largest part (>90%) of spilt diesel and crude oil very rapidly (within 6 minutes).
- Approx. 16% of (crude) oil could be squeezed out simply from porous bags of SBE.

Practical implications

Spent bleaching earths (SBEs), are inexpensive, being generally free of cost at their source, and, being widespread and usually stored in bulk prior to disposal, e.g. to landfill, are available at short notice from the closest of the many factories where edible oils are continuously manufactured.

Approximately 800,000 tonnes of SBEs were produced world-wide as wastes in 2001 (Crossley, 2001).

References

- Adams, JM (1987) Synthetic organic chemistry using pillared, cation-exchanged and acid-treated montmorillonite catalysts – a review. *Applied Clay Science* **2**, 309-342.
- Anderson AJC, Williams PN (1962) Refining of Oils and Fats for Edible Purposes. (Pergamon: New York).
- ASTM (1999). Standard test method for sorbent performance of adsorbents, F726-99. (American Society for Testing Materials: West Conshohocken, PA).
- Breen C, Madejová J, Komadel P (1995) Characterisation of moderately acid-treated, size-fractionated montmorillonites using IR and MAS NMR spectroscopy and thermal analysis. *Journal of Materials Chemistry* **5**, 469-474.
- Crossley P (2001) Clear opportunities for bleaching and clarifying clays. *Industrial Minerals*, March 2001, 69-75.
- Gates WP, Anderson, JS, Raven MD (2002) Mineralogy of a bentonite from Miles, Queensland, Australia and characterisation of its acid activation products. *Applied Clay Science* **20**, 189-197.
- ITOPF, 2010. The International Tanker Owners Pollution Federation Limited.
<http://www.itopf.com/information-services/data-and-statistics/statistics/> (sourced May 29, 2010)
- Komadel P (1999) Structure and chemical characterisation of modified clays In ‘Natural Microporous Materials in Environmental Technology’ (eds. P Misaelides, F Macásek, TJ Pinnavaia, C. Colella). pp. 3-18 (Kluwer: Netherlands).
- Rhodes CN, Brown DR (1994) Catalytic activity of acid-treated montmorillonite in polar and non-polar reaction media. *Catalysis Letters* **24**, 285-291.
- Siddiqui MKH (1968) Bleaching Earths. (Pergamon: Oxford).