



COVER SHEET

This is the author-version of article published as:

Frost, Ray and Carmody, Onuma and Xi, Yunfei and Kokot, Serge (2007) Adsorption of hydrocarbons on organo-clays - implications for oil spill remediation. *Journal of Colloid and Interface Science* 305(1):pp. 17-24.

Accessed from <http://eprints.qut.edu.au>

© 2007 Elsevier

Adsorption of hydrocarbons on organo-clays -implications for oil spill remediation

Onuma Carmody, Ray Frost^{*}, Yunfei Xi and Serge Kokot

Inorganic Materials Research Program, School of Physical and Chemical Sciences,
Queensland University of Technology, GPO Box 2434, Brisbane Q 4001, Australia

ABSTRACT

Organoclays synthesised by the ion exchange of sodium in Wyoming Na-Montmorillonite (SWy-2-MMT) with three surfactants octadecyltrimethylammonium bromide (ODTMA) formula $C_{21}H_{46}NBr$ b) didecyldimethylammonium bromide (DDDMA), formula $C_{22}H_{48}BrN$, and c) di(hydrogenated tallow)dimethylammonium chloride (tallow) were tested for hydrocarbon adsorption. Using diesel, hydraulic oil and engine oil an evaluation was made of the effectiveness of the sorbent materials for a range of hydrocarbon products that are likely to be involved in land-based oil spills. It was found that the hydrocarbon sorption capacity of the organo-clays depended upon the materials and surfactants used in the organoclay synthesis. Greater adsorption was obtained if the surfactant contained two or more hydrocarbon long chains. Extensive utilisation of chemometrics principally with the aid of MCDM methods, produced models which consistently ranked the organoclays well above any of the competitors including commercial benchmark materials. Thus the use of organo-clays for cleaning up oil spills is feasible due to its many desirable properties such as high hydrocarbon sorption and retention capacities, hydrophobicity. The negative effects of the use of organoclays for oil-spill cleanup are the cost, the biodegradability, and recyclability of the organo-clays

Keywords: Hydrocarbon adsorption, Oil spills, sorbents, organo-clays, chemometric analysis

^{*} Author to whom correspondence should be addressed (r.frost@qut.edu.au)
P: +61 7 3864 2407 F: +61 7 3864 1804

Introduction

Smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area and resulting strong adsorption/absorption capacities (1-4). Because of the hydration of inorganic cations on the exchange sites, the clay mineral surface is hydrophilic in nature, which make natural clays ineffective sorbents for adsorbing organic compounds (5-7). Organo-montmorillonites are synthesized by grafting cationic surfactants such as quaternary ammonium compounds into the interlayer space (8-10). It has been demonstrated (11-14) that replacement of the exchange ions by organic cations (or surfactants) can create a hydrophobic or organophilic surface. These clays are referred to as organo-clays or organophilic clays. The use of organo-clays for hydrocarbon sorption has been widely studied (15-17). Organo-clays are formed when large hydrophobic quaternary ammonium compounds are exchanged onto 2:1 layer silicates (18, 19). The exchanged cations are usually tetramethylammonium (TMA) and trimethylphenylammonium (TMPA) for organo-clays and alkyl hydrocarbon groups of C₁₀ or greater for organophilic clays. When using long-chain alkylammonium cations hydrophobic partition medium within the clay interlayer can form, and function analogously to a bulk organic phase. The intergallery distance of d(001) plane of the clay which has not been organically modified, is relatively small, and the intergallery environment is hydrophilic (20, 21). Intercalation of organic surfactant between layers of clays can not only change the surface properties from hydrophilic to hydrophobic, but also greatly increase the basal spacing of the layers. At present, there are many applications of organo-clays using as sorbents in pollution prevention and environmental remediation such as treatment of spills, waste water, hazardous waste landfills etc. different areas. Some studies (19, 22-24) have showed that replacing the inorganic exchange cations of clay minerals with organic cations can result in greatly enhanced capacity of the materials to remove organic contaminants.

Recent major oil spills (the Exxon Valdez in Alaska, 1989; the Braer in Scotland, 1993; the Sea Empress in Wales, 1996; and the Prestige in Spain, 2002), have contaminated thousands of kilometers of coastlines and caused significant environmental impact. These hydrocarbon spills damage marine ecosystem and cause wide spread contamination of the surrounding environment. The contamination of shorelines generally has the greatest environmental and economic impact due in part to the difficulties of clean-up measures. Another key impact area of oil spills is land-based spills (e.g. tanker truck accidents, and pipeline leakage and discharges). During land-based transport, oils and other oil-based products are spilled with adverse impact on the transport infrastructure as well as affecting the environment and the community. Due to the proximity of high density human population, when these spills occur, human health and environmental quality are put at risk. From literature and field experiences to date (25-27), one of the most economic and efficient means of cleaning up hydrocarbon spills on the shoreline (or land) is the use of sorbents. The source of these sorbent materials can be natural or synthetic. They can be natural organic substances, synthetic organic substances, inorganic substances, or a mixture of the three. A material may also be treated with oleophilic and hydrophobic compounds to improve performance (25-30). A process that has been widely applied is the modification of clay materials to increase hydrocarbon sorption.

Sharmasarkar *et al.* (31) demonstrated that organo-clay can be used for the containment of environmental pollutants originating from waste sites or accidental spills. A batch study was conducted using organo-clays produced from a Wyoming montmorillonite and three organic cations TMPA, trimethylammonium adamantane (Adam), and HDTMA to characterise BTEX (benzene, toluene, ethylbenzene, o-, m-, p-xylene) sorption. The results indicated that organo-clays with smaller cations had greater hydrocarbon retention. Sorption of BTEX followed the order of TMPA > Adam > HDTMA organo-clays. Jaynes and Vance (16) conducted experiments and discovered that hectorites with exchanged aromatic cations proved useful for the sorption of benzene, toluene and ethyl benzene. Wefer-Roehl and Czurda (32) discovered that organo-clays have proven useful for the adsorption of both aliphatic and aromatic hydrocarbons. Beall (33) used organo-clays, in combination with activated carbon and reverse osmosis, to treat wastewater contaminated with organic pollutants. It was found that organo-clays was superior to any other water treatment technology in applications where the water to be treated contained substantial amounts of oils and grease. Organo-clays were also used to successfully treat process and potable water.

It is clear that the use of organo-clays as an oil sorbent may be a viable option given its hydrophobic property and its ability to selectively adsorb oil in the presence of water. Thus, the aim of this study is to evaluate the performance of organo-clays for cleaning up oil spills by:

- a) assessing the performance of commercially available sorbents in current use;
- b) developing improved clay-based sorbents (organo-clays) for use in oil spill applications; and
- c) ranking overall sorbent performance on the basis of the sorption capacities and other performance criteria (i.e. environmental, cost and end use attributes).

1 Materials and Methods

1.1 Reference Sorbents

The eight sorbent materials selected for evaluation are all commonly available for cleaning up various large and small hydrocarbon spills. These sorbents are designated by abbreviations, which are related to their physico-chemical descriptions rather than their commercial names (Table 1). Their composition varies from one material to another and includes different natural organic substances and/or inorganic materials.

1.2 Organo-clays

The montmorillonite used in this study was supplied by the Clay Minerals Society as source clay SWy-2-Na-Montmorillonite (SWy-2-MMT) (Wyoming). This clay originates from the Newcastle formation, (Cretaceous), County of Crook, State of Wyoming, USA. The cation exchange capacity (CEC) is 76.4 meq per 100 g (according to the specification of its producer). The bentonite used in this study was sourced from Australia. The CEC for bentonite was not determined therefore, the CEC of SWy-2-MMT was used as a reference.

Three different types of surfactant were used in the modification of the clays: a) octadecyltrimethylammonium bromide (ODTMA), $C_{21}H_{46}NBr$, FW: 392.52; b) didecyldimethylammonium bromide (DDDMA), $C_{22}H_{48}BrN$, MW: 406.53; and c) di(hydrogenated tallow)dimethylammonium chloride (tallow). All the surfactants were sourced from Sigma-Aldrich.

The syntheses of surfactant-clay hybrids were undertaken by the following procedure: SWy-2-MMT or bentonite was first dispersed in deionised water (the ratio of clay to water was 100 g: 2,750 mL) and then stirred with a mechanical stirrer for about 10 hours. A pre-dissolved stoichiometric amount of surfactant was slowly added to the clay suspension. The reaction mixtures were stirred for about 24 hours. All organo-clay products were washed three times with deionised water to remove excess surfactants, filtered and dried at room temperature or in an oven at 50-60 °C, ground in an agate mortar, and then stored in a vacuum desiccator for about 7 days.

1.3 Hydrocarbons

Diesel, hydraulic oil and engine oil (BP Australia, Castrol Australia and Valvoline Australia) were used in this study and are described in Table 2. By using three different types of hydrocarbons in the study, an evaluation can be made of the effectiveness of the sorbent materials for a range of hydrocarbon products that are likely to be involved in land-based spills.

1.4 Sorption Capacity Tests

The method developed for the measurement of hydrocarbon sorption capacity of the various sorbents was based on *ASTM F726-99: Standard Test Method for Sorbent Performance of Adsorbents* (34). The focus of this method concerns the evaluation of sorbents performance for removing non-emulsified oils and other floating, immiscible liquids from the surface of water bodies. However, in this study, the oil spills are land-based (e.g. road pavement); in addition, the range and composition of sorbents tested (natural organic/inorganic, powder, granules...) varies significantly. Therefore, this method was adapted to evaluate sorption capacity in the presence of hydrocarbons only (i.e. oil bath).

For *hydrocarbon sorption capacity* measurements, the particular chosen hydrocarbon (250 mL) was poured into a rectangular Pyrex dish (ca. 25x20x7 cm). Approximately 20 g of sorbent were weighed and the value recorded. The sorbent material was spread evenly on a filter paper (Whatman no. 40), placed into a rectangular stainless steel wire mesh (2 mm²) basket (ca. 20x16x7 cm), and then lowered into the Pyrex dish with the hydrocarbon so that the sorbent was completely covered by the liquid. In general, after 15 min ± 20 s of immersion, the basket with the sorbent was removed and allowed to drain into a suitable pre-weighed container. For diesel, with its relatively low viscosity, 30 min ± 3 s were sufficient to catch most of the excess liquid but for hydraulic and engine oils, due to their higher viscosity, a drain time of 1 min ± 3 s was required to reach the same point. The saturated sorbent was then immediately transferred to another suitable pre-weighed dish and weighed. All tests were carried out in triplicate with the mean of the three runs used for calculations. If the value of any run (g/g) deviated by more than 15% (34) from the mean of the three runs, then the sample was rejected and the test repeated with three

new specimens. The hydrocarbon pick-up ratio on a weight basis was calculated as follows:

Sorption capacity (g oil/g sorbent) = S_s / S_o or $[(S_{st} - S_o) / S_o]$

where: S_o is the initial dry weight of sorbent,
 S_{st} is the weight of sorbent (after oil test)
 S_s is $(S_{st} - S_o)$ net oil adsorbed.

It should be noted that the modified method above was also applied to determine *water sorption capacity* of sorbents. There were no changes to the method other than the use of water as the test immersion liquid. The method appears quite robust with good data reproducibility.

1.5 Diesel Emulsion Extraction

In contrast to the previous method adapted from ASTM 726-99, this method was developed to evaluate the performance of sorbents for removing diesel from the surface of water bodies (i.e. diesel/water emulsion). As the sorbents would likely be used in wet weather on roads or for cleaning up spills in fresh/marine water environments, it was important to evaluate performance in the presence of water.

The diesel emulsion was prepared using the following procedure: diesel was dispersed in deionised water (the ratio of diesel to water was 10 mL: 40 mL) and the mixture was stirred with Ultra Turrax T25 homogeniser (24,000 rpm) for 2 mins. Approximately, 5 g of reference sorbent was weighed and added to the diesel emulsion. After 15 mins +/- 20s saturation time, the excess diesel emulsion was drained off and the sample reweighed. The (saturated) sample was transferred to the soxhlet extractor chamber (125 mL) and about 150 mL diethyl ether was added to the flat bottom flask. The solvent was then recycled in the soxhlet chamber (two times) for about 2 h. After the soxhlet extraction of the sorbent material using diethyl ether was completed, the extract was filtered using Whatman no. 40 filter paper to remove all particulate matter present in the extracts. The extract was then placed in a separatory funnel, mixed together thoroughly, and allowed to settle out. This process (extract washing with water) was repeated three times to completely wash the aqueous layer. After the separation process, the extract layer was drained into a flask and anhydrous sodium sulfate added to remove any residual water in the solution. The solution was then heated to evaporate the solvent to give the pure diesel compounds.

1.6 Hydrocarbon Retention Capacity

The hydrocarbon retention capacity test is a laboratory method that was developed to determine the amount of free hydrocarbons released from a sorbent material when it is subjected to pressure (compressive force) (i.e. during routine handling, transportation or disposal).

For *hydrocarbon retention capacity* measurements, approximately 100 g of reference sorbent material was weighed within +/- 2 % and the value recorded. The sample was then placed in a 250 mL beaker and saturated with 200 mL of chosen hydrocarbons for 15 min +/- 30 s. After saturation, excess hydrocarbons were drained off and the sample reweighed. The dry sample weight was subtracted from the saturated sample weight to obtain total oil adsorbed. The (saturated) sample was immediately transferred to the sample holder and the top of the sample was smoothed over with a spatula to create a horizontal surface. Then the stainless steel mesh was

placed on top of the sample with the piston positioned on top of the mesh. The top plate was then secured. The sample holder was placed on a stand and a beaker positioned underneath to capture the free liquid. To apply the required pressure (5 kN/m^2), a 2 kg free weight was applied to the piston rod for 15 min +/- 30s. The free weight was then removed and the sample transferred to a weighing pan and reweighed to within +/- 2%. The dry weight was subtracted from the sample to obtain the net oil remaining. The free liquid (hydrocarbons) in the beaker was also weighed and value recorded. All samples were duplicated with the mean of the runs used for calculations. If the value of any run deviated by more than 15 % from the mean of the two runs, then the samples were rejected and the test repeated with two new specimens. Oil retention was measured as the ratio of oil adsorbed to dry sorbent weight:

$$\text{Oil retention (\%)} = (\mathbf{O_s} - \mathbf{O_n})/\mathbf{O_s}$$

where: $\mathbf{O_s}$ = total oil adsorbed

$\mathbf{O_n}$ = net oil remaining (after oil retention test)

1.7 *Other Performance Criteria*

The other variables used in the study were obtained from the following sources:

- Ease of use – scaled (1-5) on the basis of on-site experiences with the use of sorbents to clean-up numerous road spills, and Queensland Department of main Roads (DMR) database (35);
- Biodegradation – in this exploratory work, the simple biodegradable/non-biodegradable criterion (i.e. matrix entries 1 or 0 respectively) was applied with the aid of literature (35) and manufacturer’s product information; and
- Cost – sourced (in AUS\$) from local suppliers per kilogram.

1.8 *PROMETHEE and GAIA*

PROMETHEE and GAIA Multi-Criteria Decision Making (MCDM) methods have been described in detail elsewhere (36-38); in this paper only a summary is provided to indicate the principal concepts and data treatment involved. PROMETHEE is a non-parametric method used to rank a number of actions (objects) based on the criteria (variables) in the data matrix. For each criterion, a difference, d , is calculated for all the objects in all possible ways, and a specific preference function, a threshold value and a weighting condition must be defined. The preference function is a mathematical function, which is used to calculate the degree of preference associated with each object on that variable. For an object, such preferences are summed across all variables, ultimately to give an index, termed net outranking flow, φ . A comparison of these indices for a series of objects provides their rank order.

GAIA is a data display method and is linked to the PROMETHEE procedure with the GAIA matrix being constructed from a decomposition of the φ net outranking flows (36). This new data matrix is then processed by a Principal Component Analysis (PCA) algorithm, and displayed on a GAIA biplot, which shows a distribution of objects, criteria vectors and a decision axis, π . Interpretation of such biplots provides guidelines for the PROMETHEE ranking of the objects. Detailed applications and explanations are provided in (36, 39, 40).

2 Results and Discussion

It is recognised that the many performance criteria applied to the sorbents are often competitive i.e. a sorbent with a high value of sorption capacity is not necessarily environmentally friendly or cost-effective. In general, solutions for the selection of the preferred sorbent are a compromise between performance, cost and environmental factors. To select a sorbent for an oil spill application, such materials (objects) must be ranked on the basis of a range of performance criteria (multi-variate effect values). The preferred sorbent materials can then be selected with the aid of a well described and defined model so that the rationale for selection is understood. For this purpose, there are many MCDM methods, which have been recently compared (40, 41) and described (36, 38). Among the more common and better performing models are the combination of the PROMETHEE and GAIA methods (39, 42-44). These methods were applied to the study to facilitate multi-variate data interpretation.

2.1 *Organo-clays Sorption Capacity*

The hydrocarbon sorption capacities of various modified organo-clays are given in Table 3. The hydrocarbon sorption capacity obtained for ST1 organo-clay range from 7.2 g/g for diesel, 2.2 g/g for hydraulic oil to 2.1 g/g for engine oil. Similar results were obtained for SD2 organo-clay with 5.2 g/g for diesel and 3.6 g/g for hydraulic and engine oil. These results exceeded the literature value of 1.9 g/g obtained for organo-clays used to remove heavy petroleum oil from a major chemical plant condensate (33). More importantly, SD2 and ST2 organo-clays have exceeded the study benchmark (eight reference sorbents) for all three hydrocarbons tested. This implies that, on the basis of hydrocarbon sorption capacity, the organo-clay sorbent out performs commercially available sorbents.

It is also clear that the hydrocarbon sorption capacity of the organo-clays varies depending on the materials and surfactants used in the modification process. Although the clay starting material plays a role (i.e. Na-montmorillonite vs bentonite), the clay's CEC and the use of diverse surfactants are primary determinants that facilitate hydrocarbon uptake. The influence of the clay's CEC on basal spacing and surfactant packing densities has been widely reported in literature (Wang 04, Xi, Burgentzle, Carrizosa). Xi *et al.* (04) proposed a model where at <0.4 CEC a surfactant monolayer is formed between the clay layers, at <0.8 CEC a lateral bilayer arrangement is formed, and at >1.5 CEC a pseudotrimolecular layer is formed with excess surfactant adsorbed on the clay surface. Based on this model, the organo-clays used in this study (1-1.5 CEC) generally have surfactants intercalated into the clay interlayers as well as surfactants physically adsorbed on the external surface of the clays.

The other key factor responsible for the differences in sorption capacities of organo-clays is the type of surfactants used to modify the clay. Three different surfactants were used in the modification process: a) ODTMA with one long C₁₈ group; b) DDDMA with two long C₁₈ groups; and c) Tallow with two long C₁₈ groups. From Table 3, the two long carbon chains in DDDMA and Tallow appear to enhance the sorption capacities of the organo-clays. In contrast, organo-clays (SD1) modified with ODTMA sorbed significantly less hydrocarbons. This observation suggests that the two long chains in DDDMA and Tallow provide more sites for interaction with the hydrocarbon molecules.

Overall, the study determined that the selection of smectites with different layer charges, diverse surfactant cations and use of different coverage levels is required to optimise the clay characteristics to design the most appropriate organo-clay sorbent for use as hydrocarbon spill clean-up material. In this study, the results show that Na-montmorillonite clays (1.5 CEC) modified with DDDMA (SD2) or Tallow (ST1) achieved the highest hydrocarbon sorption capacity (Table 3).

2.2 *Organo-clays vs Reference Sorbents*

To assess fully the competitiveness of organo-clays as a sorbent material, the performance of organo-clays against reference materials in current use was evaluated. The sorbent performance matrix (13 x 7) is shown in Table 4. Initially, a 13 x 3 sub-matrix consisting of the eight common sorbents and sorption capacity values of the three hydrocarbons was investigated to establish the performance of the sorbents (objects) with the three different hydrocarbons. Then, the remaining six criteria were added, one at a time, submitting each new sub-matrix (i.e. a new scenario) to the MCDM analysis to build up an understanding of the influence of each new additional criterion on the performance ranking of the sorbent materials. The PROMETHEE model parameters and threshold values for each scenario are also given in Table 4.

2.3 *Scenario 1: Hydrocarbon Sorption Capacity*

The original (13 x 3) data matrix consisted of thirteen sorbents (i.e. eight reference sorbents and five organo-clays) and the three hydrocarbon sorption criteria (diesel, hydraulic oil and engine oil). The rank order obtained for Scenario 1 is given in Table 5. From an examination of the ϕ values, SD2 and ST1 are the preferred sorbents, ranked first and second, respectively. Followed by WF (third), GC (fourth) and BD1 (fifth) in the rank order. These sorbents are the top five performers on the hydrocarbon sorption criteria. The middle ranked sorbents (BT1, SD1, OM, OZ, PM and CM) are not clearly discriminated but rather form a cluster. The least preferred sorbents are the inorganic reference sorbents, Z and S. SD2 and ST1 out performed all the reference sorbents including the rest of the organo-clays (BD1, BT1 and SD1). Clearly, the organo-clays have been shown to be competitive and to take up hydrocarbons in appreciable amounts relative to the reference sorbents.

The GAIA PC1 versus PC2 biplot (Figure 1, 100% variance described) discriminated the top performers (objects with positive PC1 scores) from the poor performers (objects with negative PC1 scores). The rank order (on PC1 axis) is also consistent with the PROMETHEE II net outranking flow values, ϕ . SD2 and ST1 objects, with the highest PC1 scores, are the preferred sorbents. These sorbents are followed by a middle cluster of WF, GC and BD1 with positive PC1 scores and lastly, a large group cluster of least preferred sorbents with negative PC1 scores.

The distribution of the objects on PC1 is influenced by the three sorption capacity criteria (DSC, HSC, ESC vectors). The three criteria strongly contribute to the discrimination pattern of the objects on PC1. The top five performers are distributed among the three criteria vectors according to their performance on the respective criterion. Thus, SD2 and BD1 perform well for all three hydrocarbons. In contrast, WF and GC have a greater affinity for the heavier hydraulic and engine oils. Similarly, ST1 has a greater affinity for diesel. The remaining sorbent objects performed poorly for all three hydrocarbons in comparison.

Projection of objects and criteria vectors on PC2 indicates that the WF/GC and ST1 have the highest and lowest scores. Most of the other objects have relatively low scores on PC2. Once again, there is a strong correlation between the heavier oils (HSC and ESC criteria vectors), while the DSC criterion vector is approximately at ninety degrees to the other two, suggesting that the DSC criterion is independent. This observation is related to the relatively high viscosity values of the first two hydrocarbons as compared to that of DSC. The decision axis, π , showing the optimal solution, roughly splits the angle between the criteria vectors, and points in the direction of the preferred performance object, SD2. This axis is long indicating a good decision. This result is reflected in the PROMETHEE II net outranking flows order (Table 5, Scenario 1).

2.4 Effects of Other Criteria on Organo-clay Performance

The original data matrix (Scenario 1) was expanded to include the other performance criteria in the PROMETHEE model (Table 4). A complete set of φ net outranking flow values (Table 5) and visual biplot results were obtained for each of the scenarios however, only Scenario 7 biplot is shown (Figure 2). In addition, only the principal effects and changes associated with Scenarios 2-7 are reported.

- *Organo-clays sorption capacity:* As discussed, differences in the hydrocarbon sorption capacity of organo-clays were obtained in the analysis. This is related to clay's CEC (1 vs 1.5), surfactants used (DDDMA vs ODTMA), and selection of clay starting material (Swy-2-MMT vs Bentonite). Organo-clays modified with the use of Swy-2-MMT at 1.5 CEC and intercalated with Tallow (ST1) and DDDMA (SD2) out performed all other sorbents (Scenario 1).
-
- *Preferred sorbent materials:* Based on the key performance criteria – hydrocarbon sorption capacities – organo-clays out performed the reference sorbents. SD2 and ST1, consistently ranked 1st and 2nd in Scenarios 1-5. However, the addition of cost and biodegradation criteria (Scenarios 6 and 7) adversely affected the rank order of SD2 and ST1 with a resultant fall in the ranking.

Model expansion and decision-making: Table 5 illustrates how sorbents may be influenced in their performance by moving up and down the rank order depending on the criterion added. In Scenario 7 (Figure 2), sorbent objects are separated on the basis of: a) organic sorbents (low cost and biodegradable); b) inorganic sorbents (low hydrocarbon sorption capacities and non biodegradable); c) organo-clays (high hydrocarbon sorption capacities, relatively high cost and non biodegradable). Organo-clays perform well for hydrocarbon sorption capacities but are relatively expensive and non-biodegradable which greatly influence its practical application (e.g. for road spills where bulk materials are required for clean-ups). In contrast, organic sorbents are cheap and biodegradable and, in the case of WF and GC, have relatively high hydrocarbon sorption capacities. Thus, the change in rank order of 1st and 2nd for WF and GC, when all criteria are considered.

3 Conclusions

Based on the PROMETHEE modelling, the organo-clay sorbents (SD2 and ST1) clearly performed best on the hydrocarbon sorption capacity criteria when compared with the project benchmark reference sorbents. The MCDM analysis demonstrated that the use of organo-clays for cleaning up oil spills is feasible due to its many desirable properties such as high hydrocarbon sorption and retention capacities, hydrophobicity. However, when the PROMETHEE model was expanded to include the cost and biodegradable criteria, alternative sorbent options became apparent, namely cellulose - based reference Sorbents ,WF and GC.

References

1. Alther, G. R., *Contaminated Soils* **8**, 189 (2003).
2. Alther, G. R., *Special Publication - Royal Society of Chemistry* **259**, 277 (2000).
3. Breen, C., Watson, R., Madejova, J., Komadel, P. and Klapyta, Z., *Langmuir* **13**, 6473 (1997).
4. Dentel, S. K., Bottero, J. Y., Khatib, K., Demougeot, H., Duguet, J. P. and Anselme, C., *Water Research* **29**, 1273 (1995).
5. Jose, C. L. V., Kozievitch, V. F. J., Diaz, F. R. V. and Buechler, P. M., *Congresso Anual - Associacao Brasileira de Metalurgia e Materiais* **57th**, 1353 (2002).
6. Kim, J. H., Shin, W. S., Kim, Y. H., Choi, S. J., Jeon, Y. W. and Song, D. I., *Water Science and Technology* **47**, 59 (2003).
7. Prost, R. and Yaron, B., *Soil Science* **166**, 880 (2001).
8. Chaiko, D., in *PCT Int. Appl.*, (University of Chicago, USA). Wo, 2002, p. 24 pp.
9. Nzungung, V. A., **1993**.
10. Soule, N. M. and Burns, S. E., *Journal of Geotechnical and Geoenvironmental Engineering* **127**, 363 (2001).
11. Booiij, E., Klopogge, J. T. and Van Veen, J. A. R., *Applied Clay Science* **11**, 155 (1996).
12. Boyd, S. A. and Jaynes, W. F., *CMS Workshop Lectures* **6**, 48 (1994).
13. Klopogge, J. T., Evans, R., Hickey, L. and Frost, R. L., *Applied Clay Science* **20**, 157 (2002).
14. Xi, Y., Frost, R. L., He, H., Klopogge, J. T. and Bostrom, T., *Langmuir In press.*, (2005).
15. Barrer, R. M., *Pillared Layered Struct.: Curr. Trends Appl., [Proc. Workshop]* **55** (1990).
16. Jaynes, W. F. and Vance, G. F., *Soil Science Society of America Journal* **60**, 1742 (1996).
17. Jaynes, W. F. and Vance, G. F., *Clays and Clay Minerals* **47**, 358 (1999).
18. Jaynes, W. F. and Boyd, S. A., *Soil Science Society of America Journal* **55**, 43 (1991).
19. Jaynes, W. F. and Boyd, S. A., *Clays and Clay Minerals* **39**, 428 (1991).
20. Xi, Y., Ding, Z., He, H. and Frost, R. L., *Journal of Colloid and Interface Science* **277**, 116 (2004).
21. Xi, Y., Frost, R. L., He, H., Klopogge, T. and Bostrom, T., *Langmuir* **21**, 8675 (2005).
22. Mortland, M. M., Shaobai, S. and Boyd, S. A., *Clays and Clay Minerals* **34**, 581 (1986).
23. Boyd, S. A., Shaobai, S., Lee, J.-F. and Mortland, M. M., *Clays and Clay Minerals* **36**, 125 (1988).
24. Jaynes, W. F. and Boyd, S. A., *Journal of the Air & Waste Management Association (1990-1992)* **40**, 1649 (1990).
25. Adebajo, M. O., Frost, R. L., Klopogge, J. T., Carmody, O. and Kokot, S., *Journal of Porous Materials* **10**, 159 (2003).
26. Choi, H. M. and Cloud, R. M., *Environmental Science and Technology* **26**, 772 (1992).

27. Teas, C., Kalligeros, S., Zankos, F., Stournas, S., Lois, E. and Anastopoulos, G., *Desalination* **140**, 259 (2001).
28. Choi, H.-M., *Journal of Environmental Science and Health, Part A: Environmental Science and Engineering & Toxic and Hazardous Substance Control* **A31**, 1441 (1996).
29. Choi, H. M. and Moreau, J. P., *Microscopy Research and Technique* **25**, 447 (1993).
30. Moreau, J. P., *Textile Research Journal* **63**, 211 (1993).
31. Sharmasarkar, S., Jaynes, W. F. and Vance, G. F., *Water, Air, and Soil Pollution* **119**, 257 (2000).
32. Wefer-Roehl, A. and Czurda, K. A., in *Clays Our Future, Proc. Int. Clay Conf., Vol. 11th* (Eds.: H. Kodama, A. R. Mermut and J. K. Torrance), ICC97 Organizing Committee, Ottawa, 1997, pp. 123.
33. Beall, G. W., *Applied Clay Science* **24**, 11 (2003).
34. Astm, *F726-99: Standard Test Method for Sorbent Performance of Adsorbents, Vol. Vol. 11.04*, American Society of Testing and Materials, Philadelphia, PA, 1999.
35. Dmr, *Vol. 2005*, Brisbane, 2005.
36. Keller, H. R., Massart, D. L. and Brans, J. P., *Chemometrics and Intelligent Laboratory Systems* **11**, 175 (1991).
37. Brans, J. P., Mareschal, B. and Vincke, P., *European Journal Operational Research* **24**, 228 (1986).
38. Brans, J. P. and Vincke, P., *Management Science* **31**, 647 (1985).
39. Ayoko, G. A., Morowska, L., Kokot, S. and Gilbert, D., *Environmental Science and Technology* **38**, 2609 (2004).
40. Kokot, S. and Ayoko, G. A., in *Encyclopaedia of Analytical Sciences*, 2nd Edition ed., Elsevier Ltd, Amsterdam, **2004**.
41. Ayoko, G., Bonire, J. J., Abdulkadir, S. S., Oluninola, P. F., Ehinmidu, J. O., Kokot, S. and Yiasel, S., *Applied Organometallic Chemistry* **17**, 749 (2003).
42. Kokot, S., King, G., Keller, H. R. and Massart, D. L., *Analytica Chimica Acta* **259**, 267 (1992).
43. Martin, N. J., St. Onge, B. and Waaub, J.-P., *International Journal of Environment and Pollution* **12**, 264 (1999).
44. Purcell, D., Leonard, G. J., O'shea, M. G. and Kokot, S., *Chem. Intel Lab Systems* **in print**, (2006).

List of Tables

Table 1	Reference sorbents used in the study
Table 2	Properties of the three hydrocarbons used in the study
Table 3	Sorption capacities of various organo-clays used in the study
Table 4	Data matrix for PROMETHEE ranking and model parameters for organo-clays and reference sorbents
Table 5	PROMETHEE II net outranking preference flows, φ , for organo-clays vs reference sorbents

Table 1.

Sorbent	Description
GC	Pelletised grain (G), cotton © and other cellulose-based material (tan/brown)
WF	Milled by-product of Australian soft wood (W) with dry mixture of cellulose fibres (F) and particulates (brown/dark brown)
OM	Organic (O)/mineral (M) powder (tan/grey)
CM	Cellulose ©/mineral (M) powder with facultative and aerobic microbial additives (tan grey)
OZ	Organic (O)/mineral powder with 20% weight zeolite (Z) (tan/grey)
PM	Organic with pecan (P) nut shells/mineral (M) powder (tan)
Z	Fine zeolite (Z) granules and powders (pink/white)
S	Fine sand (S) particles (beige)

Table 2.

Hydrocarbon	Description	Viscosity*	Specific Gravity*
BP Diesel	Clear liquid	1.2-4.6 cST @ 38°C	0.84
Castrol Hydraulic Oil (Hyspin AWH68)	Clear amber liquid	68 cST @ 40°C	0.88
Valvoline Super Diesel Engine Oil	Clear amber liquid	120 cST @ 40°C	0.89

Note: * BP Australia MSDS (2002); Castrol Australia MSDS (2002); Valvoline MSDS (2002)

Table 3.

Sorbent	Description	DSC (g/g)	HSC (g/g)	ESC (g/g)
<i>Reference Sorbents</i>				
GC	Pelletised grain, cotton-based	1.0	1.4	1.5
WF	Milled wood, cellulose fibres	2.1	2.9	2.8
OM	Organic/mineral powder	1.0	1.3	1.3
CM	Cellulose /mineral powder	0.9	1.2	1.4
OZ	Organic/zeolite powder	0.8	1.2	1.0
PM	Organic/mineral powder	1.5	3.0	3.4
Z	Zeolite	0.6	0.9	0.9
S	Sand	0.2	0.3	0.3
<i>Organo-clay Sorbents</i>				
SD1	Swy-2, 1 CEC, ODTMA	1.2	1.4	1.6
BD1	Bentonite, 1.5 CEC, DDDMA	3.5	2.2	2.1
SD2	Swy-2, 1.5 CEC, DDDMA	5.2	3.6	3.6
BT1	Bentonite, 1.5 CEC, Tallow	3.1	1.3	1.3
ST1	Swy-2, 1.5 CEC, Tallow	7.2	2.2	2.1

Note: DSC, HSC, and ESC – diesel, hydraulic oil, and engine oil hydrocarbon sorption capacity, respectively

Table 4.

	DSC	HSC	ESC	WSC	DE	HRC	EoU	Cost	Bio
<i>Model Parameters</i>									
Function	V-shaped	V-shaped	V-shaped	V-shaped	V-shaped	V-shaped	V-shaped	V-shaped	Usual (yes/not)
Min/Max	Max	Max	Max	Min	Max	Max	Max	Min	Max
Weight	1	1	1	1	1	1	1	1	1
Unit	g/g	g/g	g/g	g/g	g/g	%	5 point	\$/kg	-
<i>Reference Sorbents</i>									
OM	1.0	1.4	1.5	2.9	0.8	78	2	2.95	1
GC	2.1	2.9	2.8	4.1	0.8	74	4	2.95	1
OZ	1.0	1.3	1.3	3.2	1.1	85	2	2.95	1
PM	0.9	1.2	1.4	2.6	0.8	82	2	2.95	1
CM	0.8	1.2	1.0	2.4	0.6	83	2	2.50	1
WF	1.5	3.0	3.4	2.5	1.3	68	1	2.95	1
Z	0.6	0.9	0.9	1.0	0.04	71	3	0.60	0
S	0.2	0.3	0.3	0.3	0.01	66	3	0.50	0
<i>Organo-clays</i>									
SD1	1.2	1.4	1.6	0.3	0.8	88	2	30.00	0
BD1	3.5	2.2	2.1	0.2	0.8	89	2	30.00	0
SD2	5.2	3.6	3.6	0.2	0.9	90	2	30.00	0
BT1	3.1	1.3	1.3	0.2	0.8	89	2	30.00	0
ST2	7.2	2.2	2.1	0.2	0.9	90	2	30.00	0

Note: DSC, HSC, ESC and WSC – diesel, hydraulic oil, engine oil and water sorption capacity, respectively; DE – diesel emulsion sorption capacity; HRC – hydrocarbon retention capacity; EoU – ease of use (1-very poor, 2-poor, 3-average, 4-good, 5-excellent); Bio – biodegradable (yes=1, no=0).

Table 5.

Rank Order	Scenario 1 (SC)		Scenario 2 (+WSC)		Scenario 3 (+DE)		Scenario 4 (+HRC)		Scenario 5 (+EoU)		Scenario 6 (+Cost)		Scenario 7 (+Bio)	
	Obj	φ	Obj	φ	Obj	φ	Obj	φ	Obj	φ	Obj	φ	Obj	φ
1	SD2	0.48	SD2	0.44	SD2	0.36	SD2	0.31	SD2	0.26	SD2	0.15	WF	0.17
2	ST1	0.32	ST1	0.32	ST1	0.27	ST1	0.23	ST1	0.19	WF	0.12	GC	0.14
3	WF	0.22	BD1	0.10	WF	0.17	BD1	0.14	BD1	0.11	ST1	0.09	SD2	0.08
4	GC	0.19	WF	0.11	BD1	0.16	WF	0.12	WF	0.08	GC	0.09	OZ	0.05
5	BD1	0.13	BT1	0.05	BT1	0.05	BT1	0.05	GC	0.05	BD1	0.02	PM	0.03
6	BT1	-0.04	SD1	0	SD1	0.01	SD1	0.02	BT1	0.04	OZ	-0.02	OM	0.03
7	SD1	-0.10	GC	-0.01	GC	0	GC	-0.01	SD1	0.01	PM	-0.04	ST1	0.03
8	OM	-0.12	Z	0.15	OZ	-0.11	OZ	-0.08	OZ	-0.08	OM	-0.04	CM	0.01
9	OZ	-0.15	OM	-0.17	OM	-0.13	PM	-0.10	PM	-0.09	BT1	-0.04	BD1	0.03
10	PM	-0.15	PM	-0.18	PM	-0.13	OM	-0.11	OM	-0.10	CM	-0.06	BT1	-0.09
11	CM	-0.19	CM	-0.19	CM	-0.17	CM	-0.14	CM	-0.12	SD1	-0.07	SD1	-0.11
12	Z	-0.24	S	-0.20	Z	-0.22	Z	-0.20	Z	-0.16	Z	-0.09	Z	-0.13
13	S	-0.37	OZ	-0.21	S	-0.26	S	-0.25	S	-0.20	S	-0.12	S	-0.17
Range	0.85		0.65		0.62		0.56		0.46		0.24		0.34	
Δ	100%		93%		88%		86%		83%		86%		88%	

Note: SC – hydrocarbon sorption capacity; WSC – water sorption capacity; DE: diesel emulsion sorption capacity; EoU – ease of use; Bio – biodegradable; Δ – data variance

List of Figures

- Figure 1 GAIA biplot for Scenario 1 showing: a) most preferred objects SD2 and ST1 (highest +ve scores on PC1), middle cluster consisting of organic reference sorbents (WF and GC) and BD1, and least preferred objects - left cluster (highest -ve scores on PC1); b) criteria vectors (DSC, HSC, ESC) roughly pointing in the direction of top five ranked sorbents; and c) decision axis π , the optimal solution pointing to SD2. All criteria were assigned equal weighting.
- Figure 2 GAIA biplot for Scenario 7 showing: a) separation of sorbents – organic sorbents cluster, inorganic sorbents cluster, and organo-clays cluster; b) addition and influence of six new criteria (WSC, DE, HRC, EoU, Cost and Bio); and c) decision axis π , pointing to WF and GC and influenced by Bio, ESC, HSC and, to a lesser extent, DSC. All criteria were assigned equal weighting.

Figure 1.

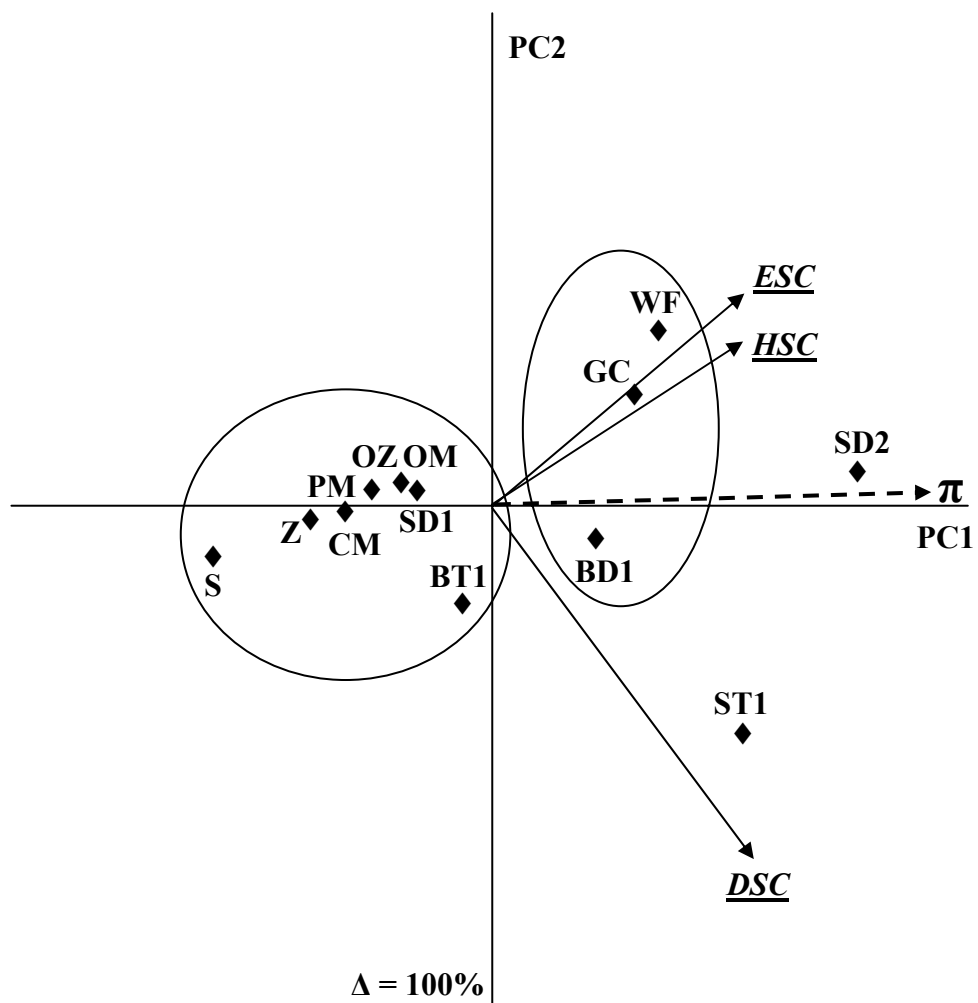


Figure 2.

