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Surface characterisation of selected sorbent materials for common hydrocarbon fuels

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ABSTRACT

The need to find the most efficient material for the clean-up of oil/fuel spills both at sea and on land is of extreme importance. Generally, this requires material selection based upon the adsorption properties of selected sorbent materials such as sand, swelling clays, organo-clays and cotton fibres. These adsorption properties are a function of the surface characterisation where hydrophobic and oleophilic properties are essential. From BET analysis, the adsorption isotherm of the selected materials was type II and IV in the IUPAC classification scheme. The main adsorption mechanism for these sorbents occurred on the external surface of the material in the pores or capillaries. ESEM studies indicate that cotton capillaries contribute significantly to the adsorption process of oil. In addition, the presence of surface wax on cotton-cellulose fibre facilitated the uptake by: a) providing a relatively hydrophobic surface for sorption of organics; and b) providing a low surface energy environment for the capillaries to aid in oil transport. Cotton fibre was observed to have several key properties such as hydrophobicity, good affinity for hydrocarbons, rapid adsorption on contact, and high adsorption and retention through interfibre capillaries. This research provides the basis for selection of cotton–cellulose fibres compared to common and other novel alternatives such as sand and organo-clays, respectively.

Keywords: Hydrocarbon adsorption, sorbents, organo-clays, BET, ESEM, contact angles

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1 Introduction

Spillages of oil and similar petroleum products are costly, common events world wide. Clean–up operations involve a range of many types of sorbents. It is important to understand at least some of the more basic characteristics, which govern their sorption behaviour. A wide range of sorbent materials was reviewed and assessed for oil spill clean-up application by Adebajo *et al.* [1]. The review focused on hydrophobic aerogels, zeolites, organo-clays, synthetic sorbents and natural sorbents as many of these materials exhibited excellent oil absorption characteristics. The common properties that these sorbent materials possess include hydrophobicity and oleophilicity, high sorption capacity, high rate of uptake, retention over time, oil recovery from sorbents and the reusability or biodegradability of sorbents. In addition, many of these sorbents show high porosity and the ability to adsorb oil in the presence of water. Based on the review, the most promising sorbent materials for further investigation and development include organo-clays and natural sorbents, particularly raw cotton.

To date, most methods have attempted to measure absorption capacity or absorbency rate from an engineering or empirical perspective [2-7]. This has been driven by the application perspectives and much effort has been made to simulate actual use conditions. Therefore, evaluation of sorbent performance has primarily been conducted on bulk materials. To provide some scientific basis for materials selection and development, this study will apply analytical techniques to assess the sorbents. The aim, where sorbent development is involved, is to use methods that not only correlate with but are also predictive of performance.

Many studies involving chemical reactions, physical chemical measurements (e.g. X-ray diffraction, infrared spectroscopy and thermal analysis), and optical and electron microscopy have been used to establish the molecular and overall structures of materials [4, 5, 8-14]. In addition to allowing an assessment of materials at the molecular level, these techniques have also provided an insight to understanding the absorption/adsorption mechanism of materials through examination of surface properties such as surface energy, chemical bonding, and morphological characteristics.

In contrast to a large volume of work undertaken on key sorbent materials (e.g. organo-clays, cellulose materials, zeolite etc), a search of literature has revealed that very limited studies have been conducted on interaction (absorption/adsorption mechanism) of liquid hydrocarbons and sorbents. Only empirical relationships, valid for specific situations and with little predictive value, have been developed [2-7]. These are mainly found in the product literature of the manufacturers of sorbent materials.

To understand the structure-property relationships of selected sorbents, the following key methods were used:

- the changes in surface characteristics as a function of sorption capacity were assessed by BET surface analyser; and

- the rate of absorption/adsorption were analysed by ESEM and contact angle measurements.

Although a wide range of techniques was available, it was not possible to cover all methods. Therefore, the above techniques were used to illustrate key properties to study the absorption and/or adsorption behaviour of selected sorbents. The BET method was used to characterise the surface properties of the sorbent materials (sand, organo-clays and cotton fibres). Various properties such as porosity, surface area, and mean pore size were measured and this information was used to compare the adsorption properties of the different sorbents. Finally, ESEM and contact angle measurements techniques were used to characterise and determine the adsorption rate and mechanism of sorbents.

2 Materials and Methods

2.1 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 surfactant used in the modification of the clay was didecyldimethylammonium bromide (DDDMA), $C_{22}H_{48}BrN$, MW: 406.53. The surfactant was sourced from Sigma-Aldrich.

The syntheses of surfactant-clay hybrids were undertaken by the following procedure: SWy-2-MMT 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.

2.2 Cotton

Raw cotton fibres used in the study were sourced from Queensland Cotton (QC), Brisbane. The cotton fibres were collected in the 2003 season from the following growing regions: Moura, Theodore, Dalby and Goondiwindi in Queensland, and Wee Waa in NSW. The ginned cotton fibres (lint) were a by-product from the classing process. A mix of fibre variety and types was used in this sorbent study.

Characterisation of cotton samples was not carried out since the by-product cotton bales were made up of samples from different growing regions (i.e. heterogenous sample). Therefore, the cotton samples used had a variety of cotton length, uniformity, strength, micronaire and colour. In addition, no cotton fibre 'conditioning' was undertaken in the experimental work. The cotton fibres were essentially used in the raw state.

2.3 Sand

Fine sand was sourced from a local supplier in Brisbane, Queensland.

2.4 Hydrocarbons

Diesel, hydraulic oil and engine oil used in this study was sourced from BP Australia, Castrol Australia and Valvoline Australia, respectively.

- BP diesel has a viscosity of 1.2-4.6 cST @ 38°C and specific gravity of 0.84.
- Castrol hydraulic oil (Hyspin AWH68) has a viscosity of 68 cST @ 40°C and specific gravity of 0.88; and
- Valvoline super diesel engine oil has a viscosity of 120 cST @ 40°C and specific gravity of 0.89.

2.5 BET Analysis

Specific surface area and pore size distributions were measured using a Gemini 2360 (Micromeritics, USA) through nitrogen adsorption at 77 K in the range of relative pressure (P/P_0) of 10^{-6}–1. Sample preparation involved degassing the samples overnight (16 hours) at 120°C under vacuum. The samples were subjected to 99-point BET surface area analysis and full adsorption isotherms were collected for all samples. In addition, micropore and mesopore volume distribution as a function of pore size were calculated on the basis of the Horvath–Kawazoe (HK) and Barret, Joyner and Halenda (BJH) method, respectively.

2.6 Electron Microscopy

A FEI Quanta 200 environmental scanning electron microscopy (ESEM/SEM) was used for surface morphological studies of the cotton fibre. The cotton fibre was mounted with carbon tape onto stainless steel stubs and coated with gold under vacuum conditions in an argon atmosphere ionisation chamber for the SEM studies. To study the adsorption properties of cotton fibres, the FEI Quanta 200 was operated in the ESEM mode. The objective was to obtain evidence to further support the observations from BET as well as contact angle measurements by studying diesel and water droplets on the cotton fibre structure. A small drop of pure water or diesel was placed on the sample which was fixed to a stainless steel stub with carbon tape. The ESEM was operated in ‘wet’ mode at an accelerating voltage of 20-30 kV and a water vapour pressure of 3 torr.

2.7 Contact Angle Measurements

Static and dynamic contact angles were measured using a FTÅ200 computer-controlled, video-based instrument (First Ten Ångstroms, USA). The instrument is built around rapid video capture of images and automatic image analysis. The instrument includes a CCD video camera, a frame grabber, an adjustable sample stage and a LED light source [15]. A drop (1 µl) of test liquid (water, diesel, hydraulic oil or engine oil) was allowed to fall onto the sample from a syringe tip to produce a sessile drop. The drop was dispensed from a syringe pump driven by a stepper motor.

Images were captured at a rate of 10 frames per second for 10 seconds. In this study, single images (a snapshot) as well as image sequences (a movie) were captured.

The contact angles were calculated by curve fitting of the captured drop profile to the theoretical shape predicted by the Lewis acid/base and Owens-Wendt models. The software fits the equations to the shape of the drop utilising all points on the drop profile. The tangent to the curve is assigned where the curve intersects the baseline. The angle between this tangent and the baseline is the contact angle. The contact angle was measured on three different points of each sample and the adsorption series were repeated at least twice. The reproducibility of contact angles measurements on different samples prepared in the same way was ±5° or better.

Adsorbent substrates were studied using the movie feature of the FTÅ200 instrument. For example, a movie was taken of the drop of liquid as it absorbs into the specimen. The contact angles (°) measured were plotted against time (t) to provide an indication of the rate of adsorption. This is the key advantage of using the FTÅ200 instrument.

3 Results and Discussion

3.1 BET Analysis

The characterisation of sorbent materials (sand, organo-clays and cotton) is problematic because the structure of the materials is complex. A *complete* characterisation is not possible. However, average properties (or simple property relationships) can be used to provide an understanding of the sorbent materials and their sorption capacity.

The adsorption process involves transferring material from a gas or fluid phase (adsorbate) to a solid phase (adsorbent). Usually, the amount adsorbed is related to the surface area and porosity of the adsorbent. Therefore, an understanding of the surface area and porosity of the material is required. This can be carried out by measuring the material's adsorption isotherm. Generally, there are many different shapes of isotherms depending on the type of adsorbent/absorbate and intermolecular interactions between the gas and the surface. These have been formally classified by Brunauer *et al.* [16]. The Brunauer, Deming, Deming and Teller (BDDT) classification has also become the basis of the modern IUPAC classification of adsorption isotherms (Figure 1). There are six broad categories of adsorption isotherms [17]:

- Type I: characterise microporous adsorbent (monolayer adsorption only) with relatively small external surfaces.
- Type II: describe adsorption on non porous or macroporous adsorbent with strong adsorbate-adsorbent interactions (unrestricted monolayer-multilayer adsorption).
- Type III: describe adsorption on non porous or macroporous adsorbent with weak adsorbate-adsorbent interactions (rarely encountered).
- Type IV: represent adsorption isotherm with hysteresis (associated with capillary condensation in mesopores).

- Type V: represent adsorption isotherm with hysteresis (pores present in the mesopore range).
- Type VI: stepped isotherm (theoretically important, but rarely encountered).

To obtain the surface area of the sorbent materials, N_2 adsorption/desorption at 77 K were carried out for sand, cotton fibre and clay/organo-clay (SWy-2-MMT and SD1, respectively) (Figure 2). The adsorption isotherms in Figure 2 correspond mainly to Type II isotherm (i.e. multi-layer physical adsorption) as classified by the IUPAC [17]. As stated, Type II isotherm describes adsorption on macroporous adsorbents with strong adsorbate-adsorbent interactions and represents unrestricted monolayer-multilayer adsorption. The resulting isotherm plot (adsorbed volume against relative pressure) was used to calculate surface area using the BET equation, devised by Brunauer *et al.* [16]. The BET instrument automatically converts the monolayer/multilayer capacity to a surface area measurement in m^2/g. A summary of the BET analysis is given in Table 1.

The BET surface areas of the sorbent materials varied from 1.2 to 27.1 m^2/g. The results obtained indicate that specific surface area of the selected sorbent materials is very low in comparison with that of other porous materials e.g. zeolites (BET surface area 601-742 m^2/g). Generally, the adsorptive capacity of a material depends on its surface area (i.e. the greater the surface area the higher the material's sorption capacity).

3.1.1 Sand

The specific surface area of 1.2 m^2/g for sand is within the expected range for quartz sands 1.0 to 4.0 m^2/g [18]. Blott *et al.* [18] observed that the higher measured surface areas for sands could be the result of the presence of high surface area materials such as clays, irregular grain shapes, and/or the surface roughness of the grains. There is no clay in the sand sample, so the shape and surface texture of the grains must be responsible for the observed surface area. In general, polycyclic, quartz-rich samples contain a higher percentage of rounded and smoothed grains, and therefore have a relatively low surface area [19]. This is possibly the case for the sand sample used in the study but sand grain morphology was not investigated. In addition, the pore volume obtained for sand (0.004 cm^3/g) suggests that internal micro-porosity is low (Table 1). Therefore, the main contribution to surface area appears to be (smooth) grain shape and (minor) surface roughness.

If the above observation is correct, the N_2 molecules would tend to adsorb on the sand particle in such a way as to form a continuous surface coating that smoothes the surface topography. Therefore, in a spill clean-up scenario using sand, the hydrocarbons would likely form a layer coating the solid grain surfaces. Thus, the main adsorption mechanism for sand is probably surface adsorption. Generally, the adsorption capacity of sand will depend on grain size, initial surface roughness (surface texture) of the material and on the specific way in which the hydrocarbons adsorbed to the surface (i.e. uniform layer or irregular/uneven patches due to surface roughness).

3.1.2 Cotton Fibre

Due to the pore and void system, the total surface area of cotton fibre exceeds the geometrical outer surface [20]. However, the total pore volume and pore size distributions are very sensitive to swelling and drying treatments of the cotton fibre [20]. It has been observed that drying the fibre results in a significant and irreversible reduction of the pore volume.

Therefore, with respect to N_2 adsorption of cotton fibre, the value obtained (8.2 m^2/g) does not represent the true surface area of the fibre. This is because the BET method requires dehydrating the cotton fibres at 120°C under vacuum, therefore removing the intramolecular water molecules and allowing the cellulose chains to collapse. The collapse of the cellulose structure also accounts for the low pore volume (0.006 cm^3/g) obtained. Thus, the internal surface area of the cotton fibres was inaccessible to the N_2 molecules. In effect, the dehydration of cotton fibre by vacuum drying promotes formation of interchain hydrogen linkages or cellulose-cellulose linkages which are too strong to be replaced by N_2 molecules [21].

Thus, the specific surface area for cotton fibre (8.2 m^2/g) corresponds to adsorption measurement mainly on the external surface. However, the low surface area value obtained in the study for cotton fibre does not explain the high sorption capacity cited in literature for cotton [2]. Therefore, other mechanisms must be responsible for the high uptake of hydrocarbons in those studies. Choi *et al.* [3] suggests that volume on or between the fibres is generally responsible for the majority of the material's sorbent capacity. As a result, it is proposed that adsorption by inter-fibre capillaries is the main adsorption mechanism for cotton sorbent. This premise will be further investigated using ESEM analysis (Section 3.2).

3.1.3 Organo-clay

The N_2 adsorption isotherms of the starting montmorillonite (SWy-2-MMT) and the resultant organo-clay (SD1) are shown in Figure 2. By examining the results of SW-2-MMT and SD1, it is clear that the modification process has decreased the specific surface area and pore volume of the organo-clay (Table 1). In contrast, the average pore size has increased for SD1 (22.9 nm) compared with SWy-2-MMT (15.6 nm). This result was unexpected since modification of the clay should ideally increase the basal spacing of the clay interlayer which implies more sorption sites are accessible.

One possible reason for the observed reduction in the surface area and pore volume of SD1 may relate to the presence of the large intercalated surfactants in the clay interlayer. Depending on the packing density of the surfactants, the internal pore spaces may be predominantly occupied by long-chained surfactants which may inhibit the adsorption of N_2 in the organo-clay [22]. This may lead to a decrease in the BET surface area and pore volume of SD1 compared with the clay starting material (SWy-2-MMT). This suggests that adsorption is mainly occurring on the external surface of the organo-clay, hence the corresponding low surface area obtained.

It was observed that the average pore size has increased with intercalation of surfactants (interlamellar expansion). Wang *et al.* [22] suggests that the organic cation exchange process may lead to the formation of a bi-dimensional porous network consisting of both micropores and mesopores. This may result in an increase in the average pore size of the organo-clays. TEM images of organoclays has been published elsewhere [23-27]. The use of organoclays for the removal of recalcitrant organic molecules from water including hydrocarbons is being explored [23]. A review of the absorption of oil has been published [1].

In summary, the BET analysis of the sorbent materials has provided the following key findings:

- adsorption isotherms are of Type II in the IUPAC classification that represent monolayer/multilayer adsorption (Figure 1). This suggests that adsorption of N_2 for the sorbent materials is moderate or, on the other hand, that the main adsorption process may be ascribed to a van der Waals force. Generally, the isotherm shows that the amount of N_2 adsorbed increases as the relative pressure increases up to a saturation point. A complete adsorption of N_2 as a monolayer onto the surface of sorbent material is shown by the plateau of the adsorption isotherm. After this point, a large uptake of N_2 is observed close to the saturation pressure and it is assumed that multilayer adsorption takes place (i.e. implying the presence of mesopores).
- adsorption isotherms for sand and SWy-2-MMT also show hysteresis loops which resemble Type IV adsorption as classified by IUPAC. According to de Boer [28], this type of hysteresis loop is attributed to cylindrical pores and/or the ‘ink bottle’ pores. This observation is consistent with the materials under investigation, namely round grains of sand creating cylindrical pores [18] and SWy-2-MMT producing ink bottle pores [22].
- there are commonalities between the three sorbents, namely the low surface area and limited pore volume available for adsorption processes in the micropores (Table 1). This suggests that the main adsorption mechanism for these sorbents occurs on the external surface of the material in the diffusion region or capillaries. This may influence the hydrocarbon sorption capacity of the sorbent materials (i.e. sand, cotton fibre and organo-clay) under investigation.

3.2 ESEM

Environmental scanning electron microscopy (SEM/ESEM) has been widely used to characterise materials, particularly their morphological properties. In this study, the technique has been extended to investigate the adsorption behaviour of cotton fibres at the micro scale. The main focus is the role of fibre morphology on the uptake of hydrocarbons. The

3.2.1 Cotton: Adsorption Mechanism

In raw cotton fibre, the principal component is cellulose, comprising 90-95% of the dry fibre weight. The remaining components are impurities such as proteinaceous material, 0.3-1% waxes, 0.7-1.2% pectins and small amounts of organic acids and ash producing inorganic materials [29]. Cotton wax is an important substance that may facilitate non-polar interaction with organic compounds such as hydrocarbons.

From the SEM image (Figure 3), an assessment of fibre morphology can be obtained. Cotton fibres have the characteristic shape of a convoluted tube which resembles a twisted ribbon, approximately 20 μm in diameter. Although not shown in the SEM image, cotton also has a thick fibre wall with a hollow tube (lumen) running down its centre [30]. The cotton fibre has a fibrillar structure (except the cuticle, which contains waxes, pectins and other proteinaceous materials). It can be observed that the fibre surface is very uneven, where the primary wall wrinkles (Figure 3).

Throughout the fibre structure there are pores and capillary spaces between the variously sized fibrils (small strands of cellulose). The network of fine fibrils makes for an organised system of continuous, very fine capillaries. Thus, cotton fibre possesses a complex porous structure. About 30% of the total fibre volume is unoccupied space with the lumen assigned to one-third of it, and two-thirds of that is pore volume and capillaries [29]. Therefore, volume on or between the fibres is generally responsible for about 90% of the adsorbent capacity. It is proposed that the volume between the fibres plays an important role in the uptake of hydrocarbons. This is demonstrated in the ESEM image in Figure 4.

In Figure 4, it can be observed that two main adsorption mechanisms are taking place on the fibre surface: a) surface adsorption where the oil is coating the fibre; and b) uptake of oil by the interfibre capillaries. It is clear from the ESEM image that uptake by the interfibre capillaries accounts for a significant amount of cotton's sorption capacity. Oil transport within the fibre mass (matrix) is quite similar to the wicking of water in capillaries. Capillary wicking is determined by two fundamental properties of the capillary: a) its effective diameter; and b) the surface energy of its inside face. Thus, the smaller the diameter of the cotton fibre or the lower the surface energy, the more readily oil would move up the capillary.

In summary, the key findings from the ESEM indicate that interfibre capillaries contribute significantly to the adsorption process of oil. In addition, the presence of surface wax on cotton fibre probably facilitates uptake by: a) providing a relatively hydrophobic surface for sorption of organics; and b) providing a low surface energy environment for the capillaries to aid in oil transport. Therefore, it is postulated that adsorption mechanisms of cotton fibres are related to:

- adsorption interactions between the surface waxes and the hydrocarbons; and
- adsorption by fibre matrix (i.e. physical trapping of hydrocarbons between the fibres – Figure 4).

3.3 Contact Angle Measurements

Following the work on ESEM, contact angle measurements were also used to determine (and visualise) the adsorption properties of the selected material, and consequently its sorption capacity. As a general rule, if $\theta > 90°$ the liquid tends to form droplets on the surface, if $\theta < 90°$ the liquid tends to spread out over the surface and if $\theta \approx 0°$ the liquid forms a thin film.

These surface properties are very important since the primary uptake of hydrocarbons as indicated by the BET analysis involves surface adsorption (i.e. non-polar interaction). Therefore, contact angle measurements are a simple way to screen the sorbent materials for further development in the study. In assessing the potential for a sorbent to take up oil, the lower the oil-solid contact angle, the greater the mutual attraction between the oil and the sorbent. Therefore, low contact angles indicate high sorption performance for hydrocarbons.

The wetting behaviour of the three sorbent materials (sand, organo-clay and cotton fibre) was investigated using ESEM images (cotton only) and the First Ten Angstroms (FTÅ200) movie sequence feature. The results from both methods are discussed below.

3.3.1 ESEM: Contact Angles of Cotton Fibres

The wetting behaviour of cotton fibres by water and oil was investigated using an ESEM. In this study, contact angles were measured for ‘single’ cotton fibres rather than bulk materials. Water droplets were formed on the fibre surfaces by varying the temperature and pressure in the ESEM chamber and oil droplets were added with the aid of a micro syringe onto the mounted sample. The contact angles were then calculated from the ESEM images using the equation devised by Carroll [31].

As the raw cotton fibre is relatively hydrophobic due to the wax coating, it is expected that the water droplets on the fibre surface would form discrete near spherical droplets. This is due to the surface tension of the water. The forces that hold the wax layer together on the fibre surface are much weaker than the forces that act between the water molecules and consequently water on the hydrophobic (waxy) surface would tend to remain in the droplet form. Since the water on the fibre surface is likely to remain in spherical droplet form, it is anticipated that the resultant contact angle would be correspondingly high (≈90°).

However, in the case of the oil droplet on the fibre surface, the opposite should occur. The cotton fibre would have at its surface a complex mixture of molecules made from carbon and hydrogen with a significant proportion of non-polar groups present. These non-polar groups have low surface energy and would be attracted to the oil molecules. Therefore, this should cause the oil droplets to spread out and form a film, essentially coating the fibre. Thus, the contact angle in this scenario should be low (<20°).

The water droplets condensed on the cotton fibre surfaces are shown in Figure 5. It can be observed that the water droplet behaved as described above. The water droplets are near spherical in shape which clearly exhibits the hydrophobic property of the raw cotton fibre. The contact angles measured from ESEM images for water gave values in the range 85° to 95°.

The oil droplet formed on the cotton fibre surface is shown in Figure 6. Once again, the oil droplet behaved as described above. The affinity of raw cotton fibre for oil is observed in the cylindrical shape of the oil droplet on the fibre. The ‘spreading’ of oil has manifested into the cylindrical coating on the fibre surface. The contact angles measured from the ESEM images for oil gave values between 15° and 20°.

3.3.2 FTÅ200: Contact Angles

The FTÅ200 instrument was used to carry out a variety of experiments dealing with contact angle measurements. The key advantage of using this instrument is the ability to capture multiple frames in 'real time' (movie sequence) to assess the adsorption properties and rates of materials. Therefore, adsorbent materials and surfaces were assessed in a dynamic way. For example, the behaviour of a drop of liquid can be tracked by evaluating the changes in contact angles over time. This information can then be plotted to give a visual display of the adsorption phenomena for the material under investigation.

In the study, sessile drop contact angles were measured for water, diesel, hydraulic oil and engine oil on the selected sorbent materials (sand, organo-clay and cotton fibre). A summary of the contact angles derived from experimental measurements is given in Table 2. Both glass and paper have also been included in Table 2 as a reference. The contact angles were measured as a function of time. Two contact angles are identified: an *initial* contact angle and a *steady-state* contact angle. The initial contact angle corresponds to the first contact of the target liquid with the dry sorbent material. The steady-state contact angle represents the equilibrium condition of the liquid on the material's surface and is probably more useful in describing adsorbing materials.

The following observations were made based on the contact angles measured in Table 2:

- *viscosity of liquid*: by comparing the initial and steady-state contact angles, it was observed that viscosity of the hydrocarbons played an important role in the wetting property of the material. Diesel is able to 'spread' on contact with the surface, compared with the heavier hydraulic and engine oils. High (initial) contact angles for the heavier oils suggest that a longer time is needed to 'wet' the material.
- *hydrophobicity of material*: based on the contact angles, it was observed for liquid water that cotton fibres (145°) and paper (110°) are completely hydrophobic (i.e. no change in the contact angle over time). Glass (35-31°) has a good affinity for water and is relatively hydrophilic. The contact angles obtained for the organo-clays (60-58°) suggest that the material is not completely hydrophobic. Sand had a high initial contact angle (100°) but after 'wetting' the material completely adsorbed the water droplet.
- *performance of sorbent material*: the measured contact angles suggest that cotton fibre is hydrophobic (water 145°) and oleophilic (diesel 0°, hydraulic oil 10° and engine oil 17°) – two key properties of a good sorbent. The initial (high) contact angles for cotton fibre are related to the fibre (matrix) surface. After contact, non-polar interaction with the fibre surface and uptake by the interfibre capillaries facilitate the adhesion between the material and the hydrocarbons. The organo-clay (SD1) appears to have an affinity for the hydrocarbons, with good wettability for diesel (4°). However, it is not completely hydrophobic which may limit its performance in comparison with cotton fibre. It was observed that sand had good wettability for all liquids: water (0°) and hydrocarbons (diesel 0°, hydraulic oil 18° and engine oil 19°). There appears to be no differentiation between the liquids for sand. The ability of sand to take-up water may restrict its performance

in wet conditions where competition from water molecules may limit its hydrocarbon sorption capacity.

The adsorption curves for the selected sorbent materials are given in Figure 7 (sand), Figure 8 (SD1 organo-clay) and Figure 9 (BC cotton). The four test liquids were used to measure changes in contact angles over time. The change in contact angles basically indicate the degree of ‘spreading’ of the liquid on the material’s surface. If the contact approaches 0°, then a thin film of the liquid is adsorbed onto the surface. The time (s) taken to achieve this condition can be measured and used to indicate the materials affinity for hydrocarbons.

The adsorption of all test liquids by sand occurred in less than 2 seconds (Figure 7). Diesel was adsorbed almost on contact whereas water and the heavier oils showed a more moderate adsorption rate in comparison as the material became wetter. It was observed that viscosity limited the ‘spread’ of the heavier oils on the surface, therefore giving a slower adsorption time. The contact angle obtained at steady-state condition after 1.2 seconds indicates that hydraulic and engine oil residue is left on the surface.

The contact angles for SD1 organo-clay showed that the steady state condition was achieved after 2 seconds to attain a plateau in Figure 8. Rapid adsorption of the liquids occurred in 1 second before an equilibrium state is established for the material. This indicates that penetration into the surface was restricted, especially for the heavier oils. Overall, the adsorption of diesel (1 second) is slower compared to sand (0.1 second). After the initial wetting of the surface, water did not spread on the surface which may mean the material is relatively hydrophobic.

The adsorption of hydrocarbons and water by cotton fibre took less than 2 seconds (Figure 9). The diesel was completely adsorbed on contact, however the heavier oils showed a quick but steady, non-linear spreading and adsorption. The water on the fibre surface is neither spreading nor adsorbing into the material mass. This hydrophobic property is displayed as a straight line in the graph in Figure 9 (i.e. no change in contact angle at equilibrium).

4 Conclusions

In practice, sorbent material is chosen on the basis of measurement of physio-chemical properties, combined with previous experience (e.g. literature review and trial and error). It is often the case that the essential physics and chemistry involved in the use of sorbents in applications is not completely understood, and is therefore difficult to correlate the useful properties of the materials with the standard characterisation measurements. As a result, choosing the optimal material for a given application cannot be done in a systematic way, and previous experience is invaluable. Commonly, for novel applications many trials are made before a suitable material is found.

In this study, an attempt was made to characterise and provide insight into the adsorption phenomena of selected sorbent materials (sand, SD1 organo-clay and BC cotton fibre) using key analytical techniques. Surface properties such as adsorption/desorption isotherms, surface area, pore volume, pore size distribution, morphology and surface energies were determined by BET, ESEM and contact angles. Although a complete understanding of the adsorption processes was not possible, given the range and complex structure of the sorbent materials, some properties/performance correlation were observed in the analysis. For adsorption of diesel by the sorbent materials, the key findings were:

- based on the BET analysis there were commonalities between the three sorbents, namely the low specific surface area and limited pore volume available for adsorption processes in the micropores (Table 1). This suggests that the main adsorption mechanism for the sorbents occurs on the external surface of the material in the diffusion region (sand and SD1 organo-clay) and/or capillaries (BC cotton fibre).
- ESEM was used to provide additional insight into the adsorption mechanism of the cotton fibre. From Figure 5, it was clear that the interfibre capillaries were responsible for retaining a significant amount of hydrocarbons. Thus, it was concluded that uptake by the interfibre capillaries was the main adsorption mechanism rather than adsorption on the fibre surface.
- the contact angle measurements indicated that sand was hydrophilic, SD1 organo-clay relatively hydrophobic and cotton fibre totally hydrophobic. In addition, the adsorption rate differed for each sorbent:
  a) sand had good wetting properties for all liquids and completely adsorbed the water and oils within two seconds;
  b) SD1 organo-clay showed rapid adsorption within the first second before achieving a steady state condition. After reaching equilibrium, further spreading of the liquids was not observed; and
  c) cotton had good wetting properties (affinity) for the hydrocarbons with adsorption time of less than two seconds. In addition, the water droplet on the fibres did not spread on contact or at equilibrium which demonstrated the hydrophobic property of the sorbent.

From surface analysis of the three sorbent materials, cotton fibre appears to be the most suitable sorbent for subsequent testing and product development. Cotton fibre was observed to have several key properties such as hydrophobicity, good affinity for hydrocarbons, rapid adsorption on contact, and high adsorption and retention through interfibre capillaries.

4.1 Acknowledgements

4.2 The financial and infra-structure support of the Queensland University of Technology Inorganic Materials Research Program of the School of Physical and Chemical Sciences is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the Surface Analysis facility through a LIEF grant. The ARC is thanked for funding the oil absorption project trough an ARC linkage grant. Queensland Main Roads department is thanked for support of this project.

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List of Tables

Table 1

Sorbent	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Mean Pore Size (nm)
Sand	1.2	0.004	11.8
BC (Goondiwindi cotton fibre)	8.2	0.006	3.0
SWy-2-MMT (clay)	27.1	0.084	15.6
SD1 (organo-clay)	8.7	0.050	22.9

Table 2.

Material	**Contact Angles (°)**							
	Diesel		**Hydraulic Oil**		**Engine Oil**		**Water**	
	I	**S**	**I**	**S**	**I**	**S**	**I**	**S**
Glass	28	6	113	18	116	22	35	31
Paper*	31	7	110	16	111	24	110	110
Sand	61	0	110	18	114	19	100	0
SD1	23	4	116	22	130	28	60	58
BC cotton	93	0	116	10	149	17	145	145

Note: I – Initial contact angle; S – Steady-state (equilibrated) contact angle; * white (treated) printing paper

List of Figures

Figure 1

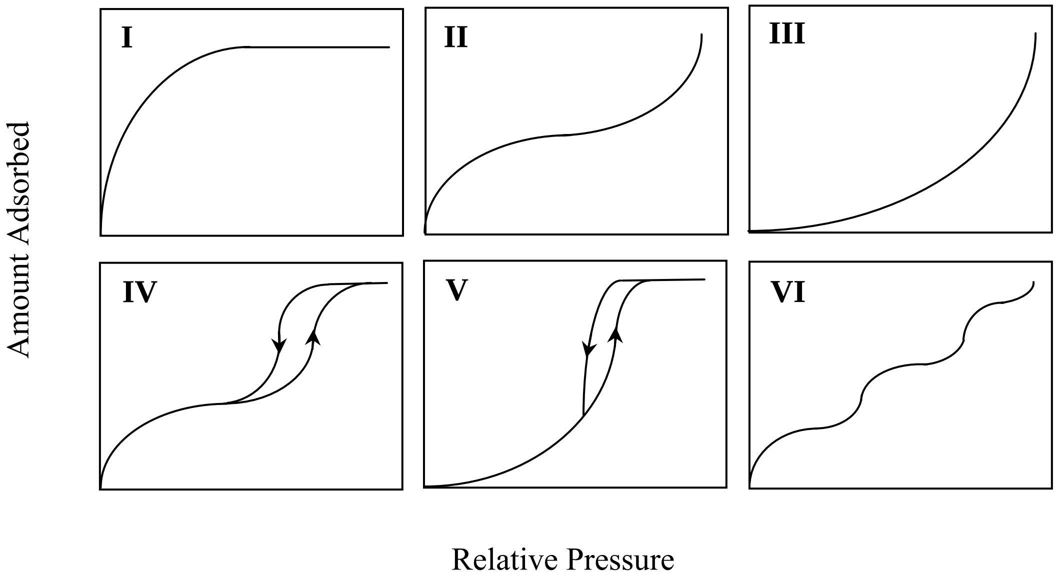


Figure 2

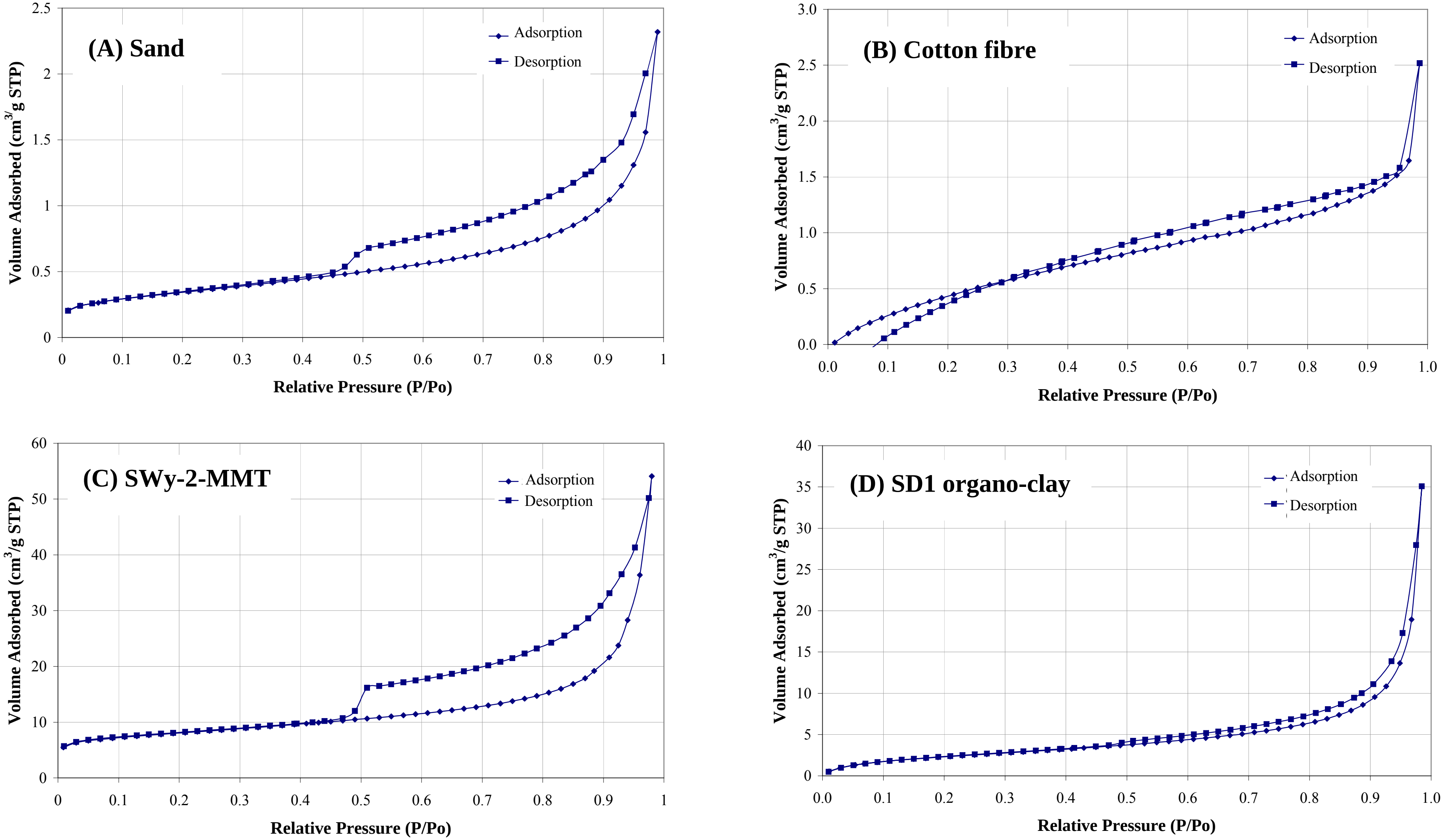

(A) Sand
Adsorption
Desorption
Volume Adsorbed (cm3/g STP)
Relative Pressure (P/Po)
0
0.5
1
1.5
2
2.5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
(B) Cotton fibre
Adsorption
Desorption
Volume Adsorbed (cm3/g STP)
Relative Pressure (P/Po)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
(C) SWy-2-MMT
Adsorption
Desorption
Volume Adsorbed (cm3/g STP)
Relative Pressure (P/Po)
0
10
20
30
40
50
60
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
(D) SD1 organo-clay
Adsorption
Desorption
Volume Adsorbed (cm3/g STP)
Relative Pressure (P/Po)
0
5
10
15
20
25
30
35
40
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

Figure 3

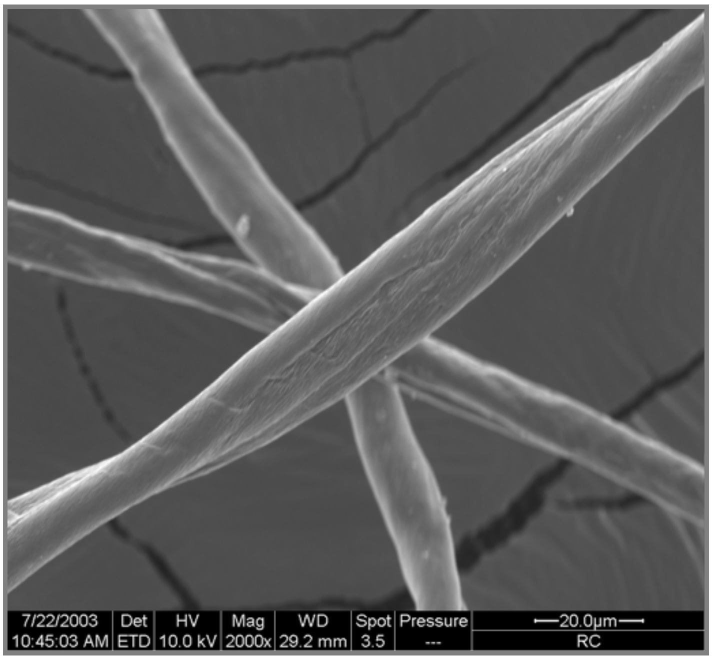


Figure 4

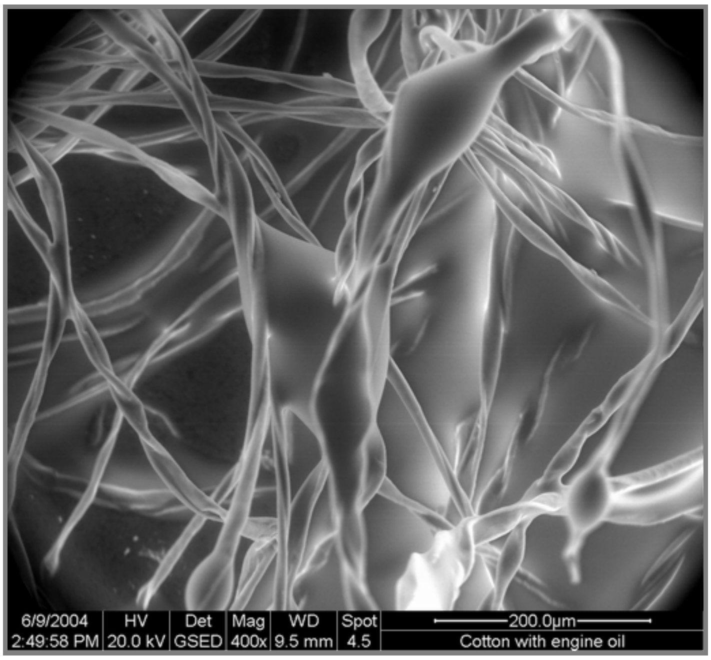


Figure 5

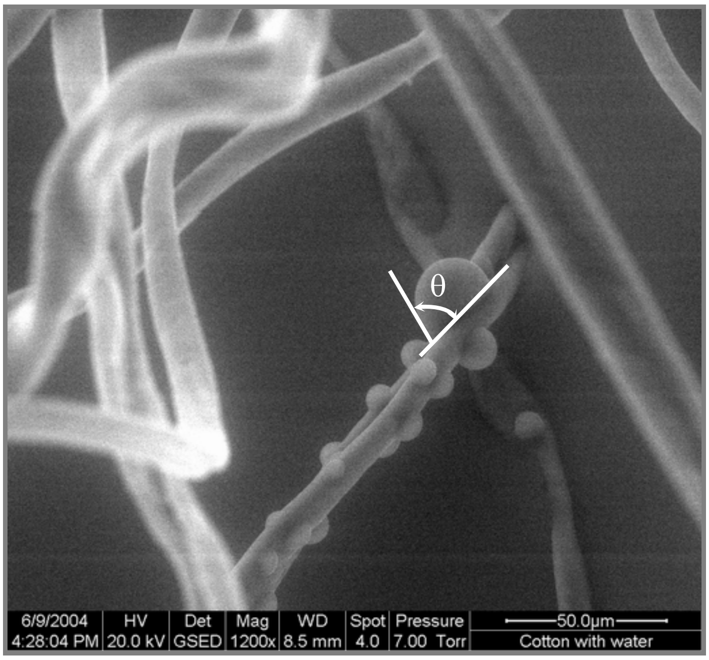


Figure 6

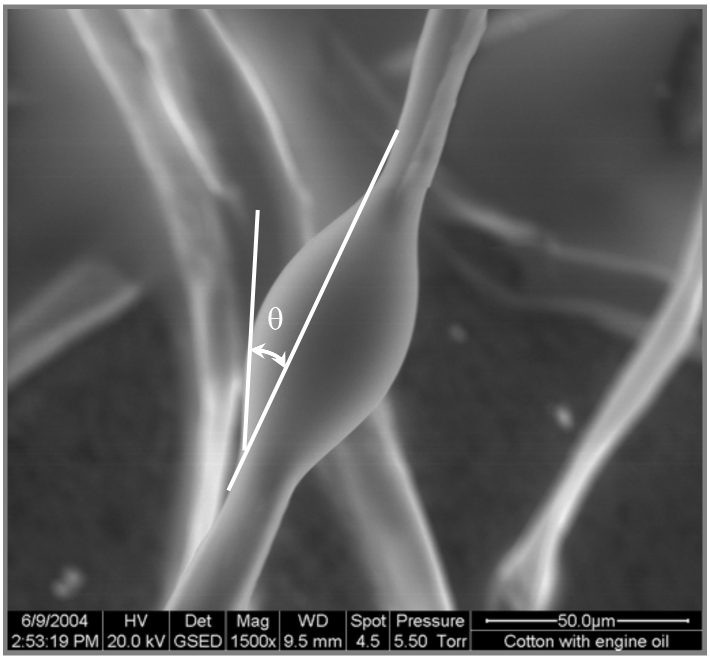


Figure 7

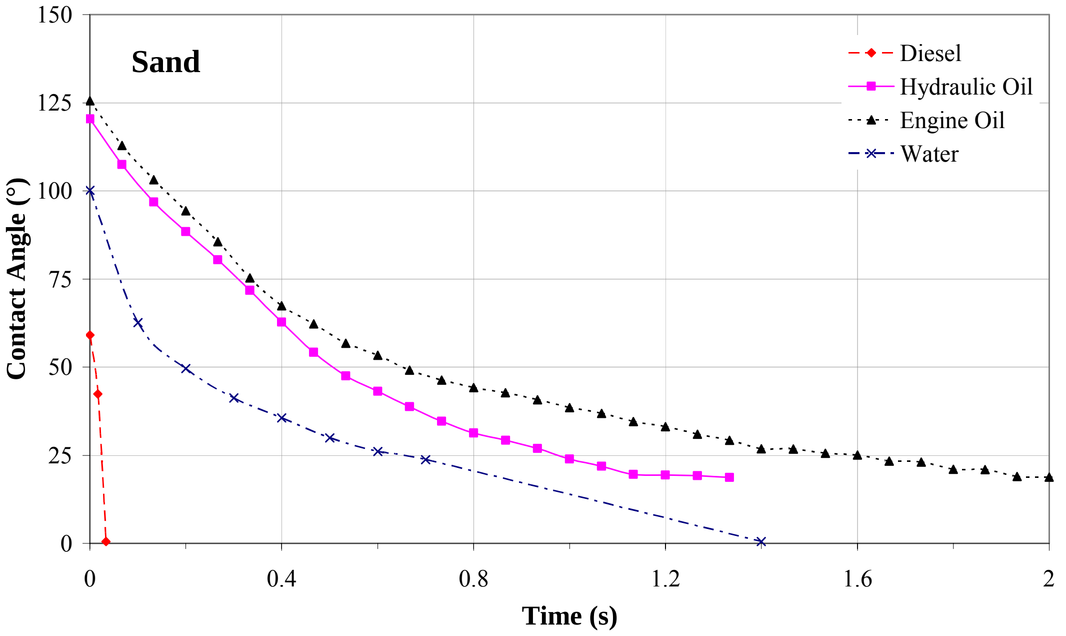


Figure 8

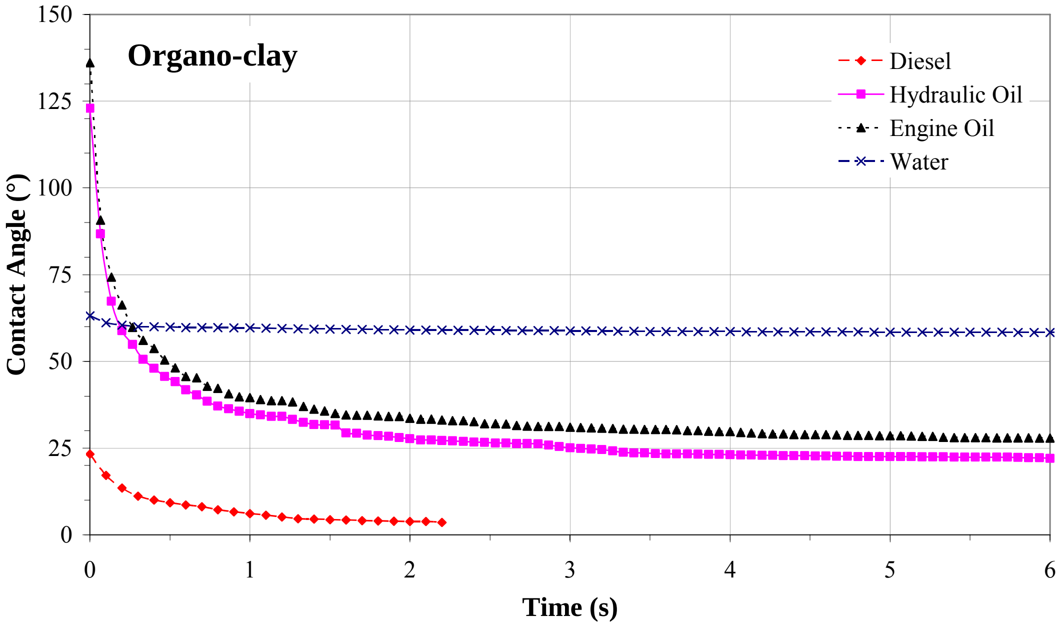
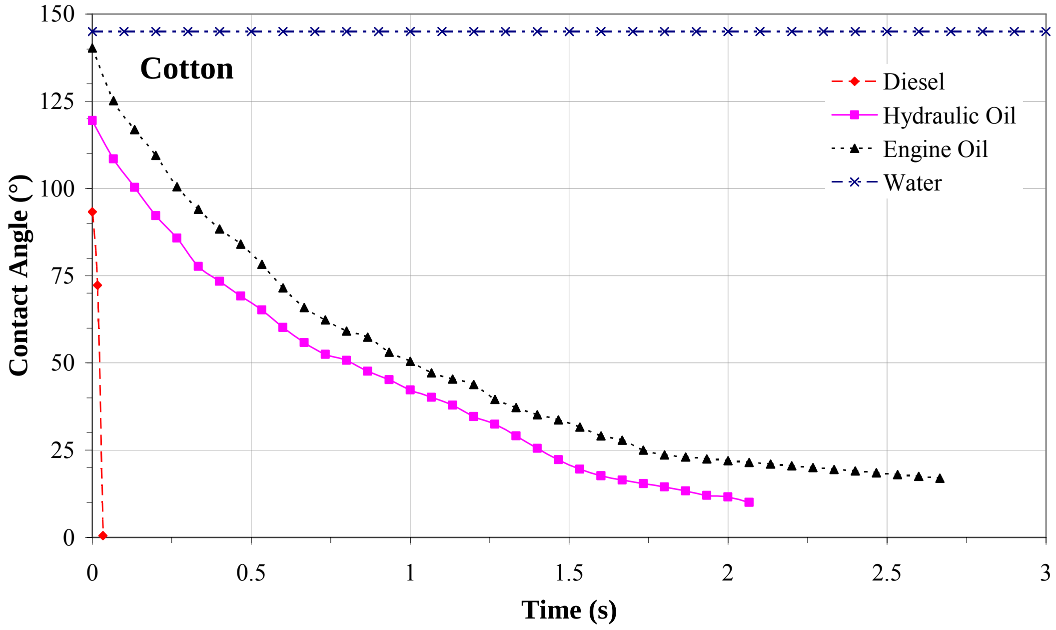


Figure 9


Cotton
Diesel
Hydraulic Oil
Engine Oil
Water
Contact Angle (°)
150
125
100
75
50
25
0
0
0.5
1
1.5
2
2.5
3
Time (s)