A comparison of wettability measurements on a synthesised water repellent sand

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ABSTRACT: Controlling the wettability of granular materials such as soil offers the opportunity to generate new materials. Such materials can completely prevent or partially restrict infiltration depending on their wettability. In this study, the wettability of a synthesised water repellent sand, isolated into four different sieve fractions was investigated by means of 2 different methods: the sessile drop method (SDM) and the Wilhelmy plate method (WPM). Both methods were shown to be effective in the measurement of contact angles (CAs) despite considerable differences in their absolute values. These differences were primarily attributed to the different methodologies which relied on different principles to measure CAs. The CAs measured with both the SDM and WPM showed a decrease in magnitude as particle size increases. The maximum differences in CAs recorded with the SDM and WPM between the particle sizes were respectively 13.3° and 26.1°. In addition to adequately describing the methodology adopted for the measurement of CAs, it is recommended to use the SDM over the WPM for soil samples with considerable clay content.

1 INTRODUCTION

Wettability is a fundamental property of solids (flat or granular) which governs the extent to which these surfaces wet. For instance, in mining engineering, the process of froth-flotation depends on the wettability of different minerals for the effective separation of valuable ones (e.g. galena – a water repellent sulphide mineral) which adhere to air bubbles and float to the top of the pulp as opposed to the relatively wettable gangue that does not (Wark, 1984). In soils, the constituting minerals (mostly silicates) are generally assumed to be completely wettable, characterised by a contact angle (CA) of 0º. However, due to coatings imparted by organic matter in their natural environment, soils have shown to exhibit a much larger CA (Hajnos et al. 2013).

The influence of wettability on unsaturated soils is important because suction is not only dependent on the degree of saturation but also on the surface tension and CA of the water menisci (Lourenço et al., 2015). In geotechnical engineering, the use of water repellent soils as a means to control infiltration is becoming increasingly recognised (Zheng et al., 2017). Potential applications of this novel technology include its use as water tight barriers and on slopes as illustrated in Lourenço et al. (2017).

However, the methods to quantify wettability have been primarily derived from the discipline of soil science where water repellent soils have been reported to prevent seed germination (Osborn et al., 1967), cause erosion (King, 1981) and preferential flow (Hendrickx et al., 1993). In this work, the measurement of wettability using 2 of these methods, namely the sessile drop method (SDM) and the Wilhelmy plate method (WPM) that have differing working principles are compared on a synthesised sand.

2 MATERIALS AND METHODS

2.1 *Soil material and preparation*

Leighton Buzzard sand (LBS) originating from quarries in southern UK was used in this study. LBS is rich in silica, mainly in the form of quartz comprising nearly 98% of the sand. The LBS sand was sieved by means of a mechanical shaker to obtain four particle sizes namely 63-212, 212-300, 300-425 and 425-600 µm. Figure 1 illustrates a monochrome scanning electron microscope image of the finest particle size of LBS used in the study.

The steps in treating the LBS samples to induce water repellency are schematically shown in Figure 2. A silanisation process using dimethyldichlorosilane (molecular weight of 129.06 & density 1.06 gcm^{-3} from Acros Organics, New Jersey, USA) was carried out. To a 10-g mass of each of the isolated air-dried particle sizes was added a volume of 100 µl of dimethyldichlorosilane from a single channel pipette (Pipetman P20 from Gilson®) followed by constant and gentle stirring for a couple of minutes. This volume corresponded to a concentration of 0.265% by mass, larger than the critical concentration defined by Chan and Lourenço (2017) to achieve maximum water repellency. The exact lifespan of the induced water repellent behaviour via the silanisation process is still unknown although Salem et al. (2010) mentioned that the water-repellent effects are certain to last for at least 3 decades. The subsequent steps in the preparation of the sample were to seal the sand in Ziploc bags for 24 hours prior to any wettability measurements.

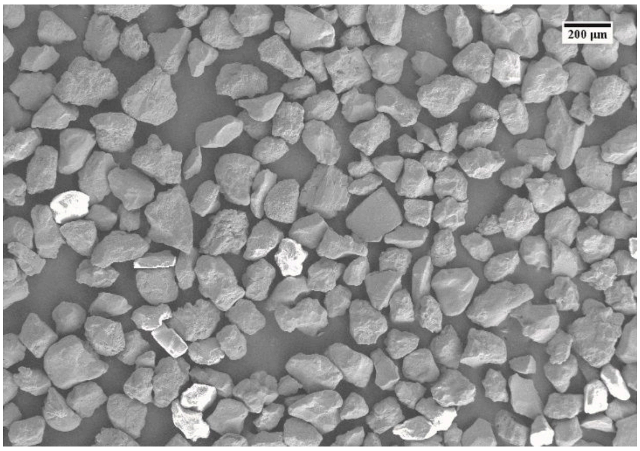

Figure 1. Scanning electron microscope image of 63-212 µm particle size of Leighton Buzzard sand

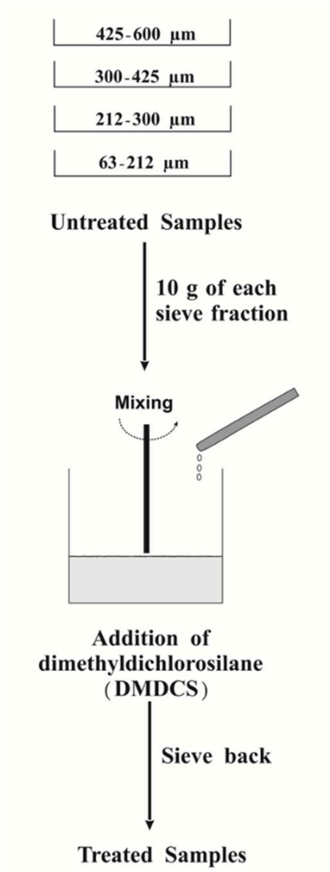

Figure 2. Schematic representation of the preparation of water repellent sand

2.2 *Wettability measurements*

2.2.1 *Sessile drop method*

The sessile drop method (SDM) makes a direct measurement of the CA at the 3-phase contact point and thus quantifies the extent to which a surface is wettable (Adamson, 1990). The SDM is the simplest and most straightforward way of determining the CA. The SDM enables the measurement of CA within the range 0° (for very wettable soils) to 180° (for non-wettable soils).

The SDM CAs were determined by a goniometer (Drop Shape Analyser 25 from KRÜSS GmbH). A 10-µl drop of de-ionised water was placed on the soil sample prepared by the method proposed by Bachmann et al. (2000). A total of 10 CAs measurements were performed on each sample. As with the study of Shang et al. (2008), the initial CA measured within 50 ms was considered to be the most representative measure of wettability. The semi-automated technique developed by Saulick et al. (2017) was used to analyse the images from the goniometer and obtain the CAs. All CAs measurements were performed at a temperature of 23 ± 1 °C and relative humidity of 65 ± 5 %.

2.2.2 *Wilhelmy plate method*

The Wilhelmy plate method (WPM) allows the measurement of the dynamic CAs (advancing and receding). This technique has traditionally been used to assess the wettability of materials in Physical Chemistry (Adamson, 1990) and its application to granular materials has been initiated by Bachmann et al. (2003). As with the SDM, the WPM also allows the measurement of CA within the range 0 to 180°. The WPM involves immersing a sample (the material whose wettability is to be determined) into a liquid (usually water) and retracting it in the opposite direction. This process is carried out while the change in mass is monitored and recorded by a tared balance connected to a computer. As the sample is inserted into the liquid, the CA obtained is called the advancing contact angle and when the sample is retracted, it is referred to as the receding contact angle.

For granular materials such as soil samples, a double-sided tape is first attached to a microscope slide on all 5 sides (the one remaining side is attached to the mass balance). A single layer of grains is then applied evenly on the microscope slide which is then lowered gently into a container of water (Figure 3a). The steps involved in the measurement of dynamic CAs are usually automated.

Besides the gravitational force (W), there are two main forces which act on the immersed sample: Buoyant and Wetting forces. The buoyant force (F_b), also called upthrust is the upward force experienced by a body when it is partly or fully immersed in water and is equal to the weight of fluid displaced by the body. As the sample moves into the liquid, F_b increases linearly and is given by Equation 1 where ρ is the density of the liquid in which the sample is immersed, V is the volume of liquid displaced by the sample and g is the acceleration due to gravity.

$$F_b = \rho V g \qquad (1)$$

The wetting force (F_w) is caused by the shape of the curved meniscus around the sample immersed (Figure 3b). For CAs < 90°, F_w increases the total downward force acting on the sample but as it becomes fully immersed, the magnitude of F_w decreases (Bachmann et al., 2003). The resultant of F_w parallel to the direction of immersion of the sample is a function of the wetted length of the sample as it is immersed (l_w), the surface tension of the liquid (γ_{lg}), which is assumed to be constant and the CA (see Equation 2). As mentioned by Bachmann et al. (2003), the evaluation of the CA requires F_w to be determined by means of a linear regression of the recorded weight curve as a function of time with an extrapolation to the zero-depth immersion (so as to correct for buoyancy).

$$F_w = l_w \gamma_{lg} \cos CA \qquad (2)$$

When the sample is partly submerged and the balance tared, the total force, F_t acting on the sample is given by Equation 3.

$$F_t = l_w \gamma_{lg} \cos CA - \rho V g \qquad (3)$$

During the derivation of Equation 3, it was assumed that the effect of the viscosity of the liquid, the surface and line forces along the smallest dimension of the microscope slide are small enough to be ignored.

In this study, a one-layer sample was carefully prepared and attached to a double-sided tape (TESA, type 4965, Hong Kong SAR) and the advancing and receding CAs were measured using the DCAT 11 Dynamic Contact Angle Meter and Tensiometer from Data Physics Corporation, Filderstadt, Germany. The maximum depth of immersion was set to 8 mm and the motor speed upon measurement of the dynamic CAs was 0.1 mm/s. Once the receding and advancing curves were obtained, the incorporated software, SCAT 12 was used to obtain the dynamic CAs.

3 RESULTS AND DISCUSSION

Figure 4 shows the contact angles determined by the SDM as a function of particle size. The lowest and highest standard deviations recorded were respectively ± 2.86° and ± 5.65°. The CAs reached by the two coarsest fractions were generally close to each other as with the two finest fractions. The CA attained by the particle size 212-300 µm was the highest (120.3 ± 5.65°) and the 300-425 µm fraction gave the lowest CA of 107.0 ± 3.06°.

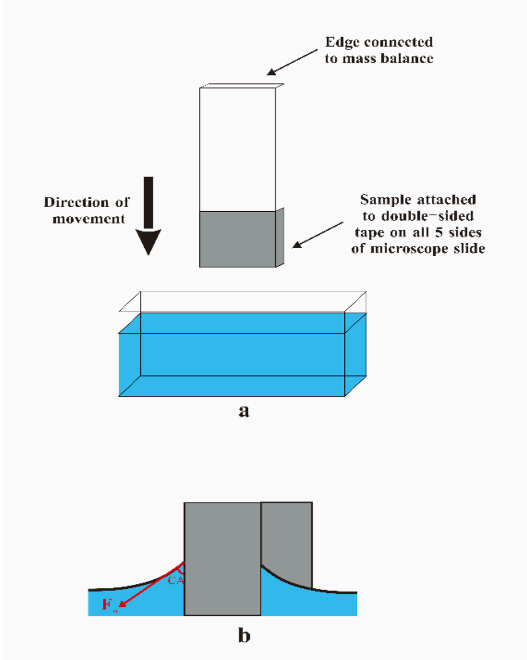

Figure 3. A schematic representation of the measurement of advancing contact angle with the Wilhelmy plate method b. wetting force, Fw acting on the immersed sample.

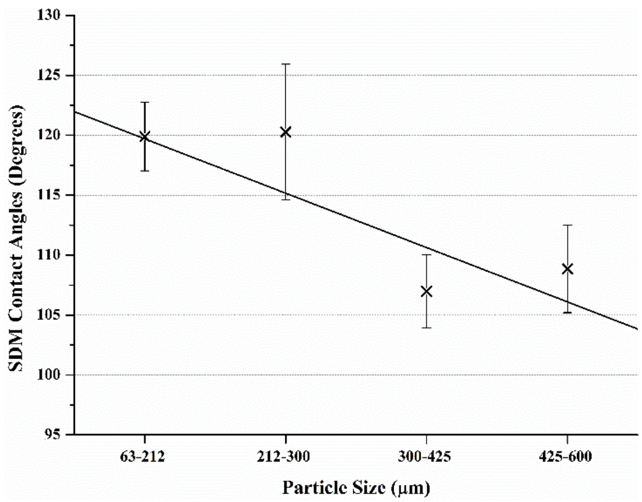

Figure 4. Contact angles measured using the sessile drop method against particle size.

The results of WPM advancing CAs against particle size are illustrated in Figure 5. The highest WPM advancing CA (154.2°) was obtained with the particle size 63-212 µm and the particle size 300-425 µm gave the lowest advancing CA (128.1°). Apart from the particle size 300-425 µm which gave a WPM receding CA of 24.0°, all remaining sizes investigated yielded receding contact angles of 0°. This last observation was also noted by Bachmann et al. (2003) who considered the measurement of CAs of soils with the WPM to be dependable and sensitive to changes in wettability.

All CAs obtained with the SDM were within the range of dynamic CAs defined by the WPM and lied closer to the advancing CAs. As with the studies of Lourenco et al. (2015) in their assessment of the wettability of naturally occurring water repellent minerals, the WPM advancing CAs were considerably larger than the CAs obtained with the SDM. A likely justification for this discrepancy is the relatively smaller footprint onto which the CAs are averaged with the SDM as compared to the WPM. A general decrease in the CAs as particle size increases was observed with both SDM and WPM. A maximum difference of 13.3° in CAs between the particle sizes was recorded with the SDM whereas with WPM, the difference was 26.1°.

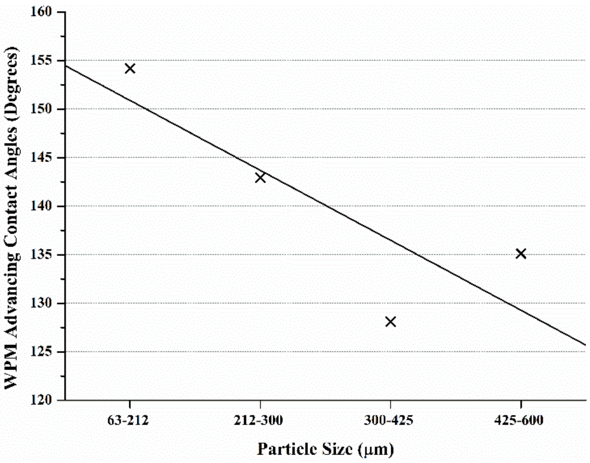

Figure 5. Contact angles measured using the Wilhelmy plate method against particle size.

4 CONCLUSIONS

The SDM and WPM used to measure the wettability of a synthesised sand have proved to be sensitive to changes in particle size. Among the particle sizes investigated, the fine fractions have generally shown to reach higher CAs than the coarser ones. However, significant differences in the magnitude of CAs were observed, indicating that the measurement of CAs are method-dependent. While both the SDM and WPM were able to distinguish between the different extents of wettability for a sandy material, it is suggested that for natural soils with considerable clay content, the SDM is to be favoured. This is because the WPM, as opposed to the SDM requires a large amount of liquid to be in contact with the soil that will lead to eventual swelling. It is also recommended that wettability measurements entail ample documentation of the methodology adopted.

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