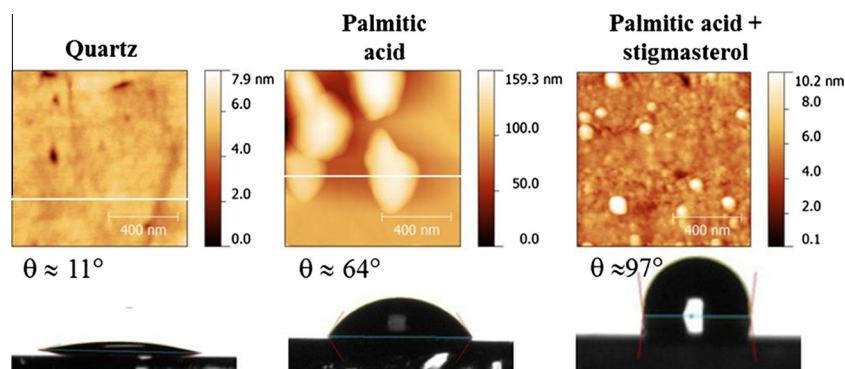# Impact of particle nanotopology on water transport through hydrophobic soils

Vi Khanh Truong, Elizabeth A. Owuor, Pandiyan Murugaraj, Russell J. Crawford *, David E. Mainwaring

School of Science, Faculty of Science, Engineering and Technology, Swinburne University of Technology, Hawthorn 3122, Australia

GRAPHICAL ABSTRACT

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ABSTRACT

The impact of non- and poorly wetting soils has become increasingly important, due to its direct influence on the water-limited potential yield of rain-fed grain crops at a time of enhanced global competition for fresh water. This study investigates the physical and compositional mechanisms underlying the influence of soil organic matter (SOM) on the wetting processes of model systems. These model systems are directly related to two sandy wheat-producing soils that have contrasting hydrophobicities. Atomic force microscopy (AFM), contact angle and Raman micro-spectroscopy measurements on model planar and particulate SOM-containing surfaces demonstrated the role of the hierarchical surface structure on the wetting dynamics of packed particulate beds. It was found that a nanoscale surface topology is superimposed over the microscale roughness of the packed particles, and this controls the extent of water ingress into particulate packed beds of these particles. Using two of the dominant component organic species found in the SOM of the two soils used in this study, it was found that the specific interactions taking place between the SOM components, rather than their absolute quantities, dictated the formation of highly hydrophobic surface nanotopologies. This hydrophobicity was demonstrated, using micro-Raman imaging, to arise from the surface being in a composite Cassie–Baxter wetting state. Raman imaging demonstrated that the particle surface nanotopography influenced the degree of air entrapment in the interstices within the particle bed. The influence of a conventional surfactant on the wetting kinetics of both the model planar surfaces and packed particulate beds was quantified in terms of their respective advancing contact angles and the capillary wetting force vector. The information obtained for all of the planar and particulate surfaces, together with that obtained for the two soils, allowed linear relationships

* Corresponding author.
    E-mail address: rcrawford@swin.edu.au (R.J. Crawford).

to be obtained in plots of the contact angle data as a function of the wetting liquid surface tensions. These linear relationships were found to reflect the mechanisms underlying the surface energy parameter requirements for wetting.

1. Introduction

Soil water repellence (SWR) or hydrophobicity is a global phenomenon, and widespread across a variety of soil types [1]. It represents one of the limits to productivity improvements, especially in broadacre grain crops grown in less favourable environments [2]. The main cause of SWR has been attributed to the presence of soil organic matter (SOM) coatings found on soil particles, which is considered to emanate from living or decomposing plants and microorganisms, together with root materials and exudates [3–5]. Several studies have been performed to extract, separate and characterise the various SOM components, which include alkanes, fatty acids and their esters, phytans, phytols and sterols [6–10]. Ma'shum et al. demonstrated that water repellence increased with the degree of SOM coating and found that addition of straight chain fatty acids and esters ranging in carbon length between C_{16}–C_{32} (which are common to non-wetting soils) induced a degree of hydrophobicity in otherwise wettable soils. This suggested that interactions between the SOM constituents themselves also play a role in soil hydrophobicity [7]. Studies have indicated that the distribution of organics in the SOM may result in dominance of non-polar groups exposed at the soil particle–air interface, which will enhance water repellence [5,11–13]. There have, however, been no mechanistic investigations detailing the physical and chemical relationships within these interfaces that dictate wetting behaviour.

The role of surface texture in wetting dynamics has also become an area of intense research interest due to its relevance in micro- and nano-technology, medical devices and biological systems. Such surfaces have traditionally been represented by two wetting regimes. A rough but chemically homogeneous surface, where water penetrates the surface asperities and wets the total surface area, yields an apparent (Wenzel) contact angle that is simply modulated by a roughness factor *r*, although wetting advancement may be controlled by significant pinning. Heterogeneous Cassie–Baxter systems arise where air remains between nanoscale protrusions on the surface, yielding a composite solid–air–water interface. Both the theoretical and experimental aspects of these states and the transitions between them have been extensively reviewed [14,15]. In this work, we apply these wetting regimes to model and real soil systems.

The micro-morphology of natural soil surfaces have been probed at the micro- and nano-scale level using scanning electron microscopy (SEM) and atomic force microscopy (AFM) [16–21]. Environmental-SEM has also been used to study the hydrophobicity of model surfaces coated with palmitic acid using moisture condensation as an indicator [21–23]. Studying the surface topology using tapping mode AFM indicated the scale of depressions and elevations present in the soil surfaces, while phase angle images allowed differentiation to be made between the structurally hard and soft regions corresponding to SOM free areas [16]. While such studies have provided morphological information that pertains to the bulk SOM, they did not selectively differentiate the underlying mode of action of the specific SOM components of the total organic soil content [17,18]. To date, investigations focusing on the specificity, interactions and microstructure of the SOM films responsible for soil water repellence are still limited. Advancing the understanding of the role of the SOM interface in wetting processes,

particularly within structure of particulate beds, would significantly contribute towards the design of effective remediation regimes that improve water transport and utilisation in such hydrophobic soils.

The wetting of water repellent soil surfaces has been commonly assessed using the molarity of ethanol droplet test (MEDT) and water droplet penetration time (WDPT) [1,24–26], both of which only indicate the degree of soil hydrophobicity in terms of the liquid surface tension needed to obtain an advancing wetting front. Additionally, the kinetics of capillary rise in porous packed beds has been extensively used to evaluate the wetting characteristics of particulate systems including minerals [27–30] and to a limited extent the wettability of soils [31–33]. Here, the initial linear portion of the kinetic curve provides a direct measure of the advancing water contact angle via the Washburn analogy to diffusional processes [34], if effects of tortuosity are removed by the use of a second fully wetting liquid that makes a 0° contact angle with the solid surface.

Surfactant amendment is one technique that has been used to alleviate water repellence [35–39], increase water infiltration rates, and reduce water run-off at the soil surface, which enhances sub-surface water migration [40–42]. In particular, non-ionic surfactants such as the ethylene oxide/polypropylene oxide based block copolymers have been extensively studied and used in the turf industry. Over the past decade, surfactant blends comprising a range of compositions of Pluronic block copolymers and alkyl polyglycosides have been shown to further improve water transport to a significant extent in some severely hydrophobic soils [36,43–45].

The present study investigated the molecular distribution of the SOM components found in non-wetting soils obtained from the grain growing regions of Western Australia, together with their role in SWR. The impact of molecular SOM interactions at the surface–air interface is modelled using palmitic acid (PA) and stigmasterol (ST) as two dominant classes of SOM, where phase behaviour is shown to produce the characteristic nanotopologies that dictate the behaviour of the advancing wetting front and hence the severity of the soil hydrophobicity with and without the presence of surfactant. Finally, we discuss the influence of surfactants on the capillary imbibition of two soils with different degrees of water hydrophobicity/repellency from Western Australia in the context of the model hydrophobic surfaces used in this study, showing a mechanistic consistency across all systems investigated.

2. Materials and methods

2.1. Materials

Trimethylchlorosilane; TMCS (>99%), palmitic acid; PA (>99%) and stigmasterol; ST (>95%), alkanes (C8–C40), isopropanol; IPA (99.9%), methanol (99.8%) and cyclohexane (99.9%) were sourced from Sigma–Aldrich, UK. Chloroform (99.8%) was obtained from Mallinckrodt Baker Inc., Phillipsburg, NJ; and ammonia; NH_3 (25%), nitric acid (>90%) and potassium hydroxide (>85%) from Merck Millipore Inc., Darmstadt, Germany. Non-ionic surfactants used included a synthetic Pluronic® block copolymer; $EO_xPO_yEO_z$ (average Molecular weight ~2800, Pluronic L-81, Sigma Aldrich),