Fatty acids as hydrophobizing agents for granular materials

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ABSTRACT

Hydrophobic (or non-wetting, water repellent) soils have a low affinity for water. The importance of soil hydrophobicity has already been recognized due to its effect on soil hydraulic properties and potential applications in ground-related constructions. The treatments coat soil particles with synthetic or natural substances (e.g. organosilane and fatty acids). Fatty acids such as stearic acid have been used widely to induce hydrophobicity, because of their similar composition to natural hydrophobic substances in soils and with the advantage of being compatible with the environment. Following an introduction to hydrophobic soils, this paper reviews fatty acids that can be employed to induce hydrophobicity in granular materials and the treatment methods used to achieve it. Results are provided for a vegetation oil (flaxseed oil) on hydrophilic sands, revealing an increase in hydrophobicity with the addition of the flaxseed oil.

Keywords: geosynthetics; ground improvement; fatty acids; soil hydrophobicity

1 INTRODUCTION

Soil hydrophobicity (or water repellency) decreases the affinity of soils for water, leading to retarded wetting of soils. This worldwide phenomenon has been studied in soil science for over a century (DeBano 2000). Recently, its importance in geotechnical engineering has been recognized because of its effect on soil strength, water infiltration and soil stability (Bardet et al. 2014; Fink et al., 1980).

Hydrophobicity shows a great potential use in the materials for ground-related construction such as hydraulic barriers and landfills. For example, Zheng et al. (2017) claimed that hydrophobic soils are a promising material for mitigating rainfall-induced landslides and stabilizing slopes. Choi et al. (2016) explored the application of hydrophobic clay as an alternative landfill cover material by investigating its hydraulic properties. An elaborate review of the fundamental, quantification and potential engineering applications in allied fields such as mining and geotechnical engineering is given in Lourenço et al. 2017.

Inducing hydrophobicity in laboratory utilizes two major types of hydrophobizing agents: silane compounds or fatty acids. Silanes share a common chemical property that they react with water and silica surfaces and then produce polydimethylsiloxane (PDMS), which forms high and stable hydrophobic surfaces (Bachmann et al. 2000). For silane-induced hydrophobicity, the controls (e.g. concentration, sand particle size, time after treatment) have been well studied (Chan and Lourenço 2016; Ng and Lourenço 2016). Another major type of agent is fatty acids, which closely simulates the chemistry of natural hydrophobic substances. Fatty acids are linear carboxylic acids containing long aliphatic chains which are hydrophobic and thus induce hydrophobicity in soils when coated on soil particle surfaces.

The objective of this paper is to review the current understanding of fatty-acids-induced hydrophobic soils. The quantification methods of hydrophobicity are firstly introduced, followed by a summary of treatment methods, mechanisms and controls of fatty-acid-induced hydrophobic soils. Induced hydrophobicity is demonstrated for sands mixed with flaxseed oil.

2 QUANTIFICATION

Wettability can be quantified by the contact angle (CA). When a drop of water is placed on the sand surface, a contact line is formed among solid, air and water, with the three-phase equilibrium governed by Young’s equation. CA of 90° is a threshold for hydrophobicity and hydrophilicity (Goebel et al. 2011).

Bachmann et al. (2000) proposed the sessile drop method to obtain CA on soils (Fig. 1(a)). Before the measurement, sands are sprayed on a glass slide with tapes, forming a thin plane layer of sand particles. A water drop from the syringe is placed on the sample surface through a needle. The shape of water drop is recorded by a camera and CA is determined.

Fig. 1(b) shows a direct measurement of CAs from a water droplet by using a drop shape analyser (KRÜSS GmbH, Hamburg, Germany). The measurement was performed in the laboratory at a temperature of 20~22℃ and relative humidity of 60~85%. For each droplet, two CAs (i.e. the left and right CA on the droplet) on a baseline were determined by a curve-fitting algorithm proposed by Saulick et al. (2017), from which an average value was obtained.

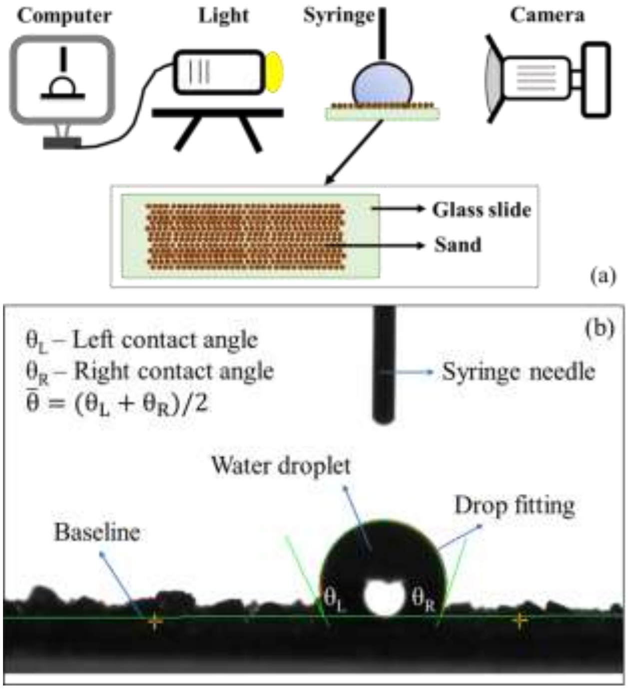

Fig. 1. (a) Schematic of sessile drop method to measure contact angle and (b) measurement of the contact angle.

3 METHODOLOGY

3.1 Hydrophobizing agents

A fatty acid contains a carboxylic group (COOH) and an aliphatic chain which is hydrophobic. In natural hydrophobic soils, fatty acids are usually found and thought to contribute hydrophobicity (Doerr et al. 2000). Inspired from this, fatty acids are recognized as a major agent for inducing hydrophobicity in laboratory. Table 1 lists examples of fatty acids that have been used in research.

3.2 Treatment methods

Two treatment methods have been applied to date: simple mixing method and solvent evaporation method. In the former one, fatty acids are directly mixed with sands that have been previously washed with water. Although it is simple and no special equipment is required, for some fatty acids with low solubility (e.g. stearic acid), this method is unsuitable. In this case a solvent evaporation method is applied, in which fatty acids are firstly dissolved in a solvent (*e.g.* diethyl ether and tetrahydrofuran), followed by mixing with washed sands. Afterwards, the fatty-acid/solvent/sand mixture is evaporated in a fume hood or a rotary evaporator until total evaporation of the solvent. These two methods have also been listed in Table 1.

4 FATTY ACIDS IN HYDROPHOBIC SANDS

At a molecular scale, fatty acids and their dissolved products interact with sand particle surfaces by chemisorption or physisorption (Graber *et al.* 2009). As shown in Fig. 2, fatty acids and their dissolved product have hydrophilic ends (COOH or COO-, respectively). Particle surfaces can be either positively charged because of metal cations, or negatively charged because of quartz or clay (e.g. Jang et al., 1995). Dissolved fatty acids can interact with positively charged surfaces (chemisorption) or with negatively charged surfaces via divalent cation bridges (physisorption), both of which form hydrophobic coatings on particles (Doerr et al., 2000).

These coatings are classified into three types: condensed, expanded and vapor coatings. For the condensed coatings, fatty acids are closely packed and steeply orientated towards the surface. The fatty acids with straight and long hydrocarbon chains (*e.g.* stearic and oleic acid) can form condensed coatings. The packing of the fatty acids in such coatings is in a crystalline state. Therefore, the coatings are solid and resistant to displacement by water. Hydrophobic sands covered by condensed coatings are usually stable.

Expanded coatings are still coherent but occupy a larger area on particle surfaces than condensed coatings. Some chemical properties can contribute to this: (1) bent hydrocarbon chains (e.g. *cis*-unsaturated acids) and (2) short hydrocarbon chains with bulky head groups. Expanded coatings are unstable in contact with water, in which fatty acids change their orientations and expose the hydrophilic ends outwards the particle surfaces (Table 1). 11-Eicosenoic acids can be either *cis* (bent chain) or *trans* (straight chain). The *cis*-11-Eicosenoic acids form expanded coatings while the *trans*-isomers form condensed coatings.

Table 1. Fatty acids used to induce hydrophobicity in soils

Fatty acids	Chemical formula	Soil	Treatment method	Contact angle	Critical Concentration	Reference
Stearic	$CH_3(CH_2)_{16}COOH$	Sand /clay	Solvent-evaporation	90°	2.2%(g/g)	Lourenço et al. (2015)
Oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	Sand	Mixing	101°	0.1%(g/g)	Subedi et al. (2012)
			Solvent-evaporation	97°	0.075%(g/g)	
Stearic	$CH_3(CH_2)_{16}COOH$		Solvent-evaporation	108°	0.6%(g/g)	
Tetradecanoic	$C_{13}H_{27}COOH$	Sand	Solvent-evaporation	-	0~4.72×10^{-6}(mol/g)	Mainwaring et al. (2013)
Stearic	$CH_3(CH_2)_{16}COOH$				0~4.72×10^{-6}(mol/g)	
Docosanoic	$C_{21}H_{43}COOH$				0~0.92×10^{-6}(mol/g)	
11-Eicosenoic	$CH_3(CH_2)_7CH{=}CH(CH_2)_9COOH$				0~17.6×10^{-6}(mol/g)	
Elaidic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$				0~17.6×10^{-6}(mol/g)	

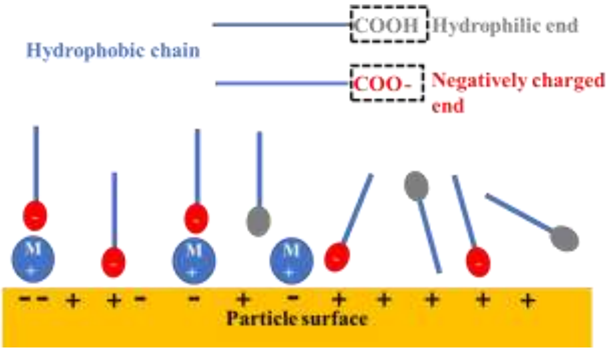

Fig. 2. Schematic of fatty acid molecules on a particle surface

5 CONTROLS

5.1 Concentration

The concentration of fatty acids is a governing factor affecting hydrophobicity. The CA-concentration relationship follows a three-region pattern as shown in Fig. 3 (a). In region A, CA increases with the concentration and reaches a peak with a small concentration. This concentration corresponding to the peak CA is named as 'critical concentration (C_{cri})' which varies from 0.1 to 0.6% for sands. After that, CA starts to decrease (Region B) and drops down further with higher concentrations (Region C). Under specific conditions, region B is negligible, and the CA-concentration curve becomes a two-region pattern (Leelamanie et al., 2008).

A conceptual model proposed by Wijewardan *et al.* (2014) is shown in Fig. 3 (b). In Region A, fatty acids start to coat the sand particles and induce hydrophobicity by their aliphatic chains. The CA of coated sand particles reaches a peak when the coating is at an optimum (a monolayer), with the concentration equal to C_{cri}. With a higher amount of fatty acids, some hydrophilic ends are exposed outward the particle surface, leading to a decreased CA. In region C, CA drops down further due to the formation of hydrophilic micelles by the fatty acids.

The major soil property affecting C_{cri} is the specific surface area of soils. For clay and silts with a larger specific surface area, C_{cri} is higher. A comparison can be seen in Table 1. For instance, by using stearic acid, C_{cri} for sands is 0.6% (g/g) with CA=108° (Subedi et al. 2013), but for a sand-clay mixture whose specific surface area is larger, 2.2% (g/g) concentration only increases CA to 90° (Lourenço *et al.* 2015).

5.2 Temperature

Temperature affects hydrophobicity. At 100~300°C, hydrophobicity can be enhanced (DeBano, 1981; Jiménez-Pinilla et al., 2016) due to melting and re-crystallization of fatty acids. For *cis*-unsaturated fatty acids, thermal *cis-trans* isomerization during heating contributes to the transformation of bent hydrocarbon chains to straight ones. Fatty acids with straight chains are easier to form condensed coatings resistant to water. At higher temperatures hydrophobicity reduces because of the combustion and evaporation of fatty acids. The threshold temperature for decreasing hydrophobicity depends on: chemical properties, oxygen availability, heating duration and the initial water content of the sands before heating.

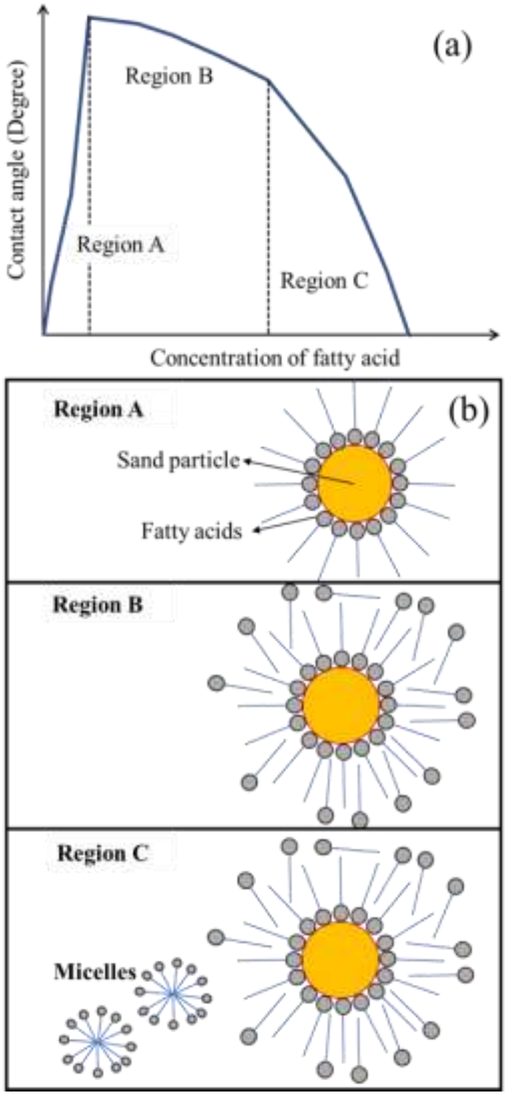

Fig. 3. Three-region pattern of concentration-contact angle relationship, (a) relation CA-concentration, (b) particle-level phenomena (after Wijewardan *et al*., 2014).

5.3 Selected results for flaxseed oil – treated sand

Vegetation oils contain high a high percentage of fatty acids and consequently could induce soil hydrophobicity. An example is flaxseed (linseed) oil which contains mostly alpha-linolenic acids and linoleic acids (Vereshchagin and Novitskaya, 1965). Given their liquid state, preparation could be conducted by mixing directly with soils. Fig.4 demonstrated the effect of mixing flaxseed oil with Leighton Buzzard sand (LBS), a clean and natural sand). The results show that the CAs increase with oil concentration and stabilize at higher concentrations. The sands were originally hydrophilic (CA=25°), and by adding 0.5% (g/g) of flaxseed oil, CAs increased to 92°. The critical concentration (*i.e.* the lowest concentration that provides the highest hydrophobicity or CAs) of flaxseed oil was 0.75% and comparable to those of other fatty acids (0.1~0.6%) in Table 1.

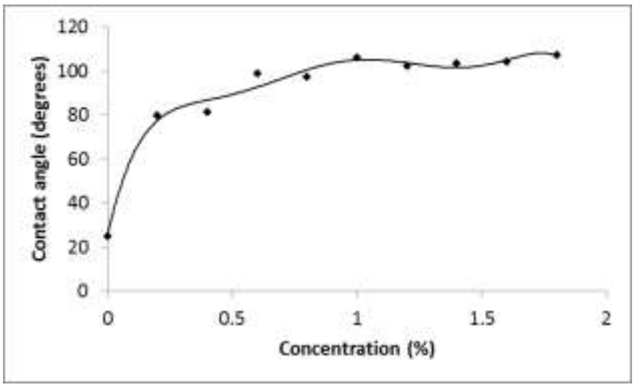

Fig. 4. Relation between flaxseed oil concentration on contact angles for a model sand.

6 CONCLUSION

This paper summarizes fundamental aspects of hydrophobic soils including their engineering applications and quantification methods, followed by an overview of two treatment methods to induce soil hydrophobicity with fatty acids. Based on a literature review, two major controls (concentration and temperature) to induce hydrophobicity and their mechanisms were discussed. The effect of concentration is showed for flaxseed oil on a sand.

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