Characterization of hydrophobicity for artificially hydrophobized autoclave aerated concrete grains

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ABSTRACT

Untreated oil-contaminated water discharge from domestic and industrial sources has led to serious environmental pollution, especially in developing countries. Many technologies (e.g., floatation and coagulation, biological treatment, membrane separation, and so on) have been developed to treat effluents. Among them, the oil-water separation utilizing hydrophobized filtration beds can be expected to be a cost-effective and quick treatment technology. Previously, hydrophobized solid grains have been preliminary tested but applicability of hydrophobized porous grains have not been fully examined in oil-water separation system. This study aimed to characterize the hydrophobicity for artificially hydrophobized porous grains of autoclave aerated concrete (AAC) grains. The AAC grains (0.106 to 0.250 mm) were coated with two hydrophobic agent (HA) such as oleic acid (OA) and stearic acid (SA) at different concentrations (5 to 750 g of HA / kg of AAC grains). The OA-coated grains exhibited high hydrophobicity with $HA \geq 50$ g/kg while for SA-coated grains, hydrophobicity became significant from $HA \geq 5$ g/kg. Both OA- and SA-coated grains gave a rapid increase with increasing HA concentration and maximum contact angles reached 140–145°, suggesting that they had a high potential to apply in the filtration beds in oil-water separation system.

Keywords: oil-contaminated water, industrial by-product, autoclave aerated concrete, hydrophobicity

1 INTRODUCTION

Excessive production of construction-demolition waste (CDW) and industrial by-products (IBPs) as well as limited recycling rate for these materials are growing problems in developing countries (e.g., Tuan et al., 2018). Along with improper management of CDW and IBPs, untreated industrial and domestic wastewater discharge into natural environment is causing serious water pollution. Especially, the direct discharge of oil contaminated water as well as an accidental oil spill in the environment bring a negative impact to human health (Gupta et al., 2012). With the viewpoints of proper management of CDW and IBPs, and environmental protection and pollution control, therefore, the development of cost effective and sustainable technologies for remediating oil-contaminated water is of great interest.

1.1 Effective utilization of industrial by-products

Among IBPs, the scrap and waste of autoclave aerated concretes (AAC) has been generated increasingly along with the manufacturing. The AAC has several advantages as a construction material including low density, high porosity, larger surface area, high heat resistance, speedy construction, and environmental friendliness (Matsushita et al., 1999; Narayanan and Ramamurthy, 2000). Additionally, the AAC is less alkaline in water compared to other cementitious materials and can be expected to utilize for the wastewater treatment (e.g., Kumara et al., 2019a, b).

1.2 Oil contaminated water

Direct discharge of industrial and domestic oil contaminated water into the environment as well as oil-spill accidents triggers serious water pollution, resulting in endangering aquatic life, threatening human health, and destructing natural landscape (Yu et al., 2017). Presently, there are many technologies to remediate oil contaminated water such as gravity separation, flotation, coagulation, chemical treatment, biological treatment, membrane separation, and so on (Jamaly et al., 2015; Jafarinejad, 2017). However, there are several drawbacks or limitations such as inadequate separation efficiency, high cost, complex operations, cost effectiveness, and source of secondary pollution (Yong et al., 2018). Sometimes, in case of emergency like oil-leakage /spillages accidents, porous materials such as sponges, foams, and textiles are commonly used (Yu et al., 2017). The major drawback is that they absorb both oil and water simultaneously, resulting in source of secondary pollutant, as it is very difficult to recycle/reuse.

Recently, many researchers tried to develop and modify the oil-water separation techniques by looking at the wettability behavior that happens at the interface of the solid, liquid, air and oil phase (Wang et al., 2015). For example, (Bigui et al., 2018) and (Yue et al., 2018) tested hydrophobized quartz sand (solid grains) as filter media in filtration beds. The tested samples were effective to treat the oil-water separation, but it needed further improvement to increase the hydrophobicity of filter beds.

On the other hand, the applicability of hydrophobized porous grains/meshes /membranes has not been fully examined compared to hydrophobized solid grains. Few researchers introduced hydrophobized porous meshes and membranes for oil-water separation. The tested materials showed a good separation ability but remained some problems such as material cost, and generation of secondary pollutant (Zeiger et al., 2017).

1.3 Objectives

In order to assess the applicability of recycled materials from CDW and IBPs for oil-water separation system for remediation of oil contaminated water, this study aims to characterize the hydrophobicity of modified wasted AAC grains in the laboratory.

2 MATERIALS AND METHODS

2.1 Autoclave aerated concrete

In this study, the base material used was AAC scrap from Vietnam. The AAC scrap was crushed and sieved with sizes ranging from 0.106 to 0.250 mm. It is one of the high porous materials having dual pore network distribution (macropores and micropores) and high surface area. The micropores (intra pores d < 10 μm) are attributed to the formation of tobermorite ($5CaO.6SiO_2.5H_2O$) and play an important role in water retention (Matsushita et al., 1999; Narayanan and Ramamurthy, 2000; Nguyen et al., 2018).

The basic physical and chemical properties of Vietnam AAC grains are shown in Table 1 below.

Table 1. Basic physical and chemical properties of AAC grains.

Tested Material	Particle size (mm)	Air-dried water content (%)	BET surface area (m^2/g)	Specific gravity	pH	EC (mS/cm)
Vietnam AAC	0.106-0.250	2.01	16.2	2.61	9.01	0.9

2.2 Hydrophobic agents

Two types of hydrophobic agent (HA) such as oleic acid (OA) and stearic acid (SA) were used because they are low cost, easy to handle, and environmental friendly. Commercially available OA (molar mass 282.46 g/mol; Kanto Chemical Co., Tokyo) and SA (molar mass 284.47 g/mol; Fujifilm Wako Pure Chemical Corporation, Osaka) were employed in this study. OA is a monounsaturated omega-9 fatty acid with a chemical formula of $CH_3(CH_2)_7CH{:}CH(CH_2)_7COOH$. SA is a saturated fatty acid ($CH_3(CH_2)_{16}COOH$).

For the impact assessment of HAs on hydrophobicity, different concentrations of HAs (OA and SA) were used ranging from 5 to 750 (g of HA / kg of AAC grains; hereafter, g/kg) based on a solvent-aided method. The ethanol (C_2H_5OH; molar mass 46.07 g/mol) and diethyl ether ($C_2H_5OC_2H_5$; molar mass 74.12 g/mol) were used as solvents for coating OA and SA, respectively.

2.1 Sample preparation

The AAC samples with particle sizes ranging from 0.106 to 0.250 mm were coated with different concentrations of OA and SA. First, the required concentrations of SA or OA were immersed in a beaker along with solvents and samples. These were kept in a draft chamber for at-least three hours to allow volatilization of the solvents. It is important to mention that SA is in solid (powder) form and OA is in liquid form at normal room temperature. Therefore, for the case of SA-coated samples, the SA and di-ethyl ether were mixed thoroughly using an electronic mixer before adding samples. After volatilization, coated samples were stored in a climate control laboratory at 20 °C for at least 48 hours to equilibrate.

After equilibrium, the degree of hydrophobicity at 'solid-air interface' was assessed by using two simple and common laboratory techniques i.e. water drop penetration time (Watson and Letey, 1970) and sessile drop method (Bachmann et al., 2000). The same technique has been previously used by many researchers for characterizing the hydrophobicity in OA and SA hydrophobized solid grains (Subedi et al., 2012; Wijewardana et al., 2015). Therefore, in this study, same approach was employed for assessment of degree of hydrophobicity at 'solid-air interface' by measuring the initial contact angle and recording the penetration time, using the Contact Angle Analyzer (Digital microscope VHX-900 series, Keyence, Japan).

2.1 Sessile drop method

In the sessile drop method (SDM), the hydrophobized AAC grains were sprinkled on an adhesive tape which was pasted onto a smooth glass slide. This glass slide was tapped to remove the excess sample. Then, it was placed on the stage of a microscopic camera and a small drop of distilled water was placed on the sample using small syringe. The horizontal microscope image recorded periodically the contact angle with time and evaluated an initial contact angle (α_i) and time dependence of contact angles. The experimental setup is shown in Fig. 1. An example of measured initial contact angle at t = 0 sec is shown in Fig. 2.

Fig. 1. Experimental set-up of SDM.

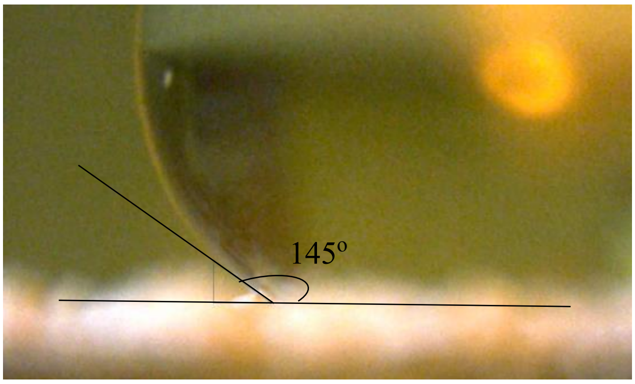

Fig. 2. Microscopic photograph of initial contact angle. The tested samples with AAC grains coated with *SA* = 500 g/kg.

2.2 Water drop penetration time

The water drop penetration time was determined via the water drop penetration test (WDPT), in which, a small drop of distilled water was placed on the smooth surface (1) of a sample using a micro syringe (2). The time was recorded by a stop watch (3) for the water droplet to penetrate into hydrophobized AAC sample. The different degrees of hydrophobicity were shown in Table 2 (Bisdom et al., 1993). The setup of WDPT is shown in Fig. 3.

Table 2. Classes of degree of hydrophobicity.

Class	WDPT (sec)	Nomenclature
0	< 10	Non water Repellency (WR)
1	10 to 60	Slightly WR
2	60 to 600	Strongly WR
3	600 to 3600	Severely WR
4	> 3600	Extremely WR

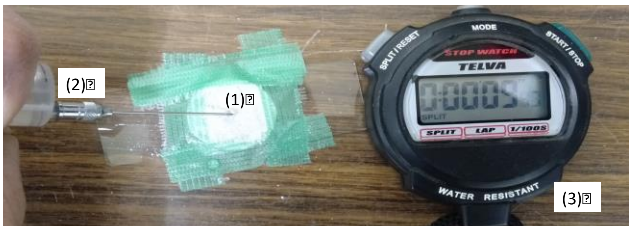

Fig. 3. Experimental set-up of WDPT.

3 RESULTS AND DISCUSSION

Measured initial contact angles from SDM and WDPT were summarized in Tables 3 and 4. For the AAC grains coated with OA, the samples coated with 5 and 10 g/kg showed no hydrophobicity, i.e., WDPT = 0 sec and SDM-α_i = 0°. With increasing in HA concentration, the hydrophobicity rapidly increased and reach approximately α_i = 140° in the range of $HA \geq 300$ g/kg. For the AAC grains coated with SA, on the other hand, the tested samples exhibited the hydrophobicity from low HA concentration. The measured α_i increased and reached approximately 147° in the range of $HA \geq 300$ g/kg. The measured α_i values are depicted as a function of HA concentration in Fig. 4. The figure clearly showed that α_i values rapidly increased with increasing in HA concentration for both OA- and SA-coated AAC grains. After reaching the maximum values, the α_i values reached a plateau and remained almost constant. Compared to the reported α_i values (approximately, 100°) for OA- and SA-coated sands (Subedi et al., 2012), the measured α_i values in this study were much higher, implying that these HAs were very good hydrophobic agents for AAC grains.

In addition, it was clear from the WDPT results that 50 g/kg of OA made the modified AAC become severely water repellent while only 5 g/kg of SA made the modified SA-coated AAC become severely water repellent. The stearic acid agent is itself a carboxylic acid, which has a carboxyl group with flexible OH-bonds, while the AAC surface contains SiO4 tetrahedra, Si-O-Si, Al-O-Al, Si-O-Al, O-SiCax, and OH groups. They might create a cross-linking between hydroxyl groups easily on the surface of AAC. While for the oxalic acid agent, which contains mostly COOH-groups, the binding was weaker.

Table 3. Test results of SDM and WDPT for OA-coated samples.

Concentrations (g/kg)	SDM, α_i (°)	WDPT (sec)	Class
5	0	0	Non WR
10	0	0	Non WR
50	126	2400	Severely WR
75	130	> 3600	Extremely WR
100	136	> 3600	Extremely WR
200	132	> 3600	Extremely WR
250	139	> 3600	Extremely WR
300	142	> 3600	Extremely WR
500	143	> 3600	Extremely WR
750	143	> 3600	Extremely WR

Table 4. Test results of SDM and WDPT for SA-coated samples.

Concentrations (g/kg)	SDM, α_i (°)	WDPT (sec)	Class
5	98	3000	Severely WR
10	100	> 3600	Extremely WR

25	142	> 3600	Extremely WR
50	134	> 3600	Extremely WR
100	143	> 3600	Extremely WR
200	140	> 3600	Extremely WR
250	138	> 3600	Extremely WR
300	144	> 3600	Extremely WR
500	145	> 3600	Extremely WR
750	146	> 3600	Extremely WR

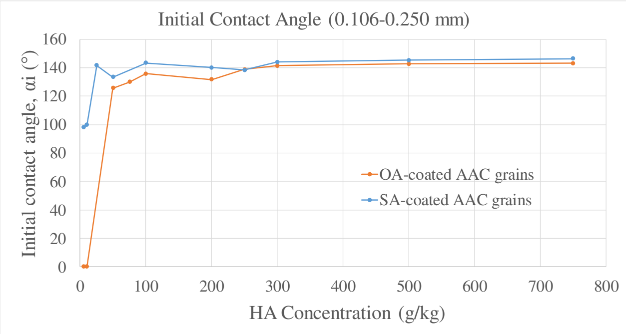

Fig. 4. Measured α_i values as a function of HA concentration.

It should be noted that the oily emulsion is quite hydrophobic and light in water. If the oil-contaminated water is put through the filtration bed filled with hydrophobic grains such as the SA- or OA-coated AAC, the repulsion shall be improved, which eventually increased the removal of oil from water.

4 CONCLUSIONS

Hydrophobicity for artificially hydrophobized AAC grains coated with OA and SA with different concentrations was assessed in the laboratory tests. The tested results showed the hydrophobized AAC grains in this study gave high α_i values (140–145°).

Nevertheless, the assessed hydrophobicity of tested samples was measured in the "solid-air interface". In order to evaluate the effectiveness of tested samples for the oil-water separation, further studies are needed to evaluate the performance in 'solid-liquid interface' by utilizing a column test under actual oily water flowing condition.

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