

Article

Contact angle and surface roughness of the imogolite membrane fabricated with different concentrations of humic acid

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Abstract

We fabricated a membrane from aqueous suspensions of imogolite and humic acid (HA) in order to apply the concept of contact angle to soil materials. This method enabled not only a direct observation of contact angles by the sessile drop method but also an analysis of surface roughness with an atomic force microscope (AFM). The membrane without the addition of the HA was found to achieve complete wetting. In contrast, the contact angle dramatically increased with an instant addition of the HA followed by a gradual increase with an increase of the HA concentration demonstrating a behavior of reaching a plateau. Results of the AFM analysis showed that the presence of the HA reduced the membrane surface roughness. From these two results, Wenzel's model rather than Cassie - Baxter's model can be utilized to describe tendency of dewetting of the surface of the fabricated membrane. In conclusion, dewetting of the fabricated membrane is mainly attributed to a hydrophobic characteristics of the HA rather than the membrane surface roughness.

Keywords: Imogolite, Humic acid, Clay membrane, Contact angle, Young's equation, Surface roughness, Wenzel's model

Introduction

Thermodynamic condition and movement of water at a solid surface of soils are major concerns in soil physics. In standard textbooks of soil physics (e.g. Yamazaki, 1977), a state of water retention of soil has been explained by using terminologies of interfacial science such as contact angle and surface tension. Contact angle is a useful index to describe water repellency and wettability of materials with a simple geometry. However, a direct determination of contact angle in soil along the lines of its principle is practically impossible because of a complicated shape and an inhomogeneous distribution of various materials in soil matrix surfaces. So far, several indirect evaluation methods of contact angles have been tested (DeBano, 2000). The water drop penetration time test has been commonly employed: to link water repellency of soil with its soil structure

(Bisdorn *et al.*, 1993); to classify wettability of soils with different hydrophobicity (Doerr, 1998); to assess effects of organic compounds, water content and clay on water repellency of a sandy soil (Leelamanie and Karube, 2007) and so on. The column wicking method indirectly gives contact angles on the basis of the speed of the capillary rise into a soil column (Ishiguro, 2003), whereas the thin-layer wicking method (a type of the Wilhelmy plate method) also provides contact angles on the basis of the speed of the capillary rise into a glass plate coated with soil colloids (van Oss *et al.*, 1992). Bachmann *et al.* (2000) proposed an application of the sessile drop method to powdered soil particles mounted on a glass slide by a double-sided adhesive tape. Shang *et al.* (2008) compared among these methods and showed their advantages and disadvantages. As seen above, there are some methods to measure wettability of soil. These

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conventional methods, however, can be used only for relative comparison with limited conditions or some assumptions. Actually, the concepts of interfacial science have not been fully utilized.

In the present study, we attempted to fabricate a flat membrane from suspensions of imogolite and humic substances in order to apply the sessile drop method, which is a standard measurement methodology of contact angles, to the surface whose roughness can be analyzed with an atomic force microscope (AFM). With this combination, the mechanism of humic substances to change wettability of the fabricated membrane is clearly demonstrated.

Materials and Methods

Imogolite

Imogolite was chosen as a membrane material because of its hollow fibrous structure. It is a hydrated aluminosilicate that characterizes a volcanic ash soil as well as allophane (Cradwick *et al.*, 1972; Levard *et al.*, 2012). A crude imogolite was sampled from a pumice horizon of a non-allophanic Andosol at Kitakami, Iwate Prefecture, Japan. The soil contains translucent membranous materials that mainly consist of imogolite, which can be easily visible to the naked eye (Figure 1). The soil was stirred with distilled water to float the translucent materials. The translucent materials were collected with a coarse sieve while plant fragments were carefully removed with tweezers. The translucent materials were twice immersed in a 5% hydrogen peroxide solution for six days at 80 °C to decompose organic constituents. After that, the residual hydrogen

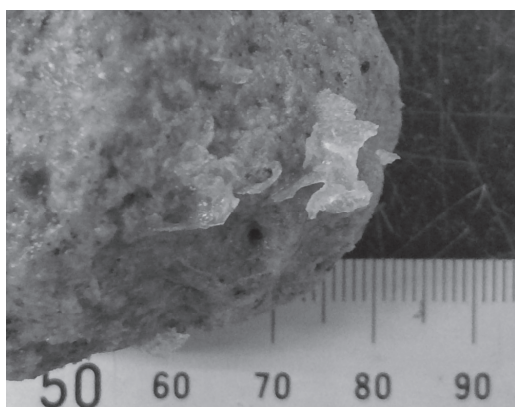


Figure 1. Translucent membranous materials in pumice soil. One division of the scale is 1 mm.

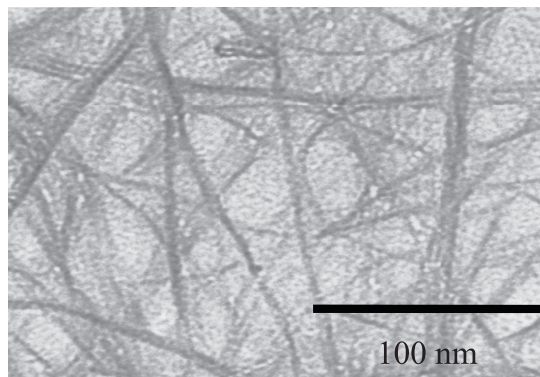


Figure 2. The purified imogolite observed with a TEM.

peroxide in the solution was boiled away for 30 min. The obtained suspension was acidified with a hydrochloric acid solution and carefully maintained pH 4–5 to avoid aggregation. The suspension was fractionated by centrifugal (H-103N, Kokusan) to obtain particles smaller than 500 nm in Stokes diameter. We hereafter refer to this fraction without iron oxide removal as the imogolite suspension. The imogolite suspension was mixed with a 4 M sodium chloride solution to have a volume ratio of 1:2 and stirred for 24 h three times to substitute exchangeable cations of imogolite with sodium ions. Then, it was dialyzed with a dialysis membrane until electric conductivity of its external solution fell below 1 $\mu\text{S}/\text{cm}$. Volume fraction of the imogolite suspension was adjusted to be 2.0 mg/L. We observed the obtained imogolite suspension with a transmission electron microscope (TEM) (JEM-100CX, JEOL Ltd.) according to the following procedure. A copper TEM grid was covered with formvar film. A thin layer of carbon was deposited onto the grid by evaporation coating. Hydrophilic treatment was made for the grid by ion sputtering. A small drop of the imogolite suspension was placed on the treated grid and dried. Figure 2 shows a TEM image of materials in the obtained imogolite suspension. We confirmed that the materials were the bundle of fibers and were similar to the literature (Karube, 1998); thereby the imogolite suspension was appropriately purified.

Humic acid

Aldrich humic acid (HA) was utilized as a model of soil organic matter. It was purified by the following procedure on the basis of Yamashita *et al.* (2013). About 30 g of the HA in a 400 mL of a 0.1 M

sodium hydroxide solution was shaken for 24 h and then centrifuged at 3,000 rpm for 30 min to remove humin. The supernatant solution was acidified to pH 1 by a hydrochloric acid solution and centrifuged at 3,000 rpm for 30 min. The obtained sediment was soaked in a mixed solution with 0.1 M sodium hydroxide and 0.3 M sodium chloride and shaken for 24 h. The sediment was again dissolved in a 0.1 M sodium hydroxide solution and the sequence of all the above procedures was repeated. The obtained solution was re-acidified to pH 1 and subsequent sediment was dispersed in an acid solution mixed with 0.1 M hydrochloric acid and 0.3 M hydrofluoric acid, and then shaken for 24 h. The sediment was dissolved in a 0.1 M sodium hydroxide solution and was sequentially passed through two ultrafiltration membranes (Macrosep, Pall Corp.) with 300,000 and 100,000 molecular weight cutoffs (MWCO). We chose this range of molecular weight because the dependencies of chemical and physicochemical properties of the same sample on molecular weight have been provided by Tanaka (2010) and Yamashita *et al.* (2013). The retentate left on 100,000 MWCO membrane was repeatedly washed with deionized water to remove sodium, chloride and fluoride ions added at the previous step until the electric conductivity of the filtrate fell below 50 $\mu\text{S}/\text{cm}$ and the color of the filtrate became almost clear, and then freeze-dried. The solution of 1 g/L HA was prepared as a stock solution.

Fabrication of imogolite membrane

The imogolite membrane was fabricated by the following procedure. The imogolite suspensions that contain 0.20 mg/L imogolite and 0 to 540 mg/L HA were prepared and shaken for 24 h to adsorb HA on imogolite. During the shaking, their pH was kept at 4.8 to avoid aggregation. No sedimentation of the

HA was visually confirmed. After that, 10 mL of each suspensions were filtered with a suction filtration apparatus so that imogolite fibers could accumulate onto the membrane filter (GVWP02500 ; Millipore) whose diameter was 25 mm and pore size was 0.22 μm . Each imogolite-accumulated filter membrane was fixed on a glass slide with a double-stick tape and dried in desiccator for more than 12 h. Figure 3(a) shows an appearance of the fabricated imogolite membrane, which its color turned light brown because of the presence of imogolite. We also confirmed from the Figure 3(b) that the fabricated membrane was flat enough to put a droplet on its surface.

Measurement of contact angle

An aliquot of 2 μL of distilled water was put on the imogolite membrane from heights of 5 mm with a syringe that connected an electric syringe pump. A sequence of the instillation of a droplet was recorded with a CCD camera. The contact angle of the droplet was determined just after an oscillation of the droplet subsided. The mean value of the contact angle was calculated from two observed data. The temperature was maintained at 20 $^{\circ}\text{C}$ during the measurements. The contact angle of membrane filter itself was 0 $^{\circ}$.

The Young's equation expresses the relationship between a shape of droplet on a flat uniform solid surface and three kinds of interfacial tension

$$\cos \theta_E = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \quad (1)$$

where θ_E is an angle between a flat solid surface and a tangent line from a contact point to an air-liquid interface, hereafter referred to as the Young's contact angle, γ_S is a solid/air interfacial tension, γ_{SL} is a solid-liquid interfacial tension and γ_L is a liquid-air interfacial tension (Adamson & Gast, 1997). If a

surface is rough, we don't directly obtain Young's contact angles by experiments. When a surface area of contact surface becomes R -times larger than its projected area because of its surface roughness, one must multiply R by the γ_S and γ_{SL} in eq. 1. Hence the Young's

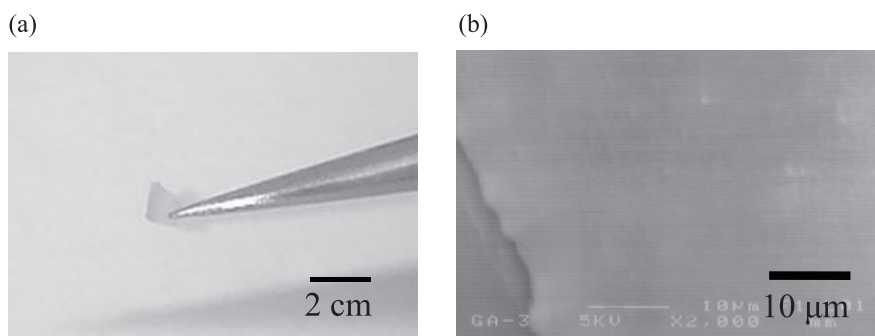


Figure 3. (a) appearance of the imogolite membrane and (b) SEM image.

equation is modified as

$$\cos \theta_R = R \frac{\gamma_S - \gamma_{SL}}{\gamma_L} = R \cos \theta_E \quad (2)$$

where θ_R is an apparent contact angle, which one can obtain as an experimental value, on a rough surface. From a practical perspective, we can only observe an apparent contact angle, θ_R , by the sessile drop method, and the ratio of actual area to projected area, R , by an AFM measurement. Therefore, we can only estimate as to the Young's contact angle by using eq 2, which is known as the Wenzel's model (Wenzel, 1936). According to this model, one can say that contact angles are sensitive not only to its hydrophobicity/hydrophilicity but also to roughness of a solid surface. This model also indicates that $\theta_R < \theta_E$ when θ_E is less than 90° (hydrophilic surface), whereas $\theta_R > \theta_E$ when θ_E is more than 90° (hydrophobic surface). That is to say, a surface roughness always magnifies the underlying wetting properties. For hydrophilic surface, it is recognized that this modified expression can only be applicable to the situation that a liquid completely contact with a surface and $\cos \theta_E$ is in the range of 0 to approximately $1/R$ (de Gennes *et al.*, 2004). Otherwise, the Cassie-Baxter's model is utilized (Cassie and Baxter, 1944). Actually, Shibuichi *et al.* (1996) demonstrated that the Wenzel's model was inapplicable when $\cos \theta_E$ was close to 1 (θ_E was close to 0°) in the case of hydrophilic surface.

Surface roughness and actual surface area of the membrane

Surface roughness profiles of the imogolite membranes fabricated with 0, 180 or 540 mg/L HA were obtained with a tapping mode AFM (Dimension 3100, Veeco). The scan rate of the AFM was set at 0.5003 Hz. The scan area was $10 \mu\text{m} \times 10 \mu\text{m}$. The roughness average (Ra) is obtained from

$$Ra = \frac{1}{L} \int_0^L |Z(x) - \bar{Z}| dx \quad (3)$$

where the $Z(x)$ is the height at position (x) of a sample over the evaluation length L and \bar{Z} is the average of the height. Thus the value of Ra means the arithmetic mean of the absolute deviation of height in a sampling length. The actual surface area for the field of view was also evaluated from the obtained profile of peaks and valleys. The value of R

in the Wenzel's model can be calculated from the ratio of the actual surface area to $100 \mu\text{m}^2$ projected area.

Results and Discussion

Figure 4 depicts the apparent contact angle of the water droplet on the imogolite membrane as a function of concentration of the HA added in the fabrication step. In the case of no addition of the HA, the apparent contact angle became zero, i.e. the complete wetting. This result demonstrated that the imogolite itself had a high affinity for water. Iwata *et al.* (1989) conducted the experiment of water vapor adsorption by allophane. They demonstrated that the allophane achieved complete wetting when a relative vapor pressure was at least 1% and had hydrophilic surface. According to their result, the hydrophilicity of the imogolite also arises from the polarities of its hydroxyl groups that are present on its aluminosilicate surface. In contrast, the apparent contact angle appeared in the case of the membranes fabricated with the HA. The apparent contact angle gradually increased with an increase of the HA up to 270 mg/L and remained constant above the threshold. Such a change of wettability of the fabricated membrane was apparently due to the adsorption of the HA on the imogolite surface. The plateau can be caused by saturated adsorption. The change from the complete wetting ($\theta = 0^\circ$) to the partial wetting ($\theta > 0^\circ$) by the presence or absence of the HA can be explained with the spreading parameter S , which measures the difference between the surface energy per unit area E of the solid surface when they are dry and wet

$$S = E_{dry} - E_{wet} = \gamma_S - (\gamma_{SL} + \gamma_L) \quad (4)$$

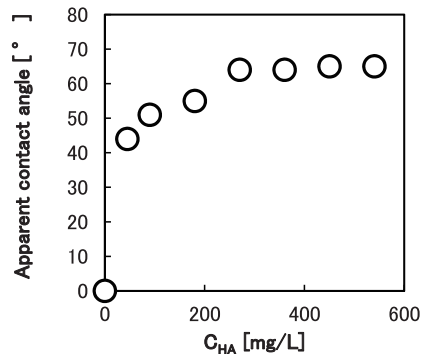


Figure 4. Apparent contact angle of the imogolite membranes as a function of the additive amount of humic acids.

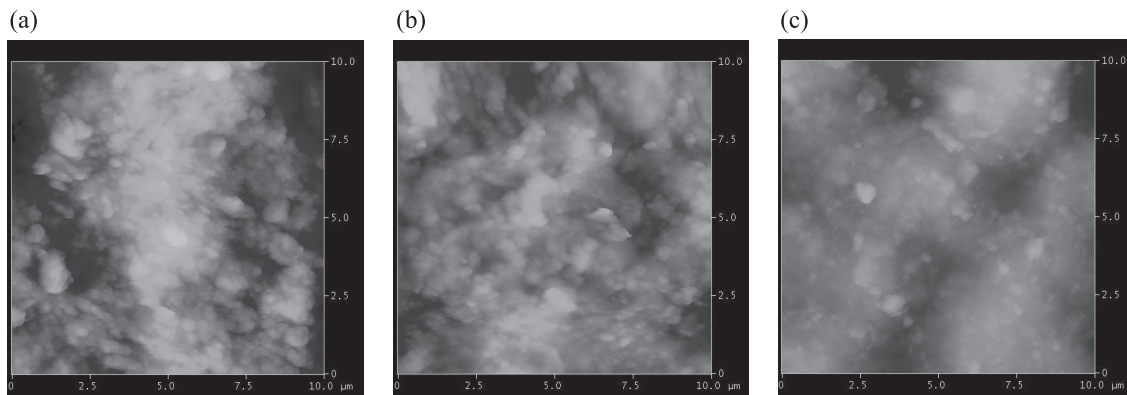


Figure 5. The image of the imogolite membrane surface with different concentrations of a humic acid (HA), which was observed by an AFM: (a) 0 mg/L HA, (b) 180 mg/L HA and (c) 540 mg/L HA. These pictures are 10 μm on a side.

A complete wetting achieves when $S > 0$ ($E_{dry} > E_{wet}$), whereas a contact angle appears when $S < 0$ ($E_{dry} < E_{wet}$). In our case, the value of S became negative when the membrane contained the HA. This sign inversion means that the HA caused the reduction of E_{dry} (or γ_s), which is equivalent to a tendency for a decreased area of their solid-liquid interface, so-called dewetting (de Gennes *et al.*, 2004). It is well known that humic acids have aromatic nuclei and long-chain hydrocarbon in their molecular structure, where they contribute to their hydrophobic characteristics (Stevenson, 1994). Meanwhile, they also have hydrophilic group such as carbonyl group. Tanaka (2012) showed the solid-state ^{13}C NMR spectra of the same HA sample that passed through the 100,000 MWCO ultrafiltration membrane. He calculated the integrated areas for the selected regions of the chemical shift (ppm) to assign the carbon structure of the HA to distribution of functional groups; 50% of aliphatic carbon (10–50 ppm), 7.0% of *o*-alkyl (50–100 ppm), 22% of double-bonded carbon (110–160 ppm) and 20% of carbonyl group (160–220 ppm), which clearly showed amphiphilicity of the HA sample. From this result, it is reasonable to support that the adsorbed HA turned its hydrophilic structure toward a hydrophilic surface of imogolite and therefore its hydrophobic structure faced to liquid phase. Hence, the imogolite membrane became more hydrophobic when the HA was added. Actually, the occurrence of the apparent contact angle of the HA-imogolite membrane implied that the membrane with the HA was more hydrophobic than that without HA, and its dewetting can be partly attributed to the hydrophobic characteristics of the HA.

Table 1 The surface roughness parameter of the imogolite membrane, apparent contact angles and the Young's angle estimated by the Wenzel's model.

C_{HA} [mg/L]	R_a [nm]	Actual surface area for 100 μm^2 [μm^2]	R [-]	l/R [-]	θ_R [$^\circ$]	θ_E [$^\circ$]	θ_E - θ_R [$^\circ$]
0	120	120	1.20	0.83	0	N/A	N/A
180	71	111	1.11	0.90	55	58.9	3.9
540	60	105	1.05	0.95	65	66.3	1.3

As mentioned in the materials and methods section, contact angles are subject to surface roughness as well as hydrophobicity. We now discuss an influence of a membrane surface roughness on contact angles. Figure 5 illustrates the AFM images of the imogolite membrane fabricated with 0, 180 or 540 mg/L HA. The luminance contrast decreased with an increase of the HA concentration. This difference qualitatively showed that the membrane was smoothed because of the HA adsorption. Table 1 lists the surface roughness parameters estimated by the AFM measurement. The R_a values revealed that the height of the roughness of the membrane was in the range from several tens to a hundred of nanometers. The decrease of the R_a values with increasing the addition of HA quantitatively proved that the HA had a capability to make the surface smoother. Such an effect reminds us of a fabric softener whose amphiphilic ingredients can lubricate rough clothing fibers. In a similar way, the HA could act as a softener detergent to the frayed imogolite fibers so that the imogolite fibers interweave each other and made smoother. The actual surface area was greater than the projected area of the field of view (100 μm^2) in all cases. The actual surface area with no addition

of the HA was the largest, and it became smaller with increasing of the addition of the HA. From the obtained values of actual surface area, the value of R can be calculated. Simultaneously, we can estimate the Young's contact angle θ_E by substituting the experimental values of R and θ_R into the eq 2. As stated in the materials and methods section, the Wenzel's model has limitation in the application ($0 < \cos \theta_E < 1/R$). In our case, the applicable conditions were calculated as $34^\circ < \theta_E < 90^\circ$, $26^\circ < \theta_E < 90^\circ$ and $18^\circ < \theta_E < 90^\circ$ for the membrane with 0, 180, and 540 mg/L HA, respectively. Therefore, our results can be applied to the Wenzel's model except for the case of no addition of the HA. The values of θ_E estimated by the Wenzel's model are shown in the Table 1. These values mean the contact angle of the surface whose roughness effect was eliminated. That is to say, the value of θ_E represents only hydrophobic effect. On the other hand, the difference between Young's and apparent contact angle ($\theta_E - \theta_R$) indicates the effect of surface roughness on the contact angles. The changes of contact angle induced by their surface roughness were determined as 3.9° and 1.3° , which corresponded to total increase of 7.0% and of 2.0%, for the membrane with 180 mg/L HA and 540 mg/L HA, respectively. As a result, we can conclude that the surface roughness has a lower impact on wettability of the membrane than the hydrophobic characteristics of the adsorbed HA.

Conclusions

We investigated contact angle and surface roughness properties of the imogolite membrane fabricated with different concentration of the HA. The contact angle without the addition of HA achieved complete wetting while the apparent contact angle increased with an increase of the concentration of HA up to approximately 70° . The reason for the appearance of dewetting of the imogolite-HA membrane was discussed in terms of the change of interfacial tensions and surface roughness. The transition of wettability by the presence or absence of the HA indicated that the adsorption of the HA can change the imogolite membrane into less hydrophilic surface. On the other hand, the influence of the membrane surface roughness on the wettability was analyzed with an AFM. The Wenzel's model combined with the obtained data represented that the membrane surface

roughness had a little effect on dewetting in the present case. Through the results of analyses of the contact angle and the surface roughness, we conclude that the tendency for dewetting of the imogolite-HA membrane is chiefly ascribed to a hydrophobic characteristics of the HA that was adsorbed on the imogolite surface rather than its surface roughness. The imogolite membrane made in the present study allows us to directly measure contact angles and demonstrate a possibility of a promising material to get more understanding of wetting phenomena of soils.

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