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Gelation Properties of Nano-tube Imogolite: Potential Application as Herbal Delivery Material

Zaenal Abidin¹*, Oliviantini Rahmadani¹, Impron², NugrahaEdy Suyatma³, Nurul Hiedayati⁴, and Naoto Matsue⁵

¹Department of Chemistry, Bogor Agricultural University, Bogor, 16680, Indonesia
²Department of Geophysics and Meteorology, Bogor Agricultural University, Bogor, Indonesia
³Department of Food Science, Bogor Agricultural University, Bogor, Indonesia
⁴Department of Pharmacology, Islamic State University, Jakarta, Indonesia
⁵Faculty of Agriculture, Ehime University, Japan

*Email: abidinzed@apps.ipb.ac.id

Abstract. Imogolite is known as variable charge aluminosilicate mineral which physicochemical properties depend on the pH solution. Dispersion and gelation properties can be adjust by change in pH solution. However, the effect of solvent on the physicochemical properties of imogolite is almost no information. Here, we studied on effect of length tube imogolite and type of solvent on its dispersion and gelation behavior. Guava extract has been used as herbal model and loaded into imogolite suspension. These results obtained important information that the length of the tube imogolite greatly affects the quality of the gel formed. The changes in the distribution of solvent polarity in certain level will affect the force of inter-surface repulsion in imogolite. Under organic solvent, formation of the gelation is not influenced by the pH solution. The obtained data is interesting because until now there is no information on the dispersion and gelation properties of imogolite in the organic solvent. Furthermore, gelation of imogolite is easily formed by addition of extract herbal into imogolite suspension. Therefore, imogolite can be used as herbal delivery material.

Keywords: imogolite, gelatin-like, guava leaf, dispersion, delivery.

1. Introduction
The discovery of fullerene nano ball and carbon nano tube had accelerated rapid development of nano scale materials [1,2]. Imogolite is nano-sized aluminum silicate with tubular morphology that exists in various soil environments. It had already been found in the soil environment long time before carbon nanotube was discovered [3]. However, imogolite research is still less developed compared to the development of other nano-materials. One of the main reasons is that imogolite cannot be synthesized
except in the dilute parent solution resulting in low yield of product. Other reason is application of imogolite still limited even it has unique structure and physico-chemical properties.

Imogolite has nano-tubular structure having inside diameter of 1.0 nm and outside diameter of 2.0 nm with a well-defined fibrous electron-diffraction pattern indicating that the tubes are uni-dimensional crystals. These tubes may be several hundred to thousand-nano meters in length. The basic structure of imogolite is built up largely of a gibbsite sheet, with orthosilicic acid coordinated from inside via oxygen of the three Al atoms with a Si/Al ratio of 0.5 [4]. The structure of imogolite is shown in Fig. 1. Imogolite also can be synthesized from chemical reagent including Si/Al.

Basically imogolite has three physical forms of suspension, gelation, and dried thin-film. The most important physical form of imogolite is suspension and gelation because the synthesis of imogolite product is in the form of clear suspension without any precipitation. The quality of imogolite synthetic is very easy to recognize by formation of gelatinous from suspension by addition of ammonia solution. Even the quality of the synthesis product is also easily seen by naked eyes from the level turbidity of suspension and the formation of white precipitate [5]. Imogolite also is easily form to be thin-film on dry condition, however the film cannot be transformed again become suspension or gelation form.
Imogolite is known as variable charge aluminosilicate mineral which surface properties depend on the pH value of the solution. Surface of imogolite are dominated by aluminol and silanol functional groups as positive and negative charge, respectively. The zero point charge of natural imogolite is around pH 7 [6]. Aluminol functional group is located in the mouth of tube as broken edge. Anion and ligands such phosphate ion is easily attached to the functional group strongly. While the inner surface along of the tube there are many silanol functional groups that can be negatively charged.

However, the negatively charged functional group cannot effectively bind the cation because the cations are difficult move to more inside tube due to blocking by other cation. For the outer surface of the tube, there are no functional groups which can bond chemically either cation or anion. Whereas water molecules are easily bonded strongly on both outer and inner surface the tube.

This study aims to study on dispersion and gelation properties of imogolite in organic solvent and to develop the application of imogolite as herbal delivery material.

2. Experimental
2.1 Materials
2.1.1 Imogolite samples
Solid silica was mixed with distilled water and put in to the dialysis membrane tube [7]. Then, the membrane was immersed into the bottle containing distilled water adjusted to a pH of 8.0 and aged at 70°C for two days. The amount of silicon in the solution was measured using Polarized Zeeman Atomic Absorption Spectroscopy (Hitachi Z-5000, Tokyo Japan) in nitrous oxide-acetylene flame. After the amount of soluble silicon species in the supernatant was measured the solution was diluted and used for the synthesis process.

Aliquots of AlCl₃ solution were simultaneously mixed with orthosilicic acid to yield Si/Al ratio of 0.5. The solution mixtures were titrated with NaOH at a rate of about 0.5 mL NaOH min⁻¹ to an OH/Al molar ratio of 2. The Si concentration of the resulting solution was 1.6 mM. All the parent solutions had pH in the range of 3.98 to 4.03. The solution mixtures were heated in an autoclave at 100°C for 6 and 24 hours. Heating for 6 and 24 hours was carried out to obtain short and long imogolite samples.

After the collected precipitates were flocculated by sodium chloride, the sample was dialyzed using cellulose tubes against distilled water until they were free of sodium and chloride ions. All of mineralogical and morphological products have been subjected by XRD (RigakuMiniflex) analysis and Scanning Electron Microscopy (SEM Hitachi High Technology S-800).

2.2 Methods
2.2.1. Gelation and measurement of weight gel. The properties of dispersion and gelation of imogolite was studied by adjusting the pH value of 5 or 8 in 1 ml of the imogolite suspension. In suspension contains 0.3 mg of imogolite. After the pH was adjusted by dropping 0.05M NaOH or HCl solution, the suspension was shaken by hand and left for 1 hour. Dispersion and gelation properties were observed and then the mixture was weight. To obtain gel, centrifugation was carried out for 2.5 minutes at 10000 rpm. The supernatants liquid was discharged and the gelation remain was weight. A fraction of the weight of the gelation imogolite or mixture an the initial solution was calculated as the degree of gelation by

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\text{Gelation} (%) = \frac{\text{Remained gel weight (g)}}{\text{Initial mixture weight (g)}} \times 100
\]

2.2.2. Extraction of Guava Leave. In this study, guava leaf was extracted using maceration method. This method was carried out at room temperature by soaking the powder of the plant sample using an
ethanol 30% as solvent. Here we used filtrate of guava extract as herbal model to know the dispersion and gelation properties. Guava extract was added into long imogolite with the ratio between long imogolite and extract of 1:10 in the mixture. Dispersion and gelation properties were observed and then the mixture was weight. To obtain gel, centrifugation was carried out for 2.5 minutes at 10000 rpm. The supernatants liquid was discharged and the gelation remain was weight.

3. Result and Discussion

3.1 Dispersion and gelation properties of imogolite in water

The products of hydrothermal reaction were clear suspension and the final pH after reaction was pH 3 for all samples. Figure 2 showed SEM image of the synthesized imogolite with various heating time. Imogolite can be synthesized by hydrothermal reaction for 6 hours with short tubes. Increasing in time reaction, the product was longer tube of imogolite. Also, the diameter of bundles is different for those samples. XRD pattern results confirmed that all of samples were imogolite without any impurities inside (data is not shown).

The properties of gelation and suspension of imogolite is influenced by several factors such as pH, tube length, type of solvent and impurities. Under the pH 5 condition, all imogolite samples are in the form of a stable suspension without forming a gelation or precipitation. The absence of precipitation at pH 5 indicates that the quality of the imogolite samples used has a high purity. Figure 3 showed the stable dispersion and gelation of imogolite samples.
3. shows stable dispersion and gelation of imogolite samples in water solution.

Gelation occurred in two types of imogolite when the addition of alkaline solution into the imogolite suspension to make pH solution of 8. However, the degree of gelation formation in the two samples is different where the longer tube has higher gelation rate compared to shorter one. The degree of gelation obtained for short and long imogolite are 11% and 25%, respectively. Figure 4 shows the degree of gelation imogolite at several pH values with various tube lengths in water solution.

At a pH less than 7, imogolite is perfectly dispersed as a stable suspension. Under acidic pH conditions, the imogolite surface will be dominant in the positive form because the aluminol functional groups are bind H⁺ ions in the form of AlOH⁺. The positively charge surface makes repulsion one to the other tubes and dispersed perfectly resulting in a stable suspension. In acidic condition also, the impurities contained in the synthetic product are easily separate with imogolite by decantation.

Under alkaline pH condition, the imogolite suspension changes to a stable gel that is easily observed. Increasing in the pH of solution causes the positively charged aluminol functional groups to release H⁺ ion and the surface of imogolite become neutral. Although the surface becomes neutral and there is no inter-surface repulsion, a stable gel can be formed easily because imogolite has tubular structure. The gel form of imogolite is very interesting because the amount of water molecule contained in the gel is very small.

The properties of gelation imogolite at alkaline pH solution are very different compared to the hydrogel organic polymer. As been known that hydrogel polymer is synthesized by several starting materials and formed three-dimensional network. These hydrogel structures consist of the main chain and cross linkage structure, in which the water molecule is trapped between three-dimensional networks. Water molecules are strongly adsorbed and slowly released from hydrogel. Gelation imogolite does not have high viscous and water molecules are easily separated by centrifugation.

In the case of imogolite hydrogels, the main component is only imogolite and affected by the length of tube. The network between of imogolite is made up by entanglement among tube without any regularity. The network also depends on the length of tube and the concentration of imogolite in the gel. The water molecules are trapped between the imogolite tubes with the other tubes interacting...
through the hydrogen bonds facilitated by the hydroxyl ion. Some hydroxyl ions will interact to hydrogen atoms at the vacant octahedral of Al-O-Al in the outer part of tubes.

This strong interaction will induce formation of gelatin-like form which many water molecules adsorbed among tubes. In the other word, water molecules and hydroxyl ion act like cross linkage agents via hydrogen bonding to hydrogel form. The longer the lengths of the tube are the larger surface area therefore the space where water molecules adsorbed are larger.

3.2 Dispersion and gelation properties of imogolite in ethanol solvent

In this study used ethanol as organic solvent because ethanol is often used in extracting herbal plant to obtain active compounds for herbal medicine. Figure 5 shows stable dispersion of imogolite samples at pH 5. Figure 6 shows the degree of gelation imogolite in several pH values with various tube lengths and ethanol solvents. The addition of ethanol 30% and 96% solvent to the pH 5 of short and long imogolite resulted in differences in the dispersion and gelation properties compared with the conditions in the water solvent. The addition of ethanol 30% into imogolite suspension indicate that short imogolite was still dispersed while formation of gelation was appeared for long imogolite. However, the gelation was not stable and difficult to separate with its suspension when centrifuged.

![Figure 5 Stable dispersion and gelation of imogolite samples in ethanol 30% and ethanol 96% solvent at pH 5 (left) and pH 8 (right).](image-url)
It is clear that changes in the solvent composition from water to ethanol make the distribution of polarity solvent and positive charge strength on the surface of imogolite change gradually. Theoretically in imogolite, the short tube contains more positive charge than long tube, so that the change in the solvent composition does not affect the force of repulsion between the positive charges on the surface. Thus, the short imogolite was still dispersed stable and difficult to be separated by centrifugation.

Whereas in the long imogolite, the positive charge on the surface is less so that the change in the distribution of polarity on the solvent give more affects in the strength of positive charge. The degree of gelation obtained for long imogolite is 15%. Interaction between ethanol molecules with positive charges on the surface via hydrogen bond is likely to change the hydration shell form. Therefore, the possibility and the force of repulsion between positive charges on the surface decreased.

Furthermore, the results obtained on the addition of ethanol 96% into imogolite suspension provided more clear on the differences of imogolite in the two types of imogolite. The ethanol 96% solvent makes the distribution of polarity solvent and positive charge strength on the surface of imogolite change totally. So the formation of gelation can more easily occur in both types of imogolite even in the acid conditions. The degree of gelation obtained for short and long imogolite are 10% and 25%, respectively.

As been explained before that under alkaline pH condition, the imogolite suspension changes to a stable gel because causes the positively charged aluminol functional groups is neutralized and the surface of imogolite become neutral. The addition of ethanol 30% solvent to short and long imogolite suspension in pH 8 resulted formation of gelation and stable which easily separated from suspension by centrifugation. The degree of gelation obtained for short and long imogolite are 8% and 20%, respectively. While the addition of ethanol 96% at pH 8, the degree of gelation obtained for short and long imogolite are 6% and 16%, respectively. The changes in the distribution of solvent polarity in certain level will affect the force of inter-surface repulsion in imogolite and accelerate formation of the gelation that is not influenced by the pH value of the environment.

From the overall results shows that the longer of tube imogolite is more easily formed gel compared to short one. Also, the degree of polarity solvent gave affect in the quantity of gelation formed. The decrease in the polarity of solvent was followed by the decrease in the degree of gelation imogolite. It can be explained that the water molecules or ethanol are trapped between the imogolite
tubes with the other tubes interacting through the hydrogen bonds facilitated by the hydroxyl ion. The strength of hydrogen bond depends on the polarity of solvent. Water molecules can form stronger hydrogen bonding than ethanol molecule. Therefore, the quantity and stability of gelation imogolite is higher in water solution. The obtained data is interesting because until now there is no information on the dispersion and gelation properties of imogolite in the organic solvent.

3.3 Potential application as herbal delivery material

One of the challenges for application of herbal medicine is the solubility of extracts and its bioavailability. Several factors to consider in the selection of solvents include evaporation rate, viscosity, environmental impact, health impact, and solvent effectiveness [8]. Based on these factors, water and ethanol 30% are often selected as solvents to extract herbal medicine plant to obtain active compounds because of both solvents has low health impacts.

Previous data shown that the addition of ethanol 30% solvent into imogolite suspension did not form a stable gelation. However, addition of herbal extract in ethanol 30% into long imogolite suspension under pH 5 condition result in gelation form. The ratio between imogolite and extract was 1:10 in the mixture. It means that extract herbal is main components in the mixture. The results may explain that the imogolite can act as a stabilizer or an emulsifier. After centrifugation, gelation of imogolite-extract was easily separated from filtrate and the degree of gelation was 45% (Figure 7).

Also, it is possible because the extract contains multi component compound that can interact strongly to the surface of imogolite. Phytochemistry analysis showed that guave contains some compounds such as phenol, steroid, triterpenoid, saponin and tannin. These compounds has possibility to interact with the surface of imogolite. The extract would be trapped into the intertubes and the gap between the imogolite tube bundles. However, the extract can not enter into the inner surface of tubular imogolite because this part is very small with a diameter of 1 nm.

From these results, we can find potential application for imogolite from gelation property as herbal delivery material. The gelation of imogolite has formed as the physically cross-linked gel via hydrogen bonding intertubes. The properties of gelation form is low viscous or thixotropic therefore imogolite can be applied as topical uses.
4. Conclusion
Imogolite can be synthesized in various sizes of length by controlling heating duration time. By adjusting pH solution, imogolite can be form a stable suspension or gelation. Characteristic of imogolite gel depends on purities of imogolite, the length of the tubes and polarity of solvents. Addition of imogolite on extract herbal can form stable complexes. Imogolite can be used as herbal delivery material.

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