A Comparison Study of Magnetic Stirrer and Sonicator Technique to Disperse 1% Span20 Treated Layered Double Hydroxides (LDHs)

S Teanmetawong¹, T Chantaramanee¹, S Lhosupasirirat¹, A Wongariyakawee⁴ and T Srikhirin¹, ², ³

¹ School of Materials Science and Innovation, Faculty of Science, Mahidol University, 999 Phutthamonthon Sai 4 Road, Salaya, Nakhon Pathom 73170, Thailand
² Physics Department, Faculty of Science, Mahidol University, Bangkok, 10400, Thailand
³ NANOTEC Center of Excellence, Mahidol University, Bangkok, 10400, Thailand
⁴ SCG Chemicals Co., Ltd., Siam Cement Road, Bang Sue, Bangkok, 10800, Thailand

toemsak.sri@mahidol.ac.th

Abstract. Effect of particle size reduction and dispersion of 2-dimensional material, layered double hydroxide (LDHs), prepared by co-precipitation method with the primary particle size of around 100 nm, was investigated. Two simple laboratory dispersing techniques including magnetic stirrer, and sonicator were applied to disperse agglomerated LDHs in 1 wt.% Span20 solution, act as a stabilizer. Magnetic stirrer showed a cluster of agglomerate particles with improved dispersion while, agglomerates with single stack LDHs were presence in case of sonicator product.

1. Introduction
Layered double hydroxides (LDHs) have a layered like structure as aluminosilicate or clay minerals. LDHs consist of a stack of positively metal hydroxide sheets. This charge is neutralized by interlayer anions solvated with water molecules in the interlayer. The chemical composition of LDHs structure can be written as \([\text{M}^{2+}_{1-x} \text{M}^{3+}_x (\text{OH})_2] \times [\text{A}^{n-}]_{\text{z}n/2}\text{H}_2\text{O}\) where \(\text{M}^{2+}\) and \(\text{M}^{3+}\) refer to divalent and trivalent metal cations, respectively. \(\text{A}^{n-}\) represents anion [1], [2]. For a large-scale production, LDHs were synthesized by co-precipitation method which LDHs were generated by precipitation from mixture of metals salt and intercalated anions solution [3].

In order to disperse LDHs particle in organic solvent, surfactant is used for rendering hydrophobicity to LDHs particles. To achieve homogenously fine colloidal dispersion, the agglomerate LDHs should be broken down and stabilized with proper type of surfactant. Thus, breaking down the large agglomeration without destroying the integrity of plate like particles and increasing interaction forces between LDHs are needed. There are several reported approaches which can be used to disperse nanoparticle. However, turbulence technique was reported to assist the adsorption of additives on fragments of the nanoparticles [4]. Magnetic stirrer provides a mechanical force through the rotating of permanent magnetic field to...
induce the movement of the magnetic bar that immersed in the suspension. Sonicator uses an ultrasound irradiation to agitate the fluid, water, normally, by bubbled cavitation effect [5]. These bubbles collapsing creates energy with combined high pressure and temperature.

In this study, the reduction of agglomerate LDHs to LDHs stacking, individual plate like structure of LDHs, using magnetic stirrer and sonicator were investigated. Span20, an industrial non-ionic surfactant type with the chemical formulation of C_{18}H_{34}O_{6}, was used as the stabilizer, figure 1a. Span20 possesses hydrophilic-lipophilic balance (HLB) value of 8.6 was used as stabilizer to prevent re-agglomeration [4].

Figure 1. (a) molecular structure of Span20, (b) magnetic stirrer and (c) sonicator model

2. Materials and methods

2.1 Materials

Unmodified surface LDHs wet cake with primary particle size, approximately 100 – 200 nm, was used as raw material and was kindly supplied by SCG Chemicals Co., Ltd., Thailand. Span20 was purchased from LobaChemie Pvt., Ltd., Mumbai, India. Methyl Ethyl Ketone or Butanone (MEK) was purchased from RCL Labscan.

Reversed Osmosis (RO) water was produced by 50 GPD auto flash (Unipure, imported by Function International Co., Ltd., Bangkok, Thailand). Magnetic stirrer was carried out by using laboratory hotplate stirrer (HTS-1003, LMS, Tokyo, Japan). Sonicator (S 70 H, Elmasonic, Singen, Germany) with fixed power at 70 W was used.

2.2 Sample preparation and dispersion

1 wt.% Span20 was mixed with 200 mL RO water at room temperature. Suspension of 5 wt.% LDHs wet cake was added in Span 20 solution. The mixture was stirred for 2 hours at room temperature. For sonicator dispersion, the suspension was mixed, stirred 1 hour and sonicated for 1 hour. The sample obtained from both techniques was separated by using centrifuge and dried in an oven at 80 °C, yielding treated LDHs powder.

2.3 Characterization

The dispersion test was carried out by redispersion of treated LDHs powder in MEK with 0.0625 wt.% and placed in sonicator for 30 minutes. The particle morphology and its distribution were observed by field emission scanning electron microscope (FE-SEM SU8010, HITACHI, Japan). Ultraviolet-visible spectroscopy (Cary 60 UV-vis, Agilent Technologies, USA) was used for monitoring the transmission of the suspension. Particle size distribution was measured by Zetasizer Nano ZS (Malvern, UK) with the measurement angle of 173° backscatter. Fourier-transform infrared spectroscopy (FTIRNICOLET 6700, Thermoscientific, USA) with ATR mode was used for identifying the existence of Span20 on LDHs. The
scanning range was from 4000 – 650 cm\(^{-1}\) wavenumber with %transmission as Y-axis. Number and resolution of scan was set as 6.4 and 2, respectively.

3. Result and discussion

3.1 Raw LDHs characteristic

![Figure 2](image)

**Figure 2.** (a) FE-SEM image and (b) particle size distribution curve of raw LDHs dispersed in MEK

Figure 2a, showed a FE-SEM image of as received LDHs. Agglomerate LDHs were found with dense packing and poor dispersion in MEK. Particle size is ranging from a few micrometers down to 100 – 200 nm. They were the agglomerate of the primary particle size. Particle size distribution (PSD), figure 2b, was a tri-modal broad distribution ranging from a few hundred nanometer up to micrometer range.

3.2 Comparison of two dispersing techniques

Figure 3a showed the appearance of 0.0625 wt.% LDHs suspension of as received LDHs and Span20 treated LDHs by stirrer and sonicator. The background cannot be seen in raw LDHs sample where the lowest %transmittance was obtained from UV-vis spectra due to the scattering of the agglomerate LDHs, figure 3b. For stirred and sonicated sample, a higher %transmittance can be observed with a clearer background. Unexpectedly, higher %transmittance was found in stirred sample. The transmission is a direct variation to the particle size distribution. The lower transmission in all wavelengths indicated a lower level of transmission of the light due to the light scattering of the suspended particle. The level of transmission was quantified in figure 3b.

Figure 4 showed FE-SEM images of 1 wt.% Span20 treated LDHs prepared by using stirrer and sonicator. Particle size reduction and Span20 treatment promoted a better dispersion and size reduction when compare to raw LDHs. It can be seen that, there were still large agglomerate particles or cluster around submicron range in stirred sample, figure 4a. Magnetic stirrer cannot completely disintegrate large agglomerate particles into the smaller particle. Individual LDHs stacking could not be obtained by stirrer. For sonicated sample, large agglomerate particles and smaller particles were found in all the area, figure 4b.
This correspond to the particle size distribution from DLS, figure 4c. Agglomerate was still found in all samples, before and after dispersing process. Multimodal distribution peak scan was found in stirred sample, which meant there were variation of particle size. Agglomerate particles in stirred sample were found in similar size to the prior dispersing process. The agglomerate size of sonicated sample was reduced where both fine and coarse particles were observed. This might be attributed to the sonicator can only scour the surface particles from the agglomerate particles [6], resulting in individual LDHs stacks with agglomerates. However, agglomerates cannot be broken further because long sonication time may induce re-agglomeration [6].

From FTIR spectra, figure 5, there were a broadband from O-H vibration, water molecule bending and a sharp band from intercalated carbonate molecules appeared around 3420, 1620 and 1364 cm⁻¹ wavenumber in all samples. The characteristic bands of LDHs were also observed at 430 and 560 cm⁻¹ which attributed to the lattice vibration of M-O and M-O-M, respectively [7]. After dispersion, it can be confirmed that Span20 appeared on LDHs particle from both techniques. Seeing that, there are CH stretching, C=O and C-O-C which are characteristic peaks of Span20, located approximately at 2850 – 3000, 1650 – 1800 and 1180 – 1200 cm⁻¹ wavenumber [8], which cannot be seen in raw LDHs. Hence, the result indicated that, stirrer and sonicator can be used to treat Span20 on LDHs particles.

4. Conclusion
Laboratory available technique, magnetic stirrer and sonicator, potentially stabilized LDHs particle by Span20. The improvement in dispersion can be obtained after dispersing process for an hour. Sonicator can separate the large agglomerate into single stack LDHs surrounding with the agglomeration. For stirrer, the agglomeration cannot be completely broken. Because, the input energy provided by magnetic stirrer and sonicator was not sufficient enough to break down all the large agglomerate particles into individual particles.

Figure 3. (a) appearance of 0.0625 wt.% of raw LDHs, magnetic stirrer and sonicator for 1 hour of 1% Span20 treated LDHs disperse in MEK, respectively and (b) UV-vis spectra with relation of % transmittance and wavelength from 329 to 800 nm of each sample
Figure 4. FESEM images of (a) stirred, (b) sonicated sample and (c) particle size distribution of (black) raw LDHs, (blue) magnetic stirrer and (green) sonicator for 1 hour.

Figure 5. FTIR spectra from 4000 to 650 cm\(^{-1}\) wavenumber of each dispersion technique (black) raw LDHs, (blue) magnetic stirrer and (green) sonicator for 1 hour.

5. References

[1] Wang Q and O’Hare D 2012 Recent Advances in the Synthesis and Application of Layered Double Hydroxide (LDH) Nanosheets Chem. Rev. 112 4124–55
[2] Benício L P F, Silva R A, Lopes J A, Eulálio D, dos Santos R M M, De Aquino L A, Vergütz L, Novais R F, Da Costa L M, Pinto F G and Tronto J 2015 Layered double hydroxides: Nanomaterials for applications in agriculture | Hidróxidos duplos lamelares: Nanomateriais para aplicações na agricultura Rev. Bras. Cienc. do Solo39 1–13

[3] Bravo-Suárez J J, Páez-Mozo E A and Oyama S T 2004 Review of the synthesis of layered double hydroxides: A thermodynamic approach Quim. Nova27 601–4

[4] Müller F, Peukert W, Polke R and Stenger F 2004 Dispersing nanoparticles in liquids Int. J. Miner. Process.74 31–41

[5] Pal N, Kumar N and Mandal A 2019 Stabilization of Dispersed Oil Droplets in Nanoemulsions by Synergistic Effects of the Gemini Surfactant, PHPA Polymer, and Silica Nanoparticle Langmuir35 2655–67

[6] Sumitomo S, Koizumi H, Uddin M A and Kato Y 2018 Comparison of dispersion behavior of agglomerated particles in liquid between ultrasonic irradiation and mechanical stirring Ultrason. Sonochem.40 822–31

[7] Tong M, Chen H, Yang Z and Wen R 2011 The effect of Zn-Al-hydrotalcites composited with calcium stearate and β-diketone on the thermal stability of PVC Int. J. Mol. Sci.12 1756–66

[8] Cortés F B, Lozano M, Santamaría O, Marquez S B, Zapata K, Ospina N and Franco C A 2018 Development and evaluation of surfactant nanocapsules for chemical Enhanced Oil Recovery (EOR) applications Molecules23 1–19