Investigation of Citrate Modified Layered Double Hydroxides by Bead Milling Technique

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Abstract. Agglomeration and low stability of layered double hydroxides (LDHs) suspended in water significantly affects its properties for water base applications. In this study, the stability of LDHs suspended in water was improved by using bead milling for size reduction and by surface treatment with tri-sodium citrate. The result showed that bead milling technique can reduce the agglomeration and induce the adsorption of tri-sodium citrate on LDHs without intercalation. Following redispersion in water, the stability of citrate-modified LDHs was >1 hr with particle size around 177 nm, whereas the particle size of unmodified LDHs was around 40 μm with fast sedimentation.

1. Introduction
Layered Double Hydroxides (LDHs) are classified as a 2 dimensional (2D) nanomaterials containing positive charged brucite-like layers which are neutralized by anions, often hydrated with water, in the interlayers. The general chemical formulation for LDHs is [M$^{II}$$_{1-x}$M$^{III}$$_{x}$(OH)$_{2}$]$(X^{2-})_{x}$(An$^{-}$)$_{x}/n$$\cdot$yH$_{2}$O where M$^{II}$, M$^{III}$ are divalent and trivalent cation, respectively [1]. LDHs possess several unique properties for example flame retardance, high mechanical properties, and anion exchangeability. They have been used in several applications, including bio nanotechnology [3], and as polymer additives [2]. LDHs are generally prepared by co-precipitation. In their agglomerated form, the individual particles (LDHs stack) are held together by Vander Waal interaction [4]. LDHs sheets have high surface energy due to abundant hydroxyl groups leading to low dispersibility in water and organic solvents. Since environmental problem can be caused by harmful organic solvents, water based formulations are gaining popularity.

Surface modification is a traditional method that is used to improve dispersibility of nanoparticles in liquid media. An anionic surfactant was considered in this work because the net cationic charge on LDH layers may induce an electrostatic attraction between the positively charged LDHs and negatively charged anions. Tri-sodium citrate (citrate) is a type of carboxylic acid salt that is widely used to promote the suspension of nanoparticle in aqueous phase [5,6]. Citrate is a harmless and inexpensive material with chemical structure as shown in Figure 1.
In this work, the effect of mechanical forces on the LDHs particle size was investigated. Bead milling is the technique that gives highest grinding energy, compared to other dispersion techniques [7]. Impact and shear forces are produced by collision between the grinding beads and particles.

The objectives of this work were to reduce the agglomerated particle size by using bead milling process and to improve the dispersibility of LDHs in water by using tri-sodium citrate as a modifier. The existence of citrate on LDHs was confirmed by Fourier Transform Infrared Spectroscopy (FT-IR). Whereas, the crystal structure of citrate-modified LDHs was observed by X-ray diffraction technique (XRD). The particle size and dispersibility of citrate-modified LDHs in water was also investigated.

2. Experimental

2.1 Materials
LDHs nanoparticle in a wet cake form with a primary particle size of 50-200 nm in the lateral dimension and around 27 nm for the stack was obtained from SCG Chemicals Co., Ltd., (Bangkok, Thailand). Analytical grade Tri-sodium Citrate was purchased from Ajax Finechem Pty Limited (Australia). Reverse osmosis water (RO) from Unipure RO-50 GPD imported by Function International Co., Ltd., (Bangkok, Thailand) was used for all experiments.

2.2 Citrate-modified LDHs preparation
Citrate-modified LDHs was prepared by mixing LDHs with 200 mL of tri-sodium citrate in RO water. The suspension was stirred by a magnetic stirrer (HTS-1003, LMS CO., LTD., Tokyo, Japan) before milling (Minicer, NETZSCH GmbH & Co. Holding K G, Germany) for various durations (15-60 minutes). The sample was cleared of excess citrate by centrifugation and dried overnight in oven (572F WTB BINDER, BINDER GmbH, Germany) at 80°C.

2.3 Characterizations
The diffraction pattern of LDHs and citrate-modified LDHs were observed by powdered X-ray diffraction (XRD) technique, (D8 Advance, Bruker, Germany), with Cu Kα radiation source (λ = 0.154 nm), step size 0.04° and time step 1.00 s.

The LDHs and citrate-modified LDHs were investigated by FTIR (NICOLET 6700, thermo scientific, USA) in ATR mode to confirm the existence of surfactants on LDHs particle.
The LDHs and citrate-modified LDHs were dispersed in RO water by a tabletop sonicator (Elmasonic S 70H, Singen, Germany) for 30 minutes. The average particle size and zeta potential of both suspensions were measured by Zetasizer Nano ZS (Malvern, UK) with a measurement angle of 173° backscatter. The measurements were repeated thrice to calculate the average particle size.

The particle morphology and particle distribution of LDHs were observed by field emission scanning electron microscope (FE-SEM) (HITACHI, SU8010, Tokyo, Japan). Before measurement, the sample suspension was dropped on a clean silicon wafer and dried in an oven.

3. Result and discussion

Bead milling technique was used for dispersing and modifying tri-sodium citrate on LDHs particle. Grinding parameters can be varied including milling time, shaft speed, feed rate, and bead size [8]. To observe the optimum milling time, the citrate-modified LDHs were redispersed in water. The particle size of citrate-modified LDHs redispersed in water at each milling time were as shown in Figure 3. At 0 minutes the average particle size was 519 nm. After 15 and 30 minutes of milling, the average particle size was reduced to around 176 nm. After 40 minutes of milling time, the average particle size increased to 268 nm which implied as the re-agglomeration of LDHs particle. At 60 minutes the average particle size decreased dramatically to 50 nm. It implied that longer milling time, high energy, may cause breaking of primary particle.

Zeta potential of citrate-modified LDHs after redispersion in water was shown in Figure 3a. The zeta potential showed negative sign with magnitude higher than 30 mV, which meant that the LDHs particles had high stability in water after modification with tri-sodium citrate [9]. A general trend of decreasing zeta potential with increasing milling time was noted.

The results showed that bead milling can reduce LDHs particle size and modify citrate on LDHs. The optimum milling time for dispersion and modification of LDHs by citrate in water was 15 minutes because it was the shortest time that provided LDHs in primary size and zeta potential lower than -30 mV. This optimum milling time was used for the preparation of citrate-modified LDHs.

![Figure 3](image-url)

**Figure 3.** Average particle size of citrate-modified LDHs redispersion in water at each milling time

FTIR results of citrate-modified LDHs particle after 15 min of grinding was shown in Figure 4a. These results were used to confirm the existence of citrate on LDHs particle after modification. For raw LDHs, the adsorption band at 1362 cm⁻¹ revealed anti-symmetric stretching mode of carbonate ion...
that intercalated into the interlayered space [10]. Characteristic bands of tri-sodium citrate were seen at 1417 cm\(^{-1}\) and 1586 cm\(^{-1}\), which were assigned to symmetric of -COO\(^-\) and asymmetric stretching [11]. The FTIR result of citrate-modified LDHs revealed the -COO\(^-\) stretching of tri-sodium citrate. First band was small shoulder at 1568 cm\(^{-1}\) and second band was at 1362 cm\(^{-1}\); however, it combined with peak of carbonated intercalated ion of LDHs. The FTIR result confirmed that tri-sodium citrate existed on LDHs particle after bead milling process. However, the intensity of characteristic bands of tri-sodium citrate on citrate-modified LDHs was low when compared to LDHs because of the small amount of tri-sodium citrate present on citrate-modified LDHs. Other techniques, such as total organic carbon analysis, could be useful to further verify the existence of citrate on LDHs particles.

The XRD pattern of Raw LDHs and citrate-modified LDHs after 15 minutes grinding was shown in Figure 4b. The 003 peaks of Raw LDHs and citrate-modified LDHs were located at the same position at 2\(\theta\) = 11.52 °. The basal spacing \(d_{003}\) was 0.76 nm which meant that after modification tri-sodium citrate did not intercalate into the interlayer of LDHs. The result corresponded with the negative sign of zeta potential of citrate modification redispersion in RO water. These results were indicative of citrate ions that were present around LDHs surfaces after modification.

The appearance of raw LDHs and citrate-modified LDHs (bead milling 15 minutes) after 1 hour holding time was shown in Figure 5a. Tri-sodium citrate-modified LDHs showed improved stability, compared to non-treated LDHs. The citrate-modified LDHs in water was stable up to 7 days. As shown in Figure 5a, the average particle size of raw LDHs in water was around 40 \(\mu\)m, which was larger than citrate-modified by bead milling -176 nm and also corresponded with the FE-SEM results. The raw LDHs revealed the presence of large agglomerated particle with particle size more than 5 \(\mu\)m, whereas the citrate-modified LDHs by bead milling technique was found in small particles with particle around 100-500 nm.

![Figure 4.](image)

(a) FTIR result and (b) XRD result of raw LDHs and citrate modification LDHs by bead milling 15 minutes

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Overall, the bead milling technique reduced the agglomerated particle size and also induced the adsorption of citrate on LDHs particle. After modification of LDHs by tri-sodium, the stability of LDHs particle in water was improved.

4. Conclusion
In this study, the bead milling technique could disperse LDHs particles and induce adsorption of citrate on them. The optimum milling time was 15 minutes. However, the tri-sodium citrate attached on LDHs surface and did not intercalate into the interlayer of LDHs. The particle size of citrate-modified LDHs after redispersion in RO-water was 177 nm with stability >1 hour.

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