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Research Paper

Intercalation and Structural Reconstruction of Ca/Al Layered Double Hydroxides

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Abstract
The intercalation of of Ca/Al layered double hydroxide (LDH) has been successfully conducted into using several intercalants with different size compounds after termal treatment process to reconstruct structure of Ca/Al LDH. Ca/Al LDH was synthesized by co-precipitation at pH 11 then calcination at various temperatures following with intercalation using water, sodium hydroxide, sodium carbonate and Keggin type of polyoxometalate $K_4[\alpha\text{-SiW}_{12}O_{40}]$. Characterization of Ca/Al LDH was carried out by XRD and FTIR analyses. XRD analysis showed that unique diffraction peak of Ca/Al LDH at 10° with interlayer space 4.67 Å. Gradual thermal treatment of Ca/Al LDH was achieved until loss unique diffraction peak at temperature 700 °C to form shrinking layer. Intercalation of water, sodium hydroxide, sodium carbonate, and polyoxometalate to shrink layer of Ca/Al LDH can create formation of well crystalline LDH to reconstruct layer structure with formation of unique diffraction at 10°. The interlayer distance of Ca/Al LDH was increased after intercalation process. Thus reconstruction structure of LDH was successfully conducted with flexibility of layer.

Keywords
Intercalation, Layered Double Hydroxides (LDH), Ca/Al, Reconstruction

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1. INTRODUCTION

Development of unique materials for separation, adsorption, selective membrane, and ion exchange is recently rapidly increased due to the application for industrial scale (Omwoma et al., 2014; Jia et al., 2019). The synthesis strategy of materials is developed from a conventional method to in-situ instrumental controlled and from original to modification ways such as grafting (Ramanathan et al., 2018), impregnation (Belin et al., 2013), encapsulation (Barkhordari and Yadollahi, 2016), and intercalation (Lesbani et al., 2020). Macromolecular materials assemblies based on host-guest construction have great attracted because the flexibility of materials can be reached for especially selective sorption and separation of economically compounds like drugs and cosmetics (Mishra et al., 2018; Woo et al., 2011). The pores, interlayer, or space of materials with host-guest properties have confined space of guest or intercalant compounds. Guest compounds can be facile in and out into host materials resulted flexibility of materials. These properties are also can occur using intercalant on layer materials. Thus, selective host is achieved for interesting applications especially for medical treatment. On the other sides, hydrophilicity and hydrophobicity of materials can be tuned by the intercalation of various intercalants into pores, interlayers, or spaces of materials. Synthetic zeolites and layered double hydroxides are two classes materials possess pores and interlayers in their structures which can be intercalated with various guests (Wu et al., 2017; Tran et al., 2018). Other materials such as cucurbit[*n*]urils (Zhang et al., 2016), cyclodextrins (Zhu et al., 2011), porous carbon materials (Zhang et al., 2016), and crown ethers (Ma et al., 2009) also have flexibility for various guests to form host-guest system materials with unique properties.

Layered double hydroxide (LDH) is inorganic layer material class with positively charged layers consists of two metallic cations M^{2+}/M^{3+} and exchangeable gallery anions (Gómez-Avilés et al., 2016; Hasannia and Yadollahi, 2015). The research of LDH is now growing rapidly due to properties and application of this materials both in the laboratory and industrially scales. The general formula of LDH is $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\bullet{}_m H_2O$, where M^{2+} and M^{3+} are di-and trivalent cations in the host layer, A^{n-} is interlayer exchangeable anions. LDH has a like-brucite structure of staked sheets in which anions within the interlayer. Cations M^{2+} and M^{3+} can be combined in order to the functionality of this material (Duan et al., 2011). On the other hand, modification of LDH is carried out to obtain unique properties which can be conducted by intercalation using various anions. The basal spacing of interlayer LDH is also increased to accommodate larger anions during intercalation process. Thus the interlayer LDH has flexibility properties and can be controlled by intercalant or guest molecules. Several intercalants with various sizes such as carbonates, sulfates, hydroxides, amino acids, and polyoxometalate compounds are commonly used as an intercalant of LDH (Carriazo et al., 2007). Calcium is abundant elements in group II periodic table and also aluminum, which use in numerous application. Ca/Al LDH thus can be easily synthesis using coprecipitation method to from Ca/Al LDH (Qu et al., 2016). Herein, we report intercalant properties for intercalation of Ca/Al LDH with various intercalant sizes such as water, hydroxide, carbonate, and polyoxometalate in order to know the effect of intercalant sizes and to know the unique intercalation properties of Ca/Al LDH.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instrumentation

Chemicals from Merck and Sigma-Aldrich were used directly without further purification such as calcium nitrate, aluminum nitrate, sodium hydroxide, and sodium carbonate. Water was purified using Purite® water purification system from Integrated Research Laboratory, Graduate School, Universitas Sriwijaya. Polyoxometalate $K_4[\alpha\text{-}SiW_{12}O_{40}]$ was synthesized according to previous reported literature (Lesbani et al., 2016).

FTIR spectrum was recorded using Shimadzu FTIR Prestige-21 spectrophotometer using KBr method, and scanning was performed from 400-4000 cm^{-1}. XRD was performed using Rigaku Miniplex-600 series and samples were scanned at 1 $deg.min^{-1}$ in the range of diffraction area 0-60°.

2.2 Synthesis of Ca/Al Layered Double Hydroxides and Characterization

Synthesis Ca/Al layered double hydroxides was conducted according to Granados-Reyes et al. (2017) by the co-precipitation method with slight modification as follow. Calcium nitrate and aluminum nitrate with molar ratio 2:1 (Ca^{2+}/Al^{3+}) was prepared by adding sodium hydroxide 2 M. The mixtures were stirred at 60 °C and pH was adjusted to 11 by adding sodium hydroxide. The mixtures were stirring until pH constant. After stable pH, the mixtures were heated using autoclave at 120 °C for 4 h. The mixtures were filtered at room temperature and washed with water and dried at 80 °C overnight to form white solid Ca/Al LDH. Calcination of Ca/Al LDH was performed at 100-700 °C. Characterization was performed using XRD and FTIR analyses.

2.3 Intercalation Process and Analysis

Several intercalants molecules were used to study layer flexibility properties of Ca/Al LDH. Sodium carbonate, sodium hydroxides, water, and silico tungstate polyoxometalate were used as intercalants. The intercalation process was performed using the small reactor batch system equipped with nitrogen flow as follow. Saturated intercalant molecules were placed on outer into the double closed tube and Ca/Al LDH was put on the inner double closed tube. The system was closed. Nitrogen was slowly flow to the small reactor and the temperature was adjusted at 60 °C. The intercalation was performed overnight. Ca/Al LDH was analyzed after intercalation stop.

3. RESULTS AND DISCUSSION

Characterization of Ca/Al LDH was performed using XRD powder analysis as shown in Figure 1. Specific diffraction of Ca/Al LDH was reported by Granados-Reyes et al. (2017) in which diffraction appeared at 10-50°. Synthesized Ca/Al LDH as shown in Figure 1 has small diffraction at 10° and high diffraction at 20-30° indicated the crystalline phase of Ca/Al LDH due to carbonate. The presence of carbonate can be explained by synthetic method because of atmospheric air conditions. This anion was located between interlayer of Ca/Al LDH. Calcination was performed at 100-700 °C in the air at 5 h. The intensity of calcite was increased by increasing temperature. Other phases were detected as calcite, mayenite, and oxide phases. The concentration of calcite was decreased at 700 °C because this compound decomposes at a lower temperature than mayenite and calcium oxide. Layer materials of Ca/Al was identified as mayenite $Ca_{12}Al_{14}O_3$ (Huang et al., 2015).

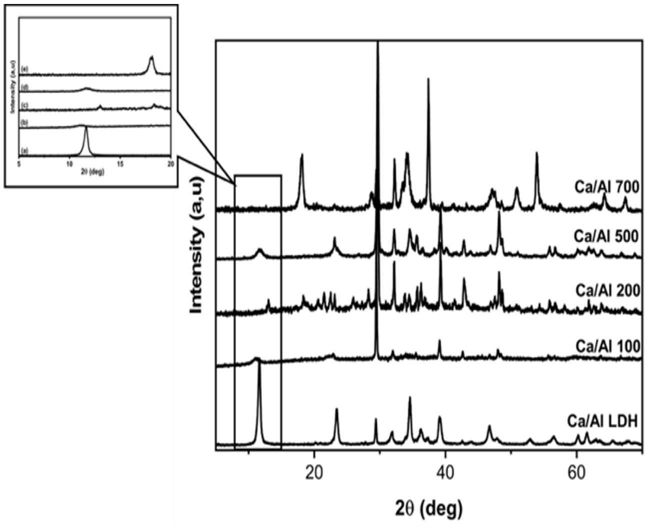

Figure 1. XRD Powder Patterns of Ca/Al LDH (A), and Ca/Al Calcined at 100 °C (B), 200 °C (C), 500 °C (D), and 700 °C (E)

Material Ca/Al LDH has gallery interlayer distance of 4.67Å at 11.3°. Gradual heating process of Ca/Al LDH caused decreasing slightly of interlayer distance due to loss of water and anions. The peak at 11.3° disappeared showed that collapse structure of layer compound. The layer was totally attached each other without anion or water of crystallization on the material. The FTIR spectrum of Ca/Al LDH are shown in Figure 2.

Figure 2 shows the main vibration peaks of Ca/Al LDH were appeared at 3520 cm^{-1} (ν O—H stretching, water) (Fitri et al., 2023), and 1460 cm^{-1} (ν N—O nitrate). The thermal treatment of Ca/Al LDH with increasing temperature will decrease the vibration at 1380 cm^{-1} and to be disappeared at temperature 700 °C due to loss of anion on interlayer space. The Ca/Al LDH was

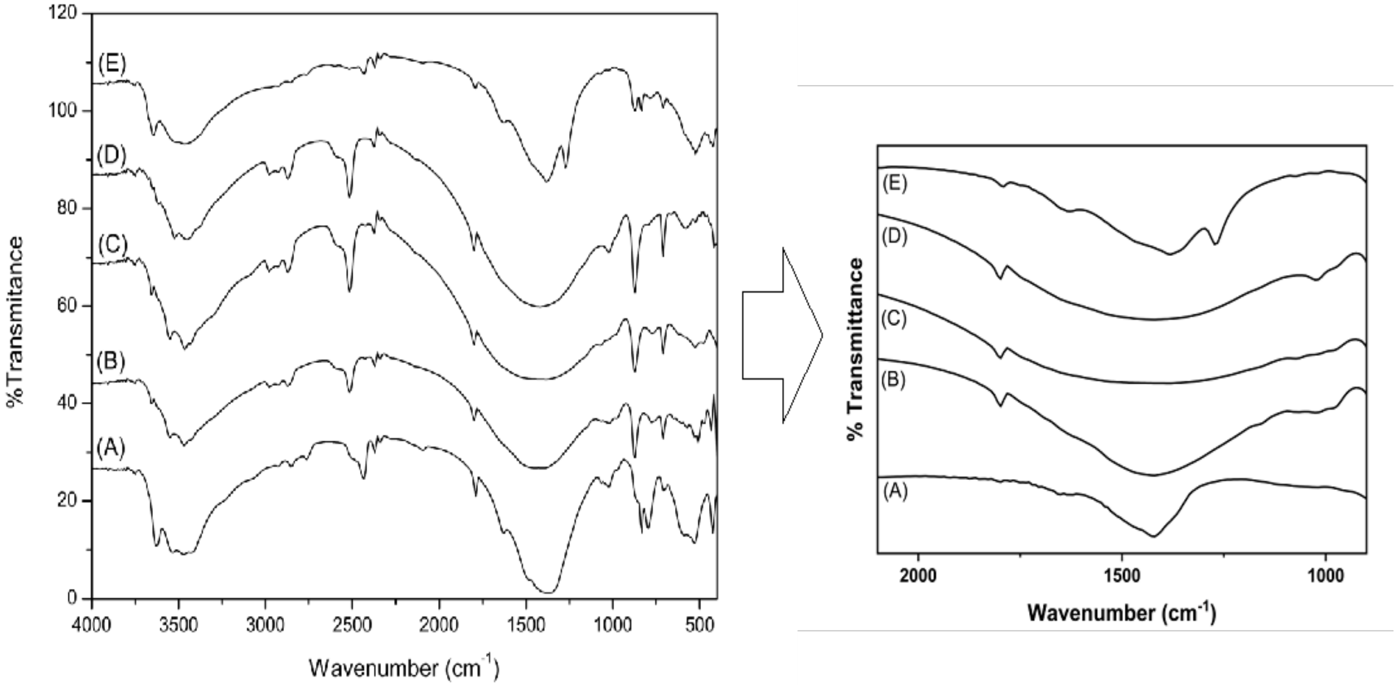

Figure 2. FTIR Spectra of Ca/Al LDH (A), and Ca/Al Calcined at 100 °C (B), 200 °C (C), 500 °C (D), and 700 °C (E)

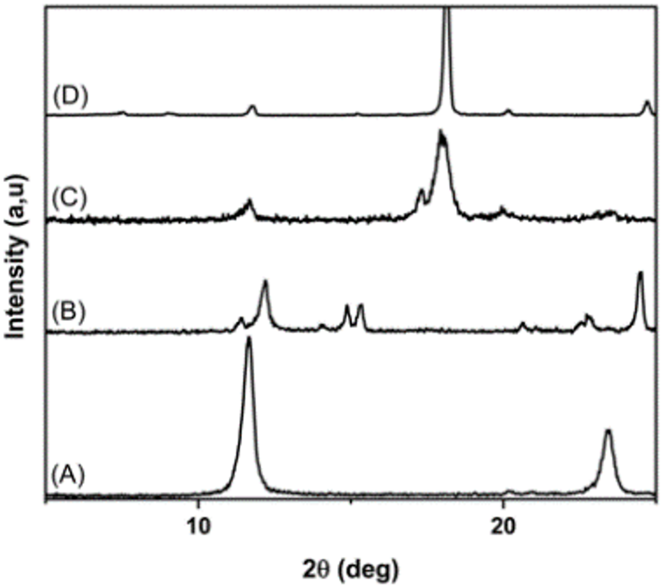

Figure 3. XRD Powder Patterns of Ca/Al LDH Intercalation with Water (A), Intercalation with Sodium Hydroxides (B), Intercalation with Sodium Carbonate (C), and Intercalation with Keggin Ion $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ (D)

Table 1. Interlayer Distance of Ca/Al LDH with Intercalation of Anions

Intercalation Ca/Al LDH	Interlayer Distance (Å)
Water	7.58
Hydroxide	5.04
Carbonate	7.53
$[\alpha - \text{SiW}_{12}\text{O}_{40}]^{4-}$	4.84

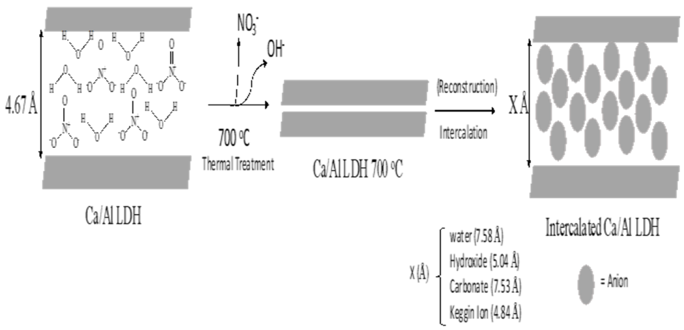

Figure 4. Schematic Illustration of Flexibility Layer of Ca/Al LDH by Thermal and Intercalation Process

shrined to be plate material at that temperature. The interesting subject is the structure of Ca/Al LDH after at 700 °C with wrinkled properties can be back to pristine structure by intercalation of anion. Here several anions were attempted to return structure of Ca/Al LDH using water, hydroxide, carbonate, and Keggin ion of polyoxometalate. Diffraction patterns of Ca/Al LDH with the inclusion of guest as shown in Figure 3 showed that unique

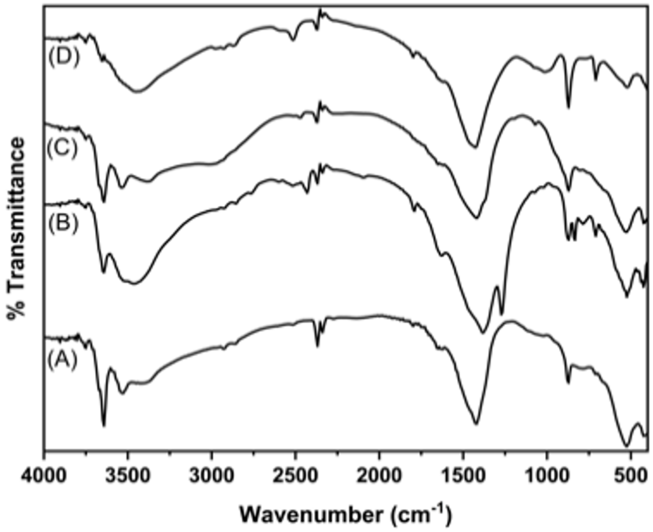

Figure 5. FTIR Spectra of Ca/Al LDH Intercalation with (A) Water; (B) Sodium Hydroxide; (C) Sodium Carbonate ; and (D) with Keggin Ion [α-$SiW_{12}O_{40}$]$^{4-}$

diffraction at 11° which was identified as interlayer distance.

The intensity of diffraction pattern of Ca/Al LDH at 11° after inclusion of anion has increased because of anion enter between layers. Water, sodium hydroxides, and sodium carbonate are frequently used as guest molecules for LDH (Zahra Mahjoubi et al., 2017). Material Ca/Al LDH with the intercalation of small molecules as anions will increase interlayer distance as shown in Table 1. Sodium hydroxides showed the lowest interlayer space after intercalation than water or carbonate. Probably sodium hydroxides come into interlayer with horizontal or diagonal orientation while water and carbonate come with vertical shapes (Hanifah and Palapa, 2016). On the other hand, Keggin ion [α-$SiW_{12}O_{40}$]$^{4-}$ with larger size than other intercalants have smaller interlayer distance. Ca/Al LDH has interlayer space 4.67Å. These spaces are not enough to accommodate Keggin ion with large size, thus the edge structure of Keggin ion [α-$SiW_{12}O_{40}$]$^{4-}$ enter to the space of interlayer distance of Ca/Al LDH.

The mechanism of shrinking and reconstructing of layer Ca/Al LDH by thermal treatment following intercalation is schematic illustration in Figure 4.

FTIR spectra of intercalation of Ca/Al LDH with water, sodium hydroxides, sodium carbonate, and Keggin ion on interlayer space of LDH are shown in Figure 5.

There are three important things can be seen from IR spectra in Figure 5 after intercalation of anions on Ca/Al LDH. First is vibration of nitrate to be sharped and boarded at wavenumber 1460 cm^{-1}, Second is vibration of Ca—O and Al—O was sharply appeared at wavenumber 650-800 cm^{-1}, and third is vibration of OH is sharped than original vibration of OH at wavenumber 3300 cm^{-1}. All IR spectrum is indicated that intercalation of various anion molecules was occurred and can reconstruct Ca/Al LDH to be a like pristine material (Starukh and Levytska, 2019).

4. CONCLUSIONS

Layer structure of Ca/Al LDH was lost after treatment at 700 °C to be shrinked material. The layer can be reconstructed by intercalation of anions. Interlayer space of Ca/Al LDH was increased by intercalation of anion molecules such as water, sodium hydroxide, sodium carbonate, and Keggin ion [α-$SiW_{12}O_{40}$]$^{4-}$. The increasing layer space was 2.69 Å for water, 2,64 Å for sodium carbonate and 0.15 Å for sodium hydroxide. Water and sodium carbonate were vertically orientation while sodium hydroxide was horizontal or diagonal orientation. On the other hand, shrinking Ca/Al LDH cannot accommodate size of higher Keggin ion [α-$SiW_{12}O_{40}$]$^{4-}$.

5. ACKNOWLEDGEMENT

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REFERENCES

Barkhordari, S. and M. Yadollahi (2016). Carboxymethyl Cellulose Capsulated Layered Double Hydroxides/Drug Nanohybrids for Cephalexin Oral Delivery. *Applied Clay Science*, **121-122**; 77–85

Belin, T., C. Mve Mfoumou, S. Mignard, and Y. Pouilloux (2013). Study of Physisorbed Carbon Dioxide on Zeolites Modified by Addition of Oxides or Acetate Impregnation. *Microporous and Mesoporous Materials*, **182**; 109–116

Carriazo, D., S. Lima, C. Martín, M. Pillinger, A. A. Valente, and V. Rives (2007). Metatungstate and Tungstoniobate-Containing *LDHs*: Preparation, Characterisation and Activity in Epoxidation of Cyclooctene. *Journal of Physics and Chemistry of Solids*, **68**(10); 1872–1880

Duan, X., J. Lu, and D. G. Evans (2011). *Assembly Chemistry of Anion-Intercalated Layered Materials*. Elsevier B.V.

Fitri, E. S., T. N. Yunita, R. Mohadi, and A. Lesbani (2023). Ca/Al and Mg/Al LDH Supported on Biochars As Effective Adsorbent and Highly Regeneration Ability for Phenol Removal from Aqueous Solution. *Indonesian Journal of Material Research*, **1**(3); 106–116

Granados-Reyes, J., P. Salagre, and Y. Cesteros (2017). Effect of the Preparation Conditions on the Catalytic Activity of Calcined Ca/Al-Layered Double Hydroxides for the Synthesis of Glycerol Carbonate. *Applied Catalysis A: General*, **536**; 9–17

Gómez-Avilés, A., P. Aranda, and E. Ruiz-Hitzky (2016). Layered Double Hydroxide/Sepiolite Heterostructured Materials. *Applied Clay Science*, **130**; 83–92

Hanifah, Y. and N. R. Palapa (2016). Mg/Al Layered Double Hydroxide: Intercalation with $H_3[\alpha-PW_{12}O_{40}]\bullet nH_2O$. *Science and Technology Indonesia*, **1**; 16–19

Hasannia, S. and B. Yadollahi (2015). *Zn-Al LDH* Nanostructures Pillared by *Fe* Substituted Keggin Type Polyoxometalate: Synthesis, Characterization and Catalytic Effect in Green Oxidation of Alcohols. *Polyhedron*, **99**(3); 260–265

Huang, J., L. Valenzano, and G. Sant (2015). Framework and

Channel Modifications in Mayenite ($_{12}$CaO·$_7$Al$_2$O$_3$) Nanocages by Cationic Doping. *Chemistry of Materials*, **27**(13); 4731–4741

Jia, Y., Y. Zhang, J. Fu, L. Yuan, Z. Li, C. Liu, D. Zhao, and X. Wang (2019). A Novel Magnetic Biochar / MgFe-Layered Double Hydroxides Composite Removing Pb^{2+} From Aqueous Solution: Isotherms, Kinetics and Thermodynamics. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **567**(January); 278–287

Lesbani, A., A. Marpaung, M. Verawaty, H. Rizki Amalia, and R. Mohadi (2016). Catalytic Desulfurization of Benzothiophene Using Keggin Type Polyoxometalates as Catalyst. *Journal of Pure and Applied Chemistry Research*, **4**(1); 5–11

Lesbani, A., T. Taher, N. R. Palapa, R. Mohadi, A. Rachmat, and Mardiyanto (2020). Preparation and Utilization of Keggin-Type Polyoxometalate Intercalated Ni-Fe Layered Double Hydroxides for Enhanced Adsorptive Removal of Cationic Dye. *SN Applied Sciences*, **2**; 470

Ma, S., C. Fan, L. Du, G. Huang, X. Yang, W. Tang, Y. Makita, and K. Ooi (2009). Intercalation of Macrocyclic Crown Ether into Well-Crystallized *LDH*: Formation of Staging Structure and Secondary Host-Guest Reaction. *Chemistry of Materials*, **21**(15); 3602–3610

Mishra, G., B. Dash, and S. Pandey (2018). Layered Double Hydroxides: A Brief Review from Fundamentals to Application as Evolving Biomaterials. *Applied Clay Science*, **153**(October 2017); 172–186

Omwoma, S., W. Chen, R. Tsunashima, and Y. F. Song (2014). Recent Advances on Polyoxometalates Intercalated Layered Double Hydroxides: From Synthetic Approaches to Functional Material Applications. *Coordination Chemistry Reviews*, **258-259**(1); 58–71

Qu, J., L. Zhong, Z. Li, M. Chen, Q. Zhang, and X. Liu (2016). Effect of Anion Addition on the Syntheses of Ca−Al Layered Double Hydroxide via a Two-Step Mechanochemical Process. *Applied Clay Science*, **124-125**; 267–270

Ramanathan, G., L. S. Liji, P. Fardim, and U. T. Sivagnanam (2018). Fabrication of 3D Dual-Layered Nanofibrous Graft Loaded with Layered Double Hydroxides and Their Effects in Osteoblastic Behavior for Bone Tissue Engineering. *Process Biochemistry*, **64**(September); 255–259

Starukh, H. and S. Levytska (2019). The Simultaneous Anionic and Cationic Dyes Removal with *Zn-Al* Layered Double Hydroxides. *Applied Clay Science*, **180**(June); 0–5

Tran, H. N., C. C. Lin, and H. P. Chao (2018). Amino Acids-Intercalated Mg/Al Layered Double Hydroxides as Dual-Electronic Adsorbent for Effective Removal of Cationic and Oxyanionic Metal Ions. *Separation and Purification Technology*, **192**; 36–45

Woo, M. A., T. Woo Kim, M. J. Paek, H. W. Ha, J. H. Choy, and S. J. Hwang (2011). Phosphate-Intercalated CaFe-Layered Double Hydroxides: Crystal Structure, Bonding Character, and Release Kinetics of Phosphate. *Journal of Solid State Chemistry*, **184**(1); 171–176

Wu, Y., X. Liu, Y. Lei, Y. Qiu, M. Wang, and H. Wang (2017). Synthesis and Characterization of 12-Tungstophosphoric Acid Intercalated Layered Double Hydroxides and Their Application as Esterification Catalysts for Deacidification of Crude Oil. *Applied Clay Science*, **150**(April); 34–41

Zahra Mahjoubi, F., A. Khalidi, A. Elhalil, R. Elmoubarki, O. Cherkaoui, S. Mhamed, and N. Barka (2017). Performance of Zn-, Mg-and Ni-Al layered double hydroxides in treating an industrial textile wastewater. *Journal of Applied Surfaces and Interfaces*, **2**(1-3); 1–11

Zhang, J., D. Xu, W. Qian, J. Zhu, and F. Yan (2016). Host-Guest Inclusion Complexes Derived Heteroatom-Doped Porous Carbon Materials. *Carbon*, **105**; 183–190

Zhu, J., J. He, X. Du, R. Lu, L. Huang, and X. Ge (2011). A Facile and Flexible Process of β-Cyclodextrin Grafted on Fe$_3$O$_4$ Magnetic Nanoparticles and Host-Guest Inclusion Studies. *Applied Surface Science*, **257**(21); 9056–9062