



## Functionalized layered double hydroxide with compound to remove cationic and anionic pollutants: A review

Siti Nabihan Ishak<sup>1</sup> and Nik Ahmad Nizam Nik Malek<sup>1,2,\*</sup>

<sup>1</sup>Department of Biosciences, Faculty of Science, Universiti Teknologi Malaysia (UTM), Johor, Malaysia.

<sup>2</sup>Centre for Sustainable Nanomaterials (CSNano), Ibnu Sina Institute for Scientific and Industrial Research (ISI-ISIR), Universiti Teknologi Malaysia (UTM), Johor, Malaysia

### Abstract

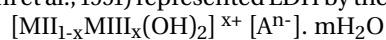
Layered double hydroxide (LDH) is one of the promising clay minerals that show great potential in various applications owing to its versatile structural properties. Prominently known for its high anion exchange capacity, this allows LDH to be considered as one of the most effective adsorbents in removing anionic toxic. However, the structural property of LDH hinders it from removing cationic toxic. Therefore, LDH have been functionalized to enhance its adsorption properties. In the present work, we aim to summarize the recent progress of functionalized LDH with different compounds for removal of both anionic and cationic toxics. The adsorption isotherm and effect of pH on absorption capacity also have been briefly reviewed.

Keywords :

Layered double hydroxide; cationic pollutants; anionic pollutants

## 1 Introduction

Layered double hydroxide (LDH) is an anionic clay with positive charge, created by the mixed hydroxides layer. The structure contributes greatly to its anionic exchange capacity. In their work, (Cavani et al., 1991) represented LDH by the general formula as follows:



Where,

MII : Divalent metal cations

MIII : Trivalent metal cation

An<sup>-</sup> : Exchangeable anion

Additionally, the layered crystal structure of these compound depends upon the nature of cation (x) and ratio of MII and MIII, where the true phase can be observed when  $0.2 < x < 0.3$  with ratio 2:1 to 4:1 of MII and MIII. As demonstrated in Figure 1.0, LDH possesses divalent and trivalent metal cations that are connected by -OH unit which lead to the formation of brucite-type octahedral sheets. The space between the layer contains exchangeable anions such as carbonate and nitrate, along with water molecule. Interestingly, LDH's lack of crosslinking between the cation layers allows the contraction and expanding interlayer spacing which allow anion to be intercalated between the layers (Dietmann et al., 2020)

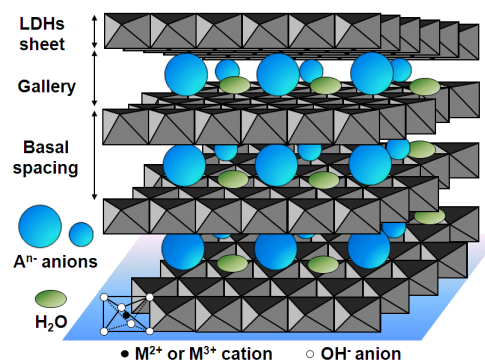


Figure 1 Structure of LDH (Bi et al., 2014)

The overview of available literature showed that LDH possesses great potential to be utilized in many applications including as adsorbents (Rathee et al., 2020; Zhao et al., 2021), wastewater purification (Teixeira et al., 2014), anion exchanger (Alibakhshi et al., 2020) and environmental application (Zaghloul et al., 2020; Zhang, Ai and Lu, 2020). The wide range of applications are contributed by its versatile structural properties such as anion exchangeability, compositional flexibility, biocompatibility, and high chemical stability. Uniquely, LDH exhibits memory effect; a condition which refers to the capability of decomposed LDH to reconstruct into its original structure when put in contact solution of anions.

The majority of scientific reports emphasized on the application of LDH to remove anionic toxic due to its capability to undergo anion exchange. However, the presence of different types of toxic compound with different charges in synthetic dye in industry requires the usage of adsorbents capable of removing both anionic and cationic toxics. Hence, to enhance the adsorption properties of LDH, numerous studies have attempted to modify LDH with other materials which allow LDH to remove anionic as well as cationic toxics.

\* Corresponding Author.

Email Address : [niknizam@utm.my](mailto:niknizam@utm.my)

<https://doi.org/10.33086/etm.v1i1.2062>

Received from 20 April 2021;

Received in revised from 30 April 2021;

Accepted 30 April 2021;

Available online 30 April 2021;

In this paper, the method to functionalize LDH and the capacity of functionalized LDH in removing anionic and cationic toxics are discussed. Next, adsorption isotherm and effect of pH on adsorption effectiveness of functionalized LDH are also presented briefly.

## 2 Synthesis of LDH and functionalized LDH

Recently, major effort has been pushed toward synthesizing LDH as it allows researchers to design and manipulate the composition and structure of LDH as well as producing LDH in high purity. Till present, several methods have been proposed to synthesis these lamellar solid, both simple and complex methods, including co-precipitation, ion exchange, hydrothermal synthesis, and ion reconstruction.

Among the aforementioned methods, co-precipitation is frequently used because it is simple, cost effective, can be applied in a large scale, and easy to handle (Hu et al., 2017; Yang et al., 2020). In short, co-precipitation is a direct method to produce LDH containing various layer of cations and interlayer anions involving simultaneous precipitation of divalent and trivalent metals. The mechanism of co-precipitation as the process of condensation of soluble source of divalent and trivalent metal together with interlayer anion in order to form a brucite-like layer.

For instance, Tran et al. (2018) have used co-precipitation method to intercalate LDH with different types of amino acid including phenylalanine, tyrosine, and serine. In a recent study conducted by Zhu et al. (2020), this method was also employed to functionalize LDH with ATMP. The authors described that the process starts with the drop-wise addition of ATMP into 100 mL Zn/Al LDH containing 0.02 mol  $Zn(NO_3)_2 \cdot 6H_2O$  and 0.01 mol  $Al(NO_3)_3 \cdot 9H_2O$  with mild agitation at pH 8. Different ratio of divalent and trivalent metal is significant in affecting the final product type of LDH (Manzi-Nshuti et al., 2009; Fahad et al., 2019). Therefore, this is crucial to optimize the ratio and carefully select type of salt for specific purpose. Next, the resulting gelatinous precipitate is aged at certain condition. The aging of the solution is vital to ensure high crystallinity of LDH (Manzi-Nshuti et al., 2009). Following this, the precipitate is filtered, dried, and ready to be collected.

Nowadays, various types of synthetic LDH can be synthesized using different types of metal cation such as Mg/Al and Zn/Al. Table 1.0 reviews the specific application of different metal cations as a source to synthesize LDH.

**Table 1** Synthesizing LDH using different metal cations in specific application.

Divalent/trivalent Application	References
Mg/Al	Control release of non-steroidal anti-inflammatory drug (Dasgupta, 2017)
Zn/Al	Removal methyl orange from aqueous solution (Mahjoubi et al., 2019)
Li/Al	Sensor for reversible sensing (Huang et al., 2019)
Co/Al	Enhance performance for brackish water desalination (Mutharasi et al., 2021)
Co/Fe	Capacitive deionization (Li et al., 2021)
Ni/Al	Self powered generator (Tian et al., 2020)
Ca/Al	Removal of selenium from caustic solution (Li et al., 2020)
Cu/Al	Antibacterial properties (Tabti et al., 2020)

Additionally, many studies have employed other materials such as oxalic anion (Badri et al., 2020), zeolite (Gustavo, Bieseki and Ribeiro, 2019), indigo carmine (Starukh and Levytska, 2019), amino acid (Tran et al., 2018), ATMP (Zhu et al., 2020a), polyoxometalate, and amino triethylene phosphonic acid to remove anionic and cationic toxics. In a recent study conducted by Badri et al. (2020), oxalic anion was intercalated within Mg/Cr LDH via ion exchange. To prepare the sample, 50g of Mg/Cr LDH was mixed with water before it was added to a solution of oxalic acid at pH 9. The suspension was stirred for 24 h under nitrogen atmosphere and finally, the mixture was dried at 100°C (Badri et al., 2020). LDH also can be functionalized with heteropoly blue using ion exchange method to enhance the adsorption of cationic toxic by LDH. The sample was prepared under nitrogen atmosphere (Bi et al., 2011).

## 3 Adsorption : cationic and anionic

Lofrano et al. (2016) defined adsorption as “a mass transfer process which involves the accumulation of substances at the interface of two phases, such as liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface”. According to Burakov et al. (2018), adsorption refers to the process that occurs when a liquid solute gathers and forms a molecular film on the surface of a solid adsorbent. In the adsorption process, the term “adsorbed” refers to the substance being adsorbed, while “adsorbent” refers to the adsorbing material (De Gisi et al., 2016). The rate of adsorption usually increases with increase in the following factors: adsorbent dose, pH, contact time, temperature, stirring speed, and initial concentration (Burakov et al., 2018). The common mechanism of adsorption by LDH and functionalized LDH are ion exchange, electrostatic interaction, physical adsorption, and chemical bonding.

To utilize LDH as an adsorbent to remove cationic and anionic toxics in wastewater from oil industry simultaneously, LDH have been functionalized with zeolite, a material with high cationic exchange capacity. The cationic and anionic exchange capacities exhibited by LDH and zeolite, respectively, allow them to exchanging cation and anion toxic in aqueous solution. The resulting functionalized LDH, Zeo-LDH has been proven to successfully removing 85–100% of cationic and 56–99.7% of anionic in water produced from petroleum production (Gustavo, Bieseki and Ribeiro, 2019).

In multiple studies, functionalized LDH has been utilized to adsorb methylene blue (MB), a cationic dye. In a recent study done by Starukh and Levytska (2019), they combined Zn/Al LDH with indigo carmine (IC), an anionic dye. Initially, the Zn/Al LDH alone was unable to remove MB, but once combined with IC, 320 mg/g of MB was successfully removed from aqueous solution (Starukh and Levytska, 2019).

An earlier study by Zhao et al. (2017) attempted to remove MB by functionalizing LDH with poly(levodopa). It has been reported that catechol groups of poly(levodopa) have a strong affinity to adsorb MB. In this work, the authors used the strategy of mussel-inspired chemistry to remove the cationic dye. In brief, simple dip-coating of LDH with levodopa (DOPA) was performed, allowing DOPA to self-polymerized and forming poly(levodopa) on the surface of LDH (Zhao et al., 2017).

## 4 Adsorption isotherm towards anionic and cationic toxics

Adsorption isotherm is conducted to predict the amount of pollutant being adsorbed to adsorbing agent and to investigate the adsorption uptake capacity which is important to design adsorption mechanism. Some of the commonly used model isotherms including Langmuir, Freundlich, and linear model for homogeneous and heterogeneous surface of material. Several reports show that functionalized LDH follows Langmuir model. This indicated

that the interaction between toxic compound with adsorbent is stronger than that of between solvent and adsorbent (Starukh and Levytska, 2019).

## 5 Effect of pH

Following functionalization of LDH, it has been reported that the effectiveness of functionalized LDH in adsorbing pollutants are influenced by pH. pH poses significant effect on the surface charge and ionic chemistry solution. At high pH (pH 3–5), the adsorption effectiveness of functionalized LDH is enhanced for the removal of cationic toxic. This is owing to the fact that the surface of LDH becomes more positive at high pH which allows them to undergo electrostatic attraction between carboxylate group in LDH and cationic metal.

In contrast, anionic toxics removal is more favorable at low pH because in this condition, the surface of LDH becomes more positive, allowing it to interact with negative charge of anionic metal. It can be explained that at low pH, hydroxyl group in LDH are converted to  $-OH_2^+$  resulting the surface of LDH to become more positive (Tran, Lin and Chao, 2018). That is consistent with the result presented by Zhu et al. (2020).

To sum, the adsorption capacity to remove cationic is ineffective at low pH and significantly increases with increasing pH. However, the adsorption experiment is conducted at pH lower than 6 in order to prevent precipitation heavy metal ion. Overall, the current research data suggests that the optimum pH in removing cationic toxic is at pH 5.

## 6 Conclusion

In this review, the current research progress in functionalized LDH to enhance the adsorption capacity in removing anionic and cationic has been briefly reviewed. In order to improve the adsorption properties, many attempts have been made such as functionalizing LDH with zeolite, amino acid, oxalic anion, and indigo carmine. The resulting the functionalized LDH with each compound exhibited great performance in removing both types of toxic. In addition, a brief discussion on adsorption isotherm is included in this review where the isotherm model used is dependent on the compound used to functionalize the LDH. Last but not least, the effect of pH demonstrated that functionalized LDH favors in removing anionic and cationic toxics at pH 3 and pH 5, respectively. It is quite evident from this review that with the appropriate choice of compound to intercalate the LDH, the resulting functionalized LDH possesses great impact in alleviating the pollution issue in our environment through adsorption and wastewater purification.

## Declaration of competing interest

The authors declare no known competing interests that could have influenced the work reported in this paper.

## Acknowledgements

The authors thank the Universiti Teknologi Malaysia for facilitating the current work.

## References

Alibakhshi, E. et al. (2020) 'The effect of interlayer spacing on

- the inhibitor release capability of layered double hydroxide based nanocontainers', *Journal of Cleaner Production*. Elsevier Ltd, 251, p. 119676. doi: 10.1016/j.jclepro.2019.119676.
- Badri, A. F. et al. (2020) 'Mg-Cr Layered Double Hydroxide with Intercalated Oxalic Anion for Removal Cationic Dyes Rhodamine B and Methylene Blue', *Journal of Environmental Treatment Techniques*, 9(1), pp. 85–94. doi: 10.47277/jett/9(1)94.
- Bi, B. et al. (2011) 'Heteropoly blue-intercalated layered double hydroxides for cationic dye removal from aqueous media', *Applied Clay Science*, 54(3–4), pp. 242–247. doi: 10.1016/j.clay.2011.09.003.
- Bi, X., Zhang, H. and Dou, L. (2014) 'Layered double hydroxide-based nanocarriers for drug delivery', *Pharmaceutics*, 6(2), pp. 298–332. doi: 10.3390/pharmaceutics6020298.
- Cavani, F., Trifirò, F. and Vaccari, A. (1991) 'Hydrotalcite-type anionic clays: Preparation, properties and applications.', *Catalysis Today*. Elsevier, 11(2), pp. 173–301. doi: 10.1016/0920-5861(91)80068-K.
- Dasgupta, S. (2017) 'Controlled release of ibuprofen using Mg Al LDH nano carrier', *IOP Conference Series: Materials Science and Engineering*, 225(1). doi: 10.1088/1757-899X/225/1/012005.
- Dietmann, K. M. et al. (2020) 'Layered double hydroxides with intercalated permanganate and peroxydisulphate anions for oxidative removal of chlorinated organic solvents contaminated water', *Minerals*, 10(5). doi: 10.3390/min10050462.
- Fahad Almojil, S. and Abdelhalim Othman, M. (2019) 'Screening Different Divalent and Trivalent Metals Containing Binary and Ternary Layered Double Hydroxides for Optimum Phosphate Uptake'. doi: 10.1038/s41598-019-52031-w.
- Gustavo, B., Bieseki, L. and Ribeiro, D. (2019) 'Development of a Zeolite A/LDH Composite for Simultaneous Cation and Anion Removal'. doi: 10.3390/ma12040661.
- Hu, Y. L. et al. (2017) 'ZnO/ZnGaNO heterostructure with enhanced photocatalytic properties prepared from a LDH precursor using a coprecipitation method', *Journal of Alloys and Compounds*. Elsevier Ltd, 709, pp. 42–53. doi: 10.1016/j.jallcom.2017.02.124.
- Huang, S. H., Liu, S. J. and Uan, J. Y. (2019) 'Controllable luminescence of a Li-Al layered double hydroxide used as a sensor for reversible sensing of carbonate', *Journal of Materials Chemistry C*, 7(36), pp. 11191–11206. doi: 10.1039/c9tc00870e.
- Li, D. et al. (2020) 'Removal of selenium from caustic solution by adsorption with Ca[*sbn*]Al layered double hydroxides', *Hydrometallurgy*. Elsevier B.V., 191, p. 105231. doi: 10.1016/j.hydromet.2019.105231.
- Li, M. et al. (no date) 'Layered Double Hydroxide Sorbents for Removal of Selenium from Power Plant Wastewaters', pp. 1–24. doi: 10.3390/chemengineering3010020.
- Li, Z. et al. (2021) 'Controllable synthesis of a hollow core-shell Co-Fe layered double hydroxide derived from Co-MOF and its application in capacitive deionization', *Journal of Colloid and Interface Science*. Academic Press Inc., 585, pp. 85–94. doi: 10.1016/j.jcis.2020.11.091.
- Mahjoubi, F. Z. et al. (2019) 'Characteristics and mechanisms of methyl orange sorption onto Zn/Al layered double hydroxide intercalated by dodecyl sulfate anion', *Scientific African*. Elsevier B.V., 6, p. e00216. doi: 10.1016/j.sciaf.2019.e00216.
- Manzi-Nshuti, C. et al. (2009) 'The role of the trivalent metal in an LDH: Synthesis, characterization and fire properties of thermally stable PMMA/LDH systems', *Polymer Degradation and Stability*. Elsevier Ltd, 94(4), pp. 705–711. doi: 10.1016/j.polymdegradstab.2008.12.012.
- Mutharasi, Y. et al. (2021) 'Novel reverse osmosis membranes incorporated with Co-Al layered double hydroxide (LDH) with enhanced performance for brackish water desalination', *Desalination*. Elsevier B.V., 498, p. 114740. doi: 10.1016/j.desal.2020.114740.

- Rathee, G., Singh, N. and Chandra, R. (2020) 'Simultaneous Elimination of Dyes and Antibiotic with a Hydrothermally Generated NiAlTi Layered Double Hydroxide Adsorbent', *Cite This: ACS Omega*, 5. doi: 10.1021/acsomega.9b03785.
- Starukh, H. and Levyska, S. (2019) 'The simultaneous anionic and cationic dyes removal with Zn-Al layered double hydroxides', *Applied Clay Science*, 180(June), pp. 0–5. doi: 10.1016/j.clay.2019.105183.
- Tabti, H. A. et al. (2020) 'Facile synthesis of Cu-LDH with different Cu/Al molar ratios: application as antibacterial inhibitors', *Research on Chemical Intermediates*. Springer Netherlands, 46(12), pp. 5377–5390. doi: 10.1007/s11164-020-04268-8.
- Teixeira, T. P. F. et al. (2014) 'Use of calcined Layered Double Hydroxides for the Removal: Kinetic, Equilibrium and Recycling Studies', *Brazilian Journal of Chemical Engineering*, 31(01), pp. 19–26. Available at: [www.abeq.org.br/bjche](http://www.abeq.org.br/bjche).
- Tian, J. et al. (2020) 'Surface charge density-dependent performance of Ni-Al layered double hydroxide-based flexible self-powered generators driven by natural water evaporation', *Nano Energy*. Elsevier Ltd, 70, p. 104502. doi: 10.1016/j.nanoen.2020.104502.
- Tran, H. N., Lin, C. C. and Chao, H. P. (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, pp. 36–45. doi: 10.1016/j.seppur.2017.09.060.
- Yang, C. et al. (2020) 'Highly efficient removal of amoxicillin from water by Mg-Al layered double hydroxide/cellulose nanocomposite beads synthesized through in-situ coprecipitation method', *International Journal of Biological Macromolecules*. Elsevier B.V., 149, pp. 93–100. doi: 10.1016/j.ijbiomac.2020.01.096.
- Zaghloul, A. et al. (2020) 'Characterization and application of tMg-Al layered double hydroxide for methyl orange removal from aqueous solution', in *Materials Today: Proceedings*. Elsevier Ltd, pp. 3793–3797. doi: 10.1016/j.matpr.2020.07.676.
- Zhang, R., Ai, Y. and Lu, Z. (2020) 'Application of Multifunctional Layered Double Hydroxides for Removing Environmental Pollutants: Recent Experimental and Theoretical Progress', *Journal of Environmental Chemical Engineering*. Elsevier Ltd, 8(4), p. 103908. doi: 10.1016/j.jece.2020.103908.
- Zhao, J. et al. (2017) 'Synthesis of functionalized MgAl-layered double hydroxides via modified mussel inspired chemistry and their application in organic dye adsorption', *Journal of Colloid and Interface Science*. Elsevier Inc., 505, pp. 168–177. doi: 10.1016/j.jcis.2017.05.087.
- Zhao, L. X. et al. (2021) 'Effectively removing indole-3-butyric acid from aqueous solution with magnetic layered double hydroxide-based adsorbents', *Journal of Hazardous Materials*. Elsevier B.V., 408, p. 124446. doi: 10.1016/j.jhazmat.2020.124446.
- Zhu, S. et al. (2020a) 'Rapid removal of toxic metals Cu<sup>2+</sup> and Pb<sup>2+</sup> by amino trimethylene phosphonic acid intercalated layered double hydroxide: A combined experimental and DFT study', *Chemical Engineering Journal*. Elsevier B.V., 392, p. 123711. doi: 10.1016/j.cej.2019.123711.
- Zhu, S. et al. (2020b) 'Rapid removal of toxic metals Cu<sup>2+</sup> and Pb<sup>2+</sup> by amino trimethylene phosphonic acid intercalated layered double hydroxide: A combined experimental and DFT study', *Chemical Engineering Journal*. Elsevier B.V., 392, p. 123711. doi: 10.1016/j.cej.2019.123711.