CHEMICAL ENGINEERING TRANSACTIONS

VOL. 86, 2021

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216

Retention of Nitrates Discharged from Photovoltaic Baths by Adsorption onto Mg-Al-LDH: Parametric Study

Nadjet Taoualit[a, *], Khalida Boutemak[b], Zoubida Chemat-Djenni[b], Ahlem Douara[a],

[a]Laboratoire des Applications Énergétiques de l'Hydrogène. Université de Blida1, Route de Soumaa, Blida, Algeria
[b]Laboratoire d'Analyse Fonctionnelle des Procédés Chimiques. Université de Blida1, Route de Soumaa, Blida, Algeria
ntaoualit@hotmail.fr

Adsorption of nitrates ions $(\mathrm{NO_3^-})$ from aqueous solutions onto an anionic synthetic clay Mg-Al-LDH has been studied using a batch adsorber. Mg-Al-LDH was prepared by co-precipitation method at constant pH and characterized by X-Ray and FTIR. Nitrates ions adsorption parameters were optimized (contact time, pH, initial NO_3^- concentration, LDH mass...). Equilibrium isotherm studies were done to evaluate the maximum adsorption capacity of Mg-Al-LDH. The localized exchange sites on the heterogeneous adsorbent surface of Mg-Al-CO_3^{2-} receive the nitrates species in multilayers with possible interactions between the adsorbed molecules by a chemisorption mechanism. Experimental kinetics data of nitrate adsorption on Mg-Al-CO_3^{2-} can be well described by the pseudo-second order model. The adsorbed quantities of nitrates at equilibrium is about 33 mg per unit mass of Mg-Al-CO_3.

1. Introduction

Thoughtless intensification of agricultural activities has resulted in water pollution from fertilizers and other chemicals. Although groundwater pollution is essentially linked to diffuse pollution of agricultural origin, that of watercourses suffers the combined effects of point-source pollution (industrial and domestic) and the runoff of agricultural pollution. Effluents from photovoltaic industry may contain harmful agents, such as acids, nanoparticles, organics, etc because the fabrication of photovoltaic (PV) cells includes the use of more than 200 organic and inorganic compounds (Aoudj et al., 2019). Among inorganic contaminants, nitrates, that may consists a threat to the environment. It should also be noted that nitrates are derived from excess nitrogen in a compartment of the cycle of this element, and when they are not eliminated or assimilated by the terrestrial biomass, they lead to a degradation of the natural environment, it is necessary to eliminate them.

Water pollution by nitrates presents a double risk. Ingested in large quantities, nitrates have toxic effects on human health. In addition, they contribute with phosphates to modify the biological balance of aquatic environments by causing eutrophication phenomena.

In Algeria, intensive soil fertilization practices in some agricultural plains and discharges of industrial and domestic effluents have increased the nitrate content of groundwater in several regions in recent years.

There are several conventional processes for the removal of nitrates from contaminated waters such as biological denitrification. It is a complex process to implement and is practically long. Physicochemical processes such as membrane processes, like reverse osmosis and electrodialysis, ion exchange and electrolysis, have some disadvantages such as incomplete removal, the need for high energy or high dose or expensive reagents. The adsorption processes have proved their effectiveness for the removal of nitrates (Ben Hamouda et al., 2017).

The main objective of this work is the shaping of an anionic synthetic clay: Mg-Al-LDH, a composite material, for removing nitrates from photovoltaic baths by discontinuous adsorption. The effect of the reactional parameters such as adsorbent mass, pH of the solution and contact time were studied. Subsequently, the Mg-Al-LDH was applied for the retention of nitrates present in the drilling of photovoltaic discharges which is located in the region of El Harrach, Algiers in Algeria.

Anionic clays or hydrotalcites, also known as layered double hydroxides (LDHs), are rare materials in nature but easy and simple to prepare in the laboratory (Carlino, 2003). These compounds have been the subject of many publications (more than 220 articles in 2005), (Géraud, 2006), much interest and research in recent years, because of their interesting properties of anion exchange, adsorption, porosity (Mishra et al., 2018).

LDH are easily synthesizable in the laboratory which requires a simple titration assembly, with an inexpensive and available material, and also allows better control of the composition of the reaction medium and gives well crystallized products (Taoualit et al., 2019). The LDH structure was determined by studies conducted by Taylor (Taylor, 1973), Brown (Brown and Gastuche, 1967) and Allmann (Allmann, 1970) in the 1970s on natural phases. The structure is constituted by a stack of brucite-type sheets $[\mathrm{M}^{\mathrm{II}}_{1-\mathrm{y}}\ \mathrm{L}^{\mathrm{III}}_{\mathrm{y}}\ (\mathrm{OH})_2]^{\mathrm{y}+}\ [\mathrm{X}^{\mathrm{n}}]_{\mathrm{y/n}}[\mathrm{H_2O}]_{\mathrm{z}}$ with common stops. The charge density being proportional to the ratio $\mathrm{y} = \frac{\mathrm{n}(\mathrm{M}^{\mathrm{III}})}{\mathrm{n}(\mathrm{M}^{\mathrm{III}}+\mathrm{L}^{\mathrm{II}})}$. A schema of LDH phases structure is given by the figure 1. While brucite has neutral sheets, the partial substitution of divalent cations by trivalent cations in LDH imposes a positive charge which is counterbalanced by the presence of anionic species and water molecules in the interlamellar space. The cations are distributed randomly in the octahedral sites of the sheets, in most phases of the hydrotalcite type (Géraud, 2006).

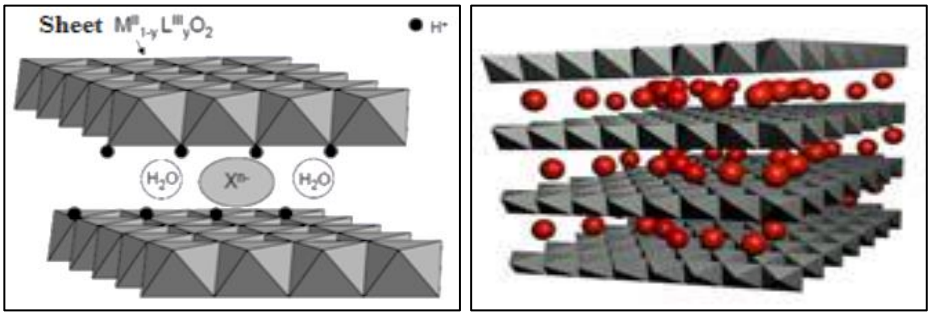

Figure 1: Schematic representation of a LDH phase structure (Géraud, 2006)

2. Materials and Methods

2.1 Preparation of Mg-Al-LDH

Mg-Al-LDH was prepared by co-precipitation method at constant pH. This method consists in titrating 100 mL of Mg(Cl_2) (98%, Fluka) and Al(Cl_3) (98%, Fluka) mixture solution, defined by a molar ratio y equal to 2 with 100 mL of Na_2CO_3 solution 1M (from Cheminova) and NaOH 2M **(**98%, Biochem) at room temperature under strong agitation during about 90 minutes while the pH was maintaining constant equal to 10. When the precipitation reaction was completed, the resulting gel was refluxed at 60°C for 15 hours to allow crystal growth. Once the heat treatment achieved, the product was filtered and washed several times with distilled water until complete elimination of excess ions on the solid (Cl^-, Na^+), then dried in an oven at 70°C, over one night. Obtained product was in the form of a sinterable solid then it was ground using an agate mortar to give a very fine white powder. Thereafter, the solid was calcined in a furnace at temperature of 600°C with an air inlet for 4hours, and a temperature rise of 5°C. min^{-1} (Vaysse, 2001).

2.2 Characterization of Mg-Al-LDH

The characterization of obtained solid was performed using the X-ray diffraction technique (XRD) and Fourier transform infrared spectrophotometer (FTIR).

2.3 Preparation and dosage of nitrates solutions

A stock solution of nitrates at $1\mathrm{g.L}^{-}$ was prepared by dissolving an appropriate quantity of KNO_3 (99.5%, purshased from Biochem) in bidistilled water. The standards solutions were obtained by successive dilutions in order to dose the residual concentration of nitrates after adsorption using UV-spectrophotometer (Shimadzu, Model UV 1700) at λmax = 220 nm. The initial pH was adjusted with dilute solutions of HCl (0.1M) and/or NaOH (0.1M).

2.4 Adsorption tests and operating conditions

The experiments were performed in batch mode, using 250 mL erlenmeyer flasks closed-cap, in which an appropriate quantity of Mg-Al-LDH was added, separately, to 100 mL of nitrates solution at fixed initial concentration and constant pH. The assembly was placed under horizontal stirring on an oscillating table at room temperature. At the end of each stirring time, which was varied from 0 to 24 hours, the samples were filtered then analyzed directly by UV-Visible at 220 nm to determine the nitrates residual concentration. The adsorbed quantities of nitrates (Q_t) at time t and at equilibrium (Q_e) per unit mass of Mg-Al-CO_3 were calculated from equation 1 and 2. The retention efficiency (E %) of nitrates on Mg-Al-LDH was calculated from equations 3 (Maghnia et al., 2017).

$$Q_t = \frac{C_0 - C_t}{m} \ x \ V \tag{1}$$

$$Q_e = \frac{C_0 - C_e}{m} \ x \ V \tag{2}$$

$$E \ (\%) = \frac{C_0 - C_t}{C_0} \ x \ 100 \tag{3}$$

Where : $C_0 \ (mg.L^{-1})$, $C_t \ (mg.L^{-1})$, $C_e \ (mg.L^{-1})$ are respectively : the initial, the final concentration of nitrates (at time 0 and t) and at equilibrium in the aqueous solution, V is the aqueous solution volume (V=100 mL) and m (g) represents the adsorbent amount.

3. Results and Discussion

3.1 Characterization of Mg-Al-LDH

Characterization by X-ray diffraction

X-ray diffraction makes it possible to identify the crystalline nature of the crystalline phases and the parameters of the elementary mesh of a solid. In our case, this technique allows to have information on the sheet and on the inter-sheet space. Indeed, this characteristic is represented by the existence of intense and symmetrical peaks at low values of 2θ (Zhitova et al., 2016). The first peak located at 2θ ≈ 15 ° was indexed as (003) and corresponds to d_{003} = 3.83A° (Figure 2a). This basic reflection can be determined using the Bragg law (λ = 2d.sinθ). This peak gives information on the inter-lamellar distance and it makes it possible to calculate the parameter c of the mesh such that: c = 3 d_{003}. The second characteristic peak located at higher values of 2θ, was indexed as (110) and corresponds to d_{110} = 1.52 A°. This basic reflection corresponds to the inte-rmetallic distance within the hydroxide layers and makes it possible to calculate approximately the parameter of the mesh a where a = 2 d_{110}. The mesh parameters c and a are then respectively 11.49 A° and 3.04 A°. According to the results, the solid Mg-Al-LDH is well of crystalline form since d_{003} < 15 A° (Rives and Ulibarri, 1999) having an X diffractogram of Stichtite type (Defontaine, 2004).

Characterization by FTIR

IR spectrum of Mg-Al-CO_3 recorded between 4000 and 400 cm^{-1} (Figure 2b) shows a general appearance similar to that of the spectra of this type of phases (Taylor, 1984).
A wide band is observed around 3455 cm^{-1} attributed to the valence vibration mode of the physi-sorbed water molecules mainly interposed in the inter-lamellar space and / or the valence mode of the OH-linked groups with carbonate anions in the presence of divalent and trivalent cations.
A shoulder assigned at 2365 cm^{-1} corresponds to the interactions of the water molecules with the carbonate anions by hydrogen bonds.
Two main peaks located around 1635 and 1381 cm^{-1}, corresponding to the elongation vibration modes of the water molecules intercalated in the interlamellar space and to the vibration modes of the carbonate anions. The intensity of these peaks decreases as a function of heat treatment indicating the departure of water and CO_3^{2-} anions (Châtelet et al., 1996).
At around of 669 cm^{-1}, an antisymmetric vibration peak $\upsilon(CO_3^{2-})$ and Mg-O is located. After calcination, the remaining broadband in the range 3000-3700 cm^{-1} is attributed to the vibrations of OH^- groups, because the hydroxyl groups are subjected to strong interaction with the carbonate ions.
On the other hand, almost all low frequency bands disappear while new bands were observed at about 669 and 853 cm^{-1} characteristic of spinel formation ($MgAl_2O_4$), (Manju and Anirudhan, 2000).

3.2 Adsorption of nitrates on Mg-Al-LDH

Adsorption of nitrates, from synthetic aqueous solution, on Mg-Al-LDH was studied with emphasis on the influence of the operating parameters such as : contact time, adsorbent amount, solution pH and initial concentration of nitrates.

Effect of contact time

Obtained results (Figure 3a) show that nitates adsorption kinetics of $C_0(NO_3^-) = 1\, g.L^{-1}$ on 1 g of adsorbent is fairly rapid. The balance is reached after 180 minutes. The highest removal efficiency is 32.8%. A contact time of 180 minutes (3 hours) was then considered sufficient for maximum adsorption.

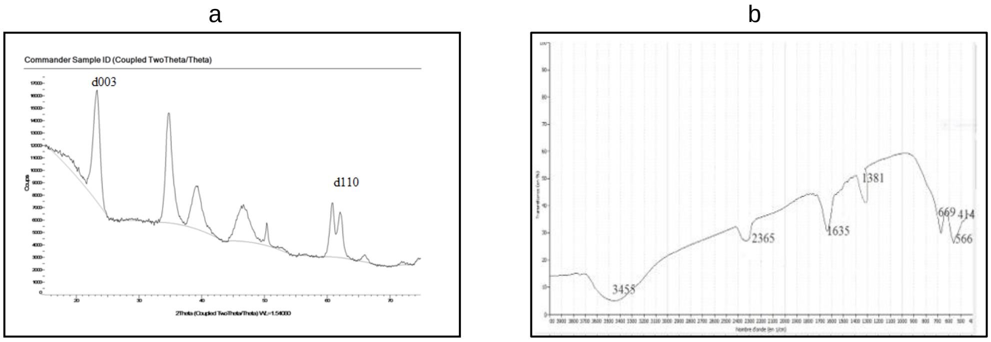

Figure 2: (a) XRD diffractogram of Mg-Al-LDH, (b) IR spectrum of calcined Mg-Al-LDH

Effect of synthetic solution pH

A range of pH was selected as: 3, 4, 5, 6, 7, 8 and 10, to study the influence of it on nitrate adsorption onto Mg-Al-LDH, while the other operating conditions were kept constants.

Obtained results (Figure 3b) show that the best yield of nitrates removal by Mg-Al-LDH is about 41% at pH 4 that was chosen for the rest of this work. The increase in nitrates retention at acid pH is due to the addition of the H^+ ions, to lower the pH, which leads to the neutralization of the OH^- ions released by LDH structure, which promotes the nitrates adsorption in acid medium. At basic pH, a decrease in the retention of nitrates is noticed, since there is a decrease in H^+ ions and the appearance of OH^- ions released by the adsorbent structure on the one hand, and by the NaOH solution of adjustment, on the other hand, which suggests that it is indeed a competition between negatively charged nitrates and the OH^- ions. This then disadvantages the adsorption of nitrates in basic medium.

Influence of the adsorbate initial concentration

Increase of initial nitrates concentration causes an increase in their adsorbed quantity (Figure 3c). Optimum retention efficiency was achieved at $C_0(NO_3^-) = 1\, g.L^{-1}$.

3.3 Modeling of adsorption kinetics

In order to investigate the nitrates adsorption processes on Mg-Al-LDH, two known order models were used to test experimental data, the pseudo-first-order model and the pseudo-second-order one.

Obtained results (Table 1) reveal that the experimental kinetic data are well described by the pseudo second-order model with correlation coefficient R^2 = 1. The pseudo-second-order model describes a rapid adsorption on reactive sites of the solid and a slow adsorption at low energy sites of the adsorbent. Therefore, the nitrates adsorption follows the chemisorption mechanism through sharing or exchange of ions between adsorbent and adsorbate (electrostatic attraction), (Tugrul et al., 2015).

Table 1: Kinetics models parameters of nitrates adsorption on Mg-Al-LDH

Pseudo-first-order model			Pseudo-second-order model		
$Ln(Q_e - Q_t) = Ln\ Q_e - K_1 t$			$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{K_2 Q_e^2}$		
$Q_e(mg.g^{-1}$	$K_1(mn^{-1})$	R^2	$Q_e(mg.g^{-1})$	$K_2(mn^{-1})$	R^2
32.8	-0.014	0.697	32.8	0.9	1

3.4 Adsorption isotherms

Equilibrium adsorption characteristics of Mg-Al-LDH can be determined using the two following classic models, Freundlich and Langmuir, to investigate nitrates adsorption isotherms. Obtained results show that data are well described by the Freundlich model (Table 2). The value of 1/n = 1.163 > 1 indicates a favorable adsorption.

Table 2: Langmuir and Freundlich isotherms parameters for nitrates retention on Mg-Al-LDH at room temperature and $C_0(NO_3^-) = 1\ g.L^{-1}$

Langmuir model			Freundlich model		
$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}}$			$Q_e = K_F\, C_e^{1/n}$		
Q_e(mg. g⁻	K_L(L. g^{-1})	R^2	$1/n$	K_F	R^2
37.037	0.25 10^{-4}	0.948	1.163	0.0176	0.992

Moreover, the Freundlich constant K_F reflects the adsorption capacity of an adsorbate considered by the solid (Monarrez, 2004), more the value of K_F is high more the retained quantity is important (Ben Hamouda et al., 2017). In the case of this paper, K_F =0.0176 **<** 1, indicating a low affinity of Mg-Al-LDH for nitrates according to the classification of Jamet (Jamet, 1988).

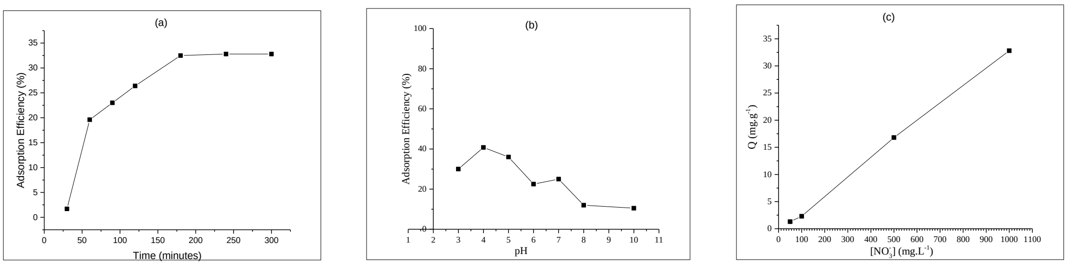

Figure 3: (a) Effect of contact time, (b) Effect of pH, (c) Effect of NO_3^- *initial concentration*

4. Application of Mg-Al-LDH for nitrates adsorption released from photovoltaïc discharges

The optimized operating conditions, previously determined (1g of Mg-Al-LDH, contact time=3 hours and pH 4), were applied for the adsorption of nitrates present in the drilling of photovoltaic discharges (located in the region of El Harrach, Algiers/Algeria) in the presence of other harmful agents. Obtained results are reported in Table 3. A low retention of nitrates on Mg-Al-LDH was obtained at pH = 4 (2.5%). When the pH decreases till the value of that of the photovoltaic discharges (pH= 0.5) the retetion efficiency increases. Adsorption is favorable in acid medium as already noted above.

Table 3: Retention results of nitrates in the PV discharges

pH	4	2.2	0.7
Efficiency E (%)	2.505	9	12

5. Conclusions

The main objective of this work is the shaping of a synthetic clay: Mg-Al-LDH, a composite material, to remove nitrates from photovoltaic baths by batch adsorption. LDHs were prepared by the direct co-precipitation method of divalent and trivalent metal salts at controlled pH, with a molar ratio of 2. Obtained material is characterized by X-ray diffraction (XRD) and infrared spectroscopy (FTIR) techniques which have confirmed that the synthesized solid corresponds well to the desired lamellar double hydroxide. XRD of calcined Mg-Al-LDH confirms its characteristic structure. FTIR analysis has also made it possible to highlight the characteristic bands of Mg-Al-LDH and confirms the dehydration and decarboxylation of this calcined adsorbent.

Experimental results showed that the kinetics of nitrate adsorption on Mg-Al-LDH reveal relatively short equilibrium times of 180 minutes. The adsorption capacity of nitrates increases with pH so that it becomes optimal at pH 4.

Nitrates adsorption onto Mg-Al-LDH is better described by the Freundlich model according to R^2. The localized sites on the adsorbent surface receive the nitrates species in multilayers with possible interactions between the adsorbed molecules.

This adsorbent surface is heterogeneous, which means that all the exchange sites have the same affinity for nitrate ions.

Experimental kinetics data of nitrate adsorption on Mg-Al-CO_3^{2-} can be well described by the pseudo-second order model. The correlation coefficient is considered satisfactory. The adsorption mechanism can be attributed to chemisorption.

The prepared LDH can be envisaged for use in the adsorption of the elements constituting the photovoltaic baths and/or of the species, harmful to the environment such as those of surface treatment baths, electroplating, copper plating, etc ...

References

Allmann Von R., 1970, Double layer structures with brucite-like ions $[\mathbf{M}_{1-x}^{II}\,\mathbf{M}_{x}^{III}\,(\mathbf{OH})_2]^{x+}$”. Chimia 24 (3), 99-108.

Aoudj S., Taoualit N., Khelifa A., Drouiche N., Berkache I., Bendjiar R., 2019, Removal of EDTA from Photovoltaic Industry Wastewater by Ag-TİO2 Photocatalyst. Chemical Engineering Transactions, 73, 79-84. doi :10.3303/CET1973014

Ben Hamouda B., Kemiha M., Azzouz N., 2017, Elimination of nitrates contained in leachate by adsorption on mixture bentonite-lime and on thermally chemically bentonite under microwave irradiation. Journal of new sciences, Volume CSIEA (24).

Brown G., and Gastuche M. C., 1967, Mixed magnesium-aluminium hydroxides. II. Structure and structural chemistry of synthetic hydroxycarbonates and related minerals and compounds. Clay Minerals 7 (2), 193-201. doi:10.1180/claymin.1967.007.2.06

Carlino S., 2003, Anionic C. 34, 135.

Châtelet L., Bottero J. Y., Yvon J., Bouchelaghem A., 1996, Competition between monovalent and divalent anions for calcined and uncalcined hydrotalcite: anion exchange and adsorption sites. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 111(3), 167-175. doi: 10.1016/0927-7757(96)03542-X

Defontaine G., 2004, Synthèse et hydratation des hydroxydes lamellaires double: études des takovites. Doctoral Thesis, University of Laurraine, France.

Géraud E., 2006, Elaboration et caractérisation de matrices Hydroxydes Doubles Lamellaires Macroporeuses. Doctoral thesis, University of Blaise Pascal, France.

Jamet P., 1988, Etude quantitative de l’adsorption et de la désorption de l’UKJ-1506 dans le sol. Agronomie, EDP Sciences, 8 (3), 227-235. https://hal.archives-ouvertes.fr/hal-00885093

Maghnia A., Ghelamallahb M. and Benghalem A., 2017, Sorptive Removal of Methyl Green from Aqueous Solutions using Activated Bentonite. Acta Physica Polonica A 132 (3), 448-450. doi: 10.12693/APhysPolA.132.448

Manju G. N., Anirudhan T. S., 2000, Treatment of arsenic(III) containing wastewater by adsorption on hydrotalcite. Indian Journal of Environmental Health 42, Part 1,1-8.

Mishra G., Dash B., Pande S., 2018, Layered Double Hydroxides: A brief review from fundamentals to application as evolving biomaterials. Applied Clay Science Volume 153, 172-186. doi: 10.1016/j.clay.2017.12.021

Rives V. and Ulibarri M. A., 1999, Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates. Coord. Chem. Rev. 181, 61-120. doi :10.1016/S0010-8545(98)00216-1

Taoualit N., Boutemak K., Chemat-Djenni Z., Aoudj S, Touati N., Abdelli W., 2019, Contribution to Copper Elimination Study by Adsorption on Double-layered Hydroxides HDL. Chemical Engineering Transactions, 73, 235-240. doi:10.3303/CET1973040

Taylor H. F. W., 1973, Crystal structures of some hydroxide minerals. Mineralogical Magazine 39 (304), 377-389. doi:10.1180/minmag.1973.039.304.01

Taylor R. M., 1984, The rapid formation of crystalline double hydroxide salts and other compounds by controlled hydrolysis. Clay Minerals, 19(4), 591-603. doi :10.1180/claymin.1984.019.4.06

Tugrul B., Erentürk S., Haciyakupoglu S., Karatepe N., Altinsoy N., Baydogan N., Baytas F., Büyük B., Demir E. and Gedi S., 2015, Kinetic and Thermodynamic Behavior of Selenium on Modified Bentonite and Activated Carbon using Radiotracer Technique. Acta Physica Polonica A, 128 (2-B), B180-B181. doi: 10.12693/APhysPolA. 128.B-180

Vaysse C., 2001, Caractérisation structurale d’hydroxydes doubles lamellaires contenant des anions oxométallates (Mo,W) ou acrylate intercalés. Doctoral thesis, University of Sciences and Technologies-Bordeaux I, France.

Zhitova E.S., Krivovichev S.V., Pekov I.V., Yakovenchuk V.N., Pakhomovsky Ya.A., 2016, Correlation between the d-value and the M2+: M3+ cation ratio in Mg–Al–CO3 layered double hydroxides. Applied Clay Science 130, 2-11. doi: 10.1016/j.clay.2016.01.031