Layered double hydroxides, especially Zn-Al, are valuable bases for intercalating various functional anions: dyes, drugs, food additives, etc. For purposeful development and optimization of the synthesis technology of functional materials based on Zn-Al layered double hydroxides, the technological parameters of Zn-Al nitrate layered double hydroxide samples (Zn:Al=4:1) synthesized at solution flow rates of 0.8 and 1.6 l/h, pH=7, 8, 9, 10 and t=10, 20, 30, 40, 50 and 60 °C were determined. The yield values of the samples were determined by the gravimetric method. The sedimentation rate was studied by measuring the normalized thickness of the precipitate layer (relative to the initial layer thickness) during 30 minutes of settling. It was found that with an increase in the synthesis pH, the yield increased from 74.68 % to 83.54 %. Increasing the flow rate of the solutions led to a decrease in yield. On the yield-synthesis temperature dependence, two sections of 10–20 °C and 30–60 °C were identified, within which an increase in temperature led to a decrease in yield. It is shown that with increasing synthesis pH, as well as the solution flow rate, the sedimentation rate increased significantly. At pH=10, almost complete sedimentation of the sample occurred within the first 5 minutes. The obtained data indicate that the pH of the zero charges of the Zn-Al-NO₃₃ layered double hydroxide particles was close to 10. It was found that increasing the temperature reduced the sedimentation rate. An abnormally low sedimentation rate at a synthesis temperature of 30 °C and an abnormally high sedimentation rate at 50 °C were detected. The obtained data confirm the previously stated hypothesis regarding the change of the mechanism or kinetics of the formation of layered double hydroxides at temperatures of 30 °C and 50 °C.

Keywords: Zn-Al layered double hydroxide, intercalation, nitrate, product yield, sedimentation rate

1. Introduction

Humanity has widely used decorative cosmetics since ancient times. They consist of various components, among which pigments are obligatory and most important [1, 2]. Pigments can be obtained both from natural sources and synthetically. The most common mineral pigments are salt and oxide substances, for example, cobalt-chromium oxide.
pigments [3], as well as spinel [4, 5], and pigments with the structure of various silicates [6, 7]. Inorganic pigments have high color stability though they have a limited range of colors. Organic pigments are characterized by a wide range of colors, but have low stability to sunlight.

Organic-inorganic hybrid materials have the complex advantages of both organic and inorganic pigments. Among pigments of this type, the most promising are layered double hydroxides (LDH) [8] intercalated with anionic dyes [9, 10].

The color palette of cosmetic pigments can be expanded by combining various metal cations and dye anions of various colors in the LDH structure. For example, Zn-Al and Acid Yellow 17 [11], Mg-Al and o-Methylene Red [12], Ni-Fe and o-Methylene Red [13], Zn-Al and Mordant Yellow 3 [14, 15], Zn-Al and Acid Yellow 3 [16], Zn-Al and Acid Green bianion 28 [17] can be used.

Some authors characterize pigments obtained by intercalation as nanocomposites. It should be noted that composite materials (organic–organic [18] or inorganic–inorganic [19]) consist of a matrix and a filler, between which there is always an interface. However, intercalated LDH pigments are mainly monophase substances, so their characterization as nanocomposites is inaccurate.

LDH can also be used to purify wastewater from anionic dyes by ion exchange to obtain dye-intercalated LDH. In particular, Evans Blue is extracted using Zn-Al LDH [20], and orange-type dyes are extracted using Mg-Al LDH [21]. Various azo dyes [22], including Remazol Brilliant Violet [23], are extracted using Ni-Al LDH, blue dyes (including Maya Blue) [24] – using Zn-Al LDH, Methyl Orange [25] – using Zn-Al LDH. Amaranth [26] is extracted from wastewater with Mg-Al LDH, Acid Yellow 42 [27] – with Mg-Al LDH, Congo Red [28] – with Ni-Al LDH, and Indigo Carmine [29] – with Mg-Fe LDH.

It is promising to use LDH as a nanocontainer for special functional anions, such as drugs [30, 31], dye anions [32], anions for sensors [33], corrosion inhibitors [34], biologically active additives [35], food additives, [36, 37], etc.

It should be noted that now there are practically no technologies for LDH production intercalated with functional ions. Therefore, the determination of the LDH process parameters as the basis for intercalation is promising.

2. Literature review and problem statement

Hydroxides of divalent metals (except for alkaline earth metals) are characterized by polymorphism and their two modifications have been described: β-modification (chemical formula Me(OH)₂, brucite structure) and α-modification (chemical formula 3Me(OH)₂·2H₂O, hydrotalcite structure). Structures intermediate between the α- and β-forms have been described for nickel hydroxide [38]. The formation of Ni(OH)₂ with a mixed layered (α+β) structure has been described in [39].

Layered double hydroxide (LDH) is an α-modification of the host metal hydroxide, in the crystal lattice of which some of the host metal cations are replaced by the guest metal cations: for example, Zn²⁺ (a host) is replaced by Al³⁺ (a guest). Because of this, an excess positive charge is formed in the crystal lattice, which can be compensated by the intercalation of additional anions into the interlayer space. Anions of precursor salts can act as such anions. But most often, anions with special functional properties are purposefully intercalated into LDH structures. Stabilizing [40] or activating anions [41, 42] can be introduced into the LDH composition.

The LDH structure consists of the following main components [43]: host metal cations, guest metal cations, and intercalated anions. It becomes possible to design an LDH with the required characteristics with a purposeful selection of all three components.

The development of a functional material based on intercalated LDH consists of choosing the type of LDH (host metal and guest metal cations), an anion for intercalation, as well as the method and conditions of synthesis.

For the synthesis of LDH-based materials, the use of Zn²⁺ as a host metal cation is the most promising. In the synthesis of LDH-based pigments, the advantage of Zn hydroxide is its white color, so Zn LDH is a good basis for a clear development of the intercalated dye color. A base LDH must be health-friendly for use in cosmetics, medicine, or as a food additive. The review paper [44] shows some negligible toxicity of Zn-Al LDH.

Al³⁺ is most often used as a guest metal cation. This is due to high structure-forming and stabilizing properties concerning the α-modification of LDH.

The choice of a functional component for intercalation into the LDH interlayer space is based on the nature of the substance, which must be anionic.

The method and conditions of synthesis directly determine the micro- and macrostructure of LDH particles. Hydroxides can be obtained by chemical precipitation, by the methods of direct (adding an alkaline solution to a metal salt solution) [45, 46], or reverse synthesis (adding a metal salt solution to an alkali solution) [47, 48], as well as by the sol-gel method [49]. Also, two-stage high-temperature synthesis [50], and homogeneous precipitation [51] can be used for their synthesis. Electrochemical methods are also used: cathodic template synthesis [52, 53] and synthesis in a slurry diaphragm electrolyzer [54]. However, not all of the methods are suitable for the synthesis of LDH intercalated with functional anions. Two types of methods can be distinguished to obtain such materials. The first one is a two-stage type, including:

1) the LDH synthesis with inorganic anions of precursor salts (mainly nitrate) by reverse precipitation [11, 16, 17], precipitation at constant pH [9, 26], homogeneous precipitation [22], etc.;

2) intercalation of a functional anion by the ion exchange method.

The two-stage type includes the method of LDH reduction from LDO (layered double oxide obtained by the LDH calcination) in the presence of a functional anion, for example, a dye anion [12]. The disadvantages of two-stage methods are the ion exchange duration, as well as the need to synthesize LDH intercalated with anions, which will be easily exchanged for functional anions. Moreover, such methods are poorly applicable in production due to complexity, long duration, and high cost.

The second method is a one-stage type. In this case, the formation of anion-intercalated LDH occurs directly during the synthesis. For this purpose, the method of co-precipitation by reverse synthesis or synthesis at constant pH is used [55, 56]. Direct one-stage synthesis is the most promising.

It should be noted that the main object of studies of LDH-based functional materials, for example, dye-intercalated Zn-Al LDH [55, 57] and Zn-Co LDH pigments [58],...
is the structure and characteristics of the synthesized materials. It should be noted that the characteristics of LDH intercalated with functional anions are determined by the parameters of the matrix – LDH intercalated with anions of precursor salts. The structural characteristics of Zn-Al-NO₃ LDH obtained by different methods were studied in [59]. At the same time, the technological parameters of the matrix (LDH intercalated with precursor salt anions) are practically not studied, which makes it difficult to develop a technology for the production of LDH-based functional materials.

3. The aim and objectives of the study

The aim of the work is to determine the technological parameters of Zn-Al nitrate layered double hydroxide under various synthesis conditions. This will allow the development of technologies for obtaining LDH-based functional materials.

To achieve the aim, the following objectives were set:
- to determine the yield of Zn-Al-nitrate layered double hydroxide samples synthesized at different temperatures, pH, and solution flow rates;
- to investigate the process of sedimentation of Zn-Al-nitrate layered double hydroxide samples synthesized at different temperatures, pH, and solution flow rates.

4. Research materials and methods

4.1. Method of samples preparation

We used crystalline hydrates of zinc and aluminum nitrates (analytical grade qualification) for the synthesis. NaOH was used in a granular form and a high analytical grade qualification.

Zn-Al-NO₃ LDH samples were obtained by chemical synthesis at constant pH [34]. LDH was synthesized with the independent supply of the Zn(NO₃)₂+Al(NO₃)₃ solution (with a molar ratio of Zn:Al=4:1) and the NaOH solution by peristaltic pumps. The solutions were fed at the same rate into a 2 L reaction beaker containing 100 mL of the initial solution. Variable synthesis conditions:
- pH – 7, 8, 9, 10;
- t – 10, 20, 30, 40, 50 and 60 °C;
- solution flow rate – 0.8 and 1.6 l/h.

Sample marking: Zn-Al-0.8-9-30, where Zn-Al is the LDH type, 0.8 is the solution flow rate (l/h), 9 is the synthesis pH, and 30 is the synthesis temperature (°C). To carry out the synthesis, the NaOH mass was calculated as the sum of the mass for the LDH formation and the mass for maintaining the required pH. The initial solution was also prepared with a pH corresponding to the pH of the synthesis. The synthesis was carried out with continuous stirring and temperature maintenance. Stirring and maintenance of the synthesis temperature continued for 60 minutes after the addition of solutions was completed. Thereafter, the LDH precipitate was filtered off from the mother liquor under a vacuum. For effective rinsing from soluble components, a two-stage procedure was used: the first drying at 70 °C (24 hours), grinding, soaking in distilled water (12 hours), filtration, and the second drying under the same conditions.

4.2. Methods of investigating the samples’ characteristics

Determination of the synthesized samples’ yield.

The yield of the samples was determined gravimetrically by weighing the sample after two-stage drying and dividing by the theoretical weight of the sample, for which the amounts of precursors were calculated.

Determination of the samples’ sedimentation rate.

The main purpose of investigating the sedimentation process was to determine the filterability of the obtained precipitate. Therefore, the investigation of the sedimentation rate was carried out immediately after the end of the precipitate aging process [60] (after turning off the heating and stirring) by measuring the thickness of the precipitate for 30 minutes.

The values of the yield and relative thickness of the precipitate layer were calculated as an average value based on the results of three repetitions of the syntheses. Statistical processing was carried out by the LSD (Least Significant Difference) calculation method.

5. Results of investigating the technological parameters of Zn-Al-nitrate layered double hydroxide samples

5.1. Results of determination of the samples yield

The yield values of Zn-Al-NO₃ samples are shown in Fig. 1.

Fig. 1. Yield of the samples synthesized at: a – different pH and solution flow rates; b – different temperatures

It should be noted that for all synthesis conditions, the LDH yield as a product was rather high and amounted to 69.9–84.4 % of the theoretical value. An increase in pH from 7 to 10 (Fig. 1, a) led to an increase in yield, while an increase in the solution flow rate from 0.8 l/h to 1.6 l/h led to a decrease in yield. An increase in temperature from 10 °C to 60 °C (Fig. 2, b) led to a decrease in yield from 84.3 % to 75.9 %. The yield of the Ni-Al-0.8-8-20 sample (obtained at 20 °C) was 81.6 %, which did not fit into the revealed dependence.
5. 2. Results of investigating samples sedimentation

The results of the sedimentation investigation are shown in Fig. 2.

![Graph showing sedimentation rate for different Zn-Al samples](image)

Fig. 2. Relative thickness of the precipitate layer for the samples obtained at: a – different pH and solutions flow rates, b – different temperatures

An increase in the synthesis pH (Fig. 2, a) led to an acceleration of sedimentation: the relative layer thickness after 30 min decreased from 71.4 % (pH=7) to 14.1 % (pH=10). At the same time, it should be noted that during synthesis with pH=7, the sedimentation rate increased with time. At the same time, as in the case of synthesis with pH=10, sedimentation almost completely ended within 5 minutes (the relative thickness of the layer after 5 minutes of sedimentation was 20.8 %, after 30 minutes – 14.1 %). Increasing the solutions flow rate from 0.8 l/h to 1.6 l/h (Fig. 2, a) led to an acceleration of sedimentation. An ambiguous effect of the synthesis temperature on the sedimentation rate was revealed (Fig. 2, b). The lowest sedimentation rate was found at a temperature of 30 °C, and the highest sedimentation rate (the smallest relative thickness after 30 minutes of sedimentation) – at 10 °C. At the same time, almost complete sedimentation within 5 min was detected for a synthesis temperature of 50 °C.

6. Discussion of the results of determining the yield and investigating the sedimentation of Zn-Al layered double hydroxide samples

In the discussion of the results, it should be taken into account that the formation of hydroxides of divalent metals occurs according to a complex mechanism [60]. During the formation of zinc hydroxide (as the hydroxide of the host metal forming the LDH crystal lattice), the rate of nucleation (formation of crystallization centers) is significantly higher than the crystal growth rate. As a result, LDH particles are formed according to a two-stage mechanism [60]:

- 1st stage (very fast) – formation of nuclei, their aggregation with the formation of a primary amorphous particle;
- 2nd stage (slow) – crystallization (aging) of the primary amorphous particle. The rate of the crystallization process is determined by many factors, the main of which are the pH of the mother liquor and the temperature.

**Determination of the LDH yield.** The analysis of the LDH yield values as a product under various synthesis conditions (Fig. 1) showed a high yield value (69.9–84.4). The decrease in the LDH yield could fundamentally be due to several reasons. First, in the process of synthesis or aging, LDH could partially decompose to LDO (layered double oxide) with a decrease in mass. Second, aluminum and zinc hydroxides are amphoteric, which could lead to partial dissolution of LDH at high pH. And third, the Zn$_{0.8}$Al$_{0.2}$$(NO_3)_2$$(OH)$$\frac{5}{2}$$H_2O formula was used to calculate the theoretical mass of LDH. At the same time, the amount of crystalline water could be lower, which would lead to a decrease in weight. An increase in the synthesis pH from 7 to 10 (Fig. 1, a) led to a slight increase in yield from 74.68 % to 83.54 %. This is probably due to the more complete precipitation of aluminum and zinc cations and possibly an increase in the amount of crystalline water. Increasing the solution flow rate from 0.8 l/h to 1.6 l/h (Fig. 1, a) led to a decrease in yield from 75.92 % to 69.98 %. The probable cause of this phenomenon may be a decrease in the amount of crystalline water. However, additional studies are needed to clarify the exact causes of this phenomenon. An increase in the synthesis temperature led to an ambiguous effect (Fig. 1, b). In general, it is possible to conclude that the yield decreased from 84.43 % (synthesis at 10 °C, Zn-Al-0.8-8-10 sample) to 75.92 % (synthesis at 60 °C, Zn-Al-0.8-8-60 sample). However, the yield value for the Zn-Al-0.8-8-20 sample, which was equal to 81.62 %, did not correspond to this dependence. Another approach seems to be more correct, which consists in separating the two sections of the yield-temperature dependence:

1) “10 °C – 20 °C” (Zn-Al-0.8-8-10, Zn-Al-0.8-8-20 samples);
2) “30 °C – 40 °C – 60 °C” (Zn-Al-0.8-8-30, Zn-Al-0.8-8-40, Zn-Al-0.8-8-50, Zn-Al-0.8-8-60 samples).

Both in the first and second sections of the dependence, there is a decrease in yield. In [34], the effect of temperature on the crystal structure of Zn-Al-NO$_3$ samples synthesized under the same conditions was studied. An analysis of the dependence of crystallinity on temperature revealed the same two sections, for which an increase in crystallinity with increasing temperature was determined. These data correlated with a decrease in yield, since an increase in crystallinity led to a decrease in the amount of crystalline water. Thus, the hypothesis put forward in [34] was confirmed. At a temperature of 30 °C, a change in the mechanism of nuclei or primary amorphous particles formation occurred.

**Investigating the sedimentation rate of LDH samples.** The analysis of the investigation of the pH influence on the sample sedimentation process (Fig. 2, a) showed that with an increase in the synthesis pH, the sedimentation rate increased. The relative thickness of the precipitate layer after 30 minutes of settling at pH=7 was 71.4 %. At the same time, the relative thickness of the layer at pH=10 was 14.2 %. In addition, it should be noted that the sample obtained at pH=7 was characterized by the sedimentation...
rate accelerating in time, and the relative thickness after 5 minutes of settling was 95.2 %. Moreover, with an increase in the synthesis pH, the sedimentation rate during the first 5 minutes of settling increased. For the Zn-Al-0.8-7-60 – Zn-Al-0.8-8-60 – Zn-Al-0.8-9-60 – Zn-Al-0.8-10-60 samples, the proportion of the precipitate thickness reduction for 5 minutes (to the total decrease in the precipitate thickness) was 16.8 %, 33.3 %, 77.7 %, and 92.3 %, respectively. This indicates a change in the state of colloidal precipitate particles. The LSD calculation showed that for the Zn-Al-0.8-8-60 and Zn-Al-0.8-9-60 samples, the values of the relative layer thickness for 25 and 30 minutes of sedimentation were statistically the same, which indicated the completion of sedimentation after 25 minutes. At the same time, for the Zn-Al-0.8-10-60 sample, sedimentation was already finished after 15 min, which probably indicated that the pH of the zero charges of the precipitate particles was close to 10. With an increase in the solution flow rate, the sedimentation rate increased (the relative thickness of the precipitate of the Zn-Al-0.8-6-60 and Zn-Al-1.6-8-60 samples after 30 minutes of settling was 52.6 % and 33.3 %, respectively). The increase in the sedimentation rate was because, with an increase in the flow rate, the local pH in the zone of formation of precipitate particles increased. In this case, sedimentation had been finished by the twenty-fifth minute of settling.

The analysis of the effect of the synthesis temperature on the sedimentation rate (Fig. 2, b) revealed two anomalies. LDH synthesized at 10 °C and 20 °C (Zn-Al-0.8-8-10 and Zn-Al-0.8-8-20 samples) were characterized by high sedimentation rates (the relative thickness of the precipitate after 30 minutes of settling was 25 % and 35.7 % respectively). An increase in the synthesis temperature reduced the sedimentation rate. For the Zn-Al-0.8-8-40 and Zn-Al-0.8-8-60 samples (synthesis temperatures 40 °C and 60 °C), the relative thickness of the precipitate after 30 minutes was 58.7 % and 52.6 %, respectively. This is probably because with an increase in the synthesis temperature, the crystallization rate increased, and it is possible that the forming particles had a smaller size, which reduced the sedimentation rate. At the same time, anomalies in the sedimentation rate for temperatures of 30 °C and 50 °C were revealed. An abnormally low sedimentation rate was revealed for the Zn-Al-0.8-8-30 sample (relative precipitate thickness 77.8 %). In this case, sedimentation was not completed after 30 minutes of settling (the difference in the relative layer thicknesses after 25 and 30 minutes exceeded the LSD). For the Zn-Al-0.8-8-50 sample, the sedimentation rate was shown to correspond to the sedimentation rate of the samples synthesized at 10 °C and 20 °C, with almost complete sedimentation occurring in the first 5 minutes. It is most probable that at temperatures of 30 °C and 50 °C, the precipitate formation mechanism changes. This confirms the hypothesis put forward in [34] about changes in the formation mechanism at these temperatures.

Additional studies are needed to clarify the formation mechanisms in detail for a more correct prediction of the Zn-Al LDH synthesis conditions.

7. Conclusions

1. The yields of Zn-Al-nitrate layered double hydroxide samples obtained by the synthesis method at a ratio of Zn:Al=4:1, a solution flow rate of 0.81/h and 1.61/h, pH=7, 8, 9, 10 and temperatures of 10, 20, 30, 40, 50, 60 °C were determined. It is shown that with an increase in the synthesis pH, the yield increases from 74.68 % to 83.54 %. Increasing the flow rate of the solutions reduces the yield. On the yield-synthesis temperature dependence, two segments were identified: 10–20 °C and 30–60 °C, within which an increase in temperature leads to a decrease in yield. The data obtained confirmed the hypothesis of a change in the mechanism or kinetics of the LDH formation at 30 °C.

2. The sedimentation rate of Zn-Al-nitrate layered double hydroxide samples obtained by synthesis at a ratio of Zn:Al=4:1, a solution flow rate of 0.81/h and 1.61/h, pH=7, 8, 9, 10 and temperatures of 10, 20, 30, 40, 50, 60 °C was studied (by measuring the precipitate thickness). It is shown that with an increase in the synthesis pH and solution flow rate, the sedimentation rate increases significantly. At pH=10, almost complete sedimentation of the sample occurs within the first 5 minutes. The data obtained indicate that the pH of the zero charges of Zn-Al-NO3 LDH particles is close to 10. When studying the effect of temperature on the sedimentation rate, it was found that an increase in temperature reduces the sedimentation rate. At the same time, an anomalously low sedimentation rate was revealed at a synthesis temperature of 30 °C and an anomalously high rate at a temperature of 50 °C, which confirms the hypothesis of a change in the mechanism or kinetics of the LDH formation at these temperatures.

References
1. Kesavan Pillai, S., Klei, P., de Beer, M., Mudaly, P. (2020). Layered double hydroxides: An advanced encapsulation and delivery system for cosmetic ingredients—an overview. Applied Clay Science, 199, 105688. doi: https://doi.org/10.1016/j.apclas.2020.105688
2. Viseras, C., Sánchez-Espejo, R., Palumbo, R., Liccardi, N., García-Villén, F., Borrero-Sánchez, A. et al. (2021). Clays in cosmetics and personal-care products. Clays and Clay Minerals, 69 (5), 561–575. doi: https://doi.org/10.1007/s42860-021-00154-5
3. Zaichuk, A. V., Amelina, A. A. (2018). Blue-green ceramic pigments in the system Ca–MgO–Al2O3–SiO2–Cr2O3 based on granulated blast-furnace slag. Voprosy Khimii i Khimicheskoi Tekhnologii, 6, 120–124. doi: https://doi.org/10.32434/0321-4095-2018-121-6-120-124
4. Zaichuk, A. V., Belyy, Ya. I. (2012). Korichnevye keramicheskie pigmenty na osnove martenovskogo shlaka. Zhurnal prikladnoy khimii, 85 (10), 1595–1600.
5. Zaichuk, A., Iovleva, J. (2013). The Study of Ceramic Pigments of Spinel Type with the Use of Slag of Aluminothermal Production of Ferrotitanium. Chemistry & Chemical Technology, 7 (2), 217–225. doi:https://doi.org/10.23939/chcht07.02.217
6. Zaichuk, A. V., Belyy, Ya. I. (2013). Sovershenstvovanie sostavov i svoystv serykh keramicheskikh pigmentov. Steklo i keramika, 6, 32–37.
7. Zaichuk, A. V., Amelina, A. A. (2017). Poluchenie uvarovitovykh keramicheskikh pigmentov s primeneniem granulirovannogo domennogo shlaka. Steklo i keramika, 3, 32–36.
8. Khan, A. I., Ragavan, A., Fong, B., Markland, C., O’Brien, M., Dunbar, T. G. et. al. (2009). Recent Developments in the Use of Layered Double Hydroxides as Host Materials for the Storage and Triggered Release of Functional Anions. Industrial & Engineering Chemistry Research, 48 (23), 10196–10205. doi: https://doi.org/10.1021/ie9012616
9. Mandal, S., Tichit, D., Lerner, D. A., Marcotte, N. (2009). Azoic Dye Hosted in Layered Double Hydroxide: Physicochemical Characterization of the Intercalated Materials. Langmuir, 25 (18), 10980–10986. doi: https://doi.org/10.1021/la901201s
10. Mandal, S., Lerner, D. A., Marcotte, N., Tichit, D. (2009). Structural characterization of azoic dye hosted layered double hydroxides. Zeitschrift Für Kristallographie. 224 (5-6), 282–286. doi: https://doi.org/10.1524/zkri.2009.1150
11. Wang, Q., Feng, Y., Feng, J., Li, D. (2011). Enhanced thermal- and photo-stability of acid yellow 17 by incorporation into layered double hydroxide. Journal of Solid State Chemistry, 184 (6), 1551–1555. doi: https://doi.org/10.1016/j.jssc.2011.04.020
12. Liu, J. Q., Zhang, X. C., Hou, W. G., Dai, Y. Y., Xiao, H., Yan, S. S. (2009). Synthesis and Characterization of Methyl-Red/ Layered Double Hydroxide (LDH) Nanocomposite. Advanced Materials Research, 79-82, 493–496. doi: https://doi.org/10.4028/www.scientific.net/amr.79-82.493
13. Tian, Y., Wang, G., Li, F., Evans, D. G. (2007). Synthesis and thermo-optical stability of α-methylene red-intercalated Ni–Fe layered double hydroxide material. Materials Letters, 61 (8-9), 1662–1666. doi: https://doi.org/10.1021/jp306778v
14. Hwang, S.-H., Jung, S.-C., Yoon, S.-M., Kim, D.-K. (2008). Preparation and characterization of dye-intercalated Zn–Al-layered double hydroxide and its surface modification by silica coating. Journal of Physics and Chemistry of Solids, 69 (5-6), 1061–1065. doi: https://doi.org/10.1016/j.jpcs.2007.11.002
15. Tang, P., Deng, F., Feng, Y., Li, D. (2012). Mordant Yellow 3 Azoic Intercalated Layered Double Hydroxides: Preparation, Thermo- and Photostability. Industrial & Engineering Chemistry Research, 51 (32), 10542–10545. doi: https://doi.org/10.1021/ie300645b
16. Tang, P., Feng, Y., Li, D. (2011). Fabrication and properties of Acid Yellow 49 dye-intercalated layered double hydroxides film on an alumina-coated aluminum substrate. Dyes and Pigments, 91 (2), 120–125. doi: https://doi.org/10.1016/j.dypig.2011.03.012
17. Tang, P., Feng, Y., Li, D. (2011). Improved thermal and photostability of an anthraquinone dye by intercalation in a zinc–aluminum layered double hydroxides host. Dyes and Pigments, 90 (3), 253–258. doi: https://doi.org/10.1016/j.dypig.2011.01.007
18. Burmistr, M. V., Boklo, V. S., Lipko, E. O., Gerasimenko, K. O., Gonza, Y. P., Vesnin, R. L. et. al. (2014). Antifriction and Construction Materials Based on Modified Phenol-Formaldehyde Resins Reinforced with Mineral and Synthetic Fibrous Fillers. Mechanics of Composite Materials, 50 (2), 213–222. doi: https://doi.org/10.1007/s11029-014-9408-0
19. Kovalenko, V., Kotok, V. (2017). Selective anodic treatment of W(C)-based superalloy scrap. Eastern-European Journal of Enterprise Technologies, 1 (5 (85)), 53–58. doi: https://doi.org/10.15587/1729-4061.2017.91205
20. Shamin, M., Dana, K. (2017). Efficient removal of Evans blue dye by Zn–Al–NO3 layered double hydroxide. International Journal of Environmental Science and Technology, 15 (6), 1275–1284. doi: https://doi.org/10.1007/s13762-017-1478-9
21. Mahjoubi, F. Z., Khalidi, A., Abdennouri, M., Barka, N. (2017). Zn–Al layered double hydroxides intercalated with carbonate, nitrate, chloride and sulphate ions: Synthesis, characterization and dye removal properties. Journal of Taibah University for Science, 11 (1), 90–100. doi: https://doi.org/10.1016/j.jtusci.2015.10.007
22. Palahagedara, M. N., Samaraweera, M., Dharmarathna, S., Kuo, C.-H., Palahagedara, L. R., Gascón, J. A., Suib, S. L. (2014). Removal of Azo Dyes: Intercalation into Sonochemically Synthesized NiAl Layered Double Hydroxide. The Journal of Physical Chemistry C, 118 (31), 17801–17809. doi: https://doi.org/10.1021/jp505260a
23. Darmograi, G., Prelot, B., Layrac, G., Tichit, D., Martin-Gassin, G., Salles, F., Zajac, J. (2015). Study of Adsorption and Intercalation of Orange-Type Dyes into Mg–Al Layered Double Hydroxide. The Journal of Physical Chemistry C, 119 (41), 23388–23397. doi: https://doi.org/10.1021/acs.jpcc.5b05510
24. Marangoni, R., Bouhent, M., Taviot-Guëzo, C., Wypych, F., Leroux, F. (2009). Zn2Al layered double hydroxides intercalated and adsorbed with anionic blue dyes: A physico-chemical characterization. Journal of Colloid and Interface Science, 333 (1), 120–127. doi: https://doi.org/10.1016/j.jcis.2009.02.001
25. El Hassani, K., Beakou, B. H., Kalhina, D., Oukani, E., Anouar, A. (2017). Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: A comparative study. Applied Clay Science, 140, 124–131. doi: https://doi.org/10.1016/j.jpcs.2017.02.010
26. Abdellauzi, K., Pavlovic, I., Bouhent, M., Benhamou, A., Barriga, C. (2017). A comparative study of the amaranth azo dye adsorption/desorption from aqueous solutions by layered double hydroxides. Applied Clay Science, 143, 142–150. doi: https://doi.org/10.1016/j.jpcs.2017.03.019
27. Santos, R. M. M. dos, Gonçalves, R. G. L., Constantino, V. R. L., Santilli, C. V., Borges, P. D., Tronto, J., Pinto, F. G. (2017). Adsorption of Acid Yellow 42 dye on calcined layered double hydroxide: Effect of time, concentration, pH and temperature. Applied Clay Science, 140, 132–139. doi: https://doi.org/10.1016/j.jclay.2017.02.005
28. Bhardwaj, D., Deka, R. C. (2017). Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide. Journal of Environmental Chemical Engineering, 5 (2), 2056–2067. doi: https://doi.org/10.1016/j.jece.2017.04.012
29. Ahmed, M. A., brick, A. A., Mohamed, A. A. (2017). An efficient adsorption of indigo carmine dye from aqueous solution on mesoporous Mg/Fe layered double hydroxide nanoparticles prepared by controlled sol-gel route. Chemosphere, 174, 280–288. doi: https://doi.org/10.1016/j.chemosphere.2017.01.147
30. Arizaga, G. G. C., Gardolinski, J. E. F. da C., Schreiner, W. H., Wypych, F. (2009). Intercalation of an oxalatooxoniobate complex into layered double hydroxide and layered zinc hydroxide nitrate. Journal of Colloid and Interface Science, 330 (2), 352–358. doi: https://doi.org/10.1016/j.jcis.2008.10.025

31. Andrade, K. N., Pérez, A. M. P., Arizaga, G. G. C. (2019). Passive and active targeting strategies in hybrid layered double hydroxides nanoparticles for tumor bioimaging and therapy. Applied Clay Science, 181, 105214. doi: https://doi.org/10.1016/j.clay.2019.105214

32. Kovalenko, V., Kotok, V., Veraloshkina, A., Zaychuk, A. (2017). Synthesis and characterisation of dyeintercalated nickelaluminium layered double hydroxide as a cosmetic pigment. Eastern-European Journal of Enterprise Technologies, 5 (12 (89)), 27–33. doi: https://doi.org/10.15587/1729-4061.2017.109814

33. Cursino, A. C. T., Rives, V., Arizaga, G. G. C., Trujillano, R., Wypych, F. (2015). Rare earth and zinc layered hydroxide salts intercalated with the 2-amino benzoate anion as organic luminescent sensitizer. Materials Research Bulletin, 70, 336–342. doi: https://doi.org/10.1016/j.materresbull.2015.04.055

34. Kovalenko, V., Kotok, V. (2019). “Smart” anticorrosion pigment based on layered double hydroxide: construction and characterization. Eastern-European Journal of Enterprise Technologies, 4 (12 (100)), 23–30. doi: https://doi.org/10.15587/1729-4061.2019.176690

35. Carabajal Arizaga, G. G., Sánchez Jiménez, C., Parra Saavedra, K. J., Macías Lamas, A. M., Puebla Pérez, A. M. (2016). Folate-intercalated layered double hydroxide as a vehicle for cyclophosphamide, a non-ionic anti-cancer drug. Micro & Nano Letters, 11 (7), 360–362. doi: https://doi.org/10.1089/mnl.2016.0106

36. Ghotbi, M. Y., Hussein, M. Z. bin, Yahaya, A. H., Rahman, M. Z. A. (2009). LDH-intercalated d-glucose: Generation of a new food additive-inorganic nanohybrid compound. Journal of Physics and Chemistry of Solids, 70 (6), 948–954. doi: https://doi.org/10.1016/j.jpcs.2009.05.007

37. Hong, M.-M., Oh, J.-M., Choy, J.-H. (2008). Encapsulation of Flavor Molecules, 4-Hydroxy-3-Methoxy Benzoic Acid, into Layered Inorganic Nanoparticles for Controlled Release of Flavor. Journal of Nanoscience and Nanotechnology, 8 (10), 5018–5021. doi: https://doi.org/10.1166/jnn.2008.1385

38. Rajamathi, M., Vishnu Kamath, P., Seshadri, R. (2000). Polymorphism in nickel hydroxide: role of interstratification. Journal of Materials Chemistry, 10 (2), 503–506. doi: https://doi.org/10.1039/a905651c

39. Kovalenko, V., Kotok, V., Yeroshkina, A., Zaychuk, A. (2017). Synthesis and characterisation of dyeintercalated nickelaluminium layered double hydroxide as a cosmetic pigment. Eastern-European Journal of Enterprise Technologies, 5 (12 (89)), 27–33. doi: https://doi.org/10.15587/1729-4061.2017.109814

40. Kotok, V., Kovalenko, V. (2018). Investigation of NiAl hydroxide with silver addition as an active substance of alkaline batteries. Eastern-European Journal of Enterprise Technologies, 3 (6 (99)), 44–52. doi: https://doi.org/10.15587/1729-4061.2019.169461

41. Kotok, V., Kovalenko, V., Vlasov, S. (2018). Investigation of NiAl hydroxide with silver addition as an active substance of alkaline batteries. Eastern-European Journal of Enterprise Technologies, 3 (6 (93)), 6–11. doi: https://doi.org/10.15587/1729-4061.2018.133465

42. Hu, M., Lei, L. (2006). Effects of particle size on the electrochemical performances of a layered double hydroxide, [Ni$_4$Al(OH)$_{10}$NO$_3$]. Journal of Solid State Electrochemistry, 11 (6), 847–852. doi: https://doi.org/10.1007/s10008-006-0231-y

43. Kotok, V. A., Kovalenko, V. L., Solovov, V. A., Kovalenko, P. V., Ananchenko, B. A. (2018). Effect of deposition time on properties of electrochromic nickel hydroxide films prepared by cathodic template synthesis. ARPN Journal of Engineering and Applied Sciences, 13 (9), 3076–3086. Available at: http://www.carpornjournals.org/jeas/research_papers/2018/jeas_0518_7034.pdf

44. Kotok, V., Kovalenko, V., Vlasov, S. (2018). Investigation of NiAl hydroxide with silver addition as an active substance of alkaline batteries. Eastern-European Journal of Enterprise Technologies, 3 (6 (93)), 6–11. doi: https://doi.org/10.15587/1729-4061.2018.133465

45. Kovalenko, V., Kotok, V. (2019). Investigation of characteristics of double Ni–Co and ternary Ni–Co–Al layered hydroxides for supercapacitor application. Eastern-European Journal of Enterprise Technologies, 2 (6 (98)), 58–66. doi: https://doi.org/10.15587/1729-4061.2019.164792

46. Xiaoyan, G., Jian-cheng, D. (2007). Preparation and electrochemical performance of nano-scale nickel hydroxide with different shapes. Materials Letters, 61 (3), 621–625. doi: https://doi.org/10.1016/j.matlet.2006.05.026

47. Kovalenko, V. L., Kotok, V. A., Sykhchin, A., Ananchenko, B. A., Chernyad’ev, E. V., Burkov, A. A. et. al. (2020). Al3$^+$ Additive in the Nickel Hydroxide Obtained by High-Temperature Two-Step Synthesis: Activator or Poisoner for Chemical Power Source Application? Journal of The Electrochemical Society, 167 (10), 100530. doi: https://doi.org/10.1149/1945-7111/abf0a2a

48. Saikia, H., Ganguli, J. N. (2012). Intercalation of Azo Dyes in Ni-Al Layered Double Hydroxides. Asian Journal of Chemistry, 24 (12), 5909–5913. Available at: https://asianjournalofchemistry.co.in/User/ViewFreeArticle.aspx?ArticleID=24_12_134
52. Kotok, V. A., Kovalenko, V. L. (2019). Non-Metallic Films Electroplating on the Low-Conductivity Substrates: The Conscious Selection of Conditions Using Ni(OH)$_2$ Deposition as an Example. Journal of The Electrochemical Society, 166 (10), D395–D408. doi: https://doi.org/10.1149/2.0561910jes

53. Kotok, V., Kovalenko, V. (2018). A study of multilayered electrochromic platings based on nickel and cobalt hydroxides. Eastern-European Journal of Enterprise Technologies, 1 (12 (91)), 29–35. doi: https://doi.org/10.15587/1729-4061.2018.121679

54. Kovalenko, V., Kotok, V. (2018). Influence of ultrasound and template on the properties of nickel hydroxide as an active substance of supercapacitors. Eastern-European Journal of Enterprise Technologies, 3 (12 (93)), 32–39. doi: https://doi.org/10.15587/1729-4061.2018.133548

55. Kovalenko, V., Kotok, V. (2020). Tartrazine-intercalated Zn–Al layered double hydroxide as a pigment for gel nail polish: synthesis and characterisation. Eastern-European Journal of Enterprise Technologies, 3 (12 (105)), 29–37. doi: https://doi.org/10.15587/1729-4061.2020.205607

56. Kovalenko, V., Kotok, V. (2020). Bifunctional indigocarmin–intercalated Ni–Al layered double hydroxide: investigation of characteristics for pigment and supercapacitor application. Eastern-European Journal of Enterprise Technologies, 2 (12 (104)), 30–39. doi: https://doi.org/10.15587/1729-4061.2020.201282

57. Kovalenko, V., Kotok, V. (2020). Determination of the applicability of Zn–Al layered double hydroxide, intercalated by food dye Orange Yellow S, as a cosmetic pigment. Eastern-European Journal of Enterprise Technologies, 5 (12 (107)), 81–89. doi: https://doi.org/10.15587/1729-4061.2020.214847

58. Kovalenko, V., Kotok, V. (2021). The determination of synthesis conditions and color properties of pigments based on layered double hydroxides with Co as a guest cation. Eastern-European Journal of Enterprise Technologies, 6 (6 (114)), 32–38. doi: https://doi.org/10.15587/1729-4061.2021.247160

59. Kovalenko, V., Borysenko, A., Kotok, V., Nafeev, R., Verbitskiy, V., Melnyk, O. (2022). Determination of the dependence of the structure of Zn-Al layered double hydroxides, as a matrix for functional anions intercalation, on synthesis conditions. Eastern-European Journal of Enterprise Technologies, 1 (12 (115)), 12–20. doi: https://doi.org/10.15587/1729-4061.2022.232738

60. Vasserman, I. M. (1980). Khimicheskoe osazhdenie iz rastvorov. Leningrad: Khimiya, 208.