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INVESTIGATION OF THE CHARACTERISTICS OF ZN-AL LAYERED DOUBLE HYDROXIDES, INTERCALATED WITH NATURAL DYES FROM SPICES, AS A COSMETIC PIGMENTS

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Pigments are the main components of cosmetics, which determine both toxicity and consumer color characteristics. Zn-Al layered double hydroxides intercalated with anionic food dyes are promising pigments. The best sources of dyes for intercalation are natural ones. The most promising are spices. Natural dyes from spices are often biologically active substances. The parameters of samples of Zn-Al (Zn:Al=3:1) hydroxides intercalated with natural food dyes, synthesized in the medium of aqueous tinctures of saffron and safflower, were studied. The crystal structure of the samples was studied by X-ray phase analysis; color characteristics were studied by spectroscopy and calculation of parameters in the CIE L*a*b system.

The possibility of synthesizing Zn-Al colored layered double hydroxides intercalated with natural dyes in the medium of saffron and safflower tinctures was shown. X-ray phase analysis showed that both pigment samples were layered double hydroxides with the α-$Zn(OH)_2$ structure. For the pigment intercalated with saffron dye, the phenomenon of partial decomposition of Zn-Al LDH to ZnO during synthesis was revealed. The color characteristics of the samples were studied. Zn-Al LDH pigment synthesized in a saffron tincture had a bright yellow color determined by intercalated saffron carotenoids (crocin and crocetin). It was suggested that safflower dye flavonoids were partially hydrolyzed (red ones – cartamine and cartamidine, and yellow – Safflor Yellow A), which led to the formation of a dark orange-brown color of the sample. The prospects of using Zn-Al LDH intercalated with saffron food dyes as a cosmetic pigment were shown

Keywords: Zn-Al layered double hydroxide, cosmetic pigment, intercalation, saffron, safflower, color, carotenoids, flavonoids

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1. Introduction

People widely use decorative cosmetics. The composition of these products includes various components, but pigments are the obligatory and most important of them [1, 2]. These pigments can be natural, artificial or synthetic, inorganic (mineral), or organic. Among the mineral pigments, the most common are salt and oxide. Inorganic pigments have high color fastness but a narrow color gamut. Organic pigments are characterized by a wide range of colors, but have low stability to sunlight.

Organo-inorganic hybrid materials combine the advantages of both organic and inorganic pigments. Among pigments of this type, the most promising are layered double hydroxides (LDHs) [3] intercalated with anionic dyes [4, 5].

The combination of various metal cations and anionic dyes of various colors in the composition of LDH will significantly expand the color palette of pigments, especially for cosmetic purposes. For example, Zn-Al and Acid Yellow 17 [6], Mg-Al and o-Methylene Red [7], Ni-Fe and o-Methylene Red [8], Zn-Al and Mordant Yellow 3 [9, 10] Zn-Al and Acid Yellow 3 [11], Zn-Al and Acid Green bianion 28 [12] are used.

Some authors use the term «nanocomposites» to describe intercalation pigments. However, composite materials (organic-organic [13] or inorganic-inorganic [14]) always have an interface between the main components - the matrix and the filler. However, intercalated LDH pigments are mainly monophasic substances; therefore, it is incorrect to describe them as nanocomposites.

LDHs were also used to purify wastewater from anionic dyes by ion exchange to obtain dye-intercalated LDHs. In particular, Evans Blue was extracted using Zn-Al LDH [15], and orange-type dyes were extracted using Zn-Al LDH [16]. Various azo dyes [17], including Remazol Brilliant Violet [18], were extracted using Ni-Al LDH, and blue dyes (including Maya Blue) [19] were extracted using Zn-Al LDH, Methyl Orange [20] was extracted using Zn-Al LDH. Amaranth [21] was extracted from wastewater using Mg-Al LDH, Acid Yellow 42 [22] was extracted using Mg-Al LDH, Congo Red [23] was extracted using Ni-Al LDH, and Indigo Carmine [24] was extracted using Mg-Fe LDH.

On the other hand, a promising direction is the use of LDH as a nano container for special functional anions, such as drugs [25, 26], dye anions [27], and anions for sensors [28] (similar to other ion exchange substances [29]), corrosion inhibitors [30], biologically active additives [31], food additives [32, 33], etc. A significant amount of functional anionic substances are found in natural sources.

The data presented indicate that it is promising to investigate the characteristics of LDHs intercalated with organic anionic compounds of natural origin.

2. Literature review and problem statement

Hydroxides of divalent metals (excluding alkaline earth ones) are characterized by polymorphism and two modifications have been described. β-modification (chemical formula $Me(OH)_2$, brucite structure) and α-modification (chemical formula $3Me(OH)_2 \cdot 2H_2O$, hydrotalcite structure). At the same time, structures intermediate between the α- and β-forms have been described for nickel hydroxide [34]. The article [35] describes the formation of $Ni(OH)_2$ with a mixed layered (α+β) structure.

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 guest metal cations. For example, Zn^{2+} (a host) is replaced by Al^{3+} (a guest). As a result 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. Counterions of precursor salts can act as such anions. But most often, anions with special functional properties purposefully intercalate into LDH structures. Stabilizing [36] or activating anions [37, 38] can be introduced into the LDH composition.

In this case, the LDH structure is formed by the following main components [39]: host metal cations, guest metal cations, and intercalated anions. The creation of an LDH with the required characteristics is possible using ionic design, with a targeted choice of these three components.

The development of a functional material based on intercalated LDH consists of the stages of choosing the type of LDH (a host metal cation and a guest metal cation), the choice of the intercalated anion, and the choice of the synthesis method and conditions.

In the LDH synthesis, the most promising is the use of Zn^{2+} as a host metal cation. In the synthesis of LDH pigments, the advantage of Zn hydroxide is the white color, therefore Zn LDH is a good basis for the full development of the color of the intercalated dye. For use in cosmetics, as a dietary supplement, or as a drug, LDH as a base must be health-friendly. The review article [40] shows the minimal toxicity of Zn-Al LDH.

As a guest metal cation, Al^{3+} is most often used, which has high structure-forming and stabilizing properties concerning the α-modification of LDH.

The choice of an intercalating substance for obtaining materials based on LDH is based on the nature of the substance. It must be anionic.

The method and conditions of synthesis determine the micro- and macrostructure of LDH particles. Hydroxides can be obtained by chemical precipitation by direct synthesis (introducing an alkaline solution into a metal salt solution) [41], reverse synthesis (introducing a metal salt solution into an alkali solution) [42, 43], and the sol-gel method. Two-stage high-temperature synthesis [44], and homogeneous deposition [45] can also be used. For synthesis, electrochemical methods are used: cathodic template synthesis [46, 47] and synthesis in a slit diaphragm electrolyzer [48]. However, not all methods can be applied to the synthesis of LDH intercalated with functional anions. In principle, two types of methods can be distinguished to obtain such materials. The first method is a two-stage type. It includes:

1) synthesis of LDHs intercalated with inorganic anions (mainly precursor salt anions) by reverse precipitation [6, 11, 12], precipitation at constant pH [4, 21], homogeneous precipitation [17], etc.;

2) introduction of a functional anion by ion-ion exchange.

One of the variants of the two-stage type is the method of LDH reduction from LDO (layered double oxide obtained by slow calcination of LDH) in a solution containing a functional anion, for example, a dye anion [7]. The disadvantages of the two-stage type are the high duration of the ion exchange, as well as the need for the synthesis of LDH with anions that can be easily exchanged for functional anions. However, such methods are not technologically advanced due to complexity, high duration, and high cost.

The second method is a one-stage type of production. In this case, the formation of dye-intercalated LDH occurs directly during the synthesis. For this purpose, the method of coprecipitation by reverse synthesis or synthesis at constant pH is used [49, 50]. Direct synthesis is the most promising.

Natural dyes are promising anionic dyes for obtaining cosmetic LDH pigment. Since ancient times, natural materials, including spices, have been used as natural water-soluble dyes. For cosmetology, yellow-orange pigments are promising. Safflower and saffron are often used as natural food dyes in this color.

Safflower, as a spice and food yellow-orange dye, is the dried petals of the Safflower plant (Carthamus tinctorius L). In Southeast Asia, Carthamus Oxyacantha is also used as a dye, spice, and medicinal plant, which is called Pholi (Wild Safflower) [51]. An aqueous extract of safflower is used as a textile dye having an antibacterial effect [52]. The main coloring component of safflower is the flavonoid cartamine [53, 54]. Its potassium salt is known [55], which confirms the anionic character of cartamine [53, 53]. In addition to cartamine, safflower colorants are cartamidine [56, 57] and Safflor Yellow A [51]. Studies [58, 59] have shown the high biological activity of cartamine and cartamidine and the prospects for their pharmacological application.

Another common dye, spice, and medicinal plant is saffron, which is the dried filaments of the autumn-blooming crocus Crocus sativus L. [60]. The main coloring and biologically active components of saffron are the water-soluble carotenoids crocin and crocetin. The high biological activity of crocin and the prospect of using it for the treatment of eye diseases (glaucoma, macular degeneration, diabetic retinopathy, and age-related macular degeneration) [61], as an antidepressant [62], and an anticancer substance [63] have been revealed.

The data presented in [34–63] show the promise of using dyes from safflower and saffron for intercalation in LDH to obtain a promising cosmetic pigment with high biological activity. However, no data on the synthesis or investigation of pigment based on LDH intercalated with safflower and saffron dyes have been found in the literature.

3. The aim and objectives the study

This work aims to investigate the characteristics of pigments based on Zn-Al LDH intercalated with natural food dyes saffron and safflower. This will make it possible to synthesize a new type of cosmetic pigments with a biologically active component.

To achieve the aim, the following tasks were set:

– to synthesize samples of Zn–Al-natural food dye directly in the medium of saffron and safflower tinctures;

– to investigate the phase composition and structures of the obtained samples;

– to investigate the color characteristics of the synthesized pigment samples.

4. Materials and research methods

4. 1. Method for obtaining samples of LDH pigments

For the synthesis, let's use crystalline hydrates of zinc and aluminum nitrates (analytical grade qualification). NaOH was used in granular form and a high analytical grade qualification. Dry commercial samples of saffron and safflower spices were used as a source of natural dyes.

Aqueous tinctures of spices were used as a medium for the synthesis of the LDH pigment. A tincture of the spice (an extract of the coloring component of the spice) was prepared by adding a weighed portion of the spice to distilled water at a temperature of 90 °C and holding it for one hour under thermostatically controlled conditions.

Before synthesis, the tincture was filtered from the spice. After that, the required amount of zinc and aluminum nitrates was dissolved in the spice tincture (at a molar ratio of Zn^{2+}:Al^{3+}=3:1).

For the synthesis of samples of Zn–Al-(natural food dye) LDH, an alkali solution was added to a solution of tincture of spices with zinc and aluminum nitrates at a temperature of 80 °C until pH=10 was reached [64, 65]. The preparation was carried out with continuous stirring, which continued for 30 minutes after the end of the synthesis. This is necessary for the process of crystallization and intercalation to proceed [66, 67]. The resulting pigment precipitate was filtered under vacuum from the mother liquor, dried for 24 hours at 80 °C, grinded, soaked in distilled water, filtered, and dried again under the same conditions. Before investigating the characteristics, LDH samples were additionally ground in an agate mortar and sifted through a 71 μm sieve.

Sample markings: Zn_3Al-(Saffron Tincture) – sample synthesized in saffron tincture; Zn_3Al-(Safflower Tincture) – sample synthesized in safflower tincture.

4. 2. Methods for investigating the characteristics of LDH samples

Investigating the characteristics of the synthesized pigment samples.

The crystal structure of the pigments was studied by X-ray phase analysis (XPA) using a DRON-3 diffractometer (Co-Kα radiation, angle range 10–90° 2Θ, scanning rate 0.1°/s).

Investigating the color characteristics of pigment samples.

To investigate the color, the pigment samples were placed in an even layer in ZIP bags. The color characteristics of gel nail polish samples were studied using an EFI Es-2000 spectrophotometer (USA). After the measurements, the color characteristics were calculated in the coordinates of the international color model CIE 1976 L*a*b: a, b, L (Lightness) and S (Saturation – color saturation) in the standard program supplied by the manufacturer of the spectrophotometer.

5. Results of the synthesis and investigation of the characteristics of intercalated Zn-Al layered double hydroxide samples

5. 1. Results of the synthesis

It was revealed that as a result of the synthesis, the colored precipitate was formed (Fig. 1).

The Zn_3Al-(Saffron Tincture) sample (Fig. 1, *a, c*), synthesized in the medium of saffron tincture, had a saturated yellow-orange color, and the Zn_3Al-(Safflower Tincture) sample (Fig. 1, *b, d*) synthesized in the medium safflower tincture, had a darker, yellow-brown color.

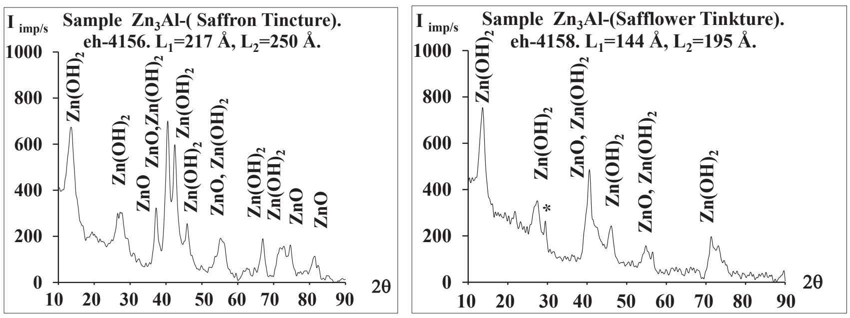
5. 2. Results of investigating the phase composition and structure of the samples

The results of the X-ray phase analysis of the samples are shown in Fig. 2.

The X-ray diffraction patterns of both samples showed clearly defined peaks of the $Zn(OH)_2$ crystal lattice, which corresponded to Zn-Al LDH. Peaks were also revealed at 2Θ=41° and 56°, which simultaneously corresponded to the oxide phase of the ZnO type and the hydroxide phase of the LDH. It should be noted that on the diffraction pattern of the Zn_3Al-(Saffron Tincture) sample (Fig. 2, *a*), the peak at 2Θ=41° was actually a part of the triple peak. At the same time, the Zn_3Al-(Safflower Tincture) sample (Fig. 2, *b*) had a single peak at 2Θ=41°.

a *b* *c* *d*

Fig. 1. Photo images of Zn-Al LDH samples intercalated with natural food dyes: *a; c* – Zn_3Al-(Saffron Tincture); *b; d* – Zn_3Al-(Safflower Tincture); *a; b* – precipitate of samples in the mother liquor; *c; d* – samples after vacuum filtration



a *b*

Fig. 2. Results of XRD analysis of the Zn-Al LDH samples intercalated with natural food dyes: *a* – Zn_3Al-(Saffron Tincture); *b* – Zn_3Al-(Safflower Tincture)

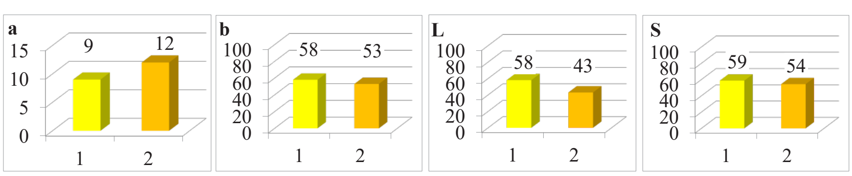
It is necessary to note the presence of an amorphous or X-ray amorphous component in both samples, as indicated by the presence of a diffuse peak in the region of angles 2Θ=10–18°. The X-ray diffraction pattern of the Zn_3Al-(Safflower Tincture) sample also revealed a peak of an unidentified phase, which was indicated by *.

5. 3. Results of investigating the color characteristics of gel nail polish samples with synthesized pigments

The color characteristics of the samples are shown in Fig. 3.

The dried and ground Zn_3Al-(Saffron Tincture) sample synthesized in safflower tincture had a bright yellow color, while the dried and ground Zn_3Al-(Safflower Tincture) sample obtained in saffron tincture was dark yellow-orange. The **a** index was higher for the Zn_3Al-(Safflower Tincture) sample, while the **b** index was higher for the Zn_3Al-(Saffron Tincture) sample.

It should be noted that the Zn_3Al-(Saffron Tincture) sample had a slightly higher saturation (Fig. 3, *d*) and higher lightness (Fig. 3, *e*) than the Zn_3Al-(Safflower Tincture) sample.



a *b* *c* *d*

Fig. 3. Color characteristics (in CIE 1976 L*a*b color model coordinates) of gel nail polishes with pigment samples. Samples: 1 – Zn_3Al-(Saffron Tincture); 2 – Zn_3Al-(Safflower Tincture); color characteristics parameters: a – chromatic component: *a; b* – chromatic component b; *c* – L (Lightness); *d* – S (Color Saturation)

6. Discussion of the results of investigating the characteristics of Zn-Al layered double hydroxides samples obtained in the medium of spice tincture

Synthesis of the samples. It was shown the possibility of obtaining colored Zn-Al LDH intercalated with natural food dyes by synthesis directly in the medium of safflower and saffron tincture. A wet sample of Zn_3Al-(Saffron Tincture) (Fig. 1, *c*) synthesized in a saffron tincture had a bright yellow-orange color. The color of the obtained substance correlated with the color of the dyes that were part of saffron – the carotenoids crocin and crocetin [60]. A wet sample of Zn_3Al-(Safflower Tincture) (Fig. 1, *d*) synthesized in safflower tincture had a darker orange-brown color. This color of the precipitate contradicted the color of safflower dyes, the main of which were the flavonoids of cartamine (red), cartamidine (red-orange), and Safflor Yellow A (yellow) [54, 56]. It is known that flavonoids are quite easily hydrolyzed at elevated temperatures with the elimination of carbohydrate residues, while the color of the substance changes towards darker, brown. An example is the purple carotenoid betanin (found in beetroots), which turns red-brown when boiled. In this case, it should be concluded that in the Zn_3Al-(Safflower Tincture) sample, both the initial flavonoid dyes and the products of their partial hydrolysis were intercalated into the LDH crystal structure. The filtrate after soaking the dried samples in distilled water for 48 hours was uncolored, which confirmed the intercalation of natural food dyes from the tinctures.

Investigation of the phase composition and structure of the samples. Analysis of XRD results (Fig. 2) showed that the main component of both samples was a phase with a crystal lattice of α-$Zn(OH)_2$ with a characteristic peak at 2Θ=14°. This clearly confirmed that the samples were precisely Zn-Al LDHs. Both diffraction patterns (Fig. 2) clearly showed a peak at 2Θ=40.6°, which simultaneously corresponded to both zinc oxide and zinc hydroxide. It should be noted the high degree of covalence of the Zn-OH bond in zinc hydroxide. As a result, even at low synthesis temperatures, partial dehydration of hydroxide to oxide occurred. It was shown in [66] that to detect ZnO in a diffraction pattern, it was necessary to use a combination of three peaks at 2Θ=37.4° (plane 100), 40.6° (plane 002), and 42.8° (plane 101).

On the diffraction pattern of the Zn_3Al-(Saffron Tincture) sample (Fig. 2, *a*) synthesized in saffron tincture, all three distinct characteristic peaks of zinc oxide were revealed at 2Θ=37.4°, 40.6°, and 42.8°. At the same time, the diffraction pattern of the Zn_3Al-(Safflower Tincture) sample (Fig. 2 *b*) clearly showed only one peak at 2Θ=40.6°. Most likely, it corresponded not to zinc oxide, but zinc hydroxide. The passage of partial decomposition of Zn-Al LDH to the oxide phase during synthesis in saffron tincture, and the absence of decomposition during synthesis in the medium of safflower tincture, were probably determined by the chemical nature of the dyes. The main dyes of saffron are the carotenoids crocin and crocetin, which do not chemically interact with LDH and only intercalate into the crystalline structure. At the same time, safflower flavonoid dyes (cartamine, cartamidine, and Safflor Yellow A) have a large number of OH groups in their structure. As a result, these substances are chemisorbed on the resulting LDH particles [27] and prevent partial decomposition to oxide.

The diffraction patterns of both samples revealed the presence of a wide halo in the range of angles 2Θ=10–18°, which indicated the presence of an amorphous or X-ray amorphous component. Most likely, such a component was an oxide component. In addition, the diffraction pattern of the Zn_3Al-(Safflower Tincture) sample revealed a peak at 2Θ=29.7°. Additional studies are needed to identify the peak.

Investigating the color characteristics of the samples. The investigation of the color characteristics of the samples confirmed the visual characteristics of the color of the samples: Zn_3Al-(Saffron Tincture) - bright yellow, Zn_3Al-(Safflower Tincture) – dark yellow-orange. The chromatic component **a** (Fig. 3, *a*) of the Zn_3Al-(Safflower Tincture) sample had a value of 9, which was lower than the value of the **a** component of the Zn_3Al-(Saffron Tincture) sample, which was 12. This indicates a color shift of the Zn_3Al-(Safflower Tincture) sample to the red zone. The value of the chromatic component **b** (Fig. 3, *b*) of the Zn_3Al-(Saffron Tincture) sample shifted to the yellow region relative to the **b** component of the Zn_3Al-(Saffron Tincture) sample. The Zn_3Al-(Saffron Tincture) sample also had a higher lightness and slightly higher color saturation. It should also be noted that, in terms of color and organoleptic properties, the Zn_3Al-(Saffron Tincture) sample synthesized in the medium of saffron tincture is more promising for use as a cosmetic pigment for gel polish for nails, powder, and eye shadow.

Further development of this investigation is the optimization of the method for preparing the tincture and synthesizing the LDH pigment (pH, temperature). The limitation of this investigation is the lack of knowledge of LDH pigment samples. The disadvantage of the investigation is the high cost of saffron as a dye source. Therefore, it is necessary to search for plant materials containing crocin and crocetin.

7. Conclusions

1. The syntheses of the samples have proved the possibility of obtaining Zn_3A layered double hydroxides intercalated with natural food dyes directly in the medium of an aqueous extract of saffron and safflower when the pH is adjusted to 10.

2. The phase composition and crystal structure of the synthesized samples have been studied. It has been shown that all samples are Zn-Al LDHs with the α-$Zn(OH)_2$ crystal lattice. For a sample of LDH pigment synthesized in the medium of saffron tincture, partial decomposition of LDH to an oxide component has been revealed. For the LDH pigment sample synthesized in safflower tincture, no degradation of LDH has been detected. This is probably due to the chemisorption of the main safflower dyes (flavonoids of cartamine, cartamidine, and Safflor Yellow A) onto the forming LDH particles.

3. The color characteristics of the obtained LDH samples have been studied. A dry milled sample of Zn-Al LDH, synthesized in the medium of saffron tincture, has a bright yellow color due to the main saffron dyes – crocin and crocetin. The dry milled sample of Zn-Al LDH synthesized in the medium of safflower tincture has a dark orange-brown color. At the same time, the main dyes of safflower are the red flavonoids of cartamine and cartamidin, and the yellow flavonoid Safflor Yellow A. It is hypothesized that the color change of this sample is due to the partial hydrolysis of dye flavonoids and the intercalation of hydrolysis products. The color coordinates of the synthesized samples have been determined in the CIE 1976 L*a*b color model. The use of Zn-Al LDH intercalated with saffron food dyes as a cosmetic pigment is shown to be promising.

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