The possibility of using aluminosilicate composite materials after modification and processing in sunflower oil

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Abstract. The paper presents the study results of the isotherms of nitrogen adsorption-desorption on blue and green powdered clays before and after the surface is modified with solutions of organic acids (oxalic, succinic) and sodium carbonate. Unlike powder of natural blue clay, the material of green clay is characterized by the presence of macropores (5%) with a diameter of more than 50 nm; 95% of volume is occupied by mesopores ranging in size 4-40 nm. According to the size distribution data, the total number of mesopores of blue and green clays has reduced after treatment with oxalic acid; it changes slightly after introduction of alkaline compound into system (sodium carbonate, 10 wt %). It was revealed that the process of adsorption of total impurity ingredients of fatty acid triglycerides provides the possibility of using acid-modified clays with a set of properties (specific surface area, pore distribution) after processing for 1 hour in sunflower oil to stabilize the digestive function of the gastrointestinal tract of poultry and improve the quality of eggs laid by them by daily evening introduction into the feed (1-3 wt %) for 1 month prior to laying.

1. Introduction

The 2000s began with an increased scientific and practical interest to studies in the field of physical and chemical properties of aluminosilicate materials [1], in particular, using them to extract impurity ingredients from aqueous media [2-3] and vegetable oils [4] with their adsorbing properties. When the surface of such materials is modified with various acid-base compounds in a science-based ratio [5], various physical and chemical processes occur due to changes in concentrations of Lewis and Bronsted sites on the surface and, therefore, sorption properties of the composites obtained in regards to a number of related ingredients of a vegetable oil. These co-ingredients may include phosphatides and impurities (usually in small quantities) that enter the solutions when extracting the target fraction from raw oil with metal equipment, as well as chlorophylls and carotenoids, free fatty acids etc. [4]. The acid-base modification of aluminosilicates provides them with a new set of properties that can be implemented into the process of refining the vegetable oils while removing even relatively inert, but unfavorable compounds, e.g. waxes. It should be noted that one of the important parameters, which demonstrate the effectiveness of the absorption of the developed material in a particular media, is the pore formation rate. Therefore, the purpose of this study is to research, in accordance with the
Brunauer-Emmet-Teller (BET) method, physical and chemical properties (specific surface, porosity, pore distribution within a volume) of the aluminosilicates (powdered blue and green clays) tested positively earlier [4] and their subsequent use after modification and processing in sunflower oil. Первый абзац каждого раздела начинается без абзацного отступа (применять стиль Bodytext). Данный раздел посвящен обоснованию актуальности и необходимости данного исследования.

2. Materials and methods

As research subjects, the materials of LLC NPF MedikoMed (Moscow) [4] were used, in particular, powders of blue (montmorillonite, formed SiO$_2$ ≤ 60%, muscovite and illite ≤ 20%, kaolinite 10-15%) and green (quartz, montmorillonite, kaolinite, muscovite, other impurities ≤ 10%) Fe (II)-containing clays (Technical Specification TU 9158-001-17033721-2014).

X-rays of samples were taken with a Bruker D8 Advance at 2 Θ = 10-70 deg. using copper cathode (CuKα-radiation, λ = 1.5406 Å).

The materials were prepared to process by calcination at 393-403 K for 2-3 hours and selection of particles of 5-20 microns in size while sifting. To find out the specific surface, 0.5g sample (natural or modified material) was put into a special container on the SORBI-M device and measured at 77 K with the four-point BET method [6]. Nitrogen gas (State standard GOST 9293-74) was used as adsorbate (high purity, volume fraction not less than 99.999%), while high quality helium (Technical Specification TU 0271-001-45905715-02) was used as the carrier gas (grade 60, volume fraction not less than 99.999%).

Adsorption isotherms were registered on powdered samples of both natural and modified materials. To treat the solid phase, oxalic (OA) "Ch " (State standard GOST 22180-76) and succinic acids "Ch" (State standard GOST 6341-65) ("Himreaktiv", Nizhny Novgorod) were used with a 6% concentration, proven suitable earlier, at a mass ratio of L:S = 1:1. The obtained organic-inorganic material was then dried, and as noted above, 5-20 microns particles were extracted. In addition to 6% organic acid solution treatment and drying, the acid-base modification was accompanied by introducing sodium carbonate (Russian national standard 32802-2014) in the system in a 1:10 mass ratio, and additional 15-18 wt % of water stirred to a uniform mixture, second drying at 393 K and sifting.

To distribute the volume of mesopores of natural and modified sorbents according to their sizes, the Kelvin equation was used (1), which expresses the vapor pressure of an adsorbate over the "liquid-vapor" border:

$$ \frac{P(r)}{P_0} = \exp \left( \frac{2 \cdot \sigma \cdot v}{r \cdot R \cdot T} \right) $$

Where $P_0$ is the saturated vapor pressure at $T$ temperature, $\sigma$ is the surface tension factor, $v$ is its molar volume [7], $r$ is the curvature radius of the boundary surface, $R$ is the absolute gas constant.

CHNS-O Analyzer Flash EA 1112 Series (Italy) was used for elemental analysis.

The natural and modified aluminosilicates were introduced into sunflower oil (acid value 3.4 mg KOH, color value 50 mg I$_2$), the amount – 30 g·l$^{-1}$. Phases were mixed with 80-120 min$^{-1}$ frequency at room temperature for 1 hour, then separated on a filter. The processed materials were added to the daily feed of poultry for 1 month prior to analysis of quality indicators of eggs laid. The diet of two groups of laying hens were supplemented with the materials in the evening for 1-3% of the feed mass.

3. Results and discussion

To refine the vegetable oils, kaolin [3], and montmorillonite [2] materials can be used. The study of the adsorption-desorption isotherms of nitrogen on the powdered blue (figure 1, a) and green clays (figure 1, b) manufactured by LLC NPF MedikoMed (Moscow) and selected based on existing data [4] shows that, during the process, a monolayer forms in both cases when these materials are used; the
graphs show a hysteresis loop. Such isotherms are considered type IV, which describes the behavior of mesoporous materials [8].

The specific surface area for powdered montmorillonite blue clay is 35 m$^2$·g$^{-1}$, whereas the specific surface area of the powdered green Fe (II)-clay is 62 m$^2$·g$^{-1}$. The reduction of area recorded after treating both aluminosilicates with 6% solution of organic acid (oxalic, succinic) can be explained by the binding of carbonyl groups of the modifier's molecules with the surface of the material and the "partial screening" effect. This theory is confirmed by elemental analysis data, according to which the atomic carbon content (1.1 wt %) in the surface layer of the modified composite increases symbatically to the 6% solution of OA at a mass ratio of L:S = 1:1 (which is in accordance with theoretical assumptions and calculations).

In turn, the subsequent introduction of an alkaline agent – sodium carbonate (10 wt %) – in the system results in partial recovery of the specific surface area when reacting with free acid molecules.

According to known facts [9], mesopores of common sorption materials are 2-50 nm in diameter, although theoretically, they can reach higher dimensions [10]. The study of the pore distribution of blue and green clays along the diameter after the 6% oxalic acid solution treatment revealed the decrease of total mesoporosity (figure 2). It should be noted that the subsequent introduction of 10 wt% alkaline modifier – sodium carbonate – in the system does not significantly affect the total number of mesopores. This is probably due to the fact that organic acid solutions, when contacting the aluminosilicate surface, partially block medium-sized pores (5-20 nm), while "craters" of 30 nm and larger in diameter are blocked to a lesser extent. Pore distribution within a volume shows that 96% of them in blue clay are 3-20 nm in size (table 1). After modifying with oxalic acid solution, powdered blue clay has few macropores 60-80 nm in diameter; there are more 13-32 nm pores and, in contrast, less 3-10 nm pores.

During subsequent sodium carbonate (10 wt %) treatment, the porosity vector of the studied aluminosilicates changes direction. The relative volume of mesopores is reduced from 7.2 to 2.3%; 13-32 nm pores are just over 1/3 of total material volume (37% against the original 54%); the total amount of small pores (< 12 nm) increases again. It is noted that, in contrast to the natural blue, a sample of the green Fe (II)-containing clay contains 5% of macropores 72 nm in diameter (table 1). The
remaining 95% of the volume are the transition pores ranging 4-40 nm in size. Thus, the powdered natural green clay is an exemplary mesoporous adsorbent that includes a small number of macropores. Due to modifying the surface of Fe (II)-containing green clay with a 6% OA solution, the total volume occupied by < 7 nm pores decreases, which, however, is leveled out by the increase in the amount of ≥ 15 nm pores in a composite material. Further sodium carbonate (10 wt %) treatment leads to recovery of mesopores to their original volume; the volumes occupied by other pores remain proportionate for composite organic-inorganic materials obtained by acid treatment of the surface. Due to the rich mineral composition (montmorillonite, kaolinite, mica, hydromica, opal-cristobalite ores etc.), the studied natural materials and the modified composites, in which base proton-accepting Brønsted sites contact with electron shell of the carbonyl oxygen of organic acids, which was noted earlier [4, 7], can be used to extract a set of related ingredients from vegetable oils with high bioactivity, such as chlorophylls, phosphatides etc. Therefore, we have studied the possibility of using the processed materials with high calcium content as enterosorbsents that ensure absorption of toxins and stabilization of the digestive functions of the gastrointestinal tract of poultry, as zeolite tuffs, silica clays, tripolites and diatomites are used, as described in [11]. Thus, table 2 shows the shell thickness assessment, as well as the egg white and yolk indices determined according to [12] in 3 days after they were laid and daily introduction of the processed material in the monthly diet of two groups of laying hens with 1 (Group I) and 3 wt % (Group II), respectively. The material was the acid-modified blue clay.

**Table 1.** Distribution of pores relative to the total volume of natural and modified aluminosilicates of LLC NPF MedikoMed (Moscow).

| Di (nm) | blue clay | blue clay + OA | blue clay + OA + sodium | green clay | green clay + OA | green clay + OA + sodium |
|--------|-----------|----------------|--------------------------|-----------|----------------|--------------------------|
| 3.50   | 19.75     | 6.27           | 19.36                    | 22.74     | 18.22          | 15.75                    |
| 4.43   | 7.46      | 2.41           | 7.60                     | 10.60     | 3.34           | 4.50                     |
| 5.86   | 25.72     | 13.80          | 16.59                    | 19.27     | 13.18          | 14.04                    |
| 8.44   | 23.28     | 15.97          | 16.33                    | 15.87     | 16.35          | 16.27                    |
| 15.00  | 20.55     | 25.66          | 20.22                    | 16.29     | 22.58          | 21.94                    |
| 9.35   | 3.24      | 28.74          | 17.56                    | 10.23     | 24.74          | 20.53                    |
| 43.56  | 0         | 0              | 0                        | 0         | 1.59           | 1.60                     |
| 71.80  | 0         | 7.15           | 2.34                     | 5.00      | 0              | 5.37                     |
| 142.29 | 0         | 0              | 0                        | 0         | 0              | 0                        |

The latter was obtained in the conditions described in the theoretical chapter of this paper, in the crude sunflower oil, which ensures cell regeneration and liver recovery in living organisms. The Group III (baseline) laying hens were fed in the evening every day for 1 month prior to the quality assessment of the laid eggs. The feed contained no processed acid-modified blue clay.

The data analysis presented in table 2 shows that the increased (1 to 3 wt. %) amount of the processed acid-modified blue clay added to the feed of poultry led to a 15% thicker egg shell, on average, when comparing Group I and Group II. It was also 41% higher than baseline Group III, which guarantees protection against external mechanical influences and bacteria. Egg white index (0.62) in this group meets the standard values (0.60-0.70), while Group II has a 19% lower value, not to mention the difference in the baseline group (26%). At the same time, the egg yolk index (it should be close to 0.50 for a laid egg) in all three groups is ≈ 0.40, which indicates a high degree of freshness of all eggs.
Table 2. Qualitative characteristics of chicken eggs laid by poultry after daily intake of enterosorbent for 1 month.

| Group indicator                      | Group (enterosorbent added to the feed) |
|--------------------------------------|----------------------------------------|
|                                      | I (1%)       | II (3%)     | III (baseline, no additives) |
| Average shell thickness (mm)         | 0.54         | 0.62        | 0.44                        |
| Egg white index                      | 0.50         | 0.62        | 0.46                        |
| Egg yolk index                       | ≈ 0.4        | ≈ 0.4       | ≈ 0.4                       |

4. Conclusion
The study revealed that it is feasible to use acid-modified LLC NPF MedikoMed clays with a specific set of properties (specific surface, pore distribution) after processing them in sunflower oil for 1 hour to stabilize the digestive functions of the gastrointestinal tract of poultry and improve the quality of the laid eggs. The effect is achieved by introducing a 1-3% of the processed material in the evening feed for 1 month before the laying.

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