Enterosorbent for farm animals

Olga Filippova¹, Elena Kiyko¹, Alexander Zazulya¹, Nadezhda Maslova¹

¹All-Russian Scientific Research Institute of Use of Machinery and Oil Products in Agriculture, side str., Novo-Rubezhny, 15, Tambov, 392022, Russia,
E-mail: filippova1968@mail.ru

Abstract. Natural mineral glauconite, which is extracted in the Bondarsky district in the Tambov region, has a high adsorption capacity. The study of its properties as an enterosorbent in the conditions of passage through the gastrointestinal tract of calves was executed. Chemical modification of the mineral was carried out by converting to Na-form. As a result of treatment, the number of bacteria in it decreased 10 times, and the number of molds decreased 3 times. The prepared enterosorbent was fed to 2 and 6-month-old calves once and for 6 and 9 days daily in the amount of 0.2 g/kg of live weight. The content of metals in the mineral, feed and excrement was determined by x-ray fluorescence analysis. According to the results of one-time feeding of enterosorbent to the calf during the milk growing period, a significant sorption effect was observed with respect to copper (13.6%), nickel (52.7%) and lead (93.8%). The use of enterosorbent in the diets of 6-month-old calves contributed to an increase in the excretion of lead from the body of animals up to 36 % of the total amount, which on average is excreted with feces.

1. Introduction

In addition to achieving high productivity of animals and preservation of young animals, among the tasks to ensure the food independence of Russia, one of the leading places is also getting clean in the ecological aspect of production. In recent years, there has been a deterioration of the environmental situation and saturation of the environment with toxic elements in many regions of the world. The need to preserve the health of the population provides for the control of the content of various pollutants, in particular heavy metals, in food. Human use of animal products (meat, milk, eggs) also provides for the production of environmentally friendly products, which can be achieved by rationing the content of metals in feed for farm animals. In case of anthropogenic contamination of soil with toxic metals, their content in forage plants may become higher than the values of MPL (maximum permissible level) [1]. However, according to researchers engaged in practical activities related to the organization of observations of the state and pollution of the environment, compounds of different metals are far from being equal as pollutants. According to the decision of the Task force on emissions of heavy metals, working under the auspices of the Europe economic Commission UNO and engaged in the collection and analysis of information on emissions of pollutants in European countries, only zinc and lead were attributed to metals whose concentration in the biosphere can be dangerous.

According to the quantitative content, metals on average in biological objects are conventionally divided into macroelements (10-2 wt.% And higher), microelements (10-2-10-5 wt.% ) and ultramicroelements (<10-5 wt.%). The importance of such elements as Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn, Mo for the vital activity of organisms is well known. Under its absence or lack disturbed normal functioning of the body. There are indications of the manifestation of biological activity V, Cr, Ni and...
Cd in the literature. As the technique of environmental experiment is increasingly improved, some of the metals previously considered toxic are now neutral and even necessary. Vital metals perform a variety of physiological functions, are part of enzymes, hormones, vitamins and other biologically active substances as activators of metabolism, reproduction, tissue respiration, neutralizers of toxic substances. For example, manganese is part of 12 different enzymes, iron-70, copper-30, and zinc-more than 300. Naturally, the lack of these elements should affect the content of the corresponding enzymes, and hence the normal functioning of the body. Thus, metal salts are absolutely necessary for the normal functioning of living organisms.

Modern technology of feeding farm animals involves the use of special feed additives-sorbents for internal use (enterosorbsents). Such additives are introduced into diets in order to minimize the action of various toxic substances that enter the body of animals with food and water, reducing the potential risk of their transfer to the human food chain. As enterosorbsents are widely used substances of mineral nature-aluminosilicates, zeolites, glauconites and others. The world practice has accumulated a great experience in its application to address a number of important environmental issues [2-8]. In agriculture, natural minerals are used in the production of animal feed as a feed additive to increase the productivity of animals and poultry, as well as to reduce the level of toxic effects of metals-pollutants and radionuclides on the animal body [9-13].

Glauconite (aluminosilicate of sedimentary origin) is a widespread clay mineral with unique sorption properties. All minerals of this group are characterized only by an external adsorbing surface. Its porosity is due to the gaps between the contacting particles. Therefore, the specific surface of such minerals is determined mainly by the dispersion of particles. The source of cationic capacity of such natural sorbents are hydroxyl groups located on the lateral faces and edges of crystallites associated with silicon atoms. Each mineralogical type of glauconite has its own characteristics in the crystal lattice formula.

Unlike zeolites, glauconites have not a frame, but a layered structure. Part of the intramolecular forces is not balanced by the interaction with the ions of chemical elements located in the cavity of one such layer. These forces can interact with the ions of chemicals contained in solutions or in the air. As a result, they accumulate on the active surfaces of the plates that make up the common crystal. Thus, the active surface area of the substance increases and this may be the main difference in the biological action of glauconite compared with zeolites.

2. Analysis of publications on the topic
Each mineralogical type of glauconite has its own characteristics in the crystal lattice formula. The specific surface of minerals of this group varies depending on the deposit. A distinctive feature of the glauconite of Bondarsky deposit of Tambov region lies in its composition. For example, it contains by 1.5-2.0 times fewer aluminum oxides than glauconite in other deposits. It also has a high content of magnesium, iron, sodium and potassium oxides, has an ability to quickly break down in the soil with the release of elements in the form of easily digestible compounds. Glauconite of Bondarsky deposit has high adsorption and cation exchange properties (specific surface-40-100 m$^2$/g, exchange capacity-15-20 mg-EQ per 100 g of rock) [14].

In addition to adsorption functions, glauconite is also characterized by ion exchange reactions. The ion exchange capacity of glauconite is due to the presence of a negative charge in the structural cell of the mineral, resulting from the replacement of four-valent silicon with trivalent aluminum or divalent magnesium in the crystal lattice. In addition, hydrogen cations of OH-groups attached to silicon atoms located on the side faces of glauconite crystals can under certain conditions enter into an exchange reaction. Molecular adsorption on glauconite in the penetration of electrolyte solutions into the free cavities of the crystal structure, available in the mineral, while sorption of cations and anions from electrolyte solutions.

The sorption capacity of glauconite of Bondarsky deposit was studied in experiments on solutions of different anionic-cationic composition on the possibility of softening of drinking and feed water high-pressure boilers [14-18]. According to the studies, glauconite concentrate can be used as a sorbent for...
water purification and bringing its hardness to a level that meets regulatory requirements. A promising possibility of using the spent sorbent as a biologically active and mineral additive in cattle feed was shown [15]. The dependence of adsorption of cations Cu$^{2+}$ and Pb$^{2+}$ from pH of a concentrate containing 95% glauconite, also studied the absorption of glauconite concentrate cations of hardness (Mg$^{2+}$,Ca$^{2+}$) in static conditions [16]. It was found that glauconite sorbs Cu$^{2+}$ and Pb$^{2+}$ ions (94-96%) with high efficiency, reducing the stiffness by only 40%. Ion exchange and sorption properties of this natural mineral allow it to pass through the digestive tract of animals to exchange with the ions of chemicals that accumulate on its active surface, and remove them from the body. Glauconite of Bondarsky deposit showed a high effectiveness as a means of prevention of diseases of the gastrointestinal tract of cattle [20].

Various physical and chemical modification methods are used to improve the operational and functional properties of natural minerals [21]. As a result of such modifications, there is a directed change in the structure of the material, leading to an increase in its specific surface area, the number of exchange centers and, as a consequence, the strengthening of sorption and ion exchange properties. For example, the translation of natural clays into Na-form increases their ion exchange properties, the ability to disperse in water [15]. This treatment leads to the replacement of protons in (-OH) - exchange centers, as well as to an increase in the interplanar distance in the structure of glauconite. In the future, the Na-form is best dispersed by mixing, and Na$^{+}$ cations are easily replaced by ions of other forms.

It was found that the exchange capacity of glauconite depends on the pH of the solution: in alkaline medium (pH ≥ 8) it significantly increases, and in acidic-decreases. With the growth of pH from 6.5 to 10 increases and the coefficient of extraction of metal cations by 7-10% [19]. Thus, it can be assumed that the ion-exchange and sorption properties of this natural mineral allow it to pass through the digestive tract of animals to exchange with the ions of chemicals that accumulate on its active surface, and remove them from the body.

The work purpose: study of sorption properties of modified concentrate glauconite of Bondarsky deposit with respect to various metals, including vital; development of method for preparing enterosorbent on the basis of modified glauconite concentrate for use in diets of farm animals, particularly cattle.

3. Methods and methodology of the works

For research, 50% concentrate glauconite of Bondarsky deposit of Tambov region (Russian State Standard TU-2164-002-03039858-08), subjected to prior chemical treatment, was used. For 20 minutes the mineral was treated with 0.1 M NaOH solution. Then washed from the alkali with distilled water and then carried out the same procedure in 0.1 M HCl followed by washing from the acid. Then for 1 hour the sorbent was transferred to Na-form in 3.0 M NaCl solution and washed again from chlorine ions. The prepared glauconite concentrate was mixed with grain flour and sugar in the form of an aqueous solution. Round boluses were formed, which were dried at ambient temperature until excess moisture evaporated. As a result, the enterosorbent was obtained for animals with increased sorption capacity in a form convenient for dosing and mixing with feed.

In order to study the sorption activity of the mineral in relation to a number of heavy metals supplied with feed to the digestive tract of animals, on the basis of one of the dairy farms of the Tambov region, a series of experiments on feeding the prepared enterosorbent to young cattle was carried out. At the preparatory stage, experiments were carried out on individual feeding of a 2-month-old calves with by enterosorbent in the amount of 0.2 g/kg of live weight once and a 6-month-old calves for 6 days. The main diet of the 6-month-old calves consisted of hay of meadow grass and wheat bran, mineral additives were not used. Boluses with glauconite were added to the diet of the calves along with bran once a day during the day feeding.

For group feeding by enterosorbent according to requirements on selection of analogs, observance of conditions of feeding and the contents, the calves of Simmental breed at the age of 6-7 months in group (experimental and control) were selected. The basic diet consisted of corn silage (5 kg), grass
silage (3 kg), castlecoole hay (3 kg), grain mixture (1.1 kg) and molasses feed (0.2 kg). During the experiment, mineral and vitamin supplements were used (table salt-25 g and premix P-62-1 – 100 g). The calves of the experimental group were fed enterosorbent daily for 9 days in the amount of 0.2 g / kg of live weight.

In the accounting period (11 days) was studied the evolution of metals with excrement. Methods for determination of metals: pre-mineralization of the samples according to GOST 26929-94, x-ray fluorescence analysis using a spectrometer “Spektrscan Max-GV”. Microbiological examination of samples of glauconite was conducted according to the GOST 10444.15-94, GOST ISO 7218-2015. Microbiological analysis of mineral samples was carried out by seeding into accumulative and differential diagnostic media with subsequent calculation of colony-forming units (CFU/g). Statistical processing of the experimental results was carried out using the Student’s criterion and the coefficient of variation (Cv) characterizing the uniformity of the data. The differences between the studied parameters were considered as statistically significant, starting from the error probability level $p \leq 0.05$.

4. Results of the research

Processing of clay minerals allows not only increasing their ion exchange abilities, but also clearing of impurities of non-clay particles. In the process of converting glauconite concentrate into sodium form, it was simultaneously washed from contamination and dried at a temperature of 65°C.

Table 1 shows the content of some elements in the initial glauconite and past technological processing. It is obvious that after the preparatory treatment in the mineral changed the content of elements and their ratio. The number of such macronutrients as calcium, magnesium and potassium has decreased especially noticeably. Structurally, glauconite is a mixture of microaggregate grains ranging in size from 0.5 to 0.001 mm, some of which, perhaps the smallest in the preparation is inevitably lost.

Microbiological studies have shown (table 2) that as a result of prior preparation (washing), the number of mesophilic aerobic and facultative anaerobic microorganisms (NMAFAnM) in the mass of glauconite decreased by an order, the contents of molds - by three times.

| Kind of microorganisms | Glaucmite (form) |
|------------------------|------------------|
| NMAFAnM, CFU/g         | $3.4 \cdot 10^3$ |
| Yeast-like mushrooms, CFU/g | $< 1 \cdot 10^1$ | $< 1 \cdot 10^1$ |
| Mold fungi, CFU/g      | 27               | 9                |
According to the rules (Russian veterinary rules and norms 13-5-01/01), in feed and raw materials for feed for farm animals, total number of molds must not be more than 5·10⁴ CFU/g, and the total amount of bacteria seeding: not more than 5·10⁵ CFU/g. Preparation of Na-form entails repeated washing with mineral by acid, alkaline and water, with the result that it significantly reduces the amount of bacteria and mold. Therefore, from the point of view of sanitary and veterinary requirements, the use of prepared glauconite in animal feeding is preferable to its untreated form.

The digestive system in calves during the milk feeding period is not yet developed, in particular, the scar in calves at this age functions like the stomach of monogastric animals, and the feed masses do not linger in the tract for 2-3 days, as in all ruminants. However, it is obvious that glauconite is not released from the body completely during the day. Part of it is delayed for a longer period. This conclusion is corroborated by the data (table 3). For example, a day after taking a mineral supplement, a significant sorption effect was observed with respect to Nickel (+52.7%) and copper (+13.6%), as well as a small effect with respect to chromium (+5.5%).

Table 3. Metal content in glauconite, milk and excrement of 2-month-old calf (in ash).

| Elements | Content in the portion of glauconite (14 g) | Content in the milk | Content in excrements / Term of selection of the sample of excrements |
|----------|----------------------------------|---------------------|-------------------------------------------------|
|          | µg | µg/l | µg/g | µg/g | After feeding |
| Cr       | 931 | 53.136 | 45.62 | 48.13 | 24.834 |
| MnO      | 2692 | 53.326 | 751.84 | 772.98 | 441.65 |
| Co       | 350 | 42.08 | 18.55 | 18.143 | 1.572 |
| Ni       | 280 | 13.8 | 26.64 | 40.673 | 28.626 |
| Cu       | 524 | 97.4 | 141.31 | 160.49 | 92.56 |
| Zn       | 1356 | 396.5 | 765.31 | 736.41 | 540.67 |
| Sr       | 3950 | 309.0 | 613.67 | 632.51 | 517.23 |
| Pb       | 1372 | 7.13 | 30.5 | – | 59.1 |

Two days later, a smaller amount of Nickel was released, which was still 7.5% more compared to the initial level, and copper and chromium – even less by 34.5 and 45.6%, respectively, in relation to the initial content. Concentrations of zinc (–29.3%), cobalt (–81%), manganese (–41.2%), strontium (–15.7%) and iron (–43%) also decreased. The content of potassium and magnesium in the excrement of the calf before feeding it a mineral supplement and 24 hours after it enters the digestive tract has not changed. After 48 hours, the concentration of these trace elements in the feces was higher by 66.3 and 46.7%, respectively.

Table 3 also shows the content of some elements in cow’s milk used in feeding a 2-month-old calf, including lead. Lead is one of the pollutant metals whose environmental pollution affects the health of animals and humans. The environmentally acceptable concentration of this element in plant feeds is 14-55 mg per 1 kg of dry matter (DM), respectively. Natural sources of lead entering in surface waters are the processes of dissolution of minerals (Galena, anglesite, cerussite, etc.). A significant increase in its content in the environment is due to the burning of coal, with removal of water objects with wastewater of ore-dressing factories, some steel plants, etc. Lead in high concentrations is high-toxic metal for living organisms.

Lead is one of the pollutant metals for which the permissible concentration limit (PCL) in milk and dairy products is set. According to TR CU 21/2011 “about food safety”, the PCL for Pb in milk is 0.1 mg/l (100 µg/l). In our experiment, lead was found in milk in trace amounts—an average of 7.13 µg/l. Also, according to the results of the analysis, it was found that in all plant feeds that were used in the diets of experimental animals, the lead content was within the norm (2-14 mg/kg of dry matter [1]).
feces of a 2-month-old calf contained 30.5 µg/g of this element. 24 hours after feeding glauconite, its concentrations in excrements were below the method detection limit definition (100% sorption effect), and after 48 hours accounted for 59.1 µg/g, that 93.8% larger than the original concentration. Probably, this element due to the weak solubility of its compounds, in small quantities getting with food, is excreted rather quickly from the body without accumulating in the intestines.

In the experiment on individual feeding of a 6-month-old calf, all feces samples released by animals during the accounting period were selected for analysis. The dynamics of lead release is shown in figure 1. The release of lead from the body in increased amounts began a day later from the first giving boluses with sorbent. The maximum level of feces was observed on day 3 (sample 4, figure 1), the difference with the average value for all days of observation was 36%.

The average content of lead in samples taken during feeding glauconite (samples 2-7, figure 1), was higher by 32.56 µg/g in relative to the period without it (samples 1 and 8-11, figure 1), which was 14.7%. The level of its content in samples taken at the end of the accounting period (samples 8-11, figure 1) was 7-22% lower relative to the initial level (sample 1, figure 1). This may be due to fluctuations in the concentration of lead in plant feeds, and with the withdrawal of its excess amount from the body of the calf as a result of feeding glauconite.

Experience in group feeding calves differed in feeding conditions-calves used a common feeder, sorbent in the concentrated feed distributed to the whole group. General samples of excrement (from all animals in the group) were also taken for analysis.

Figure 2 shows the dynamics of excretion of lead with feces during group feeding. The lead content in the samples taken during glauconite feeding had no significant differences between the group-84.2±6.8 µg/g in the experiment and 87.2±7.3 µg/g in the control (p > 0.05), the coefficients of variation –34.3 and 35.5, respectively. The average values of lead content for the accounting period of accounting
are 100.5±18.7 µg/g in the experiment (coefficient of variation-61.6) and 81.3±9.4 µg/g in the control (coefficient of variation – 38.2) (p > 0.05). The difference in containing is 23.6 %. At the same time, the maximum concentration of this metal-pollutant was noted immediately after the termination of the sorbent – on the 11th day of accounting, which was 2.7 times higher than the average value for all days of observations.

4. Results

The dynamics of the allocation of lead with feces (group feeding 6-7 monthly calves); sample 1 and 11 without glauconite, samples 2-10 with glauconite in the diet.

Thus, it can be concluded that lead is sorbed with high efficiency on glauconite, which is not released completely with feces, but accumulates in the digestive tract of animals for several days.

5. Conclusion

As a result of chemical treatment of the concentrate of glauconite of Bondarsky deposit by transfer in the sodium form in 10 times reduced bacteria and in 3 times the amount of mold fungi that is essential to the use of natural minerals in the feeding of farm animals.

It was found that the structural parts of glauconite have different ability to interact with the contents of the digestive tract of animals. Sorption of elements on glauconite depends both on their concentration in feed and the degree of assimilation in the intestine. During the milk feeding sorbent passes faster through the digestive tract of calves. Comparative analysis of the content of elements in the feces of a 2-month-old calf showed that feeding a portion of enterosorbent prepared from a modified glauconite concentrate at a dose of 0.2 g/kg of live weight to varying degrees affected the processes of assimilation and isolation of some elements. A day later, the content of Nickel (+ 52.7%), copper (+13.6%) increased in feces. There were no significant changes in the content of trace elements of zinc, cobalt, manganese, strontium, iron and macroelements of potassium, magnesium. Lead metal-pollutant was sorbed on glauconite, but was not excreted in the feces after a day, since part of the sorbent is retained in the digestive tract for a longer period. As a result of this delay, the concentration of lead in feces after two days increased by 93.8% relative to the initial concentration, and Nickel – by 7.5 %.

The use of enterosorbent in the diet of 6-7-month young cattle in a dose of 2 g/kg of live weight contributed to an increase in the excretion of lead from the body of animals up to 36% of the total amount, which on average is excreted with feces.

A thorough study of the physicochemical properties of the mineral opens up opportunities for its wide use not only in the already known quality of mineral additives in diets, but also as an enterosorbent for the treatment and prevention of nutritional toxicosis in farm animals.

References

[1] IlyinV 1991Heavy metals in the soil-plant system (Novosibirsk: Nauka) p 151
[2] Almeida NetoM, Veira M, da SilvaM2014Journal Water Process Engineering31 pp90–97
[3] Khaled A, El-T Rasha S, RostomM 2018Egyptian Journal of Petroleum27 3 pp 393 –
401doi.org/10.1016/j.ejpe.2017.07.003

[4] Liu M, Hou L, Xi B, Zhao Y, Xia X2013Applied Surface Science273 9 pp 706 – 716

[5] Rangel-Porras G, Rangel-Rivera P, Pfeiffer Perea H, Gonzalez-MunozP 2015Researche article472 pp 135 – 141

[6] Veira M, Almeida Neto A, Gilmenes M, da SilvaM2010Journal Hazardous Materials176 2 pp 109 – 118

[7] MalamisS, KatsouE 2013J. Hazard. Mater.252 pp 428 – 461

[8] VeiraM, Almeida NetoA, GilmenesM, da SilvaM2010Journal Hazardous Materials177 4 pp 362 – 371

[9] EzhkovV, YapparovA, Nefed’evE, EzhkovaA, YapparovI, GerasimovA2014Bulletin of Kazan technological University17 11 pp 41-44

[10] YapparovA, EzhkovV, YapparovI, EzhkovaA, MotinaT2015Scientific notes of the Kazan state Academy of veterinary medicine. N. E. Bauman223 pp 248– 251

[11] MotinaT, YapparovA, EzhkovaA, EzhkovV, YapparovI2015Scientific notes of the Kazan state Academy of veterinary medicine named after N. E. Bauman223 pp 121-125

[12] RyabininaE, ZotovaE, PonomarevaN2016Bulletin of Voronezh State University, Series: Chemistry, Biology, pharmacy1pp 21 – 24

[13] EzhkovV, FaizrakhmanovR, SemakinaE, EzhkovaD, Ezhkova2016Bulletin of Kazan technologic university19 20 pp 172-176

[14] TsygankovaL, ProtasovaV, VigdorovichV, AkulovA2012Bulletin of the Tomsk state University, Series: Natural and technical Sciences 17 2 pp 735-741

[15] VigdorovichV, TsygankovaL, FilippovaO, ShelleN, EsinaM, FrolovA2016Chemical engineering17 3 pp 129– 137

[16] VigdorovichV, TsygankovaL, NikolenkoD,AkulovA, RumyantsevF2010Sorption and chromatographic processes10 1 pp 121-126

[17] VigdorovichV, BoldyrevA, TsygankovaL, UryadnikovA, EsinaM, Shel'N2017Theoretical Foundations of Chemical Engineering51 5 pp 798–803doi: 10.1134/S0040579517050220

[18] VigdorovichV,TsygankovaL, EsinaM, UryadnikovA, Shel'N2017Journal Water Process Engineering 20 1 pp 180 – 186

[19] VigdorovichV, TsygankovaL, Shel'N, EsinaM, OmutkovM, PustynnikovYa 2017Polymer Science Series D10 4 pp 341 – 346 doi: 10.113451995421217040189

[20] FrolovA, FilippovaO, LobkovV 2011Bulletin of agriculture complex of upper Volga region3pp 32– 38

[21] Christidis G, Moraetis D, Keheyen E, Akhalbedashvili L, Kekelidze N, Gevorkyan R, Yeritsyan H, Sargsyane H 2003 Applied Clay Science 241–2 pp 79–91 doi:10.1016/S0169-1317(03)00150-9