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PROSPECTS OF USING CLAY WITH MEDICINAL PROPERTIES IN VETERINARY MEDICINE AND AGRICULTURE

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Summary. The article explores the potential applications of clays and clay materials in agriculture, emphasizing their role in developing effective remedies for common animal diseases and environmental cleanup. The study relies on electronic resources such as ScienceDirect, Scopus, PubMed, and ResearchGate, employing analysis and generalization as research methods. The focus is on scientific publications from 2000 to the present. Throughout history, mankind has recognized the healing properties of clay, utilized both internally through geophagy and externally in the form of medicinal poultices and rubs prepared by ancient healers. The analysis of publications highlights the focus on studying the physical and chemical properties of clay, establishing its therapeutic effects, and exploring its practical applications in medicine and veterinary medicine. The article outlines promising areas and proposes the use of clay, particularly of local origin, in domestic veterinary medicine. A notable application is in addressing gastrointestinal diseases in young animals and treating animal poisoning caused by pesticides and mycotoxins

Keywords: therapy, gastrointestinal diseases, sorbents, environmental protection

Introduction. The advancement of human and veterinary medicine in the modern era necessitates the exploration and development of effective medications suitable for both normal and extreme conditions. Criteria such as drug availability, cost, and versatility are crucial in this context. Clays, known for their potent therapeutic properties, are abundant in nature. A comprehensive investigation into clay properties enables the formulation of novel medicinal combinations that significantly enhance their efficacy.

Contemporary environmental challenges underscore the urgency of finding solutions. The escalation of environmental and food contamination by heavy metals, nitrates, pesticides, herbicides, organic compounds, and other toxins demands the creation and implementation of new, efficient, and cost-effective means for neutralizing and eliminating pollutants from diverse environmental entities. Various sorbents, including activated carbon, ion exchange resins, natural sorbents, zeolites, and vermiculites, are employed to extract and eliminate harmful substances. Clay, boasting exceptional healing and absorption properties, aligns perfectly with the requirements for its utilization in both animal health and environmental protection.

The aim of the study was analyze scientific publications from 2000 to the present about the potential applications of clays and clay materials in agriculture with focus on their role in developing effective remedies for common animal diseases and environmental cleanup.

Materials and methods. The research materials were the electronic resources Science Direct, Scopus, PubMed, and ResearchGate. Research methods – analysis and generalization. Scientific publications for the period from 2000 to the present were studied.

Results and discussion. Clay therapy, also known as bolucotherapia (from the Greek *bolos* — clay + *therapia* — treatment), or peloid therapy (from the Greek *pelos* — silt, clay + *therapia* — treatment), has been explored in this study (Konovalova, 2010).

Clay is a fine-grained sedimentary rock that is powdery when dry and malleable when wet. It is composed of one or more minerals from the kaolinite group, which is named after the Gaoling village in China, montmorillonite, or other aluminosilicates (clay minerals). It may also contain sand and carbonate particles. The main rock-forming mineral in clay is kaolinite ($Al_4Si_4O_{108}$), which contains 47% silicon oxide (SiO_2), 39% aluminium oxide (Al_2O_3), and 14% water (H_2O). Al_2O_3 and SiO_2 are significant components of clays of various colors.

The color of the clay, ranging from yellow, brown, blue, green, and purple to black, is caused by impurities of chromophore ions, including oxides of iron, titanium, magnesium, copper, nickel, and chromium (Grim, 1967). In official medicine, only white clay is used, while in folk medicine, white, blue, green, and other types are utilized. Each type of medicinal clay has a special chemical composition and healing properties. Blue clay, considered the most healing, contains elements like K, Ca, Mg, Si, Na, P, Cl, Fe, Al, I, Co, Cd, Mg, Li, Cu, Mo, Zn, Se, Ra, and others, exhibiting enveloping, bactericidal, anti-inflammatory, and other healing properties. It has a detrimental effect on pathogens such as tuberculosis, cholera, and many others, and is used to treat diseases of the throat, bronchi, and lungs. Red clay, mainly composed of iron oxide and copper, is used to treat allergies, anemia, and boost immunity (Samoilovich, 2009; Henry and Cring, 2013; Kravets and Riabiev, 2016; Young and Miller, 2019).

The most commonly used types of clay for therapeutic purposes are kaolinite (white or Chinese clay — Bolus alba, $Al_2O_3 \times 2SiO_2 \times 2H_2O$), hydrargillite

($Al_2O_3 \times 3H_2O$), diaspore ($Al_2O_3 \times H_2O$), and montmorillonite ($MgO \times Al_2O_3 \times 3SiO_2 \times 1.5H_2O$). The therapeutic effect of clay therapy is based on neurohumoral mechanisms, providing therapeutic, stimulating, and trophic effects on the pathological process. Methods of clay therapy include external use: lotions, applications, rubbing, wraps, compresses, masks, baths; and internal use: solution, powder.

History of the Use of Medicinal Clays. The healing properties of natural mineral clays have been known to man since ancient times, actively used not only in cosmetology but also in medicine. Ancient healers crafted various poultices and rubs from clay, and it was taken internally when its absorption effect was needed. Clay therapy aided in various poisonings, epidemics, and muscle pain.

The practice of eating earth, clay, and other minerals (geophagy, lithophagy) is known among both animals and humans, dating back to ancient times, and is still common in some cultures today. Clays have been used as therapeutic agents throughout human existence. Primitive tribes traditionally used different types of clay, such as bentonite, kaolinite, montmorillonite, smectite, and pascalite (Ca^{2+} montmorillonite from Wyoming, USA) (Droy-Lefaix and Tateo, 2006). Primitive tribes have used different types of clay to combat toxicity (Johns and Duquette, 1991). In Côte d'Ivoire, where clay is consumed primarily by pregnant women, the soil was found to be approximately 68% kaolinite, 27% smectite and vermiculite, and 5% other minerals (Abe et al., 2006). The use of clay is believed to address mineral deficiencies in the diet and alleviate many gastrointestinal diseases (Kikouama et al., 2002, 2009).

The earliest written sources that mention the health benefits of clay can be traced back to ancient Egyptian papyri. Even today, Egyptian and Syrian clays are recognized and popular as excellent cosmetic products. However, systematic data on using clay dates to a later historical period, specifically in Antiquity. Hippocrates (460–370 BC), often regarded as the father of medicine, was the first physician to detail the properties of clay in his works. His writings provided a comprehensive description of therapeutic and surgical methods, as well as pharmacology, emphasizing the diverse applications of clay (Hippocrates, 1936–1944).

During the medieval period, physicians like Avicenna and Amasiatsi referenced information about clay from earlier works, including Dioscorides (40–90 AD), Celsus (II century AD), and Galen (129–216 AD). However, the information from this period remains somewhat fragmentary. Avicenna, an outstanding Persian scientist, provided detailed descriptions of the properties and applications of more than twenty varieties of clay. In his Canon of Medical Science, Avicenna emphasized the importance of cleansing the body using printing clay (Tin Makhtum) as a hemostatic, wound, and ulcer healing agent, and a preventive measure against poisoning (Celsus, 1971; Avicenna, 1979–1982).

The end of the Middle Ages witnessed significant scientific and technological advancements, and medicine was no exception. In the early eighteenth century, Dr. John Quincy published *The New Dispensatorium* in London, a pharmacopeia that included descriptions of the types of clay and their applications (Lewis and Quincy, 1753). Clay was also utilized by healers known as 'hlyniuky' among the Zaporizhzhia Cossacks, and it played an active role in renowned resorts and clinics across Europe (Green Planet, 2022).

During the 20th century, clay's physical and chemical properties were extensively studied, substantiating its therapeutic effects and practical applications in medicine and animal husbandry. Both domestic and foreign scientists have contributed to the understanding of medicinal clays, and the term 'medical clays' was officially proposed by French scientists in 2006 (Tria, Zherom and Dyubuk, 2006).

For an extended historical period, spanning up to the early twentieth century, clay and clay products held a significant role in the traditional household culture, folk medicine, veterinary medicine, and magical healing practices of Ukrainians. In regions like Poltava and Slobozhanshchyna, the use of clay and its products for medicinal purposes, particularly in the preparation of homeopathic remedies, was widespread (Metka, 2010).

The current state of the problem reflects ongoing studies on the medicinal properties of clays by scientists from various countries. Essential properties of clay minerals, such as adsorption capacity (Tenorio Arvide et al., 2008) and the ability to release trace elements (Tateo and Summa, 2007; Gomes and Silva, 2007), have been established. These findings lay the foundation for the development of new drugs in both human and veterinary medicine.

Research has confirmed the effectiveness of clay minerals in binding and removing harmful compounds from the body (Xu, Han and Wang, 2004) and their antibacterial effects (Haydel, Remenih and Williams, 2008; Mpuchane et al., 2010). Clays are recognized as excellent adsorbents with physical and chemical interactions with microorganisms. They are further classified into bactericidal and non-bactericidal, with the bactericidal mechanism being chemical. Such clays demonstrate a detrimental effect on a wide range of microorganisms, including antibiotic-resistant strains (Korchak et al., 2014; Williams, 2019; Gomes C., Gomes J. and Da Silva, 2020).

Since 2006, animal health and growth have been significantly impacted by the banning of antibiotics as growth promoters in EU member states.

The use of clay minerals is considered a potential solution due to their adsorption capacity and lack of primary toxicity, making them effective preventive and therapeutic agents and feed additives that can ensure animal health and productivity (Slamova et al., 2011).

The adverse effects of non-steroidal anti-inflammatory drugs (NSAIDs) are widely recognized. Clay minerals have been reported to protect against these side effects. Experiments involving pigs and rats showed that oral administration of aspirin and phenylbutazone caused severe ulcerative damage, which was significantly reduced after treatment with smectite (Droy-Lefaix et al., 1992; Peignot, Giral and Plique, 1997).

Clays and clay minerals have been found to have a stabilizing effect on the mucosal barrier, offering protection against various lesions of the gastrointestinal mucosa. Experiments on rats demonstrated that smectite can inhibit damage caused by pathological dysregulation, preventing hemorrhagic lesions, significant bleeding, and localized ulcerative lesions (Leonard, Droy-Lefaix and Allen, 1994).

Clays have demonstrated the ability to adsorb various toxic substances, including aflatoxin (Phillips, Lemke, and Grant, 2002; Marroquín-Cardona et al., 2011), as well as toxins produced by *Yersinia pseudotuberculosis* (Carnoy et al., 2000).

The exceptional adsorption capacity of bentonites, attributed to their fine particle size, fine particle shape, and high specific surface area (Dixon et al., 2008; Tenorio Arvide, 2008), allows them to absorb large organic molecules, polymers, and complex ions. This enables them to bind mycotoxins, heavy metals, bacteria, and viruses, particularly smectites like montmorillonites (Murray, 2000; Szajewska, Dziechciarz and Mrukowicz, 2006). Kaolin, on the other hand, has been found effective in binding enterotoxins that cause diarrhea (Dominy, Davoust and Minekus, 2004).

Clays, due to their high adsorption capacity, can protect the gastrointestinal tract of animals from damage. This makes the use of clays a promising avenue for the treatment of gastrointestinal diseases in young animals and in cases of pesticide poisoning. Studies have shown that the non-selective herbicide diquat can cause erosion of the intestinal mucosa. Treatment with smectite in diquat-treated rats led to the normalization of mucus rheological properties and intestinal permeability (Theodorou et al., 1994). Both montmorillonite and bentonite are effective adsorbents that are recommended for use in the treatment of pesticide poisoning (Meredith and Vale, 1987).

In the context of dairy calves, where the incidence of morbidity exceeds 34%, and the most common diseases are gastrointestinal and respiratory, there is a growing interest in complementary and alternative therapies. Medicinal clays, being effective supplements, are easy to incorporate into daily calf care practices. However, the diverse physical and chemical compositions of different clay types necessitate systematic research (Williams and Haydel, 2010).

Research on the natural zeolite clinoptilolite revealed its effect on the absorption of immunoglobulins from colostrum and the incidence of gastrointestinal diseases in newborn calves. Adding 1.0 g of clinoptilolite per kg of body weight per day to colostrum and milk reduced diarrhea, though its impact on passive immunity was insignificant. Higher doses hurt passive immunity and caused diarrhea (Sadeghi and Shawrang, 2008).

Another study on the administration of clinoptilolite to dairy calves found a statistically higher level of antibodies against *E. coli* in the blood serum of calves fed clinoptilolite. Clinoptilolite also significantly reduced the frequency of diarrhea. The addition of clinoptilolite to colostrum and milk during the first 10 days after calving proved effective in enhancing intestinal absorption of antibodies against enterotoxigenic *E. coli* strains and reducing the frequency and duration of diarrhea in calves (Pourliotis et al., 2012).

Studies on the therapeutic efficacy of sepiolite in neonatal diarrhea in calves demonstrated that adding 2% sepiolite to the feed had no side effects on the animals. Sepiolite, as a good absorbent, effectively provides hydration by retaining water, eliminating etiological factors, and preventing diarrhea. The inclusion of sepiolite in the feed positively influenced the increase in live weight and productivity of the animals. This positive effect was observed both in the treatment and prevention of calf diarrhea, and the use of sepiolite indirectly contributed to human health by preventing the emergence of antibiotic resistance (Elitok and Fatih Baser, 2016). Consequently, utilizing clays for infections lacking effective antimicrobial agents holds promise.

Another promising application of clays lies in creating slow-release formulations and water purification. Studies have explored the modification of montmorillonite and other clays by interacting with organic cations to produce slow-release herbicide preparations and effectively remove pollutants from water through filtration. The contaminants successfully removed include hydrophobic and anionic organic molecules (herbicides), dissolved organic matter, pharmaceuticals (antibiotics and non-steroidal drugs), inorganic anions (perchlorate), microorganisms, bacteria, including cyanobacteria, and their toxins. The modification of smectite clay minerals with natural organic cations, such as L-carnitine, dimethyl ester of L-cystine, and thiamine, enhances the clay's properties for removing the herbicide simazine from the environment (Cruz-Guzmán et al., 2004; Undabeytia et al., 2020).

The efficiency of removing tetracycline and sulfonamide antibiotics from water by benzyl dimethyl hexadecylammonium (BDMHDA) micelles pre-adsorbed on montmorillonite was investigated. Micellar clay complexes (1% w/w) were found to remove 96–99.9% of antibiotics from their aqueous solutions containing 5–50 mg/l of drugs. Micellar clay complexes were found to be highly effective in removing 89–99% of tetracycline and sulfamethizole from initial solutions containing 10 mg/l of antibiotics and 8 mg/l of humic acid or 9 mg/l of fulvic acid in the presence of dissolved soil organic matter. These findings suggest that micellar clay complexes are a promising method for purifying water from tetracycline and sulfonamide antibiotics (Polubesova et al., 2006).

Simple clays, known for their significant absorption capacity for gases and organic matter, have been explored for their potential to absorb various compounds from the gaseous phase. Although this topic has not been fully explored, there are reports on the use of minerals such as kaolinite, halloysite, montmorillonite, bentonite, saponite, vermiculite, illite, sepiolite, and palygorskite to control emissions of a wide range of pollutants, including CO_2, CH_4, SO_2, H_2S, NH_3, etc. (Wal, Rutkowski and Stawiński, 2021).

Having one of the best absorption properties, the clay fully meets the requirements for its use in environmental cleaning. Since these properties of clays are still limited in livestock production, further research and implementation are promising areas. At the same time, the unsubstantiated use of clay, in addition to its benefits, may have adverse effects arising from parasites and/or harmful microorganisms and toxic substances present in the clay consumed. Current evidence indicates that geophagy poses potential risks such as heavy metal toxicity and diseases caused by clay consumption, which binds nutrients and beneficial pharmaceuticals in the gut. However, research also suggests that geophagy may have benefits in protecting against harmful pathogens and toxins through two different physiological pathways. Future research should investigate the causal relationship between geophagy and iron deficiency. Additionally, it should explore the biological and psychosocial factors associated with geophagy (Young and Miller, 2019).

In addition, the negative effects of clay may be due to the high adsorption capacity of clay. As a result, it can cause anemia by binding iron. Iron is an element that is often present in the soil, consumed by animals and humans, and thus can be a source of this mineral for the body. However, it can also be a contributing factor to anemia, according to the chelating capacity of soil clay (Kawai et al., 2009).

As a natural compound, clay is versatile: its anti-toxicity, rich mineral composition, and sorption properties, as discussed above, suggest its wider use.

Clay is richer in minerals than vegetables and fruits, and its absorption properties allow it to remove pathogens from the body. For the successful use of clay in the treatment of various diseases, it is necessary to comprehensively study their mineral composition. It is especially important to study and use local clay samples, as it is desirable to use clay not imported but taken from the place where the patient was born or lives.

In this regard, the absorption properties and ionic composition of samples of therapeutic clays located in the village of Luzhok, Derhachi District, Kharkiv Region (Ukraine) were studied. Methods for determining the trace element composition (Fe, Co, Zn, Al, Cu) in medicinal clays for medicine and veterinary medicine were developed and certified, allowing to control and regulate the concentration of the main components of medicines. The developed methods differ from the existing ones by their expressiveness, selectivity, and accuracy. A comparative analysis of the results obtained by nuclear and X-ray fluorescence spectrometry was carried out using the Q-test. It was found that the results belong to the same general population and are not burdened with systematic errors. The possibility of using clay and its combined preparations (ozone clay solutions and products for internal and external use with a regulated content of trace elements and active oxygen) in medicine and veterinary medicine for the treatment of various pathologies, disinfection of environmental objects, and the possibility of using clay for the prevention and treatment of animals with certain infectious diseases was investigated. It has been shown that combined clays do not adsorb carotene, vitamin B_{12}, and some enzymes (Melnik and Shevtsov, 2002; Melnik et al., 2002a, 2002b, 2003).

Conclusions. Given the above, we propose:

— investigate the effectiveness of clay application for gastrointestinal diseases in young animals and pesticide and mycotoxin poisoning in animals;

— develop a standard sample of therapeutic clay and study its absorption properties;

— utilize the absorption properties of clays for purifying industrial emissions from compounds (Cr, Pb, Co, Ni, Cu, Mg), treating pigsty wastewater, and improving the quality of air in livestock environments;

— create and employ combined preparations, such as ozone clay solutions, in the fields of medicine and veterinary medicine;

— explore the development of pharmaceuticals derived from local clay for both internal and external use, ensuring the regulated content of trace elements and active oxygen;

— develop regulatory documentation for the use of therapeutic clay in veterinary medicine and animal husbandry, including industry guidelines.

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