

## Different Methods of Clay Application for Humans

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### Abstract

Minerals are imperative for humanity. As a natural source of all minerals, clays can be beneficial to human health. The use of clay minerals for food, medicinal purposes, in pharmaceutical formulations, spas, beauty treatments is almost old as mankind. Clay has no toxic elements in concentrations that can harm a human body. Bentonite, montmorillonite, pascalite and other types of natural clays were applicable since prehistoric times. Concerning the physical and chemical composition of bentonite clay, it was useful as a cleaning agent for humans, mammals, birds, reptiles and insects. The aim of this work is examination of the clay applications in order to improve human health. The application of characterization analyses and thermal treatment were used for the characterization of bentonite clay, sampled from Prisjan, a village in Serbia. Considering historical development of clay, a relationship between clay and organic matter, the impact of clay on life development cycle, this work examines different methods of clay applications to improve our lives.

**Keywords:** Application; Clay; Bentonite; Humans; Health

### Introduction

Minerals have a crucial role in humankind. As the main source of life on Earth, minerals are essential for all body processes. Minerals have the impact of an assimilation of vitamins, fats, carbs, proteins, etc. From muscle contractions to the productions of hormones, minerals have a vital role in all biological functions. Clay can be considered as the natural source of all minerals consumed or used for different purposes by humans. The structure and composition of clay have no toxic effects on the human body. Clay-gels can be characterized as intermediary products between liquids and solids. The physical and chemical composition of natural clays (bentonite, montmorillonite, pascalite, etc.) subjected to modern technologies, has been examined in a lot of studies. Clays can be identified as a cleaning agents for different species of mammals, reptiles, insects. The similar activities were observed in humans. Clays can be used in nutrition, for medicine or aesthetic purposes [1]. Clays used as creams or gels can be applied for lubrication and nourishment of the body. To improve the quality of life, in home conditions, people can use clay-based products with plant extracts for the appropriate purpose. For example, the chestnut extract combined with clay can be used for varicose veins or hemorrhoids [2]. Some studies showed significant changes in the composition of natural clays during thermal treatment (from 100 to 1100°C) [3].

### Aim of the Study

The aim of this work is a multidisciplinary approach to the applications of natural clay in order to improve human health. This study is based on characterization techniques and thermal treatment of bentonite clay.

### Historical development of clay application for human health

The usage of clay minerals for human health has a long history. In the prehistoric period, *Homo-erectus* and *H- neanderthalensis* used a mixture of several clay minerals and water for cure wounds, soothe irritation and skin cleaning. The ancient Greeks used clay as an antiseptic cataplasm to cure snake bites. Marco Polo described in his travels Muslim pilgrims- phenomena of curing a fever by “pink earth” ingestion. Application of curative clay was mentioned in prominent Chinese medicine catalogue “Pen Ts’ao Kang Mu” [4].

Clay usage is related to the plant, animal and human health. Bentonite, montmorillonite, pascalite, and other types of natural clays were useful in older cultures, even before the beginning of the written history. The studies showed that volcanic ash clay had a beneficial part to Andean Indian tribes. Similar usage of clay was observed in Central Africa tribes and Aborigine in Australia. From ancient times Mexicans and South Americans knew about the benefits of clay.

Clay was used in medieval battles and wars. Application of clay was particularly important against dysentery and cholera during Balkan wars (1912-13). Under no water conditions, clay was used to maintain the hygiene of warriors [5].

The first written references about the usage of clays and description of their mineral benefits dates to the Roman period (60 BC). Throughout ancient history, clay has been used for gastrointestinal issues. Aristotle (384 - 322 BC) made the first reference about soil eating, or clay eating by humans (for therapeutic and religious purposes) [4].

In “Natural History”, Pliny the Elder described the use of clays, especially those found near Naples (volcanic muds) for stomach and intestinal ailments. During the Middle Ages, Avicenna and Averroes classified and encouraged the use of medicinal muds. Moreover, Galeno, Arabic doctor, used clays to deal with malaria [7,8]. In his research on clay application as an auxiliary medicinal product, he gave the importance of ion- exchange, emulsion, adsorption, electromechanical and diffusion properties of clay [9].

### Clay composition and methods of application on humans

From the ancient times, clay was known as volcanic ash- product. Different environmental factors (physical and chemical) influenced on clay formation. Each clay has a specific structure. In addition to that, two identical clays are impossible to find. Clays are soft minerals consisting of tiny particles that can absorb large amounts of water. As a result, clays expand due to hydration. Clays are similar to metals that can absorb minerals and organic substances [6].

On the one hand, clay has a mineral composition, on the other hand organophilic, because it contains organic residues. Moreover, clay can adsorb gases and some toxic substances. Its gel structure can be ion-exchange, binding ions of heavy metals deposited in the liver, or in the bloodstream. The organophilic composition has a reflection in binding non-biodegradable organic compounds (chloramine and others). Electrostatic Coulomb’s and Van der Waals forces are bridges between the dirty part of the skin and the clay we rub. Concerning the organic origin of clay, sprinkling clay on the wounds has antiseptic and antibiotic effects and accelerates the keratinization of the subcutaneous tissue [5].

Bentonite, as well as other types of medicinal clay, was useful in older cultures even before written sources of history. Bentonite has electrodynamic properties- it changes the electrical conductivity of water or gel [12]. Moreover, bentonite has the impact in neutralization of toxins in the intestinal tract. Some studies showed that bentonite can eliminate food allergies and food poisoning. In addition to this, it helps with *Mucus colitis* and *Spastic colitis*. Application of bentonite may prevent viral infections, stomach flu, and parasites (in the presence of clay, reproduction of parasites is impossible) [11]. Bentonite clay has a distinct water binding capacity. It represents a sort of thixotropic gel, extremely important in ion-exchange [9]. Bentonite has a possibility to adsorb protein molecules from aqueous solutions. It has application in the wine industry where it is used for removing a large amount of protein from wines. It also has an impact on both red and white wines industry. Bentonite is used as the largest laxative, and as a base for many dermatological products [24-26].

Clay has a wide spectrum of application in digestive diseases, alcoholism, arthritis, cataracts, diabetic neuropathy, pain treatment, diarrhea, hemorrhoids, stomach ulcers, anemia etc. In addition to these examples, clay adsorbs radiation caused by cell phones, microwaves, x-rays, TVs, etc [11]. The oral dose of clay (10g) helps the digestive system to remove toxins. Applied clay leads to a strange excretion of *Mycobacterium ulcerans* (Buruli ulcer) [20,21]. The usage of clay is similar to tuberculosis treatment by *Lapis lazuli* [5].

Beauty spas around the world use cosmetic capabilities of clays. In spa centers, the color of the clays mostly determines their usage. Yellowish clay is used to prevent bacterial infection on the skin while reddish clay is used for skin cleaning. The application of bluish clay reduces the development of acne. Greenish colored clays help the oily skin treatment while black clays may have the influence on general body nourishment. In Africa, cosmetic application of clay is a common practice [10].

### Clay and organic matter, possible ways of applying clay

Concerning the relationship between clay and organic matter, it is important to mention Mesolithic period and Iron Gates Gorge. This study covered four locations in Serbia, on the Danube (Lepenski Vir, Padina, Vlasac and Hajdučka vodenica). Clay origin can be in connection with burial practices which included cremation, primary inhumation, removal and reorganization of body parts, reburial of skulls and fragmentary remains [13].

As natural products, clays are subjected to different treatments (desiccation, pulverization, sterilization of heat, etc.) that provides purity of minerals. On the other hand, clays are subjected to the chemical process (homoinic clay system) [14]. Mixture of clay, water and oil builds an emulsion. The stabilization of emulsion depends on the relationship of that mixture [12].

Combined with sulfur and other minerals or used as cream, clays are important part of sunbathing emulsions [15]. Lubrication with clay may indicate a dysfunction or a possible disease. Application of clay can be divided into three segments: oral use of clay, lubrication of the skin and lubrication of medicinal mud. Oral usage of clay improves detoxification and recovery of digestive tract. Clay promotes the elimination of pathogens. Composition of clay (microelements and oligoelements) prevents reproduction of pathogens (*Candida albicans*). Consumed on an empty stomach, binding pathogens, clays have impact on the intestinal flora. Lubrication of the skin, in a form of clay crème with extract of herbs, is essential segment of beautification. Liver lubrication improves blood circulation. Liver's blood circulation affects the quality of bile salts and acids that are essential for the immune system. Clay lubrication helps in sports injuries. Mixture of soap and clay allows skin softness and smoothness. In addition to mentioned clay application, the third important segment is lubrication of medicinal mud [16]. Medicinal mud optimizes extraction of toxic substances from the human body. In addition to toxic extraction, it significantly reduces pain and infections. Americans called it "Mud that cures" [5]. Medical applications of clays, mud and other natural products have been known for ancient times [20,21].

One more way of clay application, is geophagy. Soil-eating (geophagy) was labeled as an attempt to compensate the lack of minerals in food. Different species of mammals, birds, reptiles and insects eat soil. In addition to this phenomenon, some studies showed that clay may contain many important substances from the soil. As an effective agent, clay binds to various chemical structures and inactivates them. Biologists in Canada and Alaska observed a geophagy by brown bears. One more example of geophagy was noticed in Venezuela. Producers that have cattle saw cows licking soil. In addition to this, in Africa, bisons lick clay from fresh soil. Chimpanzees, giraffes and rhinoceroses are also examples of geophagy. Mice eat soil when they are sick. The phenomena of geophagy can be used as an indicator of gastrointestinal disease in mice [5]. Geophagia (the deliberate consumption of non-food substances such as ingestion of soil/sand, clay blocks and mud) has been known for centuries. The practice of geophagia has been reported in several countries across continents including Africa (South Africa, Cameroon, Democratic Republic of Congo, Nigeria, Swaziland, Tanzania and Uganda), Asia (China, India, Philippines, and Thailand) and the Americas [22,23].

### Cosmetic and pharmaceutical application of clay

Cosmetic products make contact with different parts of human body (epidermis, nails, lips, hair, teeth, etc.). Fluids and powders applied for cosmetic purposes have poor staying properties [16]. Application of clay during skin treatment can be a better solution. As an essential part of protective creams, clays differ in composition (against dust, water, grease, sun, etc.). They are applied in a thin layer, as an impermeable flexible film that gives a hydration and strong protection to the skin [17]. The cosmetic possibilities of clay have been used worldwide. Application of clays can reduce subcutaneous fat [10]. During the annual Gerewol festival, Wodaabe tribe use clay for decoration. Himba people of Namibia use clay from head to toe to protect the skin from ultraviolet radiation [35,36].

Clays have a wide spectrum of application in pharmacy. As drug- release modifiers, clay decrease bioavailability of drugs. On one hand, via cation exchange and hydrophobic mechanisms, clay- protein interaction can localize therapeutic molecules. On the other hand, dispersed particles of clay in drug solutions, via equilibration and drying process, allow delivery of drug-clay complex in form of the tablets [18,19].

### Clay minerals and amino acids in relation to the origin of life

Miller and Urey performed the chemical experiment simulated the conditions from the early Earth period [27]. They tested the chemical origin of life by the synthesis of bio-molecules from simple precursors (e.g.  $\text{NH}_3$ ,  $\text{CH}_4$ , water). Continuous electrical sparks were fired between the electrodes simulating lightning. Addition of montmorillonite to Miller's system increased the yield of amino acids with an alkylated side chain [28,29]. Yuasa improved sparking experiment with montmorillonite, HCN and  $\text{NH}_4(\text{OH})$  [30,31].

Studies showed that clays have the important impact in the selection of protein over non- protein amino acids. In these researches, Na-montmorillonite was studied at pH 3, 7, and 10. [32]. The hypothesis that minerals of clay had a major role in the construction of proteins in the human body was confirmed in laboratory conditions by Stanley Miller in 1952 [5].

Temperature and humidity lead to the distribution and redistribution of amino acids on the surface of clay particles. Clay has the impact on the linking of amino acids into peptide chains. When moisture comes into contact with the surface of clay minerals, an active site on the surface that accelerates the formation of the peptide from the amino acid is erased. On the other hand, when moisture is absorbed, other sites become available for amino acids that build new chains. This continuous function depends on the type of clay minerals in the appropriate configuration. The special physical characteristics are responsible for curative properties of clay. In some cases, clay consists of particles smaller than bacteria. In infected mucous membrane flooded with a clay, bacteria are completely surrounded by a clay and separated from the source of nourishment. Growth and survivability of bacteria are interrupted. This can explain the reducing of infection symptoms. Moreover, it has the impact in prevention of poisoning symptoms in acute disease [33].

Minerals of clay may have contributed to the process of chemical evolution, as the result of their wide distribution in a geological era and the strong affinity for organic compounds. Clay minerals have a great role in chemical evolution which reflects in process of catalysis, adsorption of the monomers on the clay surface, polymerization of the monomers and formation of organo- clay complexes.

Clays may have the impact on the formation of amino acids of greater carbon numbers. On the other hand, clay doesn't make selection of protein amino acids over non- protein ones. Hence, under neutral or acidic pH,  $\alpha$ -amino acids can be less adsorbed than non- $\alpha$ -amino acids. Mostly, clays have no possibility to adsorb D-or L-enantiomers. However, kaolinite and montmorillonite may adsorb L-enantiomers selectively [34].

Electrical properties of clay differ from one to another. Studies showed that electrical conductivity of drinking water (from  $5,00 \times 10^{-4}$  to  $5,00 \times 10^{-2}$  (S/m)) and electrical conductivity of sea water (4.8 (S/m)) can be used for detection electrical conductivity of clay-based emulsion. Solvent emulsion based on clay for immersion in a bath (1liter per  $100 \text{ dm}^3$ ) that consists of sea salt (2 kg per  $100 \text{ dm}^3$ ), bicarbonate (500g per  $100 \text{ dm}^3$ ) and magnesium chloride aromatic salt (100g per  $100 \text{ dm}^3$ ) has electric conductivity 2 (S/m) [12].

### Experimental Methods

In this work is used bentonite clay, sampled in Prisjan, the village in the south-eastern Serbia. The chemical composition of pre-dried clay at a temperature of  $110 \text{ }^\circ\text{C}$  was: 51.82%  $\text{SiO}_2$ , 0.34%  $\text{TiO}_2$ , 26.86%  $\text{Al}_2\text{O}_3$ , 2.30%  $\text{Fe}_2\text{O}_3$ , 0.10%  $\text{MnO}$ , 1.27%  $\text{MgO}$ , 1.44%  $\text{CaO}$ , 0.75%  $\text{Na}_2\text{O}$  and 2.07%  $\text{K}_2\text{O}$ . Ignition loss was 7.2%.

## Characterization techniques

In order to characterize the bentonite clay, the Nigos- Electric dryer was used. The maximum temperature of the electric furnace was up to 1100°C. A microprocessor operated the temperature process according to the given program. A set value was generated as a series of straight segments that were adjustable by duration and inclination. An inclination segment consisted in increasing or decreasing the given value by the given speed, until reaching the given level, while the segment of holding represented the maintenance of the set value at the reached level at a certain time. After completing one program, the programmer had the ability to continue executing the next program, which could be connected to the programs.

## FTIR analysis

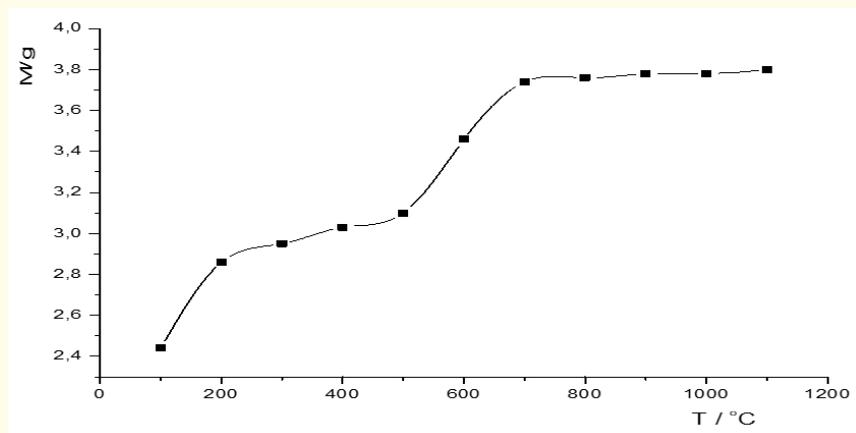
Fourier Transform Infrared Spectroscopy (FTIR) was used for characterization of organo- clay. IR spectras of prepared samples were recorded on Bomem MB-100 (Hartmann and Braun) FTIR spectroscope with a standard DTGS/KBr detector, 40 scans in the field of wave numbers 4000 - 400  $\text{cm}^{-1}$ , at a resolution of 2  $\text{cm}^{-1}$ , according to the method of pressed tablets. For sample preparation was used KBr technique. The amount of 1.5 mg of sample was homogenized with 150 mg of spectroscopically pure KBr ( $\approx 1\%$  solid solution). The mixture was subjected to vacuum and pressing pressure of 8105 Pa, to form porous tablets. Reference tablet was prepared from pure KBr.

## SEM analysis

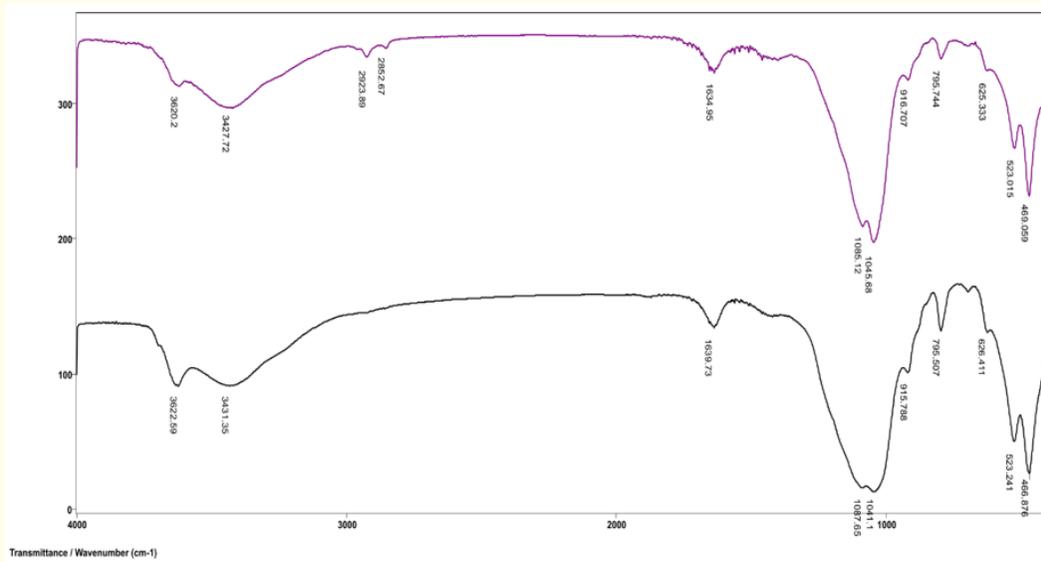
Scanning Electron Microscopy (SEM) was used for characterization of bentonite clay. Scanning electronic microscope JSM-5300 (JEOL, Japan) was used to investigate the structure of the sampled clay Preparation of samples is carried out by placing the sample on an aluminum support, with a glue or double-sided adhesive tape. The tool for spreading the layer on the sample's surface, used in this work, was JFC-1100E ION SPUTTER (JEOL Co., Japan). A potential difference of electron acceleration was 30 kV, and multiplication of the samples were 10000 and 15000 times.

## Results and Discussion

Clay changes due to dehydration, dehydroxylation, re-crystallization, shrinkage, fracture, loss of crystal structure and sintering, which occur as a result of elevated temperature, can be defined as "deformations". With increasing temperature, there is a loss in the mass of the bentonite sample. In the temperature range from 100°C to 200°C, the mass loss is high. From 300°C to 500°C we have a slight loss in mass, while for a temperature interval from 500°C to 700°C we have a maximum loss in the mass of the samples (Figure 1 and 2).

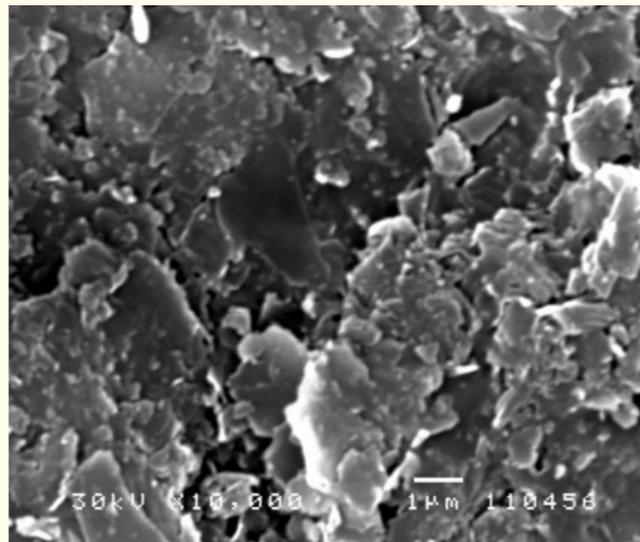


**Figure 1:** Graph of the dependence of the change in the mass of bentonite from the temperature, the starting mass of 20g.



**Figure 2:** Infrared spectrum of bentonite clay after thermal activation at a temperature of 100°C (up) and 200°C (below).

Clay was dried at 100°C. The structure of this dried sample was similar to the structure of the initial sample of bentonite clay. The porosity of this sample as higher due to partial removal of water (Figure 3 and 4).



**Figure 3:** Thermally treated clay at 100°C (increase sample 3, x 10000).

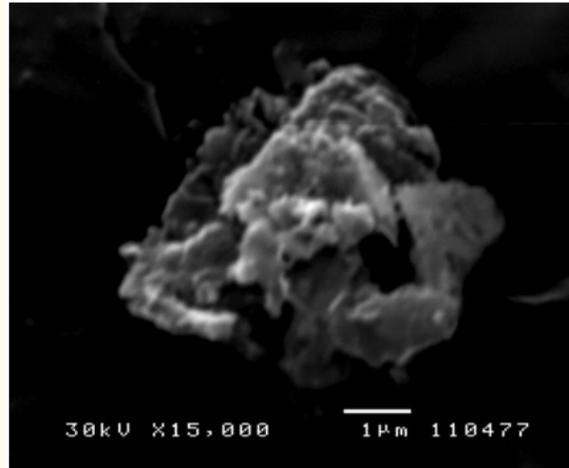


Figure 4: Thermally treated clay at 100°C (increase sample 2, x 15000).

Bentonite sample was treated with a 5% HCl ultrasound bath method in a ratio of 1: 2. During the procedure, the structure of clay changed. Hence, the porosity of bentonite increased.

In a solution of soybean isolates (5 ml), the suspension of bentonite (1g, 2g and 5g) was added and obtained by dispersing procedure at different temperatures (20°C, 40°C, 60°C and 80°C). pH of the soybean isolate (purine) solution was 6.21 pH and the electrical conductivity of the bentonite suspension with soybean isolates (purine) was measured (Figure 5).

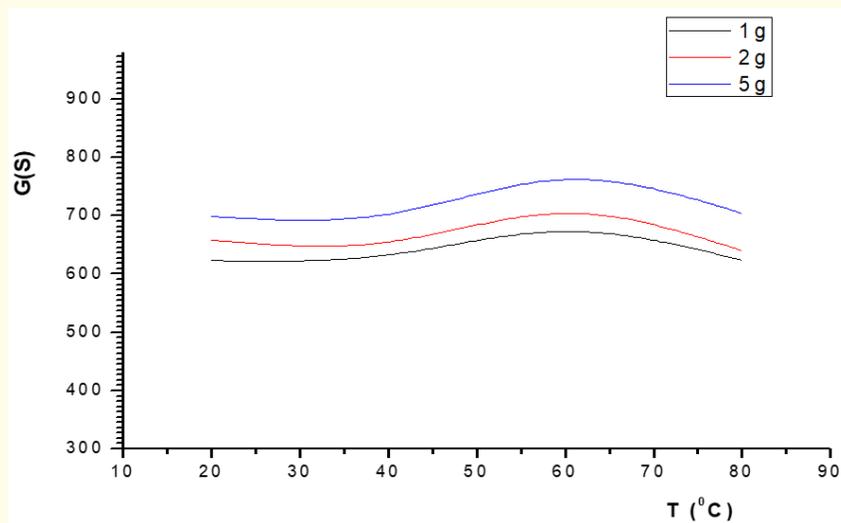


Figure 4: Graph of the dependence of electric conductivity bentonite suspension (with the addition of soybean isolates) at different dispersion temperatures of bentonite.

### Conclusion

Clay has a crucial role in solving gastrointestinal problems because it “impregnates the stomach “. The best known component of gastric juice, hydrochloric acid, activates clay components stimulating the gastric acid capabilities. Negatively charged clay nanoparticles allow the stabilization of gastric juice while positively charged soy proteins simulate food proteins. In the electrolytic process, clay particles are bonded to positively charged heavy metal ions allowing their ejection from the body. Experimental part of this paper consists of simulating the stomach reaction (stomach impregnation) during ingestion of clay. The soybean isolates and bentonite clay were used as samples during process. Dielectric constant and pH were observed during experiment. The results showed that the electrical conductivity was constant up to 40°C, at different clay concentrations. The pH value had the impact on the balance of intestinal microflora.

Human application of clay dates from the prehistoric times. Not only as a cleaner, but a catalyst, buffer, ion exchanger, adsorbent and carrier, clay can be used in a form of powder, gel, emulsion or suspension. The combination of clay with natural minerals, extracts of plants, fats and oils can significantly facilitate the synergic effect of clay application. Mostly, clay can be used for lubrication, skin treatment or bath immersion. Clay-based creams combined with oil extracts, minerals and volatiles are highly significant for the drainage of the lymphatic system. Clay application methods have significant influence in body rejuvenation system.

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