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Some Physicochemical Properties of Georgian Bentonite Clay

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Abstract

Clay minerals are known as biocompatible materials and have been utilized for medicinal aims from long ago. Currently, bentonite clays have also been widely investigated for *broad spectrum* of new *applications* in many biomedical spheres due to their unique properties - expansion and adsorption abilities - which are very useful in pharmaceutics, cosmetics, drug delivery systems and tissue engineering.

Swelling has a significant impact on the rheological and physical properties of clay. It depends on many factors including temperature, pH, and polarity. In addition, since bentonites have negative surface charge they possess high adsorption ability for cationic elements.

The priority task at the I. Kutateladze Institute of Pharmacochemistry TSMU is to extend the biopharmaceutical application of Georgian bentonite clay. Several semisolid formulations were proposed on the bases of the preparation - Tikha Ascane (TA), received from the clay of Askana Deposit (Ozurgeti region of Georgia).

In this study we investigated the swelling capability of TA in the presence of different temperatures, polarities and pH; the interaction behaviour of bentonite with cationic compounds was also evaluated. As many researches are focused on the combination clay minerals with cationic polymers for the preparation of effective therapeutic systems, we examined the suitability of TA as a substrate for the obtaining hybrid composites with biopolymer Chitosan (CS). The samples were characterized by examining FTIR spectra and morphology.

The obtained data indicate that swelling capability of TA is affected by temperature, pH, and polarity of solutions. FTIR analysis showed that cationic drug and polymer (CS) can be successfully incorporated in TA through adsorption and formation chemical bonds. Microscopic analyses demonstrated homogeneity of TA-CS composites. These results will be used in future for preparing drug - clay or drug - polymer composites based on TA for biomedical application.

Keywords: *Bentonite clay, Tikha Ascane, Swelling, Chitosan.*

Introduction

The profits of clay minerals for human health are well documented and have been utilized in traditional medicine from long ago. Presently bentonite clays have a broad spectrum of novel applications in many biomedical spheres including pharmaceutics, cosmetics, drug delivery systems, tissue engineering /1, 2/.

Bentonites possess the unique property of swelling in water to many times its dry volume, due to hydration of exchangeable cations. Since the surface of clay is negatively charged, hydronium ion (H_3O^+) from autoionization of water smoothly infiltrates into the interlayer and this hydrophilicity contributes to its swelling capacity. This ability depends on many factors such as temperature, pH, and polarity of solutions /3/.

Other characteristic of bentonite is adsorption. As it has 2:1 layer type structure with one octahedral sheet "sandwiched" within two silica-based tetrahedral sheets containing exchangeable cations, numerous molecules intercalate between the interlayers via ion exchange /4/. In particular, cationic drugs are adsorbed onto clay by these electrostatic interactions. These adsorptive interactions differ depending on the drug type and molecule size, initial drug concentration, charge, temperature and pH of solvent /1, 2, 3, 5/.

The combination of clay minerals with polymers led to the development of new hybrid materials designed for certain biological applications. In recent decade many researches are focused on cationic polymers, which are considered as promising biomaterials for the therapy of several human diseases /3, 6, 7/. Chitosan (CS) is a natural cationic polymer widely used for the preparation of effective therapeutic systems. The combined impact of the clay and biopolymer in addition to the intense interstitial interactions between them (hydrogen bonding, electrostatic interaction) could ameliorate the properties such as surface area, drug encapsulation efficacy, controlled release behaviour of the hybrid composites /6, 7, 8/.

The priority task at the I. Kutateladze Institute of Pharmacochemistry TSMU is to extend the biopharmaceutical application of Tikha Ascane (TA) - preparation, produced by Acad. Iovel Kutateladze from Georgian bentonite (Askana Deposit, Ozurgeti region, Georgia) /9, 10/. TA is registered and permitted for the medicinal and pharmaceutical application by Georgian healthcare authorities. Several semisolid formulations were proposed on the bases of this preparation /11-14/.

In this study we investigated the swelling capability of TA in presence of different temperatures, polarities and pH; the interaction behaviour with cationic compounds of bentonite was also evaluated. These results will be used in future for preparing drug - clay or drug - polymer composites based on TA for biomedical application.

Material and Methods

TA – preparation from Georgian bentonite clay was available in the Pharmaceutical Technology Direction (I. Kutateladze Institute of Pharmacochemistry, TSMU). CS of high molecular weight (CAS No.: 9012-76-4) was purchased from Aldrich. Brilliant Green (BG) (CAS: 633-03-4) was used as a model cationic drug in experiments. All the other chemicals or solvents used were commercially available and of reagent grade.

Preparation of hybrid materials

BG composites - 2% drug solution in ethanol (60%) was added to 2% clay suspension (in ultrapure water) under stirring to obtain system with 0.04% of active compound.

TA-CS complexes - Solution of chitosan was prepared by the addition of corresponding amounts of polysaccharide to 1% (v/v) acetic acid and stirred for about 6 h; the pH of the obtained solution was adjusted to 4.9 using NaOH before being mixed with the bentonite suspension. Appropriate amount of chitosan solutions were slowly added to a 2% clay suspension to obtain composites.

For spectroscopic analysis, the composites were air-dried at 50 °C and ground to powder.

Characterization

Swelling potential of TA was analyzed by the standard method according to ASTM D5890 and the swell index was calculated /15/.

All pH measurements were performed at room temperature using a pH meter (MW150, Milwaukee, Romania).

FT-IR (Fourier transform infrared) spectral analyses of tested samples were performed to determine the existence of functional groups presented in starting and synthesized materials. The IR spectra were recorded over the 4000–350 cm−1 wavenumber range on a Jasco 600 FT-IR spectrometer, equipped by a DTGS (deuterated triglycine sulphate detector) with KBr beam splitter /13, 14/.

The structure of the selected hybrid materials was examination under Light microscopy (ZEISS Jeneval Microscope CF250; 3,2x/0,06 GF planachromat 40x/0,65 GF Planachromat) /13, 14/.

All measurements were performed in triplicate. Mean values and standard deviations were computed using Microsoft Excel 2016 (Microsoft Corp.) software.

Results and Discussion

Characterization of raw materials

Swelling is a prominent feature of bentonites and has a significant impact on the rheological and physical properties of clay. It depends on many factors including temperature, solvents, pH, and time /16/. The behavior of bentonites is strongly affected by heat-treating via its influence on free and adsorbed water /3/. The swelling capacity of TA in ultrapure water was conducted in thermally controlled environments and recorded as a function of temperature (Fig.1).

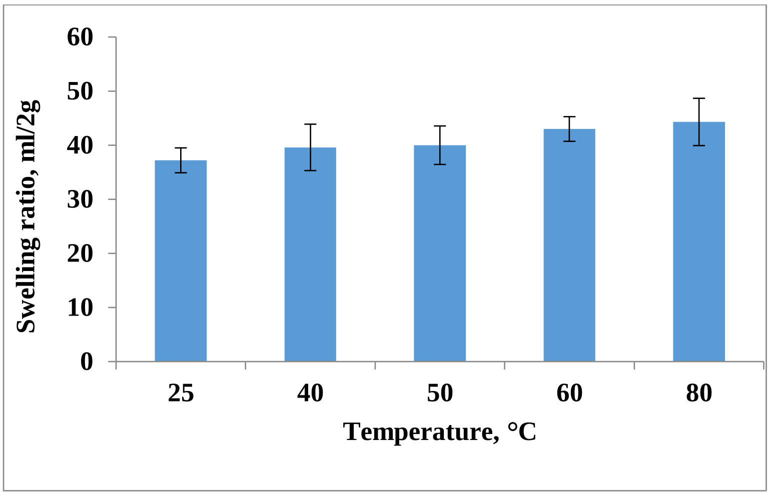


Figure 1. Impact of temperature on TA swelling potential

The study results of the temperature dependence of TA swelling ratio indicates that the expansion of clay was almost the same as temperature increased from 25 to 50 °C (Fig.1). Swelling volume begins to rise as the temperature reaches 60 °C. This indicates that high temperature impacts the motion of water molecules, interlayer cations and bentonite particle hydration consequently /16/.

Ethanol is the popular solvent to dissolve the active ingredients, as it is safe and biodegradable. Because of the polarity, it possesses 'hydrophilic' property. In this study we investigated the swelling behavior of TA using different ratio of ethanol-water solutions. By mixing alcohol with ultrapure water in varying amounts solutions with following concentration were prepared: 5, 10, 15, 20, 25, 30, 35, 40 and 60% (v/v). The obtained data are presented in Fig.2.

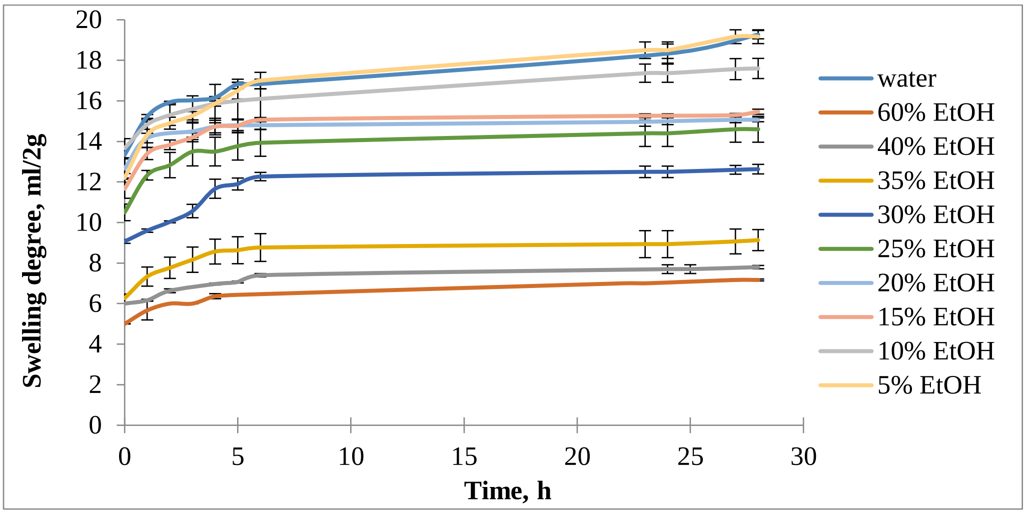


Figure 2. Swelling kinetics of TA in different alcohol concentration

The plots show that the swelling behavior of TA is notably affected by the different percentages of ethanol-water solutions; the swell degree seems to decrease with the increase of ethanol percentage. These results are consistent with published data /6/. The enlarged volume of the samples could be assigned to the interaction between the clay surfaces and fluids. The raised proportion of water expands the polarity index of the mixture. Higher polar fluids reacting with the clay surfaces form thicker diffuse bilayers that in turn produce higher swelling /6/.

Changes in pH have been observed to influence on expansion capacity of bentonites /17/. The swelling property of TA samples was evaluated in different concentration of acetic acid solutions and found that with increasing acetic acid concentration the swelling degree is decreased (Fig. 3A). This agrees with observations described by Chavali at al /18/. The rise of acid concentration lowers free swell values of clay by 31.7%, 48.9 % and 63.7 % for 0.5, 1 and 1.5 % acetic acid solution accordingly. In acidic surroundings, hydrogen ions in the pore liquid would substitute the commonly encountered exchangeable Na^{+} cations from the diffuse double layer in bentonite /17/. This process would result diminish in double layer thickness, leading in a lesser swelling /17, 19/.

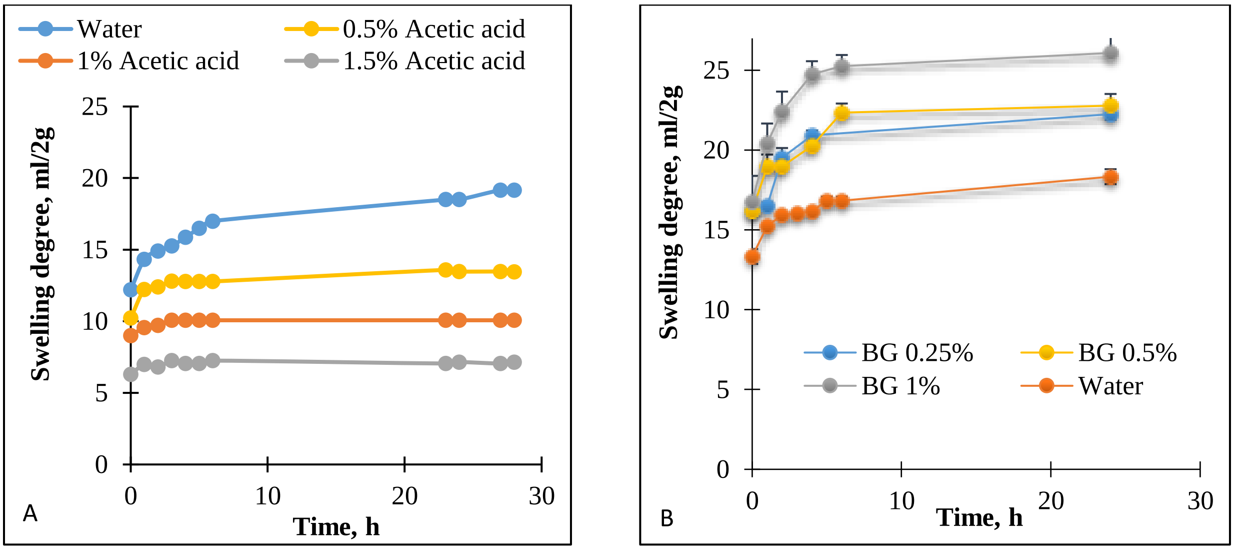


Figure 3. Swelling kinetics of TA in different concentration of: A - Acetic acid and B – BG solutions.

Bentonite has strong affinity towards basic dyes which are soluble in water forming cations /20, 21/. As a model drug, we utilised cationic triphenylmethane dye - brilliant green (BG), having an extensive experience of usage as antibacterial and antifungal agent /22/; recently the anti-proliferative action of BG has been also reported which expands its use in the therapy of cutaneous melanoma metastasis and hemangiomas /22, 23, 24/.

The swelling capability of TA was evaluated in varied concentration of BG. It was figured out, that the swelling degree is raised by 1.21, 1.24 and 1.42 times with increasing BG concentration from 0.25; 0.5 to 1%, consequently (Fig. 3B). As bentonite has the negatively charged surface lattice with exchangeable cations, BG intercalates between the interlayers by ion exchange and also through the electrostatic attraction /4/. These data are in accordance with published data /5/.

Fourier transform infrared spectroscopy was employed to examine the interaction between BG and TA in the composites (Fig. 4). The FT-IR spectra of TA-BG and pure TA are of comparable shape but some variance can be noted particularly in the region between 1700 and 900 cm−1. The peak in TA spectrum observed at 912 cm−1, which is considered as characteristic of a dioctahedral smectite (Al-Al-OH bending vibration), was shifted to 910 cm−1 after MG adsorption. No considerable shift in wavenumber was detected for the strong peak observed at 1022 cm−1, which corresponds to C-O-C groups and the stretching vibration of Si-O. The band at 1635 cm−1 corresponding to the OH stretching and bending frequencies of the hydration water was disappeared. After BG adsorption on TA, a peak attributed N–C band at 2923 cm−1 appeared. Furthermore, several adsorption peaks that arise in the range of 1580–1200 cm−1 could be ascribed to the N–C groups after BG adsorption on TA. These data indicate that the BG might not only attach on the free surface of TA by adsorption but also can form chemical bonds with bentonite /21, 25/.

TA-CS composites were prepared using diluted acetic acid as solvent for dissolving chitosan. Bentonite was first hydrated in purified water and then added to polymer solution under stirring at 60 °C. Three ratios of the TA-CS hybrid materials were prepared: 1:1, 3:1 and 1:3. Pure polymer and clay were compared with obtained composites in terms of FTIR spectra and morphological structure.

FTIR analyses of the TA-CS composite demonstrate the consolidation of specific characteristic absorptions for both ingredients (Fig. 4). The amide group in chitosan represented by the band at 1669 cm−1 are shifted in the samples to 1653 cm−1 (1:1/TA-CS), to 1660 cm−1 (1:3/TA-CS) and 1651 cm−1 (3:1/TA-CS) respectively. At 1554 cm−1, the deformation vibration of the protonated amine group in the CS is shifted towards 1529 cm−1 (1:1/TA-CS), 1537 cm−1 (1:3/TA-CS), to 1558 cm−1 (3:1/TA-CS) /7/. The peak around 1075 cm−1 most likely corresponds to the characteristic absorption frequencies of β-D-pyranoside in chitosan. The existence of the band around 1050 cm−1 in composites shows the presence of the polymer in systems. These findings show the insertion of chitosan in the TA structure.

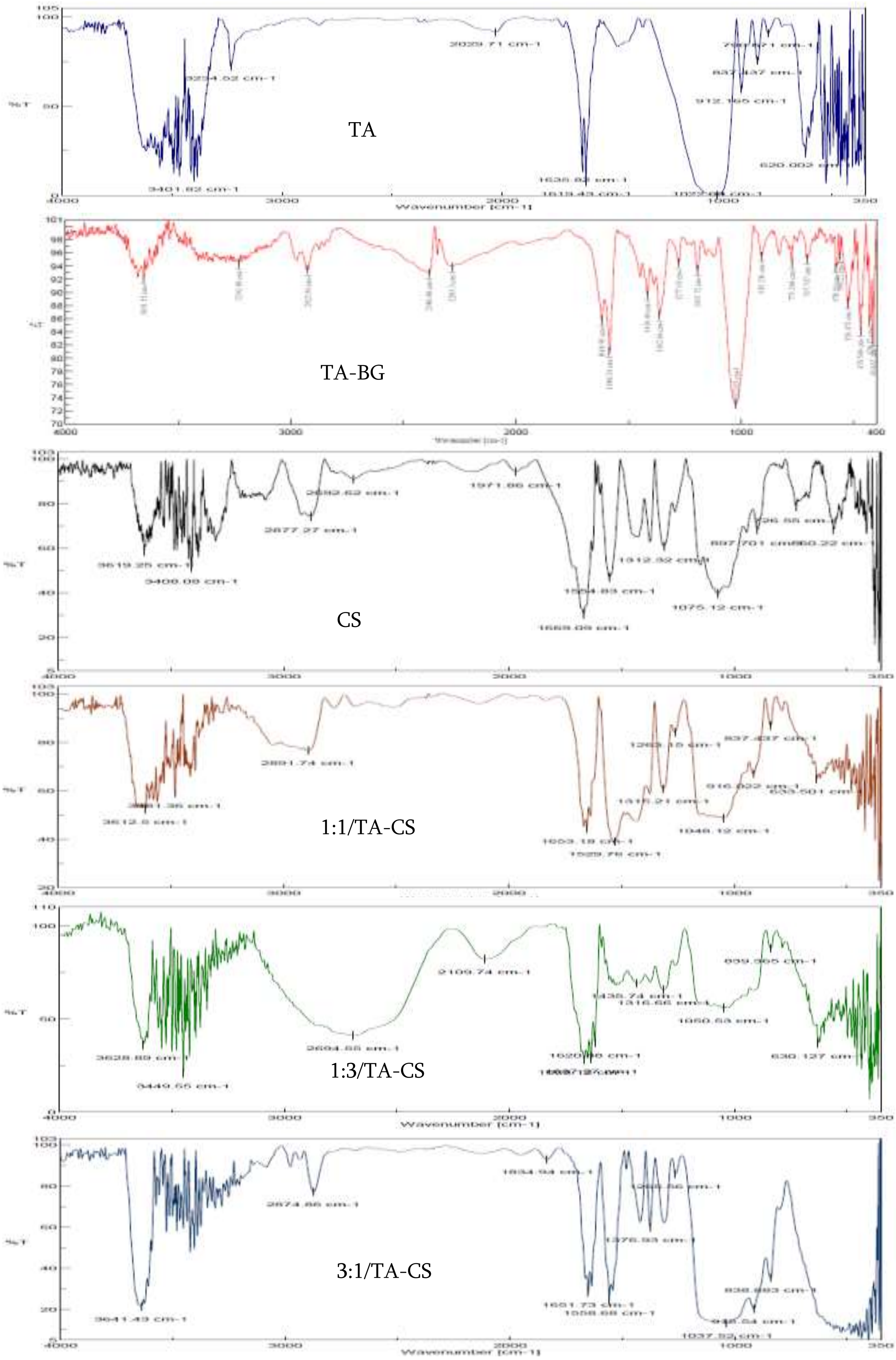
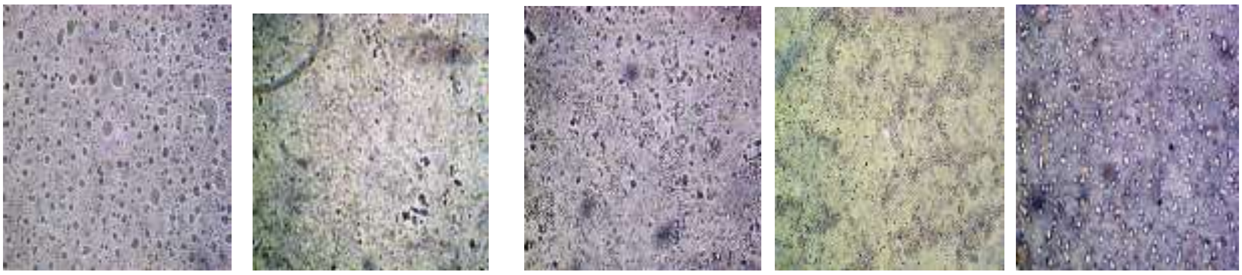


Figure 4. IR spectra of the tested samples.

The micrographs of the surface morphology of tested samples are presented in Fig 5. From visual inspection of microscopic images, the following could be observed: homogeneous appearance with small roughness and bumps characterised to TA; the well-distributed light spots belong to chitosan, and bentonite - polymer composites. The surface of the hybrid system is rough and has a porous structure, signifying that the prepared composite may have a good adsorption capability. Smoothness of the clay surface was detected to enhance with the chitosan matrix system. The presence of polymer contributed interpolated lamellar structures as result of the interaction and/or entrapment of clay particles within the polymer chitosan /6/. Microscopic analysis data are in compliance with the FTIR results, pointed out the attendance of intercalated structures in the TA-CS hybrid material through the electrostatic interaction of the silicate groups and amino TA and CS, accordingly /21/.



A B C D E

Figure 5. Light microphotographs of tested samples. A – CS; B - TA; C – TA-CS- 1:1; D – TA-CS- 3:1; E – TA-CS- 1:3.

Conclusion

The study results indicate that the expansion of clay in pure water rises as the temperature reaches 60 °C; the swell degree decreases with reducing polarity and pH of solutions. FTIR analysis showed that cationic drug and polymer (CS) can be successfully incorporated in TA through adsorption and formation chemical bonds. Microscopic analyses demonstrated homogeneity of TA-CS composites. These results will be used in future for preparing drug - clay or drug - polymer composites based on TA for biomedical application.

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საქართველოს ბენტონიტური თიხის ზოგიერთი ფიზიკურ-ქიმიური თვისება

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[1]თბილისის სახელმწიფო სამედიცინო უნივერსიტეტი, ი. ქუთათელაძის ფარმაკოქიმიის ინსტიტუტი

თიხა-მინერალები ცნობილია, როგორც ბიოთავსებადი ნედლეული, რომელიც უძველესი დროიდან გამოიყენება სამკურნალო მიზნებისთვის. ამჟამად, ბენტონიტები ფართოდაა შესწავლილი მედიცინაში მრავალმხრივი გამოყენების მიზნით მათი ისეთი უნიკალური თვისებების გამო, როგორიცაა გაჯირჯვების და ადსორბციის უნარი. გაჯირჯვება მნიშვნელოვან გავლენას ახდენს თიხის რეოლოგიურ და ფიზიკურ თვისებებზე. ის დამოკიდებულია მრავალ ფაქტორზე, მაგ. ტემპერატურა, pH და გამხსნელის პოლარობა. გარდა ამისა, ბენტონიტებს ზედაპირული უარყოფითი მუხტის გამო გააჩნიათ კათიონური ელემენტების ადსორბციის მაღალი უნარი. ი. ქუთათელაძის ფარმაკოქიმიის ინსტიტუტის (თსსუ) კვლევის ერთ-ერთი პრიორიტეტული მიმართულებაა საქართველოს ბენტონიტური თიხის გამოყენების პოტენციალის გაფართოება ბიოფარმაციაში. ასკანას საბადოს თიხიდან (ოზურგეთის რაიონი, საქართველო) მიღებული პრეპარატის - თიხა ასკანე (TA), საფუძველზე ინსტიტუტის მიერ მოწოდებულია რბილი წამლის ფორმები კანის სხვადასხვა დაავადებების სამკურნალოდ.

წარმოდგენილ ნაშრომში შესწავლილია TA -ს გაჯირჯვების უნარი სხვადასხვა ტემპერატურის, პოლარობის და pH-ის პირობებში; ასევე გამოკვლეულია ბენტონიტის ურთიერთქმედების ხასიათი კათიონურ ნაერთებთან. ვინაიდან მრავალი კვლევა ორიენტირებულია თიხა-მინერალების და კათიონური პოლიმერების კომბინაციაზე ეფექტური თერაპიული სისტემების შემუშავების მიზნით, შევისწავლეთ TA -ს როგორც სუბსტრატის გამოყენების შესაძლებლობა, ბიოპოლიმერ ქიტოზანთან (CS) ჰიბრიდული კომპოზიტების მისაღებად. ნიმუშები შეფასდა ინფრაწითელი სპექტრებისა და ერთგვაროვნების მიხედვით. დადგინდა, რომ ტემპერატურა, pH და ხსნარების პოლარობა გავლენას ახდენს TA-ს გაჯირჯვების უნარზე. FTIR ანალიზმა აჩვენა, რომ კათიონური ბუნების ნივთიერებაც და პოლიმერიც (CS) შეიძლება წარმატებით ინკორპორირდეს TA-ში ადსორბციისა და ქიმიური ბმების წარმოქმნის გზით. მიკროსკოპული ანალიზით დადგინდა TA-CS კომპოზიტების ჰომოგენურობა. მიღებული შედეგები სამომავლოდ გამოყენებული იქნება საქართვლოს ბენტონიტური თიხის პრეპარატის (TA) საფუძველზე წამალი-თიხის ან წამალი-პოლიმერული კომპოზიტების მოსამზადებლად ბიოსამედიცინო გამოყენებისთვის.

საკვანძო სიტყვები: *ბენტონიტური თიხა, თიხა -ასკანე, გაჯირჯვება, ქიტოზანი.*