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*Research Paper*

# Cosmetic Investigation of the Adsorption of Hyalunoric and Glycolic Acid on Tutmac Clay

Adnan Yildiz[1], Nur Beyaztaş[2], Tuğba Gür[3, *]

*[1]Yüzüncü Yıl University, Faculty of Education, Department of Chemistry, Van, Turkey; [2]Yüzüncü Yıl University, Faculty of Science, Department of Chemistry, Van, Turkey; [*3]Yüzüncü Yıl University, Vocational School of Health Services, Van, Turkey*

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**Abstract:** In this study, hyaluronic and glycolic acids were adsorbed on Tutmaç clay. Clay brought from the village of Tutmaç in Guzelsu town of Gurpinar district in Van. The clay we obtained in the form of large particles was first sieved with a pore size of 0.038 mm (400 mesh). This ground clay was heated in an oven at 100 °C for 24 hours and stored in a desiccator. The clay sample, that is, 0.2 gr clay, was weighed 10 times and adsorbed for 10 minutes at room temperature with 1,2,3,4.5 ml of concentrated hyaluronic acid and glycolic acid for each 0.2 gr clay. The same operations were carried out for heat-treated clay. When the adsorption process came to equilibrium, the samples were filtered on filter paper and then washed with ionized water. The solid part was dried and the Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA) and Scanning Electron Microscope (SEM) analyzes of these samples were performed, and the results were obtained by interpreting the analyzes in the central laboratory. In this study, studies were carried out on pure clay and clay treated with acids. As a result of the processes and thermal changes, it was observed that the amount of hyaluronic acid adsorbing was higher in the untreated clay, and it was concluded that these clay minerals can be used as a skin mask when suitable conditions are met. At the same time, it was concluded that the pore structure of the clay was deteriorated and it moved towards an irregular shape with the heat treatment of pure clay.

***Keywords:*** *Hyaluronic acid, Glycolic acid, Clay, Adsorption, SEM, TGA, DTA*

## Introduction

Clay minerals, which form an important part of the soil, have been formed as a result of various changes in the earth (Malayoğlu & Akar, 1999). Clay, which is a sedimentary rock formed by the agglomeration of particles of four microns or less and formed by the physical breakdown of rocks and mineral masses, has a wide range of uses in the field of health, from pharmaceutical formulations to cosmetic products (Dalgıç & Kavak, 2004; Carretero, 2002). Clays are hydrated crystalline aluminum silicates containing major elements such as iron, alkali (Na, K *etc.*) and alkaline earth (Ca, Mg etc.) metals. They are classified as three-dimensional, two-dimensional (layered) and one-dimensional (fiber structure) according to their crystal structures (Wypych, 2004). For the effect of minerals on the behavior of a soil, it is necessary to know the clay types in the soil along with the amount of clay fractions in the soil (Yılmaz, 1990). Clays have high adsorption capacity against positively charged inorganic or organic materials, thanks to their permanent negative charge and high surface area (Crini, 2006).

Adsorption is defined as the bonding of molecules with a surface due to contact effects and tensile forces on the surface (Selçuk, 1991). The adsorbate molecule may be weakly or strongly attached to the adsorbent surface. In this case, physical or chemical adsorption is mentioned (Beyhan, 2003). In the adsorption process; polymers (Kim & Guiochon, 2005), pumice stone (Veliev et al., 2006), clay (Veli & Alyüz, 2007), bentonite (Bulut *et al*., 2008) and activated carbon (Khaled et al., 2009; Bangash and Alam, 2009; Schimmel et al., 2010) are some of the commonly used adsorbents.

Hyaluronic acid (HA) is a natural linear polysaccharide that is one of the most important components of extracellular matrices (Sahiner & Jia, 2008; Jha, 2009). This natural anionic biopolymer is inherently biodegradable, biocompatible and non-toxic, and has great potential in biomedical fields (Singh, 2014; Ekici et al., 2011; Erickson *et al*., 2012; Ilgin *et al*., 2010). However, HA has low mechanical stability and rapid absorption capabilities in tissues. In order to eliminate these undesirable properties of HA, it can be used to prepare additional polymeric components from different synthetic

* *Corresponding: E-Mail: tugbagur@yyu.edu.tr, Tel: +90 553 925 74 45*

monomers and polymers and/or even natural polymers such as chitosan, silk fibroin protein, and thus in different formulations (Miranda *et al*., 2016). Superporous HA cryogel has been prepared and used in tissue integration for stem cell growth and tissue engineering in previous studies (Tavsanli & Okay, 2016; Oelschlaeger *et al*., 2016). Clay-based composites have a wide range of applications in the absorption of toxic species such as gas molecules, metal ions, organic molecules, and can be used as a rigid support in bimolecular separation (Dong *et al*., 2015, Van Scott & Yu Rj, 1974). Hyaluronic acid and glycolic acid belong to the class of alpha hydroxy acids. Since HA has the ability to absorb moisture, it is generally used in skin care products. Glycolic acid is an AHA and is widely used in the cosmetic industry and is also one of the favorite acids of the peeling process (Stiller *et al*., 1996). In studies conducted to examine the effects of AHAs on the skin, different AHAs were formulated by adding them to water or mixtures of water-miscible ethanol, propylene glycol, butylene glycol, and ethoxydiglycol at different rates. AHAs have purposes such as being effective at low relative humidity in cosmetic samples, reducing wrinkles by re-forming the skin, making the skin smooth with a bright and beautiful appearance (Berardesca & Maibach, 1995). Deep research on lactic acid has led to the idea that other AHAs will be moisturizing, and scientific studies have been concentrated in this direction and the route has begun to be drawn in different directions (Scholz *et al*., 1994).

In this study, clay-based hyaluronic and glycolic acid containing materials were prepared for potential use in cosmetic applications. Morphological and physicochemical characterization of the prepared materials were determined by SEM analysis. The thermal behavior of the obtained clays was investigated by DTA and TGA analyses.

## Material and Method

### Material

The clay used in the experimental studies was obtained from the village of Tutmac in Van Gurpınar county. The hyaluronic and glycolic acid materials were obtained from Merck. The structure of the Tutmac clay was investigated in scanning electron microscopy (SEM). Taken with a Zeiss Sigma 300 field emission scanning electron microscope (FESEM). A secondary electron (SE2) detector was used for the images. All other chemicals used in the study were of suitable analytical quality. The structure of the clay was elucidated by X-Ray Diffraction Analysis. TGA analysis was performed regarding thermal degradation and mass losses of the samples. TGA analyses were performed with Labsys Evo brand TGA device at a speed of 10 ºC /sec in the temperature range of 0-1200 ºC.

### Method

The clay sample used in the experiment was taken from the clay quarry in the vicinity of Van Gurpınar Tutmac (Krel) village and the clay sample was dried and ground in the mill, then the clay sample was passed through a 400-mesh sieve and heated in an oven at 100 ºC for 24 hours and kept in a desiccator in order to reduce the moisture content inside has been done.

The adsorption process was carried out by adding hyaluronic and glycolic acids, which are adsorbate, in different concentrations to the clay weighing 0.2 g. The prepared samples were mixed with a magnetic stirrer until they reached equilibrium at room temperature and filtered and chemical analyzes such as SEM, DTA and TGA were performed.

## Results and Discussion

The results we obtained with our study; Type and analysis of Tutmac clay, SEM image of pure clay, DTA, TGA curve, SEM image of heat-treated clay, DTA, TGA curve, SEM image of clays treated with Hyaluronic and Glycolic acid and DTA, TGA curves are shown in the figures 1 & 2.

X-Ray diffraction analysis was used to determine the type and general properties of the Tutmac clay used in our study (Figure 1). As a result of this analysis, it was seen that the structure of the clay was mixed-layered clay minerals, [Simhtite (dominant) + chlorite], [Illite + Smectite] very few, Calcite, Quartz, Serpentine group mineral and Ferdispet group mineral (very little) (Alper, 2013). Zeiss Sigma 300 field emission scanning electron microscope (FESEM) was used to obtain SEM images. When the SEM image of the untreated pure clay in Figure 2a is examined, it is seen that the existing pores in the clay structure are not fully developed, but the sedimentation in the clays has begun to show itself. When these clay samples are treated with hyaluronic and glycolic acids (Figure 2b and Figure 2c), it is observed that the layers that formed the clays in the raw sample gradually disappeared and the pores were seen more clearly. These disappearing layers are replaced by needle-like structures. The opening in these pores was more pronounced in clay treated with hyaluronic acid (Figure 2b).

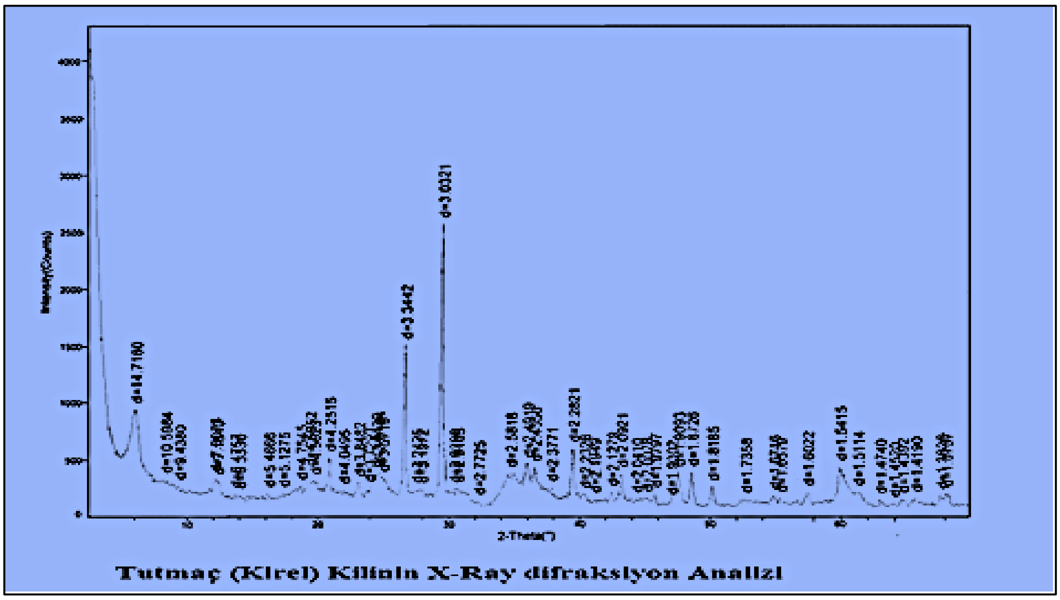
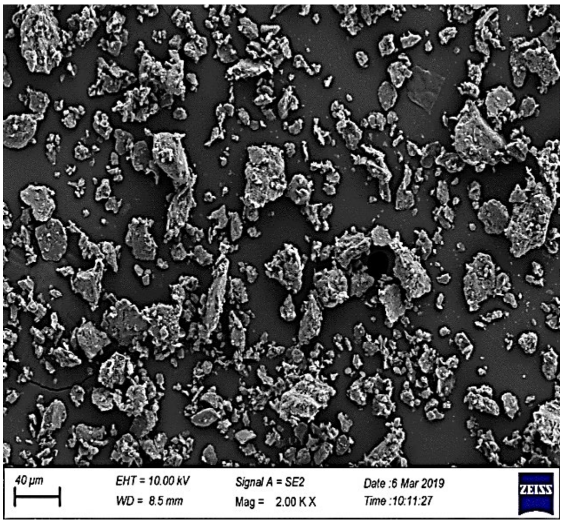
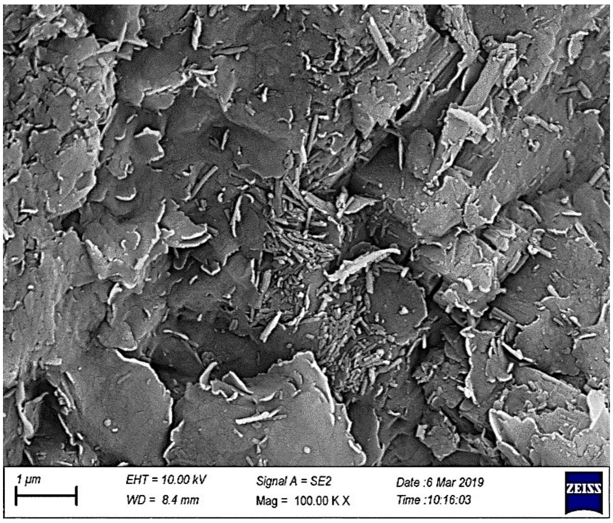


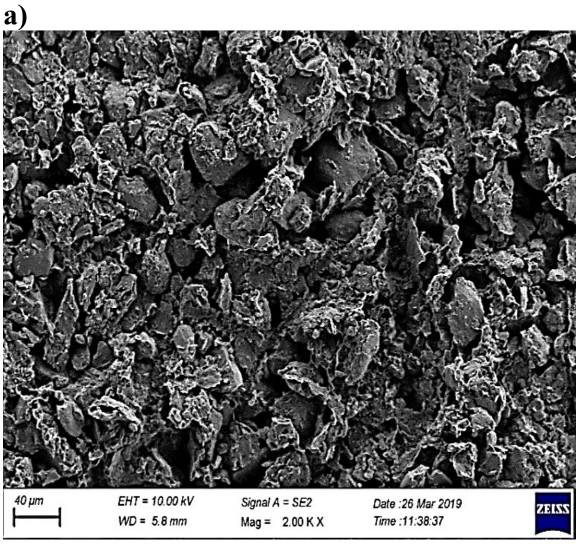

**Figure 1.** X-Ray Diffraction Analysis of Tutmaç clay



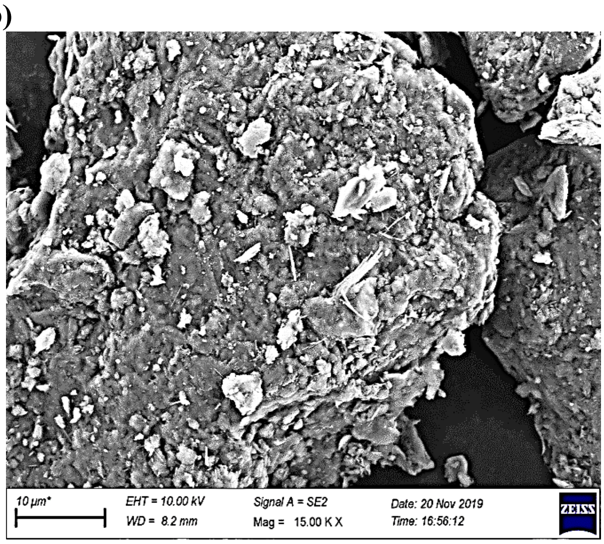

a)



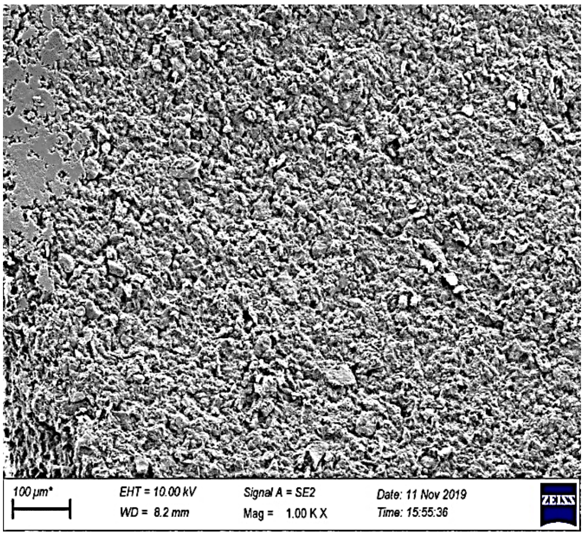

b)



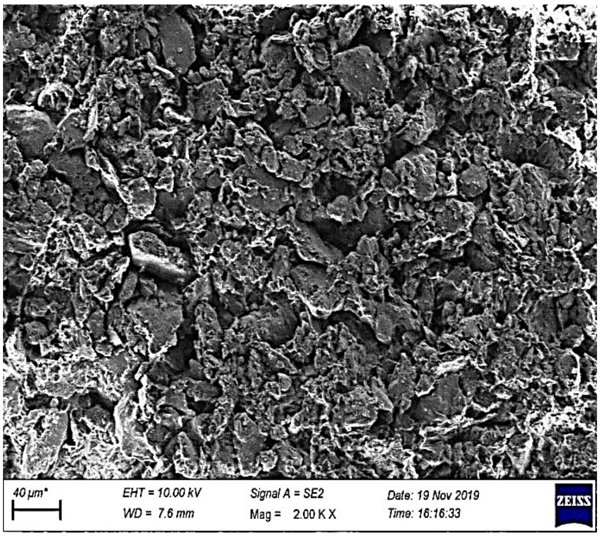

c)




d)

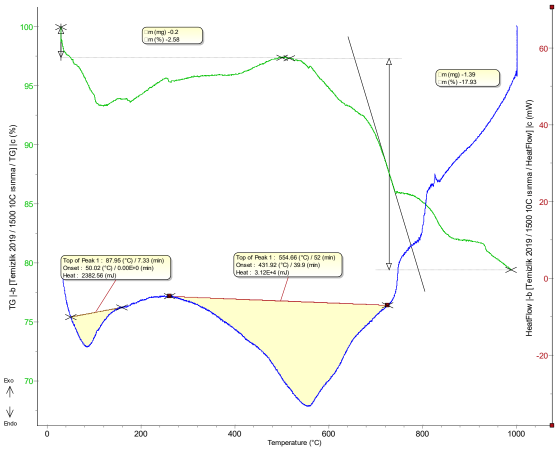



**e)**



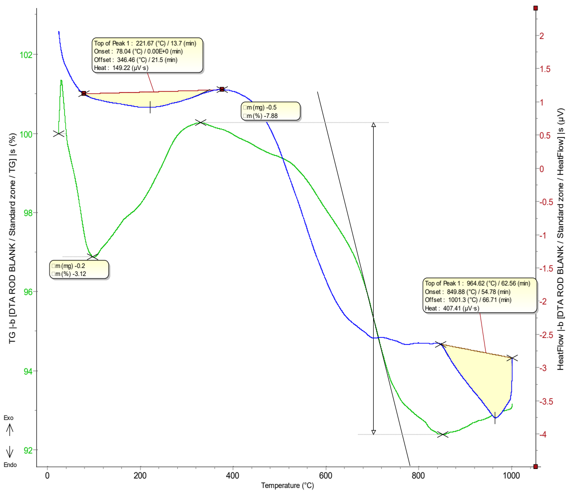

**f)**

**Figure 2.a)** SEM image of pure clay **b)** SEM image of clay treated with hyaluronic acid **c)** SEM image of clay treated with glycolic acid **d)** SEM image of pure clay heat treated at 400 ºC **e)** Pure heat treated at 400 ºC SEM image of the adsorption of clay with hyaluronic acid **f)** SEM image of the adsorption of pure clay heat-treated at 400 ºC with glycolic acid

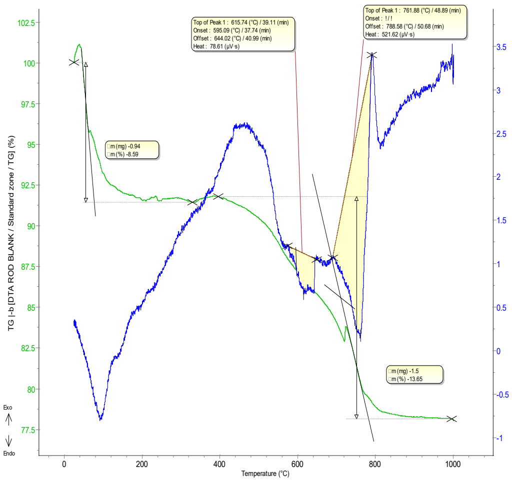



**a )**

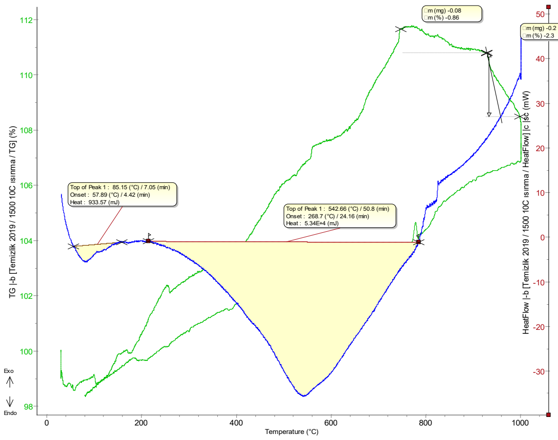

**b)**



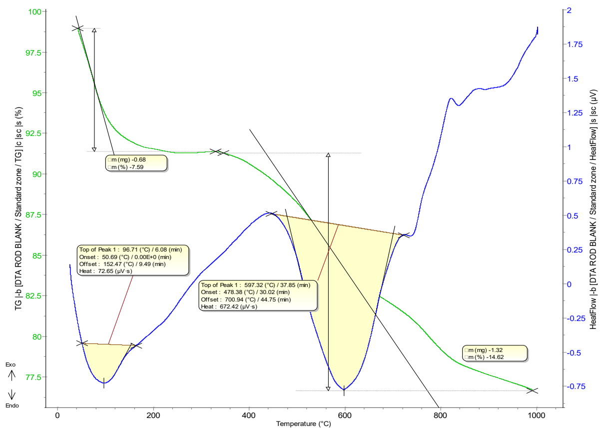

**c)**




**d)**



**e)**



**f)**

**Figure 3. a)** DTA-TGA Curve of pure clay **b)** DTA-TGA Curve of clay treated with hyaluronic acid **c)** DTA-TGA Curve of pure clay heat-treated at 400 ºC **d)** DTA-TGA curve of pure clay heat treated with glycolic acid at 400 ºC **e)** DTA-TGA Curve of pure clay heat-treated with hyaluronic acid at 400 ºC **f)** DTA-TGA curve of pure clay heat-treated with glycolic acid at 400 ºC

It is seen that the homogeneity of the clay deteriorated after the raw clay was heat treated at 400 ºC (Figure 2d). When heat-treated clay is treated with hyaluronic acid, it is observed that the porosity distribution differs with the changing temperature, more often it is observed that the crystalline structure of the clay deteriorates and turns into an amorphous structure (Figure 2e). In a study, he found that the different surface shapes and mass losses of the clays are due to the waters that bind to the clays in different ways (Yıldız, 1999). In the same study, he concluded that the surfaces of natural clays are hydrophilic and that water or water-like structures with hydrophilic properties will be more adsorbed on the surface of the clays. Our study shows parallelism with this result. The hyaluronic acid we use is a water-loving acid and therefore has a high adsorption rate. The differentiation of the surface of the clay treated with hyaluronic and glycolic acid compared to the pure clay and the presence of acicular-leafy structures are proof of the adsorption of hyaluronic and glycolic acids on the surface of the clay.

Considering the TGA and DTA values, the mass loss in the untreated clay shown in Figure 3a is 2.58%, while in Figure 9, when this clay is treated with hyaluronic acid, this mass loss is 24.56% and the difference is 21.98%. This ratio shows the hyaluronic acid retained in pure clay. Considering the TGA and DTA values in heat-treated clay in Figure 3c, the mass loss in pure clay heated at 400 ºC is 3.12%. When this heat-treated clay was treated with low concentrations of hyaluronic acid, the mass loss was 8.59% (Figure 3d). When the difference is taken into consideration before and after the treatment, it is seen that it is 5.47%. When the heat-treated clay was treated with low concentration glycolic acid, the mass loss was 7.59% (Figure 3f), and when the difference between before and after the treatment was considered, there was a difference of 4.47%.

Considering the DTA and TGA curves of the clay, the hyaluronic and glycolic acid adsorption of the heat-treated clay showed less adsorption than the un-heat-treated clay. We can conclude that this is due to the waters connected to the clay in different ways. At the same time, it was determined that the adsorption increased and decreased as a result of the binding of the waters, which are connected in different ways in the pores of the clay, with hyaluronic and glycolic acids. Adsorption decreased as a result of the removal of the water bound to the heat-treated clay. Adsorption was observed more in untreated clay. In a study, he used the sepiolite clay mineral, which belongs to a fibrous structure, and observed its thermal changes at different temperatures and reached the conclusion by investigating the temperatures at which adsorbed, zeolitic and bound water were removed (Selçuk, 1991). As a result of the thermal processes, raw and treated clay samples were examined, and it was determined that the adsorbed water on or attached to the clay mineral in the samples removed after about 105 ºC, the zeolitic waters were removed between 225-350 ºC and the crystalline water above 350 ºC (Selçuk, 1991). The clay we used in our study is a mixed clay (Figure 1). The clay mineral or similar clays we use in our study are mostly applied to the skin or body in the form of masks or mud baths for cosmetic purposes. Considering the adsorption efficiency of this study, it was observed that it provided a retention rate of 31.57%.

## Conclusions

Today, AHAs are intensively researched and their application areas are increasing day by day. The fact that AHAs are included in countless cosmetic products with their known and unknown aspects shows that these substances will be on the agenda in the coming years. With our study, we think that Tutmaç clay mineral can be modified with different modifications, namely acids or bases, and used in adsorption of different organic or inorganic substances. In line with the results obtained, we think that in cosmetic applications, hyaluronic acid and glycolic acid substances in the AHA class can be used safely with adsorption processes applied to clay.

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