Influence of Retanning on the Adsorption Capacity of Water on Cattlehide Collagen Fibers

by

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Abstract

There are plenty of hydrophilic groups in the collagen fibers in leathers. Because the affinity between these hydrophilic groups and water molecules varies with environmental changes in temperature and relative humidity, leathers will adsorb or de-adsorb water in the environment if the environmental factors change. The strength, permeability, and thermal stability of leathers may be greatly affected by the water within them. Retanning is a key operation in leather making. The main purpose of retanning is to get leathers with some special performances. The water content in leathers is around 20wt%, an amount that cannot be neglected. However, no reports are found on the interactions between collagen and water, particularly the influence of retanning on the interaction between water and collagen fibers. The state that water molecules exist in collagen fibers, the mechanism for collagen fibers to adsorb water, the de-adsorption kinetics for water molecules to escape from collagen fibers, and the influence of retanning on the adsorption of water on collagen fibers should be made clear to improve the leathermaking technology by controlling the structure and behaviors of leathers.

In the present paper, after being chrome tanned, collagen fibers were retanned with chrome, glutaraldehyde, TGR retanning agent (proprietary acrylic based), and wattle extract, respectively, to get different retanned samples. The water adsorption isotherms of the samples were obtained by the use of the gravimetric method, by which the influence of retanning on the equilibrium water adsorption capacity and the influencing mechanism were discussed. On the base of adsorption characterization and equilibrium adsorption capacity for the samples to adsorb water, different mathematics models were used to describe the adsorption process and the adsorption mechanism. Six models were chosen to fit the experimental data, and it was found that the Bradley model is the best to describe the adsorption.

Resumen

Hay una abundancia de grupos hidrofílicos presentes en las fibras colagénicas en los cueros. Cómo la afinidad entre estos grupos hidrofílicos y moléculas de agua varía con cambios en temperatura y humedad relativa, cueros adsorberán o des-adsorberán agua a medida que estos factores cambien; afectando resistencia, permeabilidad, y la estabilidad térmica. El recurtido es una operación clave en la curtición pues el recurtido tiene por objeto obtener cueros con algunas características especiales. El contenido de humedad en cueros, a menudo de 15-20 % por peso, es una cantidad que no se puede despreciar. Sin embargo, pocos informes se encuentran acerca de las interacciones entre el colágeno y el agua, específicamente de cómo el recurtido influye sobre la interacción entre el agua y las fibras colagénicas. El estado en que las moléculas de agua existen dentro de las fibras del colágeno, así como el mecanismo que rige para que las fibras colagénicas adsorban el agua, la cinética de la des-adsorción para que moléculas de agua escapen de las fibras de colágeno, y la influencia del recurtido sobre la adsorción del agua sobre las fibras del colágeno, necesita ser estudiada para mejorar la tecnología en la fabricación del cuero para controlar la estructura y los comportamientos del cuero.

En este estudio, luego de la curtición al cromo, fibras colagénicas fueron recurtidas con cromo, glutaraldehído, agente recurtiente TGR (producto comercial acrílico), extracto de mimosa, respectivamente para obtener muestras recurtidas. Las curvas isotérmicas de adsorción de humedad fueron obtenidas por un método gravimétrico, por lo cual la influencia de recurtición sobre la capacidad de adsorción bajo condiciones de equilibrio y el mecanismo que influye, fueron evaluados. Muestras con diferentes recurtidos variaron en sus cararacterísticas de adsorción de humedad y capacidad de adsorción bajo equilibrio. El recurtido por TGR aumentó la capacidad de adsorción bajo equilibrio, mientras que el recurtido por glutaraldehído la disminuyó; posiblemente debido a diferencias en los mecanismos de recurtición. Para diferentes ambientes en humedad relativa, los cueros deben

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recurtirse con diferentes agentes recurtientes para así obtener la propiedad óptima. Basados en las diferentes caracterizaciónes de adsorción y la capacidad de adsorción bajo equilibrio para las muestras, diferentes modelos matemáticos fueron empleados para describir el proceso de adsorción así como el mecanismo de adsorción. Seis modelos fueron seleccionados para acoplarse a los datos experimentales, y se encontró que el modelo de Bradley fue el superior en la descripción de la adsorción.

INTRODUCTION

Collagen is an abundant natural biopolymer. It is widely used in food, medicine, and cosmetic industries due to its unique structure, biochemistry, and biological character. There are many such hydrophilic groups as carboxylic, hydroxyl, amino, imino, and amide in protein; including collagen materials. With the changing in relative humidity of the environment, water molecules may be adsorbed from the environment or de-adsorbed (released) to the environment by the hydrophilic groups in collagen. Leather is composed of tanned collagen fibers. Therefore, for a same leather sample, different amounts of water should be contained in different environments, and the structure and behaviors of the leather sample should be different as a result. Water molecules play an important role in leather materials (modified natural polymers), and the study on the interaction between collagen fibers and water molecules is of great importance.

Water molecules in collagen fibers are important in the stabilization of the structure and the function of the materials. It may greatly affect the strength,[1-2] permeability,[3] and thermal stability[4-6] of collagen-based materials. In the preservation of raw skins or hides, the water content should be kept at a limited level to prevent them from being destroyed by bacterium. The drying process of crust leathers is a determining factor affecting the structure and behaviors of leather.[1,5] When crust leathers are being skated or set out, the water content should also be kept at a proper level. High water content will result in a bad organoleptic feeling, whilst poor tensile strength and tear resistance of leathers may mainly result from low water content. The relative humidity of the environment should also be taken into consideration when leathers or leather goods are preserved and used. Therefore, the study on the interaction between water and collagen fibers is of great importance both in theory and in application.

Regarding the interaction between water molecules and collagen fibers, however, few studies are reported. There are many problems that should be made clear in order to make full use of the water molecules in skins, hides, and leathers. For example, the procedure for collagen fibers to adsorb water molecules, the de-adsorption mechanism for water to escape from collagen fibers, and the interaction between water molecules and collagen fibers should be studied in detail.

By studying the adsorption behavior and adsorption kinetics of water molecules on collagen fibers, such adsorption information as adsorption characteristics, adsorption rates, the adsorption capacity at equilibrium, etc. may be made clear. It may help us know the controlling mechanism for collagen fibers to adsorb water, i.e. the diffusion, movement, and reaction of water molecules in collagen fibers. Furthermore, by properly choosing the mathematics model to describe the adsorption process and adsorption characteristics of water molecules on collagen fibers, one may effectively optimize the environmental conditions to process collagen materials with excellent behaviors.

Retanning, known as the "golden touching," is a very important process in leather making.[7] Basically, the overall style of the leather is determined by retanning.[7] With the same wet blues, different styles of leathers may be obtained with different retanning agents. The aim of retanning is to endow leathers with some exceptional properties to meet the needs for leathers with fullness, softness, hardness, and/or elasticity. The selective filling of some retanning favors the reduction of location differences. As to the study on the interaction between collagen fibers and water, especially the study on the influence of retanning on the interaction of collagen fibers and water, however, no reports were found.

In the present paper, after being chrome tanned, collagen fibers were retanned with chrome, glutaraldehyde, TGR retanning agent, and wattle extract, respectively, to get different retanned samples. The water adsorption isotherms of the samples were obtained by the use of the gravimetric method, by which the influence of retanning on the equilibrium water adsorption capacity and the influencing mechanism were discussed. On the base of adsorption characterization and equilibrium adsorption capacity for the samples to adsorb water, different mathematics models were used to describe the adsorption process and the adsorption mechanism. Six models were chosen to fit the experimental data, and it was found that the Bradley model is the best to describe the adsorption. The adsorption model may also be used to predict the experimental results.

EXPERIMENTAL

Main materials and apparatus

Cattlehide collagen fibers were kindly provided by Sichuan University, China. Chrome tanning liquor reduced by glucose with the basicity of 33% was prepared in our laboratory. Sulfuric acid, analytically pure, was from the Luoyang Haohua Chemical Reagent Plant, China.

Four retanning agents were applied in the present work. The retanning agents were: 1) a chrome retanning liquor, reduced by glucose, with the basicity of 38%, prepared in our laboratory; 2) glutaraldehyde (GTA), analytically pure at a 25 vol% solution, produced by the Shanghai Chemical Reagents Co., China; 3) TGR, a commercial acrylic retanning agent, supplied by the Together For Leather Company, Switzerland; and 4) the mimosa extract retanning agent, a commercial product, provided by the Henan Research Institute of Leather and Plastic, China.

The water bath constant temperature oscillator, THZ-82, was made by the Fuhua Instrument Plant in Jiangsu province, China. The analytical balance, TG328A, was from the Shanghai Balance Co. Ltd., China. The electric heated constant temperature drying oven, 101-1, was from the Hutong Electric Heating Plant in Shanghai, China.

PROCEDURES

Preparation of chrome-tanned samples

The tanning solution was prepared by mixing 48 g of sodium chloride, 600 mL of distilled water, and the concentration of chrome retanning liquor was 10 g/L (calculated as Cr_2O_3). Five grams of cattlehide collagen fibers were added to the solution. At room temperature and over a period of one month, the pH of the mixture was adjusted to 4.0 with 0.01 mol/L of sodium hydroxide. The mixture was filtered, and the filtered cake (chrome tanned collagen fibers) was washed repeatedly with distilled water until no precipitate appeared when a solution of 0.05 g/L $AgNO_3$ was dropped into the filtrate. The filtered sample was put in a desiccator with silica gel in it for more than two weeks to a constant weight.

Preparation of samples retanned with different retanning agents

The retanning process with chrome and GTA were as follows. 0.5 g of chrome-tanned cattlehide collagen fibers were placed in a wide-mouth bottle that contained retanning agent (GTA or chrome retanning liquor reduced by glucose, 5% of the chrome tanned collagen fibers in weight for the former and 1% of the collagen in weight for the latter calculated as Cr_2O_3) and 20 mL of distilled water. The mixture was shaken in the THZ-82 water bath constant temperature oscillator at 40°C for 90 minutes. The pH of the mixture was then adjusted with 0.01 M sodium hydroxide to 4.0 (chrome retanning) or 8.5 (GTA retanning), respectively. The samples were filtered and washed repeatedly with distilled water. The retanned collagen fiber was then put in a desiccator with silica gel in it for more than two weeks to constant weight.[8]

The retanning processes with TGR and the mimosa extract were as follows. Four milligram of ammonium bicarbonate and 2.5 mg of sodium acetate were dissolved in 20 mL of distilled water. Added into the solution was 0.5 g of chrome tanned collagen fibers. The pH of the solution was adjusted to 5.0-5.5. The collagen fibers were filtered and washed with distilled water. Then the collagen fibers were added to 20 mL of distilled water with retanning agent (5% of the sample in weight). The mixture was shaken at 40°C for 90 minutes in the THZ-82 water bath constant temperature oscillator. Formic acid was added to the mixture to adjust the pH of the solution to 4.0. The solution was shaken for another 20 minutes. The collagen fibers were filtered and washed repeatedly with distilled water. The retanned collagen fiber was then put in a desiccator for more than two weeks to constant weight.

Water adsorption behaviors

After being dried at room temperature, the samples were dried in an electric heated constant temperature drying oven at 104°C±2°C to constant weight. Then, the samples were exactly weighed, noted as W_0, and were air-conditioned in different environments with different relative humidity. The weight of the samples at the adsorption time of t was noted as *Wt* and the weight when equilibrium was reached was noted as *We*. The temperature when being air-conditioned was 20°C±2°C. The relative humidity of the environment was 20%, 40%, 65%, 80%, and 90%, controlled with sulfuric acid solutions of different concentrations.[9] The amount of water adsorbed by collagen fibers at the experiment time of *t* was calculated as

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

And the amount of water absorbed by collagen fibers at equilibrium (water adsorption capacity, *Me*) was calculated as

$$M_e = \frac{W_e - W_0}{W_0} \times 100 \quad (2)$$

Data processing

In order to determine the interaction mechanism between collagen fibers and water molecules in the adsorption process and to predict the equilibrium water content of the samples, the first-order and the second-order adsorption kinetics models were applied to fit the experiment data. The first-order model, also known as Lagergren first-order equation, was firstly proposed by Lagergren in 1898. It is one of the

first equations of adsorption velocity based on the adsorption content. The adsorption was considered to be driven by the adsorption gradient. The first-order equation can be expressed as follows.[10,11]

$$M_t = M_e + (M_0 - M_e)e^{-k_1 t} \quad (3)$$

where k_1 is the first-order velocity constant (h^{-1}).

The second-order model is usually used to describe the chemical adsorption, in which some covalent bonds participate. The valence linkage force between the adsorbent and the adsorbate is formed by the sharing or exchanging of their electrons. The advantage of this model is that *M*e can be derived not by the experiment data but by the equation. [24-25] The initial equation is as follow:

$$\frac{1}{M_e - M_t} = k_2 t + \frac{1}{M_e} \quad (4)$$

The linear equation is that

$$\frac{t}{M_t} = \frac{1}{k_2 M_e^{\,2}} + \frac{1}{M_e} t \quad (5)$$

in which k_2 is second-order velocity constant (h^{-1}). The fitting software is Origin 75 in this paper.

RESULTS AND DISCUSSIONS

Water adsorption isotherms

Leathers are inevitably used in conditions with a variable temperature and relative humidity. Consequently, water molecules will be adsorbed by leathers or escape from leathers when the relative humidity of the environment changes. So it is of great significance to study the water adsorption/desorption behavior of collagen fibers and to determine the isotherm type of collagen fibers at different conditions. The water adsorption of the samples retanned with chrome retanning liquor, GTA, TGR, and the mimosa extract and the samples without a retanning history are shown in Figure 1. In Figure 1, the samples were dried for 6 hours in the oven at 105 °C before adsorbing water. Figure 1 indicates that all the adsorption isotherms show the anti-S shape [12]. The water adsorption isotherms of the samples are type II. Little difference was found in the isotherms of the samples retanned by different retanning agents. By retanning, the monomolecular layer adsorption stage in the anti-S trend became weaker and weaker. A possible explanation is that the previous chrome tanning had fully opened up and fixed the collagen fibers. Retanning is only an assistant tanning, and no further opening up or fixing the collagen fibers was done by retanning. By retanning, leathers may be provided with some excellent organoleptic feeling, such as softness, fullness, smoothness and so on. The cross-linking effect of the retanning is less than that of the chrome tanning. The influence of retanning on the equilibrium water content is also less than that of tanning.

From Figure 1, we know that at the same temperature, the equilibrium water contents (water adsorption capacity, *Me*) of the samples increase with the increase of relative humidity (RH). At a low relative humidity (RH), *Me* is relatively low. When the RH is under 20%, the relevant *Me* is between 0 and 14g/100g. In this range, a slight increase in RH will move the isotherms upward remarkably. According to the BET adsorption theory, monomolecular layer adsorption is the main reaction. Water molecules are strongly bonded by the polar groups on collagen fibers, and the main adsorption mechanism is chemical adsorption. Figure 1 also tells us that retanning slightly affects the *Me* of the samples. The difference in adsorption isotherms of different retanned collagen fibers is little. The anti-S-shaped trend in the monomolecular adsorption stage becomes unclear by the retanning.

With the increase of RH, the isotherms move up slightly and then become flat, indicating the completion of the first layer adsorption. Some water molecules are adsorbed on the first adsorption layer by the Van der Waals force or hydrogen bonds between free water molecules and the water molecules bonded on collagen fibers.[13] Compared with covalent bonds, the adsorption is weaker. The equilibrium water content of samples at this stage depends mainly on the water vapor pressure, the property of the samples, and the temperature when the experiment is conducted. At this stage, the hydrogen bonds act as bridges between the water molecules and the first adsorption layer. This kind of adsorbed water may participate in bio-chemical reactions, and the force between water molecules and the first adsorption layer waters is relatively weaker in comparison to that of the first adsorption layer.

When the RH reaches 65% or more, the *M*e increases remarkably and the adsorption curves upward sharply. A possible explanation is that the increase of capillary function leads to more space for water.[14] At this stage, swelling, solvating, dispersing, and even dissolving may happen for different adsorbents. Slight effect on the *M*e of collagen fibers by retanning was found from Figure 1. Little difference was found in the isotherms of the samples retanned by different retanning agents. The monomolecular layer adsorption stage in the anti-S-shaped trend became weaker and weaker. Previous chrome tanning had fully opened the

collagen fiber bundle and stabilized the collagen fibers. Compared to the effect of chrome tanning, the effect of chrome retanning on the structure and behaviors of collagen fibers is less. The filling up effect of chrome retanning should be considered. So further retanning by chromium will decrease the space for adsorbing water, resulting in a decrease in water adsorption capacity, *M*e. With regard to the TGR retanned sample, the water adsorption capacity, *M*e, was increased by retanning. TGR is an acrylic retanning agent with many hydrophilic groups. Hydrogen bonds may be formed between water molecules and between collagen chains and water molecules, resulting in an increase of *M*e.

On the other hand, the water adsorption capacity (*M*e) is lowered by glutaraldehyde retanning. There are many such groups as amino, imino, sulfhydryl, and hydroxyl on collagen fibers that may react with GTA to form complicated insoluble products.[15] The amount of hydrophilic groups on collagen fibers is decreased and the water adsorption capacity (*M*e) is decreased as a result. Little decrease was found in the sample retanned with the mimosa extract. Although the mimosa extract had been modified, there were still few hydrophilic groups in it. The main hydrophilic group, phenol hydroxyl, can easily react with the chromium complexes existing in chrome tanned samples.[16] And the molecular weight of the mimosa extract is high. The mimosa extract may fill up the spare space to reduce the water adsorption capacity (*Me*).

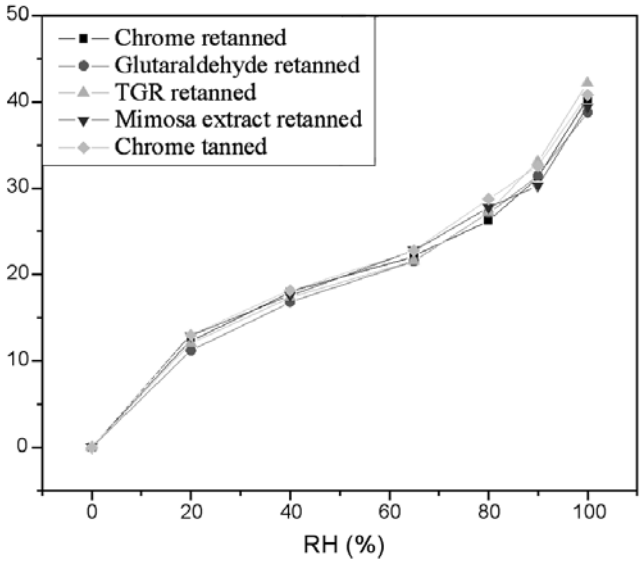

Figure 1. – Adsorption isotherms of different retanned collagen fibers.

Comparison and selection of adsorption models

There are many models to describe the water adsorption isotherms of solid materials.[17] The kinetics model of BET is based on the monomolecular layer adsorption, and the kinetics model of GAB is based on the multi-molecular-layer adsorption. The semi-empirical models of Henderson and Halsey and the empirical models of Smith and Oswin may be used to study the water adsorption isotherms of solid materials.[18] In order to find out an appropriate model to describe the adsorption isotherms of different retanned cattlehide collagen fibers, six isotherms models were employed. All the models have been successfully used in the study of the water adsorption isotherms of natural materials before. The models are listed in Table 1. In Table 1, a_w is the water activity and a_w=RH/100. The software 1stOpt1.5Pro was applied to do the non-linear regression of the isotherms curves in Figure 1. The non-linear regression results are shown in Table 2. In order to evaluate the suitability of the regression of the models, the Root Mean Square Error (RMSE), Determinants of Coefficient (DC), and correlation coefficient square (r^2) were chosen to evaluate these models. The equations to determine the RMSE, DC, and r^2 are shown as [19, 20]

$$RMSE = \sqrt{\frac{\sum (M_{e,i} - M_{e,i}^{\mathbf{II}})^2}{n}} \quad (6)$$

$$DC = 1 - \frac{\sum (M_{e,i} - M_{e,i}^{\mathbf{II}})^2}{\sum M_{e,i}^2} \quad (7)$$

$$r^2 = 1 - \frac{\sum (M_{e,i} - M_{e,i}^{\mathbf{II}})^2}{\sum (M_{e,i} - \overline{M}_{e,i})^2} \quad (8)$$

Where M_e is the experiment value, M^{II}_e is the theoretic value and $\overline{M}_e$ is the average value.

The BET model is a classical model to describe Type II adsorption isotherms. The suitable water activity range is very low, 0.1-0.4. It fits the solid materials with a uniform surface in chemical properties. [21] If a_w is less than 0.1, both the physical and chemical properties of the surface are usually not uniform. An active adsorption will exist, resulting in the unsuitability of the BET model. When a_w is more than 0.4, the adsorption data of the BET model will not correlate with the experimental data due to the assumption of infinite adsorption layers. In practice, the number of adsorption layers cannot be infinite for a porous solid at high pressure.

The GAB model, proposed by Guggenheim, Anderson, and De Boer, is a three constant model. [22] It is based on the BET multi-molecular layer theory and isothermal formula. It has found a wide application field. In the present study, RMSE is below 1.0 and both the DC and the r^2 are more than 0.99. Thus, the model of GAB is fairly good for the study. Chirife, et al [23] reported that the K of the GAB model is located in the

TABLE I

Models used in the paper

Models	Equations	Constants
BET	$\frac{M_e}{M_m} = \frac{Ca_w}{(1-a_w)[1+(C-1)a_w]}$	Mm: monolayer water content; C: Constant related to the net heat of sorption
GAB	$\frac{M_e}{M_m} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_W)}$	Mm: monolayer water content; K: constant; C: Guggenheim constant; C and K are related to temperature
Halsey	$M_e = (-\frac{D}{\ln a_w})^{1/E}$	E: parameter that characterizes the type of interaction between vapor and solid; D: constant
Oswin	$M_e = a[\frac{a_w}{(1-a_w)}]^n$	a, n: constant
Caurie	$M_e = \exp(a+ba_w)$	a, b: constant
Bradley	$\ln[\frac{1}{a_w}] = K_1K_2^{Me}$	K_1: function of the dipole moment of the absorbed vapor; K_2: function of sorptive polar groups

range of 0.56~1.0 for many materials. The result in this paper is also located in the range. It is 0.6638~0.7364. The model of Halsey is usually used in the study on the water adsorption of meat, milk, and vegetables. [24] In this study, both the DC and r^2 are more than 0.9850. The RMSE is more than 0.9029. It is a good model for the study; however, it is not the best one.

The Oswin model fits the study of water adsorption of protein and starchy foods. In the study, both the DC and r^2 are more than 0.9900. The RMSE is more than 0.2339. It is also a good model for the study, but it is not the best one. The formula and the parameters in model Caurie are good with an r^2 of more than 0.9326 and a DC of more than 0.9316. As a mathematics formula, the results of the model are reasonable. However, neither the formula nor the parameters have any experimental meaning, and the fitting result is not the best with an RMSE of more than 2.736.

The Bradley model has found a wide application in the study on water adsorption of protein. It can fit the data well in the whole range of water activity. [25] In the present study, the RMSE is less than 0.06 and the r^2 is more than 0.9999. All the parameters in the formula have their experimental meanings. K_1 is related to the dipole of adsorbate, here, water. K_2 is a function of the absorbable polar groups in the adsorbent, here, different retanned collagen fibers. They all depend on the temperature when the adsorption is studied. Little changes were found in K_1 and K_2. K_1 fell in 6.689~9.026, and K_2 was found between 0.8669 and 0.8763.

All in all, according to the three standards and the meanings of the parameters in the models, the Bradley model is the best of the six models. The parameters in the Bradley model fit the experimental data well, and the variations of parameters are small. It is very applicable for the study of water adsorption of different retanned collagen fibers. The next best model is the GAB model. As a modified BET model, the GAB model's parameters have some physical meanings and such water adsorption data as monolayer water content, *Mm*, may be obtained. Thus, the GAB model may be used as an assistant tool in the study of water adsorption of different retanned collagen fibers.

CONCLUSIONS

The water adsorption isotherms of the retanned collagen fibers are type II, anti S-shaped. There are three stages in the isotherms: when RH=0~20%, the *M*e is between 0 and 14g/100g, in which monomolecular layer adsorption is the main reaction; when the RH=20%~65%, the force, hydrogen bond, between the water molecules and the collagen fibers is weaker; and when the RH is more than 65%, the collagen fibers will adsorb water quickly. The influence of different retanning agents on the water adsorption of samples is different because of different retanning mechanisms. The Bradley model best fits the study of water adsorption of collagen fibers out of the six models.

TABLE II

Results from fitting of the experimental adsorption curves of different models

Models	Parameters	Chrome retanned	Glutaraldehyde retanned	TGR retanned	Mimosa extract retanned	Chrome tanned
BET	M_m	3.691	3.658	3.891	3.672	3.884
	C	-6.1990	-6.427	-6.365	-6.109	-6.195
	r^2	0.7425	0.7485	0.7924	0.7133	0.7464
	RMSE	6.439	6.2924	6.1105	6.7364	6.6970
	DC	0.5672	0.8375	0.6605	0.5245	0.5815
GAB	M_m	10.89	11.47	11.12	11.39	11.93
	C	167.01	29.66	73.12	88.01	62.42
	K	0.7253	0.7045	0.7364	0.7068	0.7064
	r^2	0.9951	0.9984	0.9992	0.9960	0.9984
	RMSE	0.8416	0.4779	0.3754	0.7520	0.4920
	DC	0.9951	0.9984	0.9992	0.9960	0.9984
Halsey	D	6948	3285	2641	1.002×10^4	6380
	E	3.2320	3.011	2.891	3.345	3.157
	r^2	0.9915	0.9864	0.9956	0.9864	0.9906
	RMSE	0.9029	1.154	0.6921	1.139	1.003
	DC	0.9915	0.9863	0.9956	0.9864	0.9906
Oswin	a	17.68	16.98	17.73	17.90	18.42
	n	0.2494	0.2695	0.2796	0.2418	0.2560
	r^2	0.9975	0.9952	0.9995	0.9945	0.9968
	RMSE	0.4878	0.6834	0.2339	0.7238	0.5850
	DC	0.9975	0.9952	0.9995	0.9945	0.9968
Caurie	a	1.817	1.772	1.777	1.856	1.878
	b	1.838	1.865	1.937	1.786	1.809
	r^2	0.9326	0.9480	0.9493	0.9327	0.9396
	RMSE	3.148	2.736	2.914	3.096	3.073
	DC	0.9319	0.9469	0.9487	0.9316	0.9385
Bradley	K_1	7.965	6.689	8.085	9.026	8.778
	K_2	0.8729	0.8763	0.8720	0.8669	0.8720
	r^2	0.9999	0.9999	0.9999	0.9999	0.9999
	RMSE	0.0462	0.0270	0.0189	0.0219	0.0250
	DC	0.9999	0.9999	0.9999	0.9999	0.9999

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