Study on the Adsorption Kinetics of Water Vapor on Collagen Fibers[#]

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Abstract: The adsorption behaviors and adsorption kinetics of water on collagen fibers was investigated. It is shown that water uptaking on collagen fiber is rapid in the first 6 hours, followed by a slower rate until equilibrium is reached. The water adsorption on collagen fibers at equilibrium (water adsorption capacity, *Me*) increases with increasing the relative humidity of the environment. The more the relative humidity of the environment is, the longer the time is needed to reach equilibrium. Both the Lagergren first-order adsorption kinetics model and the second-order adsorption kinetics model were employed to analyze the experimental data, while the second-order adsorption kinetics model presented a better correlation to the experimental data, suggesting that there are chemical bonds in the adsorption. Intra-particle diffusion plots showed multi-linearity with three distinct stages: initial curved portion, followed by intermediate linear portion and then, a plateau. It was proposed that the water adsorption process in the intermediate linear part should be controlled by intra-particle diffusion. The linear plots, not passing through the origin, indicated that the intra-particle diffusion was not the only one factor controlling the water adsorption rate.

Key words： collagen fibers; adsorption; water; kinetics

Introduction

Collagen is widely used in food, medicine and cosmetic industries for its unique structure, biochemistry and biological character. There are plenty of such hydrophilic groups as carboxylic, hydroxylic, amino, imino, and amido in protein, including collagen materials.

Water molecule in collagen fibers plays an important role in the stabilization of their structure and the function of the materials. It may greatly affect the strength [1-2], permeability [3], and thermal stability [4-7] of collagen-based materials. In the preserve of raw skins or hides, the water content should be kept in 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 behaviours of leather. When crust leathers are being skated or set out, the water content should also be controlled at a proper level. Therefore, study on the interaction between water and collagen fibers is of great importance both in theory and in application.

There are a lot of problems that should be made clear, in order to make full use of 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, the interaction between water molecules and collagen fibers should be studied in detail.

The kinetics curves for collagen to adsorb water molecules were obtained in the paper, and the experimental data were analyzed by both Lagergren first-order adsorption kinetics model and second-order adsorption kinetics model, respectively. It was shown that the second-order adsorption kinetic model presented a better correlation to the experimental data, suggesting the existence of chemical bonds

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in the adsorption. Intra-particle diffusion plots showed multi-linearity with three distinct stages: initial curved portion, followed by intermediate linear portion and then, a plateau. It was proposed that the water adsorption process in the intermediate linear part should be controlled by intra-particle diffusion. The linear plots, not passing through the origin, indicated that the intra-particle diffusion was not the only one factor controlling the water adsorption rate.

2 Experimental

2.1 Main materials and apparatus

Cattlehide collagen fibers, sulfuric acid. Analytical balance, TG328A. Electric heated constant temperature drying oven.

2.2 Procedures

After being dried at room temperature [8], cattlehide collagen fibers were dried at 104 ^{o}C$\pm$2 ^{o}C to constant weights. 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 ^{o}C ±2 ^{o}C. The relative humidity of the environment was controlled with different concentration of sulfuric acid solutions [9].

The amount of water adsorbed by collagen fibers at the experiment time of t was calculated as

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

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

$$M_e = \frac{W_e - W_0}{W_0} \times 100 \tag{2}$$

2.3 Data processing

Lagergren first-order adsorption kinetics model is the first model to describe adsorption behavior. It was considered that adsorption rate was based on adsorption amount, and the difference in adsorption amount was the driving force of adsorption. Lagergren first-order adsorption kinetics model may be described as [10]

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

Where k_1 is the adsorption rate constant of the first-order adsorption kinetics model (h^{-1}).

Second-order adsorption kinetics model is usually used to describe the adsorption including chemical reaction, i.e., with the participation of covalent bonds. An advantage of the model is that the adsorption amount at equilibrium, Me, may be calculated by its equation [10-11]. The equation is as follows [10]:

$$\frac{t}{M_t} = \frac{1}{k_2 M_e^{\ 2}} + \frac{1}{M_e} t \tag{4}$$

Where k_2 is the adsorption rate constant of second-order adsorption kinetics model (h^{-1}).

3 Results and discussion

3.1 Time needed to reach equilibrium for collagen fibers to adsorb water

With adsorption time for collagen fibers to adsorb water as X axis, and the amount of water adsorbed on

collagen fibers (*Mt*) as Y axis, Fig. 1 was obtained.

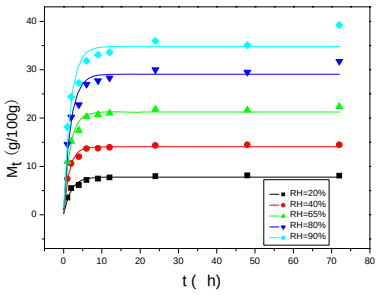

Fig. 1 Water adsorption Vs time at different relative humidity

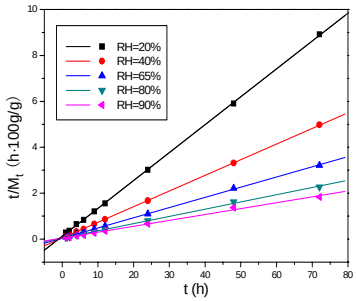

Fig. 2 Second-order kinetic model for water vapor adsorption on collagen fibers

Fig. 1 indicated that, for collagen fibers to adsorb water, a long time is needed to reach equilibrium. With increasing the relative humidity, the amount of water adsorbed on collagen fibers at equilibrium (water adsorption capacity, *Me*) increases. The adsorption may be approximately divided into three such stages as initial adsorption stage, gradually slowing adsorption stage and adsorption equilibrium stage. The amount of water adsorbed in collagen fibers, *Mt*, rapidly increases with increasing the adsorption time in the initial adsorption stage. And then, in the gradually slowing adsorption stage, the *Mt* increasing rate turns slowly gradually. After 9 hours of adsorption, equilibrium is reached. In the initial adsorption stage, the water vapor pressure in the surface of collagen fibers is less than that in the environment. The collagen fibers will adsorb water molecules from the environment rapidly, and the *Mt* will increase rapidly as a result. With the progress of water adsorption experiment, the water vapor pressure in the surface of collagen fibers tends to equal to that in the environment gradually. The adsorption rate for collagen to adsorb water molecules will be slowed down to reach a dynamic equilibrium.

3.2 Kinetics analysis for collagen fibers to adsorb water

The experimental data (see Fig. 1) was fitted according to equation (3) and equation (4), respectively, and the kinetics parameters were obtained as shown in Tab. 1. From Tab. 1, we can find that the correlation coefficient is 0.9572-0.9897 by the first-order adsorption kinetics model, whilst that is more than 0.9961 by the second-order adsorption kinetics model. Fig. 2 shows the fitting results by the second-order adsorption kinetics model (Equation (4)). Obviously, there is a better correlation between the data calculated by the second-order adsorption kinetics model and the experimental data. The theoretical equilibrium adsorption capacity, *Me*, is almost the same as the experimental value, with the maximum deviation of only 1.933% (Tab. 1). The maximum deviation of *Me* for the first-order adsorption kinetics model, however, may reach 11.26%.

The second-order adsorption kinetics model is usually used to describe the adsorption including chemical reaction [13]. It can be said that chemical adsorption does exist in the process for collagen fibers to adsorb water molecules. Water molecule is a polar molecule. There are many such polar groups as carboxylic, hydroxylic, amino, imino, and amido in collagen fiber, a kind of protein. We say that the chemical reaction in the adsorption between water and collagen fibers should be the hydrogen bonds between them. Hydrogen bonds are located between physical action and chemical reaction.

Tab. 1 Parameters of the models for water vapor adsorption on collagen fibers

Experimental		Lagergren first-order model			Second-order model		
RH%	M_e	M_e	r_1^2	k_1	M_e	r_2^2	k_2
20	8.070	7.784(-3.544%)	0.9818	0.5179	8.226(+1.933%)	0.9999	0.1206
40	14.47	14.05(-2.903%)	0.9897	0.6719	14.64(+1.175%)	0.9999	0.1009
65	22.38	21.26(-5.004%)	0.9832	0.5966	22.52(+0.6256%)	0.9997	0.04675
80	31.73	29.09(-8.320%)	0.9701	0.5299	31.72(-0.03152%)	0.9985	0.02242
90	39.25	34.83(-11.26%)	0.9572	0.5397	38.88(-0.9426%)	0.9961	0.01516

(Note: The data in the parentheses represent the percentage of the relative difference between the theoretical *Me* and experimental *Me*)

Collagen-based materials, for example, leathers, are usually porous materials. The adsorption process for porous absorbent is rather complex. In isothermal condition, there are three elementary stages in the adsorption process [14]: Process (a) is the diffusion of the adsorbate, water molecules here, in the fluid film; Process (b) includes the diffusion of adsorbate in the capillaries and on the surface of the adsorbent, collagen fibers here. The diffusion in the capillaries is the movement of adsorbate, water molecules, in the capillaries of the adsorbent (collagen fiber) in gas state, whilst the diffusion on the surface is the movement of the adsorbate, water molecules, from one site to another, not leaving the adsorbent. In the latter case, the adsorbate keeps in the same state, i. e., liquid state. Process (c) is the adsorption of water molecules on the corresponding sites of the adsorbent. The whole adsorption rate should be determined by the corresponding rates of the three elementary processes.

Intra-particle diffusion model is a popular way to study the mechanism of adsorption process. The intra-particle diffusion constant, kid, may be obtained with the following equation [15]:

$$M_t = k_{id} t^{0.5} \tag{5}$$

Regarding the model of intra-particle diffusion, Ho [16] found that there should be a linear relation between *Mt* and $t_{0.5}$, if the diffusion of adsorbate among particles is the only one factor determining the adsorption rate. The linear should pass through the origin of the coordinate, and the slope of the linear should be the intra-particle diffusion rate [17]. In the present work, the relation between the water adsorbed in the collagen fibers at the adsorption time of *t (Mt)* and $t_{0.5}$ was plotted, and Fig. 3 were obtained.

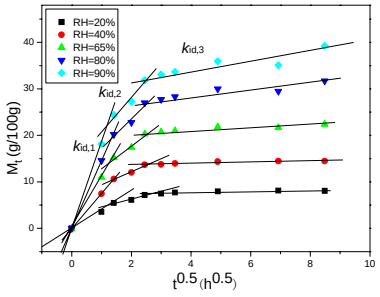

Fig. 1 Intra-particle diffusion plots for water vapor adsorption on collagen fibers

For all the samples at the environments with different relative humidity, the curves consist of three lines. Therefore, three relatively independent stages should be included in the process for collagen fibers to adsorb water molecules, and the relation among them is as:

$$(k_{id,1}) > (k_{id,2}) > (k_{id,3})$$

With increasing the relative humidity of the environment, the kid increases. The change in $k_{id,1}$, $k_{id,2}$ and $k_{id,3}$ may be resulted from the factors determining the adsorption rate. In the initial adsorption stage, the adsorption curves behave steep. The water adsorption process is mainly determined by the external membrane diffusion of water molecules on the sample surface. The second stage, a gradual adsorption stage, behaves a little gently. The water adsorption should be determined by the intra-particle diffusion of water molecules in collagen fibers. In this stage, the water adsorption rate may be affected by such factors as the size of capillaries in the samples, the affinity between water molecules and collagen fibers, etc. The platform in the last stage indicates that water adsorption equilibrium was reached. So, we may conclude that there is an intra-particle diffusion stage in the water adsorption process, and it is not the only one factor determining the water adsorption rate.

4 Conclusions

For collagen fibers to adsorb water molecules, equilibrium will be reached in about 9 hours in a low relative humidity environment. Longer time is needed to reach adsorption equilibrium in the environment with a higher relative humidity. Water adsorption at equilibrium increases with increasing the relative humidity of the environment. Chemical reaction does exist in the adsorption of water molecules in collagen fibers. There is an intra-particle diffusion stage in the water adsorption process, and it is not the only one factor determining the water adsorption rate.

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