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Adsorption and UV Protection Properties of the Extract from Honeysuckle onto Wool

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ABSTRACT: The adsorption and UV-protection properties of water-extract from honeysuckle whose main ingredient is chlorogenic acid onto wool were studied. The effect of initial pH on the adsorption was investigated, and the extent of adsorption was found to increase with decreasing pH in the range 2–7. Four kinetic equations, namely pseudo-first-order, pseudo-second-order, Elvoich, and intraparticle diffusion equations were employed to investigate the adsorption rates. The pseudo-second-order model provided the best fit to the experimental data and was indicated with the activation energy of 47.91 kJ mol⁻¹. The equilibrium adsorption data were fitted by Freundlich, Langmuir, Redlich—Peterson, and Langmuir—Nernst isotherm models. The adsorption behavior accorded with Redlich—Peterson and Langmuir—Nernst models well. The honeysuckle extract showed good build-up properties, and the UV transmittance in the range of UVA and UVB of wool treated with honeysuckle extract decreased obviously while the ultraviolet protection factors increased. The extract of honeysuckle may be developed as a natural UV-absorbing agent applied to wool finishing.

■ INTRODUCTION

In recent years, there has been growing interest in the dyeing of textiles with natural dyes, on account of their high compatibility with the environment, and because of their lower toxicity and allergic reaction. A great deal of research is being undertaken all over the world on the application of natural dyes, including the adsorption isotherms and kinetics of natural dyes which help in understanding the mechanism of adsorption processes. Comparatively, little work has been done on achromatous extracts of natural products which also have the characteristics of the natural dyes previously mentioned.

Honeysuckle (Figure 1), the dried flower bud of Lonicera japonica Thunb, is widely used as a common Chinese traditional medicine to cure the common cold and fever. The main bioactive ingredient in honeysuckle is chlorogenic acid (Figure 2), which possesses antivirus, anticancer, and anti-inflammation activities. The dried flower bud of Lonicera japonic acid (Figure 2), which possesses antivirus, anticancer, and anti-inflammation activities.

The predominant use of honeysuckle is in the field of medicine, and chlorogenic acid rich in honeysuckle is used extensively as a food preservative and cosmetics antiaging agent. In particular, people pay considerable attention to honeysuckle and chlorogenic acid in order to apply in various fields. However, at the present no information concerning the application of honeysuckle and chlorogenic acid in the textile industry, for example, the use as a finishing agent, is reported in the literature. For this reason, in the present paper, the application of honeysuckle extract onto wool was investigated.

First, water-extract of honeysuckle was obtained because water is the medium in the dyeing and finishing process, and then the effect of the initial pH on the adsorption of honeysuckle extract onto wool was investigated. Subsequently, the kinetics and thermodynamics of the adsorption of honeysuckle extract onto wool were studied using kinetic equations and thermodynamic models to fit the adsorption data with the aim of understanding the adsorption process better, and the corresponding parameters

were given. Finally, the build-up properties of honeysuckle extract onto wool and the UV protection properties of treated wool fabrics were measured.

EXPERIMENTAL SECTION

Materials. The soured and bleached wool fabric (warp 156dtex×2, weft 156dtex×2; warp density 21 threads cm⁻¹, weft density 18 threads cm⁻¹; weight 125.0 g m⁻²) was purchased from the Shanghai Textile Industry Institute of Technical Supervision.

Dry honeysuckle grown in Shandong Province was purchased from Suzhou Tianling Chinese Herbal Pieces Co. Ltd., China.

Sodium hydroxide, phosphoric acid, boric acid, acetic acid, and sodium acetate were of analytical reagent grade.

Preparation of Water Extract. Dry honeysuckle (32 g) was extracted with water in a 90 °C bath of liquor ratio 25:1 for 60 min in an oscillating dyeing machine. The extract was filtered and then diluted with water to the constant volume of 1 L. The solution obtained was applied for the following experiments, and its concentration was defined as 32 g $\rm L^{-1}$ in order to make the measure of concentration easy to handle.

Adsorption Experiments. All adsorption experiments were carried out in partially sealed and conical flasks immersed in an oscillating dyeing machine at constant temperature. The liquor ratio was 50:1. At the end of adsorption, the fabrics were washed in tap water and then dried in the open air.

(a) Effect of pH on the Adsorption of Honeysuckle Extract onto Wool. The wool fabrics were treated with 5.12 g $\rm L^{-1}$ of honeysuckle extract at 90 °C for 180 min. The treatment

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Figure 1. Honeysuckle.

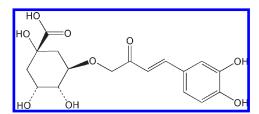


Figure 2. Chemical structure of chlorogenic acid.

solutions were adjusted to pH 2.09, 3.29, 4.10, 5.02, 6.09, and 7.00 by means of Britton-Robinson buffer solutions $(H_3PO_4-HAc-H_3BO_3/NaOH)$.

(b) Kinetic Adsorption. The wool fabrics were treated with 6.4 g L^{-1} of honeysuckle extract for different times at 65, 80, and 95 °C, respectively. The application pH (pH 3.6) was adjusted using HAc–NaAc buffer.

(c) Equilibrium Adsorption Isotherms. The wool fabrics were treated with $X ext{g L}^{-1}$ (X = 1.92, 3.84, 5.76, 7.68, 9.60, 12.80, 16.00, 19.2, 22.4, 25.60, 28.80) of honeysuckle extract at pH 3.6 using HAc—NaAc buffer for 300 min at 60, 70, 80, and 90 °C, respectively, in order to achieve equilibrium adsorption.

(d) Build-up Properties. The wool fabrics were treated with X g L^{-1} (X = 3.2, 6.4, 9.6, 12.8, 16.0) of honeysuckle extract, and the profile used was as follows: The experiments were started at 50 °C; after 5 min, the temperature was raised at a rate of 2 °C \min^{-1} up to 90 °C; at this temperature, the adsorption was continued for 60 min. HAc–NaAc buffer was used to achieve a pH of 3.6 during the process.

Measurements. The absorption spectra as well as the absorbance ($\lambda_{\text{max}} = 324 \text{ nm}$) of the honeysuckle solutions were measured using a Shimadzu UV-1800 UV/vis spectrophotometer. Using a previously established absorbance/concentration relationship at the λ_{max} of the solution, the quantity of honeysuckle extract in solution can be calculated, and the percentage of exhaustion (%E) was determined using eq 1, where m_0 and m_1 are the quantities of honeysuckle extract before and after adsorption (mg). The quantity of honeysuckle extract on

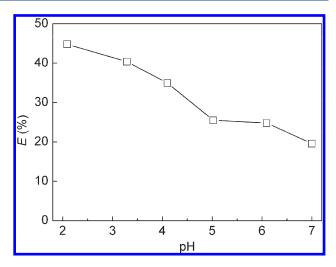


Figure 3. Effect of pH on the uptake of honeysuckle extract by wool at the initial honeysuckle extract concentration of $5.12~{\rm g\,L}^{-1}$ and $90~{\rm ^{\circ}C}$ for $180~{\rm min}$.

wool was calculated by taking into consideration the initial and final quantity of honeysuckle extract in solution and the weight of dried wool.

$$\%E = 100 \times \frac{m_0 - m_1}{m_0} \tag{1}$$

The Commission Internationale de l'Eclairage (CIE) L^* , a^* , and b^* color coordinates (lightness $[L^*]$, redness—greenness value $[a^*]$, and yellowness—blueness value $[b^*]$) of treated wool fabric were evaluated using a HunterLab UltraScan PRO reflectance spectrophotometer (illuminant D65; 10° standard observer). Each sample was folded twice so as to give a thickness of four layers. The ultraviolet protection factor (UPF) and the UV transmittance of treated wool fabric were determined in a Labsphere UV-1000F ultraviolet transmittance analyzer. Each sample was tested four times at different positions, and the average of the data was used.

An air-cooled XenoTest Alpha apparatus with xenon lamp was used to evaluate the light resistance of the wool fabric treated with 6.4 g L $^{-1}$ of honeysuckle extract. The sample was exposed for different periods (1, 2, 4, 6, 8, 10, 12, 14, 16, 18 h) according to AATCC test method TM16-2003. The desorption of honeysuckle extract from treated wool fabric in water was tested at 60 °C; the original wool sample was also treated with 6.4 g L $^{-1}$ of honeysuckle extract. The desorption rates at different times were calculated by the difference in the concentrations of honeysuckle extract on wool before and after desorption.

■ RESULTS AND DISCUSSION

pH Dependence of the Adsorption of Honeysuckle Extract onto Wool. Figure 3 clearly shows that the extent of adsorption of honeysuckle extract onto wool increased with decreasing application pH over the pH range 2.09—7.00. This may be mainly due to an increase in the protonation of the amino groups of amino acids in wool protein, which is beneficial to form ion—ion forces with ionized carboxyl groups in chlorogenic acid. The obviously decrease in the percentage of exhaustion in the pH range used indicates that the electrostatic interactions between the positively charged amino groups in wool and the anionic ionized carboxyl groups in chlorogenic acid play an important

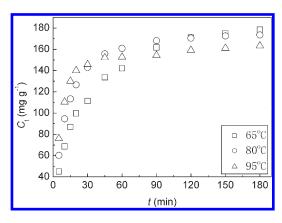


Figure 4. Adsorption kinetics of honeysuckle extract onto wool at different temperatures.

role in the adsorption of honeysuckle extract onto wool. The percentage of exhaustion at pH 7 dropped to 19.58, showing a lower extent. This implies weak nonelectrostatic interactions existing between honeysuckle extract and wool.

From the experimental results, the extract of honeysuckle can be applied under acidic conditions. Taking general processing conditions of wool fabric together, the pH value in all subsequent experiments was fixed at 3.6 and adjusted with HAc—NaAc buffer.

Adsorption Kinetics. The adsorption rate curves of the extract from honeysuckle onto wool at different temperatures are shown in Figure 4. It was found that the rate of adsorption of honeysuckle extract onto wool increased with increasing application temperature before reaching the equilibrium, which is possibly due to the higher kinetics energy of extract molecules and the higher extent of wool swelling at a higher temperature; furthermore, the amount of the adsorbed extract per gram of wool after reaching the equilibrium decreased with increasing application temperature, indicating that the adsorption process is a exothermic one. The phenomena are the result of a reduction in the affinity of honeysuckle extract to wool, which is accompanied by an elevated temperature.

A number of kinetic equations used to describe the adsorption kinetic curves were reported in literature. ^{17,18} In order to determine the mechanism of the adsorption process and potential rate-controlling steps such as chemical reaction, diffusion control, and mass transport, four kinetic models, namely pseudofirst-order, pseudo-second-order, Elovich, and intraparticle diffusion are used to analyze the experimental data.

If the adsorption rate follows a pseudo-first-order equation, the kinetic rate equation is expressed as 19

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = k(C_{\infty} - C_t) \tag{2}$$

where C_{∞} (mg g⁻¹) and C_t (mg g⁻¹) are the amount of adsorbed honeysuckle extract onto wool at equilibrium and at time t, respectively. The k (min⁻¹) is the adsorption rate constant of pseudo-first-order.

The pseudo-second-order model is usually expressed as follows:²⁰

$$\frac{t}{C_t} = \frac{1}{kC_{\infty}^2} + \frac{1}{C_{\infty}} t \tag{3}$$

where $k \text{ (g mg}^{-1} \text{ min}^{-1})$ is the equilibrium rate constant of pseudo-second-order adsorption.

Table 1. SD Values of Kinetic Models

temperature (°C)	65	80	95
pseudo-first-order equation	14.53	5.47	3.12
pseudo-second-order equation	2.10	1.97	2.24
Elovich equation	2.27	8.32	8.73
intraparticle diffusion equation	12.44	14.62	12.19

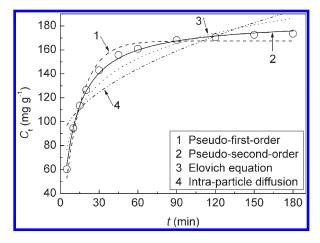


Figure 5. Different kinetic equation plots for the adsorption of honey-suckle extract onto wool at $80\,^{\circ}\text{C}$.

The Elovich equation is represented in the following:²¹

$$\frac{\mathrm{d}C_t}{\mathrm{d}t} = \alpha \exp(-\beta C_t) \tag{4}$$

where α (mol g⁻¹ min⁻¹) is the initial adsorption rate and β (g mol⁻¹) is the desorption constant related to the extent of surface coverage and activation energy for chemisorption.

The intraparticle diffusion is the rate-limiting step, and the adsorption capacity can be calculated by the following equation: 22

$$C_t = kt^{1/2} + C \tag{5}$$

where $k \text{ (mg g}^{-1} \text{ min}^{-1/2})$ and C are the internal diffusion coefficients.

The adsorption kinetic data shown in Figure 4 were investigated and fitted by the four kinetic models mentioned above using the nonlinear least-squares fitting procedure, and then, the standard deviation of the experimental values used to estimate the extent of fitting were calculated according to eq 6 and listed in Table 1.

$$SD = \left\{ \frac{1}{N} \sum_{i=1}^{N} \left[100 \times (C_{f, \exp, i} - C_{f, \text{calc}, i}) / C_{f, \text{calc}, i} \right]^{2} \right\}^{1/2}$$
(6)

where $C_{f,\exp,i}$ and $C_{f,\operatorname{calc},i}$ are the experimental and calculated values (the amount of adsorbed honeysuckle extract onto wool) in a sequence number of adsorption data, respectively; N means the total number of data sets.

By comparing the standard deviation values presented in Table 1, it is considered that the pseudo-second-order equation gave the best fit to the kinetic adsorption onto wool due to the

Table 2. Kinetic Data Obtained by the Pseudo-Second-Order Equation

temperature ($^{\circ}$ C)	$C_{\infty} (\text{mg g}^{-1})$	$k~(\mathrm{g~mg}^{-1}~\mathrm{min}^{-1})$	$t_{1/2}$ (min)
65	196.07	0.0003	19.62
80	185.13	0.0006	9.48
95	167.61	0.0012	5.06

lowest standard deviation at all temperatures. Figure 5 shows a comparison of the theoretical pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion equations with experimental data for 80 °C. The pseudo-second-order equation describes the adsorption of honeysuckle extract onto wool extremely well for all the adsorption process, whereas the pseudo-first-order, Elovich, and intraparticle diffusion equations do not give a good fit to the experimental data. This finding reflects that the adsorption of honeysuckle extract onto wool follows a pseudo-second-order equation. Similar observation was also found in the adsorption of chlorogenic acid from honeysuckle crude extracts by macroporous and polar HPD-850 resins, ²³ the dyeing of wool fiber with madder, ⁹ and the dyeing of silk and cotton fibers with lac. ^{3,12}

This suggests that the adsorption system studied belongs to the pseudo-second-order kinetic model, which is used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent force and ion exchange.²⁴ In other words, the rate limiting step of the adsorption of honeysuckle extract onto wool may be chemical adsorption.

The parameters in the pseudo-second-order equation obtained by curve-fitting are listed in Table 2. The C_{∞} values were 196.07, 185.13, and 167.61 mg g⁻¹ for 65, 80, and 95 °C, respectively, showing a decreasing trend with the increasing temperature. An increase in temperature gave rise to an increase in the pseudo-second-order rate constant k, this being attributed to the higher wool fiber swelling and the bigger size of wool fiber's void, together with the higher kinetic energy of the chlorogenic acid molecules that are accompanied by an increase in temperature. On the contrary, the half desorbing time $(t_{1/2})$ shorted with increasing temperature, and it was worth noting that the $t_{1/2}$ value at 65 °C was much bigger than those at 80 and 95 °C. The longer half desorbing time is caused by the fact that the epicuticle layer of wool exerts a resistance to the diffusion of chlorogenic acid into the interior of wool fibers.

The apparent activation energy of the adsorption of honeysuckle extract onto wool can be estimated by the Arrhenius equation²⁵ using the rate constant k of pseudo-second-order adsorption at the temperatures listed in Table 2.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

where E_a (kJ mol⁻¹), A, R, and T (K) refer to the Arrhenius activation energy, the Arrhenius factor, the gas constant, and the absolute temperature, respectively.

The activation energy $E_{\rm a}$ can be determined from the slope of the linear plot of $\ln k$ versus 1/T. The calculated value of the activation energy was $47.91~{\rm kJ~mol}^{-1}$. Usually the activation energy of physical adsorption is $5-40~{\rm kJ~mol}^{-1}$ while that of chemical adsorption is $40-800~{\rm kJ~mol}^{-1}$, so the adsorption of honeysuckle extract onto wool might be chemical adsorption,

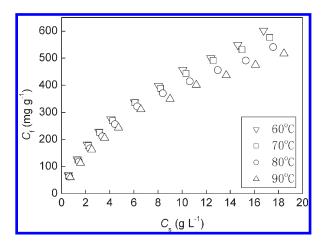


Figure 6. Adsorption isotherms of honeysuckle extracts onto wool.

which offers the evidence in support of the fact that the pseudosecond-order equation gave the best fit to the adsorption data.

Adsorption Isotherms. The adsorption isotherm of honey-suckle extract onto wool was obtained. As shown in Figure 6, increasing temperature was accompanied by a decrease in the equilibrium adsorption capacity, implying an exothermic adsorption process. This is to say, raising the temperature disfavors the adsorption of honeysuckle extract onto wool.

The adsorption isotherm describes the interaction between solutes and adsorbents and features largely in designing adsorption systems. So four isothermal models, namely Freundlich, Langmuir, Redlich—Peterson, and Langmuir—Nernst, were selected to compare the adsorption equilibrium of honeysuckle extract onto wool.

The empirical Freundlich model equation²⁷ can be written as

$$C_{\rm f} = K_{\rm F} C_{\rm s}^{1/n} \tag{8}$$

where $C_{\rm f}$ (mg g⁻¹) and $C_{\rm s}$ (g L⁻¹) are the concentrations of honeysuckle extract on wool and in the solution at equilibrium, respectively; $K_{\rm F}$ (mg g⁻¹(g L⁻¹)^{-1/n}) is the Freundlich constant, and 1/n stands for the heterogeneous factor.

The Langmuir model²⁸ is given by eq 9

$$C_{\rm f} = \frac{SK_{\rm L}C_{\rm s}}{1 + K_{\rm L}C_{\rm s}} \tag{9}$$

where $S \text{ (mg g}^{-1})$ gives the saturation capacity on wool, and $K_L \text{ (L mg}^{-1})$ is the Langmuir isotherm constant.

The Redlich-Peterson model²⁹ includes three parameters and is presented as follows:

$$C_{\rm f} = \frac{K_{\rm R}C_{\rm s}}{1 + a_{\rm R}C_{\rm s}^{\beta}} \tag{10}$$

where K_R (L g⁻¹) and a_R (L mg⁻¹) are Redlich–Peterson constants, and β is an exponent in the range 0–1.

The Langmuir—Nernst model can be described by the expression:

$$C_{\rm f} = K_{\rm P}C_{\rm s} + \frac{SK_{\rm L}C_{\rm s}}{1 + K_{\rm I}C_{\rm s}} \tag{11}$$

where $S \, (\text{mg g}^{-1})$ is the saturation capacity on wool, $K_P \, (\text{L g}^{-1})$ is the partition coefficient, and $K_L \, (\text{L mg}^{-1})$ is the Langmuir isotherm constant.

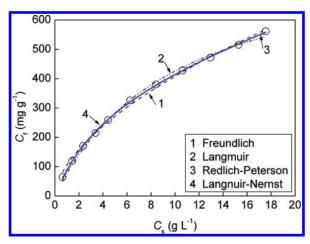


Figure 7. Different isotherm equation plots for the adsorption of honey suckle extract onto wool at 80 $^{\circ}\mathrm{C}.$

Table 3. SD Values of Isotherm Models

temperature (°C)	60	70	80	90
Freundlich	6.32	7.83	7.19	8.73
Langmuir	12.04	8.73	9.09	6.12
Redlich-Peterson	1.71	0.88	1.01	1.76
Langmuir-Nernst	1.55	1.54	2.68	1.59

All the experimental adsorption isotherms in Figure 6 were fitted to the four isotherm models using the nonlinear least-squares fitting procedure, Figure 7 presents the plots comparing the theoretical Freundlich, Langmuir, Redlich—Peterson, and Langmuir—Nernst models with experimental data at 80 °C for 300 min. The Redlich—Peterson and Langmuir—Nernst curves almost overlapped, and both of them went through all the experimental data exactly, showing a precise fitting to the experimental data. However, the fitting to Freundlich and Langmuir models was not good enough. This suggests that the adsorption behaviors of honeysuckle extract onto wool can be described by the Redlich—Peterson and Langmuir—Nernst isothermal models.

For the purpose of assessing the simulation result, all the equilibrium data were also analyzed using eq 6 and the standard deviations of the experimental data were obtained. The results were given in Table 3. The Redlich—Peterson isotherm nearly gave the lowest standard deviation values. Thus, the Redlich—Peterson isotherm is the most appropriate model to describe the adsorption behaviors of honeysuckle extract, which differs from the Langmuir model describing the adsorption of chlorogenic acid from honeysuckle crude extracts by macroporous and polar HPD-850 resins²³ and from the Langmuir and Freundlich models describing the adsorption of natural lac dyes containing carboxyl groups by silk fiber.³

The Redlich—Peterson equation is a combination of the Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation.³⁰ Its mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption.³¹ The adsorption of honeysuckle extract onto wool occurs by virtue of ion—ion forces of interaction operating between ionized carboxyl groups in chlorogenic acid and the

protonated amino groups of amino acids in wool under acid conditions. In addition, chlorogenic acid can form hydrogen-bonding forces with wool because it contains hydroxyl groups, while amino acids in wool contain amino groups and amide groups, etc. Besides, van der Waals' forces existing in chlorogenic acid molecule and amino acid molecules may contribute to the adsorption of honeysuckle extract onto wool more or less.

Isotherm parameters of the Redlich—Peterson and Langmuir—Nernst models from curve-fitting are given in Table 4. Redlich—Peterson constants $K_{\rm R}$ and $a_{\rm R}$ decreased with an increase in temperature, but β increased slightly with an increase in temperature. Equilibrium monolayer capacity $(K_{\rm R}/a_{\rm R})$ obtained with the Redlich—Peterson model changed little at 70, 80, and 90 °C, but the $K_{\rm R}/a_{\rm R}$ value at 60 °C was an exception, showing a smaller value than those at other temperatures. Similar results were observed in the Langmuir—Nernst saturation capacity S. This may be attributed to the surface barrier action of the epicuticle layer of wool which prevents chlorogenic acid from penetrating into the interior of wool fibers.

Build-up Properties. In view of the practical processing conditions, the build-up properties of honeysuckle extract onto wool were observed in a temperature-rise process in place of a constant temperature process.

The build-up properties expressed by $C_{\rm f}$ as well as the exhaustion of honeysuckle extract onto wool are depicted graphically in Figure 8. The extent of adsorption linearly increased with an increase in honeysuckle extract concentration due to a high saturation value and an incremental concentration gradient. Also Figure 8 revealed that lower exhaustion was obtained as the application concentration of extract of honeysuckle increased, with a linear relationship.

The CIE L^* , a^* , and b^* values for wool fabrics treated with different concentrations of honeysuckle extract are listed in Table 5. As can be clearly seen, the L^* , a^* , and b^* coordinates of samples changed very little with increasing honeysuckle extract concentration, which indicated that the adsorption of honeysuckle extract onto wool had an insignificant influence on the color of the treated fabric. It can be concluded from Table 5 and Figure 8 that the honeysuckle extract is not a promising natural dye for textile dyeing, although it showed good build-up properties.

UV-Protection Properties. It is surmised that honeysuckle extracts should enhance the UV-protection properties of treated fabric. Hence the UV-protection properties of treated fabric were measured and evaluated according to Australia Standard/New Zealand Standard AS/NZS 4399:1996.³²

The sunlight ultraviolet radiation in the range between 100 and 400 nm is subdivided into UVC (100–280 nm), UVB (280–315 nm), and UVA (315–400 nm) when considering the effect of ultraviolet radiation on human health and the environment. Because no UVC radiation reaches the earth's surface due to absorption by oxygen and ozone in the upper atmosphere, the transmittance of ultraviolet light including UVA and UVB through the fabrics was evaluated in the experiment. Figure 9 represents the dependence of both UPF and ultraviolet transmittance of treated wool fabrics on different honeysuckle extract concentrations. It is clear from Figure 9 that the UPF values of treated wool fabrics increased when initial honeysuckle extract concentration increased, with a dramatic increase in the concentration range of 0–3.2 g L $^{-1}$; whereas a slight increase was seen above 3.2 g L $^{-1}$. An increase in honeysuckle extract concentration caused a slight decrease in the ultraviolet

Redlich-Peterson Langmuir-Nernst $K_{\rm P} (10^{-3} {\rm L g}^{-1})$ $K_{\rm R} (10^{-3} {\rm L g}^{-1})$ $a_{\rm R} (10^{-3} {\rm L \ mg^{-1}})$ $K_{\rm R}/a_{\rm R}~({\rm mg~g}^{-1})$ β $K_{\rm L} (10^{-3} {\rm L \, mg^{-1}})$ $S \left(\text{mg g}^{-1} \right)$ temperature (°C) 1.0915 207.30 0.57 60 226.27 0.3436 338.74 18.53 70 157.08 0.5683 276.39 0.66 0.2578 404.28 14.24 80 136.16 0.4972 273.87 0.2267 401.69 0.66 13.54 293.97 90 111.80 0.3803 0.71 0.2050 400.44 10.65

Table 4. Redlich-Peterson and Langmuir-Nernst Isotherm Constants for the Adsorption of Honeysuckle Extract

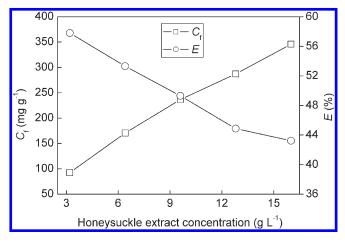


Figure 8. Influence of initial concentrations of honeysuckle extract on its uptake by wool.

Table 5. CIE L^* , a^* , and b^* Values for Wool Fabrics Treated with Different Concentrations of Honeysuckle Extract

concentration (g L^{-1})	L^*	a*	b*
0	87.69	0.06	14.27
3.2	83.28	0.44	16.49
6.4	81.88	0.79	18.50
9.6	80.23	1.04	19.60
12.8	78.92	1.23	20.40
16.0	78.78	1.50	21.41

transmittance of UVB, and a dramatic decrease in the ultraviolet transmittance of UVA in the concentration range of $0-3.2~\rm g~L^{-1}$ and, then, a slight decrease above $3.2~\rm g~L^{-1}$. It is obvious that the UV-protection properties of treated wool fabric are dependent on the extent of adsorption of honeysuckle extract onto wool since the extent of adsorption increases with the corresponding increase in the concentration of honeysuckle extract as shown in Figure 8.

According to AS/NZS 4399:1996, UPF values of less than 15, between 15 and 24, between 25 and 39, and above 40 are classified as bad, good, very good, and excellent protection against solar ultraviolet radiation, respectively. In Figure 9, as the concentration of honeysuckle extract increased from 3.2 to 16 g L⁻¹, the UPF values increased from 69.42 to 84.28. In comparison, the UPF value of the untreated wool fabrics was 21.01. When the honeysuckle extract concentration was 3.2 g L⁻¹, the treated wool fabric gave a UPF value of 69.42, which was classified in the "excellent" range. This suggests that honeysuckle

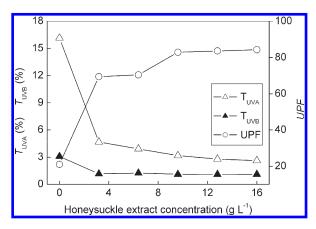


Figure 9. Ultraviolet protection factor (UPF) and ultraviolet transmittance of wool fabrics treated with different concentrations of honey-suckle extract.

extract can provide excellent UV protection for wool fabric when applied under an appropriate concentration.

The ultraviolet transmission spectra of treated wool fabrics were recorded as displayed in Figure 10. The ultraviolet transmittance of the treated wool fabrics decreased with the increasing concentration of honeysuckle extract. Compared with the untreated wool fabric, the transmittance of the treated wool fabrics decreased remarkably over the ultraviolet light range of 250–400 nm. It indicates that honeysuckle extract can absorb UVB and UVA efficiently.

A combination with Figure 9, Figure 10 reveals that the extract from honeysuckle can be applied as a natural UV-absorbing agent.

Here, it has to be mentioned that UV-protection textiles are usually subjected to light radiation and washing in the course of normal use, so the durability of their UV-protection effect is very important. In the present study, the resistance of treated wool fabrics to light and washing was evaluated. The light resistance was measured by reference to the light exposure procedure in AATCC test method TM 16-2003. The washing resistance was tested through the desorption of honeysuckle extract from the treated wool fabrics in water at 60 °C because wool fabrics would shrink and their UPF would increase if a practical washing procedure is employed. Figure 11 shows the influence of light exposure time on the UPF of treated wool fabrics after exposure to light. It is clear from Figure 11 that both the UPF values and UPF retention rates of treated wool fabrics decreased when exposure time was prolonged. But even so, the treated wool fabric gave a UPF value of 46.73 after light exposure for 18 h, which can still be classified in the excellent protection level. This suggests that honeysuckle extract can provide excellent UV protection for wool fabric and show good resistance to light. As seen in

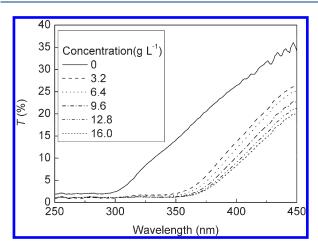


Figure 10. Transmittance spectra of wool fabrics treated with different concentrations of honeysuckle extract.

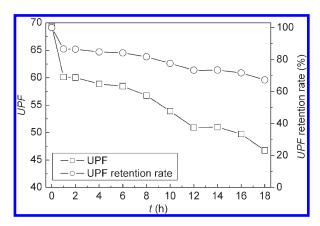


Figure 11. UPF values of treated wool fabrics after exposure to light.

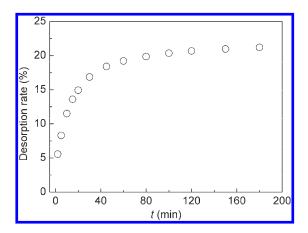


Figure 12. Desorption rate of honeysuckle extract from treated wool fabrics in water.

Figure 12, the desorption of honeysuckle extract from wool fabric increased as time was prolonged. When the desorption of honeysuckle extract exceeded 20%, it almost did not increase more. The simulated washing test indicated that the washing resistance of the honeysuckle extract adsorbed by wool might be good.

CONCLUSIONS

The adsorption of honeysuckle extract onto wool at different pH values was investigated. The uptake of honeysuckle extract by wool decreased with increasing pH in the range of 2-7. The kinetics of adsorption of honeysuckle extract onto wool was studied by using the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion equations, and the adsorption rate data were best fit by the pseudo-second-order equation which provided the lowest standard deviation values, implying that the nature of the adsorption process was chemisorption and the chemical adsorption was a rate-limiting step. The activation energy based on the kinetic equation was $47.91 \text{ kJ mol}^{-1}$.

The isotherm data were analyzed using the Freundlich, Langmuir, Redlich—Peterson, and Langmuir—Nernst models. The Redlich—Peterson model gave the best fit to the adsorption data. The adsorption of honeysuckle extract onto wool can also be successfully interpreted by the Langmuir—Nernst model. The results of adsorption study are helpful to understand adsorption mechanism of honeysuckle extract onto wool.

The extent of adsorption of honeysuckle extract onto wool linearly increased with increasing honeysuckle extract concentration, showing good build-up properties. The treated wool fabrics had much lower ultraviolet transmittance and much higher UPF values than untreated ones, and their protection capability against solar ultraviolet radiation was classified in the excellent level. It is concluded that the extract of honeysuckle may be developed as a natural UV-absorbing agent, and its UV protection effect has relatively good durability.

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