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Investigation of Adsorption Isotherms Used For Wool Dyeing by Aqueous Extraction of Cehri Fruit (Fructus Rhamni Petiolari) and Dyeing of Wool and Silk Accompanied by Various Mordants

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In this study, adsorption isotherms were obtained by processing wool with dyestuff solutions of different concentrations extracted from cehri fruit with water. These isotherms follow the Nernst equation; the Nernst constant was determined and interpreted.

In addition, wool and silk fibres were dyed with the same dyestuff solution and various mordants. Colours having a high fastness which could be used on an industrial scale were produced.
Key Words. Dyestuff adsorption; natural dyes; dyeing fibres; cehri fruit extract; wool dyeing; silk dyeing.

Introduction

Chrominance has played an important role in human life since old times. Colours contained in various parts of plants were noticed in pre-historical times therefore, much effort has been made to develop these colours and to dye various materials ever since [1]. These experimentation and skills have continued to this day passed on through the of craftsman-apprentice relationship instead of by written documentation.

Through the production of synthetic dyestuffs on an industrial scale, the use of natural dyestuffs have decreased substantially as a result of growing environmental awareness. Recently many investigations on natural dyestuffs yielding high fastness color spectra have been carried out.

Natural dyestuffs are obtained from vegetable and animal sources. Them most common are of vegetable origin. Vegetable dyestuffs are obtained by extraction from leaves, flowers, cones, fruits, body shells and roots of plants. They are most commonly used for wool dyeing, even though they can be used for silk or cotton dyeing[2]. Fibres dyed with natural dyestuff solutions are dyed directly or with a supplementary substance. These supplementary substances are called mordants, and the process is referred to as mordanting. It is possible to get hundreds of colours and shades by using different mordants with the same plant extract[3].

The evaluation of dyeing processes are based on the adsorption equilibrium of the dye distributed between dyestuff solutions and the fibres to be dyed. The dyeing distribution is expressed by isotherms drawn as the concentration of the dye is adsorbed on the fibres (C_a) against the equilibrium concentration of the dye in solution (C_d). These isotherms are classified as Nernst, Freundlich and Langmuir isotherms[4].

Langmuir and Freundlich isotherms were originally derived for the adsorption of gases by solids; the Nernst isotherm is common in dyeing processes. In this isotherm type, the distribution of substance to be adsorbed between the solid and solvent phases is expressed by a proportionality constant. There is a constant ratio between the adsorbed and aqueous concentrations of the adsorbate, and the slope of the isotherm is equal to K. If the same dyestuff adsorbed on various adsorbents gives Nernst's type isotherms, there exists a direct relationship between K and the extent of dyestuff adsorption.

The Nernst equation is given below:

$$C_a = KC_d \tag{1}$$

Experimental

Wool and silk used as fibre: The wool was provided by Diyarbakır Sümerbank Carpet Plant exported from New Zealand with PS 10Z8048 code number; the natural silk was obtained from the Antakya region and processed by hand loom.

Chemical substances used as the mordant: In mordanting, the following chemicals were used along with natural mordants such as oak gallnut and bonito.

Alum (potassium aluminum sulphate)	: $KAI\ (SO_4)_2\ 12H_2O$
Ferrous sulphate	: $FeSO_4.\ 7H_2O$
Potassium dichromate	: $K_2Cr_2O_7$
Ammonium heptamolibdate	: $(NH_4)_{12}Mo_7O_{27}.4H_2O$
Cupric sulphate	: $CuSO_4.5H_2O$
Lanthanum nitrate	: $La(NO_3)_3.6H_2O$
Mercuric nitrate	: $Hg(NO_3)_2$
Sodium bismuthate	: $NaBiO_3$

Dyestuff plant used: Cehri fruit (*Fructus Rhamni Petiolari* a species of *Rhamni Petiolaris Boiss (Rhamnaceae)* was dried from the fresh fruit. The tree is thorny and can grow up to 3m. It is fruits a deciduous tree in winter. Its fruits are 6-7 mm in diameter, dark-green-coloured, unfluffy and the inner part contains brillant-yellow-coloured seeds. The plant is common in the Central-Anatolia region[5]. Besides xanthorhamnetin which is a glycoside of rhamnetin there is rhamnazin and quercetin in its structure[6,7].

Apparatus used: Consort (C425) model digital pH-meter was used for pH measurements and Shimadzu UV-160 spectrophtometer for absorption spectra and concentration measurements.

Dyestuff extraction: Water was used as the extractant. Water was the dyestuff plant in a solid - to - liquid ratio of 1:30 (8.3 mg dye.mL^{-1} solution) mixed and left overnight. The next day, the mixture was heated 70°C for one hour. After cooling the waste materials were separated by filtration. The filtrate was diluted to its initial volume by adding water, and used as the dyestuff solution.

Mordanting: The mordanting process was carried out for one hour at 70°C with the following quantities:

For wool: 0.15 g mordant, 90 ml water and 3g wool.

For silk: 0.05 g mordant, 50 ml water and 0.5 g silk.

Dyeing: Mordanted wool and silk samples were processed with the previously prepared dyestuff solution at 8.3 mg.mL^{-1}. After rinsing, it was left at room temperature for drying.

Drawing of adsorption isotherm: The pH of the stock dyestuff solution (8.3 mg.mL^{-1} was measured as 5.09 (30° C). The absorption spectrum of cehri fruit extract (Fig. 1) showed that the maximum absorption wavelength was 350 nm, which was confirmed by the 2nd. derivative spectrum, i.e., $dA/d\lambda = 0$ at 350 nm.

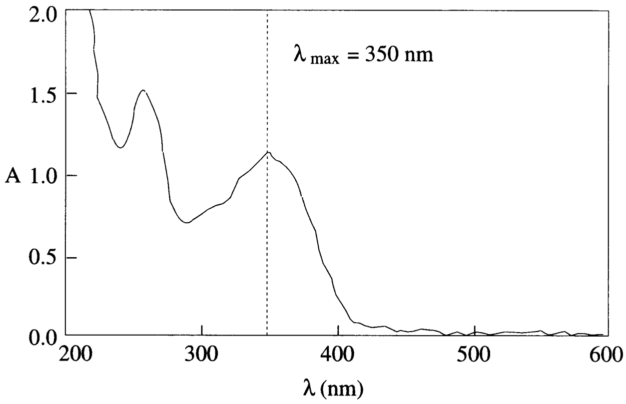

Figure 1. The absorption spectrum of the aqueous extract of cehri fruit

By suitable dilutions of the 8.3 mg.mL^{-1} stock solution, working solutions up to 0.183 mg.mL^{-1} relative concentration were prepared and their absorbances measured to yield the calibration curve seen in Figure 2.

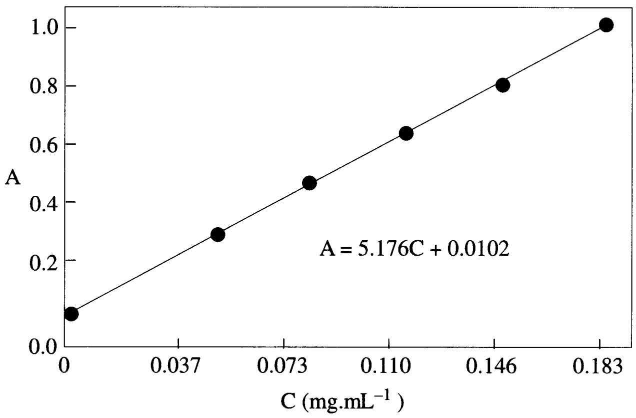

Figure 2. The working curve of the aqueous extract of cehri fruit

The solution of 5.81, 4.98, 4.15 and 3.32 mg.mL^{-1} concentration were prepared from the stock solution. The dyeing process was carried out. After dyeing each solution, the initial concentration (C_0) and equilibrium concentration (C_d) were determined by means of the calibration curve; then, by subtraction of the equilibrium concentration from the initial concentration, the adsorbed dyestuff concentration (C_4) was determined. This value was converted into milligrams of dye per gram wool. This data can be seen in Table 1.

Table 1. The adsorption data related to cehri fruit

Cehri Fruit	Wool, g	Co, mg.mL^{-1}	Cd, mg.mL^{-1}	Ca,mg	Ca, mg dye.g^{-1} wool
	2.88	8.30	5.11	3.19	1.11
pH(original) = 5,09 (30°C)	2.91	5.81	3.43	2.38	0.82
	2.59	4.98	3.18	1.80	0.70
λ_{max} = 350 mm	2.66	4.15	2.71	1.44	0.54
K = 0,210 mLg^{-1}	2.73	3.32	2.08	1.24	0.42

The adsorption isotherm in Figure 3 was obtained by recording the amount adsorbed against the equilibrium concentration.

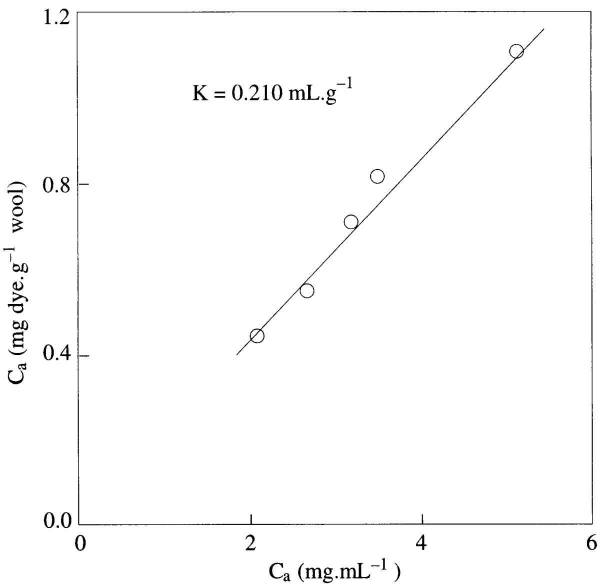

Figure 3. The adsorption isotherm of the aqueous extract of cehri fruit on wool

Light Fastness Tests: Light fastness tests of wool samples which were left under sunlight for a week at an average of 36° C, were carried out according to TS. 867 and TS. 423 grey scale definition[8,9].

Wash Fastness Tests: Dyed-wood and silk samples were washed with soapy water of 1/100 concentration at 60° C for half an hour and mixed at intervals. The degree of fastness for each washed and unwashed sample after rinsing and drying was determined by using the grey scale. The degree of fastness ranged from 1 to 5. 5 corresponds to the degree that exhibits no signs of colour change, while the other degrees show orderly fading properties. Fastness degrees relating to dyed-wool and silk samples are given in Table 2.

Colour Coding For Dyed Fibre: Colour coding was carried out by using "Farbenatlas" of. Harald Küppers[10]. In coding, letters denote the first letters of the colours in the German language and subnumbers refer to its mass technical action.

Results and Discussion

Dyeing data relating to the dyestuff extraction of cehri fruits are shown in Table 2. Besides unmordanted dyeing of wool and silk samples, vivid colors were obtained by using eleven different mordants. While the premordanting method was applied the other mordants premordanting was carried out with potassium dichromate and mordanting with potassium dichromate was conducted again. In wool dyeing, different shades of beige with unmordanted, gallnut and bonito oak and lanthanum nitrate; yellow colour in mordanting with alum, alum + curcume; dark-fume colour with ferrous sulphate; shades of green with copper sulphate, mercuric nitrate, sodium bismuthate; orange colour with potassium dichromate and ammonium heptamolibdate were obtained. In silk dyeing, beige with unmordant, gallnut and bonito oak; yellow colour with alum, potassium dichromate, sodium bismuthate, lanthanum nitrate, mercuric nitrate, alum + curcume; dark-fume colour with ferrous sulphate; celadan colour with cupric sulphate; orange colour with ammonium heptamolibdate were obtained. In dyeing both wool and silk by using mordants such as gallnut oak; bonito oak, alum, alum + curcume, ferrous sulphate, copper sulphate, and ammonium heptamolibdate, same colours were obtained. However, in both wool and silk dyeing, by using mordants such as lanthanum nitrate, mercuric nitrate, sodium bismuthate and potassium dichromate, different colour were obtained. The codes for these colours are given in Table 2. High fastness values were obtained in nearly all dyeing trials especially with mordanting processes. Normal values were obtained only in unmordanted dyeing. High fastness values in mordanting process are due to the binding effect of mordants between fibres and dyestuffs. The reason for obtaining different colours for the same dyestuff solution is due to the absorption of light-beams of different wavelengths for the electronic transitions of mordant-dyestuff interaction. The adsorption isotherm in Figure 3 was of Nernst type and by using equation (1), the Nernst constant K was calculated. There is a constant ratio between the equilibrium concentration and the adsorbed amount in this type of isotherm; the slope was equal to K. The expected concentrations of adsorbed dyestuff can be found from the equilibrium concentration by using K values.

Table 2. The dyeing data related to cehri fruit

Dyeing fibres	Using mordant	C, Flotte	Color Code	Washing fastness	Light fastness
Wool		8.30	$S_{02}O_{07}Y_{50}$	4	4-5
Wool		5.81	$S_{02}O_{07}Y_{50}$	4	4-5
Wool		4.98	$S_{02}O_{07}Y_{50}$	4	4-5
Wool		4.15	$S_{00}O_{04}Y_{41}$	4	4-5
Wool		3.32	$S_{00}O_{04}Y_{41}$	4	4-5
Wool	Oak gallnut	1:30	$S_{11}O_{11}Y_{41}$	5	5
Wool	Oak bonito	1:30	$S_{11}O_{11}Y_{33}$	5	5
Wool	Alum	1:30	$S_{00}O_{00}Y_{70}$	4	4-5
Wool	Ferrous sulphate	1:30	$S_{80}O_{11}Y_{50}$	5	5
Wool	Potassium bichromate	1:30	$S_{04}O_{33}Y_{90}$	5	5
Wool	Ammonium heptamolidate	1:30	$S_{20}O_{50}Y_{90}$	5	5
Wool	Copper Sulphate	1:30	$S_{50}O_{15}Y_{99}$	5	5
Wool	Lanthanum natrate	1:30	$S_{07}O_{07}Y_{50}$	4	4
Wool	Mercuric nitrate	1:30	$S_{50}O_{15}Y_{50}$	4	5
Wool	Sodium bizmuthate	1:30	$S_{50}O_{15}Y_{50}$	5	5
Wool	Alum + Curcume	1:30	$S_{04}O_{11}Y_{90}$	5	5
Wool	Crom→Dyeing→Crom	1:30	$S_{41}O_{41}Y_{80}$	5	5
Silk		1:30	$S_{11}O_{11}Y_{33}$	4	5
Silk	Alum	1:30	$S_{00}O_{07}Y_{60}$	5	5
Silk	Potassium bichromate	1:30	$S_{26}O_{26}Y_{90}$	5	5
Silk	Crom→Dyeing→Crom	1:30	$S_{20}O_{41}Y_{80}$	4-5	5
Silk	Ferrous sulphate	1:30	$S_{90}O_{20}Y_{90}$	5	5
Silk	Copper sulphate	1:30	$S_{04}O_{04}Y_{70}$	5	5
Silk	Ammonium heptamolibdate	1:30	$S_{20}O_{41}Y_{99}$	4-5	4
Silk	Sodium Bizmuthate	1:30	$S_{00}O_{15}Y_{70}$	4	5
Silk	Lanthanum nitrate	1:30	$S_{07}O_{15}Y_{20}$	4-5	4
Silk	Mercuric nitrate	1:30	$S_{07}O_{15}Y_{80}$	4-5	5
Silk	Oak gallnut	1:30	$S_{11}O_{15}Y_{33}$	4	4
Silk	Oak bonito	1:30	$S_{20}O_{20}Y_{33}$	4	4
Silk	Alum + curcume	1:30	$S_{00}O_{15}Y_{80}$	4	4

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