Studies of Kinetics and Thermodynamic Parameters of Cashmere Dyeing with Bio-Preparation of Rheum Undalitum L.

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Abstract

In this study dyeing Mongolian cashmere with bio-preparation extracted from of Rheum undalitum L. was investigated. Dyeing experiments were carried out varying pH, temperature and time. The results have been used to investigate the kinetic and thermodynamic parameters of dyeing cashmere. This process is pH dependent and found most suitable condition is pH 4.5. Increases in adsorption capacity with increase in temperature indicate that the dyeing process is endothermic. The thermodynamic parameters like standard standard affinity (Δμ), standard enthalpy (ΔH) and standard entropy (ΔS) were evaluated.

Keywords: *Cashmere, dyeing, natural dye, fastness rhubarb.*

INTRODUCTION

Cashmere is a natural fibre taken from the Kashmir goat's downy undercoat. One of the most luxurious and rare fibres, cashmere yarn is renowned for being light, airy, delicacy, gloss and warmth cashmere is used as a raw material for luxury woven or knit products. Around 30.0% of the world cashmere is produced in Mongolia and in 2015, 43.2% of the total livestock of Mongolia was the cashmere goats (National Statistical Office of Mongolia, 2016). The body of Mongolian goat has various colors such as reddish, red, grey, black, dark brown, and white color (Takahashi et al., 2008) [1, 2, 3].

The process of producing cashmere apparel products from fiber includes various steps from fiber preparation to garment processing. Among the many production steps, dyeing is essential in order to produce cashmere garments specially with natural dyeing for "ECO-ORGANIC PRODUCT" [4].

An international awareness about environment, ecology and pollution control creates an upsurge in the use of natural dyes in the middle of 20th century. During the last few decades, increasing attention has been paid by the researchers all over the globe towards various aspects of natural dye applications [5, 6].

Natural dyes/bio-preparations derived from flora and fauna are believed to be an eco-friendly, safe and viable substitute to synthetic colorants because of their non-toxic, non-carcinogenic and biodegradable nature [7, 8]. Moreover, natural dyes do not cause pollution and waste water problems.

Natural dyes can give suitable and elegant colours through to the brightest colour to the fibers, yarns and fabrics. The major parts of natural dyes are anthraquinone, anthocyanin and flavonoid dyes, or polyphelolic compounds most of which have yellow, red and brown shades (Bechtold and Mussak., 2009) [9].

Rheum Undalitum.L commonly known as rhubarb, is a herb of 0.3-0.8 m in height, distributed in the Altai, Khangai and Dornod area of Mongolia. The roots are the chief source of Mongolian rhubarb and finds application in medicine as a purgative and astringent tonic and their leaves, stems can also be used for colouration of textile materials [10-15].

The researchers have been reported about Rheum species major active constituents are a number of anthraquinone derivatives based on rhein, emodin, aloe-emodin and chrysophanol and tannins, flavanoids etc…. [16].

The objectives of this work are: (1) to determine optimum condition of the dyeing; (2) to estimate thermodynamic and kinetic parameters of the process; (3) to determine a suitable model describing the isotherms.

MATERIALS AND METHODS

Materials

Natural lightgrey dehaired cashmere (fineness 16.32 mkm, average length 38.6 mm) by the Gobi Co.Ltd of Mongolia was scoured with an aqueous nonionic surfactant solution at temperature of 45°C for 20 minutes, then it was throughly rinsed with cold water and air dried at room temperature.

Plant, dye bio-preparation

Fresh nature *Rheum Undalitum. L* leaves, stems were collected from Khangai area of Mongolia and dried in air 20-25^{0}C in the dark room. After completed to dry they were made into a fine powder by crushing and grinding. This powder was used in all succeeding experiments to extract bio-preparation of *Rheum Undalitum L.* for dyeing. Dyeing bio-preparation solutions by water were prepared 60 minutes, 80^{o}C temperature and M:L ratio is 1:40 [17].

Dyeing Process

Dyeing process of cashmere fibers was carried out at pH 4.5, which pH correction of the dyeing bath were used the acetic acid(CH3COON) with laboratory-grade. Dyeing process of cashmere fibers was carried out at pH 4.5 condition using a bath containing extracted *Rheum undalitum L.* bio- preperation solution at 1:50 cashmere fiber: dyeing bio-preparation ratio. The dyed cashmere fiber were washed with water and dried at room temperature. Then surface of cashmere analysis was carried out on undyed and dyed cashmere samples.

Thermodynamic studies

The thermodynamic parameters of the process such as standard affinity, $\Delta\mu^0$ (kJ/mole), standard entropy, ΔS^0 (J/mol·K) and standard enthalpy, ΔH^0 (kJ/mole) were calculated by using the following equation [1, 2, 3]:

$$-\Delta\mu^0 = RTln\frac{Df}{V} \text{ x } D_s = \mathrm{RTlnK_c} \quad (1)$$

$$K_c = \frac{C_{ad}}{C_e}\, x\, \frac{V}{m} \quad (2)$$

$$\ln K_c = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (3)$$

where, K_c is the equilibrium constant, C_{ad} is the adsorbed dye concentration (mg/l), C_e is the equilibrium dye concentration, V is the volume (l) and m is the mass of the cashmere fiber (g) R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature (in Kelvin). The various of ΔH^0 and ΔS^0 were calculated from the slopes and intercepts of the plot of $\ln K_c$ versus 1/T are linear, respectively.

Kinetics of dyeing

The kinetic studies were carried out for the time periods ranging from 30 minutes to 100 minutes, using a bath containing extracted Rheum undalitum L. bio preperation solution at 1:50 M:L ratio. Kinetics of dyeing was studied by fitting firs-order and second order reactions to experimental data.
The pseudo first-order model given by following equation [4]:

$$\log(q_t - q_e) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

The linear form of pseudo second order rate equation is given as follows [5]:

$$\frac{t}{q_t} = \frac{1}{q_t} + \frac{1}{k_2 q_{e2}} \quad (5)$$

where, k_1(min^{-1}), k_2 (g/mg min) are rate constants of pseudo-first order, pseudo-second order rate equation, q_t and q_e the amounts of dye into cashmere fiber at time t and equilibrium, respectively(mg/g);

The amounts of dye uptake by cashmere fiber were calculated using the following equation [6, 7]:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (6); \qquad q_e = \frac{(C_0 - C_e)V}{m} \quad (7)$$

where, q_t and q_e the amounts of dye into cashmere fiber at time t and equilibrium, respectively (mg/g); C_0 , C_t and C_e are the initial, time t and equilibrium concentration of dye in the solution (mg/l); V is the volume of dye bio preparation solution (L), and m is the mass of cashmere fiber (g); t is the sorption period (min).

Isotherm model

Langmuir and Freundlich isotherm model commonly used to reflect the performance of adsorbents in adsorption processes.
Langmuir model assumes monolayer adsorption given by [8]:

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (8)$$

Freundlich isotherm model assumes multilayer adsorption given by [9]:

$$\ln q_e = \ln K_f + b_f \ln C_e \qquad (9)$$

where, Q^o(mg/g) is the maximum sorption capacity, b is the Langmuir constant and K_f (l/g) and n are Freundlich constants [18-23].

RESULTS ND DISCUSSION

Effect of dyebath pH on exhaustion of bio-preparation on cashmere fiber

To investigate effect of biopreparation pH on dyeing cashmere, the pH was varied 4.5 to 6.5. The experimental results are presented in Fig. 1.

From the fig 1, obviously found dyeing cashmere was strongly pH dependent, and that dye exhaustion was superior at pH 5.0. But dye exhaustion decreased from 51.5% to 49.4% when the dyeing pH range conditions was 4.5, 5.5, 6.5. Hence, pH 5.0 was taken for further experimental work.

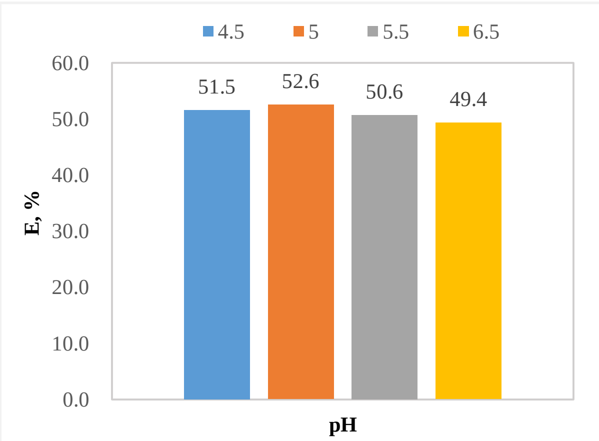

Fig. 1. Effect of dyebath pH on dye exhaustion on cashmere fiber
(initial concentration 520 mg/l, temperature 353K, t=60 min)

Effect of dyeing temperature and time periods on exhaustion of bio-preparation on cashmere fiber

The effect of temperature on dyeing cashmere is investigated at pH 5.0 condition. The temperature was varied from 333K to 363K, time was varied from 30 min to 100 min while initial concentration of bio-preparation was 520 mg/l.

From the fig. 2, dye exhaustion is increased by increasing temperature. The maximum value of dye exhaustion is reached about 53.12 % at 353K, 50 min. And in the dyeing temperature at 363K, dyed at the 40 min is 52.48%, and at the 50 min is 51.85%.

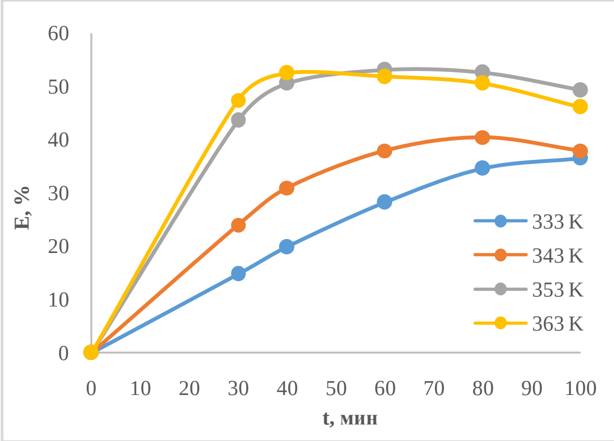

Fig. 2. Effects of dyeing temperature and time period on exhaustion of bio-preparation on cashmere fiber
(initial concentration 520 mg/l, pH=5.0, ML 1:50)

But observed dyed cashmere fiber were felted because fiber cuticle is damaged when temperature was higher.

The cashmere fibres were dyed at 80°C and 90°C and durations 40, 50 minutes respectively, so as to study of dyeing time and temperature dependences in changing the surface morphology of the wool fibre under the influence of dyeing conditions. After dyeing, the surface morphology of the wool fibre was studied using a scanning electron microscope (Fig. 3, 4).

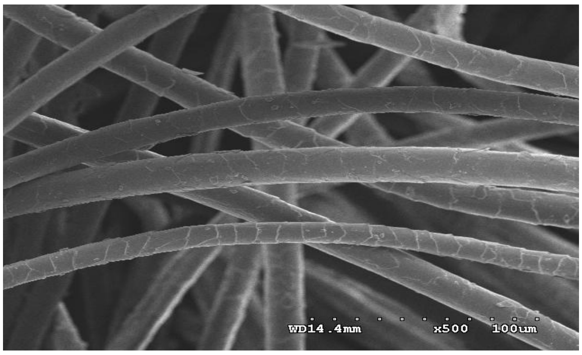

Fig. 3 SEM picture of undyed cashmere fibre

Fig. 3 shows the SEM picture of undyed cashmere fibre in which the escarpments are prominent and well defined. The undyed cashmere fibre surface may be described as a smooth fibre surface.

Fig. 4(a) and (b) are the SEM pictures of cashmere fibres dyed at 80oC 50 min and 90oC 50 min respectively. The appearance of those fibres were quite similar to the untreated fibre. There was no visible changes or damages on the scale structure of dyed at 80oC 50 min. But the fiber cuticle's scale of dyed at 90oC 50 min were slightly lifted and is observed broken.

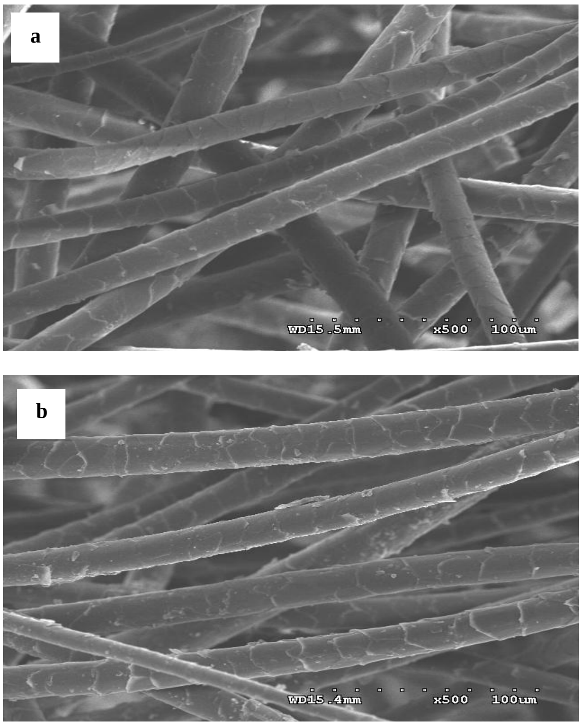

Fig.4. SEM of dyed cashmere.
a)dyed at 80°C, 50min; b)dyed at 90°C, 50min

The dye exhaustion of cashmere fiber dyed at 353K for various time periods has been carried out. The time of dyeing is calculated as 50 min. It is observed that as the time of dyeing increases from 30 min after than that the equilibrium is achieved. Similar trend was reported for the kinetics and thermodynamics of dye extracted from *Arnebia nobilis Rech.f.*on wool [24] and dyeing kinetics of wool yarn with *Rubia tinctorium L.* [25].

Therefore, 353K and 50 minute were chosen as suitable temperature and time for cashmere dyeing with the bio-preparation.

Thermodynamic and kinetic parameters

Experimental results of effect of temperature and time were used to calculate thermodynamic and kinetic parameters.
Thermodynamic parameters such as change in standard affinity ($\Delta\mu^0$), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were evaluated by the equation (1, 2, 3). ΔH^0 and ΔS^0 were calculated from the slope and intercept of the Vant Hoff's plot of $\ln K_c$ verses 1/T as shown in Fig. 5.

The thermodynamic parameters are given in Table-3.

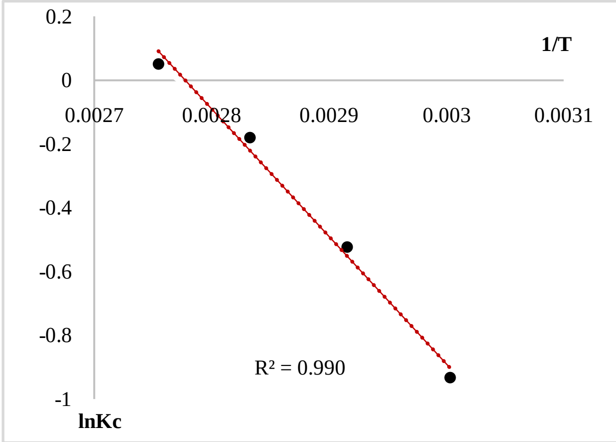

Fig 5. Vant-Hoff's plot at concentration of 520 mg/l

Table 1.
Thermodynamic parameters for cashmere dyeing with Rheum Undalitum L.

Temperature, (K)	*Bio preparation concentration, mg/l*	*$\Delta\mu^0$, (kJ/mol)*	*ΔH^0, (kJ/mol)*	*ΔS^0, (kJ/mol ·K)*
353	520	-12.50	55.90	155.67
343		-10.94		
353		-9.70		
363		-8.58		

From the table 1, positive values of ΔH^0 indicate that the dyeing of cashmere with *Rheum Undalitum L.*is endothermic process.
The negative values of $\Delta\mu^0$ is been shown where the dyeing process is spontaneous and the negative values of $\Delta\mu^0$ have been increasing slowly with rise in temperature. The increasing of the dyeing temperature will lead to higher dye affinity up to a certain temperature limit, above which the dye uptake will gradually reduce, and in this case means attached to dye fibers.
In other words practically there is a decrease in dye affinity and there are little or almost no significant changes in dye affinity with increase of dyeing temperature. Similar results were reported earlier in similar studies [26-29].

The kinetic parameters have been given in Table 2.

The k_l, and q_e have been calculated from the slope and intercept of plots of $\log(q_e\text{-}q_t)$ versus t according to pseudo-first-order model (Fig .6) and versus t according to pseudo-second-order model (Fig .7) q_e and k_2 from the slope and intercept have been calculated. From table 2, tthe correlation coefficient values for the pseudo-second-order rate equation 0.982 was found to be higher than the pseudo-first-order rate equation 0.758.

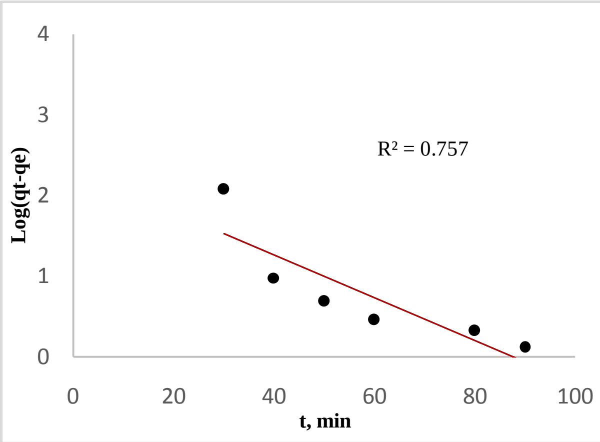

Fig. 6. Pseudo-first-order plots for cashmere dyed
(initial concentration of 520mg/l, pH=5.0, T=353K)

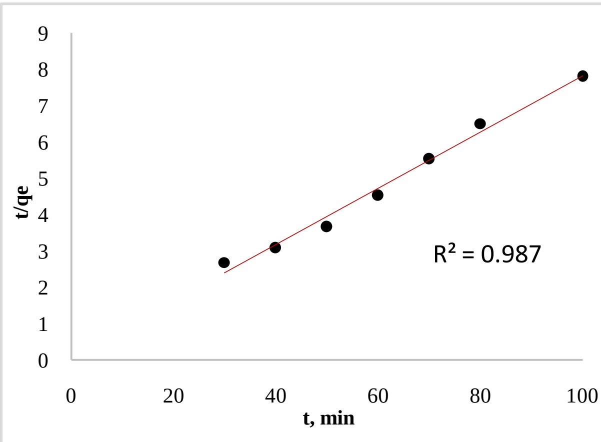

Fig. 7. Pseudo-second-order plots for cashmere dyed
(initial concentration of 520mg/l, pH=5.0, T=353K)

Table 2.

Kinetic parameters for cashmere dyeing with Rheum Undalitum L

Pseudo-first-order	**k_1, (min^{-1})**	15.4 x10^{-2}
	q_e, (mg·g^{-1})	3.97
	R^2	0.758
Pseudo-second-order	**k_2, (g·mg^{-1}·min^{-1})**	6.1 x10^{-4}
	q_e, (mg·g^{-1})	14.93
	R^2	0.982
Experimental value	**q_e, (mg·g^{-1})**	13.67

In addition, the value of the absorption capacity calculated by the pseudo-second-order is in close proximity to the experimental value.

This indicates cashmere dyeing process can be explained with pseudo-second-order equation. These data suggest that the mechanism of adsorption of pseudo-second-order is predominant and that the overall rate adsorption of *Rheum undalitum L.* dye's bio preparation is more likely to be controlled by the chemisorption process [26]. In fact, it was already expected due to the chemical attraction earlier discussed and Das et al also reported[27].

Dyeing isotherm

The isotherms of cashmere dyeing are presented in Fig 8.

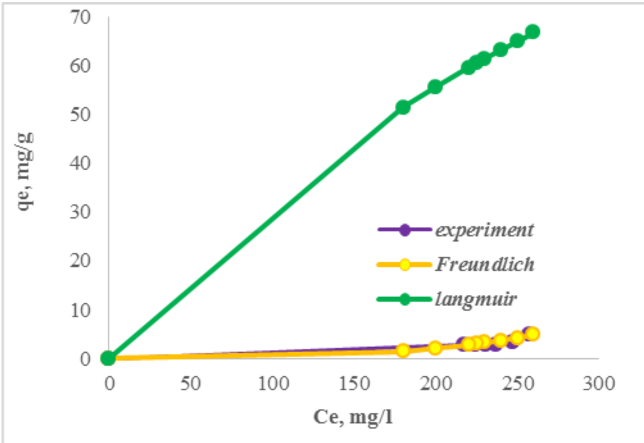

Fig. 8. Nonlinear adsorption isotherm of Langmuir, Freundlich model
and experimental values
(initial concentration of 520mg/l, pH=5.0, T=353K, t=40 min)

Experimental data was better adjusted to the Freundlich model for cashmere dyeing. The Freundlich model assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally. It predicts the formation of multilayers(Freundlich, 1906).

Possibly, the monolayer occurs with the interaction between the hydroxyl groups of the dye and the amino groups of the protein fibers[30]. The multilayer formed through chemisorption of other radicals that interact to the dye.

Therefore, the Freundlich model that emphasizes the importance of both phenomena comes naturally as the model that may represent the equilibrium data of the dyeing bio-preparation extracted from *Rheum undalitum L.* in the cashmere.
Parameters for the dyeing isotherm for cashmere dyeing are shown in Table 3.

Table 3.

Isotherm model	Isotherm constants	Corbent: cashmere
Langmuir	Q^0, mg/g	66.66
	b	0.0028
Freundlich	K_f, l/g	3.68
	n	1.26

The theoretical parameters of isotherms for cashmere dyeing

Equilibrium data were fitted to the Freundlich model, which is in total agreement with the isotherm shape for dyeing cashmere.

CONCLUSIONS

With the increase in dyeing time the dye uptake increases on cashmere up to 50 min of dyeing time and then gradually slows down and dyeing process becomes stable. The best result of dyeing the cashmere was achieved using a temperature of 80^0C, pH 5.0, 50 minutes and initial dye concentration of extracted by water with ML ratio 1:40.Also the best result of bio-preperation extracting was achieved using a temperature of 80^0C, 60 minutes and ML ratio 1:40 by water of *Rheum Undalitum L.* by the our experimental data [17].

The thermodynamics parameters of cashmere dyeing are endothermic and spontaneous. Therefore, there will be increase in dye absorption with increase in temperature of dyeing after then dyeing process slowed and dye adsorption at a certain temperature where equilibrium of dyeing is achieved.The kinetics of dyeing can be fitted by pseudo-second-order model as a correlation coefficients and values of the absorption capacity. The pseudo-second-order model may successfully represents the kinetic experimental data for cashmere dyeing. According to the kinetic and equilibrium results, it was concluded that chemisorption is quite important in the cashmere dyeing. The equilibrium data for cashmere fiber can be represented by the Freundlich model.

Considering that the dyeing process has a great contribution of chemisorption which promoted good colour fastness to laundering, it is concluded that dyeing with *Rheum Undalitum L.* has huge advantages as the textile wastewater is much more biodegradable than the textile wastewater generated with syntethic dyes.

REFERENCES

[1] National Statistical Office of Mongolia. (2016, January 24). 12 аймаг малаа 5 төрлөөр өсгөсөн байна [5 Kinds of animals are raised in 12 regions]. National Statistical Office of Mongolia. Retrieved January 12, 2016, from http://www.nso.mn/content/1#.VMpQWJX9nmJ

[2] Takahashi, H., Nyamsamba, D., Mandakh, B., Zagdsuren, Yo., Amano, T., Nomura, K., Yokohama, M., Ito, S., & Minezawa, M. (2008). Genetic structure of Mongolian goat populations using microsatellite loci analysis. AsianAustralasian Journal of Animal Sciences, 21(7), 947− 953. doi:10.5713/ajas.2008.70285.

[3] Gankhuyag, S. O. (2009). A study on the competitive advantages of cashmere industry in Mongolia. Unpublished master's thesis, National Sun Yat-sen University, Kaohsiung. Javkhlantugs, N., Ankhbayar, []E., Tegshjargal, K., Enkhjargal, D., & Ganzorig, C. (2009). AFM study of untreated and treated fibers of Mongolian goat cashmere. Materials Science Forum, 610-613, 175−178. doi:10.4028/www. scientific.net/MSF.610-613.175

[4] McGregor, B. A. (2012). Properties, processing and performance of rare natural fibres: A review and interpretation of existing research results. Canberra: Rural Industries Research and Development Corporation (RIRDC).

[5] Ahlstro¨m LH, Eskilsson C Sparr, Bjo¨ rklund E. Determination of banned azo dyes in consumer goods. TrAC Trends Anal Chem 2005;24:49–56.

[6] Shahid M, Shahid-Ul-Islam, Mohammad F. Recent advancements in natural dye applications: a review. J Clean Prod 2013;53:310–31.

[7] Islam S, Shahid M, Mohammad F. Perspectives for natural product based agents derived from industrial plants in textile applications – a review. J Clean Prod 2013;57:2–18.

[8] Yusuf M, Ahmad A, Shahid M, Khan MI, Khan SA, Manzoor N, et al. Assessment of colorimetric, antibacterial and antifungal properties of woollen yarn dyed with the extract of the leaves of henna (Lawsonia inermis). J Clean Prod 2012;27:42–50.

[9] Bechbold, T.; Mussak, R. Handbook of Natural Colorants. John Wiley&Sons Ltd, England. 2009.

[29] Anitha K and Prasad S N, Current Science, 2007, 92(12), 1681- 1682.

[10] Adeel S, Ali S, Bhatti I A and Zsila F, Asian J Chem., 2009, 21(5), 3493-3499.

[11] Sachan K and Kapoor V P, Ind J Tradit Knowl., 2007, 6(2), 270-278.

[12] Siva R, Current Science, 2007, 92(7), 916-919.

[13]Vankar P S, Shankar R and Wijayapala S, Journal of Textile and Apparel, Technology and Management, 2009, 6(1), 1-11.

[14] Samanta A K and Agarwal P, Indian J Fib Text Res., 2009, 34, 384-399.

[15] Mahangade R R, Varadarajan P V, Verma J K and Bosco H, Ind J Fib Tex Res., 2009, 34, 279-282.

[16] Debasish D, Sankar RM, Bhattacharya SC. [2008] Colouration of wool and silk with Rheum emodi. Indian J Fibre Text Res 33. 163–170.

[17] Tserendulam, S.; S.Delgermaa, S.; Nadmid, G.; Kh.Soyol-Undrakh,; Tamara, M. Eco-friendly of cashmere dyeing with Rheum Undalitum L. and Urtica Cannabina L. 2017, 11th international forum on strategic technology. IFOST 2017. Korea.

[18] Gui-zhen K, Weli-lin X, Wei-dong Y. [2008] Thermodynamic and kinetic studies of adsorption of berberine on silk. Indian J Fibre Text Res 33: 185–188.

[19] Koyuncu M. [2012]. Thermodynamic parameters and kinetics of wool yarn with aqueous extract of rubia tincorum.L. IIOABJ.Vol.5; Issue 2; 12-15.

[20] Yusan S, Gok C, Erenturk S, Aytas S. [2012] Adsorptive removal of thorium (IV) using calcined and flux calcined diatomite from Turkey: evaluation of equilibrium, kinetic and thermodynamic data. *Applied clay sci* 67-68: 106–116.

[21] Samanta AK, Konar A, Chakraborti S, Datta S. [2011] Dyeinf of jute fabric with tesu extract: part I - effects of different mordanrs and dyeing process variables. *Indian J Fibre Text Res36*: 63–73.

[22] Kumersan M, Palansisam J, Kumar PE. [2012] Application of eco-friendly natural dye on cotton using combination of mordant's. *Indian J Fibre Text Res* 37: 194–198.

[23] Al- Ghouti MA, Khraished MAM, Allen SJ, Ahmet MN. [2003] The removal of dyes from textile wastewater as study of the physical characteristics and adsorption mechanisms of diatomeceous earth. *J Environman* 69 (3): 229–238.

[24] Arora A, Deepali R, Deepti G, Gulrajani ML. [2012] Dyeing parameters of hydroxyl-naphthoquinones extracted from arnebia nobilis rech.f. *Indian J Fibre Text Res* 37: 91–97.

[25] Koyuncu.M. Thermodynamic parameters and dyeing kinetics of wool yarn with aqueous extract of Rubia tinctorumL. *IIOABJ;* Vol. 5; Issue 2;2014.12-15.

[26] Chairat M., Rattanaphani S., Bremner J.B., Rattanaphani V.An adsorption and kinetic study of Lac dyeing on silk. Dyes and Pigments; 64,231-241.DOI:10.1016/j.dyepig.2004. 6.009.

[27] Das D., Maulik S.R., Bhaattacharya S.C. Dyeing wool and silk with Bixa Orellana.2007. indian journal of Fiber and Textile research.2007.Vol.32. 366-372.

[28] Kumersan M, Palansisam J, Kumar PE. [2012] Application of eco-friendly natural dye on cotton using combination of mordant's. Indian J Fibre Text Res 37:194–198.

[29] Al-Ghouti MA, Khraished MAM, Allen SJ, Ahmet MN. [2003] The removal of dyes from textile wastewater as study of the physical characteristics and adsorption mechanisms of diatomeceous earth. J. Environment. 69 (3): 229–238.

[30] Vinod.K.N., Puttaswamy, Gowda K.N.N., Sudhakar R. Isolation of colour components from flowers of Tabebuia argentea: kinetic and adsorption studies on silk yarn. Coloration technology. 2011. 127. 205-209. DOI: 10.1111/j.1478-4408.2011.00300.x