

Preparation of Lake Pigment from Thai Lac Dye

Eakkaluk Wongwad, Ampa Jimtaisong⁺, Nisakorn Saewan and Panvipa Krisadaphong

School of Cosmetic Science, Mae Fah Luang University, Chiang Rai, Thailand, 57100

Abstract. Lac natural dye is a red color product obtained from female insect *Coccus laccae* (*Laccifer lacca* Kerr). In Thailand, lac dye is used as a natural red dyestuff for cotton and silk dyeing. Mordants, which is usually different metal salts, can form complexes with the dye molecules via coordinate bonds. These complexes are insoluble and hence improve the dye fastness. Therefore, preparation of lake pigment from Thai lac dye using four metal salts $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, AlCl_3 , CaCO_3 , and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ was investigated. The lac lake was prepared at different conditions such as pH, temperature, reaction time and metal salt concentration. The suitable condition for the lake preparation is of pH 3.5 ± 0.1 at 100°C , 2h and suitable metal salt is $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$. The UV-Vis spectra of lac lake complex showed the bathochromic shift from that of lac dye which may due to a result of coordination by lone pair electrons on the N or O donor atoms with metal ions, thus stabilizing the excited state relative to the ground state leading to longer wavelength absorption maxima and this potential coordinating between metal salt and lac dye is also illustrated in FT-IR analysis. The structure of lac dye was changed after reacted with metal salts and there is new crystalline peaks formed in XRD analysis.

Keywords: Lac natural dye, Laccaic acid, Lake pigment, Metal salt

1. Introduction

Lac natural dye is a red color obtained from female insects *Coccus laccae* (*Laccifer lacca* Kerr). Water extraction of stick-lac produces the lac dye at about 0.5-0.75% by weight of stick lac [1]. Lac dye is a mixture of at least five closely related laccaic acids derived from 2-phenlantraquinone. These five acids are Laccaic acid A, B, C, D and E, but the main major acids are Laccaic acid A and B (Laccaic acid A 71-96%; Laccaic acid B 0-20%) [2]. Laccaic acids are water soluble red dye of antraquinoid type structure. In Thailand, lac dye is used as a natural red dyestuff for cotton and silk dyeing [3]. Mordants can form complexes with the dye molecules via coordinate bonds, and different metal salts can be used as mordants in the process (e.g. potassium dicomate, tin chloride, and copper sulfate). These complexes are insoluble and hence improve the staining ability of a dye as well as increase its fastness [4]. Therefore, the water soluble dye can be converted into an insoluble pigment by making it into a lake. Carmine is red pigment used in foods and cosmetics and it is an example of lake pigment produced by reaction of natural cochineal (carminic acid) and aluminium salt. Carminic acid is an antraquinone type dye with a bright red shade, and is the most resistance to light-Induce-fading [5]. Thus, it is of interest to study the preparation of laccaic acid lake pigment which has not been extensively studied before. Therefore, the purpose of this work was to study the reaction of Thai lac dye and metal salts at different conditions such as pH, temperature, and reaction time. The properties of the resulting lake will be studied using various spectroscopy methods.

2. Experimental Procedure

2.1. Chemicals and Reagents

⁺ Corresponding author. Tel.: +66 53916843; fax: +66 5391 6831

E-mail address: ampa@mfu.ac.th

Deionized water (Milli-Q/Millipore, USA) was used for all preparations. Sodium hydroxide was of UNILAB, Philippines. Calcium carbonate was obtained from Chemex, USA. Calcium acetate monohydrate was of POCH SA, Poland. Aluminium potassium sulphate and aluminium chloride were of Ajax Fine Chem, Austria and Thai lac dye was purchased from Creasia mill Co., Ltd. Thailand. All chemicals were used as received.

2.2. Preparation of Lake Pigment

i) Effect of pH, temperature and reaction time. Thai lac dye (2g) was dissolved in 50ml of DI water and the pH of lac dye solution was adjusted from 2 to 11 using 1%w/v NaOH. 10ml of 10% w/v aluminium potassium sulphate was added and the reaction mixture were cooled to room temperature, filtered and incubated at 45 °C for 1 night and dry mass was determined. Moreover, effect of reaction temperature was studied at 50, 80, and 100 °C for 1h in suitable pH conditions. And, effect of reaction time was investigated at 1h and 2h.

ii) Effect of metal salt and its concentration. Four metal salts; aluminium potassium sulfate, aluminium chloride, calcium acetate monohydrate, and calcium carbonate were selected for this study. These metal salts were used in different concentrations, i.e. from 0.5 to 3.0g dissolved in 10ml of DI water and each of different metal salt was added into the reaction mixtures. Moreover effect of mixed metal salts for lake preparation was also prepared by selecting the pair of two metal e.g. aluminium potassium sulphate and calcium acetate monohydrate.

2.3. UV-VIS Spectroscopy

The mixture solution (1% v/v) was measured the wavelength in the range of 250 – 700 nm using UV-Vis spectrophotometer (Libra 522, Biochroms).

2.4. X-Ray Diffraction (XRD)

Powder XRD patterns were obtained at room temperature using XRD diffractometer (PANalytical/X'Pert Pro MPD), with Cu K α target tube, NaI detector, variable slits, a 0.050 step size, operated at a voltage of 30 kV, 15mA current, at 2theta (2 θ)/min scanning speed, and scanning angles ranged from 0 to 80°.

2.5. Fourier Transforms Infrared Spectroscopy (FT-IR)

The FT-IR spectra were obtained using FT-IR spectrophotometer (Perkin Elmer/FTIR Spectrum GX). The samples were mixed uniformly with potassium bromide at 1:100 (sample:KBr) ratio and incubated at 110 °C overnight. After that, the mixture was cooled down in desiccators. The KBr discs were prepared by compressing the powders (mixture of sample and KBr) in a hydraulic press. The discs were scanned in the range of 500–4000 cm^{-1} to obtain FT-IR spectra.

3. Results and Discussion

3.1. Preparation of Lake Pigment

3.1.1 Effect of pH

The Thai lac dye solution was prepared in 4% w/v concentration (pH 2.5 \pm 0.1). The effect of pH on preparing lake pigment was studied by adding different quantity of 1% w/v NaOH in the dye solution. The pH value of the mixture solution is ranging from 2.5 to 10.5. The color was changed from dark-red to dark-violet when the pH value changed from acidic to basic condition. It has been reported that depending on pH the color of anthraquinone-based compound may be a color in a spectrum from orange over red to purple [5]. Then, lake preparation was started by addition of aluminium potassium sulphate (10%w/v, pH 3.1 \pm 0.1) into each mixture solution and it was stirred at 50 °C for 1h, then cooled to room temperature and precipitates were filtered and dried at 45 °C. Yields were calculated from the dry precipitates compared with reactants, i.e. lac dye and the metal salt used. It was found that suitable pH is in the range of 3.5 to 4.5 because they are high in yield (29-65%). $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ reacted with the lac dye to form sedimentation which is less soluble in water. The metal ions can act as acceptors to electron donors to form co-ordinate bonds with the dye molecule, which is insoluble in water [3].

3.1.2 Effect of Temperature and Reaction Time

The effect of temperature was studied at 50, 80, and 100 °C, 1h. The pH of 3.5-4.5 which possessed higher yield was used for the study. Moreover, the precipitates were subjected to further wash by redissolving in DI water in order to remove some salt residues which may still present in the product. The precipitates before washing are higher in percent yield than after being washed (Table 1) which may indicate some salt contaminated and unreacted dye in the product. The data showed that higher temperature resulted in higher yield. When consider the same condition, i.e.10ml NaOH, at 50 °C showed lower yield (20.3%) and when the temperature increased to 80°C, yield slightly increased to 22.7% and further increased to 58.7% at 100 °C. The tendency of yield is in similar pattern for other pH conditions. In addition, effect of reaction time was compared between 1 and 2h, at 100 °C. It was found that the yields of all conditions (pH 3.5-4.5) increased about 12-20%. At this stage the best condition which gives highest yield is at pH 3.5±0.1 (15ml 1%w/v NaOH), and heating at 100 °C for 2h.

Table 1 Effect of temperature on preparation of lac lake pigment

Temp. (°C)	NaOH (ml)	Yield (%)	
		Before washing	After washing
50	10	44.0	20.3
	15	42.3	23.0
	20	60.0	27.0
80	10	30.0	22.7
	15	62.7	48.7
	20	71.7	45.3
100	10	108.3	58.7
	15	98.0	52.0
	20	75.3	46.3

Table 2 Effect of metal salt on preparation of lac lake pigment

NaOH (ml)	Yield (%)			
	(AlK(SO ₄) ₂ .12H ₂ O)	AlCl ₃	(Ca[CH ₃ COO] ₂ .H ₂ O)	CaCO ₃
0	-	61.3	75.3	93.0
15	83.3	48.6	84.6	100.3
20	74.3	22.6	84.6	93.0
30	-	23.6	88.3	106.6
40	-	23.6	85.6	106.6
50	-	80.7	91.0	99.0

3.1.3 Effect of Metal Salt and Its Concentration

Lake pigment used in food and cosmetic product is usually prepared in the form of aluminum or calcium lake which are already approved in issues of safety and nontoxicity [5]. Normally, the metal complexes of organic ligands exhibit light-fastness properties better than those of free ligands. This is due to the effect of coordination with a metal ion reducing the electron density at the chromophore, which in turn leads to improved resistance to photochemical oxidation [4]. Therefore, aluminium potassium sulphate (AlK(SO₄)₂.12H₂O), aluminium chloride (AlCl₃), calcium carbonate (CaCO₃), and calcium acetate monohydrate (Ca[CH₃COO]₂.H₂O) were used for study the effect of metal salt on lac lake preparation. The metal salts were prepared at concentration of 10% w/v, and each salt was added into the dye solution. Reactions of aluminum and calcium salts were differently performed. Aluminum lake was prepared by heating at 100 °C for 2h while calcium lake was reacted at ambient temperature, 30min. The precipitates of AlK(SO₄)₂.12H₂O and AlCl₃ lake are dark-red color. AlK(SO₄)₂.12H₂O gave brilliant, glossy and homogeneous product than that of AlCl₃ while Ca[CH₃COO]₂.H₂O and CaCO₃ give dark-violet precipitates, Ca[CH₃COO]₂.H₂O gives glossy and homogeneous product than that of CaCO₃. Although yield of CaCO₃ is higher (Table 2) but the complex is less preferred in aspect of appearance and color. Therefore, it can be noted that at 15ml NaOH, the lake prepared using AlK(SO₄)₂.12H₂O and Ca[CH₃COO]₂.H₂O showed good appearance and also high in percent yield (>80%). In addition, the concentration and mass ratio of dye/metal salt (AlK(SO₄)₂.12H₂O or Ca[CH₃COO]₂.H₂O) were studied. The mixture solution of lac dye (4%w/v lac dye and 15ml 1% w/v NaOH) was mixed with 10ml metal salt solution at different mass ratio in the reaction. The results showed that the highest yield when use AlK(SO₄)₂.12H₂O is at dye/metal salt ratio of 4 and at ratio of 2 for Ca[CH₃COO]₂.H₂O.

3.1.4 Preparation of Aluminum-Calcium Lake Pigment

Aluminum-calcium lakes has been prepared for using in foods, such as yogurt fruit preparation, beverages, other miscellaneous food products that may need a stable red color, and in cosmetics.¹ There are a number of particular technical advantages associated with the formation of colored metal complexes. Using

of aluminum mix with calcium is believed to be important for optimal lake formation [5]. The sequence of addition of metal salts may affect the formation of lac lake pigment. Therefore, the method of preparation of aluminium-calcium lake was studied. The dye solution is treated with the $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ under the suitable condition. Treatment of the aqueous solution with $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ compound may be performed in different ways. It may e.g. be performed by adding the $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ first and followed by adding $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ or vice versa. The results showed that, when $\text{AlK}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ was added first, the fine, glossy, and dark-red precipitates were obtained and when $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ was first added first, it gave less gloss and darker color product.

3.2. Characterization

3.2.1 UV-VIS Spectroscopy

The solubility and color shade of lac lake solution is depended on pH value and also it may affect preparation of lake pigment. Thus, the lac dye's solubility and color shade at various pH values was studied using UV-Vis spectroscopy. Lac dye contains electron-donating substituents (hydroxyl groups) in α and β positions. It is thus typical donor-acceptor structure, with the carbonyl groups as the acceptors and the electron-releasing auxochromes as the donors. The absorbance spectra of lac dye at different pH are shown in Fig. 1. The absorbance spectra shows the λ_{max} 489 nm, pH=2.58 (**1**, 0 ml NaOH) and showed bathochromic shift to λ_{max} 523 nm when pH of solution is 10.53 (**12**, 50ml NaOH). However, in the acidic region it is relatively insensitivity. The explanation is that oxygen atom of the quinone carbonyl groups in the 9-and 10-positions of the laccaic acid components of the dyes cannot be protonated because of intramolecular hydrogen bond formation with the hydroxyl groups in the 1-and 4-positions, respectively. At high pH, the phenolic and carboxylic acid groups in the anthraquinone dye components would be deprotonated. Resultant charge delocalization in the phenolate anions would lead to stabilization of the excited state with lowering of the energy of the transition [6]. The UV-VIS analysis was also studied in mixed metal complex solution; the aluminum and calcium lake pigment (Fig. 2). The addition of aluminum and calcium salt results in substantial change of the bands absorbing at the longest wavelengths, and these changes were characteristic of each metal ion. With calcium ion, the λ_{max} value of long wavelength absorption band was observed at around 524nm for $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ lake (**E**) and 529 nm for CaCO_3 lake (**D**). The λ_{max} value of approximately 483 and 490 nm were observed with aluminum ion for the $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ lake (**B**) and AlCl_3 lake (**C**). The λ_{max} at 518 and 521 nm was also present for aluminum-calcium lake (**F**), and calcium-aluminum lake (**G**) while Thai lac dye itself had a λ_{max} at 489 nm (**1**). It can be seen that the bathochromic shift occurs as a result of coordination by lone pair electrons on the N or O donor atoms with aluminum and calcium ion, thus stabilizing the excited state relative to the ground state leading to longer wavelength absorption maxima [6, 7].

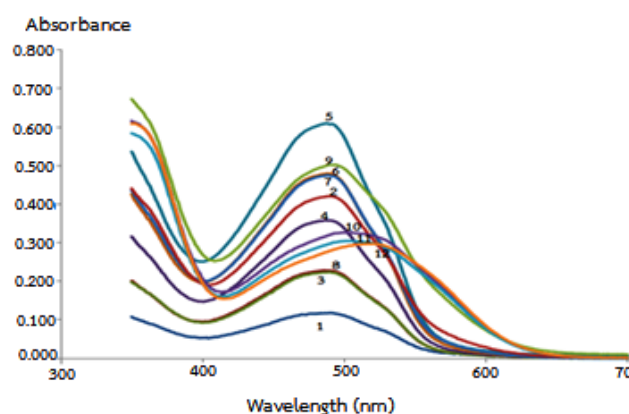


Fig. 1 UV-Vis spectra of lac dye at different pH (1) pH 2.58; (2) pH 2.86 ; (3) pH 3.29; (4) pH 3.53; (5) pH 3.63; (6) pH 4.40; (7) pH 5.18; (8) pH 5.89; (9) pH 6.14; (10) pH 8.48; (11) pH 9.65 and (12) pH 10.53

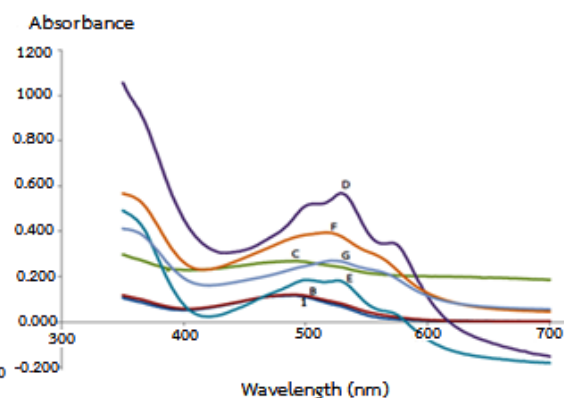


Fig. 2 UV-Vis spectra of Thai lac dye (1), $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ lake (B), AlCl_3 lake (C), CaCO_3 lake (D), $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ lake (E), aluminum-calcium lake (F), and calcium-aluminum lake (G)

3.2.2 Fourier Transforms Infrared Spectroscopy (FT-IR)

The lac dye (**1**) spectra showed vibration at 3131, 1621, 1710 cm^{-1} which corresponding to stretching vibration of $-\text{OH}$ or $-\text{NH}$, and $\text{C}=\text{O}$ or/and COOH group [8]. It also presents ring vibration around 1096 cm^{-1} (Fig. 3). It can be seen that the structure of Thai lac dye is mainly composed of $-\text{OH}$, $-\text{NH}$, $\text{C}=\text{O}$, COOH groups and aromatic ring of anthraquinone. The FT-IR spectrum of lac dye was changed after reacted with metal salt. Absorption band of lac dye at 3130 cm^{-1} shifted to higher frequency (3265-3440 cm^{-1}), indicating the $-\text{OH}$ or $-\text{NH}$ group may be taken in complexation.^{7,8} The COOH group at around 1710 cm^{-1} is shifted in **B** and **C** and disappeared in **E** and **D**. The $\text{C}=\text{O}$ group stretching (1621 cm^{-1}) is also changed. Moreover, the wavenumber of $\text{C}-\text{C}$ stretch and ring vibration at 500-1100 cm^{-1} also changed. FT-IR analysis was also performed in mixed-metal complexes; aluminum-calcium lake (**F**), and calcium-aluminum lake (**G**). The broad peak at around 3130 cm^{-1} corresponding to the stretching vibration of $-\text{OH}$ or $-\text{NH}$ group in lac dye shifted to higher frequency (3447 and 3439 cm^{-1}) in **F** and **G**.

3.2.3 X-ray Diffractometry (XRD)

The XRD pattern of Thai lac dye (**1**) exhibited its characteristic crystalline peak at around 5° , 15° and 26° . For aluminium lakes (**B** and **C**), the crystalline peak showed at around $27-28^\circ$. The XRD pattern of calcium acetate monohydrate lake (**E**) showed strong crystalline peak at around $27-28^\circ$ while that of calcium carbonate lake (**D**) crystalline peak at around $27-28^\circ$ was weakened and there are many of new diffraction peaks appeared instead. The XRD analysis was also performed in mixed metal complexes; aluminum-calcium lake (**F**), and calcium-aluminum lake (**G**) and the diffractograms are different from **1** as they showed crystalline peak at around $27-28^\circ$.

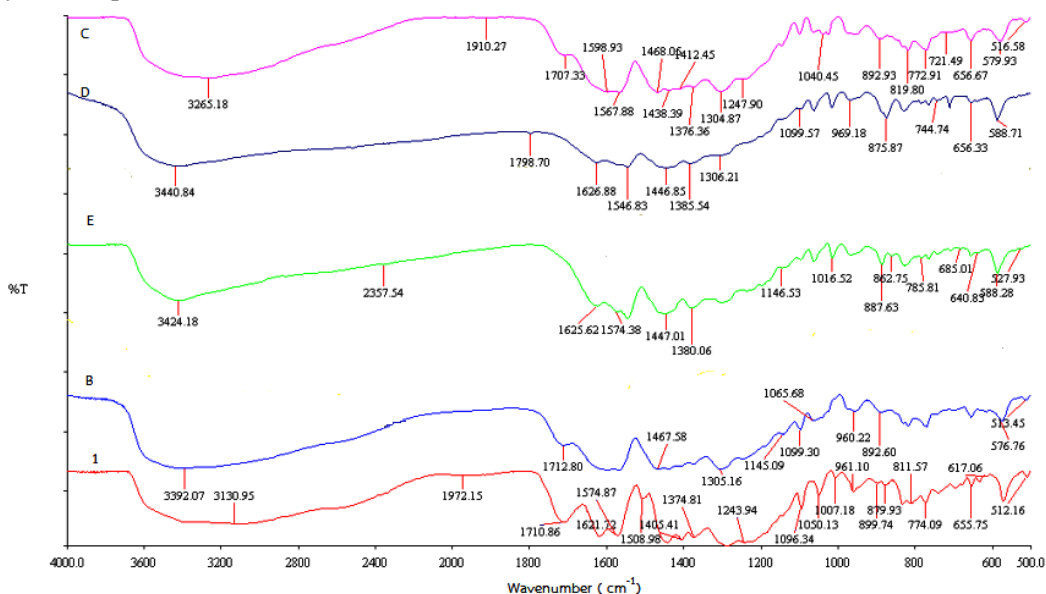


Fig. 3 FT-IR spectra of Thai lac dye (**1**), $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ lake (**B**), AlCl_3 lake (**C**), CaCO_3 lake (**D**) and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ lake (**E**)

4. Conclusion

The suitable condition for preparation of aluminium and calcium lake pigment from Thai lac dye is at pH 3.5 ± 0.1 , 100°C , 2h. $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$ showed more preferable property of lake pigment. The highest yield of $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ is at dye/metal salt ratio of 4 and at ratio of 2 for $\text{Ca}[\text{CH}_3\text{COO}]_2 \cdot \text{H}_2\text{O}$. When mixed-metal complex was prepared, the sequence of addition of metal salt affected the color and appearance of the lake pigment. The lac lake was characterized using UV-Vis, FT-IR and XRD technique. The analysis showed that the bathochromic shift of UV-Vis which may indicate a result of coordination by lone pair electrons on the N or O donor atoms with aluminum and calcium ion and this potential coordinating is also illustrated in FT-IR analysis. The new crystalline of lakes formed in XRD analysis also indicated the structure changed of lac dye after reacted with mixed metal salts.

5. Acknowledgement

The authors are grateful to the National Research Council of Thailand (NRCT) for financial support (Grant no. 55208050010). School of Cosmetic Science, Mae Fah Luang University is acknowledged for providing space and facilities.

6. References

- [1] Smith, R, and Wagner, S., (1991), “Dyes and the environmental is natural better”, *American Dyestuffs Reporter*, **80**, 32–34.
- [2] Erwin, E., (2008), “Characterization of historical organic dyestuffs by liquid chromatography-mass spectrometry”, *Analytical and Bioanalytical Chemistry*, **391(1)**, 33-57.
- [3] Kongkachuichay, P., et al., (2002), “Thermodynamics of adsorption of laccic acid on silk”, *Dyes and Pigments*, **53**, 179-185.
- [4] Taeko, N., and Keiko, M., (1980), “A study of lac dyeing with tin mordant”, *Kaseigaku Zasshi*, **31**, 19-23.
- [5] Jacobsen, S., et al, (2009) “Method for the preparation of a carminic acid lake”, US Patent Application Publication US2009/0025153 A1 (43).
- [6] Chairat, M., et al, (2004), “An absorption spectroscopic investigation of the interaction of lac dyes with metal ions”, *Dyes and Pigment*, **63**, 141-150.
- [7] Septhum, C., et al, (2007), “UV-VIS spectroscopic study of natural dyes with alum as a mordant”, *Suranaree Journal of Science and Technology*, **14**, 91-97.
- [8] J. Schmitt, H.-C., (1998), “FTIR-spectroscopy in microbial and material analysis”, *Flemming/International Biodeterioration and Biodegradation*, **41**, 1-11.