Chemical Characteristics of The Pigment Colorants Extracts from Gallnut of *Quercus infectoria*

Sa'idatul Najah Binti Ali Mohamed, Dr. Fazlena Binti Hamzah

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—An iron-gall ink is made with the tannin extracts (colorant components) from *Quercus infectoria* and is observed using UV-Vis spectrometer and was analyzed with Fourier transform infrared spectroscopy (FTIR). The aim of the study was to investigate the method of extracting the gallotannic acid from *Quercus infectoria* together with the production of iron-gall ink and characterized its properties. The UV-Vis analysis was successful in characterizing the ink and the maximum absorbance is obtained, whereas the FTIR analysis revealed the peaks of functional groups that presents in the ink. The UV-Vis spectrometer analysis shows the presence of the highest peak at 298nm. UV-Vis spectral data were mainly produced by the colorant components (i.e., dyes) found in the ink. While the FTIR data shows a broad peak at 3293cm^{-1}, indicating the presence of -OH stretch and also there is a presence of aromatic compound .**

***Keywords*— FTIR, Iron-gall ink, Quercus infectoria, UV-Vis spectrophotometer.**

I. INTRODUCTION

One of the natural remedy in dye synthesis is gallnut (*Quercus infectoria*) which naturally contains the mixture of gallotannin up to 60 – 70%, ellagic acid, starch and glucose. Ellagic acid is the content in the tannin of gallnut that is known to be the dyestuff of this natural source as it exhibits dyeing properties. It is because of its auxochrome group (-OH) together with other chromogen groups which responsible for the binding of the colour pigment on the surface of objects that are going to be dyed or coloured.

Inks consist of pigment or dyes that dispersed in a solvent either aqueous or organic. In general, compositions for writing ink consist of an inner portion of a metallic colour and outer portions of a dye stuff based colour. Ink analysis involved the inspection of documents using the naked eye, slanted lighting conditions and using special optical filters. It can be performed using optical, spectroscopic and chromatographic methods.

The aim of this research is to study more on the making of ink of black colour with the extracts of dye component from *Quercus infectoria* as well as to characterize the ink the tannin extracts from the gallnut *(Quercus infectoria)*. The making of ink sourcing from natural remedy is proposed is because to substitute the use of artificial inks and dyes that is widely used as it is not entirely safe to use. The analysis of this research study involves the use of UV-Vis spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

II. METHODOLOGY

A. Materials

1. Sample Preparation

Dried galls of *Quercus infectoria* were purchased from the local market. About 50 grams of the galls were crushed into small pieces by using a mortar and pestle and is then blended using an electric dry blender, producing a fine powder. 10 grams of the gall powder was accurately weighed in an electronic balance. The gall powder was then placed in a beaker and dissolved in a 75 ml of distilled water overnight to create a nice brown coloured solution (indicating the presence of gallotannic acid). The solution is then filtered through a filter paper in a funnel. 2.5 g of ferrous sulfate was dissolved in a 45 ml of distilled water. 2.0 g of Gum Arabic, also known as Acacia gum was dissolved in a 5 ml of distilled water. The brown solution of gallotannic acid was then added with the ferrous sulfate solution. After adding the ferrous sulfate to the solution, the colour turned from brown to black immediately. Gum Arabic solution was then added next, giving the ink some thickness as it serves as a binder for the ink.

2. UV-Vis Spectroscopic Analysis

All experimental spectroscopy was carried out on a LAMBDA™ 750 UV/Vis/NIR spectrophotometer from PerkinElmer and using plastic cuvettes with a path-length of 10 mm as the sample holder. Absorbance of the spectrum was recorded in the wavelength ranging from 200 to800 nm. The ink was used for UV-Vis analysis with distilled water as the blank solvent. Both the ink and the blank were analyzed in the same manner. From the absorbance data, the maximum absorbance from each sample of different concentration was obtained.

Figure 1: UV-Vis Spectrophotometer

3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The analysis that was carried out using the FTIR is by using the sample that is originally obtained when producing the iron-gall ink. Therefore, the sample used on the FTIR is liquid-based. The sample is first prepared, and is then dropped onto the sample holder. The equipment then collects a single-beam spectrum of the sample, which will contain absorption bands from the sample.

Figure 2: Fourier Transform Infrared (FTIR) Spectroscopy

Then, the data analysis is done by assigning the observed absorption frequency bands in the sample spectrum to appropriate normal modes of vibrations in the molecules.

III. RESULTS AND DISCUSSION

A. Ellagic Acid of Quercus infectoria

Gallnut (*Quercus infectoria*) naturally contains the mixture of gallotannin up to 60 – 70%, ellagic acid, starch and glucose [1]. Ellagic acid has the main colouring component in the gallnut extract, in which it has an affinity for dyeing substrates due to the presence of the auxochrome group (-OH) in it (Aijaz Ahmad, et al. 2012). Other than being a substance in dyeing, *Quercus infectoria* is also found to display a various pharmacological properties such as antiviral, antifungal, astringent, anti-diabetic, anaesthetic, anti-inflammation, larvicidal, wound-healing as well as antibacterial properties [1].

During the sample preparation, the extracts of *Quercus infectoria* has the brown coloured solution after it has been soaked in water overnight, this is due to the presence of gallotannic acid. Gallotannin is hydrolysed to gallic acid and glucose.

Figure 3: Powdered gallnut (*Quercus infectoria*)

Figure 4: Filtered Extracts of *Quercus infectoria*

B. Production of Ink

During the making of the iron-gall ink, it was observed that after adding the ferrous sulfate to the solution, the colour of the solution turned from brown to black immediately. This is because of the reaction of gallic acid. The gallic acid reacts with ferrous cations in which together they make ferrous gallate, which appears black in colour.

$$Gallic\ Acid + Ferrous\ Cation \rightarrow Ferrous\ Gallate$$

When the ink is used to write on paper, on the first few seconds, the ink appears in some kind of a translucent greyish brown, however, after a few more seconds, the colour of the ink on the paper gradually turned into deep black colour. It is also observed that the ink appears to be in blue-black colour when place in a bottle as can be seen in the figure below.

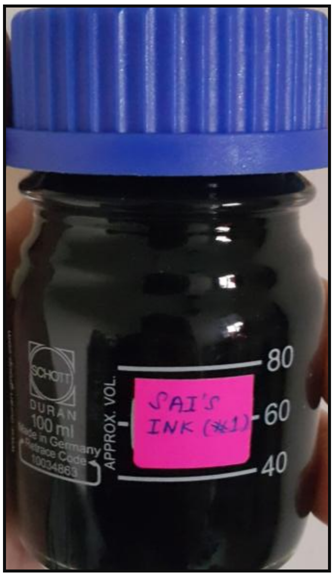

Figure 5: Iron-gall Ink

This happens due to the reaction of ferrous gallate with the presence of oxygen from the air. The black colour of iron gall ink comes from ferric pyrogallate, in which the Fe^{2+} is oxidized to Fe^{3+}.

$$Ferrous\ Gallate + Oxygen \rightarrow Ferric\ Pyrogallate + Water$$

C. Analysis of UV-Vis Spectroscopy

The ink made with the main colorant component from the extract of *Quercus infectoria* was examined by a LAMBDA™ 750 UV/Vis/NIR spectrophotometer from PerkinElmer in the wavelength ranging from 200 to 800 nm. It can be seen in Figure 2 that it shows the absorbance spectra from four samples of ink, each with different concentration as tabulated in Table 1. All of the ink samples showed one maximum absorbance peak in the wavelength range of 290 to 330 nm. Sample 1 showed the highest absorbance at wavelength 298.37.03 nm, Sample 2 at 296.74 nm, Sample 3 at 318.18 nm and lastly, Sample 4 at 327.99 nm.

Table 1: The concentration of each sample

Samples	Concentration (mM)
Sample 1	0.01
Sample 2	0.02
Sample 3	0.03
Sample 4	0.04

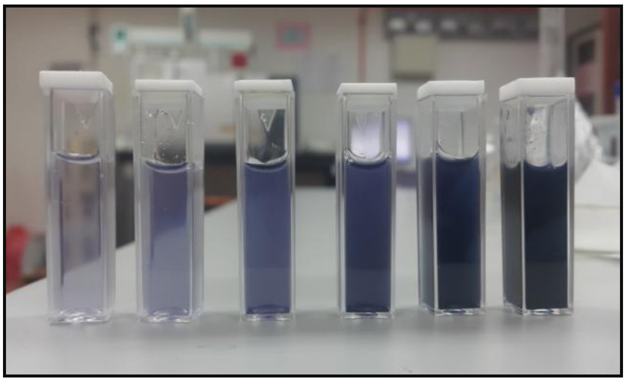

Figure 6: Ink Samples of Different Concentration (From left: Blank, Sample 1, Sample 2, Sample 3 and Sample 4)

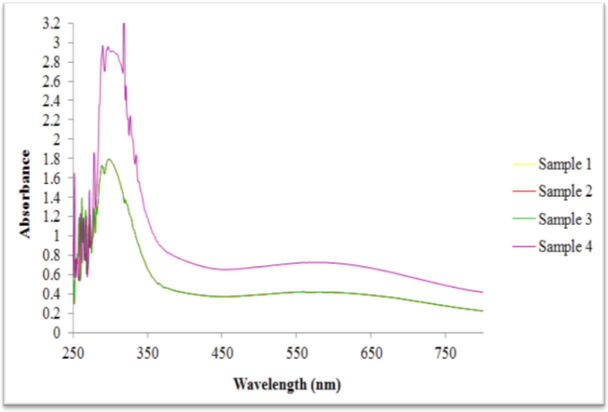

Figure 7: Graph of absorbance against wavelength (200-800 nm) of four different concentration of ink samples

The UV-Vis spectrum is usually measured in very dilute solutions and the most important criteria in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. It is known that water, ethanol and hexane are the most commonly used solvents as each is transparent in the region of UV-Vis spectrum, hence, water is used as the solvent for the analysis of UV-Vis in this study. For highly pure, non-polar solvents, they do not interact with solute molecules either in the ground or excited state. On the other hand, polar solvents such as water, may stabilize the molecular orbitals of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may be different than that of hydrocarbons. In the case of n $\rightarrow$ π^* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules are more ready than that of their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. The group of atoms containing electrons responsible for the absorption is called chromophore. Amongst the transitions of electrons that are available, the most studied transitions are n $\rightarrow$ π^*, as this type of transition absorbs at relatively longer wavelength of 280-300 nm. This is the type of transition that is shown in Figure 7, in which the average lambda max of all the samples is at 298 nm.

UV-Vis spectra are known generally to show the information mainly about the major dye component. In the previous studies, it has been stated that most of the major dye components of inks have maximum absorption at wavelength more than 500 nm [18-20], as the spectrum of colours starts with 400 nm in which it shows the spectrum of violet. As the ink samples maximum absorbance was all scanned at the wavelengths of below 500 nm, it is concluded that it only shows information about the other components of the ink than the major dye components, such as, additives. Additives are usually used to finely modify the characteristics of the ink, in this study; it would be the Gum Arabic, which serves as the binder for the ink.

D. Analysis of Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectrum for each sample was recorded in the range of 515 cm^{-1} to 4000 cm^{-1}. The IR spectra for the ink sample showed a broad peak at 3000 cm^{-1} to 3600 cm^{-1}. This indicates the presence of the NH_2 group in the ink formulations. This is because the tannin extract of *Quercus infectoria* that is the main substance of the ink has an amine group. There are three peaks that can be observed on the graph, which are at the wavelength of 3293.53 cm^{-1}, 2167.68 cm^{-1} and 1636.18 cm^{-1}.

From the graph, a broad peak can be seen in the range of 3000 cm^{-1} to 3700 cm^{-1} indicating the presence of CH_2NH_2 group in the ink sample, it can also indicates the presence of an -OH stretch. When a hydrogen atom from an aliphatic hydrocarbon is replaced by an OH group, new bands corresponding to new OH and C-O band absorption appear in the IR spectrum. A medium to strong absorption band from 3700 to 3000 cm^{-1} (see figure 8) is a strong indication that the sample is an alcohol or phenol. Similar result can be seen with the presence of NH or moisture. The exact position and shape of this band depends largely on the degree of H-bonding.

The bands considered to be of most help in diagnosing the aromatic character of the compound appear in the region 1650-1100 cm^{-1}. At about 1600, 1585, 1500 and 1450 cm^{-1}, there are normally four bands in this region and are due to C=C in-plane vibrations. The combination and hint of bands in 2170-1640 cm^{-1} region are also characteristics of aromatic rings. In addition, they are very weak and are observed only in the case of concentrated solutions of highly symmetric benzene derivatives.

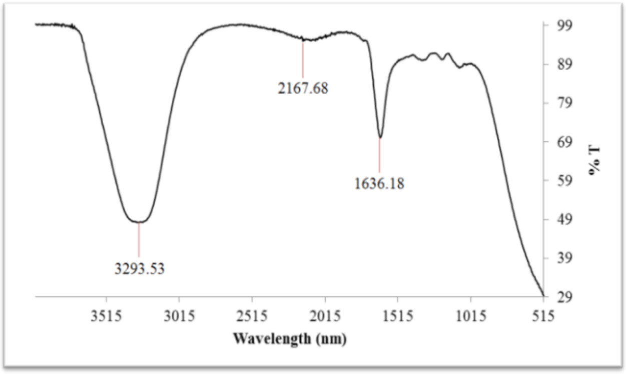

Figure 8: Graph of FTIR reading (percentage of transmittance against wavelength) with three labeled peaks

IV. Conclusion

UV-Vis analysis shows that the ink samples which are Sample 1, Sample 2, Sample 3 and Sample 4 displayed one highest peak at the wavelength in the range of 290 to 330 nm. As for the FTIR analysis, there are three peaks which are 3293.53 cm^{-1}, 2167.68 cm^{-1} and 1636.18 cm^{-1}. A broad peak is seen at 3000 cm^{-1} to 3700 cm^{-1} indicating the presence of CH_2NH_2 group in the ink sample, it can also be an -OH stretch and also there is a presence of aromatic compound indicated by the other two peaks.

Acknowledgment

Thank you to my supervisor, Dr. Fazlena Binti Hamzah, for sharing her words of wisdom during the course of this research and provides me with insight and expertise that greatly assisted the research works, although any errors are our own and should not tarnish the reputations of this esteemed person. I would like to acknowledge with gratitude to all the science officers from chemical engineering and bioprocess program, Faculty of Chemical Engineering, Universiti Teknologi MARA for the support, equipment and facilities provided. Finally, I am also grateful for the support from my family and a number of friends in encouraging me to start the work and persevere with it.

References

[1] Aijaz Ahmad, Ahmad, et al. "Dyeing, Fastness and Antimicrobial Properties of Woolen Yarns Dyed with Gallnut (Quercus infectoria Oliv.) Extract)." *Dyes & Pigments*, 2012: 53-61.
[2] Alberta Cecilian, Terence Brett. *English for graphic arts and communication.* Tangram Ediz. Scientifiche, 2009.
[3] Baird, Henry Carey. *The Manufacture of Ink: Comprising The Raw Materials, And The Preparation Op Writing, Copying, And Hektograph Inks, Safety Inks, Ink Extracts And Powders, Colored Inks, Solid Inks, Lithographic Inks And Crayons, Printing Ink, Ink Or Aniline Pencils, Marki.* Philadelphia, USA: The Collins Printing House, 1892.
[4] Engineers, NIIR Board of Consultants &. *Modern Technology of Printing & Writing Inks (with Formulae & Processes) 2nd Revised Edition.* Delhi: ASIA PACIFIC BUSINESS PRESS Inc., 2016.
[5] Kyung, Hwa Hong. "Preparation and Properties of Multi-Functional Cotton Fabric Treated by Gallnut Extract." *Textile Research Journal*, 2014: 1138–1146
[6] Myers, Vera. "Native American, Navajo Sampler of Vegetal Dyes Used in Navajo Weaving." *CulturalPatina*, 2016.
[7] Narayan, Divya. "Biochromography - Ink Synthesized from Natural Sources." *Biotech Articles*, 2016.
[8] O. , Deveoglu, Torgan E., and Karadag R. "Identification By RP-HPLC-DAD of Natural Dyestuffs from Lake Pigments Prepared with a Mixture of Weld and Dyer's Oak Dye Plants." *Journal of Liquid Chromatography & Related Technologies*, 2012: 331-342.
[9] Pereira, Jonathan. *The Elements of Materia Medica and Therapeutics, Vol. II, 3th American ed.* 1854.
[10] *Quercus infectoria, Olivier.—The Gall, or Dyer's Oak.* Henriette's Herbal, 1995 - 2016.
[11] R., Divya Lekshmi, and Ravi D. "Extraction Of Natural Dyes From Selected Plant Sources And Its." *International Journal of Textile and Fashion Technology (IJTFT)*, 2013: 53-60.
[12] Raftery, Andrew. "Making Iron Gall Ink." *RISD Museum*, 2013.
[13] Sari, Ahmet, Mustafa Soylak, and Adam Onal. "Ellagic acid from gallnut (Quercus infectoria): Extraction and determination of." *Journal of Scientific and Industrial Research*, 2005: 491-495.
[14] Schönig, Dr. Hanne. "Yemeni Women's Body Painting with Black Gall Ink." *Henna Tribe*, 2002: 1-6.
[15] Tohma, Sakura. *Making & Testing Iron Gall Ink.* Sussex, 10 March, 2015.
[16] V., Yamuna, and Sudha S. "Antimicrobial Activity of Fabrics Treated with Quercus infectoria." *Biotechnology, An Indian Journal*, 2013: 231-235.
[17] Y., Yildiz, Gunes A., Karadag R., and Yalcin B. "Natural Pigments from the Gall Oak (Quercus infectoria Olivier) Shellac." *Asian Journal of Chemistry*, 2013: 6881-6884.
[18] Thanasoulias, N. C., Parisis, N. A. & Evmiridis, N. P. (2003) Multivariate chemometrics for the forensic discrimination of blue ball-point pen inks based on their Vis spectra. *Forensic Science International* 138(1-3): 75-84.
[19] Lee, P.. & Di Gioia, A.. (2005a). Acquity UPLC seapration of triarylmethane ink dyes (part 1). Waters Corporation, Application note 720001262EN.
[20] Hofer, R. (2004) Dating of ballpoint pen ink. *Journal of Forensic Sciences* 49(6): 1353-1357.

1

FAKULTI KEJURUTERAAN KIMIA
UNIVERSITI TEKNOLOGI MARA

MANUSCRIPT APPROVAL FORM FOR FINAL YEAR PROJECT II (CGE691)

Semester : 8

Course Title : Research Project II Course Code: CBE 694

Student's Name : SA'IDATUL NAJAH BT. ALI MOHAMED Matric No. : 2013868706

Project Title : CHEMICAL CHARACTERISTICS OF THE PIGMENT COLORANT OF GALLNUT (Quercus infectoria)

Supervisor's/ Examiner's comments:

please re-do discussion on the uv-vis part. Rewrite the conclusion according to ur finding. Please improve the manuscript before submission of the final..

Supervisor's/ Examiner's signature and stamp :

DR FAZLENA HAMZAH
Head of Studies Centre
(Bioprocess Engineering)
Faculty of Chemical Engineering
Universiti Teknologi MARA
40450 Shah Alam

Date : 4/6/17