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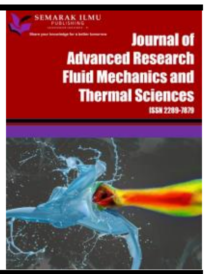

Application of Avocado Seed as Textile Natural Dye

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ABSTRACT

Organic waste that accumulates and underutilized can cause environmental pollution. Among the organic wastes that can be utilized is avocado seed waste (Persea americana mill). Avocado seeds contain anthocyanins which have the potential to give red to purple colour so that they have the potential to be used as natural dyes for textiles. This study aims to determine the quality of colour strength, the quality of colour fastness to soap washing and the quality of colour fastness to sunlight. In this research, effect of mordant types (alum, lime and ferrous sulphate) to colour strength and colour fastness were investigated. The natural dye was hot extracted from avocado seed. Maintaining extraction and dyeing processes variables, the samples were then analysed using spectrophotometer to obtain the colour strength data. Gray scale was used to assess the colour difference due to colour fastness of washing and sunlight. Experiment results showed that ferrous sulphate generated the darkest colour of R% 88.07 with very dark criteria. Colour fastness to washing was not affected by mordant type thus provided the same value of moderate. Meanwhile, the best colour fastness to sunlight was given by system with ferrous sulphate mordant with good criteria.

1. Introduction

During the transformation of raw textile fibres into finished materials, dyeing and printing processes are applied thus much increased the appearance of textile fabrics. In the dyeing process there is a reaction between a dye and a fibre, and the dye mobility into the internal part of the fibre. In general, a dyeing process includes adsorption (dyes transport from the aqueous solution onto the fibre surface) and diffusion (dyes diffusion into the fibre) processes. Besides direct absorption, dyeing process also requires dyes precipitation inside the fibre (as occur in the dyeing using vat dyes), or chemical reaction with the fibre (as occur in the dyeing using reactive dyes). As part of colouration processes, printing can be considered as partial dyeing with various colours on fabric surface to form a designed pattern [1]. Current issue in the application of synthetic dyes revealed that used synthetic

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dyes directly dissolved and discharged into the environment potentially carcinogenic effect [2-5]. It is therefore, studies on the utilisation of natural resources as dyes have been done [6-8].

One of the organic wastes that accumulate and can be utilized is seed waste from avocados. Avocado seeds are one of the groups of organic waste because the seeds from avocados are usually just thrown away and there is no use by traders or consumers. Avocado fruit is only used for avocado flesh for consumption by the residents. Due to the abundant and sustainable production of avocados, it creates organic waste that accumulates without utilizing waste. Actually, avocado seeds have various benefits for beauty, body health and as a natural textile dye. It was reported that avocado seeds contain phytochemicals include flavonoids, tannins, saponins, phenolics, antioxidant capacity, oxalates, phytates, and alkaloids [9]. Through the extraction method, avocado seeds can be used as natural dyes because they contain tannin pigments. In addition to avocado seeds, other parts of avocado can also be used for natural dyes such as avocado leaves, avocado tree bark and avocado skin.

Utami *et al.,* [10] examined the effects of solvent concentration and extraction time to the yield of dye extraction from avocado seeds. UV-Visible Spectrophotometry showed that the avocado seeds contain flavonoids while GC-MS revealed the major compound in avocado seeds is methyl ester ($C_{15}H_{26}O_2$). The compound contains a chromophore, such as a carbonyl group (C = O) which is a common feature of flavonoids.

Arlene *et al.,* [11] investigated the effects of temperature and feed to solvent ratio toward yield, colour intensity, and phenolic content of avocado seed under ultrasonic assisted extraction. It was found that temperature and feed to solvent ratio gave no effect to yield, phenolic content, and colour intensity. The highest yield of 22.6% was obtained by system with temperature extraction of 70^{o}C and feed to solvent ratio of 1:12. GC-MS analysis revealed the availability of furfural compound that assumed to generate orange colour.

Extraction of natural sensitizers from avocado peel was done using ethanol as solvent [12]. Analysis using UV-Vis generated maximum absorption peak as well as energy band gap information of 665 nm and 1.87 eV, respectively. The efficiency of natural sensitizers was about 48.25×10-12 %. It was also showed that functional group in avocado peel dye was in the range of 800 cm^{-1} to 3800 cm^{-1}. Based on the element analysis, avocado peel was categorized as anthocyanin group. GC-MS analysis showed the existence of O-H of hydroxyl group, C=O of carboxyl group and a strong peak of C-O-C ester at 3336 cm^{-1}, 1654 cm^{-1} and 1049 cm^{-1}, respectively. Furthermore, stretch band of C-O ester was visible at 1391 cm^{-1}. Lastly, two peaks at 2973 cm^{-1} and 879 cm^{-1} indicated the C-H group.

Study on the cotton and wool fabrics dyeing using avocado seeds and peels extract was done [13]. The fabrics were pre-mordanted with nontoxic metallic salts; alum and ferrous sulphate. The research provided very good washing and rubbing fastness. Fabrics pre-mordanted with ferrous sulphate possessed a different colour as well as better dyeability and light fastness. Only a slight change in chroma and hue was evidenced in the system with alum mordant. It was concluded that the natural dyes provided strong affinity to protein fibres and a relatively lower affinity to cellulosic fibres. Darker colour was observed in the samples dyed using avocado peel extract. Moreover, a more persistent hue and higher light fastness were also obtained compared to that of dyed with avocado seed extract.

It was found that avocado leaves can be used as natural dyes. Under spectrophotometer analysis at 614 nm, the Soxhlet extraction method was able to yield 68.07% at pH 4.49 and tannin of 22.07 % [14]. However, application of avocado leaves extract has its own drawbacks. Excessive use of avocado leaves will affect the growth of avocado trees. It is therefore, application of avocado leaves for natural dyes should be minimised. Except avocado seeds, avocado peel is another unused part of avocado that potential to be used as natural dyes. Phytochemicals analysis found that avocado peel contains secondary metabolites of flavonoids, tannins and anthocyanins. Avocado peel has proven to be used as natural dyes of cotton fabric [15]. It was reported that avocado production in 2018 was 410,094 tonnes [16]. Avocado consists of pulp (65–72%), stone (20–21%) and peel (7–15%) [17]. In avocado, pulp is the only usable portion, it is commonly freshly consumed. Considering the huge amount of unused avocado seed of about 82,018 tonnes/ year, there is still a lack of utilization. Among the efforts to reduce the impact of waste, avocado seeds are used as natural dyes on fabrics. Anwar *et al.,* [18] reported the utilization of avocado seeds as antioxidant tea. Another application of avocado seed was studied by Novelina *et al.,* [19] as a mixture of modified cassava flour in cookies production.

Depends on the cultivar, an avocado seed could contain about 74.47% of its dry weight [20]. This fact provides the potential of avocado seeds as natural dyes. Avocado seed could be extracted as natural dyes by firstly cut the avocado seeds into small pieces. This process ensures the starch to be crushed and the colouring matter to be released. Although previous studies on application of natural resources as textile dyes have been done [7, 8], utilisation of avocado seeds as natural dyes needs to be explored. The seeds of ripe black-purple avocado were used. High quality primissima cotton fabric was utilised in the dyeing process. Based on the background, application of avocado seed as natural dyes is reported. Dyeing quality is determined by colour strength and colour fastness.

2. Methodology

2.1 Materials

Avocado seeds were applied as sample of natural dyes. Deionized water was used for all of the solutions preparation. Commercial cotton fabric, sodium carbonate, Turkey red oil (TRO), alum, lime, and ferrous sulphate were purchased in local stores.

2.2 Procedure

Experimental research was conducted by preparing natural dyes from avocado seeds by extracting them through a pre-mordanting process with alum mordant, lime and ferrous sulphate. The mordant used were varied, i.e., alum, lime and ferrous sulphate. Colour strength, colour fastness from washing and sunlight were defined by the mordant types. During the experiment, the avocado seeds, cotton fabric, dyeing technique (pre mordanting, fixation, hot extraction), dyeing frequency 15 times, immersion time 10 minutes, fixation time 10 minutes were maintained as control.

Deionized water was used to dissolve TRO at a concentration of 2 g/L, and the resulting solution was utilised to soak the fabrics for 24 hours before washing and air drying. The mordanting agents, such as alum, ferrous sulphate, or lime, were dissolved in deionized water at a concentration of 50 g/L to produce the mordanting solution. After giving the solutions 24 hours to settle, the clear solutions were taken to begin the mordanting procedure. Each mordanting solution was applied to the fabrics for 12 hours, after which it was cleaned and allowed to air dry.

To remove contaminants and assure size uniformity, the ground avocado seed was sieved. The ratio of the ground avocado seed to deionized water was 1:5. The resultant solution was heated until it had boiled out half of its original volume. The solution was also given time to settle. To ensure that the solution was clear, the clear solution was taken and filtered. The fabrics were then soaked in an extract of avocado seed for 15 minutes at a volume ratio of 1:20. The process was done 15 times: the fabric was drained, dried, and then soaked in the dye bath.

After being dyed using avocado seed extract, the samples were tested with a UV-PC spectrophotometer model ISR-2200. The colour strength was determined using the maximum wavelength, in which the reflectance (R%) reaches the lowest value. Smaller value of R% indicates the darker colour. If the reflectance value (R%) is converted into a percentage transmittance (T%), then the maximum wavelength is at the highest T% value. Colour fastness was analysed using grey scale. The grey scale is made up of pairs of grey chips with colour differences ranging from 1 to 5. The categorization is established by the pair of grey chips on the scale that display a contrast equal to that between the original dyed specimen and the exposed specimen. Gray scale ratings were made by comparing the dyed specimens to the scale under standard lighting [21].

3. Results

3.1 Colour Strength

Table 1 shows the colour strength of cotton fabric dyed using avocado seed extract under various mordanting agents.

The pre mordanting experiments revealed that cotton fabric mordanted with 5% ferrous sulphate solution showed better effects on colour strength compared with other pre mordanting agents. Higher colour strength could be due to stable dye complex formed on the fabrics [22]. Study of Khan *et al.,* [22] exhibited the dyeing quality of cotton under various types of mordanting agents. At concentration of 5%, the colour strength was in the order of tannic acid < copper < alum < ferrous sulphate. This trend was consistent to the finding of this study. In other study [23], application of alum as mordant was given in pre mordant and post mordant process. The pre mordanted cotton fabric dyed with extract of turmeric provided better quality than that of the post mordanted.

Table 1
Colour strength

Mordant	Colour Strength		Criteria
	R%	T%	
Alum	68.49	31.51	Moderate light
Lime	63.74	36.26	Moderate light
Ferrous sulphate	11.93	88.07	Very dark

3.2 Colour Fastness to Washing

Experiments on colour fastness to washing were done under three types of mordanting agents, i.e. alum, lime, and ferrous sulphate. At mordanting agents concentration of 5%, the results of colour fastness for all mordanting agents were the same, as given in Table 2. Better colour fastness to washing was obtained by Bhatti *et al.,* [23] by applying alum mordant in the same concentration of 5%. Their research reached higher colour fastness of 4. It may due to the application of gamma radiation process applied in the research. The treatment could increase fibre resistance to shrinking and wrinkling, speed up the rate of dye absorption, increase the absorbed dye on fibres, and enhance the colour of the dyed fabric [24]. However, study of Khan *et al.,* [22] indicated non optimal concentration of mordanting agent. It was revealed by lower colour fastness than that of Bhatti *et al.,* [23] regardless the use of gamma radiation. In another study, application of eucalyptus as natural dye on cotton fabric generated washing fastness of 4 despite the absence of mordanting agent.

Table 2
Colour fastness to washing

Mordant	Colour Fastness	Criteria
Alum	3	Moderate
Lime	3	Moderate
Ferrous sulphate	3	Moderate

3.3 Colour Fastness to Sunlight

Another quality test done in this research was colour fastness to sunlight, the results are shown in Table 3. The best colour fastness to sunlight was obtained by the system mordanted using ferrous sulphate, with good level. Alum and lime pre mordanted fabrics resulted in moderate level of fastness to sunlight. Study of Uddin provided better results [25]. Applying extract of onion outer skin on silk fabric, the colour fastness to light got score of 6 and 4 for ferrous sulphate and alum mordants, respectively. Higher affinity of ferrous sulphate to dye than that of alum leads to better bounding with dye molecules. Although the mordanted fabrics with all types of mordanting agents have the same number of dye molecules ruined by light, fabric mordanted with ferrous sulphate resulted in the least fading. This is due to the deeper shades of fabrics by a greater number of dye molecules absorbed in the fabrics. Application of various mordanting agents proved that in a single mordanting process on silk, the order of colour yield was found to be ferrous sulphate > tartaric acid > tin > tannic acid > alum. It means that colour yield gradually decreased when approached from ferrous sulphate to alum. Increment of K/S values by mordanting process exhibits the capability of dye molecules in forming metal complex with the positively charged metals. In the silk fibres dyeing, dye anions and metal cations have strong appeal towards positively charged amino and negatively charged carboxyl groups, severally. It is therefore, as they enter the fibre, ionic bonding between dye and fibre was formed, followed by bonding of metal and fibre; and finally bonding of dye and metal ions. The dye-metal chelates thus generated also establish coordinate bonds with the uncharged amine (–NH2) groups of silk. Furthermore, there is a bonding formed by one molecule of dye and one site of fibre molecule. However, one mordant molecule can bond to two or more dyes molecules. Consequently, the binding of mordant molecule and fibre could hold two dyes molecules. It resulted in the increase of colour yield.

Table 3
Colour fastness to sunlight

Mordant	Colour Fastness	Criteria
Alum	3	Moderate
Lime	3	Moderate
Ferrous sulphate	4	Good

The transition metal formed a complex that able to protect chromophore from photolytic degradation, ensue the excellent light fastness. The chromophoric group absorbed photons, released their energy by resonating within the six-membered ring that was produced, accordingly, it prevents dye downgrade.

Avocado seed extract can be used as a natural dye on cotton fibre because it contains anthocyanin pigments. The chemical nature of anthocyanins is a change in colour because they are sensitive to pH and heat, anthocyanins will produce orange, red and purple colours. In dyeing with natural dyes, it is necessary to use a substance that can increase the strength of the colour called a mordant. The mordant used in this study were alum, lime and ferrous sulphate. In addition to increasing the colour strength, mordant also serves to change the colour direction of natural dyes.

The results of the colour strength on primissima cotton fabric dyed with avocado seed extract generated different colours according to the type of mordant. Fabric samples from avocado seed extract pre mordanted using alum produced a very light red colour and the brightest colour, because the chemical properties of alum which has acidic properties when reacted to anthocyanins. While the sample pre mordanted using lime generated pink because the chemical properties of lime. The reaction between lime and alkaline changed the colour to light reddish. Samples pre mordanted in ferrous sulphate mordant gave the darkest colour, i.e., blackish purple because the ferrous sulphate contains iron, sulphur and oxygen.

Mordants are crucial for enhancing fabric colour. Different ratios of the utilised mordants generated certain range of hues. The variety of hues could be generated by the same dye when it was treated with various mordants was astounding, but each mordant had a specific range of hues that it could produce. Only alum and tin produced bright, clear yellows; chrome produced yellow-golds or oranges; copper produced yellow-greens; and iron produced various shades of brown. In the past, dyers had to decide between lightfastness and their preferred hues. The chromemordants present a middle ground. In comparison to dyeing produced with alum or tin mordants, they offer dyeing with good lightfastness and only marginally duller yellows or gold tones [21]. The study revealed that the degree of colour shift was significantly influenced by the mordant's elemental composition. Alum and tin mordants caused the most colour change, whereas chrome, copper, and iron mordants caused the least amount of colour change. With alum and tin mordants, the overall colour shift was at least three times greater than with any other mordant.

Pruthi *et al.,* [26] showed that alum enhanced the dye absorption in the silk dyeing with barberry bark under various mordant combinations. The mordanting process was carried out simultaneously. As previously mentioned, alum outperformed ferrous sulphate and chrome in terms of the percentage of colour absorption. It was also reported that application of mordants combination resulted in slight improvement in fastness properties as compared to single mordant. The obtained shades were also brighter and deeper in comparison with single mordant. On the basis of this study, it can be concluded that it is recommended to proceed silk dyeing using simultaneous mordanting method as it gave maximum dye absorption. It was also proven that alum enhanced the dye absorption thus it should be used in combination with other mordants

Based on the results of the colour fastness test against soap washing on the utilisation of avocado seed extract, alum mordant, lime mordant and ferrous sulphate mordant, it resulted in a score of 3 with fairly good criteria. The mordant process which is only carried out at the beginning (pre-mordanting) affects the level of colour fastness to washing because the anthocyanins contained in the dye solution from avocado seeds that have been attached to the cotton fibre are not colour locked after dyeing so that the colour is easily separated from the fibre.

Based on the results of the colour fastness test against sunlight, the immersion of avocado seed extract on ferrous sulphate produced a better value than alum mordant and lime mordant. Ferrous sulphate mordant showed good criteria with a score of 4 while alum and lime with a value of 3 were quite good criteria. Overall, it generated an average value of colour fastness to sunlight which is quite good against sun exposure.

4. Conclusions

The results of the descriptive analysis showed that the darkest colour strength results were in ferrous sulphate mordant with R% 11.93. The results of the colour fastness test from washing soap showed that alum, lime and ferrous sulphate mordant produced a value of 3 with good enough criteria, the results of the colour fastness test against sunlight showed mordant alum and lime produced a value of 3 with moderate criteria and mordant ferrous sulphate resulted in a value of 4 with good criteria. The conclusion of this study is the quality of colour strength showed the good criteria for strength and the average fastness test.

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