https://doi.org/10.24867/GRID-2024-p85 Original scientific paper

PREPARATION OF ECO-FRIENDLY INKS FOR PRIMARY & SECONDARY PACKAGING

Madhan S, Nirmala JP, Kanchana M
Anna University, College of Engineering, Department of Printing and Packaging Technology, Guindy, Chennai – 600025, India

Abstract: *In this period of the 21st century we can see synthetic pigments everywhere. The primary reason for the widespread use of such synthetic chemicals is that they are cheaper than natively generated substances. The goal of this work is to create ink using an eco-friendly pigment produced from Indian-Almond leaves. In general, the prints over the FMCG packages are to communicate the people about the product inside the packages without. The organic pigments have been extracted from the Indian-Almond leaves at various stages of maturation using an aqueous extraction method. Furthermore, the pigments are combined with solvents, binders, and printing paste to apply the ink to the substrate's surface. These are non-toxic and commonly utilized in FMCG Packages. This allows us to boost the use of eco-friendly inks in FMCG packaging instead of synthetic chemicals-based inks.*

Key words: Natural pigment, Eco-friendly, Terminalia Catappa, Almond leaf, Non-toxic ink, Printing inks.

1. INTRODUCTION

The Chinese and Egyptians, since ancient times, have been using colour pigments on a larger scale. Chlorophyll is a green pigment, along with other coloured pigments in plants, which takes part in photosynthesis for the absorption of as much light energy as possible. Plant pigments are very diverse compounds like porphyrins, carotenoids, anthocyanins, and betalains. Plants, animals, and minerals are the origin sources of pigments. The six carotenoids found in plants include lutein, beta-carotene, zeaxanthin, antheraxanthin, violaxanthin, and neoxanthin. All of these have non-toxic short-term and long-term toxicity profiles, which therefore pose no risk to humans even upon long-term ingestion and have no adverse impact on health. Furthermore, poisonous pigments of plants have not been detected in any extract from plant species.

Carotenoids are a class of liposoluble plant pigment which has a characteristic appearance in three colours such as red, yellow, and orange. The unusual, conjugated double-bond structure of the molecules determines the colour difference. Water and organic solvents such as acetone, methanol, ethanol, and isopropanol are effective in extracting these colours. They are categorized into xanthophylls such as lutenin and xanthophylls or carotenes such as beta-carotene and astaxanthin according to the presence of oxygen-containing functional groups at the ends of the long hydrocarbon chain (Richins et al., 2010). Carotenoids are tetraphene's, which are made up of eight isoprene units, making them the most abundant plant-derived chemicals in the terpene class. The most common carotenoid found among plants is lutein. It is a yellow pigment that can be obtained from fruits and vegetables. Two of the rarest carotenoids include lactucaxanthin, which is found in carrots, and lutein epoxide, which can be found in some woody species. More than 600 carotenoids are known to exist in nature. Due to the additional health effects of some of them, such as protection against neurological diseases, retinal degeneration, and inflammation, they have uses in food and feed processing too. The extracted colorant and pigment can also be used as ink (Umale & Mahanwar, 2012).

Among the most popular processes used for the extraction of plant pigments, one can distinguish the aqueous extraction using water and organic solvents; however, important factors include cast, toxicity, and flammability. consumption: ages compared with other processes are that this water extraction process is cost effective, simple, fast, with less solvent consumption; the yields and qualities of the extracts are improved, and it is better for industrial applications. Some of these dyes are hydrophobic in nature, like phenolic compounds and carotenoids; therefore, they can hardly be dissolved in water. Consequently, to improve the mechanism of extraction of natural dye by breaking membranes of plant cells and releasing or transferring colours in water, water extraction can be improved with the application of an acidic, neutral, and basic concept at different temperatures. However, the type of solvent applied, the temperature, and the pH all play a major role in determining extraction yields and the subsequent physical and chemical properties of plant pigment extracts, which in turn provide the solubility of a solute. Thus, applying the

aqueous extraction in different contexts can yield fluctuating yields and alter the pigment concentrations (Khan et al., 2014).

Terminalia catappa is a big tropical tree from the Combretaceae family of leadwood trees. It is from Asia, Australia, the Pacific, Madagascar, and the Seychelles. The oval, glossy, dark green, leathery leaves are 10-14 cm wide and 15-25 cm long. They are deciduous trees; they have a dry season. Before the fall, they turn yellow-brown or reddish pink because of phenolic compounds contained in them, such as violaxanthin, lutein, and zeaxanthin (Thomson & Evans, 2006).

The other names for Terminalia catappa are country almond, sea almond, and tropical almond, which grow mainly in the tropics of Africa, Asia, and Australia. In India, these trees commonly occur in some of the states like Tamil Nadu, Maharashtra, Karnataka, Andhra Pradesh, and Kerala. This plant is a monoecious angiosperm, belonging to the Combretaceae family, which includes the leadwood trees. This tree reaches treetop heights ranging between 20 to 45 meters and is very resistant to drought, wind, and salt. Leaves contain flavonoids such as punicalin, punicalagin, and tercatin, saponines, and phytosterols. Because of this high chemical content, leaves find a lot of application in therapy. For example, the leaves which fall in Taiwan are used as herbal remedy against liver diseases. The leaves are used to make an herbal tea that treats dysentery and diarrhoea in China. The leaves may also hold chemicals that inhibit cancer (Boonsong, Laohakunjit & Kerdchoechuen, 2012).

Its extracts have been shown to be active against Plasmodium falciparum strains, both sensitive (HB3) and chloroquine resistant (FcB1). Left in the aquarium, the leaves retain the capability to decrease pH and heavy metal content of water. It is quite effective against bacteria and parasites for many types and has been used for a long period. It is also believed to inhibit fungus growth on fish eggs.

Printing over the package in the packaging industry is generally done with petroleum-based inks to show the brand name and product information. To create an attraction regarding brand visibility, they use some attractive coloured synthetic dyes/pigments. Packaging industries use methyl alcohol, isopropanol, alongside traditional ingredients like titanium dioxide and propylene glycol. To replace these conventional chemicals, identify the organic compounds present in the Indian almond tree leaf which have multiple colouring compounds. Extraction of pigments from the collected leaves at different maturity stages will be mixed with appropriate solvents and binders to prepare organic and eco-friendly inks for primary and secondary packaging.

2. MATERIALS AND METHODS

2.1 Collection of Materials

The concept of collecting raw materials at the right time to get a desired output. T. Catappa leaves in three different colours such as green, yellow brown, and reddish pink are collected from Anna University, CEG campus, Chennai. As T. Catappa leaves are available, samples are collected and immediately processed with no storage before analysis (Figure 1).

Figure 1: Different coloured leaves

2.2 Methods

Several types of extraction methods getting referred for the processing, like:

- ultrasound Assisted Extraction,
- microwave Assisted Extraction,
- acid Method of Extraction,
- alkaline Method of Extraction,

- aqueous Method of Extraction,
- fermentation - Extraction,
- reflex Boiling - Extraction,
- soxhlet - Extraction.

From these we choose the aqueous extraction method. Because this is a simple and cost-effective method.

2.2.1 Aqueous Method of Extraction

The Aqueous extraction method used only leaves in two colours, because this study has been conducted throughout the summer, and there will be an insufficient quantity of red leaves. Thus, this experiment compared green and yellow leaves.
The leaves of T. Catappa were cleaned with distilled water to remove dust particles before chopping into small pieces by following this extraction procedure.

Green leaf:
150g of chopped leaves along with 1liter of distilled water, which underwent maceration for various time periods up to 14 days (Figure 2). The sample solution was agitated every 24 hours and filtered into container bottles by using cotton cloths. Thus, the isolated pigment being examined using Thin Layer Chromatography (Figure 3).

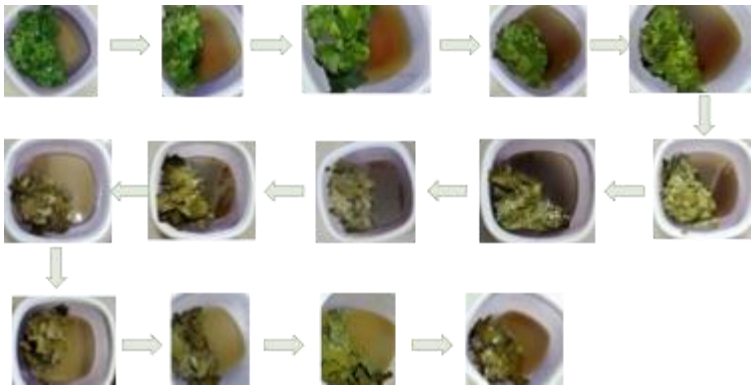

Figure 2: Colour changes of the green leaf solution from day 1-14

Figure 3: Green leaf extracts

Yellow leaf:
Weight of cut leaves 16.5g was added with distilled water 200ml which underwent maceration for a variety of times ranging from 2 days to 4 days (Figure 4). Sample solution was agitated every 24 hours and filtered into container bottles through cotton cloths. The Thin Layer Chromatography was applied to analyze the isolated pigment (Figure 5).

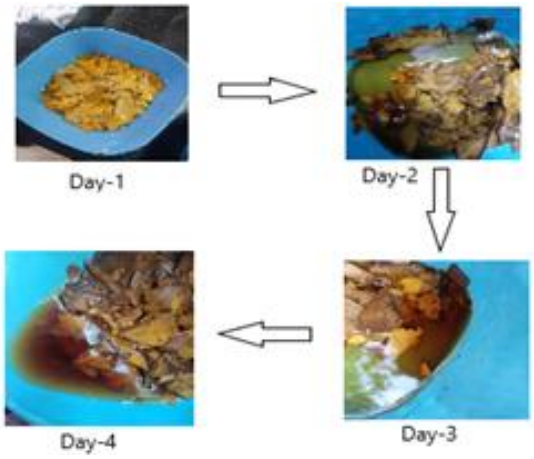

Figure 4: Colour changes of the yellow leaf solution from day 1-4

Figure 5: Yellow leaf extracts

Red Leaf:
Added 15g of cut leaves with 200ml of distilled water, it was allowed to undergo maceration at various times ranging from 2-4 days (Figure 6). Shake sample solution every 24 hours and filter it into container bottles through cotton cloths. Thus, pigment isolated has been analyzed by using Thin Layer Chromatography.

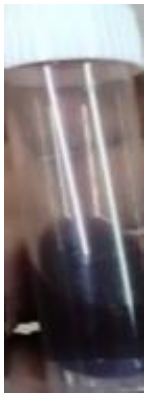

Figure 6: Red leaf extract

2.3 Pigment

The green, yellow, and red-coloured extracts were centrifuged for four hours. After which, the centrifugate is removed and the residue is cooked in a hot air oven for one hour. In this process of heating, the water evaporates, thus leaving the extracts in either pastry or powdery form.

2.4 Binder & Solvent

The binder's function is to disperse and carry the ink pigment onto the substrate, stabilize pigment and additive dispersion, avoiding setting, and confer properties to the prints, such as ink transfer behavior, setting, and drying characteristics. There are several natural binders. With this in our mind, we decided to make use of corn starch. Because of the affordability of its cost.
The binder preparation comprised 100% corn starch. For this, 2g of cornstarch was added to 100 ml of distilled water and continuously stirred at 54°C for 5 hours with a magnetic stirrer at 900 RPM (Figure 7).

Figure 7: Binder

When ink is introduced to a printing plate or cylinder from a cartridge, the solvents are employed to maintain the ink liquid until it is transferred onto the surface that will be printed on. Here water has been used as the solvent for the prepared ink.

2.5 Preparation of ink

Ink has been prepared by dissolving pigments in a solvent and adding binder. The proportions of pigment, solvent, and binder are 1:1:1 in addition with the xanthan gum as an additive (10% of total ink volume) and the prepared ink applied on both the paper and film (Figure 8). The drying time of the ink on the paper has been shorter than the film. The density and colour values have been determined by using a spectrophotometer.

Figure 8: Ink prepared by green, yellow and red pigment

3. TESTING AND RESULTS

3.1 Phenolic compound identification

The purpose of this test is to find out if the extracts contain any phenolic compounds. As a result of the displacement of the chloride anions by the aromatic rings, ferric chloride interacts with the aromatic alcohol to generate a purple solution. 5 ml of ethanol poured into the tiny baker. Ferric chloride has been

added in three drops (it does not react with aliphatic alcohol). 1 ml of extract has been added to the solution. The solution immediately generates dark purple hue complexes. The presence of phenolic chemicals in the extracts is indicated by this colour change (Figure 9).

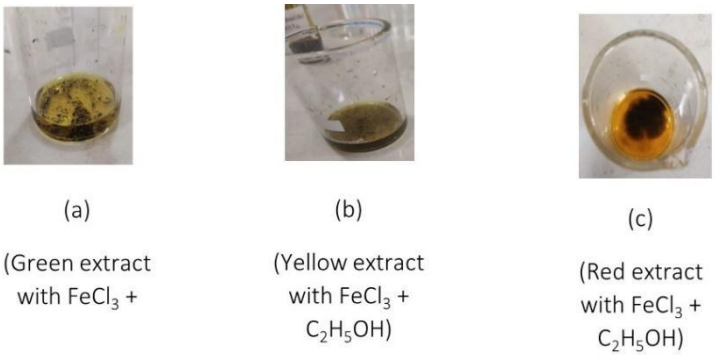

Figure 9: Testing the extracts with Ferric Chloride and Ethanol

3.2 Colour value and ink density

The Spectro densitometer is used to measure the color value and density of ink applied in a 1x1 cm² area on 75 GSM white paper and LDPE film. We measured three times to determine the approximate values of hue and density, and then subsequently averaging the values (Figure 10).

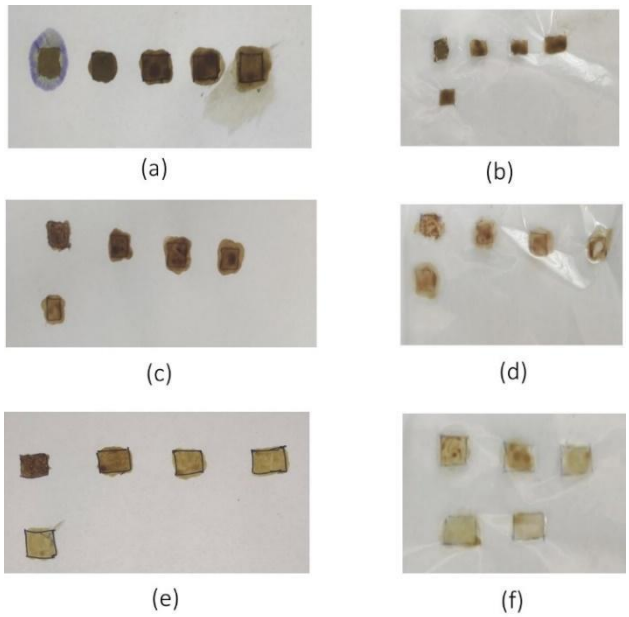

Figure 10: Colour patches in paper and LDPE Film

Here (a), (c), (e) are the figures representing the green, red, yellow inks extracted from the same colour of the leaves applied on the paper substrate. Then, the remaining (b), (d), (f) are the figures representing the green, red, yellow inks applied on the film substrate.

The drying time for the ink on the paper substrate is nearly 3 minutes, and for the film substrate it is nearly 15 minutes at room temperature. After a while of drying, the ink on the film gets peeled-off as a layer. Because both the substrate film (LDPE) and the binder (corn starch, a semi-crystalline biopolymer) used for colorant mixing are polymers.

The colour difference has been calculated by using the Equation (1):

$$\Delta E = \sqrt{((L1 - L2)^2 + (a1 - a2)^2 + (b1 - b2)^2)} \quad (1)$$

Where:

ΔE = colour difference
L1 = lightness value of the reference
L2 = lightness value of the sample
a1 = “a” value of the reference
a2 = “a” value of the sample
b1 = “b” value of the reference
b2 = “b” value of the sample

For reference, we take the printed patches with a colorant and binder ratio of 1:0, and for the sample, we take the remaining 1:1, 1:2, 1:3, and 1:4 in both the paper and the film.

3.2.1 Result for colour value and density

We can see from Figure 11 that there is a decrease in colour difference in paper when the binder ratio rises, and a similar drop in colour difference in film.
We saw from Figure 11 that the colour difference in both the paper and the film grows as the binder ratio increases.
Based on graph 3, we can see that as the binder ratio rises, the colour difference in paper likewise rises; however, in film, the colour difference reduces as the binder ratio rises (Figure 11).

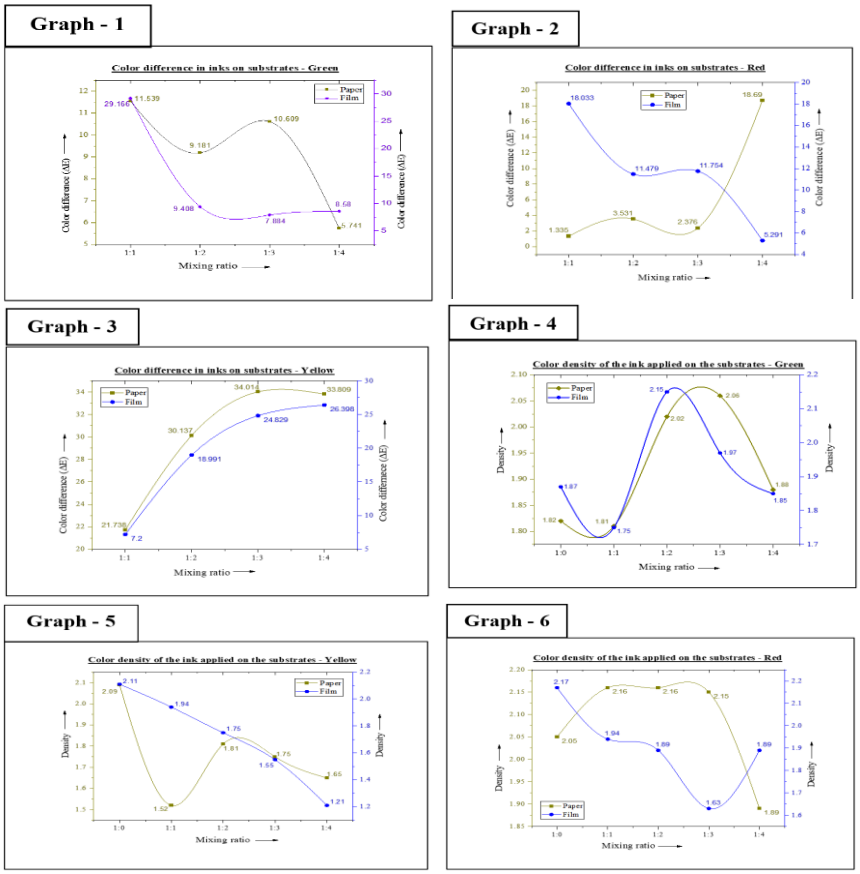

Figure 11: Colour difference and colour density graphs

3.3 Thin-layer chromatography

Silica gel plates had been activated through an oven for two hours at 100°C. The mobile phase was methanol to dichloromethane (DCM) in a 5:10 mixture. Extracts were spread out to 0.7cm from the bottom of the silica gel plate using a capillary tube with the appropriate spacing, and the silica gel plate was left to expand (pigment segregation) for about 8 minutes in a beaker comprising a mobile phase. The beaker has a lid. Pull out the TLC plate from the container when the solvent face is about 0.4cm from top of the plate.

An Rf value is a measure of the rate at which the pigment travels along the plate and is determined by dividing the total length travelled by the spot by the total length travelled by the solvent. The Rf values for each pigment have been derived by Equation (2):

$$Rf\ value\ = \frac{Total\ length\ travelled\ by\ a\ solute\ (Pigment)}{Total\ length\ travelled\ by\ a\ solvent} \quad (2)$$

Figure 12 depicts a chromatogram of TLC. The pigments have been separated, as evidenced by their respective spots. The Rf value of each site has been determined, and the results are compared to literature. Table 1 shows the identification of pigments from T. Catappa leaf extract using TLC. Spot 1 has an Rf of 0.39. It has been recognized as chlorophyll B. Spot 2 has an Rf of 0.78. It has been recognized as anthocyanins. Spot 3 has an Rf of 0.43. It has been identified as Lutein-Chlorophyll.

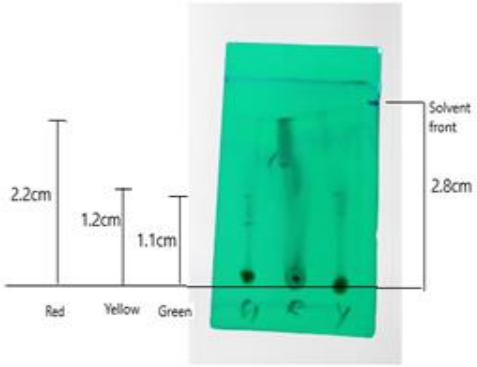

Figure 12: Thin layer Chromatography

Organic solvents can dissolve photosynthetic pigments including beta-carotene, xanthophylls, and chlorophylls. A thin silica film can be used to separate and identify pigments extracted in an organic solvent.

Table 1: Pigment confirmation

Colour of the Extract	Experimental Rf value	Literature Rf value	Pigment
Green	0.39	0.42	Chlorophyll b
Red	0.79	0.78	Anthocyanin
Yellow	0.43	0.42	Lutin-Chlorophyll

3.4 Rub resistance

Rub resistance test is used to check how much cycle of rub can be withstand by the print over the substrate (Figure 13). This test can be taken to the printed sample with the various weight of 0.5, 1 & 2 LBS at various CPM of 21, 42, 85 & 105 depending on the printed sample.

Figure 13: Rub Resistance Tester

The rub resistance test results that the print over the 75GSM white paper for 50 cycles at 42 CPM speed has no removal of ink from the substrate (Figure 14).

Figure 14: Before and After rub test

From the rub test, even though the substrate getting torn-off, the ink not getting removed from the paper substrate.

4. CONCLUSION

In the research done on T. Catappa leaf pigment extracts, violaxanthin, lutein, and zeaxanthin responsible for red, green, and yellow colours were present respectively. This work further illustrates that ethanol as a solvent can also identify such chemicals with specificity. Moreover, the advantages of aqueous extraction besides being low-cost operation go to facilities that are sensitive to environmental concerns, a minimum of energy usage, and being nonflammable and nontoxic. The Terminalia catappa leaf is made up of flavonoids, phenolic compounds that have antibacterial, anticancer, and antioxidant activities. Colorants can be used in the packaging industry to give attractive colour to improve their visual appeal. Also, they print detailed information of the product over the packages to instruct the consumers. The main advantage of pigments extracted from Terminalia catappa leaves is that they are biodegradable and renewable. In future, it may look at employing the pigment as a colouring agent in ecofriendly printing inks for degradable paper bags to replace the synthetic inks. As an alternative to artificial colours, the pigment derived from T. catappa leaves can be used to reduce the number of synthetic pigments used.

5. REFERENCES

Boonsong, P., Laohakunjit, N. & Kerdchoechuen, O. (2012) Natural pigments from six species of Thai plants extracted by water for hair dyeing product application. *Journal of Cleaner Production*. 37, 93-106. Available from: doi: 10.1016/j.jclepro.2012.06.013

Khan, A., Kumar, V., Singh, B. & Singh, R. (2013) Evaluation of wound healing property of Terminalia catappa on excision wound models in Wistar rats. *Arzneimittel-Forschung/Drug Research*. 64, 476-481. Available from: doi: 10.1055/s-0033-1357203

Richins, R. D., Hernandez, L., Dungan, B., Hambly, S., Holguin, F. O. & O'Connell, M. A. (2010) A “Green” extraction protocol to recover red pigments from hot capsicum fruit. *HortScience*. 45, 1084-1087. Available from: doi: 10.21273/HORTSCI.45.7.1084

Thomson, L. & Evans, B. (2006) Species Profiles for Pacific Island Agroforestry. *Agroforestry-Trees of Life, Trees for Life*. 2.2, 1–20.

Umale, S. & Mahanwar, P. A. (2012) Extraction of colorant from leaves of Terminalia catappa using non-conventional technique. *International Journal of Basic & Applied Sciences IJBAS-IJENS*. 12 (1), 79-88. Available from: doi: 10.1109/14393348