Optimising Syzygium Cordatum Dye Extraction

Nombuso Faith Gamedze
Department of Textiles and Apparel Design
University of Swaziland
P.O. Luyengo.
Swaziland, M205.

Pinkie Eunice Zwane
Department of Textiles and Apparel Design
University of Swaziland
P.O. Luyengo.
Swaziland, M205.

Lawrance Hunter
Faculty of Science
Department of Textile Science
CSIR and Nelson Mandela University
PO Box 77000

Abstract:- The increasing global awareness of eco-friendly and sustainable production and products has encouraged the use of natural fibres and dyes. Although research has been undertaken on the sources and applications of natural dyes, only a few such sources have been used on a commercial scale due to the costs and complexity of the associated extraction and dyeing processes, lack of appropriate technologies, and challenges with respect to dye fastness and shade reproducibility. The present investigation was carried out to optimize the extraction of natural dye from the bark of the *Syzygium cordatum* (water berry) tree. The bark was collected from recently fallen trees and twigs pruned from old trees, since the latter have greater dye content than the younger ones. The bark was dried in an open room for two weeks, crushed with a hammer and ground into powder. The conditions for dye extraction using a methanol/water mixture, were optimized by means of Response Surface Methodology (RSM), with the help of Design Expert Version 7.0. The central composite design (CCD) was applied to design experiments for the evaluation of the interactive effects of the three most important extraction variables, namely temperature, time and liquor volume on 25g dye powder. The following optimized dye extraction conditions were found: 70^{0}C temperature, 51minutes extraction time and 1:16 for material-to-liquor ratio.

***Keywords**:- Syzygium cordatum, natural dye, dye extraction, cotton dyeing.*

I. INTRODUCTION

There has been a renewed interest in using colour components of natural origin, instead of synthetic dyes, largely due to an increased awareness of sustainability and environmental issues relating to the production and application of synthetic dyes, including the harmful effects of synthetic dye effluents, which can be both toxic and non-biodegradable (Kechi *et al*., 2013). A major obstacle in the wide application of natural dyes is their scarcity, since not many countries have plants and animals insufficient quantities from which natural dyes can be sourced sustainably and economically viable. Furthermore, low dye yields, inadequate dye fixation, fastness and shade range matching and reproducibility as well as limitations in their application, lack of standard dyeing procedures also limit the use of natural dyes. Though compatible with the environment, dyeing with natural dyes is still largely confined to artisan and craftsman due to the above mentioned issues (Samanta and Agarwal, 2009; Patel, 2011). Optimizing the extraction variables, for a particular natural dye source, plays a major role in terms of colour yield, and cost effectiveness on the cost of extraction process impacting significantly on overall dyeing cost.

According to Toerien and Khumalo (2010), a study, involving Swazi indigeneous knowledge systems, showed that use of natural dyestuff, in handcraft production, was prevalent in the Hhohho region, with a few carefully selected varieties of plants being used. The local dye plant varieties used include the *Slerocarya birrea (*Marula), *Trichilia emetic (*Natal mahogany), *Calprunia aurea* (Common calprunia), *Pterocarpusangolensis* (Wild teak), *Tagetes minuta* (Khakhi weed), *Steculia murex* (Lowveld chestnut), *Syzigium cordatum* (Water berry), *Bidenspilosa* (Black jack), and *Rhus dentate* (Nana berry). The challenge with these natural dyes is the non-colourfastness when in use.

Syzygium cordatum was selected for this study because it is found in abundance in many parts of the country. It belongs to the *Myrtaceae,* family is an ever green water-loving tree, found to have a number of uses. The red to dark purple oval berries are eaten as a fresh fruit, used to make an alcoholic drink and also cooked to give good quality jelly. The flowers are used by bees to produce very good quality honey. The leaves and fruits act as food for game, like kudu, nyala, bush buck and grey duiker. Good quality timber used for furniture, window frames and rafters, is sourced from Syzygium cordatum which is a very good source of firewood and charcoal The bark of *Syzygium cordatum* contains colouring materials, such as tannins and polyphenols, and yields a red-brown dye, while the fruit is used as a purple dye (Toerien and Khumalo, 2010). The bark and wood contain proanthocyanidins, pentacylic triterpenoids, steroidal triterpenoids, ellagic acid and gallic acid and tannins which are active compounds (Fern, 2014). They occur as glycosides, containing a number of phenolic hydroxyl groups in their structure. The roots and bark of Syzygium cordatum are reported to have medicinal value used to relieve indigestion and giddiness, due to the phenolic compounds, an extract of the leaves is used as a purgative and to treat diarrhoea (Fern, 2014), as well as for the treatment of respiratory ailments, including tuberculosis (Chalannavar *et al*., 2014).

In Swaziland, the extraction and application of natural dyes from a variety of indigenous trees, such as *Szyzgium cordatum,* and herbs have neither been optimized nor standardized. This makes it difficult to produce the same shade in every dyeing operation and to be cost effective. In light of this; the present study was aimed at investigating, and optimising the process of dye extraction from the bark of the *Syzygium cordatum* tree. The main objective of the study was to: optimize the method of extracting dye from the *Syzygium cordatum* bark. It was felt that the outcome of this study will be of value to rural women of Swaziland, who create a variety of dyed cotton handicrafts, as they would be able to cost effectively and optimally extract and apply this dye in an environmentally friendly and sustainable way.

- *Experimental*

The experimental design, Design Expert Version 7.0 statistical package was employed for the experimental design, with the Response Surface Methodology (RSM) as the tool used for optimisation of the extraction process. The central composite design (CCD) was applied to design experiments to evaluate the interactive effects of the three most important extraction variables, namely temperature, time and liquor ratio, using 25g of bark powder in each case. This approach decreased the required number of experiments.

II. DYE SOURCE

The *Syzygium cordatum* bark, as the natural dye source was collected from indigenous trees around the *Umtiphofu* River in the Lowveld of Swaziland. The bark was collected from recently fallen trees, broken branches and twigs pruned from old trees, due to their greater dye content. The collected bark was dried under shade for two weeks, then crushed with a hammer and ground into a crude powder using Thomas-Wiley laboratory mill Model 4. Grinding of the bark was done to ensure a uniform particle size with a large surface area to facilitate quick dye extraction.

III. OPTIMISATION OF DYE EXTRACTION

The dye was extracted from the 25g of ground bark powder in analytical reagent methanol/distilled water mixture under varying conditions of time of extraction, temperature of extraction bath and liquor volume in each experiment (Kumaresan *et al.*, 2013) Nominal levels for each independent variable were chosen as shown in Table 1, and the experimental sequence was randomized in order to minimize the effects of uncontrolled factors. In all trials, 600mL beakers, containing 25g ground bark powder and varying volumes (200, 300, and 400mL) of a 1:2 ratio mixture of methanol/water, were used and placed in a Labcon water bath. Foil paper was used to minimize evaporation of liquor from the beakers. After extraction, the extract was filtered through Whatmans filter paper, the filtrate was collected and its absorbance recorded as a measure of the dye concentration using Boeco Model S-22 UV-VIS range spectrophotometer, with all measurements being done in triplicate

Factor	Variable	Units	Low	Medium	High
A	Time	Minutes	30	60	90
B	Temperature	Degrees celcious	50	60	70
C	Liquor	millilitres	200	300	400

Table 1. Nominal levels of independent variables

IV. DETERMINATION OF OPTIMAL EXTRACTION CONDITIONS

To determine the best powder to liquor ratio, 25g of ground bark was soaked in three beakers having 200, 300 and 400mL, respectively, of the methanol/water mixture which was at a temperature 70^{0}C for 60 minutes. To determine the best extraction time, the ground bark was soaked in 300mL of the methanol/water at 70^{0}C for 30, 60 and 90 minutes, respectively. The best extraction temperature was determined by soaking 25g the ground bark in 300mL methanol/water mixture for 60 minutes at temperatures of 50, 60 and 70^{0}C, respectively. The flow charts for the extraction of the dye under the various conditions are given in Figures 1 to 3. Experiment conditions used in the study were based on reviewed literature of various natural dyes studies (Kumaresan *et al.*, 2013, Kechi et al., 2013, and Kulkarni et al., 2011) and the methods used as combination of the above studies.

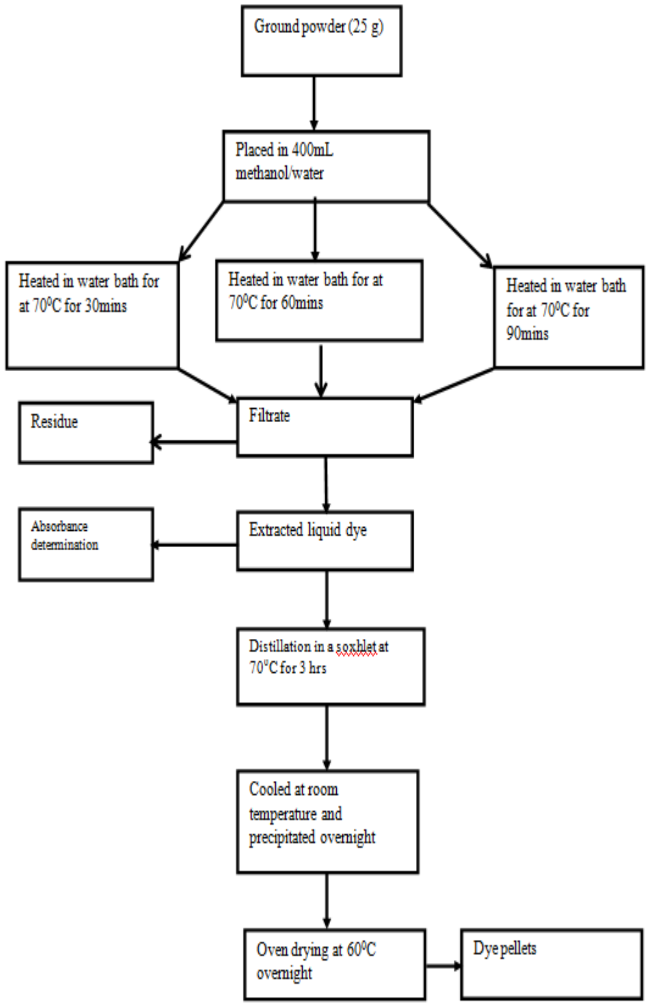

Fig 1:- Determination of best extraction time (Factor1)

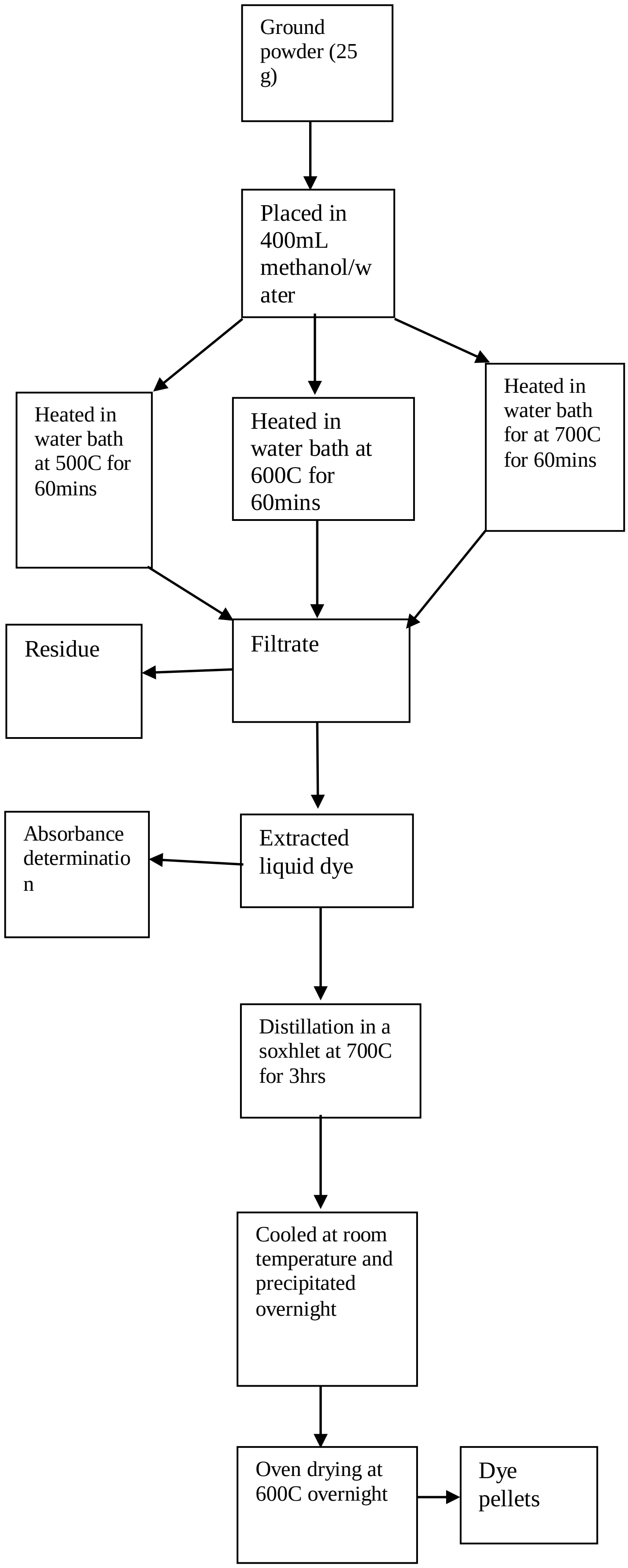

Fig 2:- Determination of best extraction temperature (Factor 2)

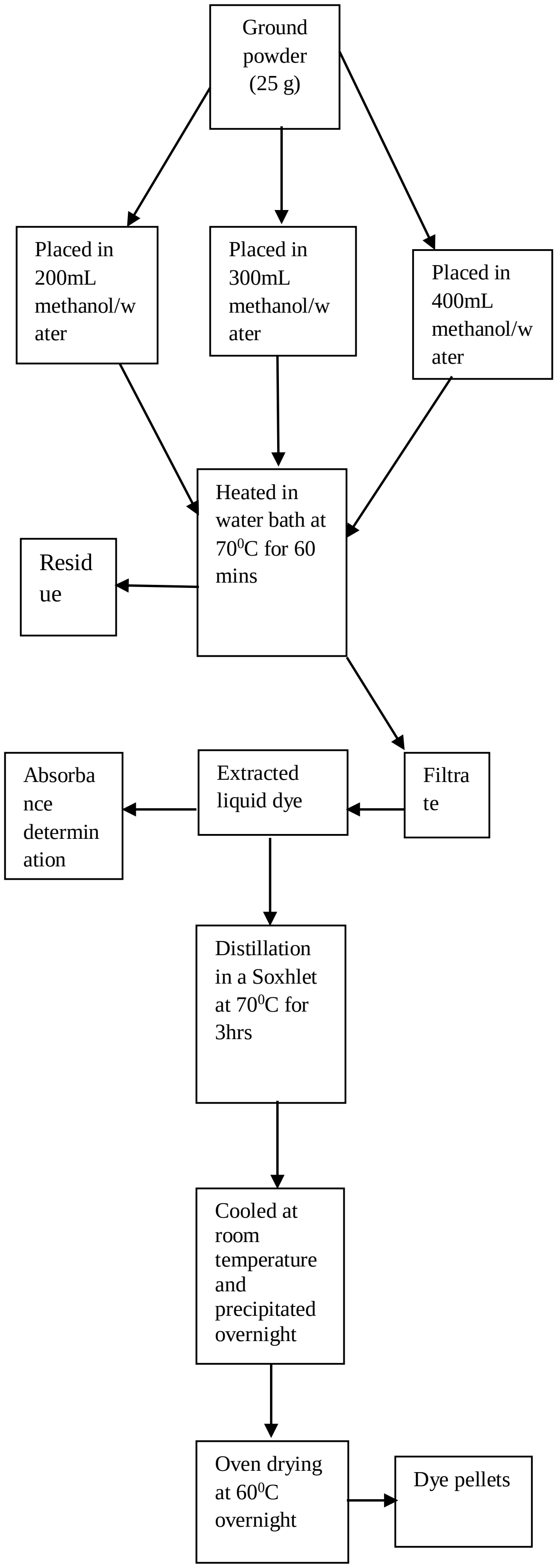

Fig 3:- Determination of best powder to extraction liquor ratio (Factor 3)

After the concentrations of the filtrate were measured, the dye filtrate was placed in a Soxhlet apparatus and heated at 70^{0}C for 3hours. This distillation process was carried out to recover the methanol and produce a concentrated aqueous dye solution. The recovered methanol can be reused, thereby reducing the cost of extraction. After distillation, the aqueous dye solution was kept overnight at room temperature to allow precipitation. After the formation of precipitate at the base of the flask, methanol/water was obtained by decanting the solution and then drying the precipitate in the oven overnight at 60^{0}C (Kulkarni *et al*., 2011). Thereafter, the precipitate was left in the open air to dry for two days, resulting in dye pellets being formed.

V. CRUDE DYE YIELD

To determine the crude dye yield, three samples were randomly selected from the 48 extractions performed, under optimized conditions. Samples were conditioned at room temperature in the absence of the standard atmospheric conditions. The weight of the crude dye determined by means of an electronic digital balance (AE Adam pw 254) to 0.0001g accuracy. The weight was used to calculate the dye yield defined as the quantity of crude dye powder obtained after evaporation of the extracted dye solution obtained under the optimized extraction conditions (Kechi *et al*. 2013). Crude solid dye yield was the weight of crude dye pellets as a percentage of the original weight 25g of the bark powder used for extraction, using the following equation:

$$W_{dy}(\%) = \frac{W_{be} - W_{ae}}{W_{be}} \times 100$$

Where W_{dy} = percentage crude dye yield; W_{be} = weight (25g) of original bark powder; W_{ae} = weight (g) of dye pellets after evaporation and drying of extract.

➢ *Results and Discussion*

This chapter presents and discusses the results obtained in this study, with the aim of optimising the process of dye extraction.

VI. OPTIMISATION OF DYE EXTRACTION

Table 2 presents the nominal experimental conditions, as well as the actual absorbance results obtained under the different extraction conditions. According to Table 2, Trial 6 was best, since it produced the maximum absorbance at both 650nm (0.81) and 700nm (0.65). The conditions for Trial 6 were: 60mins for time, 60^{0}C for temperature and 400 mL for liquor volume. From Table 2, it is evident that an increase in time even with the highest temperature range did not give good absorbances at both wavelength. Using a liquor ratio of 400mL with the highest temperature of 70^{0}c for 30 minutes gave the second highest absorbance result with the other trials producing relatively low absorbances.

Trial	Factor 1 Time (min)	Factor 2 Temperature (^{0}C)	Factor 3 liquor volume (mL)	Absorbance at 650 nm	Absorbance at 700 nm
1	60.00	60.00	300.00	0.31	0.17
2	60.00	60.00	300.00	0.36	0.24
3	30.00	60.00	300.00	0.17	0.10
4	90.00	50.00	400.00	0.42	0.28
5	60.00	70.00	300.00	0.32	0.23
6	60.00	60.00	400.00	0.81	0.65
7	60.00	60.00	300.00	0.41	0.31
8	30.00	70.00	400.00	0.64	0.45
9	60.00	50.00	300.00	0.52	0.40
10	90.00	50.00	200.00	0.43	0.28
11	90.00	60.00	300.00	0.22	0.13
12	30.00	50.00	400.00	0.43	0.33
13	30.00	50.00	200.00	0.22	0.13
14	60.00	60.00	300.00	0.56	0.39
15	60.00	60.00	300.00	0.20	0.13
16	90.00	70.00	200.00	0.39	0.29
17	90.00	70.00	400.00	0.49	0.36
18	60.00	60.00	200.00	0.27	0.17
19	30.00	70.00	200.00	0.62	0.47

Table 2. Actual absorbance results

The results of the design experiments for each response were further optimized by the RSM, using the CCD experiment to generate the optimal conditions. Table 3 presents the extraction conditions, in terms of time, temperature and liquor volume generated by the CCD analysis. The results show that there was basically one set of conditions which gave the highest desirability of 0.874, namely $\pm$50min, 70^{0}C and 400mL liquor ratio of 1:16 and therefore represent the optimum conditions for extraction of the *Syzygium cordatum* dye from the ground bark powder. The *Syzygium cordatum* bark powder was found to discharge colour more easily at the highest temperature (70^{0}c) of the methanol/water mixture as reflected in the increased absorbance and desirability at 0.874 (Table3). This means that there were more dye solutes, greater colour depth and a minimum extraction time. It was observed that the colour of the dye extract was dark red. An increase in the extraction time did not increase absorbance; if anything, it rather tended to decrease it. The optimum bark powder mass (25g) to liquor volume (mL) was 1:16 (25:400). Srivastava *et al*. (2008) found that colour strength increased with an increase in extraction temperature, up to 40^{0}C, which is much lower than that of 70^{0}C found in the present study. This may be attributed to their plant source *Canner indica* flowers, which had soft tissues compared to the hard bark used in the present study.

VII. CRUDE DYE YIELD

The crude dye yield results are given in Table 4. A crude dye yield of 20.3% was obtained under the optimal extraction condition, of $\pm$50min, 70^{0}C and 400mL. The above mentioned dye yield obtained, is termed crude, because no attempt was made to isolate the colourants present in the filtrate to obtain pure dye. Nonetheless, it can be expected that the actual amount of pure dye after isolation of the dye would be much lower, as reported by Vankara *et al.* (2007), who obtained only 9% of dye when using the methanolic extract from leaves of *Bischofia javanica* methanolic extract. Findings of this study closely affirm the results of other studies. For example, Kulkarni *et al.* (2011) obtained 19.2% crude dye yield in an ethanol/water (40:60) extraction from pomegranate peel while 20% crude dye yield was reported for the *Fesson* flower and the bark of the evergreen *Rhamnus alternus L.*, which contains a number of glycosides, as is the case with *Syzygium cordatum* bark. The dye yields obtained by Kechi *et al*. (2013), from ten different plant sources, varied from 14 to 26%, which a few plants gave higher dye yield.

Number	Time (min)	Temp (^{0}C)	Liquor vol (mL)	R1 (absorbance 650nm)	R2 (absorbance 700nm)	Desirability
1	51	70.0	400.00	0.750	0.566	0.874
2	51	70.0	400.00	0.750	0.566	0.874
3	51	70.0	399.96	0.749	0.566	0.874
4	53	70.0	400.00	0.748	0.566	0.873
5	52	69.9	399.94	0.748	0.565	0.872
6	51	69.9	400.00	0.747	0.564	0.870
7	55	70.0	400.00	0.745	0.565	0.869
8	52	69.6	400.00	0.742	0.566	0.863
9	59	70.0	400.00	0.736	0.568	0.856
10	62	70.0	400.00	0.723	0.549	0.838
11	54	70.0	393.09	0.717	0.541	0.826
12	64	51.7	400.00	0.651	0.503	0.742
13	60	63.8	400.00	0.656	0.495	0.738
14	39	66.2	400.00	0.656	0.486	0.729
15	58	53.1	400.00	0.640	0.494	0.724
16	57	59.4	400.00	0.634	0.481	0.708
17	54	70.0	200.00	0.584	0.455	0.646
18	54	70.0	200.00	0.584	0.455	0.646
19	55	70.0	200.00	0.583	0.455	0.646
20	56	70.0	200.00	0.583	0.455	0.645
21	56	70.0	204.52	0.570	0.453	0.625
22	66	50.0	200.18	0.481	0.336	0.458

Table 3. Results generated by CCD matrices

Kechi *et al*. (2013) emphasized that the quantity of natural dye source required for dyeing of textile material is relatively high, due to the low dye yield and low colour strength, this also being observed in the present study. The use of more sophisticated methods, such as ultrasonic extraction, can possibly improve dye yields (Kulkarni *et al*., 2011).

Bark powder (g)	Residue (g)	Crude dye yield %
25	19.8	20.8
25	19.9	20.4
25	20.2	19.8
Average	Mean	20.3

Table 4. Crude dye yield

VIII. CONCLUSION

The ultimate objective of this study was to optimize and standardize the conditions of dye extraction and dyeing of cotton and to provide the information to the Swaziland craft industry to apply in practice, this paper dealing with the extraction of the dye. Due to the low water solubility of natural dyes, especially those containing polyphenols, such as *Syzygium cordatum* bark used in the study, a 1:2 methanol/water mixture was used for dye extraction. The optimum dye extraction conditions, for a 25g sample of *Syzygium cordatum* bark powder, as derived from a CCD analysis, were an extraction temperature of 70^{0}C, $\pm$51min extraction time and 1:16 bark powder (g): methanol/water (mL) solution ratio. Under these optimum conditions, a dark red dye solution was obtained, with the crude dye yield from the ground bark being 20.3%. According to the results of the study, the dye extracted from the bark of the *Syzygium cordatum* tree dye can be regarded as a valuable and environmentally friendly natural colorant which is easily extractable in fairly large quantities. By optimizing extraction, artisans will be able to create reproducibly dyed products, within the minimum time and with less experimentation, thereby improving their efficiency.

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