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Spathodea campanulata Beauv. flower dye extraction: Mass transfer enhancement through process optimization

Pravinkumar D Patil[1,*], Late C R Rao[2], A I Wasif[3] & S V Anekar[4]

[1]Department of Technology, Shivaji University, Kolhapur, Maharashtra, India.

[2]Vignan University, Vadlamudi, Guntur, Andhra Pradesh, India.

[3]Textile and Engineering Institute, DKTES, Ichalkaranji, Maharashtra, India

[4]T.K.I.E.T Warananagar, Maharashtra, India

E-mail: pdpchem@gmail.com

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The natural dyes are re-gaining importance because of ecological issues of most of the synthetic dyes. Mass transfer enhancement has been carried out in the study using the optimized extraction conditions to obtain maximum dye yield from flower petals of 'African Tulip tree'. Taguchi design has been implemented to investigate the optimum extraction conditions. The overall effort is to meet the challenges to reintroduce natural dyes. The investigated optimum parameters for extraction include: '150 micron particle size', '1:20 solid-solvent ratio', 'one hour extraction' and 'enzyme addition as an assistance for extraction'. The absorbance values, mass transfer rates and subsequent dye yields obtained from optimized extraction have been compared against control extraction. It is seen that using optimized extraction conditions; the mass transfer rate is enhanced triply as compared to control extraction. It ultimately result in increased dye yield to the tune of about 10.75%.

Keywords: Mass transfer, Natural dye, *Spathodea campanulata*, Taguchi optimization

The use of natural dyestuffs for various purposes dates back to remote antiquity. Natural dyes are the colorants extracted from vegetative matter, animal residues or from minerals. These dyestuffs include roots, leaves, barks, trunks, fruits and flowers of plants, animal sources such as cochineal and shellfish or sometimes soils or clay. These dyes were used for various purposes such as coloration of clothing, food, leather tanning, painting etc[1]. However with the invention of synthetic dyes like aniline, alizarin and indigo in the mid 1800's, natural dyes lost their economic significance. Today, synthetic dyes have market dominance because of their varied colours, vast, easy production and very good fastness properties. Some major existing limitations and technical problems in the procurement of natural dyes made us shift our focus from natural to synthetic dyes[2]. As regards the synthetic dyes, within a period of one and half century, some serious drawbacks have been revealed. The research showed that most of the synthetic dyes are suspected to release harmful chemicals that are allergic, carcinogenic and detrimental to human health. Ecology and environment problems related to synthetic dyes have increased public awareness. In 1996, Germany became the first country to ban certain azo dyes. About 74 azo dyes have been banned worldwide in view of their carcinogenic nature[3,4]. Because of increasing environment related consciousness; resurgence of natural dyes is being seen. Natural dyes like other natural products are becoming more popular. Better biodegradability and 'non-toxic, eco-friendly properties' are the major advantages of natural dyes. The other benefit of natural dyes is that there is significant reduction in the amount of toxic effluent resulting from the synthetic dye processes[5,6].

In spite of these strong and positive aspects of natural dyes, the present international consumption of natural dyes is very low than the synthetic dyes. The difficulty in upbringing natural dyes is their existing limitations and technical drawbacks. Low colour yield, inadequate and inefficient dye extraction methods are among the major problems to reintroduce the natural dyes[7]. The greatest challenge is to increase the yield of these dyes. Present research work has been carried out to address this particular issue. The plant part selected for the study is the flower petals of *Spathodea campanulata Beauv.* tree[8].

Extraction of dyes from their raw dyestuffs is basically a solid-liquid extraction operation. When a solid material is brought in contact with a solvent, the soluble components in the solid material move to the solvent. The extraction of plant material results in the mass transfer of soluble colour ingredient to the solvent and this takes place in a concentration gradient. The rate of mass transfer decreases as the concentration of dye in the solvent increases, until equilibrium is reached i.e. the concentrations of dye at the interface and the solvent are the same. Thereafter, there will no longer be mass transfer of dye from plant material to the solvent[9].

One of the steps to improve the mass transfer during extraction of dyes from their dyestuff is to find out the optimum conditions of extraction and to exploit them for efficient extraction of the dye. This research mainly focuses employing optimized extraction conditions to get maximum dye from the source and to further calculate the mass transfer rates during the extraction[10].

Experimental Section

Raw material for dye extraction

Spathodea, a monotypic genus in the flowering plant family Bignoniaceous has a single species '*Spathodea campanualata*' commonly known as 'African tulip tree'. It grows between 7-25 m tall. Native to tropical dry forests of Africa but it is seen now as an ornamental tree everywhere[11].

Locally, the flowers from the road side trees were collected as the raw dyestuff. Petals separated from their buds, were dried in a tray dryer. The dry petal mass was ground in a domestic mixer-grinder giving mixed particle sizes. The powder was sieved to get three different sizes of the dyestuff required for experimental work.

Chemicals and equipments used

- Cellulase and pectinase enzymes : HIMEDIA
- 9.5 *p*H Buffer tablets: Merck
- Weighing balance : Shimadzu AUX220
- Domestic microwave oven: Samsung DE68-02233G
- Orbital Shaker-incubator : Nanolab India Model NLSIC-23#25/50
- Syringe and holder assembly with nylon membrane filters (0.2 micron porosity): HIMEDIA
- UV-VIS Spectrophotometer: Shimadzu, Germany, Model UV1800

Taguchi optimization followed in the natural dye extraction

The objective in the extraction of natural dye was to increase yield of the product through efficient mass transfer operation. A standardized version forwarded by Dr. Genichi Taguchi, was used for dye extraction optimization[12]. In this research effort, Taguchi method was mainly used to achieve efficient extraction of dye. The four factors investigated in the work (Table 1). Absorbance of the colour extract was considered as the response variable.

L9 orthogonal arrays were selected with 9 experimental runs. There were 4 factors for investigation with 3 levels each[13]. Each of the nine runs was conducted in duplicate. The other parameters ascertained from the literature survey included extraction temperature 60°C, speed of the orbital shaker 150 rpm, microwave power and irradiation time 300Watt and 40 second respectively, enzymes proportion as 2% of cellulase and 1% pectinase both on weight of raw dyestuff basis[14,15]. Water was used as a solvent in the extraction experiments.

Method of data analysis in the extraction optimization experiment

Using Minitab software version 13, analysis was conducted for the response variable. The General Linear Model (GLM) approach was used to perform analysis of variance and regression of each response variable. Calculations were performed using a regression approach. Conclusions were obtained using calculated results and the graphs.

Conduct of dye extraction with optimized parameters and control parameters

The solid-liquid extraction was carried out using optimum parameters as suggested by the Taguchi Design. The particular experiment was named as optimum extraction experiment. Also the control experiment was conducted simultaneously with predetermined control parameters. The control parameters included course particle size (425 micron), 1:20 solid to solvent proportion, three hours of extraction and there was no specific assistance for extraction.

Table 1 — The control factors and levels

Factor↓ Level→	0	1	2
Particle size, microns	150	300	425
Solid: liquid ratio, g:mL	1:10	1:20	1:30
Time, min	60	120	180
Method	Microwave assistance	Enzyme assistance	Microwave + Enzyme assistance

It was aimed to compare control extraction performance with that of the optimized extraction. UV-VIS spectra were obtained for the extracts from the two experiments (Fig.1).

Analysis of data

Statistical analysis

The analysis suggested the optimum set of parameters (Table 2 and Table 3). The F-value for each parameter indicated which parameter has significant effect on extraction and is simply a ratio of the squared deviation to the mean of squared error. Usually, larger F-value shows greater effect on the extraction value due to the change of the process parameter. Optimal combination of process parameters was predicted using ANOVA. (Fig.2)

Analysis of data for yield and mass transfer rate calculation

Chemical nature of the colorant

The FT-IR and UV-VIS spectroscopy analysis as well support the presence of colourant namely n-hexadecanoic acid. Its molecular formula is $C_{16}H_{32}O_2$ with molecular weight (MW) 256. The colourant structure is shown in Fig. 3.

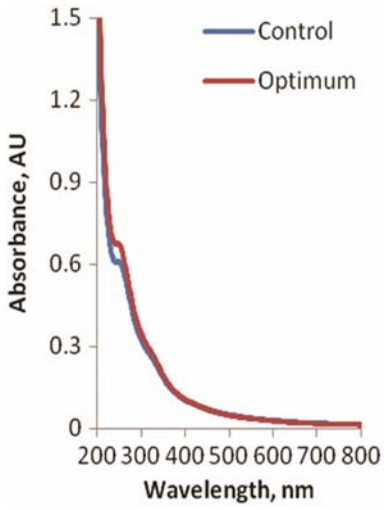

Fig. 1 — UV-vis spectra of the extracts (λ_{max}=247 nm)

Determination of dye yield

To find out the concentration of the dye extracted, the dye powder obtained from the spray drier was used to prepare solutions of different concentrations. These solutions were tested for their respective absorbance values using UV-vis spectrophotometer.

The dye concentrations were plotted against the respective absorbance values. The graph showed the BEST-FIT line. (Table 4) The slope of this line is the product of path length and molar extinction coefficient. Using slope and absorbance, the concentration and dye yields were determined and compared for the control extraction and optimum extraction.

Beer-Lambert law is used to determine concentration of an absorbing species in solution.

$$A = \log_{10} (I_o/I) = [\varepsilon \times L] \times [c] = \text{slope} \times [c] \quad ...(1)$$

$$\text{Thus, Concentration} = \text{Absorbance/Slope} \quad ...(2)$$

$$\text{The trend line is } Y = 1.003X \quad ...(3)$$

The concentration values and the molecular mass of predicted colourants were used to calculate dye yields.

Table 3 — Least squares means for absorbance

Parameter	Level	Mean	SE Mean
Particle size	0	0.5725	0.001174
	1	0.3915	0.001174
	2	0.4767	0.001174
Solid-Liquid ratio	0	0.6075	0.001174
	1	0.4597	0.001174
	2	0.3735	0.001174
Time of extraction	0	0.4903	0.001174
	1	0.4897	0.001174
	2	0.4607	0.001174
Method of assistance	0	0.4638	0.001174
	1	0.5688	0.001174
	2	0.4080	0.001174

Table 2 — Analysis of variance for absorbance, using adjusted SS for tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Replica	1	0.000001	0.000001	0.000001	0.11	0.751
Particle size	2	0.098397	0.098397	0.049198	5953.42	0.000
Solid-Liquid ratio	2	0.168071	0.168071	0.084035	1.00E+04	0.000
Time of extraction	2	0.003443	0.003443	0.001722	208.32	0.000
Method of assistance	2	0.080019	0.080019	0.04001	4841.51	0.000
Error	8	0.000066	0.000066	0.00000		
Total	17	0.349997				

Table 4—Absorbance vs. Concentration

Absorbance	Concentration, g /litre
0.000	0
0.1	0.1
0.2	0.2
0.28	0.3
0.42	0.4
0.5	0.5

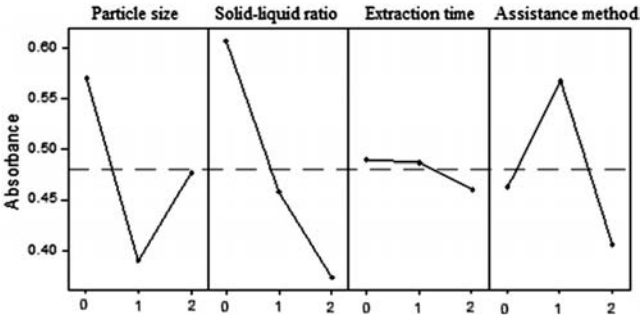

Fig. 2 — Optimal combination of process parameters predicted using ANNOVA

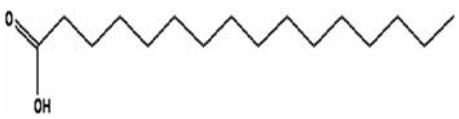

Fig. 3 — Structure of *n*-hexadecanoic acid

Control extraction

C = Absorbance ÷ slope = 0.609 ÷ 1.003 = 0.6072 mole per liter ...(4)

Original extract (0.5 mL) is diluted to 100 mL (means 200 times). Therefore the original concentration is 0.6072 × 200 = 121.44 mole per litre.

The colourant with the molecular weight 256 is present in the extract. Therefore presence of the colourant in the extract is 121.44 ÷ 256 = 0.4743 g per liter which is 0.04743 g per 100 mL. However, the source of the colourant is from 3 g of the raw dyestuff.

% yield = [quantity of colour extracted ÷ quantity of raw material taken] × 100

= [0.04743 ÷ 3] × 100 = 1.581 …(5)

Optimum extraction

C = Absorbance ÷ slope = 0.609 ÷ 1.003 = 0.6072 mole per liter ...(6)

Original extract (0.5 mL) is diluted to 100 mL (means 200 times). Therefore the original concentration is 0.672 × 200 = 134.39 mole per liter. The colourant with the molecular weight 256 is present in the extract. Therefore presence of the colourant in the extract is 134.39 ÷ 256 = 0.5249 g per liter which is 0.0525 g per 100 mL. However; the source of the colourant is from 3 g of the raw dyestuff.

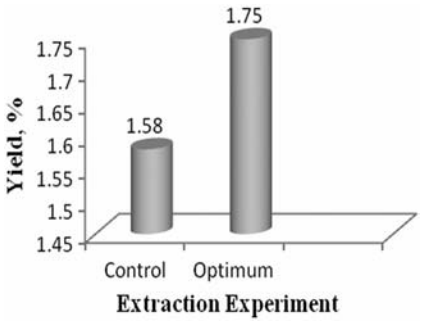

Fig. 4 — Extraction yield of dye

% yield = [quantity of colour extracted ÷ quantity of raw material taken] × 100

= [0.0525 ÷ 3] × 100 = 1.75 ...(7)

Extraction efficiency and mass transfer rate enhancement

Extraction efficiency enhancement calculations

Figure 4 shows graphical comparison of control extraction against optimum. The improvement in extraction efficiency was noticed:

Extraction efficiency enhancement

= [Yield (Optimum-Control)]/ Yield (Control)

= [1.75-1.58] / 1.58 = 10.75% ...(8)

Mass transfer rate enhancement calculations

Further by using the absorbance values of the two extraction experiments, the rates of diffusion or the rate of mass transfer were calculated and compared. The mass transfer rate can be expressed in terms of AU/hour, moles/lit. hour or g of solute transferred/hour. The graphical comparison mass transfer rates indicated significant enhancement in the mass transfer rate in case of optimized extraction. (Fig. 5)

The formula for the rate of diffusion is as follows:

Mass transfer Rate = absorbance/time = A/t, AU/hour

For experiment with control parameters:

The rate of extraction mass transfer = 0.609 ÷ 3

= 0.203 absorbance units per hour …(9)

= 121.44 ÷ 3 = 40.48 *moles per liter per hour* …(10)

= 1.58 ÷ 3 = 0.53g per hour …(11)

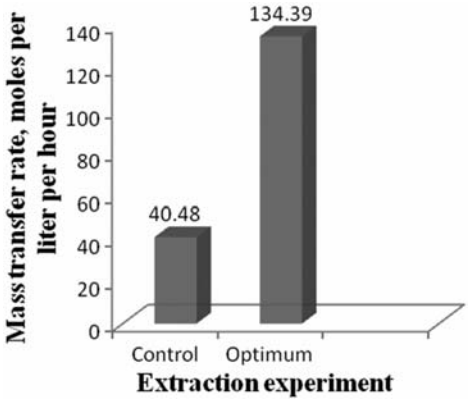

Fig. 5 — Enhancement of Mass transfer rates for the dye

For experiment with optimum set of parameter:

Rate of extraction mass transfer= absorbance/time

The rate of extraction mas transfer = 0.674 ÷ 1
= 0.674 absorbance units per hour …(12)

= 134.39 ÷ 1 = 134.39 *moles per liter per hour* …(13)

When optimized extraction was compared against control, the enhancement in mass transfer rate was as follows:

Mass transfer rate enhancement = Rate (Optimum)/ Rate (Control) = 0.674/0.203 = 3.32 …(14)

Results and Discussion

Optimization results

Variance analysis results showed statistical significance of chosen parameters. Optimal combination of process parameters was predicted using ANOVA. The resultant optimum set of parameters was: dyestuff particle size 150 microns, solid-solvent ratio 1:20, Extraction time one hour and enzyme addition as assistance method.

The finest particle size was found as the optimum parameter. This might be due the fact that the finest size has got the highest contact surface area thereby increasing the absorbance value and therefore the extraction efficiency. The optimum ratio found was 1:20. It meant that 20 parts of the solvent were adequate enough for complete transfer of dye from one part of the solid dyestuff. Dynamic dye transfer equilibrium might have reached with the particular ratio. Therefore there was no further mass transfer resulting to maxima of absorbance.

In the context of extraction time, absorbance values were 0.4903, 0.4897 and 0.4607 for 0, 1 and 2 levels respectively indicating one hour as optimum time for extraction. Improved extraction of the colorant was seen through the highest absorbance in the enzyme method. Enzymes loosen the structural integrity of the plant material making their cells easily breakable. This might be the reason for maximum releasing of the solute colorant from its raw material source. This has resulted in the increased dye yield.

Comparison of Absorbance, Mass transfer rate enhancement and Dye yields

Optimized extraction was compared with the control experiment with respect to the absorbance, mass transfer rate and dye yield. The enhancement in mass transfer rate was calculated. The significant increase in absorbance values, mass transfer rates and dye yield in case of the extraction with the optimum set of conditions might be due to combined effect of all the parameters used at their optimum values. The use of all these levels in one experiment resulted in the attainment of mass transfer equilibrium. Thus it leads to the finding that the optimization of extraction process is beneficial for mass transfer rate enhancement in the natural dye production. In turns the use of optimized extraction conditions gives rise to increased dye yield increasing the productivity of dye.

Conclusion

Optimum extraction conditions obtained from Taguchi design are successfully used to conduct natural dye extraction operation in an efficient way. The result shows significant increase in the absorbance of the colour extract. It indicates that mass transfer rate and therefore yield of the colourant is increased when optimal extraction conditions are used for the extraction. The results are pretty encouraging to notice excellent mass transfer enhancement of about 3.32 times as against control extraction. It saves material as well as time required for extraction. This research can certainly contribute to the future scale-up of *Spathodea campanulata Beauv.* flower dye production useful for textile, food, pharmaceutical, dye-sensitized solar cell applications and cosmetic industries.

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