Studies on dyeing with shikonin extracted from Ratanjot by supercritical carbon dioxide

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Shikonin (di-hydroxy 1, 4-napthaquinone), extracted from Ratanjot (Onosma echiodes) by supercritical carbon dioxide, has been used to study the kinetics of dyeing on polyester. The main component of this dye has been separated chromatographically, analyzed spectroscopically and then used to study the diffusion coefficient. There is not much difference between the diffusion coefficients of shikonin and main component. On comparing the dyeing results of shikonin with those of other napthaquinone natural dyes (juglone, lawsone and crude Ratanjot), it is found that the diffusion coefficient of shikonin and main component is intermediate between juglone and lawsone. The diffusion coefficient of the dye extracted by supercritical carbon dioxide is found to be higher than the crude Ratanjot dye.

Keywords: Diffusion coefficient, Kinetic studies, Polyester, Ratanjot, Shikonin, Supercritical carbon dioxide

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1 Introduction

Shikonin is a historical natural dye that has been used since centuries BC. This dye also holds immense importance in the field of pharmaceuticals, cosmetics and food colourants. It is an enantiomeric napthaquinone natural dye. The main compound shikonin (di-hydroxy 1,4-napthaquinone\(^1\)) and its enantiomer alkannin (Fig. 1) are present in various plants of Boraginaceae family. In India, shikonin and alkannin are present in the root bark of Ratanjot (Onosma echiodes) along with their other derivatives, like deoxyshikonin, acetylshikonin, hydroxyalkanna, etc (ref. 2). Shikonin being hydrophobic in nature can be extracted with solvents or by supercritical carbon dioxide.

The studies have already been done with napthaquinone based isomeric dyes lawsone and juglone (2-hydroxy and 5-hydroxy napthaquinone)\(^3\) and also with crude dye from Ratanjot\(^4\). These dyes exhibited high affinity towards hydrophobic fibres and there is evidence of dye aggregation in solution as well as inside the fibre.

The present paper reports the kinetic of dyeing of shikonin extracted from Ratanjot by supercritical carbon dioxide and also of its major component separated by column chromatography. A comparison of diffusion coefficients of shikonin and its component with those of the other napthaquinone natural dyes has also been made.

2 Materials and Methods

2.1 Materials

'Seef shikonin' — shikonin extracted from Ratanjot by supercritical carbon dioxide was procured from Alps Industries Ltd, Ghaziabad, India. The main component of this dye (Component A) was then separated by column chromatography using silica gel (mesh size 60-120) obtained from Qualigens, India. A high temperature, high pressure (HTHP) beaker dyeing machine was used to carry out the dyeing studies.

Scoured and bleached polyester fabric of 64.30 g/m\(^2\) from JCT Fabrics, India, was used for the dyeing
studies. The radius of the polyester fibre was found to be 0.00085 cm, measured using projection microscope.

The solvents, reagents and chemicals, all of laboratory grade, were obtained from Qualigen, India.

Ultraviolet-visible (UV-Vis) spectra were recorded in ethyl acetate on a Pharmacia LKB Biochrome 4060 spectrophotometer. Fourier transform infrared spectra was registered on KBr discs using Perkin Elmer Spectrum BX FTIR spectrophotometer.

2.2 Methods

2.2.1 Extraction and Characterization of Shikonin

The main component from scfe shikonin was separated by chromatographic techniques. The optimum conditions for the preparative column chromatography were ascertained by thin layer chromatographic (TLC) analysis. Column chromatography was then carried out to separate the components from scfe shikonin. The ratio of dye to silica gel was 1:500 (w/w). A mobile phase comprising hexane: ethyl acetate (98:2 v/v) was used to separate the main component (Component A). The purity of the eluted fractions was determined by TLC analysis with solvent system hexane: ethyl acetate (80:20 v/v). The extracted fractions were then analysed spectrophotometrically.

2.2.2 Preparation of Fabric

The fabric was scoured by using 1g/L of non-ionic detergent (Lissapol N) for 1 h at 90°C with a material-to-liquor ratio of 1:30. This was followed by repeated rinsing in hot and cold water followed by drying at room temperature.

2.2.3 Kinetic Studies

For the kinetic studies, an infinite bath was prepared at a material-to-liquor ratio of 1:1000. Sodium lauryl sulphate (5g/L) was used as a dispersing agent for the dye and the dye bath pH was adjusted to 3.0±0.2 using acetic acid. Dyeing was carried out at 130°C for 1-72 h. The dye was dispersed in the dye

![UV-Vis spectrum of scfe shikonin](image)

Fig. 2—UV-Vis spectrum of scfe shikonin

![FTIR spectrum of scfe shikonin](image)

Fig. 3—FTIR spectrum of scfe shikonin
bath using high-speed stirrer to obtain a suitable dispersion.

The amount of dye on the fibre was estimated by dissolving the dyed fabric in 0-chlorophenol and the absorbance values were measured spectrophotometrically.

3 Results and Discussion

3.1 Spectral Analysis

The UV-Vis spectrum of sefe shikonin (Fig. 2) shows absorption bands at \(\lambda_{\text{max}}\) 207, 216, 274, 521 and 559 nm. The peak at 274 nm is due to the quinonoid absorption. In the FTIR spectrum (Fig. 3), main peaks are observed at 3434 (O-H stretching), 2928 (methyl symmetric), 2847 (methyl asymmetric), 1738 (carbonyl), 1611 (C=C aromatic ring), 1574 (conjugation of carbon with other unsaturated function with the benzene ring), 1454 (methyl C-H bending), 1230 (aromatic alcohol) and 784 cm\(^{-1}\) (aromatic ring out of plane C-H bending).

The UV-Vis spectrum of Component A shows absorption bands at \(\lambda_{\text{max}}\) 275, 488, 520 and 561 nm (Fig. 4). In the FTIR spectrum (Fig. 5), the important peaks are obtained at 3433 (O-H stretching), 2924 (methyl symmetric), 2853 (methyl asymmetric stretching), 2361 (enole), 1718 (carbonyl), 1615 (C=C aromatic), 1210 (aromatic alcohol), 1141 (C-O stretching band of tertiary alcohol) and 1080 cm\(^{-1}\) (primary alcohol). This component is the major fraction of sefe shikonin that could be separated by column chromatography and the IR spectra indicate that the hydroxyl group content is more in this fraction. Moreover, in this component the peak at 1517 cm\(^{-1}\) which is related to the additional carbonyl group is absent, which indicates that this fraction cannot be compounds like acetyl shikonin, butylshikonins or isovaleryl shikonin, as these compounds have additional carbonyl group. Hence, it can be predicted that the Component A
3.2 Kinetic Studies

For the measurement of diffusion coefficient, the dyeing was carried out on polyester fabric with scfe shikonin and Component A at 130°C. The experimental values for concentration \( C \) at time \( t \) \( (C_t) \) and also at infinite \( (\alpha) \) time \( (C_\alpha) \) were obtained for calculating \( C_t / C_\alpha \). These were used to calculate the apparent diffusion coefficient \( (D) \) using Hill’s equation for an infinite dye bath, its approximations given by Urbanik, Rais and Militky and Etters’ equations. Values obtained from all the equations are found to be comparable (Table 1). There is not much difference in the \( D \) values of scfe shikonin and Component A. The \( D \) value of scfe shikonin is slightly higher than that of the Component A. This may be due to the difference in the compounds present in the two dyes and difference in their structure and polarity as this affects the rate of diffusion.

The \( D \) values obtained for scfe shikonin and Component A were compared with those of other naturally occurring naphthaquinones dyes, like juglone and Lawson, on polyester. The diffusion coefficients of all these dyes are shown in Table 2. The \( D \) values of shikonin, in general, are found to lie between the \( D \) values of juglone and lawson. Juglone has \( D \) value much higher than that of shikonin and lawson has \( D \) value much lower than that of shikonin. When compared with the crude Ratanjot extracted by solvent extraction, it is observed that the \( D \) value of the dye extracted by supercritical carbon dioxide is much higher than that of the crude dye. This may be due to the better purity of the dye in the case of extraction done by supercritical carbon dioxide.

4 Conclusions

Shikonin extracted by supercritical carbon dioxide from Ratanjot has a higher diffusion coefficient than the crude Ratanjot dye obtained by solvent extraction. The diffusion coefficient of the composite dye obtained by supercritical carbon dioxide is slightly higher than that of the main component shikonin in it. The diffusion coefficient of shikonin lies between the diffusion coefficient values of juglone and lawson.

References

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<th>Table 1—Calculated values of diffusion coefficient of scfe shikonin and Component A on polyester</th>
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<td>Dye</td>
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<tr>
<td>Scfe shikonin</td>
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<td>Component A</td>
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\( C_t \)—Concentration of dye in fibre at time \( t \) and \( C_\alpha \)—Concentration of dye in fibre at time \( \alpha \)

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<th>Table 2—Values of diffusion coefficient of naphthaquinones on polyester at 130°C</th>
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<td>Dye structure</td>
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<td>5-hydroxy 1,4-naphthaquinone</td>
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<td>2-hydroxy 1,4-napthaquinone</td>
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<td>Di-hydroxy 1,4-napthaquinone</td>
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contains the compound shikonin, nearly free from other derivatives.