

Reclamation of Pure Lac Dye from Lac Effluents

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A simple and economical method has been developed for the recovery of lac dye in pure state from sticklac wash water. The dye is first recovered from acid-treated wash water as calcium salt and is then regenerated in pure form by converting the calcium salt to sodium salt followed by elution through a cation exchange resin. The pure dye is non-toxic and is recommended for use as a food colour and in cosmetic preparations.

IN an earlier communication¹, the preparation of lac dye of 70-75% purity from lac effluents for use in dyeing wool and silk was reported. This lac dye, known as laccaic acid², is a mixture of five components³⁻¹⁰. It was an important article of commerce till the turn of the present century, when it was completely replaced by synthetic dyes. In the absence of

its proper utilization, as much as ~250 tonnes of the dye from 25,000 tonnes of sticklac are washed into the gutters. The dye is very fast to animal fibres, but not to synthetic and vegetable fibres. Extensive toxicity tests carried out at the Central Drug Research Institute, Lucknow, have shown that it is free from toxicity (Venkataraman, K., private communica-

tion). According to the report, the maximum ineffective dose should not exceed 0.1 mg/kg body weight and the recommended proportion of the dye to be used in foodstuff may not exceed 0.01%.

Fruitful utilization of the dye depends on its economical recovery from the sticklac wash water as well as its purity. The present investigation was aimed at these objectives.

At the outset, the quantities of water-soluble dye present in *palas*, *ber* and *kusmi* sticklacs were determined colorimetrically against a 0.1% aqueous solution of pure lac dye. It was found that on an average, in *ari*, the dye is present to the extent of 1.1, 1.16 and 0.82% and in *phunki* its content is 0.93, 0.91 and 0.5% respectively. It has also been found that nearly 60% of the dye settled down along with the sludge when the wash water was treated with sulphuric acid; the rest of the dye remained in the clear aqueous liquor. Recovery of dye from this clear liquor as an insoluble salt by treatment with chemicals, such as potash alum, zinc oxide, lead carbonate, calcium carbonate (precipitated chalk) and quicklime was tried. Calcium carbonate was found to serve the purpose very well and the insoluble calcium salt of the dye along with calcium sulphate and excess calcium carbonate could be collected easily after allowing some time for settling and then filtering. Quicklime was found to be second best in this respect.

The method as standardized on the basis of the results of a few successful preliminary trials with washings of various types of sticklacs is described below.

Method for the recovery of dye

The sticklac wash water is acidified as usual¹¹ with sulphuric acid (0.1% on the vol. of water) and the precipitate allowed to settle in the tanks. The supernatant clear liquor is decanted and treated with the requisite quantity of calcium carbonate (precipitated chalk) or quicklime till the liquor becomes colourless. The calcium salt which separates is collected and dried. The acid precipitated sludge is separately extracted thrice with boiling water for complete removal of the dye, the water in each extraction being nearly 15 times the weight of the sludge. After filtration, the calcium salt of the dye is precipitated as before and dried.

The combined calcium salt, if necessary, is extracted with hexane to remove any adherent wax. It may then be treated for reclaiming the dye with dilute mineral acid. Alternatively, the dye may be recovered by converting it into sodium salt followed by passage through a cation exchange resin.

In the first method, the salt is reacted with an excess amount of a 10% aqueous solution of hydrochloric or sulphuric acid, preferably in a glass or enamelled vessel. The mixture is heated up to 85°C, filtered hot and the filtrate allowed to stand for 7-10 days at room temperature, when the dye crystallizes out. The dye is separated, washed with ice-cold water and dried. The filtrate contains some quantity of dye and can be reused for treating the next batch of salt.

In the second method, the salt is triturated with the requisite quantity of sodium carbonate as a 10% solution. Calcium is precipitated as calcium carbonate and the dye goes into solution as sodium salt. The calcium carbonate is filtered off and the filtrate, violet in colour, dried on a steam-bath, preferably under reduced pressure to yield the sodium salt of the dye. Alternatively, the filtrate is passed through a column of cation exchange resin and on concentration of the eluate, preferably under reduced pressure, pure dye in the form of bright red crystals separates out on keeping the concentrate for three to four days.

The dye obtained by the first process has a high ash content and low water solubility, while that obtained by the second method is purer and completely water soluble. Hence, the second process is preferable. The dye can be used in the form of sodium salt as such. The dye thus obtained is further purified by several crystallizations from hot water or acetone-water mixture (30:10). It is highly soluble in formic and acetic acids, methyl alcohol and 10% aqueous acetone. The aqueous solution is red in colour, but turns orange in acid and violet in alkaline media. It melts within the range 170°-175°C with charring and the acid value varies within 238 and 240.

The average yield of pure dye from *Rangeeni* sticklac (*phunki*) was 0.8-0.9%. Thus, the recovery of dye from the wash water appears to be almost complete under the above conditions.

RECLAMATION OF LAC DYE FROM LAC EFFLUENTS

Table 1—Cost estimate for the production of pure lac dye from sticklac wash water

(Basis : Wash water from 4 charges of 6 quintals each per day, 300 days a year)

INVESTMENT	Rs	
(A) Equipment		
Wooden vats (200 litres cap.), 8 Nos.	8,000.00	
Steam coils, 4 Nos.	1,000.00	
Ion exchange columns, 2 Nos.	10,000.00	
Vacuum distilling unit, 1 No.	10,000.00	
Stainless steel crystallising pans, 4 Nos.	1,000.00	
Distilled water plants, 2 Nos.	2,000.00	32,000.00
(B) Working capital for 3 months (3 × 25 days) to cover cost of chemicals, labour, etc.	18,000.00	18,000.00
Total capital outlay	50,000.00	50,000.00
Production cost per day		
Direct costs		
Chemicals, etc.		
Sulphuric acid (tech), 5 kg	7.00	
Calcium carbonate (precipitated chalk), 10 kg	140.00	
Sodium carbonate, 5 kg	8.00	
Sulphuric acid (pure), 5 kg	25.00	
Cloth, 2 m	10.00	
Utilities		
Water, power, steam, etc.	20.00	
Labour and supervision	30.00	240.00
Indirect costs		
Depreciation of equipment @ 10%	10.00	
Interest on working capital @ 10%	6.00	16.66
Total cost of production of 20 kg pure dye per day		Rs 256.66
Cost of production per kg of pure lac dye		Rs 12.83

In a recent work¹² we have developed a unique method for the production of shellac directly from sticklac by extracting the resin with alcohol or acetone. The residue left over after extraction contains the full complement of wax and dye (the dye as its Na/K salts) along with insect debris, sand and other insoluble impurities. The pure dye (4% on the residue) may be recovered easily by extraction with water, passing the extract through a cation-exchange resin and then concentrating the eluate under vacuum. Alternatively, the aqueous extract may be treated with excess of acetic acid,

warmed to coagulate any proteinous matter, filtered and concentrated to yield the pure dye.

Cost estimate

Based on the experimental findings, cost estimate for the production of ~ 26 kg of calcium salt of dye or ~ 20 kg of pure lac dye per day from sticklac wash water has been prepared (Table 1). The recovery of the dye as calcium salt should be carried out at the existing lac factories, where necessary building facilities are available. Hence, in the calculations, the cost of building and wash water has not been taken into consideration. The pure dye can be prepared from the calcium salt at site if desired or the salt may be passed on to the interested dye manufacturers. However, to get a clear picture, the total cost of production up to the pure dye stage has been worked out. Though precipitated chalk is costlier than quicklime, the former has been preferred for convenience, as the insoluble residue comprises only calcium salt of the dye along with some calcium carbonate and sulphate. The excess of calcium carbonate and that regenerated during treatment of calcium salt of the dye with sodium carbonate may be used again and again for the preparation of dye salt, supplementing it with fresh chalk whenever necessary. The byproduct calcium sulphate after necessary purification may be put to some use. The clear and neutral mother liquor left after precipitation of the dye salt may be reused for washing sticklac.

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References

- GHOSE, A. K., MUKHERJEE, M. & SENGUPTA, S. C., *Res. & Ind., New Delhi*, **9** (1964), 129.
- SCHMIDT, R. E., *Ber. dt. chem. Ges.*, **20** (1887), 1285.
- BHIDE, N. S., JOSHI, B. S., PATWARDHAN, A. V., SRINIVASAN, R. & VENKATARAMAN, K., *Bull. natn. Inst. Sci. India*, No. 28 (1965), 114.
- PANDHARE, E. D., RAMA RAO, A. V., SRINIVASAN, R. & VENKATARAMAN, K., *Tetrahedron (suppl.)*, **8** (1966), 229.
- PANDHARE, E. D., RAMA RAO, A. V. & SHAIKH, I. N., *Indian J. Chem.*, **7** (1969), 977.
- BURWOOD, R., READ, G., SCHOFIELD, K. & WRIGHT, D. E., *J. chem. Soc.*, (1965), 6067; (1967), 842.
- BURWOOD, R., READ, G. & SCHOFIELD, K., *Tetrahedron Lett.*, (1966), 3059.

8. BHIDE, N. S., PANDHARE, E. D., RAMA RAO, A. V.,
SHAikh, I. N. & SRINIVASAN, R., *Tetrahedron Lett.*,
7 (1969), 987.
9. RAMA RAO, A. V., SHAIKH, I. N. & VENKATARAMAN,
K., *Tetrahedron Lett.*, 7 (1969), 188.
10. MEHANDALE, A. R., RAMA RAO, A. V., SHAIKH,
I. N. & VENKATARAMAN, K., *Tetrahedron Lett.*
(1968), 2231.
11. BHOWMIK, T. & GHOSE, A. K., *Res. & Ind., New
Delhi*, 3 (1958), 320.
12. GHOSE, A. K. & SENGUPTA, S. C., *Res & Ind., New
Delhi*, 21 (1976), 98.