

**REMOVAL OF IONIC DYES FROM WATER BY LIQUID-  
LIQUID EXTRACTION USING REVERSE MICELLES**

**By**

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in fulfillment of the requirements of the degree of  
Doctor of Philosophy**

**to the**



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## CERTIFICATE

This is to certify that the thesis entitled **REMOVAL OF IONIC DYES FROM WATER BY LIQUID-LIQUID EXTRACTION USING REVERSE MICELLES** submitted by **Mr. Prabhat Pandit** to the Indian Institute of Technology Delhi, for the award of the degree of the Doctor of Philosophy is a record of the bonafide research work carried out by him. Mr. Prabhat Pandit has worked under my supervision for the submission of this thesis, which to my knowledge has reached the requisite standard.

This thesis, or any part thereof has not been submitted to any university or institution for the award of any degree or diploma.

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*Prabhat Pandit*  
10/11/03  
(Prabhat Pandit)

*Dedicated*

*to my wife, children*

*and*

*parents*

*for bearing some trying times*

**To see a World in a Grain of Sand  
And a Heaven in a Wild Flower,  
Hold Infinity in the palm of your hand,  
And Eternity in an hour**

**- William Blake**

## ABSTRACT

Effluent water from carpet manufacturing, dyeing, textile industries, and pulp and paper contains various types of dyes and they should be removed before discharging the effluent to environment to avoid health hazards and destruction of the ecosystem. In the present study, solvent extraction using reverse micelles is proposed for the removal of organic dyes from water. Towards this approach, the dye is solubilised in the aqueous core of the reverse micelles, which are present in the organic phase. The organic phase is subsequently separated from the aqueous phase leading to significant removal of dye from the aqueous phase. The use of reverse micelles for the removal of dye from aqueous phase is not found in the literature. The experiments were conducted by mixing a known quantity of dye in aqueous phase and solvent containing surfactants in a simple mixer. The separation of solvent phase from aqueous phase due to gravity results in separation of dye from the aqueous phase. The different ionic dyes e.g., eosin yellow, methylene blue, malachite green, methyl orange, orange G in aqueous phase and different surfactants e.g., sodium dodecylbenzene sulphonate (SDBS), hexadecyl trimethyl ammonium bromide (HTAB), cetyl pyridinium chloride (CPC), and sodium-2-diethyl hexyl sulfosuccinate (AOT) in different solvents were used in the experimental study. Amyl alcohol, benzyl alcohol, methyl benzoate and iso-octane were used as the solvents for hosting the dyes in the reverse micelles. The experimental data on percentage removal for different ionic dyes indicate that only small quantity of dye is transferred to the solvent phase when no surfactant is used.

Further, the dye is not removed from water when surfactant having similar charge to that of dye is used. Thus, the electrostatic attraction between cationic (or anionic) dye and anionic (or cationic) surfactants is responsible for dye solubilisation in reverse micelles.

The removal of dye from aqueous phase by forming reverse micelles in the solvent phase is studied in detail to elucidate the effect of process variables on the percentage removal of dye. The percentage removal of dye from the aqueous phase increases with the decrease in dye concentration and with the increase in surfactant concentration. The increase in percentage removal of dye is attributed to increase in number of reverse micelles with the increase in surfactant concentration. A limited quantity of dye is encapsulated for a given surfactant concentration. The COD of the water after treatment through liquid-liquid extraction using reverse micelles decreases significantly (~80%) as compared to that of the original dye solution. Two different cationic surfactants, HTAB and CPC or anionic surfactants, SDBS and AOT resulted in the same percentage of dye removal. The increase in the organic to aqueous phase volumetric ratio increases the solubilisation of the dyes in the solvent phase leading to larger removal of the dyes from aqueous phase. The percentage dye removal increases with the increase in pH for methyl orange, orange G and eosin yellow. The percentage dye removal decreases with the increase in pH for methylene blue and malachite green. Further, the percentage dye removal decreases with the increase in KCl concentration for methylene blue and orange G. Although no effect of solvent nature

on dye solubilisation capacity has been established, amyl alcohol is found to be the best solvent as far as phase separation time is concerned.

Two mathematical models based on ion-exchange reaction between surfactant and dye and electrostatic adsorption (Stern adsorption isotherm) of dye on surfactant head groups in the reverse micelles have been tested. The experimental data could be fitted to a straight line in accordance to the ion exchange reaction model for all the dyes. The slopes and intercepts of the straight lines provided the values of equilibrium constants of the ion-exchange reactions. The predictions of the electrostatic model are in good agreement with the experimental data for varying dye, solvent, surfactant type and concentrations.

The recovery of dye and solvent from the solvent to aqueous phase is possible using a counter-ionic surfactant. The back transfer is governed by the concentration of the counter-ionic surfactant, pH and KCl concentration in the aqueous phase. The mixture of cationic and anionic dyes was successfully separated from aqueous phase by treating with reverse micelles of anionic surfactants and cationic surfactants in step-wise manner.

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