Recovery of Reactive (Triazine) Dyes from Textile Effluent by Solvent Extraction Process

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In the present work, triazine reactive dyes are recovered from the textile effluent by the solvent extraction process using surfactants. Work is carried out on three different triazine dyes *i.e.*, reactive blue 171, reactive red 141 and reactive yellow 84. As these dyes are anionic in nature so cationic surfactant *i.e.*, hexadecyl trimethyl ammonium bromide (HTAB) is used for the forward extraction of dye into solvent phase. For the backward extraction of dye into aqueous phase an anionic surfactant is used to counter the charge effect *i.e.*, sodium dodecyl benzene sulfonate (SDBS). The cationic surfactant is chosen in such a way that it forms reverse micelle with solvent. Isoamyl alcohol is selected as solvent for the present studies, since the other lower alcohols are soluble in water, where as it is almost immiscible and forms distinct upper layer in aqueous solution. The effects of different parameters, such as the surfactant concentration, pH and electrolyte (NaCl) concentration are studied in the present work.

Key Words: Triazine dyes, Reverse micelle, Surfactant, Solvent extraction, Electrostatic interaction.

INTRODUCTION

Colour that contributes so much to the beauty of nature is essential to the attractiveness and acceptance of the textile products used by the modern society. All the textile industries use dye to colour the fabric to make it appealing to the customers. Many classes of dyes are available such as direct dyes, vat dyes, sulphur dyes and reactive dyes. All the dyes have some unique properties but triazine class of reactive dyes is the first choice of dyers because of its low cost and high colour fastness to washing, rubbing and light[1,2]. Even after the technological process developments by various scientists, *ca.* 20-30 %[3,4] of dyes remain unused that should be removed before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem. Effluent containing dye is responsible for water-borne diseases exhibiting symptoms such as hemorrhage, nausea, dermatitis, ulceration of the skin and mucous membranes, kidney damage and a loss of bone marrow leading to anemia[5,6]. Most dyestuffs are designed to be resistant to environmental conditions such as light, pH and microbial attack[7-9]. Hence, their presence in effluent is undesired and it is essential to remove dyes from effluents before their discharge

to the environment. Several techniques has been developed for the removal of colour from the effluent such as Flocculation-Coagulation[10,11], adsorption[12-14], membrane-separation[15], electrochemical[16], reverses osmosis, ozone oxidation[17] and biological treatment[18-20]. In the separation of dyes based on the flocculation-coagulation process, dye forms a complex with the flocculant and thus the reuse of dye are not possible. Removal of dye by adsorption on wood charcoal, sugarcane bagasse, coconut coir pith, eucalyptus bark and activated charcoal is studied in detail[21]. Although adsorption methods are capable of removing the dyes from effluent but regeneration of most of the adsorbents is difficult except for activated charcoal. The adsorption treatment using activated charcoal as the adsorbent is quite expensive[22,23]. All other methods such as membrane- separation and reverse osmosis are also expensive and economically not viable.

In the present work the application of reverse micelles in removing and recovering three different triazine dyes from textile effluent by solvent extraction process is studied. The purpose of the present study is to show that the un-used dyes can be removed and recovered from the effluent by solvent extraction process using reverse micelle. The effect of various parameters such as surfactant concentration, pH, salt concentration and size of dye molecule is also studied in the present work. For the present study, effluent is generated in the laboratory using actual method of dyeing[24] on 100 % ready for dyeing cotton cloth. As the dyeing is done on laboratory scale so the percentage of un-used dye in the effluent is relatively higher ($\approx$ 40 %) in comparison to the industrial effluent.

EXPERIMENTAL

All dyes are supplied by colour division of Atul India Limited. Isoamyl alcohol, glacial acetic acid, sodium carbonate, sodium chloride, hydrochloric acid.

Surfactants: The surfactants used are:

(i) Hexadecyl trimethyl ammonium bromide (HTAB, chempure): It is a cationic surfactant having critical micelle concentration (CMC) value of 350 mg/L and molecular weight of 364.6.

(ii) Sodium dodecylbenzene sulfonate (SDBS, chempure): It is an anionic surfactant having critical micelle concentration (CMC) value of 500 mg/L and molecular weight of 348.5.

Cotton cloth: For dyeing purpose 100 % ready for dyeing cotton cloth is used which is procured from the local market. The specifications of the fabric used are: Warp yarn count:1/30 cc, Weft yarn count: 1/40 cc, EPI/PPI:70/42, Fabric width: 100 cm, Fabric weight: 90 GSM.

Effluent: Effluent was generated in the laboratory by dyeing cotton cloth with the actual dyeing process.

Dyeing process: Dye bath was prepared by dissolving 0.8 g w/w (for 0.1 % depth of shade for 80 g fabric) of dye in 2 L of water. To this added 80 g of cotton cloth to maintain a M:L ratio of 1:25. Started heating on the hot plate and increased the temperature to 45 °C at a rate of 2 °C/min. Then added 3 g of sodium chloride

to the dye bath and further increased the temperature to 85 °C. Then added 3 g more of sodium chloride and run the bath for 15 min. Then added 4 g of sodium carbonate and run the bath for 20 min. Cooled the bath and removed the fabric for washing and neutralization. Drain was collected in a bottle for further use as an effluent.

General procedure: The experiments were conducted in two steps. The first step is the dye removal step, where dye was removed from the effluent by solvent extraction process using reverse micelle. The second step is the dye recovery step, where dye is backward extracted to water by using anionic surfactant.

Dye removal: 50 mL of the effluent was added to 25 mL of isoamyl alcohol having 120 mg of cationic (HTAB) surfactant. The aqueous and solvent phases were mixed using a mechanical stirrer (Universal Motor) at a fixed rpm of 4000 for 2 min. The two-phase dispersion was transferred to a separating funnel to separate the aqueous and solvent phases by gravity. This resulted in the formation of two clear liquid phases in 1 h. The solvent phase containing the dye encapsulated in the reverse micelle and the clear aqueous phase. The samples were collected from the aqueous phase and analyzed in spectrophotometer (Analytik Jena Specord 200) to determine the amount of dye separated.

Recovery of dye: The experiments on backward transfer of dye into aqueous phase were conducted using process similar to forward extraction. To the 25 mL of the solvent phase containing the extracted dye was added 50 mL of fresh aqueous phase containing 550 mg of anionic surfactant (SDBS). The aqueous and solvent phases were mixed using a mechanical stirrer (Universal Motor) at a fixed rpm of 4000 for 2 min. The two-phase dispersion was transferred to a separating funnel to separate the aqueous and solvent phases by gravity. This resulted in the formation of two clear liquid phases in 1 h: an aqueous phase containing dye and a clear solvent phase. The aqueous phase was analyzed using spectrophotometer (Analytik Jena Specord 200) to quantify the dye recovered.

Detection method: All colour measurements were carried out with spectrophotometer (Analytik Jena Specord 200) operating in the visible range in absorbance mode. Absorbance values were recorded at the wavelength for maximum absorbance (λ_{max}) corresponding to each dye. Results reported are average of five readings in each case.

% Dye removal: It is calculated by the following formula:

$$\% \text{ Dye removal} = \frac{Ab_1 - Ab_2}{Ab_1} \times 100$$

% Dye recovery: It is calculated by the following formula:

$$\% \text{ Dye recovery} = \frac{Ab_3}{Ab_1} \times 100$$

where Ab_1 = Absorbance of original effluent, Ab_2 = Absorbance after dye extracted from effluent, Ab_3 = Absorbance after recovery of dye in aqueous layer.

RESULTS AND DISCUSSION

The removal of dye from the effluent using solvent extraction process was very low without surfactant. It is clear from the Fig. 1 that the removal is only 4.0, 4.6 and 5.2 % in yellow 84, red 141 and blue 171, respectively in the absence of surfactant (0 mg HTAB). This may be due to the partial physical interaction between anionic dye molecules and organic solvent and partition of dye from higher concentration in aqueous layer to a lower concentration in solvent. Whereas, after the addition of surfactant in solvent, the removal percentage is increased drastically which may be due to the formation of reverse micelle of surfactant in organic layer with entrapment of dye anion. It is shown in Fig. 1 that the complete removal of dye is possible by the solvent process using reverse micelle. Effect of various parameters on the percentage removal of dye is discussed as below:
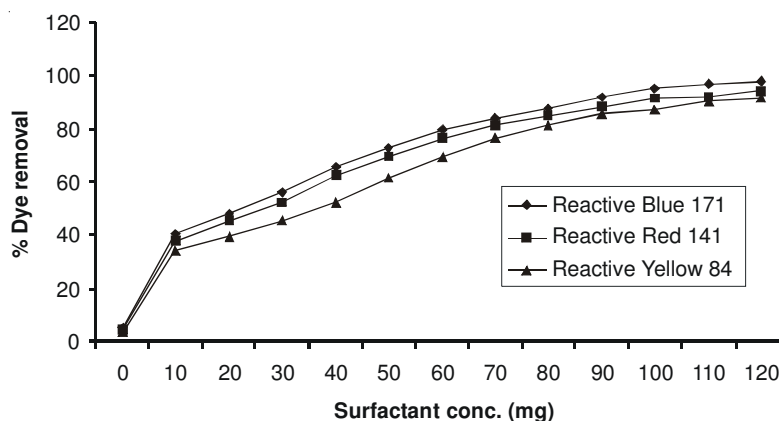

Fig. 1. Effect of surfactant concentration on the percentage removal of colour

Effect of surfactant concentration: For the studies a mixture of effluent with organic solvent into 2:1 ratio is used. It is clear from the Fig. 1 that with the increase of surfactant concentration percentage removal of dye increases with constant amount of isoamyl alcohol in mixture because with the increasing amount of surfactant the number of reverse micelle increases linearly which increases the number of dye molecules to be encapsulated. This can be further understood by thermodynamic model based on the mass action kinetics:

For a pseudo reaction of dye molecule D with n number of reverse micelle M

$$D + n\,M \longrightarrow DM$$
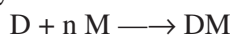
where D = Dye molecule, M = Reverse micelle, DM = Reverse micelle with entrapped dye molecule.

Reverse micelle conc. M is related to the surfactant conc. [S] as

$$[M] = \frac{[S]}{\text{Aggregation number}}$$

Aggregation number (Nag) is assumed to be independent of surfactant conc.[25]. So increase in surfactant conc. leads to the increase in number of reverse micelle, consequently more number of dye molecules gets encapsulated increasing the percentage removal of dye.

Effect of pH: Fig. 2 shows the effect of pH on the percentage removal of dye from effluent. It is clear from the Fig. 2 that the dye removal decreases with the decrease of pH. It is maximum (98.3 % in blue 171) in alkaline medium at pH 12 and reduces to 59.1 % in acidic medium at pH 4. This reduction with the decrease in pH can be explained on the basis of electrostatic force of attraction between the anionic dye and cationic group of surfactant. In the acidic medium, due to the protonation of dyes, magnitude of anionic charge of dyes gets reduced. Since the electrostatic force of attraction depends upon the magnitude of charge. Lower the magnitude of charge lesser is the attraction among ions. So in acidic medium less dye is attracted towards the opposite charge reverse micelle and hence percentage removal of colour is reduced.
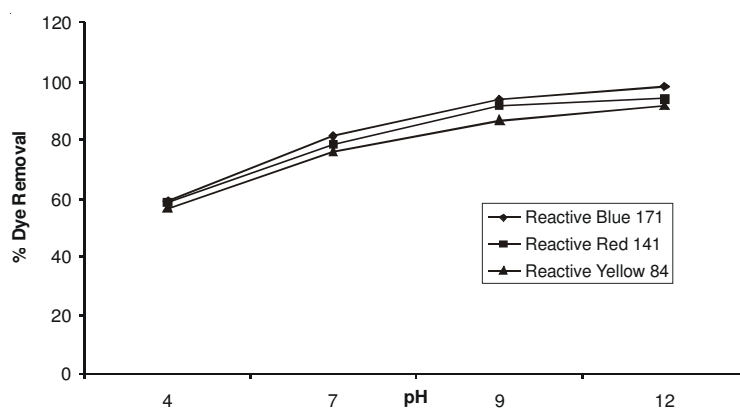

Fig. 2.   Effect of pH on the percentage removal of colour with 120 mg hexadecyl trimethyl ammonium bromide

Effect of salt concentration: Fig. 3 shows the effect of salt concentration on the percentage removal of dye. It is clear from the figure that the percentage removal of colour decreases with increase in salt concentration. With the pure dye solution removal is more than 97 % in all three dyes. But in case of effluent, due to the presence of salts, removal of dyes decreases from 97.2 to 81.3 % in yellow 84. With further addition of salts, sharp decrease in the removal of dyes is observed *i.e.*, 60.6 % with 3 g NaCl and 48.3 % with 5 g NaCl in case of yellow 84. Similar trend are shown by other dyes also.

The decrease in removal of dyes in the presence of salts is due the fact that anions of the salt may start competing with the dye anions and block the reverse micelles. Thus, a number of reverse micelles gets blocked and as a consequence of this removal of dye decreases.
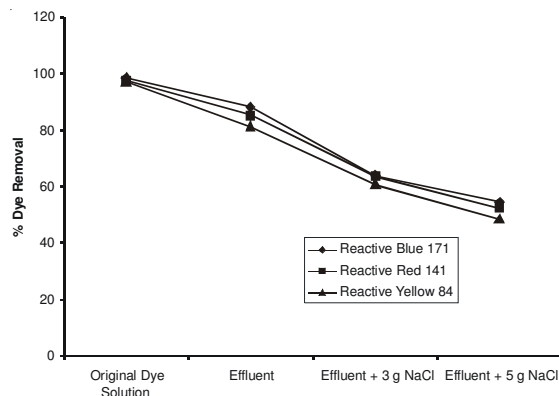
Fig. 3.   Effect of NaCl concentration on the percentage removal of colour with 80 mg
hexadecyl trimethyl ammonium bromide

Recovery of dye: It is clear from the Fig. 4 that the recovery of dye into aqueous phase from solvent phase is 85, 78 and 74 % in reactive blue 171, reactive red 141 and reactive yellow 84, respectively. This backward transfer of dye into the aqueous phase in the presence of anionic surfactant is due to the breaking of reverse micelles of hexadecyl trimethyl ammonium bromide in solvent layer by counterionic sodium dodecylbenzene sulfonate. After the breaking of reverse micelle, encapsulated dye gets released and passes into aqueous layer due to its ionic nature
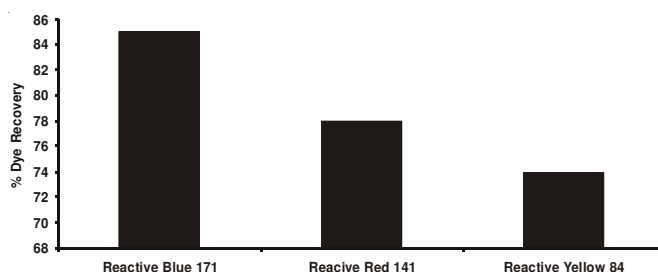

Fig. 4. Percentage dye recovery using sodium dodecylbenzene sulfonate

From the results it is observed that weight of dye molecule is also playing an important role in the dye removal. Removal and recovery of dye are maximum with the blue 171 dye which has lowest molecular weight and minimum with the yellow 84 which has the highest molecular weight among the three dyes used. Possibly with lower molecular weight the size of dye anion is relatively smaller which helps in more encapsulation of dye molecules by surfactant reverse micelle.

Conclusion

The present work describes the almost complete removal and recovery of reactive (triazine) dyes from textile effluent by solvent extraction process using surfactant. Further it is also observed that the process of dye recovery is effected by the parameters

like surfactant concentration, pH, salt concentration and molecular weight of the dye. (**a**) Almost complete removal of dye from the effluent is possible with solvent process and the remaining clean water can be released or re-used. (**b**) The above recovered dye can be re-used for dyeing. This is a significant economical help to the society. (**c**) Solvent and surfactant used in the forward extraction can be recovered and re-cycled. (**d**) Organic carbon content of the effluent is reduced significantly, hence pollution hazard can be minimized. All the above, this process is greatly helpful in maintaining a green earth and pollution free environment.

ACKNOWLEDGEMENTS

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