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Research Article

EFFICIENT GEMINI SURFACTANT AIDED EXTRACTION OF HAZARDOUS REACTIVE DYE FROM EFFLUENT

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ABSTRACT

Reactive dyes are hazardous due to their property of forming covalent bond with $-NH_2$ and –SH group of proteins in living organisms. Hence their removal is mandatory from the effluent before discharging into main stream. Different methods have been employed for the satisfactory removal of dyes. Current methods for their removal largely rely on adsorption techniques which are costly and produce another waste to be disposed off, whereas the concept of reverse micelles acting to encapsulate the dye in aqueous micro pool in solvent environment provides a useful chemistry. The removal of the reactive red RB from aqueous phase in amyl alcohol solvent using cationic surfactants was successful giving 100% removal within seconds. The effect of dye and surfactant concentration, solvent, temperature, salts like NaCl, KCl, NH_4Cl and $MgCl_2$ were studied. The percentage removal of dye depends upon the size of the reverse micelle of the surfactant. The solvent used for the dye removal can be recovered by distillation method and can be reused.

Keywords: *Reverse Micelle, Effluent, Reactive Dye, Solvent Extraction*

INTRODUCTION

The ever-developing dye industry has adversely affected the environment by producing 3,84,000 tons of waste each year. In 1856 when the synthetic dyes came into existence, they completely replenished natural dyes due to their properties like cheaper to produce, brighter, more color-fast, and easy to apply to fabric. Depending on exposure time and dye concentration, dyes can have acute or chronic effects on exposed flora and fauna and even its presence in small quantities (less than 1 ppm) is highly visible in water due to their brilliance. It affects the aquatic life as the light absorption by dyes diminishes photosynthetic activity of algae and seriously influences on the food chain. Dyes can remain in the environment for an extended period of time, because of high thermal and photo stability. Textile dyes can cause allergies such as contact dermatitis and respiratory diseases, allergic reaction in eyes, skin irritation, irritation to mucous membrane and the upper respiratory tract. Effluent containing dyes is responsible for water-borne diseases exhibiting symptoms such as haemorrhage, nausea, dermatitis, ulceration of the skin and mucous membranes, kidney damage and a loss of bone marrow leading to anaemia (Anliker *et al.*, 1981).

Dyes are mostly introduced into the environment through industrial effluents. An important portion of the commercial synthetic dyes are reactive dyes, mainly because of their excellent binding ability initiated by the formation of a covalent bond between their reactive groups and the surface groups of the textile and cellulose fibres. Hence, extensively used in textile industries for dyeing wool, silk, modified acrylic fibres and polyamide fibres which up to 50% of the dyes may be lost to the effluent (Easton, 1985). Reactive dyes are present in a hydrolyzed state in the exhausted dyebath or wash-water, a form that cannot be reused in the dyeing process. Moreover, their photolytical/chemical stability and extremely low physical affinity (Reife, 1993) for various adsorbents make conventional treatment a rather difficult task. Their release to the environment is hazardous, due to their toxicity, mutagenicity, and non biodegradability

(Asouhidou *et al.*, 2009). Also, reactive dyes tend to pass through conventional treatment systems unaffected (Pearce *et al*., 2003). Additionally, reactive dyes are resistant to natural biodegradation, due to the aromatic rings in their structure (Karacakaya *et al.,* 2009).

Public perception of water quality is greatly influenced by the color. Hence, their presence in wastewater is unwanted, and it is mandatory to remove dyes from effluents before their discharge to the environment. Several studies have been performed for the treatment of effluents. The three main categories are chemical, physical and biological methods. The conventional biological treatments are less effective for treating wastewater containing azo dyes (Arslan *et al*., 1999).

In literature, various techniques have been proposed to remove dyes from water, such as oxidation (Xu *et al.,* 2005) adsorption (Khraisheh *et al.,* 2005) flocculation-precipitation (Golob *et al*., 2005), membrane separation (Sostar *et al.*, 2005) electro-coagulation (Alinsafi *et al.,* 2005**)** electrochemical destruction (Jain *et al.*, 2004), photo catalysis (Hachem *et al*., 2001) ultrasound (Vinodgopal *et al.*,1998). All the methods have been compared but these methods have advantages as well as disadvantages (Ahmet *et al.*, 2003). Due to the high cost and other disadvantages of the above methods, a new method for dye removal has been tried.

This method is based on the solvent extraction method using reverse micelles of surfactants (Pandit *et al.*, 2002; Pandit *et al.,* 2004). In this method, the dye is extracted into the reverse micelle of the surfactant soluble in a solvent by electrostatic attraction and is tightly held there. Reverse micelles are nanometer size aggregates of surfactant molecules surrounding a microscopic water core in non polar solvents. These inverted aggregates are drawn together by hydrogen bonding in the presence of minimal amounts of water and they are thermodynamically stable.

The tendency of many water soluble solutes to partition into the aqueous inner core of reverse micelles present in the organic phase has spawned a great deal of interest in using such systems as continuous extractants for proteins (Dungan *et al.*, 1991) amino acids (Rabie *et al.*, 1996) and enzymes(Krei *et al.*, 1992).

In the continuation of our work for the removal of the anionic dyes from the effluent (Mangat *et al.*, 2014a; Mangat *et al.*, 2014b) which have been removed by laboratory synthesized surfactants (Mangat *et al.*, 2014c; Mangat *et al.,* 2013). The removal of reactive dye was attempted with the laboratory synthesised cationic gemini surfactant (Mangat *et al.*, 2014d).

Since effluents containing reactive dyes contain certain salts, and the pH of effluent is alkaline so the attempts have been made to study the extraction process in the presence of salts and as a function of temperature and concentration of dye, surfactant and salt at alkaline pH.

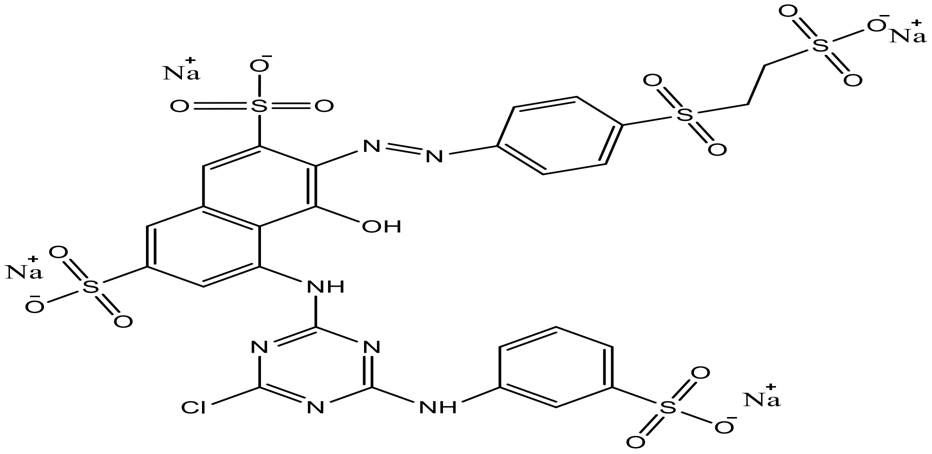
MATERIALS AND METHODS

Chemicals

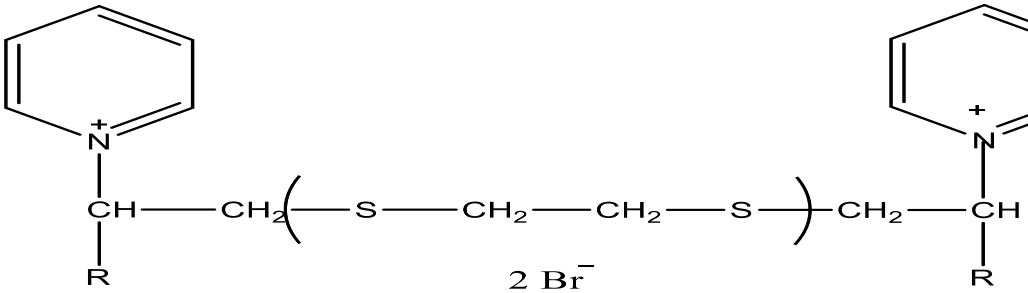
The cationic gemini surfactant used to prepare reverse micelles was 1,1'- (1,1'-(ethane-1,2-diylbis-(sulfanediyl)) bis (octadecane-2, 1-diyl) dipyridinium bromide (CMC = 0.02 mm and Molecular weight = 915.15). Reactive Red is anionic in nature with sulfate and amino groups attached to the aromatic moieties. The reactive red dye has four different parts

- The chromogen i.e. azo group
- The water solubilising group (ionic groups, often sulphonate salts), which has the expected effect of improving the solubility, since reactive dyes must be in solution for application to fibres. This means that reactive dyes are not unlike acid dyes in nature.
- The bridging group links the chromogen and the fibre-reactive group. Frequently the bridging group is an amino, -NH-, group. This is usually for convenience rather than for any specific purpose.
- The fibre-reactive group is the only part of the molecule able to react with the fibre.

The structure and the properties are given in Figure 1



Reactive Red RB (MW = 968.21)
$C_{27}H_{18}N_7ClNa_4O_{15}S_5$



18-2-18 (MW = 915.15)
CMC = 0.02 mM
$C_{48}H_{86}Br_2N_2S_2$

Figure1. Structure of the Dye RB and the Surfactant

The solvent used for dye removal from water was amyl alcohol (3-methyl butan-1-ol). Freshly prepared distilled water was used in all the experiments. The pH was varied by adding analytical grade HCl and NaOH. Analytical grade NaCl, KCl, NH_4Cl and $MgCl_2$ were used to study the effect of salt. These chemicals were acquired from E. Merck, India and the dye was obtained from Ranbaxy, India.

Experimental Setup

A simple magnetic stirrer (Remi, India) was used for the mixing of the solvent and the aqueous phase. The speed of the stirrer can be measured accurately (rpm). A separating funnel was used to separate the solvent and aqueous phases by gravity. A UV-V is spectrophotometer (Shimadzu, UV 1800) has been used to measure the color intensity after and before dye removal in the aqueous phase.

To succeed as a viable alternative to the conventional extraction process, a solvent is used in the reverse micellar extraction technique, which is easily and cost effectively separated from solvent/aqueous phase dispersion in the presence of surfactant. The reverse micelles are formed in the solvent phase. Process optimization was carried out with benzyl alcohol, octanol, decanol and amyl alcohol. Amyl alcohol has been found to be the best solvent for the removal of dye from water using the reverse micelles technique and hence it has been selected as a solvent for further use. Amyl alcohol is sparingly soluble in water at 298 K and at atmospheric pressure. The dispersion of amyl alcohol in water is easy to separate into pure phases in a separating funnel by gravity. A 110 ml mixture of amyl alcohol/water dispersion in 1:10 ratio separates in 2-5 hour into pure phases within a range of the surfactant concentration.

Method

Different concentrations of the dye were prepared by adding different amount of dyes (mg) in 100 ml of the solution. A known quantity of cationic surfactant above the critical micelle concentration (CMC) was added to 10 ml of amyl alcohol. The aqueous phase and amyl alcohol were mixed thoroughly using the magnetic stirrer for 5 min at 25ºC. The whole solution was transferred to a separating funnel to separate the solvent and aqueous phases by gravity. The heavier aqueous phase was collected at the bottom of the separating funnel, whereas the lighter amyl alcohol was collected at the top. The residual concentration of dye in aqueous phase was analysed by UV-V is spectrophotometer to determine the amount of dye extracted. The dye concentration in amyl alcohol was determined to check the mass balance. The experiments were repeated to check the accuracy and the data were found to be accurate within ±5% error.

Calculation

The extraction performance was determined with the % removal (E), given by equation 1

$$\mathbf{E} = \frac{D_{i-D_{aq}}}{D_i} \times \mathbf{100} \qquad \textbf{(1)}$$

Where,
D_i = initial concentration of dye taken
D_{aq} = concentration of dye left in the aqueous media after the two layers separates
D_{org} = concentration of dye encapsulated in the reverse micelles in the organic phase

RESULTS AND DISCUSSION

The efficient removal of the dye depends upon the size compatibility of the dye with the size of core of the reverse micelle. Depending upon this the surfactant chosen for the removal of RB is 18-2-18. Initial studies were carried out in which the 0.1 mm (9.68 mg/100 ml) of RB was treated with 1 mg of surfactant 18-2-18 and the percentage removal was satisfactory (64.90 %). So the studies were extended as a function of solvent, surfactant, dye and salt concentration and as a function of temperature and are discussed as follows:

Effect of Solvent

To study the effect of the solvent, the concentration of the dye RB (30 mg/100 ml) and the surfactant (4 mg/10 ml) is kept constant and studies have been carried out using different solvents viz. amyl alcohol, benzyl alcohol, octanol, decanol are studied for the removal of RB. The results are reported in Table 1.

Table 1: Effect of the Solvent on the Percentage Removal (E) of RB

S.No	Solvent	E
1.	Amyl Alcohol	51.26
2.	Benzyl Alcohol	49.00
3.	Octanol	51.10
4.	Decanol	50.36

The result in the Table 1 shows that the best solvent for the removal of the dye is amyl alcohol. Hence, all the experiments were done using amyl alcohol.

Effect of Surfactant Concentration

To optimize the surfactant concentration, the dye concentration and solvent to water mass ratio have been kept constant and the effect of the surfactant concentration has been studied by increasing surfactant concentration from 2 mg to 10 mg/10 ml. The results are shown in the Figure 2. As can be seen from the

Figure, for the lower concentrations of the dye (upto 20 mg/ 100 ml) there is an increase in the E and after certain concentration of the surfactant, the percentage removal decreases after it reaches 100 % due to saturation. This Figure shows that upto 20 mg of RB, maximum removal is at 6 mg of the surfactant and further it decreases with the increase in the surfactant concentration.

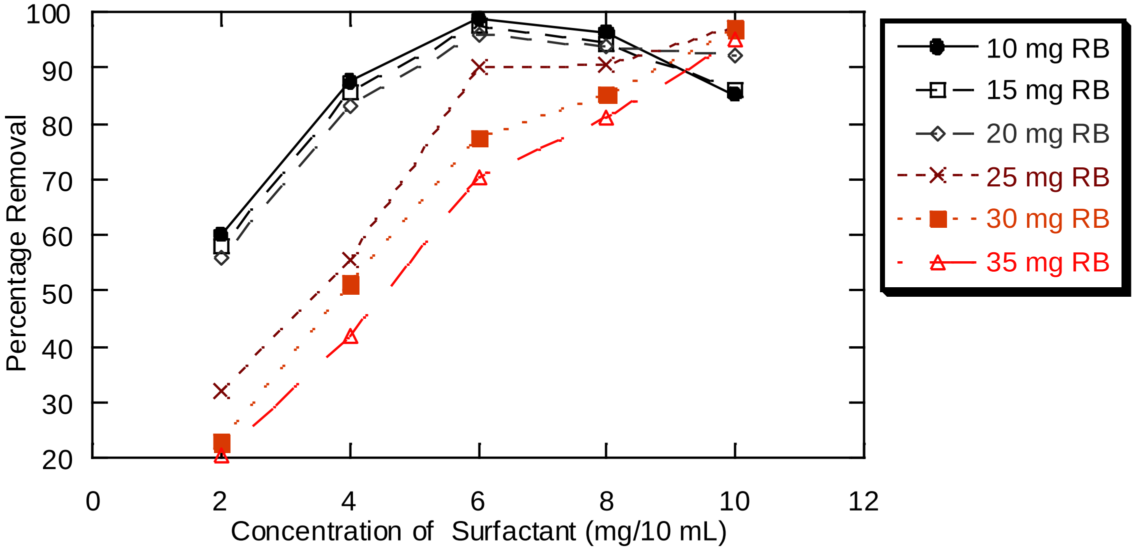


Figure 2: Effect of the Surfactant and Dye Concentration on the Percentage Removal of RB

This can be explained on the basis of the fact, that the dye molecules occupy the vacant sites in RM and that after saturation, further increase in the surfactant concentration above (6 mg/10 ml) causes aggregation of the reverse micelles into lamella and the removal decreases. The formation of the lamellae has been confirmed from the TEM (Figure 3) of the solution above 6 mg of the surfactant concentration. However, at high dye (above 20 mg/100 ml) and surfactant concentrations (above 6 mg/10 ml), there are increased electrostatic in the system which prevents the formation of lamellae and more RM sites are available to the dye molecule for the encapsulation, increasing the solubility of the dye in the organic phase leading to the higher E values with surfactant concentration.

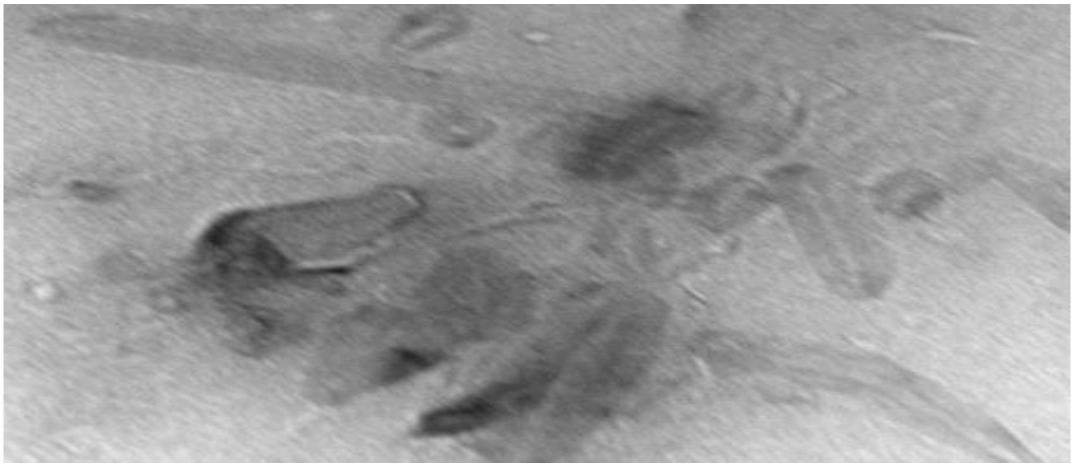


Figure 3: Tem Showing Formation of Lamellae at Higher Concentration of the Surfactant

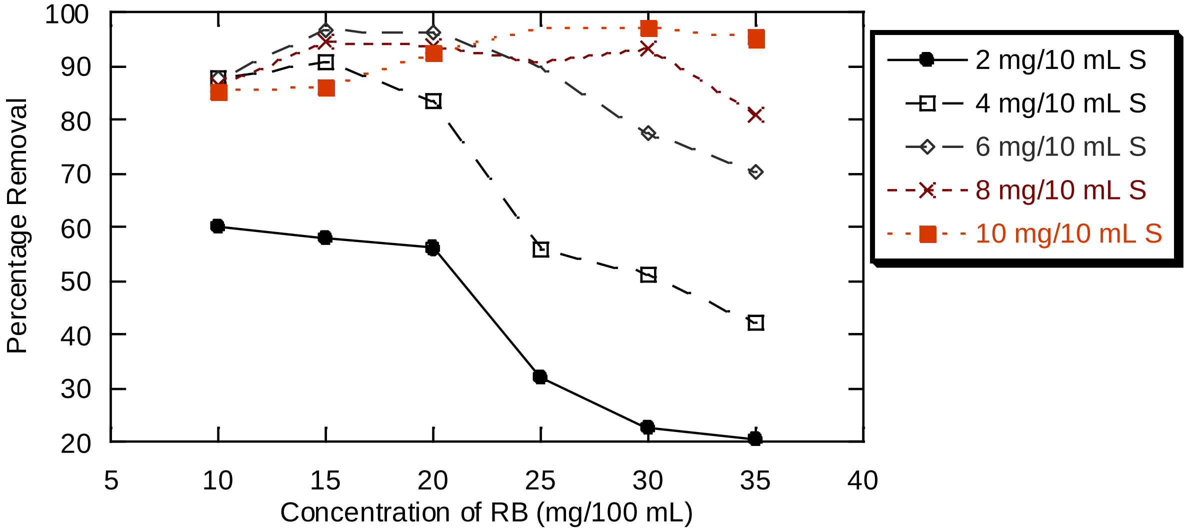


Figure 4: Effect of the Dye Concentration on the Percentage Removal of RB

Effect of Dye Concentration

To know the extent to which the dye can be effectively removed from the solution, the effect of the dye concentration has been studied by increasing the concentration of the dye from 10 mg to 30 mg/ 100 ml, in the varying range of surfactant concentration of 2 mg/10 ml to 10 mg/10 ml and is depicted in Figure 4. It can be seen that upto 6 mg of surfactant, E decreases with increase in dye concentration. At low dye concentration, the reverse micelles are available for the dye molecules and beyond certain level, saturation of sites occur and no further extraction takes place leading to the decrease in the extraction. At higher concentrations of the surfactant (above 6 mg) the surfactant exists in lamellae form at low concentrations of the dye as shown by the TEM, hence E decreases. But as the high concentration of the dye prevents the surfactant to form lamellae, hence reverse micelles are available for the dye up take leading to the increase in removal.

Effect of Electrolytes

Reactive dyes are used for dyeing processes in the presence of salts. The presence of salts in reactive dye solutions allows better aggregation of dye molecules which improves their fixation onto the fibres. The number of intermolecular forces suggested to explain this aggregation are, Vander Waals forces, ion dipole forces, dipole-dipole forces. Therefore, the effect of salt on the removal of the dye with the application of the reverse micelle by solvent extraction method has been studied using salts viz. NaCl, NH_4Cl, KCl and $MgCl_2$ taking 2 g to 8 g/100 ml concentration. On the addition of different salts to the dye solution, there is a decrease in the E value as shown in Figure 5. The effect of each salt is different depending on the extent of their effect on aggregation of the dye. The decrease in the dye removal is in the form NaCl > KCl > $MgCl_2$ > NH_4Cl at a concentration of 2 gm of the salts.

Figure 5 shows that minimal addition of NaCl and KCl causes a decline in the percentage removal from 96% to zero % or nearly zero %. This may be due to the fact that even in the presence of minimum amount of these salts, the dye molecules aggregate more effectively due to the electropositive nature of these ions thereby increasing the size of the dye. This prevents the dye from fitting into the core of the reverse micelle affecting the removal of the reactive dye. In case of $MgCl_2$, the decrease is substantive (upto 15.90%) because of the double charge of the ion. In case of NH_4Cl, there is decline in removal percentage from 96 % to 46.75 % i.e. reduces to almost half of the initial value. Further on an increase in the salt concentration, there is more drop in E values as salt concentration affects the extent of aggregation of the dye molecules.

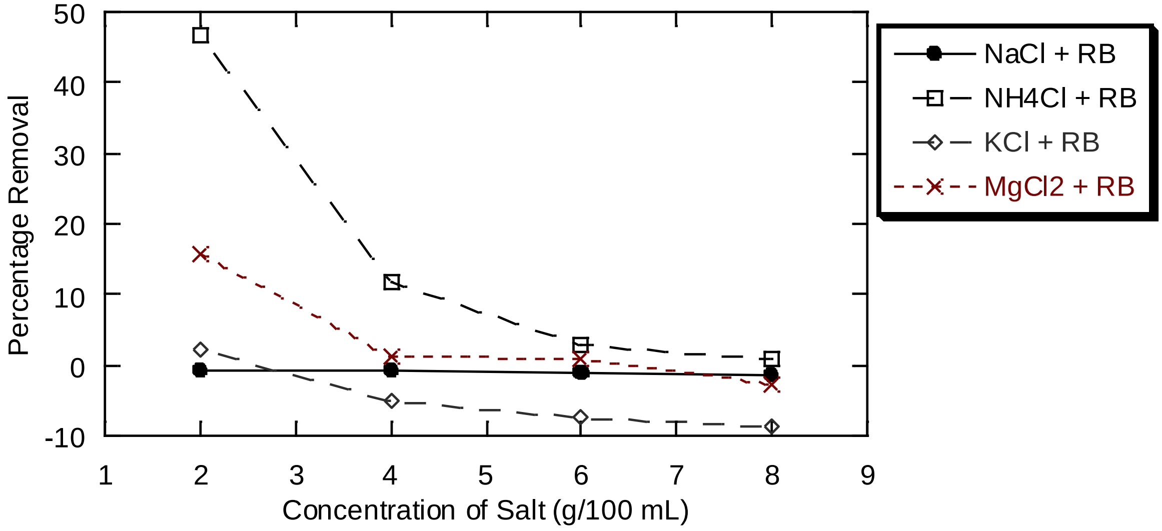


Figure 5: Effect of Salt Concentration on Dye Removal

Effect of Temperature

The effect of temperature has been studied at two temperatures viz. 293.15 and 308.15 K and is given in Table 2. The results show that the effect of the temperature on the percentage removal depends upon the surfactant concentration. At lower concentration of the surfactant (upto 6 mg), percentage removal decreases on increasing the temperature. This is because at higher temperature, the immiscibility of the two solvents decreases and the equilibrium is disturbed. The solvent is lost to the aqueous layer leading to the decrease in the E values. However at higher surfactant concentrations (10 mg), there is an increase in the percentage removal reaching to 100 %. This is because higher temperature delays the formation of lamellae and the reverse micelles are available for the entrapment of the dye molecules leading to higher E values. Though the removal is increased at high temperature but the equilibrium being disturbed leading to loss of the solvent and hence the purpose of the process is defeated. Hence the removal of the dye should be carried out at lower temperatures.

Table 2: Effect of Temperature on the Removal of the Dye

S. No	**Surfactant Concentration (mg/10 mL)**	**15 mg/100 mL RB**		**20 mg/100 mL RB**	
		293.15 K	308.15 K	293.15 K	308.15 K
1.	2	58.09	36.78	56.11	34.50
2.	4	85.67	78.92	83.35	77.40
3.	6	97.62	96.23	96.05	94.75
4.	8	94.43	98.92	93.71	97.10
5.	10	86.16	100	92.40	100

Conclusion

Dye removal via solvent extraction method involving the application of reverse micelles shows promising and excellent results of 100 % removal. The dye removal increases with the increase in concentration of the surfactant and decreases with an increase in dye concentration. The salts have negative effect on dye removal due to aggregation of dye molecules in their presence leading to decrease in the percentage removal. The lower temperature gives better removal at lower concentrations. Higher temperature causes increase in dye removal at high surfactant concentration by preventing them to form lamellae, but the solvent mixes with the aqueous layer. Though the use of solvents is employed, which naturally require enclosure and recovery, this method is fundamentally eco friendly to nature. However, to consider the full economic model and the important final carbon footprint, the energy usage in distillation for the solvent recovery and final cooling would need to be compared with the direct adsorption technique.

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