Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.906323

54 (2015) 2739–2747
May

Taylor & Francis
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Effect of pH, salt concentration and chain length of surfactants on the MO removal from water by pyridinium-based gemini surfactant

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Received 28 August 2013; Accepted 9 March 2014

ABSTRACT

Dye stuffs are an environmental problem, and their presence in drinking water and bio ecosystems such as rivers and water ways have long been recognized as deleterious. 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 methyl orange from aqueous phase in amyl alcohol solvent using cationic surfactants was studied. 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, containing encapsulated dye in reverse micelles, from aqueous phase due to gravity results in the separation of dye from water. The effects of dye and surfactant concentration, pH, salts like KCl and $MgCl_2$ were studied. The percentage removal of the 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 micelles; Cationic gemini surfactant; Liquid–liquid extraction method; Salt effect; Partition coefficient

1. Introduction

The ever-developing dye industry has adversely affected the environment. As with any industry, production creates a considerable amount of waste. Textile manufacturers generate about 3,84,000 tons of waste each year. Efforts should be focused on managing resources, recycling and proper disposal of waste. Earlier, natural dyes were used which were degradable. Things began to change around 1856 when the synthetic dyes came into existence. They are cheaper to produce, brighter, more colour-fast and easy to apply to fabric. The chemicals used to produce dyes and their breakdown products are often highly toxic, carcinogenic and mutagenic to life. 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 influence on the food chain.

There is ample evidence of their harmful effects. Triple primary cancers involving kidney, urinary

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bladder and liver of dye workers have been reported. Mathur et al. studied the mutagenicity of textile dyes and the effluents containing these dyes, and the influence on the health of textile dyeing workers and the environment [1]. The degradation product of dyes could be carcinogenic. Depending on their chemical complexity, structure and synthetic origin, dyes are resistant to fading on exposure to light, water, some chemicals and microbial attack [2,3]. They are very stable and many decompose only at temperatures higher than 200°C due to their high thermal and photostability. Effluent containing dyes are 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 [4]. Public perception of water quality is greatly influenced by the colour. Hence, their presence in wastewater is unwanted, and it is mandatory to remove dyes from effluents before their discharge into 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 [5]. In literature, various techniques have been proposed to remove dyes from water, such as oxidation [6,7], adsorption [8–11], flocculation–precipitation [12], membrane separation [13], electro-coagulation [14–16], electrochemical destruction [17], photo catalysis [18,19] and ultrasound [20,21]. All the methods have been compared, but these methods have advantages as well as disadvantages [22,23]. 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 [24,25]. 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-sized 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 [26–29], amino acids [30,31] and enzymes [32].

Keeping in view, the above work and the perception on solvent extraction method using reverse micelles of surfactants, the removal of anionic dyes was attempted with the laboratory-synthesized cationic surfactants [33].

2. Experimental section

2.1. Materials

The six cationic gemini surfactants used to prepare reverse micelles were 4,4´-(propane-1,3-diyl)bis{1-(2-(dodecyloxy)-2-oxoethyl}; 4,4´-(propane-1,3-diyl)bis{1-(2-(tetradecyloxy)-2-oxoethyl}; 4,4´-(propane-1,3-diyl) bis{1-(2-(hexadecyloxy)-2-oxoethyl} dipyridinium chlorides; 4,4´-(propane-1,3-diyl)bis{1-(2-(dodecyloxy)-2-oxoethyl}; 4,4´-(propane-1,3-diyl)-bis{1-(2-(tetradecyloxy)-2-oxoethyl} and 4,4´-(propane-1,3-diyl)bis{1-(2-(hexadecyloxy)-2-oxoethyl} dipyridinium bromides [34]. The physical properties have been given in Table 1. The surfactant $C_{12}PBr$ has 1.02 mM critical micelle concentration (CMC) in the solvent. The CMC in water is given in Table 1 for all the six surfactants. Methyl orange is anionic in nature with sulphate and amino groups attached to one of the two aromatic moieties, which are themselves connected through the azo group $[Na^+–SO_3–C_6H_4–N=N–C_6H_4\,N–(CH_3)_2]$.

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 KCl and $MgCl_2$ were used to study the effect of salt. These chemicals and the dyes were acquired from E. Merck, India.

2.2. Experimental set-up

A simple magnetic stirrer (Remi, India) was used for 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–vis spectrophotometer (Shimadzu, UV 1800) has been used to measure the colour intensity before and after 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 butanol, ethyl acetate, amyl alcohol and octanol. Amyl alcohol has been found to be the best solvent for the removal of dye from water using the reverse micelles technique. Amyl alcohol is sparingly soluble in water at 298 K

Table 1
Physical properties of surfactants

S. no.	Name	Formula	MW	CMC (mM)
1.	4,4´-(propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium chloride (C_{16}PCl)	$C_{51}H_{88}Cl_2N_2O_4$	864.16	0.059
2.	(4,4´-(propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl) dipyridinium chloride (C_{14}PCl)	$C_{47}H_{80}Cl_2N_2O_4$	808.06	0.144
3.	(4,4´-(propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl) dipyridinium chloride (C_{12}PCl)	$C_{43}H_{72}Cl_2N_2O_4$	750.49	0.359
4.	4,4´-(propane-1,3-diyl)bis(1-(2-(hexadecyloxy)-2-oxoethyl) dipyridinium bromide (C_{16}PBr)	$C_{51}H_{88}Br_2N_2O_4$	953.06	0.036
5.	(4,4´-(propane-1,3-diyl)bis(1-(2-(tetradecyloxy)-2-oxoethyl) dipyridinium bromide (C_{14}PBr)	$C_{47}H_{80}Br_2N_2O_4$	896.96	0.121
6.	(4,4´-(propane-1,3-diyl)bis(1-(2-(dodecyloxy)-2-oxoethyl) dipyridinium bromide (C_{12}PBr)	$C_{43}H_{72}Br_2N_2O_4$	840.85	0.172

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 h into pure phases within a range of the surfactant concentration. Fig. 1 represents the process taking place in the solvent extraction process for the removal of the dye.

2.3. Methods

2.3.1. Removal of the dye

Different concentrations of the dye were prepared. A known quantity of cationic surfactant [S] (in the range of 4–12 mg) above the 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 25˚C. 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–vis 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.

2.3.2. Calculation

The extraction performance was determined with the partition coefficient (K) and % removal (E), given by Eqs. (1) and (2) [35]:

$$\mathrm{K} = \frac{D_{\mathrm{org}}}{D_{\mathrm{aq}}} \tag{1}$$

$$\mathrm{E} = \frac{D_i - D_{\mathrm{aq}}}{D_i} \times 100 \tag{2}$$

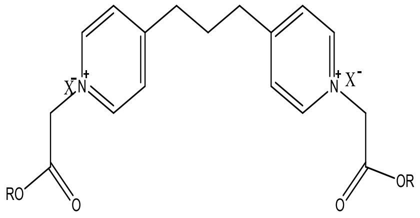
where D_i = initial concentration of dye taken, D_{aq} = concentration of dye left in the aqueous media after the dye extraction and D_{org} = concentration of dye encapsulated in the reverse micelles in the organic phase

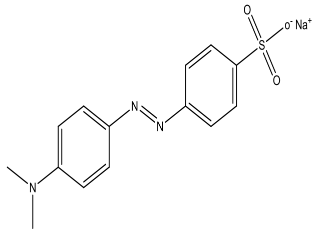
3. Results and discussion

The percentage removal of the dye with the application of surfactant is probably due to the formation of reverse micelle of surfactant in organic layer with entrapment of the dye anion in its core. In the first experiment, the different concentrations of MO were treated with all the six cationic surfactants (5 × cmc). The results are plotted in Fig. 2, which reveals that the surfactant with a chain length of 12 carbons (C_{12}PX) shows better removal and it decreases with increase in chain length. This can be explained on the basis that the size of the core of the reverse micelles increases with the chain length. As with the increase in the size of the core, the compatibility of the core and dye gets disturbed leading to decrease in percentage removal. The removal of MO (2 mg/100 mL) by the surfactant (C_{16}PX) is very poor i.e. 32.5%. Hence further experiments were not carried out by (C_{16}PX).

Fig. 2 shows that Chlorides shows better removal than bromides when taken in terms of CMC concentrations, as chlorides form reverse micelles at higher concentrations. However, it was observed that for the

The structure of the surfactant and MO is given below





Gemini cationic Surfactant

Where X = Cl, Br and

R = $CH_3(CH_2)_{11}$-; $CH_3(CH_2)_{13}$-and $CH_3(CH_2)_{15}$-.

Methyl Orange (MW = 327.00)

$C_{14}H_{14}O_3SNaN_3$

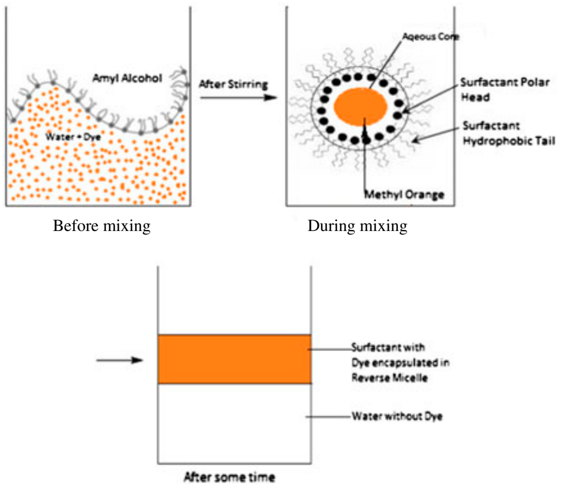


Fig. 1. Diagrammatic representation of the process taking place in the solvent extraction process for the removal of the dye.

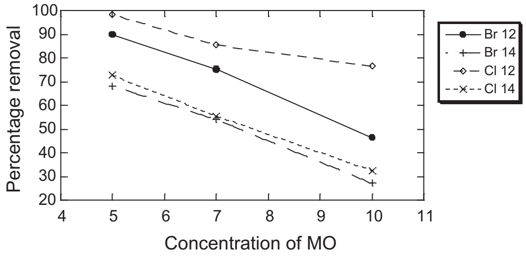


Fig. 2. Percentage removal of MO by the four cationic surfactants (5 × cmc).

same amount of surfactant taken in mg, bromides shows better removal of the dye. This may be because bromides are more hydrophobic and facilitate the surfactant to form micelles faster in comparison to chlorides [33]. Thus taking this in account, further studies was carried out using bromide surfactant (C_{12}PBr). The removal of the dye from the effluents is effected by many factors. Effect of various parameters on the percentage removal of dye is discussed.

3.1. Calibration curve

Table 2 shows the absorbance measurements of known aqueous (dye + water) mixture. By applying linear regression on this data, the calibration curve (Fig. 3) was obtained and used to determine dye concentration in aqueous phase.

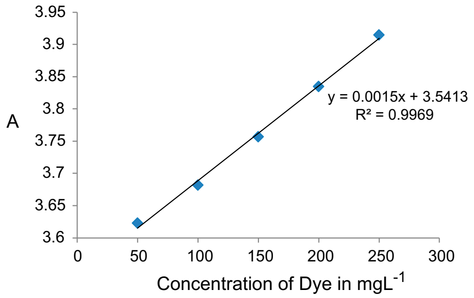


Fig. 3. Calibration curves of absorbance vs. concentration of dye in water.

3.2. Effect of surfactant concentration

In this section, dye concentration and solvent to water mass ratio were kept constant and the effect of the surfactant concentration has been studied by increasing the concentration of $C_{12}PBr$ from 4 mg to 12 mg/10 mL of the solvent. The percentage removal of the dye has been studied as the function of surfactant concentration. The results are shown in the Fig. 4 and the partition coefficient is given in Table 3. Fig. 4 shows that an increase in the surfactant concentration causes an increase in the partition coefficient *K*, leading to an increase in the percentage removal of the dye (*E*). This can be attributed to the fact that by increasing the amount of the surfactant, the number of reverse micelles increase linearly, which increases the number of dye molecules to be encapsulated in the micellar core. This can be further supported by thermodynamic model based on the mass action kinetics:

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

$$D + n[M] — \mathrm{DM} + [(n-1)M] \tag{3}$$

where D = dye molecule, M = reverse micelle, DM = reverse micelle with entrapped dye molecule. Reverse micellar concentration, *M*, is related to the surfactant concentration, [*S*] as follows:

$$[M] = \frac{[S]}{\mathrm{Nag}} \tag{4}$$

Aggregation number (Nag) is assumed to be independent of the surfactant concentration. So an increase in the surfactant concentration leads to enhanced reverse micelle formation in solvent. Consequently, more number of dye molecules gets encapsulated increasing the solubility of the dye in the organic phase. This causes a great reduction of dye concentration in aqueous phase thereby explaining the higher *E* values and increase in the *K* with surfactant concentration.

Table 2
Absorbance (A) vs. dye concentration in water

Dye concentration (mg L^{-1})	Absorbance
50	3.623
100	3.682
150	3.757
200	3.835
250	3.915

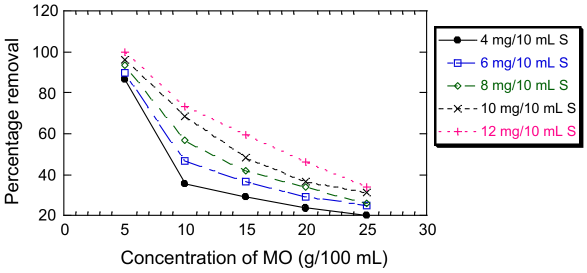


Fig. 4. Effect of the surfactant [s] ($C_{12}PBr$) and dye concentration on the removal of MO dye.

3.3. Effect of concentration of dye

The effect of the dye concentration has been studied by increasing the concentration of the dye from 5 mg to 25 mg/100 mL by keeping the ($C_{12}PBr$) surfactant concentration constant in the range of 4–12 mg. Partition coefficient and percentage removal (E) are shown in Fig. 4 and in Table 4. The partition coefficient K and the percentage removal (E) of MO decrease with an increase in the concentration of dye at constant concentration of surfactant as shown in Fig. 4. It may be due to the fact that the number of reverse micelles formed remains constant at particular concentration of the surfactant. With an increase in MO concentration, the intake of the dye in the reverse micelles does not take place i.e. organic phase tends to become saturated with the dye leading to the enhanced dye concentration in the water phase.

3.4. Effect of pH

It has been found that pH of aqueous solution significantly influences the extraction efficiency; especially for pH-sensitive dyes; as pH of the aqueous phase affects the degree of ionization of a dye molecule. For instance, in the aqueous solution, the sulphonate groups of MO ($D\text{-}SO_3Na$) are completely dissociated in anionic form. The effect of pH on the removal of MO was investigated in the pH range of 2–8 (by adding 0.1 N HCl or 0.1 N NaOH solutions), with initial MO concentration (15 mg/100 mL), volume of solvent (10.0 mL) and 4, 6, 8, 10 and 12 mg of the surfactant. The results shown in Fig. 5 reveal that the extraction efficiency was initially decreased to pH 6.0 and slightly increased at pH 8.0. To correlate the pH effect on the dye and surfactant, the ionic behaviour of the dye and surfactant in both the aqueous and non-polar phases has been studied as a function of pH and the results are shown in Table 5. It can be seen from the table that the surfactant and the dye show maximum conductance at pH 2 which explains the

Table 3
Partition coefficient (K) and % removal (E) by varying the concentration of the surfactant

Before extraction			After extraction			
S. no.	D_i (g/100 mL)	D_{sur} (mg/10 mL)	D_{aq} (g/100 mL)	D_{org} (g/100 mL)	K	E
1.	15	4	10.64	4.36	0.4097	29.06
2.	15	6	9.52	5.48	0.5756	36.53
3.	15	8	8.72	6.28	0.7202	41.86
4.	15	10	7.76	7.24	0.9329	48.26
5.	15	12	6.08	8.92	1.4671	59.48

Table 4
Partition coefficient (K) and % removal (E) by varying the concentration of dye at fixed surfactant concentration (10 mg)

Before extraction		After extraction			
S. no.	D_i (g/100 mL)	D_{aq} (g/100 mL)	D_{org} (g/100 mL)	K	E
1.	5	0.19	4.81	25.31	96.20
2.	10	3.14	6.86	2.184	68.60
3.	15	7.76	7.24	0.932	48.26
4.	20	12.74	7.26	0.5698	36.30
5.	25	17.23	7.77	0.4509	31.06

ease with which the dye enters the reverse micelles leading to higher extraction.

At low pH, the N^+ of pyridine of the surfactant gets more polar facilitating the intake of the dye into the reverse micelles by increased electrostatic interaction. At the pH range of 4–7, the dye exist as zwitterionic as the azo groups get protonated and the positive charge on N of pyridine of the surfactant is reduced leading to decrease in the extraction of dye into organic phase. However at higher pH (at 8 and above), the dye exist as negatively charge molecule, hence, leading to an increase in the extraction of the dye.

3.5. Effect of salts

The effect of salt on the removal of the dye with the application of the reverse micelle by solvent extraction method has been studied. In this study the experiments were carried out using salts viz. KCl, KBr, $MgBr_2$ and $MgCl_2$. The salts have their effects on the percentage removal depending upon their effect on the CMC of the surfactant. Not much change has been observed between the effects of Cl^- and Br^- of the salts and studies have been done using KCl and $MgCl_2$. Thus, the results of the two salts KCl and $MgCl_2$ have been discussed below. The effect of the salt KCl and $MgCl_2$ has been studied by adding salt in the range from 2 to 8 g/100 mL to the dye solution and their effects on the percentage removal of MO from water in the presence of surfactant are shown in Figs. 6 and 7, respectively.

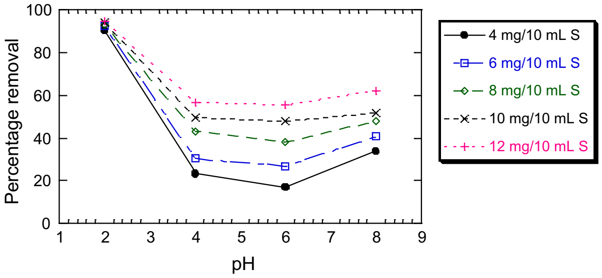


Fig. 5. Effect of pH on the percentage removal of MO (15 mg/100 mL).

3.5.1. Effect of KCl

It can be seen from Fig. 6 that the percentage removal of MO is increased with the increase in KCl concentration for a given dye concentration (15 mg/100 mL). The difference in the decrease in MO concentration in water leading to the increase in MO concentration in amyl alcohol suggests early formation of reverse micelles in the presence of salt at the amyl alcohol–water interface. Thus the presence of inorganic salts, in fact, decreases the CMC of surfactants. The equilibrium of Eq. (1) shifts in forward direction leading to an increase in the electrostatic interaction of the reverse micelles and the dye molecules. This

Table 5
Representing the conductance of surfactant and dye at different pH

S. no.	pH	Conductance of surfactant in amyl alcohol (µScm^{-1})	Conductance of surfactant in water	Conductance of dye
1.	2	5.4	2.6 mScm^{-1}	2.84 µScm^{-1}
2.	4	1.9	156 µScm^{-1}	116 µScm^{-1}
3.	6	1.3	54.4 µScm^{-1}	57.2 µScm^{-1}
4.	8	4.3	234 µScm^{-1}	62.5 µScm^{-1}

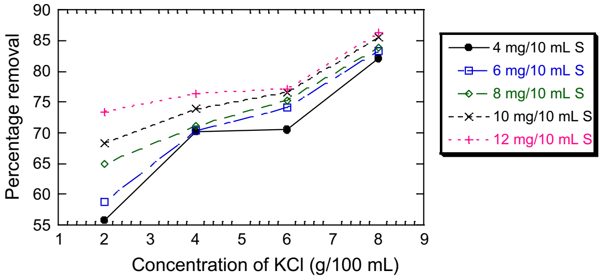


Fig. 6. The effect of salt KCl on the removal of MO.

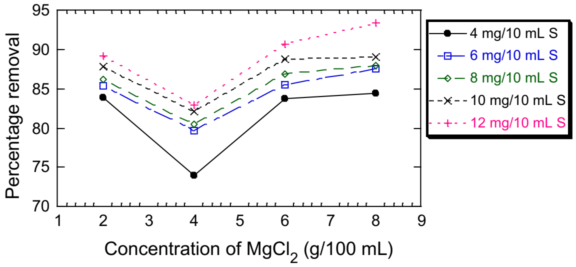


Fig. 7. Effect of $MgCl_2$ on the percentage removal of MO (15 mg/100 mL).

causes an increase in the E value. Rabie et al. proposed a similar view for low protein extraction in the presence of NaBr [36]. However, it should be noted that the dye molecule might not behave in a fashion similar to that of the protein molecule, since they are complicated in nature.

3.5.2. *Effect of salt $MgCl_2$*

Fig. 7 shows that the effect of $MgCl_2$ on the removal of MO from the solution is different from that of effect of KCl as the Mg^{2+} has different effect on the CMC. At lower concentration of 2 g/100 mL, the percentage removal of MO is higher than in absence of salt. As the concentration of the salt is increased, the percentage removal decreases up to 4 g/100 mL and then it increases up to 8 g/100 mL. Presence of $MgCl_2$ enhances the overall extraction to a higher degree than in case of KCl. However, the effect of the salt is nearly constant accept at concentration of 4 g/100 mL.

Both the salts have different effects on the removal process. Figs. 8 and 9 show the percentage removal of the dye in the presence of two salts at different concentrations and without the presence of the salts. Both the figures show the percentage removal in trend $E\,(MgCl_2) > E\,(KCl) > E\,(Dye)$. $MgCl_2$ gives better extraction than KCl due to its double charge.

The above data show that the cation plays an important part in the removal of the dye. The removal of MO in the presence of both the salts increased though they follow a different trend. The percentage removal of MO is more in the presence of Mg^{2+} than in the presence of K^+. The more is the charge on the ion the more it facilitates the removal of the dye as the presence of the salt lowers the CMC of the surfactant [24]. The extent of lowering the CMC of the surfactant is different in both the cases. $MgCl_2$ lowers the CMC of the surfactant to a higher extent, and hence shows better removal of the dye than KCl.

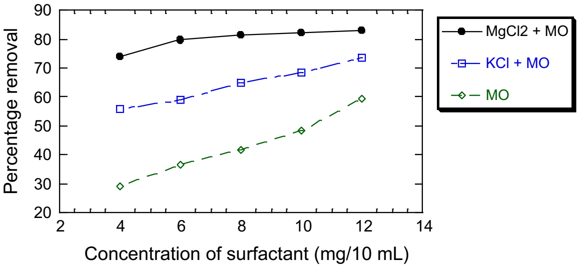


Fig. 8. Percentage removal of MO (15 mg/100 mL) at different concentrations of surfactant in the presence of 0.2 mol of KCl and 0.2 mol of $MgCl_2$ separately.

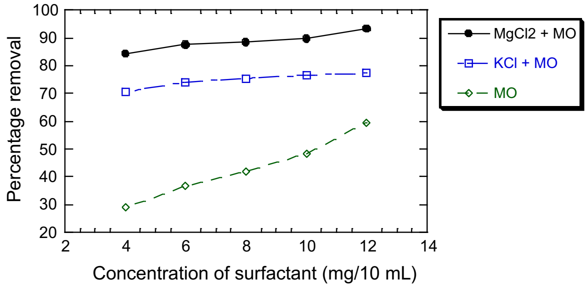


Fig. 9. Percentage removal of MO (15 mg/100 mL) at different concentrations of surfactant in the presence of 0.8 N of KCl and $MgCl_2$ and without salt separately.

4. Conclusion

Dye removal via solvent extraction method with the application of reverse micelles shows promising and excellent results. It was found that the surfactants were selective in dye removal depending upon the size of their reverse micelles in relation to the molecular size of the dye. It is found that bromo-analogues are more efficient than chloro-analogues as the CMC of bromo-analogues is lower than chloro-analogues due to greater hydrophobic nature of bromide ions. The dye removal increases with the increase in concentration of surfactant because with the increasing amount of surfactant the number of reverse micelle is assumed to increase linearly, which in turn increases the number of dye molecules that can be encapsulated. The effect of pH and salt concentration is explained based on charge-transfer mechanism and electrostatic interactions and dye-surfactant complex formation. Though the use of solvents is employed, which naturally require enclosure and recovery, this method is fundamentally eco-friendly in nature. However, to consider the full economic model and the important final carbon footprint, the energy usage in distillation and final cooling would need to be compared with the direct adsorption technique.

Acknowledgements

The investigators are thankful to the UGC for providing research grant for this work and the Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh for TEM analysis.

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