Journal of Pharmaceutics and Drug Research
JPDR, 3(3): 396-404
www.scitcentral.com

ISSN: 2640-6152

Research Article: Open Access

Synthesis of Biodegradable Cationic Surfactant and its Application in Water Treatment

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Received April 13, 2020; Revised April 14, 2020; Accepted April 16, 2020

ABSTRACT

The surfactant was synthesized using long-chain fatty acid and halo-alcohol at 60°C. Several popular methods used to characterize the surfactant includes surface tension, density, specific conductance and UV spectroscopy. The surface tension of the micelle is 28 mN/m. The lower surface tension of micelle indicating the decrease of entropy due to ordering during the formation of sebacic acid-derived surfactant shown in the mechanism. The surface tension of the dye mixture decreases with the addition of synthesised micelle from 35 to 26 mN/m. The adsorption reaction was performed at room temperature. The density of dye solution decreases by the addition of surfactant from 1.36 g/cm^2 to1 g/cm^2 which is nearly same as the density of water. The 96% dye removal as the conversion was reported using a synthesized surfactant at a wavelength of 280 nm at 12 h of reaction, which is a homogenous catalysis reaction. The absorbance value of the dye sample was reported to be 0.039 at 562 nm after treating it with a surfactant which was initially observed to 4 at same wavelength.

Keywords: Sebacic acid, Methyl red dye, Surface tension, Tween 20, Surfactant

INTRODUCTION

Nanotechnology is one of the emerging multidisciplinary research areas. The various types of nanoparticles, such as micelle, metallic nanoparticles, nanotubes, and polymeric nanoparticles, have been reported [1,2]. The design of different nanoparticles and their applications is one of the best utilizations of nanotechnology. The synthesis and application of surfactant can be a homogenous catalysis reaction for waste water treatment [3-6]. Surfactants are usually organic compounds which contain both hydrophobic group (tails) and hydrophilic group (heads). Surfactants are used in lubricants as an ingredient, such as shaving creams, and also in car engine lubricants, which helps to keep particles away from the engine parts. Surfactants are used as cleaning agents and help cleaning agents to remove dirt from the surface being cleaned [2]. Surfactant can be non-ionic, anionic and cationic and their synthesis depends on the utilization. Very few studies have been reported the synthesis of biodegradable cationic surfactant and their applications for the dye removal study [5]. This lead to the synthesis of the sebacic acid-derived micelle and monomeric surfactants by esterification of the halogenated carboxylic acid with short-chain fatty alcohols or acids with 2-chloroethanol forming suitable esters such as 2-propylbromoacetate, 2-butybromoacetate, 2-octylbromoacetate, 2-chlorobenzoacetate, 2-chloromethylcinnamate, followed by their subsequent treatment with different spacers (4,4-trimethylenedipyridine, 1-methylimidazole). The identification of these surfactants is based on surface tension study [1-6]. A series of parameters such as the chemical structure of the surfactants, surface tension, critical micelle concentration (CMC), viscosity, density, conductance and pH are also determined. The synthesized ionic liquids are also applied for the dye removal from the water but the cost of ionic liquids is the main drawback to commercialize this process [5-9]. Textile dyes are extensively used in many manufacturing processes in the textile industry, but it has been proved that these dyes are very harmful to human health as well as for the environment [1,8,10]. The chemicals which are used during the preparation of dyes like azo dyes may cause carcinogenic effects [2,7]. The discharge of these dyes into water bodies have very toxic effects on aquatic animals and humans [2]. The dye molecules have a shape like narrow strips of paper,

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Citation: Kaur P, Kour S, Sharma M, Rehmani S & Singh H. (2020) Synthesis of Biodegradable Cationic Surfactant and Its Application in Water Treatment. J Pharm Drug Res, 3(3): 396-404.

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that is having length and breadth but relatively little thickness [1,2]. Basically, dyes are the compounds that are used to impart colour to the fabric and on any surface shells. Nowadays, the decolourization of wastewater from textile and other manufacturing industries is a major issue [3] because dyes are water-soluble compounds, and they impart very intense colour into the water as well as it makes the water acidic and the second reason is, they have great affinity of the dye to the fibre due to forces of attraction [4]. Main reason behind higher morbidity rates of kidney, liver, bladder cancers, etc. is the discharge of organic contaminants from various industries such as electroplating, textile production, and cosmetics [4-6,9].

HARMFUL EFFECTS OF DYES

Textile dyes are extensively used in many manufacturing processes in the textile industry, but it has been proved that these dyes are very harmful to human health as well as for the environment. The chemicals which are used during the preparation of dyes like azo dyes may cause carcinogenic effects. The discharge of these dyes into water bodies have very toxic effects on the variety of organism such as aquatic animals [8-12]. Dyes cause so many skin irritation, itchy or blocked nose, sneezing, and sore eyes. Synthetic dyes, such as reactive, vat, and disperse dyes, are skin sensitive [13]. Textile effluents contain so many organic and inorganic compounds [14]. During the process of dyeing, the total dye is not fixed on the fabric; some of the portions remain unfixed to the fabric and get washed out. This unfixed dye content is considered as textile effluent [15]. There are so many treatments used to treat this water, such as primary, secondary, and tertiary treatment processes like flocculation, trickling filters, and electrodialysis, etc. But these treatments are not effective for dye removal and for chemical removal. [16,17]. Due to their demerits, it is gaining interest to remove dye from wastewater by using different methods [9-12]. Organic compounds in wastewater, such as dyes and pigments in industry effluents, are toxic or have a lethal effect on aquatic living and humans as already discussed earlier [5,10-13]. Stability of organic contaminants, especially methyl blue, methyl red and methyl orange, to light, heat, or oxidizing agents makes them difficult to remove by various conventional wastewater treatments (chemical and biological) [10-15]. Decolourization is done by using methods such as Adsorption, Filtration, Precipitation, Degradation, Photodegradation, Chemical degradation etc [11-13]. This article is focused not only for the synthesis of biodegradable cationic surfactant but also to its utilization to remove organic dye.

The new sebacic acid-based cationic surfactant has excellent potentials for adsorptive removal of organic dyes and other organic ingredients for water remediation application. The Methyl red dye is chosen as model representative organic pollutants for efficient adsorptive removal from the simulated industrial wastewater using the new Gemini cationic surfactant adsorbent. The work reports an excellent adsorbent for the fast and efficient removal of organic dyes from industrial wastewater. This process of dye removal can be a pre-treatment step for dye effluent treatment to make useful waste for irrigation and other purposes.

EXPERIMENTAL SECTION

Chemicals and materials

Sodium hydroxide (NaOH), hydrochloric acid (HCl), concentrated sulphuric acid (H_2SO_4), Sebacic acid ($C_{10}H_{18}O_4$), NaCl and KCl analytical grade were purchased from E. Merck, India and used as received. Amyl alcohol (3-methyl butan-1-ol), decanol, benzyl alcohol, methyl benzoate, octanol, ethyl acetate, Ethanol - (C_2H_5OH), acetone (CH_3COCH_3) and toluene (C_7H_8) were obtained from S.D. fine chemicals. Methyl red dye is collected from Merck.

Preparation of dye solutions

1g.L^{-1} stock solution of dyes was prepared by dissolving the appropriate amount of dye in water and stored in bottles. The solution was diluted by adding a suitable amount of water to the stock solution as per requirement.

Preparation of surfactant

Surfactants are prepared by the use of long-chain fatty acid and halo-alcohol and by the addition of a small amount of sulphuric acid **(Figure 1)**. After the addition, stirred this solution for near about 72 h by the use of magnetic stirrer at 60°C. After that, add a pinch of (0.1 M) 4,4,4-triethylenedipyridene then again stirred this solution for near about 24 h. Then washed this solution with chloroform in separating funnel. The bottom layer is collected as a surfactant from separating funnel. The methodology described in scheme 1 **(Figure 2)** for dye removal study and separation of surfactant.

Instrumentation

The dye concentration before and after extraction was carried out by using shimadzo-1900 spectrophotometer. The dyes were analyzed at their respective $\lambda_{max.}$ The dye concentrations removed was calculated from the absorbance of the initial and treated dye solution.

The instrument used for analysis of refractive index and density of the liquid sample was Rudolf analytical instrument (DDM2911). Rudolf research analytical instrument (DDM2911) was used for the analysis of density and refractive index of the liquid sample (red dye mixture and synthesized cationic surfactant).

The pH measurements were performed using a pH meter (ELICO model LI-127, India). The surface tension of synthesized micelle is measured using the Kyowa interface science surface tensiometer (Dy-300 model). The instrument was calibrated with deionized water, and 2-3 mL of sample was used for each test.

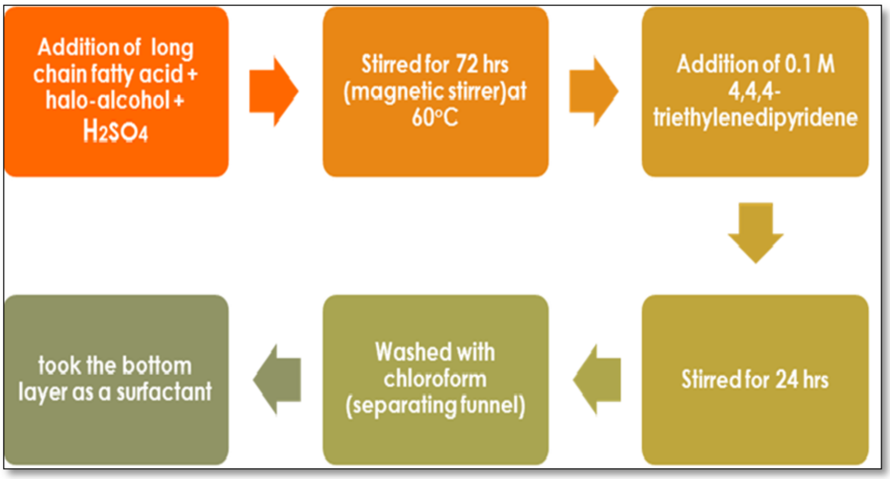


Figure 1. Preparation of Cationic Surfactant.

Figure 2. Scheme 1: Dye removal by using solvent extraction method.

Experimental setup

For the preparation of surfactant, a simple Magnetic Stirrer were used. The speed of the stirrer was measured accurately in rpm. Then a separating funnel is used to separate the aqueous and solvent by gravity.

After the preparation of surfactant, it was used to remove dye from the waste water of dye. A particular solvent which is cost effective, is used in the reverse micelle extraction process. Solvent is separated from aqueous phase and solvent dispersion in the spreading in the appearance of surfactant. There are so many solvents such as amyl alcohol, butanol, methyl benzoate, ethyl acetate, octanol and decanol etc. are used for the elimination of dye in the reverse miceller extraction process. Among these solvents' amyl alcohol has been found the best out of all other solvents for the removal of dyes in reverse miceller extraction process. The formation of reverse micelles occurs in the solvent phase. Amyl alcohol is easily soluble into water at room temperature and pressure. The time taken to separate a 100ml of the mixture of amyl alcohol is usually 2-5 h if kept within a range of surfactant concentrations [18,19].

RESULTS AND DISCUSSION

The physical properties of the synthesized micelle are described in **Table 1**. The sebacic acid derived liquid surfactant with a density of 1.35 g/cm^2 having a surface tension of 28 mN/m and a pH 1. We have shown the comparative study of physicochemical properties of synthesised cationic surfactant (sabacic acid based) with the reported cationic surfactant in detailed **(Figure 3 and Table 2)**. Physico-chemical property of dye before treating with surfactant and after treating with surfactant is shown in **Table 3**. The red dye sample with a pH of 1 before treatment with a surfactant exhibit refractive index of 1.33 and a density of 1.35g/cm^2 at a temperature of 25°C. While the same dye after treatment with a surfactant becomes less acidic (pH 3) and colourless, and the density of the dye decreases to 1 g/cm^2 and refractive index increase up to 1.69 at the constant temperature of 25°C.

The adsorption reaction using micelle to demonstrate the effect of synthesized cationic surfactant to remove the organic dye (Methyl red), was performed at a different time on stream (2-24 h). The experiments also carried out at Methyl red dye to synthesized surfactant (adsorbent) with the addition of Tween 20, non-ionic surfactant. Tween 20 is a non-ionic hydrophobic surfactant, which is polyethoxylated sorbitol ester. It can act as wetting agent, dispersant and solubilizer [17-22]. The U.V result of reactant (Methyl red dye) shows absorbance at 500 nm wavelength before reaction with micelle. The absorbance of dye mixture after treating with sebacic acid derived micelle did not offer any absorbance at 500 nm. At 2 h of reaction, absorbance reported 3.9 ml at the U.V. range using 4 ml cationic surfactant in 100 ml dye solution. It concludes that after adding cationic surfactant (2 ml) and 8 ml non-ionic surfactant (Tween 20) and 10 amyl alcohol in the water sample no change in absorbance. It shows after adding cationic surfactant (6 ml) and 4 ml non-ionic surfactant (Tween 20) and 10 amyl alcohol in the dye sample, the absorbance shifted to UV region. The absorbance showed 0.039 in the UV region after 24 h of separation.

Figure 4 demonstrates the UV results of Methyl red dye after adsorbing on the cationic surfactant with different concentrations. The Methyl red dye mixture shows the absorption peak at 500nm wavelength with sharp intensity **(Figure 4-Graph 1)** which is not observed after adsorption reaction with cationic surfactant **(Figure 4-Graph 2, 3 and 4)**. The minor absorption peaks reported at 200 nm in the dye mixture after adsorption on surfactant, which may be due to the presence of choloro ethanol and amyl alcohol. These results showed that synthesized cationic surfactant has a positive effect of removing the organic dye.

Table 1. Physical properties of sebacic acid-derived surfactant.

Physical properties	**Surfactant**
`pH	1
Colour	Colourless
Density (g/cm^2) at 25˚C	1.35
Surface tension (mN/m)	28
Physical state	Liquid

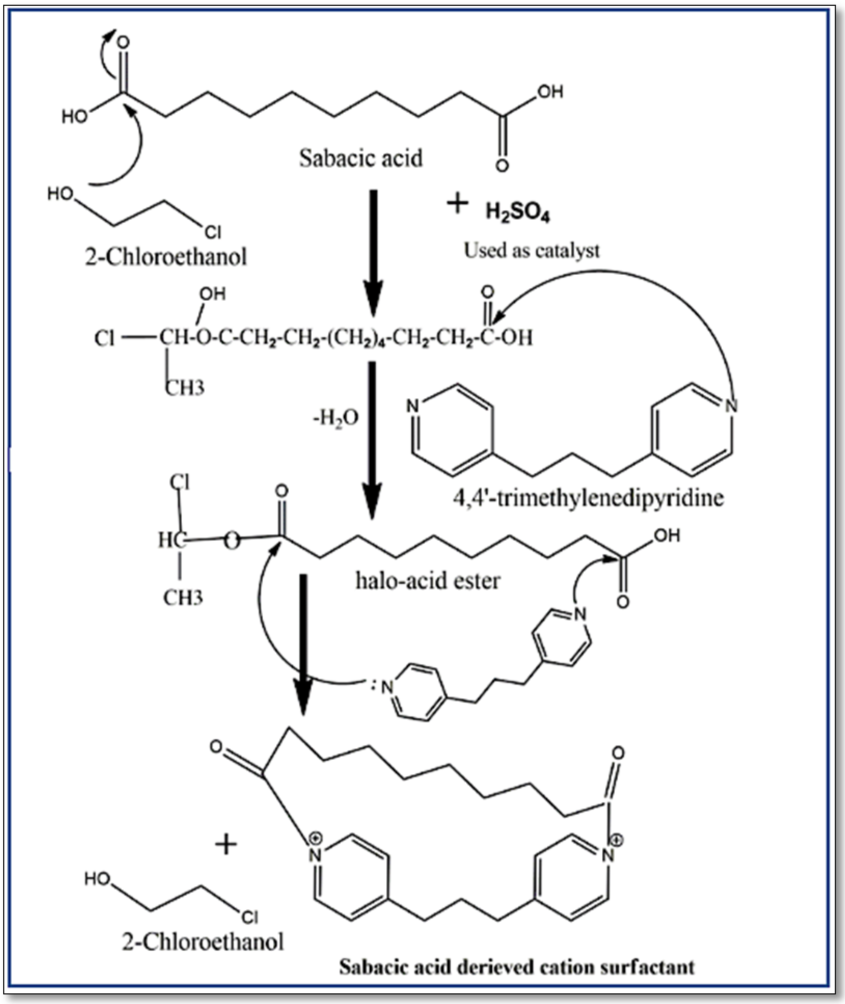


Figure 3. Sabacic acid derived cation surfactant.

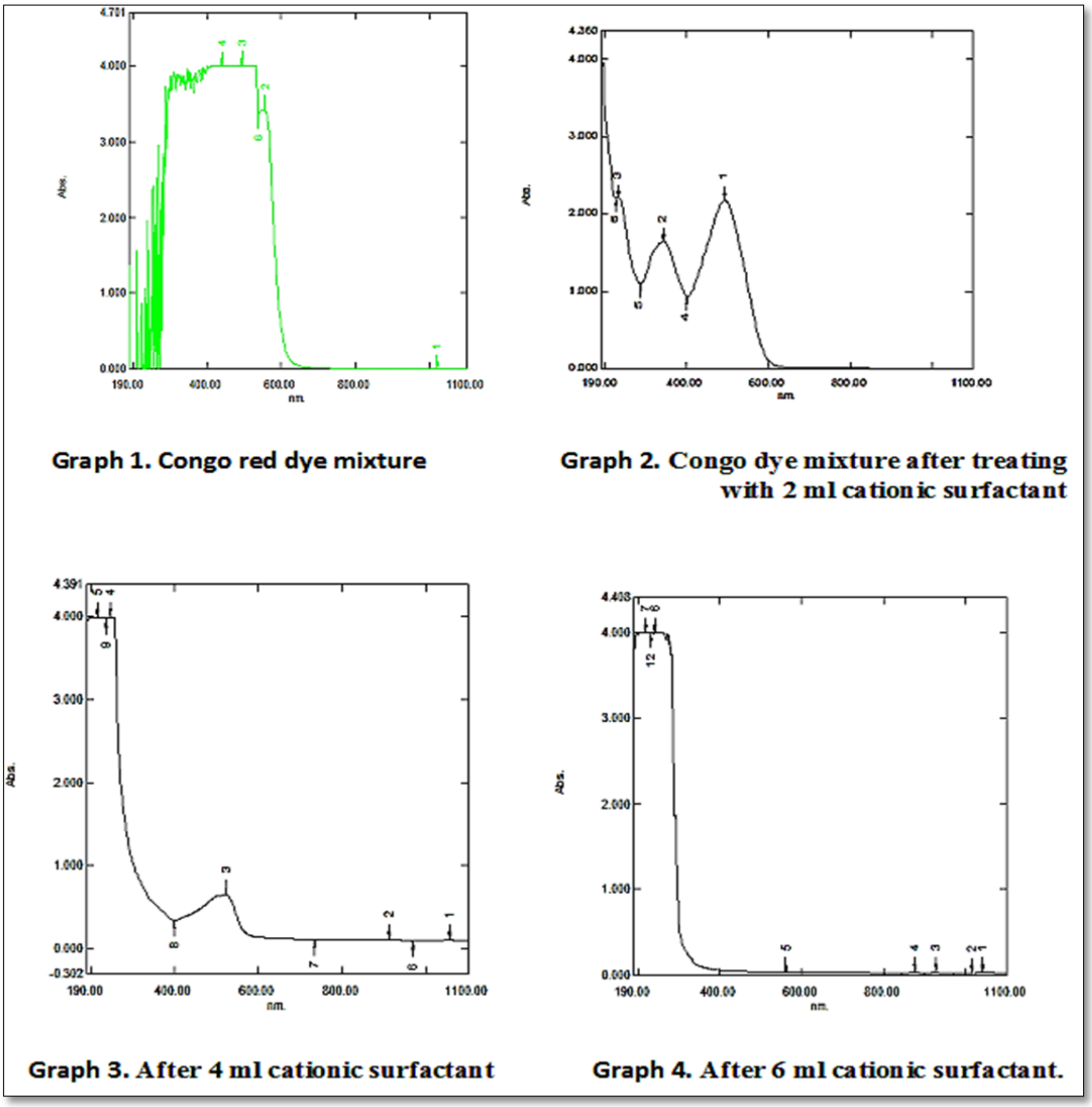
Table 2. Physical properties of synthesised surfactant and comparison with of reported surfactants.

Physical properties	Synthesized Surfactant	CTAB*	BAC*	Cetrimonium chloride
pH	1	2	-	3-5
Colour	Colourless	White powder	White or yellow	Colourless or yellow
Density (g/cm^2) at 25°C	1.35 g/cm^3	1 g/cm^3	0.98 g/cm^3	0.96 g/cm^3
Surface tension	32.84 mN/M	0.95Mm	41 mN/M	33 mN/M
Physical state	Liquid at room temperature	Solid	Powder	Liquid

**BAC= Benzalkonium Chloride, CTAB=Cetyl Trimethyl Ammonium Bromide.*

Table 3. Physico-chemical properties of dye sample before and after adsorption on surfactant.

Physical properties	Methyl red dyes	Dye solution after treating with surfactant
pH	1	3
Colour	Red	Almost colourless
Density (g/cm^2)	1.35	1.00
Refractive index at 25 ˚C	1.33	1.69
Surface tension (mN/m)	35	26
Conductance (Seimen)	6.61	9.76



Graph 1. Congo red dye mixture

Graph 2. Congo dye mixture after treating with 2 ml cationic surfactant

Graph 3. After 4 ml cationic surfactant

Graph 4. After 6 ml cationic surfactant.

Figure 4. UV-spectra: **Graph 1:** Methyl red dye mixture with 50% water, **Graph 2:** Methyl dye mixture after treating with 2 ml cationic surfactant **Graph 3:** After 4 ml cationic surfactant **Graph 4:** After 6 ml cationic surfactant.

Table 4 shows the comparative study for the removal of dye removal using different techniques reported in the literature. Various techniques such as adsorption oxidation degradation and photochemical reaction was reported in this manuscript. We have done the adsorption study of methyl red dye using sebacic acid derived surfactant to remove dye. Photo catalytic method to remove dye was reported to be 92% dye removal capacity using Titanium based catalysts [23]. The methyl red dye removal study using Fenton reagent with CrK $(SO_4)_2$ salt reported 57% dye removal capacity [23-26].

The adsorption of dye using cationic surfactant (sabacic acid derived) was found to be more suitable (96% dye removal) than the other reported techniques. It is a good example of a homogenous catalysis reaction as a surfactant can act as a homogenous catalyst, and its application for wastewater treatment at atmospheric conditions. At the end of the reaction, the dark colour dye can be visualized and can be separated using the solvent extraction method. **Figure 5** shows the decolourization of the dye sample after treating it with synthesized micelle.

Table 4. The study to remove dyes via different techniques reported in the literature.

Dye removal technique	Name	Surfactant/Catalyst	Percentage of removal	References
Solvent extraction	**Methyl red dye**	Cationic surfactant	96%	My research
Adsorption	**Methyl red dye**	Activated carbon	83%	25
Photochemical	**Methyl red dye**	TiO_2	92%	23
Adsorption	**Malachite green**	Graphene oxide	48%	26
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with NaCl	47%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with $NaIO_3$	26%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with $CaCl_2$	44%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with $CuSO_4$	29%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with Na_2SO_4	40%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with CrK $(SO_4)_2$	57%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with $Ca_3(PO_4)_2$	92%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with Mg $(NO_3)_2$	45%	24
Oxidation & Degradation	**Methyl red dye**	Fenton reagent with Co $(NO_3)_2$	45%	24

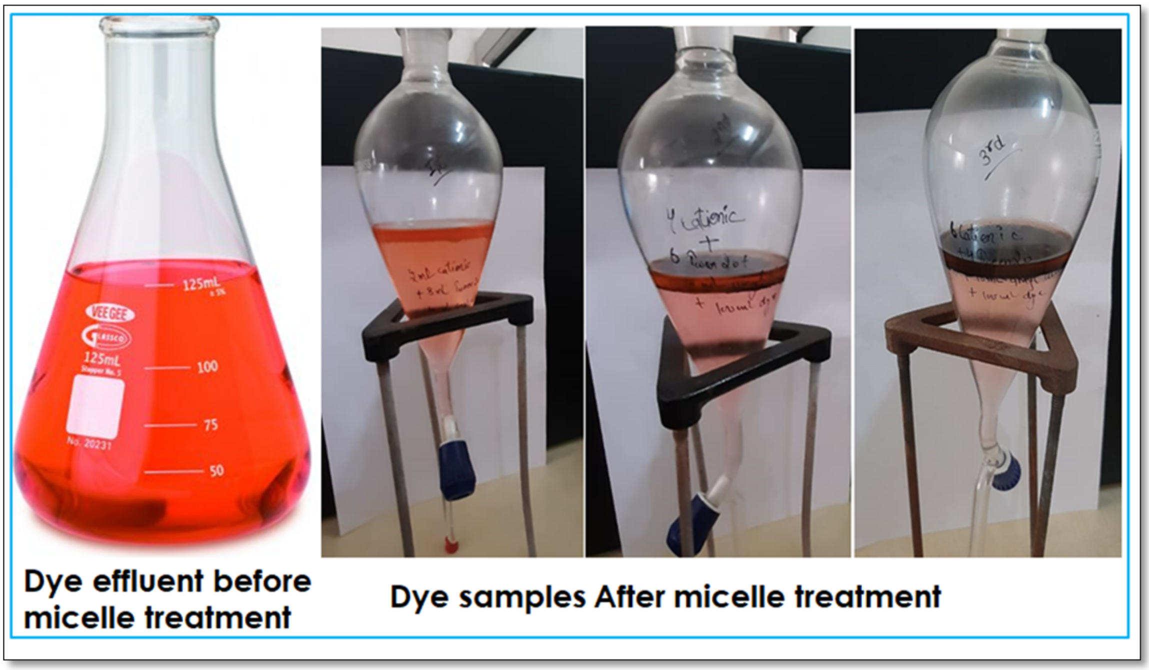


Figure 5. Visible identification (decolourization) of dye before and after the reaction with micelle.

CONCLUDING REMARKS

This work systematically demonstrates the synthesis of sebacic acid derived micelle using 4,4,4-triethylenedipyridene, inorganic-organic polymer complex stabilizing agent. The plausible mechanism of synthesises describes the ester formation initially to form biodegradable cationic surfactant. The application of surfactant studied for the dye removal by adsorption mechanism. The U.V. spectroscopic results show adsorption potential of dye after treating of surfactant with dye mixture at room temperature. The decolourization of Methyl red dye with micelle also shows the positive adsorption process. The Methyl red dye showed significantly higher adsorption on the synthesized cationic surfactant compared to nonionic surfactant (tween 20) under identical experimental conditions. The lower surface tension of micelle (28 mN/m) and no peak observation in the U.V analysis of the dye mixture after adsorbing on sebacic acid derived micelle shows the potential of synthesized micelle to remove dye sample.

ACKNOWLEDGMENT

P.K. thanks RIMT University for M.Phil. S.K. acknowledges RIMT University for Ph.D. We thank CSIR-CSIO, Chandigarh, for surface tension analysis.

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