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Reverse Micellar Extraction of Acid Dyes from Simulated Textile Effluent

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Abstract: Textile industry produces effluent which contributes to water pollution since it utilizes many organic and inorganic chemicals especially dye. Decolorization of textile effluent is very important before discharging to the environment to avoid health hazards. Among several methods, the most promising method in terms of simplicity and efficiency for dye removal from effluent is solvent extraction using reverse micelles. This study explores the solvent extraction method to remove mixture of Acid Blue-1, Acid Yellow-17 and Acid Orange-7 dyes from textile effluent using cationic surfactant and a suitable organic solvent. In this method, dye is dissolved in aqueous phase and mixed with organic solvent containing surfactant. The effect of different parameters such as concentration of surfactant, concentration of dye, pH, electrolyte concentration, nature of solvent etc. has been studied in the present work. Almost 100% dye has been extracted from the aqueous phase at 100ppm initial dye concentration.

Keywords: Reverse micelles, Surfactant, Solvent extraction, Acid dyes.

INTRODUCTION

Water resources are of critical importance for both human development and natural ecosystem. Increasing environmental contamination from industrial and textile effluent is of major concern. Many industries use dyes to color their products, especially textile industry and also consumes substantial amount of water. It is estimated that the production of different dyes and the pigments in the world is over 10,000 per year [1]. Unfortunately, the exact amount of dyes produced in the world is not known. The global consumption of textiles is around 30 million tones with a growth rate of 3% per annum, and the coloration of these textiles needs approximately 8×10^5 tones of dyes [2]. Effluent from textile industry contains various types of dyes and they should be removed before discharging the effluent to the environment to avoid health hazards and destruction of the ecosystem. Dye effluent is responsible for many water borne diseases exhibiting symptoms like hemorrhage, nausea, dermatitis, ulceration of the skin, kidney damage, loss of bone marrow leading to anemia [3, 4]. Most dyestuffs are designed to be resistant to environmental conditions like light, pH, and microbial attack [5]. Hence, their presence is unwanted and should be removed from effluent before discharging to the environment. Several techniques are available for the removal of dyes from effluent like adsorption [6-8], flocculation-coagulation [9, 10], membrane separation [11], ozone oxidation [12, 13], biological treatments [14-16] etc. the physical methods are non-destructive and merely transfer the pollutants from one medium to another, thus giving secondary treatment [17].

But these methods are not economically viable due to high dosage and production of a large quantity of sludge [18-20]. Removal of dyes by adsorption on wood [21], silica [22], eucalyptus bark [23], tea waste [24], activated carbon [25] etc. has been proposed. These adsorption methods are capable of removing dyes from effluent but regeneration of most of the adsorbents is difficult except activated carbon. And adsorption treatment using activated carbon is quite expensive [26].

All other methods are also expensive and economically not viable. Thus a new technique is required for the removal of dyes from effluent that must be simple, cost-effective and environment friendly. In recent years, much attention has been focused on separation techniques like solvent extraction or liquid-liquid extraction. Liquid- liquid extraction defines as purification enrichment separation and analysis of various compounds [27]. It is based on the principal that a solute can distribute itself in a certain ratio between immiscible solvents. Thus, the selection of both a diluent and an extractant determines equilibrium for a given system and the efficiency of extraction process depends on its mass transfer rate [28]. The advantages of solvent extraction includes high throughput, ease of automatic operation and of scale up and high purification [29].

Thus, application of solvent extraction for removing dyes from textile effluent by the use of surfactants has been studied in the present work. The purpose of present work is to show the removal of acid dyes by solvent extraction process using reverse micelles. The reverse micelles are nanometer-sized aggregates of surfactant molecules surrounding microscopic water core in nonpolar solvents [30]. The use of reverse micelles in the removal of dyes from water was demonstrated by Pandit and Basu [31]. The recovery of acid dye from wastewater by solvent extraction and multistage counter current extraction and stripping experiments were carried out by Hu *et al* [32]. In the present study, the effect of different parameters such as concentration of surfactant, concentration of dye, pH, electrolyte concentration, nature of solvent etc. has been studied. Upon reviewing the literature it was observed that multistage separation of mixture of dyes has not been explored and the same has been carried out for multistage separation of dyes by surfactant after optimization of parameters. We have optimized pH, temperature, ionic strength, surfactant concentration, dye concentration and nature of extracting solvent. An interesting trend has been observed.

EXPERIMENTAL

Materials and Methods

Simulated textile effluent to dye wool was prepared in the lab by mixing three dyes Acid Blue-1 (AB-1), Acid Orange-7 (AO-7) and Acid Yellow-17 (AY-17). The surfactant used to prepare reverse micelle was HTAB (Hexadecyl trimethyl ammonium bromide). HTAB is a cationic surfactant. The solvent used for removal of dye from water was isoamyl alcohol. Freshly prepared distilled water was used in the experiment. Analytical grade HCl and NaOH were used for the variation of pH. A UV-Visible spectrophotometer (Systronics 2201) was used to measure the absorbance and concentration of dye in the aqueous phase. A simple stirrer was used for mixing of the solvent and aqueous phase. A schematic diagram of the experimental set up is shown in **Figure 1**.
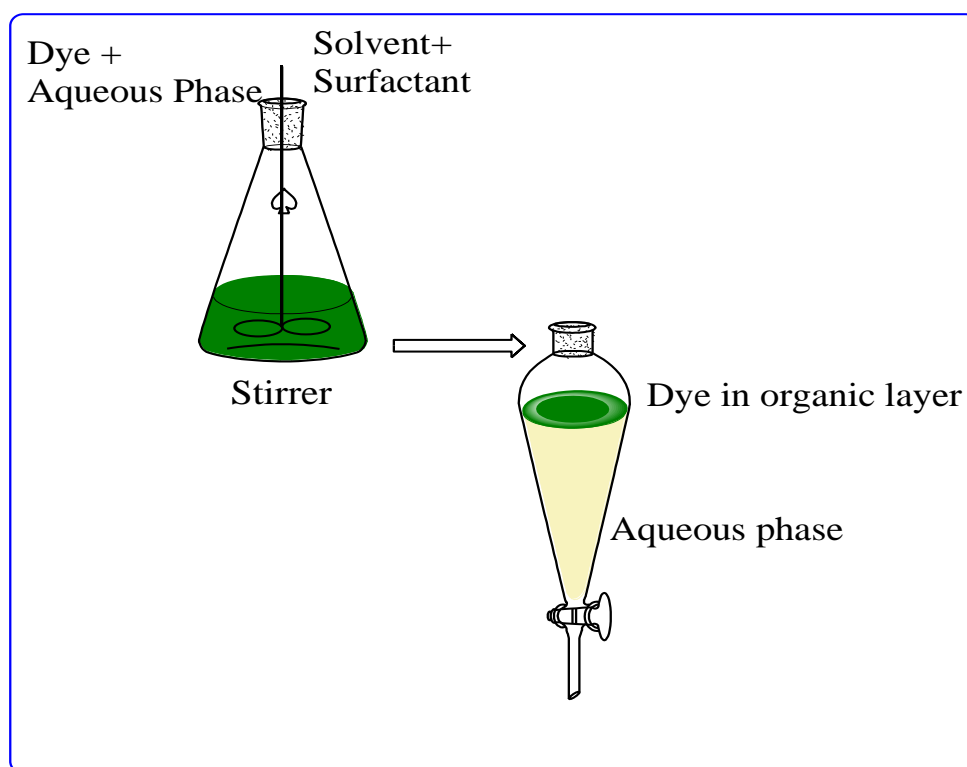

Figure 1: Schematic diagram of the experimental set up of solvent extraction to remove dye from aqueous solution.

EXPERIMENTAL METHOD

A given volume of aqueous solution with known dye concentration was added to a known volume of the organic solvent containing known quantity of cationic surfactant. The concentration of surfactants used is at its critical micelle concentration level. The two phases were then mixed thoroughly using a stirrer at a fixed rpm for about 15 min. The two phases were then transferred to the separating funnel to separate organic layer and the aqueous phase. A sample of the aqueous layer was then analyzed for the absorbance and concentration measurement of dyes in the aqueous phase [33, 34]. The wavelength of maximum absorbance (λ_{max}) for AY-17, AO-7 and AB-1 were 401.6nm, 484.8nm and 639.2nm respectively. The structure of dyes is shown in **Figure 2**. The distribution ratio (D) and the percentage of extraction (E) were calculated using equations (1) and (2).

$$D = \frac{[Dye]_{org}}{[Dye]_{aq}}$$

… (1)

$$E = 100 \times \frac{[Dye]_{aq0} - [Dye]_{aq}}{[Dye]_{aq0}}$$

… (2)

Where $[Dye]_{org}$ is the dye concentration in organic phase (mg L^{-1}), $[Dye]_{aq0}$ is initial dye concentration of aqueous phase (mg L^{-1}) and $[Dye]_{aq}$ the dye concentration of aqueous phase after extraction (mg L^{-1}).
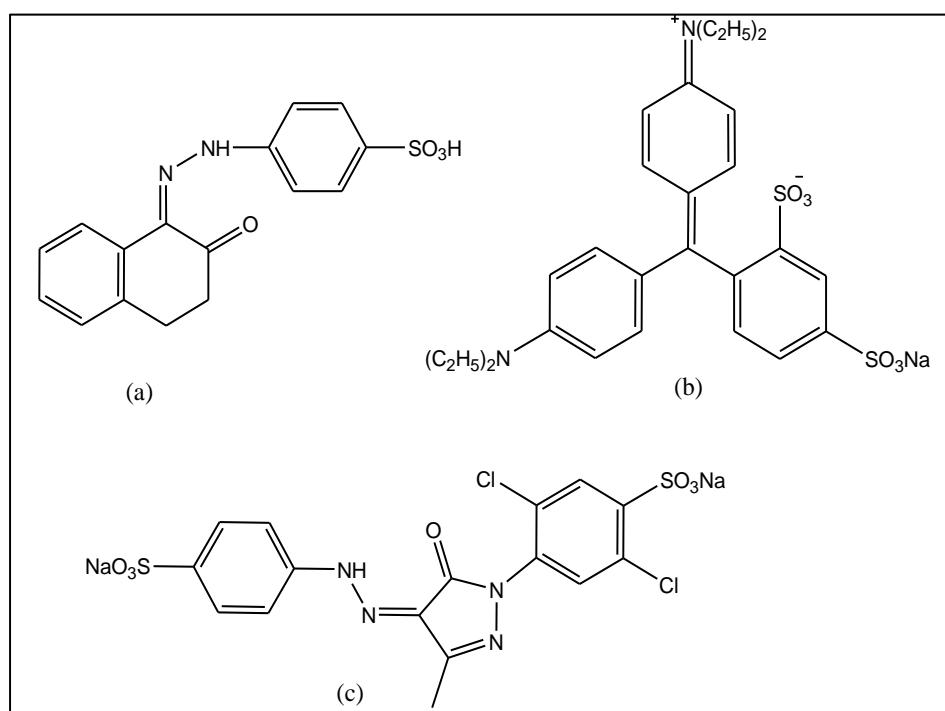

Figure 2: Structure of dyes used (a) Acid Orange-7 (b) Acid Blue-1 (c) Acid Yellow-17.

RESULTS AND DISCUSSION

Effect of Equilibration Time: The equilibration time for the removal of dyes was studied by varying the time between 1-30 min. The maximum extraction of dye at 1.0 min was 80% and further increase in equilibration time increases the extraction of dye. At 15.0 min more than 90% dye was found to be extracted and remained constant upto 30 min. When individual dyes were studied, the equilibration time of extraction for AO-7, AY-17 and AB-1 was 5.0 min., 5.0 min. and 15.0 min. respectively. The effect of time has been shown in **Figure 3**. It has been observed that order of extraction of dyes is AO-7 > AB-1 > AY-17.
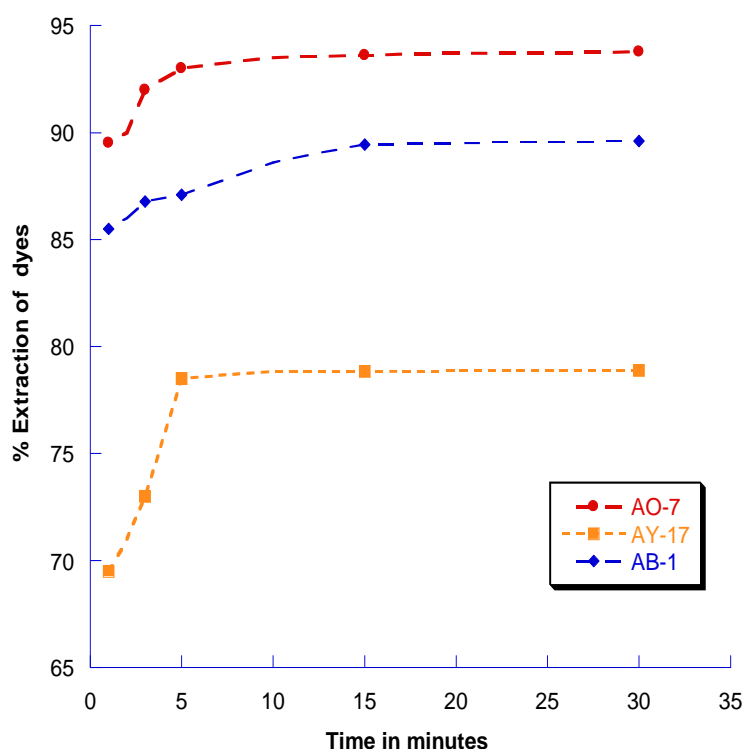
Figure 3: Effect of time on extraction of dyes.

When surfactant was added to the aqueous phase it gets dissociated in the form of ions which aggregate together to form micelles against entropy driving rule. Micellar formation is assumed to be enthalpy driven. The energy is provided by stirring due to which immediate micellization occurs. When organic solvent is added to the aqueous phase containing micelles, phase transfer causes reverse micellization. Phase transfer of micelles from aqueous to organic is incredibly quick. Interactions among tails of reverse micelles are hydrophobic in aqueous phase which changes to Van der Waal in organic phase. Phase transfer is faster in aqueous medium in the presence of dye ions due to strong electrostatic interactions among dye ions and surfactant heads which are oppositely charged.

The magnitude of forces control the kinetics, the order of energy released is directly related to the forces of attraction. This is a well-known fact that electrostatic forces of attraction are stronger than Vander Waal forces of attraction which are stronger than hydrophobic forces of attraction; hence this becomes the driving force. This process is exceptionally fast and seems to be first order but beyond measurements. Therefore majority of the dye has been extracted in first few minutes.

EFFECT OF SURFACTANT CONCENTRATION

By changing the amount of surfactant from 0.08 mM to 0.67 mM per 50ml of dye solution in constant amount of organic solvent. As number of ions of surfactant increases, the number of micelles also increases as shown in **Figure 4**. The rate of phase transfer depends upon number of micelles and the number of dye ions in aqueous medium. When reverse micelles are formed the dye ions get entrapped among them. Because with increase in concentration of surfactant the number of micelles increases linearly and the number of dye molecules encapsulated also increases linearly.
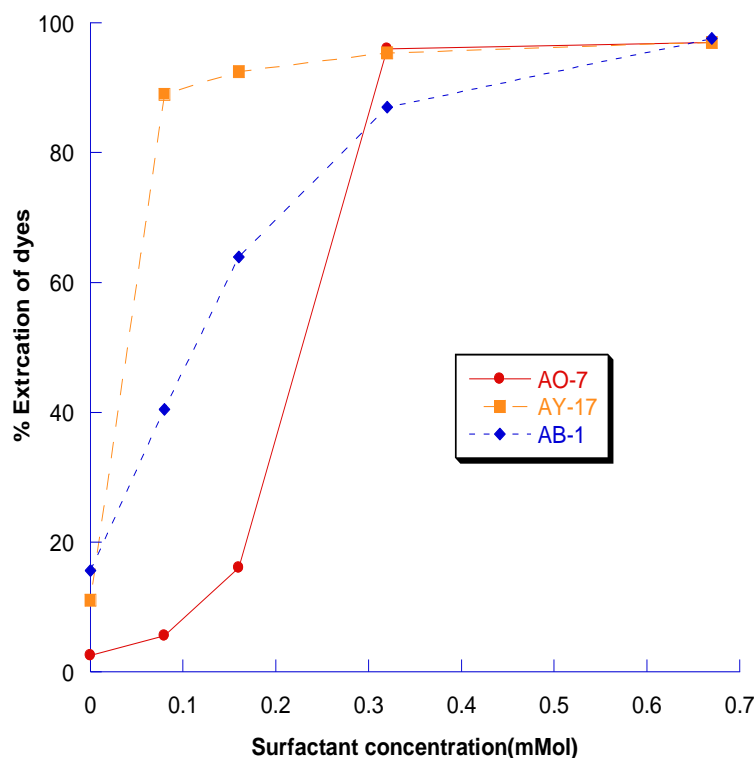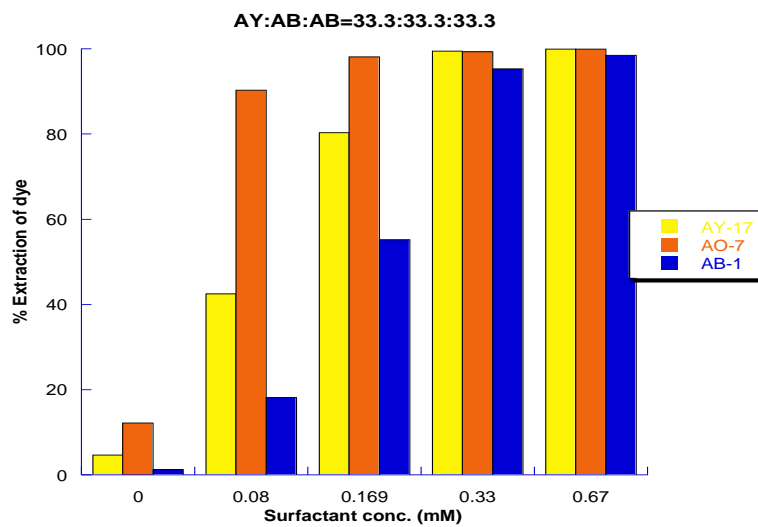
Figure 4: Effect of surfactant concentration on extraction of single dye from aqueous medium
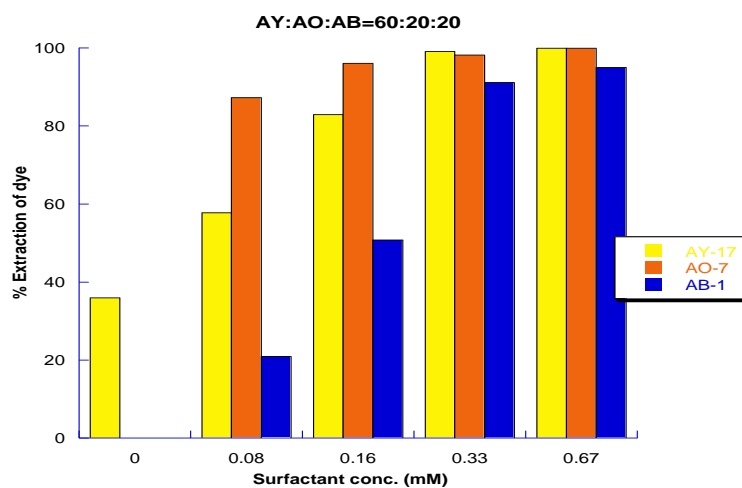
EFFECT OF INITIAL DYE CONCENTRATION

The variation of concentration of ternary dyes has been studied at original pH which was 6.45. Solutions were prepared by mixing ternary dyes in different ratios (AY-17+AO-7+AB-1=100ppm). This was observed that when the dyes are mixed in 1:1:1 ratio, maximum dye extracted was AO-7 (95-99%) as shown in **Figure 5**. The order of extraction of dyes follows the order AO-7>AY-17>AB-1. In the aqueous solution containing three dyes AY-17, AO-7 and AB-1in different ratios, it has been observed that AO-7 is extracted almost completely as compared to AY-17 and AB-1. The reason for the removal of AO-7 is its small size and low molar mass. When the dyes have been mixed in other ratios like (3:1:1), (1:3:1), (1:1:3) and (2:2:1) respectively, the order of extraction of dyes remained the same i.e. AO-7>AY-17>AB-1 as shown in **Figure 5**. This suggests that the electrostatic interactions are more effective at certain optimum cavity size of reverse micelle. The head group of HTAB is very small creating a small sized cavity that entraps small dye ions completely. After almost 100% removal of AO-7, remaining reverse micelles rearranges and entraps AY-17 dye ions. After removal of AY-17, concentration of reverse micelles decreases per unit volume.
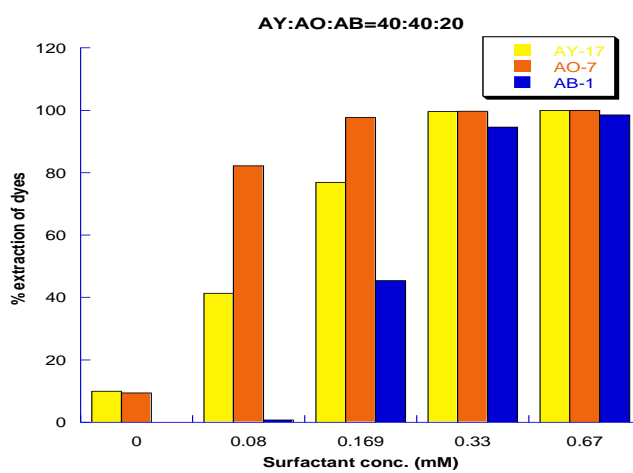
Big sized dye ions hardly get encapsulated in small sized cavity of reverse micelles. Small electrostatic forces on polar surfaces of dye and micellar head core creates weak, superficial attraction; creating a temporary and reversible complex which dissociates even before separation. This has been observed that when concentration of surfactant is excess, large number of reverse micelles are formed. They encapsulate all the type of dye ions irrespective of their sizes, due to formation of lamelles at higher concentration of surfactants which can sandwich any type of dye ion by electrostatic interaction. At lower surfactant concentration reverse micelles are spherical, at slightly higher concentration oval shaped and at highest concentration lamelles are formed.

AY:AB:AB=33.3:33.3:33.3

(i)

AY:AO:AB=60:20:20

(ii)

AY:AO:AB=40:40:20

(iii)

AY:AO:AB=20:60:20
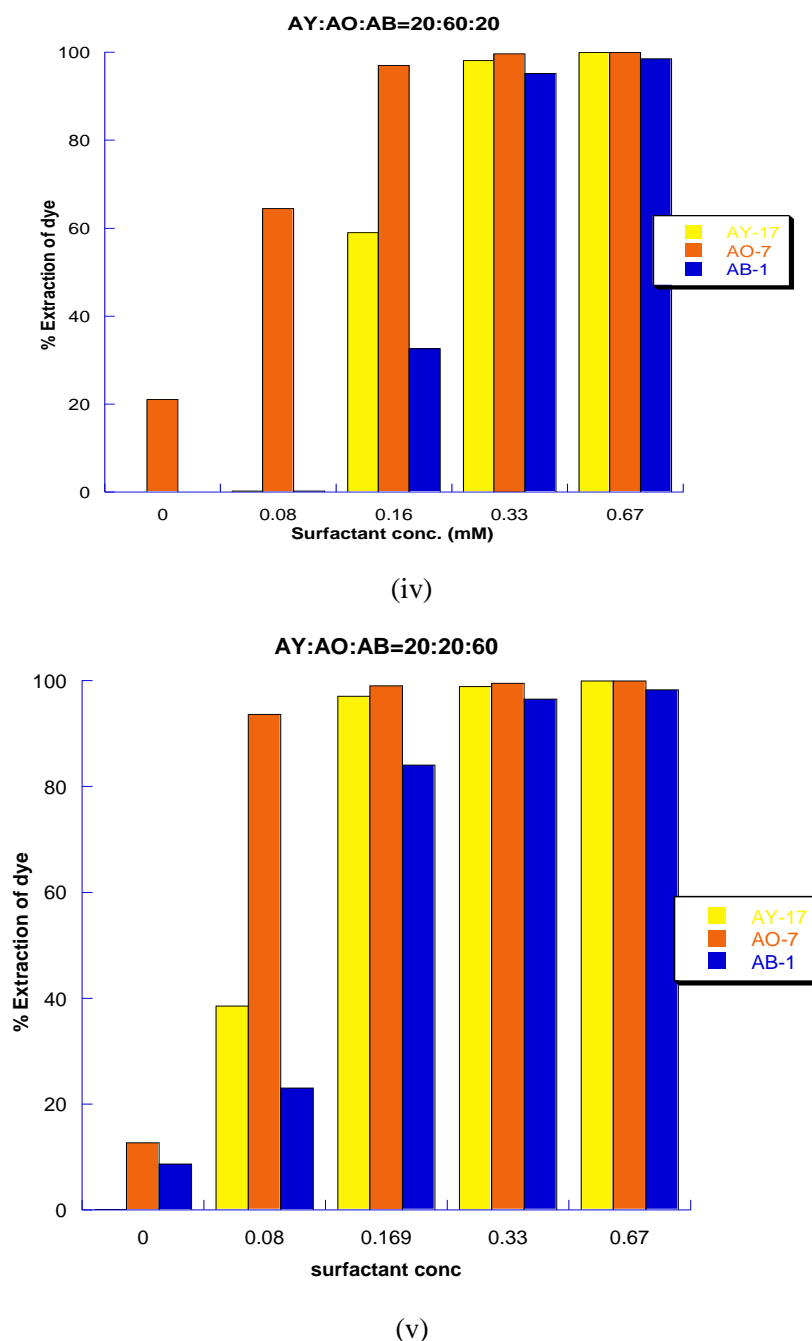

(iv)

AY:AO:AB=20:20:60

(v)

Figure 5: Effect of surfactant concentration on different composition of dyes (i)-(v).

EFFECT OF TEMPERATURE

The effect of temperature on extraction of dyes from aqueous phase has been studied at 298, 308 and 318K. It has been observed that the extraction rate for the dyes remained unchanged. This is due to the reason that micellization of HTAB is entropy driven. The HTAB system entropy effect dominates over the entire range of temperature. Thus, effect of temperature is not significant. Thus further studies were carried out at 303K. The effect of temperature on extraction of dyes is shown in **Figure 6**. When micelles of HTAB are formed, it displaces large number of water molecules out of core which is hydrophobic, so formation is increasing entropy of water, though entropy of surfactant ions

is decreasing. Net entropy of the system causing micellization increases. Reverse micellization is driven by electrostatic interactions.
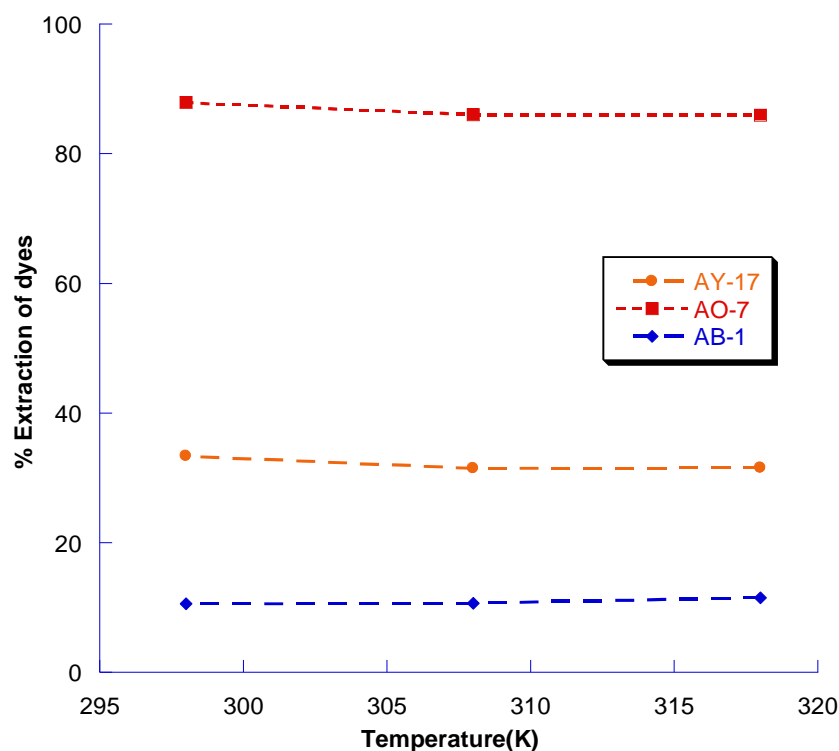

Figure 6: Effect of temperature on extraction of dyes.

EFFECT OF pH

The effect of pH on the extraction of ternary mixture of AB-1, AY-17 & AO-7 present in textile effluent was investigated at different pH values 2.0 to 9.0 at 303K. The result shows that efficiency of extraction is maximum for AY-17 and AO-7 dye at pH 5 but minimum for AB-1 as shown in Figure 7. Electrostatic interaction is one of the major interactions in reverse micelle extraction, thus changing the pH of aqueous solution will directly affect the extraction of dyes. The dye is highly protonated at very low pH because the solution becomes highly acidic and is rich in positive charge. So the extraction of anionic AB-1 dye which is rich in negative charge is maximum at low pH.

At low pH, H^+ ion concentration is high which allows the anionic dye to form an ion-pair complex with cationic surfactant, whereas AO-7 and AY-17 dyes are maximum extracted at pH 5. Thus these dyes get less protonated in highly acidic medium, thereby reducing the negative charge of anionic dyes. Since the electrostatic force of attraction depends upon the magnitude of charge, lower the magnitude of charge lesser is the attraction among ions.

The pKa values of AO-7, AY-17 and AB-1 were found to be 8.3, 9.4 and 8.26 respectively. Furthermore, at pH lower than their pKa values, the dyes are protonated and their ionic character increases leading to more solubilizaton of dyes in micelles. At higher pH above pKa values the dyes are deprotonated and their behavior looks like that of hydrophilic molecule, so that they are less solubilized in micelles. Thus, dye extraction of acid dyes increases at acidic pH.
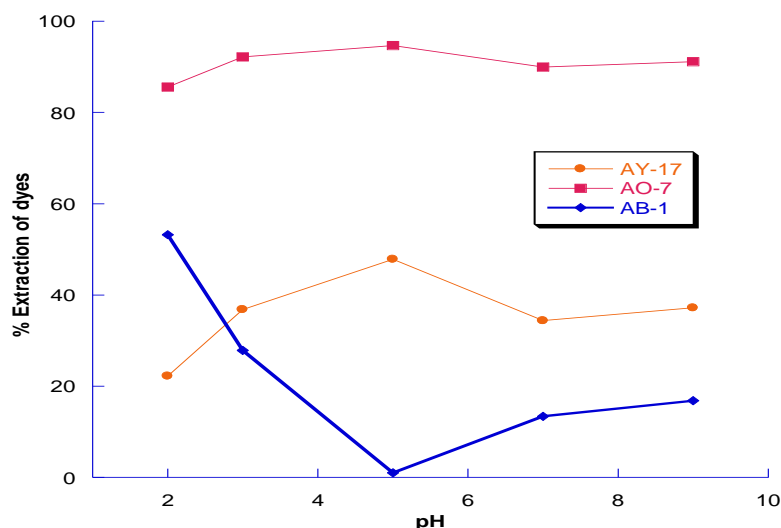
Figure 7: Effect of pH on extraction of ternary mixture of dyes

EFFECT OF SALT CONCENTRATION

In actual textile dye bath effluent, some salts are present along with dye like NaCl, $MgCl_2$ and $AlCl_3$ etc. and hence their influence on the extraction was investigated. The effect of NaCl, $MgCl_2$ and $AlCl_3$ on the percentage extraction of AO-7, AY-17 and AB-1 from aqueous solution at its original pH is shown in **Figure 8**. The effect of increase in concentration of salts on extraction of dyes from ternary mixture follows the order NaCl > $MgCl_2$ > $AlCl_3$, because the size of cation decreases whereas positive charge increases. Due to small size and high positive charge Al^{+3} penetrate deeply into the core of micelles and suppress the micellization of cationic surfactant due to competitive interactions. Increase in concentration of $AlCl_3$ decreases the extraction of all the three dyes in ternary mixture. As shown in **Figure 8**, the extraction of AB-1 is highly suppressed in presence of these electrolytes as compared to AY-17 and AO-7 because of its high molecular mass. The order of extraction of dyes in presence of these salts is in the order AO-7 >AY-17> AB-1. It is also observed that with increase in concentration of NaCl, extraction of dyes slightly increases.
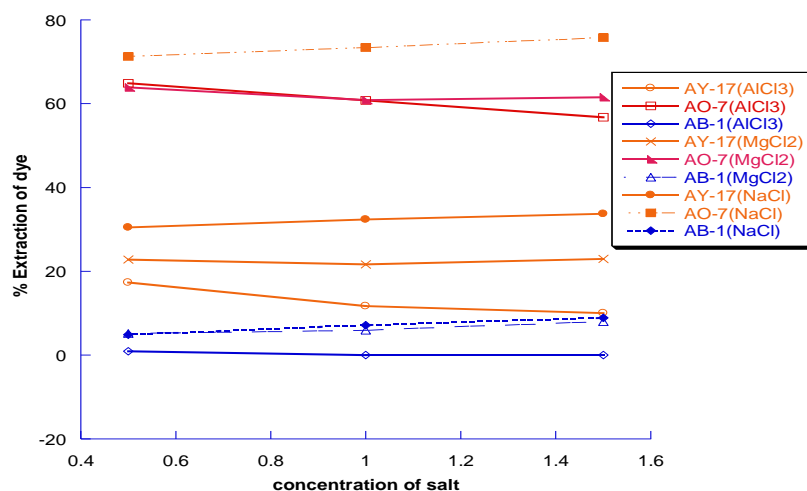

Figure 8: Effect of different salt concentration.

EFFECT OF SOLVENT

Different types of solvents such as butanol, 1, 4-Dioxane, hexane, amyl alcohol and isoamyl alcohol were tried for extraction study. Among them, isoamyl alcohol, amyl alcohol and butanol extracted the dye effectively. Maximum extraction of dyes was found in isoamyl alcohol. Thus, isoamyl alcohol was used for further studies. The effect of solvent on extraction of dyes is shown in **Figure 9**.
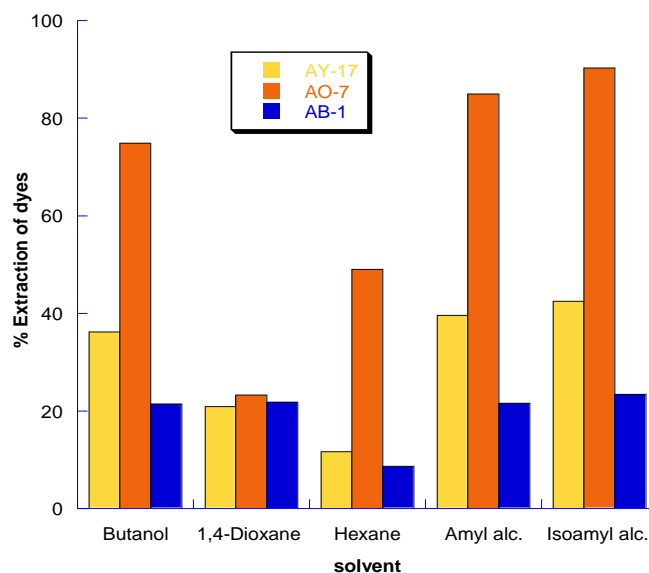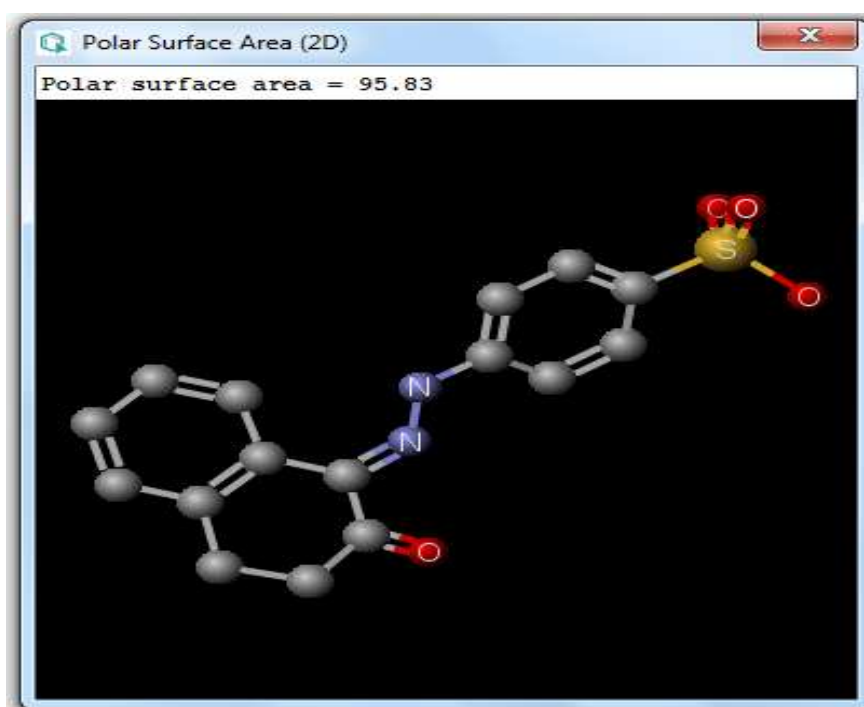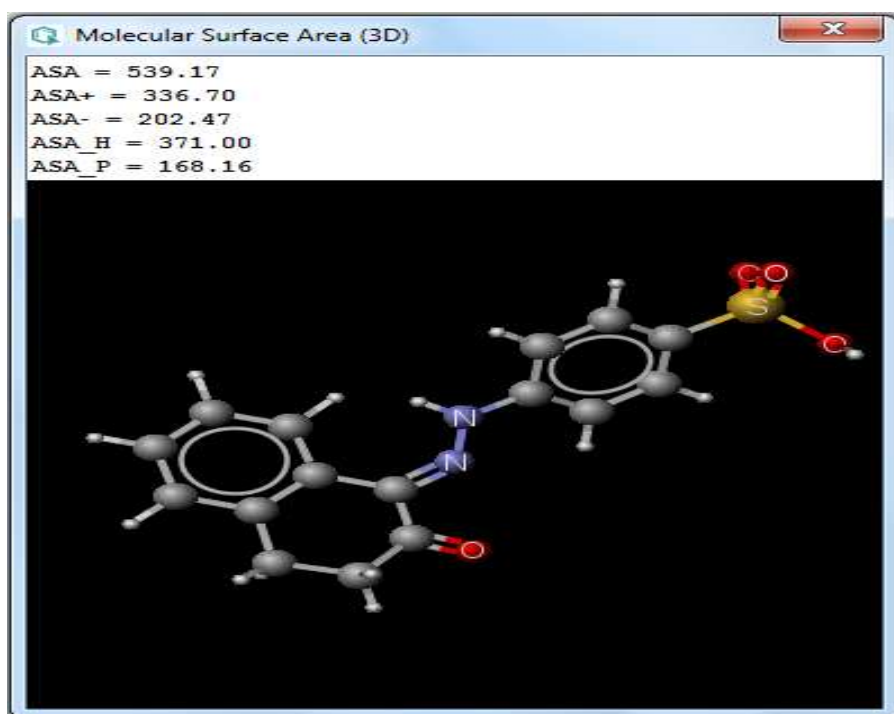

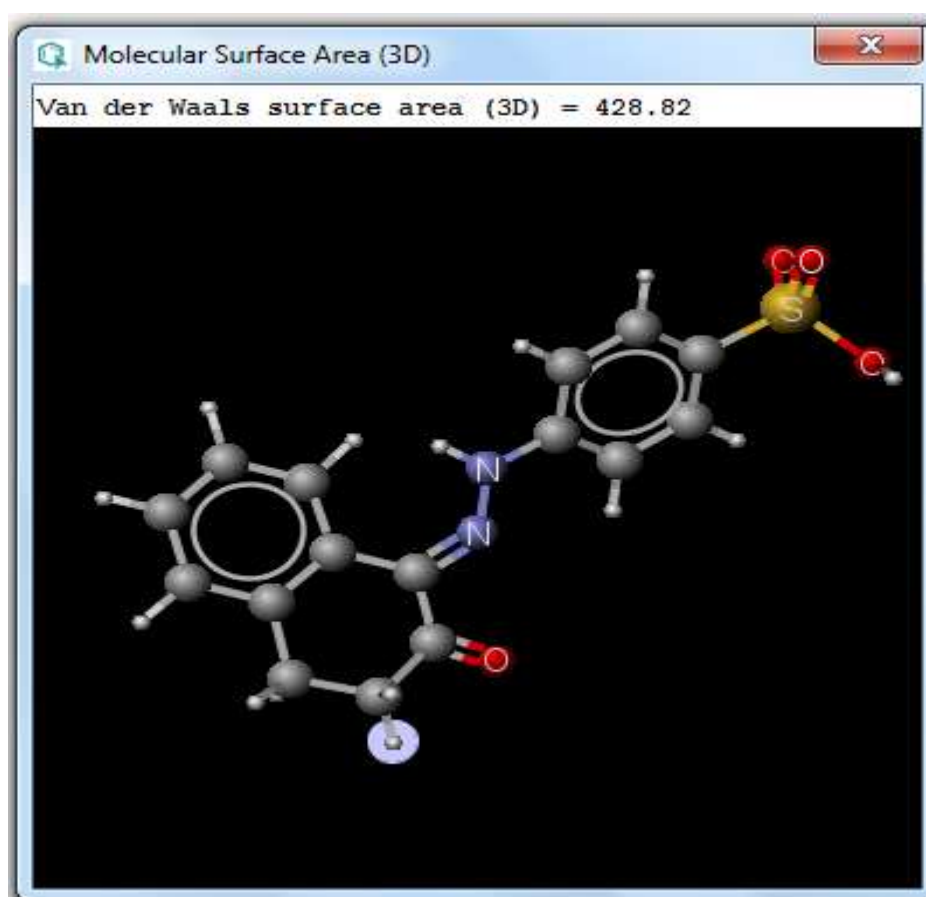**Figure 9:** Effect of solvent on extraction of dyes.

1) **Compound A**

Polar Surface Area (2D)
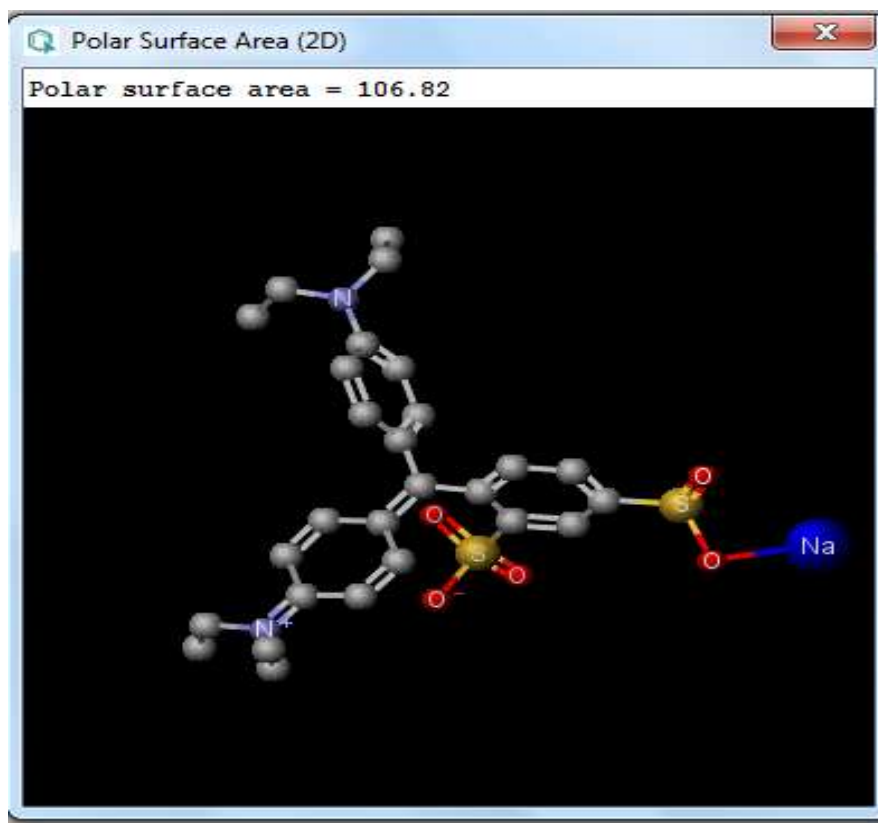
Molecular Surface Area (3D): Solvent Accessible

Molecular Surface Area (3D): Van der Waals

2)   Compound B

Polar Surface Area (2D)

Molecular Surface Area (3D): Solvent Accessible

Molecular Surface Area (3D): Van der Waals

3)   Compound C

Polar Surface Area (2D)

Molecular Surface Area (3D): Solvent Accessible
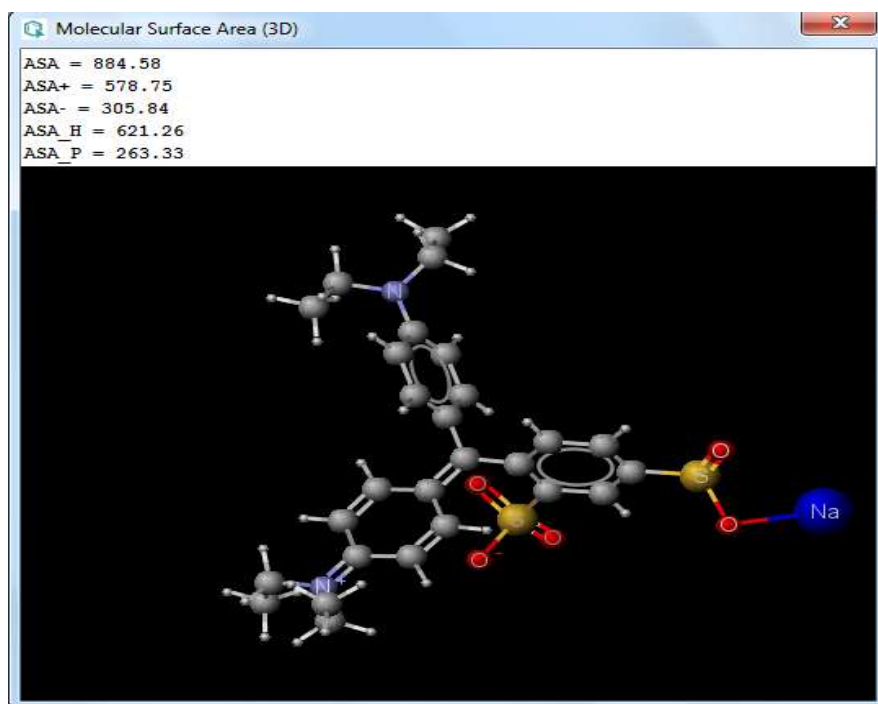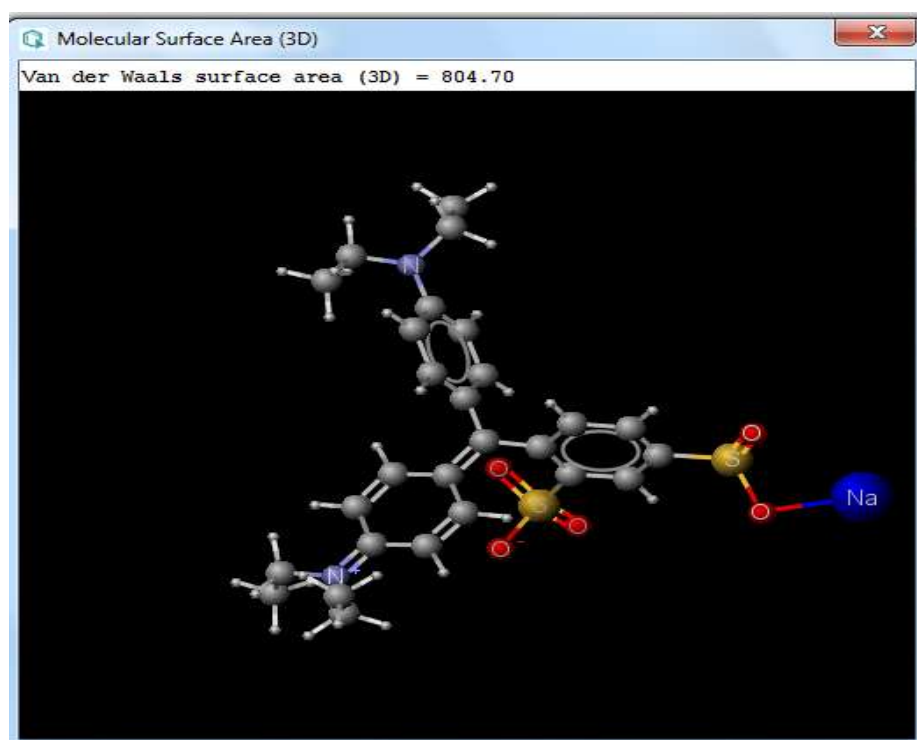

Molecular Surface Area (3D): Van der Waals
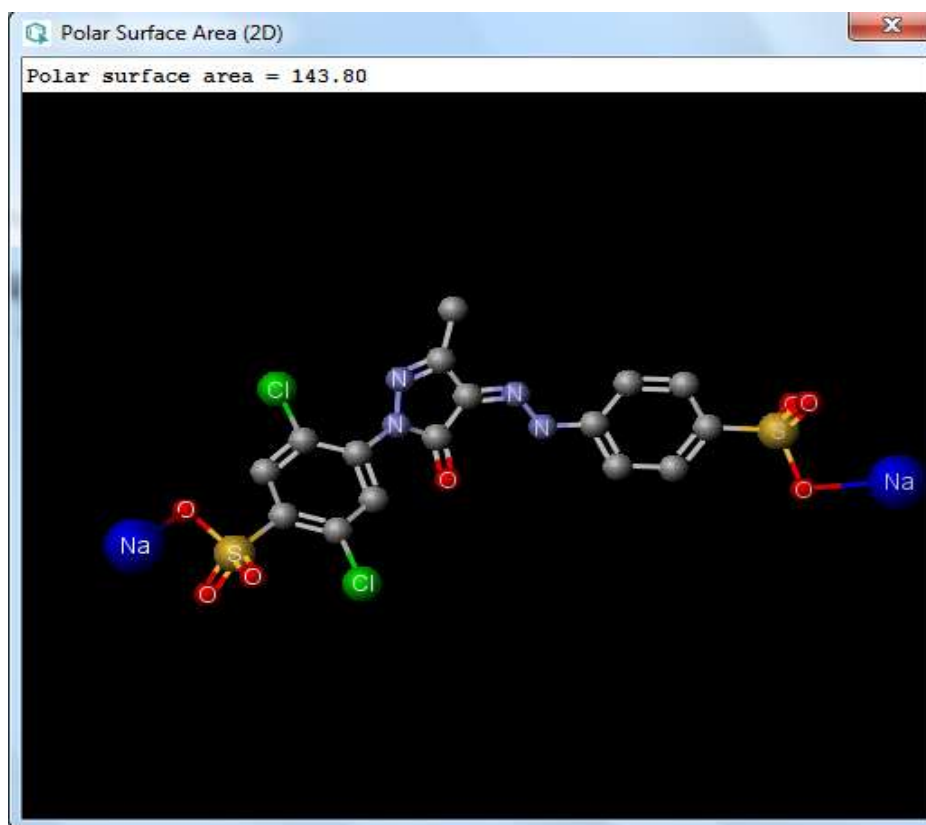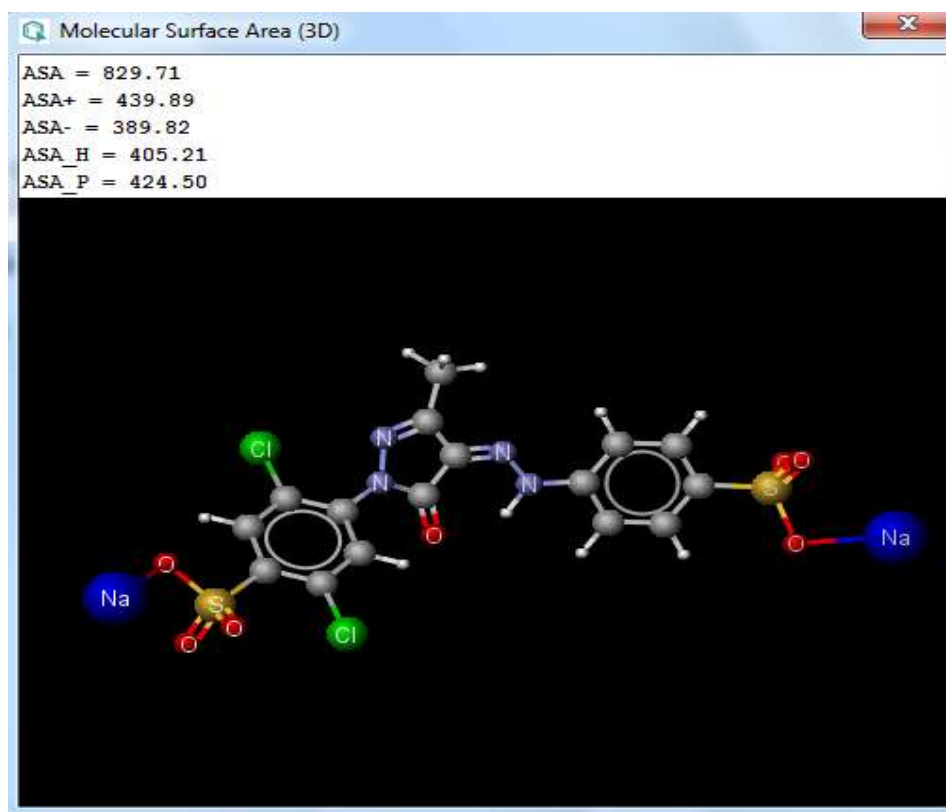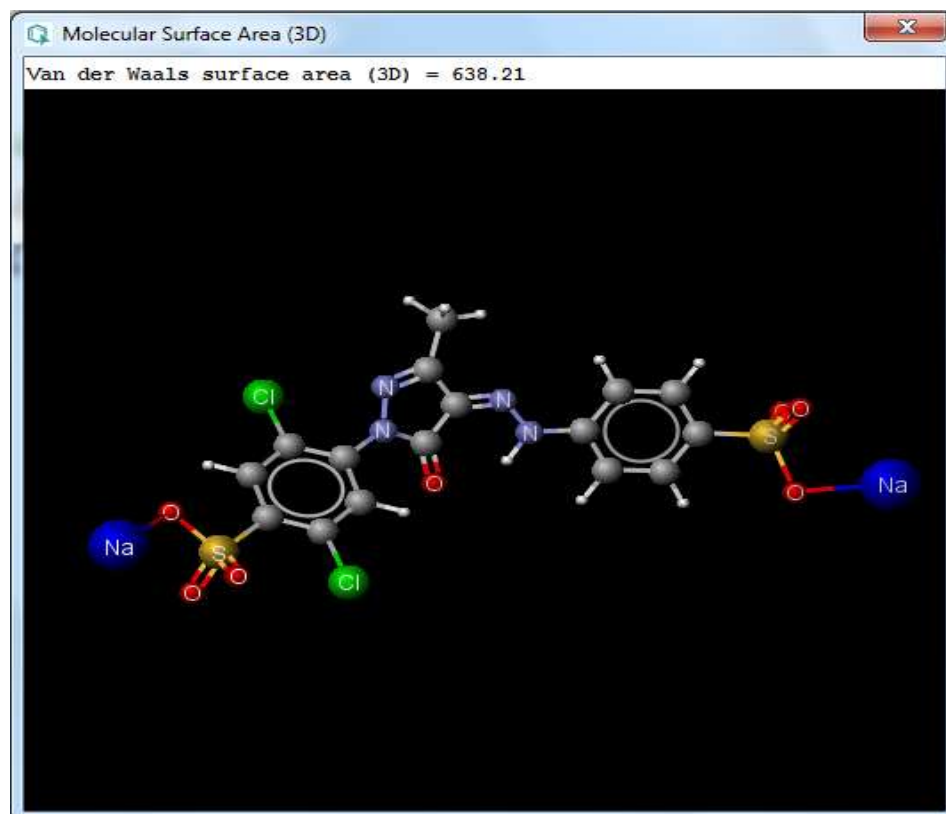
CONCLUSION

Anionic dyes Acid Blue-1, Acid Orange-7 and Acid Yellow-17 used in textile industry to dye wool, nylon, silk are extracted from the aqueous solution by solvent extraction method using HTAB surfactant. Experimental results show that different parameters like dye concentration, surfactant concentration, equilibration time also effect the removal of dyes. Almost complete removal of dyes from the effluent is possible with solvent extraction. The solvent used can be recovered and recycled.

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