Langmuir-Hinshelwood (L-H) adsorption isotherm and photodegradation of copper surfactants derived from long chain saturated fatty acid catalyzed by zinc oxide

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Photocatalysis process is a relatively novel subject with tremendous potential in the near future because of its environmental applications. Large molecules such as copper stearate soap (CS) and copper palmitate (CP) cannot be metabolized rapidly by microorganisms naturally. Photocatalytic degradation has been considered to be an efficient and rapid process for the degradation of copper soaps derived from long chain saturated fatty acid. The zinc oxide as semiconductor can be effectively used as a catalyst for the photochemical degradation of surfactants causing environment pollution. The progress of the reaction has been monitored spectrophotometrically by measuring the absorbance of the reaction mixture at definite time intervals. Different parameters such as the concentration of soap, dose of semiconductor, light intensity, effect of solvent polarity were varied to achieve the optimum rate of photodegradation. The observations revealed that CS and CP soaps were degraded successfully by using ZnO under UV. The disappearance of copper surfactants follows a pseudo-first order kinetics according to the Langmuir-Hinshelwood (L-H) model. A tentative mechanism has been proposed for the photodegradation of copper surfactants.

Keywords: Zinc oxide, photocatalytic degradation, semiconductor, copper surfactants.

Introduction

It is the prime objective of environmental education to make people aware about the importance of protection and conservation of our environment because indiscriminate release of various pollutants in the environment leads to serious health hazards. The extensive use of surfactants as lubricants, stabilizers, repellants, protectors, insecticide etc.[1]. Physicochemical studies, synthesis and characterization of antifungal agents containing Cu[II] soaps and their complexes derived from various oil has been studied earlier by Sharma *et al.*[2]. In our earlier communications on studies of CMC, solute-solvent and solute-solute interactions[3], ultrasonic studies[4,5], biocidal activities[6,7], thermal degradation[8,9], photo degradation[11] of Cu[II] soaps derived from edible and non-edible oils in methanol-benzene system at 303 K have been reported. Photochemistry plays a significant role in many reactions of biological, synthetic and industrial importance in which energy received from sun can be better utilized for converting the pollutants into less toxic materials. Extensive research in photocatalysis resulted in various applications based on the use of semiconductors ZnO is an attractive semiconductor for numerous applications because of its hardness, chemical stability, optical transparency, large excitation energy and piezoelectric properties[12]. Ameta *et al.* carried out the photodegradation of naphthol green B dye using antimony trisulphide as a heterogeneous catalyst[13]. Attia has reported the photocatalytic oxidation of iodide ion in the aqueous suspension of zinc oxide and its sensitization with riboflavin carried out the photocatalytic degradation of aniline blue dye using different semiconductors such as ZnO, ZnS and SnO2[14]. Kothari *et al.* reported the photocatalytic degradation of evans blue, an azo dye and its mixture with amaranth in presence of ZnO[15]. Photocatalytic mineralization of methylene blue using buoyant TiO2-coated polystyrene beads was observed by Fabiyi and Skelton[16]. Mixed ligand complexes of copper plays important role in numerous chemical and biological systems, like water softening, electroplating, dyeing, antioxidant, photosynthesis in plants, removal of

undesirable and harmful metals from living organisms etc.[17,18]. It has created a new problem in environmental pollution because these are either slowly biodegraded or these do not biodegraded at all. It is, therefore necessary to search out an alternate and quicker method for the treatment of these pollutants. This pressing demand results in the origin of the present investigation. Zinc oxide has been used as an effective catalyst for carrying out number of chemical reactions, but limited work has been reported on degradation of surfactants[19]. Different methods of surfactants treatment are being used for the removal of these from their solutions. In the present work, ZnO was used as a semiconductor. Further, this method is more advantageous over other methods, since it does not add further to pollution. The present study involves the photocatalytic degradation of copper stearate and copper palmitate surfactants by heterogeneous photocatalytic process using ZnO as semiconductor and the degradation was studied spectrophotometrically in non-aqueous and non-polar solvent benzene which has been chosen due to maximum solubility of solute molecule in solvent. Further the study deals with the effect of various parameters such as concentration of soap, catalyst loading, light intensity, effect of solvent on photocatalytic degradation of copper surfactants.

Materials and methods:

Synthesis:

Firstly copper surfactants were prepared by direct metathesis of corresponding potassium soap with slight excess of required amount of copper sulphate at 50–55°C (Scheme 1)[20]. After washing with hot water and the alcohol, the sample was dried at 80–100°C and recrystallized from hot benzene (60°C). The physical and analytical data of copper surfactants are given in Table 1. Elemental analysis was done for surfactants for their metal content following standard procedures[21].

$$RCOOH \xrightarrow[\text{EtOH}]{\text{KOH}} RCOOK \xrightarrow[\text{Benzene}]{\text{Cu}^{II}} (RCOO)_2Cu \qquad (1)$$
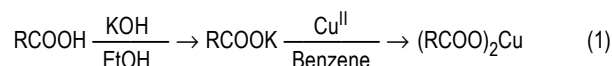
Scheme 1. Synthesis of copper surfactants.

Results and discussion

Photo-chemical degradation studies:

Solutions of the surfactants were prepared in hot benzene (Qualigens). The solutions were clear and free from solid impurities. For each observation 25.0 ml of solution was taken in a reaction flask and ZnO as semiconductor was added to it. The infrared fraction of light was eliminated by keeping a water filter between irradiation source and reaction mixture. The pre-aerated reaction mixture was exposed to tungsten lamp. Irradiation was carried out in a covered glass bottle (Pyrex, 50 ml) for the protection of evaporation of the solvent with a 200 W tungsten lamp (visible light, Philips). Absorbance of the reaction mixture was observed at regular time intervals. In a control experiment, photocatalytic degradation was carried out in the absence of ZnO. It was observed that there was no appreciable photodegradation of copper surfactants, indicating that for photodegradation of copper surfactants semiconductor ZnO plays a key role. A 3.0 ml aliquot was taken from the reaction mixture at regular time intervals and the absorbance measured spectrophotometrically at λ_{max} value of 420 nm. It was observed that the absorbance of the solution decreases with increasing the time of exposure, which indicates that the concentration of copper surfactants decreases with increasing time. The calculation of degradation efficiency ψ was made by the relation[22].

$$\text{Degradation \%} = \frac{A^0 - A}{A^0} \times 100 \qquad (2)$$

Here A^0 is initial absorbance, and A is absorbance after degradation of copper surfactants at time t. A plot of 2 + log A versus time was linear following pseudo-first order kinetics.

Table 1. Analytical and physical data of copper surfactant derived from saturated fatty acids

Compound	Molecular weight	M.p. (°C)	Color	Found (Calcd.) (%)			
				Cu	C	H	O
$C_{36}H_{70}O_4Cu$ (Copper stearate)	630.42	82	Blue	9.52 (10.07)	67.95 (68.56)	11.01 (11.19)	10.02 (10.15)
$C_{32}H_{62}O_4Cu$ (Copper palmitate)	573.54	80	Blue	11.01 (11.06)	66.10 (66.91)	10.82 (10.87)	11.03 (11.14)

The rate constant, *k* was calculated by using the expression[23].

$$k = 2.303 \times slope \qquad (3)$$

To predict the effect of various factors on the rate of degradation process, the concentration of the surfactant was varied from 0.40–0.96 g L^{-1} photocatalyst (semiconductor) were used ranging from 0.01 to 0.06 g, the light intensity was varied from 26 to 54 mW cm^{-2} with the help of a solarimeter (CEL India, Model SM 201) and the percentage of methanol varied from 20 to 80% to observe solvent effect. According to calibration curve, λ_{max} was found at 420 nm and the progress of the photocatalytic reactions was observed by measuring the absorbance at 420 nm (λ_{max}) in regular time intervals by UV-Visible spectrophotometer (Systronics, Model 106). The effects of the various parameters such as concentration of soap, dose of semiconductor, effect of light intensity, effect of polarity of solvent on the rate of photocatalytic degradation are as follows:

Effect of concentration of soap:

The rate of photocatalytic degradation of CS and CP is likely to be affected by change in concentration of the surfactant and therefore, the concentration of CS and CP was varied from 0.40–0.96 g L^{-1}. The results are graphically presented in Fig. 1 with RSD. The rate of photocatalytic degradation was found to increase with increasing concentration of CS soap up to 0.56 g L^{-1} while for CP up to 0.8 g L^{-1}. Further increase in the surfactant concentration resulted in a

Table 2. Effect of concentration of copper surfactant on degradation efficiency

Concentration of surfactants (g L^{-1})	Degradation efficiency (%)	
	CS	CP
0.40	34.91	23.55
0.48	36.11	35.74
0.56	**66.49**	45.94
0.64	49.92	49.02
0.72	40.01	59.42
0.80	38.60	**62.85**
0.88	35.78	53.16
0.96	32.15	41.82

Constant parameters: Light intensity, 042 mW cm^{-2}, solvent-benzene, dose of ZnO, 0.04 g.

decrease the rate of degradation (Table 2) which was also coincide by rate constant *k* (Fig. 2). The increase in the rate may be due to the fact that as the concentration of copper surfactant was increased more surfactant molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The decrease in the rate may be attributed to the fact that the surfactant molecules will start acting as a filter for the incident light and it will not permit the desired light intensity to reach the semiconductor particles, thus decreasing the rate of photocatalytic degradation.
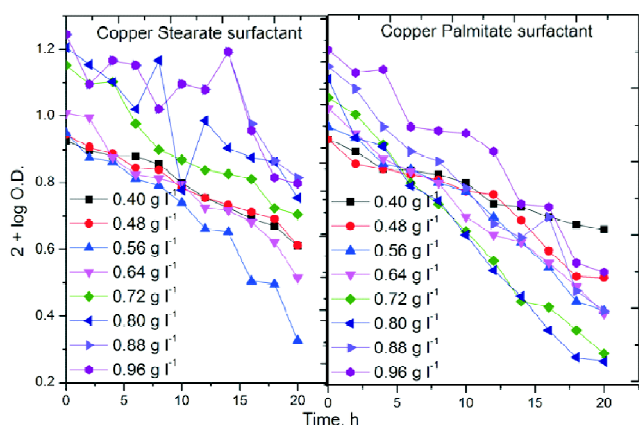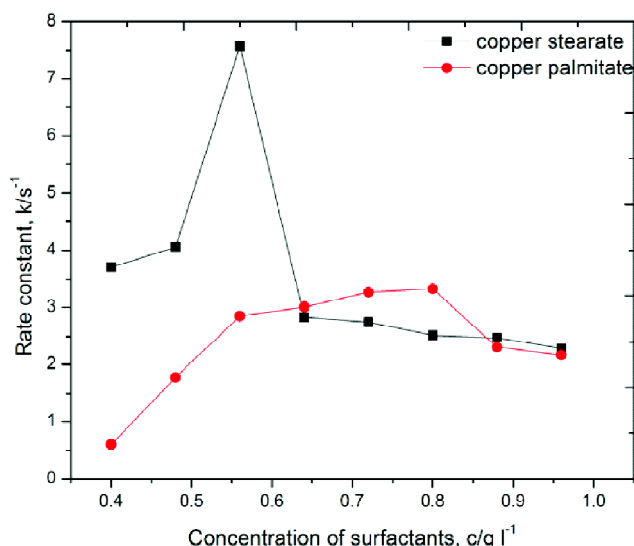

Fig. 1. Plot of 2 + log *A* versus time on effect of concentration of copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light intensity, 42 mW cm^{-2}, solvent-benzene, at constant dose of ZnO, 0.04 g).

Fig. 2. Plot of rate constant *k* versus concentration of copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light intensity, 42 mW cm^{-2}, solvent-benzene, dose of ZnO, 0.04 g).

Selection of suitable catalyst:

The rate of photocatalytic degradation was carried out on three different catalysts i.e. ZnO, TiO$_2$, ZnS. It was found that higher rate constant k observed for ZnO, therefore for present study ZnO wastaken (Fig. 3).
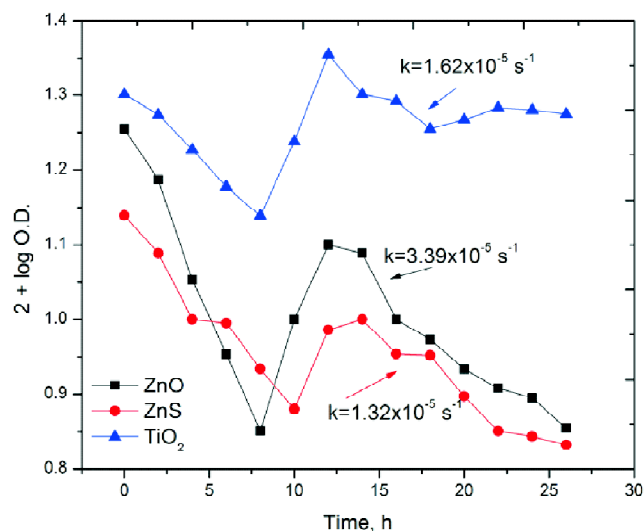

Fig. 3. Selection of suitable catalyst for degradation of copper surfactant derived from copper.

Effect of dose of semiconductor (ZnO):

The dose of semiconductor is also likely to affect the process of surfactant degradation and hence, different doses of photocatalyst were used ranging from 0.01 g to 0.06 g. The results are graphically presented in Fig. 4 (RSD ±0.2%). A perusal of the results indicates that the rate of photodegradation of copper surfactant increase with an increase in the dose of semiconductor and then ultimately, it becomes almost constant after a certain dose. The rate was found to be maximum at 0.04 g (Table 3) which was also coincide by rate constant k (Fig. 5). This may be attributed to the fact that as the dose of semiconductor was increased, the exposed surface area also increases but after a certain limit, if the dose of semiconductor was further increased, then there will be no increase in the exposed surface area of photocatalyst after this particular dose would only increase the thickness of the layer at the bottom of the vessel, once the bottom of the reaction vessel was completely covered by the semiconductor. This multilayer structure would not permit the entire semiconductor particles to be exposed to light and as such, the rate of the reaction became almost constant.
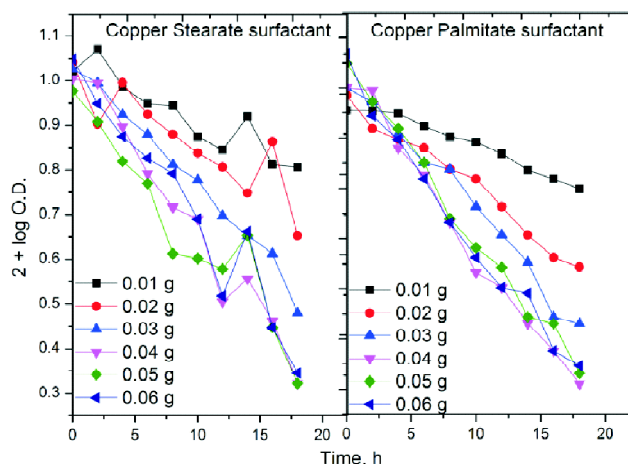

Fig. 4. Plot of 2 + log A versus time on effect of dose of semiconductor on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light intensity, 42 mW cm^{-2}, solvent-benzene, concentration of CS, 0.4 g L^{-1}).

Table 3. Effect of dose of semiconductor on degradation efficiency of copper surfactants

Dose of ZnO	Degradation efficiency (%)	
(g)	CS	CP
0.01	22.08	17.29
0.02	38.31	35.67
0.03	54.20	47.90
0.04	**68.93**	**59.90**
0.05	68.02	59.96
0.06	68.16	59.21

Constant parameters: Light intensity, 42 mW cm^{-2}, solvent-benzene, concentration of CS, 0.4 g L^{-1}.
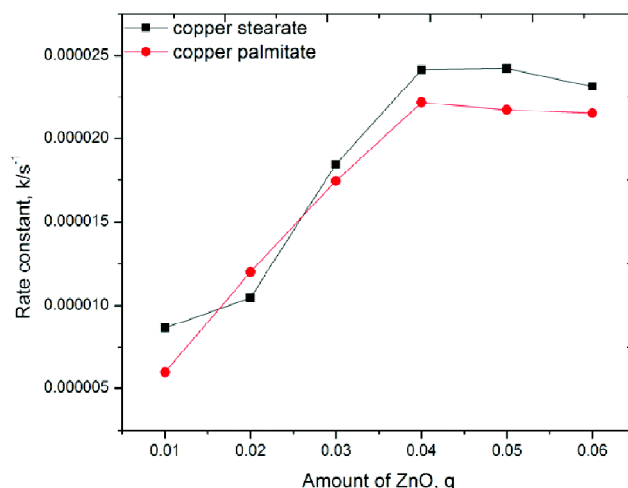

Fig. 5. Plot of rate constant k versus dose of semiconductor on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light intensity, 42 mW cm^{-2}, solvent-benzene, concentration of CS, 0.4 g L^{-1}).

Effect of light intensity:

The effect of light intensity on the photocatalytic degradation of copper surfactant was also studied. The light intensity was varied from 26 to 54 mW cm^{-2}. The results are graphically presented in Fig. 6 (RSD ±0.2%).
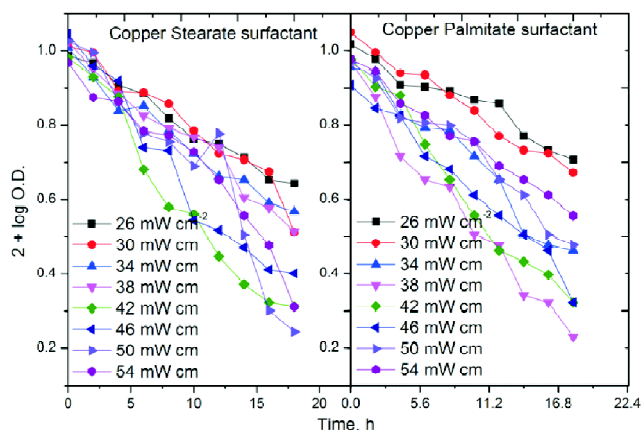

Fig. 6. Plot of 2 + log *A* versus time on effect of light intensity on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Solvent-benzene, dose of ZnO, 0.04 g, concentration of CS, 0.4 g L^{-1}).

The data indicate that the rate of photocatalytic degradation of CS was found to increase with increasing light intensity upto 42 mW cm^{-2} while for CP upto 38 mW cm^{-2} (Table 4) which was also coincide by rate constant *k* (Fig. 7). Further increase in the light intensity resulted in a decrease in the rate of degradation. As the number of photons striking per unit area of semiconductor powder increases with the increase in light intensity, there is a corresponding increase

Table 4. Effect of light Intensity on degradation efficiency of copper surfactants

Light Intensity	Degradation efficiency (%)	
(mW cm^{-2})	CS	CP
26	35.77	31.50
30	41.42	36.99
34	44.66	52.53
38	50.88	**77.21**
42	**69.21**	68.02
46	62.67	65.45
50	57.22	31.69
54	48.84	24.17

Constant parameters: Dose of ZnO, 0.04 g; solvent-benzene, concentration of CS, 0.4 g L^{-1}.
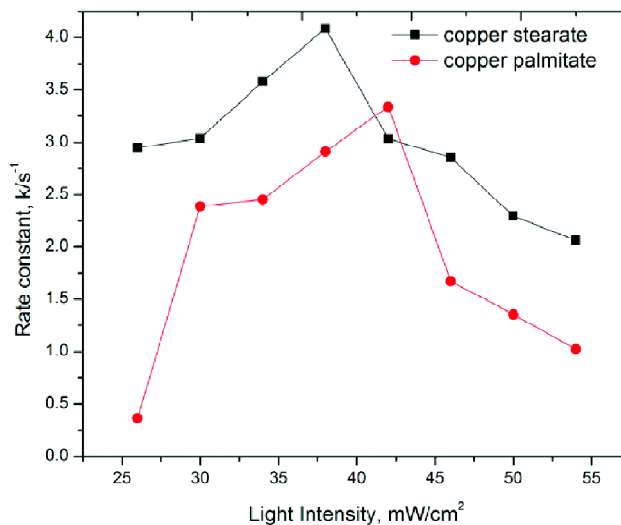

Fig. 7. Plot of rate constant *k* versus effect of light intensity on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Solvent-benzene, dose of ZnO, 0.04 g, concentration of CS, 0.4 g L^{-1}).

in the rate of photocatalytic degradation of soap. As a result, more electron-hole pairs are generated, which results in an overall increase in the rate of the reaction. The rate of photocatalytic degradation was found to decrease with a further increase in the light intensity due to thermal side effects.

Effect of solvent:

The rate of photocatalytic degradation of copper surfactant is also affected by the change in solvent. The percentage of methanol was varied from 20 to 80%. The results are graphically presented in Fig. 8 (RSD ±0.2%).
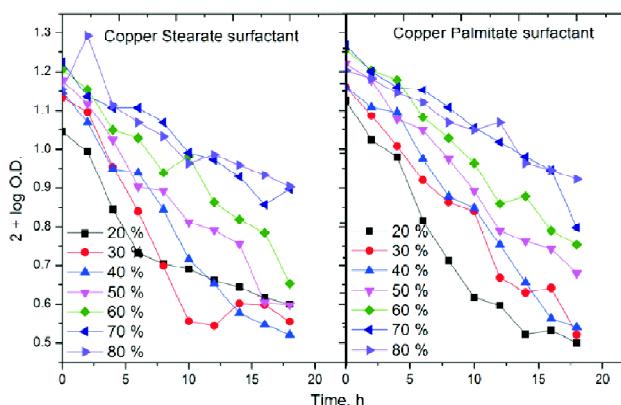

Fig. 8. Plot of 2 + log *A* versus time on effect of solvent on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light Intensity, 42 mW cm^{-2}, dose of ZnO, 0.04 g, concentration of CS, 0.40 g L^{-1}).

It was observed that the rate of degradation continuously decreases with increase in the polar solvent such as methanol. In the case of copper surfactants degradation, it has been clearly observed that rate decreases with the increase in polarity of solvent (Table 5) which was also coinciding by rate constant k (Fig. 9). Surfactants are surface-active compounds and they behave differently due to micellar activity. It may be suggested from the above observations that the polarity inhibits the reactivity of the surfactant molecule.

Table 5. Effect of solvent polarity on degradation efficiency of copper surfactants

Polarity of solvent	Degradation efficiency (%)	
(%)	CS	CP
20	53.20	62.00
30	52.15	61.34
40	51.45	59.55
50	50.41	49.42
60	47.06	44.62
70	28.00	41.36
80	22.97	26.58

Constant parameters: Dose of catalyst, 0.04 g, concentration of CS, 0.4 g L^{-1}, light Intensity, 42 mW cm^{-2}, solvent-benzene.
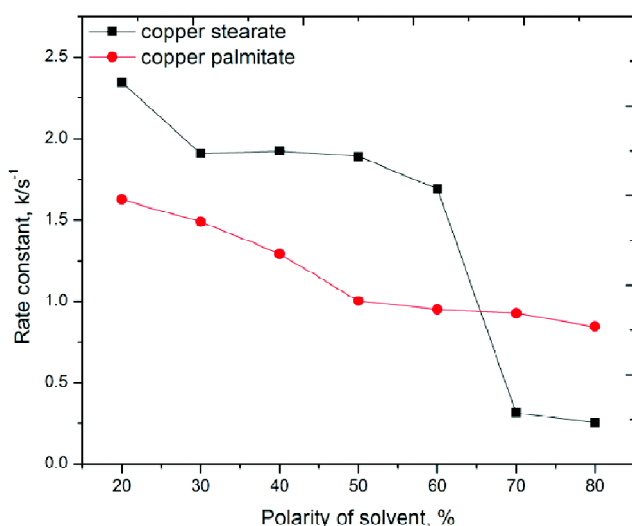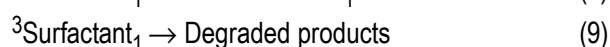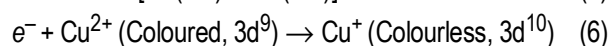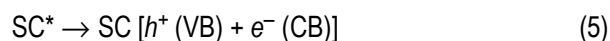

Fig. 9. Plot of rate constant k versus effect of solvent on copper surfactant derived from copper stearate and copper palmitate (Constant parameters: Light Intensity, 42 mW cm^{-2}, dose of ZnO, 0.04 g, concentration of CS, 0.40 g L^{-1}).

Mechanism:

A tentative mechanism for the photocatalytic degradation may be proposed as[24]

$$SC \xrightarrow{h\nu} SC^* \tag{4}$$

$$SC^* \rightarrow SC\ [h^+\ (VB) + e^-\ (CB)] \tag{5}$$

$$e^- + Cu^{2+}\ (Coloured,\ 3d^9) \rightarrow Cu^+\ (Colourless,\ 3d^{10}) \tag{6}$$

$$^1Surfactant_0 \xrightarrow{h\nu} {}^1Surfactant_1 \tag{7}$$

$$^1Surfactant_1 \xrightarrow{ISC} {}^3Surfactant_1 \tag{8}$$

$$^3Surfactant_1 \rightarrow Degraded\ products \tag{9}$$

Initially on exposure to light the semiconductor (SC) will be excited to give SC*, the excited state of semiconductor. This excited state will provide an electron in the conduction band (CB) and a hole in the valence band (VB).

When the solution of soap in the benzene was exposed to light in the presence of a semiconductor, the soap molecule may be first excited to its first excited singlet state. These excited molecules are transferred to corresponding triplet state through Inter System Crossing (ISC) and triplet state of soap molecules oxidized with atmospheric oxygen, convert in to degraded products. The decoloration of the soap solution also suggests that some of the Cu^{2+} ion of the soap may reduce to Cu^+ to some extent during the process of degradation.

Langmuir isotherm:

Langmuir isotherm[25] can be expressed by the:

$$1/q_e = 1/Q^0 + 1/bQ^0C_e \tag{10}$$

where q_e is the amount adsorbed (mol/g) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). Q^0 and b are the Langmuir constants related to maximum adsorption capacity and energy adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, L shaped graph obtain with slope $1/bQ^0$ for both the solutions, which shows that there is no strong competition between the solvent and the adsorbate to occupy the ZnO surface sites (Fig. 10).
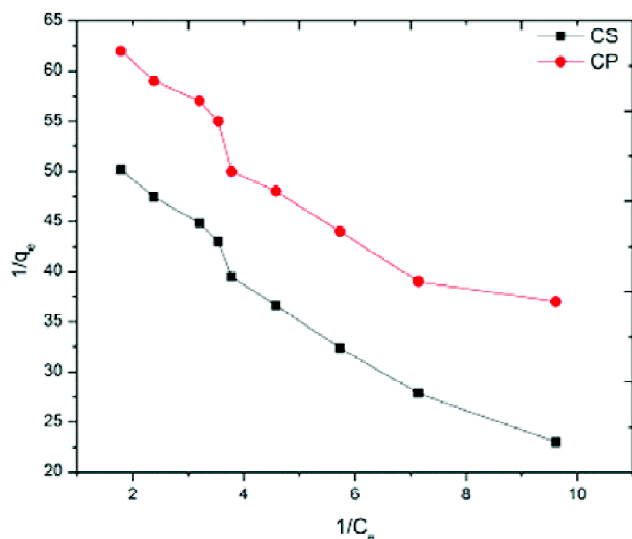
Fig. 10. Copper surfactants L-H isotherm on ZnO at constant parameters: Concentration, 0.4 g/L, temperature, 30±0.1°C.

Conclusion

Photocatalysis has been predicted as a promising technology for degradation of pollutants. This work reports a simple, novel, and cost-effective degradation of copper surfactants in the presence of ZnO. The photocatalytic efficiency for copper stearate observed higher than that of copper palmitate it is suggested that CS has higher molecular weight (630.42) compare to CP (573.54) which co-related by higher rate constant *k* for CS compare to CP catalyst was examined by using it for the photocatalytic degradation of CS soap. The optimum reaction conditions of copper surfactants degradation with ZnO were experimentally determined. The photochemical degradation of copper surfactants follows pseudo-first order kinetics. Experimental results indicate that the CS surfactant degrades best at concentration 0.56 g L^{-1} with light intensity 42 mW cm^{-2} and catalyst loading 0.04 g, 20% methanol polarity with degradation efficiency 65.55%. Similarly CP surfactant degrades best at concentration 0.8 g L^{-1} with light intensity 38 mW cm^{-2} and catalyst loading 0.04 g, 20% methanol polarity with degradation efficiency 60.15%.

Acknowledgement

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