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An investigation and Environmental Aspects of Copper(II) Surfactant with Photocatalytic Degradation

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ABSTRACT

Surfactants have wide use all over the world in various field of the national economy, will continue to expand its scope of application and the consumption is also increasing. Photodegradation is a branch of science, which attracted the attention of science community all over the world due to selection of light as energy source to degrade large molecules to smaller size molecules which does not degrade easily. Copper(II) Soya Thiourea complex has been synthesised and photocatalytic degradation of this complex carried by using ZnO as semiconductor catalyst in non aqueous solvent benzene. Concentration effect on Copper (II) Soya Thiourea complex with reference of optical density, photodegradation and percent degradation has been studied here. Using light as an energy source to drive a reaction results in chemistry is much more 'green', helping to eliminate the requirement for harsh reactants which are often toxic and unrecoverable. Photocatalysis also has applications in wide area of renewable energy. Analysis of biological activities of Copper soap complex is also done with Staphylococcus aureus to anticipate that it will generate new hopes in the field of biological applications.

Keywords : Copper(II) Soya Thiourea Complex, optical density, concentration of complex, percent degradation, Staphylococcus aureus.

I. INTRODUCTION

The scientific and technological implications of photocatalytic degradation processes are well recognized today, in so far as it allow the possibility of performing chemical reactions aimed at , elimination of pollutants without the concourse of elevated temperatures and pressures and using (sun)light as the only energy input. Copper (II) soap complexes with nitrogen and sulphur containing ligands play most prominent role in different fields of science and technology. Study of photodegradation of biologically active molecules in various solvents under different conditions may provide significant information towards safe and green chemistry.

The goal of this work to conclude a outline about feature and structure of Copper soap complexes synthesized from natural edible oils with long chain fatty acids and accurate kinetics of photocatalytic degradation of Copper (II) soap complexes containing N and S as donor atoms, as a function of various operating parameters such as catalyst loading, light intensity, initial concentration in polar and non-polar solvent. A large number of surfactants containing waste water are discharged into the environment, resulting in harming aquatic life (flora and fauna), polluting the water and endangering human health. When the concentration of the surfactant reaches to 0.1mg/L, the water may appear persistent foams and excess of bubbles are not easy to disappear in the water, forming foam insulating layer. Along with in human body they damage the enzyme activity and thus disrupt the body's normal physiological function.[1] Hence Photodegradation and biodegradation are the degradation processes which can naturally clean up the environment. [2] While comparing with other elimination methods, photocatalytic degradation has a unique advantage like simple and cost-effective approach. [3-5]

Several Copper(II) complex systems have been used for the degradation of lignin [6], polycyclic aromatic hydrocarbons [7], and synthetic dyes. [8] Recently work on transition metal complexes of heterocyclic ligands and polymetallic complexes have been done and also their structure and biological characteristics have been discussed.[9-12]

In this study, we measure the photocatalytic efficiency of the Copper soap complex derived from complexation of N and S containing ligand such as Thiourea with Copper soap. Therefore, proper design of ligands and also complexation with suitable metal ions are expected to improve the biological efficacy of Copper complexes. Although a lot of work has been done in the field of photocatalysis but no work has been reported by photodegradation of Copper (II) Soya Thiourea complex.

II. METHODS AND MATERIAL

SYNTHESIS OF COPPER (II) SOYA SOAP AND THIOUREA COMPLEX

Copper (II) Soyabean soap derived from saturated edible oil Soyabean (Glycine Max) has been synthesized by refluxing oil with ethyl alcohol and 1N KOH for three hours (Direct Metathesis). [13, 14] Neutralization of excess KOH was done by 1N HCl solution. Saturated solution of copper sulphate used for conversion of neutralized potassium soap into copper (II) soap. The purity of these complexes was checked by elemental analysis and determination of their melting point. The fatty acids composition of these edible oils was recognized via GLC of their methyl esters.

SYNTHESIS OF COMPLEX

A solution of ligand in 15 ml of ethanol was taken and solution of purified Copper (II) Soyasoap in benzene was added in 1:1 ratio and refluxed for 1 hrs. The formed precipitate was filtered off, washed with purified hot benzene, and dried. The sticky product was clearly green in color and soluble in benzene non-polar and organic solvents but insoluble in polar solvent water. All the complexes were stable at room temperature and their physicochemical properties are studied earlier. [15]

Here: CS soap- Copper(II) Soya soap

CST complex- Copper(II) Soya Thiourea complex

METHOD OF KINETICS AND DEGRADATION STUDIES

The photocatalytic activity of the complex has been evaluated by measuring the rate of degradation and the kinetics of photodegradation of CST complex. Covered glass bottles (pyrex-50 ml) containing 25 ml solutions were used for shielding of evaporation of solvent during irradiation with a 200 W tungsten lamp (visible light, Philips). A water strain was used to eliminate thermal emission in degradation method.[16]

The reaction mixture, containing ZnO as photocatalyst has exposed to a 200 W tungsten lamp (Philip) for light

radiation 18 mWcm2-to 42 mWcm2-. The reported absorbance maxima were 680 nm for blank.

III. RESULTS AND DISCUSSION

A graph plotted between 2+ log OD and time for each system and through observed optical density, 2+ log OD was calculated. Two-step degradation rate (K1, K2) with different time interval was observed through slopes of that particular graph.

Rate of reaction was determined by this phrase.[16]

K= 2.303 x slope

Here K represents rate of photocatalytic degradation and slope is calculated by the graph plotted between 2 + log OD and time.

Percent degradation of the complex has calculated by this expression. [17]

% degradation= Ao-At/Ao *100.

Here Ao = initial concentration of Copper (II) soap complex

At = concentration of Copper (II) soap complex after irradiation

MEASUREMENT OF OPTICAL DENSITY AND TIME

The photocatalytic activity of Copper (II) soap complex in pure solvent was studied under UV - visible light. Optical density was recorded for each solution with constant parameters at regular time interval (i.e. every 2 hours interval). Numerous plots were plotted between optical density recorded in terms of absorbance 'A' and other variables like concentration, amount of catalyst, light intensity and polarity of solvents. These plots were analysed for the calculation of rate of reaction K for different steps (i.e. K1, K2, K3) of the degradation of the complex molecule.

CATALYST EFFECT

Copper (II) Soya Thiourea (CST) complex was chosen to show the effect of amount of catalyst on optical density during degradation. This system was treated with different amount of catalyst to measurement of OD. 0.01 g and 0.06 g of ZnO. Results are shown in Table-1 with Figure -1

Table -1 Catalyst effect of Copper(II) soap complexes and Optical Density.

Concentration - .0008M Solvent -Benzene

Light intensity - 34 mWcm2- ZnO - .01 g and 0.6g

OD - Optical density

Time Hours	**[CST] Complex ZnO – 0.1g**	**[CST] Complex ZnO – 0.6g**
	2+Log OD	2+Log OD
0	1.22	1.19
2	1.06	1.139
4	0.934	0.991
6	0.812	0.869
8	0.591	0.863
10	0.431	0.633
12	0.612	0.863
14	0.431	0.698
16	0.38	0.602
18	0.301	0.505
20	0.23	0.301

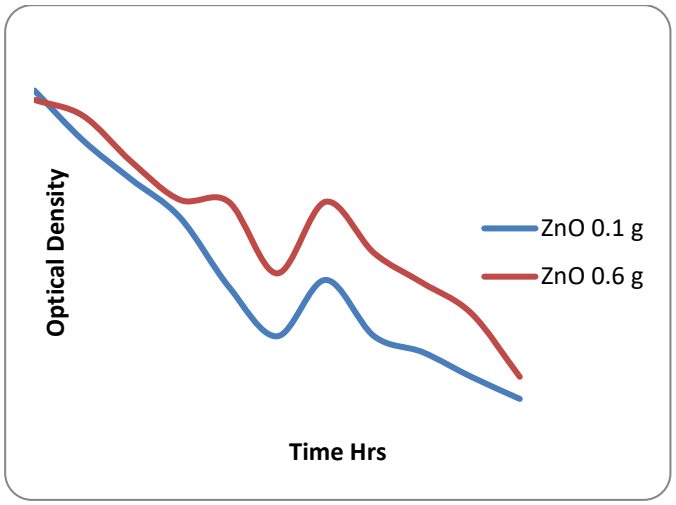

Figure -1 Catalyst effect of Copper(II) soap complexes and Optical Density.

PHOTODEGRADATION OF COPPER(II)SOYA THIOUREA COMPLEX (CST)
EFFECT OF CONCENTRATION

The effect of variation in the CST complex concentration on the rate of reaction was observed by using different concentrations of CST complex in gram mole per litre by keeping other parameters constant.

Two values of rate constant for kinetics of degradation in two-step were obtain by plotting the graphs between concentration and optical density which follows the order $K_1 > K_2$. The perusals of the results may suggest that the co-ordination bond between metal surfactant and ligand (Thiourea) and along with mono; polyunsaturated bonds of the long chain fatty acid component of the solute may degrade in first step and then saturated long chain fatty acid segment undergoes degradation in second phase. These observations also recommend that the rate of degradation of CST complex is increases with increasing the concentration of solute and further decreases; this can be explained to the fact that initially extra complex molecules were available for excitation and energy transfer and therefore increase in the rate was observed. A decrease in the rate of photocatalytic degradation of CST complex was observed with the further increase in the concentration of the solute molecules in the solution. This may be attribute to the fact that at higher concentration of complex, molecules act as filter for the incident light, the desired light intensity cannot reach at the surface of the semiconductor particles, and a decrease in the degradation rate was observed. Results are graphically represented in Figure 2

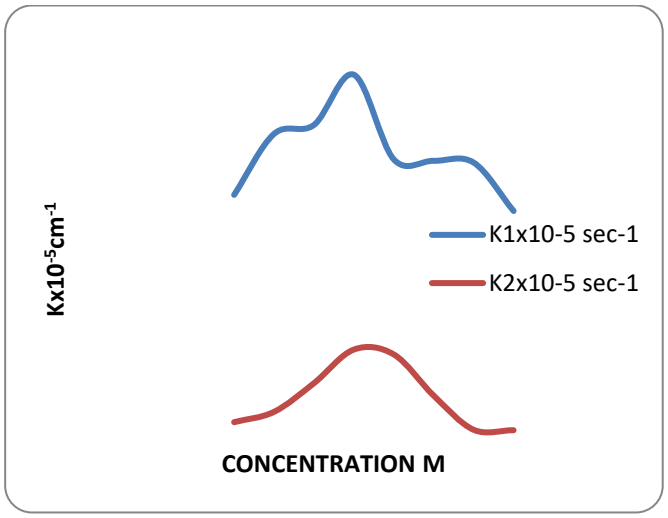

Figure- 2 Effect of Concentration on Copper(II) Soya Thiourea complex

Analysis of Percent Degradation with concentration of Copper(II) Soya Thiourea complex

As the initial concentration of Copper (II) soap complexes increases, more molecules are available for excitation and energy transfer. [18] This dependence is perhaps related to the formation of several monolayers of complex on the ZnO surface, which is favored at high concentrations till the critical level is reached, the surface is not completely covered leading to constant reaction rates. [19]

On the other hand, as the initial concentrations of the complex increase more and more, complex molecules have been adsorbed on the surface of the catalyst and significant amount of UV absorption has been hindered by Copper(II) soap complex molecules. Hence, the penetration of light to the surface of the catalyst decreases. Figure-3 shows that the rate of percent degradation of CSU complex

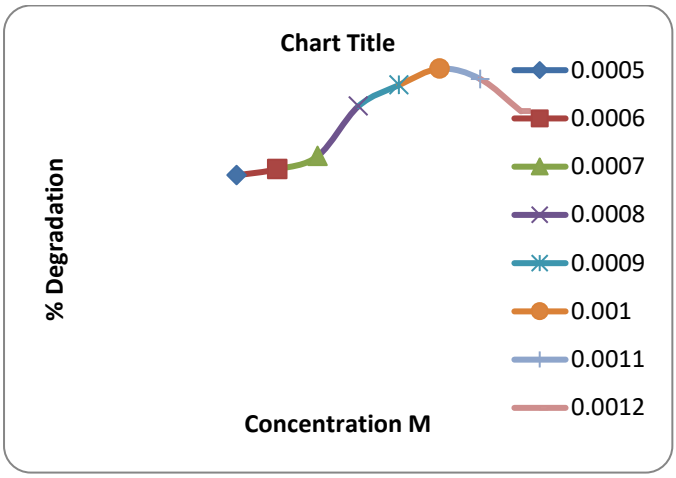

Figure-3 Percent Degradation of Copper(II) Soya Thiourea complex

Microbial Studies of Copper (II) Soya Complexes

Microbial studies have also been completed subsequently to identify with the toxicity pattern of and Copper (II) Soya Thiourea complex against S*taphylococcus aureus* at varying concentrations using Mueller-Hinton Agar plates in Kirby-Bauer disc diffusion method. Copper (II) complex shows higher resistivity at higher concentration. Hence it is obvious that concentration performs an essential role in increasing the degree of inhibition.

IV. CONCLUSION

All the above studies lead to the conclusion that in general, the photocatalytic degradation depends strongly on the concentration of solution. The increase in the concentration of Copper (II) complex increases rapidly degradation rate. Further increase in concentration of complex, there is a decrease in rate of degradation was observed. The entire physico-chemical and microbial investigations reported by us will execute a considerable role in their application in industries and a variety of numerous fields.

V. LIST OF TABLES AND FIGURES

Table -1 Catalyst effect of Copper(II) soap complexes and Optical Density.

Figure -1 Catalyst effect of Copper(II) soap complexes and Optical Density.

Figure- 2 Effect of Concentration on Copper(II) Soya Thiourea complex.

Figure-3 Percent Degradation of Copper(II) Soya Thiourea complex .

VI DECLARATIONS

VII ACKNOWLEDGEMENTS

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VIII CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

IX FUNDING

Not Applicable.

X ETHICS STATEMENT

Not Applicable.

XI INFORMED CONSENT

Not Applicable.

XII DATA AVAILABILITY

Not Applicable.

VI. REFERENCES

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