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Experimental and Theoretical Study of Copper(II) Soya Complexes in Photocatalytic Degradation

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ABSTRACT: Photodegradation is considered as familiar and interdisciplinary field in science and technology, because it includes the development of novel methods for the protection and conservation of our environment. The goal of this work to conclude a outline about photocatalytic degradation of Copper soap complexes synthesized from natural edible oils with long chain fatty acids and accurate kinetics of photocatalytic degradation of Copper (II) Soya Thiourea complex containing N and S as donor atoms, as a function of various operating parameters such as catalyst loading light intensity, reactivity in polar and non-polar solvent. Photocatalysis also has applications in wide area of renewable energy.

KEYWORDS: Copper (II) Soya Thiourea complex, photodegradation, light intensity, polarity of solvent, optical density.

I. INTRODUCTION

Copper (II) soap complexes with nitrogen and sulphur containing ligands play most prominent role in different fields of science and technology. Anionic surfactants which bear Copper ion are gaining popularity on account of their utilitarian effect such as herbicide, fungicide etc. Copper(II) soaps and their complexes show an important role in specific fields such as fungicide, pesticide, herbicide and other anti microbial activities etc. These molecules may cause pollution which is a big challenge to material scientists. Study of photodegradation of biologically active molecules in various solvents under different conditions may provide significant information towards safe and green chemistry. Several Copper(II) complex systems have been used for the degradation of lignin [1], polycyclic aromatic hydrocarbons [2], and synthetic dyes. [3,4]

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.[5-9] The effectiveness of Copper soaps as insecticides fungicides, bactericides, and herbicides were also studied.[10-16]

In this article, we will discuss the photocatalytic degradation of Copper (II) soap complexes derived from edible oil (Mustard oil and Soyabean oil), which has been carried out in the presence of semiconducting Zinc oxide (ZnO) and observed spectrophotometerically. Studies like time of irradiation and polarity of solvent with Copper (II) soap complex concentrations are also discussed. Research works based on Zinc oxide are emerging techniques related to the purification of water and air.

II. EXPERIMENTAL

Copper(II) soaps were synthesized by direct metathesis [17] and complexes were synthsised by refluxing 1:1 ratio of Copper(II) Mustard soap and Copper(II) soya soap with ligand like urea, thiourea. [18] The formed precipitate was filtered off, washed with purified hot benzene, and dried. The sticky product was passing through a filter, washed several times with ethanol and dried. Formed product is clearly green in color and soluble in benzene non-polar and organic solvents but insoluble in polar solvent water.

Complexes are abbreviated as:
Copper Mustard Thiourea complex-[CMT]
Copper Soya Thiourea complex-[CST]

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The photocatalytic activity of the complexes has been evaluated by measuring the rate of degradation and the kinetics of photodegradation of CMT and CST complexes. 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.

Amount of catalyst (ZnO) used for the study were range from 0.01 g to 0.06 g. The reaction mixture, containing ZnO as photocatalyst has exposed to a 200 W tungsten lamp (Philip) for light radiation 18 $mWcm^{2-}$ to 42 $mWcm^{2-}$. Variation in the light intensity had done by changing the distance between the light source and reaction mixture and Suryamapi (CEL model SM 201) measured it. Calibration of the spectrophotometer was done after each observation. During analysis, absorbance measured with reference to benzene blank. The reported absorbance maxima were 680 nm for blank.

III. RESULT 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 (K_1, K_2) with different time interval was observed through slopes of that particular graphs.
Rate of reaction was determined by this phrase.[19]
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.

IV. EFFECT OF LIGHT INTENSITY ON COPPER(II) SOYATHIOUREA COMPLEX

The light intensity effect on the photocatalytic degradation was also been studied. The experiments were carried out at the optimum initial concentration (.0008 M) and catalyst dosage (.02 g) in polar solvent (benzene). As indicated from the data it has been observed that rate of photocatalytic degradation of CST complex increases with increasing in intensity of light initially due to the number of photon striking per unit area of semiconductor particles also increases , further increase in light intensity causes decrease in the degradation rate. Photocatalytic degradation was found to reduce with enhancing in light intensity might be due to thermal-effect. The results are tabulated in Table **-1**

Table-1 Effect of light intensity on Copper (II) SoyaThiourea complex.

Solvent -Benzene
Amount of ZnO -0.02 g
[CST] - 0.0008M.

S. No.	Intensity of light $mWcm^{2-}$	K_1x10^{-5} sec^{-1}	K_2x10^{-5} sec^{-1}
1.	18	9.11	4.26
2.	22	9.63	8.31
3.	26	10.71	6.87
4.	30	9.59	6.23
5.	34	6.39	5.99
6.	38	5.95	5.71
7.	42	5.31	1.27

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

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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.

V. EFFECT OF SOLVENT POLARITY ON COPPER(II) SOYA THIOUREA COMPLEX

The rate of photocatalytic degradation of CST complex was also affected by solvent polarity. The percentage of polar solvent methanol was chosen as 20%, 30%, 40%, 50%, 60%, 70% and 80% with non-polar benzene. Other parameters like light intensity, concentration of CST and amount of semiconductor was kept constant for this observation.

It was observed that rate of degradation is increases with increase in polarity of solvent and after a certain limit rate of degradation decreases. It may be due to increase in early participation of macromolecular solute to get excited by absorbing the electron and degradation starts earlier through various steps of degradation, including metal- ligand bond breaking and degradation of polyunsaturated, monounsaturated, saturated bonds in long chain fatty acid segments of the complex molecule in solution . The results are graphically represented in Figure- 2

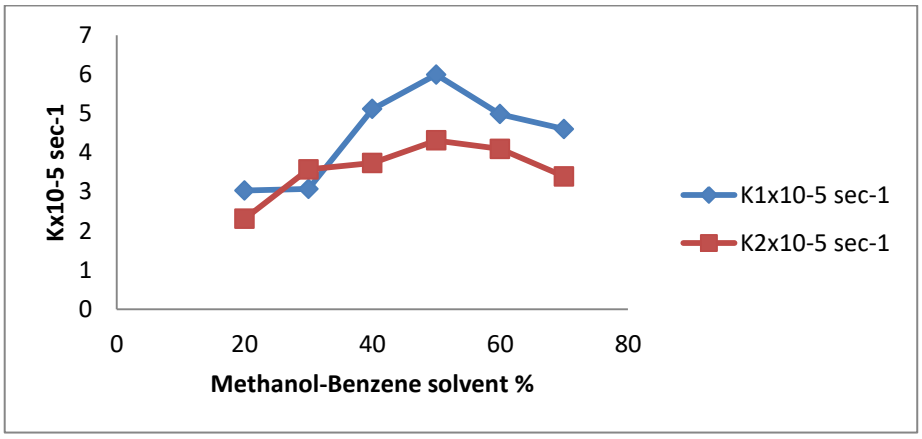

Figure-2 Effect of solvent polarity on Copper (II) SoyaThiourea complex.

VI. CONCLUSION

This study includes synthesis of Copper (II) soap complex (CST) and photocatalytic degradation of complex system (CST and CMT) in solution phase in non polar and non aqueous media by using ZnO as semiconductor under UV visible light intensity. The rate of photocatalytic degradation of Copper (II) soap complexes increases by increase in light intensity and solvent polarity but after a certain limit it decreases. Percent degradation of Copper (II) soap complexes complex also affected by different parameters.

The work described here the comparative study of Copper (II) Mustard Thiourea and Copper(II) Soya Thiourea complexes against light intensity and solvent polarity. Our results point out that CMB complex shows higher resistivity at higher concentration. On studying the experimental data it reveals that phodegradation in two-step were obtain by plotting the graphs between concentration and optical density which follows the order $K_1 > K_2$. Thus the photocatalytic degradation processes may provide an original contribution in a relatively new field of scientific knowledge.

VII. CONSENT FOR PUBLICATION

Not applicable.

VIII. FUNDING

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IX. CONFLICT OF INTEREST

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

X. ACKNOWLEDGEMENTS

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