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Study of Photocatalytic Degradation of Copper Mustard Urea Complex Using ZnO as Semiconductor in Non Aqueous Media

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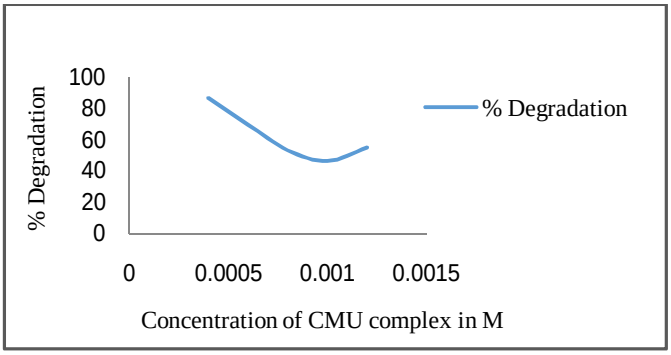
ABSTRACT

Photocatalytic degradation has been considered to be an efficient and rapid process for degradation for Copper Mustard complex. Heterogeneous catalysis appeared as a new emerging "Advanced oxidation process"(AOP), as illustrated by the many studies. This article recalls and demonstrates the photocatalytic degradation of Copper Mustard Urea complex by heterogeneous photocatalytic process using ZnO as semiconductor. The degradation was studied spectrophotometrically in non-aqueous and non polar solvent benzene. Photo-degradation of copper soap complex increase with increasing concentration of soap complex and further decrease with some extent, similarly amount of semiconductor, light intensity and polarity of solvent are some other factors which were also affect rate of degradation in different manner. Total degradation was calculated and compared with respect to various factors. Tentative mechanism has been also proposed for photo-degradation of copper soap complex.

Graphical Abstract



Percent degradation of CMU complex.

Keywords: Copper(II) Mustard Urea complex, Zinc oxide as semiconductor, Non-aqueous media Photocatalytic degradation,.

INTRODUCTION

Photocatalysis is the acceleration of a photoreaction in the presence of catalyst. In catalyzed photolysis, light is absorbed by an adsorbed subtract. Photocalysis has become one of the most effective approaches to degrade highly toxic naturally produce compounds, like cyanotoxins that cannot be removed through conventional treatment process [1].

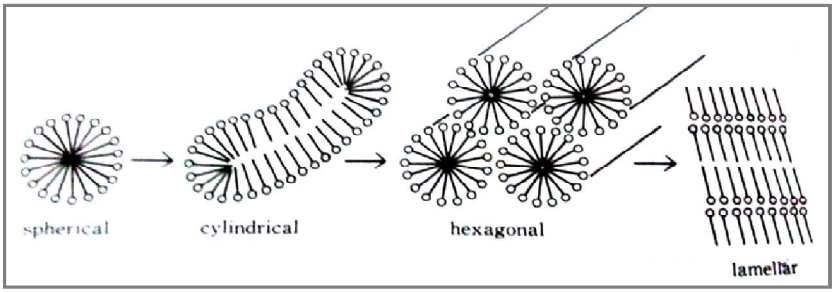
Photocatalytic degradation has been considered to be an efficient and rapid process for degradation of copper soap derived from edible and non edible oils. Heterogeneous photocatalysis on semiconductor surfaces has attracted a lot of attention due to application like water disinfection, degradation and complete mineralization of organic contaminants in waste water and purification and water splitting for hydrogen production [1-3]. ZnO nano particles are also known to be one of the multifunctional inorganic nanoparticles with effective anti bacterial activity. ZnO nano structures exhibits high catalytic efficiency, strong adsorption ability and Au used more and more frequently in the manufacture of sunscreen [4].

In parallel to this initial contribution from photo electrochemistry, photocatalysis receive valuable contribution from other chemical sub disciplines and become a major discipline owing to mutual enrichment of scientist arising from different fields: photochemistry, electrochemistry, analytical chemistry, surface science, electronics and catalysis also [5]. Photocatalytic techniques may prove to be faster and more economical than the traditional techniques of treating pollutant.

Present study involves the degradation of complex derived from copper mustard soap with urea ligand. From the analytical data the stoichiometry of complex has been observed to be 1:1 (metal: ligand). Magnetic moment studies suggest the dimeric nature of complex [6].

Shape and Structure of Micelles: A micelles is an aggregates of surfactant molecules dispersed in a liquid colloid. The aggregation process depends, on the amphiphilic species and the condition of the system in they are dissolved. Hartley proposed that micelles are spherical with the charge groups situated at the miceller surface [6], whereas, Mc Bain suggested that lamellar and spherical forms coexist [7]. X-ray studies by Harkins *et al* [8]. Then suggested the sandwich or lamellar model. Later, Debye and Anacker proposed that micelles are rod shaped rather than spherical or disk like [9].

Micelles of ionic surfactants are aggregates composed of a compressive core surrounded by a less compressive surface structure [10] and with a rather fluid environment (of viscosity 8-17 centipoise (cP) for solubilized nitrobenzene in SDS and cetyltrimethylammonium bromide micelles) [11]. Copper ion attached to micelles have essentially the same hydration shell near the micellar surface as in bulk phase and do not penetrate into the non polar part of the micelles [12] so the volume change caused by the binding of divalent metal ions to micelles is very small [13].



Change in micelle shape and structure with changing surfactant concentration.
[Y. Moroi, Micelles: Theoretical and Applied Aspects]

MATERIALS AND METHODS

Initially copper mustard soap is prepared by direct metathesis of corresponding potassium hydroxide with oils to get soap with slight excess of required amount of copper sulphate at 50-55°C [**14**]. After washing with hot distilled water and alcohol, the sample was dried at 60-80°C and recrystallized with hot benzene.

$$RCOOH \xrightarrow[EtOH]{KOH} RCOOK \xrightarrow{Cu^{+2}} R(COO)_2K$$

The prepared soap derived from edible oil was refluxed with ligand urea in 1:1 ratio using benzene as solvent for one hour (Table 1). It was then filtered hot, dried, recrystallized and purified in hot benzene. The complex is dark green and soluble in benzene. Physical parameters are recorded on the basis of its elemental analysis, 1:1 (metal:ligand) type of stoichiometry has been suggested (Table 2).

Table 1. Fatty acid composition of oil used for copper soap/complex synthesis [**15**]

Name of oil	% Fatty acids					
Composition	16:0	18:0	18:1	18:2	18:3	Other acids
Mustard oil	2	1	25	18	10	(C_{20}-C_{41}%)

Table 2. The composition and physical data of complex

Name of Complex	Color	M.P. C°	Yeild %	Metal Content		S.V.	S.E.	Average Molecular eight
				Obs.	Cal.			
Copper mustard urea CMU	Dark green	68	92	8.46	8.35	-	-	759.724

CMU: Copper mustard urea complex, S.V: Saponification value, S.E: Saponification equivalent

The solutions of the complex with different concentration were ranging from .0004 to .0013 gm mole lit^{-1} prepared. The solvent methanol was chosen to access the effect of polarity on photodegradation and solutions were made in 20%, 30%, 40%, 50%, 60% and 80% methanol and benzene solvent mixture. Different amount of catalyst were taken varied from .01, .02, .03, .04, .05 and .06 gm to study the effect of these on the degradation at the same complex solution.

Photocatalytic degradation of CMU complex was observed at lambda maximum 680nm. Irradiation was carried out in covered glass bottles for the protection of evaporation of solvent with a 200 W tungsten lamp. A water filter was used to avoid thermal degradation .Concentration of soap complex remains constant during experiment to know the effect of light intensity. Intensity of light is varied from 18 $mWCm^{-2}$ to 46 $mWCm^{-2}$ with the help of solar meter (CEL India Model SM 201). Absorption of light is recorded by U.V. visible spectrophotometer (SYSTRONIC MODEL 106) at different intervals of time.

RESULTS AND DISCUSSION

plot of 2+ logs O.D. (absorbance) versus time was linear and follows pseudo first order kinetics. Rate of the reaction was calculated using the following equation:

$$K=2.303x \text{ slope}$$

The results obtained by analysis are shown in table 3 and graphically presented in figure 1

Table 3. Change in Optical Density during different Time intervals

Time (h)	Optical Density(O.D.)	2+Log O.D.	Time (h)	Optical Density(O.D.)	2+Log O.D.
0	.202	1.305	12	.118	1.071
2	.131	1.117	14	.079	.897
4	.116	1.064	16	.087	.939
6	.079	.897	18	.094	.973
8	.107	1.029	20	.085	.929
10	.089	.949	22	.054	.732

Light intensity - 32 $mWcm^{-2,}$ Solvent –Benzene, Amount of ZnO-0.02 gm,
[CMU complex]-Concentration of Copper Mustard Urea Complex .0008M

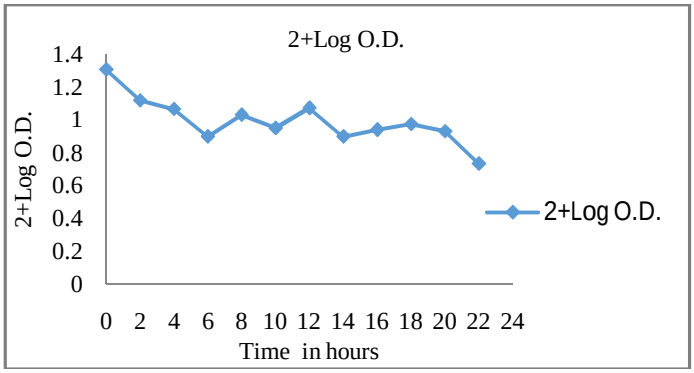


Figure 1. Change in Optical Density during different Time intervals

The effects of different parameters on the rate of photocatalytic degradation are as follows:

Effect of concentration of soap complex: Results are tabulated in table 4 and graphically presented in figure 2 A perusals of the results may suggest that Copper and ligand (Urea) bond is co-ordinate bond which may degrade easily at first step. Polyunsaturated segment of CMU complex at second step and then saturated segment undergoes degradation at third step as already studied in our previous studies. The results of Thermogravimetric analysis reveal that CMU system undergoes stepwise thermal degradation in three steps corresponding to the decomposition of polyunsaturated, monounsaturated

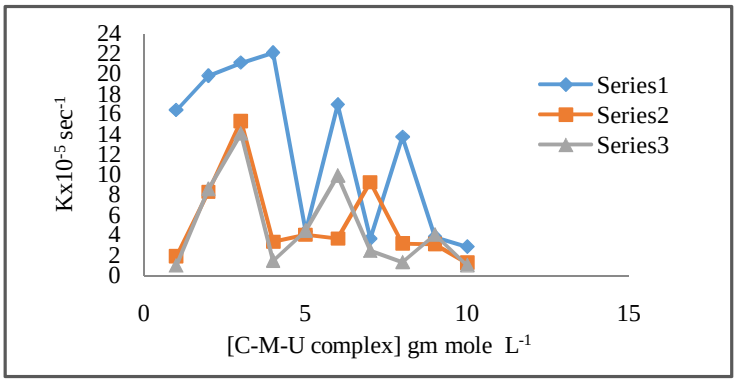
Table 4. Effect of Concentration of Copper Mustard Urea Complex

[CMU Complex] in M	K_1x10^{-5} sec^{-1}	K_2x10^{-5} sec^{-1}	K_3x10^{-5} sec^{-1}
.0004	16.4	1.91	1.03
.0005	19.8	8.31	8.6
.0006	21.1	15.35	14.09
.0007	22.09	3.35	1.5
.0008	4.37	4.05	4.47
.0009	16.95	3.67	9.91
.0010	3.67	9.27	2.48
.0011	13.75	3.19	1.35
.0012	3.85	3.1	4.05
.0013	2.87	1.27	1.06

Light intensity- 32 $mWcm^{-2}$, Solvent-Benzene, Amount of ZnO-0.02 gm

and unsaturated fatty acid components of their corresponding edible oil [17]. Three values of rate constant for kinetics of degradation in three steps were obtained by plotting the graphs between concentration and optical density which follow the order $K_1>K_2>K_3$. This observation suggest that the rate of degradation of metal ligand bond increase with increasing concentration of CMU and further

increase in the complex concentration results in decrease in the rate of degradation . The initial increase in the rate may be due to the fact that as the concentration of the complex increase more complex molecules were available for excitation and energy transfer and hence increase in the rate was observed. Further decrease in the rate of may be attribute to the fact that at higher concentration, the complex molecules start acting as a filter for the incident light and they may not permit the desired light intensity to reach the semiconductor particles, thus decreasing the rate of photocatalytic degradation of CMU complexes was observed at higher concentration of solute in solution.



Here: Series-1 =k_1x10^{-5}, Series-2 =k_2x10^{-5}, Series-3 =k_3x10^{-5}

Figure 2. Effect of Concentration of Copper Mustard Urea Complex

Percent- degradation of CMU complex: Photocatalytic degradation of CMU complex was carried out by using ZnO as semiconductor under light of 34 $mWcm^{-2}$. Complex degradation was initially identified by color change. Initially the color of complex was dark green- blue which was gradually fades to light green after 2 h. Further light green was disappears slowly and solution becomes almost colorless after completion 18 h light exposure (Table 5, Figure 3).

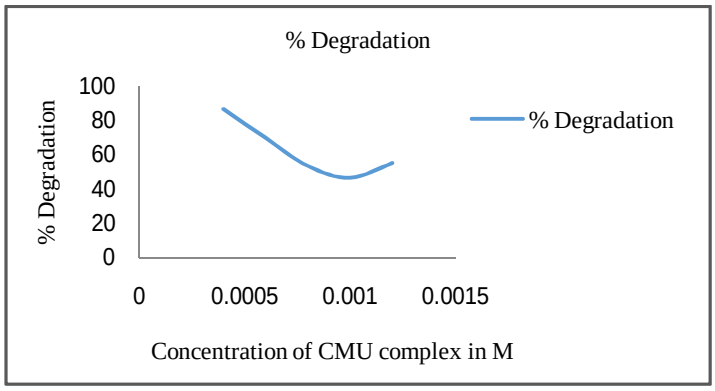


Figure 3. Percent degradation of CMU complex.

Percentage of complex degradation was estimated by the following equation [18].

$$\% \text{ degradation} = A_o - A_t / A_o * 100$$

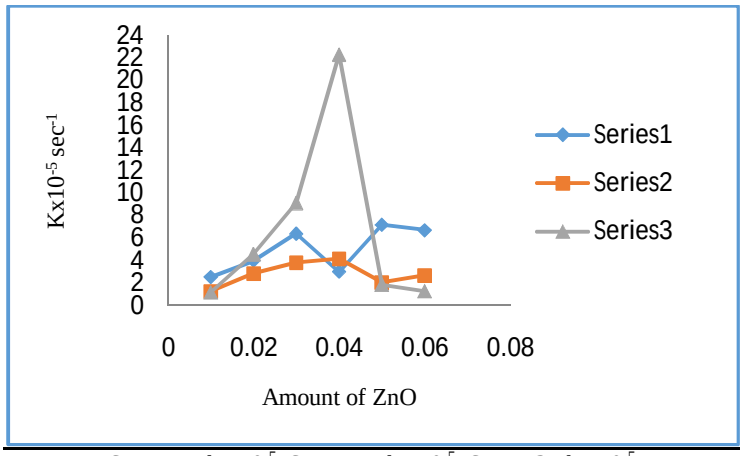
Table 5. Percent- degradation of CMU complex

S.No.	Concentration of complex M	Ai	At	% Degradation
1	0.0004	0.271	0.036	86.71
2	0.0006	0.156	0.047	69.87
3	0.0008	0.202	0.094	53.46
4	0.0010	0.086	0.046	46.51
5	0.0012	0.279	0.125	55.19

Effect of amount of semiconductor: Photocatalytic degradation of copper soap complex is also affected by the different amount of catalyst. Range of semiconductor used for this is .01, .02, .03, .04 and0.06 gm. The results are reported in table 6. Light intensity - 32 $mWcm^{-2}$, Solvent-Benzene, [CMU complex]-Concentration of Copper Mustard Urea Complex, Concentration of Complex in gm mole lit^{-1} - 0.0008 M (Figure 4).

Table 6. Effect of Amount of Semiconductor on Copper Mustard Urea Complex

Amount of ZnO(gm)	K_1x10^{-5} sec^{-1}	K_2x10^{-5} sec^{-1}	K_3x10^{-5} sec^{-1}
.01	2.55	1.27	1.17
.02	3.99	2.87	4.55
.03	6.39	3.8	9.11
.04	3.03	4.15	22.3
.05	7.19	2.07	1.83
.06	6.71	2.7	1.27



Series-1 =k_1x10^{-5}, Series-2 =k_2x10^{-5}, Series-3 =k_3x10^{-5}

Figure 4. Effect of Amount of Semiconductor on Copper Mustard Urea Complex.

In order to get better insight into the different amount of ZnO and the effect of amount on the degradation rate of complex, studies were done and optical densities were measured. A perusal of figure 4 shown that there is a sharp increases in degradation rate upto .04 gm and further decreases with the increase in amount of ZnO. This may be attribute to the fact that the amount of ZnO was increase the exposed surface area also increase but if the amount of ZnO increased the exposed surface area but further increase in amount caused decrease in degradation rate which may be due to deposition and increase in the thickness of layer of catalyst at the bottom of reaction vessel without participating in degradation mechanism. Other studies also support our observations in which this fact was confirming by taking the vessels of different dimension [**19, 20, 21**].

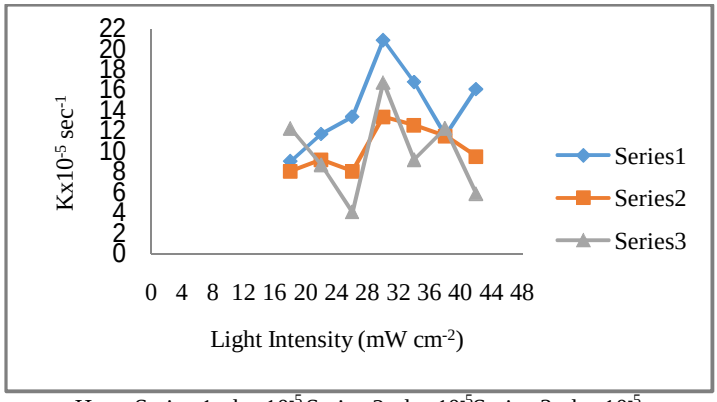
Effect of light intensity: Photocatalytic degradation of CMU complex was also affected by light intensity. The light intensity was varied from 18, 22, 26, 30, 34 and 42 mW cm^{-2} to 42 $mWcm^{-2}$. The results are tabulated in table 7 and presented in figure 5.

The data indicates that the rate of photocatalytic degradation of CMU complex was found to highest at 30 $mWcm^{-2}$. Further increase in light intensity resulted decrease in the rate of degradation. Value of K1>>K2 shows that the rate of degradation of unsaturated segment is much higher than that of the saturated segment at light intensity 30 $mWcm^{-2}$ as the number of photon striking per unit area of ZnO powder increase with increase in the light intensity, there is a corresponding increase in the rate of photocatalytic degradation of complex [**22, 23**] the rate of photocatalytic degradation was found to decrease with further increase in light intensity due to thermal effect [**17**].Solvent-Benzene,

Amount of ZnO-0.02 gm, [CMU complex]-Concentration of Copper Mustard Urea Complex, Concentration of Complex in gm mole L^{-1} - 0.0008M.

Table 7. Effect of Light Intensity on Copper Mustard Urea Complex

Light Intensity ($mWcm^{-2}$)	K_1x10^{-5} sec^{-1}	K_2x10^{-5} sec^{-1}	K_3x10^{-5} sec^{-1}
18	9.03	8.06	12.28
22	11.7	9.2	8.7
26	13.4	8.06	4.09
30	20.9	13.4	16.8
34	16.8	12.6	9.2
38	11.5	11.5	12.28
42	16.1	9.5	5.88



Here: Series-1 $=k_1x10^{-5}$ Series-2 $=k_2x10^{-5}$Series-3 $=k_3x10^{-5}$

Figure 5. Effect of Light Intensity on Copper Mustard Urea Complex.

Effect of solvent: The studies were done in different compositions of methanol and benzene to assess the effect of polarity on the rate of degradation at constant concentration of the complex molecule. Other two parameters light intensity and amount of catalyst were kept also constant for the observations. The rate of photocatalytic degradation of CMU complexes is found to be affected significantly with the variation in the composition of polar and non polar solvent in solvent mixture. The percentage of polar solvent methanol was chosen as 20%, 40%, 60%, 80% for study. Results are shown in table 8. Light intensity-32 $mWcm^{-2}$, Solvent-Benzene and Methanol, Amount of ZnO-0.02 gm, [CMU complex]-Concentration of Copper Mustard Urea Complex, Concentration of Complex in gm mole L^{-1}-0.0008 M.

Table 8. Effect of solvent on Copper Mustard Urea Complex

% of methanol	K_1x10^{-5} sec^{-1}	K_2x10^{-5} sec^{-1}	K_3x10^{-5} sec^{-1}
20	.533	2.55	1.7
30	2.13	3.83	2.07
40	.959	.799	2.71
50	2.71	1.11	.533
60	2.98	2.39	4.15
70	2.34	.799	1.81
80	3.83	.959	3.03

Effect of solvent on Copper Mustard Urea Complex: A perusal of data suggests that the rate of degradation increases with the increase in percentage of polar component in solvent mixture, which may be due to the increase in early participation of the macromolecular solute to get excited by absorbing the electron and degradation starts earlier through various steps including copper ligand bond breaking, polyunsaturated and monounsaturated segment's /breaking /degradation in the system.

Mechanism: On the basis of experimental observation, a tentative mechanism for photocatalytic degradation of copper mustard urea complex may be proposed as:

$$^{1}CMU_{0} \xrightarrow{hv} {}^{1}CMU_{1} \quad \ldots(1)$$

$$^{1}CMU_{1} \xrightarrow{ISC} {}^{3}CMU_{1} \quad \ldots(2)$$

$$^{3}CMU_{1} + O \longrightarrow \text{Products [epoxides]} \quad \ldots(3)$$

$$Cu^{+2} + e^{-} \longrightarrow Cu^{+} \quad \ldots(4)$$

- When the solution of the copper soap complex in the benzene or benzene-methanol was exposed to light in the presence of semiconductor, the complex molecule may be first excited to its first excited singlet state. These excited molecules are transferred to corresponding triplet state through ISC [**24**] and then it reacts with atomic oxygen(which is produced in during the reaction) to give products.

- IR spectral studies of degraded complex molecule in solid phase that the peak at 1620 cm^{-1} due to >c=c< stretching has been clearly disappear which may be attribute to the fact that double bond react with available atmospheric oxygen to form epoxide [**25, 26, 27**] as product.

- IR ,NMR, and thermal studies also support the proposed mechanism in which >c=c< site present in all the natural oil segment of the complex molecules reacts/ breaks /degrades first and the soap complex derived from the natural oils degrade comparatively faster than saturated segment of copper mustard urea complexes [**4**].

- The decolouration of the copper soap complexes also suggests that some of Cu^{+2} ion of the complex may reduced to Cu^{+} or Cu^{0} to some extent during the process of degradation by trapping photogenerated electron in the system.

- The literature survey reveals that the presence of oxygen may also affect the photodegradation of complex molecules as the main oxidation products of the esters are keto or hydroxy compounds [**28-32**].

APPLICATION

Photodegradation has been considered in many reaction of biological, synthetic and industrial importance here energy received from sun can be better utilized for converting the pollutants into less toxic or almost harmless materials. Photo degradation plays a vital role in specific phenomena such as foaming, wetting, detergency, emulsification, fungicides etc. The study will provide many information towards green and safe chemistry.

CONCLUSION

Present study suggests that the rate of photocatalytic degradation of copper soap complexes increases by increasing concentration of complex to a certain limit and then decreases which may be due to increase in aggregation of macromolecules in solution which decreases the probability and the rate of degradation including various steps of metal ligand breaking, unsaturated segment and saturated segment bond breaking of complex respectively. Rate of degradation also increases with increasing amount of semiconductor at some extent and further decreases. Further, the degradation rate increases with increase in light intensity upto certain intensity and then decreases. The increase of polar solvent content in solvent mixture also contributes to the kinetics and affects the rate of photodegradation significantly.

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