Research Article

Degradation Kinetics of Copper (II) Soap Derived from *Pongamia Pinnata* (Karanj) in Presence of Irradiated Semiconducting ZnO

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Abstract

Photocatalysis process is a relatively novel subject with tremendous potential in the near future because of its environmental applications. Large molecules such as Copper Pongamia Soap (CPm) 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 edible and non-edible oils. The present study involves the photocatalytic degradation of Copper Pongamia Soap by heterogeneous photocatalytic process using ZnO as semiconductor and the degradation was studied spectrophotometrically in non aqueous and non-polar solvent benzene. An attempt has been made to study the effect of process parameters viz- concentration of soap, catalyst loading, light intensity, effect of solvent on photocatalytic degradation of Copper Pongamia Soap. A tentative mechanism has been proposed for the photodegradation of Copper Pongamia Soap.

Keywords: Copper Pongamia Soap, Zinc oxide, Photocatalytic degradation

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Introduction

A kind of pollution, which has emerged in last few years, is the surfactant or detergent pollution. As it is well known fact that detergent do not prefer biodegradable pathways and on the other hand the chemical degradation of the surfactants will add a new member in the list of existing types of pollution [1]. The extensive use of surfactants has created a new problem in environmental pollution because surfactants are either slowly biodegraded or these do not biodegrade at all. Thus photocatalytic technique may prove to be faster and more economical than the traditional techniques of treating these types of pollutants. The importance of these types of research is increasing recently and has become a subject of major public health concern and scientific interest.

Synthesis, characterization, antifungal activities and thermogravimetric analysis of Copper (II) Soaps and their complexes derived from *Azadirachta Indica* (Neem) and *Pongamia Pinnata* (Karanj) have been studied by Sharma et al [2-3]. Viscometric studies at various temperature, apparent molar volume, ultrasound, surface tension and antifungal activities related with micellar features of copper soaps in various organic solvents have been studied by Mehta et al [4]. Photochemistry using semiconductor nanoclusters, is involved in a group of waste treatment methods called Advanced Oxidation Processes (AOPs) such as photofenton, photocatalysis and sonolysis. Extensive research in photocatalysis resulted in various applications based on the use of semiconductors [5-6]. ZnO is an attractive semiconductor for numerous applications [7-10] because of its hardness, chemical stability, optical transparency, large excitation energy and piezoelectric properties. Gulati et al [11] used ZnO particulate system in photobleaching of toludine blue. Park and Kim [12] reported the photocatalytic decomposition of carboxylic acid derivatives in presence of semiconductors, whereas Miyoshi et al [13] have studied the light induced decomposition of saturated carboxylic acid on iron oxide incorporated clay suspended in aqueous solution. Vora et al [14] used ZnO to observe degradation kinetics of 2, 4-dinitroaniline. Teka and Reda [15] studied the comparative study on the photocatalytic degradation of malachite green using zinc oxide under different sources of radiation.

Some dyes, surfactants and other organic pollutants have been studied time to time but no attention has been received by the photodegradation of metallic soaps such as CPm Soap, although it has various applications. All the above facts lead us to conduct the present work.

Experimental

Firstly Copper Pongamia Soap is prepared by direct metathesis of corresponding potassium soap with slight excess of required amount of copper sulphate at 50-55^{0}C [16]. After washing with hot water and the alcohol, the sample was dried at 80-100^{0}C and recrystallized with hot benzene.

$$RCOOH \xrightarrow[EtOH]{KOH} RCOOK \xrightarrow{Cu^{+2}} (RCOO)_2Cu$$

Solution of the soap was prepared in hot benzene (Qualigens). The photocatalytic degradation was observed upon addition of zinc oxide (Merck 99%) to the soap solution. 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). A water filter was used to cut thermal radiations. The solutions were clear and free from solid impurities. To predict the effect of various factors on the rate of degradation process, the concentration of the soap was varied from 400 ppm to 960 ppm, photocatalyst (semiconductor) were used ranging from 0.01 to 0.06 gm, the light intensity was varied from 18 mW cm^{-2} to 46 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 680 nm and the progress of the photocatalytic reactions was observed by measuring the absorbance at 680 nm (λ_{max}) in regular time intervals by UV-visible spectrophotometer (Systronics Model 106).

Results and Discussions

The synthesized compound is abbreviated as follows:-

- Copper Pongamia Soap (CPm Soap)
- The composition of Karanj oil and physical & analytical data of CPm soap are given in **Table-1 and 2** respectively.

Elemental Analysis was done for soap for their metal content following standard procedures [17]. Molecular weights of copper soaps were determined from saponification value [18]. The saponifiaction equivalent or saponification value is a measure of the average length of the fatty acid that makes up a fat. The saponification equivalent (S.E.) is the amount of material saponified by one gram equivalent of potassium hydroxide, whilst the saponification value (S.V.) is the number of milligrams of KOH required to hydrolyze one gram of fat, indicating the number of ester groups in the fat.

$$S.E. = \frac{56100}{S.V.}$$

Thus S.E. may be taken as average molecular weight of the oil. Value of S.E. is determined by experiment and from these values average molecular weight of Copper Pongamia Soap is calculated.

Table 1 Percentage Fatty Acid Composition of Oil used for Preparation of Copper Soap

(a)

Name of Oil	Percentage fatty acids (Carbon Numbers)							
	16:0	18:0	18:1	18:2	20:0	20.1	22:0	24:0
Karanj Oil	5.2	5.0	57.3	13.8	2.7	10.3	4.1	1.6

(b)

Name of Oil	Percentage fatty acids		
	Saturated	Monounsaturated	Polyunsaturated
Karanj Oil	18.6	67.6	13.8

Table 2 Analytical and Physical data of Copper soap derived from Karanj Oil

S.V. = Saponification Value S.E. = Saponification Equivalent

Name of Soap	Color	M.P.(^{0}C)	Metal Content		S.V. of oil	S.E. of oil	Average Mol. Wt. of soap
			Observed	Calculated			
CPm	Dark Green	51	9.4996	9.3426	181.5	309.091	679.682

Photocatalytic degradation of CPm Soap was observed at λ_{max} 680 nm. The optical density (O.D.) decreases with increasing time. The rate of degradation is favorably affected by ZnO. A plot of 2 + log O.D. (absorbance) versus time was linear and this reaction follows pseudo-first order kinetics. The rate constants of this reaction were determined by the expression [19]–

$$k = 2.303 \times \text{slope}$$

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

(a) Effect of Concentration of Soap

The rate of photocatalytic degradation of CPm Soap is likely to be affected by the change in concentration of soap varied from 400 ppm (0.40 g/l) to 960 ppm (0.96 g/l). The results are tabulated in **Table-3** and graphically presented in **Figure-1**.

Table 3 Effect of Concentration of Copper Pongamia Soap

Light Intensity	-	30 mW cm^{-2}	Solvent	-	Benzene
Amount of ZnO	-	0.03 g			
[CPm Soap]	-	Concentration of Copper Pongamia Soap			
ppm	-	parts per million			

[CPm Soap] (ppm)	[CPm Soap] (gm/l)	$k_1 x10^5 (sec^{-1})$	$k_2 x10^5 (sec^{-1})$
400	0.40	2.84	2.08
480	0.48	4.19	3.76
560	0.56	4.59	4.13
640	0.64	5.65	4.99
720	0.72	7.56	6.16
800	0.80	1.94	2.55
880	0.88	1.25	1.96
960	0.96	0.95	1.59

It was observed that polyunsaturated segment of the CPm soap is degrading first and then saturated segment undergoes degradation. The values of $k_1 > k_2$, also suggests that the rate of degradation of polyunsaturated segment is higher than the saturated segment of the referred system [3]. The rate of photocatalytic degradation of unsaturated segment was found to increase with increasing concentration of CPm soap upto 720 ppm and the rate of degradation of saturated segment was also found to increase with increasing concentration of CPm soap upto 720 ppm. Further increase in the soap concentration resulted in a decrease in the rate of degradation. The increase in the rate may be due to the fact that as the concentration of soap was increased, more soap molecules were available for excitation and energy transfer and hence, an increase in the rate was observed. The decrease in the rate of photocatalytic degradation may be attributed to the fact that the soap 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 of CPm soap [11, 20].

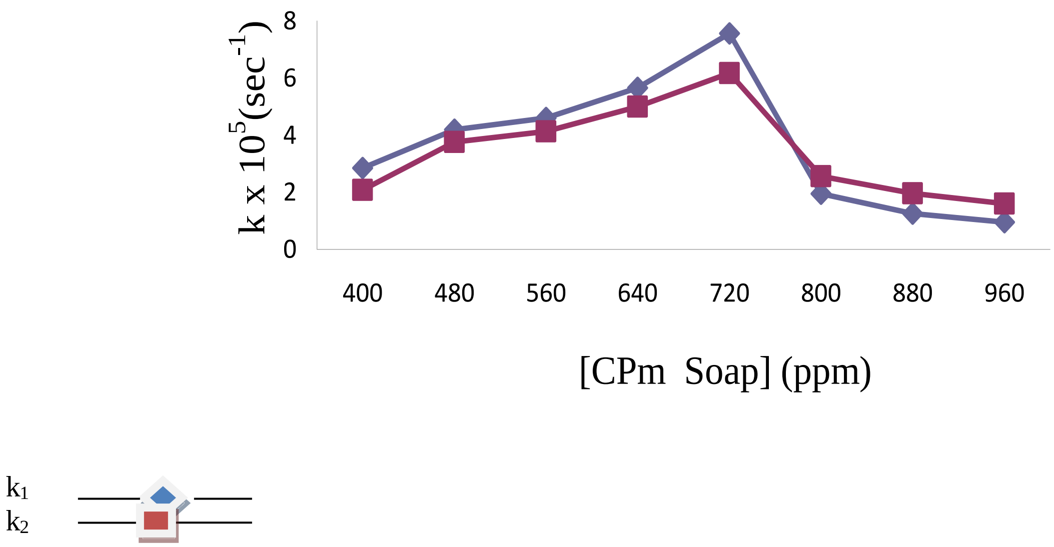

Figure 1 Effect of Concentration of Copper Pongamia Soap

(b) Effect of amount of Semiconductor (ZnO)

The amount of semiconductor is also likely to affect the process of photocatalytic degradation. For this purpose different amount of semiconductor ranging from 0.01 g to 0.06 g were used. The results are reported in **Table-4** and graphically presented in **Figure 2**.

Table 4 Effect of Amount of Semiconductor on Copper Pongamia Soap

Light Intensity - 30 mW cm^{-2} Solvent - Benzene
[CPm Soap] - 720 ppm (0.72 g/l)

Amount of ZnO (g)	$k_1 x10^5 (sec^{-1})$	$k_2 x10^5 (sec^{-1})$
0.01	2.01	1.91
0.02	2.39	2.13
0.03	2.68	2.61
0.04	2.70	2.62
0.05	2.78	2.58
0.06	2.72	2.60

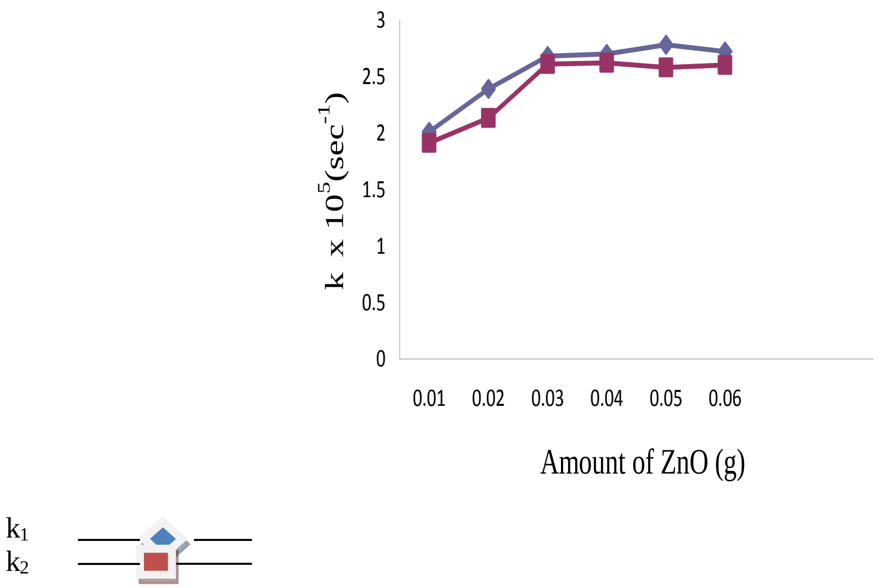

Figure 2 Effect of Amount of Semiconductor (ZnO) on Copper Pongamia Soap

A perusal of the **Figure-2** suggests that there is a sharp increase in degradation rate up to the 0.03 g amount of ZnO for both unsaturated and saturated segment then remains almost constant. This may be attributed to the fact that as the amount of ZnO was increased, the exposed surface area also increases but after certain limit, and if the amount of ZnO was further increased then there will be no increase in the exposed surface area of the ZnO (Photocatalyst). It may be considered like a saturation point, above which an increase in the amount of semiconductor has negligible change or there will be no effect on the rate of photocatalytic degradation of CPm soap. As any increase in the amount of semiconductor above this point will only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking the vessels of different dimensions [21-22].

(c) Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of CPm soap was also studied. The light intensity was varied from 18 mW cm^{-2} to 46 mWcm^{-2}. The results are tabulated in **Table-5** and presented in **Figure-3**.
The data indicate that the rate of photocatalytic degradation of CPm soap was found to increase with increasing light intensity upto 30 mW cm^{-2}. Further increase in the light intensity resulted in a decrease in the rate of degradation. The values of k_1>>k_2 show that the rate of degradation of unsaturated segment is much higher than that of the saturated segment, at light intensity 30 mW cm^{-2}. As the number of photons striking per unit area of semiconductor powder increases with the increase in light intensity, there is a corresponding increase in the rate of photocatalytic degradation of soap [23-24]. The rate of photocatalytic degradation was found to decrease with further increase in the light intensity due to thermal effects [19].

Table 5 Effect of Light Intensity on Copper Pongamia Soap

[CPm Soap] - 720 ppm (0.72 g/l) Solvent - Benzene
Amount of ZnO - 0.03 g

Light Intensity (mW cm^{-2})	$k_1 x 10^5 (sec^{-1})$	$k_2 x 10^5 (sec^{-1})$
18	2.50	0.67
22	2.87	0.97
26	3.19	1.37
30	5.94	2.30
34	5.41	1.89
38	4.56	1.55
42	3.93	1.09
46	3.34	0.82

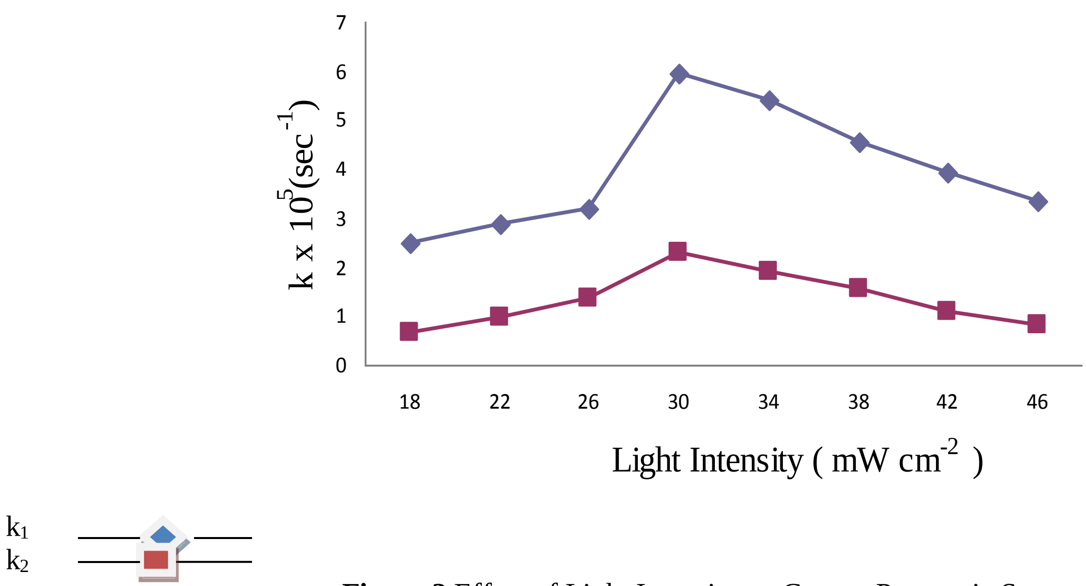

Figure 3 Effect of Light Intensity on Copper Pongamia Soap

(d) Effect of Solvent

The rate of photocatalytic degradation of CPm soap is also affected by the change in solvent. The percentage of methanol (polar solvent) was varied from 20 % to 80 %. Results are presented in **Table-6** and **Figure-4**.

Table 6 Effect of Solvent on Copper Pongamia Soap

Light Intensity - 30 mW cm^{-2}
[CPm Soap] - 720 ppm (0.72 g/l)
Amount of ZnO - 0.03 g

Percentage of Methanol (%)	$k_1 x 10^5 (Sec^{-1})$	$k_2 x 10^5 (Sec^{-1})$
20	5.65	3.33
30	4.20	2.53
40	2.39	2.25
50	2.13	1.86
60	1.82	1.37
70	1.23	0.95
80	0.99	0.71

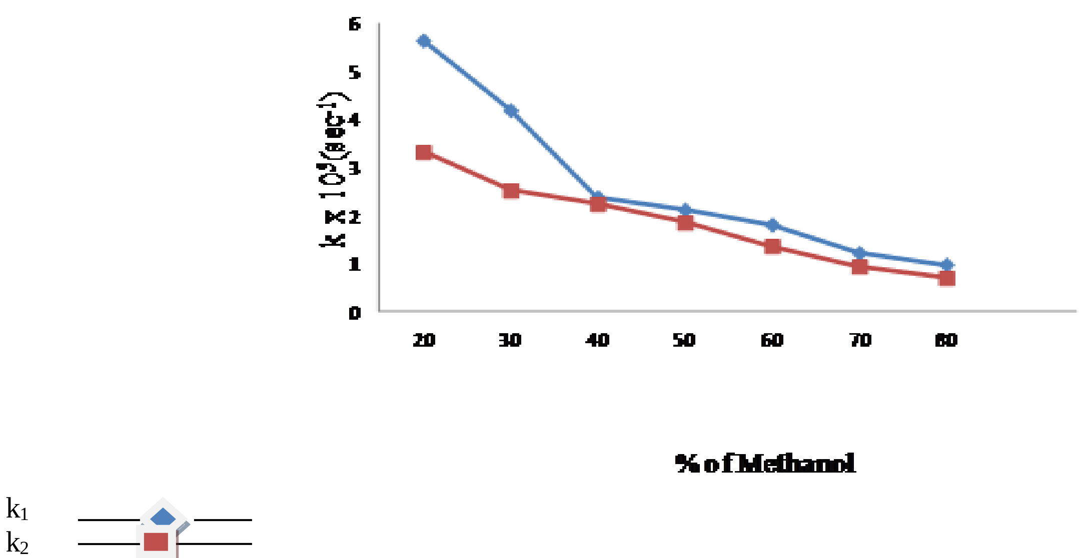

Figure 4 Effect of Solvent on Copper Pongamia Soap

It was observed that the rate of degradation continuously decreases with increase in the polar solvent such as methanol. In the case of soap degradation, it has been clearly observed that rate decreases with the increase of polarity of solvent. Soaps are surface active compounds and they behave differently due to miceller activity. The unsaturated segment of CPm soap is degraded fast as compared to the saturated segment of soap. It may be suggested from the above observations that the polarity inhibits the reactivity of the soap molecule.

Mechanism

A tentative mechanism for the photocatalytic degradation may be proposed as :

$$SC \xrightarrow{h\nu} SC^* \quad \text{.......... (1)}$$

$$SC^* \longrightarrow SC\,[h^+\,(VB)] + e^-\,(CB) \quad \text{.......... (2)}$$

$$h^+ + ZnO \longrightarrow O + Zn^+ \quad \text{.......... (3)}$$

$$e^- + Zn^+ \longrightarrow Zn \quad \text{.......... (4)}$$

$$e^- + O_2 \longrightarrow O_2^{-\cdot} \quad \text{.......... (5)}$$

$$h^+ + O_2^{-\cdot} \longrightarrow O_2 \quad \text{.......... (6)}$$

$$Zn + O_2 \longrightarrow ZnO + O \quad \text{.......... (7)}$$

$$ZnO \longrightarrow Zn + \tfrac{1}{2}\,O_2 \quad \text{.......... (8)}$$

$$^1Soap_0 \xrightarrow{h\nu} {}^1Soap_1 \quad \text{.......... (9)}$$

$$^1Soap_1 \xrightarrow{ISC} {}^3Soap_1 \quad \text{......... (10)}$$

$$^3Soap_1 + O \longrightarrow \text{Products [epoxides]} \quad \text{......... (11)}$$

$$Cu^{+2} + e^- \longrightarrow Cu^+ \quad \text{......... (12)}$$

- 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) [25]. The hole in the valence band may react with ZnO to produce atomic oxygen and Zn^+, while electron in the conduction band reduces the Zn^+ ion to Zn and this electron may be utilized by atmospheric oxygen to give superoxide anion radical [25]. This radical may react with h^+ and form atmospheric oxygen. This oxygen molecule may utilized by Zn to regenerate the semiconductor.

- 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) [25] and then it reacts with atomic oxygen (which is produced in above steps) to give products.

- IR spectral studies of degraded soap molecule in solid phase suggests that the peak at 1620 cm^{-1} due to >C =C< stretching has been clearly disappeared which may be attributed to the fact that double bond reacts with available atmospheric oxygen to form epoxide [18, 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 soap molecules reacts / breaks / degrades first and the soap derived from natural oils degrade comparatively faster than saturated segment of stearate and palmitate soaps [3].

- The discoloration of the soap solution also suggests that some of the Cu^{2+} ion of the soap may reduce 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 soap molecule as the main oxidation products of the esters are keto or hydroxy compounds [28].

- Several mechanism of C-C bond fission is there in the oxidation. In α -mechanism only one C-C bond is broken to form C_m and C_{n-m} products, while in β mechanism, two C-C bonds are broken in the β-position to form C_m, C_{n-m-1} , CO_2 etc.The α and β mechanisms of C-C bond scission may be regarded as a result of peroxy radical isomerisation to form labile dihydroperoxide [28].

Conclusion

The present study suggests that the rate of photocatalytic degradation increases by increase in the concentration of soap to a certain limit and then continuously decreases. Rate of degradation also increases when the amount of semiconductor was increased and further, the rate becomes constant, thus, an optimum quantity of semiconductor is required. It is also observed that degradation increases with light intensity to a limit and then decreases on further increasing the light intensity. The effect of polar solvent inhibits the rate of degradation.

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