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Use of Zinc Oxide as Photocatalyst for Photodegradation of Copper Soap Derived From *Azadirecta Indica* (Neem) Oil

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ABSTRACT

Large molecules such as copper neem soap (CN soap) can not be metabolized rapidly by microorganisms naturally. Thus, if macromolecules were dissected into smaller plural entities by radiations, they would not persist in the environment for a long period. 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. Seed oil of *Azadirecta Indica* (Neem) is ecofriendly, nontoxic, insect repellant and having antiviral, antifungal, antiseptic and antibacterial properties. The seed oil of neem has been chosen and soap has been synthesized using direct metathesis method. The photocatalytic degradation of copper neem soap was studied spectrophotometrically in non aqueous and non polar solvent benzene using zinc oxide as semiconductor. The effect of various parameters such as concentration of soap, amount of semiconductor, effect of light intensity, effect of polarity of the solvent etc., on the rate of this photocatalytic degradation has been observed. The studies suggest 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 increases and further increase in the amount of semiconductor the rate becomes constant. It is also observed that degradation is maximum at light intensity 34 mW cm^{-2} and effect of polar solvent inhibits the rate of degradation. A tentative mechanism has been proposed for the photocatalytic degradation of CN soap.

Keywords: *Azadirecta Indica* (Neem), Zinc oxide, Photocatalytic degradation

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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 has created a new problem in environmental pollution; because surfactants are either slowly biodegraded or these do not biodegrade 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. 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 [1-2].

Synthesis, characterization and antifungal activities of copper (II) soaps and their complexes derived from *Azardirecta Indica* (Neem) and *Pongamia Pinnata* (Karanj) oil have been studied earlier by Sharma and Khan [3]. 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. 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 [4-5]. ZnO is an attractive semiconductor for numerous applications [6-12] because of its hardness, chemical stability, optical transparency, large excitation energy and piezoelectric properties.

Tang et al [13] and Papadam et al [14] reported photocatalytic degradation of dyes by aqueous TiO_2 suspension. Photocatalytic degradation has been considered to be an efficient process for the degradation of copper soaps derived from natural edible and non edible oils. Some dyes, surfactants and other organic pollutants have been studied [15-16] from time to time but no attention bas been received by the photodegradation of metallic soaps such as CN soap, although it has various applications. All the above facts lead us to conduct the present work.

EXPERIMENTAL

Firstly copper neem soap is prepared by direct metathesis of corresponding potassium soap with slight excess of required amount of copper sulphate at 50-55^{0}C [17-19]. After washing with hot water and the alcohol, the sample was dried at 80-100^{0}C and recrystallized with hot benzene.

$$\mathrm{RCOOH} \xrightarrow[\mathrm{EtOH}]{\mathrm{KOH}} \mathrm{RCOOK} \xrightarrow{\mathrm{Cu^{+2}}} \mathrm{(RCOO)_2\,Cu}$$

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 solvent with a 200 W tungsten lamp (visible light, Philips). A water filter was used to cut thermal radiations. The solution must be 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 were 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 Neem Soap (CN Soap)
- The composition of neem oil and physical & analytical data of CN soap are given in Table-1 and 2 respectively. Elemental Analysis was done for soaps for their metal content following standard procedures [20]. Molecular weights of copper soaps were determined from saponification value [21]. 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.

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

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 neem soaps are calculated.

Table – 1(a)(b): Percentage Fatty Acid Composition of Oils used for Preparation of Copper Soap

Name of Oil	Percentage fatty acids (Carbon Numbers)				
	16:0	18:0	18:2	20:0	20.1
Neem Oil	14.9	14.4	61.9	7.5	1.3

Name of Oil	Percentage fatty acids		
	Saturated	Monounsaturated	Polyunsaturated
Neem Oil	30.6	61.9	7.5

Table – 2: Analytical and Physical data of Copper soaps derived from Neem 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			
CN	Dark Green	50	10.3632	10.1087	198	283.33	628.166

EFFECT OF CONCENTRATION OF SOAP

The rate of photocatalytic degradation of CN Soap is likely to be affected by the change in concentration of soap. The results are tabulated in Table-3 and graphically presented in Figure 1.

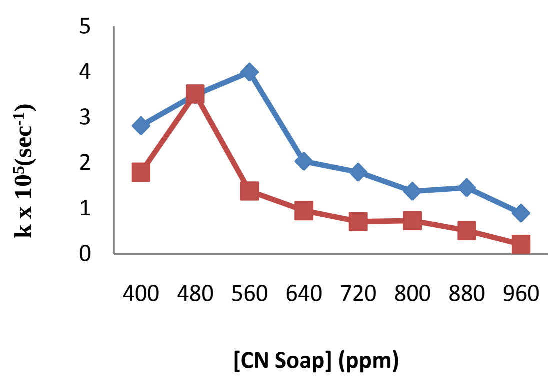
On observation of the Table-3 and the Figure.-1, it may be suggested that polyunsaturated segment of the CN soap is degrading first and then saturated system undergoes degradation. The values of k1 > k_2, also suggests that the rate of degradation of polyunsaturated segment is higher than the saturated segment, of the referred system.

The rate of photocatalytic degradation of unsaturated segment was found to increase with increasing concentration of soap upto 560 ppm and the rate of degradation of saturated segment was found to increase with increasing concentration of soap upto 480 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 CN soap [22].

Table – 3: Effect of Concentration of Copper Neem Soap

Light Intensity-34 mW cm^{-2} Solvent - Benzene
Amount of ZnO - 0.02 g
[CN Soap] – Concentration of Copper Neem Soap
ppm – parts per million

[CN Soap](ppm)	[CN Soap] (gm/l)	$k_1 x10^5 (sec^{-1})$	$k_2 x10^5 (sec^{-1})$
400	0.40	2.81	1.79
480	0.48	3.49	3.51
560	0.56	3.99	1.38
640	0.64	2.03	0.95
720	0.72	1.79	0.71
800	0.80	1.37	0.73
880	0.88	1.45	0.51
960	0.96	0.89	0.21



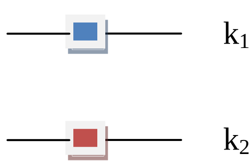


Figure:-1 Effect of Concentration of Copper Neem Soap

EFFECT OF AMOUNT OF SEMICONDUCTOR

The amount of semiconductor is also likely to affect the process of photocatalytic degradation. The results are reported in the Table-4 and graphically presented in Figure-2.
It has been observed that the rate of photocatalytic degradation of CN soap increases with an increase in the amount of semiconductor and then ultimately, it becomes almost constant after a certain amount. The rate for unsaturated segment of CN soap was found to be maximum at 0.04 g and as such the rate for saturated segment of soap was also found to be maximum at 0.04 g. 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

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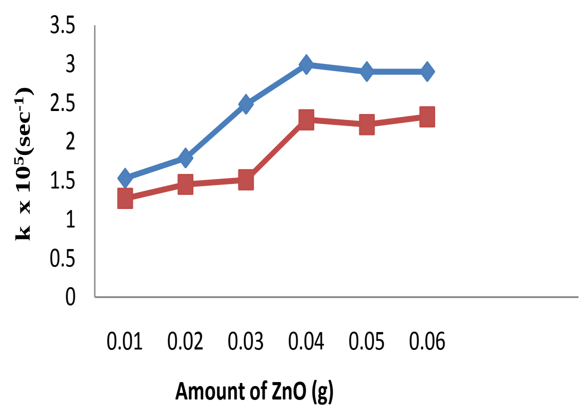
semiconductor has negligible change or there will be no effect on the rate of photocatalytic degradation of CN soap [23]. As any increase in the amount of semiconductor above this point will only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking the vessels of different dimensions.

Table – 4: Effect of Amount of Semiconductor

Light Intensity- 34 mW cm^{-2} Solvent - Benzene

[CN Soap]- 640 ppm (0.64 g/l)

Amount of ZnO (g)	$k_1 x 10^5 (sec^{-1})$	$k_2 x 10^5 (sec^{-1})$
0.01	1.53	1.27
0.02	1.79	1.45
0.03	2.48	1.51
0.04	2.99	2.28
0.05	2.90	2.22
0.06	2.90	2.32



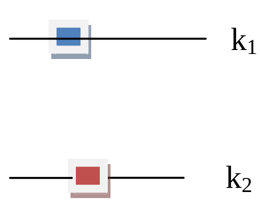


Figure: - 2 Effect of Amount of Semiconductor (ZnO)

EFFECT OF LIGHT INTENSITY

The effect of light intensity on the photocatalytic degradation of CN soap was also studied. The results are tabulated in Table -5 and Figure-3.

The data indicate that the rate of photocatalytic degradation was found to increase with increasing light intensity upto 34mW 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 34mW 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 [15]. The rate of photocatalytic degradation was found to decrease with a further increase in the light intensity.

Table - 5: Effect of Light Intensity
[CN Soap]- 640 ppm (0.64 g/l) Solvent – Benzene
Amount of ZnO - 0.02 g

Light Intensity ($mW\ cm^{-2}$)	$k_1 x10^5 (sec^{-1})$	$k_2 x10^5 (sec^{-1})$
18	1.59	0.42
22	2.13	0.83
26	2.28	0.95
30	4.79	1.27
34	5.27	2.39
38	4.26	1.06
42	4.18	0.91
46	3.01	0.49

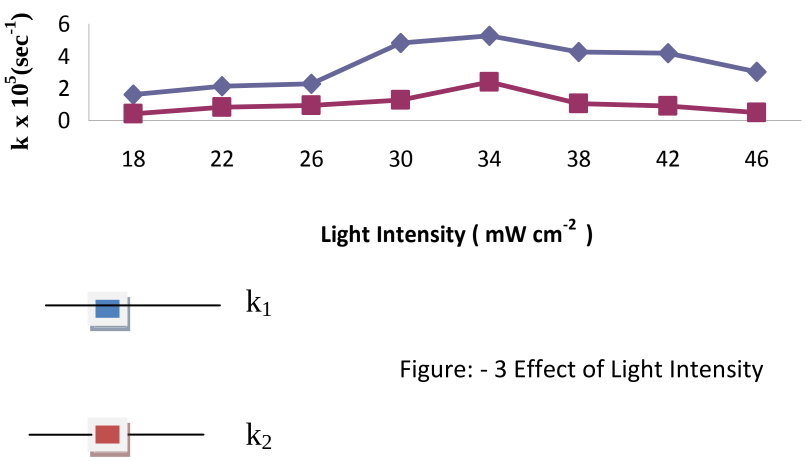


Figure: - 3 Effect of Light Intensity

EFFECT OF SOLVENT

The rate of photocatalytic degradation of CN soap is also affected by the change in solvent. The results are presented in Table-6 and Figure-4. 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 CN 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. Further it is also suggested that for the better use of molecule (CN soap) in applications like antifungal and antibacterial etc., the medium should be non polar in nature.

Table - 6: Effect of Solvent

Light Intensity- 34 mW cm^{-2}, [CN Soap]- 640 ppm (0.64 g/l), Amount of ZnO-0.02 g

Percentage of Methanol	$k_1 x 10^5 (Sec^{-1})$	$k_2 x 10^5 (Sec^{-1})$
20 %	5.26	2.70
30 %	3.78	2.19
40 %	2.04	1.88
50 %	1.34	1.54
60 %	1.27	1.06
70 %	1.09	0.82
80 %	0.74	0.47

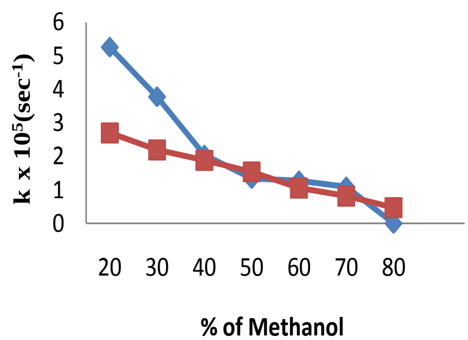
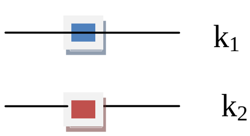


Figure: - 4 Effect of Solvent



CONCLUSION

The studies suggest 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 increases and further increase in the amount of semiconductor the rate becomes constant, thus an optimum quantity of semiconductor is required. It is also observed that degradation is maximum at light intensity 34 mW cm^{-2} and effect of polar solvent inhibits the rate of degradation.

MECHANISM

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

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

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

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

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

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

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

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

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

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

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

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

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

- 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) [24].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 [24]. 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) 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 disappears which may be attributed to the fact that double bond reacts with available atmospheric oxygen to form epoxide [21, 25-27] as product.

- Mass spectroscopy, 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 [28].

- The decoloration 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 [29].

- 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 [29].

- Some experiments regarding identification of products are running in our laboratory and confirmed results will be communicated later.

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