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Photocatalytic and Environmental Degradation Studies Using Copper(II) Surfactants

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ABSTRACT

Copper(II)-based surfactants are an important class of metal-containing surface-active agents that exhibit unique physicochemical, antimicrobial, catalytic, and environmental properties. Their widespread applications in detergents, coatings, corrosion inhibition, wastewater treatment, and pharmaceuticals have increased concerns regarding their environmental fate and toxicity. This investigation focuses on the synthesis, characterization, environmental behavior, and photocatalytic degradation of Copper(II) surfactants. 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. Particular emphasis is placed on understanding how photocatalytic processes can reduce the persistence and ecological impact of these compounds in aquatic environments. The study highlights the effectiveness of semiconductor photocatalyst such as and Zinc Oxide in degrading Copper(II) surfactants under ultraviolet or visible-light irradiation. Analysis of biological activities of Copper soap complex is also done with Staphylococcus aureus to anticipated that it will generate new hopes in the field of biological applications. The study suggests that the complex exhibits notable antibacterial properties, indicating its potential usefulness in biological applications. These findings provide promising prospects for further exploration of Copper soap complexes as effective antimicrobial agents in pharmaceutical and biomedical fields.

Keywords: Copper(II) Soya Thiourea Complex, optical density, photocatalytic degradation, Staphylococcus aureus, antimicrobial .

INTRODUCTION

Surfactants are amphiphilic compounds containing both hydrophilic and hydrophobic groups. Copper(II) surfactants are coordination compounds formed by the interaction of copper ions with surfactant ligands. These compounds possess enhanced biological activity and surface properties compared with conventional surfactants. Photocatalytic degradation is an advanced oxidation process that utilizes light energy and a semiconductor catalyst to generate highly reactive species capable of mineralizing organic pollutants. The scientific and technological significance of photocatalytic degradation processes is widely recognized today, as they enable chemical reactions aimed at the elimination of pollutants without the need for elevated temperatures or pressures. These processes utilize light, particularly solar radiation, as the sole energy source, making them an energy-efficient and environmentally friendly approach for pollutant degradation and environmental remediation. The objective of this work is to provide an overview of the structural features and properties of Copper soap complexes synthesized from natural edible oils containing long-chain fatty acids, along with a detailed study of the kinetics of photocatalytic degradation of Copper(II) soap complexes containing nitrogen and sulfur donor atoms. The degradation behavior has been examined as a function of various operational parameters, including catalyst loading, light intensity, and initial concentration in both polar and non-polar solvents.

A large volume of surfactant-containing wastewater is continuously discharged into the environment, leading to adverse effects on aquatic ecosystems, including flora and fauna, as well as contributing to water pollution and potential risks to human health. When the concentration of surfactants reaches approximately 0.1 mg/L, persistent foaming may occur in water bodies. These stable foams and excessive bubble formation are difficult to dissipate and can create a foam layer that acts as an insulating barrier on the water surface, further disturbing natural ecological processes. 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. CuO nanoparticles as effective photocatalysts and electrochemical sensors, offering promising applications in environmental remediation and heavy metal detection. [3-5]Several Copper(II) complex systems have been used for the degradation of lignin [6], polycyclic aromatic hydrocarbons and synthetic dyes. [7]

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.[8] Although extensive research has been carried out in the field of photocatalysis and photodegradation of various metal complexes, to the best of our knowledge, no report is available on the photodegradation behavior of the Copper(II) Soya Soap–Thiourea complex. Therefore, this study provides new insights into its photocatalytic activity and potential applications in environmental remediation.

MATERIAL AND METHOD

Synthesis of Copper (II) Soya soap and Thiourea complex

Preparation of Soya Soap:

Soya oil(Glycine Max) contains fatty acids such as oleic, linoleic, palmitic, and stearic acids. Saponification of soya oil with Potassium hydroxide (Direct Metathesis). [9,10] produces Potassium soya soap.

General reaction:

Triglyceride + 3KOH → Glycerol + 3RCOOK

where RCOONa represents sodium salts of fatty acids.

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 were 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. [11]

Here: CS soap- Copper(II) Soya soap

In the present study, the photocatalytic efficiency of a Copper soap complex derived from the complexation of nitrogen- and sulfur-containing ligands, such as thiourea, with Copper soap has been investigated. It is expected that appropriate ligand design and complexation with suitable metal ions can enhance the biological and photocatalytic performance of Copper-based complexes.Kinetics and Photodegradation Studies.

The photocatalytic activity of the Copper(II) soya soap–thiourea (CST) complex was evaluated by determining its degradation rate and photodegradation kinetics under visible light irradiation. For the experiments, 25 mL of the CST complex solution was placed in 50 mL Pyrex glass bottles covered with glass stoppers to minimize solvent evaporation during irradiation.A 200 W tungsten lamp (Philips) was used as the visible-light source. To

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eliminate thermal effects and ensure that only photochemical reactions occurred, a circulating water filter was placed between the lamp and the reaction vessel. The reaction mixture contained ZnO as the photocatalyst. The photocatalytic degradation experiments were carried out at different light intensities ranging from 18 mW cm^{-2} to 42 mW cm^{-2}. The light intensity was varied by adjusting the distance between the tungsten lamp and the reaction mixture. The intensity of incident light was measured using a Suryamapi photometer (CEL Model SM-201). At regular irradiation intervals, aliquots of the reaction mixture were analyzed spectrophotometrically. The UV–Visible spectrophotometer was calibrated before each measurement to ensure accuracy and reproducibility of the results. Absorbance measurements were recorded using benzene as the reference blank. The CST complex exhibited a maximum absorbance λ_{max} at 680 nm, and the decrease in absorbance at this wavelength was used to monitor the progress of photodegradation.

RESULTS AND DISCUSSION

The photocatalytic degradation of the Copper(II) soya soap–thiourea (CST) complex was monitored spectrophotometrically by measuring the optical density (OD) at regular irradiation intervals. A graph was plotted between 2+ log OD and irradiation time for each experimental system. The values of 2+ log OD and was calculated from the observed optical density data.The degradation process exhibited two distinct stages, and therefore two degradation rate constants (K_1, K_2) with different time interval was observed through slopes of that particular graph.

Rate of reaction was determined by this phrase.[12]

K= 2.303 x slope

The presence of two rate constants indicates that the degradation proceeds through a two-step mechanism. The first stage corresponds to the rapid decomposition of the parent CST complex, while the second stage is associated with the slower degradation of intermediate products formed during 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. K_1, K_2, K_3) of the degradation of the complex molecule.

Catalyst effect:

The effect of catalyst loading on the photocatalytic degradation of the Copper(II) Soya Soap–Thiourea (CST) complex was investigated using different amounts of ZnO photocatalyst. The CST complex was selected as the model system, and the degradation process was monitored by measuring the optical density (OD) at regular intervals under visible light irradiation.

The amount of ZnO catalyst was varied from 0.01 g to 0.06 g while keeping all other experimental parameters constant, such as the concentration of the CST complex .0008 M, irradiation time, reaction volume 25 ml, and light intensity34 $mWcm^{2-}$. The changes in optical density were used to evaluate the extent of photodegradation.

It was observed that the optical density of the CST complex decreased progressively with increasing catalyst concentration, indicating enhanced photocatalytic degradation. The increase in ZnO loading provides a greater surface area and a larger number of active sites for photon absorption and generation of electron–hole pairs. Consequently, the production of reactive oxygen species such as hydroxyl radicals and superoxide radicals increases, leading to a higher degradation rate.

At lower catalyst loading (0.01 g), fewer active sites were available, resulting in slower degradation and comparatively higher optical density values. As the catalyst amount was increased, the degradation efficiency improved significantly due to the enhanced generation of reactive species.

However, beyond an optimum catalyst concentration, the rate of degradation may not increase proportionally because excessive catalyst particles can cause aggregation and light scattering, reducing the penetration of light into the reaction medium. This phenomenon decreases the effective utilization of incident radiation and may limit further enhancement of photocatalytic activity.

Therefore, the study indicates that catalyst loading is an important parameter affecting the photocatalytic degradation of the CST complex. An optimum amount of ZnO catalyst provides maximum degradation efficiency by balancing the availability of active sites and effective light absorption. Results are shown in Table-1 and Figure – 1.

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

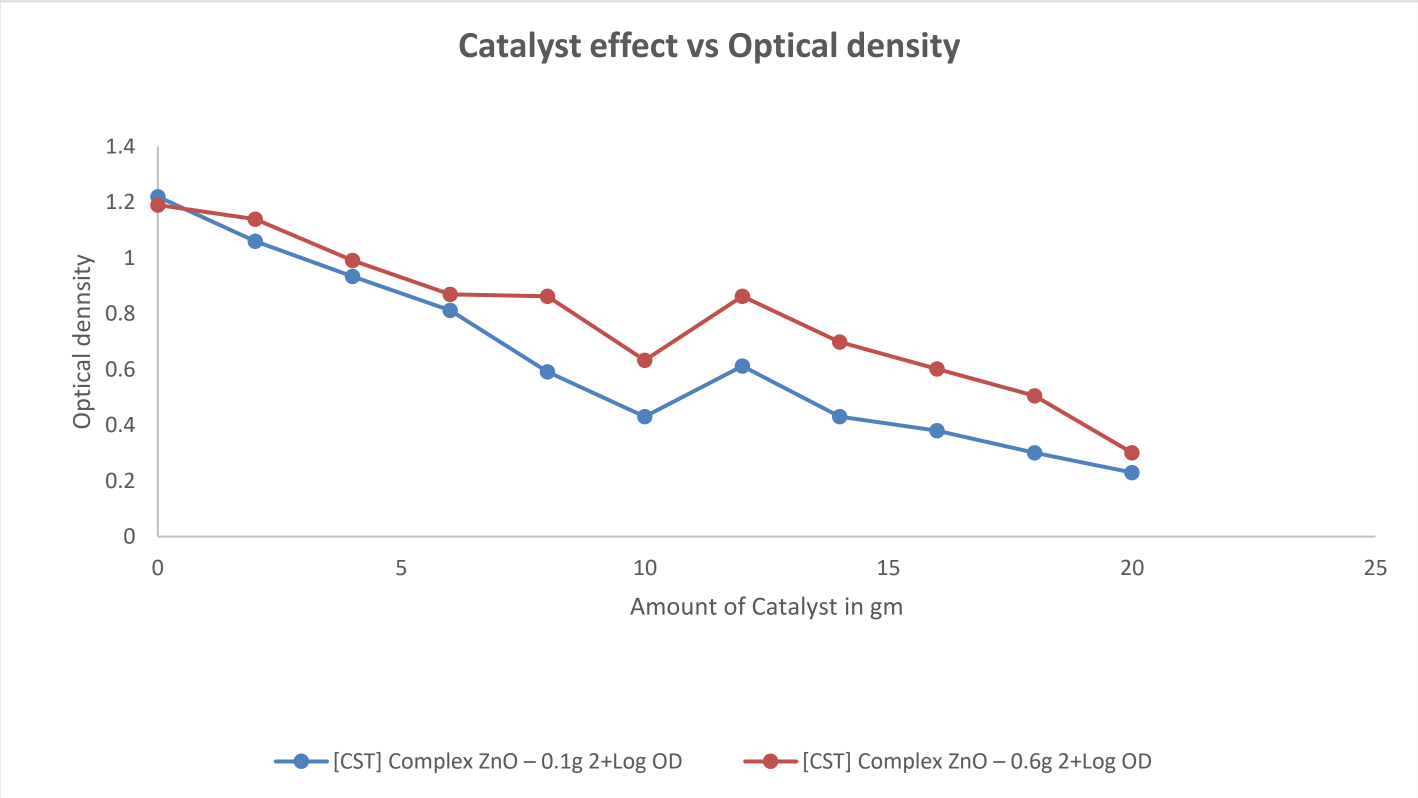

Figure -1 Catalyst effect of Copper(II) soap complexes and Optical Density.

Microbial Studies of Copper (II) Soya Complexes

Microbial studies were carried out to evaluate the toxicity pattern and antibacterial activity of the Copper(II) Soya Soap–Thiourea (CST) complex against Staphylococcus aureus. The antibacterial activity was investigated at different concentrations using the Kirby–Bauer disc diffusion method on Mueller–Hinton agar plates. Sterile discs containing varying concentrations of the CST complex were placed on agar plates inoculated with Staphylococcus aureus. After incubation, the antimicrobial activity was assessed by measuring the diameter of the inhibition zones around the discs.

Figure-2 Results of antimicrobial susceptibility test of Copper (II) Soya Thiourea complex against Staphylococcus aureus

These observations suggest that concentration plays a vital role in determining the antibacterial efficacy of the Copper(II) complex. The enhanced inhibition at higher concentrations may be attributed to increased interaction of the metal complex with bacterial cell membranes, leading to disruption of essential cellular functions and suppression of bacterial growth.[13] Therefore, it can be concluded that the Copper(II) Soya Soap–Thiourea complex possesses concentration-dependent antibacterial activity and may serve as a potential antimicrobial agent against Staphylococcus aureus.

CONCLUSION

The present study demonstrates that the photocatalytic degradation of Copper(II) Soya Soap–Thiourea (CST) complexes is strongly influenced by the catalyst. The optical density initially increases with an increase in the amount of catalyst, owing to the greater availability of molecules for photocatalytic reaction. However, beyond an optimum level, a decrease in the degradation rate is observed. This may be attributed to reduce light penetration, increased solution opacity, and limited availability of active sites on the photocatalyst surface.

Furthermore, microbial studies demonstrated that the Copper(II) Soya Soap–Thiourea complex possesses appreciable antibacterial activity against Staphylococcus aureus. The degree of inhibition increased with increasing concentration of the complex, indicating a concentration-dependent antimicrobial effect.

Overall, the physicochemical, photocatalytic, kinetic, and microbial investigations reported in this study provide valuable insights into the behavior and potential applications of Copper(II) Soya Soap–Thiourea complexes. These findings suggest that such complexes may find significant applications in environmental remediation, wastewater treatment, antimicrobial formulations, catalysis, and various industrial processes. Further studies on degradation mechanisms, toxicity assessment of degradation products, and large-scale applications may enhance their practical utility in diverse fields.

DECLARATIONS

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Conflict of interest

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

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Ethics statement

Not Applicable.

Informed consent

Not Applicable.

Data availability

Not Applicable.

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