

PHOTO-CATALYTIC DEGRADATION OF SURFACTANTS HEXADECYLTRIMETHYL-AMMONIUM CHLORIDE IN AQUEOUS MEDIUM - A KINETIC STUDY

Suhail A. Soomro^{1,*}, Shaheen Aziz¹, Abdul Rehman Memon¹, Mukhtar ul Hasan², Abdul Jabbar Chaudhary²

e-mail: suhail.soomro@yahoo.com

¹ Department of Chemical Engineering, Mehran University of Engineering & Technology, Jamshoro, Pakistan

²Institute for the Environment, Brunel University, West London, UK.

ABSTRACT: *Surfactants in the environment are a prerequisite for the sustainable development of human health and ecosystems. Surfactants are important in daily life in households as well as in industrial cleansing processes. It is important to have a detailed knowledge about their lifetime in the environment, their biodegradability in wastewater treatment plants and in natural waters, and their ecotoxicity.*

Most of the issues on environmental acceptability focus on the effects on the environment associated with the use and disposal of these surfactants. These effects are taken into account by a risk assessment. The first step in a risk assessment is to estimate the concentrations of surfactants in the environmental compartment of interest, such as wastewater treatment plant effluents, surface waters, sediments, and soils. This estimate is generated either by actual measurement or by prediction via modelling. The measured or predicted concentrations are then compared to the concentrations of surfactant known to be toxic to organisms living in these environmental compartments.

There are many situations where industry is producing both heavy metals ions and organic pollutants. Successful treatment of effluents of this type to achieve legislative compliance will depend on whether the heavy metals effect the process of degradation of the organic species and whether the presence of organic molecules hinder the process of removal of heavy metals.

Degradation of cationic surfactant was studied with a photolytic cell system. Compressed air was used as oxidant and the temperature was maintained at 25-30°C. Effect of UV source, hydrogen peroxide (H₂O₂) and titanium (TiO₂) on Hexadecyltrimethyl-ammonium chloride (C₁₉H₄₂NCl) were recorded. HPLC and IR were used to analyse the rate of degradation of Hexadecyltrimethyl-ammonium chloride (C₁₉H₄₂NCl).

Keywords: *Hexadecyltrimethyl-ammonium chloride, photolytic cell, catalysts, hydrogen peroxide (H₂O₂), titanium dioxide (TiO₂), rate of reaction.*

INTRODUCTION

Surfactants (surface-active agents) can be anionic, amphoteric, polymeric and non-ionic. They are held in industries such as agro-chemical, mining and oilfield. Surfactants have a hydrophilic head which attaches to water, and a hydrophobic part of the molecule that avoids water. The hydrophobic part of the molecule is also free to attach to grease, fat, or oil on the surface.

Heterogeneous photocatalysis is a well-known technology used to solve the problem of water pollution [1, 2]. Even in the nuclear industry, during decontamination of protective clothing and contaminated materials, detergents are employed to bring down the level of radioactive contamination to within safe limits. However, the surfactant present in these wastes interferes in the chemical treatment process, reducing the decontamination [3]. Although surfactants have been studied in complex water soil systems [4, 5], the effects are not well understood. Different methods have been used to destroy and reduce the levels of organic pollutants including treatment with activate sludge [6] Clinical oxidation [7] biological oxidation [8] thermal degradation [9] ozonization [10] and photo-oxidation with ultraviolet radiation [9].

The present experiments were conducted using surfactants as a model on account of the possible contamination of the environment by surfactants arising from the widespread use of soaps and detergents [10] of low biodegradability [11], and the inhibiting effect to the

biodegradation of some other pollutants [12,13]. The surfactant used was Sodium dodecylbenzenesulfonate (DBS) It has a molecular weight of 430.6 and has abbreviations such as NAC.

EXPERIMENTAL METHODS

The photocatalytic cell system was used to analyse the samples for degradation of industrial effluents (figure 1). Compressed air was used as the oxidant. The temperature in the system was measured by thermometer. The reaction chamber was maintained at 25-30°C by a water cooling jacket which surrounded the UV probe.

The degradation of Hexadecyltrimethyl-ammonium chloride (C₁₉H₄₂NCl) were studied by using UV source, hydrogen peroxide (H₂O₂) and titanium dioxide (TiO₂). 50ppm solution of Hexadecyltrimethyl-ammonium chloride were prepared and used to study the effects of the UV source, hydrogen peroxide (H₂O₂) and titanium dioxide (TiO₂) on degradation of surfactant. 5 cm³dm⁻³ & 10 cm³dm⁻³of H₂O₂ were prepared. Also, samples of another catalyst, namely TiO₂ were prepared in 01 gm dm⁻³ & 02 gm dm⁻³ concentrations, following the same procedure as for H₂O₂. The analysis of DBS was carried out by using High Performance liquid Chromatography (HPLC) and Infrared Spectroscopy (IR).

RESULTS AND DISCUSSION

Effect of UV source on the degradation of Hexadecyltrimethyl-ammonium Chloride

The first set of experiment was focused to observe the effect of UV source on the degradation of surfactant, Hexadecyltrimethyl-ammonium chloride using 15 watt & 400 watt UV lamps. The time intervals of the UV exposure to the sample were set to 02, 04, 06 and 08 hours. It was observed that percentage degradation of surfactant sample was 7.7% in 02 hours, 12.9% in 04 hours & 21.5% in 06 hours & 32.7% in 8 hours (Table-1). The same trend is shown for the 400watt UV lamp as for 150 watt lamp, degradation increases from 10.2% in 02 hours to 60.3% in 08 hours

Table-1 Effect of UV source

Time (h)	Degradation of $C_{19}H_{42}NCl$ (%)	
	150Watt Lamp	400Watt Lamp
2	8.7	12.2
4	13.9	24.8
6	21.5	46.1
8	34.7	62.3

Table-2 Effect of H_2O_2

Time, (h)	Degradation of $C_{19}H_{42}NCl$, (%)		
	No catalyst	H_2O_2 ($5\text{ cm}^3\text{ dm}^{-3}$)	H_2O_2 ($10\text{ cm}^3\text{ dm}^{-3}$)
2	12.2	20.8	27.1
4	24.8	35.5	53.0
6	46.1	59.6	78.9
8	62.3	79.9	99.8

Table-3 Effect of TiO_2 on degradation of

Time, (h)	Degradation of $C_{19}H_{42}NCl$, (%)		
	No catalyst	TiO_2 (1g dm^{-3})	TiO_2 (2g dm^{-3})
2	12.2	18.6	25.1
4	24.8	41.5	48.0
6	46.1	66.6	77.9
8	62.3	82.7	95.8

Effect of H_2O_2 on the degradation of Hexadecyltrimethyl-ammonium Chloride

In this set of experiments, the effect of degradation were studied by using hydrogen peroxide (H_2O_2) in two concentrations, i.e., $5\text{ cm}^3\text{ dm}^{-3}$ and $10\text{ cm}^3\text{ dm}^{-3}$ in addition when no catalyst was used. It was observed that the degradation was 10.2% at 02 hours, when no catalyst were used. it increases from 10.2% to 60% in 08 hours. The degradation was 19.8% at 02 hours, when $5\text{ cm}^3\text{ dm}^{-3}$ concentration solution of hydrogen peroxide were used. It increases further to achieve 78.9% degradation in 08 hours time. Further increase in the concentration of catalyst shows 25.1% degradation in 02 hours and reached 99.8% degradation when time were increased to 08 hours.

Effect of TiO_2 on the degradation of Hexadecyltrimethyl-ammonium Chloride

In order to see the optimum degradation, another catalyst; titanium dioxide (TiO_2) were used in 1g dm^{-3} and 2g dm^{-3} concentration, keeping the time interval same as in the previous set of experiments. It was observed that at 02 hours time & 1g dm^{-3} concentration, the degradation achieved was 17.6%. As the time increased, the degradation also increased to 82.7%. The 2g dm^{-3} concentration showed better degradation at 02 hours, i.e., 24.1%. After passing 08 hours, the degradation was 95.8%.

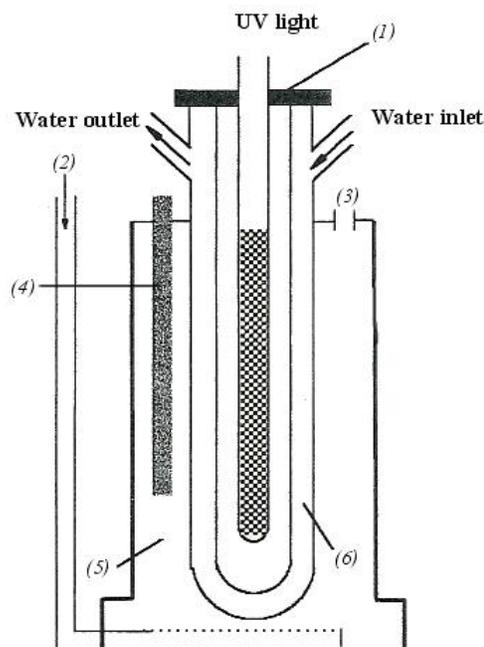


Figure 1 The photolytic cell system [(1) UV probe (2) inlet (3) outlet (4) thermometer (5) reaction chamber (6) cooling jacket]

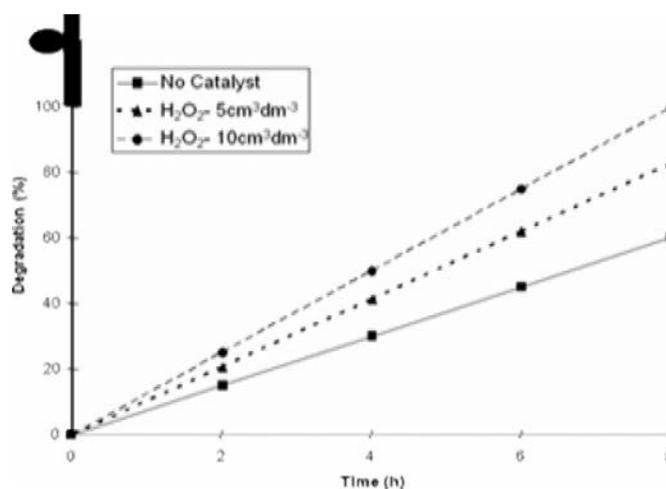


Figure 2 Effect of H_2O_2 on the Degradation of Hexadecyltrimethyl-ammonium Chloride

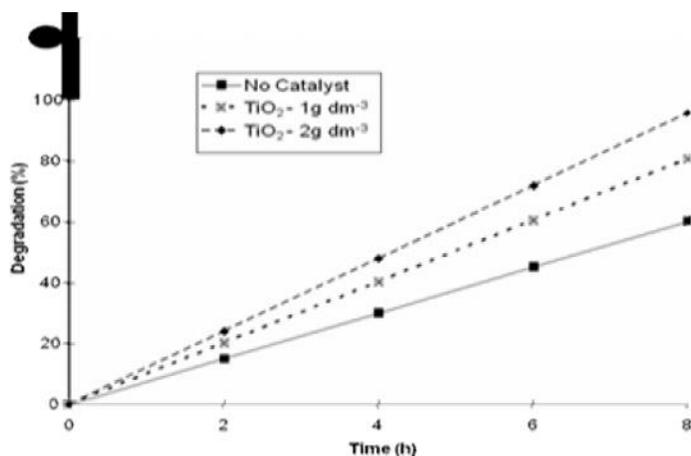


Figure 3 Effect of TiO₂ on the Degradation of Hexadecyltrimethyl-ammonium Chloride

CONCLUSION

- 400 W UV source is required to achieve a complete degradation of the surfactant.
- Complete degradation of the surfactant was achieved using 1% H₂O₂ or 2g/L TiO₂.
- This increase in degradation is attributed to the ease of formation of free radical in the presence of an oxidant or a catalyst.
- Two intermediate species were detected by HPLC indicating the presence of carboxylic acids.
- The effect of heavy metals on the degradation is being carried out.

REFERENCES

- [1] Hoffman, M.R.Martin, S.T.Choi, W.Y et.al, Environmental Applications semiconductor photocatalysis, *Chem.Rev.*, 96, 1995.

- [2] Alfano, Bahnemann, D.Cassano et.al, Photocatalysis in water environments using artificial and solar lights, *Catal. Today*, 58,199, 2000.
- [3] Chitra S, Chandran Sandhya, Sasidhar P, Lal KB, Amalraj RV, Biodegradation of surfactant bearing wastes, *Indian Environ Prot*, **11** (9) 689-692, (1991),.
- [4] Aronstein B.N., Y.M.Calvillo and M.Alexander, Effect of surfactants at low concentrations, *Environ. Science. Technol.*, **25**, 1728-1731, 1991.
- [5] Laha S and R.G.Luthy, Inhibition of phenanthrene mineralization by noionic surfactants, *Environ Svi. Technol.*, **25**, 1920-1930, 1991..
- [6] Hashimoto, N.; Sumino, T.; *J. Ferment. Bioeng.* **86**, 424, 1998.
- [7] Basu, S.; Wei, I. W. *Chem. Eng Commun.*, **164**, 111, 1998.
- [8] Dilaconi. C.; Ricco, G.; Tanzarella, C.; Tomei, M. *C. Ann. Chim.*, **88**, 849, 1998.
- [9] Peuravuori, J.; Paaso, N.; Pihlaja, K. *Thermochim. Acta* **325**, 181, 1999
- [10] Karsa D.R., Industrial applications of surfactants IV, *The Royal Society of Chemistry*, 1-22, 1999.
- [11] Scott M.J and Jones M.N., Review: the biodegradation of surfactants in the environment, *Biochimica et Biophysica Acta*, 1508, 235, 2000.
- [12] Urano K and Saito M., Biodegradation of surfactants and inhibition of surfactants to biodegradation of other pollutants, *Chemosphere*, **14**, 1333, 1985.