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Wastewater and sludge treatment

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A technical paper on

Removal of triclosan in municipal wastewater treatment

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviation / Symbol	Meaning
µ	Micro
AOP	Advanced oxidation process
C_{efl}	Effluent concentration
C_{inf}	Influent concentration
C_0	Initial concentration of triclosan
C_t	Concentration of triclosan at time (t)
COD	Chemical oxygen demand
DSDD	dibenzo-dichloro-p-dioxin
DO	Dissolved oxygen
g	Gram
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
L	Litre
mg	Mili gram
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
MWTP	Municipal wastewater treatment plant
nm	Nanometer
OUR	Oxygen uptake rate
SPE	Solid phase extraction
SRT	Solid retention time
SVI	Sludge volume index
TCS	Triclosan
TOC	Total organic carbon
UV	Ultraviolet
WWTP	Wastewater treatment plant

ABSTRACT

Triclosan (TCS) is a multiuse ordinary component for the daily household personal care and consumer products like toothpastes, shampoo and soaps because of its antibacterial and antiseptic properties. The large-scale use of TCS allocates this compound different ways to become a part of the environment. This technical paper deals with the removal of TSC in waste water treatment plants with the help of photocatalytic degradation and activated sludge processes on a lab-scale reactor. The use of systematic procedure involving solid-phase extraction (SPE) and high-performance liquid chromatography (HPLC) determined the removal efficiency of TCS during activated sludge process. The determined efficiency was 92.5%, 95.4%, 99.1% and 99.9% for different Hydraulic retention time (HRT) values of 18h, 24h, 48h, and 52h respectively. On the other side during degradation of TCS in TiO_2-only condition was just 30% in 20min, at the same time higher removal efficiency of 75% and 82% in 20min was achieved for photolysis and photocatalysis respectively. Adding 2-propanol, a radical scavenger significantly decreases the removal efficiency of photolysis and photocatalysis. These effects have also been discussed in the paper. Results show that photocatalysis is more efficient than photolysis as it is achieved by radicals, these radicals further degrade the harmful intermediates produced.

1. INTRODUCTION

Water is the most abundant natural resource available on the earth, but only 1% of the available water is suitable for human consumption. The main reason that supply of fresh water become unsuitable for consumption is constant contamination of natural water sources by organic and inorganic pollutants [1]. Many chemically potential compounds and elements are known, but currently emerging contaminants and pollutants are receiving great attention. These pollutants can be found in various product that are used on a daily basis, like hormones, medications and cleaning products [2]. Triclosan (TCS) is an important emerging pollutant. It is causing serious environmental problems due to its incomplete elimination [3]. It is an antimicrobial agent currently used in toothpastes, mouth washes, liquid soaps. Approximately 1500 ton triclosan is produced globally per year, and approximately 300 ton is applied in Europe. In various municipal wastewater treatment samples, triclosan has been detected at a concentration of 0.5-4.5 μgL^{-1} [4].

2. STATE OF ART

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol), is used in personal and health care products, as a broad-spectrum antibacterial agent, with concentrations ranging from 0.1-1% [5]. TCS is a synthetic organic compound which has antimicrobial and fungicidal effects, having main applications in personal care products (soaps, toothpastes and creams) and some toys [2]. Although TCS is referred to a low toxic compound, it is a main element that triggers formation of more toxic dioxins. Studies have found that dioxins may cause reproductive and developmental abnormalities in humans (E.g. Chlorinated dioxins are well known carcinogens) [6]. A risk assessment study has shown that TCS in surface water could negatively affect a range of aquatic organisms [7]. TCS samples have been found in treated waste waters, ground water, surface water and even drinking water, with concentrations ranging between 0.1 - 20 μgL^{-1}. The occurrence and fate of these contaminants have always bothered the wastewater engineers and therefore have been a subject of many monitoring studies in recent years. Conventional wastewater treatment methods have been ineffective in their treatment, being one of the reasons for these emerging pollutants to enter the

environment [8]. Therefore, effective alternative wastewater treatment techniques are required for treating these harmful pollutants.

Following figure 1 shows molecular structure of TCS [9].

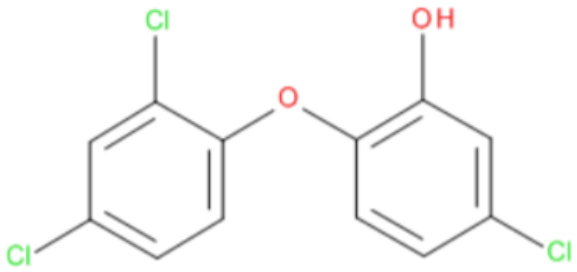


Fig 1: Triclosan Molecule

3. REMOVAL OF TRICLOSAN IN WASTEWATER TREATMENT

The conventional method i.e. biodegradation of TCS in municipal wastewater treatment plants (MWTPs) and the Photocatalytic oxidation of TCS have been discussed below in detail.

3.1 BIODEGRADATION OF TRICLOSAN

The activated sludge process has been used since the early 1900s in biological wastewater treatment; it is a suspended culture system. The name of the process is derived from the fact that the living and active microorganisms are returned to the reactor to increase the speed of biological reactions with the availability of increased biomass. There are two possibilities including complete mix flow or purge flow process [10]. The extended aeration as modification of the process was used. The modification of activated sludge process includes increase in aeration time of about 18-24h with high mixed liquor suspended solids between 3500-5000 mg/L [11].

Ciba-Geigy Company, Switzerland firstly synthesized TCS with its broad-spectrum antimicrobial properties under its trade name IRGASAN DP300 [12]. TCS has been detected as eco-toxic to aquatic environment specially algae. In Europe, the use of TCS has increased to 350 tons as an antimicrobial component in many products.

The following table shows the chemical properties of TCS.

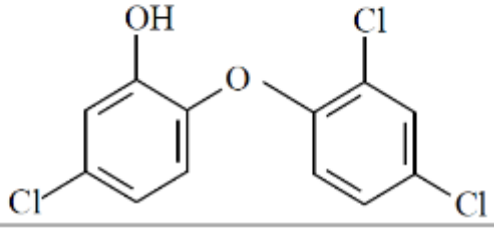
INCI Name	Triclosan
Chemical Name	2,4,4'-trichloro-2'-hydroxy-diphenylether
Scientific name	(5-chloro-2-(2,4-dichloro-phenoxy)-phenol
Trade Names	Irgasan® DP300, Irgasan® PG60, Irgacare® MP, Irgacare® CF100, Irgacide® LP10, ; Cloxifenolum, Irgagard® B 1000, Lexol 300, Ster-Zac
Molecular Formula	$C_{12}H_7Cl_3O_2$
Molecular Weight	289.5
Physical form	White crystalline powder
Chemical structure	

Table 1: Chemical Properties of TCS

Materials and methods

Recent research in the field of wastewater and sludge treatment regarding removal of TCS in the wastewater provided the data of removal efficiency of different plants using different methods. In Europe the wastewater treatment plants using a technique of primary settling in the activated sludge process resulted in removal efficiency of about 58-73%. The experimental data shows that the biodegradation of TCS under anaerobic conditions is not possible [13],[14]. Ammonia-oxidizing bacteria takes part in the biodegradation of the TCS, And the research shows a considerable reduction in the production of nitrate due to the toxic effects and competitive behaviour of TCS present in the wastewater samples [15].

In another research, it was observed in a conventional activated sludge process that up to 85-95% of the influent TCS was biodegraded and 1.5-4.5% of it was sorbed to sludge. The research was concluded on a result that the biodegradation of TCS is possible at both low and high concentration using activated sludge process. The data shows that the acclimation of microorganisms is decisive for the biodegradation of TCS [16].

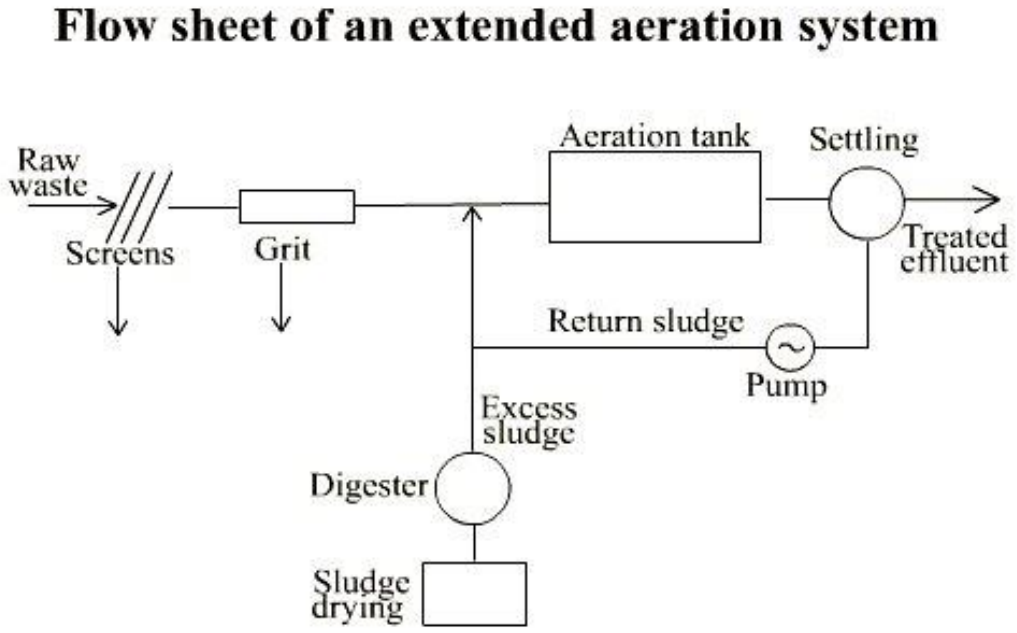


Fig 2: Extended activated sludge process [17].

Activated sludge samples

For experiments on lab-scale five batch bioreactors were used. The activated sludge samples were taken from a WWTP, as the plant was designed for the treatment of wastewater using activated sludge treatment process with a flow rate of 230,000 m^3/day and solid retention time (SRT) of 2-4 days. The samples taken from the plant were kept in the operational bioreactors for three months to acclimate the microorganisms under lab conditions. Aeration pumps were used to get dissolved oxygen (DO) concentration of 5mg/L. after achieving the concentration of MLSS more than 5000 mg/L, TCS was added starting with the lowest concentration of 0.01mgL^{-1} [17].

Batch Reactor system

Batch bioreactors used in the experiments were maintained and the treatment efficiencies were detected by the measurement of influent and effluent concentrations of COD, MLSS, and oxygen uptake rate (OUR). The starting concentrations of MLSS and COD were maintained within the range of 4000-5000 mg/L and 900-1120 mg/L,

respectively. The operational time for the reactors was 60h in batch mode and samples were examined after every 12h. Different parameters like MLSS, pH, COD, MLVSS, DO, OUR and sludge volume index (SVI) were measured in the samples from the reactors.

Bioreactors	A	B	C	D
pH	7.1	6.9	7.4	7.2
D.O (mg/L)	4.8	5.1	4.9	5.3
MLSS (mg/L)	5142	5283	4971	5036
MLVSS (mg/L)	4215	4230	3768	3957
F/M gCOD/g MLSS/ day	0.197	0.212	0.185	0.198
SVI (ml/g)	89	89.5	92	94
OUR (mg/L O_2 / h	25	27	26	27.5
COD in (mg/L)	900	1057	998	1083
COD out (mg/L)	153	204	162	218

Table 2: Operational conditions for the bioreactors [17].

3.2 PHOTOCATALYTIC OXIDATION OF TRICLOSAN

Advanced oxidation processes (AOPs) have been developed in the past years [18], which have a potential of mineralizing most of the contaminants. Conventional oxidation process chemically attacks the pollutants resulting in change of the chemical structure of the specific molecules, in comparison to these, the AOPs provide hydroxyl radicals having oxidation potential. Solar energy is used as an advanced natural source for oxidation [19], from which photocatalytic degradation is considered to be the most favoured and a greener technology as there are no wastewater problems and also the process is favoured by mild pressure and temperature conditions [18].

Photolysis could be a promising technique for degradation of TCS in wastewater treatment, but it has a major drawback that during photolysis it forms harmful intermediates of dioxins- and phenol- types, which are carcinogenic in nature [6]. According to Hyun-Seok S et al. TCS when treated with photolysis under lowlight intensity (max wavelength = 365nm) it may form dibenzo-dichloro-p-dioxin (DCDD) and dibenzo-p-dioxin. To reduce the formation of these intermediate dioxins, oxidants like OH radicals are useful. Photocatalytic reaction is the alternative to increase the

production of OH radicals. TiO_2 based photocatalysts have been extensively used for the degradation of water pollutants. This treatment method is based on the formation of pairs of electrons (e^-_{CB}) and positive holes (h^+_{VB}), when UV irradiation of wavelength smaller than 387.5nm is subjected over the photocatalysts. Hydroxyl OH radicals are photogenerated due to the presence of water and oxygen [6]. Following figure 3 shows a pictorial abstract of the photocatalytic degradation technique (data from [19]).

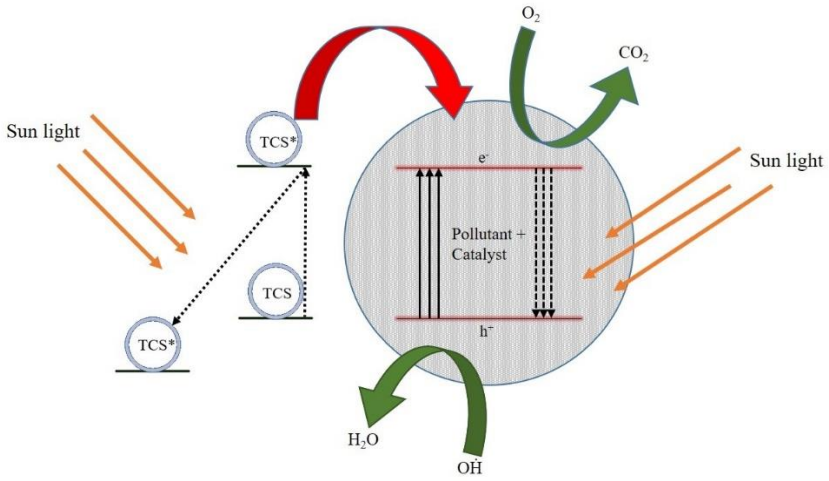


Fig 3: Pictorial abstract of photocatalytic degradation technique (data from [19])

The study carried out by Hyun-Seok S et al. [20] looked into the kinetics and the mechanisms of photolysis and the photocatalysis of TCS. The experiments of TiO_2 photocatalysis and photolysis of TCS were investigated and the results were compared with TiO_2-only in dark condition, 2-propanol (as a scavenger) was added to both photocatalysis and photolysis to study the consequences of OH radical in both cases. This study is discussed in details below.

Materials and methods

Triclosan (Merck, solid phase), methanol (J.T. Baker), and $FeSO_4 \cdot 7H_2O$ (J.T. Baker), $CH_3CHOHCH_3$ (Aldrich), $MgSO_4$ (Aldrich) and TiO_2 (P-25, Degussa Chemical Co., Germany) were used as received. Experiments were performed in a photoreactor system, having a metering pump (Cole-Parmer) circulating the contents by $0.1 Lmin^{-1}$, and a glass reservoir with a capacity of 1.5L. Medium pressure Hg-vapor UV-A lamp with maximum wavelength of 365nm was used. Experiments were at atmospheric pressure at 293K. In every experiment the initial concentration of TCS was $1.73x10^{-2}$

mM. The light intensity of $1.37x10^{-4}EinsteinL^{-1}min^{-1}$ was used in every experiment. TiO_2 concentration of $0.1gL^{-1}$ was used in the photocatalytic and the adsorption experiments. 2-propanol (as OH scavenger) with concentration of 1.3mM was used. An ultraviolet persulfate oxidation TOC analyser with an infrared detector (Phoenix 8000TM, TekMar Dohrmann) was used to carry out a TOC measurement to measure the mineralization of TCS. pH of the reaction during experiments was measured using a pH meter (Orion, Model 52A).

4. RESULTS AND DISCUSSION

Biodegradation of TCS:

The objective of the experiment is to estimate the removal efficiency of TCS in wastewater treatment plants based on literature. The research examined the capacity of extended activated sludge process to remove TCS during wastewater treatment. Standard solutions of TCS ranging between 0.01-10mg/L were prepared for the experimental data. Fig 4 shows the removal efficiency of TCS during biodegradation in MWTP.

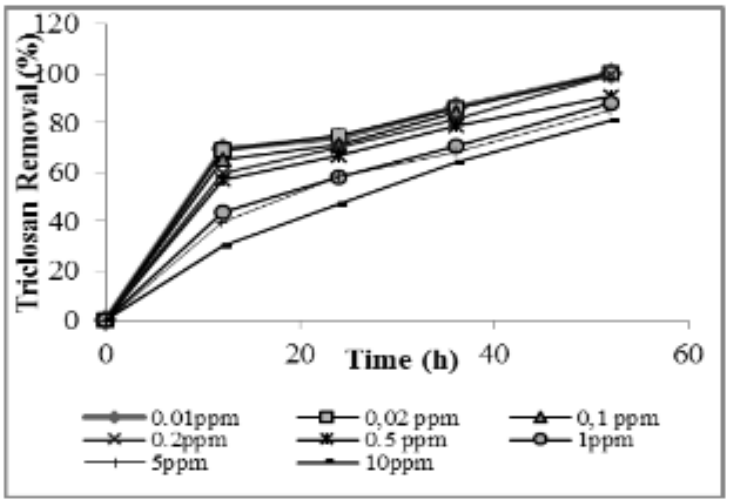


Fig 4: TCS (%) removal with time [17].

The percentage removal of TCS was calculated using following mathematical expression: [17]

$$\text{Removal efficiency (\%)} = (C_{inf} - C_{efl}) \div C_{inf} \times 100$$

Photocatalytic oxidation of TCS:

At first, comparison of the TCS removal with TiO_2 only, photolysis and photocatalytic condition is done. From fig we can see almost 30% of TCS removal was achieved after 20min with TiO_2-only in dark condition, following by achieving equilibrium after further 10min. TOC reduction in TiO_2-only condition is same as TCS removal, which tells that TCS adsorption over TiO_2 is not a chemical reaction. Photolytic and photocatalytic efficiencies of TCS at same times were 75% and 82% respectively, but TOC removal efficiency is higher in photocatalysis than photolysis.

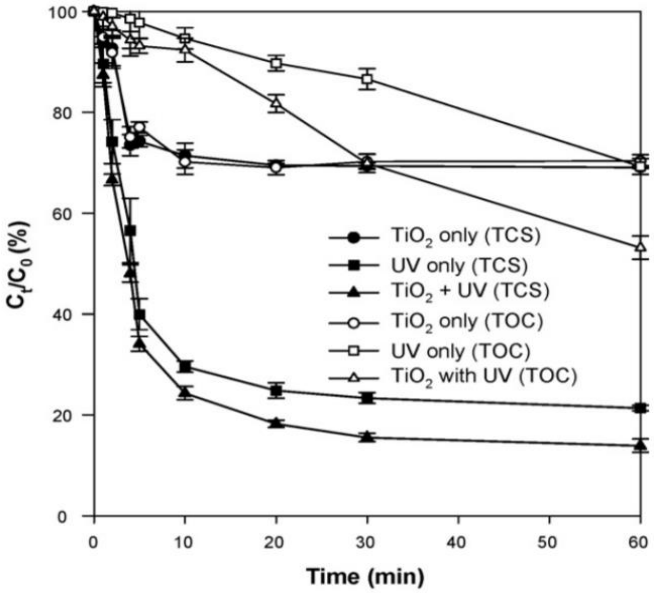


Fig 5: Comparison of triclosan (TCS) and TOC removal efficiency at TiO_2-only (adsorption), photolysis (UV-only), and TiO_2 photocatalysis [20].

Further the effects of pH and initial concentrations on adsorption were seen. The adsorption of TCS increased as the pH of solution containing TCS decreased. Compared to neutral and acidic pH, less adsorption of TCS with TiO_2 is achieved due to the repulsive forces between TCS and TiO_2 catalyst in pH higher than 8. Fig 6b shows that after 30 and 90 min the initial pH of 8 and 10 reduces to 7.5 and 7.9 respectively. We can see that the best condition for TCS adsorption is neutral pH.

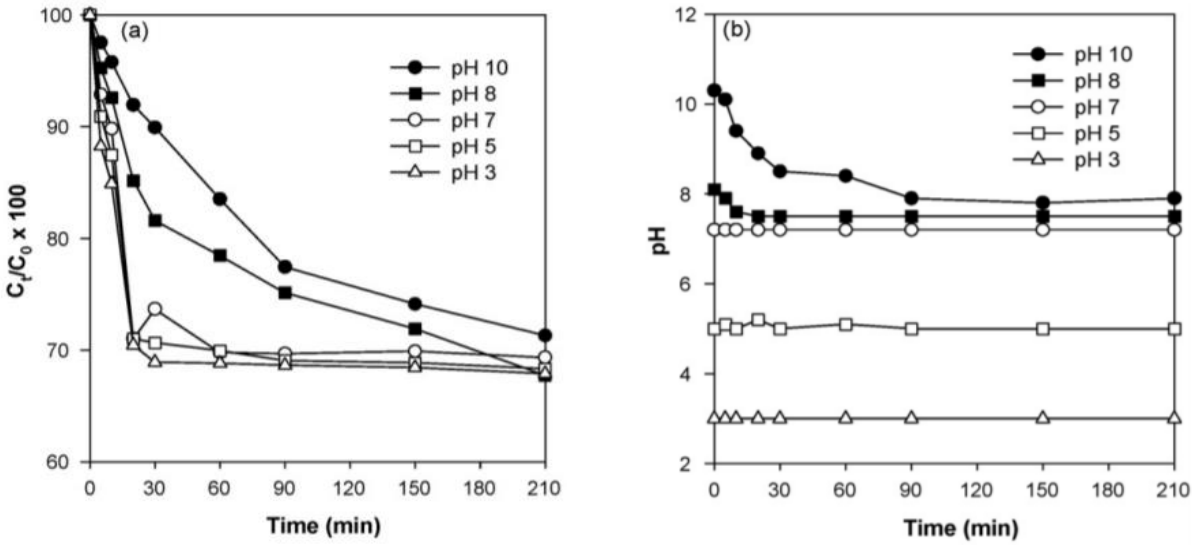


Fig 6: (a) Effect of pH and initial concentrations on adsorption (b) pH change in the adsorption of triclosan by TiO_2 (the deviation of pH ±0.3).

After addition of 2-propanol, the degradation efficiency of TCS gradually decreased for both photolytic and photocatalytic conditions (Fig 7). With 2-propanol it is almost 40% for 2h time, which is way less than initial efficiency with TiO_2 (~80%).

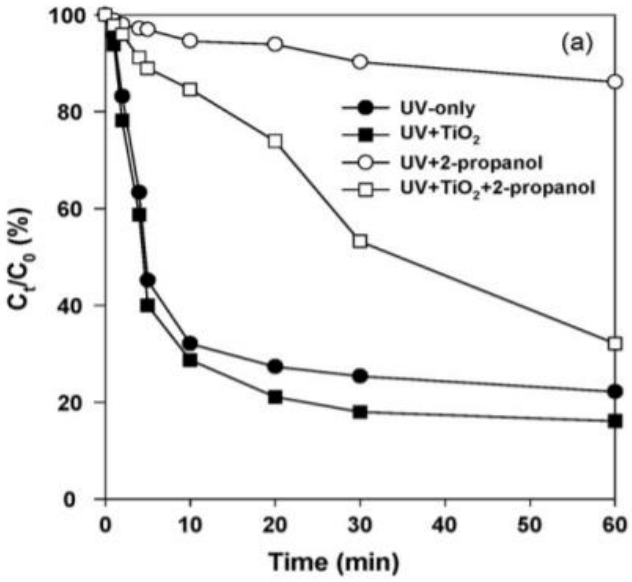


Fig 7: Photolysis and photocatalysis efficiencies of triclosan for 60 min with 2-propanol and without 2-propanol.

Fig 8 below shows the photogeneration of dioxins- and phenol- type intermediates during photolysis and photocatalysis. The disappearance of these dioxin- type intermediates depend upon the formation of OH radicals during photocatalysis. Considering the degradation of photocatalysis and toxicity of these intermediates,

photocatalysis is becomes more effective than photolysis in TCS treatment in wastewater. Fig 8 shows the mechanism for photocatalysis and photolysis for TCS proposed by Hyun-Seok et al. [20].

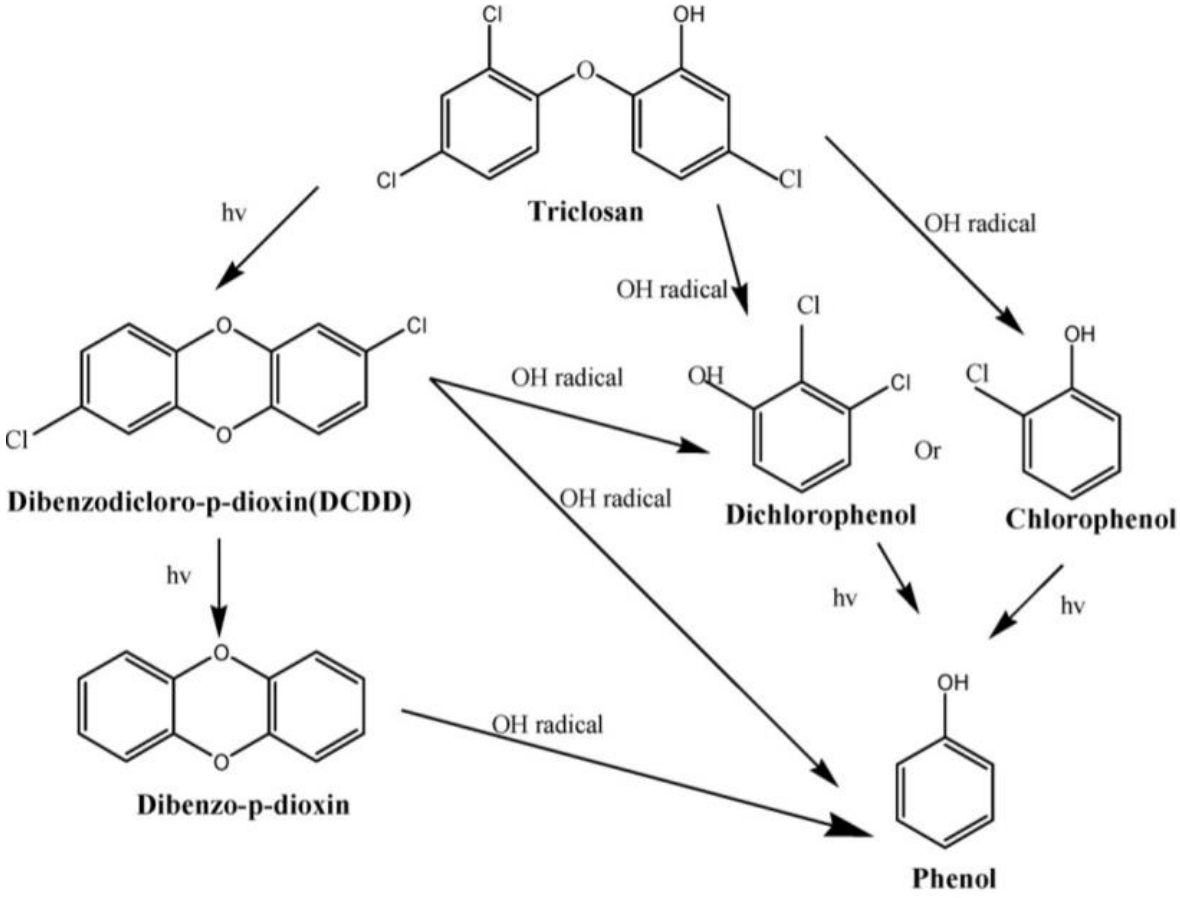


Fig 8: Proposed mechanism of photocatalysis and photolysis of TCS [20].

5. CONCLUSION

The results show that for the extensive removal of TCS from the wastewater, extended activated sludge reactors can be used. The efficiency of the reactors can be improved by increasing the aeration time. The results show that the TCS even in high concentration did not affect the activated sludge process in Wastewater treatment plants. The removal efficiency directly depends upon the mean residence time and amount of air used during the process. TCS when treated under lowlight irradiation produces harmful dioxins- due to its high sensitivity to photolysis. These dioxins- are carcinogenic in nature. So, a more efficient and advanced method is needed so as the formation of these harmful intermediate products can be avoided. Oxidising these

intermediates with OH radicals using photocatalytic oxidation is found to be more efficient in reduction of formation of these dioxins- , also the pollutants are mineralized into inorganic substances when irradiated under UV light using TiO_2 catalyst, which can further be easily treated. Further research is required to find more efficient catalyst for photocatalytic oxidation to achieve more removal of TCS from wastewater.

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