

Triclosan Removal from Synthetic Wastewater by TiO_2/UV and O_3/UV Processes

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Abstract: Triclosan is an important broad spectrum antimicrobial agent which has been incorporated into a variety of personal care products, because of its favourable safety profile. Triclosan is relatively stable and occurs in low concentrations thereby making it difficult to remove or degrade in the natural aquatic environment. Advanced Oxidation Processes (AOPs) have proved to be effective in degradation of triclosan. In this study, a heterogeneous advanced oxidation process (AOP) using TiO_2/UV was compared with homogeneous AOP using O_3/UV for the removal of triclosan from wastewater. The performance was evaluated in terms of efficiency of removal of triclosan by both the processes. The effect of pH, oxidant dosage and contact time were also considered and favourable reaction conditions were found. Homogeneous AOP (O_3/UV) was found to have higher triclosan removal efficiency (>90%) under optimum reaction conditions. It was found that TiO_2/UV process required more oxidant dosage and reaction time than the O_3/UV process to ensure significant triclosan removal efficiency. However, prolonged irradiation using heterogeneous AOP (TiO_2/UV) ensured complete removal of triclosan. Even so, selection of a particular treatment option depends on various factors such as the type of wastewater and potential reuse application of treated wastewater.

Keywords: AOP, O_3/UV , TiO_2/UV , Triclosan, Wastewater

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I. Introduction

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol) (TCS) is a nonionic, colourless substance that was developed in the 1960s. It has been added as an antimicrobial to a substantial number of personal care products. The widespread use of this compound is of concern since recent studies report inadequate TCS removal after wastewater treatment as well as detection of TCS in surface waters. Such discharge of TCS may likely cause several effects on the environment and human health, including bioaccumulation of TCS and methyltriclosan in algae and snails; algal growth repressing effects; the formation of hazardous degradation products and the improvement of microbial resistance [1]. Triclosan is hard to remove or degrade in the natural environment because of its stable chemical structure and low concentration [2]. It is a relatively stable, hydrophobic compound with a high potential for bioaccumulation. The long term effects caused by exposure to low concentrations of triclosan are being studied extensively in recent times [3, 4, 5, 6]. Moreover, the formation of transformation products such as methyl triclosan, chlorinated triclosan and dioxins from triclosan has already been reported in the literature [7, 8].

Advanced Oxidation Processes (AOPs) have proved to be effective in degradation of recalcitrant organic compounds like triclosan [9]. AOPs are generally defined as the treatment methods that generate hydroxyl radicals (OH^\cdot), which are responsible for oxidizing and mineralizing almost all types of organic molecules, yielding carbon dioxide and inorganic ions as the end products of the reactions [10].

Fenton and Fenton-like oxidation have appeared to be effective treatment option for the removal of triclosan [11, 12]. Complete triclosan removal was achieved from 10 mg/L concentration solution at very low iron and H_2O_2 doses (1 mg/L and 5 mg/L respectively) and room temperature. The aromatic by-products formed during these reactions were found to have significantly lower ecotoxicity and higher rates of conversion to organic acids. Electro-Fenton systems using undivided electrolytic cells containing platinum or Boron Doped Diamond (BDD) anode and a carbon felt or O_2 diffusion cathode has also been used for efficient removal of Triclosan from aqueous solutions with a small catalytic amount of iron (Fe^{3+}) [13]. The triclosan decay rate in these cells followed the sequence: Pt/carbon felt > BDD/carbon felt > Pt/ O_2 diffusion > BDD/ O_2 diffusion, in agreement with the generation rate of hydroxyl radicals from Fenton's reaction, which is the main oxidant of triclosan. According to a study conducted by Martínez-Zapata et al. (2013) [14], the oxidation of triclosan by hydroxyl radical caused significant reduction in the production of dioxin-group intermediates. It also resulted in improvement of effective mineralization of triclosan. Triclosan exhibited a mineralization of 72% at basic pH after 19 hours when subjected to direct photolysis.

Some of the other techniques adopted for degradation of triclosan are Photo-degradation [14], Sono chemical degradation [15], Membrane filtration [16], Ozonation [17, 18], Photocatalysis using titanium dioxide [10,19], Solar photocatalysis using titanium dioxide [20] etc.

Ozone has been reported to be an effective oxidant for the degradation of a variety of persistent organic compounds in water as well as wastewater. Although ozonation of organic pollutants has been investigated in numerous studies, data on the removal of triclosan are scarce and incomplete. Heterogeneous photocatalytic processes have also received an increasing attention in the recent decades because they have the potential to completely mineralize several organic pollutants present in aqueous wastes. TiO_2 is a suitable photocatalyst because of its photo-stability, high activity and availability. Hence, these processes were chosen for the removal of triclosan from synthetic wastewater. The objective of this work was to compare the O_3/UV process with the TiO_2/UV process for the removal of triclosan from synthetic wastewater.

II. Material And Methods

2.1 Chemicals

All the chemicals were analytical grade reagents and were used without further purification. Triclosan (TCS) was procured from Himedia. Sulphuric acid (H_2SO_4), Sodium Hydroxide (NaOH) and Titanium dioxide (TiO_2) were procured from Merck India. Ozone by was supplied by an ozonator.

2.2 Experimental methods

Three replicates of each experiment were carried out. The data reproducibility was better than $\pm 10\%$ in all the cases. Experiments were conducted in the batch process using batch reactors. The set up consisted of a closed chamber containing a reactor (1L Volume) with a magnetic stirrer. Irradiation was done by an 8W UV-C lamp which was covered with quartz jacket. 1 litre solutions of different initial concentrations were prepared from the 10 mM stock solution of TCS. The pH of the solution was adjusted to the required range using 0.01N

NaOH and 0.01N H_2SO_4 . An appropriate amount of TiO_2 was added to the solution to initiate the heterogeneous reaction and solution was mixed thoroughly using the magnetic stirrer. In the case of the homogenous AOP, ozone from the ozonator was supplied through a diffuser at the bottom of the reactor. The samples to be analyzed were drawn from the reactor and filtered through 0.45- μm filter membrane before analysis. Samples were analyzed immediately after filtration to avoid any possible contamination.

2.3 Analytical Methods

pH was measured using a digital pH meter (Lovibond-pH meter). Triclosan was analyzed using High Performance Liquid Chromatography (HPLC) at 30°C. Agilent Binary LC was used in this study which was fitted with a reversed phase ZORBAX C18 silica (100mm 4.6 mm, 3.5 micron pore size) column. The diode array detector (DAD) was to be set to an adsorption wavelength of 280 nm, which is the excitation wavelength for triclosan. An 80/20 solution of methanol and DI water was used as a carrier solution at a flow rate of 1.0 mL/min. Each value represents the mean of independent experiments performed in triplicates, with an average standard deviation of $\leq 10\%$.

III. Results And Discussion

3.1 Homogeneous Advanced Oxidation Process using O_3/UV

3.1.1 pH

The ozonation was carried out in alkaline pH so as to achieve optimum decomposition of ozone. A constant ozone dosage as well as time of reaction was maintained and concentration of TCS was varied from 0.1mM to 0.5 mM. The rate of removal of TCS was plotted against pH. Figure 1 shows the effect of pH on the TCS removal by an O_3/UV process for samples having different initial concentration of TCS. It is observed that, as pH rises, the rate of removal of TCS also increases. This may be due to the fact that the rate of decomposition of ozone is favoured by the formation of hydroxyl radical at higher pH values [21, 22]. Maximum TCS removal is observed at pH 12 in all the cases. It is also seen that the removal rate decreases with the increase in the initial concentration of TCS, which maybe overcome by increasing the ozone dosage corresponding to the increase in the initial concentration of TCS. However, selection of optimum pH for large scale treatment of water containing TCS depends on process economics as well as the purpose for which the treated water will be used.

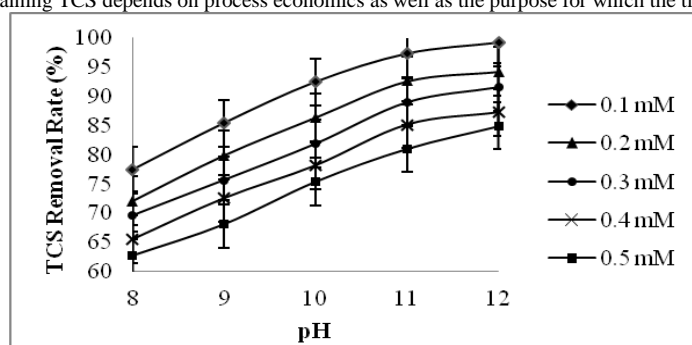


Fig. 1 Effect of pH of TCS removal rate

3.1.2 Ozone dosage

The ozone dosage was added in terms of molar ratio with respect to the initial TCS concentration. The molar ratio of ozone to TCS was varied in the range 1 to 5, while a pH of 10 and time of reaction of about 120 minutes were maintained constant. Near complete ozonation of triclosan was detected in the sample with a molar ratio of ozone: TCS = 5. Ozonation was substantial in the samples with a molar ratio of ozone: TCS = 4 and ozone: TCS = 3, whereas, less in the sample with molar ratio of ozone: TCS = 2 and ozone: TCS = 1. The TCS removal rate increased with the increase in ozone dosage in the reactions. The dosage of ozone required for the removal of TCS from water varies with the initial concentration of TCS in the water. Higher ozone concentrations may result in complete removal of TCS as well as the by-products formed during the reaction [18]. Increasing the initial pH can also considerably improve the rate of removal of TCS from the water sample, as evident in the section 3.1.1. Figure 2 shows the change in the removal rate of TCS with the increasing dosages of ozone.

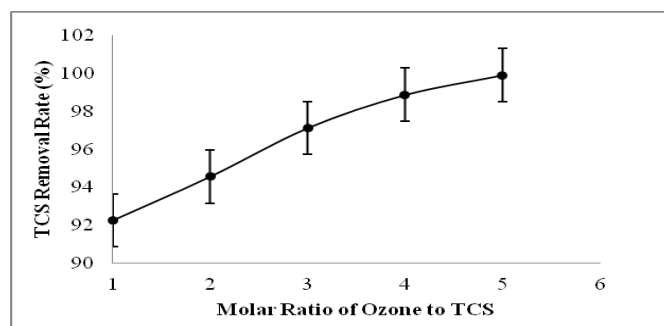


Fig. 2 Effect of Ozone dosage on TCS removal rate

3.1.3 Contact Time

Contact time or the time of reaction plays an important role in determining the rate of any reaction. Optimum contact time not only ensures the achievement of required level of pollutant removal, but also ensures avoiding unnecessary delay. The effect of contact time or reaction time was studied by varying the initial pH of water maintaining a constant ratio of ozone: TCS = 5. TCS/TCS_0 (ratio of final concentration to initial concentration) was plotted against the time of contact. It is observed that the removal of TCS increases with increase in the reaction time. Nearly 50% removal is observed within 90 minutes at high pH of 11 and 12. The rate of removal is slightly less at lower pH values (Figure 3). Hence, it can be concluded that the treatment time can be considerably reduced by increasing the initial pH of the water sample.

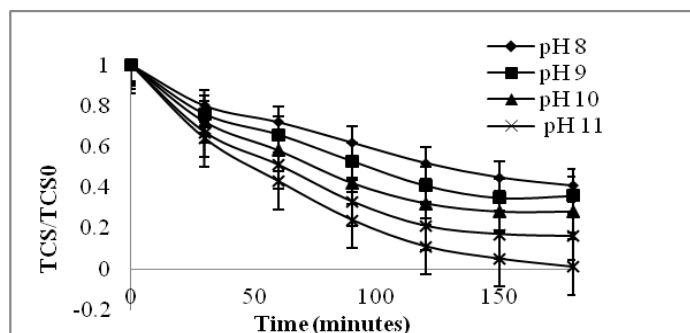


Fig. 3 Effect of contact time on TCS removal

3.2 Heterogeneous Advanced Oxidation Process using TiO_2/UV

3.2.1 pH

Figure 4 shows the effect of pH on the TCS removal from the water sample. A constant TiO_2 dosage as well as time of reaction of about 120 minutes was maintained. The different values of pH for which the treatment process was carried out were 4, 6, 8 and 10. It is observed that as the pH increases from acidic to alkaline; the percentage TCS removal reaches a minimum at near-neutral pH. This may be due to the fact that isoelectric pH of titanium dioxide is typically about 7 [23]. The surface of a commercially available TiO_2 molecule is positively charged under acidic conditions ($\text{pH} < 6.9$) and negatively charged under alkaline conditions ($\text{pH} > 7.0$). Hence, the removal efficiency reaches a minimum at the isoelectric pH. TiO_2 has been reported to have a higher oxidative capacity at low pH. However, the excess H^+ ions present at a low pH can significantly reduce the hydroxyl radicals, thereby decreasing the overall rate of reaction of TCS removal. Subsequently, TiO_2 displays an apparent increase in the rate of removal of TCS at higher pH. This may be attributed to the increase in the production of hydroxyl radicals at higher pH, which increases the rate of reaction of TCS removal [24].

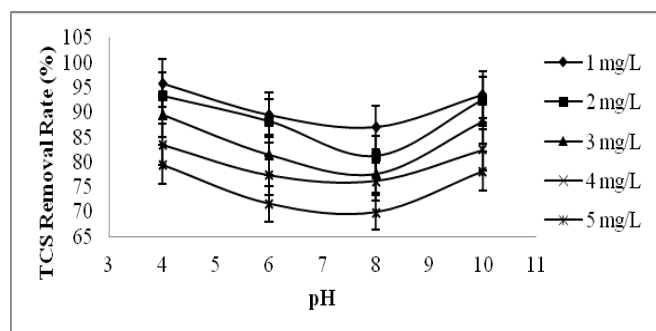


Fig. 4 Effect of pH of TCS removal rate

3.2.2 Dosage

The dosage of TiO_2 was varied from 10 g/L to 70 g/L for an initial TCS concentration of 10 mg/L in the water sample. The contact time was maintained at 120 minutes. It is observed from Figure 5 that the TCS removal rate increased with increase in the TiO_2 dosage up to an optimum value, after which the TCS removal started decreasing. Generally, an increase in catalyst concentration results in a rapid increase in pollutant removal, as observed in the graph. The increase in the concentration of TiO_2 increased the amount of photocatalyst, increasing the number of active sites available, which in turn increased the number of OH^\cdot radicals generated. However, when TiO_2 concentration exceeds the optimum value, the removal rate declined due to the interference of the light by the suspension of TiO_2 particles in the water sample [24].

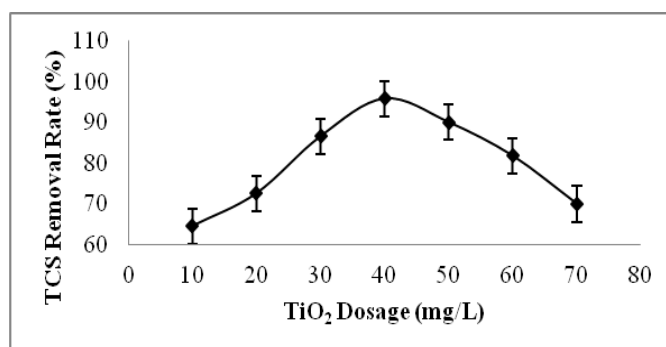


Fig. 5 Effect of TiO_2 dosage on TCS removal rate

3.2.3 Contact Time

The effect of contact time or irradiation time was studied for varied initial pH of water containing fixed amount of TCS and TiO_2 . TCS/TCS_0 (ratio of final concentration to initial concentration) was plotted against the contact time. It is observed that the removal of TCS increases with increase in the reaction time. However, it is observed that maximum removal takes place within 120 minutes. The removal rates are higher for acidic and alkaline pH as compared to near neutral pH which is same as observed in section 3.2.1. Longer irradiation

time (>480 minutes) helped in achieving complete removal of TCS. However, it is not economically feasible to have such long duration of treatment.

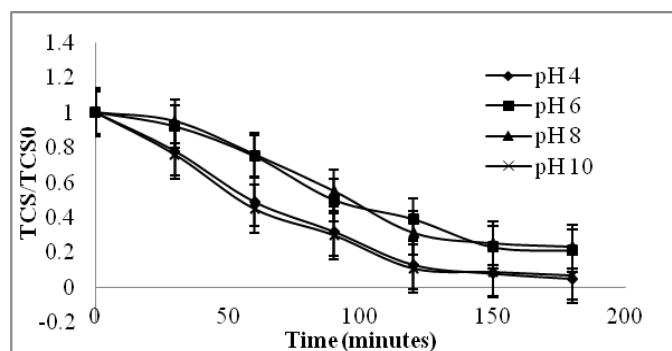


Fig. 6 Effect of contact time on TCS removal

IV. Conclusion

In this study, removal of triclosan was studied using ozone as well as titanium dioxide in the presence of UV. The outcomes of the present study are:

- Homogeneous AOP (O_3/UV) was found to have high triclosan removal efficiency (>90%) under optimum reaction conditions (alkaline pH and the molar ratio of O_3 to TCS = 5).
- Increasing the ozone concentration may lead to complete oxidation of TCS as well as its by-products.
- Prolonged irradiation using heterogeneous AOP (TiO_2/UV) ensured complete removal of triclosan.
- TiO_2/UV had comparatively lower removal efficiency as compared to O_3/UV process with respect to the reaction time as well as oxidant dosage.
- O_3/UV process has an added advantage over the TiO_2/UV process that additional expenses would be avoided for the removal and disposal or reuse of the catalyst after the triclosan has been removed from the wastewater.
- Formation of intermediates during the oxidation reactions has to be investigated to determine the necessary steps to be taken for further treatment.
- Solar irradiation can be used as an alternative source of light to off-set the higher operational costs likely to be encountered while using UV rays.

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